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Lantern-type dinuclear $Cr^{III}Pt^{II}$ and $V^{IV}Pt^{II}$ complexes bridged by pyridine-2-thiolate. Synthesis and characterization†

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Reaction of complex $[Pt(4\text{-Hmpyt})_4]Cl_2$ with $Na[CrO(hmp)_2]$ in toluene gave the lantern-type binuclear [ClCr(4-mpyt)$_4$Pt] **1** (4-Hmpyt = 4-methylpyridine-2-thiol; H_2hmp = 2-hydroxy-2-methylpropionic acid). The Cl^- ligand of **1** was readily replaced by OH^- to give [(HO)Cr(4-mpyt)$_4$Pt] **2**. [OV(L)$_4$Pt] type complexes (L = 4-mpyt **3a**; L = pyt **3b**) were obtained from the reaction of $[Pt(LH)_4]Cl_2$ with $[VO(acac)_2]$ (Hpyt = pyridine-2-thiol; acac = acetylacetonato) in toluene at 160 °C in the presence of $KHCO_3$. Compounds **1**, **2·2CH$_3$CN** and **3a** were characterized by single-crystal X-ray crystallography. These complexes have a common XM(4-mpyt)$_4$Pt core (M = Cr, X = Cl (**1**), OH (**2**); M = V, X = O (**3a**)) in which the 4-mpyt ligands bridge the Pt and M atoms to give a square-planar PtS_4 and a square-pyramidal MN_4X co-ordination sphere. The core has a crystallographically imposed 4-fold axis (**2·2CH$_3$CN**, **3a**) or an approximate one (**1**). In the crystal structure of **1** a pair of [ClCr(4-mpyt)$_4$Pt] units are combined to form a dimer through two Pt · · · S interactions (2.89(1) and 3.30(1) Å) between the PtS_4 planes of the respective monomers. The M · · · Pt distances range from 2.497(2) to 2.604(7) Å. The cyclic voltammogram (CV) of **1** in CH_3CN shows a reversible wave for $[ClCr(4\text{-mpyt})_4Pt]^{0/-1}$ with $E_{1/2} = -1.12$ V *vs.* Ag/Ag$^+$, whereas **2** gives an irreversible reduction peak at −1.90 V and reoxidation peaks at −1.12 V. Addition of hydrochloric acid, however, results in a dramatic change of the CV pattern to exhibit a reversible wave at $E_{1/2} = -1.12$ V, the shape and potential are similar to those of **1** indicating the generation of [ClCr(4-mpyt)$_4$Pt] by replacement of OH ligand by HCl.

Introduction

Intermetallic interactions in polymetallic complexes have attracted much interest in view of their physical and chemical properties[1a–w] as well as catalytic activity.[2a–c] A suitable system must be found to explore the intermetallic interaction. The so-called lantern-type binuclear complexes in which two metal atoms are connected by four bidentate ligands prepared in our laboratory is one such system.[3,4] The selective synthesis of a heterometallic dinuclear complex [M(bridge)M′] is more difficult than the synthesis of a homometallic dinuclear complex due to the generation of [M(bridge)M] and [M′(bridge)M′] complexes as side products.[5a–o] In the course of the synthesis of [Pt$_2$(bridge)$_4$], [Pd$_2$(bridge)$_4$] and [Pt$_2$(bridge)$_4$X$_2$] complexes, it turned out that [Pt(R-pytH)$_4$]Cl$_2$ acts as a suitable ligand for different kinds of metal ions (R-pytH = 4-methylpyridine-2-thiol or pyridine-2-thiol).[6] In this complex, R-pytH ligands co-ordinate to the Pt atom *via* the S atoms, whereas the pyridine N atoms are protonated and protected from further co-ordination. This complex can act as a tetradentate ligand when deprotonated forming the lantern-type [M(R-pyt)$_4$Pt] complexes. In these complexes, the M atom is surrounded by four N atoms and the Pt atom is surrounded by four S atoms forming an asymmetric co-ordination sphere. Since the N atoms of the pyridine are much harder than the S atoms of the thiolate, first row transition metal ions should be good candidates for co-ordination. The metal ion should also have the tendency to form square planar or square pyramidal geometries. Ni^{II} or Co^{II} can be used to form the bimetallic lantern-type complexes [(CH$_3$CN)M(4-mpyt)$_4$Pt].[6,7] In this work, lantern-type complexes containing ($V{=}O^{2+}$) and ($Cr{=}O^{3+}$) have been prepared.

