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Article

Half-Lantern Pt(II) and Pt(III) Complexes. New Cyclometalated Platinum Derivatives

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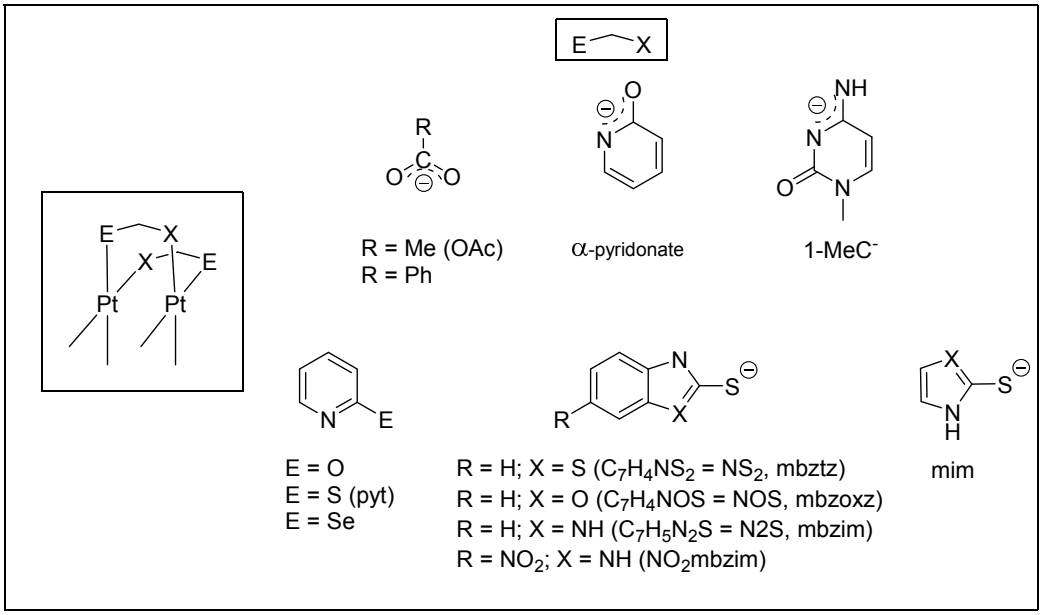
Abstract: The divalent complex [{Pt(bzq)(μ-*L*)}$_2$] (**1**) [Hbzq = benzo[h]quinolone, H*L* = $CF_3C_4H_2N_2SH$: 4-(trifluoromethyl)pyrimidine-2-thiol] was obtained from equimolar amounts of [Pt(bzq)(NCMe)$_2$]ClO_4 and 4-(trifluoromethyl)pyrimidine-2-thiol with an excess of NEt_3. The presence of a low intensity absorption band at 486 nm (CH_2Cl_2), assignable to a metal-metal-to-ligand charge transfer transition (^{1}MMLCT) [dσ*(Pt)$_2$→π*(bzq)], is indicative of the existence of two platinum centers located in close proximity because the rigidity of the half-lantern structure allows the preservation of these interactions in solution. Compound **1** undergoes two-electron oxidation upon treatment with halogens X_2 (X_2: Cl_2, Br_2 or I_2) to give the corresponding dihalodiplatinum (III) complexes [{Pt(bzq)(μ-*L*)*X*}$_2$] (*L* = $CF_3C_4H_2N_2S$-κN,S; *X*: Cl **2**, Br **3**, I **4**). Complexes **2**–**4** were also obtained by reaction of **1** with H*X* (molar ratio 1:2, 10% excess of H*X*) in THF with yields of about 80% and compound **2** was also obtained by reaction of [{Pt(bzq)(μ-Cl)}$_2$] with H*L* (4-(trifluoromethyl)pyrimidine-2-thiol) in molar ratio 1:2 in THF, although in small yield. The X-ray structures of **2** and **3** confirmed the half-lantern structure and the *anti* configuration of the molecules. Both of them show Pt–Pt distances (2.61188(15) Å **2**, 2.61767(16) Å **3**) in the low range of those observed in Pt$_2$(III,III)X_2 half-lantern complexes.

Keywords: half-lantern compounds; cyclometalated; platinum (II); platinum (III)

1. Introduction

Half-lantern compounds of platinum with two four-bond bridging groups have been known for a long time (Scheme 1). Cationic complexes derived from Cisplatin and analogues relevant to antitumor activity have been widely investigated over the last 40 years [1]. Bridging ligands for dinuclear *cis*-diaminoplatinum complexes include mainly carboxylate, α-pyridonate, amidates, and anionic nucleobases [1,2]. Some examples of divalent Pt_2(II,II) complexes are *cis*-$[Pt_2(\mu\text{-}OAc)_2(NH_3)_4]^{2+}$ [3,4], *ht*-$[Pt_2(\mu\text{-}C_5H_4NO)_2(NH_3)_4]^{2+}$ (C_5H_4NO = α-pyridonate) [5] or *ht-cis*-$[(NH_3)_2Pt(1\text{-}MeC^{-}\text{-}N3,N4)_2Pt(NH_3)_2](NO_3)_2$ (1-MeC: 1-Methylcytosine) [6], which exhibit Pt–Pt distances in the range 2.9–3.0 Å, indicating the absence of a formal metal-metal bond between the two d^8 metal ions [7]. The dimers usually stack in the crystal lattice to form infinite chains [1,3,4], with Pt–Pt separations of ~3.15 Å and hydrogen bonding between the oxygen atoms of the bridging ligands and the protons of the amine ligands, stabilizing the intermolecular interactions.

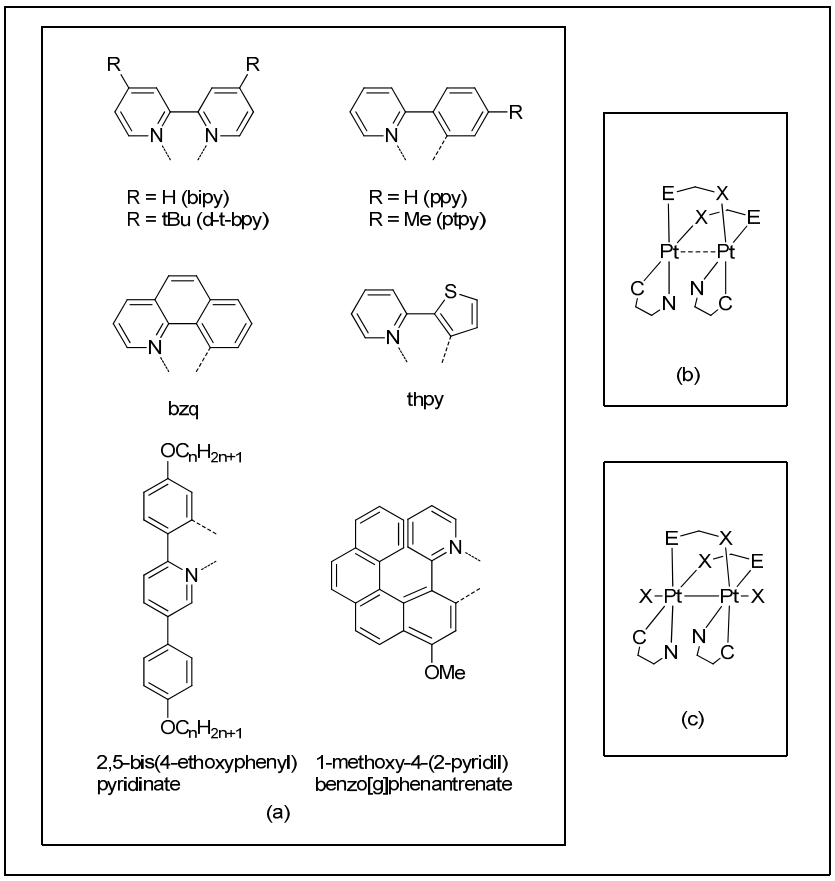
Scheme 1. Schematic structures and four-bond bridging groups.



