

Figure 4. Polyhedral edge lengths (Å) of $\text{Cd}(\text{AMNU})_4^{2-}$ anions. The four short edges of length 2.238 and 2.705 Å are the dodecahedral m edges spanned by the four bidentate ligands.

$\text{CMP}(\text{H}_2\text{O})_n^{19b}$ (2.58–2.87 Å).

The Cd–N distances of 2.302 (2) and 2.341 (2) Å are in the normal range observed in other similar cadmium complexes with pyrimidine derivatives (2.21–2.34 Å).¹⁹

The AMNU ligands are essentially planar (Table III) with the exocyclic atoms deviating somewhat. The cadmium atom deviates to a greater extent, -0.065 Å from the near plane through the ring atoms.

The geometry of the ligand (Figure 3) is in agreement with that reported for this ligand in the complex $[\text{Zn}(\text{AMNU})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}^{8d}$ in spite of the fact that, in this case, the ligand is bidentate (N5, O4), being bound by neither O2 nor N1 with the Zn(II) ion.

A very interesting aspect of this structure is the tetradentate character of the ligand. Thus far, this is the first metal complex of uracil derivatives that is found to involve N5, O4, N1, and O2 atoms, causing the uracil derivative to act as a bridging ligand.

The packing within the crystal is such as to produce an infinite planar network. Different networks are held together by hydrogen bonds formed between one proton of an amino group and the O5 atom of one nitroso group of position $x + 1/2, -y + 1/2, -z - 1/4$. The N6–O5 and O5...H61 distances are 2.797 (3) and 2.215 (3) Å, respectively. These separations are smaller than 2.9 and 2.6 Å (sums of the van der Waals radii of N...O and H...O, respectively) suggested by Ladd²⁰ as a criterion for the existence of a hydrogen bond.

Acknowledgment. We are indebted to R. Oberti and L. Ungaretti for their collaboration.

Registry No. $\text{Cd}(\text{AMNU})_2$, 100494-96-0.

Supplementary Material Available: According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (19 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.

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Notes

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Dioxomolybdenum(VI)-Substituted 2,6-Pyridinedimethanol Complexes: New Five-Coordinate Species

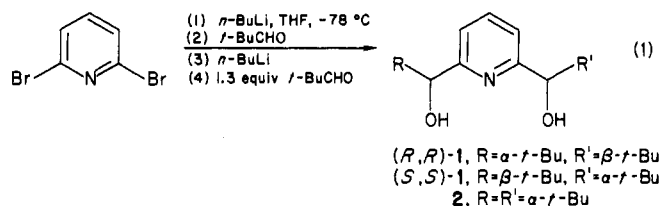
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Dioxomolybdenum(VI) complexes with sterically bulky ligands have attracted recent interest as molybdoenzyme models.^{1,2} Our interest in this area lies in the development of new asymmetric oxidation catalysts. While exploring the utility of *threo*- α, α -di-*tert*-butyl-2,6-pyridinedimethanol (**1**) as a new C_2 symmetric chiral ligand, we prepared the corresponding dioxomolybdenum(VI) complex. X-ray crystallographic analysis revealed a novel five-coordinate MoO_2NO_2 structure, which we describe herein.

Results

Pyridinediol **1** was prepared in a single pot from 2,6-dibromopyridine by two successive lithiation and pivalaldehyde trap cycles (eq 1).³ The *threo* isomer **1**, distinguished by the presence of two peaks on chiral stationary phase HPLC,⁴ was readily separated from the *meso* isomer **2** by flash chromatography.⁵



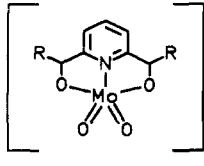
Resolution was accomplished by multiple recrystallizations of the dibenzoyltartrate salt. The analogous *threo*-diisopropyl ligand was prepared similarly but not resolved.

Dioxomolybdenum(VI) complexes were prepared from the corresponding pyridinediols by reaction with $\text{MoO}_2(\text{acac})_2$ in dichloromethane followed by removal of volatiles in vacuo and recrystallization from dichloromethane/ether. Pertinent spectroscopic data are given in Table I. The solid-state IR spectra (KBr) show a similarity between the racemic *t*-Bu and racemic *i*-Pr complexes, **4** and **7**, with Holm's unsubstituted complex **3**.⁶ The homochiral *t*-Bu and *meso*-*t*-Bu complexes, **5** and **6**, in contrast, do not show the band near 850 cm^{-1} . The solution-state IR spectra, taken in bromoform due to its transparency in the ν_{MoO} region, are the same for the substituted complexes **4–7**, each lacking the band near 850 cm^{-1} . Similar solution-state behavior among the substituted complexes is also seen in the ^1H NMR spectra (CDCl_3). The molecular weight of the homochiral *t*-Bu complex **5**, measured in dichloromethane by the Signer method,⁷ indicated it to be monomeric in solution.

