

Editorial

Metal Complexes with N-donor Ligands

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Complexes of transition and non-transition metals with a wide variety of N-donor ligands (like ammonia, amines, urea derivatives, Schiff bases, or N-heterocycles) comprise a highly important class of compounds in chemistry, biochemistry, material science, and the chemical industry [1–14].

The coordination chemistry of metal complexes with N-bases has high variability depending on the chemical and stereochemical nature of the central atoms, as well as the basicity, number, and arrangement of N-donor ligands within the structure of organic ligands. The reactivity of complexes strongly depends on the coordination modes, coordination sites, geometrical parameters, the presence/absence of co-ligands, and the secondary interactions between the ligands and anionic components [2,4,11,14]. These structural features and the ligand–central atom or ligand–anion interactions in the solid or solution phase offer facile routes that can be used to prepare and study several industrially important materials. For instance, the interaction of oxidizing anions with reducing N-base ligands within these complex compounds can result in mixed oxides with nanometric sizes that can be used as catalysts in various technologically important reactions, such as CO₂ reduction, Fischer–Tropsch synthesis, CO oxidation, etc. [3,12,13].

Despite intensive development over more than two hundred years, the chemistry of complexes with N-donor ligands, even if the ligand is as simple a molecule as ammonia, remains one of the most diverse and rapidly developing areas of modern chemistry. This is also promoted by the various applications of these complexes and their decomposition/reaction products, including synthesizing inorganic and organic chemicals, pharmaceuticals, polymers, ceramics, heat-resistant materials, semiconductors, etc. The complexes in and of themselves (or their thermal decomposition products) are catalysts of important chemical processes.

These ten articles form a Special Issue of *Inorganics* which seeks to reflect data on the latest advances in the chemistry of certain complexes of N-donor ligands. The papers illustrate the very comprehensive world of the inorganic complex chemistry of metals with N-donor heterocyclic ligands, including pyridine, pyrazoles, Schiff bases, cyclometallated arylpyridines, N-heterocyclic stannylenes, and simple ammonia complexes, as well as novel approaches to the synthesis of indeno[1,2-*b*]quinoxaline-ring-containing oxime complexes with spontaneous resolution processes.

The reactivity of chiral N-heterocyclic stannylene [{MeHCN(tBu)}Sn] (Compound 1) with the chalcogenide elements O₂, S, Se, and Te was investigated by Prof. A. L. Johnson's group [15]. The reaction of 1 with molecular oxygen resulted in a cyclic tristannoxane complex [{MeHCN(tBu)}₂Sn(μ-O)]₃, whereas S, Se, and Te yielded cyclo-distannachalcogenide complexes [{MeHCN(tBu)}₂Sn(μ-E)]₃ (E = S, Se, Te). The reaction products were characterized in detail with multinuclear NMR and single-crystal studies, and their assemblies and structural features were reported in detail.

The synthesis of a series of iron(III) complexes with N-phenylpyrazole-based ligands was carried out by Prof. Matthias Bauer and co-workers [16]. This paper was inspired by the success of cyclometallated iron(III) complexes in utilizing a bis-tridentate ligand motif and tried to use phenyl-1H-pyrazole as a bidentate ligand. Five complexes of the



Citation: Kótai, L. Metal Complexes with N-donor Ligands. *Inorganics* **2024**, *12*, 130. <https://doi.org/10.3390/inorganics12050130>

Received: 26 March 2024

Revised: 8 April 2024

Accepted: 26 April 2024

Published: 29 April 2024



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tris(1-phenylpyrazolato-N,C2)iron(III) core scaffold were presented, including the parent complex and four meta-substituted (phenyl ring) derivatives, which were investigated by single-crystal diffraction, UV-vis spectroscopy, cyclic voltammetry, X-ray absorption, and emission spectroscopy, and offered unique insight into their electronic structure, including DFT calculations.

Some organosilicon pyridine-2-olates ($R\text{Si}(\text{pyO})_3$, $R = \text{Me, Ph, Bn, and Allyl}$; $\text{pyO} = \text{pyridine-2-olate}$) that serve as tripodal ligands toward CuCl were studied by Prof. J. Wagler's group [17] in the preparation of complexes of the $R\text{Si}(\mu^2\text{-pyO})_3\text{CuCl}$ type. For $R = \text{allyl}$, the formation of a stable isomer compound, $(\kappa\text{O-pyO})\text{Si}(\mu^2\text{-pyO})_2(\mu^2\text{-Allyl})\text{CuCl}$, was observed. The computational analyses of this isomerization process were also performed. The presence of dry air as an oxygen source in the reactions of ligands and CuCl afforded Cu(II) complexes of $R\text{Si}(\mu^2\text{-pyO})_4\text{CuCl}$ in good yields. The reaction of $\text{Ph}_2\text{Si}(\text{pyO})_2$ and CuCl in an equimolar ratio afforded a series of $(\text{CuCl})_n$ ladder-type oligonuclear Cu(I) complexes $\text{Ph}_2\text{Si}(\mu^2\text{-pyO})_2(\text{CuCl})_n(\mu^2\text{-pyO})_2\text{SiPh}_2$ ($n = 2, 3, 4$), depending on the reaction conditions. In all of the above compounds, the pyO group was found to be Si-O -bound and, in the case of μ^2 coordination, Cu-N -bound.

