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# Reactivity of Oxomolybdenum(VI), -(V), and -(IV) Compounds as Controlled by Sulfur Chelate Ligands

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A series of *cis*-dioxomolybdenum(VI) complexes of the type $MoO_2(L\text{-}L)_2$ was prepared with a variety of chelating monoanions (L-L) to examine their relative stabilities. Also prepared were some related molybdenum(V) and -(IV) compounds. Reactivity of the oxo ligand in $MoO_2(L\text{-}L)_2$ was investigated to examine the ligand effects. Complexes $MoO_2(L\text{-}L)_2$, with L-L = dialkyldithiocarbamato ($R_2$dtc) or similar sulfur-containing ligands, were found effective in the dehydrogenation of hydrazobenzene to azobenzene and oxygenation of $PPh_3$, while those with O,O and O,N chelate ligands were inactive. Condensation of monoarylhydrazine with $MoO_2(L\text{-}L)_2$ occurs to give $MoO({=}NNHAr)(L\text{-}L)_2$ (L-L = thioxinato), $Mo(N{=}NAr)_2(L\text{-}L)_2$ (L-L = oxinato) or $Mo_2(N{=}NAr)_3(L\text{-}L)_4$ (L-L = $R_2$dtc), depending on the chelating ligands. These reactivities are discussed in terms of the electronic effect of the ligands.

Molybdenum enzymes are characterized by their redox capabilities.[2] Nitrogenase and xanthine oxidase are typical examples. In oxidases, mono- or dioxomolybdenum species may play an important role. Thus, it is of interest to investigate the oxidative ability of oxomolybdenum species coordinated with various types of chelates containing sulfur donor atoms. We have examined a series of mono- and dioxomolybdenum sulfur-chelated complexes as reagents for selective oxidation of various organic compounds.

Nitrogen fixation has been proposed to proceed stepwise through diazene (HN=NH) and hydrazine ($H_2NNH_2$) stages.[3] An alternative proposal considers the formation of a [hydrazenido(2−)]metal intermediate ($M{=}NNH_2$) by protonation at the coordinated dinitrogen followed by diazene formation and disproportionation to ammonia and dinitrogen based on experimental evidence obtained in $Mo(N_2)_2(PMe_2Ph)_4$.[4] We have examined the reaction of various hydrazine derivatives with a series of chelated oxomolybdenum compounds. In the course of our study, Chatt et al.[5] have reported a similar reaction of arylhydrazine with $MoO_2(R_2dtc)_2$ to give $PhN_2Mo(R_2dtc)_3$. The coordinating atoms of the chelating ligands were varied to reveal the effect of the auxiliary ligands in the reaction.

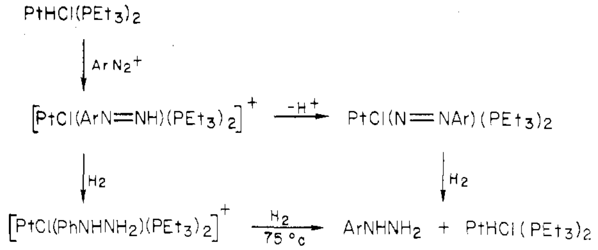
Reaction of monoaryldiazonium salts with group 8 metal complexes has been reported to give aryldiazene or aryldiazenido(1−) complexes,[6] some of which are reduced to arylhydrazine complexes.[7] For example, a platinum(II) complex reacts as shown in Scheme I. By contrast, some oxo complexes of group 6 metals react with arylhydrazines forming arylhydrazido(2−) metal species, M=NNHAr (Scheme II). In the reaction with $ReCl_3(PMe_2Ph)_3$, reductive cleavage of the N–N bond of arylhydrazine was observed together with formation of aryldiazenido(1−) complexes.[8] One of the N–N cleavage products was found to remain coordinated in the product, $[ReCl_2(NH_3)(PhN_2H)(PMe_2Ph)_2]^+$, by X-ray analysis.

Since the dehydrogenation and the reductive cleavage of the N–N bond are closely connected with the redox ability of the molybdenum species, the reaction of arylhydrazines with oxomolybdenum complexes was studied by varying the coligands to see the electronic effect on these reactions.

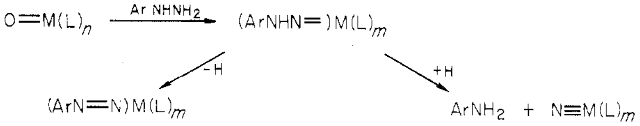
## Results and Discussion

**Relative Thermal Stability of Formal Oxidation State of the Metal in Oxomolybdenum Bis Chelates.** Since redox properties of molybdenum complexes are one of their most important features, indispensable for understanding the function of the metal center in the enzymic reaction, the relative thermal stabilities of various oxomolybdenum complexes were qualitatively assessed from preparative studies. Oxomolybdenum complexes of general empirical formulas $MoO_2(L\text{-}L)_2$, $Mo_2O_3(L\text{-}L)_4$, and $MoO(L\text{-}L)_2$ have been reported with various chelate ligands L-L.[2a] In general, hard chelate ligands with O,O- or N,O-coordinating atoms, e.g., acac, sal, ox (oxinato), are known to prefer higher oxidation states,[2a] i.e., Mo(VI) over Mo(V) or Mo(IV). When the ligand softness is increased by incorporation of sulfur in the coordinating atoms, the oxomolybdenum complexes tend to prefer lower oxidation states. Thus, we have found that addition of an S,S chelate such as an alkyl xanthato ($ROCS_2^-$) ion to an aqueous solution of $MoO_4^{2-}/HCl$ yields a binuclear Mo(V) complex $Mo_2O_3(xan)_4$. This may suggest instability toward reduction of the corresponding Mo(VI) complex, $MoO_2(xan)_2$, under the preparative conditions. The dialkyldithiocarbamato Mo(VI) complexes $MoO_2(R_2dtc)_2$ are readily reduced to the Mo(V) state with various weak reducing agents as described in this paper.

