Inorg. Chem. **1982**, *21*, 3772-3776

Contribution from the Molecular Structure Center and Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Tetranuclear Dialkyl Dithiophosphate Complexes of Molybdenum(V) with Nitride Ligands

MARK E. NOBLE, KIRSTEN FOLTING, J. C. HUFFMAN,* and R. A. D. WENTWORTH*

Received February 26, 1982

The syntheses of the tetranuclear, ferromagnetic compounds $[MoN(S_2P(OR)_2)_2]_4$ (R = CH_3 and C_2H_5) are described along with their unusual dissociative and chemical stabilities. The compound with R = CH_3 crystallizes in the monoclinic space group $A2/a$ with a = 18.632 (8) Å, b = 24.384 (12) Å, c = 12.600 (5) Å, β = 92.16 (1)°, and Z = 4 at −163 °C. The structure was solved by direct methods (LSAM) using 3813 unique reflections with $F > 2.33\sigma(F)$. Final residuals were $R(F) = 0.082$ and $R_w(F) = 0.075$. The chiral molecule contains a nearly square and planar $[MoN]_4$ ring in which all bond distances are identical within experimental error. This portion of the structure contrasts markedly with the alternating triple and single bonds found in the $[MoN]_4$ rings in the lattice of $MoNCl_3$, and the differences in the structures are substantiated by the disparate values of ν(MoN). Explanations for the ferromagnetism are given in terms of a superexchange mechanism and molecular orbital theory.

Introduction

Although our previous studies of multiple bonding between molybdenum and nitrogen have focused on the structures and reactivities of imido[1-3] and arylimido[4-9] complexes, we have also diverted part of our attention to a study of nitrido complexes of Mo(V). Previous preparative studies by others have led to the isolation of the Mo(V) complexes $MoNCl_2(PR_3)_2$,[10] as well as the Mo(VI) complexes $MoNCl_3$,[11] $MoNCl_5^{2-}$,[10,12] and $MoN(S_2CNR_2)_3$.[10] Only $MoNCl_3$ and $MoN(S_2CNR_2)_3$ have been characterized by X-ray methods.[13,14]

Our initial goal was the synthesis and structural characterization of a compound whose simplest formula is $MoN(S_2P(OR)_2)_2$ because of its possible utility as a reagent in additional synthetic studies.

Experimental Section

Reagents and Procedures. All reactions were performed under nitrogen with use of standard vacuum line techniques. Solvents were dried and distilled under vacuum prior to use. Trimethylsilyl azide was used as received. Diethylammonium dialkyl dithiophosphates were prepared by the slow addition of a solution of diethylamine in ether to an ice-cold solution of the appropriate dialkyldithiophosphoric acid in ether. The precipitate was collected, washed, and dried. Although $[(C_2H_5)_2NH_2](S_2P(OC_2H_5)_2)$ was used as obtained from this procedure, $[(C_2H_5)_2NH_2](S_2P(OCH_3)_2)$ was subsequently recrystallized from acetone/ether.

The preparation of $MoCl_3(THF)_3$ from $MoCl_4(THF)_2$ was conducted using Sn rather than Zn as previously reported.[15] Freshly acid-washed Sn (30 mesh, 10.6 mmol) was added to a slurry of $MoCl_4(THF)_2$ (26.5 mmol) in tetrahydrofuran (37 mL) at 0 °C. After the mixture was stirred for 24 h at the same temperature, the bright orange powder was filtered, washed with the same solvent, and dried under vacuum. Anal. Calcd: Cl, 25.4. Found: Cl, 25.7. Yields are typically 80–90%.

Table I. Spectroscopic Properties of $[MoN(S_2P(OR)_2)_2]_4$

R	λ_{max},[a,b] nm	ν(MoN),[c] cm^{-1}
CH_3	298 (19 700), 344 (15 700), 396 (10 700), 497 (1800), ~627 (144)	925
C_2H_5	303 (20 100), 345 (16 100), 399 (11 300), 504 (1750), ~637 (161)	923

[a] Obtained in CH_2Cl_2. Molar extinction coefficients appear in parentheses. [b] First, second, third, and fifth bands obey the Beer–Lambert law. No attempt was made to test the validity of this law with the fourth band. [c] Obtained in KBr pellets.

Physical and Analytical Methods. Infrared spectra were obtained in KBr pellets on a Perkin-Elmer Model 283 spectrophotometer. A Cary 14 spectrophotometer was used to obtain electronic spectra. Molecular weights were determined in 1,2-$C_2H_4Cl_2$ with a Mechrolab 301A osmometer operating at 37 °C. Magnetic moments were derived from susceptibility data obtained on a Varian HR 220 NMR spectrometer by a modified[16] form of the method of Evans.[17] Susceptibilities were obtained in CH_2Cl_2 and were corrected for diamagnetism.

Analyses for Cl and S were obtained with use of standard gravimetric procedures following digestion in basic peroxide. Alternatively, analyses for S as well as C, H, and N were obtained from Galbraith Laboratories, Inc., Knoxville, TN.

