Hydroxo and Oxo Complexes of Platinum(II) Stabilized by Phosphanes: Synthesis and Characterization − X-ray Structures of *cis*-$[L_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (L = PMe_2Ph, $PMePh_2$) and $[\{cis\text{-}(PMe_2Ph)_2Pt\}_3(\mu\text{-}O)_2]Cl_2$

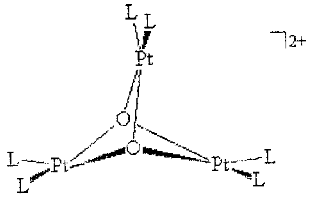
Bruno Longato,*[a,c] Giuliano Bandoli,[b] and Alessandro Dolmella[b]

Keywords: Platinum / Oxo and hydroxo ligands / X-ray diffraction / Deprotonation reactions

The dinuclear hydroxo complexes *cis*-$[L_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (L = PMe_2Ph and $PMePh_2$) have been characterized by single-crystal X-ray analysis, and their reactivity towards chloride ions has been investigated. Reaction of *cis*-$[L_2Pt(\mu\text{-}OH)]_2X_2$ (L = PMe_3, PMe_2Ph; X = NO_3^-, ClO_4^-) with $(NEt_4)Cl{\cdot}H_2O$ or $(AsPh_4)Cl$, in a 1:2 molar ratio, afforded a mixture of *cis*-$[L_2PtCl_2]$ and $[\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2]^{2+}$ in ca. equimolar amounts. The trinuclear oxo compounds, separated by fractional crystallization of the reaction mixtures, were fully characterized by spectroscopic techniques, and the derivative $[\{cis\text{-}(PMe_2Ph)_2Pt\}_3(\mu\text{-}O)_2]Cl_2$ was also characterized by X-ray diffraction methods. Under the same experimental conditions, the structurally analogous hydroxo complex, stabilized by the less basic and more hindered $PMePh_2$ ligand, reacted with Cl^- to give *cis*-$[(PMePh_2)_2PtCl_2]$ as the only isolable species. The ^{31}P NMR spectroscopic analysis of the reaction mixtures allowed the detection of a moderately stable product, which is most likely to be the neutral hydroxo complex *cis*-$[L_2PtCl(OH)]$.

Introduction

Oxo complexes of platinum(II) stabilized by phosphanes of the type $[L_2Pt(\mu\text{-}O)]_2$ (L = PPh_3, PMe_2Ph; L_2 = bidentate phosphanes) have recently been described by P. R. Sharp.[1] They were obtained by deprotonation of the corresponding hydroxo bridged complexes $[L_2Pt(\mu\text{-}OH)]_2^{2+}$ with strong bases such as $LiN(SiMe_3)_2$. A common feature of the bridging oxo ligands, and their chalcogenide analogues,[2] is the ability to bind ions such as Li^+, Ag^+, Cu^+, and other metal centers, thus affording stable and well-characterized heteropolymetallic complexes. An exception is represented by the adduct $[cis\text{-}L_2Pt(\mu\text{-}O)]_2{\cdot}2LiBF_4$ (L = PMe_2Ph), which decomposes in THF to give $[\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2](BF_4)_2$ (Scheme 1), the trinuclear species in which each oxygen atom is symmetrically coordinated to three $[L_2Pt]^{2+}$ units.[3]



Scheme 1

We have now found that oxo complexes of this type are also formed when the hydroxo complexes *cis*-$[L_2Pt(\mu\text{-}OH)]_2^{2+}$ (L = PMe_3 and PMe_2Ph) react with chloride ions in aprotic solvents. The nucleophilic attack of Cl^- at the metal center affords a mixture of the mononuclear dichloro *cis*-$[L_2PtCl_2]$ species and the trinuclear $[\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2]^{2+}$ species in which the relative quantity of the two compounds is strongly dependent on the amount of added chloride. A large excess of Cl^- ions leads to the formation of *cis*-$[L_2PtCl_2]$ as the main product, whereas relatively good yields of the oxo complex are formed when the molar ratio $n_{(Cl^-)}/n_{(\text{hydroxo complex})}$ approaches the value of 2:1. This finding contrasts the observations reported by Bushnell for the strictly related hydroxo complex stabilized by PEt_3.[4] In that case, addition of LiCl to a solution of $[cis\text{-}(PEt_3)_2Pt(\mu\text{-}OH)]_2^{2+}$, in a 2:1 molar ratio, gave the substitution product *cis*-$[(PEt_3)_2PtCl_2]$ and about half of the starting hydroxo complex remained unreacted.

---

[a] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova,
Via Marzolo 1, 35131 Padova, Italy
Fax: (internat.) +39-049-8275161
E-mail: longato@chin.unipd.it
[b] Dipartimento di Scienze Farmaceutiche, Università di Padova, Via Marzolo 5, 35131 Padova, Italy
[c] Istituto di Scienze e Tecnologie Molecolari, CNR, c/o Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Marzolo 1, 35131 Padova, Italy.

DOI: 10.1002/ejic.200300446

In this paper, in addition to the X-ray structures of *cis*-$[L_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (L = PMe_2Ph, $PMePh_2$), we report on the details of the reaction of this class of dinuclear compounds with chloride ions. The facile deprotonation of the bridging hydroxo ligands, induced by the presence of the nucleophile Cl^-, offers an alternative route for the synthesis of the oxo compounds $[\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2]^{2+}$ (L = PMe_2Ph, and PMe_3), one of which has not previously been described. The products have been isolated as pure compounds and characterized by spectroscopic methods, and the species $[\{cis\text{-}(PMe_2Ph)_2Pt\}_3(\mu\text{-}O)_2]Cl_2$ has also been characterized by single-crystal X-ray diffraction analysis. Moreover, the study of the reaction by ^{31}P NMR spectroscopy allowed the detection of unstable products, which are tentatively attributed to the mononuclear complexes *cis*-$[L_2PtCl(OH)]$ (L = PMe_3, PMe_2Ph, $PMePh_2$).

