The Production of Class-II Mixed-valence Complexes in the Redox Reaction between Dithiomalonamide and Platinum(IV) or Palladium(IV) †

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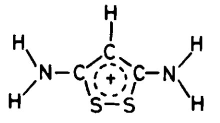
Due to its joint reducing and complexing properties, dithiomalonamide (HL) reacts with $[\mathrm{PtX_6}]^{2-}$ and $[\mathrm{PdX_6}]^{2-}$ ions to afford two types of complexes which, on the basis of microanalytical data, may be formulated as $\mathrm{M(HL)X_3}$ and $\mathrm{M(HL)_2X_3}$ respectively. A detailed investigation of their behaviour in solution (^{1}H, ^{13}C, and ^{195}Pt n.m.r.) and in the solid state (i.r., visible, x.p.s., and electrical conductivity measurements) has been performed. The experimental data show the two types of complexes to be mixed-valence compounds which are best formulated as $[\mathrm{M^{II}(HL)_2}][\mathrm{M^{IV}X_6}]$ and $[\mathrm{M^{II}(HL)_2}][\mathrm{M^{IV}(HL)_2X_2}]\mathrm{X_4}$ respectively. In these complexes, dithiomalonamide co-ordinates to palladium and platinum either *via* SN or $\mathrm{S_2}$ donation. They are recognised as semiconductors with electrical conductivities up to $-10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

The unusual stoicheiometry associated with platinum and palladium complexes $\mathrm{ML_2X_3}$ (M = Pt or Pd; L = $\mathrm{NH_3}$, mono- or di-amine; X = monoanion) has been a subject of interest for some years. Since the work of Brosset [1] devoted to the crystal structure of '$\mathrm{Pt(NH_3)_2Br_3}$' and the numerous studies related to Wolfram's red salt,[2,3] the early suggestions regarding the occurrence of platinum (or palladium) in the oxidation state +3 have been contradicted and the complexes recognised as mixed-valence species. They consist of square-planar $\mathrm{M^{II}}$ and tetragonal-bipyramidal $\mathrm{M^{IV}}$ units alternately arranged in $\cdots\mathrm{M^{II}}\cdots\mathrm{X{-}M^{IV}{-}X}\cdots\mathrm{M^{II}}$ chains.[2,4–6] Evidence for electronic interactions within the chains has been obtained from electrical conductivity measurements.[7–9] Furthermore, several complexes have been studied as single crystals and they were found to behave as highly anisotropic semiconductors.

These structural studies and the results of physical measurements are consistent with 'class-II mixed-valence compounds' according to the classification of Robin and Day.[10]

In spite of the increasing interest given to low-dimensional mixed-valence compounds related to the problems of electron-transfer phenomena, the examples known are restricted to species involving nitrogen-donor ligands. However, in a recent paper, we have described some new class-II mixed-valence compounds prepared from thioureas, thioamides, and related ligands.[11,12]

In the present paper, we report on the possibility of obtaining platinum and palladium mixed-valence complexes by reacting $[\mathrm{PtX_6}]^{2-}$ and $[\mathrm{PdX_6}]^{2-}$ with dithiomalonamide. This possibility rests on the fact that dithiomalonamide is known to be readily oxidized to the ion shown below.[13] In addition,



dithiomalonamide is a versatile ligand which (*i*) displays four potential donor sites and, therefore, may lead to SS-, SN-, or NN-chelation, and (*ii*) can co-ordinate either as a neutral (HL) or as an anionic (L$^-$) ligand.

We succeeded in preparing two types of platinum and palladium mixed-valence complexes, $[\mathrm{M(HL)_2}][\mathrm{MX_6}]$ and $[\mathrm{M(HL)_2}][\mathrm{M(HL)_2X_2}]\mathrm{X_4}$. However, no crystal suitable for an *X*-ray diffraction study has yet been obtained. In order to achieve a precise characterisation of these compounds, we have performed a detailed investigation of their behaviour in solution (^{1}H, ^{13}C, and ^{195}Pt n.m.r.) and in the solid state (i.r., visible, x.p.s., electrical conductivity determination). Some nickel(II), platinum(II), and palladium(II) compounds are included for comparison.

Experimental

Reagents.—Dithiomalonamide was prepared using Lawesson reagent, *i.e.* 2,4-bis(*p*-methoxyphenyl)-2,4-dithioxo-1,3,2,4-dithiaphosphetane, as thiation agent.[14] Malonamide (0.01 mol) and an excess of Lawesson reagent (0.005 mol) in dry toluene (15 cm^3) were kept at 100 °C for 4 h. After cooling and evaporation of the solvent, dithiomalonamide was obtained (100% yield). The product, purified on a silica-gel column (60 Merck; ether–acetone eluant), was identified by chemical analysis, i.r., and n.m.r. spectroscopy.

