encountering other unfavorable energy factors that limit the twisting. In this case, the final Cl···Cl distances are in the range 3.30-3.35 Å, but they would be shorter if there were no twisting.

The 4:0 or totally polar arrangement makes possible the formation of one strong axial Os-Cl bond in exchange for some Cl···Cl repulsive energy, whereas a 2:2 arrangement would presumably preclude any axial bonding, even though Cl···Cl repulsions would be much less. The axial Os-Cl bond here, with a distance of 2.433 (2) Å, is apparently a fairly strong one and may be compared with those in $Ru_2Cl(chp)_4$ and the $Os_2Cl_2(O_2CR)_4$ compounds.[4,19] The present axial Os-Cl distance is appreciably shorter than those in $Os_2Cl_2(hp)_4$, where they are 2.505 (5) Å.[20] The average Os-O and Os-N distances, 2.002 [6] Å and 2.088 [6] Å, respectively, and the mean angles, Os-Os-O = 89.6 [2]°, O-Os-O(cis) = 89.9 [2]°, and N-Os-N(cis) = 89.8 [2]°, are within the expected ranges.

We may finally turn to a comparison of the present Os-Os bond length, 2.348 (1) Å, with Os-Os distances found in other comparable Os_2 compounds. It is 0.034 Å longer than that in the tetraacetate starting material.[19] This is a rather small increase for a bond order decrease of 0.5, but this need not be surprising since the change from Os_2^{6+} to Os_2^{5+} may also increase the overlap in all the bonding orbitals, thus tending to strengthen the bond. Exactly this type of situation where there are countervailing—and nearly offsetting—factors has been thoroughly documented before for the series $[Re_2Cl_4(PMe_2Ph)_4]^{n+}$ (n = 2, 1, 0).[21]

Acknowledgment. We thank the National Science Foundation for support.

Registry No. $Os_2Cl(chp)_4\cdot 2(CH_3)_2CO$, 101471-02-7; $Os_2Cl(chp)_4$, 101420-22-8; $Os_2Cl_4(chp)_2(H_2O)$, 101403-87-6; $Os_2Cl_4(chp)_2(py)$, 101403-86-5; $Os_2Cl_2(O_2CCH_3)_4$, 81519-41-7; Os, 7440-04-2.

Supplementary Material Available: Full listings of bond angles, bond distances, positional parameters, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (23 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

---

(19) Cotton, F. A.; Chakravarty, A. R.; Tocher, D. A.; Stephenson, T. A. *Inorg. Chim, Acta* **1984**, *87*, 115.

(20) Cotton, F. A.; Thompson, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6437.

(21) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Preparation and Structural Characterization of $Os_2Cl_4(chp)_2(L)$ (chp = 6-Chloro-2-hydroxypyridinato; L = H_2O, Pyridine): A New Class of $M_2X_4(LL)_2$ Complexes Possessing an Eclipsed Conformation Where LL Is a Substituted Hydroxypyridinato Ligand

F. Albert Cotton,* Kim R. Dunbar, and Marek Matusz

Received November 4, 1985

The melt reaction of 6-chloro-2-hydroxypyridine with $Os_2(O_2CCH_3)_4Cl_2$ at 145 °C affords two products. A polar compound, $Os_2(chp)_4Cl$, was recently characterized, and details of the X-ray structure and spectroscopic data are fully described in the preceding paper.[1] We now wish to report the identification of the second product, $Os_2Cl_4(chp)_2$, which has been isolated as two different adducts: $Os_2Cl_4(chp)_2(py)$ (**1**) and $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)_2CO$ (**2**). Crystals of **1** were grown by vapor diffusion of hexane into a solution of the compound in acetone-pyridine (40:1). The crystallographic data for **1** are as follows: monoclinic, space group $C2/c$, a = 14.718 (2) Å, b = 12.860 (3) Å, c = 11.553 (2) Å, β = 100.5 (1)°, V = 2150 (1) Å^3, Z = 4. The structure was refined to R = 0.027 (R_w = 0.033). The molecule has crystallographically imposed C_2 symmetry with a twofold axis lying along the Os-Os bond axis. The Os-Os distance is 2.322 (1) Å, Os(1)-N(axial) = 2.238 (14) Å, Os-Cl(av) = 2.29 (3) Å, Os(1)-N(1) = 2.095 (9) Å, Os(2)-O(1) = 1.980 (8) Å. Crystals of **2** were grown by slow evaporation in air of an acetone solution of the complex. Pertinent crystallographic data are as follows: triclinic, space group $P\bar{1}$, a = 9.445 (2) Å, b = 15.148 (3) Å, c = 7.855 (2) Å, α = 94.92 (2)°, β = 98.50 (2)°, γ = 75.73 (1)°, V = 1075.7 (4) Å^3, Z = 2. The structure was refined to R = 0.039 (R_w = 0.065). The molecule possesses virtual C_{2v} symmetry although there is a lack of crystallographically imposed symmetry. The interstitial acetone molecule interacts significantly with the diosmium unit via hydrogen bonding to the axial water molecule. The hydrogen atoms were not located during the crystallographic refinement, but the distance between the oxygen atoms of acetone and water is only 2.726 Å, clearly indicating the presence of hydrogen bonds. The title compounds are formally derivatives of $[Os_2Cl_8]^{2-}$, a species that has only recently been prepared and structurally characterized.[2a] In addition, **1** and **2** are the first examples of an $Os_2X_4(LL)_2$ class of compounds, a type unknown for platinum metals. Furthermore, there are no reported examples of $M_2X_4(LL)_2$ complexes with an overall eclipsed conformation that contain a substituted hydroxypyridinate anion as the trans bidentate ligand. The electrochemistry of **1** and **2**, as determined by cyclic voltammetry, reveals a reversible reduction process located at $E_{1/2}$ = +0.15 V vs. Ag/AgCl for **1** and $E_{1/2}$ = +0.46 V vs. Ag/AgCl for **2**. A solution of $Os_2Cl_4(chp)_2(py)$ in dichloromethane exhibits a band at 555 nm (ϵ = 2815 M^{-1} cm^{-1}), and an acetone solution of $Os_2Cl_4(chp)_2(H_2O)$ displays an absorption maximum at 549 nm (ϵ = 3440 M^{-1} cm^{-1}).