Neutral Pt_2 (II,II) complexes with bulkier monodentate ancillary ligands [2] and carboxylate-bridging groups, such as $[Pt_2(\mu\text{-}OAc)_2(\eta^1\text{-}OAc)_2(PPh_3)_2]$ [8], show a increase of the metal-metal distance of up to 3.10 Å. In spite of this, in $[Pt_2Cl_2(\mu\text{-}O_2CMe)_2(PMe_2Ph)_2]$ the ^{31}P and ^{195}Pt NMR data [J(Pt–P') ≈ 30 Hz; J(Pt–Pt') ≈ 1000 Hz)] strongly support $M\cdots M$ interactions [9]. In complexes with pyridine-2-chalcogenolates (2-PyE^{-}, E = O, S, Se) [2], when E = O, binuclear half-lantern complexes are formed $[Pt_2Cl_2(\mu\text{-}PyE)_2(PR_3)_2]$ but no $M\cdots M$ interactions are detected from the NMR spectra. As the chalcogen size increases, monomeric complexes are predominantly formed. Four-bond ligands with a larger bite size, such as xanthates, dithiocarbamates, or dithiophosphates, render exclusively mononuclear complexes [2]. Therefore, the metal-metal separation is significantly affected by the bite

size and orientation of the bridging ligands, as well as by the bulkiness of the ancillary ones. Planar di- or tert-dentated polyimines and cyclometalated ligands do not hinder the face-to-face orientation of the metal planes, allowing metal-metal interactions to exist (Scheme 2a,b). Many of these half-lantern compounds exhibit luminescence from triplet metal-metal-to-ligand charge transfer (^{3}MMLCT) excited states. The MMLCT transition involves charge transfer between a filled Pt–Pt antibonding (dσ*) orbital and an empty ligand-based π* orbital [dσ*(Pt)$_2$→π*(*L*)] of the polyimine or the cyclometalated ligand.

Scheme 2. Schematic Pt_2(II,II) and Pt_2(III,III) structures with diimines and cyclometalated ligands.



Considering half-lantern complexes containing diimines, Kato and co-workers were able to isolate and characterize the *syn* and *anti* isomers of $[Pt_2(pyt)_2(bipy)_2][PF_6]_2$ from the mixture of both, obtained from $[PtCl_2(bipy)]$, pyridine-2-thiol and NH_4PF_6 [10]. The *syn* isomer has a head-to-head configuration of two bridging pyt and Pt···Pt separation of 2.923(1) Å. The *anti* isomer shows a head-to-tail arrangement of them and inter-metallic distance of 2.997(1) Å.

Tzeng and co-workers prepared the dinuclear diimine complexes *syn*- or *anti*-$[Pt_2(\mu\text{-}NS)_2(dtbpy)_2]^{2+}$ dtbpy = 4,4'-di-tert-butyl-2,2'-bipyridine, NHS = pyridine-2-thiol (Hpyt), 2-mercaptobenzothiazole (HNS_2), 2-mercaptobenzimidazole (HN_2S), 2-mercaptobenzoxazole (HNOS)) by reaction of the mononuclear derivative $[Pt(dtbpy)Cl_2]$ with the corresponding HNS in the presence of NaOMe [11,12]. The *anti*-$[Pt_2(pyt)_2(dtbpy)_2]^{2+}$ isomer shows a Pt···Pt distance of 2.917(2) Å and also shows photoluminescence at room temperature in the solid state (λ_{max} = 606 nm) [12]. The *syn*- or *anti*-$[Pt_2(\mu\text{-}NS)_2(dtbpy)_2]^{2+}$ (NS = NS_2, N_2S, NOS) exhibit intramolecular Pt···Pt distances

of 2.9727–3.0079 Å, which lead to Pt···Pt and π-π interactions in the solid state and, additionally, intermolecular Pt···Pt and π-π contacts in the *syn* isomers.

Changing diimines by *C*, *N*-cyclometalated fragments allowed neutral half-lantern Pt(II) complexes, such as complexes $[Pt_2(C^N)_2(pyt)_2]$ (Hpyt = pyridine-2-thiol, HC^N = 2-phenylpyridine (Hppy), 2-(*p*-tolyl)pyridine (Hptpy), 2-(2-thienyl)pyridine (Hthpy), benzo[h]quinolone (Hbzq)) to be prepared from $(NBu_4)[Pt(C^N)Cl_2]$ and Hpyt with an excess of tributylamine (NBu_3) [13,14]. These dinuclear complexes have a rigid dinuclear framework and only exhibit head-to-tail conformation due to the different *trans* influence of C and N of the C^N ligand, whereas the pyt group prefers the *N*-coordination at the *trans* position to C (Scheme 2b). Complexes $[Pt_2(C^N)_2(pyt)_2]$ (C^N = ppy, ptpy, thpy, bzq) display short Pt···Pt distance (2.82–2.88 Å), suggesting the existence of strong Pt···Pt interactions, and exhibit red luminescence at room temperature both in solid state (λ_{max} = 633–711 nm) and in solution (λ_{max} = 650–715 nm) derived from a ^{3}MMLCT origin.

The half-lantern Pt(II) complexes $[\{Pt(bzq)(\mu\text{-}C_7H_4NS_2\text{-}\kappa N,S)\}_2]\cdot Me_2CO$ and $[\{Pt(bzq)(\mu\text{-}C_7H_4NOS\text{-}\kappa N,S)\}_2]$ (Hbzq: benzo[h]quinolone; $C_7H_4NS_2$: 2-mercaptobenzothiazolate, C_7H_4NOS: 2-mercaptobenzoxazolate) were prepared selectively (yield *ca.* 80%) by reaction of $[Pt(bzq)(NCMe)_2]ClO_4$ and KC_7H_4NYS (*Y* = S, O) in 1:1 molar ratio in acetone/methanol (2:1) at room temperature [15,16]. Complex $[\{Pt(bzq)(\mu\text{-}C_7H_4NOS\text{-}\kappa N,S)\}_2]$ and the analogous $[\{Pt(ppy)(\mu\text{-}C_7H_4NOS\text{-}\kappa N,S)\}_2]$ were also obtained by one-pot reaction between $[\{Pt(C^N)(\mu\text{-}Cl)\}_2]$ (C^N, bzq, ppy) and NOSH in a ratio of 1.0:4.2 in THF at r.t. in the presence of NaOAc in yields of 32%–35% [17]. All three complexes show an *anti* configuration, with the N of the bridging groups coordinated at the *trans* position to C, and intermetallic distances of 2.91 Å, 2.97 Å (bzq) and 3.02 Å (ppy). The bzq complexes show significant π-π interactions that are absent in the ppy one. These compounds were isolated as orangish-red solids, which exhibit a weak absorption at ~500 nm and intense orangish-red photoluminescence at room temperature both in solid state (λ_{max} = 665–691 nm) and in toluene solution (λ_{max} = 660–677 nm) [15,16]. TD-DFT studies on complexes $[\{Pt(bzq)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)\}_2]$ (*Y* = S, O) [15,16] proved the ^{1,3}MMLCT character of their lower energy absorption and emission, which is affected by the strength of the π···π interactions. Complexes $[\{Pt(pbt)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)\}_2]$ (pbt: 2-phenylbenzothiazole; *Y* = S: 2-mercaptobenzothiazolate, *Y* = O: 2-mercaptobenzoxazolate) were prepared later by a similar procedure with yields of 60%–70% [18].

The half-lantern Pt_2(II,II) complexes show complex and interesting redox chemistry [19]. Oxidation of *cis*-diaminoplatinum Pt_2 (II,II) leads to oligomeric mixed-valence "platinum blues" with oxidation states varying +2.25, +2.5 and 3. Apart from these, discrete *cis*-diaminoplatinum (III) dimers, such as, *ht*-$[Pt_2(\mu\text{-}C_5H_4NO)_2(NH_3)_4X_2]^{2+}$ (C_5H_4NO = α-pyridonate, *X* = NO_3, NO_2, Cl, Br) [20,21], *ht-cis*-$[(OH_2)(NH_3)_2Pt(1\text{-}MeC^-\text{-}N3,N4)_2\text{-}Pt(NH_3)_2(OH_2)](ClO_4)_4\cdot H_2O$ [22], or *cis*-$[Pt_2(\mu\text{-}OAc)_2X_2(NH_3)_4]^{2+}$ (*X* = Cl, Br) [4] are known, with bond distances of ~2.6 Å. The diamagnetic nature of these compounds and the shortening of the Pt−Pt distance with respect to the Pt_2(II,II) are consequences of the formation of a metal-metal σ bond.