Experimental

Materials and measurements

4-Hmpyt (4-methylpyridine-2-thiol)[8] and [Pt(4-Hmpyt)$_4$]Cl$_2$[6] were prepared by previously reported methods. Sodium bis(2-methyl-2-hydroxybutyrato)oxochromate(V) was prepared according to the method reported by Krumpolc and Rocek.[9] All other chemicals were purchased from Wako, Nacalai or Aldrich, and used without further purification. Solvents were dried and distilled before use. Silica-gel 60 (70–230 mesh) and Florisil (100–200 mesh) were purchased from MERCK Co. and Floridin Co., respectively.

Electronic spectra were recorded on a HITACHI 3410 spectrophotometer at room temperature. Electrochemical measurements were performed with a Bioanalytical Systems Inc. CV-50W Voltammetric Analyzer. Cyclic voltammograms were measured at 20 °C using a glassy-carbon-disk working electrode and a Ag–Ag$^+$ reference electrode, (Bu$_4$N)PF$_6$ or (Bu$_4$N)Cl (0.1 mol dm^{-3}) was used as the supporting electrolyte and acetonitrile was used as the solvent. The formal potential of the ferrocenium–ferrocene couple was +0.52 V with respect to the reference electrode. Controlled potential coulometry

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† Electronic supplementary information (ESI) available: cyclic voltammograms of complexes **1**, **2** and **3b**. See http://www.rsc.org/suppdata/dt/a9/a909241b/

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Table 1 Crystal data and structure refinements for **1**, **2** and **3a**

	1	**2**·2CH$_3$CN	**3a**
Formula	$C_{24}H_{24}ClCrN_4PtS_4$	$C_{28}H_{31}CrN_6OPtS_4$	$C_{24}H_{24}N_4OPtS_4V$
M	779.26	842.92	758.75
Crystal system	Monoclinic	Tetragonal	Tetragonal
Space group	$P2_1/n$ (no. 14)	$P4/ncc$ (no. 130)	$P4/ncc$ (no. 130)
a/Å	16.457(3)	14.929(5)	15.350(2)
b/Å	18.945(3)	14.929(5)	15.350(2)
c/Å	18.671(3)	14.320(7)	14.270(3)
β/°	101.39(1)		
U/Å^3	5706(1)	3191(1)	3362(1)
T/K	296	296	296
Z	8	4	4
D_c/Mg m^{-3}	1.814	1.754	1.499
F(000)	3032	1660	1476
μ(Mo-Kα)/mm^{-1}	5.666	4.996	4.686
Measured reflections	17673	2706	2719
Independent reflections	5336 [*R*(int) = 0.088]	1253 [*R*(int) = 0.019]	714
*R*1, *wR*2	0.046, 0.048	0.035, 0.038	0.062, 0.102

was carried out using a Huso HECS 343B coulometer and a Nichia NP IR1000 Potentio Galvanostat. A reticulated vitreous carbon was used as the working electrode. Magnetic susceptibility measurements were performed on powder samples at 0.1 T after zero field cooling, in the temperature range 1.8–300 K with a Quantum Design SQUID magnetometer MPMS2.

The mass spectra were recorded on a JEOL MS 700T (JEOL, Japan) sector mass spectrometer. FAB mass spectra were obtained using a 3-nitrobenzyl alcohol matrix. Electrospray ionization (ESI) mass spectra were obtained using a methanol mobile phase. Methanol solutions were directly injected into a API-II (the equipment of Atomic pressure Ionization for MS 700T) attached to the spectrometer. A Harvard pump II was used to deliver the solution to the API-II at a flow rate of 50 mL min^{-1}. Pressure in the mass analyzer region was usually about 5×10^{-3} Pa. Complexes **1** and **2** gave a strong signal in their positive and negative spectra.

