reconversion of acetylene complexes to the starting oxomolybdenum(IV) complexes, a reaction which might be useful in synthesis. The surprising lack of reaction exhibited by Ac = HFB contrasts strikingly with its most rapid hydrolysis and, if the above speculation concerning the mechanism is correct, indicates that the HFB adducts do *not* dissociate in solution.

The thiourethane product formed by reaction of the HFB and DMAC adducts with alcohol apparently comes from attack on the positively charged α-carbon of the dithiocarbamate ligand. These observations suggest that the hydrolysis reactions might take a similar course for the HFB and DMAC complexes, where no olefins were formed. This reactivity is very similar to that observed[49] for the reaction of the alkylxanthate complexes $Mo_2O_3(S_2COR)_4$ with alcohols (eq 7), where the organic products were identified as the *O,O*-dialkylthiocarbonates. *No* formation of thiourethane was

$$Mo_2O_3(S_2COR)_4 + 2R'OH \rightarrow ROC({=}S)OR' + Mo_2O_2S_2(S_2COR)_2 + H_2O \quad (7)$$

observed from reaction of $Mo_2O_3(S_2CNEt_2)_4$ with alcohol. The fate of the molybdenum in these reaction mixtures is unknown. The reaction of the MP adduct with alcohol not only forms the thiourethane as for the DMAC and HFB adducts but also adds dtcH across the acetylene (as for the hydrolysis of the MP adducts) forming the olefinic product. No reaction occurred between the DTA complex and alcohols, which is perhaps cosistent with the stability of this complex to hydrolysis.

The variability of the reactivity of these acetylenic complexes toward the same reagent is striking, the nature of the acetylene having a very significant effect. The binding of acetylene also radically alters the susceptibility of the dithiocarbamate ligands to attack by water and alcohol as evidenced by a comparison with $MoO_2(S_2CNR_2)_2$, $OMo(S_2CNR_2)_2$, and $Mo_2O_3(S_2CNR_2)_4$ which are stable toward these reagents. These reactions are not simple and in many cases, no molybdenum-containing products could be isolated and/or identified. They show that marked changes of reactivity patterns with changes in coordination occur and these may be particularly significant for the understanding of the role of molybdenum in enzymes, where apparently small changes in the environment of molybdenum can drastically alter its catalytic capability and substrate selectivity.[3,50,51]

Acknowledgment. We are grateful to R. A. D. Wentworth and E. A. Maatta for informing us of their experimental results before publication and to E. I. Stiefel and G. D. Watt for continuing helpful discussions.

Registry No. $OMo(S_2CNMe_2)_2(DMAC)$, 39584-77-5; $OMo(S_2CNEt_2)_2(DMAC)$, 55723-31-4; $OMo(S_2CNMe_2)_2(MP)$, 73367-33-6; $OMo(S_2CNEt_2)_2(MP)$, 73367-34-7; $OMo(S_2CNMe_2)_2(HFB)$, 73367-35-8; $OMo(S_2CNEt_2)_2(HFB)$, 73367-36-9; $OMo(S_2CNMe_2)_2(DTA)\cdot C_6H_6$, 73367-38-1; $OMo(S_2CNEt_2)_2(DTA)$, 73367-39-2; $OMo(S_2CNEt_2)_2(C_2H_2)$, 66060-13-7; $OMo(S_2CNMe_2)_2$, 39587-09-2; $OMo(S_2CNEt_2)_2$, 25395-92-0; $Mo_2O_4(S_2CNMe_2)_2$, 50860-30-5; *trans*-$(Me_2NCS_2)CH{=}CH(CO_2Me)$, 73377-27-2; *cis*-$(Me_2NCS_2)CH{=}CH(CO_2Me)$, 25924-87-2; Me_2NCS_2Na, 128-04-1; MP, 922-67-8; $(Me_2NCS_2)(CO_2Me)C{=}C(H)(CO_2Me)$, 73377-28-3; DMAC, 762-42-5; Me_2NH, 124-40-3; Et_2NH, 109-89-7; methanol, 67-56-1; water, 7732-18-5.