Oxidation of C, *N*-cyclometalated Pt_2(II,II) compounds do not lead to mixed-valence oligomeric species but rather to discrete Pt_2(III,III) dimers [13] (Scheme 2c). By way of example, complexes $[\{Pt(bzq)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)\}_2]$ (*Y* = S, O) undergo two-center, two-electron oxidation in their reactions with halogens (X_2 = Cl, Br, I) [15,16] to give $[\{Pt(bzq)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)X\}_2]$ (*Y* = S, O;

X = Cl, Br, I) which show Pt−Pt distances (2.63 to 2.68 Å), about 10% shorter than their starting complexes (2.91, 2.97 Å). The half-lantern $Pt_2(III,III)X_2$ compounds (*X* = Cl, Br, I) seem to be quite stable, being the final products of diverse kinds of reactions. The dichloro compounds $[Pt_2(C^N)_2(\mu\text{-pyt})_2Cl_2]$ (Hpyt = pyridine-2-thiol, HC^N = 2-phenylpyridine (Hppy), 2-(*p*-tolyl)pyridine (Hptpy), 2-(2-thienyl)pyridine (Hthpy), benzo[h]quinolone (Hbzq)) were the final products of the reactions between $(NBu_4)[Pt(C^N)Cl_2]$ and Hpyt in the absence of a base [13]; otherwise, in the presence of NBu_3, the divalent compounds $[Pt_2(C^N)_2(\mu\text{-pyt})_2]$ were formed. Compound $[Pt_2(ppy)_2(\mu\text{-pyt})_2Cl_2]$, which shows a Pt-Pt distance of 2.6150(8) Å, was also obtained by reaction of the corresponding $Pt_2(II,II)$ derivative with HCl or by recrystallization of $Pt_2(II,II)$ from chloroform [14].

$Pt_2(III,III)Cl_2$ derivatives can also be obtained by using the dinuclear complexes $[\{Pt(C^N)(\mu\text{-Cl})\}_2]$ as starting materials. Examples of this synthetic route are the synthesis of $[\{Pt(ppy)(\mu\text{-N^S})Cl\}_2]$ (HN^S = 2-mercaptobenzimidazole (mbzimH), 5-nitro-2-mercaptobenzimidazole (NO_2-mbzimH), 2-mercaptobenzothiazole (mbztzH), 2-mercaptobenzoxazole (mbzoxzH), 2-mercaptoimidazoline (mimH)) by reaction of $[\{Pt(C^N)(\mu\text{-Cl})\}_2]$ and HN^S in $CHCl_3$ at room temperature [23]. The Pt−Pt distances in these trivalent dinuclear complexes range from 2.6185(14) Å to 2.6445(3) Å.

Carboxylate-bridged $Pt_2(III,III)Cl_2$ derivatives such as $[\{Pt(C^N)(\mu\text{-}O_2CR)Cl\}_2]$ (C^N = 2,5-bis(4-ethoxyphenyl)pyridine-H, *R* = Me [24], 1-methoxy-4-(2-pyridyl)benzo[*g*] phenantrene-H, *R* = Ph [25,26]) could be obtained by reaction of the mononuclear [Pt(C^N)Cl(DMSO)] with acetic acid [24] or by reaction of the dinuclear $[\{Pt(C^N)(\mu\text{-Cl})\}_2]$ with AgO_2CPh [25,26]. The metal-metal distances in these di-μ-carboxylate complexes are 2.5730(3) Å [24] and 2.5952(6) Å [26], both of which are quite shorter than those observed in the above described complexes containing two N^S bridging groups.

None of the described half-lantern $Pt_2(III,III)$ complexes are luminescent in the visible region. In general, the d^7−d^7 complexes are no emitter, both in solution and in solid state, there being just a few exceptions, for example, $[Pt_2(\mu\text{-pop})_4X_2]^{4-}$ (pop = *P*,*P*-pyrophosphite,$P_2O_5H_2^{2-}$, *X* = Cl, Br, SCN, or py) [27,28], which exhibit red luminescence in an alcohol glass or in solid state at low temperature and $[\{Pt(\kappa^2\text{-As,C-}C_6H_3\text{-5-CHMe}_2\text{-2-AsPh}_2)_2X\}_2]$ (*X* = Cl, Br, I, CN) [29] that emit in the visible to NIR region even at room temperature.

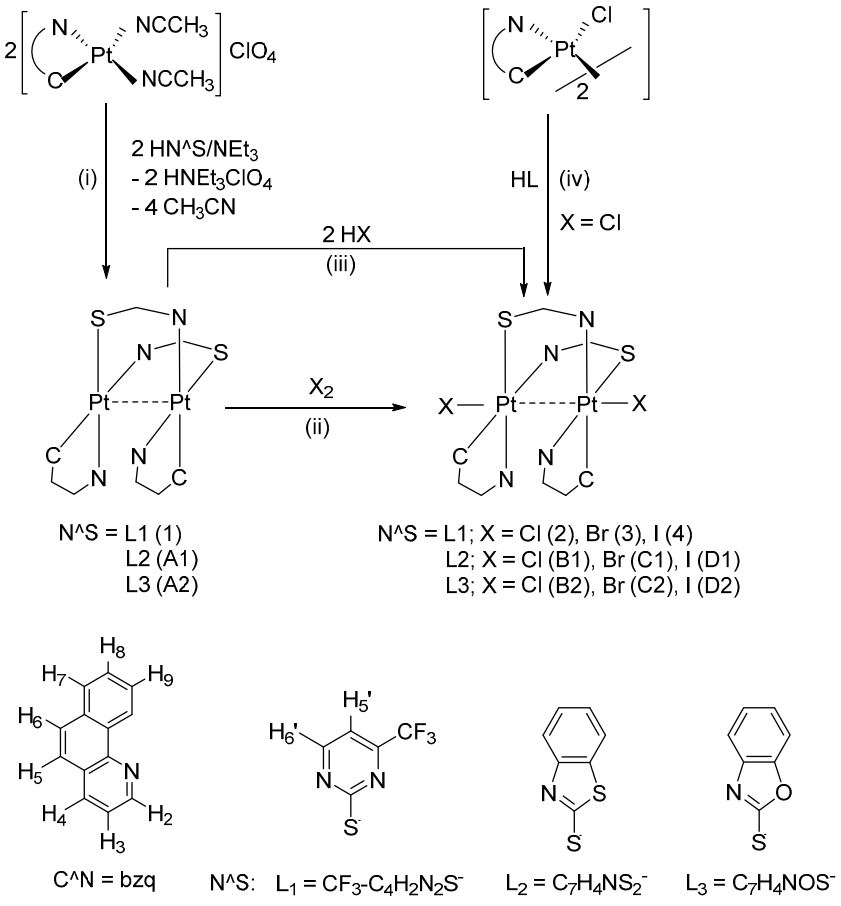
In the course of our research on half-lantern Pt(II) complexes, we have prepared a new $Pt_2(II,II)$ derivative, $[\{Pt(bzq)(\mu\text{-L})\}_2]$ [Hbzq = benzo[h]quinolone, HL = $CF_3C_4H_2N_2SH$: 4-(trifluoromethyl)pyrimidine-2-thiol] and the two-electron-oxidized dihalodiplatinum (III) complexes $[\{Pt(bzq)(\mu\text{-}L)X\}_2]$ (*L* = $CF_3C_4H_2N_2S$-κN,S; *X*: Cl, Br, I). In spite of the similarities of $[\{Pt(bzq)(\mu\text{-}CF_3C_4H_2N_2S\text{-}\kappa N,S)\}_2]$ with compounds $[\{Pt(bzq)(\mu\text{-}C_7H_4NY\text{S-}\kappa N,S)\}_2]$ (*Y* = S, O) [15,16], it showed not luminescence in the visible region and, as expected, the $Pt_2(III,III)X_2$ neither did.

