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# Atoms in Highly Symmetric Environments: H in Rhodium and Cobalt Cages, H in an Octahedral Hole in MgO, and Metal Atoms Ca-Zn in $C_{20}$ Fullerenes

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**Abstract:** An atom trapped in a crystal vacancy, a metal cage, or a fullerene might have many immediate neighbors. Then, the familiar concept of valency or even coordination number seems inadequate to describe the environment of that atom. This difficulty in terminology is illustrated here by four systems: H atoms in tetragonal-pyramidal rhodium cages, H atom in an octahedral cobalt cage, H atom in a MgO octahedral hole, and metal atoms in C<sub>20</sub> fullerenes. Density functional theory defines structure and energetics for the systems. Interactions of the atom with its container are characterized by the quantum theory of atoms in molecules (QTAIM) and the theory of non-covalent interactions (NCI). We establish that H atoms in H<sub>2</sub>Rh<sub>13</sub>(CO)<sub>24</sub><sup>3-</sup> trianion cannot be considered pentavalent, H atom in HCo<sub>6</sub>(CO)<sub>15</sub><sup>1-</sup> anion cannot be considered hexavalent, and H atom in MgO cannot be considered hexavalent. Instead, one should consider the H atom to be set in an environmental field defined by its 5, 6, and 6 neighbors; with interactions described by QTAIM. This point is further illustrated by the electronic structures and QTAIM parameters of M@C<sub>20</sub>, M=Ca to Zn. The analysis describes the systematic deformation and restoration of the symmetric fullerene in that series.

Keywords: QTAIM; fullerene inclusion complexes; hypervalence; hypercoordination

# 1. Introduction

# 1.1. Background

Chemical species can be systematically described with the assumption that individual atoms can be bound to specific numbers of neighbors. Local geometry and the strength of bonds are easily rationalized by, for example, the tetravalency of carbon, the divalency of oxygen, and similar assignments to other common atoms. Departures from such simple counts are exceptional (though not rare) and require special description. Molecules with larger than normal numbers of bound partners, i.e., "hypervalent compounds", were identified by Musher [1]. Many of these species may be written as  $X_n G Y_m$  where G is a member of groups 14, 15, and 16. This includes for example ClF<sub>3</sub>, F<sub>3</sub>PO, PF<sub>5</sub>, XeF<sub>6</sub>, and IF<sub>7</sub>; these species have unusual tri-, penta- or hepta-valency, with the number of valence pairs in the neighborhood of a central atom exceeding the familiar value of four. If all bonds are covalent and we adopt the Lewis model of pair bonding, then, from the elementary valence-bond view, d atomic orbitals (AOs) are needed to mix with s and p AOs to form local hybrids on the central atom. An alternative representation assigns ionic structures to the ligands, so that trigonal-bipyramidal PF<sub>5</sub> for example is assigned  $F_3P^{2+}$  ( $F^{1-}$ )<sub>2</sub> with two negatively charged fluorides at the poles, and three PF bonds and a lone pair in the equatorial plane. These conceptual alternatives have been discussed mainly in pedagogical settings [2,3]. The question of the nature of bonding in such species is evaded by the noncommittal term "hypercoordinate" species apparently first coined by Schleyer [4].



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Hypercoordinated species need not display hypervalence, whether involving *d* atomic orbitals or an expanded octet. High coordination numbers can be achieved by trapping a species in a strongly coordinating medium. This trap may be a cage, organic or metalorganic, or a hole in an otherwise orderly solid. In this work we examine H atoms in an oxide hole in MgO, in cages of rhodium atoms as in H<sub>2</sub>Rh<sub>13</sub>CO<sub>24</sub><sup>3–</sup> and of Co atoms as in HCo<sub>6</sub>(CO)<sub>15</sub><sup>1–</sup>. We study a wider range of atoms within C<sub>20</sub> fullerenes.

#### 1.2. Hypercoordinated H Atom

The hydrogen atom takes part in a range of interactions beyond its normal monovalence/monocoordination, including a number of forms of hydrogen bonding, agostic interactions, hydride bridging, and multicenter bonding. Kühl [5] has reviewed this behavior.

H atoms trapped within metal clusters have been ascribed coordination numbers as high as 4, 5, and 6 [6–9].

In solids, high coordination numbers for H atom have been reported. Quoting from Janotti and van der Walle [10],

"[We] discuss hydrogen as a substitutional impurity in the binary metal oxides ZnO and MgO. Contrary to expectations, hydrogen on a substitutional oxygen site forms genuine chemical bonds with all of its metal—atom nearest-neighbours, in a truly multicoordinated configuration."

# Their computed charge density leads the authors to conclude that

*"hydrogen is equally bonded to all four Zn neighbours in ZnO, and to all six neighbours in MgO."* 

The six-fold hypercoordination in MgO has, to our knowledge, not been further examined.

#### 1.3. Endohedral Atoms in Fullerenes

Atoms, clusters, and molecular species have been incorporated in fullerenes [11]. The most thoroughly studied inclusion complexes employ larger fullerenes ( $C_{60}$  and greater). Molecules placed in  $C_{60}$  include  $H_2$ , HF,  $H_2O$ , and HF. Recently methane@ $C_{60}$  has been reported [12], and target species with captives  $O_2$ ,  $N_2$ , CO, NO, ammonia, methanol, formaldehyde, and carbon dioxide are sought. Larger molecules can be enclosed in larger fullerenes, with one extreme being  $C_{60}$  in  $C_{240}$  [13].

Electronic structure modeling of endohedral complexes of fullerenes  $C_n$  with  $n \ge 60$  begins with the work of Cioslowski and Fleishmann on  $C_{60}$  species [14]. They characterized the charge distribution by RHF and a mixed basis (4-31G for C atoms and the DZP basis for guests). Their calculations for inclusion complexes of closed shell species  $F^{1-}$ , Ne, Na<sup>1+</sup>,  $Mg^{2+}$ , and  $Al^{3+}$  complexes imposed icosahedral symmetry for the most part; however, an estimate of the force constants revealed geometrical instability (symmetry breaking) for all species other than Ne $@C_{60}$ . Investigation of finite displacements of the Na cation in  $Na(+)@C_{60}$  found a minimum energy geometry with that ion 0.660 Å from the center point. Atoms-in-molecules analysis (AIM) [15,16] for Ne $^{\circ}$ C<sub>60</sub> found all C atoms connected to Ne by interaction lines (often called bond paths), which are loci of points which have maximum density in two dimensions; we call these features "ridges" in the density. Intuitively recognizable C-C and C=C bonds correspond to density ridges in the fullerene shell. These are characterized by critical points, for which  $\nabla \rho = 0$ , which have maxima normal to the interaction line and a minimum along the line. Substantial densities are found at these points, 0.266 and 0.308 atomic units respectively. Sixty other interaction lines were found, each connecting a C atom to the central neon atom. Because such lines can hardly be identified as bonds, an alternative terminology is called for; perhaps "interaction lines" would serve. Following Shahbazian [17], we refer to the CPs on such paths as "line critical points", or LCPs. These LCPs have small density values, 0.0024 atomic units. The corresponding Laplacian values (-0.563 and -0.753 for C-C and C=C BCPs, and +0.0145 for the LCP) indicate normal covalent bonding in the cage and weak closed shell—closed shell interactions between the Ne atom and the fullerene cage. Cioslowski and Fleishmann [14]

remarked that a reasonable model of their results would represent C60 as a spherical shell of charge, polarizable and responsive to the central atom or ion.

Jalife et al. reviewed noble gas inclusion complexes in fullerenes [18]. In the intervening three decades, X-ray structures for  $C_{60}$  inclusion complexes had become available for He [19], Xe [20] and Kr [21]. The QTAIM analysis reported by Cerpa et al. [22] revealed a multitude of cage C-to-noble gas paths and located associated line critical points with very small densities and small positive Laplacians. These authors remarked that the number of bond paths and BCPs was a consequence of the symmetry of the cage and had no necessary correspondence to chemical constructs. The apparent paradoxes in application of QTAIM to endohedral complexes was further explored by Popov and Dunsch [23]. Estrada-Salas and Valladares [24] studied endohedral and exohedral complexes of Mn, Fe, Co, Cu, and Zn with  $C_{60}$ , optimizing structures with BPW91 and a DNP basis.

