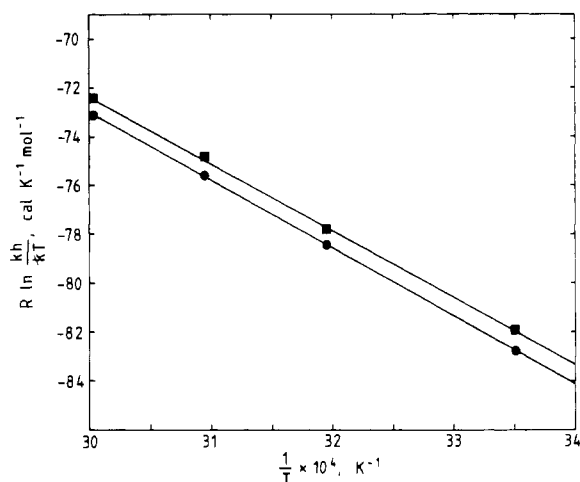


**Table I.** Solvent-Exchange Data for *cis*-Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> in Acidic Aqueous Solution

reacn medium	temp, °C	k, s <sup>-1</sup>	ΔH <sup>‡</sup> , kcal mol <sup>-1</sup>	ΔS <sup>‡</sup> , cal K <sup>-1</sup> mol <sup>-1</sup>	ref
2 M HNO <sub>3</sub>	25.5	(7.91 ± 0.19) × 10 <sup>-6</sup>	27.4 ± 0.5	+9.8 ± 1.6	a
	40.0	(6.50 ± 0.10) × 10 <sup>-5</sup>			
	50.0	(2.98 ± 0.05) × 10 <sup>-4</sup>			
	60.0	(1.01 ± 0.04) × 10 <sup>-3</sup>			
2 M HClO <sub>4</sub>	25.5	(4.98 ± 0.08) × 10 <sup>-6</sup>	27.8 ± 0.5	+10.4 ± 1.4	a
	40.0	(4.62 ± 0.01) × 10 <sup>-5</sup>			
	50.0	(2.05 ± 0.02) × 10 <sup>-4</sup>			
	60.0	(6.93 ± 0.24) × 10 <sup>-4</sup>			
0.8 M HClO <sub>4</sub>	25.0	7.5 × 10 <sup>-6</sup>	29.2 ± 0.4	+15.8 ± 1.4	20
	39.9	7.7 × 10 <sup>-5</sup>			

<sup>a</sup>This work.



**Figure 3.** Plot of  $R \ln(kh/kT)$  vs.  $1/T$ : (■) [HNO<sub>3</sub>] = 2 M; (●) [HClO<sub>4</sub>] = 2 M. Conditions: [Co(III)] = 0.12 M.

nitrate complexes could represent at most only a few percent of the cobalt(III) species in solution and can therefore not rule out their possible participation as unstable intermediates.

On the average the exchange rate constant is approximately 50% higher in nitric acid than in perchloric acid medium. The activation parameters are identical within the low experimental error limits and are in close agreement with those reported by Kruse and Taube.<sup>20</sup> However, the enhancement in nitric acid medium is observed at each temperature and must be due to slightly smaller values for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  (see Figure 3). The catalytic effect of the nitrate medium is rather disappointing in the light of the very strong effects observed for the substitution reaction with oxalic acid.<sup>6-8</sup> From this we conclude that direct chemical effects cannot account for the observed data but that these are most probably due to secondary medium effects. We can offer a few possible explanations, of which one has been mentioned above.

Earlier similar observations<sup>2,3</sup> led to the suggestion that some interaction occurs between water in the first solvation sphere of the nitrate ion and coordinated water. If these water molecules exchange, i.e. coordinated water replaces the water of solvation around the nitrate ion, it is expected to show up in  $\Delta S^\ddagger$  as a solvational effect. In such a case nitrate ions influence the magnitude of the rate constant but not the mechanism of the process. Such an interaction of nitrate ion with the coordinated water molecule could be due to its higher basicity than perchlorate ion and could result in the partial formation of an aquohydroxo complex ion. This process could also be visualized in terms of specific ion-pair formation accompanied by the partial deprotonation effect. Such an interaction would then result in a more labile coordinated water molecule since it is known that *cis*-Co(en)<sub>2</sub>(H<sub>2</sub>O)OH<sup>2+</sup> is ca. 100 times more labile than the diaquo complex species.<sup>20</sup> It follows that only a weak interaction could account for the observed 50% enhancement in the exchange rate constant. Deprotonation of coordinated water accompanied by an increase in the solvent-exchange lability has also been reported

for the Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> species, where Fe(H<sub>2</sub>O)<sub>5</sub>OH<sup>2+</sup> is suggested to exchange its coordinated solvent according to a dissociative reaction mode compared to a much slower associative reaction mode for the Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> species.<sup>29,30</sup>

