2702 *Inorg. Chem.* **1997,** *36,* 2702−2703

Synthesis of *trans*-$[Mo(O)(F)(dppe)_2](BF_4)$, *trans*-$[Mo(O)(OH)(dppe)_2](ClO_4)$, and *trans*-$[Mo(O)_2(dppe)_2]\cdot 2L$ ($L = H_2O, CH_3OH, CH_3CH_2OH, CH_3CHOHCH_3$). Crystal Structure of *trans*-$[Mo(O)_2(dppe)_2]\cdot 2CH_3OH$

Jesper Bendix,[*,†] Henrik Birkedal,[‡] and Anders Bøgevig[†]

Department of Inorganic Chemistry and Centre for Crystallographic Studies, University of Copenhagen, Universitetsparken 5,
DK-2100 Copenhagen, Denmark

Received November 22, 1996

Dioxo complexes of second- and third-row transition metal centers with d^2 electronic configurations are numerous in the chemistry of technetium,[1] rhenium,[2] ruthenium,[3] and osmium.[4] The photochemical and photophysical properties of these compounds have received much interest.[4a,5] However, for molybdenum and tungsten only two types of *trans*-dioxo d^2 systems have been described. These are the *trans*-$[M(O)_2(CN)_4]^{4-}$ ions[6] and the matrix-isolated *trans*-$[M(O)_2(CO)_4]$ ($M = Mo,W$) complexes.[7] Recently, Cotton and Feng have reported calculations on *trans*-$[Mo(Q)_2(PH_3)_4]$ ($Q = O, S, Se, Te$) complexes and partial structural data on *trans*-$[Mo(O)_2(dppee)_2]$ (dppee = *cis*-$Ph_2PCH{=}CHPPh_2$).[8] Here we report synthesis and characterization of new members of this class of compounds, *trans*-$[Mo(O)_2(dppe)_2]\cdot 2L$ (**1**·2L) ($L = H_2O, CH_3OH, CH_3CH_2OH, CH_3CHOHCH_3$) (dppe = $Ph_2PCH_2CH_2PPh_2$), together with a high-yield synthesis of the compounds *trans*-$[Mo(O)(OH)(dppe)_2](X)$ ($X = ClO_4$ (**2**), HSO_4 (**3**)). We also report an efficient route to *trans*-$[Mo(O)(F)(dppe)_2](BF_4)$ (**4**), which serves as the starting material for the synthesis of **1**−**3**.

The synthesis of **4** was achieved by letting $Na_3[Mo(HCOO)_6]$[9] react with dppe in acetone solution containing an excess of aqueous HBF_4. The reaction was performed in contact with air, which acts as the oxidizing agent. The yield of the pink crystals is 74%.[10] This compound has been obtained before but only as a byproduct, and no yield was given. The crystal structure of **4** has been reported.[11]

The compounds **1**·2L were synthesized in high yield (80%−90%) by letting **4** react with 40% aqueous tetraethylammonium hydroxide in acetone−L (3:2) mixtures. The yellow compounds, obtained by crystallization, are nearly insoluble in most solvents, but react fast with electrophilic solvents including halogenated methanes. In positive FAB mass spectra the main peak stems from *trans*-$[Mo(O)(OH)(dppe)_2]^+$.

From supensions of the compounds **1**·2L in methanol, yellow-orange salts of the corresponding acid, *trans*-$[Mo(O)(OH)(dppe)_2]^+$, can be obtained quantitatively by reaction with excess of acids.[12] In this way **2** and **3** were prepared. In positive FAB mass spectra the unfragmented cation gives the main peak. This cation has been claimed to have been obtained as its tetrafluoroborate salt in the yield of one crystal as a byproduct in a complex reaction mixture.[13] In view of the description of the compound as pink and our observation of facile conversion of **1** as well as **2** and **3** to **4** by treatment with aqueous HBF_4, we believe ref 13 to actually describe **4**.

The magnetic susceptibility of **1**·$2CH_3OH$, measured by the Faraday method and corrected for diamagnetism, is temperature independent (TIP, 80−270 K) with a value of around 130×10^{-6} cgsu, corresponding to a room-temperature magnetic moment of 0.55 μ_B. This value is in the range expected for low-spin d^2 systems. Contrary to many reports[14] such systems cannot be completely diamagnetic but should, irrespective of the magnitude of the spin−orbit coupling, have room-temperature magnetic moments around 0.5 μ_B.[15] The origin of the TIP is simple. The component parallel to the multiple donor-atom axis originates entirely from admixture of the lowest $^1A_2(D_4)$ term, while the perpendicular components stem primarily (>98%) from mixing with the lowest $^1E(D_4)$. The calculated susceptibility tensor is prolate and quite anisotropic with $\chi_\parallel/\chi_\perp \approx 2$.