Supplementary Material Available: A listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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Formation of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$, a Complex with a Bridging Imido Ligand, and Its Reactions with Acids

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The nature of the reaction between $MoO(S_2P(OEt)_2)_2$ and HN_3 is discussed. The decomposition of a purple intermediate, thought to be $Mo_2O_2(NH)(S_2P(OEt)_2)_4$, results in the formation of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$. The structure of the latter includes bridging oxo and imido ligands. The reaction of this complex with HCl results in the protonation of the imido ligand (substantiated by ^{15}N labeling) and the formation of $Mo_2O_2(NH_2)Cl(S_2P(OEt)_2)_2$. Similarly, the reaction with $HS_2P(OEt)_2$ results in the formation of $Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$. The site of protonation was again substantiated by ^{15}N labeling. The contrasting behaviors of terminal and bridging imido ligands as well as bridging oxo ligands to protonation are compared.

Introduction

Several recent studies have focused on the reactions of dithiocarbamate complexes of oxomolybdenum(IV) with small, easily reduced compounds.[1,2] Of primary interest for present purposes is the oxidation of $MoO(S_2CNR_2)_2$ by HN_3 with the latter distributed between acidic aqueous and organic phases.[2] The products of this reaction are $MoO_2(S_2CNR_2)_2$, N_2, and NH_3. These results were interpreted in terms of an initial abstraction of the NH ligand to give $MoO(NH)(S_2CNR_2)_2$ and N_2, followed by hydrolysis of the intermediate to yield the remainder of the products. Subsequently, we have been able to demonstrate the abstraction of NR ligands from various

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[1] See, for example: (a) Schneider, P. W.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 9640; (b) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612; (c) Maatta, E. A.; Wentworth, R. A. D.; Newton, W. E.; McDonald, J. W.; Watt, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 1320; (d) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 524.

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aryl azides by the isolation of $Mo(NR)_2(S_2CNEt_2)_2$ and $MoO(NR)(S_2CNEt_2)_2$.[3,4] Futhermore, these studies have shown that the removal of a terminal arylimido ligand by protonation depends upon the electronic configuration at the nitrogen atom of that ligand.

We have also briefly indicated[5] that the oxidation of $MoO(S_2P(OEt)_2)_2$ with HN_3 can result in the formation of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$. Spectroscopic studies of this compound and X-ray studies of its adduct with tetrahydrofuran have shown[5] that the imido ligand occupies a bridging site in the dinuclear complex which is otherwise similar to many other complexes containing a Mo_2O_2 core. The purpose of this paper is to delineate some further aspects of the complex reaction between $MoO(S_2P(OEt)_2)_2$ and HN_3, to describe the less than straightforward preparation of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ in detail, and to explore the nature of the reactions of this compound with two monoprotic acids. The site of protonation has been determined unambiguously from ^1H NMR studies by labeling with ^{15}N.

Experimental Section

Materials and Procedures. A literature method[1b] was used to prepare $MoO(S_2P(OEt)_2)_2$. Phenyl azide was obtained by the method described previously.[4] All subsequent reactions were routinely performed either under an argon atmosphere or under vacuum. Solvents were dried and distilled directly into the reaction vessels. The evolution of N_2 was quantitated by measuring the pressure of the gas after pumping it into an evacuated manifold of known volume. Labeling with ^{15}N was accomplished by using KN_3 in which the azide ion was enriched to 95 atom % in ^{15}N in a single terminal site (Stohler Isotope Chemicals).

Infrared spectra were recorded by using a Perkin-Elmer Model 283 spectrophotometer and Nujol mulls. Proton NMR spectra were obtained by using a Varian HR-220 NMR spectrometer with Me_4Si as an internal standard while ^{31}P NMR spectra were obtained by using a Varian XL-100-15 FT NMR spectrometer. Chemical shifts are referenced to the upfield signal from external H_3PO_4. Mass spectra were recorded with a Varian CH-7 mass spectrometer. Molecular weights were determined in 1,2-$C_2H_4Cl_2$ by using a Mechrolab 301A osmometer operating at 37 °C.

The titration of aqueous Mo(V) with $Cr_2O_7^{2-}$ was accomplished according to a published procedure.[6] Elemental analyses were obtained from Galbraith Laboratories.

