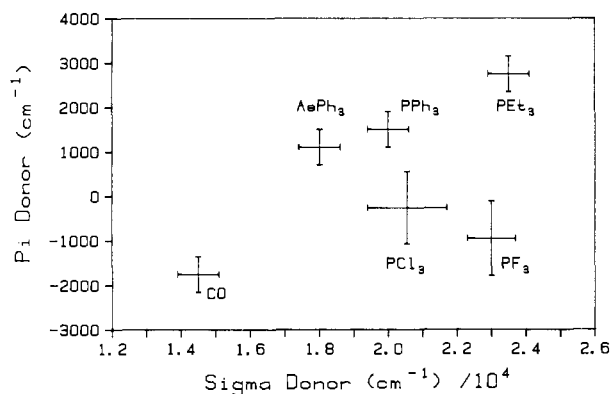


**Table II.** Band Assignments and Calculated Transition Energies for  $(\text{Pr}_4\text{N})[\text{PtCl}_3(\text{PF}_3)]$  and  $(\text{Pr}_4\text{N})[\text{PtCl}_3(\text{PCl}_3)]^a$ 

Pt-PF <sub>3</sub>			Pt-PCl <sub>3</sub>		
obsd	calcd	assgnt	obsd	calcd	
Singlet d-d					
32 300	32 663	<sup>1</sup> B <sub>1</sub>	29 940	30 055	
36 200	35 985	<sup>1</sup> A <sub>2</sub>	33 800	33 822	
39 900	39 947	<sup>1</sup> B <sub>2</sub>	37 700	37 027	
	40 162	<sup>1</sup> A <sub>1</sub>		38 028	
Triplet d-d					
	22 657	B <sub>2</sub>		20 480	
	22 837	A <sub>1</sub>		20 543	
23 000	23 048	B <sub>1</sub>	21 600	20 934	
(22 900-23 800)			(21 050-22 030)		
	24 677	A <sub>2</sub>		22 098	
	25 789	B <sub>2</sub>		23 383	
26 000	26 127	B <sub>1</sub>	23 540	23 553	
(25 600-26 700)			(22 990-24 100)		
	26 177	A <sub>2</sub>		23 883	
	26 781	A <sub>1</sub>		24 414	
28 700	28 875	B <sub>2</sub>	26 700	26 706	
(28 170-29 400)			(25 970-27 030)		
	29 638	A <sub>1</sub>		26 851	
	30 428	A <sub>2</sub>		27 793	
	31 650	B <sub>1</sub>		29 266	

<sup>a</sup>The transition energies for  $\text{PtCl}_3(\text{PF}_3)^-$  were calculated by using the following parameters ( $\text{cm}^{-1}$ ):  $I_{\sigma}^{\text{Cl}}$  = 11 800,  $I_{\pi}^{\text{Cl}}$  = 3000,  $L_{\pi}^{\perp,\text{Cl}}$  = 2700,  $I_{\sigma}^{\text{PF}_3}$  = 22 900,  $I_{\pi}^{\text{PF}_3}$  = 1020,  $L_{\pi}^{\perp,\text{PF}_3}$  = -2050,  $B$  = 630,  $C$  = 3000,  $\text{SOC}$  = 2850,  $\sigma_{\text{sd}}$  = 14 575. The transition energies for  $\text{PtCl}_3(\text{PCl}_3)^-$  were calculated by using the following parameters ( $\text{cm}^{-1}$ ):  $I_{\sigma}^{\text{Cl}}$  = 11 800,  $I_{\pi}^{\text{Cl}}$  = 3000,  $L_{\pi}^{\perp,\text{Cl}}$  = 2700,  $I_{\sigma}^{\text{PCl}_3}$  = 20 000,  $I_{\pi}^{\text{PCl}_3}$  = 1450,  $L_{\pi}^{\perp,\text{PCl}_3}$  = -1150,  $B$  = 630,  $C$  = 3000,  $\text{SOC}$  = 2850,  $\sigma_{\text{sd}}$  = 13 850.



**Figure 4.** Two-dimensional spectrochemical series for the phosphine ligands and other ligands of interest in organometallic chemistry. The  $\pi$  acceptor strength increases from top to bottom. The  $\sigma$  donor strength increases from left to right.