2. Results and Discussion

The divalent complex $[\{Pt(bzq)(\mu\text{-}L)\}_2]$ (**1**) [Hbzq = benzo[h]quinolone, H*L* = $CF_3C_4H_2N_2SH$: 4-(trifluoromethyl)pyrimidine-2-thiol] was obtained by refluxing equimolar amounts of $[Pt(bzq)(NCMe)_2]ClO_4$ and 4-(trifluoromethyl)pyrimidine-2-thiol with an excess of NEt_3 in

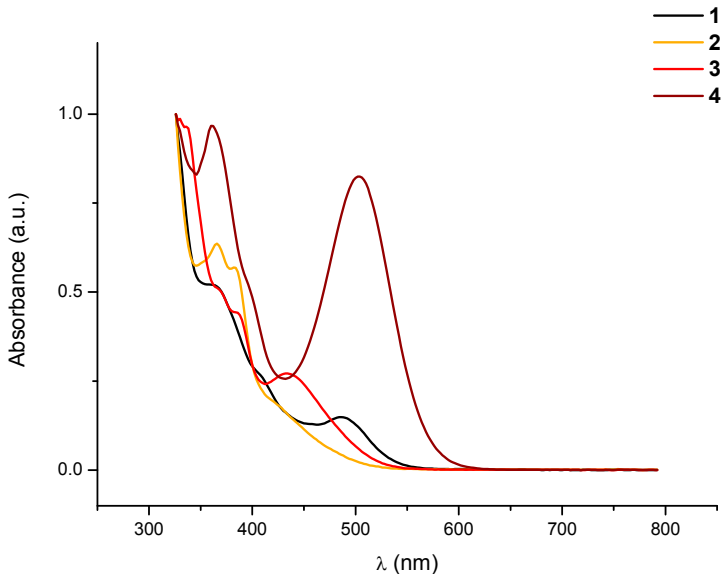
acetone-methanol. Compound **1** precipitated in the reaction mixture from which it was separated and obtained as a pinkish-red, air-stable solid in a good yield (92%) (see Scheme 3, path i, and Experimental Section). No single crystals of **1** could be grown for X-ray purposes, but evidences from other techniques lead us to propose the structure represented in Scheme 3. The dinuclear nature of **1** is revealed from its mass spectrum that shows two important peaks at *m*/*z* 1105.1 (97%) and 925.2 (100%) corresponding to $[M]^+$ and $([M\text{-}CF_3\text{-}C_4H_2N_2S]^+$ respectively. The electronic absorption spectrum of **1** recorded in CH_2Cl_2 (Figure 1) also provided some structural information. It shows a low intensity band centered at 486 nm (CH_2Cl_2), which can be tentatively assigned to a metal-metal-to-ligand charge transfer transition, (^{1}MMLCT) [dσ*(Pt)$_2$→π*(bzq)] as in the analogous half-lantern compounds [{Pt(bzq)(μ-C_7H_4NYS-κN,S)}$_2$] (*Y* = O, 480 nm CH_2Cl_2; *Y* = S, 487 nm CH_2Cl_2) [15,16]. The presence of this band due to Pt···Pt interactions is indicative of the existence of two platinum centers located in close proximity. The rigidity of the half-lantern structure would allow the preservation of these interactions in solution. The presence of only one set of signals corresponding to the bzq and the bridging $CF_3C_4H_2N_2S$-κN,S ligands, indicates that compound **1** exists as one single, symmetric isomer, most probably the *anti* one, as observed in the previously reported analogous compounds [{Pt(bzq)(μ-C_7H_4NYS-κN,S)}$_2$] (*Y* = O, S). The scarce solubility of **1** in most common solvents precludes obtaining more information about its structure in solution by other means, such as a NOE spectrum.

Scheme 3. Reaction scheme and numbering for NMR purposes.



As expected from the presumed short Pt–Pt distance, compound **1** undergoes two-electron oxidation upon treatment with halogens X_2 (X_2 = Cl_2, Br_2 or I_2) to give the corresponding dihalodiplatinum (III) complexes [{Pt(bzq)(μ-*L*)*X*}$_2$] (*L* = $CF_3C_4H_2N_2S$-κN,S; *X*: Cl **2**, Br **3**, I **4**) as yellowish-orange, orange and pinkish-red solids, respectively, in very high yield (Scheme 3, path ii and Experimental Section). The IR and ^{1}H-NMR spectra of **2**–**4** are very similar and show small changes with respect to the starting complex **1** ones; the different colors of these complexes are revealed in their UV-vis spectra (Figure 1). The X-ray studies confirmed that these Pt(III) complexes are isostructural (see below). Complexes **2**–**4** were also obtained by reaction of **1** with H*X* (molar ratio 1:2, 10% excess of H*X*) in THF with yields of about 80% (Scheme 3 path iii and Experimental Section).

Figure 1. Normalized absorption spectra in CH_2Cl_2 solution (10^{-}4 M) of **1**–**4** at room temperature.



Compound **2** was also obtained by reaction of [{Pt(bzq)(μ-Cl)}$_2$] with HL (4-(trifluoromethyl)pyrimidine-2-thiol) in molar ratio 1:2 in THF (Scheme 3 path iv and Experimental Section). This pathway rendered compound **2** with a moderate yield, as previously observed in the synthesis of the analogous compounds [{Pt(2-PhPy)(μ-*L*)Cl}$_2$] (H*L* = 2-mercaptobenzimidazole, 5-nitro-2-mercaptobenzimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptoimidazoline) [23]. The use of [{Pt(bzq)(μ-Cl)}$_2$] as starting material, has important limitations: (a) it exclusively renders the dichloro compound, preventing comparison of dichloro with dibromo and diiodo derivatives and (b) it proceeds with low yield, probably because side reactions occurred simultaneously.

The X-ray structures of **2** and **3** are shown in Figures 2 and 3 respectively and a selection of bond distances and angles is listed in Table 1. They confirmed the expected half-lantern structure and the *anti* configuration of the molecule. Each Pt (III) center has a distorted octahedral environment with the axial positions occupied by an halogen atom (Cl **2**, Br **3**) and the other Pt(III) center, and with the X–Pt–Pt angles being close to 174°. Compounds **2** and **3** show Pt-Pt distances (2.61188(15) Å **2**, 2.61767(16) Å **3**), similar to that of [$Pt_2(ppy)_2(μ\text{-}pyt)_2Cl_2$] (2.6150(8) Å) [14], all three being in the low range of those observed in Pt_2(III,III)X_2 half-lantern complexes [15,16]. The shortening of the Pt-Pt distance in **2** and **3** with respect to those of the analogous compounds (*X* = Cl: 2.6420(3) Å **B1**,

2.6383(3) Å **B2**; Br: 2.6435(4) Å **C1**, 2.6671(9) Å **C2**) [15,16] seems to be related to the NCS angle values of the 4-membered bridges. These angles are close to 120° in **2** and **3** (120.47(22)° **2**, 121.23(24)° **3**) and clearly smaller than those in **B1**(128.4(4)°), **C1**(129.03(52)°), **B2** (128.2(5)°) and **C2** (131.56(00)°). In addition, the Pt-Pt distances in **2** and **3** were shorter in the dichloro than in the dibromo derivative, in accordance with the larger *trans*-influence of Br with respect to Cl [30], as was previously observed in $[Pt_2(P_2O_5H_2)_4X_2]^{4-}$ (*X* = Cl, Br, I) [31], $[Pt_2(\mu\text{-}\kappa As,\kappa C\text{-}C_6H_3\text{-}5\text{-}CHMe_2\text{-}2\text{-}AsPh_2)_4X_2]$ (*X* = Cl, Br, I) [29], $[Pt_2(\mu\text{-}\kappa As,\kappa C\text{-}C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4X_2]$ (*X* = Cl, Br, I) [32] or $[\{Pt(bzq)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)X\}_2]$ (*Y* = O, S; *X* = Cl, Br, I) [15,16]. The Pt(III)−*X* distances are in the range of those found in other complexes with these kinds of ligands. In these dinuclear Pt_2(III,III)X_2 complexes, the two platinum coordination planes are almost parallel, with a small interplanar angle [9.79(5)° **2**, 9.76(6)° **3**] and the Pt-Pt line is almost perpendicular to the two Pt square coordination planes, the biggest angle being 5.44(4)° (Pt1−Pt2 line and Pt1 plane for compound **2**). The crystal packing of these two complexes does not show intermolecular interactions among neighbor molecules.

Table 1. Selected Bond Distances (Å) and angles (deg) of **2** and **3**.

