valato)dichloroditechnetate(III).[23] The slightly larger Tc–N bond lengths are consistent with the 0.04 Å larger covalent radius of nitrogen compared with oxygen.[24] It is interesting that the Tc–N distances are the same as those reported for $(Me_4N)_3[Fe(NCS)_6]$, 2.03 (2)–2.06 (2) Å.[25] Since technetium(III) has the same octahedral covalent radius as iron(III), it might substitute for iron(III) in biological systems.

Other features of the geometry (Table III) are normal. The relatively low accuracy of the structure determination results from the small amount of high-angle data. The Tc–N–C and N–C–S angles are all within 10° of linearity. The average N–C (1.12 (5) Å) and C–S (1.64 (4) Å) distances agree with those found for the iron(III) analogue, 1.14 (4) and 1.62 (4) Å, respectively, as do the various bond angles (cf. ref 25). There was no evidence for disorder of the tetra-*n*-butylammonium carbon atoms.

The tetraphenylarsonium salt in a KBr pellet and solutions of $[Tc(NCS)_6]^{3-}$ exhibit a single, strong band in the cyanide stretching region of the infrared spectra (Table IV), consistent with octahedral symmetry. In the case of $(n\text{-}Bu_4N)_3[Tc(NCS)_6]$, two bands are observed in the infrared and three in the Raman spectra, rather than the one infrared-active and two Raman-active bands predicted for an octahedral anion. Unfortunately, satisfactory Raman spectra in solution have not been obtainable for $[Tc(NCS)_6]^{3-}$, to date. The observed behavior of the $n\text{-}Bu_4N^+$ salt must be due to solid-state effects; the X-ray structure determination reveals there to be two crystallographically independent thiocyanate ligands. The octahedral iron(III) thiocyanate complex $(Me_4N)_3[Fe(NCS)_6]$ displays three bands in the cyanide stretching region of the infrared spectrum in the solid,[10] and, yet, and X-ray structure has confirmed it as a generally octahedral six-coordinate complex,[25] although there are two crystallographically distinct octahedra, one of which has a markedly nonlinear Fe–N–C–S moiety (Fe–N–C = 146 (2)°).

The observed magnetic moment of the technetium(III) complex, 3.0–3.3 μ_B at 298 K, is in the range expected for a d^4 ion with two unpaired electrons.[13] No EPR spectrum was obtainable at room temperature or 77 K. Equivalent conductance measurements (Figure 2) on $(n\text{-}Bu_4N)_3[Tc(NCS)_6]$ in acetonitrile are consistent with a 1:3 electrolyte; cf. $(Me_4N)_3[Fe(NCS)_6]$. The optical spectrum has an intense band at approximately 400 nm ($\epsilon \sim 22\,000$), which is solvent dependent in shape and intensity.

The voltammetric behavior of the hexakis(isothiocyanato)technetate(III) ion is summarized in Table V. The complex exhibits an irreversible one-electron reduction at −1.10 V vs. SCE. More importantly, a reversible one-electron oxidation at 0.18 V vs. SCE is observed. As mentioned earlier, solutions of $[Tc(NCS)_6]^{3-}$ are air sensitive and convert to $[Tc(NCS)_6]^{2-}$ upon exposure to oxygen. This reaction can be monitored spectrophotometrically. An isosbestic point occurs at ~435 nm; as the band at 400 nm decreases, the band at 500 nm increases. Addition of cerium(IV) or thiocyanogen, $(SCN)_2$, oxidizes solutions of $[Tc(NCS)_6]^{3-}$ rapidly to $[Tc(NCS)_6]^{2-}$. In addition, bubbling NO through a purged dichloromethane solution of $[Tc(NCS)_6]^{3-}$ rapidly produces $[Tc(NCS)_6]^{2-}$. The behavior described is consistent with both species, comprising a one-electron reversible redox couple, eq 2, with $E_{1/2} = 0.18$ V vs. SCE.

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Registry No. $(NH_4)_2[Tc(NCS)_6]$, 72622-85-6; $(Ph_4As)_2[Tc(NCS)_6]$, 71128-60-4; $(n\text{-}Bu_4N)_3[Tc(NCS)_6]$, 72622-87-8; $(Ph_4As)_3[Tc(NCS)_6]$, 72622-88-9; $(n\text{-}Bu_4N)_2[Re(NCS)_6]$, 16985-65-2; NH_4SCN, 1762-95-4; $(NH_4)_2[TcBr_6]$, 29462-54-2; $(NH_4)_2[TcCl_6]$, 18717-26-5; NH_4TcO_4, 13598-66-8; TcO_2, 12036-16-7.

Supplementary Material Available: Tables S1–S3 listing respectively observed and calculated structure factor amplitudes, the root-mean-square amplitudes of thermal vibration along principal axes, and the hydrogen atom positional and thermal parameters (8 pages). Ordering information is given on any current masthead page.

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Contribution No. 3378 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Complexes of (Arylimido)molybdenum(V)

A. WINSTON EDELBLUT and R. A. D. WENTWORTH*

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The preparations of the paramagnetic Mo(V) complexes $Mo(NR)(S_2P(OEt)_2)_3$ and $Mo(NR)Cl(S_2P(OEt)_2)_2$ (R = Ph and tol) from $Mo(CO)_4Cl_2$, $NH_4S_2P(OEt)_2$, and the aryl azides are described. The stability of the imido ligand in each complex to protonation is demonstrated. The isotropic ESR spectra of these complexes are notable. Every ligand in these complexes contains a magnetic nucleus (^{14}N, ^{31}P, and $^{35,37}Cl$), and coupling to each of these nuclei is manifested in the ESR spectra. Superhyperfine coupling constants are obtained unambiguously, however, only after ^{15}N labeling. Stereochemistries cannot be deduced with certainty either from ESR or infrared spectra or from chemical evidence. The reaction of $Mo(Ntol)(S_2P(OEt)_2)_3$ with H_2S produces the unusual tetranuclear compound $[Mo(Ntol)S(S_2P(OEt)_2)]_4$. The equilibrium constant relating this complex to the dinuclear compound has been determined. A rationalization of the tetranuclear nature of the compound is discussed, and a structure is suggested.

Introduction

The affinity of the oxo ligand for molybdenum in its higher oxidation states is well-known.[1,2] Simple arguments concerning the participation of the metal's d orbitals in π bonding with this ligand provide an adequate explanation for stereochemistry as well as bond distances, stretching force constants, and ^{17}O chemical shifts.[3,4] Recently, we recognized that one or more NR (R = H, alkyl, or aryl) ligands should bind to molybdenum in a manner which is fundamentally equivalent to the binding of an identical number of oxo ligands since each

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type of ligand can serve as either a two- or a four-electron donor in terms of the EAN rule.[5,6] This equivalence suggests that a homologous series of complexes could be realized. Indeed, we have postulated the transitory existence of $MoO(NH)(S_2CNEt_2)_2$[7] and demonstrated the existences of $Mo(NR)_2(S_2CNEt_2)_2$ (R = Ph[5,6,8] or tol[6,8]), $MoO(NPh)(S_2CNEt_2)_2$,[6] $Mo(NR)Cl_2(S_2CNEt_2)_2$,[6] and $Mo_2O_3(NH)(S_2P(OEt)_2)_2 \cdot THF$.[9] The analogous oxo complexes are $MoO_2(S_2CNEt_2)_2$, $MoOCl_2(S_2CNEt_2)_2$, and $Mo_2O_4(S_2P(OEt)_2)_2$. Although the latter is unknown, the corresponding dithiocarbamates are well-known. Other analogies exist between $Mo(NR)(S_2CNEt_2)_3^+$ (R = Me[10] and Ph[6]) and $MoO(S_2CNEt_2)_3^+$[11] as well as within the chemistries of rhenium[12] and osmium.[13]

Because of our successful preparation of $Mo(NR)_2(S_2CNEt_2)_2$ (R = Ph or tol) from $Mo(CO)_2(S_2CNEt_2)_2$ and the corresponding aryl azides,[5,6] we were interested in similar reactions employing dithiophosphate ligands with the recognition that $MoO_2(S_2P(OR)_2)_2$ does not appear to have an independent existence.[14] However, we recognized that the Mo(V) complexes $MoOCl(S_2P(OR)_2)_2$ and $MoO(S_2P(OR)_2)_3$ have been prepared in solution and characterized by their ESR spectra.[15] The results of our investigation are reported herein.