$\text{cm}^{-1}$ . The uncertainties in these values are larger than those in the ligand field parameters obtained from other platinum compounds in which the transition energies could be measured with high accuracy from single-crystal polarized absorption spectra. In addition, the  $\pi$  values are the average of the in-plane and out-of-plane components, which reflect the different magnitudes of  $\pi$  interaction of the ligand with the  $d_{xy}$  and the  $d_{xz}$  orbitals, respectively. It is important to note that the sign of the  $\pi$  parameter does not have an intrinsic meaning. Only the relative values can be interpreted. These parameters are the result of a complete calculation in which no approximations regarding the  $\pi$  parameters have been made. It has long been known that the AOM  $\pi$  parameter for amines is not zero.<sup>20</sup> When the complete fit to experimental spectra is obtained and the  $\pi$  value for amine is allowed to vary in order to obtain the best fit, the  $\pi$  value is generally greater than zero. Thus, the small positive value of the  $\pi$  parameter for the  $\text{PCl}_3$  ligand should be interpreted to mean that the ligand is a poorer  $\pi$  acceptor (or conversely a better  $\pi$  donor) than the  $\text{PF}_3$  ligand and a much better  $\pi$  acceptor (or poorer donor) than the chloride ligand. The values of the Racah  $B$  and  $C$  parameters are a measure of the nephelauxetic effect.

Because the variations of these parameters are small compared to the uncertainties, no meaningful comparisons can be made.

The relationship of the ligand field parameters of both  $\text{PF}_3$  and  $\text{PCl}_3$  to those of other phosphine ligands and ligands of interest in organometallic chemistry are shown in the two-dimensional spectrochemical series in Figure 4. The results show that  $\text{PF}_3$  is a surprisingly good  $\sigma$  donor. Its  $\sigma$  donor interaction with platinum is stronger than that of  $\text{CO}$ ,  $\text{PPh}_3$ , and  $\text{PCl}_3$  but weaker than that of  $\text{PEt}_3$ . The large  $\sigma$  donor interaction is consistent with a large synergistic effect.<sup>2</sup> The  $\pi$  back-bonding ability of  $\text{PF}_3$  is stronger than that of any of the other phosphines which have been studied by electronic spectroscopy but slightly weaker than that of  $\text{CO}$ .

**Acknowledgment.** We thank the National Science Foundation (Grant CHE 85-09329) for support of this work.

**Registry No.**  $(\text{Pr}_4\text{N})[\text{PtCl}_3(\text{PF}_3)]$ , 113258-11-0;  $(\text{Pr}_4\text{N})[\text{PtCl}_3(\text{PCl}_3)]$ , 113258-12-1;  $\text{PF}_3$ , 7783-55-3;  $\text{PCl}_3$ , 7719-12-2.

Contribution from the Research School of Chemistry,  
The Australian National University,  
G.P.O. Box 4, Canberra, ACT 2601, Australia

#### Platinum(IV) Cage Chemistry: Crystal Structure of [1,8-Bis(hydroxylamino)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosa]platinum(IV) Trifluoromethanesulfonate Hydrate

Karl S. Hagen,<sup>\*,†</sup> Peter A. Lay, and Alan M. Sargeson\*

Received July 28, 1987

We recently reported the synthesis and properties of platinum(IV) cage complexes prepared by the template synthesis about  $[\text{Pt}(\text{en})_3]^{4+}$ .<sup>1</sup> Reaction of  $[\text{Pt}(\text{en})_3]^{4+}$  with formaldehyde and ammonia resulted in the preparation of  $[\text{Pt}(\text{sep})]^{4+}$ ,<sup>1-3</sup> while the use of  $\text{CH}_2\text{NO}_2^-$  as a nucleophile resulted in the preparation of  $[\text{Pt}((\text{NO}_2)_2\text{sar})]^{4+}$ .<sup>1-3</sup> On reduction of this complex by  $\text{SnCl}_2/\text{HCl}$ , a complex believed to be  $[\text{Pt}((\text{NH}_2)_2\text{sar})]^{4+}$  was formed;<sup>1,3</sup> however, additional work indicated that this complex could be the bis(hydroxylamine) species  $[\text{Pt}(\text{NHOH})_2\text{sar}]^{4+}$ .<sup>4,5</sup> We therefore embarked on a crystallographic analysis of this complex. Such a study was also of interest to determine the coordination geometry about the platinum for comparison with the structure of  $[\text{Pt}(\text{sep})](\text{S}_2\text{O}_6)_2 \cdot 5/2\text{H}_2\text{O}$ , which has an approximate trigonal-prismatic geometry.<sup>2</sup> It was also necessary to check the identity of the cage complex obtained from the  $\text{SnCl}_2/\text{HCl}$  reduction of  $[\text{Pt}((\text{NO}_2)_2\text{sar})]^{4+}$  ion in order to reinterpret the electrochemical and spectroscopic properties of the product, if necessary.