Hydrochloric acid used was 37% and acetic acid was glacial. All reagents were of pure chemical grade.

Synthesis of $[\mathrm{PtL_2}]$ *and* $[\mathrm{PdL_2}]$.—A warmed aqueous solution of potassium tetrachloroplatinate (0.005 mol) was added to a stirred solution of dithiomalonamide (0.01 mol) in hot water. A mustard-coloured product separates immediately; it was washed with ethanol and dried under vacuum.

Orange $[\mathrm{PdL_2}]$ was prepared by the same method as the platinum analogue.

Synthesis of $[\mathrm{Pt(HL)_2}]\mathrm{Cl_2}$.—A warmed solution of dithiomalonamide (0.01 mol) in HCl (37%) or in glacial acetic acid was added to a stirred potassium tetrachloroplatinate (0.005 mol) solution in the same solvent. The product separated immediately. It was washed with ethanol and dried *in vacuo.*

Synthesis of $[\mathrm{Pd(HL)_2}]\mathrm{Cl_2}$.—This complex was obtained similarly to its platinum analogue. However, in this case, the reaction first gave the intermediate complex $[\mathrm{Pd(HL)Cl_2}]$ as a first step when the Pd : HL molar ratio is 1 : 1. The desired complex, $[\mathrm{Pd(HL)_2}]\mathrm{Cl_2}$, only precipitates when Pd : HL reaches the value 1 : 2. The compound was washed with ethanol and dried *in vacuo.*

Synthesis of the Mixed-valence Compounds $\mathrm{Pt(HL)Cl_3}$ *and* $\mathrm{Pd(HL)Cl_3}$.—A warmed aqueous solution of $\mathrm{H_2PtCl_6}$ (0.01

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† *Supplementary data available* (No. SUP 23958, 2 pp.): relevant i.r. data for the complexes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: Torr ≈ 133 Pa, eV ≈ 1.60×10^{-19} J.

Table 1. Elemental analyses * (%)

Compound	C	H	N	M	Cl
$[PtL_2]$	15.8 (15.15)	2.1 (2.20)	12.0 (12.15)	42.1 (42.25)	—
$[PdL_2]$	19.2 (19.35)	2.8 (2.70)	15.2 (15.05)	28.2 (28.55)	—
$[Pt(HL)_2]Cl_2$	14.3 (13.5)	2.1 (2.25)	10.5 (10.5)	35.7 (36.55)	13.4 (13.25)
$[Pd(HL)_2]Cl_2$	16.7 (16.15)	2.3 (2.70)	—	24.1 (23.95)	15.7 (15.9)
$[Pt(HL)_2][PtCl_6]$	8.6 (8.25)	1.3 (1.35)	6.1 (6.45)	44.0 (44.8)	25.2 (24.8)
$[Pd(HL)_2][PdCl_6]$	10.0 (10.4)	1.9 (1.75)	8.0 (8.10)	31.7 (30.65)	30.6 (30.8)
$[Pt(HL)_2][Pt(HL)_2Cl_2]Cl_4$	12.0 (12.65)	2.1 (2.10)	10.0 (9.85)	35.3 (34.25)	19.3 (18.7)
$[Pd(HL)_2][Pd(HL)_2Cl_2]Cl_4$	14.7 (15.0)	2.4 (2.50)	11.1 (11.65)	22.0 (22.1)	20.3 (22.2)

* Calculated values are given in parentheses.

Table 2. N.m.r. (^{13}C and ^{195}Pt) parameters for dithiomalonamide (HL) and its palladium and platinum complexes

	$\delta(^{13}C)$ p.p.m.				
Compound	C=S	CH_2	CH	$\delta(^{195}Pt)$/p.p.m.	Co-ordination mode
$H_2NC(S)CH_2C(S)NH_2$ [a]	199.4	58.0	—	—	—
$[PtL_2]$	171.9	—	97.4	−4 064	MS_4
$[PdL_2]$	176.2	—	98.3	—	MS_4
$[NiL_2]$	177.5	—	96.8	—	—
$[Pt(HL)_2]Cl_2$ [b]	169.3 189.2	59.0	—	−3 761	MS_2N_2
$[Pt(HL)_2][PtCl_6]$	172.1	58.6	—	+410 −4 065	MS_4 MCl_6
$[Pd(HL)_2][PdCl_6]$	176.3	57.2	—	—	MS_4 MCl_6
$[Pt(HL)_2][Pt(HL)_2Cl_2]Cl_4$	163.6 169.4 188.3	59.7	—	−3 564 −3 816	MS_2N_2 MS_2N_2
$[Pd(HL)_2][Pd(HL)_2Cl_2]Cl_4$	172.4 176.3 189.1	56.8	—	—	MS_2N_2 MS_2N_2