Reaction of $MoO(S_2P(OEt)_2)_2$ with HN_3. In a typical reaction, a sixfold molar excess of sodium azide was added to an evacuated, stirred, two-phase medium consisting of 10 mL of 1 M HCl and 1 mmol of $MoO(S_2P(OEt)_2)_2$ in 25 mL of CH_2Cl_2. Initially, the organic phase assumed a purple color. After the evolution of N_2 appeared to cease (about 4 h), the organic phase was virtually colorless while the aqueous phase was yellow-orange. After an additional 8 h, it was shown that 1.5 ± 0.1 mmol of N_2 had evolved. The electronic spectrum of a diluted aliquot of the aqueous layer indicated the presence[7] of $Mo_2O_4^{2+}$ while the potentiometric titration of another aliquot with $Cr_2O_7^{2-}$ indicated that at least 99% of the available molybdenum was in the aqueous layer as Mo(V). Evaporation of the organic phase led to the recovery of 0.95 mmol of the disulfide $(EtO)_2P(S)SSP(S)OEt)_2$. The identification of this compound was accomplished from its mass spectrum and by comparing its infrared and ^1H NMR spectra with those of an authentic sample. Finally, NH_3 was identified qualitatively in the aqueous phase by a spot test with *p*-nitrobenzenediazonium chloride.[8]

$Mo_2O_3(NH)(S_2P(OEt)_2)_2$. The addition of 0.5 mmol of sodium azide to a mixture of 1 mL of 6 M HCl and 0.5 mmol of $MoO(S_2P(PEt)_2)_2$ in 5 mL of CH_2Cl_2 produced a vigorous evolution of N_2 and an immediate purple color. The reaction was quenched by immersing the flask in liquid nitrogen, and 50 mL of CH_2Cl_2 was introduced by distillation. The reaction mixture was warmed until only the organic phase had thawed. Quick filtration through a cold frit allowed the separation of the two phases. The purple, organic phase became yellow on standing about 10 min. The solvent was removed by distillation, and the residue was washed with petroleum ether. Two recrystallizations from benzene–heptane afforded feathery yellow crystals in 63% yield. Anal. Calcd for $Mo_2O_3(NH)(S_2P(OEt)_2)_2$: C, 15.4; H, 3.4; N, 2.2; S, 20.5. Found: C, 15.3; H, 3.5; N, 2.2; S, 20.5. Labeling with ^{15}N was accomplished according to the same procedure.

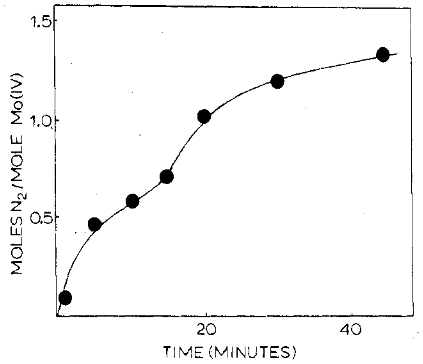

Figure 1. Time-dependent evolution of N_2 from the reaction of $MoO(S_2P(OEt)_2)_2$ with HN_3. The size of the circles indicates the approximate error in the measurements.

$Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$. When 0.65 mmol of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ in 50 mL of CH_2Cl_2 was stirred with 5 mL of 1 M HCl, a gradual color change from yellow to orange occurred in the organic phase. When the aqueous phase attained a greenish hue, the reaction was quenched in liquid nitrogen. Warming allowed the organic phase to be removed by filtration through $MgSO_4$. The organic solvent was then removed by distillation, and crystallization of the residue from CH_2Cl_2–heptane afforded orange needles. Anal. Calcd for $Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$: C, 14.5; H, 3.3; N, 2.1. Found: C, 14.6; H, 3.3; N, 2.1. The ^{15}N-labeled complex was prepared by an identical procedure.

$Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$. This compound was prepared from the reaction of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ (1 mmol) with excess $HS_2P(OEt)_2$ in anhydrous methyl alcohol. The reaction was accompanied by the formation of yellow precipitate. Crystallization of the latter from methyl alcohol–ether afforded yellow needles. Anal. Calcd for $Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$: C, 17.8; H, 4.0; N, 1.8. Found: C, 17.5; H, 3.9; N, 1.7. The ^{15}N-labeled complex was prepared analogously.

$Mo_2O_2(NPh)(S_2P(OEt)_2)_4$. Phenyl azide (1.25 mmol) was added to 2.50 mmol of $MoO(S_2P(OEt)_2)_2$ in 25 mL of CH_2Cl_2. The reaction was allowed to proceed until the solution was deep purple. Heptane was added, and solvent was removed partially by distillation. The deep purple crystals were removed by filtration and recrystallized from CH_2Cl_2–heptane by the same procedure. Anal. Calcd for $Mo_2O_3(NPh)(S_2P(OEt)_2)_4$: C, 25.0; H, 4.3; N, 1.3; S, 24.3. Found: C, 25.1; H, 4.4; N, 1.3; S, 24.5.