Modeling of neutral alkali metal and transition metal inclusion complexes in  $C_{20}$  has been pursued for more than a decade. An and co-authors [25] studied Li, Na, K, Rb, and Cs atoms in icosahedral C<sub>20</sub> with DFT (PW91/DNP). Garg and co-workers [26] evaluated structures, energies, and magnetic moments with an alternative DFT model PBE with a pseudo potential representing core electrons and a DZP basis for valence electrons. Baei et al. [27] treated  $C_{20}$  inclusion complexes of transition metals Sc-Zn with DFT (PBE/6-31G(d) for C, LANL2DZ for metals), finding that inclusion complexes M@C<sub>20</sub> of the later transition metals (Co-Zn) were not stable compared to the isolated metal atom M and the C<sub>20</sub> fullerene. Vibrational analysis showed that the centrosymmetric structures for Sc, Cr, Fe, Ni had saddle-point character and would spontaneously break symmetry. Gonzalez, Lujan, and Beran [28] modeled TM@C<sub>20</sub> for group 11 and 12 transition metals, Zhao, Li, and Wang [29] considered a broad sample of transition metals with configurations in 3d (Sc-Zn), 4d (Y-Cd) and 5d (Lu-Hg) shells, with the PBE functional and a numerical basis of double-zeta quality but apparently no relativistic corrections. They found maximum spin polarization for Mn, and most effective binding of Ti and V. Sarkar, Paul, and Misra [30] treated transition metals Ti, V, Cr, Mn, Fe, Co, and Ni in all spin states with UB3LYP expressed in a mixed basis, 6-31++G(d,p) for C and LANL2DZ for metals. They found that the structures all retained centrosymmetry and that maximum multiplicity state was most stable in every case except for Cr and Fe, which prefer the triplet. While details of binding energy and structure are not disclosed, the authors provide the range of M-C distances; these show that the endohedral complexes are nearly not perfectly centrosymmetric.

In this report we address first the description of coordination of H atom captured in metal cages and in a salt crystal [6–10]. QTAIM provides a unified description of the environment of the captured H atom. Despite claims to the contrary, the QTAIM results show that it is misleading to use the chemical terminology of pair bonds in these cases. Such time-honored representations of molecules are even less well suited to the description of the environment of atoms isolated in a small fullerene. The structures of  $C_{20}$  systems enfolding metal atoms are not systematically established, nor is the thermodynamics of capture well established.

#### 2. Systems Studied

The choice of systems was guided by theoretical concerns—the characterization of H atom confined in a structure with many immediate neighbors—and the need to refine the description of structure and bonding in the smallest metal atom endohedral fullerenes. Such analysis must precede the study of electrical, magnetic, and spectroscopic properties, which for these systems may be particularly interesting and useful.

#### 2.1. H Atom Capture in Inorganic Vacancies

The high-symmetry environments we have chosen include a rhodium trianion with H atoms occupying nearly square-pyramidal cage sites  $[H_2Re_{13}(CO)_{24}]^{3-}$ , [7] and a cobalt nearly-octahedral cage of cobalt atoms enclosing a single H atom  $[HCo_6(CO)_{15})]^{1-}$ , [8,9] a fragment of MgO crystal with a H atom occupying a hole left by removal of an O atom, [10]

and fullerenes C20 with inclusion complexes of single atoms including uncharged transition metals and noble gases. We have experimental data for some of these species [7,9] and have constructed some computational models for others to advance the discussion. In the following discussion we provide brief initial discussions of these systems.

#### 2.1.1. H Atoms in the Rhodium Square-Pyramidal Cages

In  $[H_2Rh_{13}(CO)_{24}]^{3-}$  which has a rhodium cage structure [7] there would seem to be six equivalent square-pyramidal open sites (three above the equator, three below). Idealized forms are shown in Figure 1. Each of the open sites is enclosed by four Rh atoms forming a square face of the polyhedron and the central metal atom. The electronic structure of the experimental system is represented by QTAIM interaction lines connecting nuclear centers in Figure 2.



**Figure 1.** The idealized rhodium cage Rh<sub>13</sub> is composed of a fragment of a hexagonal close packed structure. (**a**) the three layers of (3, 6, 3) rings. Rhodium atoms form a truncated trigonal prism; the 13th Rh is at the center of the cluster. H atoms occupy square pyramidal arrays of Rh atoms, sharing the central Rh as a shared apex. (**b**) A reoriented view with the polyhedron resting on a square base of four Rh atoms; the Rh atom at the center of the midplane completes the square pyramids.

QTAIM critical points of types (3, -3)—that is, nuclear attractors, or atomic centers are shown in Figure 2, along with interaction lines (which have maximum density in two dimensions, a "ridge" in the density) connecting the nuclear attractors. The object is oriented to suggest a left-right symmetry, which is imperfect. The symmetry of the experimentally studied structure is reduced in part by the bridging carbon dioxide fragments which reduce the symmetry to C<sub>s</sub>. Symmetry is further reduced by the counterions in the crystal. Then the "square" pyramidal holes are deformed into three nonequivalent sets of two equivalent quadrilateral pyramidal holes. In the experimental system [7], the trapped H atoms occupy two non-equivalent holes.

More detailed description of the experimental system is in the Supplementary Material. Discussion of a symmetrized model is deferred to the section on results.



**Figure 2.** The experimental X-ray structure [7] of the complex  $[H_2Rh_{13}(CO)_{24}]^{3-}$  as represented in the AIM topology. Oxygen atoms are color-coded red, rhodium atoms are dark green, carbon atoms dark gray, and hydrogen atoms are light gray. Of the 24 CO ligands, 12 are attached each to a single Rh and 12 bridge two rhodium atoms. The bridging reduces the global symmetry to C<sub>s</sub>. Even that plane of symmetry is broken in the crystal since the H atoms occupy nonequivalent sites.

2.1.2. H Atom in a Cobalt Octahedral Cage

Two views of the  $C_{2v}$ —symmetric framework in  $[HCo_6(CO)_{15}]^{1-}$  anion [8,9] appear in Figure 3. This symmetric structure was obtained by geometry optimization with density functional theory, using the model  $\omega$ B97XD/cc-pVTZ (see Methods and Software section for details). According to the QTAIM analysis, there are six interaction lines connecting Co atoms with the trapped H atom



**Figure 3.** Two views of  $HCo_6(CO)_{15}^{1-}$  with color code red = O atom, gray = C atom, pink = Co atom, light gray = H atom. System optimized in  $C_{2v}$  symmetry with DFT model  $\omega$ B97XD/def2-SVP. Connections are QTAIM features, ridges in the electron density linking nuclear centers. (a) A view along the  $C_2$  axis (b) An offset view revealing the hexacoordinated H atom and displaying the lines connecting the H atomic center with Co atoms according to QTAIM.

## 2.1.3. H Atom in a Magnesium Oxide Crystal Vacancy

Figure 4 shows a fragment of a MgO crystal, with a neutral H atom replacing an oxygen atom [10]. In the perfect crystal each magnesium atom is coordinated with six oxygen atoms, and each oxygen atom by is coordinated with six magnesium atoms. The distortion of the crystal arising from the substitution of neutral H for the O dianion is evident. Some Mg atoms depart from the mean  $(MgO)_n$  plane since they are more weakly attracted by H than by  $O^{-2}$ .



**Figure 4.** A fragment of a MgO crystal, with one oxygen hole occupied by H atom, as represented in the AIM topology. The fragment has a net +2 charge. Solid and dashed lines, ridge lines in the electron density, lead between nuclear attractors; solid lines denote stronger interactions than dashed lines.

Figure 4 includes QTAIM interaction paths between nuclear attractors—that is, critical points of type (3, -3). Solid lines denote strong interactions, as between neighboring atomic centers of opposite charge. Interactions over longer distances and between ions of like charge are weaker, as shown by broken lines. The single H atom shown here interacts with two neighboring Mg atoms and four neighboring O atoms.

#### 2.1.4. Endohedral M in C20 Fullerene

Illustrating use of QTAIM analysis [14,15] for M@C<sub>20</sub>, Figure 5 describes Ne@C20. The structure is optimized in  $\omega$ B97XD/cc-pVDZ, and is shown in the QTAIM topology. Solid black lines connect nuclear attractors' (3, -3) critical points (atomic centers). The lines represent ridges in the electron density function and suggest that the central Ne atom interacts strongly with all 20 of the C atoms of the fullerene container. Green dots on these connectors mark a minimum density along the ridge; these points are termed line critical points (LCPs). These are termed (3, -1) extreme points. At those points, the gradient of the density is zero and the matrix of second derivatives has one positive root corresponding the increase in density along the interaction line (call this *z*), and the decrease in density in the other two dimensions (*x* and *y*).



**Figure 5.** Ne@C<sub>20</sub>, as represented in the AIM topology. View along the three-fold axis in symmetry  $D_{3d}$ . Carbons are coded gray, Ne is light blue.

#### 3. Methods and Software

We used density functional theory to compute the ground state energies and harmonic vibrational frequencies, and electron distribution. For the fullerenes our choice of functional was  $\omega$ B97XD [31]. This functional is gradient-corrected, its exchange is scaled for distance, and the functional includes an empirical term describing dispersion interactions, Grimme's D2 formulation [32]. The cc-pVDZ basis [33,34] was used for fullerenes and inclusion complexes. For the rhodium system, we used the Ahlrichs–Weigend basis SVP [35,36] and the Stuttgart basis SDD, [37] each of which incorporates a relativistic pseudopotential. These basis sets are all available for download [38]. Gaussian 09 [39] and Gaussian 16 [40] produced optimized structures and the wfx files required by QTAIM analysis. QTAIM treats the molecular charge density  $\rho$  and its gradients  $\nabla \rho$ , and identifies interaction lines between atomic centers. Atomic centers have three negative roots of the matrix of second derivatives of the density with respect to Cartesian displacement coordinates  $\left[\partial^2 \rho / \partial x_i \partial x_i\right]$ and are denoted as (3, -3) critical points (CPs). The interaction lines are loci of points with maximum density (negative curvature) in two dimensions, a "ridge" in the density. The minimum density point along the ridge (a saddle point with two negative and one positive curvature) may be called a line critical point (LCP) of type (3, -1).