[a] HL. [b] The Pd analogue, $[Pd(HL)_2]Cl_2$, decomposed in Me_2SO solution.

mol dm^{-3}) was added to a stirred solution of dithomalonamide (0.06 mol dm^{-3}). A yellow-orange product precipitated rapidly. It was washed with ethanol and dry diethyl ether, and dried *in vacuo*.

The brick-red palladium product was prepared by the same method as used for the platinum analogue, using potassium hexachloropalladate.

Synthesis of the Mixed-valence Compounds $Pt(HL)_2Cl_3$ *and* $Pd(HL)_2Cl_3$.—An aqueous solution of H_2PtCl_6 (0.01 mol dm^{-3}) was added to a stirred solution of dithiomalonamide (0.06 mol dm^{-3}) in HCl (37%). A yellow-orange product precipitated rapidly. It was washed with ethanol and dry diethyl ether, and dried *in vacuo*.

The same procedure was used to prepare the red palladium analogue.

Synthesis of the Mixed-valence Compounds $M(HL)Br_3$, $M(HL)_2Br_3$, $M(HL)I_3$, *and* $M(HL)_2I_3$.—The bromo derivatives were prepared by the same method as used for the chloro analogues using potassium hexabromo-platinate or -palladate instead of the chloro compounds.

Aqueous solutions of H_2PtCl_6 or K_2PdCl_6 (0.01 mol dm^{-3}) were added to an aqueous solution of KI (0.1 mol dm^{-3}). The resulting solution was allowed to react with dithiomalonamide, either in water for obtaining $M(HL)I_3$, or in glacial acetic acid for $M(HL)_2I_3$.

Analytical data of the compounds are reported in Table 1.

Physical Measurements.—Routine i.r. spectra were recorded on a Perkin-Elmer 577 spectrophotometer using KBr pellets. Chloro samples exhibit the same spectra in Nujol mulls.

Powder reflectance spectra were obtained with a Cary 14 spectrophotometer at room temperature. The compounds were diluted in KBr and studied as KBr pellets.

Nuclear magnetic resonance. All n.m.r. spectra were recorded on a WH250 Bruker spectrometer operating in the Fourier-transform mode and equipped with a wide-band probe (23—103 MHz). The complexes were dissolved in $(CD_3)_2SO$, the ^2H resonance of which provided the field/frequency locking signal; ^1H noise-modulated decoupling ensured complete proton decoupling of the spectra.

Typical parameters for ^{13}C spectra were: pulse width 20 μs, impulse delay 1 s; 2 000—5 000 accumulations were usually necessary to achieve a satisfactory signal to noise ratio. The ^{13}C shifts were measured relative to the solvent $(CD_3)_2SO$, however, δ values reported are quoted with respect to $SiMe_4$.

Typical parameters for ^{195}Pt spectra were: pulse width 20 μs, impulse delay 1 s; 500—3 000 transients were collected. Previous papers reporting ^{195}Pt chemical shifts mention the use of different compounds as the reference zero. We have adopted the convention suggested by Kerrisson and Sadler,[15] which conforms to that of IUPAC, using ^{195}Pt of H_2PtCl_6 in D_2O solution as external zero reference at 57 770 768 MHz. The dependence of the chemical shift of the solvent was examined in the case of H_2PtCl_6 by using a solution in $(CD_3)_2SO$.

Solutions for n.m.r. spectra were nearly saturated and data were collected on freshly prepared samples. The data given were quite reproducible and there was no evidence of solvolysis or decomposition of the complexes during the course of the measurements.

The chemical shifts are given in Table 2. A positive shift implies that the sample resonance occurs at a higher frequency and that the ^{195}Pt nucleus is less shielded than in the reference.

X-Ray photoelectron spectroscopy. The *X*-ray photoelectron spectroscopic (x.p.s.) measurements were obtained with an AEI ES 200B spectrometer using Mg-K_α radiation (1 253.6 eV) as the *X*-ray excitation source; the powdered samples were compressed into a copper grid. All spectra were run at a pressure of *ca.* 5×10^{-8} Torr. The C(1*s*) line from oil contamination (binding energy 285 eV) was used as an internal standard for calibrating the spectra.