Bonds and angles	**2** CH_2Cl_2	**3**·CH_2Cl_2
Pt(1)−C(1)	2.015(3)	2.013(3)
Pt(1)−N(1)	2.090(2)	2.092(2)
Pt(1)−$N_{\mu\text{-}N\text{^}S}$	2.151(2)	2.165(3)
Pt(1)−$S_{\mu\text{-}N\text{^}S}$	2.3016(7)	2.2995(8)
Pt(1)−*X*(1)	2.4305(7)	2.5593(3)
Pt(1)−Pt(2)	2.61188(15)	2.61767(16)
Pt(2)−C(14)	2.015(3)	2.015(3)
Pt(2)−N(2)	2.078(2)	2.080(3)
Pt(2)−$N_{\mu\text{-}N\text{^}S}$	2.151(2)	2.156(3)
Pt(2)−$S_{\mu\text{-}N\text{^}S}$	2.3036(7)	2.3047(8)
Pt(2)−*X*(2)	2.4381(7)	2.5692(3)
C(1)−Pt(1)−N(1)	81.44(11)	81.55(11)
N(1)−Pt(1)−$N_{\mu\text{-}N\text{^}S}$	93.43(9)	93.37(10)
C(1)−Pt(1)−$S_{\mu\text{-}N\text{^}S}$	96.52(8)	96.25(9)
$N_{\mu\text{-}N\text{^}S}$−Pt(1)−$S_{\mu\text{-}N\text{^}S}$	88.46(6)	88.70(7)
C(14)−Pt(2)−N(2)	81.68(11)	81.56(12)
N(2)−Pt(2)−$N_{\mu\text{-}N\text{^}S}$	93.87(9)	93.69(10)
C(14)−Pt(2)−$S_{\mu\text{-}N\text{^}S}$	96.35(9)	96.31(9)
$N_{\mu\text{-}N\text{^}S}$−Pt(2)−$S_{\mu\text{-}N\text{^}S}$	88.13(7)	88.48(7)
C(1)−Pt(1)−*X*(1)	86.94(8)	86.29(9)
N(1)−Pt(1)−*X*(1)	88.94(6)	88.73(7)
$N_{\mu\text{-}N\text{^}S}$−Pt(1)−*X*(1)	91.44(6)	92.14(7)
$S_{\mu\text{-}N\text{^}S}$−Pt(1)−*X*(1)	86.47(2)	86.71(2)
Pt(2)−Pt(1)−*X*(1)	173.389(18)	173.901()
C(14)−Pt(2)−*X*(2)	89.04(8)	88.22(9)
N(2)−Pt(2)−*X*(2)	88.51(6)	88.71(7)
$N_{\mu\text{-}N\text{^}S}$−Pt(2)−*X*(2)	91.36(6)	92.34(7)
$S_{\mu\text{-}N\text{^}S}$−Pt(2)−*X*(2)	88.25(2)	88.09(2)
Pt(1)−Pt(2)−*X*(2)	175.352(1)	175.567(9)

Differently to the analogous compounds [{Pt(bzq)(μ-C_7H_4NOS-κN,S)}$_2$] (**A1**) and [{Pt(bzq)(μ-$C_7H_4NS_2$-κN,S)}$_2$] (**A2**), compound **1** showed no luminescence either in solid or in solution and, as expected, neither did the d^7–d^7 compounds **2**–**4**.

Figure 2. Molecular Structure of compound **2**. Ellipsoids are drawn at their 50% probability level; solvent molecules and hydrogen atoms were omitted for clarity.

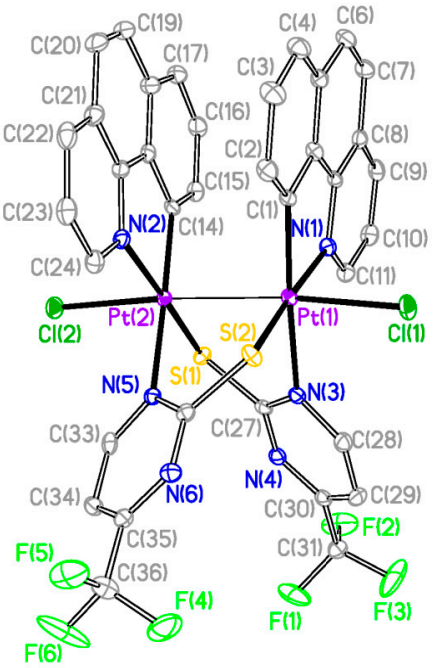
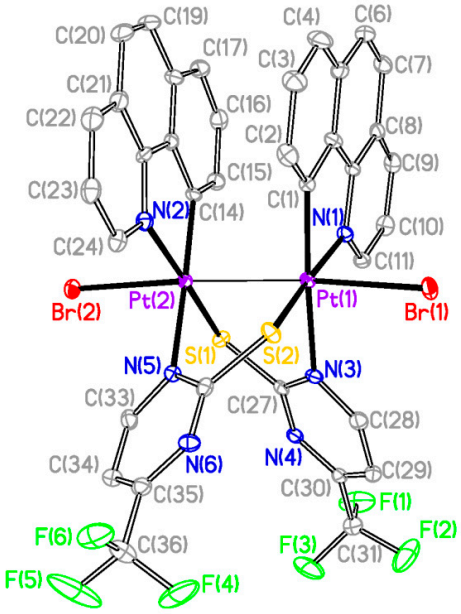


Figure 3. Molecular Structure of compound **3**. Ellipsoids are drawn at their 50% probability level; solvent molecules and hydrogen atoms were omitted for clarity.



3. Experimental Section

General procedures and materials. Elemental analyses were carried out with a Perkin Elmer (Waltham, MA, USA) 2400 CHNS analyzer. IR spectra were recorded on a Perkin-Elmer (Waltham, MA, USA) Spectrum 100 FT-IR Spectrometer (ATR in the range 250–4000 cm^{-1}). Mass spectral analyses were performed with a Microflex MALDI-TOF Bruker or an Autoflex III MALDI-TOF Bruker (Madison, WI, USA), instruments. NMR spectra were recorded on a Bruker (Madison, WI, USA) AV-400 spectrometer using the standard references: $SiMe_4$; *J* is given in Hz and assignments are based on ^1H-^1H-COSY experiments. Absorption spectra were recorded on a Thermo Electron Corporation (Waltham, MA, USA) evolution 600 spectrophotometer and diffuse reflectance UV-vis (DRUV) spectra were recorded on a Thermo Electron Corporation (Waltham, MA, USA) Evolution 600 spectrophotometer equipped with a Praying Mantis integrating sphere. The solid samples were homogeneously diluted with silica. The mixtures were placed in a homemade cell equipped with quartz window.

The starting material $[Pt(bzq)(NCMe)_2]ClO_4$ was prepared, as described elsewhere [33]. $(CF_3)C_4H_2N_2SH$ was used as purchased from Aldrich (St. Louis, MO, USA).

$[\{Pt(bzq)(\mu\text{-}(CF_3)C_4H_2N_2S\text{-}\kappa N,S)\}_2]$ (**1**). A yellowish-orange suspension of $[Pt(bzq)(NCMe)_2]ClO_4$ (0.251 g, 0.453 mmol) in acetone (20 mL) was treated with a solution of $(CF_3)C_4H_2N_2SH$ (0.082 g, 0.453 mmol) in methanol (10 mL) and NEt_3 (0.5 mL). The mixture was stirred and refluxed for 2 h and then was concentrated to about 15 mL. The resulting pinkish-red solid was filtered-off, washed with MeOH (2 × 3 mL) and Et_2O (2 × 5 mL) and dried, **1**. Yield: 0.231 g, 92%. Anal. Calcd for $C_{36}H_{20}F_6N_6Pt_2S_2$: C, 39.13; H, 1.82; N, 7.61; Found: C, 39.10; H, 1.99; N, 7.55; ^1H-NMR (CD_2Cl_2, 400.16 MHz, 298K): δ 9.10 (2H, d, ^3J(H6',H5') = 5.7; H6'), 7.97 (2H, dd, ^3J(H4,H3) = 7.9, ^4J(H4,H2) = 1.0, H4), 7.93 (2H, dd, ^3J(H2,H3) = 5.2; H2), 7.32 (2H, dd, H3), 7.20 (4H, m, H9, H5'), 7.16 (4H, AB, ^3J(H5,H6) = 8.6, H5, H6), 6.86 (2H, d, ^3J(H7,H8) = 7.5; H7), 6.64 (2H, dd, ^3J(H8,H9) = 7.5, H8) ppm; ^{19}F-NMR (CD_2Cl_2, 376 MHz, 298K): δ −70.9 (s, CF_3) ppm; MS ($MALDI^+$): *m*/*z* 925.2 ($[M - CF_3\text{-}C_4H_2N_2S]^+$, 100%), 1105.1 ($M^+$, 97%); IR ($cm^{-1}$): 1620 d, 1575 m, 1545 m, 1450 d, 1426 m, 1405 m, 1328 f, 1314 mf, 1205 f, 1178 m, 1144 f, 1113 mf, 1087 f, 1053 m, 998 m, 928 m, 841 f, 823 f, 762 m, 751 m, 730 f, 710 f, 671 f, 654 m, 526 m, 469 m, 288 m, 281 m, 264 m.