QTAIM reports the Laplacian of the density at LCPs, and energy densities G (kinetic) and potential (V) as well. The mathematical formulation of these quantities has been clearly described [41]. This report also defines the delocalization index (DI) which counts the number of shared electron pairs. These quantities have been used widely to characterize the strength and degree of covalency of bonding.

Non-covalent interactions (NCIs) appear in regions of low density and small values of the reduced density gradient (RDG) [42]. These may be attractive (as van der Waals forces or H-bonding) or repulsive (most closed shell–closed shell interactions, such as steric effects. A useful description of the RDG, its graphical characterization, and its interpretation is given by Contreras-Garcia et al. [43,44].

QTAIM results were obtained with AIMALL [45] and Multiwfn [46,47] software. NCIPLOT software was obtained by download from the Contreras-Garcia group [44].

For the model structure for the rhodium cage, we began with idealized geometric forms (a dodecahedron of 12 Rh atoms with one more at the center of the figure) for the  $Rh_{13}$ 

cluster, and introduced terminal and then bridging CO groups to mimic the connectivity of the X-ray structure. Two H atoms were introduced along the approximately fourfold axis passing through the central Rh and the tetragonal faces of Rh atoms. The energies of these starting forms were optimized in  $\omega$ B97XD/SDD and  $\omega$ B97XD/def2-tzvp models. For H@MgO, structures were taken from the X-ray analysis.

Initial M@C<sub>20</sub> structures were obtained by placing the M atom at the center of the  $D_{3d}$  form of  $C_{20}$ . [46] The optimization did not enforce symmetry, and several systems were found to depart substantially from this initial symmetry.

#### 4. Results

In this section we present details of the QTAIM and NCI analyses for the three cageconfined H atom systems (Section 4.1, parts Sections 4.1.1–4.1.3) and metal endohedral C20 fullerenes (Section 4.2, parts Sections 4.2.1–4.2.15). Summary remarks on the QTAIM analysis for members of the M@C20 series are to be found in Section 4.2.14, and an overview of the NCI results is to be found in Section 4.2.15.

#### 4.1. Captured H Atoms

In the following sections we describe geometries of systems in which foreign atoms are captured. Some structures are simply borrowed from reported X-ray crystallography studies (as in the H-doped MgO solid sample and the experimentally known unsymmetric rhodium cage compound), while other structures are found by geometry optimization in  $\omega$ B97XD/cc-pVDZ. These include all the M@C<sub>20</sub> fullerenes and the modeled high-symmetry rhodium and cobalt cage compounds.

### 4.1.1. H Atoms in Rhodium Cages

The unsymmetric experimental rhodium cage [7] and the symmetrized analog capture H atom in a square-pyramidal environment, as shown above in Figure 2. The QTAIM analysis is unwieldy owing to the low symmetry of the species; it can be found in supplementary information. An idealized  $D_{4h}$  structure of a simplified structure  $H_2Re_{13}(CO)_{12}]^{3-}$ , is shown in Figure 6a. Then H atoms occupy square-pyramidal holes and have five Rh atoms as neighbors in a square pyramid. Each Rh is bound to a CO carbon and four Rh neighbors, as in the experimental structure. A further idealization of the rhodium system with bridging carbonyls and formula  $H_2Re_{13}(CO)_{24}]^{3-}$  is shown in Figure 6b.



**Figure 6.** Two views of a symmetrized  $H_2Rh_{13}(CO)_{24}^{3-}$  trianion. The color code has Rh in blue–green, C in dark gray, O in red, and H in light gray. (a) The H atoms are seen on a diagonal in the 3-6-3 orientation of the three rhodium layers. (b) A view of H atom through a nearly square base.





**Figure 7.** Two symmetrized models of Rh13 species containing H atoms in square-pyramidal holes. (**a**) A simplified complex  $[H_2Re_{13}(CO)_{12}]^{3-}$  as represented in the AIM topology. Color-coding as in Figure 3. The paths imply coordination of H atoms with five rhodium atoms. (**b**) a  $D_{4h}$ —symmetric model of  $[H_2Re_{13}(CO)_{24}]^{3-}$  with H atoms in equivalent square-pyramidal holes.

**Table 1.** The coordination around the two H atoms in of  $[H_2Rh_{13}(CO)_{24}]^{3-}$  trianion. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units, (absolute electrons per Bohr-cubed for the density, for example), as are the kinetic and potential energy densities G and V. Density was computed in  $\omega$ B97XD/SDD.

Coordination	Length	Density $\rho$ at LCP	$\nabla^2\rho$ at LCP	DI	G	V	Н
a a'	1 5963 1 6590	0 1271 0 1114	$\pm 0.2826 \pm 0.2450$	0.3734,	0.1250,	-0.1799,	-0.0549,
a, a	1.0700, 1.0070	0.12/1, 0.1114	10.2020, 10.2450	0.3075	+0.1037	-0.1465	-0.0428
h h/	1 0012 1 0155	0.0012 0.0975	0 1009 0 1007	0.2284,	0.0812,	-0.1125,	-0.0313,
D, D	1.8013, 1.8133	0.0912, 0.0875	+0.1998, +0.1902	0.2286	0.0767	-0.1160	-0.0393
/	1 7410 1 7500	0.00(2, 0.0012	0.0000 0.0000	0.2694,	0.0896,	-0.1229,	-0.0333,
С, С	1.7419, 1.7326	0.0963, 0.0913	+0.2260, +0.2069	0.2622	0.0829	-0.1142	-0.0313
ינ נ	1 7040 1 7922	0.0000 0.0000	0.0150.0001	0.2451,	0.0845,	-0.1154,	-0.0309,
a, a	1.7949, 1.7832	0.0909, 0.0969	+0.2150, 2221	0.2668	0.0893	-0.1235	-0.0342
DL II	1 9105 1 7926	0.0027.0.007(	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0.2038,	0.0914,	-0.1241,	-0.0327,
Rh-H	1.0103,1.7830	0.0937, 0.0976	+0.2353, +0.2356	0.2226	0.0942	-0.1293	-0.0351

Table 1 contains QTAIM data for the symmetrized H<sub>2</sub>Rh<sub>13</sub>(CO)<sub>24</sub><sup>3-</sup> trianion. The structure is obtained by optimization with  $\omega$ B97XD/SDD. Symmetrization is far from perfect but it is clear that the distance from H to the central Rh (2.628 ± 0.04 Å) is larger than the distance from H to the Rh atoms making up the square bases (1.786 ± 0.026 Å). The Laplacian values are all positive, indicating a depletion of charge at the H-Rh LCPs, characteristic of closed shell interactions. However, the delocalization index (DI), which reflects the number of shared electron pairs [48], suggests that covalent interactions are significant. If the ratio |V|/G < 1, we take the bonding to be mainly ionic, while if the ratio exceeds 2, the bonding is covalent. In this case, the ratio lies between 1 and 2, and bonding is considered "mixed" [48]. The bond strength measure -V/2 [49,50] assigns

the interaction energy (about 0.05 to 0.06 Hartree) to the H-Rh interaction energy. For a detailed guide to the mathematical formulation of these QTAIM constructs see [48].

The delocalization index DI is an estimate of electron pairs shared between atoms. Negative values for H = G + V, or values of |V|/G > 1 (here they average about 1.4) suggest that covalent interactions are significant.

The DI index for H atom and the five surrounding Rh atoms is  $1.304 \pm 0.026$ , which does exceed the ideal limit of 1.00 for perfectly covalent dihydrogen. However, if a pentavalent species is to share five electron pairs, we see that it is seriously misleading to describe hydrogen atom in the Rh square pyramid as being pentavalent. It is of course pentacoordinate since it interacts with five immediate neighbors.

A view of the NCI surfaces for  $H_2Rh_{13}(CO)_{24}^{3-}$  trianion is given in Figure 8.



**Figure 8.** Surfaces inclosing zones of non-covalent interaction, color coded blue for attraction and red for repulsion. Atoms are coded red for O, blue-green for Rh and C, and light gray for H. Two H atoms are pointed out by horizontal gold arrows, and the central Rh is designated by a vertical gold arrow. The H atoms are each in a plane defined by a square face of the Rh cage. Those base Rh atoms visible from this perspective are labeled.

NCI zones appear around the outer surface of the Rh dodecahedron, but there are no such zones near H atoms. This suggests that dispersion and steric interactions between H atom and Rh atoms making up its cage are not significant. The bonding is weak according to QTAIM but results predominantly from covalent/orbital mixing interactions.