#### Experimental Section

$[\text{Pt}(\text{NHOH})_2\text{sar}]^{4+}$  was prepared by the  $\text{SnCl}_2/\text{HCl}$  reduction of  $[\text{Pt}((\text{NO}_2)_2\text{sar})]^{4+}$ <sup>1</sup> and was recrystallized from hot 6 M  $\text{CF}_3\text{SO}_3\text{H}$ . After slow cooling to room temperature, the solution was cooled at 4 °C for 2 days, affording colorless crystals of  $[\text{Pt}((\text{NHOH})_2\text{sar})](\text{CF}_3\text{SO}_3)_4 \cdot \text{H}_2\text{O}$ .<sup>6</sup> X-ray photographs of a crystal mounted on a quartz fiber revealed only  $\bar{1}$  Laue symmetry, indicating a triclinic space group. Successful solution and refinement of the structure establishes it to be  $P\bar{1}$ . The orientation matrix and unit cell dimensions were calculated by least-squares treatment of 25 machine-centered reflections ( $2\theta < 26^\circ$ ) on a Nicolet R3m four-circle diffractometer using graphite-monochromatized  $\text{Mo K}\alpha$  radiation. Crystallographic details are given in Table I. Three check reflection intensities were measured every 100 reflections and exhibited no decay. The data were processed with the program XTape of the SHELXTL program package (Nicolet XRD Corp., Madison, WI), and an analytical absorption correction was applied to the data. The positions of the heavy atoms were obtained from a Patterson

<sup>†</sup> Current address: Department of Chemistry, Emory University, Atlanta, GA 30322.

**Table I.** Crystallographic Data for  $[\text{Pt}((\text{NHOH})_2\text{sar})](\text{CF}_3\text{SO}_3)_4 \cdot \text{H}_2\text{O}$  at 293 K

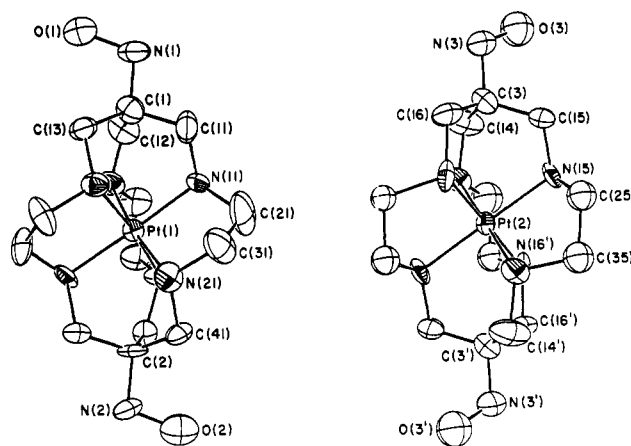
formula	$\text{C}_{18}\text{H}_{36}\text{F}_{12}\text{N}_8\text{O}_{15}\text{S}_4\text{Pt}$
color	colorless
mol wt	1155.9
<i>a</i> , Å	11.183 (2)
<i>b</i> , Å	17.337 (5)
<i>c</i> , Å	17.496 (6)
$\alpha$ , deg	60.53 (2)
$\beta$ , deg	82.14 (2)
$\gamma$ , deg	72.79 (2)
vol, Å <sup>3</sup>	2821 (1)
cryst syst	triclinic
space group	$P\bar{1}$
$d_{\text{calcd}}$ g/cm <sup>3</sup>	2.04
$d_{\text{obsd}}$ g/cm <sup>3</sup> <sup>a</sup>	2.03
<i>Z</i>	3
radiation	Mo K $\alpha$ (0.710 69 Å)
abs coeff, $\mu$ , cm <sup>-1</sup>	40.61
max, min transmission	0.8, 0.2
cryst size, mm	0.03 × 0.40 × 0.50
scan speed in $2\theta$ , deg/min	4.9–29
scan range, deg	2
bkgd/scan time ratio	0.1
data collected	$\pm h, \pm k, +l$ ( $3^\circ \leq 2\theta \leq 40^\circ$ )
no. of unique data ( $I > 3\sigma(I)$ )	4490
no. of variables	630
goodness of fit <sup>b</sup>	2.6
<i>R</i> , %	5.8
<i>R</i> <sub>w</sub> , %	6.2