Preparation of dinuclear complexes

[ClCr(4-mpyt)$_4$Pt] 1. [Pt(4-Hmpyt)$_4$]Cl$_2$ (90 mg, 0.117 mmol) was reacted with Na[CrO(hmp)$_2$] (35 mg, 0.117 mmol) in toluene (10 mL) under argon in a sealed tube at *ca.* 160 °C for 1 h. The resulting red solution was chromatographed on a silica gel column (30 × 100 mm) using toluene as eluent to give an orange-red micro-crystalline solid **1** after removal of solvent *in vacuo*. Yield 57 mg (62%) (Found: C, 36.80; H, 3.05; N, 7.52%. $C_{24}H_{24}N_4S_4ClCrPt$ requires C, 36.99; H, 3.10; N, 7.19%); UV/VIS λ_{max}/nm (CH$_2$Cl$_2$): 526 (*ε*/dm^3 mol^{-1} cm^{-1} 1450, sh), 510 (1747), 478 (1798, sh), 428 (1901) and 378 (6445, sh); FAB$^+$ MS: *m*/*z* 779 (M^+), 743 ([M − Cl]$^+$), 655 ([M − 4-mpyt]$^+$) and 620 ([M + H − 4-mpyt − Cl]$^+$).

[(HO)Cr(4-mpyt)$_4$Pt]·2CH$_3$CN 2·2CH$_3$CN. To a solution of [ClCr(4-mpyt)$_4$Pt] **1** (39 mg, 0.05 mmol) dissolved in acetonitrile (20 mL) was added a 0.2 mL aqueous solution of NaOH (0.025 mol dm^{-3}), and the mixture was stirred for 2 days at *ca.* 20 °C to give a brown solution. The brown microcrystalline product **2** was obtained by column chromatography with florisil (30 × 100 mm) using CH$_2$Cl$_2$ as the eluent. Yellow crystals of **2**·2CH$_3$CN was obtained by recrystallization from acetonitrile (35.8 mg, 94%) (Found: C, 38.53; H, 3.41; N, 7.06%. $C_{26}H_{28}N_5S_4OCrPt$ requires C, 38.99; H, 3.40; N, 8.74%); UV/VIS λ_{max}/nm (CH$_2$Cl$_2$): 476 (*ε*/dm^3 mol^{-1} cm^{-1} 917) and 418 (1702); μ_{eff} = 3.95 (298 K), 3.87 (120 K) μ_B; FAB$^+$ MS: *m*/*z* 760 (M^+), 743 ([M + H − H$_2$O]$^+$), 636 ([M + H − 4-Hmpyt]$^+$) and 619 ([M + H − 4-mpyt − H$_2$O]$^+$).

[OV(4-mpyt)$_4$Pt]·C$_7$H$_8$ 3a·C$_7$H$_8$. [Pt(4-Hmpyt)$_4$]Cl$_2$ (90 mg, 0.117 mmol), [VO(acac)$_2$] (31 mg, 0.117 mmol), KHCO$_3$ (47 mg, 0.469 mmol) and toluene (10 mL) were mixed in a tube, and the tube was sealed under argon. The green solution turned red after stirring for 1 h at *ca.* 160 °C. The red solution was cooled and passed through a silica-gel column with a 10 : 1 (v/v) mixture of toluene with acetonitrile as the eluent. Red microcrystalline **3a** was obtained from the first eluting band. Yield 21.8 mg (25%) (Found: C, 43.38; H, 3.68; N, 6.55%. $C_{31}H_{32}N_4S_4OPtV$ requires C, 43.76; H, 3.79; N, 6.58%); UV/VIS λ_{max}/nm (CH$_3$CN): 533 (*ε*/dm^3 mol^{-1} cm^{-1} 525), 486 (464, sh), 418 (1172) and 381 (2800, sh); FAB$^+$ MS: *m*/*z* 759 ([M + H]$^+$) and 634 ([M + H − 4-Hmpyt]$^+$).

[OV(pyt)$_4$Pt] 3b. Complex **3b** was prepared in a similar manner to **3a**. [Pt(pytH)$_4$]Cl$_2$ was used in place of the 4-mpyt analogue. Yield 15.6 mg (19%) (Found: C, 35.35; H, 2.47; N, 7.22%. $C_{20}H_{16}N_4S_4OPtV$ requires C, 34.19; H, 2.30; N, 7.97%); UV/VIS λ_{max}/nm (CH$_3$CN): 784 (*ε*/dm^3 mol^{-1} cm^{-1} 43.5, sh), 554 (715) and 514 (610); FAB$^+$ MS: *m*/*z* 703 ([M + H]$^+$) and 592 ([M + H − Hpyt]$^+$).

