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Lantern type heterobimetallic complexes. Tetra-μ-4-methylpyridine-2-thiolato bridged platinum(II)cobalt(II) and oxidation complexes †

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A lantern type bimetallic complex $[(CH_3CN)Co(4\text{-mpyt})_4Pt]$ **1** (4-Hmpyt = 4-methylpyridine-2-thiol) was obtained by the reaction of $[Pt(4\text{-Hmpyt})_4]Cl_2$ with $CoCl_2$ in the presence of base and recrystallization from acetonitrile. The complex was characterized by single-crystal X-ray crystallography and is paramagnetic. It has a tetragonal $Co(4\text{-mpyt})_4Pt$ core in which 4-mpyt ligands bridge Pt and Co atoms. The Pt atom has a square-planar co-ordination by four S atoms, whereas the Co atom has a square-pyramidal co-ordination by five N atoms, the N atom of acetonitrile being located at the axial position of Co. The Co · · · Pt distance is 2.573(2) Å. Oxidation of **1** yielded diamagnetic $[Co^{II}(4\text{-mpyt})_4Pt^{III}X]$ type complexes (X = Cl **2a**, Br **2b**, N_3 **2c** or NCS **2d**): **2a** and **2b** were obtained by the reaction of **1** with iodobenzene dichloride or Ce^{IV} in the presence of Br^- respectively, while the reaction with pseudo-halides in air gave **2c** and **2d**. They have been characterized by variable-temperature ^1H NMR and X-ray photoelectron spectroscopies. Complexes **2a**–**2d** exist as the oligomer $[\{Co(4\text{-mpyt})_4PtX\}_n]$ where up to four tetragonal $[Co(4\text{-mpyt})_4PtX]$ units are linked by Pt–X–Co bridges. Cyclic voltammetry (CV) of **1** in acetonitrile displayed a one-electron oxidation peak at −0.05 V and two rereduction peaks at −0.17 and −0.40 V *vs.* an $Ag–Ag^+$ electrode at 25 °C. The CVs of **1** and **2a** show similar temperature dependences which can be interpreted on the basis of the dissociation–association equilibrium of the $Co^{II}Pt^{III}$ species in the co-ordinating solvent.

Introduction

Binuclear complexes with metal–metal bonds have attracted considerable interest for studying metal–metal bonding[1a–q] and catalytic activity[2a,b] in the simplest manner. Most of those studies have been made for homometal complexes and much less for heteronuclear metal–metal complexes.[1a,3a–o] A heteronuclear complex is produced by bridging different kinds of metal ions with appropriate ligands, but the synthetic reaction may afford two different homonuclear complexes at the same time. Sometimes the latter are produced dominantly over the former. This tendency causes the difficulty in the synthesis of heteronuclear metal complexes.

The complex $[Pt(4\text{-Hmpyt})_4]Cl_2$ (4-Hmpyt = 4-methylpyridine-2-thiol), in which the Pt atom is co-ordinated by four sulfur atoms in a square-planar configuration and pyridine nitrogens are protonated, acts as a binucleating reagent upon deprotonation of its nitrogen atoms which capture another metal ion to give a $[Pt(4\text{-mpyt})_4M]$ type complex. By reaction of $[Pt(4\text{-Hmpyt})_4]Cl_2$ with $Ni(CH_3CO_2)_2$ we have prepared a lantern type binuclear $[Pt^{II}(4\text{-mpyt})_4Ni^{II}]$, where the Pt and Ni atoms are co-ordinated by four S and four N in pyridine, respectively.[4a] Such a $d^8 \cdots d^8$ complex has a potential ability to form a d^7–d^7 complex.[5,6] The d^7–d^7 complex could also be derived from a $d^8 \cdots d^7$ complex by one-electron oxidation. In addition to the $Ni^{II}Pt^{II}$ complex, an attempt has been made to prepare lantern type $Co^{II}Pt^{II}$ and $Co^{II}Pt^{III}$ complexes. We report here the syntheses and characterizations of the binuclear $Co^{II}Pt^{II}$ and $Co^{II}Pt^{III}$ complexes.

Experimental

Materials and measurements

4-Methylpyridine-2-thiol was prepared from 4-methylpyridine by modifying the literature method.[7] The complex $[Pt(4\text{-Hmpyt})_4]Cl_2$ was prepared as described previously.[4a] Iodobenzene dichloride was prepared by the literature method.[8] Solvents were dried and distilled before use. All other chemicals were purchased from Wako, Nacalai and Aldrich, and used without further purification. Silica gel column chromatography was used for purification of the products.

Electronic spectra were recorded on an Hitachi 330 spectrophotometer at room temperature, ^1H NMR spectra on JEOL-GX400 and -α400 spectrometers at 25 °C, $SiMe_4$ being used as internal standard.

Electrochemical measurements were performed with a Bioanalytical Systems Inc. CV-50W Voltammetric Analyzer. Cyclic voltammograms were recorded between 25 and −25 °C by use of a glassy-carbon-disc working electrode and an $Ag–Ag^+$ reference electrode, acetonitrile and 0.1 mol dm^{-3} Bu_4NPF_6 being used as a solvent and supporting electrolyte respectively.[9] The formal potential of the ferrocenium–ferrocene couple was +0.52 V with respect to this reference electrode. Controlled potential coulometry was carried out with a Hokuto 501 potentiostat. The working electrode was reticulated vitreous carbon.