$[MoN(S_2P(OCH_3)_2)_2]_4$. A combination of $MoCl_3(THF)_3$ (12 mmol), $(CH_3)_3SiN_3$ (12 mmol), and tetrahydrofuran (50 mL) was warmed at 45–50 °C for 1 h. The red-orange solution was evaporated to a glass to remove $(CH_3)_3SiCl$. The addition of $[(C_2H_5)_2NH_2](S_2P(OCH_3)_2)$ (28.1 mmol) and tetrahydrofuran (65 mL) resulted in a slurry, which was stirred for 3 h. After the volume was halved, filtration provided 93% of nearly colorless crystals of $[(C_2H_5)_2NH_2]Cl$. The deep orange-brown filtrate was treated with methyl alcohol (50 mL) and evaporated to a small volume, which results in the removal of most of the tetrahydrofuran. Methyl alcohol (30 mL) was then added. The resulting precipitate was filtered, washed with the same solvent, and dried. The crude product was recrystallized slowly from a mixture of tetrahydrofuran and methyl alcohol to give deep orange-brown crystals (61%). Anal. Calcd. for $[MoN(S_2P(OCH_3)_2)_2]_4$: C, 11.3; H, 2.9; N, 3.3; S, 30.2; M_r 1697. Found: C, 11.0; H, 2.8;

---

(1) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1978**, *17*, 922.
(2) Edelblut, A. W.; Haymore, B. L.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1978**, *100*, 2250.
(3) Edelblut, A. W.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 2006.
(4) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.
(5) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409.
(6) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1055.
(7) Edelblut, A. W.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1110.
(8) Edelblut, A. W.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1981**, *103*, 1927.
(9) Noble, M. E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1982**, *21*, 2101.
(10) Chatt, J.; Dilworth, J. R. *J. Indian Chem. Soc.* **1977**, *54*, 13.
(11) Kolitsch, W.; Dehnicke, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1970**, *25B*, 1080.
(12) Bereman, R. D. *Inorg. Chem.* **1972**, *11*, 1149.
(13) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalle, M. *J. Less-Common Met.* **1977**, *54*, 487.
(14) Strahle, J. *Z. Anorg. Allg. Chem.* **1970**, *375*, 239.
(15) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639.
(16) Modification followed the nuclear screening equation for parallel magnetic field orientation given by: Becconsall, J. K. *Mol. Phys.* **1968**, *15*, 129.
(17) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

0020-1669/82/1321-3772$01.25/0

N, 3.0; S, 29.7; M_r (osmometry, 2.8×10^{-2} M) 1700 ± 30. Magnetic moment (CH_2Cl_2, 2.2×10^{-2} M): 4.8 μ_B (22 and −38 °C). IR: 2984 (w), 2942 (m), 2882 (w), 2837 (w), 1453 (m), 1181 (m), 1040 (sh), 1013 (s), 925 (m), 796 (s), 656 (m), 642 (m), 526 (w), 384 (w), 347 (w), and 299 (w) cm^{-1}.

The electronic spectrum of the compound in CH_2Cl_2 consists of the five bands shown in Table I. The molar extinction coefficients of the first three were obtained from plots of absorbance against concentration ((0.55–5.5) × 10^{-5} M) while that of the fourth was obtained from the absorbance of the most concentrated solution. The molar extinction coefficient of the fifth band was again obtained from adherence to the Beer–Lambert law ((0.46–4.6) × 10^{-3} M).

$[MoN(S_2P(OC_2H_5)_2)_2]_4$. A combination of $MoCl_3(THF)_3$ (7.5 mmol), $(CH_3)_3SiN_3$ (7.5 mmol), and tetrahydrofuran (20 mL) was warmed at 45–50 °C for 1 h. Evaporation gave a glass to which was added $[(C_2H_5)_2NH_2](S_2P(OC_2H_5)_2)$ (16.1 mmol) and tetrahydrofuran (20 mL). This slurry was stirred overnight. The solvent was again removed and replaced by ether (25 mL). Filtration afforded impure $[(C_2H_5)_2]NH_2Cl$. The solvent from the deep orange-brown filtrate was removed once again. The addition of methyl alcohol (20 mL) caused the slow deposition of deep orange-brown crystals, which were collected, washed with the same solvent, and dried (yield 54%). Anal. Calcd for $[MoN(S_2P(OC_2H_5)_2)_2]_4$: C, 20.0; H, 4.2; N, 2.9; S, 26.7; M_r 1922. Found: C, 20.1; H, 4.0; N, 2.9; S, 27.0; M_r (osmometry, 4×10^{-2} M) 1530 ± 30 (see the discussion of results). Magnetic moment (CH_2Cl_2, 2.2×10^{-2} M): 4.8 μ_B (25 °C). IR: 2975 (m), 2928 (w), 2892 (w), 1470 (w), 1437 (w), 1389 (m), 1160 (m), 1095 (w), 1035 (sh), 1011 (s), 959 (s), 923 (m), 815 (m), 785 (m), 651 (m), 638 (m), 432 (w), 385 (w), 354 (w), and 294 (w) cm^{-1}.