# 4.1.2. The H Atom Captured in a Six-Coordinate Cobalt Cage

Figure 9a shows the cobalt cage compound  $HCo_6(CO)_{15}^{1-}$  anion, by the density ridge lines connecting nuclear centers (in QTAIM terminology, (3, -3) critical points, meaning that density decreases in all three directions from the critical point. The density ridge or line critical points (LCPs) are minima along the line, and are called (3, -1) points. The trapped H atom interacts with all six Co atoms. Figure 9b schematizes those interactions and provides a labeling scheme, which is used in Table 2, summarizing QTAIM parameters.



**Figure 9.** Two views of the  $HCo_6(CO)_{15}^{1-}$  anion (a)  $C_s$ —symmetric  $HCo_6(CO)_{15}^{1-}$  anion as represented in the AIM topology. Solid lines connect nuclear attractors (large spheres; H is light gray, Co is pink, Ne is light blue, carbon is dark gray) Green dots on these connectors represent line critical points and reinforce the suggestion that the central H atom interacts strongly with six Co atoms of the Co cage. (b) Labeling scheme for interaction lines.

**Table 2.** The coordination around H atom in  $HCo_6(CO)_{15}^{1-}$  anion. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units (e.g., absolute electrons per Bohrcubed for the density), as are the kinetic and potential energy densities G and V. Geometry was optimized in  $\omega$ B97XD/def2-SVP. There are no interaction lines nor LCPs from Co to Co.

Coordination	Length	Density	ρ at LCP	$\nabla^2\rho$ at LCP	
a, a'	1.7933	0.0	689	+0.1267	
b	1.8158	0.0	0.0642		
d	1.9129	0.0	+0.1337		
с	1.8158	0.0	+0.1376		
e	1.9130	0.0	+0.1338		
Co a-a'	2.4666	*	*		
Co b-b'	2.4647		*		
Co a-b (a'-b')	2.7959		*	*	
	DI	G	V	Н	
a, a'	0.2731	0.0529	-0.0741	-0.0212	
b	0.2341	0.0519	-0.0694	-0.0175	
d	0.1971	0.0442	-0.0580	-0.0138	
с	0.2341	0.0519	0.0519 -0.0694		
e	0.1918	0.0442	-0.0551	-0.0551	

<sup>1</sup> There are no interaction lines connecting Cobalt atoms.

The delocalization index DI is an estimate of electron pairs shared between atoms. Negative values for H = G + V, or values of |V|/G > 1 (here they average about 1.4) suggest that covalent interactions are significant.

Values of QTAIM collected in Table 2 attest to weak Co-H bonding with a degree of covalency. The delocalization index DI is an estimate of electron pairs shared between atoms. Negative values for H, or values of |V|/G > 1 suggest that covalent interactions are significant. Here |V|/G averages about 1.3, so bonding is mixed. This is appropriate for these weakly charged systems and consistent with the modest values of the DI. The positive values of the Laplacian are characteristic of closed shell—closed shell interaction, so we must infer a delicate balance between weak covalent interaction and near-canceling steric repulsion and attractive dispersion.

The total DI of 1.4033 electron pairs shared among the six immediate Co neighbors of H atom, is comparable to the DI of H in the rhodium cage. In analogy to the Rh case, if hexavalency implies that six electron pairs participate in bonding with H, it cannot be

said that H is hexavalent. It is surely hexacoordinate; there is a small degree of covalency associated with those six interactions.

The NCI graphical analysis for the  $HCo_6(CO)_{15}^{1-}$  anion (Figure 10) shows noncovalent interactions between Co atoms but no evident NCI from Co to H atom. Evidently the dispersion and steric NCIs tend to cancel.



**Figure 10.** Two views of the NCI surfaces of  $HCo_6(CO)_{15}^{1-}$  anion (**a**) side view showing zones of weak interaction (**b**) a tilted view revealing the H atom.

#### 4.1.3. Hydrogen Atom in MgO

The H atom in the system H@MgO takes the place of an O atom in the crystal's rock salt structure. The interaction lines derived from QTAIM analysis are shown in Figure 11a.



**Figure 11.** Two views of the H-doped MgO crystal, according to the QTAIM topology. (a)  $D_{4h}$ —symmetric fragment, with three layers. Color code red = O atom, green = Mg, and light gray = H atom. Note distortion of top and bottom layers, arising from the weaker interaction of H with Mg compared with the interaction of O with Mg. (b) view normal to the middle layer, with six interaction lines. Two (from H to Mg, coded b) lie in the plane, and four (from H to O, labeled a) lie in a perpendicular plane. The interaction from Mg to O is labeled x.

The QTAIM analysis assigns charges of  $\pm 1.7671$  to Mg,  $\pm 1.7858$  to O, and  $\pm 0.7839$  to H. (Units are absolute electrons,  $\pm 1.91$ ). Table 3 shows small densities at line critical points and positive values for the Laplacian, indicating charge depletion at the LCPs. This is characteristic of closed shell–closed shell interactions. The delocalization index DI four interactions to suggests minimal electron pair sharing, and the H index shows that the weak H ... O interaction is balanced between covalent and ionic character. H ... Mg

tilts slightly to the covalent side, while Mg ... O is decidedly ionic; the ratio |V|/G is 0.83. Mg ... O is also the strongest interaction according to -V/2, ca 0.024 Hartrees.

**Table 3.** The coordination around H atom. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density $\rho$ at LCP	$\nabla^2\rho$ at LCP	DI	G	V	Н
a (H O)	2.6108	0.0177	+0.0399	0.0880	0.0107	-0.0113	-0.0006
b (H Mg)	2.4025	0.0265	+0.1241	0.0746	0.0286	-0.0263	+0.0023
x (MgO)	1.9109	0.0556	+0.2731	0.1440	0.0583	-0.0483	-0.0100

With four H ... O interactions and two H ... Mg interactions identified by QTAIM the total number of electron pairs shared with H and neighbors is 0.50; that value falls short of the total Mg ... O DI of  $6 \times 0.144 = 0.86$  shared pairs. Again, although H has six neighbors, it is far from hexavalent. Of course, the high degree of ionicity in the salt virtually precludes covalency.

The non-covalent interaction analysis produces surfaces enclosing regions of low density and low reduced density gradient. Figure 12 provides a view through the top layer of MgO.



**Figure 12.** A view through the top layer of MgO. Mg atoms (pink) are seen in the corners and the center of a square array, and O atoms are shown in red.

Behind the central Mg atom is a surface enclosing the H atom and blocking it from view. The blue–green color coding suggests that the Mg-H interaction is weak. Behind every edge-Mg lies an O atom, with a blue NCI zone between them. This is a strongly attractive ion-ion NCI. A similar but darker blue ring can be seen between edge O atoms and the Mg atoms behind them. The NCI visualization is entirely consistent with the semi-quantitative QTAIM description

# 4.2. Neutral Metal Atoms in C<sub>20</sub> Fullerene: Overview of Binding, QTAIM Interaction Ridges, and Non-Covalent Interactions

The following sections deal with a series of inclusion complexes  $M@C_{20}$ . First (Section 4.2.1) we report the thermodynamic energy change associated with capture of

neutral atoms in the  $C_{20}$  cage. The reference point for bonding analysis (Section 4.2.2) is Ne@C<sub>20</sub>, which retains high (D<sub>3d</sub>) symmetry for the C<sub>20</sub> shell. Ne interacts almost identically with each of the shell carbons, in keeping with that high symmetry. NCI analysis shows regions of repulsion between Ne and each C.

Sections 4.2.3–4.2.13 are each devoted to a single endohedral complex M@C20 for M in the series Ca to Zn. In each case the interaction lines define a structure, and the QTAIM properties of line critical points (LCPs) are compiled. Key variables include the LCP electron density, its Laplacian, the delocalization index, and he kinetic and potential energy densities. Both the LCP electron density and the LCP potential energy density have been considered useful measures of interaction strength. The ratio of kinetic to potential energy density K/V, as well as their sum H has been used to judge the relative degree of ionic and covalent interaction, while the delocalization index is considered a measure of the number of shared electron pairs.

General description of behavior of the QTAIM quantities of the  $M@C_{20}$  is found in Section 4.2.14, and an overall view of the NCI analysis is in Section 4.2.15.

# 4.2.1. Energetics for $M + C_{20} \rightarrow M@C_{20}$ for the Series M = Ca-Zn

In this section, we describe the set of  $M@C_{20}$  fullerene inclusion complexes. The set of M lies in the first transition row and range from Ca to Zn. The atoms are all neutral, of configuration  $d^n$  (n = 0 to 10). We chose maximum multiplicity since the set of d AOs span a single irreducible representation in the reference I<sub>h</sub>-symmetrical structure of C<sub>20</sub>. While all M@C<sub>20</sub> structures occupy a relative minimum in the potential surface (all vibrational frequencies are real) some species are thermodynamically unstable according to our unrestricted  $\omega$ B97XD/cc-pVDZ calculations. Our estimates of the thermodynamic stability of the endohedral metal species M@C20 relative to separate M and C<sub>20</sub> (Table 4) disagree sharply with those of Garg et al. [26] and Gonzalez and co-workers [28]. Since these investigators used rather different computational models and the structures they used are not defined in detail the discrepancy is difficult to resolve.