Molecular weight measurements were performed with a

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† *Supplementary data available*: variable temperature ^1H NMR spectra. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/3177/, otherwise available from BLDSC (No. SUP 57425, 4 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

Knauer model 11.00 vapour pressure osmometer using dichloromethane as a solvent.

The XPS spectra were recorded on a VG Scientific ESCA LAB MKII spectrometer by use of monochromated Mg-Kα (1253.6 eV) radiation, the standard technique being employed.

Preparations

[(CH$_3$CN)Co(4-mpyt)$_4$Pt]·CH$_3$CN 1·CH$_3$CN. The mixture of [Pt(4-Hmpyt)$_4$]Cl$_2$ (200 mg, 0.26 mmol), CoCl$_2$·6H$_2$O (105 mg, 0.26 mmol), KHCO$_3$ (105 mg, 1.04 mmol) and toluene (10 cm^3) in a sealed tube with a greaseless bulb was heated for 3 h at 120 °C under a nitrogen atmosphere. The solid compounds were dissolved in toluene, the solution changing from green to red-orange. After cooling to room temperature, the product was purified by short silica gel column chromatography under a nitrogen atmosphere using acetonitrile as an eluent. Red crystals of **1**·CH$_3$CN were obtained by concentrating the red eluate (135 mg, 62%) (Found: C, 39.98; H, 3.53; N, 9.95. $C_{28}H_{30}CoN_6PtS_4$ requires C, 40.38; H, 3.63; N, 10.09%); μ_{eff}(room temperature) = 3.20 μ_B.

[Co(4-mpyt)$_4$PtCl]·CHCl$_3$ 2a·CHCl$_3$. Iodobenzene dichloride (9 mg, 0.03 mmol) dissolved in chloroform (3 cm^3) was added to a chloroform solution (5 cm^3) of complex **1** (50 mg, 0.06 mmol) at −40 °C and stirred for 2 min under a nitrogen atmosphere. After addition of chilled *n*-hexane (10 cm^3), the solution was left in a refrigerator (−40 °C). Dark brown microcrystals were recrystallized from chloroform to give **2a**·CHCl$_3$ (48 mg, 84%) (Found: C, 32.83; H, 2.76; N, 6.21. $C_{25}H_{25}Cl_4CoN_4PtS_4$ requires C, 33.16; H, 2.78; N, 6.19%); δ_H(CD$_2$Cl$_2$) 8.71 (2 H, br, H6), 6.97 (1 H, br, H3), 6.89 (1 H, br, H3), 6.54 (2 H, br, H5) and 2.20 (6 H, s, CH$_3$).

[Co(4-mpyt)$_4$PtBr]·3CHCl$_3$ 2b·3CHCl$_3$. A methanol solution (3 cm^3) of potassium bromide (7 mg, 0.06 mmol) was added to a chloroform solution (5 cm^3) of complex **1** (50 mg, 0.06 mmol) at −30 °C and stirred for 2 min under a nitrogen atmosphere. Addition of ammonium cerium(IV) nitrate (35 mg, 0.06 mmol) in methanol (3 cm^3) gave rise to a change from orange to green-black. After stirring for 2 min, chilled *n*-hexane (10 cm^3) was added. Green-black **2b**·3CHCl$_3$ was obtained by recrystallization from chloroform (33 mg, 44%) (Found: C, 26.31; H, 2.19; N, 4.83. $C_{27}H_{27}BrCl_9CoN_4PtS_4$ requires C, 27.28; H, 2.29; N, 4.71%); δ_H(CD$_2$Cl$_2$) 8.71 (2 H, br, H6), 6.98 (1 H, br, H3), 6.91 (1 H, br, H3), 6.51 (2 H, br, H5) and 2.17 (6 H, s, CH$_3$).

[Co(4-mpyt)$_4$Pt(N$_3$)] 2c. A methanol solution (3 cm^3) of sodium azide (4.3 mg, 0.06 mmol) was added to a chloroform solution (5 cm^3) of complex **1** (50 mg, 0.06 mmol) at −30 °C and stirred for 2 min. After addition of chilled *n*-hexane (10 cm^3), the resulting solution was left in a refrigerator. Brown-black **2c** was obtained by recrystallization from chloroform (47 mg, 94%) (Found: C, 35.92; H, 3.03; N, 12.02. $C_{24}H_{24}CoN_7PtS_4$ requires C, 36.31; H, 3.05; N, 12.37%); δ_H(CD$_2$Cl$_2$) 7.88 (2 H, d, H6, $^3J_{HH}$ = 6.4), 6.95 (2 H, br, H3), 6.61 (2 H, d, H5, $^3J_{HH}$ = 6.4 Hz) and 2.17 (6 H, s, CH$_3$). Complex **2c** was also obtained from **2a** by the substitution reaction [Co(4-mpyt)$_4$PtCl] + NaN$_3$ $\longrightarrow$ [Co(4-mpyt)$_4$Pt(N$_3$)] + NaCl at −30 °C in methanol–chloroform.