The electronic spectrum of the compound in CH_2Cl_2 consists of five bands. The wavelengths of their maxima are also given in Table I. Molar extinction coefficients were obtained by procedures that were identical with those used for $[MoN(S_2P(OCH_3)_2)_2]_4$.

Attempted Reactions of $[MoN(S_2P(OCH_3)_2)_2]_4$ with $HS_2P(OC_2H_5)_2$ or $KS_2P(OCH_3)_2$. A combination of $[MoN(S_2P(OCH_3)_2)_2]_4$ (0.13 mmol), $HS_2P(OC_2H_5)_2$ (1.12 mmol), and tetrahydrofuran (15 mL) was stirred for 24 h without any apparent reaction. The solvent was removed by evaporation, and the residue was triturated with methyl alcohol, filtered, and dried. The infrared spectrum of the solid was identical with that of $[MoN(S_2P(OCH_3)_2)_2]_4$. The ^1H NMR spectrum of the extracts, after alcohol removal and dissolution in CCl_4, revealed only a trace of $HS_2P(OCH_3)_2$.

When a comparable quantity of $KS_2P(OCH_3)_2$ was used instead of $HS_2P(OC_2H_5)_2$ with the other conditions remaining the same, $[MoN(S_2P(OCH_3)_2)_2]_4$ was again recovered from the solution after 24 h.

Exchange between $[MoN(S_2P(OCH_3)_2)_2]_4$ and $KS_2P(OC_2H_5)_2$. A solution composed of $[MoN(S_2P(OCH_3)_2)_2]_4$ (0.075 mmol), $KS_2P(OC_2H_5)_2$ (0.30 mmol), and tetrahydrofuran (25 mL) was prepared in each of six reaction vessels. At the completion of a predetermined time, methyl alcohol (5 mL) was added to one of the flasks to precipitate the bulk of the tetranuclear substances. After it was stirred for 5 min, the mixture was cooled to −78 °C and filtered. Water (half the volume of the filtrate) was added to the filtrate to remove the remainder of the tetranuclear substances as an oil. Centrifugation gave a clear supernatant liquid, which was decanted and evaporated to dryness. The residue was dissolved in acetone-d_6 and examined by ^1H NMR spectroscopy. After 1, 2, 4, 8, 12, and 18 h, the quantities of $S_2P(OCH_3)_2^-$ liberated during the reaction were 0.015, 0.024, 0.051, 0.090, 0.13, and 0.17 mmol, respectively.

Crystallography. A small, well-formed parallelepiped of maximum dimension 0.21 mm was initially chosen for the X-ray analysis. The sample (crystal I) was mounted on a glass fiber affixed to a translation-only goniometer head with silicone grease and transferred to the goniostat, where it was cooled to −150 °C. The modified Picker goniostat and gaseous nitrogen cooling system used in the study have been described previously.[18]

A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that could be indexed as monoclinic, space group $A2/a$ (nonstandard setting of $C2/c$ (No. 15)), or the noncentrosymmetric equivalent, Aa. Statistical tests and the solution and refinement indicated the centrosymmetric choice to be correct (see below). A least-squares fit of angular data from 50 reflections yielded the cell dimensions shown in Table II. Data for I were collected with use of a standard moving-crystal–moving-detector technique for those data with 6° < 2θ < 45°. Diffractometer data are as follows: 4°/min scan rate, 5-s stationary background counts, scan width of 2.0° + (dispersion correction), Mo Kα radiation and graphite monochromator (0, 0, 2 plane), source to sample distance 23.5 cm; sample to detector distance 22.5 cm; aperture 3 × 4 mm. It was noted during data collection that 45% of the data were "unobserved" when the criterion $I_{obsd} \geq 2.33\sigma(I)$ was used. Such a high value is unusual for low-temperature data and is usually indicative of disorder or poor crystal quality.

Table II. Crystal Data

space group	$A2/a$
temp, °C	−163
a, Å	18.632 (8)
b, Å	24.384 (12)
c, Å	12.600 (5)
β, deg	92.16 (1)
V, Å^3	5720.2
Z	4
d_{calcd}, g/cm^3	1.971
fw	1697.08
cryst size, mm	0.14 × 0.16 × 0.17
λ, Å	0.71069
μ(Mo Kα), cm^{-1}	16.75
no. of unique data	5055
no. of data with $F > 2.33\sigma(F)$	3259
$R(F)$	0.082
$R_w(F)$	0.075
goodness of fit	1.745
largest Δ/σ	0.05

Direct methods (LSAM) located the molybdenum atoms, and Fourier techniques readily located all remaining non-hydrogen atoms. Full-matrix least squares using anisotropic thermal parameters converged to $R(F) = 0.125$ and $R_w(F) = 0.102$. Several of the refined atoms had large thermal amplitudes, although there was no apparent disorder present.