X-Ray photoelectron spectra were deconvoluted using a program requiring input for the number of peaks and the height, half-width, and position for each peak suspected of comprising the multiplets. Based on these parameters, a spectrum is calculated which can be compared to the experimental spectrum. In all the deconvoluted spectra, we have had a good fit between calculated and experimental spectra. All the spectra were deconvoluted at least twice (for two different runs of the samples). Agreement between two deconvolutions was excellent.

Powder conductivities were determined on compressed pellets with a Wayne Kerr Automatic Component Bridge B 605. The pellets were pressed and their resistance directly measured in a 'conductivity press' by applying a force of 100 kg on 3-mm diameter pistons moving in a glass capillary tube.

Results and Discussion

Dithiomalonamide has been shown to exist in the dithione form in acetone.[16] From our own results, we may infer that this form also prevails in dimethyl sulphoxide. The ^{1}H spectrum displays two peaks with integrated areas in the ratio 2 : 1. The sharp resonance at 3.95 p.p.m. is assigned to the methylenic protons in agreement with the assignments of Martin and Master.[16] The position of the second signal strongly depends on the nature of the solvent since it is observed at 9.65 p.p.m. in $(CD_3)_2SO$ and at 2.75 p.p.m. in $(CD_3)_2CO$. The latter value is identical with that quoted in the literature.[16] The two signals of the ^{13}C spectrum are attributed to the methylenic carbon (58 p.p.m.) and to the C=S carbon (199.4 p.p.m.) since, in a ^{1}H-coupled spectrum, the high-field signal appears as a triplet while the low-field signal remains a singlet. The chemical shifts of ligand and complexes are quoted in Table 2.

Platinum(II) *and Palladium*(II) *Complexes*.—On the basis of the microanalytical data, two types of complexes have been obtained, $[ML_2]$ and $[M(HL)_2]Cl_2$. These formulations are supported by molecular weight and conductibility measurements performed in Me_2SO. These data are in close agreement with the conclusions of Martin and Master [16] concerning the nickel analogues.

N.m.r. spectroscopy affords a clear distinction between the two types of complexes. The ^{1}H spectra of the $[ML_2]$ complexes comprise two peaks with integrated areas in the ratio 1 : 4. The resonance at *ca.* 7.2 p.p.m. is assigned to NH_2 protons (intensity 4), while the signal at *ca.* 5.6 p.p.m. (5.60 p.p.m. for $[PtL_2]$, 5.55 p.p.m. for $[PdL_2]$, and 5.62 p.p.m. for $[NiL_2]$) is attributed to one proton (intensity 1) linked to a sp^2 carbon and the ligand is consequently assumed to react in its deprotonated form. The observed equivalence of the NH_2 protons suggests SS- or NN-symmetrical chelation.

The ^{13}C spectra of the three $[ML_2]$ complexes display two lines (see Table 1). The resonance at 97.4 p.p.m. ($[PtL_2]$) which appears as a doublet in the ^{1}H-coupled spectrum may be attributed to a sp^2 type carbon. It is noteworthy that a single C=S signal is observed at 171.9 p.p.m. ($[PtL_2]$) excluding SN co-ordination. Furthermore, the important co-ordination shift of the C=S carbon (*ca.* 30 p.p.m.) undoubtedly indicates that co-ordination occurs through sulphur atoms inducing a loss of multiplicity of the C=S linkage. By removal of a proton from the CH_2 group, the six-membered ring would acquire aromatic character, as in acetylacetonates. The shift of the ^{195}Pt nucleus in $[PtL_2]$ (δ −4 064 p.p.m.) is strongly reminiscent of the value (−4 045 p.p.m.) observed in the thiourea (L′) complex $[PtL'_4]Cl_2$ where four sulphur atoms are co-ordinated to platinum.[17] Finally, the whole set of n.m.r. data related to the $[ML_2]$ complexes emphasizes their similarity and supports the occurrence of a MS_4 co-ordination sphere.