Discussion of Results

Oxidation of $MoO(S_2P(OEt)_2)_2$ with HN_3. When a solution of $MoO(S_2P(OEt)_2)_2$ in CH_2Cl_2 is stirred with an aqueous solution of NaN_3, the evolution of N_2 is exceedingly slow. Since the reaction is much more rapid in the presence of 1 M HCl, it is clear that HN_3 is a more efficient oxidant than N_3^-, in accord with our previous results with $MoO(S_2CNR_2)_2$.[2] However, the stoichiometry of the reaction, given in eq 1 and

$$2MoO(S_2P(OEt)_2)_2 + 3HN_3 + 2H_3O^+ \rightarrow Mo_2O_4^{2+} + 2(EtO)_2P(S)SSP(S)(OEt)_2 + 3N_2 + 3NH_3 \quad (1)$$

suggested by the results in the Experimental Section, differs considerably from that experienced by the dithiocarbamate complex since now both the metal and the ligand suffer oxidation. The complexity of eq 1 and the appearance of a purple intermediate indicate that several steps must be involved.

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

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

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Table I. Molecular Weight Data and Selected Infrared Frequencies[a]

compd	mol wt[b]	ν(NH)	$\nu(Mo_2O)$	ν(PS)
$Mo_2O_3(NH)(S_2P(OEt)_2)_2$	635 ± 10 (625)	3365 (w)[c]	719 (m) 522 (m)	632 (m)
$Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$	645 ± 10 (662)	3363 (w) 3217 (m)	703 (m) 530 (w)	629 (m)
$Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$	785 ± 10 (811)	3245 (w,b)	755 (m) 533 (m)	660 (m) 638 (w)

[a] Spectra were obtained in Nujol mulls except where indicated. Band positions are reported in cm^{-1}; m = medium, w = weak, b = broad. [b] Values in parentheses are the calculated molecular weights. [c] Obtained in $1,2\text{-}C_2H_4Cl_2$.

When the rate of dinitrogen evolution was followed, two distinct steps were observed as shown in Figure 1. The fastest step occurs with the formation of the purple intermediate and the liberation of approximately one-third of the total amount of gas. We suggest that these observations are satisfied by the sequential reactions in eq 2 and 3.

$$MoO(S_2P(OEt)_2)_2 + HN_3 \rightarrow MoO(NH)(S_2P(OEt)_2)_2 + N_2 \quad (2)$$

$$MoO(NH)(S_2P(OEt)_2)_2 + MoO(S_2P(OEt)_2)_2 \rightarrow Mo_2O_2(NH)(S_2P(OEt)_2)_4 \quad (3)$$

Since $Mo_2O_2(NH)(S_2P(OEt)_2)_4$ is isoelectronic with purple $Mo_2O_3(S_2P(OEt)_2)_4$, a similar color might be expected. Our efforts to isolate this dinuclear complex in pure form have not been successful, but we have shown that the reaction of $MoO(S_2P(OEt)_2)_2$ with 0.5 equiv of phenyl azide leads to purple $Mo_2O_2(NPh)(S_2P(OEt)_2)_4$. Although very good analytical results were obtained from this compound, the rapid decomposition of this compound to undetermined products in CH_2Cl_2 solutions prevented a study of its properties in solution. It is also unfortunate that the infrared spectrum of this compound is dominated by bands due to intraligand vibrations so that the structure of this compound remains in doubt. Nevertheless, the isolation of this compound lends support to the conjecture that the formation of the purple intermediate is in accord with eq 2 and 3.

Subsequent steps in this reaction are not understood. Although we have obtained $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ by allowing decomposition of solutions of the purple intermediate, a reaction which possibly proceeds according to eq 4 by utilizing residual water in the CH_2Cl_2 solution, it is possible that significant quantities of this complex are not involved in the overall reaction in eq 1.

$$Mo_2O_2(NH)(S_2P(OEt)_2)_4 + H_2O \rightarrow Mo_2O_3(NH)(S_2P(OEt)_2)_2 + 2HS_2P(OEt)_2 \quad (4)$$

The prejudice is based on the reaction of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ with HN_3 which leads to a dark precipitate (of unknown composition). This precipitate is not observed in the original reaction.

