these four carbons form the largest P–N–C angles. These large angles do not appear to be unambiguously associated with the short nonbonded C–C distances, however, since analysis of the structural data for $Fe(CO)_4(\mathbf{1})$ and *trans*-$Fe(CO)_3(\mathbf{1})_2$ reveals that similar nonbonded interactions do not involve large P–N–C angles. The cone angles of **1** (168°) and **2** (164°) calculated from the X-ray structural data of $[Ag(\mathbf{1})_2]BPh_4$ and $OP(NMeCH_2)_3CCH_3$,[48] respectively, are indeed of comparable size as was assumed at the onset from models. Interestingly the cone angle of **1** is larger in $[Ag(\mathbf{1})_2]BPh_4$ than when it is measured from space-filling models (157°). Since $[Ag(\mathbf{1})_2]BPh_4$ shows no evidence of ligand–ligand repulsion, the ligand cone angle might be expected to decrease in more crowded complexes.

From the structural data for $[Ag(\mathbf{1})_2]BPh_4$ it can be concluded that because of considerable similarities to structures of a variety of other PN_3 compounds, the ligand conformations observed are not determined by lattice effects. Our results also lend further credence to conclusions from theoretical work, which suggests that structures C and D in Figure 1 represent the most stable conformations of tris(dialkylamino)phosphines, with the energy difference between the two being rather small. Finally, the bulk of the structural data indicates that tris(dialkylamino)phosphines are not idealized symmetrical structures but they prefer (at least in the solid state) a conformation wherein one or more of the nitrogens assumes some pyramidal character.

Acknowledgment. J.G.V. is grateful to the National Science Foundation for generous support of this research in the form of a grant and to Iowa State University for computational funds. The authors thank J. H. Benson and B. J. Helland for their assistance in collecting X-ray data.

Registry No. **1**, 1608-26-0; **2**, 14418-26-9; **3**, 1194-53-2; $[Ag(\mathbf{1})_2]BPh_4$, 87883-94-1; $[Ag(\mathbf{1})_2I]$, 87883-95-2; $[Ag(\mathbf{1})_2Cl]$, 87883-96-3; $[Ag(\mathbf{1})_2NO_3]$, 87883-97-4; $[Ag(\mathbf{1})]BF_4$, 87883-99-6; $[Ag(\mathbf{1})_2CN]$, 87884-00-2; $[Ag(\mathbf{1})_3]BPh_4$, 87884-02-4; $[Ag(\mathbf{2})BF_4]$, 87884-03-5; $[Ag(\mathbf{2})_2]PF_4$, 87884-05-7; $[Ag(\mathbf{2})_3]BPh_4$, 87884-07-9; $[Ag(\mathbf{3})BF_4]$, 87884-08-0; $[Ag(\mathbf{3})_4]BF_4$, 87884-10-4; $[Ag(\mathbf{3})_4]Cl$, 87884-11-5; $[Ag(\mathbf{3})_4]I$, 87884-12-6; $[Ag(\mathbf{3})_3I]$, 87884-13-7.

Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factors and a computer drawing of the unit cell (15 pages). Ordering information is given on any current masthead page.

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[48] These cone angles were calculated by assuming an M–P distance of 2.28 Å, a C–H bond length of 1.00 Å, a hydrogen van der Waals radius of 1.00 Å, and tetrahedral angles around carbon. The P–M–H angle was calculated for a coplanar arrangement of the M–P–C–H bonds for C_7, C_{10}, and C_{11} in the ligand of the silver complex. These angles were then doubled, and the average was taken to give 168°. A similar treatment of the structural data for the $P(NCH_3CH_2)_3CCH_3$ moiety in $OP(NCH_3CH_2)_3CCH_3$ (Clardy, J. C.; Kolpa, R. L.; Verkade, J. G. *Phorphous Relat. Group V Elem.* **1974**, *4*, 133) gave an average cone angle of 164°.

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Preparation and Characterization of Binuclear (1,4,7-Triazacyclononane)molybdenum(III) Complexes. Crystal Structures of $[Mo^{III}_2(\mu\text{-}OH)_2Cl_2(C_6H_{15}N_3)_2]I_2$ and $[Mo^{III}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(C_6H_{15}N_3)_2]I_3\cdot H_2O$

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Binuclear complexes of molybdenum(III) have been prepared by hydrolysis of the mononuclear $LMoCl_3$ (**2**) in aqueous solution containing acetate or hydrogen carbonate ions: $[LMo(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)_2)MoL]I_3\cdot H_2O$ (**3a**), $[LMo(\mu\text{-}OH)_2(\mu\text{-}CO_3)MoL]I_2\cdot H_2O$ (**4**) (L = 1,4,7-triazacyclononane). The reactions of the μ-carbonato complex with aqueous CH_3SO_3H, HCOOH, and HCl afford the complexes $[LMo(\mu\text{-}OH)_2(OH_2)_2MoL]I_4$ (**5**), $[LMo(\mu\text{-}OH)_2(\mu\text{-}O_2CH))MoL]I_3$ (**3b**), and $[LClMo(\mu\text{-}OH)_2MoClL]I_2$ (**6**), respectively. **5** is readily oxidized by $HClO_4$ or O_2 forming a Mo(V) dimer, $[Mo_2O_2(\mu\text{-}O)_2L_2]I_2$. Crystals of **3a** belong to the space group $P2_1/a$ with $a = 9.833$ (2) Å, $b = 19.261$ (8) Å, $c = 14.967$ (2) Å, $\beta = 100.00$ (2)°, $V = 2792$ (6) Å^3, and $Z = 4$. Crystals of **6** belong to the space group $C2/c$ with $a = 12.889$ (6) Å, $b = 14.219$ (4) Å, $c = 14.280$ (4) Å, $\beta = 116.70$ (3)°, $V = 2338$ (6) Å^3, and $Z = 4$. The structures refined to $R = 0.053$ and 0.057 for **3a** and **6**, respectively. The structure of **3a** consists of a binuclear cation of two distorted octahedra bridged by one acetate and two hydroxo ligands. The Mo–Mo distance is 2.471 (2) Å, and the formal bond order may be three ($\sigma^2\pi^2\delta^2$). The structure of **6** consists also of a binuclear cation of two distorted octahedra sharing an edge. The $Mo(\mu\text{-}OH)_2Mo$ ring is planar, the Mo–Mo distance being 2.501 (3) Å ($Mo\equiv Mo$, $\sigma^2\pi^2\delta^2$).