The situation is markedly different in the case of the $[Pt(HL)_2]Cl_2$ complex since three signals are observed in the ^{13}C spectrum. On the basis of their δ values and the multiplicity of their corresponding ^{1}H coupled resonances, they are attributed to a CH_2 (δ 59.0 p.p.m.) and two C=S carbons (δ 169.3 and 189.2 p.p.m.), respectively. The presence of a CH_2 group is in agreement with the $[M(HL)_2]Cl_2$ formulation which implies that the ligand is not deprotonated. From the inequivalence of the thiocarbonyl carbons, co-ordination may be inferred to occur *via* two sulphur and two nitrogen atoms. This is further supported by consideration of the δ values. One of these shifts (δ 169.3 p.p.m.) is almost identical with the value (171.9 p.p.m.) observed for the $[PtL_2]$ complex and, therefore, may be associated with thiocarbonyl groups S-linked to the metal. The second value (189.2 p.p.m.), much less different from the shift in the free ligand, may be ascribed to thiocarbonyl groups not directly bonded to the metal.

A S_2N_2 co-ordination is also consistent with the ^{195}Pt resonance data. As previously mentioned, a MS_4 co-ordination would be characterized by a shift of *ca.* −4 050 p.p.m. The value observed (−3 761 p.p.m.) may be related to the deshielding effects of the nitrogen atoms. It is known that substitution of sulphur atoms by more electronegative ligands causes a deshielding of the ^{195}Pt nucleus.[17] For instance, the chemical shift δ(^{195}Pt) moves from −4 045 p.p.m. in $[PtL'_4]^{2+}$ to −3 779 p.p.m. in $[PtL'_2Cl_2]$ (L′ = thiourea).

Finally, the combined ^{1}H, ^{13}C, and ^{195}Pt n.m.r. data support the occurrence of MS_4 and MS_2N_2 type co-ordination in $[ML_2]$ complexes and $[M(HL)_2]Cl_2$ complexes, respectively.

In the case of $[Ni(HL)_2]Cl_2$, a S_2N_2 co-ordination has been suggested by Peyronel *et al.*[18] on the basis of i.r. data. However, Martin and Master [16] have interpreted the i.r. spectra of both types of M^{II} complexes, $[ML_2]$ and $[M(HL)_2]Cl_2$, in terms of S_4 co-ordination. This disagreement emphasizes the difficulties in interpreting the i.r. spectra of thioamides and their complexes due to the fact that many relevant vibrations are strongly coupled with other modes.[19] Besides the absence of any ν(M−Cl) vibration in the two $[M(HL)_2]Cl_2$ complexes, we note, in the case of the palladium complex, the presence of two vibrations attributable to ν(Pd−N) (500 cm^{-1}) and ν(Pd−S) (350 cm^{-1}), supporting a S_2N_2 co-ordination. However, the main interest of the i.r. spectra is to show the great similarity between the platinum and palladium homologues.

Mixed-valence Complexes.—According to the experimental conditions, two types of complexes may be obtained. On the basis of analytical data, they are represented by the crude formulations $M(HL)X_3$ and $M(HL)_2X_3$ (M = Pt or Pd; X = Cl, Br, or I). They are virtually insoluble in all common organic solvents, except Me_2SO.

X-Ray photoelectron spectroscopy has been used to obtain more precise information on the oxidation state of the metal in these complexes. The x.p.s. experiments have only been conducted on the platinum chloro complexes. However, keeping in mind the general resemblance between the platinum compounds and their palladium analogues, the results of this solid-state investigation may be easily extended to palladium complexes.

Table 3. Binding energies [a] (eV) for the $4f$ levels of platinum

Compound	Pt^{IV}		Pt^{II}	
	$4f_{\frac{7}{2}}$	$4f_{\frac{5}{2}}$	$4f_{\frac{7}{2}}$	$4f_{\frac{5}{2}}$
K_2PtCl_6 [b]	75.7	79.0	—	—
K_2PtCl_4 [b]	—	—	73.2	76.4
$[Pt(NH_2Et)_4][Pt(NH_2Et)_4Cl_2]Cl_4$ [c]	76.4 (1.75)	79.8 (1.8)	74.1 (1.6)	77.4 (1.6)
$[PtL'_4][PtCl_6]$ [d]	74.6 (1.4)	77.9 (1.6)	72.5 (1.6)	75.8 (1.4)
$[Pt(en)_2][Pt(en)_2Cl_2][BF_4]_4$ [e]	74.6	77.2	72.6	75.3
$[Pt(HL)_2][PtCl_6]$	75.5 (1.8)	78.9 (1.7)	73.2 (1.7)	76.6 (1.8)
$[Pt(HL)_2][Pt(HL)_2Cl_2]Cl_4$	74.2 (1.8)	77.5 (1.9)	72.4 (1.8)	75.7 (1.8)

[a] Binding energies are accurate to ±0.2 eV; full-width at half-maximum values are given in parentheses. [b] Ref. 24. [c] Wolfram's red salt; ref. 25. [d] L′ = Thiourea; ref. 11. [e] en = Ethylenediamine; ref. 32.

