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Spectroscopic Study and X-ray Structure of Bis(N-methylimidazole)bis(2,4,6-trichlorophenolato)cobalt(II)

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The preparation, spectroscopic study and X-ray structure of the mixed-valence compound $Pt(NMIz)_4PtCl_6$ *are described; NMIz stands for N-methylimidazole.*

The crystal and molecular structure has been determined by a single crystal X-ray analysis using three-dimensional diffractometer data. The compound crystallizes in the triclinic system, with four formula units in the unit cell, space group $F\bar{1}$ *and lattice parameters* a = *15.228(11),* b = *17.855(12),* c = *11.177(8)* Å, α = *91.98(6),* β = *106.94(6),* γ = *115.76(7)°.*

The structure was solved and refined using the heavy-atom method and subsequent least-squares techniques. Refinements using 2335 observed reflections (Mo-Kα radiation) led to final values for R and R_w *of 0.077 and 0.075 respectively.*

The Pt(II) ions are surrounded in a square-planar geometry by four NMIz ligands (Pt–N = 1.986–2.012(14) Å *and N–Pt–N = 92.6(6)°). Pt(IV) is octahedrally coordinated by the six* Cl^- *ions (Pt–Cl = 2.313–2.323(6) and Cl–Pt–Cl = 88.3–89.9(2)°). In addition there is an interaction between the* $Pt(NMIz)_4^{2+}$ *ions and the* $PtCl_6^{2-}$ *ions (with Pt...Cl = 3.538(5)* Å *and Pt(II)... Cl–Pt(IV) = 144.1°) and Pt(II). Pt(IV) = 5.588* Å*), resulting in a chain-type behaviour along the c-axis.*

Optical, infrared and far-infrared spectra agree with this structure. No clear intervalence charge-transfer absorption could be detected which might be related to the relatively long Pt(II)...Pt(IV) distance in this compound.

Introduction

In recent years much work has been done on linear-chain platinum compounds, which may have a high electric conductivity [1]. Three types of linear-chain platinum compounds have been described in the literature:

1) Compounds consisting of a linear array of stacked square-planar platinum compounds, like $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ with a non-integral oxidation state, and the Magnus Green Salt $[Pt(NH_3)_4]\cdot PtCl_4$.

2) Mixed-valence compounds consisting of chains of alternating square-planar PtL_2X_2 and octahedral PtL_2X_4 units, with a halogen atom bridging between two platinum ions.

3) Mixed-valence compounds consisting of chains of alternating square-planar PtL_4^{2+} ions and octahedral $PtL_4X_2^{2+}$ ions, with the halogen atoms of the trans-$PtL_4X_2^{2+}$ ions bridging between the platinum ions. A well known example is Wolffram's red salt $[Pt(C_2H_5NH_2)_4]\cdot[Pt(C_2H_5NH_2)_4Cl_2]Cl_4$.

During the work on platinum compounds of N-methylimidazole, an interesting mixed-valence compound of formula $Pt(NMIz)_4PtCl_6$ was found [2]. We now describe the characterization of this compound together with its crystal and molecular structure.

Experimental

Starting Materials

The compounds $Pt(NMIz)_4Cl_2\cdot 2H_2O$ and $Pt(NMIz)_4PtCl_4$ were synthesized as described earlier [2]. K_2PtCl_6 was obtained by oxidation of an aqueous solution of K_2PtCl_4 with a mixture of 2 *N* HCl and a few ml of H_2O_2 (30%). Evaporation of the solvent and addition of KCl yielded the desired compound. K_2PtCl_4 was commercially available (Drijfhout, Amsterdam).

