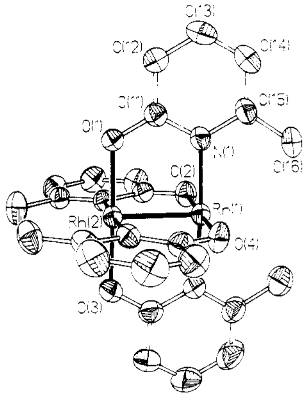

Figure 1. Molecular structure of $Rh_2(mhp)_4$ in **3**. Thermal motion is shown as 50% probability ellipsoids.

data are summarized in Table I. Atomic coordinates are given in Table II. Table III compares the essential results with those of previously determined $M_2(mhp)_4$ and $M_2(chp)_4$ structures. Detailed results, together with structure factor tables, are available as supplementary material.

Results and Discussion

The molecular structure of **3** is depicted in Figure 1; the atom-numbering scheme is the same as in all our studies of $M_2(mhp)_4$ structures. The structure is essentially the same as for **1**, **2**, and the other related dimers.

The molecular structure of $Mo_2(mhp)_4$ varies insignificantly with crystal packing in all three crystal structures; no significant differences are observed in the bond lengths or even in the conformational twist about the Mo–Mo bond. It might be expected that the eclipsed conformation of a quadruple bond, which contains a δ component, would be particularly insensitive to factors favoring a twisting distortion, but torsion angles of up to 30° have been observed, whereby the δ component has been estimated to lose only approximately 50% of its contribution to the Mo–Mo bonding.[9]

The single Rh–Rh bond shows a greater variation of twist, reflecting its inherently weaker nature and the σ symmetry of the net Rh–Rh bond. The range of observed Rh–Rh bond lengths in these $Rh_2(mhp)_4$ structures is, however, very small, and the differences observed are of dubious significance in the absence of special precautions in the determination of unit cell parameters.

When all the crystallographic results now available for molecules of this type are considered together, it appears that the torsional conformation of the $M_2(mhp)_4$ and $M_2(chp)_4$ molecules is determined by a balance of several factors, which are given as follows, in decreasing order of importance.

(1) Bonding Characteristics of the M_2 Unit Bridged by Four Ligands of the mhp Type. The preference here is always for an eclipsed conformation, with that for the Mo–Mo quadruple bond being significantly more marked than that for the Rh–Rh single bond.

(2) Intramolecular Steric Interactions between the Ligands, Notably the Me···Me or Cl···Cl Interactions of Mutually Trans Ligands. A twist away from the eclipsed conformation relieves this repulsion. We have already discussed this effect for $M_2(mhp)_4$ complexes[3,4] and note that the known $M_2(chp)_4$ structures also fit into this pattern (Table III). These $M_2(chp)_4$ complexes (and $Rh_2(mhp)_4$) are all isostructural (space group *Pbca*), so variations in packing forces are slight. The relatively small increase in mean torsion angle in moving from $Mo_2(chp)_4$ to $Rh_2(chp)_4$, compared with the rather larger difference for the corresponding mhp complexes, mirrors the smaller variation in [mean d(M–N) – mean d(M–O)] for the chp complexes; i.e., the intramolecular steric repulsion effect shows much less variation for the chp complexes. Moreover, in both groups of complexes $M_2(mhp)_4$ and $M_2(chp)_4$ with M = Cr, Mo, or W,[2,6] the largest degree of twisting distortion is for M = Cr; here steric interaction will be at its greatest for each triad, because of the shorter Cr–N bonds. Although these torsion angles, and differences between them, are small, a satisfactory and convincing overall pattern does emerge from the complete set of known structures. Extreme steric effects, with twists of around 20°, are observed when four mhp or chp ligands are arranged about a Rh_2 unit, such that three methyl groups or chlorine atoms lie at one end of the molecule.[7,10]

(3) Intermolecular Interactions between Molecules and with Solvent Molecules. For normal van der Waals interactions (when the solvent of crystallization is methanol, CH_2Cl_2, or nonexistent), the effect is a minor one, overlaid on factors 1 and 2. In the case of $[Rh_2(mhp)_4]{\cdot}H_2O$, however, the rather stronger hydrogen bonds[7] have a much greater effect on the torsional conformation of the dimeric molecule.

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Registry No. 1, 67634-80-4; **2**, 86257-95-6; **3**, 86177-69-7.

Supplementary Material Available: Listings of bond lengths and angles, thermal parameters, atomic coordinates, and structure factors (80 pages). Ordering information is given on any current masthead page.