Scheme I



Scheme II



Replacement of the dialkyl group(s) in dithiocarbamato ligands with an aryl or hydrogen group on the N atom causes marked destabilization of the *cis*-dioxomolybdenum(VI) species, $MoO_2(S\text{-}S)_2$, resulting in facile formation of monooxo-bridged binuclear Mo(V) complexes, $Mo_2O_3(S\text{-}S)_4$. Thus, reaction of sodium *N*-phenyl-*N*-methyldithiocarbamate with $MoO_4^{2-}$ at room temperature at pH 5–6 gave at first a yellow $MoO_2(S\text{-}S)_2$ species which on standing changed into the purple Mo(V) complex $Mo_2O_3[Ph(CH_3)NCS_2]_4$. The observed preference for the Mo(V) oxidation state by the $Ph(CH_3)NCS_2^-$ complex seems to be due to the electron-attracting inductive effect of the *N*-phenyl group. A similar inductive effect of the *N*-phenyl group on the spectroscopic properties of $Fe(CO)_2(R_2dtc)_2$ complexes has recently been reported.[9] It was found that monoalkyldithiocarbamato ligands ($RNHCS_2^-$) also give unstable *cis*-dioxomolybdenum(VI) species. Incipient formation of an unstable *cis*-dioxomolybdenum(VI) species was followed by precipitation of the binuclear Mo(V) complexes $Mo_2O_3(RNHCS_2)_4$, R = cy-

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**Table I.** Reactions[a] of $MO_2L_2$ with $PPh_3$ and Hydrazobenzene

| $MO_2L_2$[b] | hydrazobenzene |  | $PPh_3$ |  |
|---|---|---|---|---|
|  | conditions | products | conditions | products |
| $MoO_2(dtc)_2$ | 25 °C, 1 h | $Mo_2O_3(dtc)_4$ + PhN=NPh | 25 °C, 1 min | $Mo_2O_3(dtc)_4$ + $O{=}PPh_3$ |
| $MoO_2(tox)_2$ | 25 °C, 6 h | $Mo_2O_3(tox)_4$ + PhN=NPh | 25 °C, 10 min | $Mo_2O_3(tox)_4$ + $O{=}PPh_3$ |
| $MoO_2(ox)_2$ or $MoO_2(acac)_2$ | 60 °C, 3 h | no reaction | 40 °C, 3.5 h | no reaction |
| $WO_2(tox)_2$ or $WO_2(ox)_2$ | 60 °C, 3 h | no reaction | 40 °C, 5 h | no reaction |

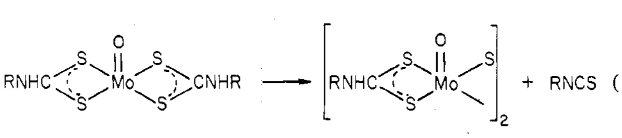
[a] Molar ratio 1:2 in $CH_2Cl_2$. [b] Abbreviations: dtc, diethyldithiocarbamato; tox, thiooxinato (8-mercaptoquinolinato); ox, oxinato (8-hydroxyquinolinato).

clo-hexyl (cHx) or *l*-neomenthyl. A further change to a dark brown ill-defined compound occurs upon standing for a few hours together with formation of alkyl isothiocyanate, RNCS.

A novel S,S-chelate ligand, $PhNHNHCS_2^-$, behaved similarly to $RNHCS_2^-$ in the reaction with $MoO_4^{2-}$, giving directly purple $Mo_2O_3(RNHNHCS_2)_4$. Attempts were made to prepare a dtc ligand with a long-chain alkyl group to create an effective hydrophobic site around the Mo center. Thus, $n\text{-}C_{12}H_{25}NHCS_2^-$ ($C_{12}$-dtc) was reacted with a $MoO_4^{2-}/S_2O_4^{2-}$ system to give at first a pink amorphous precipitate (probably $MoO(C_{12}\text{-dtc})_2$) which decomposed slowly on standing. The presence of the long-chain alkyl group makes isolation and purification of a monooxomolybdenum(IV) complex very difficult because of the waxlike property and air sensitivity.

Monooxomolybdenum(IV) complexes with two dialkyldithiocarbamato ($R_2$dtc) ligands, $MoO(R_2dtc)_2$, are known to be thermally stable compounds implying stabilization of the lower valency state by four sulfur donor atoms. Monooxomolybdenum(IV) species with two monoalkyldithiocarbamato ($RNHCS_2^-$) ligands were readily obtained by performing the same reaction under reducing conditions. Thus, $MoO((cHx)NHCS_2)_2$ was obtained as a pink powder from the reaction with a $MoO_4^{2-}/S_2O_4^{2-}$ system under $N_2$. The use of a relatively bulky N substituent probably helps to isolate the complex as a precipitate from the aqueous reaction mixture.

The (neomenthyldithiocarbamato)molybdenum(IV) complex $MoO(\textit{neo}\text{-Men-dtc})_2$ is converted to a doubly sulfur-bridged binuclear Mo(V) complex when dissolved in $CH_2Cl_2$. A similar conversion of $Mo_2O_3(xan)_4$ to give a doubly sulfur-bridged complex $Mo_2O_2S_2(xan)_2$ has been reported.[10] In our case the desulfurization of the carbamato ligand is accompanied by formation of isothiocyanate, (cHx)NCS, or *neo*-Men-NCS. This reaction demonstrates the propensity of the (monoalkyldithiocarbamato)molybdenum(IV) complex to undergo extrusion of a sulfur atom and release of an RNCS molecule and provides a new route to the doubly sulfur bridged Mo(V) complexes $Mo_2O_2S_2(RNHCS_2)_2$ (eq 1). Similar cleavage of the ($i$-Pr)$_2$dtc ligand in "$Mo^{II}[(i\text{-Pr})_2dtc]_2$" to bridging sulfide and $\eta^2$-coordinated ($i$-Pr)$_2$NCS has recently been shown.[11]



(1)

R = neomenthyl or cyclohexyl

Attempts were also made to prepare oxo complexes of Mo(VI) and Mo(V) with thioxanthato ($RSCS_2^-$) ligands. Upon addition of $n\text{-}PrSCS_2^-$ (Pr-txt) to "Mo(V)" species formed from $MoCl_5$ and water, a purple suspension of $Mo_2O_3(\text{Pr-txt})_4$ instantly resulted. In the process of isolating the complex, it changed to a deep blue solution at room temperature and gave blue well-formed crystals of $Mo(\text{Pr-txt})_4$. Other alkyl thioxanthato Mo complexes behaved similarly, but the isolation of pure crystalline compounds was unsuccessful. For example, the *S*-benzyl derivative $Mo_2O_3(\text{Bz-txt})_4$ was very unstable and changed to a green unidentifiable material. Very recently some $Mo(RSCS_2)_4$ complexes were prepared for R = Et, *i*-Pr, and *t*-Bu.[12]

The above-mentioned results as a whole show an apparent control of stability of *cis*-dioxomolybdenum(VI) vs. oxomolybdenum(V) species through the substituent Y on chelates of the type $YCS_2^-$. Thus, when the electron-donating alkyl groups are on the $R_2$dtc ligand, i.e. Y = $R_2N$, the *cis*-dioxomolybdenum(VI) species are stabilized to some extent. When the electron donation becomes weaker, as with Y = NHR or Y = N(Ph)R, the *cis*-dioxomolybdenum(VI) complexes are less stable. The xanthato ligands (Y = OR) destabilize the molybdenum(VI) but stabilize oxomolybdenum(V) species. Thioxanthato ligand (Y = SR) readily removes all the oxo groups in Mo(VI) species leading to Mo(IV) compounds.