<sup>a</sup> Measured by neutral buoyancy in  $\text{CCl}_4/\text{C}_2\text{H}_4\text{Br}_2$ . <sup>b</sup> Goodness of fit =  $[w(|F_o| - |F_c|)^2 / (n_o - n_v)]^{1/2}$ , where  $n_o$  and  $n_v$  denote the numbers of data and variables, respectively.

synthesis, and the remaining non-hydrogen atoms were found by successive difference Fourier maps and least-squares refinement. One of the cations (Pt(2)) is located on an inversion center, necessitating a disorder of the ethane bridging portion of the ligand. Final least-squares refinement was performed on two blocks of 287 and 343 parameters with use of SHELX 76. Neutral-atom scattering factors with anomalous dispersion corrections were used throughout.<sup>7</sup> Due to the high number of parameters, selected carbon, oxygen, and fluorine atoms were refined isotropically and hydrogen atoms were not included. A disorder of the hydroxylamine oxygen atoms, O(3a) and O(3b), of cation Pt(2) was modeled with occupancies of 0.8 and 0.2, respectively. The final difference map included three peaks of height greater than  $1 e/\text{Å}^3$  around the Pt atoms. Large thermal parameters of anion oxygen and fluorine atoms were indicative of disorder. Final *R* factors are given in Table I.

## Results and Discussion

The X-ray crystal structure established the presence of hydroxylamine substituents for the complex that had NMR (<sup>1</sup>H and <sup>13</sup>C) and electronic absorption spectra identical with those reported for the supposed  $[\text{Pt}((\text{NH}_2)_2\text{sar})]^{4+}$  ion.<sup>1</sup> This confirmed the suspicion arising from a reanalysis of the spectroscopic data, which implied the presence of hydroxylamine substituents.<sup>4</sup> The diamagnetism of the complex evident from the NMR spectroscopic data indicated a Pt(IV) oxidation state with NHOH substituents instead of Pt(II) with  $\text{NH}_2\text{OH}^+$  substituents. The hydroxylamine sites are not protonated despite the isolation from 6 M acid. It is apparent that reductants with sufficient potential to reduce the



**Figure 1.** Structure of the Pt(1) and Pt(2) cations depicting 50% thermal ellipsoids. Selected distances (Å) and angles (deg) about Pt(1): Pt(1)–N(11) = 2.07 (1), Pt(1)–N(12) = 2.06 (1), Pt(1)–N(13) = 2.07 (2), Pt(1)–N(21) = 2.04 (1), Pt(1)–N(22) = 2.09 (1), Pt(1)–N(23) = 2.03 (1); N(12)–Pt(1)–N(11) = 87.4 (5), N(13)–Pt(1)–N(11) = 91.7 (5), N(13)–Pt(1)–N(12) = 93.5 (6), N(22)–Pt(1)–N(21) = 94.3 (5), N(23)–Pt(1)–N(21) = 89.6 (5), N(23)–Pt(1)–N(22) = 86.5 (5), N(21)–Pt(1)–N(11) = 85.7 (5), N(22)–Pt(1)–N(12) = 84.1 (6), N(23)–Pt(1)–N(13) = 86.3 (5), N(21)–Pt(1)–N(13) = 88.9 (6), N(22)–Pt(1)–N(11) = 95.6 (5), N(23)–Pt(1)–N(12) = 97.4 (5), N(23)–Pt(1)–N(11) = 174.9 (6), N(21)–Pt(1)–N(12) = 172.7 (5), N(22)–Pt(1)–N(13) = 172.1 (4).