Because of the large values of the final residuals, a second crystal (II) of dimensions 0.14 × 0.16 × 0.17 mm was examined. The temperature was lowered to −163 °C, and data were collected at a scan rate of 2.5°/min with 15-s stationary background counts at each extreme of the scan. All other diffractometer data were the same as for I. The improved signal to noise ratio for crystal II, due to the slower scan, resulted in only 36% of the data being unobserved. Since an examination of ψ scans and several symmetry-related intensities indicated that the maximum absorption correction was less than 5% ($\mu = 16.75$ cm^{-1}), no absorption correction was performed. Cell dimensions for II were identical, within experimental error, with those of I.

Refinement with data for crystal II proceeded smoothly to final residuals of $R(F) = 0.082$ and $R_w(F) = 0.074$ for the 3259 data with $I > 2.33\sigma(I)$. Estimated errors for the bond lengths and angles are still somewhat large, and thermal amplitudes of many of the atoms are still considered excessive for low-temperature data. Attempts to refine the data in the noncentrosymmetric space group Aa led to residuals that were not significantly (on the basis of Hamilton's test[19]) lower, indicating the centrosymmetric space group was the proper choice. A final difference Fourier was essentially featureless, with the largest peak being 0.45 e/Å^2. Several difference maps were generated in which various individual atoms were removed, and the resultant electron density was carefully examined. In all cases the removed atom reappeared and there was no evidence of doubling.

Final values of the fractional coordinates are given in Table III. The observed and calculated structure amplitudes, anisotropic thermal parameters, and a complete listing of all bonded distances and angles are available as supplementary material.

Results and Discussion

Syntheses. Solutions of a useful but uncharacterized Mo(V) intermediate, whose preparation was previously described by Chatt and Dilworth,[10] were prepared by the oxidation of $MoCl_3(THF)_3$ with $(CH_3)_3SiN_3$ in tetrahydrofuran. The

---

(18) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

(19) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

Table III. Fractional Coordinates (×10^4)[a]

atom	*x*	*y*	*z*
Mo(1)	2370 (1)	3360 (1)	3524 (1)
Mo(2)	2357 (1)	4890 (1)	3531 (2)
S(1)	1974 (2)	3293 (2)	1462 (3)
S(2)	1054 (4)	3142 (3)	3548 (4)
S(3)	2599 (4)	2283 (2)	3467 (4)
S(4)	3652 (3)	3309 (2)	3064 (4)
S(5)	2347 (2)	4922 (2)	1439 (3)
S(6)	3649 (2)	5090 (2)	3195 (4)
S(7)	2143 (2)	5969 (2)	3481 (3)
S(8)	1020 (2)	4955 (2)	3503 (3)
N(1)	2500*	3334 (7)	5000*
N(2)	2354 (7)	4125 (5)	3441 (9)
N(3)	2500*	4927 (6)	5000*
P(1)	1006 (3)	3114 (2)	1966 (4)
P(2)	3570 (4)	2483 (2)	3075 (5)
P(3)	3395 (3)	5065 (2)	1635 (4)
P(4)	1111 (2)	5777 (2)	3482 (3)
O(1)	370 (6)	3487 (6)	1453 (12)
O(2)	677 (6)	2552 (6)	1518 (9)
O(3)	3819 (7)	2234 (5)	2005 (11)
O(4)	4132 (14)	2211 (7)	3892 (17)
O(5)	3888 (7)	4629 (8)	1035 (18)
O(6)	3673 (7)	5578 (7)	1011 (11)
O(7)	633 (6)	6020 (4)	2541 (9)
O(8)	744 (7)	6053 (5)	4469 (10)
C(1)	373 (11)	4069 (8)	1712 (20)
C(2)	998 (11)	2032 (7)	1825 (17)
C(3)	3438 (10)	2354 (8)	1002 (14)
C(4)	4741 (13)	2309 (11)	4198 (30)
C(5)	3772 (13)	4128 (8)	801 (22)
C(6)	3307 (12)	6090 (8)	1150 (21)
C(7)	807 (11)	5870 (9)	1453 (14)
C(8)	26 (9)	5877 (8)	4734 (15)

[a] Fractional coordinates marked with an asterisk belong to atoms on the crystallographic 2-fold axis.

addition of salts of $S_2P(OR)_2^-$ (R = CH_3 and C_2H_5) to these solutions produced $[MoN(S_2P(OR)_2)_2]_4$ in good yields. Other routes to the same compounds, which have been explored briefly and successfully without attempts to optimize conditions, are the addition of salts of $S_2P(OR)_2^-$ to slurries of $MoNCl_2(P(C_6H_5)_3)_2$ and the addition of $(CH_3)_3SiN_3$ and salts of $S_2P(OR)_2^-$ to slurries of $MoCl_4(THF)_2$. We assume that the disulfide, $(RO)_2P(S)SSP(S)(OR)_2$, is also formed in the second reaction.

Spectroscopic Properties. The electronic spectrum of both compounds in CH_2Cl_2 consists of five bands that are similarly positioned with comparable molar extinction coefficients as shown in Table I. The absorbances of four of the five bands in each spectrum adhere to the Beer–Lambert law without exception. The behavior of the intensity of the other band as a function of concentration was not investigated.