Experimental Section

Reagents and Procedures. The ammonium salt of diethyldithiophosphoric acid was used without further purification while the aryl azides PhN_3 and $tolN_3$ were prepared as previously described.[6] Labeling the aryl azides with ^{15}N was accomplished by the conversion of $Ph^{15}NH_2$ (99 atom %; Stohler Chemical) to $Ph^{15}N^{14}NPF_6$ in 84% yield by a reaction with $^{14}NO_2^-$.[16] The labeled diazonium salt was then converted to $Ph^{15}N^{14}N^{14}N$ in quantitative yield through the stereospecific[17] reaction with $^{14}N_3^-$. An established method[18] was used to prepare $Mo(CO)_4Cl_2$. All subsequent reactions were routinely performed under an argon atmosphere. Solvents were dried and distilled directly into the reaction vessels.

$Mo(NR)(S_2P(OEt)_2)_3$ (R = Ph or tol). The preparations of these complexes were accomplished by the slow addition of $Mo(CO)_4Cl_2$ (11 mmol) to a heterogeneous mixture of $NH_4S_2P(OEt)_2$ (10 g) and aryl azide (17 mmol) in 100 mL of ether. After 24 h, the solution was filtered and the solvent was removed under reduced pressure. Crystallization of the remaining oil occurred on the addition of 75 mL of methanol. Bronze crystals (about 35%) were obtained after recrystallization from CH_2Cl_2/methanol. Anal. Calcd for $Mo(NPh)(S_2P(OEt)_2)_3$: C, 29.1; H, 4.7; S, 25.9; N, 1.8. Found: C, 28.8; H, 4.8; S, 25.9; N, 1.9. Calcd for $Mo(Ntol)(S_2P(OEt)_2)_3$: C, 30.2; H, 4.9; S, 25.4; N, 1.9; mol wt 757. Found: C, 30.3; H, 4.9; S, 25.2; N, 1.8; mol wt (osmometry) 743 ± 6. Magnetic moment (CH_2Cl_2, 33 °C): 1.5 μ_B. IR (Nujol): (R = Ph) 1290 (w), 1158 (w), 1102 (w), 1051 (m), 1011 (s), 952 (s), 812 (s), 798 (s), 770 (s), 685 (w), 651 (s), 635 (s), 539 (w), 515 (m), 298 (m) cm^{-1}; (R = tol) 1292 (w), 1163 (m), 1102 (w), 1047 (s), 1015 (s), 1002 (s), 972 (s), 945 (s), 815 (s), 780 (s), 645 (s), 634 (s), 549 (w), 535 (w), 522 (w), 312 (w) cm^{-1}. The spectrum between 380 and 1600 nm consisted of a single band at 462 nm (ϵ 2150). The infrared spectrum of $Mo(^{15}NPh)(S_2P(OEt)_2)$ was not perceptibly different from the spectrum described above with the exception that the weak band at 539 cm^{-1} shifted to 534 cm^{-1}.

$Mo(NR)Cl(S_2P(OEt)_2)_2$ (R = Ph or tol). A solution of $Mo(NR)(S_2P(OEt)_2)_3$ (1.2 mmol) in 20 mL of ether was stirred under gaseous HCl (4 mmol) until a yellow-green color appeared (about 15 min). The solvent was removed under reduced pressure, and the yellow oil was stirred with pentane to remove the protonated ligand and to cause solidification. Recrystallization of this product from CH_2Cl_2/methanol gave a yellow powder (about 85%). Anal. Calcd for $Mo(NPh)Cl(S_2P(OEt)_2)_2$: C, 28.4; H, 4.2; S, 21.6; N, 2.4; Cl, 6.0. Found: C, 28.3; H, 4.2; S, 19.5; N, 2.3; Cl, 5.9. Calcd for $Mo(Ntol)Cl(S_2P(OEt)_2)_2$: C, 29.7; H, 4.5; S, 21.1; N, 2.3; mol wt 607. Found: C, 29.6; H, 4.5; S, 20.9; N, 2.2; mol wt (MS) 607. Magnetic moment (CH_2Cl_2, 33 °C): 1.5 μ_B. IR (Nujol): (R = Ph) 1290 (w), 1160 (w), 1100 (w), 1050 (m), 1000 (s), 980 (s), 812 (s), 795 (m), 760 (m), 680 (w), 635 (s), 542 (w), 522 (w), 385 (w), 362 (w), 305 (m) cm^{-1}; (R = tol) 1295 (w), 1164 (m), 1102 (w), 1052 (m), 1001 (s), 970 (s), 816 (s), 794 (s), 776 (m), 642 (s), 525 (m), 428 (m), 360 (w), 308 (m) cm^{-1}. The spectrum between 380 and 1600 nm consisted of a very narrow band at 1410 nm (ϵ 7) which is undoubtedly part of the vibrational spectrum. The infrared spectrum of $Mo(^{15}NPh)Cl(S_2P(OEt)_2)_2$ was identical with that described above except that the weak bands at 542 and 385 cm^{-1} were shifted to 533 and 376 cm^{-1}.

Alternatively, $Mo(CO)_4Cl_2$ (11 mmol) was allowed to react with the aryl azide (17 mmol) and $NH_4S_2P(OEt)_2$ (4.5 g) in 100 mL of ether for about 24 h. The product was obtained from the yellow solution by the method described above.

$[Mo(Ntol)S(S_2P(OEt)_2)]_4$. When a solution of $Mo(Ntol)(S_2P(OEt)_2)_3$ (2 mmol) and $tolN_3$ (2 mmol) in 10 mL of dry methanol was refluxed, the burgundy red product precipitated from the resulting green solution. After the product was washed with methanol, it was recrystallized from CH_2Cl_2/methanol. A yield of about 10% was realized. The presence of $tolN_3$ is not essential to this reaction, but it does optimize the yield. Anal. Calcd for $[Mo(Ntol)S(S_2P(OEt)_2)]_4$: C, 31.6; H, 4.1; S, 23.0; N, 3.4; mol wt 1673. Found: C, 31.6; H, 4.1; S, 22.8; N, 3.3; mol wt (osmometry, ~0.025 M) 1623 ± 20. ^1H NMR (CD_2Cl_2): δ 0.81 (3 H, t, CH_3), 1.53 (3 H, t, CH_3), 2.00 (3 H, s, aryl CH_3), 3.64 (2 H, m, OCH_2), 4.52 (2 H, m, OCH_2), 6.26 (4 H, q, aryl H). ^{31}P NMR (CD_2Cl_2): 111.0 (s) ppm. IR (Nujol): 1320 (m), 1160 (w), 1098 (w), 1030 (s), 1010 (s), 1053 (s), 811 (m), 768 (m), 642 (m), 532 (w), 431 (w), 311 (w), 294 (w), 273 (w) cm^{-1}.

A better preparative method involved the reaction of $Mo(Ntol)(S_2P(OEt)_2)_3$ (1.3 mmol) with H_2S (1 atm) in 25 mL of methanol for 8 h. After recrystallization, the yield was 53%.