Synthesis of the Compound

The compound $Pt(NMIz)_4PtCl_4$ was dissolved in concentrated HCl. Upon standing bright red crystals

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TABLE I. Final Atomic Coordinates for Non-hydrogen Atoms ($\times 10^4$) and Thermal Parameters[a] ($\times 10^3$) with e.s.d's in Parentheses.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	0	0	0	33(1)	20(1)	27(1)	4(1)	13(1)	17(1)
Pt(2)	0	0	5000	32(1)	18(1)	26(1)	6(1)	11(1)	13(1)
Cl(1)	−1475(4)	130(3)	4006(5)	41(2)	44(3)	74(3)	27(2)	16(2)	26(2)
Cl(2)	−17(5)	−489(3)	3036(4)	101(4)	45(3)	38(2)	11(2)	37(3)	43(3)
Cl(3)	978(3)	1383(2)	4812(4)	49(2)	21(2)	45(2)	11(2)	16(2)	14(2)
N(11)	3026(10)	1872(8)	917(13)	42(8)	22(6)	37(7)	5(5)	12(6)	12(6)
N(31)	1422(10)	963(7)	706(11)	50(8)	23(6)	27(6)	9(5)	25(6)	24(6)
N(12)	−1222(11)	1415(8)	1186(13)	47(8)	24(6)	42(7)	9(5)	24(6)	26(6)
N(32)	−653(10)	724(7)	295(11)	45(7)	27(6)	22(6)	9(5)	17(5)	30(6)
C(21)	2145(14)	1210(10)	155(16)	51(10)	29(8)	36(9)	5(7)	18(8)	22(7)
C(41)	1869(13)	1498(10)	1885(16)	41(9)	35(9)	39(9)	3(7)	17(7)	24(7)
C(51)	2865(14)	2082(10)	2035(17)	50(10)	32(8)	43(9)	3(7)	21(8)	25(8)
C(61)	4001(13)	2307(12)	651(21)	27(9)	48(11)	75(14)	−12(10)	25(9)	3(8)
C(22)	−628(12)	1001(9)	1428(16)	39(8)	18(7)	46(9)	3(6)	24(7)	18(6)
C(42)	−1254(13)	941(11)	−679(15)	45(9)	47(10)	37(8)	23(7)	22(7)	37(8)
C(52)	−1581(13)	1413(10)	−69(17)	41(9)	32(8)	51(10)	15(7)	23(8)	24(7)
C(62)	−1441(14)	1801(11)	2173(17)	65(12)	46(10)	40(9)	−1(8)	24(8)	42(9)

[a] Anisotropic thermal parameters are in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{12}hka^*b^*)]$.

of the title compound were formed. The crystals were filtered, washed with water, ethanol and dry diethylether and dried *in vacuo* at room temperature. The compound could also be prepared by mixing equimolar amounts of $Pt(NMIz)_4Cl_2 \cdot 2H_2O$ and K_2PtCl_6 dissolved in water. The compound precipitated immediately, and was filtered, washed with water, ethanol and dry diethylether and dried *in vacuo* at room temperature. Analytical results: %C: 20.3 (calc. 20.6); %H:2.6(2.3); %N: 12.0(12.0); %Pt: 41.3(41.9); %Cl: 23.0(22.9).

Physical Methods

Infrared and far-infrared spectra and X-ray powder diffraction photographs were obtained as described earlier [2]. UV–visible light spectra were recorded on a Beckman DK2 spectrometer, furnished with a reflectance attachment (35.000–4.000 cm^{-1}). $BaSO_4$ was taken as the reference material.

Crystal Data

A red crystal (of dimensions *ca.* 0.10 × 0.18 × 0.35 mm) was mounted along the elongation direction and preliminary rotation and Weissenberg photographs were taken. On rotation photographs very weak Bragg layer lines can be discerned. From this feature it can be concluded that the metal–halogen–metal chains are running along *c* with a repeat distance of two metal–metal separations along the chain. The diffraction pattern indicates that the crystals belong to the Laue group $F\bar{1}$; the stronger reflections of the layers with $l = 2n$ have either *h* or *k* even, and the weaker reflections of the layers with $l = 2n + 1$ have either *h* or *k* odd. Approximate unit-cell parameters were obtained from the Weissenberg photographs and refined later by a least-squares procedure, using the θ-values of 20 high-angle reflections accurately measured on a Siemens AED single-crystal diffractometer. The most significant crystal data are as follows: $C_{16}H_{24}Cl_6N_8Pt_2$, M.W. = 931.32, triclinic, a = 15.228(11), b = 17.855(12), c = 11.177(8) Å, α = 91.98(6), β = 106.94(6), γ = 115.76(7)°: V = 2572(4) Å^3, Z = 4, D_c = 2.405 g cm^{-3}, μ(MoKα) = 116.34 cm^{-1}; space group $F\bar{1}$ (from structure determination).