In respect to the above, our original suggestion<sup>6</sup> of nitrate-catalyzed formation of a five-coordinate intermediate is not that unrealistic, even if it occurs only to a minor extent. However, the present results do force us to modify our earlier view from a direct catalytic effect (which should show up in  $\Delta H^\ddagger$ ) to an indirect medium effect with very similar activation parameters. The more dissociative nature of the solvent exchange on *cis*-Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> in the presence of nitrate ion is furthermore in agreement with the slightly more positive  $\Delta V^\ddagger$  value found for the substitution reaction with oxalic acid in nitrate as compared to that in perchlorate medium.<sup>16</sup>

In conclusion, the effect of nitrate on the solvent exchange of *cis*-Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> is small and is of the same order as found for the exchange of Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> at 2-4 M ionic strength and 27 °C.<sup>9</sup> Whether this effect can really account for the large effect observed during the reaction with oxalic acid remains unanswered, and the possible involvement of oxalic acid itself with the solvent-exchange process cannot be excluded. It is further obvious that a diaquo arrangement is required,<sup>6-8</sup> since such catalytic effects do not show up for monoquo species.<sup>31</sup> This in turn is also in line with our suggestion of the partial formation of an aquohydroxo intermediate to account for the nitrate effect.

The results of this investigation demonstrate the sensitivity and accuracy of the method employed to determine the solvent-exchange rate constants. Further studies on the medium and pH dependencies of such exchange reactions involving Co(III) and Cr(III) complexes are presently under way.

**Acknowledgment.** We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

**Registry No.** *cis*-[Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup>, 21247-59-6; NO<sub>3</sub><sup>-</sup>, 14797-55-8; H<sub>2</sub>O, 7732-18-5.

(29) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55.

(30) Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212.

(31) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1975**, *14*, 10.

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### Mononuclear, Low-Valent Osmium Nitrosyl Complexes

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Received September 6, 1984

Recently we have reported novel {RuNO}<sup>5</sup> and {RuNO}<sup>7</sup> complexes.<sup>1</sup> Only one monomeric osmium(I) complex, [Os(N-

**Table I.** Analytical Data and Nitrosyl Stretching Frequencies ( $\text{cm}^{-1}$ ) for the Complexes

compds	mp, °C	anal. found (calcd)					$\nu_{\text{NO}}$ , $\text{cm}^{-1}$	$\nu'_{\text{NO}}$ , <sup>a</sup> $\text{cm}^{-1}$
		% C	% H	% N	% Cl/Br	% P		
$\text{Os}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2$	312	53.2 (53.01)	3.7 (3.68)	1.6 (1.72)	8.9 (8.71)	7.4 (7.61)	1845	1845
$\text{Os}(\text{NO})\text{ClBr}(\text{PPh}_3)_2$	330	50.4 (50.26)	3.3 (3.49)	1.8 (1.63)	13.6 (13.44)	7.0 (7.21)	1842	1842
$\text{Os}(\text{NO})\text{Cl}(\text{PPh}_3)_3$	90	62.4 (62.22)	4.1 (4.32)	1.5 (1.34)	3.4 (3.41)	8.8 (8.93)	1640	1620
$\text{Os}(\text{NO})\text{Br}(\text{PPh}_3)_3$	90	60.0 (59.67)	4.3 (4.14)	1.2 (1.22)	7.5 (7.37)	8.6 (8.56)	1635	1615
$\text{Os}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$	260	50.8 (50.8)	3.8 (3.53)	1.5 (1.65)	12.7 (12.53)	7.6 (7.50)	1850	1850
$\text{Os}(\text{NO})\text{Cl}_2\text{Br}(\text{PPh}_3)_2$	270	48.4 (48.26)	3.5 (3.35)	1.4 (1.56)	16.9 (16.87)	6.8 (6.92)	1860	1860
$\text{Os}(\text{NO})\text{Br}_3(\text{PPh}_3)_2$	262	44.0 (43.90)	3.2 (3.05)	1.3 (1.42)	24.5 (24.39)	6.5 (6.30)	1860	1860