**Table 4.** Electronic energy of endohedral complexes for Ca-Zn (Hartrees), binding energy (eV), and number of QTAIM lines from the metal to fullerene carbons. Negative BE, which is the electronic energy change in the reaction  $M + C_{20} \rightarrow M@C_{20}$  with no corrections for effects of the medium, means the complex is more stable. LN refers to the number of QTAIM lines connecting the metal to C atoms of the fullerene. These values do not incorporate zero-point vibrational energies.

Atom M	LN	$E (M + C_{20})$	E (M@C <sub>20</sub> )	BE (eV)	<b>BE (eV)</b> <sup>1</sup>
<sup>1</sup> Ca d <sup>0</sup>	10	-1438.799965	-1438.515743	+7.73a	
$^{2}$ Sc d <sup>1</sup>	20	-1521.861237	-1521.890211	-0.79a	
<sup>3</sup> Ti d <sup>2</sup>	20	-1610.588977	-1610.724727	-3.69a	3.80 <i>b</i>
$^{4}V d^{3}$	12	-1705.143352	-1705.194267	-1.39a	1.93b
<sup>5</sup> Cr d <sup>4</sup>	8	-1805.655613	-1805.591705	+1.74a	-3.23b
<sup>6</sup> Mn d <sup>5</sup>	4	-1912.089623	-1912.078599	+0.30a	-6.31b
<sup>5</sup> Fe d <sup>6</sup>	5	-2024.881830	-2024.791288	+2.46a	-3.47b
$^{4}$ Co d <sup>7</sup>	8	-2144.000844	-2143.843613	+4.28a	-4.19b
<sup>3</sup> Ni d <sup>8</sup>	8	-2269.221160	-2269.386339	-4.49a	-4.75b
$^{2}$ Cu d $^{9}$	6	-2401.807669	-2401.507195	+8.18 <i>a</i>	−7.52b, −2.17c
$^1$ Zn d $^{10}$	10	-2540.729908	-2540.386014	+9.36 <i>a</i>	-4.31c

<sup>1</sup> BE values labeled a are from this work; those labeled b and c are from [26,28] respectively.

Misra and co-workers reported [30] that the triplet Fe@C<sub>20</sub> was lower in energy than the maximum-multiplicity quintet; we confirmed that finding, with our  $\omega$ B97/XD/cc-pVDZ placing the triplet 0.09 eV lower than the quintet. The structure of the triplet is quite different from that of the quintet. Similarly, for Cr, we find the triplet more stable by 0.57 eV, and of distinct structure. Neither of these revisions alter the thermodynamic instability of the endohedral species.

# 4.2.2. The Ne@C<sub>20</sub> Reference System

As a reference for further discussion of the series  $M@C_{20}$  with M being members of the first transition series of the periodic table, we report the QTAIM analysis for Ne@C20. Figure 13 displays the connectivity for this system.



**Figure 13.** Two views of Ne $@C_{20}$ , according to the QTAIM analysis. (a) Structure of Ne $@C_{20}$  according to QTAIM analysis. Color coding has C atoms in dark gray, Ne atom in light blue–gray. (b) Schlegel diagram for the C<sub>20</sub>, with the central atom represented by the dot.

Solid black "interaction lines" follow ridges in the electron density and connect nuclear centers, i.e., (3, -3) critical points. Green dots mark line critical points (LCPs) of type (3, -1). (b) an adaptation of a Schlegel representation of the  $C_{20}$  cage, with the Ne atom shown as a dot. In  $D_{3d}$  symmetry, there are three distinct Ne-C connections: along the  $D_3$  axis; to a C which is a neighbor to a C on the axis; and to a C, which has no such neighbor on the axis

The numerical results of a QTAIM analysis for Ne@C<sub>20</sub> are shown in Table 5. In  $D_{3d}$  symmetry there are four distinct types of CC interactions in the fullerene shell, with density at the LCPs ranging from 0.22 to 0.28 atomic units. This is typical of carbon-carbon bonds. There are 20 Ne-C interaction lines, in three symmetry equivalent sets of two, six, and twelve. In contrast to the CC LCP densities, the Ne-C LCP densities are much smaller. The Laplacian values are negative for CC interactions, suggesting charge accumulation characteristic of covalent bonding. Laplacian values for Ne-C lines are smaller and positive, suggesting charge depletion at the LCPs, characteristic of closed shell–closed shell interactions.

**Table 5.** The coordination around Ne atom in Ne@C<sub>20</sub>. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density ρ at LCP	$\nabla^2\rho$ at LCP	DI	G	V	Н
a (to C along D3 axis)	2.0183	0.0591	+0.3438	0.0825	0.0870	-0.0879	-0.0009
b (to a neighboring C)	2.0336	0.0566	+0.3227	0.0762	0.0822	-0.0822	+0.0023
c (to a non-neighboring C)	2.1047	0.0512	+0.3042	0.0642	0.0746	-0.0732	+0.0014

DI (delocalization index) is a measure of electron sharing. H (=G + V) < 0 suggests a degree of covalent bonding.

Energy density values at LCPs further distinguish the interactions. The Ne-C interaction, for which H is near zero and |V|/G is near 1, is not dominated by either extreme of ionic or covalent interaction. DI, an index of electron pair sharing, is very small for the Ne-C interactions, in contrast to the CC bonds which are highly covalent and have multiple bond character.

We use the properties of Ne-C bonds, as revealed in QTAIM analysis, as a basis for comparison for the series of  $M@C_{20}$  systems. Explicitly these are LCP densities in the range 0.05 to 0.06; Laplacian values near 0.33; DI near 0.08; and balanced covalent/ionic interactions.

We take the averages of QTAIM parameters for Ne@C<sub>20</sub> as a reference for discussion of the M@C<sub>20</sub> species described below. That is, we will consider departures from 1: the D<sub>3d</sub> symmetry; 2. The mean Ne-C distances, 2.02 (short) and 2.10 (long); The LCP density 0.055; the mean Laplacian +0.32; the mean DI 0.075; the kinetic energy density 0.0821; the potential energy density V; and the near-perfect balance between G and V (H = G + V near zero).

Though there are 20 interactions between Ne and C in Ne $^{\circ}C_{20}$  identified by QTAIM, one would never claim twenty-fold valency of the noble gas. It is already remarkable that QTAIM would consider ca. 1.50 electron pairs to be shared between Ne and the C<sub>20</sub> shell.

The NCI analysis shown in Figure 14 displays small NCI zones at ring critical points and considerably larger zones between the central Ne and the fullerene shell. The color coding has blue as attractive and red as repulsive, so we infer that for the Ne-C connection the steric (Pauli pressure) repulsion is larger than the dispersive (London force) attraction.



**Figure 14.** View down a threefold axis for  $D_{3d}$  Ne@C<sub>20</sub>. Color coding of NCI zones has red designating repulsive, blue attractive, and green weak interactions. Here we see small NCI repulsions at ring centers and larger zones between Ne and C.

In the following sections we present results for  $M@C_{20}$ , with a minimum of discussion. Comparisons are deferred to Section 4.2.14. Presentation of results for each metal (Sections 4.2.3–4.2.13) follows the format established for the  $Zn@C_{20}$  example.

NCI results are presented in summary form, in Section 4.2.15.

# 4.2.3. QTAIM Analysis for Ca@C<sub>20</sub> (d<sup>0</sup> Spin Singlet)

Figure 15a displays the C and Ca nuclei, that is, (3, -3) critical points, as spheres. Interaction lines between atoms and their (3, -1) critical points define the structure of the electron density distribution. Figure 15b provides a schematic view of the ten interactions between Ca and fullerene C atoms, and defines the labeling used in Table 6.

**Table 6.** The coordination around Ca atom (triplet). Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density <b>ρ</b>	$ abla^2 ho$	DI	G	V	Н
Ca to C in polar 5-rings	2.1112	0.0782	+0.3418	0.1654	0.0992	-0.1128	-0.0136



**Figure 15.** Two representations of connectivity of Ca in  $C_{20}$  fullerene. (a) Ten interaction lines connecting nuclear centers (QTAIM attractors of type (3, -3)); two types of connection are seen, along the  $C_3$  axis in  $D_{3d}$  symmetry and normal to that axis. (b) The ten interaction lines are symmetry equivalent ( $D_{5d}$ ) extending from the metal Ca to two symmetry-equivalent five membered rings on the surface.

Table 6 shows that the fullerene inclusion complex  $Ca@C_{20}$  retains high symmetry (all Ca-C distances are identical). A small density is found at the LCPs, and according to the Laplacian, charge is depleted. This is characteristic of closed shell–closed shell interactions, but the delocalization index (DI) indicates a degree of electron pair sharing. The small and negative value of H indicates a near balance of ionic and covalent bonding.