hydroxylamine substituents to amine substituents also reduce the Pt(IV) center with concomitant rupture of the cage structure.<sup>1</sup> This precluded the use of Zn/HCl as a reductant, for example, where the major product is the  $[\text{M}((\text{NH}_2)_2\text{sar})]^{2+}$  species for other metal ions.<sup>8–12</sup> Reduction of other nitro-capped cage complexes with  $\text{SnCl}_2/\text{HCl}$  also results in the predominant formation of hydroxylamine species.<sup>4</sup> The very acidic nature of the protons on coordinated nitrogen of  $[\text{Pt}((\text{NO}_2)_2\text{sar})]^{4+}$  results in deprotonation of the complex even under dilute acidic conditions. Since deprotonation of platinum cage complexes shifts the Pt(IV)–Pt(II) reduction potential to considerably more negative values,<sup>1</sup> destructive reduction at the metal center is curtailed. In addition, the  $[\text{Pt}((\text{NHOH})_2\text{sar})]\text{Cl}_4$  complex is only sparingly soluble under the HCl conditions used for the reduction, thereby minimizing destruction of the product. These factors fortuitously combine to allow moderate (~50%) yields of the product,  $[\text{Pt}((\text{NHOH})_2\text{sar})]^{4+}$ , under reducing conditions that normally lead to cage rupture.<sup>1</sup>

The structure consists of discrete anions and cations, with one situated on an inversion center (Pt(2)), while the other is at a general position (Pt(1)). There are, therefore, three formula units per unit cell. However, all three water molecules are associated with Pt(2). Apart from the disorder problems the anions are unexceptional and will not be discussed. The two cations are depicted in Figure 1, and selected bond distances and angles are included in the legend. Both inversion-related cations (of occupancy 0.5) share a common stereochemistry of the capping groups (1,1,1-tris(aminomethyl)ethane) but necessarily have different stereochemistries for the ethane bridging units, and the figure includes those of only one of the two orientations. The water oxygen atoms are distributed evenly between the ethane bridging groups with C...O distances ranging from 3.25 to 3.64 Å. However, C...O distances of the ethane bridging groups of the other orientation are only 1.06–1.36 Å. Cation Pt(1) exhibits no disorder

- Boucher, H. A.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 4652.
- Mikami, M.; Konno, M.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *35B*, 3096.
- Abbreviations: sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; sar = sarcophagine = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; en = 1,2-ethanediamine;  $(\text{NO}_2)_2\text{sar}$  = 1,8- $(\text{NO}_2)_2\text{sar}$ ;  $(\text{NH}_2)_2\text{sar}$  = 1,8- $(\text{NH}_2)_2\text{sar}$ ;  $(\text{NHOH})_2\text{sar}$  = 1,8- $(\text{NHOH})_2\text{sar}$ .
- Lay, P. A.; Sargeson, A. M., to be submitted for publication.
- Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1986**, *25*, 4801.
- Anal. Calcd for  $\text{C}_{18}\text{H}_{36}\text{N}_8\text{F}_{12}\text{O}_{15}\text{S}_4\text{Pt}$ : C, 18.70; H, 3.14; N, 9.69. Found: C, 18.92; H, 3.04; N, 9.49.
- International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99, 149.

- Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478.
- Harrowfield, J. M.; Herlt, A. J.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Mulac, W. A.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5503.
- Geue, R. J.; McCarthy, M. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 8282.
- Gahan, L. R.; Hambley, T. W.; Sargeson, A. M.; Snow, M. R. *Inorg. Chem.* **1982**, *21*, 2699.
- Hammershøi, A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 3554.

and as seen from the view in Figure 1 has a pseudo-2-fold axis passing through the C(22) and C(32) bond and Pt(1). The metrical details (in the form minimum, maximum, and mean) of the coordination about Pt are the Pt-N distance of 2.03 (1), 2.09 (1), and 2.06 (2) Å, the bite angle about Pt of the five-membered rings of 84.1 (6), 86.3 (5), and 85 (1)°, the bite angle about Pt of the six-membered rings of 86.5 (5), 94.3 (5), and 91 (3)°, and the angle of the trans nitrogen atoms of 172.1 (4), 174.9 (6), and 173 (1)°. The variation in these quantities indicates large deviations from octahedral geometry, although the twist angle between the two triangular faces of cation Pt(2) necessarily is 60°, corresponding to octahedral geometry, whereas the average of that of cation Pt(1) is 52°. These indicate a considerable difference from the near-trigonal-prismatic value of 16° for [Pt(sep)]<sup>4+</sup>.<sup>2</sup> Two of the ethane bridging groups of cation Pt(1) adopt an "ob" configuration and the other "lel", whereas all three of cation Pt(2) are of the "lel" form.