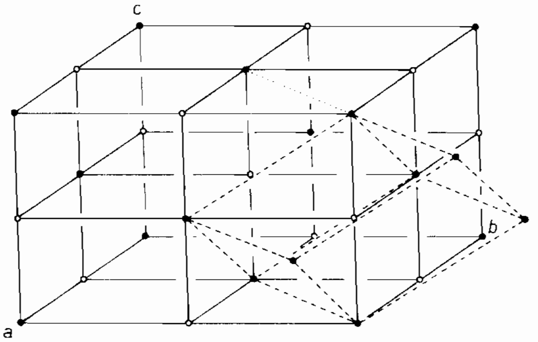

Fig. 1. Relation between the *F* and the primitive reduced cell. The white and black circles indicate the centres of symmetry on which the Pt^{II} and Pt^{IV} atoms lie respectively.

The primitive reduced cell (having the parameters: a = 8.865, b = 10.368, c = 8.026 Å, α = 98.59, β = 101.60, γ = 113.08°) is obtained by applying the matrix: ||½, ½, 0/0, −½, −½/−½, 0, −½||. Figure 1

TABLE II. Calculated Atomic Coordinates for Hydrogen Atoms ($\times 10^3$).

	x/a	*y/b*	*z/c*
H(21)	204	92	−77
H(41)	149	146	258
H(51)	341	259	283
H(611)	457	281	144
H(612)	386	256	−21
H(613)	429	186	52
H(22)	−23	92	234
H(42)	−143	78	−169
H(52)	−203	172	−52
H(621)	−106	171	309
H(622)	−227	151	198
H(623)	−116	247	217

shows the relation between the primitive reduced cell and the *F* cell: the white and black circles indicate the centres of symmetry on which lie the Pt^{II} and Pt^{IV} atoms, respectively. By considering these Pt atoms only, this figure shows also the presence of a subcell with translations a/2, b/2 and c/2, which justifies that the reflections with *h, k* and *l* odd are very weak.

Intensity data were collected on the same diffractometer by the $\theta/2\theta$ scan technique, using the Nb-filtered Mo-Kα radiation ($\bar{\lambda}$ = 0.71069 Å). 3281 independent reflections with θ in the range 2.5–29° were measured, 2335 of them were considered as observed and used in the analysis having $I > 2\sigma(I)$. A standard reflection was monitored after each measurement of 20 reflections, their intensities showing good stability. The Lorentz and polarization corrections were applied to the intensity data, but no absorption correction was made. The first absolute scaling and the mean isotropic temperature factor were obtained by the Wilson method.

The structure was determined by the heavy-atom method, and refined by least squares full-matrix cycles using the SHELX system of computer programs [3] with initially isotropic and then anisotropic thermal parameters. The coordinates of the hydrogen atoms were calculated in the geometrical positions and included in the final structure factor calculations. In the last cycles of refinement the weighting scheme $1/w = \sigma^2(F_o) + 0.001F_o^2$ was used. The final *R* value was 0.077, and R_w = 0.075 (observed reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of Pt and Cl) were taken from the International Tables [4]. The atomic fractional coordinates and thermal parameters of the non-hydrogen atoms are given in Table I, the calculated coordinates of the hydrogen atoms are given in Table II. A list of observed and calculated structure factors is available from the authors on request.