The electronic spectra of *trans*-$[Mo(O)_2(dppe)_2]$ and *trans*-$[Mo(O)(OH)(dppe)_2]^+$ are shown in Figure 1 together with the spectrum obtained by protonating *trans*-$[Mo(O)(OH)(dppe)_2]^+$ with CF_3SO_3H. The blue species produced in the latter case is believed to be the *trans*-$[Mo(O)(H_2O)(dppe)_2]^{2+}$ ion. The latter protonation reaction can be reversed by dilution. We favor the oxo−aqua formulation over the tautomeric dihydroxo formulation by analogy with the known[16] behavior of the cyanide complexes. It should, however, be noted that the isoelectronic *trans*-$[Mo(NH)(OH)(dppe)_2]^+$ upon protonation crystallizes as a salt of the *trans*-$[Mo(NH_2)(OH)(dppe)_2]^{2+}$ ion.[17] We observe no bands in the spectrum of **1** with wavelength above 400 nm. The spectrum was recorded within 1 min immediately after dissolving **1** because the compound reacts fast with halogenated organic solvents to give solutions with spectra which strongly

---

[†] Department of Inorganic Chemistry.

[‡] Centre for Crystallographic Studies.

(1) (a) Trop, H. S.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1980**, *19*, 1993. (b) Fackler, P. H.; Lindsay, M. J.; Clarke, M. J. *Inorg. Chem. Acta* **1985**, *109*, 39.

(2) (a) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373. (b) Yam, V. W.; Tam, K.; Cheng, M.; Peng, S.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1992**, 1727.

(3) (a) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315. (b) Tokita, Y.; Yamaguchi, K; Watanabe, Y.; Morishima, I. *Inorg. Chem.* **1993**, *32*, 329.

(4) (a) Che, C.; Yam, V. W.; Cho, K.; Gray, H. B. *J. Chem. Soc., Chem. Commun.* **1987**, 948. (b) Malin, J. M.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1977**, *16*, 615. (c) Kruse, F. H. *Acta Crystallogr.* **1961**, *14*, 1035.

(5) (a) Yam, V. W.; Che, C. *Coord. Chem. Rev.* **1990**, *97*, 93. (b) Lam, H.; Chin, K.; Che, C.; Wang, R.; Mak, T. C. *Inorg. Chim. Acta* **1993**, *204*, 133. (c) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346.

(6) (a) Day, V. W.; Hoard, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 3374. (b) Lippard, S. J.; Russ, B. J. *Inorg. Chem.* **1967**, *6*, 1943.

(7) Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 3051.

(8) Cotton, F. A.; Feng, X. *Inorg. Chem.* **1996**, *35*, 4921.

(9) Brorson, M.; Schäffer, C. E. *Acta Chem. Scand. A* **1986**, *40*, 358.

(10) Anal. Calcd for $C_{52}H_{48}BF_5OP_4Mo$: C, 61.56; H, 4.77. Found: C, 61.62; H, 4.82.

(11) Cotton, F. A.; Eglin, J. L.; Wiesinger, K. J. *Inorg. Chim. Acta* **1992**, *195*, 11.

(12) Anal. Calcd for $C_{52}H_{49}ClO_6P_4Mo$: C, 60.92; H, 4.82; Cl, 3.46. Found: C, 59.94; H, 4.65; Cl, 3.53.

(13) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1978**, *17*, 668.

(14) (a) Novotny, M.; Lippard, S. J. *Inorg. Chem.* **1974**, *13*, 828. (b) Fackler, P. H.; Lindsay, M. J.; Clarke, M. J.; Kastner, M. E. *Inorg. Chim. Acta* **1985**, *109*, 39.

(15) Bendix, J. To be published.

(16) (a) Robinson, P. R.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1975**, *14*, 2035.

(17) Adachi, T.; Hughes, D. L.; Ibrahim, S. K.; Okamoyo, S.; Pickett, J.; Yabanouchi, N.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1081.