[Co(4-mpyt)$_4$Pt(SCN)]·2CHCl$_3$ 2d·2CHCl$_3$. A methanol solution (3 cm^3) of sodium thiocyanate (5 mg, 0.06 mmol) was added to a chloroform solution (5 cm^3) of complex **1** (50 mg, 0.06 mmol) at −30 °C with stirring. After chilled *n*-hexane (10 cm^3) was added, the solution was left in a refrigerator overnight. Black crystals of **2d**·2CHCl$_3$ (53 mg, 81%) were obtained (Found: C, 35.34; H, 2.92; N, 7.97. $C_{26}H_{26}Cl_2CoN_5PtS_5$ requires C, 34.94; H, 2.93; N, 7.84%); δ_H(CD$_2$Cl$_2$) 8.03 (2 H, br, H6), 7.00 (1 H, br, H3), 6.92 (1 H, br, H3), 6.62 (2 H, br, H5) and 2.20 (6 H, s, CH$_3$).

[(CH$_3$CN)Ni(4-mpyt)$_4$Pt]·CH$_3$CN 3·CH$_3$CN. The preparation of complex **3** was reported previously.[4a] The complex [Pt(4-Hmpyt)$_4$]Cl$_2$ (767 mg, 1.0 mmol), Ni(CH$_3$CO$_2$)$_2$·4H$_2$O (249 mg, 1.0 mmol), KHCO$_3$ (400 mg, 4.0 mmol) and 15 g of naphthalene were put in a sealed tube with a greaseless bulb and heated for 1 h at 120 °C under a nitrogen atmosphere. The solution gradually turned from yellow to red-brown during the reaction. After cooling to room temperature, naphthalene was removed by treatment with *n*-hexane. The orange precipitate was purified by silica gel chromatography using acetonitrile–dichloromethane (1:10, v/v) as eluent. Red crystals of **3**·CH$_3$CN (525 mg, 63%) were obtained (Found: C, 40.20; H, 3.59; N, 10.03. Calc. for $C_{28}H_{30}N_6NiPtS_4$: C, 40.39; H, 3.63; N, 10.10%); μ_{eff}(room temperature) = 2.83 μ_B.

Crystallography

Crystal data. *Compound* 1. $C_{28}H_{30}CoN_6PtS_4$, M = 832.85, orthorhombic, space group *Pbca* (no. 61), a = 21.381(4), b = 18.292(4), c = 16.692(5) Å, U = 6527(2) Å^3, T = 296 K, Z = 8, D_c = 1.695 Mg m^{-3}, $F(000)$ = 3272, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 5.1 mm^{-1}, $wR(F^2)$ 0.057, $R1$ = 0.051.

Compound 3. $C_{28}H_{30}N_6NiPtS_4$, M = 832.62, orthorhombic, space group *Pbca* (no. 61), a = 21.362(3), b = 18.237(2), c = 16.608(2) Å, U = 6470(2) Å^3, T = 296 K, Z = 8, D_c = 1.709 Mg m^{-3}, $F(000)$ = 3280, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 5.2 mm^{-1}, $wR(F^2)$ 0.039, $R1$ = 0.032.

Data collection and reduction. *Compound* 1. Single crystals of compound **1** were obtained by slow evaporation of its acetonitrile solution. A red prism with dimensions 0.50 × 0.30 × 0.20 mm was mounted in a glass capillary. A total of 10294 intensities were measured to $2\theta_{max}$ 60°, all independent. An absorption correction based on empirical ψ scans was applied, with transmission factors 0.791–0.998. Cell constants were refined from setting angles of 25 reflections in the range 2θ 21.9–23.4°. For every intensity measurement three standard reflections, monitored every 150, showed no significant variation during data collection.

Compound 3. Single crystals of compound **3** were obtained by slow evaporation of dichloromethane into an acetonitrile solution. A red prism with dimensions 0.40 × 0.40 × 0.20 mm was mounted in a glass capillary. A total of 10275 intensities were measured to $2\theta_{max}$ 60°, of which 10272 were independent (R_{int} = 0.510). An absorption correction based on empirical ψ scans was applied, with transmission factor 0.618–0.992. Cell constants were refined from setting angles of 25 reflections in the range 2θ 29.5–30.0°. For every intensity measurement three standard reflections, monitored every 150, showed no significant variation during data collection.

Structure solution and refinement. The two structures were solved by the direct method, and the positional and thermal parameters refined by full-matrix least squares on F. Positions of almost all hydrogen atoms were found on the Fourier-difference map and the remaining ones were located on the calculated positions (C–H 0.95 Å). The positional and isotropic thermal parameters were included in the least-squares calculation. All calculations were carried out by use of the TEXSAN crystallographic software package.[10]

CCDC reference number 186/1117.

See http://www.rsc.org/suppdata/dt/1998/3177/ for crystallographic files in .cif format.