<sup>a</sup> Corrected NO stretching frequencies have been calculated by Ibers' empirical rules.<sup>13</sup>

$\text{H}_3)_6\text{Br}_2$ ,<sup>2</sup> and three dimeric osmium(I) complexes,  $[\text{Os}(\text{CO})_4\text{X}]_2$  ( $\text{X} = \text{Br}, \text{I}$ ) and  $[(\text{C}_5\text{H}_5)\text{Os}(\text{CO})_2]_2$ ,<sup>3</sup> have been reported so far. The synthesis of  $\text{Os}(\text{NO})\text{Cl}(\text{PPh}_3)_3$  has been reported recently.<sup>4</sup> We now report the first examples of the  $\{\text{OsNO}\}^7$  complexes  $\text{Os}(\text{NO})\text{ClX}(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and a simple synthetic route to  $\text{Os}(\text{NO})\text{X}(\text{PPh}_3)_3$  and their spectral studies.

### Experimental Section

All the reagents used were AnalaR or of chemically pure grade. The solvents were dried and freshly distilled before use. The reactions were carried out under a pure, dry nitrogen atmosphere.

Dichlorotris(triphenylphosphine)osmium(II), nitrosyl chloride, and nitrosyl bromide were prepared by the literature methods.<sup>5-7</sup> Carbon, hydrogen, and nitrogen analyses were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur, India. Halogen estimation was carried out by standard methods.<sup>8</sup> For the estimation of phosphorus, samples were decomposed with sodium peroxide, sugar, and sodium nitrate in the ratio 20:1:3 in a Parr bomb crucible and extracted with water. The solution was neutralized with dilute  $\text{H}_2\text{SO}_4$  and an excess of concentrated  $\text{H}_2\text{SO}_4$  (0.5 mL) added. It was heated until the evolution of  $\text{SO}_3$  fumes ceased, cooled, and diluted with water. From the filtrate of the solution phosphorus was estimated as phosphoammonium molybdate. The IR spectra of the samples were recorded with a Perkin-Elmer Model 580 spectrophotometer in the range 4000–250  $\text{cm}^{-1}$ . Samples were prepared as KBr pellets and CsI pellets. The electron spectra were recorded in benzene solution on a Varian 634S spectrophotometer. The magnetic measurements were made on a Gouy balance. EPR spectra were recorded on a Varian Associates E-Line EPR Century Series Model E-104 A spectrometer system. Molecular weights were determined by field desorption mass spectrometry. Analytical data and nitrosyl stretching frequencies of the complexes are given in Table I.

**(a) Preparation of Dichloronitrosylbis(triphenylphosphine)osmium,  $\text{Os}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2$  (1).** A saturated solution of  $\text{NOCl}$  in dichloromethane (15 mL) was added dropwise to a stirred solution of  $\text{OsCl}_2(\text{PPh}_3)_3$  (0.2 g) with  $\text{PPh}_3$  (1.0 g) in dichloromethane (20 mL). The reaction mixture was refluxed for 1 h, and the solution was concentrated to 10 mL under reduced pressure. On addition of hot methanol (30 mL), the fine yellow crystalline complex **1** separated. This was centrifuged, washed with methanol and diethyl ether, and dried in vacuo (yield 0.128 g, 82%); mp 312 °C; mol wt (field desorption MS) 815 (obsd), 815.2 (calcd).

In the absence of  $\text{PPh}_3$ , the above reaction leads to the formation of the red-brown complex  $\text{Os}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$ , which was isolated by a procedure similar to that given above (yield 0.146 g, 90%); mp 260 °C;  $\nu_{\text{NO}}$  1850  $\text{cm}^{-1}$ .

**(b) Preparation of Bromochloronitrosylbis(triphenylphosphine)osmium,  $\text{Os}(\text{NO})\text{ClBr}(\text{PPh}_3)_2$  (2).** A solution of nitrosyl bromide (5 mL, ca. 2 M) in dichloromethane was added dropwise to a stirred solution of  $\text{OsCl}_2(\text{PPh}_3)_3$  (0.2 g) with  $\text{PPh}_3$  (1.0 g) in dichloromethane (20 mL). The reaction mixture was refluxed for 1 h, and the cream-colored complex **2** was isolated by a procedure similar to that given in part a (yield 0.123 g, 75%); mp 330 °C; mol wt 859 (obsd), 859.7 (calcd).