**Oxidation Reactions with Dioxomolybdenum(VI) Chelates.** We have examined the reactivity toward (a) hydrazines, (b) tertiary phosphines, and (c) alcohols of a series of Mo(VI) chelates spanning (a) O,O chelation (e.g., acac), (b) O,N chelation (e.g., 8-hydroxyquinolinato (oxinato)), (c) S,N chelation (e.g., 8-mercaptoquinolinato (thiooxinato, tox) or $\beta$-aminoethanethiol), and (d) S,S chelation (e.g., dialkyldithiocarbamato ($R_2$dtc) or alkyl xanthato (xan)). The oxidizing ability of *cis*-dioxomolybdenum chelates $MoO_2(L\text{-}L)_2$ (L-L = chelating anion) is best illustrated by the reactions with hydrazobenzene. As shown in Table I, the reaction proceeds with the complexes containing S,S and S,N chelation, i.e., with L-L = $R_2$dtc and tox. Neither the O,O nor N,O chelates of the type $MoO_2(L\text{-}L)_2$ oxidize hydrazobenzene below 80 °C. The reactions with monoarylhydrazines will be described in a later part of this paper. The asymmetrically disubstituted hydrazine $Et_2NNH_2$ was inert at room temperature to all the dioxomolybdenum chelates so far examined.

In the oxidation of tertiary phosphine,[13] e.g., $Ph_3P$ or $n\text{-}Bu_3P$, various molybdenum(VI) chelates display a similar trend (Table I). Again, the presence of sulfur ligands enhances oxidative ability of dioxomolybdenum(VI) complexes. Note that $MoO_2(acac)_2$ and $MoO_2(ox)_2$ are poor oxidants. Stoichiometric oxidation of $Ph_3P$ with $MoO_2(Et_2dtc)_2$ has already been reported and was found to be useful for analysis of $Ph_3P$.[13] We have found that $MoO_2(tox)_2$ is an effective catalyst for aerial oxidation of $Ph_3P$ in EtOH.

The observed trend in the oxidative reactions of dioxomolybdenum complexes reflects the ability of sulfur chelates to stabilize the lower oxidation state of molybdenum as described above. Since tungsten is usually an antagonist[14] for molybdenum in biological systems, the oxidative ability of an isostructural tungsten complex $WO_2(tox)_2$ was examined. It failed to show the reactivity of the Mo analogue. Here again, W compounds are more difficult to reduce than the corresponding Mo compounds.

The oxidizing ability of the molybdenum(VI) dithiocarbamates is also demonstrated by the reaction with primary alcohols. Thus, benzyl alcohol reduced $MoO_2(Et_2dtc)_2$ to $Mo_2O_3(Et_2dtc)_4$ at room temperature. The reaction mixture was examined by GLC, and almost quantitative formation of benzaldehyde was found. Secondary alcohols, such as 2-propanol and *l*-menthol also reduced $MoO_2(Et_2dtc)_2$, but *t*-BuOH did not. Benzhydrol, $Ph_2CHOH$, reduced the complex slowly and the organic product was examined by the IR spectrum; no specific assignment could be made at this time but benzophenone is not among the products. Indoline also reacts with $MoO_2(Et_2dtc)_2$ to give $Mo_2O_3(Et_2dtc)_4$ but the organic product was not the expected dehydrogenated one, indole, and not readily identifiable by conventional spectroscopy. Detailed characterization of all of these reaction products requires considerable investigation and is beyond the scope of this paper.

Dioxomolybdenum(VI) chelates $MoO_2L_2$ in the absence of sulfur coordination were found to be inert in these reactions. Attempts to oxidize aldehydes with $MoO_2(Et_2dtc)_2$ were unsuccessful, intractable brown solids being the products. A recent report of Miller and Wentworth[15] pointed out the absence of oxidation of aldehydes by $MoO_2(cys\text{-}OEt)_2$.

We have also examined oxidation of primary alcohols by $MoO_2(cys\text{-}OEt)_2$ and have found no reaction below 50 °C.

The observed oxidizing ability of dioxomolybdenum(VI) complexes can be related to their Mo=O stretching frequencies. As shown in Table II, the frequency decreases on successive introduction of sulfur atom coordination. The lower the frequency, the higher is the ability to transfer an oxygen atom to a substrate, e.g., phosphine. The corresponding tungsten analogues have higher W=O stretching frequencies as compared to those of the molybdenum analogues. This trend is in accord with the well-known inertness of tungsten(VI) compounds toward reduction. Since the tungsten atom is heavier than the molybdenum atom, the higher W=O stretching frequency indicates larger force constants associated with it.

**Condensation Reactions of Dioxomolybdenum(VI) Complexes ($MoO_2(L\text{-}L)_2$) with Arylhydrazines.** Reactivity of dioxomolybdenum(VI) complexes toward arylhydrazines and the resulting products depend on the identity of the chelates. Thus, the dioxo complexes with N,O or N,S chelates slowly react with phenylhydrazine in ethanol to give at first the mono-condensation products $MoO(=NNHPh)(L\text{-}L)_2$ (L-L = tox) admixed with the starting material. The second condensation occurs with difficulty even on refluxing in ethanol, but in the presence of excess phenylhydrazine the condensation product is converted to the bis(phenyldiazenido) complex ($Mo(N=NPh)_2(L\text{-}L)_2$, L-L = ox or tox) obtained as red or brown crystals. Chatt et al. also briefly reported the same product for L-L = ox.[16]

In the case of an S,S chelate $MoO_2(R_2dtc)_2$ the same reaction with arylhydrazine at room temperature smoothly gives a brown mono-condensation product "$MoO(=NNHPh)(R_2dtc)_2$" which further reacts with arylhydrazine resulting in an aryldiazenido complex $Mo_2(=NN\ Ph)_3(R_2dtc)_4$ through the presumed intermediate, bis-condensation product "$Mo(=NNHPh)_2(R_2dtc)_2$". Group 8 metal complexes of arylhydrazido(2−) (M=NNHAr) and aryldiazene M(NH=NAr) are likewise readily converted into aryldiazenido complexes MN=NAr through electron transfer and deprotonation. The reaction of $WO_2(tox)_2$ with excess phenylhydrazine proceeded slowly even at 80 °C to give the mono-condensation product $WO(=NNHPh)(tox)_2$. Thus, the tungsten complex $WO_2(tox)_2$ is hard to condense with $PhNHNH_2$.