Results and discussion

Initially complex **1** was prepared by the reaction of [Pt(4-Hmpyt)$_4$]Cl$_2$ with CoCl$_2$ in the presence of base in naphthalene similar to the preparation of **3** in low yield, presumably owing to the difficulty in removing naphthalene completely from the

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** (M = Co) and **3** (M = Ni)

	1·CH_3CN	**3**·CH_3CN
Pt···M	2.573(2)	2.531(1)
Pt–S(1)	2.328(4)	2.321(2)
Pt–S(2)	2.329(4)	2.322(2)
Pt–S(3)	2.323(5)	2.324(2)
Pt–S(4)	2.331(5)	2.321(2)
M–N(1)	2.16(1)	2.130(5)
M–N(2)	2.14(1)	2.104(5)
M–N(3)	2.16(1)	2.119(5)
M–N(4)	2.16(1)	2.124(4)
M–N(5)	2.17(2)	2.119(5)
S(1)–Pt–S(2)	90.4(2)	90.85(6)
S(1)–Pt–S(4)	88.9(2)	89.74(6)
S(2)–Pt–S(3)	90.9(2)	90.58(6)
S(3)–Pt–S(4)	89.7(2)	88.82(6)
N(1)–M–N(2)	91.6(5)	89.6(2)
N(1)–M–N(4)	89.1(5)	89.4(2)
N(2)–M–N(3)	89.9(5)	91.2(2)
N(3)–M–N(4)	88.9(5)	89.5(2)
N(1)–M–N(5)	94.1(6)	90.5(2)
N(2)–M–N(5)	93.5(5)	92.9(2)
N(3)–M–N(5)	91.3(6)	93.4(2)
N(4)–M–N(5)	91.3(5)	90.7(2)
M–N(5)–C(26)	162(2)	164.3(5)

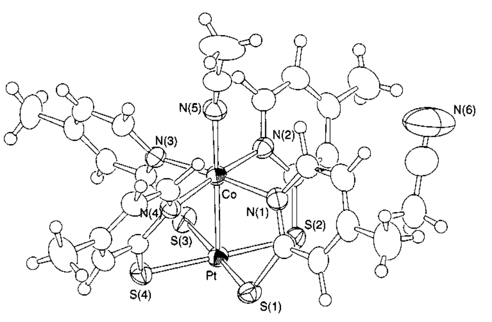
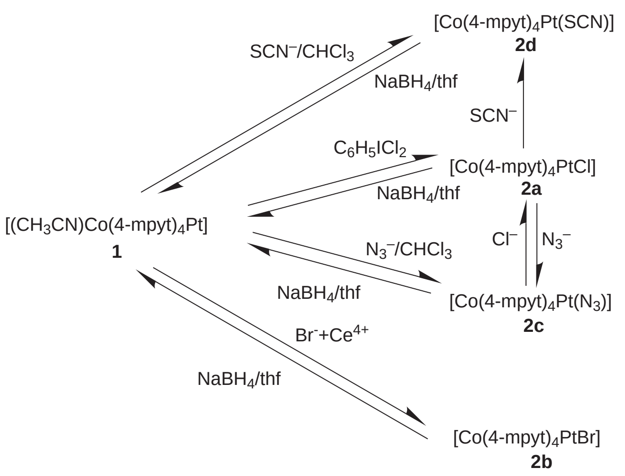


Fig. 1 An ORTEP drawing of [$(CH_3CN)Co(4\text{-mpyt})_4Pt$]·$CH_3CN$ **1**·CH_3CN.

reaction mixture. The yield was improved significantly using toluene instead of naphthalene as a solvent. Complex **1** is immediately decomposed upon dissolution in chloroform at room temperature but is more stable in acetonitrile than in non-co-ordinating solvents. Presumably ligation of acetonitrile to the Co atom stabilizes **1**.

An ORTEP drawing of complex **1** (Fig. 1) shows that it is isostructural with the $Ni^{II}Pt^{II}$ complex as inferred from the similar cell dimensions of **1**·CH_3CN to those of **3**·CH_3CN.[4b] Table 1 lists selected bond lengths and angles of **1** and **3**. Complex **1** has an approximate tetragonal symmetry and the four S and four N atoms are co-ordinated to the heavier and the lighter metal atom respectively. While the former has a square-planar co-ordination by four S atoms, the latter is co-ordinated to four N atoms at the basal sites and an acetonitrile molecule at the axial site to give a square-pyramidal co-ordination. The CoN_4 equatorial co-ordination square is parallel to, but rotated by 28.7° (mean) from, the PtS_4 co-ordination squares. The Co atom deviates from the four N co-ordination plane toward the apical MeCN ligand by 0.10 Å. The $Pt^{II}\cdots Co^{II}$ distance is 0.042 Å less than $Pt^{II}\cdots Ni^{II}$, and the Co–N (4-mpyt$^-$) and (MeCN) distances are also slightly longer than the corresponding Ni–N distances of **3**·CH_3CN, reflecting a larger atomic and covalent radius for Co than Ni. Compound **1** is paramagnetic with $\mu_{eff} = 3.20\ \mu_B$ (298 K), which suggests no appreciable intermetallic interaction in this complex.



Scheme 1 Reactions of $(CoPt)^{4+/5+}$ complexes.