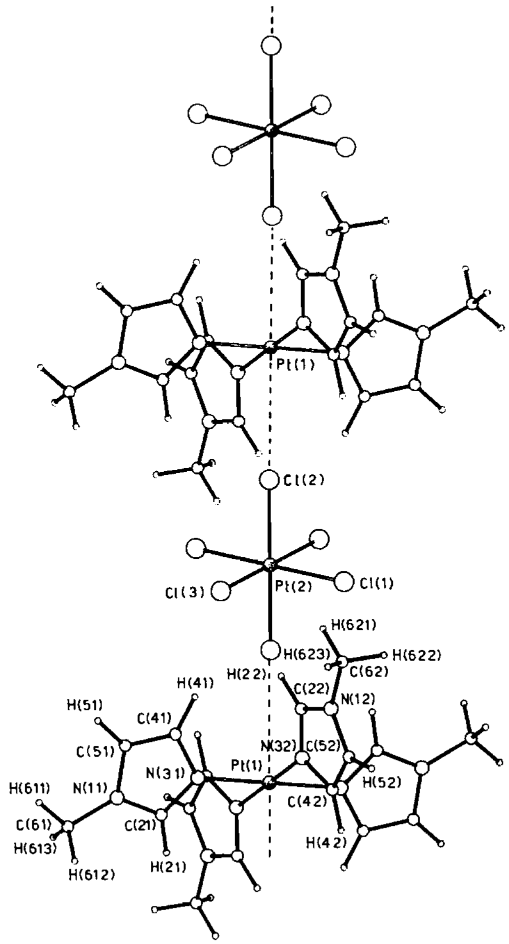

Fig. 2. Alternating Pt^{II} and Pt^{IV} complexes along *c*.

All the calculations were carried out on the CYBER 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support of the University of Parma.

Results and Discussion

Synthesis and Spectroscopic Properties

The formation of the compound from $Pt(NMIz)_4PtCl_4$ and the corresponding bromide [5] in concentrated HCl (or HBr) solution must be due to air oxidation. The compounds formed from $Pt(NMIz)_4PtX_4$ in HX and from $Pt(NMIz)_4^{2+}$ and PtX_6^{2-} are completely identical as deduced from X-ray powder diffraction patterns and infrared spectra [5].

The chloro and bromo compounds are mutually isomorphous as concluded from X-ray powder

TABLE III. Bond Distances (Å) and Angles (°).

Pt(1)–N(31)	1.986(14)	N(31)–Pt(1)–N(32)	92.6(6)
Pt(1)–N(32)	2.012(14)	N(31)–Pt(1)–Cl(2)′	87.1(4)
Pt(1)–Cl(2)′	3.538(5)	N(32)–Pt(1)–Cl(2)′	94.0(4)
Pt(2)–Cl(1)	2.313(6)	Cl(1)–Pt(2)–Cl(2)	89.3(2)
Pt(2)–Cl(2)	2.323(5)	Cl(1)–Pt(2)–Cl(3)	88.3(2)
Pt(2)–Cl(3)	2.320(5)	Cl(2)–Pt(2)–Cl(3)	89.9(2)
N(11)–C(21)	1.345(24)	C(51)–N(11)–C(21)	108.3(1.5)
C(21)–N(31)	1.333(24)	N(11)–C(21)–N(31)	110.6(1.5)
N(31)–C(41)	1.392(21)	C(21)–N(31)–C(41)	106.6(1.4)
C(41)–C(51)	1.372(28)	N(31)–C(41)–C(51)	109.7(1.6)
C(51)–N(11)	1.410(23)	C(41)–C(51)–N(11)	104.3(1.6)
N(11)–C(61)	1.472(25)	C(61)–N(11)–C(21)	126.5(1.6)
		C(61)–N(11)–C(51)	125.2(1.6)
N(12)–C(22)	1.375(24)	C(52)–N(12)–C(22)	111.1(1.5)
C(22)–N(32)	1.327(21)	N(12)–C(22)–N(32)	105.2(1.4)
N(32)–C(42)	1.389(22)	C(22)–N(32)–C(42)	111.6(1.5)
C(42)–C(52)	1.395(28)	N(32)–C(42)–C(52)	105.1(1.4)
C(52)–N(12)	1.348(23)	C(42)–C(52)–N(12)	106.7(1.6)
N(12)–C(62)	1.471(25)	C(62)–N(12)–C(22)	124.1(1.4)
		C(62)–N(12)–C(52)	124.8(1.6)

diffraction photographs and infrared spectra [5]. The compound is insoluble in all common solvents.