Crystallography

The structure determinations were carried out using a Rigaku AFC-7S diffractometer and a graphite-monochromated Mo-Kα radiation source (*λ* 0.71069 Å). For **1**, **2**·2CH$_3$CN and **3a** the cell constants were refined from setting angles of 25 reflections in the range $2\theta = 25.2$–$29.4°$. For every intensity measurement, three standard reflections, monitored every 150 reflections, showed no significant variation during data collection. Absorption correction based on empirical *Ψ* scans was applied for all of the F_o data. Experimental details are listed in Table 1.

The structures were solved by the direct method. Positional and thermal parameters were refined by full-matrix least-squares on *F*. For each structure most of the hydrogen atoms were found from the difference synthesis but the remaining ones were located on the calculated positions (C–H, 0.95 Å). They were included in the least-squares calculations with isotropic thermal parameters being used. All calculations were carried out by use of the TEXSAN crystallographic software package.[10]

CCDC reference number 186/1841.

See http://www.rsc.org/suppdata/dt/a9/a909241b/ for crystallographic files in .cif format.

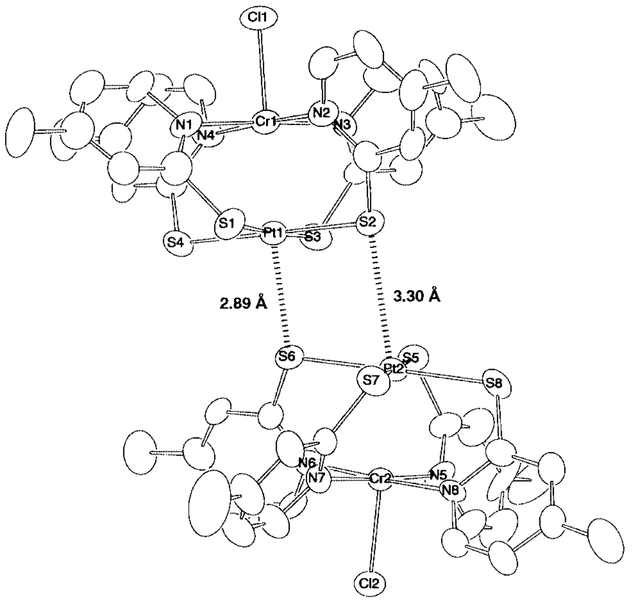


Fig. 1 ORTEP[11] drawing of [ClCr(4-mpyt)$_4$Pt] **1**.

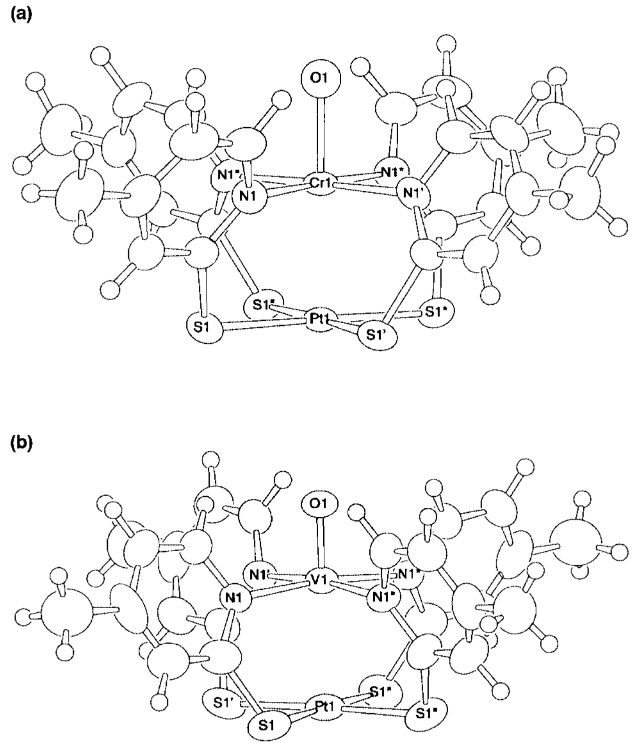


Fig. 2 ORTEP drawing of [(HO)Cr(4-mpyt)$_4$Pt] **2** (a) and [OV(4-mpyt)$_4$Pt] **3a** (b).