The reaction of complex **1** with iodobenzene dichloride in chloroform gave dark brown diamagnetic **2a**, and the bromo-analogue **2b** was obtained by the reaction of **1** with $(NH_4)_2Ce(NO_3)_6$ in the presence of KBr. These reactions were carried out under a nitrogen atmosphere and at temperatures below −30 °C, taking precautions against the decomposition of **1** prior to the reaction. However, the reactions of **1** with NaN_3 and NaSCN in chloroform–methanol in air at −30 °C afforded diamagnetic **2c** and **2d** without strong oxidant, and no appreciable decomposition of **1**. Formation of **2a** and **2b** was also observed in the reaction of **1** with NaX (X = Cl or Br) in air at < −30 °C, but not so selective as those of **2c** and **2d**.[12] The 1:1 reaction of **2a** with NaN_3 and NaSCN in chloroform–methanol gives **2c** and **2d**. Complex **2c** reverts back to **2a** on reaction with twice as many moles of iodobenzene dichloride in dichloromethane.[13] The reactions of **2a** with $Bu^n{}_4NBr$ gave **2b**, but that of **2b** with $Bu^n{}_4NCl$ afforded a mixture of **2a** and **2b**. In the oxidation of **1** one electron may be removed from either Co^{II} or Pt^{II} to give a $Co^{II}Pt^{III}$ or $Co^{III}Pt^{II}$ complex. In the former case the d^7–d^7 bond formation is responsible for the diamagnetic nature of the products. In the latter the strong preference of Co^{III} for octahedral six-co-ordination to give a monomeric complex may result in a destruction of the {$Co(4\text{-mpyt})_4Pt$} core structure. That **2a**–**2d** are $Co^{II}Pt^{III}$ complexes is supported by XPS data as shown later as well as the following facts. As described below, **2a** shows a cyclic voltammogram similar to that of **1** in pattern as well as peak potentials for redox waves in acetonitrile at −1.0 to +0.5 V *vs.* Ag^+–Ag at room temperature. This electrochemical interconversion process suggests the possibility of the chemical reconversion of **2a** into **1**. Indeed the reaction of **2a**–**2d** with $NaBH_4$ in thf gives a red-orange compound identified as **1** based on the UV/VIS spectrum. The $\mathbf{1} \longleftrightarrow \mathbf{2}$ redox interconversions and the substitution reactions among **2a**–**2d** strongly indicate the retention of the {$Co(4\text{-mpyt})_4Pt$} core structure during the reactions (Scheme 1).

As the preparation of single crystals of complexes **2a**–**2d** has been unsuccessful, their structures have been investigated by using the results of reactivity, electrochemical measurement, ^1H NMR spectra, and osmometric molecular weight measurement. Fig. 2 shows the dynamic behaviour of the ^1H NMR spectrum of **2c**. At 20 °C all protons exhibit a sharp signal except for H3, the broad signal of which begins to split into two peaks at −5 °C. At much lower temperature, however, the H5, H6 and CH_3 signals also become broad. At −80 °C the CH_3 signal splits into more than three and each of the H3, H5 and H6 signals into more than four peaks. On the other hand, **2a** gives, even at 20 °C, a broad signal for all protons and two peaks for H3. The extent of the broadening is similar to that of **2c** at −40 °C. At −60 °C the H6 signal splits into six peaks and the CH_3 signal into three. Signal-pattern variations with temperature for **2b** and **2d** resemble those of **2a** than **2c**. At −60 °C the CH_3 signal

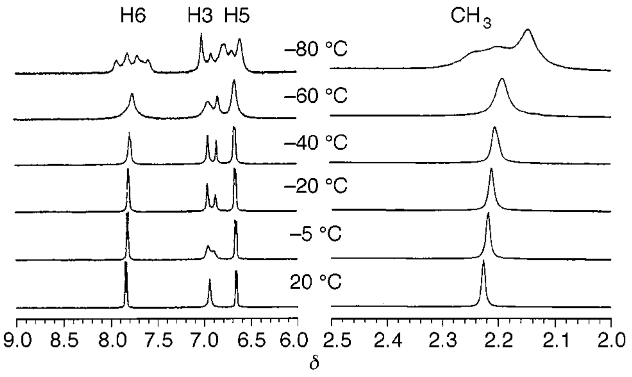


Fig. 2 The variable temperature ^{1}H NMR spectra of [Co(4-mpyt)$_4$-Pt(N$_3$)] **2c**.

of **2d** split into more than eight peaks which indicates the complex behaviour of **2d** in solution.[14] These spectra could not be explained on the basis of a tetragonal [Co(4-mpyt)$_4$PtX] monomer structure simply supposed from the analytical results.

The existence of [Co(4-mpyt)$_4$PtX] cores was confirmed by the redox reactions, electrochemistry and XPS measurement. The osmometric molecular weights of **2a** and **2d** at 2.40 mg per 1 ml CH$_2$Cl$_2$ and 8.38 mg per 1 ml CH$_2$Cl$_2$ were 4060 ± 400 and 3430 ± 400, respectively.[15] The result shows the existence of a tetrameric unit of [{Co(4-mpyt)$_4$PtX}$_4$] for **2a** and **2d** in CH$_2$Cl$_2$ solution.