Many studies have been recently devoted to Pt^0, Pt^{II}, and Pt^{IV} compounds.[20-22] The data already published assume that the areas of the peaks are directly proportional to the number of elements from which they are derived and that binding energies $Pt(4f_{\frac{5}{2}})$ and $Pt(4f_{\frac{7}{2}})$ increase with the oxidation number of the metal. A difference of *ca.* 2 eV is generally observed between the platinum(II) complexes and their platinum(IV) analogues.

The close similarity of the x.p.s. spectra of the two complexes clearly appears. In both cases the Pt(4*f*) signal looks like a triplet which can be resolved into two doublets of equal intensity. The values of the binding energies reported in Table 3, together with published data related to thioamido mixed-valence compounds, are consistent with the simultaneous occurrence of platinum(II) and platinum(IV) in both complexes. The areas of the two signals [platinum(II) and platinum(IV), respectively] are identical only for brief *X*-ray exposure. With time, spectral changes indicative of a surface reduction of platinum(IV) to platinum(II) are observed. Such *X*-ray damage has already been reported for some platinum(IV) and mixed-valence platinum compounds.[23-25]

The chlorine 2*p* spectra of the two platinum complexes show only an ill resolved line which cannot be reliably deconvoluted. This may be due either to the presence of several different chlorine atoms in the complexes or to the occurrence of Cl_2 or HCl resulting from the photoredox process. Finally, it is noteworthy that the x.p.s. study clearly demonstrates the mixed-valence character of both types of complexes but does not afford any clear distinction between them.

As previously mentioned, the coupling of the relevant i.r. vibrations with other modes prevents the definitive use of this spectroscopy in diagnosing the mode of co-ordination. Moreover, the simultaneous presence of ligands co-ordinated to metal in two different oxidation states is expected to increase the complexity of the spectra. The main absorption bands with their tentative assignment are available as SUP No. 23958. Again, we note the resemblance between the platinum and palladium complexes.

The use of solution studies to characterize mixed-valence complexes deserves a preliminary comment since the specific character of these complexes is known to disappear in solution. However, their component entities (ionic or molecular) recover their individuality and thus become separately amenable to characterization by n.m.r. spectroscopy.

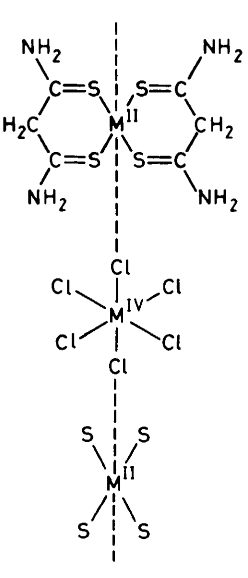
Furthermore, we have recently shown[26] that ^{13}C n.m.r. spectra related to class-II mixed-valence complexes are practically not affected by the physical state of the sample since almost identical δ values are obtained from solution and solid-state spectra.

The ^{195}Pt spectra of $Pt(HL)Cl_3$ comprises two lines located at +410 and −4 065 p.p.m., indicating the occurrence of two types of platinum nuclei. The shift of the low-field signal is particularly characteristic and may be ascribed to $[PtCl_6]^{2-}$. Considering the mixed-valence nature of the complex, the second signal must be attributed to a platinum(II) moiety. This highly shielded shift (−4 065 p.p.m.) is consistent with a PtS_4 co-ordination mode which has been observed in $[PtL_2]$ [$\delta(^{195}Pt) = -4\,064$ p.p.m.]. This conclusion is further supported by the ^{13}C n.m.r. spectra which unambiguously show the presence of one type of C=S carbon (δ 172.1 p.p.m.). This shift is identical with the value quoted for $[PtL_2]$ in which the metal is co-ordinated to the ligands *via* their sulphur atoms. According to our previous work,[17] if the ligands were bonded to platinum(IV), the thiocarbonyl carbon would be more shielded (δ *ca.* 164 p.p.m.). Finally, the n.m.r. data allow the $M(HL)Cl_3$ complexes to be suitably represented by the formula $[Pt^{II}(HL)_2][Pt^{IV}Cl_6]$, each ligand being S_2-bonded to the platinum(II) [structure (1)].

The ^{195}Pt spectrum of $Pt(HL)_2Cl_3$ comprises two resonances (−3 816 and −3 564 p.p.m.), again indicating the presence of two types of platinum nuclei. However, due to the proximity of these δ values, each of them is hardly attributable either to a platinum(II) or to a platinum(IV).