The infrared spectra of $[MoN(S_2P(OR)_2)_2]_4$ contain all of the characteristic bands due to the bidentate ligands that are usually observed in the spectra of other complexes of molybdenum containing these ligands, the acid forms of the ligands, the derived disulfides, and simple salts containing the ligands. However, the spectrum of the compound with R = CH_3 also contains an isolated, well-resolved band at 925 cm^{-1}, which can only arise from motions involving the metal and nitrogen atoms as shown in Table I. A well-resolved shoulder at 923 cm^{-1} in the spectrum of the compound with R = C_2H_5 has received an identical assignment. These frequencies are considerably less than those found with other nitrido complexes of either Mo(V) or Mo(VI). The known mononuclear complexes have $\nu(Mo{\equiv}N)$ between 1000 and 1050 cm^{-1},[10] while $MoNCl_3$ with its alternating Mo≡N and Mo—N bonds in a $[MoN]_4$ ring has $\nu(Mo{\equiv}N)$ at 1045 cm^{-1}.[11] Consequently, a reduction in the order of the bond between the metal and nitrogen atoms in $[MoN(S_2P(OR)_2)_2]_4$ is to be expected.

Molecular Weights and Magnetism in Solution. The molecular weight of $[MoN(S_2P(OCH_3)_2)_2]_4$ in 1,2-$C_2H_4Cl_2$, established by osmometry, was found to be 1700 ± 30. The theoretical value is 1697. Moreover, this composition is retained at lower concentrations since the Beer–Lambert law is rigidly followed in CH_2Cl_2 at four different wavelengths. These results may be compared to those found[7] for the unrelated compound $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$, where osmometry gave unambiguous evidence for the tetranuclear composition but marked deviations from the Beer–Lambert law in more dilute solutions indicated a concentration-dependent dissociation. Since there is no detectable dissociation of $[MoN(S_2P(OCH_3)_2)_2]_4$ in CH_2Cl_2, magnetic studies were conducted in that solvent. The results indicated a magnetic moment of 4.8 μ_B for four molybdenum atoms (or 2.4 μ_B/Mo atom) at both 22 and −38 °C.

In contrast to that for $[MoN(S_2P(OCH_3)_2)_2]_4$, the measured molecular weight of $[MoN(S_2P(OC_2H_5)_2)_2]_4$ is only 1530 ± 30 while the theoretical value is 1922. The absorption spectrum of this compound, however, mimics that of $[MoN(S_2P(OCH_3)_2)_2]_4$ and also adheres strictly to the Beer–Lambert law. Moreover, the magnetic moment is again 4.8 μ_B. Since the spectroscopic and magnetic results are in accord with a nondissociable tetranuclear compound, the only reasonable explanation for the low value of the molecular weight is solvent of crystallization which is not detected by the elemental analysis. For example, the presence of one molecule of methyl alcohol (the solvent that caused the compound to crystallize) for every four tetranuclear molecules would lead to a calculated molecular weight of 1544.[20] When the compound was recrystallized from a mixture of benzene and petroleum ether, the observed molecular weight increased but only to 1760 ± 30. This result suggests that one type of solvent of crystallization was replaced by another with an accompanying change in the ratio of solvent and tetramer in the lattice. Neither type was detected in the infrared spectra because the intense bands due to the bidentate ligand would easily obscure the weaker bands from limited quantities of a solvent of crystallization. Although the exact composition of the compound remains unknown, the tetranuclear nature of the species which contains molybdenum is clearly established by the spectroscopic and magnetic results.

The magnetic moments of both compounds are consistent with ferromagnetic coupling, a ground state characterized by $S = 2$ (which would have a spin-only magnetic moment of 4.90 μ_B), and no appreciable population of an excited state with a lower value of S. No ESR signal was observed with a solution of $[MoN(S_2P(OC_2H_5)_2)_2]_4$ at either room temperature or −178 °C, undoubtedly due to an unfavorable relaxation rate in the ground state.

Chemical Stability. When excess gaseous HCl was admitted to a solution of $[MoN(S_2P(OCH_3)_2)_2]_4$ in tetrahydrofuran, rapid formation of NH_4Cl was observed. However, the same tetranuclear compound was recovered unscathed after contact with $HS_2P(OC_2H_5)_2$ for 24 h in the same solvent. A trace of $HS_2P(OCH_3)_2$ in the solution suggested a very slow exchange between the bound bidentate ligand and the acid. Similarly, no reaction was observed after 18 h when H_2S, *t*-C_4H_9SH, or CH_3I was added to solutions of this compound in the same solvent. Thus, the compound is unstable with respect to strong acids but unable to react with weaker acids or electrophilic reagents of moderate strength.