Results and discussion

Positive-ion FAB mass spectra showed distinct peaks for $\mathbf{1}^+$ ($m/z = 779$), $\mathbf{2}^+$ ($m/z = 760$) for **1** and **2** but **3**·H^+ for **3a** and **b** ($m/z = 759$ for **a**, 703 for **b**). These observations supported the chemical formulae for **1**, **2** and **3**. The negative-ion FAB mass spectrum for **2** gave a peak corresponding to OCr(4-mpyt)$_4$Pt$^-$ ($m/z = 759$) as the molecular peak. Negative ESI mass spectra of **2** showed, in addition to the peaks for the species found in the FAB mass spectra, a peak corresponding to HOCr(4-mpyt)$_4$Pt·OCr(4-mpyt)$_4$Pt$^-$ ($m/z = 1520$) indicating the presence of oligomers in solution.

Figs. 1 and 2 show the molecular structures of **1**, **2** and **3a**. They all have a common lantern-type structure. Four 4-mpyt ligands bridge the two metal atoms. The Pt atom has a square-planar co-ordination by 4 S atoms, and the Cr/V atoms are co-ordinated by 4 N and a Cl/O atom in a square-pyramidal fashion with Cl or O at the apical position. Square-planar co-ordination is characteristic of Pt^{II} complexes and the Cr is trivalent as indicated from the magnetic moment as well as the chemical formula. Square-pyramidal co-ordination is rare for the Cr^{III} state which has a strong preference for octahedral co-ordination.[1a] Complexes **2** and **3a** have the crystallographically imposed 4-fold axis which passes through Pt···M–L (M = Cr or V; L = Cl or O), and **1** has an approximate one. Selected bond lengths and angles are listed in Tables 2 and 3.

Table 2 Selected bond lengths (Å) and angles (°) for [ClCr(4-mpyt)$_4$Pt] **1** with estimated standard deviations (e.s.d.s) in parentheses

Pt(1)···Cr(1)	2.495(2)	Pt(2)···Cr(2)	2.499(2)
Pt(1)–S(1)	2.304(4)	Pt(2)–S(5)	2.324(4)
Pt(1)–S(2)	2.329(4)	Pt(2)–S(6)	2.323(4)
Pt(1)–S(3)	2.294(4)	Pt(2)–S(7)	2.338(4)
Pt(1)–S(4)	2.325(4)	Pt(2)–S(8)	2.317(4)
Cr(1)–N(1)	2.09(1)	Cr(2)–N(5)	2.12(1)
Cr(1)–N(2)	2.08(1)	Cr(2)–N(6)	2.09(1)
Cr(1)–N(3)	2.09(1)	Cr(2)–N(7)	2.10(1)
Cr(1)–N(4)	2.11(1)	Cr(2)–N(8)	2.11(1)
Cr(1)–Cl(1)	2.334(4)	Cr(2)–Cl(2)	2.347(4)
S(1)–Pt(1)–S(2)	89.5(1)	S(5)–Pt(2)–S(6)	90.3(1)
S(1)–Pt(1)–S(4)	90.4(1)	S(5)–Pt(2)–S(8)	87.9(1)
S(2)–Pt(1)–S(3)	90.5(1)	S(6)–Pt(2)–S(7)	90.3(1)
S(3)–Pt(1)–S(4)	89.6(1)	S(7)–Pt(2)–S(8)	91.5(1)
N(1)–Cr(1)–N(2)	89.0(4)	N(5)–Cr(2)–N(6)	88.4(4)
N(1)–Cr(1)–N(4)	90.0(4)	N(5)–Cr(2)–N(8)	91.1(4)
N(2)–Cr(1)–N(3)	89.0(4)	N(6)–Cr(2)–N(7)	93.4(4)
N(3)–Cr(1)–N(4)	91.9(4)	N(7)–Cr(2)–N(8)	87.0(4)
Cl(1)–Cr(1)–N(1)	90.9(3)	Cl(2)–Cr(2)–N(5)	92.0(3)
Cl(1)–Cr(1)–N(2)	92.0(3)	Cl(2)–Cr(2)–N(6)	90.6(3)
Cl(1)–Cr(1)–N(3)	91.7(3)	Cl(2)–Cr(2)–N(7)	91.0(3)
Cl(1)–Cr(1)–N(4)	91.2(3)	Cl(2)–Cr(2)–N(8)	92.3(3)
Pt(1)–Cr(1)–Cl(1)	178.2(1)	Pt(2)–Cr(2)–Cl(2)	179.2(1)