Four signals are observed in the ^{13}C spectrum of $Pt(HL)_2Cl_3$. The signal at 59.7 p.p.m. is attributable to a CH_2 group, while the three low-field signals (δ 163.6, 169.4, and 188.3 p.p.m.) may be assigned to thiocarbonyl carbons. By comparison with the shifts observed in the case of $[Pt(HL)_2]Cl_2$, the signal at 169.4 p.p.m. corresponds to a C=S group S-bonded to platinum(II) while the signal at 188.3 p.p.m. is attributable to a C=S group not directly bonded to the metal. The strong shielding of the third signal (163.6 p.p.m.) is characteristic of a thiocarbonyl group S-bonded to a platinum(IV).[17] These data are consistent with a formulation analogous to that of Wolfram's red salt, *i.e.* $[Pt^{II}(HL)_2][Pt^{IV}(HL)_2Cl_2]Cl_4$, the non-deprotonated ligand chelating platinum(II) and platinum(IV) *via* a SN co-ordination mode [structure (2)].

It is noteworthy that the $[Pt(HL)_2]^{2+}$ moiety which is involved in a S_2N_2 co-ordination scheme in $[Pt(HL)_2]Cl_2$ displays either a S_4 or a S_2N_2 co-ordination mode in the mixed-valence complexes $[Pt(HL)_2][PtCl_6]$ and $[Pt(HL)_2][Pt(HL)_2Cl_2]Cl_4$, respectively. In connection with this versatility of the HL ligand, we may return to the redox process operating in the reaction of $[MCl_6]^{2-}$ with dithiomalonamide. From all the data already mentioned, it is obvious that two types of mixed-valence compounds may be obtained depending on the experimental conditions. The nature of these compounds, *i.e.* $[Pt(HL)_2][PtCl_6]$ and $[Pt(HL)_2][Pt(HL)_2Cl_2]Cl_4$, implies that the last step of the whole process involves, in the first case, $[Pt^{II}(HL)_2]^{2+}$ previously formed and $[Pt^{IV}Cl_6]^{2-}$, and, in the second case, $[Pt^{II}(HL)_2]^{2+}$ and $[Pt^{IV}(HL)_2Cl_2]^{2+}$ with both ions



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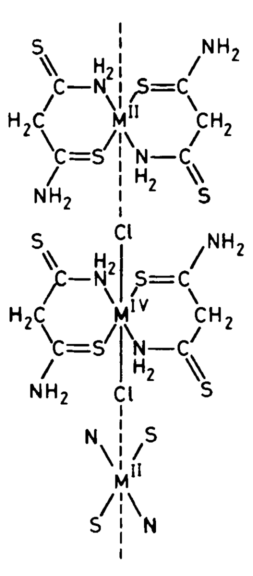

(2)

resulting from former reactions. Thus we suggest that, in neutral medium, $[Pt^{IV}Cl_6]^{2-}$ which is added to a large excess of ligand is reduced and complexed to yield a platinum(II) entity, $[Pt^{II}(HL)_2]^{2+}$, which, according to the behaviour of platinum(II) complexes in neutral medium, may display a S_4 co-ordination mode. This species then reacts with $[Pt^{IV}Cl_6]^{2-}$, which is now in excess due to the consumption of ligand in the previous process, to yield the mixed-valence species $[Pt(HL)_2][PtCl_6]$. In acidic medium, $[PtCl_6]^{2-}$ first complexes the ligand to yield a S_2N_2-co-ordinated platinum(IV) cation, $[Pt^{IV}(HL)_2Cl_2]^{2+}$, which is then reduced to the corresponding platinum(II) species, $[Pt^{II}(HL)_2]^{2+}$. The simultaneous presence of the platinum(IV) and platinum(II) species allows the mixed-valence complex $[Pt(HL)_2][Pt(HL)_2Cl_2]Cl_4$ to precipitate.

Characteristic properties of the mixed-valence complexes. Complexes having platinum (or palladium) atoms in two different oxidation states and bridged by halogen atoms are known to display a characteristic absorption in their visible spectra as well as the electrical behaviour of semiconductors. In this respect, the data quoted in Table 4 may be favourably compared with the data obtained for various mixed-valence[7,8,27–29] amine complexes. The values related to dithiomalonamide complexes, which reflect the conductivity parameters averaged over all directions in the crystal, are typical of semiconductors.