Physical and Analytical Methods. The molecular weights of $Mo(Ntol)(S_2P(OEt)_2)_3$ and $[(Ntol)MoS(S_2P(OEt)_2)]_4$ were determined by osmometry in 1,2-$C_2H_4Cl_2$ using a Mechrolab 301A instrument operating at 37 °C, while that of $Mo(Ntol)Cl(S_2P(OEt)_2)_2$ was obtained from its mass spectrum by using a Varian Associates CH 7 mass spectrometer. Infrared spectra were obtained from Nujol mulls between CsI plates by using a Perkin-Elmer 283 infrared spectrometer. A Varian Associates HR-220 NMR spectrometer was used for ^1H NMR measurements with Me_4Si as the internal reference. The ^{31}P NMR spectrum, measured downfield from external H_3PO_4, was obtained on a Varian Associates XL-100 spectrometer. Magnetic moments were determined by using the method of Evans.[19] Spectra were obtained at 33 ± 1 °C by using a Varian Associates T-60 spectrometer with CH_2Cl_2 as the solvent and internal reference. The molar susceptibility in each case was corrected for diamagnetism. ESR spectra of CH_2Cl_2 solutions containing Mo(V) complexes were recorded on a Varian Associates E-Line Century Series spectrometer operating near 9.1 GHz. The frequency was determined with a Hewlett-Packard 5248L electronic counter in conjunction with DPPH as a field marker. Degassed solutions were cooled in a nitrogen stream at temperatures which are accurate to ±1 °C. Superhyperfine coupling constants were obtained by using the program ESRCON.[20] This

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Table I. Possible Superhyperfine Coupling Constants (G)

		^{14}N compd				^{15}N compd				
compd	case[a]	$A(^{14}N)$	$A(^{31}P')$	$A(^{31}P'')$	$A(^{35,37}Cl)$	$A(^{15}N)$	$A(^{31}P')$	$A(^{31}P'')$	$A(^{35,37}Cl)$	$A(^{15}N)/A(^{14}N)$
$Mo(NPh)Cl(S_2P(OEt)_2)_2$	a	3.72	1.88		2.11	5.37	1.94		2.24	1.45
	b	1.94	5.56		2.08	1.94	5.37		2.24	1.00
$Mo(NPh)(S_2P(OEt)_2)_3$	c	3.61	1.62	1.62		5.06	1.64	1.64		1.40
	d	1.80	5.41	1.46		(1.64)[b]	(5.06)[b]	(1.64)[b]		0.91

[a] The possible coupling assignments are delineated in the text. [b] Obtained by interchanging the assignments from (c).

Table II. Isotropic ESR Parameters for $Mo(NR)Cl(S_2P(OEt)_2)_2$ and $Mo(NR)(S_2P(OEt)_2)_3$ in CH_2Cl_2

compd	R	g	$A(^{95,97}Mo)$, G	$A(^{31}P)$, G	$A(^{31}P')$, G	$A(^{31}P'')$, G	$A(^{35,37}Cl)$, G	$A(^{14}N)$, G	T, °C
$Mo(NR)Cl(S_2P(OEt)_2)_2$	Ph	1.971	45	49.1	1.9		2.1	3.7	−51
	tol	1.971	46	52.5	1.9		2.1	3.7	−48
$Mo(NR)(S_2P(OEt)_2)_3$	Ph	1.975	43	44.9	1.6	1.6		3.6	−51
	tol	1.980	41	46.0	1.6	1.7		3.7	−54

program optimizes approximate coupling constants and line widths obtained directly from a spectrum by a least-squares fit. Simulated spectra were then constructed for visual comparison.

Elemental (C, H, N, and S) analyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tenn. The chloride analysis was obtained by first digesting the sample in basic peroxide solution followed by standard gravimetric procedures.

Discussion of Results

Reactions. The oxidation of $Mo(CO)_4Cl_2$ with excess quantities of RN_3 (R = Ph or tol) in the presence of $(NH_4)S_2P(OEt)_2$ gives high yields of the Mo(V) complex $Mo(NR)(S_2P(OEt)_2)_3$ (1.5 μ_B). Reactions of these compounds with HCl in CH_2Cl_2 result in $Mo(NR)Cl(S_2P(OEt)_2)_2$ (1.5 μ_B) as shown in eq 1. This compound can also be prepared

$$Mo(NR)(S_2P(OEt)_2)_3 + HCl \rightarrow Mo(NR)Cl(S_2P(OEt)_2)_2 + HS_2P(OEt)_2 \quad (1)$$

by the oxidation of $Mo(CO)_4Cl_2$ with excess RN_3 in the presence of salts of $S_2P(OEt)_2^-$. When solutions of $Mo(Ntol)(S_2P(OEt)_2)_3$ in methanol are allowed to stand for long periods of time, small quantities of a diamagnetic, tetranuclear compound, $[Mo(Ntol)S(S_2P(OEt)_2)]_4$, precipitate. Other products are unknown. For reasons we do not understand, somewhat better yields are obtained if $tolN_3$ is also present. However, a straightforward preparation of this compound in relatively high yield can be obtained from the reaction of $Mo(Ntol)(S_2P(OEt)_2)_3$ with H_2S in methanol as shown in eq 2.

$$Mo(NR)(S_2P(OEt)_2)_3 + H_2S \rightarrow \tfrac{1}{4}[Mo(NR)S(S_2P(OEt)_2)]_4 + 2HS_2P(OEt)_2 \quad (2)$$

The reaction of $Mo(NR)(S_2P(OEt)_2)_3$ with HCl to produce $Mo(NR)Cl(S_2P(OEt)_2)_2$ illustrates the stability of the imido groups in both the reactant and the product to protonation. Moreover, the reactions shown in eq 1 and 2 follow a straightforward pattern. While the monoprotic acid causes the removal of only one dithiophosphate ligand, two are removed by the diprotic acid. The lability of this ligand under acidic conditions has been previously observed in the ligand-exchange reaction between $MoO(S_2P(OEt)_2)_2$ and $MoO(S_2P(OMe)_2)_2$ which occurs in CH_2Cl_2 only when HCl has been added.[21]

ESR Spectroscopy. The isotropic ESR spectrum of each of the paramagnetic complexes was obtained in CH_2Cl_2 near −50 °C, the highest temperature which afforded maximum resolution of the superhyperfine lines.

The spectra of $Mo(NR)Cl(S_2P(OEt)_2)_2$ (R = Ph and tol) are very similar (see Figure 1 for R = Ph). Each consists of the usual hyperfine lines due to $^{95,97}Mo$ superimposed on a doublet due to superhyperfine coupling to a phosphorus nucleus (^{31}P). We find $g = 1.971$, $A(^{95,97}Mo) = 45$ G, and $A(^{31}P) = 49.0$ G for $Mo(NPh)Cl(S_2P(OEt)_2)_2$. Each component of the doublet is further divided into nine lines, as shown in Figure 1, with an approximate intensity distribution of 1:2:3:4:4:4:3:2:1 and a spacing of about 2.1 G. This pattern can only result from coupling to the other phosphorus nucleus ($^{31}P'$), the ^{14}N nucleus of the imido ligand, and the $^{35,37}Cl$ nuclei. Resolution of the superhyperfine lines due to the different isotopes of the Cl atom was not obtained here nor was it obtained with $MoOCl(S_2P(OEt)_2)_2$.[15] As shown by the stick diagrams in Figure 2, there are two possible assignments which lead to a nine-line spectrum with the correct intensity distribution: (a) $A(^{31}P') \approx A(^{35,37}Cl) \approx {}^{1}/_{2}A(^{14}N) \approx 2.1$ G and (b) $A(^{35,37}Cl) \approx A(^{14}N) \approx {}^{1}/_{3}A(^{31}P') \approx 2.1$ G. Further refinement by computer led to the parameters given in Table I. Each assignment leads to an accurate simulation of the observed spectrum (Figure 1). This dilemma was successfully resolved by ^{15}N labeling. The change in nuclear spin will lead to changes in the pattern of superhyperfine lines, but, more importantly, it will do so in an entirely predictable manner since the ratio of the nuclear g values leads to $A(^{15}N)/A(^{14}N) = 1.40$. As shown in Figure 3 for the low-field portion of the principal doublet, a pattern of seven lines was obtained with an intensity distribution of approximately 1:2:3:4:3:2:1 and a splitting of approximately 2.3 G. The original superhyperfine coupling constants shown in Table I were then used as starting points for the computer's solution of the assignments. Although convergence was obtained in both instances without major modification of either $A(^{31}P')$ or $A(^{35,37}Cl)$, $A(^{15}N)/A(^{14}N)$ is 1.45 for (a) and 1.00 for (b). Clearly, (a) is the correct assignment. Complete details of both spectra are given in Table II. The parameters for $MoOCl(S_2P(OEt)_2)_2$, which are $g = 1.962$, $A(^{95,97}Mo) = 46$ G, $A(^{31}P) = 43$ G, and $A(^{35,37}Cl) = 3.5$ G,[15] are in reasonable agreement with those obtained from the imido complexes. Resolution of additional superhyperfine lines due to the remaining phosphorus atom in the oxo complex was not obtained.[15]