# 4.2.4. Sc@C<sub>20</sub> (d<sup>1</sup> Spin Doublet)

Figure 16a shows the QTAIM interactions lines for  $Sc@C_{20}$  while Figure 16b schematizes the interactions using an adaptation of the Schlegel diagram for the cage. Similar to the case of Ca@C<sub>20</sub>, symmetry is approximately preserved upon introduction of the endohedral atom. QTAIM data collected in Table 7 indicate approximate symmetry, weak interactions, modest pair sharing, and a balance between covalent and ionic interaction between Sc and C.

**Table 7.** The coordination around Sc atom (doublet). Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density ρ	$ abla^2 ho$	DI	G	V	Н
Sa C to a CE	2.118	0.0832	+0.3233	0.1852	0.1009	-0.1201	-0.03
50- C 10 a C5	to	to	to	to	to	to	to
ring	2.106	0.0810	+0.3158	0.1784	0.0842	-0.1172	-0.02

DI (delocalization index) is a dimensionless measure of electron sharing. Energy densities G and V are in Hartrees/cubic Bohr, i.e., atomic units. H (which = G + V) < 0 suggests a degree of covalent bonding.



**Figure 16.** Two representations of connectivity of Sc in C<sub>20</sub> fullerene. (a) Twenty lines with  $\nabla \rho = 0$  connecting nuclear centers (QTAIM attractors of type (3, -3)); two types of connection are seen, along the C<sub>3</sub> axis in D<sub>3d</sub> symmetry and normal to that axis. (b) Adaptation of a Schlegel diagram for M@C<sub>20</sub> (dodecahedral); QTAIM interaction lines extend from the metal (Sc, represented by the central dot) to each vertex.

There are 20 C-Sc interaction lines, with greater LCP density and DI than is found for Ca@C<sub>20</sub>. Sc is near the center of the fullerene. Counterintuitively, the basin charge for the Sc atom is +1.47 |e| with charge on C atoms—or more properly (3, -3) CPs—about -0.07 |e|.

# 4.2.5. Ti@C<sub>20</sub> (d<sup>2</sup> Spin Triplet)

Figure 17a shows the QTAIM interaction lines defining the density for  $TiC_{20}$ . Ti interacts with all twenty fullerene carbons; the Schlegel diagram in Figure 17b displays the fullerene net and the central atom.



**Figure 17.** Two representations of connectivity of Ti in C20 fullerene. (a) Twenty lines with  $\nabla \rho = 0$  connecting nuclear centers (QTAIM attractors of type (3, -3)); two types of connection are seen, along the C3 axis in D3d symmetry and normal to that axis. (b) Adaptation of a Schlegel diagram for M@C20 (dodecahedral); QTAIM interaction lines extend from the metal (Ti, represented by the central dot) to each vertex.

Table 8 collects the Ti-C interatomic distances and QTAIM parameters for the Ti-C interaction LCPs. These have increased relative to Ne $@C_{20}$ , Ca $@C_{20}$ , and Sc $@C_{20}$ , indicating a strengthening interaction between the fullerene cage and the endohedral metal atom.

**Table 8.** The coordination around Ti atom (triplet). Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density $\rho$	$ abla^2 ho$	DI	G	V	Н
Ti C square plane	2.087	0.0851	+0.3228	0.2230	0.1016	-0.1225	-0.0209
Ti-C four triangles C4	2.101	0.0877	+0.3190	0.2121	0.0901	-0.1228	-0.0327
Ti-C four triangles S4	2.101	0.0874	+0.3148	0.2233	0.0980	-0.1173	-0.0193

DI (delocalization index) is a measure of electron pair sharing. H (= G + V) < 0 suggests a degree of covalent bonding.

# 4.2.6. V@C<sub>20</sub> (d<sup>3</sup> Spin Quartet)

Figure 18a,b displays the interactions in  $V@C_{20}$ , and the V-C interaction lines respectively. Figure 18b defines the labeling system for Table 9.



**Figure 18.** Two representations of connectivity of V in C<sub>20</sub> fullerene. (a) Twelve lines with  $\nabla \rho = 0$  connecting nuclear centers (QTAIM attractors of type (3, -3)). (b) Labeling scheme for interaction lines.

**Table 9.** The coordination around V atom (quartet). Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density <b>ρ</b>	$ abla^2 ho$	DI	G	V	Н
a, a'	2.1356	0.0719	+0.2772	0.1737	0.0830	-0.0967	-0.0137
b, b′	2.0790	0.0917	+0.3026	0.3749	0.1272	-0.1686	-0.0414
с	1.9737	0.1214	+0.3958	0.2337	0.1165	-0.1686	-0.0531
d	2.1088	0.0839	+0.2454	0.4793	0.1141	-0.1553	-0.0412
e, e'	1.9785	0.1135	0.3426	0.2814	0.1014	-0.1272	-0.0258
f, f'	1.9915	0.1112	0.3179	0.3706	0.1196	-0.1598	-0.0402
g, g'	2.0299	0.1036	0.2801	0.3550	0.1059	-0.1419	-0.0360

 $\overline{DI}$  (delocalization index) is a measure of electron pair sharing. H (=G + V) < 0 suggests a degree of covalent bonding.

Table 9 shows that the symmetry for  $V@C_{20}$  is disrupted, and some interactions have become strong. The negative value of H and its larger magnitude relative to values for Ca-Ti indicates that covalent bonding has become more significant.

# 4.2.7. Cr@C<sub>20</sub> (d<sup>4</sup> Spin Quintet)

QTAIM interaction lines characterize the electron density in  $Cr@C_{20}$  (Figure 19a) and are the basis for the schematic representation in Figure 19b, which defines the labeling used in Table 10.



**Figure 19.** Two representations of connectivity of Cr in C<sub>20</sub> fullerene. (a) Ten lines with  $\nabla \rho = 0$  connecting nuclear centers (QTAIM attractors of type (3, -3)). (b) Labeling scheme for interaction lines.

**Table 10.** The coordination around Cr atom (quintet) in Cr@C<sub>20</sub>. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density <b>ρ</b>	$ abla^2 ho$	DI	G	V	Н
а	2.0919	0.0928	+0.1693	0.4136	0.0928	-0.1108	-0.0180
b, b′	1.8910	0.1249	+0.2496	0.3498	0.1249	-0.1772	-0.0523
c, c′	1.9854	0.1165	+0.2913	0.3903	0.1165	-0.1686	-0.0531
d, d'	1.9880	0.1142	+0.3196	0.3869	0.1142	-0.1687	-0.0545
e	1.9068	0.1221	+0.2656	0.4725	0.1221	-0.1765	-0.0544
f, f′	2.0248	0.1138	+0.3373	0.3498	0.1138	-0.1739	-0.0601

 $\overline{\text{DI}}$  (delocalization index) is a measure of electron sharing. H (=G + V) < 0 suggests a degree of covalent bonding.

QTAIM entries for  $CrC_{20}$  in Table 10 indicate a continuation of a trend toward greater distortion of the fullerene and stronger and more covalent interactions its carbon atoms with the endohedral atom.

# 4.2.8. Mn@C<sub>20</sub> (d<sup>5</sup> Spin Sextet)

Figure 20a displays the QTAIM interactions lines characterizing the fullerene framework and connections between certain C atoms and the endohedral Mn atom. In Figure 20b we see the labeling scheme for entries in Table 11. Note the sudden decrease in the number of lines connecting Mn and C atoms.

Coordination	Length	Density ρ	$ abla^2 ho$	DI	G	V	Н
а	1.9048	0.1390	+0.2419	0.5599	0.1269	-0.1935	-0.0666
b, b'	1.9074	0.1259	+0.2296	0.4752	0.1274	-0.2022	-0.0748
e	2.2543	0.0625	+0.1928	0.1152	0.0475	-0.0647	-0.0172

**Table 11.** The coordination around Mn atom (sextet) in Mn@C<sub>20</sub>. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

 $\overline{DI}$  (delocalization index) is a measure of electron sharing. H (=G + V) < 0 suggests a degree of covalent bonding.



**Figure 20.** Two representations of connectivity of Mn in C<sub>20</sub> fullerene. (a) Four lines with  $\nabla \rho = 0$  connecting nuclear centers (QTAIM attractors of type (3, -3)). (b) Labeling scheme for interaction lines.

Table 11 shows the shortening of Mn-C bonds and the enhanced, density, DI, and covalency in this system.

# 4.2.9. Fe@C<sub>20</sub> (d<sup>6</sup> Spin Quintet)

Interaction lines obtained from QTAIM analysis for  $Fe@C_{20}$  are shown in Figure 21a. The notation used in Table 12 is defined in Figure 21b.



**Figure 21.** Two representations of connectivity of Fe in C<sub>20</sub> fullerene. (a) Five lines with  $\nabla \rho = 0$  connecting nuclear centers (QTAIM attractors of type (3, -3)). (b) Labeling scheme for interaction lines.