The tetramers of the {Co(4-mpyt)$_4$Pt} core are the key point for understanding the complex ^{1}H NMR behaviour. Molecular weight measurements indicate only the average value, so it is likely there are equilibria involving oligomers, namely the trimer, tetramer and pentamer, their ratio being determined by the concentration, solvent, axial ligand, temperature and so on. Such oligomeric aggregation is consistent with the highly symmetric spectra at the high temperature limit, and the very complex signals at lower temperature. The signals at room temperature tend to cause broadening at higher concentration. The most plausible model for this type of aggregation involves stacking through the Pt–X–Co interaction. At high temperature rapid exchange of the {Co(4-mpyt)$_4$Pt} core between oligomers averages the signals to give a highly symmetrical signal. At lower temperature the exchange between oligomers is slowed as is the rate of rotation around the aggregation axis. Finally, each oligomer as well as the rotamer contributes to the NMR signal, resulting in the very complex pattern. Thus, the methyl singlet for **2d** at 20 °C splits in to more than eight peaks at −60 °C.[14] There is no evidence for terminal ligation at either platinum or cobalt; the oxidation state of the metals might determine the co-ordination site of the outer axial ligand.

Fig. 3 shows a plausible structure of the [{Co(4-mpyt)$_4$PtX}$_n$] oligomer. The Pt–X bonds in the bridging Pt–X–Co segment, similar to those in [XPt(bridge)$_4$PtX] complexes,[6] may be significantly longer than those of the in-plane bonds. In the tetramer there are at least four different environments for the protons.

In the presence of an excess of halide ion, however, the oligomer may be decomposed into [XCo(4-mpyt)$_4$PtX]$^-$ monomer owing to the ligation of halide ion to Co^{II}. Indeed a CDCl$_3$ solution of complex **2a** showed sharp ^{1}H NMR signals even at room temperature (Fig. 4) on addition of a large excess of Bu$^n{}_4$NCl or Bu$^n{}_4$NBr, and each of the spectra was explainable based on the tetragonal [XCo(4-mpyt)$_4$PtX]$^-$ monomer.[16]

The UV/VIS spectral data are given in Table 2. In view of the transition energy and ε value the absorption bands of complex **1** are assignable as d–d transitions localized on the CoN$_5$ core. In contrast to **1**, **2a**–**2d** show much more intense absorption in CH$_2$Cl$_2$, which indicates participation of two metal atoms in these electronic transitions. These observations strongly indicates that **2a**–**2d** possess a Pt–Co bond.

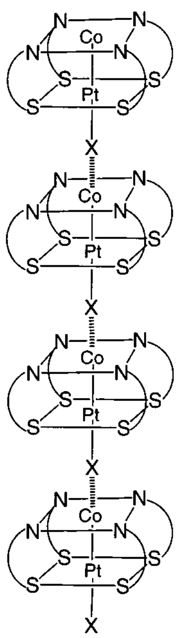


Fig. 3 The tetramer model of [{Co(4-mpyt)$_4$PtX}$_4$] (X = Cl **2a**, Br **2b**, N$_3$ **2c** or SCN **2d**).

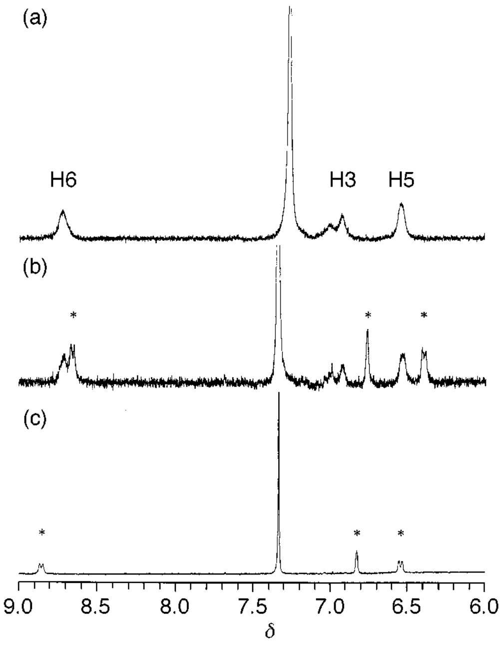


Fig. 4 The ^{1}H NMR spectra of [Co(4-mpyt)$_4$PtCl] (a), [Co(4-mpyt)$_4$-PtCl] + 1000 equivalents Bu$^n{}_4$NCl (b) and [Co(4-mpyt)$_4$PtCl] + 1000 equivalents Bu$^n{}_4$NBr (c). Asterisks denote signals assignable to [XCo-(4-mpyt)$_4$PtX]$^-$.