In both series, $[M(HL)_2][MX_6]$ and $[M(HL)_2][M(HL)_2X_2]X_4$, the conductivity values depend on the nature of the halogen (X), on the metal (M), and on the co-ordination sphere around the metal. As already reported by Interrante *et al.*[7,29] and Kida and co-workers,[30] changing of the halide ion in such class-II mixed-valence compounds increases the conductivity in the sequence Cl < Br < I. Similarly, but to a much lesser extent, the conductivity of a given palladium complex is always larger than that of its platinum analogue. A rather important increase (*ca.* 10^2) of the conductivity is also observed in going from $[M(HL)_2][MCl_6]$ to $[M(HL)_2][M(HL)_2Cl_2]Cl_4$.

Table 4. Conductivity measurements (Ω^{-1} cm^{-1})

Complex	M = Pt	M = Pd
$[M(NH_3)_2Cl_2][M(NH_3)_2Cl_4]$ *	—	7×10^{-10}
$[M(NH_3)_2Br_2][M(NH_3)_2Br_4]$ *	3×10^{-10}	5×10^{-8}
$[M(en)Cl_2][M(en)Cl_4]$ *	—	1×10^{-15}
$[M(en)Br_2][M(en)Br_4]$ *	—	5×10^{-13}
$[M(en)I_2][M(en)I_4]$ *	—	1×10^{-9}
$[M(HL)_2][MCl_6]$	3.25×10^{-8}	7.63×10^{-8}
$[M(HL)_2][MBr_6]$	8.67×10^{-8}	2.99×10^{-7}
$[M(HL)_2][MI_6]$	2.23×10^{-7}	6.51×10^{-7}
$[M(HL)_2][M(HL)_2Cl_2]Cl_4$	1.43×10^{-6}	3.52×10^{-6}
$[M(HL)_2][M(HL)_2Br_2]Br_4$	0.86×10^{-5}	1.72×10^{-5}
$[M(HL)_2][M(HL)_2I_2]I_4$	7.96×10^{-5}	9.77×10^{-5}

* Ref. 29.

These results may be interpreted on the basis of the band theory. In a sample composed of isolated M^{II} and M^{IV} species, the d_{z^2} band gap represents the difference between the energies of the two d_{z^2} orbitals. In a mixed-valence complex the gap will depend on the difference of length between the M^{II}–X and the M^{IV}–X distances. As these distances become similar, metal(II) and metal(IV) become more metal(III)-like and the two d_{z^2} bands tend to merge in one. Comparison between Reilhen's green salt, $[Pt(NH_2Et)_4][Pt(NH_2Et)_4Br_2]Br_4$,[31] and Wolfram's red salt,[32] shows the band gap to be smaller for the bromo complex than for the chloro analogue. This result is in good agreement with our own experimental data relating to the variation of conductivity of the complexes $[M(HL)_2][M(HL)_2X_2]X_4$ (X = Cl, Br, or I). Finally, it should be underlined that the high conductivity of the $[M(HL)_2][M(HL)_2X_2]X_4$ complexes with respect to their $[M(HL)_2][MX_6]$ analogues is probably related to the fact that in the former complexes the environments of the two metal centres, M^{II} and M^{IV}, are much more similar than in the latter.

Considering the u.v.–visible spectra of the mixed-valence complexes, some difficulties have been encountered in identifying the absorption classically attributed to a charge-transfer transition between the two metallic centres through the bridging halogen atom. First of all, since no sufficiently large single crystal was available, the reflectance spectra of the mixed-valence compounds were related to microcrystalline samples. Then the absorption is partially obscured by a large band attributable to the platinum(II) moiety. Indeed, one of the most characteristic features of the $[ML_2]$ and $[M(HL)_2]X_2$ spectra is the presence of a strong charge transfer band (L→M) next to the *d–d* transition assigned to the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ ($x^2 - y^2 \rightarrow xy$) in-plane transition. This band has been ascribed by Martin and Master[16] and Peyronel *et al.*[18] by comparison with the very similar spectrum of bis(dithioacetylacetonato)nickel(II) for which a complete study of energy levels has been given by Siiman and Fresco.[33] As a matter of fact, a low intensity absorption is discernible in the visible region of the spectra of the mixed-valence compounds (*ca.* 20 000 cm^{-1} for the chloro complexes and *ca.* 18 000 cm^{-1} for the bromo derivatives). It may be attributed to the transition from d_{z^2} (M^{II}) to the molecular orbital p_z (halogen) and d_{z^2} (M^{IV}). The difficulty in locating precisely this absorption which is barely resolved from the tail of the large platinum(II) absorption prevents any detailed analysis of its behaviour.

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Received 31*st October* 1983; *Paper* 3/1939