A group of 18 lanthanide-containing 1D-coordination polymers ($3\text{-}(2\text{-pyridyl})\text{pyrazole}$ ($[\text{Ln}_2(2\text{-PyPzH})_4\text{Cl}_6]$, $\text{Ln} = \text{La, Nd, and Sm}$), dinuclear polymorphic complexes ($\alpha\text{-, } \beta\text{-}[\text{Ln}_2(2\text{-PyPzH})_4\text{Cl}_6]$, $\text{Ln} = \text{Sm, Eu, Gd}$, $\alpha\text{-}[\text{Tb}_2(2\text{-PyPzH})_4\text{Cl}_6]$, and $[\text{Gd}_2(2\text{-PyPzH})_3(2\text{-PyPz})\text{Cl}_5]$), mononuclear complexes ($[\text{Ce}(2\text{-PyPzH})_3\text{Cl}_3]$, $[\text{Ln}(2\text{-PyPzH})_2\text{Cl}_3]$, $\text{Ln} = \text{Tb, Dy, Ho, and Er}$), and salt-like complexes ($[\text{Gd}_3(2\text{-PyPzH})_8\text{Cl}_8]\text{Cl}$ and $[\text{PyH}][\text{Tb}(2\text{-PyPzH})_2\text{Cl}_4]$) were obtained by Prof. K. Müller-Buschbaum's group [18] in the reaction between the ligand and lanthanide chlorides at various temperatures. The antenna effect via the ligand-to-metal energy transfer was observed for certain complexes, and the highest luminescence efficiency was observed by a quantum yield of 92% in the $[\text{Tb}(2\text{-PyPzH})_2\text{Cl}_3]$ complex. The cerium ion in $[\text{Ce}(2\text{-PyPzH})_3\text{Cl}_3]$ exhibited an orange 5D-based broadband emission at ~ 600 nm, which is a good example of the strong reduction of 5D-excited states of Ce(III) .

One article in the Special Issue, authored by Prof. A. S. Potapov [19], is devoted to studying the spontaneous resolution reactions of iridium(III) and rhodium(III) (i.e., half-sandwich coordination compounds) with 11H-indeno[1,2-*b*]quinoxalin-11-one oxime. The half-sandwich complexes were synthesized via the reaction between the proligand with $[\text{M}(\text{Cp}^*)\text{Cl}_2]_2$ ($\text{M} = \text{Ir, Rh}$) dimers and the N-donor ligand in methanol. $[\text{Ir}(\text{Cp}^*)(\text{L})\text{Cl}]$ crystallizes in a centrosymmetric space group as a true racemate, whereas $[\text{Rh}(\text{Cp}^*)(\text{L})\text{Cl}]$ (2) forms a racemic conglomerate. The intermolecular $\text{C-H}\cdots\text{C}$ contacts between a pair of Ir complex enantiomers link the molecules into centrosymmetric dimers and lead to the formation of heterochiral crystals with an iridium complex. However, the intramolecular $\text{CH}\cdots\text{Cl}$ and $\text{CH}\cdots\text{C}$ contacts in the Rh complex bind all three ligands around the chiral Rh(III) metal center; thus, the combination of intermolecular $\text{CH}\cdots\text{O}$ and $\text{CH}\cdots\text{C}$ contacts was found to lead to the formation of homochiral supramolecular structures.

The reaction of 2-acetylpyridine-aminoguanidine with zinc(II) sulfate resulted in two different types of complexes, i.e., $[\text{Zn}(\text{H}_2\text{O})_6](\text{H}_2\text{L})_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ and $[\text{Zn}(\text{L})(\text{H}_2\text{O})(\text{SO}_4)] \cdot \text{H}_2\text{O}$, depending on the presence or absence of lithium acetate as a deprotonating agent, as demonstrated in the paper by Prof. M. Rodic and V. M. Leovac [20]. The first complex obtained in the absence of lithium acetate, the doubly protonated Schiff base acts as a counter ion, whereas in the presence of lithium acetate, deprotonation and coordination took place, and the Schiff base became a tridentate N3 ligand that could coordinate through pyridine, azomethine, and the imino nitrogen of the aminoguanidine residue, resulting in a two-fused five-membered chelate ring. Both complexes and the parent ligand showed strong photoluminescence.