Introduction

An extensive range of binuclear Mo(V) compounds with the $Mo_2O_4^{2+}$ unit [bis(μ-oxo)bis(oxomolybdenum(V))] and O,N-donor ligands have been prepared in aqueous solution and have been characterized by X-ray analysis.[2] The short Mo–Mo distances (2.59–2.53 Å) and the observed diamagnetism indicate that a weak interaction (Mo–Mo single bond) exists between the two metal atoms.

Hydroxo-bridged binuclear diamagnetic complexes of molybdenum(III) containing O,N-donor ligands (e.g., edta) are known to a much lesser degree.[2a] Their preparation in aqueous solution was achieved via reduction of the corresponding Mo(V) dimers with strong reductants (e.g., zinc amalgam). Thus, bis(μ-hydroxo)(μ-acetato)(μ-ethylenediaminetetraacetato)dimolybdenum(III) has been fully characterized. The short Mo–Mo distance of 2.43 Å and its diamagnetism indicate the presence of a strong Mo–Mo interaction.[3] Paramagnetic,

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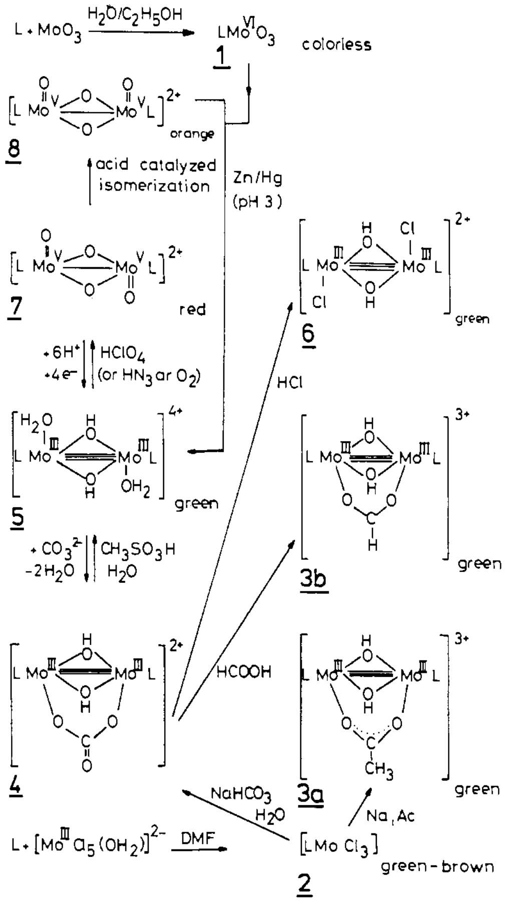
[1] (a) Ruhr-Universität Bochum. (b) Universität Heidelberg.

[2] (a) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1. The first structure was determined in 1965: Cotton, F. A.; Morehouse, S. M. *Inorg. Chem.* **1965**, *4*, 1377. More recent structure determinations are: (b) Kojima, A.; Ooi, S.; Sasaki, Y.; Suzuki, K.; Saito, K.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2457. (c) Cotton, F. A.; Ilsey, W. H. *Inorg. Chim. Acta* **1982**, *59*, 213. (d) Moynihan, K. J.; Boorman, P. M.; Ball, J. M.; Patel, V. D.; Kerr, K. A. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2258. (e) Shibahara, I.; Kuroya, H.; Matsumoto, K.; Ooi, S. *Inorg. Chim. Acta* **1981**, *54*, L75.

[3] (a) Kneale, G. G.; Geddes, A. J.; Sasaki, Y.; Shibahara, T.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1975**, 356. (b) Shibahara, T.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1978**, 95. (c) Kneale, G. G.; Geddes, A. J. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1233.

Scheme I



mononuclear complexes of the type $LMoX_3$ (L = N_3-donor ligand; X = Cl, Br) have also been prepared[4] but to our knowledge have not succesfully been used as starting material for the preparation of binuclear Mo(III) complexes in aqueous solution.

In this paper we describe the preparation, characterization, and crystal structures of a series of binuclear complexes of Mo(III).

Results and Discussion

Syntheses of Complexes. The hydrolysis of the mononuclear $([9]aneN_3)MoCl_3$ (**2**) in an oxygen-free aqueous solution of sodium hydrogen carbonate at 70 °C affords the green, diamagnetic, binuclear cation (μ-carbonato)bis(μ-hydroxo)bis-[(1,4,7-triazacyclononane)molybdenum(III)], which has been isolated as its crystalline iodide salt, **4** (Scheme I).[5] Although solutions of **4** are very air sensitive, the green crystalline compound is only moderately sensitive. Hydrolysis of **2** in an oxygen-free, aqueous solution of sodium acetate yields the green, diamagnetic (μ-acetato)bis(μ-hydroxo)bis[(1,4,7-triazacyclononane)molybdenum(III)] cation (**3a**), which is also obtained as crystalline iodide salt. **3a** is also oxygen sensitive.

The μ-carbonato complex **4** is a useful starting material for the syntheses of binuclear complexes of molybdenum(III). When **4** is reacted with acetic acid (or formic acid), complex **3a** (or **3b**) is formed; whereas methanesulfonic acid removes the carbonate bridge with concomitant addition of two coordinated water molecules generating the very oxygen-sensitive bis(μ-hydroxo)bis[aqua(1,4,7-triazacyclononane)molybdenum(III)] cation, **5**. Green, diamagnetic precipitates are obtained from such solutions by adding sodium iodide or bromide. When **4** reacts with hydrochloric acid (0.5 M), the green, diamagnetic, chloro complex **6** is formed.

Table I. Electronic Absorption Spectra of Complexes[a]

complex	λ_{max}, nm (ϵ(dimer), $M^{-1}\ cm^{-1}$)
3a	375 (1.3×10^3), 626 (69), 754 (55)
3b	377 (1.2×10^3), 626 (76), 755 (57)
4	366 (1.2×10^3), 450 (sh), 630 (71), 735 (sh)
5	379 (1.4×10^3), 490 (sh), 643 (147), 715 (sh)
6	384 (1.2×10^3), 430 (sh), 650 (164), 765 (115)
7	312 (3.6×10^3), 525 (380)
8	284 (7.0×10^3), 378 (410)

[a] Aqueous solutions.