Complexes corresponding to $Mo(NR)(S_2P(OEt)_2)_3$ also afford very similar spectra. The most prominent feature in each spectrum is again a doublet as shown in Figure 4 for R = Ph. We obtained $g = 1.975$, $A(^{95,97}Mo) = 43$ G, and $A(^{31}P) = 45.1$ G for this complex. Each component of the doublet consists of seven lines with an approximate intensity distribution of 1:2:2:2:2:2:1 and a spacing of approximately 1.8 G. Two interpretations are again possible: (c) $A(^{31}P') \approx A(^{31}P'') \approx {}^{1}/_{2}A(^{14}N) \approx 1.8$ G or (d) $A(^{31}P'') \approx A(^{14}N) \approx {}^{1}/_{3}A(^{31}P') \approx 1.8$ G. Stick diagrams for each of these assignments are shown in Figure 2. Further refinement by computer led to the results shown in Table I. After ^{15}N labeling, this portion

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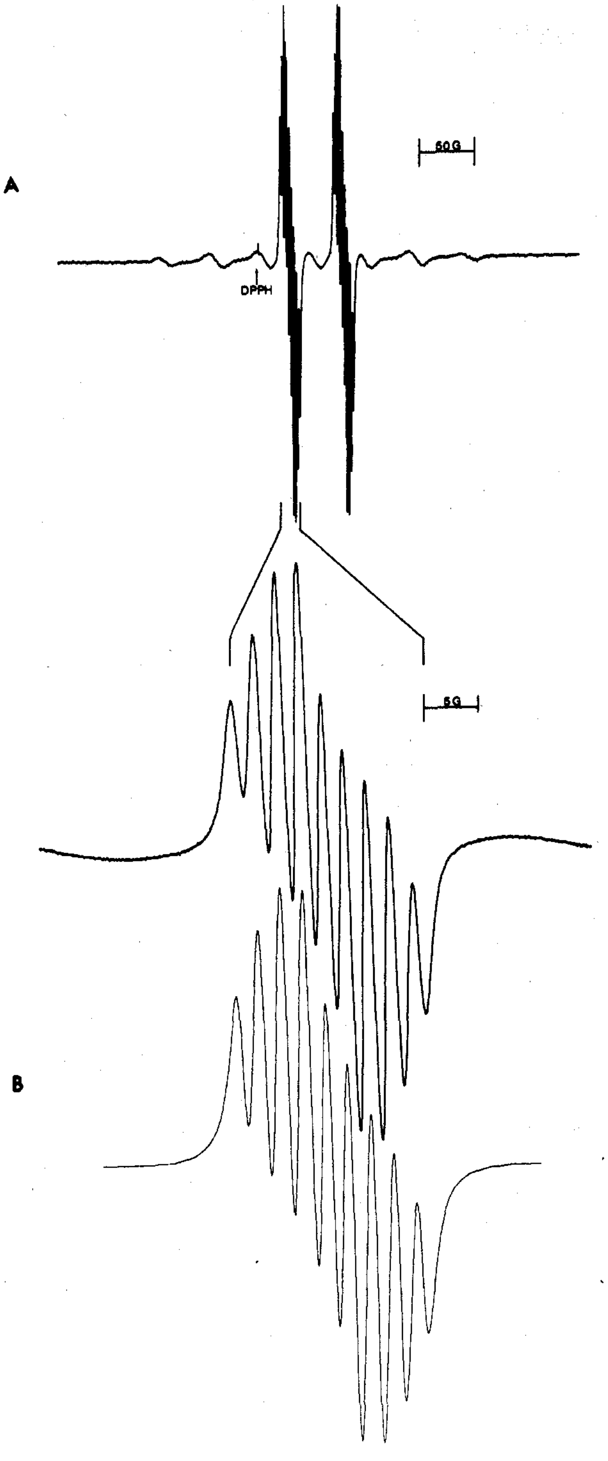


Figure 1. Observed (A) and calculated (B) ESR spectra of Mo(NPh)Cl($S_2P(OEt)_2)_2$ at -51 °C in CH_2Cl_2.

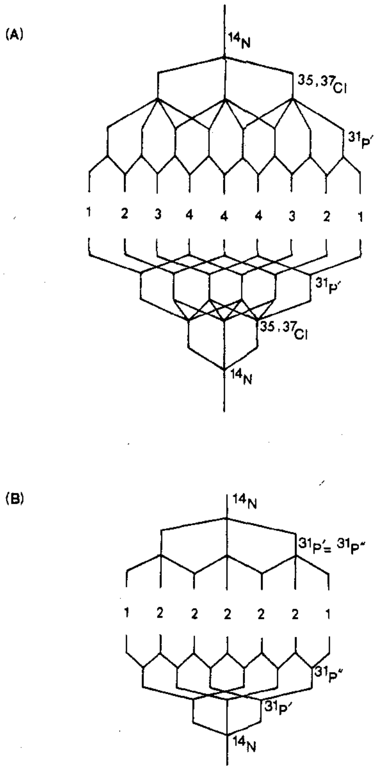


Figure 2. Possible spectroscopic assignments for (A) Mo(NR)Cl($S_2P(OEt)_2)_2$ and (B) Mo(NR)($S_2P(OEt)_2)_3$ which lead to the observed spectra.

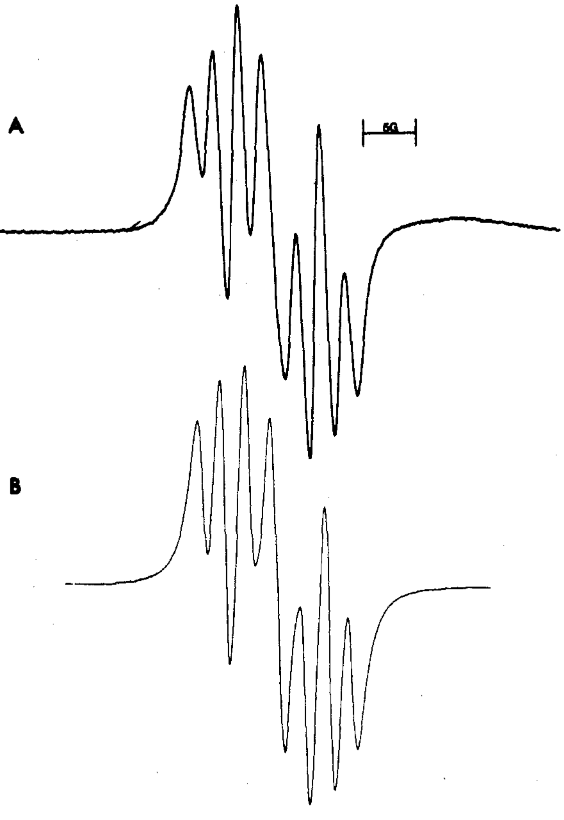


Figure 3. Observed (A) and calculated (B) low-field components of the principal doublet in the ESR spectrum of Mo(^{15}NPh)Cl($S_2P(OEt)_2)_2$.

of the spectrum (Figure 5) consists of two triplets with the larger splitting being about 5.4 G and the smaller splittings being about 1.6 G. While two assignments of this spectrum are possible in principle (Table I), only the one stemming from (c) leads to the expected ratio of $A(^{15}N)/A(^{14}N) = 1.40$. As shown in Table II, the spectra of Mo(NPh)($S_2P(OEt)_2)_3$ and Mo(Ntol)($S_2P(OEt)_2)_3$ yield similar g values and coupling constants. The ESR spectrum of MoO($S_2P(OEt)_2)_3$ also consists of a doublet.[15] No other superhyperfine coupling was observed and, strangely, neither the values of g nor $A(^{31}P)$ were reported.