$[\{Pt(bzq)(\mu\text{-}(CF_3)C_4H_2N_2S\text{-}\kappa N,S)Cl\}_2]$ (**2**). (Method A) A solution of Cl_2 in CCl_4 0.25M (0.602 mL, 0.151 mmol) was added to a pinkish-red suspension of **1** (0.1513 g, 0.137 mmol) in THF (4 mL). The resulting orange mixture was stirred for 4 h and concentrated to 2 mL. Addition of Et_2O (5 mL) to the residue rendered a yellowish-orange solid that was filtered-off and washed with Et_2O (2 × 4 mL), **2**. Yield: 0.134 g, 83%. Anal. Calcd for $C_{36}H_{20}Cl_2F_6N_6Pt_2S_2$: C, 36.77; H, 1.71; N, 7.15; Found: C, 36.65; H, 2.06; N, 7.08; ^1H-NMR (CD_2Cl_2, 400.16 MHz, 298K): δ 10.00 (2H, d, ^3J(H6',H5') = 6.1; H6'), 8.13 (2H, dd, ^3J(H2,H3) = 5.6, ^4J(H2,H4) = 1.0, ^3J(Pt,H2) = 22.5, H2), 8.06 (2H, dd, ^3J(H4,H3) = 8.1, ^4J(H4,H2) = 1.0, H4), 7.55 (2H, dd, H3), 7.40 (2H, d, H5'), 7.29 (4H, AB, ^3J(H5,H6) = 8.8, H5, H6), 7.04 (2H, dd, ^3J(H9,H8) = 7.5; ^4J(H9,H7) = 0.8 Hz, ^3J(Pt,H9) = 31.6, H9), 6.93 (2H, d, ^3J(H7,H8) = 8.0; H7), 6.75 (2H, dd, H8) ppm; ^{19}F-NMR (CD_2Cl_2, 376 MHz, 298K):δ −70.6 (s, CF_3) ppm. IR (cm^{-1}): 1621 d, 1586 m, 1575 m, 1549 m, 1454 d, 1436 m, 1407 m, 1343 f, 1332 f, 1322 mf, 1205 f, 1185 m, 1142 f, 1116 mf, 928 m, 844 m, 830 mf, 819 m, 764 m, 731 f, 711 f, 674 f,

654 m, 514 m, 467 m, 438 m. (Method B) A solution of HCl in H_2O 1M (299 μL, 0.299 mmol) was added to a pinkish-red suspension of **1** (0.150 g, 0.136 mmol) in THF (10 mL) and the mixture was stirred for 51 h in the darkness. During this time, a yellowish-orange solid was precipitated. The solvent was evaporated to ca. 2 mL and Et_2O (10 mL) was added to the reaction mixture. The yellowish-orange solid **2**·THF was filtered-off, washed with Et_2O (2 × 5 mL) and dried to the air. Yield: 0.1368 g, 81%. (Method C) A yellow solution of $C_5H_3N_2F_3S$ (0.062 g, 0.348 mmol) in THF (20 mL) was added drop by drop to a yellow suspension of [{Pt(bzq)(μ-Cl)}$_2$] (0.142 g, 0.174 mmol) in THF (10 mL). Then, the mixture was stirred for 70 h to give a yellow solution that was evaporated to dryness. Addition of acetone (15 mL) to the residue rendered a yellowish- orange solid, **2**, that was filtered-off, washed with acetone (2 × 5 mL) and Et_2O (2 × 5 mL) and dried to the air. Yield: 0.0341 g, 24%.

[{Pt(bzq)(μ-(CF_3)$C_4H_2N_2$S-κN,S)Br}$_2$] (**3**). (Method A) was prepared in the same way as **2**, but using Br_2 (0.149 mmol 7.66 μL, *d* = 3.119 g/mL), **1** (0.150 g, 0.136 mmol). Orange solid **3**, Yield: 0.154 g, 90%. Anal. Calcd for $Br_2C_{36}H_{20}F_6N_6Pt_2S_2$: C, 34.19; H, 1.59; N, 6.65; Found: C, 33.80; H, 1.61; N, 6.71. ^{1}H-NMR (CD_2Cl_2, 400.16 MHz, 298K): δ 10.14 (2H, d, ^3J(H6',H5') = 6.0; H6'), 8.19 (2H, dd, ^3J(H2,H3) = 5.5, ^4J(H2,H4) = 1.3, ^3J(Pt,H2) = 22.2, H2), 8.05 (2H, dd, ^3J(H4,H3) = 7.8, ^4J(H4,H2) = 1.3, H4), 7.56 (2H, dd, H3), 7.38 (2H, d, H5'), 7.29 (4H, AB, ^3J(H5,H6) = 8.8 Hz, H5, H6), 7.00 (2H, dd, ^3J(H9,H8) = 7.6; ^4J(H9,H7) = 0.7, ^3J(Pt,H9) = 31.7, H9), 6.90 (2H, d, ^3J(H7,H8) = 8.0; H7), 6.74 ppm (2H, dd, H8); ^{19}F-NMR (CD_2Cl_2, 376 MHz, 298K):δ −70.6 (s, CF_3) ppm. IR (cm^{-1}): 1621 d, 1586 m, 1575 m, 1549 m, 1454 m, 1436 m, 1407 m, 1343 f, 1332 f, 1322 mf, 1205 f, 1185 f, 1142 f, 1116 mf, 1053 m, 928 m, 844 f, 830 mf, 819 f, 764 f, 731 f, 711 f, 674 f, 654 m, 514 m, 467 m, 438 m, 271 m. (Method B) A solution of HBr in H_2O 1M (296 μL, 0.296 mmol) was added to a pinkish-red suspension of **1** (0.149 g, 0.135 mmol) in THF (20 mL) and the mixture was stirred for 72 h in the darkness, while an orange solid was precipitated. The solvent was evaporated to ca. 2 mL and Et_2O (10 mL) was added to the reaction mixture. The orange solid **3**·THF was filtered-off, washed with Et_2O (2 × 5 mL) and dried to the air. Yield: 0.127 g, 70%.

[{Pt(bzq)(μ-(CF_3)$C_4H_2N_2$S-κN,S)I}$_2$] (**4**). (Method A) was prepared in the same way as **2**, but using a solution of I_2 (0.038 g, 0.151 mmol) in THF (4 mL), a suspension of **1** (0.152 g, 0.137 mmol) in THF (4 mL). Pinkish-red solid **4**, Yield: 0.162 g, 87%. Anal. Calcd for $C_{36}H_{20}I_2F_6N_6Pt_2S_2$: C, 31.82; H, 1.48; N, 6.19; Found: C, 31.58; H, 1.32; N, 6.28. ^{1}H-NMR (CD_2Cl_2, 400.16 MHz, 298K): δ 10.34 (2H, d, ^3J(H6',H5') = 6.0; H6'), 8.28 (2H, dd, ^3J(H2,H3) = 5.4, ^4J(H2,H4) = 1.1, H2), 8.05 (2H, dd, ^3J(H4,H3) = 8.0, ^4J(H4,H2) = 1.1, H4), 7.57 (2H, dd, H3), 7.35 (2H, d, H5'), 7.30 (4H, AB, ^3J(H5,H6) = 8.7 Hz, H5, H6), 6.93 (2H, dd, ^3J(H9,H8) = 7.5; ^4J(H9,H7) = 0.8, ^3J(Pt,H9) = 31.4, H9), 6.86 (2H, d, ^3J(H7,H8) = 7.8; H7), 6.71 (2H, dd, H8) ppm; ^{19}F-NMR (CD_2Cl_2, 376 MHz, 298K): δ-70.6 (s, CF_3) ppm; IR (cm^{-1}): 1620 d, 1585 m, 1574 m, 1546 m, 1453 m, 1436 m, 1407 m, 1332 mf, 1322 mf, 1205 f, 1187 m, 1158 m, 1138 f, 1116 mf, 928 m, 845 m, 829 mf, 819 m, 763 f, 731 f, 709 f, 673 f, 653 m, 512 m, 482m, 467 m, 438 m. (Method B) A solution of HI in H_2O 1M (292 μL, 0.292 mmol) was added to a pinkish-red suspension of **1** (0.147 g, 0.133 mmol) in THF (10 mL) and the mixture was stirred for 26 h in absence of light. During this time, a reddish-garnet solid was precipitated. The solvent was evaporated to ~2 mL and 10 mL of Et_2O was added. The reddish-garnet solid **4**·THF was filtered-off, washed with Et_2O (2 × 5 mL) and dried. Yield: 0.156 g, 82%.