Interestingly, the reaction of oxygen-free aqueous solutions of **4** of **5** with perchloric acid (0.1 M) at 20 °C yielded a cherry red solution within 60 min from which red, diamagnetic crystals of bis(μ-oxo)bis[oxo(1,4,7-triazacyclononane)molybdenum(V)] diiodide (**7**) were precipitated at 2 °C.[5] The same product was obtained by using HN_3 as the oxidant of **4**. The controlled oxidation of **5** with dioxygen (stoichiometric reaction) also yielded **7** quite rapidly at room temperature (pH 7). The crystal structure of $(\mathbf{7})I_2$ revealed the first binuclear molybdenum(V) complex with a $Mo_2O_4^{2+}$ entity, the terminal Mo=O groups being trans with respect to each other. **7** is irreversibly converted to the yellow complex **8** containing the bis(μ-oxo)bis[oxo(1,4,7-triazacyclononane)molybdenum(V)] cation with the Mo=O groups in the well-known cis position. The conversion **7** → **8** occurs via an acid-catalyzed reaction path.[5] Aqueous solutions of **7** are indefinitely stable.

Under more acidic reaction conditions such as 0.7 M perchloric acid and elevated temperatures (40 °C), **4** (or **5**) was converted to **8**, which contains the orange cation bis(μ-oxo)-bis[oxo(1,4,7-triazacyclononane)molybdenum(V)]. A variety of solid salts of **8** have been prepared (Cl^-, Br^-, I^-, ClO_4^-, SCN^-). Identical products were obtianed when a suspension of $(NH_4)_2MoCl_5{\cdot}H_2O$ in dimethyl sulfoxide was reacted with 1,4,7-triazacyclononane at 50 °C.[6] The reduction of $(\mathbf{8})I_2$ or $(\mathbf{8})Br_2$ in oxygen-free aqueous HI or HBr (pH 3) with zinc amalgam yielded **5** within 20 min at 20 °C.

It has not been possible to oxidize the Mo(V) dimer further to Mo(VI) with retention of the binuclear Mo_2O_4 structure. The reaction of 1,4,7-triazacyclononane with MoO_3 in aqueous solution afforded the colorless, mononuclear $([9]aneN_3)MoO_3$ (**1**). This reaction is identical with the procedure reported for the preparation of $(dien)MoO_3$.[7] The reduction of **1** in trifluormethanesulfonic acid (10^{-3} M) with zinc amalgam afforded under an argon atmosphere the Mo(III) dimer **5**. A binuclear Mo(VI) species has been obtained from a completely different reaction.[8] The yellow $[([9]aneN_3)_2Mo_2O_5](ClO_4)_2$ salt most probably contains the well-known μ-oxo-bridged $Mo_2O_5^{2+}$ unit. We have not found a simple preparative route from this species to the series **8**, **7**, **5** or from **8** to the Mo(VI) dimer.

In Table I the electronic spectra of the new complexes are summarized. The electronic spectra of the Mo(V) dimer **8** and those of Mo(III) dimers **3a**, **3b**, **4**, **5**, and **6** are very similar to those reported for $[Mo_2O_4(edta)]^{2-}$,[10] $[Mo^{III}_2(\mu\text{-}OH)_2(O_2CCH_3)(edta)]^-$,[3b] and $[Mo^{III}_2(\mu\text{-}OH)_2(H_2O)_2(edta)]$.[3b] Peaks in the visible region 600–750 nm (ϵ 50–150 $M^{-1}\ cm^{-1}$) observed for complexes **3a**, **3b**, **4**, **5**, and **6** are believed to be

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(4) (a) Brenčič, J. V.; Leban, I. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1292. (b) Millar, M.; Lincoln, S. S.; Koch, S. A. *J. Am. Chem. Soc.* **1982**, *104*, 288.

(5) Wieghardt, K.; Hahn, M.; Weiss, J.; Swiridoff, W. *Angew. Chem.* **1983**, *95*, 499; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 491.

(6) We thank Dr. W. Schmidt, Universität Hannover, 1978, for suggesting this preparation.

(7) (a) Marzluff, W. F. *Inorg. Chem.* **1964**, *3*, 395. (b) Cotton, F. A.; Elder, R. C. *Ibid.* **1964**, *3*, 397.

(8) From reaction of $([9]aneN_3)Mo(CO)_3$ in aqueous solution—among a variety of other products—$[([9]aneN_3)_2Mo_2O_5](ClO_4)_2$ can be isolated: Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.*, in press.

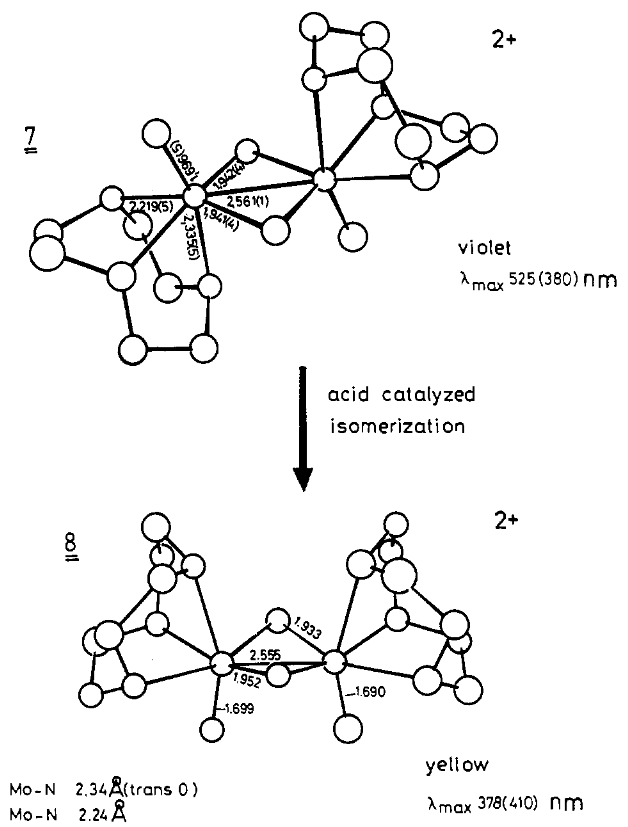


Figure 1. Ball and stick representation of the isomeric cations **7** and **8** of $[([9]aneN_3)_2Mo_2O_4]^{2+}$.

characteristic of Mo(III) dimers.[3b]

The IR spectra of the dimeric complexes show some interesting features concerning their Mo_2O_2 structural units and Mo–O stretching frequencies of terminal oxo or aqua ligands. The latter frequency is observed at 940 cm^{-1} for the Mo(V) dimer **8** and at 909 cm^{-1} for the Mo(V) dimer **7**. The antisymmetric oxo-bridge vibration is observed at 740 cm^{-1} for **8** and the respective vibration for **7** at 729 cm^{-1} whereas for the Mo(III) dimers **4**, **5**, and **6** this band is probably shifted to 620 cm^{-1}.