Introduction

Early research efforts in the development of multiply bonded dimetal complexes were focused primarily upon transition metals from groups V-VII (5-7)[28] with little attention being directed toward the platinum-group elements.[3] Since the discovery of the first osmium-osmium triple bond, there has been a growing interest in the preparation of new diruthenium[4-7] and diosmium[8-11] systems.

---

(1) Cotton, F. A.; Dunbar, K. R.; Matusz, M. *Inorg. Chem.*, preceding paper in this issue.

(2) (a) Fanwick, P. E.; King, M. K.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5009. (b) Agaskar, P.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A., manuscript in preparation.

(3) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(4) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4030.

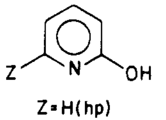
(5) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6409.

(6) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 172.

0020-1669/86/1325-1589$01.50/0

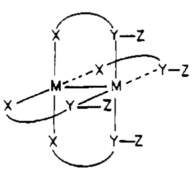
Indeed, there have been major synthetic advances in these areas during the past 2 years, especially in the preparation of compounds containing diruthenium multiple bonds. The most recent achievement in diosmium chemistry is the isolation and structural characterization of $[Os_2X_8]^{2-}$ (X = Cl, Br).[2a,b] The $[M_2X_8]^{n-}$ compounds have played a central role in the historical development of multiple bonds,[3] and they continue to be important starting materials especially for M = Mo, Re. The electron-rich triply bonded $[Os_2X_8]^{2-}$ complexes represent the first example of this kind for the platinum-group metals.

The ligand 2-hydroxypyridine and a variety of its 6-substituted derivatives have also been broadly useful in the preparation of multiply bonded systems. A substituent in position 6 of the hydroxypyridine ring impedes axial coordination in dimetal complexes and allows for isolation of discrete molecules rather than polymeric chains. Among the frequently used 6-substituted 2-hydroxypyridines are

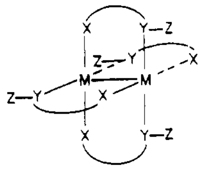


Z = H(hp)
Z = Cl(chp)
Z = CH_3(mhp)
Z = F(fhp)

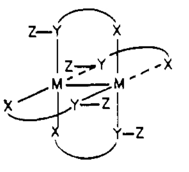
Complexes of the type $M_2(zhp)_4$ have attracted the most attention. The arrangement of zhp ligands around the dimetal unit can be entirely polar (also called 4:0), illustrated schematically in I. A series of unprecedented compounds containing this arrangement of ligands was prepared by the reaction of Li(fhp) with $M_2(O_2CCH_3)_4$ (M = Cr, Mo) and by treatment of a reduced solution of WCl_4 with Na(fhp).[12] Additional examples of polar complexes include $Rh(fhp)_4(Me_2SO)$,[13] $Ru_2(fhp)_4Cl$,[14] $Ru_2Cl(hp)_4(Hhp)$,[6] and $Ru_2Cl(PhNNpy)_4$.[6] Finally, two isostructural compounds, $M_2(chp)_4Cl$ (M = Ru, Os; chp = 6-chloro-2-hydroxypyridinate) have been recently synthesized in this laboratory.[1,7] The preferred 4:0 arrangement of the fhp ligands is reasonable, because four fluorine atoms can be accommodated on one end of the molecule without excessive crowding. On the other hand, chlorine atoms are much larger, and it was previously thought that the polar arrangement would be unlikely because of strong repulsive forces. Actually, the polar $M_2(chp)_4Cl$ molecules can be made, but they are twisted from an ideal eclipsed conformation by 19° in the case of ruthenium[7] and by 15° in the case of osmium[1] to relieve the Cl···Cl contacts.



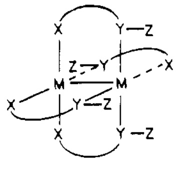
I



II



III



IV

The transoid arrangement, as represented in II (also called the 2:2 arrangement), is found in the group of compounds $M_2(mhp)_4$ (M = Cr, Mo, W, Ru, Rh).[15-17] The methyl substituents are much too bulky to allow for a stable 4:0 compound. The cisoid structure, III, is encountered in $Re_2(hp)_4Cl_2$.[18] Finally, the 3:1 arrangement of mhp and chp ligands, IV, is found in Rh(II) dimers. The compounds $Rh_2(mhp)_4L$ (or $Rh_2(chp)_4L$) possess a lone axial ligand on the less sterically hindered side of the molecule.[17]

The initial investigation of the reaction between Hchp and $Os_2(O_2CCH_3)_4Cl_2$ led to the discovery of $Os_2(chp)_4Cl$.[1] The second product of the reaction, the purple species mentioned in the previous paper,[1] has been isolated and fully characterized. We now present details of the molecular structures and spectroscopic properties of the two adducts $Os_2Cl_4(chp)_2(L)$ (L = py, H_2O). These molecules comprise a previously unknown class of trans bridged hydroxypyridine complexes $M_2X_4(LL)_2$. This mixed-ligand compound may be regarded as a partially substituted derivative of either $[M_2(chp)_4]^{2+}$ or $[M_2Cl_8]^{2-}$. A complex of the type $Os_2Cl_4(LL)_2(L')$ is of special interest because it could prove to be an attractive starting material for halide substitution reactions. The trans bridging chp ligands may help to preserve the integrity of the dimetal unit during ligand displacement processes. Furthermore, these $Os_2Cl_4(chp)_2(L)$ species are the first examples of diosmium(III) compounds with an axial ligand other than a halide. Although the presence of axial halide(s) in diruthenium and diosmium compounds has previously been a general feature of their chemistry, our present results suggest that this was merely a consequence of fulfilling the electrical-charge requirements of the $Os^{III}Os^{III}$ (or $Os^{II}Os^{III}$)[1,19] and $Ru^{II}Ru^{III}$ dimetal cores.