Crystals of the homochiral *t*-Bu complex **5** suitable for X-ray crystallography were grown by slow evaporation of a dichloromethane solution. Crystallography revealed two discrete mono-

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Table I. Selected Spectroscopic Data for Dioxomolybdenum(VI) Complexes


R	isomer	compd no.	ν_{MoO} , cm^{-1}		$^1\text{H NMR}$, δ		
			solid	solution	4-H	3,5-H	α -H
H ⁶		3	909, 850				
<i>t</i> -Bu	racemic	4	934, 857	943, 918	8.10	7.57	5.70
<i>t</i> -Bu	homochiral	5	929, 916	943, 918	8.09	7.56	5.69
<i>t</i> -Bu	<i>meso</i>	6	940, 914	943, 917	8.07	7.50	5.61
<i>i</i> -Pr	racemic	7	934, 868	943, 919	8.14	7.43	5.90

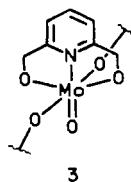
Table II. Selected Bond Distances (Å) and Angles (deg)

5a		5b	
Mo1-N11	2.163 (5)	Mo2-N21	2.184 (5)
Mo1-O11	1.898 (4)	Mo2-O21	1.922 (4)
Mo1-O12	1.919 (4)	Mo2-O22	1.920 (5)
Mo1-O13	1.696 (4)	Mo2-O23	1.693 (5)
Mo1-O14	1.698 (4)	Mo2-O24	1.704 (5)
O13-Mo1-O14	109.7 (3)	O23-Mo2-O24	109.9 (3)
O13-Mo1-N11	130.5 (3)	O23-Mo2-N21	127.3 (3)
O12-Mo1-O13	97.2 (2)	O22-Mo2-O23	98.9 (2)
O12-Mo1-N11	72.1 (2)	O22-Mo2-N21	72.4 (2)
O12-Mo1-O11	144.8 (2)	O22-Mo2-O21	144.9 (2)

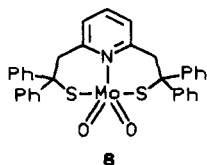
nuclear species of similar structure within the asymmetric unit, **5a** and **5b** (Figure 1). Selected bond distances and angles are shown in Table II. The molybdenums are five-coordinate with distorted trigonal-bipyramidal geometry; the nitrogen and oxo ligands are equatorial, and the alkoxides are axial. The absolute configuration of **5** was determined (vide infra) and found to agree with the configuration of **1** predicted by Pirkle's model.⁴

Discussion

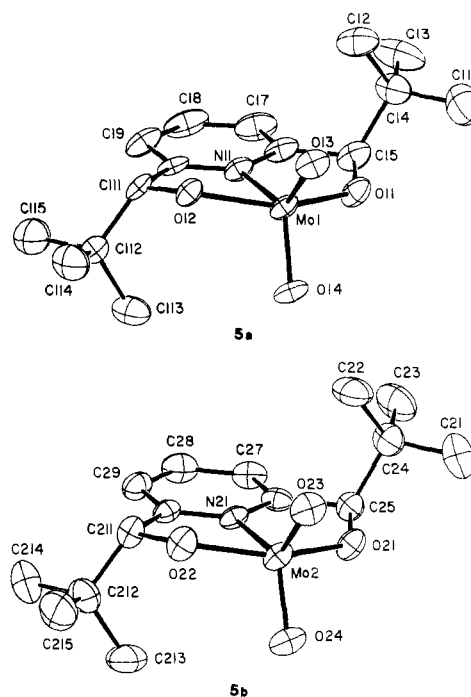
Dioxomolybdenum(VI) complexes are generally six-coordinate. For MoO₂(tridentate) complexes, the sixth ligand can be a donor such as Me₂SO, or a bridging oxo as in **3**.^{1a} The first example



of a five-coordinate dioxo Mo(VI) complex was Holm's pyridinedithiol complex, **8**.⁸ Complex **5** is the second example of this structural type, the first bis(alkoxide).⁹



The coordination geometries of **5** and **8** are similar. The Mo-O_{oxo} bond lengths in **5a** and **5b** (average 1.698 Å) are essentially the same as found in **8** (average 1.694 Å). The O=Mo=O angles in **5a** and **5b** (average 109.8°) are slightly smaller than in **8** (110.5°). The diolate O-Mo-O angles in **5a** and **5b** (average 144.9°) are the same as the corresponding O-Mo-O angle in **3** (145.0°) but smaller than the analogous S-Mo-S angle in **8** (156.4°).