Description of Crystal Structures. The crystal structures of $(\mathbf{7})I_2$ and $(\mathbf{8})(SCN)_2{\cdot}KSCN$ have been reported elsewhere.[5] The structure of **8** is similar to that of a variety of compounds containing the $Mo_2O_4^{2+}$ structural unit.[2] The Mo–Mo distance of 2.555 (1) Å is also well in the range observed for these complexes (2.53–2.58 Å). The central $Mo(O_2)Mo$ ring is strongly puckered, and the terminal Mo═O groups are cis with respect to each other. Together with the observed diamagnetism of the complex **8**, these data suggest the formation of a direct metal–metal bond of bond order one.

The most striking difference between **7** and **8** is that the terminal oxo ligands of the bis(μ-oxo)bis[oxomolybdenum(V)] cation adopt a trans position with respect to each other and the Mo_2O_2 four-membered ring is planar. For comparative purposes pertinent bond lengths together with a perspective view of the cations **7** and **8** are given in Figure 1. Bond lengths in $(\mathbf{8})(SCN)_2{\cdot}KSCN$ and $(\mathbf{7})I_2$ do not differ significantly; the Mo–Mo metal bond distances are identical within experimental error (2.55 Å).

The crystal structure of $[([9]aneN_3)_2Mo_2(\mu\text{-}OH)_2Cl_2]I_2$ (**6**) consists of the dimeric cation $[([9]aneN_3)Mo_2(\mu\text{-}OH)_2Cl_2]^{2+}$ and uncoordinated iodide anions. **6** has crystallographically imposed C_i symmetry. Each molybdenum atom is in a distorted-octahedral environment of three facially coordinated nitrogens of the amine ligand, two cis oxygens of hydroxo bridges, and one bound chlorine ligand. The two molybdenum atoms are connected via two hydroxo bridges (edge-sharing octahedra). Figure 2 gives a perspective view of the cation **6**. In Tables II and III selected bond lengths and angles are summarized.

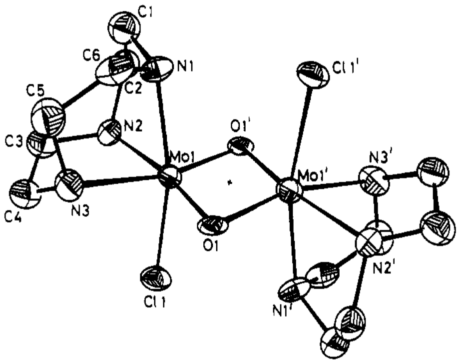


Figure 2. Perspective view of the cation $[([9]aneN_3)_2Mo_2Cl_2(\mu\text{-}OH)_2]^{2+}$ (**6**) and atomic-labeling scheme.

Table II. Selected Bond Lengths (Å) of Complexes 6 and 3a with Standard Deviations in Parentheses

	Complex 6		
Mo1-Mo1′	2.501 (3)	Mo1-N1	2.197 (12)
Mo1-O1	2.126 (9)	Mo1-N2	2.231 (14)
Mo1-O1′	2.135 (11)	Mo1-N3	2.216 (12)
Mo1-Cl	2.438 (5)		
	Complex 3a		
Mo3-Mo5	2.471 (2)	Mo5-O2	2.066 (10)
Mo3-O1	2.082 (10)	Mo5-O4	2.078 (11)
Mo3-O2	2.071 (9)	Mo5-N4	2.196 (12)
Mo3-O3	2.094 (11)	Mo5-N5	2.219 (13)
Mo3-N1	2.199 (12)	Mo5-N6	2.214 (12)
Mo3-N2	2.218 (12)	O3-C20	1.311 (21)
Mo3-N3	2.234 (12)	O4-C20	1.261 (20)
Mo5-O1	2.084 (9)	C19-C20	1.500 (23)

Table III. Selected Bond Angles (deg) of the Binuclear Cations 6 and 3a

	Complex 6		
O1-Mo1-O1′	108.1 (3)	O1′-Mo1-N2	86.4 (4)
O1-Mo1-Cl1	94.4 (3)	Cl1-Mo1-N1	164.9 (3)
Mo1-Mo1-Cl1	96.8 (1)	Cl1-Mo1-N3	88.2 (4)
O1-Mo1-Cl1	93.5 (3)	Cl-Mo1-N2	92.1 (4)
N1-Mo1-N2	78.6 (5)	O1-Mo1-N2	163.6 (4)
N2-Mo1-N3	79.7 (5)	O1-Mo1-N1	97.7 (4)
N3-Mo1-N1	78.6 (5)	O1-Mo1-N3	85.5 (4)
Mo1-O1-Mo1′	71.9 (3)	O1-Mo1-Cl1	94.4 (3)
	Complex 3a		
O1-Mo3-O2	106.3 (4)	Mo5-Mo3-O3	87.2 (3)
O1-Mo3-O3	89.1 (4)	O2-Mo3-O3	95.3 (4)
O2-Mo3-N1	95.9 (4)	O1-Mo3-N1	99.4 (4)
O2-Mo3-N2	165.2 (4)	O3-Mo3-N1	163.3 (4)
N1-Mo3-N2	80.8 (4)	O1-Mo3-N2	88.4 (4)
O1-Mo3-O3	167.0 (4)	O3-Mo3-N2	85.1 (4)
O3-Mo3-N3	88.4 (4)	O2-Mo3-N3	86.6 (4)
N2-Mo3-N3	78.6 (5)	N1-Mo3-N3	80.1 (5)
O1-Mo5-O4	89.2 (4)	O1-Mo5-O2	106.4 (4)
O1-Mo5-N4	166.4 (4)	O2-Mo5-O4	93.7 (4)
O4-Mo5-N4	89.4 (4)	O2-Mo5-N4	87.2 (4)
O2-Mo5-N5	94.8 (4)	O1-Mo5-N5	99.4 (4)
N4-Mo5-N5	79.5 (5)	O4-Mo5-N5	165.6 (5)
O2-Mo5-N6	166.8 (4)	O1-Mo5-N6	86.3 (4)
N4-Mo5-N6	80.1 (4)	O4-Mo5-N6	89.6 (5)
O4-Mo5-Mo3	86.0 (3)	N5-Mo5-N6	79.6 (5)
N5-Mo5-Mo3	108.4 (4)	Mo5-Mo3-N1	109.4 (3)
Mo5-O1-Mo3	72.7 (3)	Mo5-O2-Mo3	73.4 (3)
C20-O3-Mo3	121.8 (10)	Mo5-O4-C20	125.3 (11)
O3-C20-O4	119.5 (15)	O3-C20-C19	117.7 (15)
O4-C20-C19	122.8 (16)		