X-ray Structure Determinations. Crystal data and other details of the structure analyses are presented in Table 2. Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into concentrated solutions of the complexes in 3 mL of CH_2Cl_2. Crystals were mounted at the end of quartz fibres. The radiation used in both cases was graphite monochromated MoKα (λ = 0.71073 Å). X-ray intensity data were collected on an Oxford Diffraction Xcalibur diffractometer. The diffraction frames were integrated and corrected from absorption using the CrysAlis RED program [34]. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 with SHELXL-97 [35]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their attached parent atoms. Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table 2. CCDC 1011979–1011980 contain the supplementary crystallographic data for compounds **2**·CH_2Cl_2 and **3**·CH_2Cl_2 [36].

Table 2. Crystal data and structure refinement for complexes [{Pt(bzq)(μ-(CF$_3$)C$_4$H$_2$N$_2$S-κN,S)Cl}$_2$]·CH_2Cl_2 (**2**·CH_2Cl_2), [{Pt(bzq)(μ-(CF$_3$)C$_4$H$_2$N$_2$S-κN,S)Br}$_2$]·CH_2Cl_2 (**3**·CH_2Cl_2).

Parameters	**2**·CH_2Cl_2	**3**·CH_2Cl_2
	$C_{37}H_{22}Cl_4F_6N_6Pt_2S_2$	$C_{37}H_{22}Br_2Cl_2F_6N_6Pt_2S_2$
M_t [g mol^{-1}]	1260.71	1349.63
T [K]	100(2)	100(2)
λ [Å]	0.71073	0.71073
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a [Å]	11.3613(3)	11.4798(2)
b [Å]	11.8938(3)	11.8668(2)
c [Å]	14.2579(3)	14.4711(3)
α [°]	90.003(2)	88.942(2)
β [°]	98.289(2)	81.111(2)
γ [°]	101.170(2)	78.410(2)
V [Å^3]	1869.64(8)	1907.83(6)
Z	2	2
ρ [g cm^{-3}]	2.239	2.349
μ [mm^{-1}]	7.942	9.737
F(000)	1192	1264
2θ range [°]	4.21–28.88	4.19–28.88
no. of reflns collected	41040	41763
no. of unique reflns	8961	9166
R(int)	0.0302	0.0318
final R indices [$I > 2\theta(I)$] [a]		
R_1	0.0207	0.0232
wR_2	0.0446	0.0516
R indices (all data)		
R_1	0.0250	0.0277
wR_2	0.0465	0.0534
Goodness-of-fit on F^2 [b]	1.024	1.058

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] Goodness-of-fit = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

4. Conclusions

The divalent complex [{Pt(bzq)(μ-L)}$_2$] (**1**) [Hbzq = benzo[h]quinolone, HL = $CF_3C_4H_2N_2SH$: 4-(trifluoromethyl)pyrimidine-2-thiol] was obtained from equimolar amounts of [Pt(bzq)(NCMe)$_2$]ClO_4 and 4-(trifluoromethyl)pyrimidine-2-thiol with an excess of NEt_3. The electronic absorption spectra of **1** shows a low intensity band at 486 nm (CH_2Cl_2) assignable to a metal-metal-to-ligand charge transfer transition, (^{1}MMLCT) [dσ*(Pt)$_2$→π*(bzq)], due to the presence of two platinum centers located in close proximity.

As expected, compound **1** undergoes two-center two-electron oxidation upon treatment with halogens X_2 (X_2: Cl_2, Br_2 or I_2) to give the corresponding dihalodiplatinum (III) complexes [{Pt(bzq)(μ-L)*X*}$_2$] (L = $CF_3C_4H_2N_2S$-κN,S; *X*: Cl **2**, Br **3**, I **4**) in a very high yield. Complexes **2**–**4** were also obtained by reaction of **1** with H*X* (molar ratio 1:2, 10% excess of H*X*) and compound **2** even by reaction of [{Pt(bzq)(μ-Cl)}$_2$] and HL (4-(trifluoromethyl)pyrimidine-2-thiol) in 1:2 molar ratio, albeit in moderate-low yield. The use of [{Pt(bzq)(μ-Cl)}$_2$] as the starting material has significant limitations: it exclusively renders the dichloro compound preventing the comparison of dichloro with dibromo and diyodo derivatives, and it proceeds with a low yield, probably because of side reactions occurring simultaneously.

The X-ray structures of **2** and **3** confirmed the half-lantern structure and the *anti* configuration of the molecules. Both of them show Pt−Pt distances (~2.61 Å) in the low range of those observed in Pt$_2$(III,III)X_2 half-lantern complexes, and their values are in accordance with the larger *trans*-influence of Br with respect to Cl. The Pt-Pt distance in Pt$_2$(III,III)X_2 compounds also seems to be related to the NCS angle values of the 4-member bridges, these being close to 120° in **2** and **3**, which is clearly less than that observed in other dichloro- and dibromo-compounds compounds (~129°) exhibiting longer intermetallic separations (~2.64 Å).

Compounds **1**–**4** showed not luminescence in the visible region.

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Author Contributions

Violeta Sicilia: Responsible for research publication. Pilar Borja: Research performer. phD student. Antonio Martín: Crystallographer.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Lippert, B. Impact of Cisplatin on the recent development of Pt coordination chemistry: A case study. *Coordin. Chem. Rev.* **1999**, *182*, 263–295.
2. Jain, V.K.; Jain, L. The chemistry of binuclear palladium(II) and platinum(II) complexes. *Coordin. Chem. Rev.* **2005**, *249*, 3075–3197.
3. Sakai, K.; Takeshita, M.; Tanaka, Y.; Ue, T.; Yanagisawa, M.; Kosaka, M.; Tsubomura, T.; Ato, M.; Nakano, T. A new one-dimensional platinum system consisting of carboxylate-bridged cis-diammineplatinum dimers. *J. Am. Chem. Soc.* **1998**, *120*, 11353–11363.
4. Wilson, J.J.; Lippard, S.J. Acetate-Bridged Platinum(III) Complexes Derived from Cisplatin. *Inorg. Chem.* **2012**, *51*, 9852–9864.
5. Hollis, L.S.; Lippard, S.J. New Reaction Chemistry of *cis*-Diammineplatinum(II) with α-Pyridone—Crystalline Relatives of the α-Pyridone Blue. *J. Am. Chem. Soc.* **1981**, *103*, 1230–1232.
6. Faggiani, R.; Lippert, B.; Lock, C.J.L.; Speranzini, R.A. Unusual Platinum Complexes of Deprotonated 1-Methylcytosine: Bis(μ-1-Methylcytosinato-*N*-3,*N*-4)-bis(*cis*-Diammineplatinum(II)) Dinitrate Dihydrate, $[(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2](NO_3)_2{\cdot}2H_2O$, and [Diaquahydrogen(1+)] [bis(μ-1-Methylcytosinato-*N*-3,*N*-4)-Bis(*cis*-Nitrodiammine-Platinum)(Pt–Pt)] Dinitrate, $(H_5O_2)[(NH_3)_2(NO_2)Pt(C_5H_6N_3O)_2Pt(NH_3)_2(NO_2)](NO_3)_2)_2$. *J. Am. Chem. Soc.* **1981**, *103*, 1111–1120.
7. Cotton, F.A.; Walton, R.A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, UK, 1993.
8. Moiseev, I.I.; Kozitsyna, N.Y.; Kochubey, D.I.; Kolomijchuk, V.N.; Zamaraev, K.I. Synthesis and Characterization of Platinum and Palladium Clusters with Phosphide Ligands. *J. Organomet. Chem.* **1993**, *451*, 231–241.
9. Kannan, S.; Jain, V.K. P-31 and Pt-195 NMR-Studies of Carboxylato-Bridged Dinuclear Platinum(II) Complexes. *Magn. Reson. Chem.* **1990**, *28*, 1007–1010.
10. Kato, M.; Omura, A.; Toshikawa, A.; Kishi, S.; Sugimoto, Y. Vapor-induced luminescence switching in crystals of the syn isomer of a dinuclear (bipyridine)platinum(II) complex bridged with pyridine-2-thiolate ions. *Angew. Chem. Int. Ed. Engl*. **2002**, *41*, 3183–3185.
11. Tzeng, B.C.; Chiu, T.H.; Lin, S.Y.; Yang, C.M.; Chang, T.Y.; Huang, C.H.; Chang, A.H.H.; Leo, G.H. Structural Isomerism of Luminescent Dinuclear Pt(II)-Thiolate Diimines. *Cryst. Growth Des.* **2009**, *9*, 5356–5362.
12. Tzeng, B.C.; Fu, W.F.; Che, C.M.; Chao, H.Y.; Cheung, K.K.; Peng, S.M. Structures and photoluminescence of dinuclear platinum(II) and palladium(II) complexes with bridging thiolates and 2,2'-bipyridine or 2,2':6',2''-terpyridine ligands. *J. Chem. Soc., Dalton Trans.* **1999**, 1017–1024.
13. Aoki, R.; Kobayashi, A.; Chang, H.C.; Kato, M. Structures and Luminescence Properties of Cyclometalated Dinuclear Platinum(II) Complexes Bridged by Pyridinethiolate Ions. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 218–225.