The oxidation states of the metal atoms were investigated by XPS. The platinum (4f$_{\frac{7}{2}}$) binding energy of complex **2a** is 0.5 eV higher than the corresponding one of **1** but the cobalt (2p$_{\frac{3}{2}}$) binding energy of **2a** agrees with that of **1** within the experimental error (Table 3). In the case of the [XPt^{III}(4-mpyt)$_4$Pt^{III}X] and [Pt^{II}(4-mpyt)$_4$Pt^{II}] couple, the platinum (4f$_{\frac{7}{2}}$) binding energy of the former is 1.2 eV higher than that of the latter, the usual difference for a +1 increment of the oxidation state. The increment of the platinum (4f$_{\frac{7}{2}}$) binding energy for **2a**–**1** is less than that of [XPt^{III}(4-mpyt)$_4$Pt^{III}X] and [Pt^{II}(4-mpyt)$_4$Pt^{II}]. However the significant increase in binding energy of **2a** in comparison with **1** indicates the Pt atom in **2a** to be in the trivalent state, one odd electron of which is coupled with that of Co^{II} to give diamagnetic **2a**. Thus **2a** is considered as a Co^{II}Pt^{III} complex. From analogy to Pt$^{III}{}_2$ complexes, a plausible structure for

Table 2 The UV/VIS absorption spectral data [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]

Co^{II}–Pt^{II} **1**[a]	Co^{II}–Pt^{III}–Cl **2a**[b]	Co^{II}–Pt^{III}–Br **2b**[b]	Co^{II}–Pt^{III}–N_3 **2c**[b]	Co^{II}–Pt^{III}–SCN **2d**[b]	Ni^{II}–Pt^{II} **3**[a]
540 (360)	530 (4000, sh)	520 (3350, sh)	550 (6700)	515 (4980, sh)	510 (160, sh)
470 (355, sh)	435 (8480)	430 (6370, sh)	445 (12700)	425 (11030)	350 (10100, sh)
	410 (8400, sh)	400 (7300)		400 (10200, sh)	310 (17100, sh)
					282 (24800)

[a] Measured in CH_3CN. [b] In CH_2Cl_2.

Table 3 XPS Data (eV)

Compound	Pt($4f_{7/2}$)	Co($2p_{3/2}$)
1 [(CH_3CN)Co(4-mpyt)$_4$Pt]	72.9	779.8
2a [Co(4-mpyt)$_4$PtCl]	73.4	779.9
[Pt(4-mpyt)$_4$Pt]	73.0	
[IPt(4-mpyt)$_4$PtI]	74.2	

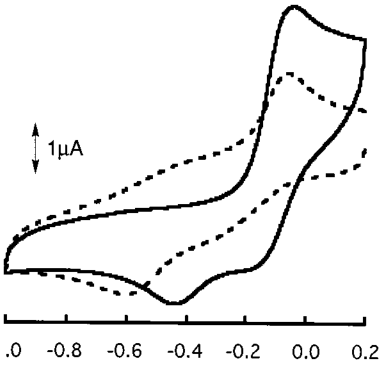


Fig. 5 Cyclic voltammograms of [(CH_3CN)Co(4-mpyt)$_4$Pt] **1** (——) and [Co(4-mpyt)$_4$PtCl] **2a** (– – –) in 0.1 mol dm^{-3} Bu_4NPF_6–CH_3CN at a glassy-carbon electrode with a scan rate of 50 mV s^{-1}.

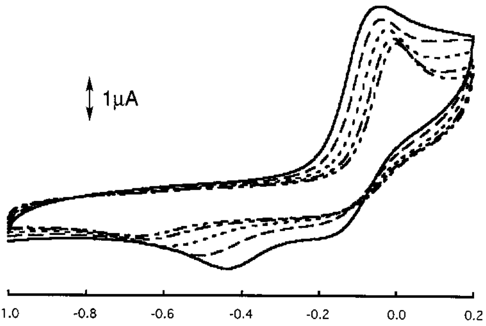


Fig. 6 Cyclic voltammograms of [(CH_3CN)Co(4-mpyt)$_4$Pt] **1** in 0.1 mol dm^{-3} Bu_4NPF_6–CH_3CN at a glassy-carbon electrode with a scan rate of 50 mV s^{-1} at 25 (——), 5 (– – –), −6 (- - -), −17 (—— - ——) and −26 °C (—- - -).

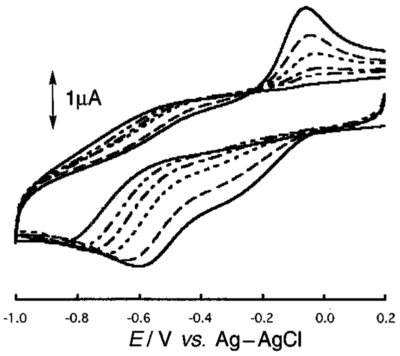
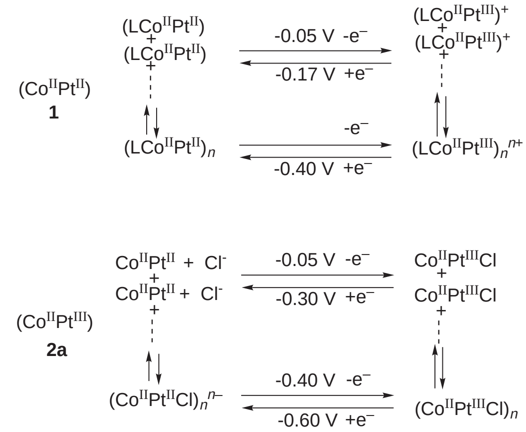


Fig. 7 Cyclic voltammograms of [Co(4-mpyt)$_4$PtCl] **2a** in 0.1 mol dm^{-3} Bu_4NPF_6–CH_3CN at a glassy-carbon electrode with a scan rate of 50 mV s^{-1} at 25 (——), 15 (– – –), 4 (- - -), −5 (—— - ——), −12 (—- - -) and −25 °C (— — —).