**Figure 1.** Geometry of the two crystallographically independent molecules of **5** showing the atomic-labeling scheme and 30% probability thermal ellipsoids. Hydrogen atoms are not shown.

The solid-state structure of **5** is probably preserved in the solution state since it is also monomeric (vide supra). The solution IR ν_{MoO} bands at 943 and 918 cm^{-1} can thus be correlated with the five-coordinate structure of **5**. Accordingly, **4**, **6**, and **7** must also be five-coordinate in solution. The solid-state IR spectrum of the *meso* complex **6** is similar to that of **5** and **8** (8: 950, 915 cm^{-1} ; null^{1a}), implying that it is also five-coordinate as a solid. The low ν_{MoO} bands in the solid-state IR spectra of the racemic complexes **4** and **7** imply that they, like **3**, are polymeric in the solid state.⁶ Thus the tendency of these Mo(VI)-dioxo-pyridinediol complexes to become six-coordinate by polymerizing is subtly dependent on the stereochemistry of the ligands: two molecules of **5** will not associate, but **5** will associate with its enantiomer to form the racemic polymer **4**. The study of **5** and other complexes with **1** as asymmetric catalysts will be reported in due course.¹⁰

Experimental Section

The preparation of the pyridinediol ligands will be reported elsewhere.¹⁰ The preparation of **5** is typical for complexes **4**-**7**. Bromoform was distilled immediately before use as an IR solvent.

5. A dry N₂-flushed 25-mL flask was charged with 100 mg of (+)-**1** (0.398 mmol, enantiomer retained more on the Pirkle column⁴), 5.2 mL of dichloromethane (dried over 4A molecular sieves), and 126 mg of MoO₂(*acac*)₂ (0.386 mmol, Alfa, purified by filtering in dichloromethane and drying in vacuo). The initial slightly cloudy greenish yellow solution decolorized gradually while being stirred at room temperature for 23 h. Volatiles were removed in vacuo (2 mm), giving 146.4 mg of a very pale tan solid. Recrystallization from dichloromethane/ether yielded 128.5 mg (88%) of a white crystalline air-stable solid: mp 256-263 °C dec; $[\alpha]_{\text{D}}^{25}$ -38.0° (c 1.02, CH₂Cl₂). Anal. Calcd for C₁₅H₂₃NO₄Mo: C, 47.75; H, 6.15; N, 3.71. Found: C, 47.79; H, 6.27; N, 3.64. Selected spectroscopic data are given in Table I.

Crystallography. X-ray data were collected on an Enraf-Nonius CAD4F-11 diffractometer using Mo K α radiation. Details of the data collection, reduction, and refinement procedures have been described elsewhere.¹¹ A total of 6155 reflections (+*h*, +*k*, \pm l), as well as Friedel pairs (-*h*, -*k*, \pm l), were collected in the range 3° ≤ 2θ ≤ 50° with the 5269 reflections having F_o > 4σ(F_o) being used in the structure refinement, which was by full-matrix least-squares techniques (382 variables) using SHELX-76. All non-hydrogen atoms were refined anisotropically. Hy-

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drogen atoms were placed in calculated positions (C-H = 0.95 Å) and were constrained to ride on their respective carbon atoms.

The absolute configuration was assigned by first assuming the *R,R* configuration. Six final cycles of least-squares refinement converged at $R_1 = 0.0448$ and $R_2 = 0.0493$. Anomalous dispersion due to Mo was included in the calculation. The alternate hand of the structure was then refined to convergence from the same starting point, again with six cycles of least-squares refinement, giving a final $R_1 = 0.0466$ and $R_2 = 0.0515$. Thus the original assignment of configuration, depicted in Figure 1, was shown to be correct.

Crystal data: $a = 6.881(3)$ Å, $b = 12.679(2)$ Å, $c = 20.176(4)$ Å, $\beta = 92.03(3)^\circ$, $V = 1759.1$ Å³, space group = $P2_1$, $Z = 4$, $M_r = 377.3$, $\rho(\text{calcd}) = 1.425$ g cm⁻³, $\mu = 7.2$ cm⁻¹. A semiempirical absorption correction was applied. Figure 1 shows the geometry of **5a** and **5b** along with the atomic numbering scheme. Table II shows selected bond distances and angles.

Acknowledgment. We thank the National Science Foundation for financial support (Grant CHE-8308355). We also thank the Biomedical Research Support-Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10RR02243-01). J.M.H. thanks the Fannie and John Hertz Foundation for a graduate fellowship (1982-1985).