The bis(phenyldiazenido) complex with $R_2dtc$ ligands was found to react with an excess reducing agent (e.g., $PhNHNH_2$ or $NaBH_4$) to give N–N cleavage products, among which an arylamine (aniline) is found in substantial yield (maximum 50%) (see Scheme III). The determination of ammonia in these reactions has not been attempted due to the small amounts involved and the possible decomposition of arylhydrazine during the analytical process. Formation of a binuclear deep purple compound $Mo_2(N_2Ph)_3(R_2dtc)_4$ in the reaction of $MoO_2(R_2dtc)_2$ (R = Me, Et) with phenylhydrazine in a 1:3 ratio at 80 °C is based on the elemental analysis and IR and NMR spectra. No strong IR absorption in the Mo=O stretching region was found and the ratio of the NMR peak areas assigned to Ph vs. Me or Et groups indicates the stated composition. The solution molecular weight was not obtainable due to limited solubility in benzene. In this reaction, one aryldiazenido ligand seems to have been lost by reductive cleavage due to electron transfer followed by protonation from the solvent. The reductive cleavage and protolysis would give a reactive coordinatively unsaturated molybdenum species (probably $Mo(N_2Ar)(R_2dtc)_2$) which reacts with $Mo(N_2Ar)_2(R_2dtc)_2$ to give the observed product. The exact structure of this novel compound is now under investigation.

Scheme III

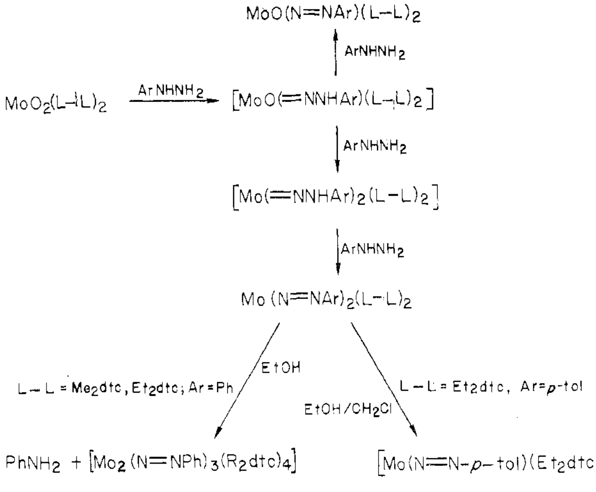


**Table II.** Infrared Oxomolybdenum and Oxotungsten Stretching Frequencies[a] ($\nu_{M=O}$) in $cm^{-1}$

| | $\nu_{M=O}$(asym) | $\nu_{M=O}$(sym) |
|---|---|---|
| $MoO_2(dtc)_2$[b] | 878 | 910 |
| $MoO_2(tox)_2$ | 890 | 920 |
| $MoO_2(ox)_2$ | 902 | 926 |
| $MoO_2(sal)_2$ | 909 | 938 |
| $WO_2(tox)_2$ | 897 | 940 |

[a] In Nujol mulls. [b] For abbreviations, see Table I.

A compound of composition "$Mo(Et_2dtc)_2(N_2C_7H_7)$" was isolated by the reaction of $MoO_2(Et_2dtc)_2$ with *p*-tolylhydrazine in $EtOH/CH_2Cl_2$ as red-brown microcrystals characterized by analysis, NMR spectra, and IR spectra (see Tables III–V), but the molecular weight was not obtainable due to its limited solubility. Chatt et al.[16] have recently communicated the isolation of the related compound $Mo(N_2Ph)(R_2dtc)_3$ from $MoO_2(Et_2dtc)_2$ and $PhNHNH_2$ in the presence of $Et_2dtc^-$. Here the reductive cleavage of one of the $N_2Ph$ ligands is thought to be followed by coordination of $R_2dtc^-$ ligand. The reactions described above are summarized in Scheme III. The characterization of the complexes isolated in an analytically pure state are listed in Tables III–V. The reductive cleavage of the N=N bond occurred only for the complexes with S,S chelate ligands and therefore seems due to the characteristic properties associated with the dithiocarbamato ligand.

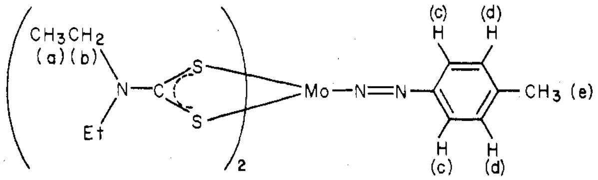
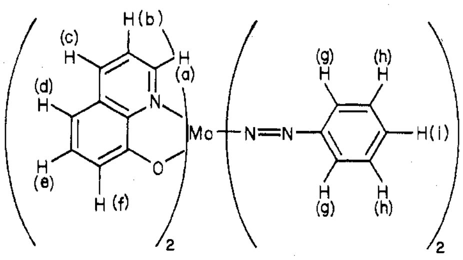
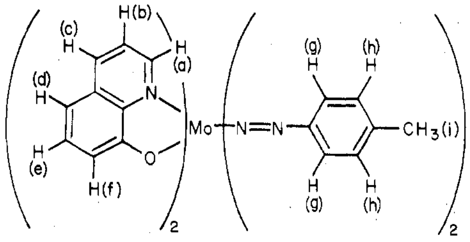
According to previous reports,[6] the aryldiazenido and arylhydrazido ligands are readily interconvertible through a protonation/deprotonation process with electron transfer to or from the metal. The same transformation is involved in the (aryldiazenido)molybdenum complexes (eq 2).

$$(R_2dtc)_2Mo(N=NAr)_2 + 2H^+ \rightleftarrows (R_2dtc)_2Mo(=NNHAr)_2 \quad (2)$$