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X-ray Diffraction and Thermal Analysis of Molybdenum(VI) Oxide Hemihydrate: Monoclinic $MoO_3{\cdot}{}^1/_2H_2O$[1]

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Molybdenum(VI) oxide is known to form a rich family of crystalline hydrates that include a monoclinic dihydrate, $MoO_3{\cdot}2H_2O$,[5] two monohydrates, the yellow monoclinic $MoO_3{\cdot}H_2O$[6] and the white triclinic $MoO_3{\cdot}H_2O$,[7] and a white hemihydrate.[8] A molybdenum oxide hemihydrate phase has

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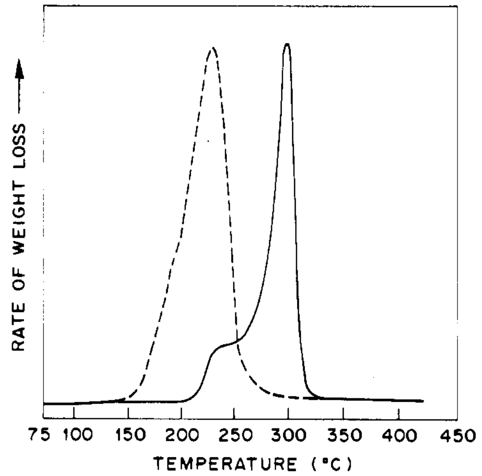

Figure 1. Derivative thermogravimetric analysis of monoclinic $MoO_3\cdot{}^1/_2H_2O$ (—) and triclinic $MoO_3\cdot H_2O$ (- - -).

been prepared during the study of molybdenum-containing precipitates from nitric acid solution. The range of preparative conditions and the stability of this hemihydrate in nitric acid, a thermogravimetric study of its decomposition and comparison with that of white triclinic $MoO_3\cdot H_2O$,[7] and the results of an X-ray diffraction study are described here.

Experimental Procedure

To prepare the hemihydrate, aliquots of 3 M nitric acid solution containing 0.73–1.15 M molybdenum (prepared by dissolving molybdenum metal in the acid) were mixed with concentrated nitric acid and water so that the final concentrations covered the ranges of 0.10–0.31 M molybdenum in 4–10 M nitric acid. The solutions were thermostated for several weeks at 50 and 70 °C. The white precipitates that gradually formed were removed from the solution by filtration, washed with nitric acid, and dried over powdered phosphorus pentoxide for a minimum of 2 weeks. In a separate experiment, small single crystals were isolated from a 6 M acid solution that was initially 0.23 M in molybdenum and had been equilibrated at 70 °C.

The white triclinic monohydrate was prepared by a similar procedure in which 1.9 M nitric acid was used, and the solution was maintained at 50 °C. The powder diffraction pattern[7] served to confirm the identity of the monohydrate.

Thermogravimetric (TGA) analyses were performed on a Du Pont thermal analyzer. Samples were heated at the rate of 5–10°/min in a flowing argon atmosphere. The identity of the evolved gas was determined by heating the samples in the inlet port of a mass spectrometer while the mass/charge ratios were monitored from 0 to 100 as a function of temperature.

X-ray diffraction line positions were obtained from both high-resolution (measuring circle diameters of 401 and 346 mm) diffractometers and a 114-mm Debye–Scherrer powder camera using copper radiation. One powder sample was run with an internal standard of high-purity tungsten ($a = 3.1652 \pm 0.0002$ Å) (plus and minus figures refer to one standard deviation). 2θ line positions were obtained by computer resolution of the doublet $K\alpha_1$–$K\alpha_2$ due to the copper radiation. The integrated line intensities were determined by using the diffractometer technique with a scintillation counter. Standard oscillating and Weissenberg photographic techniques, as well as computer programs ITO[9] and DICVOL,[10] were used to determine the crystal system and index the powder diffraction lines. Unit-cell parameters were refined with use of a locally modified version of the least-squares computer program LCS-2.[11]

Results and Discussion

A thermogravimetric derivative scan of monoclinic $MoO_3\cdot{}^1/_2H_2O$ is shown in Figure 1 along with that for the white triclinic $MoO_3\cdot H_2O$ for comparison. The major weight loss of the hemihydrate occurs near 315 °C, while a minor (and slightly variable) loss occurs at 250 °C. This variability appeared to be somewhat related to the dryness of the sample, although the small peak could never be eliminated. Some samples that were dried less stringently (in air, over anhydrous magnesium perchlorate, and/or dried for a shorter time period, for example) gave a peak of slightly greater intensity at 250 °C. Drying over phosphorus pentoxide for periods greater than 2 weeks gave no noticeable decrease in the weight-loss peak at 250 °C.