Experimental Section

Starting Materials. $Os_2(O_2CCH_3)_4Cl_2$ was prepared by a literature procedure[20] in ca. 60% yield. Osmium tetraoxide was purchased from Stevens Metallurgical Corp. The ligand 6-chloro-2-hydroxypyridine was obtained from Aldrich Chemical Co. and was purified by sublimation prior to use.

Preparation of $Os_2Cl_4(chp)_2(py)$ (1) and $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)_2CO$ (2). The syntheses of these compounds are described in the Experimental Section of the preceding paper.[1]

Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were recorded as KBr disks on a Perkin-Elmer 785 spectrophotometer. The electronic spectra were recorded on acetone or dichloromethane solutions with a Cary 17D spectrophotometer. Electrochemical measurements were done by using a Bioanalytical Systems, Inc. Model BAS 100 electrochemical analyzer. Experiments were carried out in dichloromethane or THF containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. A three-electrode system was used, with a platinum disk and platinum wire as the working and auxiliary eleectrodes, respectively. Ag/AgCl was used as a reference electrode (the ferrocene–ferrocenium couple is located at $E_{1/2}$ = +0.52 V). The measurements were made at room temperature with a full positive-feedback resistance compensation and are uncorrected for the junction potentials.

X-ray Crystallographic Procedures. Single crystals of **1** were grown by vapor diffusion of hexane into an acetone–pyridine (40:1) solution of the compound. Suitable crystals of **2** were grown by slow evaporation of an acetone solution in air. The structures were determined by application of procedures fully described elsewhere.[21,22] Lorentz, polari-

---

(7) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 1263.

(8) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4693.

(9) (a) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 501. (b) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4697.

(10) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chim. Acta* **1984**, *89*, L15.

(11) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 1334.

(12) Cotton, F. A.; Falvello, L. R.; Han, S.; Wang, W.; *Inorg. Chem.* **1983**, *22*, 4106.

(13) Cotton, F. A.; Han, S.; Wang, W. *Inorg. Chem.* **1984**, *23*, 4762.

(14) Chakravarty, A. R.; Cotton, F. A.; Schwotzer, W. *Polyhedron*, in press.

(15) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(16) (a) Berry, M.; Garner, C. D.; Hiller, I. H.; MacDowell, A. A. *Inorg. Chim. Acta* **1981**, *53*, L61. (b) Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3112. (c) Lindsay, A. J.; Tooze, R. P.; Motevalli, M.; Hursthouse, M. B.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1383.

(17) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981** *20*, 584.

(18) Cotton, F. A.; Gage, L. D. *Inorg. Chem.* **1979**, *18*, 1716.

(19) Cotton, F. A.; Dunbar, K. R.; Matusz, M. *Polyhedron*, in press.

(20) Behling, T.; Wilkinson, G.; Stephenson, T. A.; Tocher, D. A.; Walkinshaw, M. D. *J. Chem. Soc., Dalton Trans* **1983**, 2109.

(21) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, Texas, with a VAX-SDP software package.

Table I. Crystal Data

formula	$Os_2Cl_6O_2N_3C_{15}H_{11}$ (**1**)	$Os_2Cl_6O_4N_2C_{13}H_{14}$ (**2**)
fw	858.39	855.39
space group	$C2/c$	$P\bar{1}$
systematic absences	hkl: $h + k \neq 2n$ $h0l$: $l \neq 2n$	none
a, Å	14.718 (2)	9.445 (2)
b, Å	12.860 (3)	15.148 (3)
c, Å	11.553 (2)	7.855 (2)
α, deg	90.0	94.92 (2)
β, deg	100.50 (1)	98.50 (2)
γ, deg	90.0	75.73 (1)
V, Å^3	2150 (1)	1075.7 (4)
Z	4	2
d_{calcd}, g/cm^3	2.652	2.641
cryst size, mm	0.12 × 0.15 × 0.20	0.40 × 0.20 × 0.08
μ(Mo Kα), cm^{-1}	125.97	125.9
data collcn instrument	CAD-4	P3
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
orientation reflcns: no. range (2θ), deg	25; $12 < 2\theta < 25$	25; $20 < 2\theta < 30$
temp, °C	27	27
scan method	ω–2θ	ω–2θ
data collcn range (2θ), deg	4–50	4–50
no. of unique data; total with $F_o{}^2 > 3\sigma(F_o{}^2)$	1736; 1123	3094; 2897
no. of params refined	151	244
trans factors: max; min	0.999; 0.660	0.999; 0.287
R^a	0.0273	0.039
$R_w{}^B$	0.0325	0.065
quality-of-fit indicator^c	0.856	1.526
largest shift/esd, final cycle	0.25	0.35
largest peak, e/Å^3	0.60	1.56

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2|F_o|$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

zation, and absorption corrections were applied to the data. The pertinent crystallographic data for **1** and **2** are summarized in Table I. Positional parameters are presented in Table II. Selected bond distances and angles for **1** and **2** are presented in Tables III and IV, respectively.

Structure of $Os_2Cl_4(chp)_2(py)$ (1). An irregular crystal of approximate dimensions 0.12 × 0.15 × 0.20 mm was mounted on the tip of a glass fiber. The diffraction data were collected on a CAD4 diffractometer. The unit cell was indexed on 25 reflections found by an automatic search routine and were in the range $12° < 2\theta < 25°$. Application of direct methods (MULTAN 11/82) revealed the approximate location of the diosmium coordination sphere; however, the unit was slightly displaced from the crystallographic twofold axis. A deliberate placement of the Os atoms on the symmetry element led to successful refinement of these positions. The non-hydrogen atoms were located in the first difference Fourier map, and they were anisotropically refined. A subsequent difference map disclosed the positions of the hydrogen atoms, which were then included in the refinement.