---

(20) When this compound or one similar to it is placed in 1,2-$C_2H_4Cl_2$ with a concentration suitable for a molecular weight measurement, the vapor pressure would be essentially that of 1,2-$C_2H_4Cl_2$ since the mole fraction of methyl alcohol in that solvent would be exceedingly small (less than 0.01). As a consequence, the osmotic pressure should be a reasonably true indicator of the weighted-average molecular weight of the two solutes.

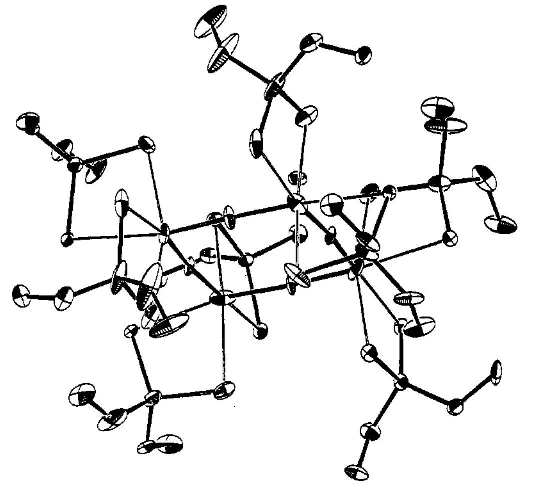

Figure 1. ORTEP drawing of $[MoN(S_2P(OCH_3)_2)_2]_4$ with thermal ellipsoids at the 20% probability level.

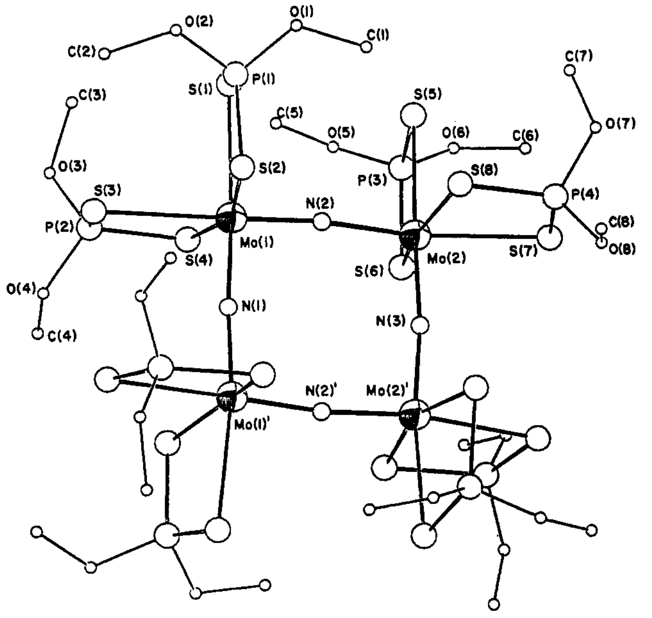

Figure 2. Ball-and-stick drawing of $[MoN(S_2P(OCH_3)_2)_2]_4$, which gives the numbering scheme and a view of the $[MoN]_4$ ring.

The compound is also stable with respect to nucleophilic substitution by either $(C_6H_5)_3P$ or $(C_6H_5)_3PO$ since it failed to react with these reagents after 18 h in tetrahydrofuran. Similarly, nucleophilic addition of $S_2P(OCH_3)_2^-$ was not observed when the tetranuclear compound was in contact with $KS_2P(OCH_3)_2$ for 24 h in the same solvent. However, an additional study indicated that exchange between the tetranuclear compound and $KS_2P(OC_2H_5)_2$ occurred steadily, albeit slowly, during 18 h. These results may be contrasted to the almost nonexistent exchange between $[MoN(S_2P(OCH_3)_2)_2]_4$ and $HS_2P(OC_2H_5)_2$ during a somewhat longer period of time.

The remarkable chemical stabilities of these compounds preclude their use in the syntheses of imido and alkylimido compounds of Mo(V). Nevertheless, the structures of these compounds and an explanation for the observed ferromagnetism are still questions of interest.

Structure. There are two lines of evidence from which the structure of these compounds, particularly in the vicinity of the metal atoms, was determined: an examination of $[MoN(S_2P(OCH_3)_2)_2]_4$ with X-rays and infrared spectroscopy.

Table IV. Selected Bond Distances (Å) and Angles (Deg)[a]

Mo(1)-N(1)	1.867 (2)	Mo(1)-S(3)	2.661 (5)
Mo(1)-N(2)	1.868 (12)	Mo(1)-S(4)	2.483 (6)
Mo(2)-N(2)	1.870 (12)	Mo(2)-S(5)	2.637 (4)
Mo(2)-N(3)	1.862 (2)	Mo(2)-S(6)	2.508 (5)
Mo(1)-S(1)	2.680 (4)	Mo(2)-S(7)	2.661 (4)
Mo(1)-S(2)	2.510 (6)	Mo(2)-S(8)	2.469 (5)
N(1)-Mo(1)-N(2)	95.3 (6)	Mo(1)-N(1)-Mo(1')	176.1 (11)
N(2)-Mo(2)-N(3)	96.2 (6)	Mo(1)-N(2)-Mo(2)	173.2 (7)
		Mo(2)-N(3)-Mo(2)	174.5 (10)

[a] Additional bond distances and angles can be obtained by rotation about the crystallographic 2-fold axis.