Table 3 Selected bond lengths (Å) and angles (°) for [(HO)Cr(4-mpyt)$_4$Pt] **2** and [OV(4-mpyt)$_4$Pt] **3a** with e.s.d.s in parentheses

B	**2**·2CH$_3$CN	**3a**
Pt···M	2.509(3)	2.604(7)
Pt–S	2.321(3)	2.323(8)
M–O	1.89(1)	1.59(3)
M–N	2.101(9)	2.13(2)
S–C(1)	1.73(1)	1.72(3)
S–Pt–S	90.00(1)	89.99(1)
M–Pt–S	90.20(7)	90.8(2)
Pt–M–N	89.3(2)	86.6(6)
O–M–N	90.7(2)	93.4(6)
N–M–N	89.99(1)	89.80(7)

The asymmetric unit of **1** comprises two crystallographically independent molecules which are combined to form a dimer through two intermolecular Pt···S interactions (Fig. 1). There are no appreciable differences between the corresponding molecular parameters of the respective monomers. One of the Pt···S distances is ≈0.5 Å longer than Pt–S co-ordination bonds and indicates a weak intermonomer interaction. The Cr–Cl lengths are slightly longer than those in *trans*-[CrCl$_2$(H$_2$O)$_4$]Cl·2H$_2$O (2.286(1) Å)[12] and *trans*-[CrCl$_2$(en)$_2$]Cl·HCl·2H$_2$O (2.33(1) Å).[13] Cr–O(H) length is ≈0.1 Å shorter than Cr–OH$_2$ distances (2.002(3)–2.013(3) Å) in *trans*-[CrCl$_2$(H$_2$O)$_4$]Cl·2H$_2$O[12] but significantly shorter than those (1.919(7)–1.988(2) Å) in hydroxo bridged dinuclear Cr^{III} complexes.[14]

The Cr···Pt distances of **1** and **2** are among the shortest M···Pt distances in the series of [M(R-pyt)$_4$Pt] (M = V, Cr,

Table 4 Structural data for lantern-type [XM(4-mpyt)$_4$M′X] compounds

Compound	Oxidation state	Bite distance/Å	M–M distance/Å	Deviation/ Å	Twist angle/°	N–C–S^h/°	Pt–S^h/Å	M–N^h/Å	Ref.
cis-[Pt$_2$(4-mpyt)$_4$]·C$_7$H$_8$	(II, II)	2.74	2.680(2)	0.00	13.1	122.9(17)	2.284(7)	2.08(2)	3
trans-[Pt$_2$(4-mpyt)$_4$]	(II, II)	2.73	2.683(3)	−0.02	17.1	—	—	—	15
trans-[IPt(4-mpyt)$_4$PtI]·3C$_6$H$_6$	(III, III)	2.73	2.539(1)	−0.06	32.0	—	2.335(8)	2.09(2)	15
cis-[PtPd(4-mpyt)$_4$]$_{0.67}$·[Pd$_2$(4-mpyt)$_4$]$_{0.33}$·CH$_2$Cl$_2$	(II, II)	2.74	2.673(1)	0.03	1.8	124.9(6)	2.293(2)	2.081(6)	16
[(CH$_3$CN)Ni(4-mpyt)$_4$Pt]·CH$_3$CN	(II, II)	2.70	2.531(1)	−0.018,^{a} −0.07^c	29.6(1)	119.8(4)	2.322(2)	2.119(5)	7
[(CH$_3$CN)Ni(4-mpyt)$_4$Pd]·CH$_3$CN	(II, II)	2.71	2.541(4)^g	−0.03,^{b} −0.07^c	29.9	118.7(17)	2.326(8)	2.116(18)	17
[(CH$_3$CN)Co(4-mpyt)$_4$Pt]·CH$_3$CN	(II, II)	2.70	2.573(2)	−0.013,^{a} −0.095^d	28.7(4)	119.0(10)	2.328(5)	2.16(1)	7
[ClCr(4-mpyt)$_4$Pt] **1**	(II, III)	2.69	2.497(2)^g	−0.020,^{a,g} −0.054^{f,g}	30.5(4)	120.3(10)	2.323(4)	2.10(1)	This work
[(HO)]Cr(4-mpyt)$_4$Pt]·2CH$_3$CN **2**·2CH$_3$CN	(II, III)	2.70	2.509(3)	−0.012,^{a} −0.018^f	29.1(8)	120.6(8)	2.321(3)	2.101(9)	This work
[OV(4-mpyt)$_4$Pt] **3a**	(II, IV)	2.70	2.604(7)	0.032,^{a} −0.126^e	25.6(6)	121(2)	2.323(8)	2.13(2)	This work

The deviation for the: ^{a} Pt, ^{b} Pd, ^{c} Ni, ^{d} Co, ^{e} V and ^{f} Cr atom. ^{g} The mean value between two independent molecules. ^{h} The mean value.