Structure of $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)_2CO$ (2). A thin crystal with well-developed faces and of approximate dimensions 0.40 × 0.20 × 0.08 mm was mounted on the tip of a glass fiber. The diffraction data were collected on a Syntex P3 autodiffractometer equipped with a graphite-monochromated Mo K$_\alpha$ (λ = 0.71073 Å) radiation. The unit cell was indexed on 25 strong reflections in the range $20° < 2\theta < 30°$ selected from a preliminary data collection. The positions of two Os atoms were determined from a three-dimensional Patterson map, and the remaining non-hydrogen atoms were located by alternating difference Fourier maps and least-squares refinements. During the final cycles of the refinement, it became clear that absorption problems still affected the results, despite an earlier absorption correction based on ψ scans. This problem has been encountered before for thin crystals with a very high absorption coefficient. The program DIFABS[23] was applied to the data, and this procedure reduced the number of residual peaks above 1 e/Å^3 to half of the previous number. The remaining peaks in the final difference Fourier map that were larger than 1 e/Å^3 were all very close to the heavy atoms. The non-hydrogen atoms in $Os_2Cl_4(chp)_2(H_2O)$ and in the acetone solvent molecule were refined anisotropically. The hydrogen atoms were not located in this structure.

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $Os_2Cl_4(chp)_2(py)$ (**1**) and $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)CO$ (**2**)[a]

atom	x	y	z	B, Å^2
		Compound **1**		
Os(1)	0.000	0.29405 (5)	0.250	2.22 (1)
Os(2)	0.000	0.11350 (4)	0.250	2.11 (1)
Cl(1)	0.1187 (3)	0.3417 (3)	0.1628 (3)	3.94 (7)
Cl(2)	0.1285 (2)	0.0881 (2)	0.1631 (3)	3.20 (6)
Cl(3)	−0.0887 (3)	0.4928 (2)	0.0980 (3)	4.70 (9)
O(1)	−0.0798 (5)	0.1116 (5)	0.0923 (6)	2.7 (2)
N(1)	−0.0873 (6)	0.2899 (6)	0.0851 (6)	2.3 (2)
N(2)	0.000	−0.0605 (9)	0.250	2.7 (3)
C(1)	−0.1089 (6)	0.1959 (8)	0.0362 (8)	1.9 (2)
C(2)	−0.1650 (7)	0.1893 (8)	−0.0768 (8)	2.2 (2)
C(3)	−0.1936 (7)	0.2811 (9)	−0.1351 (9)	2.8 (2)
C(4)	−0.1704 (9)	0.3765 (9)	−0.081 (1)	3.1 (3)
C(5)	−0.1182 (9)	0.3777 (9)	0.025 (1)	3.1 (3)
C(6)	0.0469 (9)	−0.1125 (9)	0.341 (1)	3.5 (3)
C(7)	0.0480 (9)	−0.2204 (8)	0.343 (1)	3.9 (3)
C(8)	0.000	−0.274 (1)	0.250	3.1 (4)
H(2)	−0.184 (6)	0.120 (7)	−0.101 (8)	2 (2)*
H(3)	−0.241 (8)	0.265 (8)	−0.196 (9)	3 (3)*
H(4)	−0.188 (8)	0.43 (1)	−0.12 (1)	6 (4)*
H(6)	0.079 (7)	−0.080 (8)	0.418 (8)	3 (3)*
H(7)	0.066 (5)	−0.245 (6)	0.382 (6)	2 (2)*
H(8)	0.000	−0.352 (9)	0.250	1 (3)*
		Compound **2**		
Os(1)	0.22881 (5)	0.20487 (3)	0.15920 (7)	2.16 (1)
Os(2)	0.37319 (5)	0.30676 (3)	0.23933 (7)	2.12 (1)
Cl(1)	0.2089 (4)	0.2112 (2)	−0.1356 (5)	3.42 (8)
Cl(2)	0.2060 (4)	0.1662 (3)	0.4304 (5)	4.07 (8)
Cl(3)	0.3956 (4)	0.3225 (3)	0.5308 (5)	3.54 (8)
Cl(4)	0.4310 (4)	0.3483 (3)	−0.0076 (5)	3.92 (8)
O(1)	0.048 (1)	0.3033 (5)	0.158 (1)	2.6 (2)
O(2)	0.406 (1)	0.1028 (6)	0.158 (1)	3.2 (2)
N(2)	0.556 (1)	0.1979 (7)	0.251 (2)	3.1 (3)
N(1)	0.183 (1)	0.4106 (7)	0.227 (2)	3.3 (3)
Cl(5)	0.7153 (4)	0.3162 (3)	0.3503 (6)	4.34 (9)
Cl(6)	0.3573 (5)	0.5220 (3)	0.3083 (7)	5.2 (1)
C(6)	0.534 (1)	0.1101 (9)	0.208 (2)	2.9 (3)
C(7)	0.655 (2)	0.0360 (9)	0.234 (2)	3.6 (3)
C(8)	0.795 (2)	0.045 (1)	0.293 (2)	4.6 (4)
C(9)	0.817 (2)	0.136 (1)	0.334 (2)	4.2 (4)
C(10)	0.697 (2)	0.208 (1)	0.311 (2)	3.2 (3)
C(1)	0.052 (1)	0.3875 (9)	0.194 (2)	2.2 (3)
C(2)	−0.083 (2)	0.457 (1)	0.192 (2)	4.0 (3)
C(3)	−0.076 (2)	0.548 (1)	0.234 (2)	3.9 (4)
C(4)	0.064 (2)	0.5683 (9)	0.278 (3)	4.8 (4)
C(5)	0.185 (2)	0.5008 (9)	0.268 (2)	3.5 (3)
O(3)	0.093 (1)	0.1021 (7)	0.082 (2)	4.6 (3)
O(4)	0.123 (1)	−0.0717 (7)	0.175 (2)	5.2 (3)
C(11)	0.233 (2)	−0.130 (1)	0.203 (2)	4.0 (4)
C(12)	0.379 (2)	−0.109 (1)	0.270 (3)	5.7 (5)
C(13)	0.228 (2)	−0.228 (1)	0.189 (3)	5.3 (5)

[a] Values marked with an asterisk indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Results and Discussion

High-temperature melt reactions have been used effectively in diruthenium chemistry to carry out ligand substitution.[6,24] These

---

(22) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. (c) North, A. C. T.; Philips, D. C.; Matthews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A39*, 158.