Results and Discussion

Synthesis and Characterization of the Hydroxo Complexes *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)]_2X_2$ [X = NO_3^- (1a), ClO_4^- (1b)] and *cis*-$[(PMePh_2)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (2)

We have already shown that the removal of the chloride ligands from the trimethylphosphane complex *cis*-$[(PMe_3)_2PtCl_2]$ with $AgNO_3$, followed by neutralization of the resulting solution, afforded the hydroxo compound *cis*-$[L_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (L = PMe_3). This compound is a dinuclear cationic complex, which is very soluble in water when the anion is the nitrate group.[5] More recently, we have prepared the complex *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (**1a**) using the same procedure. This compound is still moderately soluble in water.[6] As previously observed for the PMe_3 analogue, the conversion of **1a** into the perchlorate salt results in a drastic decrease in the solubility. The compound *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ (**1b**) can be obtained in a quantitative yield from **1a** by metathetical exchange. The complex *cis*-$[(PMePh_2)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (**2**), which was prepared in a good yield using a slightly modified procedure, is virtually insoluble in water.

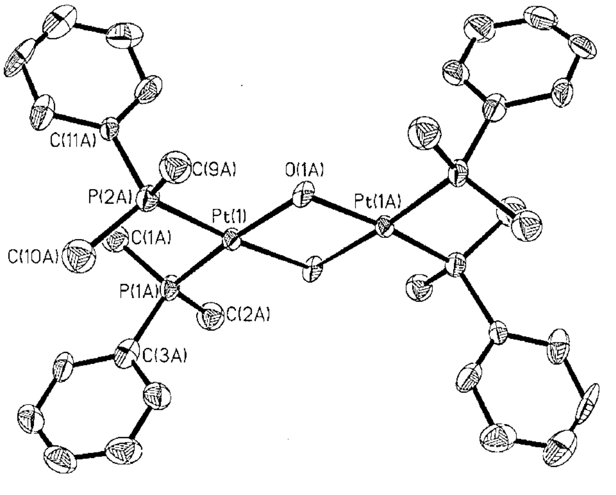


Figure 1. ORTEP drawing of **1a** showing 40% probability thermal ellipsoids and the essential atom numbering scheme; for clarity, the nitrate anions are omitted and only unit **I** is shown

The dinuclear nature of **1a** and **2** has been confirmed by single-crystal X-ray analysis. The ORTEP drawings of the two cations, *cis*-$[L_2Pt(\mu\text{-}OH)]_2^{2+}$, are shown in Figures 1 and 2, while the relevant bond lengths and angles are reported in Table 1. The unit cell of **1a** comprises two moieties denoted as **I** and **II**.

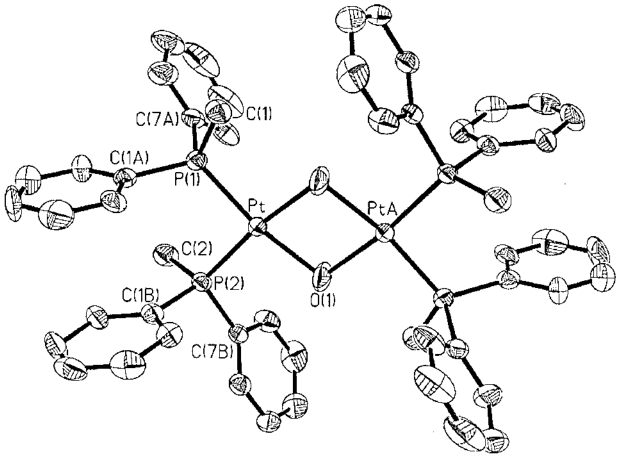


Figure 2. ORTEP drawing of **2** showing 40% probability thermal ellipsoids and the essential atom numbering scheme; for clarity, the nitrate anions are omitted

Table 1. Selected bond lengths [Å] and angles [°] for the complexes **1a** and **2**

	1a		**2**
	Unit I	Unit II	
Pt−P(1)	2.217(4)	2.234(4)	2.211(3)
Pt−P(2)	2.236(4)	2.219(4)	2.219(2)
Pt−O(1)	2.06(1)	2.08(1)	2.053(9)
Pt−O(1)[a]	2.08(1)	2.07(1)	2.073(8)
Pt···Pt[a]	3.233(1)	3.211(1)	3.174(1)
P(1)−Pt−P(2)	93.6(2)	94.9(2)	96.5(1)
P(1)−Pt−O(1)	172.3(3)	171.7(3)	170.0(2)
P(2)−Pt−O(1)[a]	171.4(3)	171.5(3)	172.4(3)
O(1)−Pt−O(1)[a]	77.5(4)	78.5(4)	79.4(4)
P(2)−Pt−O(1)[a]	95.0(3)	93.6(3)	91.1(2)
P(2)−Pt−O(1)	94.0(3)	93.1(3)	93.0(2)
Pt−O(1)−Pt[a]	102.5(4)	101.5(4)	100.6(2)

[a] At *x*, *y*, 1 − *z* in **1a**; at *x*, 1 − *y*, *z* in **2**.

The $P_4Pt_2O_2$ skeleton is essentially planar, within 0.03, 0.04, and 0.05 Å in **1a−I**, **1a−II**, and **2**, respectively. Comparison of the structural parameters of **1a** and **2** with those of the PMe_3 analogue shows only minor differences. In particular, the P−Pt−P and O−Pt−O angles are 93.6(2) and 77.5(4), 94.9(2) and 78.5(4), and 96.5(1)° and 79.4(4)° in **1a−I**, **1a−II**, and **2**, respectively, while the corresponding values in the PMe_3 analogue are 95.4(1) and 75.9(4)°. However, more significant changes are observed in the O···O and Pt···Pt distances. The O···O distance is relatively short in the PMe_3 derivative (2.54 Å), however, this distance is longer in

1a and **2**, 2.61 Å and 2.64 Å, respectively; the latter value is the same as that observed for the structurally analogous complex that is stabilized by NH_3 ligands,[7] and only slightly shorter than that found in the PPh_3 derivative (2.66 Å).[3] An increase in the O···O separation is accompanied by a decrease in the Pt···Pt distance; 3.222 Å (average) in **1a**, 3.174(1) Å in **2** and 3.261 Å in the PMe_3 complex. This trend probably reflects the different repulsion effects at the metal centers due to the diverse basicity of the PR_3 ligands.[3]

As found in the PMe_3 analogue, in **1a** the hydroxo ligands interact via hydrogen-bonding with the nitrate anions. In particular, the atoms that are involved in this hydrogen-bonding interaction are O(6) (at x, y, $1 - z$) in unit **I** (O···O separation of 2.74 Å and an O−H···O angle of 167°) and O(2) (at x, $y + 1$, z) in unit **II** (separation of 2.79 Å and an angle of 178°). This hydrogen-bonding system is not present in the crystal packing of **2**, where the shortest O···O distance is 3.18 Å.