Table V. Least-Squares Analysis of the Planarity of the $[MoN]_4$ Ring and the Equatorial Sulfur Atoms[a]

atom	Δ, Å[b]	atom	Δ, Å	atom	Δ, Å
Mo(1)	0.013	N(2)	−0.009	S(3)	−0.445
Mo(2)	−0.013	N(3)	0.000	S(5)	0.327
N(1)	0.000	S(1)	−0.368	S(7)	−0.402

[a] The equation for the plane that was defined by the four molybdenum atoms is $(1.8541 \times 10^{-4})x + (4.5576 \times 10^{-10})y - (1.7150 \times 10^{-1})z = 3.7777 \times 10^{-1}$. [b] Displacement from the plane. The displacement of the remainder of the atoms can be obtained by rotation about the crystallographic 2-fold axis.

The X-ray analysis of $[MoN(S_2P(OCH_3)_2)_2]_4$, which led to the molecular structure shown in Figures 1 and 2, indicated a nearly square and planar array of molybdenum and nitrogen atoms in an eight-membered ring. This ring resembles (but is not identical with) the $[MoN]_4$ riings in $MoNCl_3$.[14] The donor atoms of the bidentate dithiophosphate ligands complete a distorted octahedron around each metal atom. The chiral molecule possesses a crystallographic 2-fold axis, which passes through N(1) and N(3). Some pertinent bond distances and bond angles are given in Table IV while a least-squares analysis of the planarity of the ring is given in Table V.

Relatively large amplitudes of vibration are associated with several of the peripheral atoms. This problem is particularly acute with C(4), O(4), C(5), and O(5) and the corresponding atoms related to these by the crystallographic 2-fold axis. As a consequence, the positional parameters for these atoms have a large error. However, the positions of the atoms within the ring and those immediately adjacent to it are sufficiently well determined to warrant some discussion.

A detailed view of the ring is shown in Figure 2. All Mo-N distances are identical within experimental error with a value of 1.87 Å.[21] This bond distance may be compared to the terminal Mo≡N distance of 1.62 Å found in $MoN(S_2CN(C_2H_5)_2)_3$[13] and the average bridging Mo≡N and Mo—N distances of 1.65 and 2.17 Å, respectively, in $MoNCl_3$.[14] While the ring in $MoNCl_3$ clearly consists of alternating triple and single bonds, it would appear that the corresponding bonds in the compound described herein are all double or at least partial double bonds.

Distortions to the octahedral stereochemistry about each metal atom enter from four sources. First, each N-Mo-N bond angle is slightly opened probably because of the repulsion between the π-electron systems of adjacent Mo-N bonds. Second, the eight equatorial sulfur atoms are alternately displaced by 0.33-0.45 Å above and below the plane of the ring (Table V), which is due, at least in part, to the inability of the four-membered chelate rings to span the adjacent sites of a regular octahedron. Third, a trans effect due to each nitrogen atom causes the eight equatorial Mo-S distances to be 0.13-0.18 Å longer than the eight axial Mo-S distances. Fourth, each axial sulfur atom is bent away from its two

---

(21) While the Mo(1)-N(1) and Mo(2)-N(3) bond distances show a higher degree of precision than the remaining Mo-N bond distances, the increased precision is due to N(1) and N(3) lying on the crystallographic 2-fold axis. As a consequence, only the error in the coordinates of Mo(1) and Mo(3) influences the precision of these bond distances.

nearest axial neighbors so that the average distance between nearest neighbors is 4.32 Å. In the absence of this effect, the shortest distance between two axial sulfur atoms would be the edge length of the ring or 3.73 Å. Since the latter is approximately twice the van der Waals radius (1.85 ± 0.05 Å, according to Pauling[22]), the larger observed distance is not due to repulsion but is again probably due to the small chelate rings.

When the $[MoN]_4$ rings in $[MoN(S_2P(OCH_3)_2)_2]_4$ and $MoNCl_3$ are compared, however, a somewhat disturbing similarity is revealed. Although the sum of the Mo≡N and Mo—N bond distances in $MoNCl_3$ is somewhat longer than twice the Mo–N bond distance in our compound, slight angular distortions cause the Mo–Mo distances to be nearly identical in both compounds. It is also noteworthy that the longest axis of the thermal ellipsoid for each metal atom lies principally in the plane of the ring and tangentially to that ring. This effect could be due to an undetected disorder in the molybdenum atoms. If so, the lattice could consist of a statically or dynamically disordered array of $[MoN]_4$ rings with each ring having the alternating triple and single bonds which are found in $MoNCl_3$. This possibility, however, can be excluded because of the spectroscopic results and, to a lesser degree, the chemical results.