Additional Characterization of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$. We have previously discussed[5] the characterization of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ in solution by spectroscopic methods. These results and others are included in Tables I and II. Additional evidence for the integrity of the bridging NH ligand when this compound is in solution has been obtained from studies of the ^{15}N-labeled complex. The ^1H NMR spectrum contains a sharp doublet due to coupling with the ^{15}N nucleus (J_{NH} = 83 Hz) as shown in Figure 2. The broad resonance within this doublet is due to the hydrogen atom bound to ^{14}N. The intensity of this resonance is approximately equal to that of the doublet. Since the azide ion used in the preparation of the labeled complex was enriched to 95% in a single terminal site, these results imply that abstraction of NH from HN_3 by Mo(IV) occurs from only terminal sites, as would be expected.

Table II. ^1H NMR Spectra of Compounds Containing Bridging Imido and Amido Ligands in CD_2Cl_2[a, b]

	chemical shift, δ		
	$S_2P(OEt)_2$		
compd	CH_3	CH_2[c]	NH or NH_2
$Mo_2O_3(NH)(S_2P(OEt)_2)_2$	1.42 (t, 6 H) 1.70 (t, 6 H)	4.34 (m, 4 H) 5.09 (m, 4 H)	13.27 (s, 2 H)
$Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$	1.22 (t, 6 H) 1.54 (t, 6 H)	3.83 (m, 4 H) 4.53 (m, 4 H)	5.95 (s, 1 H) 6.14 (s, 1 H)
$Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$	1.30 (t, 6 H) 1.58 (t, 6 H) 1.78 (t, 6 H)	3.82 (m, 4 H) 3.98 (m, 4 H)[d] 4.47 (m, 4 H)	6.59 (s, 1 H) 9.82 (s, 1 H)

[a] Spectra are reported at 16 °C except for that of $Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$ which is reported at −33 °C. [b] s = singlet, t = triplet, q = quintet, and m = multiplet. [c] Multiplet arises from two overlapping quartets unless otherwise noted. [d] Poorly defined.

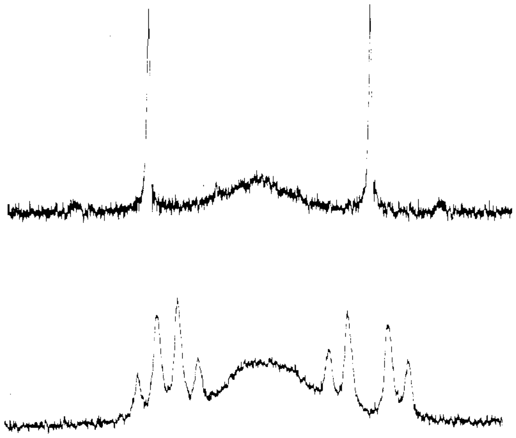

Figure 2. ^1H NMR spectra of ^{15}N-labeled $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ (top) and $Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$ (bottom).

It is worth noting that strong absorptions in the infrared spectrum due to the P–O–C linkages[9] dominate the region in which bands due to terminal MoO groups are expected to be found, and no assignment of ν(MoO) is possible. We have, however, tentatively assigned $\nu(Mo_2O)$ in Table I by using previous assignments[10] obtained with $Mo_2O_3S(S_2CNEt_2)_2$. In addition, a probable assignment for ν(PS), based upon other work,[9,11] is given in Table I.

Reaction of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ with Acids. The reaction of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ with HCl leads to protonation of the bridging imido ligand and the formation of $Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$. Data for this compound can be found in Tables I and II. The ^1H NMR spectrum contains two broad and closely spaced singlets at about 5.95 and 6.14 ppm due to inequivalent hydrogen atoms of a bridging amido ligand. The spectrum of the labeled complex in this region, which is also shown in Figure 2, contains the doubled AB portions of an ABX pattern with A = B = ^1H and X = ^{15}N (J_{AB} = 8 Hz, J_{AX} = 78 Hz, and J_{BX} = 70 Hz). The original two resonances due to the unenriched complex now appear as a very broad, unresolved resonance. The remainder of the spectrum consists of signals due to two pairs of inequivalent

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(9) Rudzinski, W.; Behnke, G. T.; Fernando, Q. *Inorg. Chem.* **1977**, *16*, 1206.

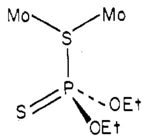
(10) Newton, W. E.; McDonald, J. W. *J. Less-Common Met.* **1977**, *54*, 51.