The Mo–N bonds in **6** are equivalent within experimental error (average 2.215 Å) and are identical with those in **7** (2.218 Å) and **8** (2.243 Å), which are not affected by a trans Mo═O group. The Mo–N and Mo—Cl bond lengths agree well with

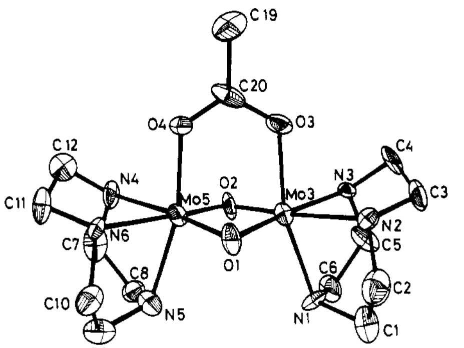


Figure 3. Perspective view of the cation $[([9]aneN_3)_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]^{2+}$ (**3a**) and atomic-labeling scheme.

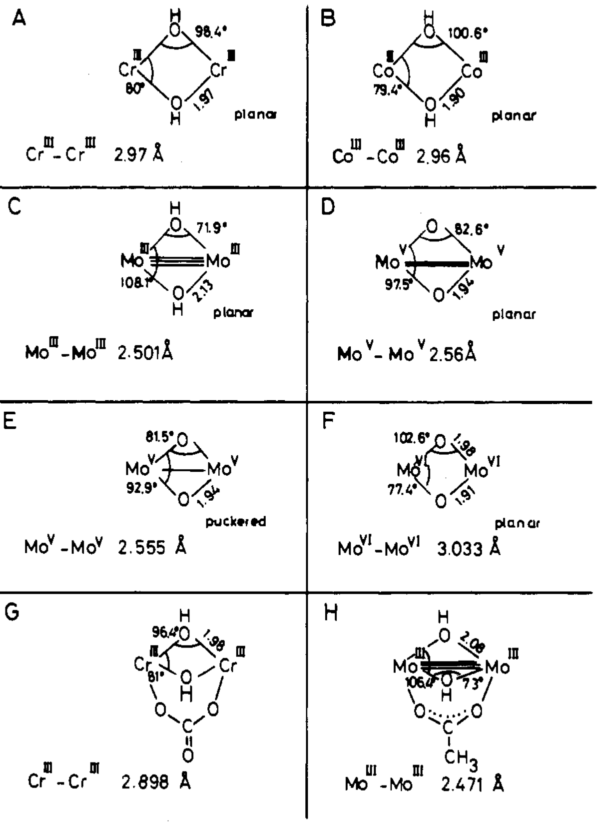
those found in monomeric complexes of molybdenum(III).[4]

The Mo–O distances of the hydroxo bridges (2.13 (1) Å) are significantly longer than those in **7** and **8** (1.94 Å) despite a somewhat shorter Mo–Mo distance of 2.501 (3) Å, which is to be compared with 2.561 (1) Å found in **7** and 2.555 (1) Å in **8**. This shortening of the Mo–Mo distance and lengthening of the Mo–O bonds yield comparatively larger O–Mo–O and smaller Mo–O–Mo bond angles, the first of which is acute whereas the latter is obtuse. As in **7**, the four-membered Mo_2O_4 ring in **6** is planar.

The crystal structure of $[([9]aneN_3)_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]I_3{\cdot}H_2O$ (**3a**) consists of the binuclear cation (μ-acetato)bis(μ-hydroxo)bis[(1,4,7-triazacyclononane)molybdenum(III)] and of uncoordinated iodide ions. Two distorted octahedra are connected via one acetato and two hydroxo bridges (Figure 3). Mo–N and Mo–O bond lengths agree well with those in **6** and in the $[Mo_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)\text{edta}]^-$ anion.[3] The Mo–Mo distance is short (2.471 (2) Å) and may be compared with 2.430 (3) Å in the Mo^{III}(edta) dimer[3b] and 2.501 (3) Å in **6**.

The Mo–Mo Bond Order in Mo^{III} Dimers. Direct metal–metal bonds have been discussed in bridged binuclear complexes of molybdenum in various formal oxidation states.[9] The observed coupling of electron spins for such d^1–d^1, d^2–d^2, d^3–d^3, and d^4–d^4 dimers at room temperature alone cannot be taken as evidence for direct Mo–Mo interactions since the spins could get coupled by molecular orbital delocalization through the bridging groups. But, the latter mechanism does not lead to short metal–metal distances. The above series of structurally well-characterized complexes presents the opportunity to study the effect of changing oxidation states of the Mo centers (e.g., addition or subtraction of valence electrons) without extensively altering the immediate environment of the molybdenum atoms. Furthermore, it is fortunate for our purpose that the same binuclear structure type has been studied previously for some other transition metals (e.g., Cr(III),[10] Co(III),[11] Rh(III)[12]). These represent cases where no direct metal–metal interactions have to be invoked (the Cr(III) dimers are antiferromagnetic and the Co(III) and Rh(III) complexes have d^6 low-spin configuration). In Chart I a comparison of the arrangements of the various M_2O_2 four-membered rings are summarized. Clearly, direct interactions of Mo–Mo atoms in the oxidation states V and III are evident from this compilation. Within the four-membered rings of Cr(III), Co(III), Rh(III), or Mo(VI) dimers, the metal–metal distances are greater than 2.9 Å and, consequently, the M–O–M angles are obtuse and the O–M–O bond angles are acute, indicating the absence of direct M···M interactions. In contrast, in the Mo(V) and Mo(III) dimers **8**, **7**, and **6**, Mo–Mo distances smaller than 2.6 Å are observed, and now the Mo–O–Mo angles are acute whereas the O–Mo–O angles are obtuse.