Coordination	Length	Density ρ	$ abla^2 ho$	DI	G	V	Н
а	1.8598	0.1380	+0.2087	0.5135	0.1269	-0.1935	-0.0666
b, b′	1.8588	0.1376	+0.2076	0.5150	0.1274	-0.2025	-0.0851
d	1.9874	0.1046	+0.3675	0.2707	0.0693	-0.1721	-0.1028
e	2.3621	0.0453	+0.1686	0.1059	0.0475	-0.0529	-0.0054

**Table 12.** The coordination around Fe atom (quintet) in Fe@C<sub>20</sub>. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

 $\overline{DI}$  (delocalization index) is a measure of electron sharing. H (=G + V) < 0 suggests a degree of covalent bonding.

QTAIM parameters collected in Table 12 show that the Fe complex has more interaction lines than Mn, and that the covalency is higher for Fe than for Mn. The departure from high symmetry of the fullerene of Fe@C<sub>20</sub> is even greater than that seen in Mn@C<sub>20</sub>.

# 4.2.10. Co@C<sub>20</sub> (d<sup>7</sup> Spin Quartet)

Figure 22a shows QTAIM interaction lines for  $Co@C_{20}$ ; note the lack of connection between C atoms in the base. Figure 22b defines the labeling scheme used in Table 13.



**Figure 22.** Two representations of connectivity of Co in C<sub>20</sub> fullerene. (a) Eight lines with  $\nabla \rho = 0$  connecting nuclear centers (QTAIM attractors of type (3, -3)). (b) Labeling scheme for interaction lines.

**Table 13.** The coordination around Co atom (quintet). Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density <b>ρ</b>	$ abla^2 ho$	DI	G	V	Н
а	1.8973	0.1336	+0.3179	0.4173	0.1366	-0.1935	-0.0569
b, b′	1.8438	0.1442	+0.2913	0.4750	0.1442	-0.2155	-0.0713
c, c'	1.8445	0.1444	+0.2914	0.4725	0.1442	-0.2156	-0.0714
d, d'	1.8374	0.1358	+0.2370	0.5672	0.1360	-0.2127	-0.0767
e	1.8975	0.1336	+0.3183	0.4184	0.1366	-0.1938	-0.0400

DI (delocalization index) is a measure of electron sharing. H (=G + V) < 0 suggests a degree of covalent bonding.

Table 13 shows the compression of the C20 cage, and the increase in bond strength measures density, DI, and |V|/2.

# 4.2.11. Ni@C<sub>20</sub> (d<sup>8</sup> Spin Triplet)

Figure 23a shows QTAIM interaction lines deduced from the density for Ni@C<sub>20</sub>; note the lack of connection between C atoms in the base. The system of notation used in Table 14 is defined in Figure 23b.



**Figure 23.** Two representations of connectivity of Ni in C<sub>20</sub> fullerene. (a) Eight lines with  $\nabla \rho = 0$  connect nuclear centers (QTAIM attractors of type (3, -3)). (b) Labeling scheme for interaction lines.

**Table 14.** The coordination around Ni atom (triplet) in Ni@C<sub>20</sub>. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density <b>ρ</b>	$ abla^2 ho$	DI	G	V	Н
а	1.9285	0.1137	+0.2350	0.3770	0.1171	-0.1571	-0.0400
b, b′	1.8518	0.1297	+0.2836	0.4426	0.1369	-0.2030	-0.0661
c, c'	1.8516	0.1297	+0.2835	0.4427	0.1369	-0.2030	-0.0661
d, d′	1.8306	0.1329	+0.2347	0.5188	0.1289	-0.1991	-0.0702
e	1.9285	0.1137	+0.2683	0.3770	0.1171	-0.1571	-0.0400

DI (delocalization index) is a measure of electron sharing. H (=G + V) < 0 suggests a degree of covalent bonding.

Table 14 shows that the Ni $@C_{20}$  endohedral fullerene is still seriously compressed; the strength of Ni-C bonding is reflected in a relatively large LCP density, DI, and |V|/2.

# 4.2.12. Cu@C<sub>20</sub> (d<sup>9</sup> Spin Doublet)

Figure 24a depicts the interaction lines connecting nuclear centers for  $Cu@C_{20}$  and Figure 24b defines the notation used in Table 15.

**Table 15.** The coordination around Cu atom (doublet) in Cu@C<sub>20</sub>. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units.

Coordination	Length	Density $\rho$	$ abla^2  ho$	DI	G	V	Н
a, a'	2.0034	0.0785	+0.3038	0.2454	0.1077	-0.1395	-0.0318
b, b′	1.9726	0.0978	+0.3177	0.2348	0.1155	-0.1586	-0.0475
d	1.9766	0.0967	+0.3128	0.2604	0.0956	-0.1475	-0.0531
е	2.0520	0.0785	+0.2960	0.1740	0.0642	-0.1172	-0.0530

DI (delocalization index) is a measure of electron sharing. H (=G + V) < 0 suggests a degree of covalent bonding.



**Figure 24.** Two representations of connectivity of Cu in C<sub>20</sub> fullerene. (a) Six lines with  $\nabla \rho = 0$  connect nuclear centers (QTAIM attractors of type (3, -3)). (b) Labeling scheme for interaction lines.

Table 15 shows that while the fullerene in  $Cu@C_{20}$  is compressed relative to C20 itself, the size reduction and the departure from symmetry is minor.

# 4.2.13. Zn@C<sub>20</sub>

Figure 25 shows the network of interaction lines as defined by a QTAIM analysis, and a schematic representation of interactions with the labeling scheme used in Table 16.



**Figure 25.** Two representations of connectivity of Zn in C<sub>20</sub> fullerene. (a) Ten lines with  $\nabla \rho = 0$  connecting nuclear centers (QTAIM attractors of type (3, -3)). (b) Labeling scheme for interaction lines.

Coordination	Length	Density <b>ρ</b>	$ abla^2 ho$	DI	G	V	Н
a, a'	2.0792	0.0763	+0.2898	0.1333	0.0950	-0.1175	-0.0225
b, b′	2.0788	0.0763	+0.2897	0.1332	0.0948	-0.1172	-0.0220
d	2.0792	0.0765	+0.2901	0.1334	0.0964	-0.1174	-0.0110
e	2.0786	0.0761	+0.2960	0.1334	0.0948	-0.1173	-0.0221
f, f'	2.0775	0.0762	+0.2891	0.1330	0.0947	-0.1171	-0.0218
g, g'	2.0786	0.0762	0.2894	0.1333	0.0948	-0.1173	-0.0221

**Table 16.** The coordination around Zn atom (doublet) in Zn@C<sub>20</sub>. Interatomic distances are in Angstroms. Density  $\rho$  and its Laplacian  $\nabla^2 \rho$  are in atomic units. To a good approximation the system is D<sub>5d</sub>—symmetric.

DI (delocalization index) is a measure of electron sharing. H (=G + V) < 0 suggests a degree of covalent bonding.

In Table 16 we find a very uniform set of QTAIM parameters, characteristic of a near-perfect symmetry in the  $Zn@C_{20}$  system.

# 4.2.14. Summary Remarks on QTAIM Description of M@C<sub>20</sub>

Calculations with a  $\omega$ B97XD/cc-pVDZ density functional model have produced structures and energetics for the M@C<sub>20</sub> inclusion complexes of fullerenes, with metals M = Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. A reference is provided by the Ne@C<sub>20</sub> and Ar@C<sub>20</sub> complexes, which are centrosymmetric. In some cases (vanadium, manganese, and iron especially—see Figure 26) the inclusion complexes depart seriously from the high symmetry assumed in initial model-building. All reported structures occupy relative minima in the potential surfaces (they are stable with respect to small distortions). However, the inclusion complexes are not always thermodynamically stable relative to symmetric  $C_{20}$  and free gas phase metal.



**Figure 26.** A M3 (max—mean—min) plot for M to C distances in the series  $M@C_{20}$ , M from Ca to Zn. The radius of I<sub>h</sub>—symmetric C<sub>20</sub> is 2.030 A and the Ne-C distances in the D<sub>3d</sub> Ne reference vary from 2.0183 to 2.1047 A. Most species display M-C distances within this range, though Mn and Fe have large ranges of M-C distances; Co and Ni shrink the C<sub>20</sub> envelope. Argon expands C<sub>20</sub> to Ar-C distances ranging from 2.159 to 2.187 A.

We take the averages of QTAIM parameters for Ne@C<sub>20</sub> as a reference for discussion of the M@C<sub>20</sub> species described below (see Table 17). That is, we will consider departures from (a) the D<sub>3d</sub> symmetry; (b) the mean Ne-C distances, which range from 2.02 (short) to 2.10 (long); (c) the mean LCP density 0.055; (d) the mean Laplacian +0.32; (e) the mean DI 0.075; (f) the mean kinetic energy density 0.082; (g) the potential energy density V, and (h) the near-perfect balance between G and V (H = G + V near zero).