(23) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(24) Malinski, T.; Chang, D.; Feldman, F. N.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 3225.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $Os_2Cl_4(chp)_2(py)$ (**1**)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist
Os(1)	Os(2)	2.322 (1)	Os(2)	N(2)	2.238 (14)
Os(1)	Cl(1)	2.255 (4)	Cl(3)	C(5)	1.723 (13)
Os(1)	N(1)	2.095 (9)	O(1)	C(1)	1.295 (13)
Os(2)	Cl(2)	2.320 (4)	N(1)	C(1)	1.347 (14)
Os(2)	O(1)	1.980 (8)	N(2)	C(6)	1.326 (15)

atom 1	atom 2	atom 3	angle
Os(2)	Os(1)	Cl(1)	105.8 (1)
Os(2)	Os(1)	N(1)	88.5 (3)
Cl(1)	Os(1)	N(1)	89.8 (3)
Os(1)	Os(2)	Cl(2)	98.10 (9)
Os(1)	Os(2)	O(1)	90.7 (2)
Os(1)	Os(2)	N(2)	180.00 (0)
Cl(2)	Os(2)	O(1)	89.7 (3)
Cl(2)	Os(2)	N(2)	81.90 (9)
O(1)	Os(2)	N(2)	89.3 (2)
Os(2)	O(1)	C(1)	122.4 (7)
Os(1)	N(1)	C(1)	117.5 (7)
Os(1)	N(1)	C(5)	122.5 (9)
C(1)	N(1)	C(5)	120 (1)
Os(2)	N(2)	C(6)	120.3 (9)
O(1)	C(1)	N(1)	121 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)_2CO$ (**2**)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist
Os(1)	Os(2)	2.293 (1)	O(1)	C(1)	1.292 (13)
Os(1)	Cl(1)	2.303 (3)	O(2)	C(6)	1.252 (14)
Os(1)	Cl(2)	2.311 (3)	N(2)	C(6)	1.400 (15)
Os(1)	O(1)	1.974 (7)	N(2)	C(10)	1.38 (2)
Os(1)	O(2)	1.976 (7)	N(1)	C(1)	1.351 (15)
Os(1)	O(3)	2.246 (9)	N(1)	C(5)	1.381 (14)
Os(2)	Cl(3)	2.265 (3)	Cl(5)	C(10)	1.690 (12)
Os(2)	Cl(4)	2.269 (3)	Cl(6)	C(5)	1.714 (14)
Os(2)	N(2)	2.071 (9)	C(6)	C(7)	1.39 (2)
Os(2)	N(1)	2.071 (9)			

atom 1	atom 2	atom 3	angle
Os(2)	Os(1)	Cl(1)	98.91 (8)
Os(2)	Os(1)	Cl(2)	98.63 (8)
Os(2)	Os(1)	O(1)	91.3 (2)
Os(2)	Os(1)	O(2)	90.9 (3)
Os(2)	Os(1)	O(3)	178.5 (2)
Cl(1)	Os(1)	Cl(2)	162.4 (1)
Cl(1)	Os(1)	O(1)	88.9 (3)
Cl(1)	Os(1)	O(2)	90.9 (3)
Cl(1)	Os(1)	O(3)	81.4 (3)
Cl(2)	Os(1)	O(1)	91.1 (3)
Cl(2)	Os(1)	O(2)	88.4 (3)
Cl(2)	Os(1)	O(3)	81.0 (3)
O(1)	Os(1)	O(2)	177.8 (3)
O(1)	Os(1)	O(3)	90.1 (3)
O(2)	Os(1)	O(3)	87.7 (3)
Os(1)	Os(2)	Cl(3)	106.35 (9)
Os(1)	Os(2)	Cl(4)	106.50 (9)
Os(1)	Os(2)	N(2)	88.4 (3)
Os(1)	Os(2)	N(1)	88.5 (3)
Cl(3)	Os(2)	Cl(4)	147.1 (1)
Cl(3)	Os(2)	N(2)	90.7 (3)
Cl(3)	Os(2)	N(1)	89.3 (3)
Cl(4)	Os(2)	N(2)	90.3 (3)
Cl(4)	Os(2)	N(1)	91.4 (3)
N(2)	Os(2)	N(1)	176.8 (4)
Os(1)	O(1)	C(1)	121.7 (7)
Os(1)	O(2)	C(6)	124.4 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

reactions typically produce high yields of a single product resulting from complete ligand replacement. In the present example, the reaction of molten Hchp with $Os_2(O_2CCH_3)_4Cl_2$ produces two isolable species. One product, $Os_2(chp)_4Cl$, which is the subject of the preceding paper,[1] results from complete ligand substitution and a concomitant reduction from Os_2^{6+} to Os_2^{5+}. The yield of this product varies from 20 to 40%, depending upon reaction conditions. We discovered during the course of our investigation that the formation of $Os_2(chp)_4Cl$ is favored when the reaction is performed under a constant purge of dinitrogen rather than in a small, closed tube that has been sealed in air. Conversely, the yields of the second product, $Os_2Cl_4(chp)_2(L)$, are maximized ($\cong$45%) when the sealed-tube method is employed.

The formation of the title compounds, $Os_2Cl_4(chp)_2(L)$ (L = py, H_2O), from the reaction we have described is rather unexpected, since they do not result from a simple substitution process. The starting material, $Os_2(O_2CCH_3)_4Cl_2$, possesses two axial chlorine atoms, whereas the products **1** and **2** each contain four equatorial chloride ligands. It is worth noting that the possibility exists for a rational synthesis of $Os_2Cl_4(chp)_2$ from $[Os_2Cl_8]^{2-}$. The latter complex has been recently reported by Walton et al.,[2a] and perhaps four chloride ligands of $[Os_2Cl_8]^{2-}$ could be substituted by two chp ligands to give the desired product in quantitative yields. If such a reaction were to be successful, it would doubtless be a superior method for the preparation of **1** and **2**.