The infrared spectrum shows the absorption bands due to ligand vibrations. The spectrum shows the same features as other platinum–N-methylimidazole compounds [2, 5]. The far-infrared spectrum reveals the presence of a strong absorption band at 322 cm^{-1}, which can be assigned to the Pt–Cl stretching vibration.

In the visible spectra no clear indications have been found for the occurrence of intervalence charge-transfer transitions. A very broad absorption band starts at 600 nm with a small shoulder at 500 nm in the spectrum.

Description of the Structure

Many examples of mixed-valence platinum compounds with alternating Pt(II) and Pt(IV) complexes, joined in chains with halides bridging between the platinum atoms, are reported in the literature [6–11]. In the structures of these compounds generally one-dimensional order along the metal–halogen–metal chain is present with a repeat distance along the chain of one metal–metal distance. The environment around the Pt(II) and Pt(IV) atoms differs substantially only in the intrachain metal–halide distances.

Figure 2 shows the molecular structure of $Pt(NMIz)_4PtCl_6$ together with the atomic numbering scheme. In the structure the chemical environments of the Pt(II) and Pt(IV) atoms are completely different: *i.e.* octahedral $PtCl_6^{2-}$ ions and square-planar $Pt(NMIz)_4^{2+}$ ions are present. A long Pt(1)——Cl(2) interaction of 3.538 Å joins alternating Pt(II) and Pt(IV) complexes in chains running along *c*. The repeat distance along the chain amounts to two metal–metal separations.

Bond distances and bond angles are given in Table III.

The Pt(IV)–Cl distances of 2.313, 2.320 and 2.323 Å agree well with those found in K_2PtCl_6 [12]. The Pt(II)–N distances of 1.986 and 2.012 Å in the square-planar cations are in good agreement with those found for other compounds of Pt(II) with heterocyclic nitrogen-donor ligands [13–15].

A comparison of the present chain structure with that of other mixed-valence linear chain platinum compounds [6–11] reveals the following differences.

The chain in the present compound is not linear, the Pt(1)–Cl(2)–Pt(2) angle being 1.44°. The Pt(II)–Pt(IV) distance of 5.588 Å in the present compound is significantly longer than that in the other compounds described in the literature with chloride bridged-Pt(II) and Pt(IV) atoms [6, 7, 9, 11]. For comparison this value amounts to 5.48 Å in $[Pt(en)Cl_2]$. $[Pt(en)Cl_4]$, to 5.45 Å in $[Pt(en)_2][Pt(en)_2Cl_2]\cdot(ClO_4)_4$, to 5.40 Å in $[Pt(tn)_2][Pt(tn)_2Cl_2](BF_4)_4$ and to 5.39 Å in $[Pt(C_2H_5NH_2)_4][Pt(C_2H_5NH_2)_4Cl_2]Cl_4$. The longer distance in the present compound can be explained by the longer Pt(II)–Cl distance, which is probably due