S0020-1669(96)01407-3 CCC: $14.00

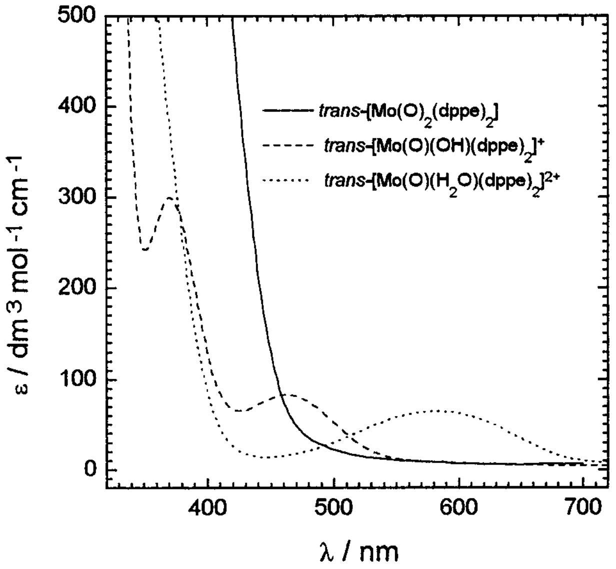

Figure 1. Electronic spectra of *trans*-$[Mo(O)_2(dppe)_2]$ in $CHCl_3$ (solid line), $[Mo(O)(OH)(dppe)_2]^+$ in acetone (dashed line), and $[Mo(O)(OH_2)(dppe)_2]^{2+}$ in acetone (dotted line). Spectral characteristics [λ/nm (ϵ/$dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}$)]:*trans*-$[Mo(O)_2(dppe)_2]$, 373 (360), 462 (95.3); *trans*-$[Mo(O)(OH)(dppe)_2]^+$, 362 (274), 509, (87.8); *trans*-$[Mo(O)(OH_2)(dppe)_2]^{2+}$, 587 (85.0).

resemble that of *trans*-$[Mo(O)(OH)(dppe)_2]^+$. In ref 8 two bands of d−d character were reported as shoulders in the spectrum of *trans*-$[Mo(O)_2(dppee)_2]$. These bands were assigned as $^1A_g(D_{2h}) \rightarrow {}^3B_{1g}(D_{2h})$ and $^1A_g(D_{2h}) \rightarrow {}^1B_{1g}(D_{2h})$ corresponding respectively to the triplet and the singlet components of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. While the featureless spectrum of **1** contains no information regarding the energetic ordering of the metal d^2 states in the dioxo compound, the quoted assignments cannot hold for the monooxo species. The pronounced dependence of the position of the lowest energy band on the nature of the axial ligands (cf. Figure 1) rules out the possibility that the transition is of $d_{xy} \rightarrow d_{x^2-y^2}$ character. In the traditional ligand-field description of *trans*-dioxo d^2 systems[18] the lowest energy transition is $^1A_g(D_{4h}) \rightarrow {}^3E_g(D_{4h})$ of $d_{xy} \rightarrow \{d_{zx},d_{yz}\}$ character. The shift of the lowest energy band upon protonation can then be explained as a consequence of the decreasing π-donor strength along the series $O^{2-} > OH^- > H_2O$. This is also in accordance with the fact that for *trans*-$[Mo(O)(Cl)(dppe)_2]^+$ the lowest energy absorption ($\lambda_{max} = 566$ nm; $\epsilon = 64.9$ $dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}$) places chloride only a little above water with regard to π-donor strength.

The crystal structure of $\mathbf{1}{\cdot}2CH_3OH$ (Figure 2) has been determined by single-crystal X-ray diffraction.[19] The crystallographic results are of high accuracy; all hydrogen atoms were located from the difference electron density map and could be refined freely. The molybdenum ion is situated at an inversion center. The Mo−O distance is 1.8184(8) Å, which is slightly shorter than the distances found in the cyano complexes: 1.828(14) Å in $K_4[Mo(O)_2(CN)_4]{\cdot}6H_2O$[20] and 1.834(9) Å in $NaK_3[Mo(O)_2(CN)_4]{\cdot}6H_2O$.[6a] As the Mo−O distance in **1** compares well with those found in the related cyanide systems, it seems unlikely that the value (1.833(5) Å) reported in ref 13 for the Mo−oxo distance in a *monooxo* complex is genuine. Our preliminary structural results on cations of the type *trans*-$[Mo(O)(X)(dppe)_2]^+$ show that they almost invariably exhibit disorder among the oxo and the *trans* ligand. This we believe to have caused a severe overestimation of the Mo−oxo distance in the earlier study. The angle between *trans* and *cis* ligand axes is, in the cyano complexes, very close to 90°, the deviations being in both cases less than 1°. In $\mathbf{1}{\cdot}2CH_3OH$, however, the O═Mo═O axis is tilted with respect to the $Mo-P_4$ plane, the angle being 82.5°. This tilt is most likely due to a steric effect caused by the bulkiness of the hydrogen-bonded methanol molecules. In this hydrogen bond, the O1···HMe distance is 1.88(3) Å, the O1···OMe distance is 2.717(2) Å, while the O···H−O angle is 173(2)°. On distance-based criteria this is thus a medium strength hydrogen bond.