**Table III.** Elemental Analyses

| | % found | | | % calcd | | |
|---|---|---|---|---|---|---|
| | C | H | N | C | H | N |
| $MoO(tox)_2(N_2Ph)$ | 53.82 | 3.41 | 10.24 | 53.63 | 3.19 | 10.42 |
| $Mo(tox)_2(N_2Ph)_2$ | 57.44 | 3.52 | 12.95 | 57.51 | 3.54 | 13.41 |
| $Mo(ox)_2(N_2Ph)_2$ | 60.30 | 3.83 | 13.49 | 60.61 | 3.73 | 14.14 |
| $MoO(ox)_2(N_2\text{-}p\text{-}tol)$ | 58.14 | 3.64 | 10.86 | 57.81 | 3.69 | 10.79 |
| $WO(tox)_2(NNHPh)$ | 46.41 | 3.38 | 8.75 | 46.02 | 2.90 | 8.94 |
| $Mo_2(N_2Ph)_3(Me_2dtc)_4$ | 36.27 | 4.03 | 13.84 | 36.10 | 3.97 | 14.04 |
| $Mo_2(N_2Ph)_3(Et_2dtc)_4$ | 41.61 | 5.19 | 12.76 | 41.19 | 5.14 | 12.59 |
| $Mo(Et_2dtc)_2(N_2\text{-}p\text{-}tol)$ | 40.08 | 5.10 | 11.07 | 39.98 | 5.32 | 10.95 |
| $Mo_2O_4(Et_2dtc)_2$ | 21.38 | 3.58 | 4.92 | 21.74 | 3.65 | 5.07 |
| $MoO((cHx)(H)dtc)_2$ | 36.38 | 5.17 | 6.08 | 36.51 | 5.25 | 6.08 |
| $Mo_2O_2S_2((l\text{-}neo\text{-}Men)(H)dtc)_2$ | 35.25 | 5.51 | 3.78 | 35.28 | 5.38 | 3.74 |
| $Mo(n\text{-}PrSCS_2)_4$ | 27.49 | 4.02 | | 27.41 | 4.03 | |
| $Mo_2O_2S_2((cHx)_2dtc)_2$ | 38.65 | 5.60 | 3.58 | 39.00 | 5.54 | 3.50 |
| $Mo_2O_2S_2((i\text{-}Pr)_2dtc)_2$ | 26.06 | 4.32 | 4.24 | 26.24 | 4.40 | 4.37 |

**Table IV.** $^1$H NMR Data[a] of (Aryldiazenido)molybdenum Complexes

| complexes | | δ | ratio | mult | J, Hz |
|---|---|---|---|---|---|
|  | H(a) | 1.20 | 12 H | t | 6.6 |
| | H(b) | 3.76 | 8 H | q | 7.2 |
| | H(c) | 7.04 | 4 H | d | 8.7 |
| | H(d) | 7.88 | | d | 9.0 |
| | H(e) | 2.30 | 3 H | s | |
|  | H(a) | 8.66 | 2 H | d | 4.8 |
| | H(f) | 8.40 | 2 H | d | 8.6 |
| | H(b–e, g–i) | 7.26–7.72 | 18 H | m | |
|  | H(a) | 8.52–8.72 | 2 H | b | |
| | H(f) | 8.30–8.40 | 2 H | b | |
| | H(b–e, g, h) | 7.16–7.76 | 16 H | m | |
| | H(i) | 2.34 | 6 H | s | |

[a] Collected in $Me_2SO\text{-}d_6$.

**Table V.** Properties and Spectral Data of Aryldiazenido(1–) and Arylhydrazido(2–) Complexes

| complexes | color | mp, °C | $\lambda_{max}$,[a] nm | IR,[b] cm$^{-1}$ |
|---|---|---|---|---|
| $Mo(tox)_2(NNPh)_2$ | dark brown | 227–229 | 360 sh, 437,[c] 524 sh | 1638 m, 1616 m, 1574 m, 1539 s, sh, 1521 vs, 1507 s, sh |
| $MoO(tox)_2NNPh$ | brown | 228–231 | 432, 660 sh | 1595 w, 1559 w, sh, 1511 s, 1500 s, 1487 s, 890 m |
| $Mo(ox)_2(NNPh)_2$ | brownish red | 228–231 | 398, 511 | 1633 m, 1606 m, 1575 s, 1537 s, 1500 s, 1487 s |
| $WO(tox)_2NNHPh$ | brown | 180–188 (color change) | | 3240 w ($\nu_{NH}$), 903 s ($\nu_{W=O}$) |
| | | 196–203 | 407, 455 sh, 522 sh | 1606 m, 1505 s, 1445 s |
| $Mo(Et_2dtc)_2NN\text{-}p\text{-}tolyl$ | brown | 112–115 | 413, 545 sh | 1614 w, 1576 w, sh, 1538 s, sh, 1449 vs, 1446 s, sh |
| $MoO(ox)_2NN\text{-}p\text{-}tolyl$ | reddish brown | 252–254 (color change) 300 | 393, 515 | 1640 m, 1609 m, 1576 s, 1538 s, 1490 vs, 898 s, 923 m, sh ($\nu_{Mo=O}$) |

[a] In $C_6H_6$. [b] Measured in Nujol. [c] Measured in $CH_2Cl_2$.

The proton basicity at the uncoordinated nitrogen atom and ease of redox reaction at the metal appear to be responsible for this transformation. Note the relative stability of [hydrazido(2–)] tungsten complex compared to that of molybdenum analogue. Sulfur chelates seem to enhance the basicity and at the same time promote the redox reaction. Further protonation at the NH part of M=NNHR grouping coupled with the electron transfer would give an amine, $NH_2R$, and a nitride complex (M≡N). The formation of aniline in the reaction of $Mo(N{=}NAr)_2(R_2dtc)_2$ may be explicable in this way.

**ESCA Binding Energies of Relevant Molybdenum Chelates.** The binding energies of some representative molybdenum complexes containing sulfur chelates or a diazene ligand have

**Table VI.** Binding Energies (eV) of Molybdenum Complexes[a,d]

| compd | Mo(3d 3/2)[c] | Mo(3d 5/2)[c] |
|---|---|---|
| $MoO_2(S_2CNEt_2)_2$[b] | 234.5 | 231.5 |
| $Mo_2O_3(S_2CNEt_2)_4$[b] | 232.9 | 229.9 |
| $Mo_2O_3(tox)_4$ | 233.3 | 230.3 |
| $MoO(N{=}NC_6H_4CH_3)(ox)_2$ | 232.4 | 229.6 |
| $Mo(N{=}NPh)_2(ox)_2$ | 232.5 | 229.4 |
| $Mo_2(N{=}NPh)_3(S_2CNEt_2)_4$[b] | 231.6 | 228.5 |

[a] Measured by a Shimadzu-Du Pont Model 850, and the data were calibrated with the Au(4f 7/2) peak at 83.3 eV. [b] A weak peak exists at 226.0 eV. [c] The data are accurate to ±0.2 eV. The Mg Kα line was used as the X-ray source. [d] These values may be compared with the known values Mo(3d 5/2) (eV) in relevant metals and complexes: Mo(metal), 227.0; $Mo(CO)_6$, 227.6; $MoO_2$, 231.0; $MoS_2$, 228.1; $MoO_2(acac)_2$, 231.0 (S. O. Grim and L. J. Matienzo, *Inorg. Chem.*, **14,** 1014 (1975); W. B. Hughes and B. A. Baldwin, *ibid.*, **13,** 1531 (1974)).

been measured (see Table VI). The presence of sulfur donor atoms lowers the binding energy and effective charge on molybdenum. The presence of a diazene ligand also lowers the binding energy indicating the diazene ligand to be a soft ligand similar to the sulfur ones (see Table VI). The coexistence of these two ligands in the same complex, e.g., in $Mo_2(N{=}NPh)_3(dtc)_4$, results in the lowest observed value in the table. The observed trend in lowering the binding energy is also correlated to the increased covalency of Mo–S bonds as compared to the corresponding ones for Mo–O or Mo–N bonds. Covalency enhances $\pi$ interaction between metal d orbitals and ligand $p\pi$ orbitals. Increased delocalization of electrons in the metal–ligand $\pi$ orbitals is thus implied. The delocalization is also apparently correlated with the experimentally observed effects of sulfur ligands on the oxidation states of the metal as caused by a slight change even in remote parts of the ligand.