The spectroscopic characterization of compounds **1** and **2** has been carried out in [D$_6$]DMSO. In the ^1H NMR spectra, the OH resonances are observed as broad singlets at $\delta = 4.11$ (L = PMe_2Ph) and 3.53 (L = $PMePh_2$), values similar to that observed for the PMe_3 analogue ($\delta = 3.46$).[5] The ^{31}P NMR spectra, obtained at 36.23 MHz, exhibit a singlet flanked by the typical pattern due to the ^{195}Pt satellites. Each component of the doublet, which is assigned to the isotopomer $[L_2{}^{195}Pt(OH)_2PtL_2]^{2+}$ ($^1J_{P,Pt}$ = 3457 Hz for **1** and 3571 Hz for **2**), is flanked by a couple of very weak resonances, separated by 304 Hz for **1** and 232 Hz for **2**, due to the contribution of the less abundant isotopomer $[L_2{}^{195}Pt(OH)_2{}^{195}PtL_2]^{2+}$ (relative abundance 11.4%). As previously noticed for *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)]_2(BF_4)_2$,[3] the main resonance does not show resolved satellites, which are assigned to the $^3J_{P,Pt}$ coupling, indicating that the magnetic interaction between the ^{31}P and ^{195}Pt nuclei through three bonds is presumably too small to be observed.

Lability of the Bridging Hydroxo Ligands in *cis*-$[L_2Pt(\mu\text{-}OH)]_2^{2+}$ (L = PMe_3, PMe_2Ph, and $PMePh_2$)

The ^1H and ^{31}P NMR spectroscopic parameters of **1** and **2** do not exhibit appreciable changes with the concentration (in the 10^{-2} to 10^{-3} M range), suggesting that these dinuclear hydroxo-bridged complexes do not dissociate significantly in DMSO solution. However, the lability of the Pt−O bonds becomes evident when solutions of **1** and **2** are mixed. The ^{31}P NMR spectrum of a freshly prepared mixture shows, after a few minutes, the growth of two new singlets, symmetrically flanked by ^{195}Pt satellites at $\delta = -5.15$ ($^1J_{P,Pt}$ = 3541 Hz) and −16.15 ($^1J_{P,Pt}$ = 3478 Hz). These values for the chemical shifts and the coupling constants are intermediate between those found for the pure compounds (Table 2), and are consistent with the formation of the mixed complex *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)_2Pt(PMePh_2)_2]^{2+}$. A similar exchange also occurs when **1** or **2** are mixed with *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$.

Table 2. ^1H and ^{31}P NMR spectroscopic data for *cis*- $[L_2Pt(\mu\text{-}OH)_2PtL'_2](NO_3)_2$ in [D$_6$]DMSO at 27 °C

L,L	δ_P [ppm]	$^1J_{P,Pt}$ [Hz]	δ_{OH} [ppm]
L = L′ = PMe_3	−24.5	3358	3.46
L = L′ = PMe_2Ph	−15.5	3457	4.11
L = L′ = $PMePh_2$	−5.32	3571	3.53
L = PMe_3	−24.30	3363	3.40
L′ = PMe_2Ph	−15.73	3446	
L = PMe_3	−24.87	3377	4.01
L′ = $PMePh_2$	−4.94	3522	
L = PMe_2Ph	−16.15	3478	3.90
L′ = $PMePh_2$	−5.15	3541	

In all the cases, the NMR spectrum of the resulting mixture shows the resonances of the starting complexes and two new singlets which are assigned to the species *cis*-$[L_2Pt(\mu\text{-}OH)_2PtL'_2]^{2+}$ (L = PMe_3, L′ = PMe_2Ph or $PMePh_2$). After a few hours at room temperature, the relative intensities of the signals due to the mixed complexes are approximately the same as those expected for a statistical distribution of the *cis*-$[L_2Pt(OH)]^+$ units according to the equilibrium reaction [Equation (1)].

$$cis\text{-}[L_2Pt(\mu\text{-}OH)]_2^{2+} + cis\text{-}[L'_2Pt(\mu\text{-}OH)]_2^{2+} \rightleftarrows 2\,cis\text{-}[L_2Pt(\mu\text{-}OH)_2PtL'_2]^{2+} \quad (1)$$

This exchange reaction is followed by a further redistribution of the neutral ligands around the metal center as indicated by the appearance of additional doublets due to the {*cis*-LL′Pt} moieties in the ^{31}P NMR spectra.[8] The lability of the bridging hydroxo ligands has previously been observed in the structurally related Ni^{II} complexes $[NiR(PMe_3)(\mu\text{-}OH)]_2$ (R= CH_2Ph; CH_2CMe_2Ph).[9]

Synthesis and Characterization of the Oxo Complexes [{*cis*-L_2Pt}$_3(\mu\text{-}O)_2$]X_2 (L = PMe_3, X= ClO_4^-, 3; L = PMe_2Ph, X = Cl^-, 4)

When chloride ions were added to solutions of *cis*-$[L_2Pt(\mu\text{-}OH)]_2X_2$ (X = NO_3^-, ClO_4^-; L = PMe_3, PMe_2Ph) in DMSO or CH_2Cl_2/DMSO, at room temperature, a mixture of the species *cis*-$[L_2PtCl_2]$ and [{*cis*-L_2Pt}$_3(\mu\text{-}O)_2$]$^{2+}$ (L = PMe_3, **3**; PMe_2Ph, **4**) was formed. {^1H}^{31}P NMR analysis of the resulting pale yellow solutions shows that the relative quantity of the two products is strongly dependent on the stoichiometric ratio of the reactants. A large excess of Cl^- ions (molar ratio > 10), added as solid $(NEt_4)Cl\cdot H_2O$ or $(PPh_4)Cl$, affords the corresponding *cis*-$[L_2PtCl_2]$ as the only detectable species. At lower concentrations of the chloride ions, the solutions contain increasing amounts of the oxo complexes [{*cis*-L_2Pt}$_3(\mu\text{-}O)_2$]$^{2+}$.