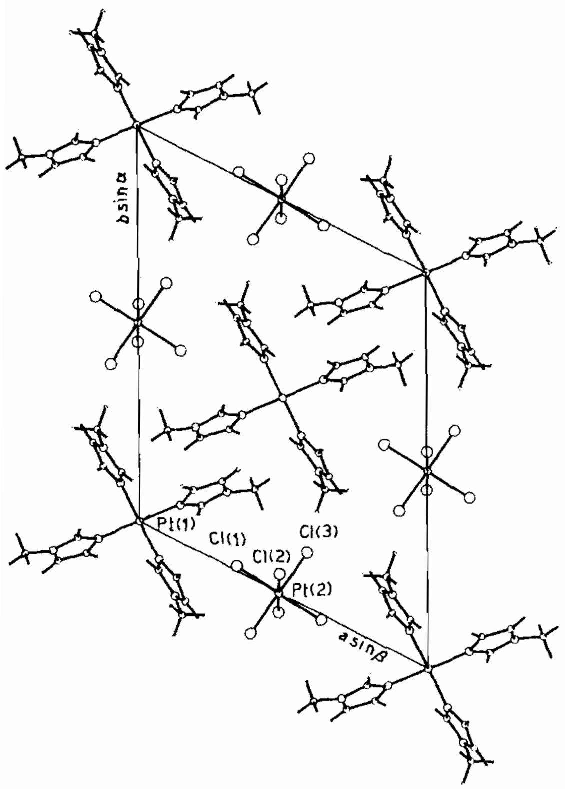

Fig. 3. Projection along c of the complexes with Pt at $z = 0$.

to the relative steric hindrance of the N-methylimidazole ligands with respect to the aliphatic amines.

The dihedral angle between the planes of the two crystallographically independent NMIz ligands is 106.2°, whereas the dihedral angle between each of these ligand planes and the square plane around Pt(II) is 51.9 and 108.4° for N(11)C(21)N(31)-C(41)C(51) and N(12)C(22)N(32)C(42)C(52) respectively.

The structural parameters of the two independent imidazole rings are very similar and are well within the range observed in other NMIz compounds [13, 16–19]. The major differences in the two independent ligands concern the N–C–N angles; N(11)–C(21)–N(31) = 110.6° and N(12)–C(22)–N(32) = 105.2°. This could be due to the fact that C(22)–H(22) is involved in an intrachain C–H——Cl interaction, with C(22)——Cl(3) = 2.69 Å, and C(22)–H(22)–Cl(3) = 159°.

The packing of the $Pt(NMIz)_4^{2+}$ cations and the $PtCl_6^{2+}$ anions in the structure is represented in Figs. 3 and 4.

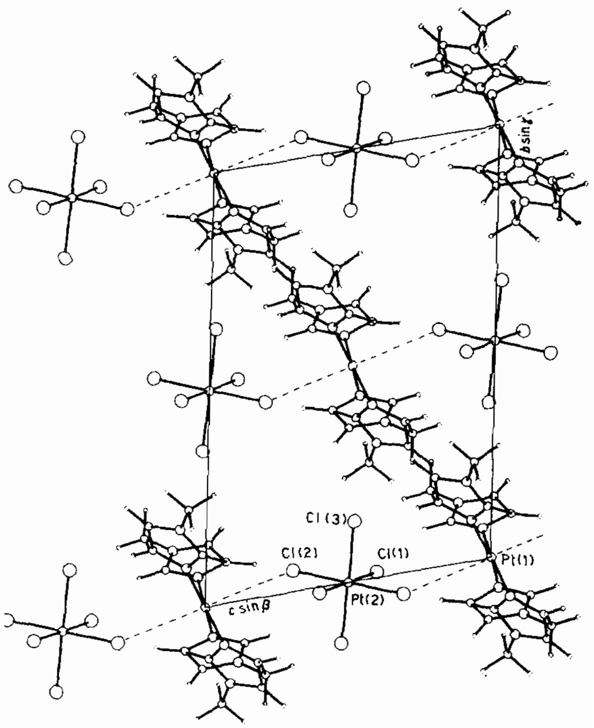

Fig. 4. Projection along a of the complexes with Pt at $x = 0$.

Conclusion

The present structure represents the first example of a mixed-valence chain compound of platinum with a zig-zag chain and with completely different ligand environments of the Pt(II) and Pt(IV) atoms. The fact that no low-energy intervalence charge-transfer absorption is found, agrees with the relative long Pt. . .Cl–Pt distance.

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