The results and observations presented above clearly indicate that the mechanism(s) for product formation are quite complicated. One clear aspect, however, is that chloride ion must be scavenged to form **1** and **2** from $Os_2(O_2CCH_3)_4Cl_2$. The source of free chloride may be the excess Hchp, the diosmium starting material, or both. It should be pointed out that one axial chloride is lost from the diosmium unit for each molecule of $Os_2(chp)_4Cl$ that is formed in the reaction. If this process were the only source of chloride ion in the reaction that leads to compounds **1** and **2**, the maximum $Os_2Cl_4(chp)_2(L)$:$Os_2(chp)_4Cl$ ratio would be 1:2. We have, however, demonstrated that this is not the case by carefully determining the product yields from several independent preparative trials. Thus, there must be one, or more, additional chloride-transfer processes.

Solutions of $Os_2Cl_4(chp)_4(L)$ can be obtained by washing the crude reaction product with THF or acetone. The axial ligand L, that is present at this time is most likely a neutral one, such as Hchp. Initial attempts to isolate a crystalline compound from anhydrous acetone under anaerobic conditions were without success. Acetone solutions containing pyridine and acetone solutions that were exposed to moist laboratory air, however, readily produced single crystals of **1** and **2**, respectively.

Spectroscopic and Magnetic Properties. The electronic properties of triply bonded diosmium compounds have been much discussed. It appears that in general there is a diamagnetic ground state based on a $\sigma^2\pi^4\delta^{*2}\delta^2$ or $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration, with a spin triplet state arising from the $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$ and/or $\sigma^2\pi^4\delta^2\pi^{*2}$ configurations,[20,25] lying a few hundred wave numbers higher in energy. Complexes such as $[n\text{-}Bu_4N]_2[Os_2Cl_8]$[2b] and $Os_2(O_2CR)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (R = CH_3, C_2H_5)[9b] contain short Os–Os distances (2.1 – 2.3 Å) and are essentially diamagnetic, presumably because the singlet–triplet separation is much greater than kT. Complexes **1** and **2** of this work have Os–Os bond distances that lie in the shorter range and thus might also be expected to show little paramagnetism. Neither complex gives an EPR signal at room temperature or below (to −196 °C). $Os_2Cl_4(chp)_2(py)$ is not sufficiently soluble to allow for an Evans method magnetic susceptibility measurement. The water adduct $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)_2CO$, however, dissolves in acetone, and the room-temperature magnetic moment was found to be 1.65 μ_B/Os_2 unit. This value is very close to those found for the $Os_2(O_2CR)_4Cl_2$ and $Os_2(hp)_4Cl_2$ complexes.[20,26]

Electrochemistry. A cyclic voltammogram of a solution of **2** in 0.2 M tetra-*n*-butylammonium hexafluorophosphate in CH_2Cl_2 revealed a reversible process at $E_{1/2}$ = +0.15 V vs. a Ag/AgCl reference electrode (see Figure 1). This is an easily accessible

---

(25) Stephenson, T. A.; Tocher, D. A.; Walkinshaw, M. D. *J. Organomet. Chem.* **1982**, *232*, C51.

(26) Tetrick, S. M.; Coombe, V. T.; Heath, G. A.; Stephenson, T. A.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 4567.

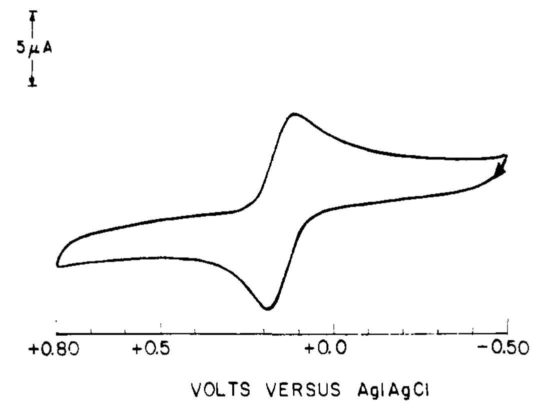


Figure 1. Cyclic voltammogram of $Os_2Cl_4(chp)_2(py)$ (measured at 200 mV/s in 0.2 M TBAH-CH_2Cl_2 at a Pt-disk electrode).

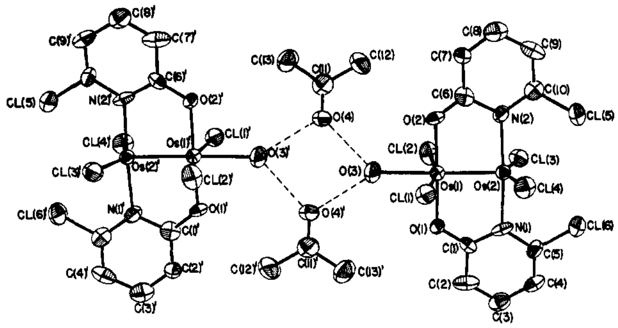


Figure 3. ORTEP diagram of the molecule $Os_2Cl_4(chp)_2(H_2O)$ and the lattice acetone molecule, which is hydrogen bonded to the axial water ligand O(3). This figure includes the two symmetry-related molecules that are generated by the inversion center. The hydrogen bonding is drawn with a broken line.

reduction that corresponds to the $Os_2^{6+} + e^- \rightarrow Os_2^{5+}$ process. Our result is consistent with the redox chemistry observed for other known triply bonded diosmium compounds.[8,11,26] It has been shown that Os_2^{6+} compounds can also be easily chemically reduced with cobaltocene to give the Os_2^{5+} core.[26]

Our attempt to obtain a cyclic voltammogram of **1** in acetone was unsuccessful. The cyclic voltammogram of **1** in THF solution reveals a reversible reduction at $E_{1/2}$ = +0.46 V vs. Ag/AgCl. It is not clear whether the shift in the reduction potential is a genuine reflection of different electronic properties of $Os_2Cl_4(chp)_2(L)$ with L = pyridine vs. L = water or whether this is a solvent-dependent effect. Because of solubility differences, we were not able to obtain a cyclic voltammogram of **1** and **2** in the same solvent.

It has been noted previously that the increase in the formal reduction potential for the Os_2^{6+}/Os_2^{5+} couple follows the order of decreasing Os≡Os triple-bond length in a linear fashion.[11] Compounds **1** and **2** follow that general trend rather well, showing a decrease in reduction potential (from +0.46 to +0.15 V) with increasing bond length (from 2.293 to 2.322 Å) for **1** and 2, respectively.