In the absence of  $\text{PPh}_3$ , the red-violet complex  $\text{Os}(\text{NO})\text{Cl}_2\text{Br}(\text{PPh}_3)_2$  is formed (yield 0.147 g, 86%); mp 270 °C;  $\nu_{\text{NO}}$  1860  $\text{cm}^{-1}$ .

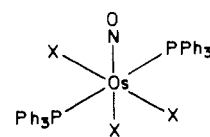
**(c) Preparation of Tribromonitrosylbis(triphenylphosphine)osmium,  $\text{Os}(\text{NO})\text{Br}_3(\text{PPh}_3)_2$ .** A solution of nitrosyl bromide (5 mL, ca. 2 M) in dichloromethane was added dropwise to a stirred solution of  $\text{OsH}_4(\text{PPh}_3)_3$  (0.2 g) in dichloromethane (20 mL). The reaction mixture was refluxed for 15 min, and the violet crystals of  $\text{Os}(\text{NO})\text{Br}_3(\text{PPh}_3)_2$  were isolated by a procedure similar to that given in part a (yield 0.171 g, 85%); mp 262 °C;  $\nu_{\text{NO}}$  1860  $\text{cm}^{-1}$ .

**(d) Preparation of Chloronitrosyltris(triphenylphosphine)osmium,  $\text{Os}(\text{NO})\text{Cl}(\text{PPh}_3)_3$  (3).** Triphenylphosphine (0.8 g) was added to a solution of  $\text{Os}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$  (0.2 g) in benzene (25 mL). The resulting solution was refluxed for 36 h. It was concentrated to 5 mL under reduced pressure. On addition of *n*-hexane, the green complex **3** precipitated. This was centrifuged, washed with *n*-hexane, and dried in vacuo (yield, 0.166 g, 84%); mp 90 °C.

**(e) Preparation of Bromonitrosyltris(triphenylphosphine)osmium,  $\text{Os}(\text{NO})\text{Br}(\text{PPh}_3)_3$  (4).** Triphenylphosphine (0.8 g) was added to a solution of  $\text{Os}(\text{NO})\text{Br}_3(\text{PPh}_3)_2$  (0.2 g) in benzene (25 mL). The resulting solution was refluxed for 36 h. It was concentrated to 5 mL under reduced pressure. The green complex **4** was isolated by a procedure similar to that in part d (yield 0.124 g, 60%); mp 90 °C.

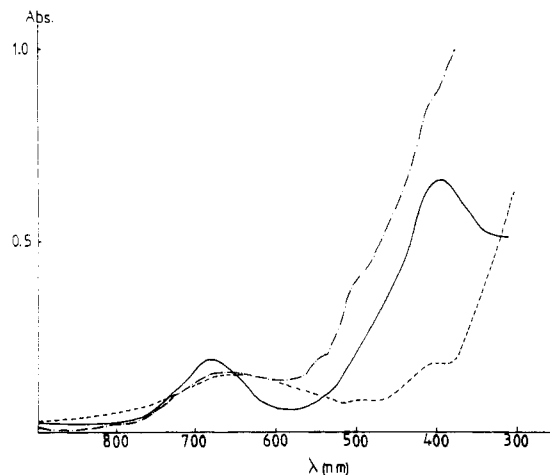
### Results and Discussion

**Magnetic and Spectroscopic Data.** The complexes  $\text{Os}(\text{NO})\text{X}_3(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}$ , yellow, mp 300 °C;  $\text{X} = \text{Br}$ , yellow, mp 260 °C) have been reported by Araneo et al.<sup>9</sup> The orange complex  $\text{Os}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$  has also been reported.<sup>10</sup> Our complexes differ in color and, for the chloro complex, in melting point also, from the complexes reported by Araneo et al. The size of crystals of these complexes are too small to determine X-ray crystal structure. X-ray powder pattern data showed that all the  $\{\text{OsNO}\}^6$  complexes were found to be isomorphous with  $\text{Os}(\text{NS})\text{Cl}_3(\text{PPh}_3)_2$ , which has been prepared by a similar method, that is, the reaction of solvated thionitrosyl chloride with  $\text{OsCl}_2(\text{PPh}_3)_3$ , and whose X-ray crystal structure has been previously determined.<sup>11</sup> It is therefore possible to assign the following structure to  $\{\text{OsNO}\}^6$  complexes:

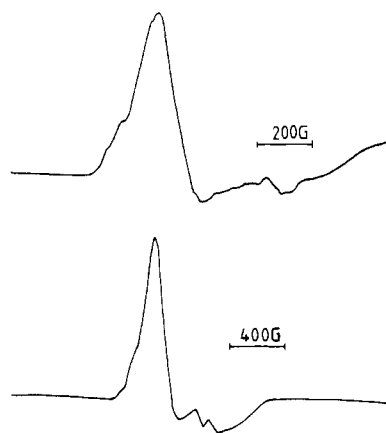


- Pandey, K. K.; Ahuja, S. R.; Poonia, N. S.; Bharti, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1268.
- Watt, G. W.; Potrafke, E. M.; Klett, D. S. *Inorg. Chem.* **1963**, *2*, 868.
- Fischer, E. O.; Vogler, A. *Angew. Chem.* **1965**, *4*, 700.
- Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939.
- Oudeman, A.; Van-Rantwijk, F.; Van-Bekkum, H. *J. Coord. Chem.* **1974**, *4*, 1.
- Shell International Research Maatschappij, Neth. Appl. Pat. 61 512 661 (Cl. CO.1b), 1967.
- Burns, W. G.; Bernstein, H. J. *J. Chem. Phys.* **1950**, *18*, 1669.
- Vogel, A. I. "A Textbook of Quantitative Inorganic Analysis", 3rd ed.; Longmans Green: London, 1961.

- Araneo, A.; Valenzio, V.; Cariati, F. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1877.
- Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 2947.
- Roesky, H. W.; Pandey, K. K.; Clegg, W.; Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 719.



**Figure 1.** Absorption spectra (concentration of compounds  $10^{-4}$  M): (---)  $\text{Os}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2$ ; (—)  $\text{Os}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$ ; (-·-·)  $\text{Os}(\text{NO})\text{Cl}(\text{PPh}_3)_3$ . See text for absorption maxima.



**Figure 2.** ESR spectra of  $\text{Os}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2$  at 295 K:  $g_{\text{av}} = 2.485$ ,  $g_{\perp} = 2.492$ ,  $g_{\parallel} = 2.481$ .

The complex **1** is a nonelectrolyte. Its IR spectrum exhibits  $\nu_{\text{NO}}$  (Table I),  $\nu_{\text{OsCl}} = 325 \text{ cm}^{-1}$ , and bands due to  $\text{PPh}_3$ . The magnetic moment for **1** at  $22^\circ \text{C}$  ( $\mu = 1.52 \mu_{\text{B}}$ ) is lower than the spin-only value. ESR spectra are shown in Figure 2. For a linear  $\{\text{MNO}\}^7$  system, the unpaired electron could be either in  $\sigma_{\text{NO}}\text{-d}_z$  in the case of tetragonal-pyramidal geometry<sup>12</sup> ( $g_z \approx 2.0$ ), or in  $\text{d}_{x^2-y^2}$  in the case of distorted-trigonal-bipyramidal geometry ( $g_z > 2.0$ ). The UV/visible spectrum (Figure 1) in benzene shows  $\lambda_{\text{max}}$  ( $\epsilon$ ) 805 (5.56), 750 (16.5), 675 (43.5), 555 (52.2), 520 (106), 405 (243), and 275 nm (24124). The lowest energy bands correspond to  $d \rightarrow d$  transitions with the occupied metal orbital having some Cl character. Complex **2** is a nonelectrolyte:  $\nu_{\text{NO}}$  (Table I),  $\nu_{\text{OsCl}} = 320 \text{ cm}^{-1}$ ;  $\mu = 1.46 \mu_{\text{B}}$ ; ESR ( $g_{\text{av}} = 2.3495$ ,  $g_{\perp} = 2.4198$ ,  $g_{\parallel} = 2.3136$ ; UV/visible  $\lambda_{\text{max}}$  ( $\epsilon$ ) 810 (13.58), 770 (23.78), 682 (52.3), 560 (120), 515 (136), 390 (308), 278 nm (21062). The corrected  $\nu_{\text{NO}}$  (Table I) falling above  $1610 \text{ cm}^{-1}$  gives added evidence for the presence of linear nitrosyl groups in these complexes. If the rules that have been suggested by Ibers<sup>14</sup> and Hoffmann et al.<sup>15</sup> for pentacoordinated nitrosyl complexes are combined with empirical rules of stereochemistry, the geometry about the osmium atom is probably a distorted trigonal bipyramid with axial phosphine ligands and two Cl atoms, the NO group occupying the equatorial plane (the molecule has  $C_{2v}$  symmetry<sup>16</sup>). These five-coordinated linear  $\{\text{OsNO}\}^7$  complexes can be regarded

as complexes between  $\text{Os}(\text{I})$  and  $\text{NO}^+$ .