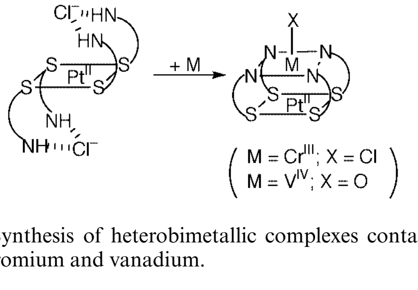
Co, Ni) type complexes (Table 4). Although a slight difference between Cr···Pt distances of **1** and **2** seems to result from the influence of the apical ligand on Cr···Pt interaction, there are no other observations suggestive of the interaction. In most square-pyramidal 5-co-ordinate structures, the metal atom deviates from the basal plane towards the apical ligand, but the deviations of Cr atoms in **1** and **2**·2CH$_3$CN are less than 0.06 Å.

2·2CH$_3$CN and **3a** crystallize in the same space group. Since Pt and Cr or V atoms lie on the crystallographic 4-fold axis, dinuclear complexes in the crystal structure are disposed in a fashion very similar to each other: **2**·2CH$_3$CN and **3** have linear ···Pt···Cr–OH···Pt···Cr–OH··· and ···Pt···V=O···Pt···V=O chains along the *c*-axis respectively, indicating an important contribution of the dipole–dipole interaction to lattice energy. The intermolecular O···Pt distance is 2.71(1) Å in the former and 2.94(1) Å in the latter. The H atom of the OH ligand may have more than 4-fold disorder about the 4-fold axis. The V atom in **3a** deviates from the 4 N plane by 0.13(2) Å. The deviation is much less than those in [VO(pc)$_2$] (pc = phthalocyaninate) (0.575(1) Å),[18] [VO(etp)$_2$] (etp = etioporphyrinate) (0.49(1) Å)[19] and [VO(etp)]$_2$(H$_2$Q) (H$_2$Q = quinol) (0.51(1) Å)[19] but greater than those of Cr atoms in **1** and **2**, making the Pt···V distance the longest in the series of [M(R-pyt)$_4$Pt] (M = V, Cr, Co, Ni). The V=O length is comparable to those of [VO(acac)$_2$] (1.571(10) Å)[20] and [VO(etp)$_2$] (1.599(6) Å).[19]

Single crystals suitable for X-ray work have not been obtained for **3b** as yet, but the analytical formula consistent with the MS data indicates a structure very similar to **3a**. As shown in the table, the Pt–M distance is longest for M = V ion and shortest for the Cr^{3+} ion, even though, all of the structural parameters in [Pt(R-pyt)$_4$MX] resemble each other. This fact indicates that the pyridine thiolate bridged system is suitable for the preparation of heterometallic dinuclear complexes.

In this work we were successful in preparing **3a** first by making use of V=O^{2+} which is capable of having a square-pyramidal co-ordination geometry. Since CrO^{3+} resembles V=O^{2+} in co-ordination geometry, an attempt was made to prepare a binuclear Cr···Pt complex by reaction of [Pt(4-Hmpyt)$_4$] with Na[CrO(hmp)$_2$], despite the possibility that the Cr^{V} could be reduced. However, the reaction affords **1** where the Cr^{III} atom, having a strong preference for octahedral co-ordination, participates in the lantern-type dinuclear framework at the expense of adopting an unfavourable square-pyramidal geometry.

In the synthetic reaction of [OV(L)$_4$Pt] complex, the yield is higher for L = 4-mpyt than the L = pyt, presumably because of the lower solubility of the pyt than the 4-mpyt complex. Compounds **1** and **3** were obtained in higher yield by doing the reaction in a non-polar solvent such as naphthalene or toluene than in a polar solvent such as DME or alcohols. The reaction in polar solvents gave a significant amount of [Pt(4-mpyt)$_4$Pt]. According to the preparative work and the structural evidence, the reaction system using [Pt(R-pytH)$_4$]$^{2+}$ with metal ions presents a general route to prepare [Pt(R-pyt)$_4$MX] while retaining its starting atomic arrangement as shown in Scheme 1.