Chart I[a]



[a] The data were taken from single-crystal X-ray investigations of the following complexes: (A) $[Cr_3([9]aneN_3)_2(OH)_5]I_5{\cdot}5H_2O$, ref 10; (B) $[Co_2([9]aneN_3)_2(OH)_2(OH_2)_2](ClO_4)_4{\cdot}4H_2O$, ref 11; (C) **6**, this work; (D) **7**, ref 5; (E) $(\mathbf{8})(SCN)_2{\cdot}KSCN$, ref 5; (F) $(Et_2NHOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$, ref 13; (G) $[([9]aneN_3)_2Cr_2(OH)_2CO_3]I_2{\cdot}H_2O$, ref 14; (H) **3a**, this work; identical values are reported for $K[Mo_2(OH)_2(O_2CCH_3)(\text{edta})]$, ref 3.

Interestingly, the same picture emerges for the μ-carboxylato-bridged complex **3a** and Sykes' $[Mo_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(\text{edta})]^-$, which exhibit short Mo–Mo distances as compared to the bis(μ-hydroxo)(μ-acetato)bis[triamminecobalt(III)] cation for which a Co–Co distance of 2.804 (1) Å has been determined.[15] For the (μ-carbonato)bis(μ-hydroxo)bis[(1,4,7-triazacyclononane)chromium(III)] cation[17] a Cr–Cr distance of 2.898 Å has been determined.

Therefore, we feel that these facts are excellent evidence that there is metal–metal bonding in the Mo(V) and Mo(III) dimers, but there remains the question of the actual bond order in the Mo(III) dimers if one accepts one direct single bond (σ bond) between the Mo(V) ions in **7** and **8**. Recently ex-

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perimental and theoretical evidence for double bonds between alkoxo-bridged dimolybdenum(IV) and ditungsten(IV) has been presented.[16,17] In the bis(μ-alkoxo)-bridged complex $Mo_2(O\text{-}i\text{-}Pr)_8$ a double bond ($\sigma^2\pi^2$) has been proposed on the basis of a Mo–Mo distance of 2.523 (3) Å and its diamagnetism.[17] Fenske–Hall type molecular orbital calculations for the model system $[Mo_2Cl_4(\mu\text{-}OH)_2(OH)_2(H_2O)_2]$ have been carried out.[16] A Mo–Mo double bond of the $\sigma^2\pi^2$ type has been proposed. In this model two edge-sharing octahedra were connected via two hydroxo bridges.

So far the scarcity of the experimental data concerning hydroxo-bridged species of Mo(III) has suppressed a more detailed description of the bonding situation of this structure type. But, since additional structures in this class are now known,[3] the bis(hydroxy) bridge appears to be the common structural unit for aqueous dimeric Mo(III) systems as Stiefel suggested in 1977.[2a] To our knowledge there are no bis(μ-alkoxo)-bridged Mo(III) dimers known that could complement the present discussion. The $Mo_2(OCH_2CMe_3)_6$ complex contains a direct Mo≡Mo triple bond (2.222 (2) Å) and no alkoxo bridges.[18]

All bis(μ-hydroxo)-bridged Mo(III) dimers are diamagnetic. Since there is a small but significant *decrease* of the Mo–Mo bond length in going from the bis(μ-oxo)bis[oxomolybdenum(V)] species (**7**, d(Mo–Mo) = 2.561 (1) Å) to the bis(μ-hydroxo)dimolybdenum(III) species (**6**, d(Mo–Mo) = 2.501 (3) Å) whereas all other comparable Mo—O bond lengths *increase*, we propose a Mo≡Mo triple bond of the $\sigma^2\pi^2\delta^2$ type in this class of compounds. The alternative formulation of $\sigma^2\pi^2\delta^{*2}$, which has been proposed for $[(H_2edta)Tc(\mu\text{-}O)_2Tc(edtaH_2)]$,[19] cannot be ruled out although oxidation of **6** to **7** or **8** results in a significant *increase* of Mo–Mo bond length.

Experimental Section

All new compounds were isolated as crystalline solids that gave satisfactory analyses (supplementary material). These were obtained by Beller, Microanalytical Laboratory, Göttingen. 1,4,7-Triazacyclononane has been prepared by procedures described in the literature.[11,20] Complexes **2**, **4**, and **7** have been prepared as described previously.[5]

([9]aneN$_3$)MoO$_3$ (1). A suspension of 1,4,7-triazacyclononane (2 g, 15 mmol) and MoO_3 (1.1 g, 7.2 mmol) in 50 mL of water was heated with stirring until a clear solution was obtained. To this solution was quickly added 100 mL of ethanol at 20 °C. A colorless precipitate formed, which was filtered off, washed with ethanol and ether, and air-dried. Recrystallization from 25 mL of hot water, addition of ethanol at 20 °C until the solution became turbid, and cooling (0 °C) afforded 2.5 g (60%) of colorless, needle-shaped crystals. The product was dried in vacuo over P_2O_5 for 2 days. Anal. C, H, N, Mo.

[([9]aneN$_3$)$_2$Mo$_2$(μ-OH)$_2$(μ-CH$_3$–CO$_2$)]I$_3$·H$_2$O (3a). To an oxygen-free (Ar-purged) solution of sodium acetate (5 g) in 35 mL of water was added $([9]aneN_3)MoCl_3$[5] (0.5 g). The suspension was heated to 70 °C until a clear dark green solution was obtained to which 15 g of solid sodium iodide was added. After the mixture was allowed to stand at 2 °C for 12 h, green crystals precipitated, which were filtered off, washed with ethanol and ether, and dried an argon atmosphere. Solutions of **3a** are very air sensitive, and the green crystals, only moderately air sensitive. Anal. C, H, N, Mo, I.