Molecular Structure. $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)_2CO$ (2). The positional parameters of **2** are given in Table II, and selected bond distances and angles are listed in Table III. Figure 2[27] presents a labeled ORTEP diagram of $Os_2Cl_4(chp)_2(H_2O)$. The molecule consists of a diosmium unit with two trans chp ligands and four equatorial chloride ligands. Water occupies one of the axial positions, and the other axial site is blocked both by the chlorine atoms from the chp ligands and by the equatorial chloride ligands that are bent toward the axial site with a Cl(3)–Os(2)–Cl(4) angle of 147.1 (1)°. The equatorial ligands on Os(1) are not quite as "swept back" from the center of the molecule, and the angle Cl(1)–Os(1)–Cl(2) is 162.4 (1)°. This is a reasonable result, because Os(1) is also coordinated to the axial water molecule. In addition, this axial water forms hydrogen bonds to an acetone molecule in the lattice. Figure 3 illustrates the situation by showing one diosmium and one acetone molecule, along with their symmetry-generated counterparts across the inversion center. The hydrogen atoms of the water molecue (not shown) interact with O(4) and O(4)' of two acetone molecules. The O(3)–O(4) distance of 2.725 Å is consistent with the presence of hydrogen bonding. Figure 4[27] is a stereoview of a unit cell packing, also showing the hydrogen bonding. The acetone molecule that is shown in the diagram is from a unit cell different from the one outlined in the picture. The Os(1)–Os(2) distance of 2.293 (1) Å places **2** in the range of relatively short triple bonds. This distance is, however, significantly longer than the Os–Os distances found in $[Os_2Cl_8]^{2-}$ and $[Os_2Br_8]^{2-}$, ($[PPN]_2Os_2Cl_8$, 2.195 (2) Å;[2a] $[n\text{-}Bu_4N]_2Os_2Cl_8$, 2.182 Å;[2b] $[n\text{-}Bu_4N]_2Os_2Br_8$, 2.196 Å[2b]). The longer distances found in **1** and **2** may be attributed to the presence of an axial ligand. The Os(1)–O(3) distance is 2.246 (9) Å, indicating strong axial ligation. The average Os–N and Os–O distances are 2.071 [1] Å and 1.975 [7] Å, respectively. The average Os–Cl distance is 2.24 [1] Å. All of these are within expected ranges. The molecule exhibits a small torsional twist from the ideal eclipsed conformation by approximately 3.7°.

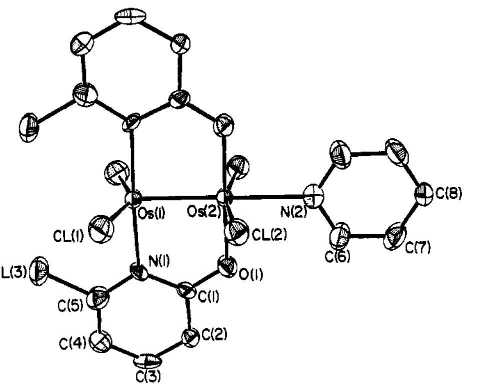


Figure 5. ORTEP diagram of $Os_2Cl_4(chp)_2(py)$ (**1**) with the indicated atom-labeling scheme. The atoms are represented by thermal vibration ellipsoids at the 50% level. Hydrogen atoms have been omitted for clarity.

$Os_2Cl_4(chp)_2(py)$ (1). The positional parameters and the selected bond distances and bond angles are contained in Tables II and IV, respectively. The molecule is depicted by an ORTEP diagram that is labeled with the unique atoms (see Figure 5). The structure consists of the same arrangement of chlorides and chp ligands that was described for **2**. The angles N(1)–Os(1)–Cl(1) and O(1)–Os(2)–Cl(2) are 89.8 (3) and 89.7 (3)°, respectively. Again, the trans chloride ligands are nonlinear, with Cl(2)–Os(1)–Cl(1)' = 148.4 (2)° and Cl(2)–Os(2)–Cl(2)' = 163.8 (1)°. The torsional twist in this molecule is almost negligible (1.5°). The Os(1)–Os(2) distance is 2.322 (1) Å, slightly longer than in compound **1**.

Structural Comparison of 1 and 2. The isolation of two separate adducts of $Os_2Cl_4(chp)_2(L)$ presents an opportunity to examine the influence of axial ligation upon the osmium–osmium interaction. What we see is a very clear example of the influence of axial ligation in weakening the metal–metal bond. In **2** we have the weaker base (H_2O) more weakly bonded (Os–O = 2.246 Å) and an Os–Os bond length of 2.293 (1) Å. In **1** we have the stronger base (pyridine) more strongly bonded (Os–N = 2.238 Å), and accordingly, the Os–Os bond length is greater, namely 2.322 (1) Å. This inverse relationship between axial M–L bonding and M–M bonding is found quite generally.

---

[27] Figures 2 and 4 can be found in the supplementary material. The reader should refer to Figure 3, which contains all the pertinent information.

[28] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Concluding Remarks

This study documents the existence of a previously unknown class of compounds that are unique in several respects. First, and most importantly, they constitute the only members of an $M_2Cl_4(LL)_2$ general class of compounds, in which there is an overall eclipsed conformation with two trans bidentate ligands (LL) that are anions of a substituted hydroxypyridine. We are working to extend this class of compounds to include examples with other transition metals. Secondly, they are the first reported examples in diosmium chemistry of an $Os_2Cl_4(LL)_2$ structural type. Finally, **1** and **2** are the first diosmium compounds that contain a neutral donor molecule as an axial ligand. Previous compounds have always possessed either one or two halides in the axial positions. The investigation of the reactivity of $Os_2Cl_4(chp)_2(L)$ (L = py, H_2O) is currently under way. These complexes, in which the Os-Os bond is supported by trans bridging ligands, may provide us with the opportunity to study substitution reactions that might otherwise (e.g., for the $Os_2Cl_8^{2-}$ ion) result in disruption of the dimetal unit.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. **1**, 101403-86-5; **2**, 101403-88-7; Os, 7440-04-2.