The notable differences in ν(MoN) that occur in the infrared spectra of $[MoN(S_2P(OR)_2)_2]_4$ and $MoNCl_3$ indicate that the alternating triple and single bonds in the $[MoN]_4$ rings of $MoNCl_3$ have been replaced by a cyclic array of delocalized Mo=N or Mo$\overset{\cdot\,\cdot}{-}$N bonds in the $[MoN]_4$ rings of $[MoN(S_2P(OR)_2)_2]_4$. Neither a static nor a dynamic disorder could give rise to the observed disparity in the values of ν(MoN). Moreover, the unusual dissociative and chemical stabilities that are associated with our compounds can be explained more easily in terms of a delocalized pattern of bonding.

Explanations for Ferromagnetism. Inspection of the spin-state correlation diagram given by Martin[23] for a square d^1–d^1–d^1–d^1 tetramer indicates that gross ferromagnetism will result if coupling along the edges of the square is ferromagnetic while diagonal coupling may then be weakly antiferromagnetic, nonexistent, or ferromagnetic. An exchange mechanism for a $[MoN]_4$ ring that satisfies these requirements will involve 180° superexchange along the edges and direct exchange across the diagonals. A dominant role for the latter can be safely discounted, in agreement with the conclusions from the correlation diagram, because the diagonal distance in a $[MoN]_4$ ring is greater than 5 Å. Ferromagnetism along the edges will result when a filled orbital from each nitrogen atom is able to transfer an electron to a nonorthogonal, half-filled metal orbital on one side and a nonorthogonal, empty metal orbital on the other side. This requirement indicates that a p–t_{2g} pathway for superexchange assumes a dominant role while the antiferromagnetic contribution from a p_σ–e_g pathway has less importance.[23] The spatial orientation of the orbitals is also stipulated by this requirement. Each of the four unpaired electrons must occupy one of four metal orbitals which are related by the 4-fold axis of the square and which have nodal surfaces in the plane of the square. Either one of two of the t_{2g} orbitals will meet this demand while the third will not. The filled p orbitals from the nitrogen atoms must also have nodal surfaces in the plane of the square.

Another explanation for the ferromagnetism and an appraisal of the effects of delocalization can be obtained from a standard application of molecular orbital theory to the π-electron system of the ring. For ease, it will be assumed that the point group for $[MoN(S_2P(OR)_2)_2]_4$ is D_4. It will also be convenient to define two types of orbitals: those with nodal surfaces in the plane of the ring, which will be called out-of-plane orbitals, and those with nodal surfaces perpendicular to the plane of the ring, which will be called in-plane orbitals.

Since the eight out-of-plane metal d orbitals span the $a_1 + a_2 + b_1 + b_2 + 2e$ representations while the four out-of-plane nitrogen p orbitals span the $a_2 + b_2 + e$ representations, the out-of-plane $a_1 + b_1 + e$ orbitals from the metal atom are nonbonding with respect to the ring. Similarly, the four in-plane metal d orbitals span the $a_1 + b_2 + e$ representations while the corresponding p orbitals from the nitrogen atoms span the $a_1 + b_1 + e$ representations. Since spatial orientation prevents the overlap of the in-plane b_2 orbital from the metal atoms with the out-of-plane b_2 orbital from the nitrogen atoms, the former will also be nonbonding with respect to the ring. Moreover, spatial orientation also precludes the overlap of the out-of-plane b_1 orbital from the metal atoms with the in-plane b_1 orbital from the nitrogen atoms so that the latter can be used for a lone pair of electrons which are delocalized over the four nitrogen atoms.

Twenty electrons (four from each nitrogen atom and one from each metal atom) are available to the system described in this analysis. A set of seven bonding orbitals, out-of-plane $a_2 + b_2 + e$ and in-plane $a_1 + e$, will be filled with fourteen of these electrons. Another two electrons will occupy the b_1 orbital to form the delocalized lone pair described above. The remaining four electrons will be distributed in the out-of-plane $a_1 + b_1 + e$ and in-plane b_2 orbitals, which are nonbonding with respect to the ring. Since only seven bonding orbitals are available and are filled, the π bond order for each bond in the eight-membered ring is $^7/_8$.

All of the orbitals that are nonbonding with respect to the ring, however, will interact with appropriate combinations of filled and empty sulfur π orbitals. As a result, the actual distribution of electrons in these orbitals will depend on the extent to which the degeneracy is removed by these interactions. The observed magnetism indicates that at least four of these five orbitals must have similar energies.

Acknowledgment. Support for this research was provided by USDA Grant No. 59-2184-0-1-434-0. The authors also acknowledge support from the Marshall H. Wrubel Computing Center for use of the computing facilities.

Registry No. $[MoN(S_2P(OCH_3)_2)_2]_4$, 82621-45-2; $[MoN(S_2P(OC_2H_5)_2)_2]_4$, 82638-70-8.

Supplementary Material Available: Listings of all bond distances and angles and observed and calculated structure factor amplitudes (36 pages). Ordering information is given on any current masthead page.

---

[22] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[23] Martin, R. L. In "New Pathways in Inorganic Chemistry"; Ebsworth, E. A. V., Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: London, 1968; pp 175–231.