14. Koshiyama, T.; Omura, A.; Kato, M. Redox-controlled luminescence of a cyclometalated dinuclear platinum complex bridged with pyridine-2-thiolate ions. *Chem. Lett.* **2004**, *33*, 1386–1387.
15. Sicilia, V.; Borja, P.; Casas, J.M.; Fuertes, S.; Martin, A. Selective synthesis of new half-lantern benzoquinolate platinum complexes. DFT and photophysical studies on the platinum (II,II) derivative. *J. Organomet. Chem.* **2013**, *731*, 10–17.
16. Sicilia, V.; Fornies, J.; Casas, J.M.; Martin, A.; Lopez, J.A.; Larraz, C.; Borja, P.; Ovejero, C.; Tordera, D.; Bolink, H. Highly Luminescent Half-Lantern Cyclometalated Platinum(II) Complex: Synthesis, Structure, Luminescence Studies, and Reactivity. *Inorg. Chem.* **2012**, *51*, 3427–3435.
17. Wang, Z.; Jiang, L.; Liu, Z.P.; Gan, C.R.R.; Liu, Z.L.; Zhang, X.H.; Zhao, J.; Hor, T.S.A. Facile formation and redox of benzoxazole-2-thiolate-bridged dinuclear Pt(II/III) complexes. *Dalton Trans.* **2012**, *41*, 12568–12576.
18. Katlenok, E.A.; Balashev, K.P. Binuclear cyclometallated complexes of 2-phenylbenzothiazole with 2-mercaptothiazole and 2-mercaptobenzoxazole bridging ligands. *Russ. J. Gen. Chem.* **2014**, *84*, 791–792.
19. Katlenok, E.A.; Balashev, K.P. Optical and electrochemical properties of cyclometalated Pd(II) and Pt(II) complexes with a metal-metal chemical bond. *Opt. Spectrosc.* **2014**, *116*, 100–104.
20. Hollis, L.S.; Lippard, S.J. Redox Properties of *cis*-Diammineplatinum α-Pyridone Blue and Related Complexes—Synthesis, Structure, and Electrochemical-Behavior of *cis*-Diammineplatinum(III) Dimers with Bridging α-Pyridonate Ligands. *Inorg. Chem.* **1983**, *22*, 2605–2614.
21. Hollis, L.S.; Roberts, M.M.; Lippard, S.J. Synthesis and Structures of Platinum(III) Complexes of Alpha-Pyridone, $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X](NO_3)_2 \cdot nH_2O$ (X^- = Cl^-, NO_2^-, Br^-). *Inorg. Chem.* **1983**, *22*, 3637–3644.
22. Kampf, G.; Willermann, M.; Freisinger, E.; Lippert, B. Diplatinum(III) complexes with bridging 1-methylcytosinate ligands and variable axial ligands, including guanine nucleobases. *Inorg. Chim. Acta* **2002**, *330*, 179–188.
23. Rodriguez, A.; Romero, M.J.; Fernandez, A.; Lopez-Torres, M.; Vazquez-Garcia, D.; Naya, L.; Vila, J.M.; Fernandez, J.J. Dinuclear cyclometallated platinum(III) complexes. Relationship between molecular structure and crystal packing. *Polyhedron* **2014**, *67*, 160–170.
24. Santoro, A.; Wegrzyn, M.; Whitwood, A.C.; Donnio, B.; Bruce, D.W. Oxidation of Organoplatinum(II) by Coordinated Dimethylsulfoxide: Metal-Metal Bonded, Dinuclear, Liquid-Crystalline Complexes of Platinum(III). *J. Am. Chem. Soc.* **2010**, *132*, 10689–10691.
25. Anger, E.; Rudolph, M.; Norel, L.; Zrig, S.; Shen, C.S.; Vanthuyne, N.; Toupet, L.; Williams, J.A.G.; Roussel, C.; Autschbach, J.; *et al*. Multifunctional and Reactive Enantiopure Organometallic Helicenes: Tuning Chiroptical Properties by Structural Variations of Mono- and bis(Platinahelicene)s. *Chem. Eur. J*. **2011**, *17*, 14178–14198.
26. Anger, E.; Rudolph, M.; Shen, C.S.; Vanthuyne, N.; Toupet, L.; Roussel, C.; Autschbach, J.; Crassous, J.; Reau, R. From Hetero- to Homochiral bis(Metallahelicene)s Based on a Pt-III–Pt-III Bonded Scaffold: Isomerization, Structure, and Chiroptical Properties. *J. Am. Chem. Soc.* **2011**, *133*, 3800–3803.
27. Roundhill, D.M.; Gray, H.B.; Che, C.M. Pyrophosphito-Bridged Diplatinum Chemistry. *Acc. Chem. Res.* **1989**, *22*, 55–61.

28. Stiegman, A.E.; Miskowski, V.M.; Gray, H.B. Metal Metal Excited-State Emission from Binuclear Platinum(III) Complexes. *J. Am. Chem. Soc.* **1986**, *108*, 2781–2782.
29. Bennett, M.A.; Bhargava, S.K.; Cheng, E.C.C.; Lam, W.H.; Lee, T.K.M.; Priver, S.H.; Wagler, J.; Willis, A.C.; Yam, V.W.W. Unprecedented Near-Infrared (NIR) Emission in Diplatinum(III) (d(7)–d(7)) Complexes at Room Temperature. *J. Am. Chem. Soc.* **2010**, *132*, 7094–7103.
30. Flemming, J.P.; Pilon, M.C.; Borbulevitch, O.Y.; Antipin, M.Y.; Grushin, V.V. The trans influence of F, Cl, Br and I ligands in a series of square-planar Pd(II) complexes. Relative affinities of halide anions for the metal centre in trans-[$(Ph_3P)_2$Pd(Ph)*X*]. *Inorg. Chim. Acta* **1998**, *280*, 87–98.
31. Alexander, K.A.; Bryan, S.A.; Fronczek, F.R.; Fultz, W.C.; Rheingold, A.L.; Roundhill, D.M.; Stein, P.; Watkins, S.F. Crystal and Molecular-Structures of Dihalotetrakis(Pyrophosphito)Diplatinum(III) Complexes—Integrative Use of Structural and Vibrational Data to Assess Intermetallic Bonding and the Trans Influence of the Pt(III)–Pt(III) Bond. *Inorg. Chem.* **1985**, *24*, 2803–2808.
32. Bennett, M.A.; Bhargava, S.K.; Bond, A.M.; Edwards, A.J.; Guo, S.X.; Priver, S.H.; Rae, A.D.; Willis, A.C. Synthesis, characterization, and electrochemical relationships of dinuclear complexes of platinum(II) and platinum(III) containing ortho-metalated tertiary arsine ligands. *Inorg. Chem.* **2004**, *43*, 7752–7763.
33. Fornies, J.; Fuertes, S.; Lopez, J.A.; Martin, A.; Sicilia, V. New water soluble and luminescent platinum(II) compounds, vapochromic behavior of [$K(H_2O)$][$Pt(bzq)(CN)_2$], new examples of the influence of the counterion on the photophysical properties of d(8) square-planar complexes. *Inorg. Chem.* **2008**, *47*, 7166–7176.
34. *CysAlis RED, CCD Camera Data Reduction Program*; Oxford Diffraction: Oxford, UK, 2004.
35. Sheldrick, G.M. SHELX-97, a program for the refinement of crystal structures. *Acta Cryst.* **2008**, *64*, 112–122.
36. Cambridge Crystallographic Data Centre. Available online: www.ccdc.cam.ac.uk/data_request/cif (accessed on 31 May 2014).