When the molar ratio $n_{(\mathrm{Cl}^-)}/n_{(\mathrm{Pt\ complex})}$ is in the range 1−2, the relative intensity of the ^{31}P resonances which are assigned to the dichloro and oxo complexes approach the value expected from the following reaction [Equation (2)].

$$2\ cis\text{-}[L_2Pt(\mu\text{-}OH)]_2^{2+} + 2\ Cl^- \rightleftarrows cis\text{-}[L_2PtCl_2] + [\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2]^{2+} + 2\ H_2O \quad (2)$$

The trinuclear complexes were obtained as pure compounds (^{31}P NMR spectroscopy) after precipitation with Et_2O, followed by fractional crystallization. The elemental analysis of the product isolated from the reaction of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ with $(NEt_4)Cl$ was consistent with the separation of the oxo species as the perchlorate salt, $[\{cis\text{-}(PMe_3)_2Pt\}_3(\mu\text{-}O)_2](ClO_4)_2$ (**3**). The presence of the ClO_4^- ion was clearly evidenced by the typical absorption at 1093 cm^{-1} in the IR spectrum of the solid.

The crystallization of the product obtained from the reaction of *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ with Cl^- gave crystals of $[\{cis\text{-}(PMe_2Ph)_2Pt\}_3(\mu\text{-}O)_2]Cl_2$ (**4**), i.e. the chloride salt of the oxo species, as established by single-crystal X-ray analysis. The structure of the dication of **4** is shown in Figures 3 and 4, while the relevant data are presented in Table 3.

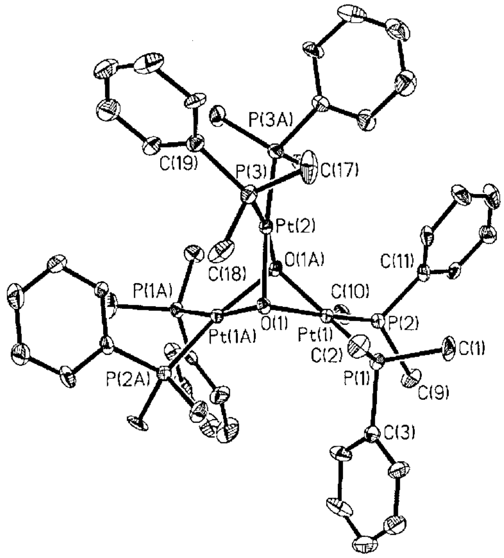


Figure 3. ORTEP drawing of **4** showing 35% probability thermal ellipsoids and the essential atom numbering scheme; for clarity, the chloride anions are omitted

The oxygen atoms cap a triangle formed by three $(PMe_2Ph)_2Pt$ units in which the average Pt···Pt distance is 2.884 Å. Comparison of this structure with that containing BF_4^- as the counterion[3] does not reveal any significant differences. For example, the Pt−O distances and the angles around the oxygen atoms are almost equal, averaging 2.087(5) Å and 87.4(2)° in **4** and 2.083(8) Å and 87.4(3)° in that previously determined. The three dihedral angles formed by the three P_2PtO_2 mean planes are 61.3, 58.7, and 61.3° in **4** and compare with the values of 61.8, 59.1, and 59.5° in the BF_4^- derivative.

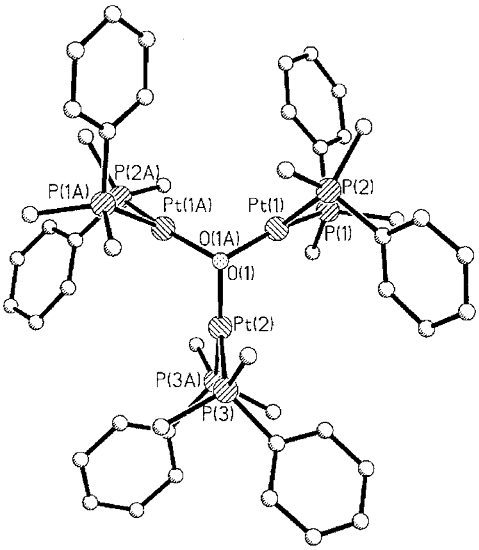


Figure 4. The dication of **4** viewed along the O(1)···O(1A) line

Table 3. Selected bond lengths [Å] and angles [°] for complex **4**

Pt(1)−O(1)	2.089(5)	Pt(1)−P(1)	2.229(2)
Pt(1)−O(1A)[a]	2.078(5)	Pt(1)−P(2)	2.230(2)
Pt(2)−O(1)	2.094(5)	Pt(2)−P(3)	2.233(2)
Pt(1)···Pt(2)	2.883(1)	Pt(2)···Pt(1A)	2.883(1)
Pt(1)···Pt(1A)	2.886(1)		
		P(3)−Pt(2)−O(1)	94.2(2)
P(1)−Pt(1)−P(2)	97.1(1)	P(3)−Pt(2)−P(3A)	97.9(1)
P(1)−Pt(1)−O(1)	94.8(1)	O(1)−Pt(2)−O(1A)	73.9(3)
O(1)−Pt(1)−O(1A)	74.3(2)	P(3)−Pt(2)−O(1A)	167.6(2)
O(1A)−Pt(1)−P(2)	94.2(1)	Pt(1)−O(1)−Pt(2)	87.1(2)
P(1)−Pt(1)−O(1A)	167.5(1)	Pt(1)−O(1)−Pt(1A)	87.7(2)
P(2)−Pt(1)−O(1)	167.7(1)	Pt(2)−O(1)−Pt(1A)	87.4(2)

[a] At $1/2 - x$, $y - 1/2$, $1/2 - z$.