Each ligand in Mo(NR)Cl($S_2P(OEt)_2)_2$ and Mo(NR)($S_2P(OEt)_2)_3$ contains an atom which possesses a nuclear spin. The ESR spectra which we have obtained represent rare examples in which the influences of each ligand in the coordination sphere are manifested in the spectra. Moreover, we note that the isotropic g values for the imido complexes are

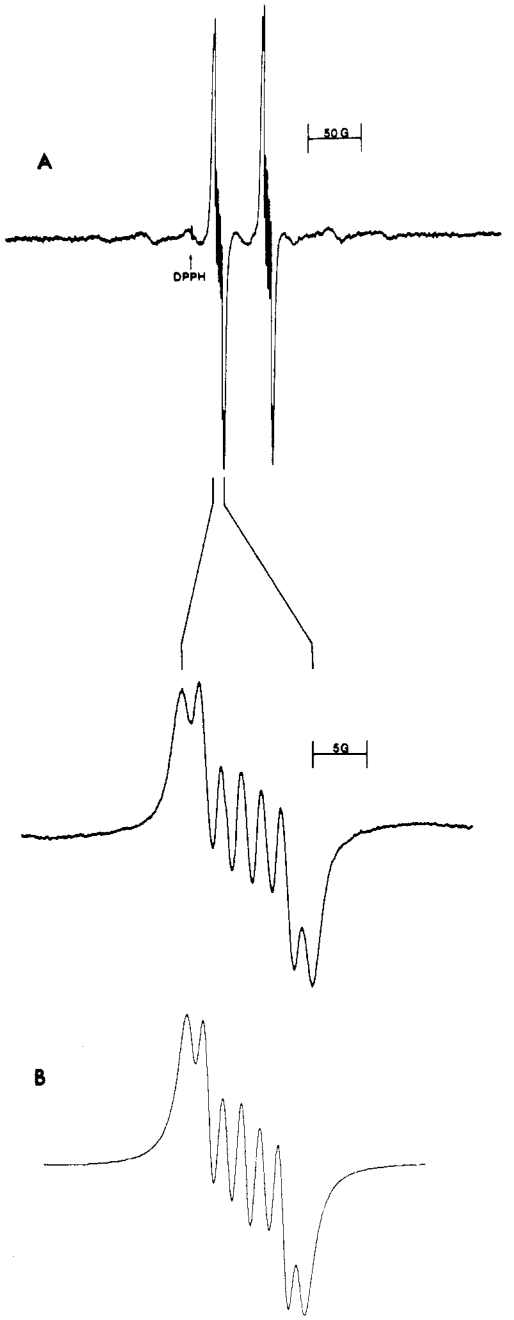


Figure 4. Observed (A) and calculated (B) ESR spectra of Mo$(NPh)(S_2P(OEt)_2)_3$ at −51 °C in CH_2Cl_2.

similar to those found for xanthine, aldehyde, and sulfite oxidases while the isotropic values of $A(^{95,97}Mo)$ are similar to those found in xanthine and sulfite oxidases as well as nitrate reductase.[2] However, no similarity in structure can be inferred or is intended from this comparison.

Stereochemistry of Mononuclear Complexes. Both $MoOCl(S_2P(OEt)_2)_2$ and $Mo(NR)Cl(S_2P(OEt)_2)_2$ can be viewed as octahedral complexes with 17-electron configurations. The oxo and imido ligands function as four-electron donors, which suggests the bonding patterns given by **1** and **2**. While complexes containing **1** are well-known,[22] $[(\eta^5$-

$$\underset{\mathbf{1}}{\mathrm{Mo{\equiv}O}} \qquad \underset{\mathbf{2}}{\mathrm{Mo{\equiv}N{-}R}}$$

$C_5H_5)Mo(NR)S]_2$,[23] $Mo(Ntol)Cl_2(PhCONNtol)(PMe_2Ph)$,[24] and $Mo(NPh)Cl_2(S_2CNEt_2)_2$[25] are the only authenticated examples containing **2** although corresponding rhenium complexes are known.[26] Since a remarkable feature of the imido complexes containing **2** is the absence of an appreciable trans effect, five-coordination and a 15-electron configuration would seem to be a more unlikely possibility for $Mo(NR)Cl(S_2P(OEt)_2)_2$. Furthermore, crystallographic studies[27] have demonstrated cis-octahedral coordination in $MoOCl(tox)_2$ (tox = 8-mercaptoquinolate) even though the oxo ligand exerts a rather large trans effect.

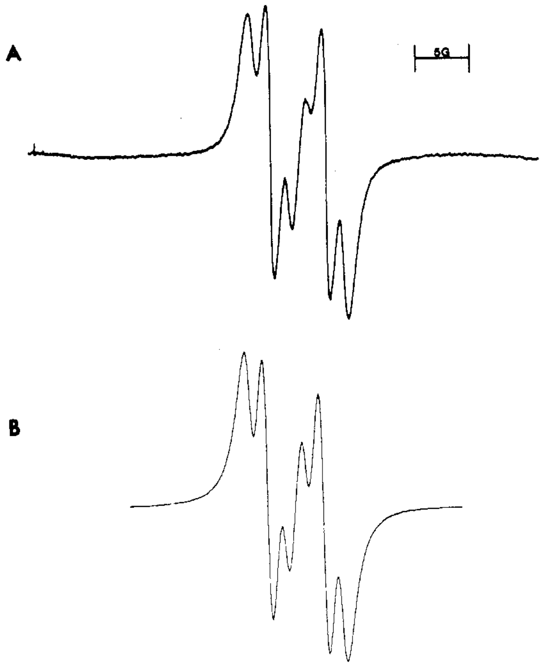
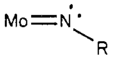


Figure 5. Observed (A) and calculated (B) low-field components of the principal doublet in the ESR spectrum of $Mo(^{15}NPh)(S_2P(OEt)_2)_3$.

Structural possibilities for $Mo(NR)(S_2P(OEt)_2)_3$ are more varied, and, unfortunately, no structurally characterized precedents exist. Coordination numbers of 5 and 6 with two or one dangling ligands are again possible and would again lead to 15- and 17-electron configurations. However, seven-coordinate structures must also be examined. Seven-coordinate d^0 complexes corresponding to M(monodentate)(bidentate)$_3$ appear to favor a somewhat distorted pentagonal bipyramid.[28,29] If an additional electron is introduced into either a nonbonding or weakly antibonding orbital, this geometry may continue to prevail for the d^1 complex. Although the d_{xz} and d_{yz} orbitals of a regular pentagonal bipyramid are degenerate, the Jahn–Teller theorem requires the stabilization of one of these orbitals in a d^1 complex. Cylindrically symmetric π bonding will then be destroyed, and electron density will inevitably be shifted to the nitrogen atom. The limiting structure, which would have a 17-electron configuration, would include **3**. However, the geometry of the poorly characterized



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d^1 complex $Ti(CN)_7^{4-}$ has been inferred to be a capped trigonal

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[22] See ref 1, 2, and 4 for example.