Initially, there was no reason to suspect that the product from the SnCl<sub>2</sub>/HCl reduction of [Pt((NO<sub>2</sub>)<sub>2</sub>sar)]<sup>3+</sup> was anything but [Pt((NH<sub>2</sub>)<sub>2</sub>sar)]<sup>4+</sup>, as the <sup>1</sup>H and <sup>13</sup>C NMR spectra and the microanalytical data<sup>1</sup> were all consistent with this formulation. For instance, the <sup>1</sup>H NMR and UV/vis spectra do not allow the complexes [Co((NH<sub>2</sub>)<sub>2</sub>sar)]<sup>3+</sup> and [Co((NHOH)<sub>2</sub>sar)]<sup>3+</sup> to be distinguished,<sup>4,13</sup> so it is also expected that they will be similar for the Pt analogue. Further, the microanalytical data for both the Cl<sup>-</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> salts<sup>1</sup> are equally consistent with a hydrated form of [Pt((NH<sub>2</sub>)<sub>2</sub>sar)]<sup>4+</sup> or [Pt((NHOH)<sub>2</sub>sar)]<sup>4+</sup>. The first indication that the supposed "[Pt((NH<sub>2</sub>)<sub>2</sub>sar)]<sup>4+</sup>" complex was not the major product of the SnCl<sub>2</sub>/HCl reduction of [Pt((NO<sub>2</sub>)<sub>2</sub>sar-H)]<sup>3+</sup> arose from the study of the SnCl<sub>2</sub>/HCl reductions of [Co((NO<sub>2</sub>)<sub>2</sub>sar)]<sup>3+</sup>, where the major product is [Co((NHOH)<sub>2</sub>sar)]<sup>3+</sup>.<sup>4</sup> This in turn led to a reexamination of the <sup>1</sup>H-decoupled <sup>13</sup>C NMR spectrum<sup>1</sup> of "[Pt((NH<sub>2</sub>)<sub>2</sub>sar)]<sup>4+</sup>", which indicated that the chemical shift of the quaternary carbons was more in keeping with those bound to hydroxylamine substituents rather than amine substituents.<sup>4,5</sup>

The interpretation of the electrochemical experiments reported in the initial paper<sup>1</sup> are not affected by the present result, as the complexes [Pt((NH<sub>2</sub>)<sub>2</sub>sar)]<sup>4+</sup> and [Pt((NHOH)<sub>2</sub>sar)]<sup>4+</sup> are expected to have identical reduction potentials, by analogy with their cobalt counterparts.<sup>14</sup> Moreover, the hydroxylamine substituent is not electroactive under the conditions reported in the original paper;<sup>1</sup> thus, the transient reduction product of the pulse radiolysis and electrochemical experiments is not due to a hydroxylamine radical anion but to the Pt(III) complex [Pt<sup>III</sup>(NHOH)<sub>2</sub>sar]<sup>3+</sup>.

The X-ray data on [Pt((NHOH)<sub>2</sub>sar)](CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O also throw light on the ESR spectra of the Pt(III) complexes observed in the γ-radiolysis of solid samples of this complex and the analogous chloride salt.<sup>1</sup> It was expected that these Pt(III) complexes should give rise to a central peak due to the isotopes <sup>190</sup>Pt, <sup>192</sup>Pt, <sup>194</sup>Pt, <sup>196</sup>Pt, and <sup>198</sup>Pt with a doublet centered about this peak due to the <sup>195</sup>Pt (*I* = 1/2) isotope. While this was observed for the chloride salt, the spectrum due to the Pt(III) trapped in [Pt((NHOH)<sub>2</sub>sar)](CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub> is more complex and looks more like two overlapping Pt(III) signals of equal intensity. The presence of two structurally distinct Pt(IV) ions in the [Pt((NHOH)<sub>2</sub>sar)](CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O lattice resolves this apparent discrepancy.