Attempts to determine the structure of **3** by X-ray analysis were unsuccessful. However the ^{31}P NMR spectrum of this complex shows a pattern that is very similar to that shown in the spectrum of **4**. Both complexes are characterized by a singlet (at $\delta = -30.3$ and -19.5 ppm for **3** and **4**, respectively, in [D$_6$]DMSO) that is symmetrically flanked by satellites which can be assigned to the $^3J_{\mathrm{P,Pt}}$ (ca. 13 Hz) and $^1J_{\mathrm{P,Pt}}$ couplings (in the range 3356−3396 Hz for **3** and 3410−3460 Hz for **4**).

Dinuclear oxo complexes of platinum(II) stabilized by phosphanes are obtained by reacting the corresponding hydroxo compounds with strong bases [Equation (3)].

$$cis\text{-}[L_2Pt(\mu\text{-}OH)]_2(BF_4)_2 + 2\ LiNR_2 \rightleftarrows [cis\text{-}L_2Pt(\mu\text{-}O)]_2{\cdot}2LiBF_4 + 2\ HNR_2 \quad (3)$$

The bridging oxo ligands generally associate one or two molecules of $LiBF_4$, depending on the type of phosphane used. In solution, when L is PMe_2Ph, the dinuclear oxo complex decomposes to form the stable species $[\{cis\text{-}(PMe_2Ph)_2Pt\}_3(\mu\text{-}O)_2](BF_4)_2$ in a high yield.[3] In the reaction of **1**, and its PMe_3 analogue, with Cl^- ions [Equation (2)], the ^{31}P NMR spectra obtained immediately after the addition of the chloride ions do not show signals which can be assigned to the dinuclear oxo complex. The formation of *cis*-$[L_2PtCl_2]$ and $[\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2]^{2+}$ instead is accompanied by the formation of a relatively stable species; it has tentatively been suggested that this species is the mixed complex *cis*-[$L_2PtCl(OH)$], although a dinuclear species of the type $[\{cis\text{-}L_2Pt\}_2(\mu\text{-}Cl)(\mu\text{-}OH)]^{2+}$ cannot be ruled out.[10] In a typical experiment, increasing amounts of $(AsPh_4)Cl$ as a solid were added to a CD_2Cl_2 solution of **1a** and the ^{31}P NMR spectrum of the resulting solution immediately obtained. Figure 5(a) shows the spectrum that is observed when the molar ratio $n_{(\mathbf{1a})}/n_{(Cl^-)}$ is 1.0. The main resonance signal is the singlet, whose chemical shift and coupling constant are very similar to those of unchanged **1a**. The signals of the oxo species (at $\delta = -19.5$) and the dichloro complex (at $\delta = -14.4$) exhibit relative intensities of 5.6:1, whereas the resonances assigned to *cis*-[$L_2PtCl(OH)$], characterized by an AX multiplet, (at ca. $\delta = -12$ and -24 ppm; $^2J_{P,P} = 24$ Hz) are only just detectable.

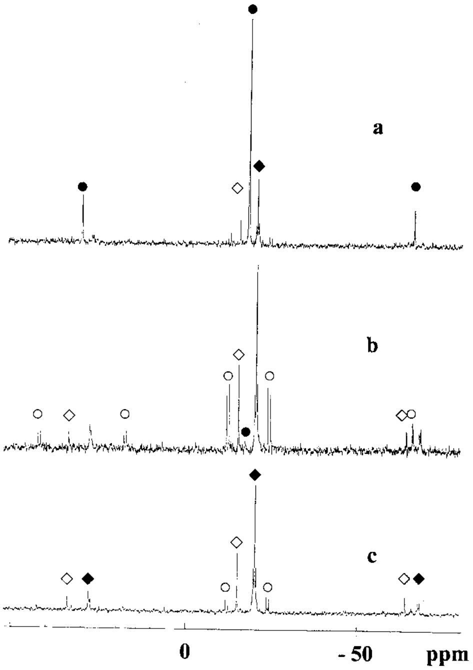


Figure 5. $\{^1H\}^{31}P$ NMR spectrum (at 36.23 MHz) of a solution ($3.73\cdot10^{-2}$ M) of **1a** in CD_2Cl_2 at 27 °C: (**a**) immediately after the addition of $(AsPh_4)Cl$ (molar ratio **1a**/Cl^- = 1:1); the labels (solid circle and solid diamond) refer to the complexes *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)]_2^{2+}$ and *cis*-$[\{(PMe_2Ph)_2Pt\}_3(\mu\text{-}O)_2]^{2+}$, respectively; (**b**) ca. half an hour after (a), following the addition of a further amount of $(AsPh_4)Cl$ (molar ratio **1a**/Cl^- = 1:2); (**c**) after 12 h at 33 °C); the labels (open circle and open diamond) refer to the complexes *cis*-$[(PMe_2Ph)_2PtCl_2]$ and *cis*-$[(PMe_2Ph)_2PtCl(OH)]$, respectively

The further addition of chloride ions ($n_{(\mathbf{1a})}/n_{(Cl^-)} = 1:2$), carried out after ca. 0.5 h, leads to the almost complete disappearance of the resonances due to the starting complex, whereas the AX multiplet became more intense to allow the detection of the platinum-195 satellites (Figure 5, b). The doublet at lower field ($\delta = -11.97$, $^1J_{P,Pt}$ 3930 Hz) is assigned to the PMe_2Ph molecule *trans* to the chloride ion, and the resonance at -23.86 ppm, with a lower P−Pt coupling constant (3020 Hz), is assigned to the phosphane *trans* to the hydroxo ligand. The intensities of these signals slowly decrease, whereas the relative intensities of the signals at $\delta = -19.5$ and -14.4 ppm remain apparently unchanged as shown in Figure 5(c), which represents the spectrum of the same solution left for 12 h at 33 °C.