M@C20	Density M-C LCP	Laplacian M-C LCP	Н (G-V)	-V/2	Radius (C20)	vdW Radius <sup>1</sup> Q	Range of DI
Ne	0.0591 0.0512	0.344 0.322	<0.010	0.044 0.041	2.034 2.018	$\begin{array}{c} 154 \\ -0.004 \end{array}$	0.082 0.076
Са	0.7840	0.340	-0.014	0.056	2.111	194 1.028	0.165
Sc	0.0832 0.0810	0.323 0.316	$-0.03 \\ -0.02$	0.060 0.058	2.118 2.106	184 1.474	0.185 0.178
Ti	0.0874 0.0851	0.3228 0.3150	$-0.033 \\ -0.019$	-0.1227 -0.1173	2.0814 2.0814	176 1.732	0.2223 0.2120
V	0.1135 0.1036	0.396 0.280	$-0.036 \\ -0.0193$	0.071 0.064	2.03 1.97	171 1.620	0.355 0.281
Cr	0.1249 0.1138	+0.2496 0.3373	$-0.060 \\ -0.052$	0.089 0.084	1.891 2.025	166 1.432	0.472 0.350
Mn	0.1350 0.1259	0.2419 0.2296	$-0.067 \\ -0.075$	0.1011 0.0967	2.10 2.09	161 1.362	0.560 0.475
Fe	0.1380 0.1046	0.2076 0.3675	$-0.067 \\ -0.085$	0.0967 0.1012	1.86 1.99	156 1.298	0.514 0.377
Со	$0.1358 \\ 0.1444$	0.2370 0.3183	$-0.040 \\ -0.077$	0.0967 0.1077	1.837 1.897	152 0.920	0.519 0.377
Ni	0.1329 0.1137	0.2347 0.3183	$-0.077 \\ -0.040$	0.0995 0.0786	1.831 1.923	149 0.834	0.519 0.377
Cu	0.0978 0.0785	0.3177 0.3038	$-0.053 \\ -0.032$	0.0793 0.0698	1.973 2.003	145 0.999	0.260 0.245
Zn	0.0762	0.2930	-0.022	0.0586	2.079	142 1.404	0.133
Ar	0.1202 0.0742	0.3305 0.1568	$-0.052 \\ -0.010$	0.0721 0.0516	2.180 1.968	$     188 \\     -0.051 $	0.366 0.156

**Table 17.** Ne@C<sub>20</sub> is a reference, with LCP densities in the range 0.05 to 0.06; Laplacian values near 0.33; DI near 0.08; and balanced covalent/ionic interactions (|H| near zero). All energies are in Hartrees; the van der Waals radii are in picometers and charges are in absolute electrons |e|.

<sup>1</sup> van der Waals radii are from [51].

A detailed numerical comparison with the Ne reference is compiled in Table 17. Entries show maximum and minimum values for the several parameters, which for distorted systems can span a considerable range.

A few examples will illustrate broad trends. Figure 26 shows M-C distances for the series Ca-Zn. The vertical lines through dots representing mean values are not error bars but rather represent the range of values of the bond distance. The range of values reflects the departure from a perfect sphere, which is minimal for Ca, Sc, and Ti at the beginning of the row, and Cu and Zn at the end. There is recognizable shortening beginning with V, and serious shortening for Co and Ni.

These features are imposed on the trend in van der Waals radii of the endohedral atoms [51]. The van der Waals radii decrease monotonically across the row, with argon then increasing sharply.

Figure 27 shows the electron density at line critical points for M-C interactions. The magnitude of the density is associated with the strength of the interaction. It shows a broad maximum extending from Mn to Ni. The vertical lines through dots representing mean values represent the range of values of the LCP densities. Ne@C<sub>20</sub> values range from to 0.0521 to 0.0591. M@C<sub>20</sub> density values at LCPs are substantially higher for Mn-Ni. Ar@C<sub>20</sub> values range from 0.0744 to 0.1202, reflecting the larger interaction of Ar with the C<sub>20</sub> fullerene compared with the effect of Ne.



Figure 27. A similar M3 plot for the electron density at M-C line critical points.

According to Figure 28, covalent bonding as measured by mean DI passes through a broad maximum extending from Mn to Ni. The vertical lines through dots representing mean values represent the range of values of the DI The range of values increases beginning with V, for which we see the first major distortion of the fullerene cage. Mean DI and its variance decrease sharply for Cu and Ni.



**Figure 28.** Delocalization Index for the series Ca-Zn. Ne@C20 values ranged from 0.064 to 0.082, and Ar@C<sub>20</sub> values from 0.156 to 0.366, once again reflecting the strong interaction between Ar and the  $C_{20}$  cage.

The LCP density reaches a maximum about 0.14 at Fe and Co, more than twice the value for Ne@C<sub>20</sub>. The bonding strength measure -V/2 is largest for Mn through Ni, up to four times the value for the Ne inclusion complex. The mean delocalization index is large for Cr through Ni, reaching a fivefold increase over the value for Ni@C<sub>20</sub>. These features

are reflected in the mean radius of the fullerene, which declines from the Ne $@C_{20}$  value (ca. 2.02 A) to 1.83 for Fe and Co.

The behavior of all measures of bonding suggests tighter M-C binding and greater distortion of the fullerene as we pass from weakly bound and very symmetric  $Ca@C_{20}$  to the late transition metals. The  $C_{20}$  cage distorts as the metals interact more strongly with particular areas of the surface. However, binding weakens and symmetry is re-established at the end of the passage with Cu and Zn. Neon provides a limit of minimal interaction between fullerene and its captured atom, while argon is large enough to have an impact on the cage structure.

4.2.15. Non-Covalent Interactions in M@C<sub>20</sub>

Figure 29 presents graphics for the zones of non-covalent interaction for all species Ca-Zn with Ne $^{\circ}C_{20}$  for reference.

Ca (d <sup>0</sup> )	Sc (d1)	Ti (d² triplet)
V (d³ quartet)	Cr (d4 quintet)	Mn (d <sup>5</sup> sextet)
Fe (d <sup>6</sup> quintet)	Co (D <sup>7</sup> quartet)	Ni (d <sup>s</sup> triplet)
Cu (doublet d)	Zn (singlet d10)	Ne (singlet)

**Figure 29.** NCI zones for  $M@C_{20}$  for M = Ca to Zn and Ne.

We find only the repulsive NCI zones at ring critical points (RCPs) of the  $C_{20}$  fivecarbon rings for calcium, scandium, chromium, manganese, copper and zinc. In contrast, the Neon endohedral system displays pronounced repulsive NCI zones between the captured atom and the  $C_{20}$  fullerene. These compounds are approximately centrosymmetric. More interesting are the non-centrosymmetric cases chromium, manganese, and iron. We note the severe increase of a CC distance for cobalt and nickel complexes. Although these endohedral complexes occupy relative minima in potential energy, attested by the absence of imaginary vibrational frequencies, this suggests that the Co and Ni complexes can easily lose their captured atom.

# 5. Conclusions

The valency theory is challenged by chemical systems which enclose single atoms in a container. We have addressed H atoms in  $H_2Rh_{13}(CO)_{24}{}^{3-}$  trianion, for which each H is enclosed in a square-pyramidal rhodium cage; H atom in  $HCo_6(CO)_{15}{}^{1-}$  anion, for which the H atom in trapped an octahedral cobalt cage, H@MgO in which the H atom occupies a hole from which O atom is absent. Ionic bonding dominates for MgO, but covalency as reflected in QTAIM theory is prominent in the H to metal interactions of the Rh and Co molecules. In these cases, the H atom shares about 1.4 electron pairs with its metallic neighbors, justifying a characterization of the bonding as hypervalent, but far short of penta- or hexa-valency.

We modeled endohedral complexes of metal atoms Ca-Zn in  $C_{20}$  fullerenes using density functional theory, which provided energetics and structures for  $M@C_{20}$  species. Our values for energetics of  $M + C_{20} \rightarrow M@C_{20}$  are at variance with values from prior studies. Lack of detail of structures impedes resolution of this issue.

We found patterns in the density-based parameters of the QTAIM theory for  $M@C_{20}$ . There seems to be a link between strength of the strength of individual M-C interaction and the number of unpaired electrons in these systems. Interactions between the trapped metal atom and the  $C_{20}$  wrapping and the accompanying distortion of  $C_{20}$  reach a peak late in the transition series (Mn-Ni), but decline for the more symmetric Cu and Ni species. This is reflected in the size of the  $C_{20}$  shell, the extent of its distortion upon trapping of the metal atom, the magnitude of the density at line critical points, the number of electron pairs shared in bonding, and the extent of covalent bonding.

The confusion in terminology for the interaction of atoms with many neighbors is, we believe, resolved by the examples given for H atom captured in cages. Rather than speaking of valency or even coordination number in these cases, it is recommended to consider that a field is defined by the cage, with spatial properties well described by the constructs of QTAIM. This is reminiscent of the crystal field theory.

The properties of transition metals confined within a  $C_{20}$  fullerene cannot be reliably described without first establishing stable structures and then reasonable energetics. This work will continue; once these properties are well characterized electrical and magnetic properties of these species can be estimated reliably.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/ 10.3390/sym13071281/s1, Coordinates of all species as .mol2 files, and a sumviz file readable by AIMALL providing QTAIM parameters for the  $1 H_2 Rh_{13} (CO)_{24}^{3-}$  trianion in its X-ray structure.

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