It is also clear that the observed ESR signals are not due to reduction of the hydroxylamine substituents, because of the appreciable <sup>195</sup>Pt hyperfine splitting of the signals (~60 G) and the prolonged life of these paramagnetic species. The irradiated solid samples could be kept for weeks at room temperature and in the presence of O<sub>2</sub> in the solid state without any noticeable deterioration of the signal.

**Acknowledgment.** We are grateful to Dr. W. T. Robinson and the University of Canterbury, Christchurch, New Zealand, for

use of X-ray diffraction facilities, and to the ANU Microanalytical Service.

**Registry No.** [Pt((NHOH)<sub>2</sub>sar)](CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O, 115731-60-7.

**Supplementary Material Available:** For [Pt((NHOH)<sub>2</sub>sar)](CF<sub>3</sub>SO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O, tables of positional parameters, thermal parameters, and bond distances and angles and a full labeling scheme for cations Pt(1) and Pt(2) (13 pages); listings of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

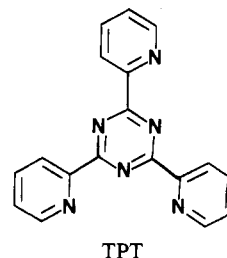
Contribution from the Departments of Chemistry,  
Auburn University at Montgomery,  
Montgomery, Alabama 36193-0401,  
and University of Delaware, Newark, Delaware 19716

### Ruthenium Carbonyl Complexes of 2,4,6-Tris(2-pyridyl)-1,3,5-triazine. Crystal Structure of Methoxide-Substituted [μ-2,4,6-Tris(2-pyridyl)-1,3,5-triazine]bis[dicarbonyldichloro- ruthenium(II)]

Nicholas C. Thomas,\*† B. Lachele Foley,†  
and Arnold L. Rheingold‡

Received December 17, 1987

The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPT) has been studied extensively as an analytical reagent for various metals.<sup>1-3</sup> It functions primarily as a tridentate ligand, similar to 2,2':6',2''-terpyridine (tpy), forming complexes of the general type [M(TPT)<sub>2</sub>]<sup>2+</sup> (M = Ru,<sup>1</sup> Co,<sup>2,3</sup> Fe<sup>4,5</sup>), M(TPT)(NO<sub>3</sub>)<sub>3</sub> (M = lanthanide<sup>6</sup>), or M(TPT)Cl<sub>2</sub> (M = Co,<sup>3</sup> Sc,<sup>7</sup> Fe or Zn<sup>8</sup>). The



TPT

coordination of a second metal to TPT is not usually observed due to deactivation of the triazine ring by the inductive effect of the first metal and as a result of steric interaction between the hydrogen atoms and the metal ion.<sup>6</sup> Further work has indicated that TPT is a more versatile ligand than tpy and that it may function simultaneously as a tridentate and bidentate ligand in dicobalt<sup>3</sup> and dimercury<sup>9</sup> complexes. Only a few TPT complexes have been examined crystallographically.<sup>10</sup>

Our continuing interest<sup>11</sup> in reactions of N-donor heterocyclic molecules with polymeric dicarbonyldichlororuthenium(II), [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub>, led to the reaction of this complex with TPT in methanol. In the absence of light, the bimetallic complex (μ-TPT)[Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub> has been obtained from this reaction. By contrast, a similar reaction in the presence of visible light yields {μ-C<sub>3</sub>N<sub>3</sub>(OMe)(py)<sub>2</sub>(pyH)}[Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>, formed by photochemically activated nucleophilic attack by methanol at the triazine ring. X-ray crystallographic and spectroscopic data for the complex are reported.

#### Experimental Section

2,4,6-Tris(2-pyridyl)-1,3,5-triazine and methanol (HPLC grade) were obtained from Aldrich and used without further purification. Polymeric dicarbonyldichlororuthenium(II) was prepared according to the reported method.<sup>12</sup> Microanalyses were obtained by Galbraith Laboratories, Knoxville, TN. Infrared spectra were recorded as Nujol mulls between

(13) The protons due to the -NH<sub>2</sub> and -NHOH substituents are not observed in D<sub>2</sub>O solutions because of rapid exchange.

(14) Bond, A. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* 1983, 22, 2010.

\*Auburn University at Montgomery.

†University of Delaware.