**Correlation of Redox Reactions with the Nature of Chelate Ligands.** The observed ease of various redox reactions of oxomolybdenum chelates has now been shown to be strongly influenced by the nature of the chelating ligands. In particular, the complexes with S,S ligands of dithio acid type exhibit redox behavior sensitively controlled by the nature of the Y group of the S,S chelates $YCS_2^-$.

The relative ease of reduction of Mo(VI) to Mo(V) in complexes of the type $MoO_2(L\text{-}L)_2$ may be quantitatively expressed by the reported values of the one-electron reduction potential: −0.83 V ($Me_2SO$) for $MoO_2(Et_2dtc)_2$ and −1.07 V ($Me_2SO$) for $MoO_2(ox)_2$.[17] In the binuclear Mo(V) complexes, a doubly sulfur-bridged complex $Mo_2O_2S_2(Et_2dtc)_2$ is reported[17] to be reduced to a postulated tetranuclear cluster anion $[Mo_4O_4S_4(Et_2dtc)_4]^-$, at the negative electrode potential of −1.00 V ($Me_2SO$). This value should be compared with the corresponding value of $Mo_2O_4(Et_2dtc)_2$, −1.23 V ($Me_2SO$).[17]

The electron delocalization effect of the dtc or xan chelates seems to be important since the chelating aliphatic dithiol complex $[Mo_2O_2S_2(SCH_2CH_2S)_2]^{2-}$ is found to be more difficult to reduce to the Mo(IV) state (reduction potential at −1.85 V[18]) probably because of the accumulation of electron density by the two thiolates coordinated and by the overall negative charges creating an electrostatic barrier.

Comparison of the chemical properties of isostructural Mo and W complexes revealed an interesting difference in their reactivity. For example, the Mo congeners are more easily reduced and condensed with hydrazine derivatives than the W analogues.

In conclusion, the reactivity of oxo ligands on molybdenum is increased by sulfur coligands. For example, dehydrogenation of hydrazines or alcohols, oxygen-atom transfer to tertiary phosphines,[13] and condensation with arylhydrazines[4] are remarkably accelerated by use of suitable sulfur coligands. All of the oxo ligands of $MoO_4^{2-}$ are also readily eliminated in the presence of excess thioxanthate anion to give $Mo(txt)_4$ even at room temperature. The observed trend should have some implications about the reaction pathways in molybdenum enzymes where redox reactions are presumed to be promoted by coordination of thiolato ligands in a special environment.

## Experimental Section

**Instruments.** Infared spectra were taken on a Jasco Model IR-S, NMR spectra on a Jeol JNM 4H-100, visible spectra on a Hitachi EPS-3T, and GLC on a column packed with poly(ethylene glycol) 6000. All reactions were carried out under pure nitrogen.

**Preparation of Molybdenum Complexes.** $MoO_2(Et_2dtc)_2$,[19] $MoO_2(ox)_2$,[20] $MoO_2(tox)_2$,[21] $MoO_2(sal)_2$,[22] $WO_2(tox)_2$,[21] $Mo_2O_3(tox)_4$,[21] $Mo_2O_3(Et_2dtc)_4$,[23] and $MoO(Et_2dtc)_2$[24] were prepared by methods in the literature. The following complexes have been prepared as described.

**Di-μ-oxo-bis[oxo(diethyldithiocarbamato)molybdenum(V)], $Mo_2O_4(Et_2dtc)_2$.** Aniline (5 mL) was added to $MoO_2(Et_2dtc)_2$ (210 mg) to give a yellow solution which was heated to 80 °C for 20 min. The color changed to green ($\lambda_{max}$ 565 nm). Ethanol was added to the reaction mixture to precipitate yellow crystals which were filtered, washed with ethanol, and dried (10–15% yield). The analytical values agree with the above composition confirming the purity of the product prepared by this method. The role of aniline is to reduce the metal to the Mo(V) stage and also to eliminate the $Et_2dtc$ ligand as thiourea derivatives $(RNH)_2C{=}S$. The preparative method[13b] starting from aqueous $MoCl_5$ solutions was found to give only traces of the desired complex. Since two different structures (syn and anti) are possible, the complex prepared by our method may be different from the one reported by Newton et al.[25] because the complex behaved somewhat differently in the reaction with organic thiols probably due to difference in the solubility.

**Di-μ-oxo-bis[oxo(dicyclohexyldithiocarbamato)molybdenum(V)], $Mo_2O_4((cHx)_2dtc)_2$.** This was prepared in a similar way as described above.

**Di-μ-sulfido-bis[oxo(diethyldithiocarbamato)molybdenum(V)], $Mo_2O_2S_2(Et_2dtc)_2$.** Hydrogen sulfide was passed through a solution of $Na_2MoO_4{\cdot}2H_2O$ (12 mmol) in water (50 mL). To the resulting deep red solution was added a solution of sodium diethyldithiocarbamate (12 mmol) in water (30 mL). Hydrochloric (2 N) acid was added dropwise to the solution until the pH was 8. A brown precipitate was formed, and the mixture was stirred for several hours. The precipitate was filtered off, washed with water, and dried in vacuo. The yield was 1.5 g. Recrystallization from toluene gave golden yellow crystals.

The corresponding *N,N*-dicyclohexyl and *N,N*-diisopropyl complexes, $Mo_2O_2S_2(S_2(cHx)_2dtc)_2$ and $Mo_2O_2S_2(i\text{-}Pr_2dtc)_2$, were prepared by the same method.