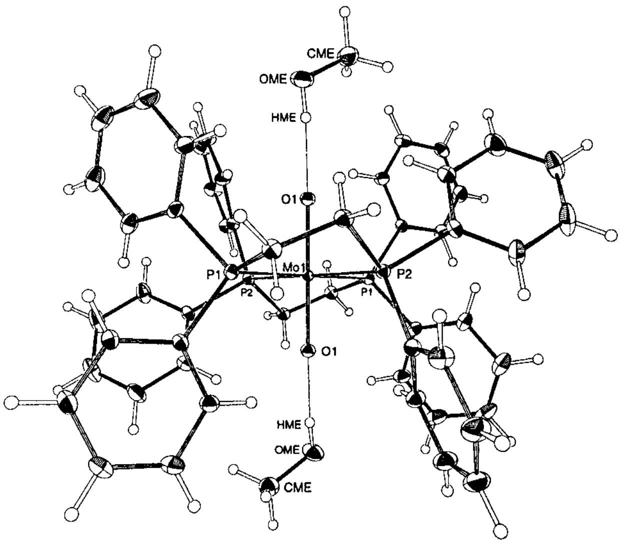

Figure 2. ORTEP-II drawing of *trans*-$[Mo(O)_2(dppe)_2]{\cdot}2CH_3OH$.

From ^{31}P-NMR spectroscopy the increased electron-donating strength along the series $F^- < OH^- < O^{2-}$ is seen to lead to a parallel variation of the shielding of the phosphorus nuclei. The chemical shifts in $CDCl_3$ (downfield relative to 85% H_3PO_4) are respectively 39.84 ppm (**4**), 37.16 ppm (**3**), and 34.94 ppm (**1**).

Further studies revisiting the bond lengths in *trans*-$[Mo(O)(OH)(dppe)_2]^+$, which has been presented as an example of bond-stretch isomerism,[21] are being carried out.

Acknowledgment. We thank Prof. C. E. Schäffer and Dr. S. Larsen for valuable discussions and Mr. F. Hansen and Dr. K. Marthi for their valuable technical assistance.

Supporting Information Available: Text giving a detailed account of the syntheses, text and tables giving X-ray experimental details and structure solution, atomic coordinates and displacement parameters, and bond lengths and angles, and figures showing FAB mass spectra of $\mathbf{1}{\cdot}2CH_3OH$, **2**, and **4**, TGA plots for $\mathbf{1}{\cdot}2L$, and magnetic susceptibility plots for $\mathbf{1}{\cdot}2CH_3OH$ and **4** (16 pages). Ordering information is given on any current masterhead page.

IC9614071

---

[18] (a) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111. (b) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346.

[19] Anal. Calcd for $C_{54}H_{56}O_4P_4Mo$: C, 65.59; H, 5.71. Found: C, 64.71; H, 5.79. Crystal and refinement data: Triclinic yellow plates, space group $P\bar{1}$, $a = 9.454(3)$ Å, $b = 11.426(2)$ Å, $c = 13.141(2)$ Å, $\alpha = 110.86(2)°$, $\beta = 99.11(2)°$, $\gamma = 110.08(2)°$, $Z = 1$, $T = 122.0(5)$ K, 16 624 measured and 13 699 independent reflections, residuals on all data of $R1 = 4.04\%$ and $wR2 = 7.48\%$, refinement on F^2.

[20] Schlupp, R.; le Carpentier, J. M.; Weiss, R. *Rev. Chim. Miner.* **1970**, *7*, 63.

[21] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.