A similar behavior was observed with the hydroxo complex stabilized by PMe_3. The spectrum of a mixture containing *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2X_2$ and Cl^- in a 1:2 molar ratio shows, in addition to the resonances assigned to the oxo complex **3** (52% of relative intensity) and *cis*-$[(PMe_3)_2PtCl_2]$ (relative intensity 20%), an AX multiplet ($^2J_{P,P} = 20$ Hz) at $\delta = -21.0$ and -34.0 ppm which disappears after 24 h. These results lead to conclusion that the species responsible for the AX multiplet, the mononuclear hydroxo complex *cis*-$[(PMe_3)_2PtCl(OH)]$, slowly decomposes leaving a pale yellow solution in which the only detectable resonances are those of the colorless species *cis*-$[L_2PtCl_2]$ and $[\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2]^{2+}$.

Once formed, the species $[\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2]^{2+}$ are unreactive towards an excess of Cl^-ions. In fact, the ^{31}P NMR spectrum of the isolated complex **3** (in **4**) in DMSO is unaffected by the addition of $AsPh_4Cl$ (molar ratio 1:3), after several days at room temperature. The stability of the Pt−O bonds in these trinuclear oxo complexes is confirmed by the observation that they do not undergo intermolecular exchange. Unlike their hydroxo precursors, when mixed in DMSO, **3** and **4** maintain their structure as is observed by the absence of new resonances in the ^{31}P NMR spectrum of the resulting mixture.

Reactivity of *cis*-$[(PMePh_2)_2Pt(\mu\text{-}OH)]_2^{2+}$ with Cl^-

Under the same conditions as those used for the PMe_3 and PMe_2Ph analogues, complex **2** does not form stable oxo species when treated with Cl^-. The ^{31}P NMR spectrum of a solution of **2** in $CDCl_3$ (or CH_2Cl_2/$[D_6]$DMSO mixtures) containing $(NEt_4)Cl{\cdot}H_2O$ (or $AsPh_4Cl$) in a 1:2 molar ratio, exhibit an intense singlet at $\delta = -1.08$ ($^1J_{P,Pt} = 3634$ Hz) and an AX multiplet ($\delta = 1.97$, $^1J_{P,Pt} = 4030$ Hz and -9.03 ppm, $^1J_{P,Pt} = 3100$ Hz, with $^2J_{P,P} = 23$ Hz) as the main resonance signals. These signals are assigned to *cis*-$[(PMePh_2)_2PtCl_2]$ and to the neutral complex *cis*-$[(PMePh_2)_2PtCl(OH)]$. Two relatively weak signals are seen at $\delta = -8.85$ (singlet, $^1J_{P,Pt} = 3602$ Hz) and at $\delta = -5.72$ (broad singlet). After 12 h at room temperature, the AX multiplet disappears, the resonance at $\delta = -5.72$ ppm also disappears and is replaced by a very weak singlet at $\delta = -5.92$ due to unchanged complex **2**. A further change in the ^{31}P NMR spectrum occurs after several days, leading to the complete disappearance of the resonance at $\delta = -8.85$. The low concentration and the moderate stability of the species responsible for this singlet prevents better characterization. The absence of the fine structure observed for **3** and **4**, however, seems to exclude the formation of the analogous trinuclear species *cis*-$[\{(PMePh_2)_2Pt\}_3(\mu\text{-}O)_2]^{2+}$. On the other hand, the formation of a mononuclear species of the type *cis*-$[(PMePh_2)_2Pt(OH)_2]$, (the analogue *cis*-$[(PMe_3)_2Pt(OH)_2]$ (known to be unstable in chlorinated solvents) as has been seen before),[11] is not supported by the value of $^1J_{P,Pt}$ coupling constant. The observed value (3602 Hz), in fact, is only slightly lower than that of the dichloro complex, *cis*-$[(PMePh_2)_2PtCl_2]$ ($^1J_{P,Pt}$ = 3627 Hz); however, the difference between the observed value and those for *cis*-$[(PMe_3)_2Pt(OH)_2]$ (3254 Hz, in CD_2Cl_2) and *cis*-$[(PMe_3)_2PtCl_2]$ (3470 Hz) is large.[11] Similar considerations seem to exclude the formation of *cis*-$[(PMePh_2)_2Pt(\mu\text{-}O)]_2$ since such oxo species should have a $^1J_{P,Pt}$ value that is much lower than that of the precursor hydroxo complex.[3]

Conclusions

The structures of complexes **1** and **2** reported here represent further examples of the preference for the $\{L_2Pt(OH)\}^+$ moiety (L = phosphanes or diphosphanes) to form dinuclear species. This feature is in common with most of the monohydroxo complexes of Pt^{II} with N-donor ligands, although examples of the formation of hydroxo complexes with higher nuclearity from some diamines are known.[12]

An interesting feature of the phosphano-based complexes *cis*-$[L_2Pt(\mu\text{-}OH)]_2{}^{2+}$ (L = PMe_3, PMe_2Ph, and $PMePh_2$) is their reactivity towards Cl^- ions. Unlike the isostructural hydroxo compounds containing the chelate ligands 2,2′-bipyridine or phenanthroline, which are inert towards LiCl even at 100 °C,[13] they react with Cl^- ions under very mild conditions. When an excess of chloride ions is used, the substitution of the OH^- ligands, to give *cis*-$[L_2PtCl_2]$, is the predominant process. At lower concentrations of Cl^- ions, however, other reaction pathways become competitive, leading to the concomitant formation of the stable complexes $[\{cis\text{-}L_2Pt\}_3(\mu\text{-}O)_2]^{2+}$ when L is PMe_3 or PMe_2Ph, but an unstable and not yet fully characterized species when L is $PMePh_2$.

Experimental Section

Reagent and Chemicals: Reagent grade chemicals $(NEt_4)Cl\cdot H_2O$ (Ega-Chemie) and $(AsPh_4)Cl$ (Fluka) were used as received. The complexes *cis*-$[(PMePh_2)_2PtCl_2]$,[14] *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2X_2$ (X = NO_3,[5] ClO_4),[15] and *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)]_2(NO_3,)_2$ [6] were synthesized as previously reported.

Instrumentation: ^1H and $\{^1H\}^{31}P$ spectra were obtained with JEOL 90Q and/or Bruker 300AVANCE spectrometers. ^1H chemical shifts are referred to the residual peak of the deuterated solvent ($[D_6]DMSO$), whereas the external reference for ^{31}P is H_3PO_4 (85% w/w in H_2O). IR spectra in the range 4000−400 cm^{-1} were recorded as KBr pellets with a Perkin−Elmer 283 spectrophotometer.