Registry No. (*R,R*)-1, 100994-70-5; 2, 100994-71-6; 4, 100994-68-1; 5, 101053-54-7; 6, 101053-55-8; 7, 100994-69-2; MoO₂(acac)₂, 17524-05-9; *t*-BuCHO, 630-19-3; 2,6-dibromopyridine, 626-05-1; 2,6-dibromopyridine *N*-oxide, 25373-69-7.

Supplementary Material Available: Listings of final positional and thermal parameters and final observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Single-Crystal Polarized Electronic Absorption Spectra and Ligand Field Parameters for the Trichloro(triethylphosphine)platinate(II) Ion

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Received August 1, 1985

The bonding properties of phosphine ligands have been studied by a variety of techniques. The most extensive studies have been IR spectroscopic investigations of changes in carbonyl stretching frequencies in phosphine-carbonyl compounds. In addition, NMR spectroscopy and X-ray crystallography have been used as the basis for discussion of σ - and π -bonding properties.

Electronic absorption spectroscopic measurements of the position of phosphine in the spectrochemical series are relatively scarce. The major factors contributing to the scarcity are the relatively high energies of the d-d bands, which frequently cause them to be obscured by charge-transfer bands, and the relatively large extinction coefficients, which make studies of single crystals difficult. Phosphine ligands have been studied the most extensively in tetrahedral Ni(II) and Co(II) complexes.¹⁻⁸ The results have indicated that phosphines are strong ligands in the spectrochemical series. Jørgensen has concluded that the triethylphosphine ligand

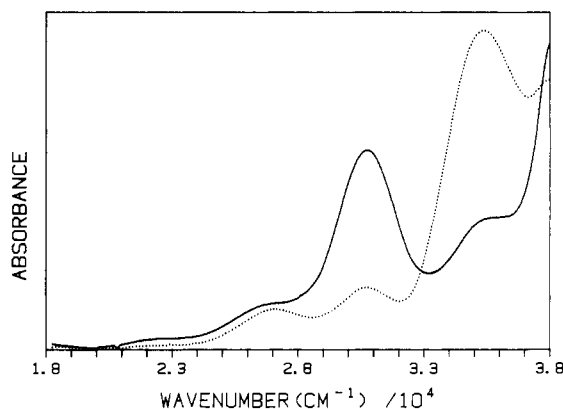


Figure 1. Single-crystal polarized electronic absorption spectrum of $(\text{Pr}_4\text{N})[\text{PtCl}_3\text{PEt}_3]$ at room temperature. The two curves were obtained in orthogonal polarization directions.

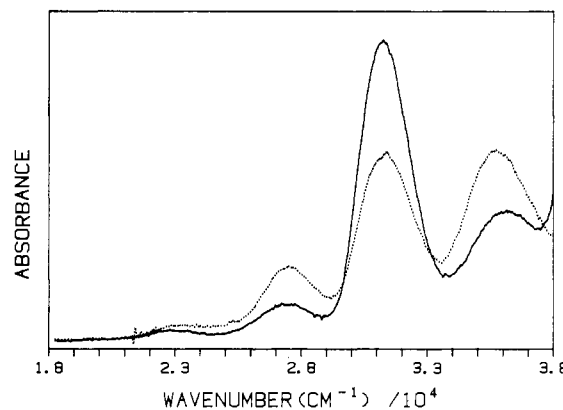


Figure 2. Single-crystal polarized electronic absorption spectrum of $(\text{Pr}_4\text{N})[\text{PtCl}_3\text{PEt}_3]$ at 10 K. The two curves were obtained in orthogonal polarization directions.

“has a spectrochemical position slightly above the amines.”⁹ Triphenylphosphine is a better σ donor and a better π acceptor than halides.¹

A series of compounds that is proving amenable to detailed electronic spectroscopic study is the PtCl_3L^- series where the ligand L can range from “Werner” ligands such as amines and halides¹⁰⁻¹³ to ligands of interest in organometallic chemistry such as ethylenes, CO, and phosphines.¹⁴⁻¹⁶ Microspectroscopic techniques allow measurements to be made on single crystals even when the extinction coefficients are greater than 10^3 .¹⁴ We report here the low-temperature single-crystal polarized electronic absorption spectra of $\text{PtCl}_3\text{PEt}_3^-$ and the angular overlap ligand field analysis of the σ and π interactions with the metal d orbitals.

Experimental Section

$(\text{Pr}_4\text{N})[\text{PtCl}_3\text{PEt}_3]$ was prepared according to the method of Duddell et al.¹⁷ Single crystals were grown between quartz plates that were stored in a covered dish. A drop of a solution of the complex in chloroform was put onto one plate, and a second plate was pressed on top of the first. The dish was covered and allowed to stand for several hours

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