The major weight loss of the monohydrate occurs at 225 °C, while a very small loss is observed near ~175 °C. Both losses occur at temperatures some 75–90 °C lower than for the hemihydrate. Results of mass spectral studies indicated a major evolution of water at temperatures corresponding to the observed peaks, confirming that the weight loss in each compound is due to water evolution. For the monoclinic hemihydrate prepared in this work, four samples exhibited an average weight loss of 6.8 ± 0.2%, corresponding to the formula $MoO_3\cdot(0.58 \pm 0.02)H_2O$. If the minor TGA peak is assumed to be due to adsorbed water, the major peak is from 76 to 93% of the total loss, depending on how the peaks are resolved. The estimate of the hydrate stoichiometry and uncertainty then becomes $MoO_3\cdot(0.49 \pm 0.05)H_2O$. The average weight loss from the known monohydrate was 11.55 ± 0.13% for four samples, corresponding to the stoichiometry $MoO_3\cdot(1.04 \pm 0.01)H_2O$. The TGA residue from the thermal analysis of each compound had been heated to 600 °C. The residues were determined by X-ray analysis to be orthorhombic MoO_3 (molybdite) in all cases.

The X-ray powder pattern of each compound was determined via several techniques because the crystalline habit (thin needles) caused a significant degree of preferred orientation of the sample. The integrated I/I_0 values listed in the table, which are taken from one powder experiment, were judged to be semiquantitatively representative of all the experiments that were performed. Although useful for identification purposes, care should be taken in using these line intensities for any quantitative purpose. From one sample preparation, a small single crystal of the hemihydrate ~2.5 mm in length and <0.1 mm in diameter was isolated and used for the oscillation and Weissenberg measurements. The X-ray powder pattern of white, monoclinic $MoO_3\cdot{}^1/_2H_2O$ to a 2θ of 67.50° is tabulated in Table I.

Computer indexing of the powder pattern by using programs ITO and DICVOL was hindered both by absence of an observed 010 line and by the paucity of lines that had any nonzero k dependence. Nonetheless, these programs were successful in determining the a, c, and β values of the unit cell. The oscillation and Weissenberg studies confirmed these values and provided the true b value. All of the experimentally observed lines were successfully accounted for by the indexing procedure.

Use of the refined unit-cell parameters $a = 9.658 \pm 0.004$ Å, $b = 3.710 \pm 0.002$ Å, $c = 7.087 \pm 0.003$ Å, and $\beta = 102.43 \pm 0.02°$ with $Z = 4$ resulted in a calculated density of 4.128 g/cm^3 compared with the observed powder density of 4.024 g/cm^3. The figure of merit of the indexing (M_{20})[12] was 21.7 on the basis of the 20 observed lines with highest d values. No systematic line extinctions were observed. This is consistent with the crystal's belonging to one of the space groups $P2$, Pm, or $P2/m$.

Throughout the experiments made in this study (which spanned a period of up to 10 months), this monoclinic hemihydrate appeared to be the stable phase in the range of concentrations from ~4 to 10 M nitric acid and temperatures

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Table I. X-ray Line Positions for Monoclinic $MoO_3\cdot{}^1/_2H_2O$

I/I_0[a]	*hkl*	2*θ*, deg calcd	2*θ*, deg exptl[b]	*d*, Å exptl[c]
1	100	9.369	9.38	9.42
100	001	12.782	12.79	6.916
0.6	$10\bar{1}$	14.139	14.15	6.254
12	101	17.436	17.48	5.069
89	200	18.803	18.82	4.711
0.7	$20\bar{1}$	20.364	20.46	4.337
79	201	25.014	25.04	3.553
64	002	25.725	25.72	3.461
11	$11\bar{1}$	27.932	27.92	3.192
95	$20\bar{2}$ $30\bar{1}$	28.499 28.523	28.49	3.130
28	102	29.320	29.31	3.045
5	111	29.789	29.79	2.997
1	301	33.729	33.74	2.654
1	211	34.915	35.02	2.560
8	$40\bar{1}$	37.527	37.51	2.396
3	400	38.137	38.15	2.357
35	003	39.013	38.99	2.308
70	$20\bar{3}$	39.593	39.58	2.275
12	$40\bar{2}$	41.407	41.38	2.180
27	302	42.788	42.73	2.114
47	401	43.075	43.07	2.099
2	$11\bar{3}$	45.498	45.48	1.993
2	013	46.306	46.29	1.960
5	$50\bar{1}$	47.093	47.04	1.930
13	203	47.415	47.40	1.916
20	500	48.205	48.21	1.886
7	$40\bar{3}$	48.895	48.90	1.861
8	$31\bar{3}$	50.122	50.07	1.820
5	$12\bar{1}$ 402	51.324 51.330	51.37	1.777
11	004	52.875	52.85	1.731
9	303	54.090	54.01	1.696
15	$50\bar{3}$	55.886	55.93	1.643
4	$60\bar{1}$	57.188	57.13	1.611
9	$11\bar{4}$ 320	57.634 57.647	57.63	1.598
12	$40\bar{4}$	58.983	58.98	1.565
22	$31\bar{4}$	60.581	60.65	1.526
12	321	60.864	60.88	1.520
6	$51\bar{3}$	61.664	61.72	1.502
4	$61\bar{1}$	62.891	62.86	1.477
4	$61\bar{2}$	64.640	64.68	1.440
11	$10\bar{5}$ 205	66.024 66.081	66.05	1.413
5	$32\bar{3}$	67.507	67.49	1.387