**Di-μ-sulfido-bis[oxo(neomethyldithiocarbamato)molybdenum(V)], $Mo_2O_2S_2$(*neo*-Men(H)-dtc)$_2$.** A solution of $Na_2MoO_4{\cdot}2H_2O$ (0.55 g) in $H_2O$ (10 mL) was added to a solution of sodium neomethyldithiocarbamate (1.4 g) in methanol (20 mL). The mixture was added dropwise to a solution of $Na_2S_2O_4$ (5 g) in water (20 mL). A pink precipitate (probably $MoO[S_2CN(H)$-*neo*-Men$]_2$) was formed and washed with water and water–ethanol (1:1). The product was dissolved in dichloromethane and warmed. The color changed through purple to green, and a yellow precipitate was formed. The precipitate was filtered off, washed with dichloromethane, and then dried in vacuo. The filtrate was evaporated and the residual oil was sublimed in vacuo to give a liquid product showing a strong IR peak at 2100 cm$^{-1}$.

**Oxo(monocyclohexyldithiocarbamato)molybdenum(IV), MoO-((cHx)(H)dtc)$_2$.** Sodium *N*-cyclohexyldithiocarbamate (5.5 g) and $Na_2MoO_4{\cdot}2H_2O$ (2.4 g) in water (60 mL) and ethanol (6 mL) were mixed. This solution was added dropwise into $Na_2S_2O_4$ (10.6 g) dissolved in water (45 mL). A reddish purple precipitate was formed and slowly became pink. The suspension was stirred overnight at room temperature. The pink precipitate was filtered off, washed with water and ethanol–water (1:1), and then dried under high vacuum: yield 40% (1.85 g); mp 119–121 °C; IR (1535 (s), 1450 (s), 1410 (m), 1250 (m), 1155 (m), 1087 (m), 980 (m), 920 (s) cm$^{-1}$.

**Tetrakis(*n*-propyl thioxanthato)molybdenum(IV), Mo($S_2CS$-*n*-Pr)$_4$.** A yellow solution of sodium *n*-propyl thioxanthate (0.3 mol) in ethanol was added dropwise to a solution of molybdenum pentachloride (0.01

mol) in water (100 mL) at 0 °C. A purple tar was formed and extracted with toluene. The toluene solution was concentrated and *n*-hexane was added to give black crystals: yield 10% (0.7 g); mp 96 °C; IR 1295 (m), 1240 (m), 1010 (s), 960 (s), 680 (m) $cm^{-1}$; $\lambda_{max}$ 450, 503, 620, 863 nm.

**Reaction of Dioxomolybdenum(VI) Complexes with Arylhydrazines. (a) $Mo(ox)_2(NNPh)_2$.** Phenylhydrazine (148 $\mu$L, 1.50 mmol) was added dropwise into a yellow suspension of $MoO_2(ox)_2$ (209 mg, 0.502 mmol) in 20 mL of ethanol. While the reaction mixture was refluxed for 3 h, the color changed to brownish red, and brownish red microcrystals separated out. They were filtered off, washed with ethanol, and dried in vacuo. The yield was 268.3 mg (88.7%). The crude crystals were recrystallized from acetone; yield 50.9%.

**(b) $MoO(tox)_2NNPh$ and $Mo(tox)_2(NNPh)_2$.** Phenylhydrazine (132 $\mu$L, 1.34 mmol) was added dropwise into an orange suspension of $MoO_2(tox)_2$ (200.6 mg, 0.447 mmol) in 17.5 mL of ethanol. Brown microcrystals of $MoO(tox)_2NNPh$ precipitated from the reaction mixture during refluxing for 5 h and were filtered. From the filtrate, the brown microcrystals of $Mo(tox)_2(NNPh)_2$ crystallized out after the filtrate was allowed to stand for 3 days. Both products were washed with ethanol and dried in vacuo. The yields of $MoO(tox)_2NNPh$ and $Mo(tox)_2(NNPh)_2$ were 218.1 mg (90.8%) and 4.0 mg (1.4%), respectively.

**(c) $WO(tox)_2NNHPh$.** Phenylhydrazine (28.5 $\mu$L, 0.290 mmol) was added dropwise into a greenish yellow suspension of $WO_2(tox)_2$ (51.8 mg, $9.66 \times 10^{-2}$ mmol) in 20 mL of ethanol. After being stirred for 17.5 h, the reaction mixture was refluxed for 6 h. During the period of refluxing, a dark brown solution resulted. This was filtered and concentrated to half of the original volume. By the period of concentration brown microcrystals were separated. They were filtered off, washed with ethanol, and dried in vacuo. The yield was 27.0 mg (44.6%).

**(d) $MoO(ox)_2NN$-*p*-tol.** A light brown solution of *p*-tolylhydrazine hydrochloride (122.1 mg, 0.775 mmol) in 10 mL of ethanol was neutralized with 1.24 mL of 0.5 N NaOH solution. This solution was added into a suspension of $MoO_2(ox)_2$ (107.6 mg, 0.258 mmol) in 3 mL of ethanol. While the reaction mixture was refluxed for 4 h, brown microcrystals were separated. They were filtered off, washed with ethanol, and dried in vacuo. The yield was 101.5 mg (75.6%).

**Reduction of $Mo_2(Et_2dtc)_4(NNPh)_3$ by Sodium Borohydride.** Sodium borohydride (56.4 mg, 1.50 mmol) was added into a suspension of $Mo_2(Et_2dtc)_4(NNPh)_3$ (88.6 mg, 0.149 mmol) in ethanol (10 mL). The reaction mixture was stirred at 20 °C for 24 h. The resultant suspension was evaporated, and ethanol was trapped in a methanol–dry ice bath. Aniline in the trapped liquid was analyzed quantitatively by GLC with naphthalene as a reference substance. The aryldiazenido complexes containing ox or tox ligands also react with sodium borohydride under the stated conditions. However, no aniline was detected among the product.

**Reaction of $MoO_2(R_2dtc)_2$ with Arylhydrazine. (a) Molar Ratio 1:1 in Ethanol (R = Et).** The reaction at room temperature proceeded during several hours to give brown microcrystals: mp 149–151 °C; $\lambda_{max}(C_6H_6)$ 416, 534 nm; IR(Mo═O) 913 $cm^{-1}$. The analytical and spectroscopic data indicated the presence of mono-condensation product ($MoO(Et_2dtc)_2$(═NNHPh)) since the NMR spectrum showed the presence of NH at 1.96 ppm in $CDCl_3$.

**(b) Molar Ratio 1:3 in Ethanol (R = Me).** The reaction with phenylhydrazine went smoothly on refluxing for 1 h to give deep purple microcrystals in 90% yield: mp 216–217 °C; $\lambda_{max}(C_6H_6)$ 420, 547 nm. The NMR spectrum ($CDCl_3$) showed three sharp methyl resonances together with peaks due to the phenyl groups in a proton ratio of 24:15. No strong IR peaks were found in the Mo═O stretching region. Although the molecular weight in solution could not be measured due to the limited solubility, the analytical data indicate the composition to be $Mo_2(Me_2dtc)_4(N_2Ph)_3$. The mass spectrum showed peaks due to $Mo(Me_2dtc)_3(N_2Ph)$[16] upon heating at the sampling port.