[([9]aneN$_3$)$_2$Mo$_2$(μ-OH)$_2$(μ-H–COO)]I$_3$ (3b). In 25 mL of aqueous formic acid (0.5 M) was dissolved $(4)I_2$ (0.5 g) within 1 h at 20 °C under an argon atmosphere. The solution was stirred further for 3 h after which time solid sodium iodide (5 g) was added. Green crystals precipitated immediately, which were filtered off, washed with ethanol and ether, and dried under argon. Aqueous solutions of 3b are very air sensitive, and crystals, only moderately air sensitive. Anal. C, H, N, I, Mo.

Table IV. Summary of Crystal Data and Intensity Collection for Binuclear Complexes of Molybdenum

	6	3a
A. Crystal Parameters at 22 °C[a]		
system	monoclinic	monoclinic
space group	$C2/c$	$P2_1/a$
a, Å	12.889 (6)	9.833 (2)
b, Å	14.219 (4)	19.261 (8)
c, Å	14.280 (4)	14.967 (2)
β, deg	116.70 (3)	100.00 (2)
V, Å^3	2338	2792
formula	$C_{12}H_{32}Cl_2I_2Mo_2N_6O_2$	$C_{14}H_{35}I_3Mo_2N_6O_4$
fw	809	924
Z	4	4
μ(Mo Kα), cm^{-1}	39.1	42.0
B. Intensity Measurement		
cryst dimens, mm	0.2 × 0.2 × 0.6	0.2 × 0.15 × 0.4
diffractometer	Syntex R3	Syntex R3
temp, °C	22	22°
data collcn	θ–2θ	θ–2θ
max 2θ, deg	45	55
std reflcns	2 every 100 reflcns	
no. of data for $I > 2.5\sigma(I)$	1109	2063
no. of parameters varied	137	299
R[b]	0.057	0.053
R_w[b]	0.050	0.041

[a] Unit cell parameters were obtained by a least-squares analysis of the setting angles of 25 reflections. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table V. Atom Coordinates (× 10^4) of $[([9]aneN_3)_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)]I_3 \cdot H_2O$

atom	x	y	z
I1	2677 (1)	1376 (1)	4857 (1)
I2	1364 (1)	8912 (1)	7138 (1)
I3	2185 (2)	8072 (1)	575 (1)
Mo3	2987 (2)	9413 (1)	3043 (1)
Mo5	3536 (2)	385 (1)	2090 (1)
O1	4278 (10)	249 (5)	3470 (7)
O2	2045 (11)	−367 (5)	1726 (6)
O3	4674 (11)	−1110 (6)	2677 (7)
O4	5128 (11)	−239 (6)	1801 (7)
C19	6707 (15)	−1217 (10)	1992 (11)
C20	5449 (16)	−826 (9)	2148 (11)
N1	1209 (11)	−305 (7)	3679 (7)
N2	3659 (13)	−1066 (7)	4396 (8)
N3	1823 (12)	−1589 (6)	2888 (8)
C2	3082 (20)	−624 (10)	5016 (11)
C3	3176 (20)	−1798 (9)	4433 (11)
C4	2739 (21)	−2076 (8)	3479 (12)
C5	417 (21)	−1499 (9)	3144 (14)
C6	6 (20)	−750 (10)	3191 (15)
N4	3125 (13)	725 (7)	667 (8)
N5	2038 (13)	1236 (7)	2167 (8)
N6	4924 (12)	1297 (7)	2176 (8)
C7	1928 (19)	1228 (10)	503 (12)
C8	1125 (16)	1222 (10)	1269 (12)
C9	2761 (20)	1925 (10)	2347 (11)
C10	4307 (18)	1838 (10)	2701 (11)
C11	5003 (18)	1569 (9)	1239 (12)
C12	4480 (17)	1040 (10)	506 (11)
O10	2836 (13)	4648 (7)	641 (8)

[([9]aneN$_3$)$_2$Mo$_2$(μ-OH)$_2$(H$_2$O)$_2$]I$_4$ (5). In 30 mL of aqueous methanesulfonic acid (0.5 M) was dissolved $(4)I_2$ (0,5 g) within 1 h at 20 °C with stirring under an argon atmosphere. After 2 h of stirring, sodium iodide (15 g) was added to the clear green solution. A green precipitate formed immediately, which was filtered off, washed with ethanol and ether, and dried under argon. Anal. C, H, N, I, Mo. A mixed bromide–iodide salt of the complex cation **5** was obtained by reacting $(4)I_2$ (0.5 g) with 40 mL of hydrobromic acid

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Table VI. Atom Coordinates (×10^4) of $[([9]aneN_3)_2Mo_2Cl_2(\mu\text{-}OH)_2]I_2$

atom	*x*	*y*	*z*
Mo1	977 (1)	375 (1)	479 (1)
I	5533 (1)	8342 (1)	4794 (1)
O1	626 (8)	922 (7)	4653 (7)
Cl1	−916 (4)	1278 (3)	5996 (3)
N1	1427 (11)	201 (8)	7042 (9)
N2	2852 (11)	9967 (9)	6045 (10)
N3	1784 (11)	8388 (9)	6490 (9)
C1	2352 (16)	918 (11)	7245 (13)
C2	3328 (14)	518 (13)	7048 (14)
C3	3443 (15)	9039 (14)	6190 (14)
C4	−3066 (16)	1633 (13)	3192 (13)
C5	1514 (15)	8463 (11)	7404 (13)
C6	1810 (15)	9447 (12)	7861 (12)

(0.5 M) at 20 °C under argon. Anal. ($[([9]aneN_3)_2Mo_2(OH)_2(H_2O)_2]Br_{3.5}I_{0.5}$) C, H, N, Br, I, Mo.

$[([9]aneN_3)_2Mo_2(\mu\text{-}OH)_2Cl_2]I_2$ (6). (4)I_2 (0.5 g) was dissolved in 30 mL of hydrochloric acid (0.5 M at 20 °C under an argon atmosphere. Upon addition of sodium iodide (5 g), green crystals precipitated, which were filtered off, washed with ethanol and ether, and dried under argon. Anal. C, H, N, I, Mo.