[23] L. F. Dahl, P. D. Frisch, and G. R. Gust, *J. Less-Common Met.*, **36**, 255 (1974).

[24] M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, S. A. A. Jayaweera, and A. Quick, *J. Chem. Soc., Dalton Trans.*, 914 (1979).

[25] E. A. Maatta, B. L. Haymore, and R. A. D. Wentworth, unpublished results.

[26] D. Bright and J. A. Ibers, *Inorg. Chem.*, **7**, 1099 (1968); **8**, 703 (1969).

[27] K. Yamanouchi and J. H. Enemark, *Inorg. Chem.*, **18**, 1626 (1979).

[28] R. Hoffmann, B. F. Beier, E. L. Muetterties, and A. R. Rossi, *Inorg. Chem.*, **16**, 511 (1977).

[29] M. G. B. Drew, *Prog. Inorg. Chem.*, **23**, 67 (1977).

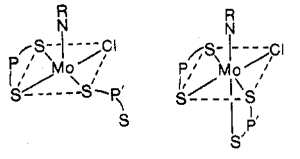

Figure 6. Possible structures for $Mo(NR)Cl(S_2P(OEt)_2)_2$.

prism with the cap over a tetragonal face of the prism.[30] Since the d_{xz} and d_{yz} orbitals cannot be degenerate in this geometry,[28] cylindrically symmetric π bonding cannot occur. A bent imido ligand (**3**) and a 17-electron configuration may then result.

Although the isotropic g values indicate that the ground states of $Mo(NR)Cl(S_2P(OEt)_2)_2$ and $Mo(NR)(S_2P(OEt)_2)_3$ are orbital singlets, they are to be expected in any case because of the Jahn–Teller theorem. Some structural differentiation is possible, however, from the magnitudes of the superhyperfine coupling constants with the use of an approach described by others.[31] The magnitude of $A(^{31}P)$ obtained for $Mo(NR)Cl(S_2P(OEt)_2)_2$ is in accord with the square pyramid or the cis octahedron in Figure 6. The electronic configuration for each structure would include a half-filled d_{xy} orbital. The spectrum of the corresponding oxo complex was previously interpreted in terms of the cis octahedron.[15,32] A doublet in the ESR spectrum of $MoOCl(S_2(i\text{-}Pr)_2)_2$ with $A(^{31}P) = 26$ G has also been interpreted[33] in terms of this geometry while the spectrum of $MoO(S_2P(i\text{-}Pr)_2)(o\text{-}OC_6H_4S)$, a complex which is almost certainly square pyramidal, also consists of a doublet with $A(^{31}P) = 38$ G.[31] These geometries do not allow direct coupling to either $^{31}P'$ or ^{14}N in the imido complexes so that rather small superhyperfine coupling constants for these nuclei should result. Indirect coupling either by spin polarization through appropriate bonds or by the inclusion of other symmetry-allowed orbitals in the ground state must be involved.

The criteria for the structure of $Mo(NR)(S_2P(OEt)_2)_3$ are also easily delineated. The structure must possess a ground state which permits strong coupling with the unique ^{31}P nucleus, weaker but apparently equivalent coupling with $^{31}P'$ and $^{31}P''$, and weak coupling with ^{14}N. Moreover, the structure must permit nearly identical values of $A(^{95,97}Mo)$, $A(^{31}P)$, $A(^{31}P')$, and $A(^{14}N)$ for both $Mo(NR)Cl(S_2P(OEt)_2)_2$ and $Mo(NR)(S_2P(OEt)_2)_3$ as shown in Table II. Four structures which appear to fulfill these criteria for the most part are shown in Figure 7. Although it is possible that the structures of $Mo(NR)Cl(S_2P(OEt)_2)_2$ and $Mo(NR)(S_2P(OEt)_2)_3$ are based on identical polyhedra because of the close similarity of all spectroscopic parameters, none of the structures in Figure 7 are readily dismissed. Although the cis octahedron has been suggested[15] for $MoO(S_2P(OEt)_2)_3$ apparently on the sole basis of the superhyperfine doublet in the ESR spectrum, this feature should also result from each of the structures in Figure 7.

A half-filled d_{xy} orbital with strong coupling to ^{31}P is again expected from either the square pyramid with two dangling ligands or the cis octahedron with one dangling ligand. The plane of symmetry in the former allows $A(^{31}P') = A(^{31}P'')$. This criterion is also exactly fulfilled with the cis octahedron providing the molecule is fluxional on the ESR time scale. Although we have examined the ESR spectra of $Mo(NPh)(S_2P(OEt)_2)_3$ in solutions of CH_2Cl_2 and Freon-22 at temperatures ranging from −50 to −100 °C, we have failed to detect a fluxional process.[34] If we assume that a fluxional process is operative, that the signs of $A(^{31}P')$ and $A(^{31}P'')$ are identical, that $A(^{31}P')$ obtained from the spectrum of $Mo(NR)Cl(S_2P(OEt)_2)_2$ has the same sign, and that its magnitude of 1.9 G is indicative of the geometric location of $^{31}P'$ within the cis octahedron of Figure 6, we would then expect to find $A(^{31}P') \approx 1.9$ G and $A(^{31}P'') \approx 1.3$ G in the slow-exchange region. Because our resolution is probably no better than about 1 G, a fluxional process could remain undetected since little spectroscopic differences would occur between the fast-exchange and slow-exchange regions.[35] Alternatively, it is possible that our original assignment of $A(^{31}P') = A(^{31}P'') = 1.6$ G is merely an artifact brought about by a fitting procedure which utilizes lines of equal width. A static molecule with $A(^{31}P') \approx 1.9$ G and $A(^{31}P'') \approx 1.3$ G then becomes a real possibility which is not invalidated by our ^{15}N-labeling studies. Although the fluxionality of $Mo(NR)(S_2P(OEt)_2)_3$ remains as an interesting question, it is clear that it is not a question which must be given great weight in discussing the possible stereochemistry of these compounds.

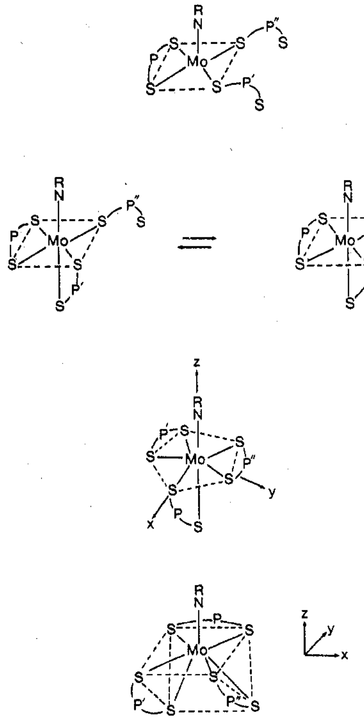

Figure 7. Possible structures for $Mo(NR)(S_2P(OEt)_2)_3$.

The only seven-coordinate structures which will satisfy the necessary criteria exactly are the pentagonal bipyramid and capped trigonal prism shown in Figure 7. The imido ligand occupies an apical site in each structure so that each possesses

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(30) D. Nicholls, T. A. Ryan, and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 635 (1974).

(31) E. I. Stiefel, W. E. Newton, and N. Pariyadath, *J. Less-Common Met.*, **54**, 513 (1977).

(32) Since trans effects due to oxo ligands are large while those due to **2** are virtually nonexistent, square-pyramidal coordination is more likely in $MoOCl(S_2P(OEt)_2)_2$ than in its imido analogues.

(33) J. W. McDonald, *Inorg. Chim. Acta*, **35**, 93 (1979).