Syntheses of the Complexes

Preparation of *cis*-$[(PMe_2Ph)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ (1b): A solution of $AgNO_3$ (1.15 g, 6.77 mmol) in H_2O (20 mL) was added to a suspension of *cis*-$[(PMe_2Ph)_2PtCl_2]$ (1.84 g, 3.38 mmol) in H_2O (200 mL). The AgCl precipitate formed immediately was removed by filtration, and the resulting solution was neutralized with NaOH (0.092 M). Addition of $NaClO_4\cdot H_2O$ (0.48 g, 3.4 mmol) led to the immediate precipitation of a white microcrystalline solid, which was collected by filtration, washed with H_2O, EtOH, and Et_2O. The yield of the dry product **1b** was 1.29 g (92%). $C_{16}H_{23}ClO_5P_2Pt$ (587.8): calcd. C 32.69, H 3.94; found C 32.41, H 4.01. ^1H NMR at 89.55 MHz in $[D_6]DMSO$: δ = 7.5−7.7 (5 H, Ph), 4.09 (broad s, 1 H, OH), 1.54 (apparent doublet, J_{PH} = 11.7, $^3J_{PtH}$ = 35.6 Hz, 6 H, CH_3) ppm. $\{^1H\}^{31}P$ NMR at 36.23 MHz in $[D_6]DMSO$: δ = −14.50 (s, $^1J_{P,Pt}$ = 3456 Hz; $^2J_{Pt,Pt}$ = 304 Hz) ppm.

Caution*: *The above perchlorate is a potential explosive!

Preparation of *cis*-$[(PMePh_2)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (2): A solution of $AgNO_3$ (0.794 g, 4.67 mmol) in EtOH (10 mL) and H_2O (2 mL) was added to a solution of *cis*-$[(PMePh_2)_2PtCl_2]$ (1.56 g, 2.34 mmol) in CH_2Cl_2 (20 mL). The AgCl precipitate formed immediately was filtered, and an aqueous solution (25.4 mL) of NaOH (0.092 M) was added to the resulting solution. The solution was concentrated under vacuum, and a white precipitate was obtained, which was recovered by filtration, washed twice with H_2O (10 mL) and dried under vacuum. The yield of the pure product **2** was 1.11 g (70%). $C_{26}H_{27}NO_4P_2Pt$ (674.5): calcd. C 46.29, H 4.03, N 2.08; found C 45.73, H 3.96, N 1.99. ^1H NMR at 89.55 MHz in $[D_6]DMSO$: δ = 7.5−7.8 (10 H, Ph), 3.53 (s broad, 1 H, OH), 1.62 [apparent doublet, J_{PH} = 10.7 Hz, 3 H, CH_3] ppm. $\{^1H\}^{31}P$ NMR in $[D_6]DMSO$: δ = −5.32 (s, $^1J_{P,Pt}$ = 3578, $^2J_{Pt,Pt}$ = 232 Hz) ppm.

Preparation of $[\{cis\text{-}(PMe_3)_2Pt\}_3(\mu\text{-}O)_2](ClO_4)_2$ (3): A solution of $(NEt_4)Cl\cdot H_2O$ (228 mg, 1.24 mmol) in CH_2Cl_2 (20 mL) was added to a stirred solution of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ (576 mg, 0.62 mmol) in DMSO (15 mL), and the resulting pale yellow solution was left at room temperature for 18 h. Addition of Et_2O (100 mL) afforded a white precipitate which was recovered by filtration, dissolved in a minimum amount of CH_2Cl_2 and precipitated by addition of Et_2O. The crude solid (265 mg) was further purified from CH_2Cl_2/Et_2O, and a microcrystalline product was obtained which was recovered by filtration, washed with EtOH and dried under vacuum. The yield of the pure compound **3** was 91 mg [23%, based on Equation (2)]. $C_{18}H_{54}Cl_2O_{10}P_6Pt_3$ (1272): calcd. C 16.99, H 4.28; found C 16.78, H 4.16. ^1H NMR in $[D_6]DMSO$: δ = 1.59 (d, $J_{H,P}$ = 10.3, $^3J_{H,Pt}$ = 34 Hz) ppm. $\{^1H\}^{31}P$ NMR in CD_2Cl_2 (at 36.23 MHz): δ = −31.7 ($^1J_{P,Pt}$ = 3376−3406 Hz) ppm. Crystallization of the solid from $CH_2Cl_2/CHCl_3$ (1:1) gave needle-shaped colorless crystals unsuitable for X-ray diffraction analysis.

Preparation of $[\{cis\text{-}(PMe_2Ph)_2Pt\}_3(\mu\text{-}O)_2]Cl_2$ (4): A solution of $(NEt_4)Cl\cdot H_2O$ (166 mg, 0.90 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of **1b** (533 mg, 0.49 mmol) in DMSO (6 mL). The resulting pale yellow solution was left at ca. 20 °C for 24 h. Addition of Et_2O (120 mL) gave a waxy solid which was rapidly washed with H_2O and then with Et_2O. The dried solid (360 mg) was purified twice by dissolution in CH_2Cl_2 and precipitation with toluene. The yield of **4**, free of the perchlorate salt, was 126 mg [yield 34%, based on Equation (2)]. $C_{48}H_{66}Cl_2O_2P_6Pt_3$ (1517.0): calcd. C 38.00, H 4.38; found C 37.85, H 4.29. ^1H NMR in $[D_6]DMSO$: δ = 7.96−7.53 (complex multiplets, 5 H, Ph), 1.52 (d, $J_{H,P}$ = 10.2 Hz with unresolved ^{195}Pt satellites) ppm. $\{^1H\}^{31}P$ NMR in CD_2Cl_2: δ = −20.1 ($^1J_{P,Pt}$ = 3460−3487 Hz) ppm.