Supplementary Material Available: Full listings of bond angles, bond distances, and anisotropic equivalent displacement parameters and Figures 2 and 4 (9 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (21 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

Contribution from the Department of Physical and Life Sciences, University of Portland, Portland, Oregon 97203, and Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794

Synthesis, Structure, and Interconversion of Polypyrazolylborate Complexes of Molybdenum(V)

Sandra Lincoln*[1a] and Stephen A. Koch*[1b]

Received May 28, 1985

A series of oxomolybdenum(V) complexes with the hydrotripyrazolylborate ($HB(pz)_3^-$) ligand has been synthesized and characterized. $HB(pz)_3MoOCl_2$ (**1**) was prepared by the reaction of O_2 with $HB(pz)_3MoCl_3$. A pair of $(HB(pz)_3MoOCl)_2O$ geometric isomers (**2a**, **2b**) and $(HB(pz)_3)_2Mo_2O_2(\mu\text{-}O)_2$ (**3**) were obtained from the reaction of $MoCl_5$ and $KHB(pz)_3$ in dilute HCl. A Mo(V) tetramer, $Mo_4(HB(pz)_3)_2(O)_4(\mu\text{-}O)_4(\mu\text{-}OMe)_2(HOMe)_2$ (**4**), was synthesized from the reaction of **3** with MeOH. Compounds **1**, **2a**, **2b**, and **4** were structurally characterized by X-ray diffraction. The unit cell parameters are as follows: for **1**, a = 15.273 (2) Å, b = 7.698 (1) Å, c = 13.442 (2) Å, β = 108.84 (1)°, V = 1495.9 (6) Å^3, Z = 4, Cc; for **2a**, a = 16.140 (5) Å, b = 11.163 (2) Å, c = 17.337 (4) Å, β = 116.18 (2)°, V = 2803 (1) Å^3, Z = 4, $P2_1/c$; for **2b**, a = 7.763 (4) Å, b = 13.128 (4) Å, c = 14.823 (4) Å, β = 96.61 (3)°, V = 1501 (2) Å^3, Z = 2, $P2_1/c$; for **4**, a = 14.763 (6) Å, b = 8.965 (3) Å, c = 14.076 (4) Å, β = 104.25 (3)°, V = 1806 (2) Å^3, Z = 2, $P2_1/c$. Compounds **2a** and **2b**, which are geometric isomers, have the structures typical of $Mo_2O_3^{4+}$ dimers with linear Mo-O-Mo bridges. Compounds **2a** and **2b** provide the first example of Mo=O distortional isomers with a d^1 electronic configuration: the Mo-oxo distance in **2a** is 1.670 (4) Å while the corresponding distance in **2b** is 1.779 (6) Å. The yellow-brown colors of **2a** and **2b** with intense bands at 21 645 cm^{-1} indicate that the previous interpretations of the electronic spectra of $Mo_2O_3^{4+}$ complexes must be reevaluated. The chemical and crystallographic characterization of **4** indicated that it is a Mo(V) tetramer with a zigzag chain of four Mo atoms. The importance of correctly distinguishing between a coordinated alkoxide and a coordinated alcohol has been demonstrated in the structure of **4** and by the reformulation of two Mo(V) tetramers that had been previously reported in the literature as mixed-valence complexes.

Introduction

Molybdenum serves an important role in certain metalloproteins and in heterogeneous catalysts. In both cases sulfur and oxygen ligands are particularly important. The biochemistry of the molybdenum-containing enzymes[2] has provided much of the inspiration for the extensive development in the coordination chemistry of molybdenum with sulfur and oxygen ligands.[3-6] More recently, the widespread industrial use of molybdenum oxides and molybdenum sulfides as oxidation and hydroprocessing catalysts[7,8] has also begun to suggest research problems in molybdenum coordination chemistry.[9] One of our research goals has been to synthesize molybdenum cluster complexes with oxygen and sulfur donor ligands that would contain structural features found in the solid-state molybdenum oxides and sulfides. This paper describes some of our efforts in this area. In this, and our related publications,[10-12] we have been making use of the tridentate polypyrazolylborate ligand to control three of the coordination sites of the molybdenum center.

Experimental Section

All organic solvents were dried by standard procedures. Unless otherwise noted, reactions were carried out under a nitrogen atmosphere by using Schlenk glassware and vacuum-line procedures. ^{1}H NMR spectra were obtained with a Varian HFT-80 spectrometer.

$HB(pz)_3MoOCl_2$ (1). $HB(pz)_3MoCl_3$[10] (1.0 g, 2.4 mmol) was dissolved in dry CH_2Cl_2 (90 mL); dioxygen (27 mL, 1.2 mmol) was added, and the reaction was stirred for several hours. After filtration to remove

---

(1) (a) University of Portland. (b) SUNY at Stony Brook.

(2) (a) Coughlan, M. *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: New York, 1980. (b) Newton, W. E.; Otsuka, S. *Molybdenum Chemistry of Biological Significance*; Plenum: New York, 1980.

(3) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1-223 and references therein.

(4) Stiefel, E. I. In *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: New York, 1980; pp 41-98.

(5) Pope, M. T.; Still, E. R.; Williams, R. J. P. In *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: New York, 1980; pp 1-40.

(6) Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99.

(7) Grasseli, R. K. In *Surface Properties and Catalysis by Non-Metals: Oxides, Sulfides and Other Transition Metal Compounds*; D. Reidel: Dordrecht, 1983; pp 272-304.

(8) (a) Topsøe, H.; Clausen, B. S. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 395. (b) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 361.

(9) (a) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119. (b) Chisholm, M. H. *ACS Symp. Ser.* **1983**, *No. 211*, 243. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

(10) Millar, M.; Lincoln, S.; Koch, S. A. *J. Am. Chem. Soc.* **1982**, *104*, 288.

(11) Koch, S. A.; Lincoln, S. *Inorg. Chem.* **1982**, *21*, 2904.

(12) Lincoln, S.; Soong, S.-L.; Koch, S. A.; Sato, M.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1355.

0020-1669/86/1325-1594$01.50/0