(34) Although the appearance of the superhyperfine spectrum is slightly different at the lowest temperatures, each member of the principal doublet is again composed of seven lines. The spectrum was simulated successfully with $A(^{14}N) = 3.7$ G, $A(^{31}P') = A(^{31}P'') = 1.4$ G, and a slight decrease in the average line width from 1.5 to 1.3 G.

(35) If, however, $A(^{31}P')$ and $A(^{31}P'')$ are of opposite sign, then, taking the former to be positive, we would expect that $A(^{31}P') \approx 1.9$ G and $A(^{31}P'') \approx -5.1$ G in the slow-exchange region. Nine of the expected 12 lines should be easily observed. Our results indicate that, if a fluxional process were occurring in a system in which $A(^{31}P')$ and $A(^{31}P'')$ were of opposite sign, fast exchange ($k \approx 10^9$ s^{-1} or greater) would still be operative near −100 °C. In contrast, the faster of two fluxional processes in $Fe(\eta^3\text{-cyclooctenyl})(P(OMe)_3)_3$, the only known example of a transition-metal complex which is fluxional on the ESR time scale (S. D. Ittel, P. J. Krusic, and P. Meakin, *J. Am. Chem. Soc.*, **100**, 3264 (1978)), occurs with a rate constant of approximately 10^8 s^{-1} at −100 °C. It is very unlikely that the activation barrier would be lower for a fluxional process involving a six-coordinate molybdenum complex than for one involving a five-coordinate iron complex.

C_s symmetry. The unpaired electron will be found in the $d_{x^2-y^2}$ orbital in the capped trigonal prism,[28] and we have assumed[36] that it would be found in the d_{xz} orbital in the pentagonal bipyramid. Substantial bending of the imido ligand would be implied in both cases. Although the d_{xz} and d_{yz} orbitals are strongly coupled by spin–orbit interactions, the lack of a strong g shift indicates that a large difference in the energies of these orbitals would necessarily exist if the structure of the compound were pentagonal bipyramidal. This interpretation would also be supported by the absence of any ligand field bands below 20 000 cm^{-1} in the absorption spectrum. If the compound were a capped trigonal prism, on the other hand, a large difference in the energies of the d_{xz} and d_{yz} orbitals must occur because the former is heavily involved in σ bonding.[28] Since overlap of the half-filled orbital on the metal atom and the 2s orbital of the nitrogen atom is zero in each geometry regardless of the actual degree of bending, no direct contribution to the isotropic value of $A(^{14}N)$ may occur. Additional seven-coordinate structures may become possible if the restriction $A(^{31}P') = A(^{31}P'')$ is relaxed as with the cis octahedron.

Two other lines of evidence are also available. First, the imido ligands in $Mo(NR)Cl(S_2P(OEt)_2)_2$ and $Mo(NR)(S_2P(OEt)_2)_3$ are remarkably stable to protonation. According to previous results with dithiocarbamate complexes, this stability could indicate the inert[6] linkage in **2** and either square-pyramidal or octahedral geometry in each of the Mo(V) complexes. However, it is equally possible that $Mo(NR)(S_2P(OEt)_2)_3$ is seven-coordinate with a bent imido ligand and with appreciable electron density on the nitrogen atom, providing one or more of the ligating sulfur atoms are inherently more basic sites for protonation. The reaction of this complex with HCl might then involve protonation of a ligating sulfur atom, opening of the chelate ring, and loss of the protonated ligand. Second, infrared spectroscopy can, in principle, distinguish between **2** and **3**. The spectra of the imido complexes, however, are dominated by strong absorptions between 1160 and 360 cm^{-1} which can be attributed to the dithiophosphate ligand.[37] Their occurrence vitiates the possibility of unambiguously assigning ν(MoN), a frequency which is expected to occur between 1000 and 900 cm^{-1} for **2**.[6] Furthermore, labeling the nitrogen atom did not result in the detection of any shifted bands. A fundamental difference in the spectra of $Mo(NR)Cl(S_2P(OEt)_2)_2$ and $Mo(NR)(S_2P(OEt)_2)_3$, however, does occur in the region near 640 cm^{-1}. Only one strong band due to the $P\overset{\cdots}{-}S$ antisymmetric stretching motion[37] occurs in the spectrum of the former while two strong bands are found in the spectrum of the latter. These bands could be due to bidentate ligands in a seven-coordinate complex of relatively low symmetry, but one of these absorptions might also be due to a free P═S group in a complex with a low coordination number. We note that this absorption occurs at 650 cm^{-1} in the spectrum of $HSP(S)(OEt)_2$ and at 660 cm^{-1} in that of $EtSP(S)(OEt)_2$.[38]

It is clear that neither evidence from ESR and infrared spectroscopies nor chemical evidence provides an unambiguous structural assignment for either the imido complexes or their oxo analogues. However, we remain biased against five-coordinate geometries for either $Mo(NR)Cl(S_2P(OEt)_2)_2$ or $Mo(NR)(S_2P(OEt)_2)_3$ because of the lack of a strong trans effect for a linear imido ligand in structures which have been examined to date. Furthermore, the many similarities between the ESR parameters for each type of complex lead to a bias in favor of an octahedral geometry for each. This view will allow ready explanations for the inertness of the imido ligand to protonation, the removal of a dangling dithiophosphate ligand by acid, and the doubling of infrared bands near 640 cm^{-1}. A crystallographic determination of the structure is clearly required to remove all ambiguities. To date, however, we have experienced considerable difficulty in obtaining suitable crystals.

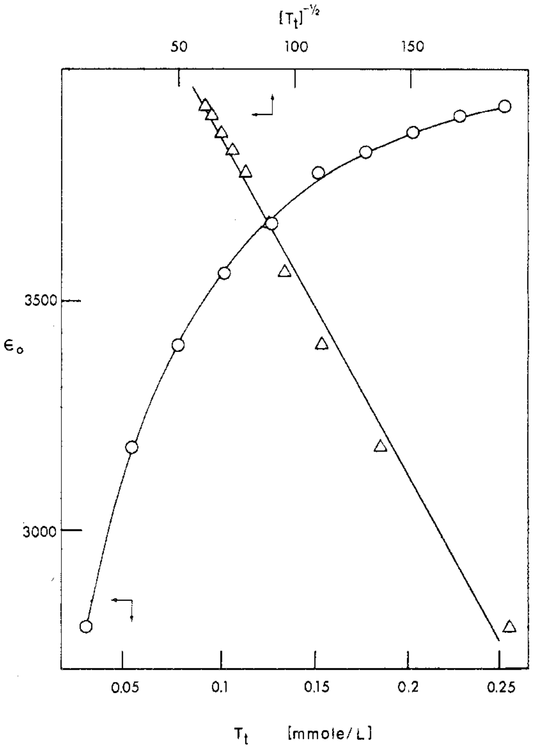

Figure 8. Behavior of ϵ_o at 585 nm with respect to the formal concentration of $[Mo(Ntol)S(S_2P(OEt)_2)]_4$ (○) and its inverse square root (△) according to eq 4.

Possible Stereochemistry of $[Mo(Ntol)S(S_2P(OEt)_2)]_4$. The tetranuclear nature of this compound was established by osmometry in $1,2\text{-}C_2H_4Cl_2$. We have also examined the concentration dependence of the electronic spectrum under more dilute conditions in CH_2Cl_2. The band at 585 nm does not follow the Beer–Lambert law as shown in Figure 8. The behavior of the apparent extinction coefficient of this band leads us to believe that we are observing the effects of the equilibrium shown in eq 3 with the band arising principally

$$2[Mo(Ntol)S(S_2P(OEt)_2)]_2 \rightleftharpoons [Mo(Ntol)S(S_2P(OEt)_2)]_4 \tag{3}$$

from the tetranuclear compound. The spectroscopic data can then be readily used to evaluate the equilibrium constant of eq 3 if the concentration of the dinuclear compound is neglected with respect to the total formal concentration of the tetranuclear compound (T_T). The result for a path length of 1 cm is shown in eq 4, where ϵ_o is the observed extinction

$$\epsilon_o = -\tfrac{1}{2}\epsilon_T K^{1/2} T_T^{-1/2} + \epsilon_T \tag{4}$$

coefficient and ϵ_T is that due to the tetranuclear compound. When this equation is applied to the data (Figure 8), we obtain $K = 6.3 \times 10^4$ M^{-1} and $\epsilon_T = 4450$ M^{-1} cm^{-1}. The remarkable stability of the tetranuclear compound is reflected by the magnitude of the equilibrium constant.