The seventh paper in the Special Issue explored the structure and vibrational spectroscopic properties of the hemipyridine solvate of bis(pyridine)silver(I) perchlorate ($[\text{Agpy}_2\text{ClO}_4] \cdot 0.5\text{py}$), as presented by L. Kótai and his group [21]. The compound was prepared via the trituration of $[\text{Agpy}_2\text{ClO}_4]$ and $4[\text{Agpy}_2\text{ClO}_4] \cdot [\text{Agpy}_4]\text{ClO}_4$ (as the source of the solvate pyridine) in a mixed solvent of acetone–benzene = 1:1 ($v = v$) at room tempera-

ture. The solvate pyridine was connected to the perchlorate anion via its α -CH. Correlation analysis was also performed to assign the perchlorate and pyridine vibrational modes.

Prof. M. Thomas and coworkers investigated the spin states of two mononuclear iron(II) complexes with tridentate Schiff bases derived from pyridine-2,6-dicarboxaldehyde [22]. To study the spin-crossover (SCO) active species, two mononuclear Fe(II) complexes, $[\text{Fe}(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ and $[\text{Fe}(\text{L}^2)_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$, were synthesized from N6-coordinating tridentate Schiff bases derived from 2,6-bis[(benzylimino)methyl]pyridine. The complexes had Fe–N6-distorted octahedral coordination geometry and remained locked in an LS state throughout the magnetic measurement temperature range of 5 to 350 K.

One study by Prof. L. S. Vojinovic-Jesic and coworkers investigated the synthesis, spectroscopic, thermal, and biochemical properties of certain Zn(II) compounds with a pyrazole-type ligand (ethyl-5-amino-1-methyl-1H-pyrazole-4-carboxylate [23]). The reactions of this pyrazole derivative with zinc(II) halogenides in methanolic solution, or zinc(II) nitrate and acetate in acetonic solution, were studied. The following compounds were synthesized: ZnL_2Cl_2 , $[\text{ZnL}_2\text{Br}_2]$, $\text{ZnL}_2\text{I}_2 \cdot 0.5\text{MeOH}$, $[\text{Zn}(\text{L})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$, and $\{\text{ZnL}(\text{OAc})_2\}_2$.

A multi-centered solid-phase quasi-intramolecular redox reaction observed during the thermal decomposition of [(chlorido)pentaamminecobalt(III)] permanganate was described by L. Kótai's group [24] as an easy reaction route to prepare a pure-phase CoMn_2O_4 spinel. A previously unknown complex and its deuterated analog were synthesized and studied using IR and Raman spectroscopy. The presence of N–H...O–Mn hydrogen bonds initiated a solid-phase quasi-intramolecular redox reaction at $\sim 120^\circ\text{C}$ in which the Co(III) centers were also involved. The amorphous reaction product transformed after dissolving in water. The insoluble residue may contain the $\{\text{Mn}_{4-6}^{\text{III}}\text{Mn}_{0-2}^{\text{IV}}\text{O}_{12}\}_n(4-6)^{n-}$ framework, which can embed $2 \times n$ ($\text{Co}^{\text{II,III}}$) cations in the tunnels and $4 \times n$ ammonia. Its heating led to a solid $\text{Co}^{\text{II}}\text{M}^{\text{III}}_2\text{O}_4$ spinel which had an average particle size of 16.8 nm and exhibited photocatalytic activity following Congo red UV degradation.

The Special Issue also contains two important reviews by Prof. R. N. Mehrotra [25] concerning the chemistry of transition metal salts with ammonia–ligand complexes and XO_4 -type oxoanions (M=Mn, Tc, and Re), and NMR and single-crystal data regarding Au(III) cyclometallated compounds with 2-arylpyridines and their derivatives or analogues [26] were reviewed.

The first study summarized data on the challenging preparation routes of the ammine complexes of transition metals with oxidizing anions. These complexes play an important role in the development of new oxidants in organic chemistry and in the preparation of mixed oxide catalysts. The available data on the permanganate, pertechnetate, and perhenate compounds were comprehensively reviewed. The role of the ammine complexes of transition metal permanganate salts in various organic oxidation reactions (like the oxidation of benzyl alcohols and the regeneration of oxo-compounds from oximes and phenylhydrazones, including the kinetics of these processes) was evaluated in detail.

The second review, written by Prof. L. Pazderski and P. A. Abramov, systematically evaluated the data on the NMR spectroscopic and structural features of Au(III) cyclometallated compounds with 2-arylpyridines and their analogues (2-arylquinolines, 1- and 3-arylisquinolines, and 7,8-benzoquinoline), with a total of 113 references. The parameters for 554 species containing $\kappa^2\text{-N}(1),\text{C}(6')\text{-Au(III)}$, or analogous moieties (i.e., chelated by the nitrogen of the pyridine-like ring and the deprotonated ortho-carbon of the phenyl-like ring) were collected. The NMR spectroscopic data and/or single-crystal X-ray diffraction data (207 X-ray structures) were described. The biological or catalytic activity and luminescence properties of compounds were also discussed.

These papers contain important contributions on the intensively studied modern areas of the inorganic complex chemistry of N-donor ligand-containing compounds. These two comprehensive review papers offer a broad overview of the discussed compound types.

Conflicts of Interest: The author declares no conflict of interest.

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