(11) Edelblut, A. W.; Wentworth, R. A. D., unpublished results.

ethyl groups. Although the molecular weight of this compound in 1,2-$C_2H_4Cl_2$ is in accord with a molecular species, ionic behavior in this solvent is easily masked by strong ion pairing. The initial molar conductivity of this complex[12] in CH_3CN (1.33 mM) is 32 Ω^{-1} cm^2 mol^{-1}, a result which is only consistent with a molecular species.[13] When the solution is allowed to stand, the molar conductivity increases to 140 Ω^{-1} cm^2 mol^{-1} which is probably indicative of a slow ionization. The structure of this complex probably consists of a distorted confacial bioctahedron with two terminal oxo ligands, two terminal dithiophosphate ligands, and bridging oxo, amido, and chloro ligands. Precedent for this general structure is available[14] from X-ray studies of other dinulcear Mo(V) complexes.

When $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ reacts with $HS_2P(OEt)_2$, $Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$ is formed. The ^{31}P NMR spectrum consists of two narrow signals at 104.7 and 95.5 ppm with an intensity ratio of 2:1. The ^1H NMR spectrum at 16 °C contains broadened resonances due to three types of ethyl groups with an intensity ratio of 1:1:1 and broad signals of equal intensity due to the hydrogen atoms of the bridging amido ligand. Due to the broadened nature of the resonance at 1.58 ppm, the spectrum was also obtained at −33 °C, but no additional resolution occurred. The spectrum is described in Table II. Finally, the spectrum of the ^{15}N-labeled complex contains the characteristic doubled AB portion of an ABX spectrum due to the amido ligand (J_{AB} = 8 Hz, J_{AX} = 77 Hz, and J_{AX} = 69 Hz).

The third dithiophosphate ligand in this complex presumably occupies a bridging site along with the oxo and amido ligands. However, two modes of bridging are possible (**1** and **2**). A confacial bioctahedron would occur again in **1** while the structure involving **2** can be described as an edge-shared bioctahedron. There would appear to be no structural precedent for **2** among the oxo complexes of Mo(V). In principle, the NMR data could distinguish between these structures. Although ethyl groups of the bridging dithiophosphate ligand in **1** would be equivalent when averaged over the various confirmations, the methylene hydrogen atoms of this ligand would be diastereotopic. The ethyl groups in **2**, however, would not be equivalent because of the inequivalence of the remainder of the bridging ligands. While the three sets of signals of equal intensity that are actually observed suggest **1**, the possibility of accidental degeneracy with **2** is not easily discounted. Furthermore, two of the resonances due to the methylene hydrogen atoms are sharp quintets (due to overlap of the two quartets which arise from coupling with the ^{31}P nucleus), but the central resonance at 3.98 ppm is poorly defined. Although the poor definition of this resonance is undoubtedly caused by one of the effects described above, we are unable to judge which effect is causing the poor resolution. Although we prefer **1**, no structural assignment is possible. It is worth noting that the infrared spectrum of this compound, unlike those of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ and $Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$, contains two bands which can be assigned[10] to ν(PS) as shown in Table I. Unfortunately, this observation is readily explicable in terms of the structures implied by either **1** and **2**.



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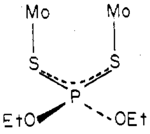

2

Protonation of Terminal and Bridging Imido Ligands. Although only a limited number of systems have been studied, it has been suggested previously[4] that the basicity of the nitrogen atom in a terminal NR (R = aryl) ligand will depend upon the electronic configuration at the nitrogen atom which, in turn, is dictated to a large extent by the EAN rule as well as the natures of R and the remainder of the ligands. Thus, the linear moiety (**3**) which results when the electron count is precisely 18 appears to be incapable of protonation. No differences in behavior are expected with complexes bearing terminal NH ligands as in **3**. Indeed, the NH group in the 18-electron complex, $Mo(NH)X(dppe)_2^+$ (X = halogen and dppe = $Ph_2PCH_2CH_2PPh_2$), appears to function only as an acid and not as a base.[15] The bent moiety (**4**), which is to be expected in electron-rich complexes,[3] will act as a base since it has a pair of electrons available for protonation.[4] Furthermore, attack at the molybdenum atom of the protonated molecule by either the conjugate base of the acid or other nucleophiles will force an additional pair of electrons onto the nitrogen atom and allow subsequent protonation of the amido ligand. This process can continue until the original imido ligand is lost as the amine. Since the number of electrons available to an imido ligand for bonding to the metal atom is identical with that of an oxo ligand, patterns of protonation or resistance to protonation for these ligands in terminal sites are virtually identical.[4]

3

4

In contrast to complexes with terminal imido ligands, the structural data[5] for $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ are consistent with the use of eight orbitals on each molybdenum atom in bonding to the ligands and the adjacent metal atom. The ninth orbital, which is virtually nonbonding and directed away from the terminal MoO bond, has weak acceptor properties as is evidenced by the formation of an adduct with tetrahydrofuran. The $Mo_2O(NH)$ core in this complex is isoelectronic with the well-characterized Mo_2O_2 core found in many dinuclear Mo(V) complexes.