Complex **3** is a nonelectrolyte, and its solutions are air sensitive:  $\nu_{\text{NO}}$  (Table I),  $\nu_{\text{OsCl}} = 325 \text{ cm}^{-1}$ ; UV/visible  $\lambda_{\text{max}}$  ( $\epsilon$ ) 750 (62), 640 (250), 495 (167), 400 (292), 270 nm (41660). Complex **4** is also a nonelectrolyte:  $\nu_{\text{NO}}$  (Table I); UV/visible  $\lambda_{\text{max}}$  ( $\epsilon$ ) 755 (65), 640 (162), 515 (286), 400 (315), 275 nm (40980). Complex **4** is more stable in solution than **3**. Complexes **3** and **4** are expected to be distorted trigonal bipyramids with equatorial phosphine ligands and axial NO group trans to X (X = Cl, Br), and the molecules have  $C_{3v}$  symmetry.<sup>15</sup>

**Acknowledgment.** We thank the CSIR, New Delhi, India, for a fellowship (to S.R.A.).

**Registry No.** **1**, 96689-07-5; **2**, 96689-08-6; **3**, 86645-90-1; **4**, 96689-09-7;  $\text{OsCl}_2(\text{PPh}_3)_3$ , 40802-32-2;  $\text{Os}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$ , 29292-10-2;  $\text{Os}(\text{NO})\text{Cl}_2\text{Br}(\text{PPh}_3)_2$ , 78106-84-0;  $\text{Os}(\text{NO})\text{Br}_3(\text{PPh}_3)_2$ , 29292-11-3.

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### Synthesis, Structure, and Properties of Chlorobis(acetato)bis(6-methyl-2-hydroxypyridinato)diruthenium(II,III), the First $\text{Ru}_2^{5+}$ Compound with a Mixed Set of Bridging Ligands

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Received October 17, 1984

In the chemistry of metal-metal multiple bonds,<sup>1</sup> the oxidation state of the metal center as well as the steric properties of the equatorial and axial ligands plays an important role in determining the coordination geometry and the stability of the complex. Among diruthenium complexes it has been found<sup>2-13</sup> that most of the stable compounds have diruthenium centers with a formal oxidation state of +2.5 for each metal atom. In recent years a few  $\text{Ru}(\text{II})\text{Ru}(\text{II})$ <sup>14-17</sup> and  $\text{Ru}(\text{III})\text{Ru}(\text{III})$ <sup>17,18</sup> complexes have

- (12) Feltham, R. D.; Enemark, J. H. *Top. Inorg. Organomet. Stereochem.* **1981**, *12*, 155.  
 (13) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060.  
 (14) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2610.  
 (15) Hoffmann, R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666.  
 (16) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

- (1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.  
 (2) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285.  
 (3) Bennett, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1.  
 (4) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599.  
 (5) (a) Mukaida, M.; Nomura, T.; Ishimori, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2462; **1972**, *45*, 2143. (b) Togano, T.; Mukaida, M.; Nomura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2085.  
 (6) Martin, D. S.; Newman, R. A.; Vlasnik, L. M. *Inorg. Chem.* **1980**, *19*, 3404.  
 (7) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2276.  
 (8) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.  
 (9) Chavan, M. Y.; Feldman, F. N.; Lin, X. Q.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 2373.  
 (10) Malinski, T.; Chang, D.; Feldman, F. N.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 3225.  
 (11) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6409.  
 (12) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 172.  
 (13) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 1263.  
 (14) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowell, A. A.; Clegg, W. *Inorg. Chim. Acta* **1981**, *53*, L61. Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3112.  
 (15) Lindsay, A. J.; Tooze, R. P.; Motevalli, M.; Hursthouse, M. B.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1383.  
 (16) Collman, J. P.; Barnes, C. E.; Swepton, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500. Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030.