$[([9]aneN_3)_2Mo_2O_4]X_2$ (8), X = Cl^-, Br^-, I^-, or ClO_4^-. A. To a suspension of $(NH_4)_2MoCl_5(OH_2)$ (3.3 g) in 30 mL of dimethyl sulfoxide (Me_2SO) was added a solution of 1,4,7-triazacyclononane (1.3 g) in 10 mL of ethanol under an argon atmosphere. The solution was kept at 50 °C with stirring for 3 h during which time a yellow precipitate formed. The microcrystals of (8)Cl_2 were filtered off, washed with ethanol and ether, and air-dried. The crude product was recrystallized from a minimum amount of water and sodium chloride.

A bromide, iodide, or perchlorate salt of **8** was obtained from aqueous solutions of the above chloride by adding sodium bromide, sodium iodide, and sodium perchlorate, respectively. Anal. C, H, N, Hal, Mo.

B. Identical products were obtained by dissolving (4)I_2 (1.0 g) in 20 mL of perchloric acid (0.7 M) at 40 °C. Within 1 h a clear yellow solution was generated from which the above salts were obtained upon addition of the respective sodium halide salt.

X-ray Crystallography. Details of the measurements of cell dimension and of intensity using suitable crystals for X-ray data collections of **6** and **3a**, respectively, are summarized in Table IV. The data were corrected for Lorentz and polarization effects. Empirical corrections for absorption effects were carried out in all cases.[21] The structures were solved via three-dimensional Patterson syntheses, which yielded the positions of the molybdenum, iodine, and chlorine atoms, respectively. Subsequent Fourier syntheses revealed the locations of all remaining non-hydrogen atoms. Idealized positions of H atoms bound to carbon atoms were calculated (on the basis of d(C–H) = 0.96 Å and regular tetrahedral geometry about the C atoms) and were refined as rigid moieties with fixed isotropic thermal parameters (U = 0.067 $Å^2$ for **3a**, and U = 0.054 $Å^2$ for **6**) and anisotropic thermal parameters for the C atoms (supplementary material). Refinements were carried out with use of anisotropic thermal parameters for all other atoms. The function minimized during least-squares refinement was $\sum w_i(|F_o| - |F_c|)^2$ ($w_i = 1/\sigma^2(F)$). The positions of H atoms bound to nitrogens of the amine ligands were not located for **6** and **3a**; the H atoms of the hydroxo bridges were also not located and were not included in final refinement cycles. In structure **6** a statistical disorder of the iodide positions was found. The least-squares analysis of the occupancy factor revealed an 85% occupancy of the uncoordinated iodide positions by iodide and 15% by chloride.

Final positional parameters for **3a** and **6** are given in Tables V and VI, respectively. Calculated positions of hydrogen atoms and anisotropic thermal parameters and listings of observed and calculated structure factors are available as supplementary material.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this research.

Registry No. 1, 87938-79-2; 2, 85923-29-1; **3a**·I_3·H_2O, 87938-80-5; **3b**·I_3, 87938-81-6; 4·I_2, 85939-37-3; 5·I_4, 87938-82-7; 5·$Br_{3.5}$·$I_{0.5}$, 87984-19-8; 6·I_2, 87938-83-8; 7·I_2, 85923-30-4; 8 (X = Cl^-), 87938-84-9; 8 (X = Br^-), 87984-15-4; 8 (X = I^-), 87984-16-5; 8 (X = ClO_4^-), 87984-18-7; $(NH_4)_2MoCl_5(OH_2)$, 13820-59-2.

Supplementary Material Available: Listings of elemental analyses of new compounds, anisotropic thermal parameters, calculated hydrogen atom parameters, and structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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(21) Computations were carried out on a NOVA (general data) computer using the SHELXTL program package (Revision 3.0, July 1981) by G. M. Sheldrick, University of Göttingen.

Contribution from Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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A Linear μ-Oxo-Diosmium(IV) Molecule in Which Two Bis(diphenylphosphino)methane Ligands Bridge an Entire M–O–M Unit: $Os_2(\mu\text{-}O)(\mu\text{-}Ph_2PCH_2PPh_2)_2Cl_6$

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The title compound, $Os_2(\mu\text{-}O)(\mu\text{-}dppm)_2Cl_6\cdot 2CHCl_3$ (dppm = $(PPh_2)_2CH_2$), was prepared by reacting $OsCl_3$ with dppm. The crystal and molecular structure of this compound has been determined from three-dimensional X-ray study. The compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a = 11.138 (3) Å, b = 24.461 (5) Å, c = 12.769 (3) Å, β = 105.82 (3)°, and V = 3347 (3) $Å^3$ with Z = 4. The structure was refined to R = 0.044 (R_w = 0.052). The complex molecule, which lies on a crystallographic inversion center, has a linear Os–O–Os central unit with an Os–O bond distance 1.792 (1) Å. The complex is diamagnetic. The equivalence of all phosphorus atoms is evidenced from both the ^{31}P NMR spectrum (chemical shift 30.9 ppm) and the X-ray structure. The dihedral angles O–Os–P–C of two phosphine bridges are 22.2 and 27.2°. A dichloromethane solution of the complex displays one one-electron oxidative response at +1.62 V (ΔE_p = 200 mV) and two one-electron reductive processes at +0.09 V (ΔE_p = 180 mV) and −1.13 V. The coulometrically reduced (at −0.15 V) solution of the dimer exhibits a rhombic EPR spectrum with g_1 = 2.022 and g_2 = 1.578. The electronic spectrum of the dichloromethane solution shows absorption bands at 355 (ϵ = 26 000), 425 (18 500), 490 (9600), and 705 nm (760). The spectroelectrochemical behavior of this complex can be interpreted by using a qualitative molecular orbital scheme, framed on the assumption that a strong Os–Os interaction exists through the linear oxide bridge.

Introduction

Both ruthenium and osmium are known to combine with potentially bridging ligands to form dinuclear complexes in which there are multiple metal-to-metal bonds.[1] However, the known range of this chemistry is still not great and an effort is being made in this laboratory to extend it. As part of this

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(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982; pp 192–198.

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