A study of the reactions of $Mo_2O_4(S_2CNEt_2)_2$ with various acids has indicated[16] that one or both of the bridging oxo ligands can be removed as water by protonation. However, the nucleophilicity of the conjugate base of the acid rather than the acidity of the acid appears to exert a dominant influence. We infer that simple protonation of a bridging oxo ligand is not a favored reaction and that protonation of this ligand is coupled to nucleophilic addition of the conjugate base to one of the metal atoms. The nonbonding orbital of the metal would be used to accept the additional ligand. Since the symmetric combination of the nonbonding orbitals is of the same symmetry as the corresponding combination of the metal's d_{xz} and d_{yz} orbitals as well as the bridging oxo ligands' π orbitals, the addition of the conjugate base may directly enhance the electron density at a bridging oxo ligand and assist protonation. The remaining oxo ligand will be a better π donor than the hydroxo ligand which is formed by this reaction. The enhanced electron density at the hydroxy ligand would favor subsequent protonation to form water, a ligand which should be readily lost. Capture of the two, singly bound conjugate bases by the

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(12) We are indebted to Dr. K. F. Miller of the Kettering Research Laboratory for obtaining this result.

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adjacent metal atoms to form a confacial bioctahedron may occur as steps throughout this process.[17] This scheme, while not necessarily entirely accurate, provides a consistent explanation for the reactivity of $Mo_2O_4(S_2CNEt_2)_2$ toward acids and for the known structure of $Mo_2O_3(SPh)_2S_2CNEt_2)_2$[14b] and the presumed structure[16] of $Mo_2O_3(SCH_2CH_2O)(S_2CNEt_2)_2$. Interestingly, diprotic acids whose conjugate bases are powerful, inflexible chelating agents can remove the last bridging oxo ligand to yield mononuclear complexes.

Although the initial portion of this scheme would presumably apply to the reactions of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ with acids which were studied, one important aspect must be different. Since initial protonation can occur at either the bridging oxo or imido ligands, we must assume that the relative basicities of these ligands are in the same order as those of water and ammonia so that only the imido ligand is protonated. Further protonation of the amido ligand would be difficult because it would necessarily entail rupture of a Mo–N bond, a bond whose general stability has been demonstrated by the present studies. It is conceivable that other acids,[18] particularly diprotic chelating acids, could result in protonation of both the imido and oxo ligands. If this occurs, the bridging hydroxo ligand may well be susceptible to further protonation by analogy to the protonations of $Mo_2O_4(S_2CNEt_2)_2$.

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Registry No. $MoO(S_2P(OEt)_2)_2$, 25395-91-9; $Mo_2O_3(NH)(S_2P(OEt)_2)_2$, 66741-00-2; $Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$, 73558-07-3; $Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$, 73558-08-4; $Mo_2O_2(NPh)(S_2P(OEt)_2)_4$, 73558-09-5; NaN_3, 26628-22-8; phenyl azide, 622-37-7; HN_3, 7782-79-8; $Mo_2O_2(NH_2)(SCH_2CH_2O)_2(S_2P(OEt)_2)$, 73697-78-6.

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(17) Although the reaction of $Mo_2O_4(S_2CNEt_2)_2$ with either $S_2CNEt_2^-$ or HS_2PR_2 in CH_2Cl_2 containing methyl alcohol results[16] in the formation of $Mo_2O_3L_4$ rather than a confacial bioctahedron, it may be that these chelating agents are incapable of occupying two bridging sites of a confacial bioctahedron.