Table 4. Crystal and refinement data for complexes **1a**, **2**, and **4**

Complex	**1a**	**2**	**4**
Formula	$C_{32}H_{46}N_2O_8P_4Pt_2$	$C_{52}H_{54}N_2O_8P_4Pt_2$	$C_{48}H_{66}Cl_2O_2P_6Pt_3$
Molecular mass	1100.8	1349.0	1517.0
Color	colorless	colorless	colorless
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\ -1$ (No. 2)	$P\ 2_1/n$ (No. 14)	$C\ 2/c$ (No. 15)
a [Å]	10.642(2)	9.772(2)	23.160(2)
b [Å]	11.830(2)	16.292(3)	13.404(4)
c [Å]	16.129(3)	16.040(4)	17.996(4)
α [°]	105.66(1)		
β [°]	93.78(1)	100.48(2)	99.36(2)
γ [°]	94.75(1)		
V [Å^3]	1940.3(5)	2510.9(9)	5512(2)
Z	2	2	4
D_{calc} [g cm^{-3}]	1.884	1.784	1.828
$F(000)$	1064	1320	2912
μ (Mo-K_α) [mm^{-1}]	7.41	5.75	7.90
Crystal dimensions [mm]	0.20·0.20·0.30	0.15·0.25·0.20	0.30·0.15·0.08
Θ limits [°]	2.0 / 21.0	2.0 / 22.5	1.8 / 25.0
No. of independent data	4186	3286	4549
No. of data with $I > 2\sigma\ (I)$	3162	2815	3779
No. of variables	366	308	286
$R(F)$[a]	0.050	0.049	0.031
$wR(F^2)$[b]	0.121	0.131	0.066
Largest peak in ΔF [e·Å^{-3}]	1.3	1.7	0.8
GOF[c]	1.004	1.193	1.011

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$. [c] $\mathrm{GOF} = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$.

X-ray Data Collection, Structure Solution and Refinement of 1a, 2, and 4:[16] The X-ray data collections were performed at room temperature with a Nicolet−Siemens four-circle R3m/V diffractometer on single-crystals mounted in thin-walled glass capillaries with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å).

Crystals of **1a** and **2** were obtained by slow diffusion of vapors of Et_2O into a saturated solution of the corresponding compound in ethanol, whereas crystals of **4** were obtained by slow evaporation of a $CH_2Cl_2/C_6H_5CH_3$ solution of the complex, at room temperature.

A summary of the X-ray analyses carried out on the complexes is listed in Table 4. The cell dimensions for the complexes were determined from the setting angles of 50 centered reflections. Intensity data were collected for unique portions of reciprocal space to the limit of observable diffraction. Corrections for X-ray absorption effects were applied on the basis of azimuthal scan data.[17] The absorption effects have been noticeable only in complex **4**, the transmission factors ranging from 0.637 to 0.996.

The unit cell of **1a** comprises two moieties denoted as **I** and **II**. The structures were solved by heavy-atom methods and refined by full-matrix least-squares against F^2. Pt, P, and phenyl C atoms of **1a** and all non-hydrogen atoms of **2** and **4** were assigned anisotropic displacement parameters. As expected, the nitrate groups of **1a** and **2** endure high thermal motions and they have been treated isotropically.

Final difference syntheses showed no chemically significant features, the largest maxima being close to the platinum. Refinements converged smoothly to residuals given in Table 4. All calculations were made with programs of the SHELXTL/PC[18] system and SHELXL-93[19] program.

Acknowledgments

This work was financially supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (PRIN 2001).

---

[1] P. R. Sharp, *J. Chem. Soc., Dalton Trans.* **2000**, 2647−2657.
[2] J. S. L. Yeo, J. J. Vittal, W. Henderson, T. S. A. Hor, *Inorg. Chem.* **2002**, *41*, 1194−1198.
[3] J. J. Li, W. Li, P. R. Sharp, *Inorg. Chem.* **1996**, *35*, 604−613.
[4] G. W. Bushnell, K. R. Dixon, R. G. Hunter, J. J McFarland, *Can. J. Chem.* **1972**, *50*, 3694−3699.
[5] G. Trovò, G. Bandoli, U. Casellato, B. Corain, M. Nicolini, B. Longato, *Inorg. Chem.* **1990**, *29*, 4616−4621.
[6] B. Longato, L. Pasquato, A. Mucci, L. Schenetti, *Eur. J. Inorg. Chem.* **2003**, 128−137.
[7] R. Faggiani, B. Lippert, C. J. L. Lock, B. Rosenberg, *J. Am. Chem. Soc.* **1977**, *99*, 777−781.
[8] D. G. Cooper, J. Powell, *J. Am. Chem. Soc.* **1973**, *95*, 1102−1108.
[9] E. Carmona, J. M. Marin, P. Palma, M. Paneque, M. L. Poveda, *Inorg. Chem.* **1989**, *28*, 1895−1900.
[10] M. E. Fakley, A. Pidcock, *J. Chem. Soc., Dalton* **1977**, 1444−1448.
[11] T. K. Miyamoto, Y. Suzuki, H. Ichida, *Chem. Lett.* **1992**, 839−842; T. K. Miyamoto, Y. Suzuki, H. Ichida, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3386−3397.
[12] R. Faggiani, B. Lippert, C. J. L. Lock, B. Rosenberg, *Inorg. Chem.* **1977**, *16*, 1192−1196; F. D. Rochon, A. Morneau, R. Melanson, *Inorg. Chem.* **1988**, *27*, 10−13.

[13] S. Wimmer, P. Castan, F. L. Wimmer, N. P. Johnson, *J. Chem. Soc., Dalton Trans.* **1989**, 403−412.

[14] S. O. Grim, R. L. Keiter, W. Mc Farlane, *Inorg. Chem.* **1967**, *6*, 1133−1137.

[15] B. Longato, G. Bandoli, A. Mucci, L. Schenetti, *Eur. J. Inorg. Chem.* **2001**, 3021−3029.

[16] CCDC-168694 (for **1a**), -168695 (for **2**), and -168696 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[17] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351−359.

[18] G. M. Sheldrick, *SHELXTL/PC*, Version 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, **1994**.

[19] G. M. Sheldrick, *SHELXL-93*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1993**.

Received July 9, 2003
Early View Article