Scheme 1 Synthesis of heterobimetallic complexes containing platinum with chromium and vanadium.

The newly synthesized complex **1** shows a relative reactivity toward hydroxide ion to produce complex **2** by the axial ligand substitution reaction. The reverse reaction does not take place

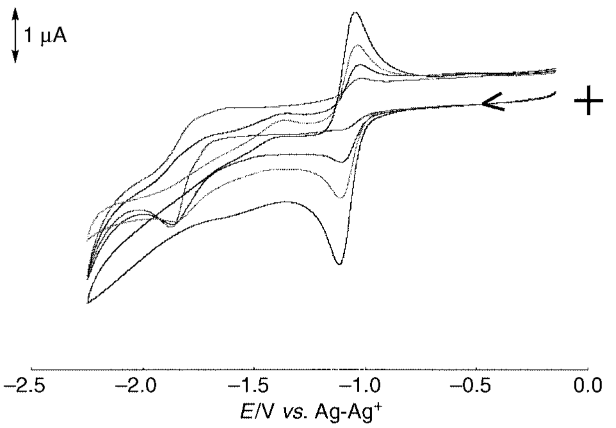


Fig. 3 Cyclic voltammogram of 0.5 mmol dm^{-3} [(HO)Cr(4-mpyt)$_4$Pt] **2** with 0, 0.75, 1.5 and 3.0 equivalents H_2SO_4 in 0.1 mol dm^{-3} Bu_4NCl–CH_3CN using a platinum electrode with a scan rate of 100 mV s^{-1}.

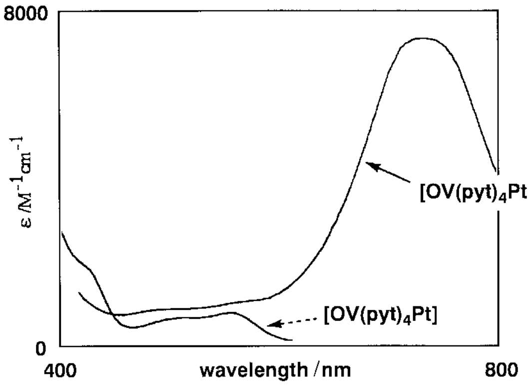


Fig. 4 Absorption spectra of [OV(pyt)$_4$Pt] **3b** (– – –) and the reduced species [OV(pyt)$_4$Pt]$^-$ (——) in DMF.

easily even in the presence of a large excess of the Cl^- ion. The displacement of OH in **2** is induced by the addition of protons to this reaction. This phenomenon is shown by the electrochemical measurements. Complex **1** shows one electron reversible couple at $E_{1/2} = -1.12$ V at 25 °C in acetonitrile, which is totally absent for complex **2** even in the presence of $(Bu)_4NCl$ as a supporting electrolyte.[20] The addition of H^+ (H_2SO_4) to the solution of **2** with $(Bu)_4NCl$ causes the peak at −1.90 V to completely disappear, and a reversible wave at −1.12 V for [ClCr(4-mpyt)$_4$Pt]$^{-1/0}$ appears (Fig. 3). This is identical to **1**. The OH ligand of **2** is unable to be replaced by Cl^- but is readily replaced in the presence of H^+. The proton probably attacks the OH ligand on **2** to give [(H_2O)Cr(4-mpyt)$_4$Pt]$^+$, and the H_2O ligand is then replaced by Cl^- to give **1**.

Interestingly, **3b** gives a reversible one electron reduction wave at $E_{1/2} = -1.45$ V (see the ESI for CVs of **1**, **2** and **3b**). The electrolysis of **3b** afforded an intense blue coloured solution which reverted back to pale red by reoxidation at −0.5 V. Treatment of **3b** with sodium metal in acetonitrile under argon also gave an intensely blue-coloured solution. The UV/Vis spectrum of the blue-coloured solution shows an intense absorption centred at 720 nm which may be due to, as inferred from its ε value (9600 dm^3 mol^{-1} cm^{-1}), a charge transfer transition within [Pt(pyt)$_4$VO]$^-$ (Fig. 4). Unfortunately, the blue species could not be isolated. The colour change in solution is totally reversible by both chemical and electrochemical reactions.

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