The tetranuclear nature of this compound was not anticipated since there are a large number[1,2] of dinuclear complexes

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[36] If bending of the imido ligand is confined to the xz plane in the pentagonal bipyramid shown in Figure 7, stabilization of the d_{xz} orbital is the natural result. Since the corresponding bonding molecular orbital will then contain less character due to the d_{xz} orbital, a shift in electron density to the nitrogen atom will occur.

[37] W. Rudzinski, G. T. Behnke, and Q. Fernando, *Inorg. Chem.*, **16**, 1206 (1977).

[38] E. M. Popov, T. A. Mastryukova, N. P. Rodionova, and M. I. Kabachnik, *J. Gen. Chem. (USSR)*, **29**, 1967 (1959).

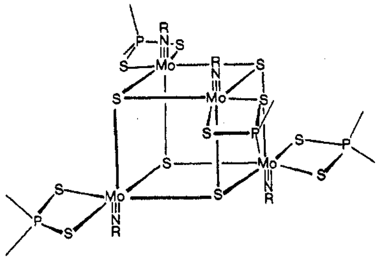

Figure 9. Probable structure of $[Mo(Ntol)S(S_2P(OEt)_2)]_4$. The ethoxy groups are not shown.

having stoichiometries of $MoX_2Y_2L_2$ (L = bidentate ligand; X = Y = O or S and X = O, Y = S). Moreover the dinuclear natures of $[(\eta^5\text{-}C_5H_5)Mo(NR)S]_2$ (R = *t*-Bu) and $[(\eta^5\text{-}C_5H_5)MoOS]_2$ have been established.[23,39] A retrospective rationale has been found, however. Replacing the cyclopentadienyl rings, each being a five-electron donor, with bidentate ligands which are three-electron donors forces the dinuclear complex to attempt to compensate for the loss of four electrons. While it may be argued that the electron-rich bridging ligands allow compensation through multiple bonding, the chemistry of the Mo_2O_4 group points to some degree of unsaturation.[40] Alternatively, compensation can occur by way of the formation of a tetranuclear complex. It is possible that $[Mo(Ntol)S(S_2P(OEt)_2)]_4$ adopts the cubic $[Mo(Ntol)]_4S_4$ cluster since this structure would provide an easy means for joining two $Mo_2(Ntol)_2S_2(S_2P(OEt)_2)_2$ systems providing these systems include cis-imido ligands rather than the centrosymmetric structure found in $[(\eta^5\text{-}C_5H_5)Mo(NR)S]_2$.[23] Although other structures may explain the ^1H and ^{31}P NMR spectra of this compound equally well, these spectra are in accord with the cubic structure (see Figure 9). We are not aware of any authenticated cubic structures containing molybdenum only, but reduced complexes containing a Mo_4S_4 cluster, $[MoOS(S_2CNEt_2)]_4{}^{n-}$ (*n* = 1 and 2), have been postulated previously.[41] Cubic Fe_3MoS_4 clusters are now known.[42]

Although the retrospective argument provides a means to rationalize the formation of this compound, it is clear from the large number of crystallographically authenticated dinuclear compounds that a very delicate balance of stereochemical forces must be operative. These forces may originate from either the imido ligand or the dithiophosphate ligand. If the former is responsible, then these forces, along with differences in trans effects, constitute two remarkable manifestations of differences in the chemistries of the imido and oxo ligands which otherwise appear to be very similar.[6]

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE 75-08188-A01) and by a grant-in-aid from Indiana University. We thank Dr. Shun Fukuzumi for aid in obtaining ESR spectra and Dr. E. I. Stiefel for helpful discussions.

Registry No. $Mo(NPh)(S_2P(OEt)_2)_3$, 72967-92-1; $Mo(Ntol)(S_2P(OEt)_2)_3$, 72967-91-0; $Mo(NPh)Cl(S_2P(OEt)_2)_2$, 72967-90-9; $Mo(Ntol)Cl(S_2P(OEt)_2)_2$, 72967-89-6; $[Mo(Ntol)S(S_2P(OEt)_2)]_4$, 73037-71-5; PhN_3, 622-37-7; $tolN_3$, 2101-86-2; $Mo(CO)_4Cl_2$, 15712-13-7; $Mo(^{15}NPh)Cl(S_2P(OEt)_2)_2$, 72967-88-5; $Mo(^{15}NPh)(S_2P(OEt)_2)_3$, 72967-87-4.

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(39) D. L. Stevenson and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3721 (1967).

(40) W. E. Newton, G. J.-J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, **98**, 5387 (1976).

(41) L. J. De Hayes, H. C. Faulkner, W. H. Doub, and D. T. Sawyer, *Inorg. Chem.*, **14**, 2110 (1975).

(42) T. E. Wolff, J. M. Berg, C. Warrick, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **100**, 4630 (1978); G. Christou, C. D. Garner, and F. E. Mabbs, *Inorg. Chim. Acta*, **29**, L189 (1978); G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, *J. Chem. Soc., Chem. Commun.*, 740 (1978).

Contribution No. 3379 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Formation of $Mo(S_2P(OEt)_2)_3$, a Molybdenum(III) Complex with Ligation Only by Sulfur, and Its Reactions with Azobenzene

A. WINSTON EDELBLUT and R. A. D. WENTWORTH*

Received July 13, 1979

The synthesis of $Mo(S_2P(OEt)_2)_3$ from $Mo(CO)_4Cl_2$, $HS_2P(OEt)_2$, and aryl azides is described. The reaction of this compound with azobenzene in ether containing HCl yields $MoCl(S_2P(OEt)_2)_3$ and benzidine rearrangement products. The reaction of the Mo(III) complex with azobenzene in methanol gives $Mo(OMe)_2(S_2P(OEt)_2)_2$ and hydrazobenzene. Possible mechanisms are discussed.

Introduction

Our interest in the reaction of aryl azides with low-valent molybdenum complexes has led to a series of (arylimido)molybdenum(VI) compounds[1,2] as well as the Mo(V) complexes $Mo(NR)(S_2P(OEt)_2)_3$ and $Mo(NR)Cl(S_2P(OEt)_2)_2$ (R = Ph and tol).[3,4] The latter were obtained from reaction of $Mo(CO)_4Cl_2$ with excess aryl azide in the presence of the bidentate ligand. However, as we show herein, if this reaction is conducted with lesser quantities of the aryl azide, the Mo(III) complex $Mo(S_2P(OEt)_2)_3$ results. Our original intention was to establish another means to prepare (arylimido)molybdenum(V) complexes by the reaction of this compound with various azobenzenes. The only precedent for this reaction is the cleavage of hexafluoroazomethane by $(Ph_2MeP)_2Ir(CO)Cl$ to give $(Ph_2MeP)_2Ir(NCF_3)Cl$.[5] While we have found that the desired reaction does not occur, the reaction with azobenzene does provide new Mo(IV) complexes and the reduction of azobenzene to hydrazobenzene.

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(1) B. L. Haymore, E. A. Maatta, and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **101**, 2063 (1979).

(2) E. A. Maatta and R. A. D. Wentworth, *Inorg. Chem.*, **18**, 2409 (1979).

(3) The abbreviations Ph and tol represent C_6H_5 and $p\text{-}CH_3C_6H_4$, respectively.

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