[a] Preferred orientation effects render these values somewhat variable (see discussion). [b] Estimated measurement error 0.011 ± 0.008°. [c] Based upon $\lambda(\text{Cu K}\alpha_1) = 1.540\,598\,1$ Å (see: Deslattes, R. D.; Henins, A. *Phys. Rev. Lett.* 1973, *31*, 972).

from ~50 to 70 °C. It precipitates under these conditions even in the presence of submolar concentrations of thorium, uranium, and plutonium.

The experimental procedure used by Vorob'ev and Davydov[8] to prepare a molybdenum oxide containing 0.5 mol of water/mol of MoO_3 falls within the range of conditions used in our study to prepare monoclinic $MoO_3\cdot{}^1/_2H_2O$. The hemihydrate prepared by Vorob'ev and Davydov and that prepared in this work may be the same compound. Work is currently under way on the characterization of a different hemihydrate phase that can be formed under slightly modified conditions.

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Matrix-Isolation Infrared Spectra of (Octaethylporphyrinato)manganese(II) and (Phthalocyaninato)manganese(II) and Their Dioxygen Adducts

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The symmetric side-on coordination of dioxygen in (dioxygen)(tetraphenylporphyrinato)manganese $Mn(TPP)O_2$, is well established by electronic[1] and ESR[1,2] studies and MO calculations.[3] We have recently provided further support for this structure through an IR study on $Mn(TPP)O_2$, which was prepared via cocondensation of Mn(TPP) vapor with isotopically scrambled dioxygen ($^{16}O_2$ + $^{16}O^{18}O$ + $^{18}O_2$) diluted in argon on a cold window at ~15 K.[4] Furthermore, we have located the $\nu(O_2)$ (ν: stretching) of $Mn(TPP)O_2$ at 983 cm^{-1}, which is between those of superoxo (1200–1100/cm^{-1}) and peroxo (900–750 cm^{-1}) and is much higher than that previously assigned (ca. 840 cm^{-1}).[5] This result has led us to conclude that the negative charge on the O_2 of $Mn(TPP)O_2$ is between those of superoxo (O_2^-) and peroxo (O_2^{2-}) adducts. The main objective of this investigation is to determine whether (dioxygen)(octaethylporphyrinato)manganese, $Mn(OEP)O_2$, and (dioxygen)(phthalocyaninato)manganese, $Mn(Pc)O_2$, prepared by matrix cocondensation techniques exhibit $\nu(O_2)$ in a range similar to that of $Mn(TPP)O_2$. Previous researchers[6] reported the isolation of crystalline $Mn(Pc)O_2$ from a DMA (*N*,*N*-dimethylacetamide) solution. They assigned a weak IR band at 1094 cm^{-1} to the $\nu(^{18}O_2)$ of $Mn(Pc)^{18}O_2$ and suggested the end-on coordination of a superoxo type dioxygen. However, the corresponding $\nu(^{16}O_2)$ was not distinct and assumed to be hidden under the tail of a strong Pc band at 1167 cm^{-1}. It is, therefore, of great interest to determine whether the $\nu(^{16}O_2)$ of $Mn(Pc)O_2$ prepared in inert-gas matrices appears near 980 cm^{-1} as found for $Mn(TPP)O_2$ or near 1167 cm^{-1} as assigned for the solid compound obtained from a DMA solution.

Experimental Section

The complex $Mn(OEP)(py)_2$ was prepared by the literature method.[7] It was placed in the Knudsen cell of our matrix-isolation system and heated under 10^{-6} torr at ~320 K for 4 h until the vacuum gauge indicated complete dissociation. The resulting Mn(OEP) was vaporized from the Knudsen cell at ~400 K and cocondensed with pure Ar or O_2 diluted in Ar at various ratios on a CsI window that was cooled to ~15 K by a CTI Model 21 closed-cycle helium refrigerator. Similar experiments were also carried out by using pure Kr or O_2 diluted in Kr. The complex Mn(Pc) was purchased from Eastman Kodak and used without purification. Procedures similar to those described above were used to deposit Mn(Pc) and $Mn(Pc)O_2$ onto the cold window. Mn(Pc) was preheated at ~450 K for 14 h to remove impurities adsorbed on the sample and evaporated on the cold window by heating at 500 K.

IR spectra were measured on a Beckman Model 4260 infrared spectrophotometer using a 25 cm^{-1}/in. chart expansion and 5 cm^{-1}/min chart speed. Rotation–vibration bands of standard molecules and

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