(18) We have also shown that the reaction of HBr with $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ gives $Mo_2O_3(NH_2)Br(S_2P(OEt)_2)_2$ with excellent analytical results. Similarly, the reaction of 2-mercaptoethanol with the imido complex leads to a compound which we formulate provisionally as $Mo_2O_2(NH_2)(S_2CH_2CH_2O)_2(S_2P(OEt)_2)$, again with excellent analytical results. The ^1H NMR spectrum in deuterated Me_2SO is complex but shows that the mercaptoethanolate ligands are not equivalent while resonances which can presumably be assigned to the bridging amido ligand occur at 8.30 and 8.65 ppm. If the formulation of this compound is correct, it represents the first example of a complex whose reaction with an acid leads to both the removal of a bridging oxo ligand as well as the protonation of the imido ligand. Reactions of the imido complex with acetic acid, thioacetic acid, 8-hydroxyquinoline, and *o*-aminothiophenol have also been observed. The death of Winston Edelblut, a tragic loss of a very promising young chemist, has prevented a thorough investigation of the products of these reactions.

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Asymmetric Transformation of α-Amino Acids Promoted by Optically Active Cobalt(III) Complexes

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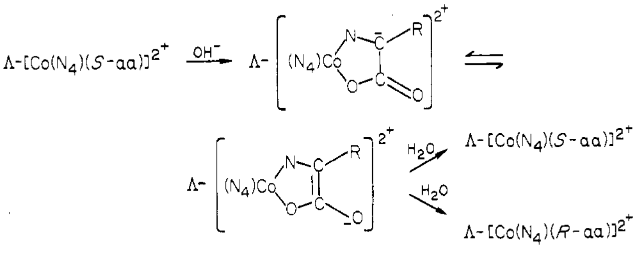
The hydroxide ion catalyzed epimerization of chelated α-amino acidates in Λ-β_2-$[Co(N_4)$(*S*- or *R*-aa)$]^{2+}$ ((N_4) = tetraamine ligand; aa = amino acidato) is an example of a "first-order asymmetric transformation" of α-amino acids promoted by chiral cobalt(III) complexes. Chiral derivatives of 2,3,2-tet (1,9-diamino-3,7-diazanonane) or triethylenetetramine were employed as quadridentate ligands. Epimerization of alaninate, valinate, and phenylalaninate moieties in Λ-β_2-$[Co(N_4)$(*S*- or *R*-aa)$]^{2+}$ were examined at pH 10–12 carbonate buffer, to give equilibrium mixtures of diastereomers (Λ-*R* and Λ-*S*). In the most discriminative case where (N_4) = *SS*-phyt and aa = α-alaninate the isomer ratio for Λ-*S*/Λ-*R* was 18/82. The energy difference between the Λ-*R* and Λ-*S* isomers is discussed in relation to the prediction of strain energy minimization calculations.

Introduction

It has been known that metal ions increase the reactivity of the α proton of chelated α-amino acids.[1] Sargeson and co-workers showed[2] that the α proton of chelated α-amino acidate moieties in dissymmetric complex ions undergoes OH^--catalyzed exchange in basic aqueous solution, to give a diastereomeric equilibrium mixture. They measured the equilibrium constants between the diastereomers Λ-$[Co(en)_2$(*R*-aa)$]^{2+}$ and Λ-$[Co(en)_2$(*S*-aa)$]^{2+}$ (aa represents the α-amino acidate coordinated as a bidentate ligand) and obtained the isomer ratio Λ-$[Co(en)_2$(*R*-val)$]^{2+}$/Λ-$[Co(en)_2$(*S*-val)$]^{2+}$ = 63/37 and Λ-$[Co(en)_2$(*R*-ala)$]^{2+}$/Λ-$[Co(en)_2$(*S*-ala)$]^{2+}$ = 50/50. Under the above conditions, the racemization of the chelated α-amino acidates occurred without change in the arrangement of three chelate rings around the cobalt(III) center (represented by Λ or Δ). The above reaction is applicable to the amino acidato complexes having the general formula $[Co(N_4)$(*R*- or *S*-aa)$]^{2+}$, where (N_4) indicates four amine nitrogen atoms of two diamines or a tetraamine.

Scheme I. Proposed Mechanism for the Epimerization of a Chelated α-Amino Acid in Basic Solution



Scheme I shows the proposed mechanism for the OH^--promoted epimerization of an α-amino acid coordinated to a dissymmetric center in Λ-$[Co(N_4)$(*S*-aa)$]^{2+}$.[2] It can be expected that the ratio of two isomers (Λ-*R*/Λ-*S*) at equilibrium will be biased from 50/50, reflecting the free energy difference between the diastereomers. On this basis the epimerization in Λ-$[Co(N_4)$(*R*- or *S*-aa)$]^{2+}$ is considered as an example of

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