Scheme 2 Square electrochemical–chemical–electrochemical–chemical step dimerization mechanism.

2a–**2d** is [Co(4-mpyt)$_4$PtX] which has a {Co(4-mpyt)$_4$Pt} core and X bound to a Pt^{III} atom.

Fig. 5 shows the cyclic voltammograms of complexes **1** and **2a** at 25 °C in acetonitrile. Both change dramatically with temperature (Figs. 6 and 7). At 25 °C **1** exhibits an oxidation peak at −0.05 V, whereas there are two rereduction peaks at −0.17 and −0.40 V on the reverse scan. The controlled-potential coulometry of **1** at +0.20 V indicated the oxidation to be a one-electron process. With the dependence on temperature, the rereduction peak at −0.17 V tends to diminish and the peak potential of the other rereduction peak at −0.40 V at 25 °C moves negatively to −0.65 V. The CV of **2a** (Fig. 7) shows two reduction peaks at −0.30 and −0.60 V at 25 °C. The temperature dependence for the reduction peaks of **2a** is quite similar to that of **1**. Both peaks diminish and the peak at −0.60 V moves negatively to −0.85 V. At 25 °C the reoxidation peak appeared at −0.05 V which is almost the same as the oxidation potential peak potential of **1**. The broad signal around −0.40 V increases and shifts to −0.60 V as the temperature decreases and is likely coupled with the reduction peak at −0.85 V. The variable temperature data suggest complementary behaviour for **1** and **2a**. The observation that the one-electron oxidized species of **1** shows two reduction peaks indicates that the two reduction processes arise from different species. As illustrated in Scheme 2, the electrode oxidation of **1** generates $LCo^{II}Pt^{III}$ species (L may be either solvent or PF_6^-), parts of which are immediately coupled together to give the $(LCo^{II}Pt^{III})_n$ oligomer. In the reverse scan the $LCo^{II}Pt^{III}$ and $(LCo^{II}Pt^{III})_n$ species stabilized by oligomer formation are reduced at −0.17 and −0.40 V, respectively, to give $LCo^{II}Pt^{II}$ and $(LCo^{II}Pt^{II})_n$. At lower temperature the equilibrium shift to oligomer takes place which diminishes the monomer reduction peak and the reduction peak of the oligomer moves to negative potential. Even though the oxidation peak at −0.05 V diminishes in peak height significantly at low temperature, the peak position does not change, which is the same as that of **1**. This phenomenon indicates the peak is assignable to the oxidation of Co–Pt. Since the stabilized oligomer of $(Co^{II}Pt^{II})_n$ is reoxidized at around −0.60 V at lower temperature, the decrease in concentration of the monomer $Co^{II}Pt^{II}$ causes a significant change in the peak intensity at −0.05 V for **2a**. These phenomena are consistent with the existence of a monomer–oligomer equilibrium for both $LCo^{II}Pt^{II}$ and $(LCo^{II}Pt^{III})_n$.

Acknowledgements

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12 A solution (3 cm^3) of LiCl (2.5 mg, 0.06 mmol) in methanol was added to a solution (5 cm^3) of complex **1** (50 mg, 0.06 mmol) in chloroform at −30 °C and stirred for 2 min. Addition of chilled *n*-hexane (10 cm^3) gave a dark brown solid, for which ^1H NMR in $CDCl_3$ disclosed that although the reaction affords **2a** a few unidentified compounds are also produced at the same time.

13 A dichloromethane solution (3 cm^3) of iodobenzene dichloride (5.2 mg, 0.019 mmol) was added to a dichloromethane solution (5 cm^3) of complex **2c** (30 mg, 0.038 mmol) at −30 °C with stirring. Addition of chilled *n*-hexane (10 cm^3) afforded a dark green precipitate, which was found to be an approximately 1 : 1 mixture of **2a** and **2c** from its ^1H NMR spectrum. Iodobenzene dichloride is thought to give rise to the oxidation followed by replacement of the azide ligand to give **2a.**

14 The variable temperature ^1H NMR spectra of $[Co(4\text{-mpyt})_4Pt(SCN)]$ **2d** is provided in the Supplementary data (SUP 57425).

15 The large uncertainties in the molecular weights arises from the low solubility of complexes **2a** and **2d**. Measured values are provided in SUP 57425 (Figs. S2 and S3).

16 A mixture of $Bu^n{}_4NX$ (X = Cl or Br) (2.5 mmol), complex **2a** (2 mg, 0.0025 mmol) and $CDCl_3$ (1 cm^3) was stirred at 20 °C for 5 min. It was filtered into an NMR sample tube and the ^1H NMR spectrum measured. In the case of X = Br the spectrum showed only tetragonal $[BrCo(4\text{-mpyt})_4PtBr]^-$ monomer; when X = Cl an approximately 1 : 1 mixture of $[ClCo(4\text{-mpyt})_4PtCl]^-$ monomer and **2a** was revealed.

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