**(c) Molar Ratio 1:3 in Ethanol (R = Et).** The reaction with phenylhydrazine was very similar to that described and gave a product of similar appearance in 62% yield: mp 101–105 °C, $\lambda_{max}$ 419, 547 nm. The analytical data also indicate the composition $Mo_2(Et_2dtc)_4(N_2Ph)_3$.

**(d) Molar Ratio 1:3 in Ethanol–Dichloromethane (R = Et).** A similar reaction with *p*-tolylhydrazine gave somewhat different results as described below. A light brown solution of *p*-tolylhydrazine (2.12 mmol) in 25 mL of ethanol was added into a yellow solution of $MoO_2(S_2CNEt_2)_2$ (201.4 mg, 0.710 mmol) in 50 mL of dichloromethane. A dark brown solution resulted after stirring for 16 h and was concentrated to 26 mL. A brown product which precipitated during the period of concentration redissolved upon heating at 45 °C on a water bath. Brown microcrystals were separated after cooling at −20 °C for 2 days. They were filtered off, washed with ethanol, and dried in vacuo. The yield was 66.0 mg (18.1%): mp 115 °C, $\lambda_{max}$ 415, 538 nm. The analytical data shown in Table III indicate composition $Mo(Et_2dtc)_2(N_2C_7H_7)$, which is supported by the $^1H$ NMR spectrum (Table IV) indicating the presence of *p*-tolyl and $Et_2dtc$ groups in 2:1 ratio. Since the complex was found to be not very stable to air in solution, accurate data on the molecular weight could not be obtained. An oligomeric structure seems probable for this complex.

**Stoichiometric Oxidation of Benzyl Alcohol with $MoO_2(Et_2dtc)_2$.** $MoO_2(Et_2dtc)_2$ (0.4 g, 0.94 mmol) was dissolved in benzyl alcohol (10 mL) with stirring. The initial yellow color turned purple on standing at room temerature. After 1 day purple crystals of $Mo_2O_3(Et_2dtc)_4$ (insoluble isomer characterized by the elemental analysis and IR spectrum) were collected, and the supernatant liquor was analyzed by GLC for benzaldehyde to find its almost quantitative yield. Similar reactions of $MoO_2(Et_2dtc)_2$ with a variety of primary and secondary alcohols, e.g., methanol, ethanol, or 2-propanol, were examined at room temperature in $CHCl_3$. In each case, $Mo_2O_3(Et_2dtc)_4$ formed after overnight standing. The organic products were not readily identified by examination of the reaction mixture by the $^1H$ NMR spectra. The reaction of $Ph_2CHOH$ with $MoO_2(Et_2dtc)_2$ proceeded in 24 h to give $Mo_2O_3(Et_2dtc)_4$, but the dehydrogenated product, $Ph_2CO$, was not found by the IR spectrum. An adduct formation with $Et_2dtc$ anion seems to be responsible for the absence of the ketonic products in these dehydrogenations.

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**Registry No.** $MoO(tox)_2(N_2Ph)$, 68539-87-7; $Mo(tox)_2(N_2Ph)_2$, 68539-88-8; $Mo(ox)_2(N_2Ph)_2$, 53540-23-1; $MoO(ox)_2(N_2$-*p*-tol), 68539-89-9; $WO(tox)_2(NNHPh)$, 68539-90-2; $Mo_2(N_2Ph)_3(Me_2dtc)_4$, 68813-08-1; $Mo_2(N_2Ph)_3(Et_2dtc)_4$, 68813-09-2; $Mo(Et_2dtc)_2(N_2$-*p*-tol), 68539-91-3; $Mo_2O_4(Et_2dtc)_2$, 50860-31-6; MoO((c-Hx)(H)dtc)$_2$, 68539-92-4; $Mo_2O_2S_2$((*l*-*neo*-Men)(H)dtc)$_2$, 68539-93-5; Mo(*n*-PrSCS$_2$)$_4$, 68525-32-6; $Mo_2O_2S_2$((c-Hx)$_2$dtc)$_2$, 68539-94-6; $Mo_2O_2S_2$((*i*-Pr)$_2$dtc)$_2$, 68539-95-7; $MoO_2(dtc)_2$, 18078-69-8; $MoO_2(tox)_2$, 17926-52-2; $MoO_2(ox)_2$, 17856-49-4; $MoO_2(sal)_2$, 53062-21-8; $WO_2(tox)_2$, 55835-57-9; $Mo(ox)_2(N_2$-*p*-tol)$_2$, 68539-96-8; $Mo_2O_3(S_2CNEt_2)_4$, 20023-86-3; $Mo_2O_3(tox)_4$, 64685-99-0; $Mo_2O_2S_2(Et_2dtc)_2$, 55723-33-6; $MoO(Et_2dtc)_2$(═NNHPh), 68539-97-9; $PPh_3$, 603-35-0; hydrazobenzene, 122-66-7; $PhNHNH_2$, 100-63-0; *p*-tolylhydrazine, 539-44-6.

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# Synthesis and Characterization of the Nickel(II)–Rubeanic Acid Complex on Interlamellar Surfaces of Molybdenum Trioxide

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A stable nickel(II)–rubeanic acid coordination polymer was first prepared in the interlayer space of $MoO_3$ by soaking hydrated nickel molybdenum trioxide in an acetone solution of rubeanic acid. The basal spacing of the rubeanic acid–Ni–$MoO_3$ complex was found to be 9.5 Å by powder X-ray diffraction. Both chemical analysis and thermogravimetry indicated that the molar ratio of nickel ion to rubeanic acid is 1:1. The most probable molecular structure of the intercalated nickel(II)–rubeanic acid complex is suggested from the infrared spectrum and magnetic susceptibility of the material.

## Introduction

The study of coordination polymers has been widely carried out and undoubtedly will be continued in the future, because many of them exhibit interesting physical properties, as evidenced from studies of their semiconductivity, magnetic susceptibility, catalytic activity, and heat resistance. However, neither the molecular weight nor the molecular structure is easily determined because of their low solubilities and, in many cases, their low degree of crystallinity. Among the coordination polymers whose structures are still uncertain at present, there is one class composed of rubeanic acid (dithiooxamide) and transition metals.[2-4] The structural irregularity of the rubeanic acid (RA) complex has prevented a theoretical interpretation of the physicochemical properties of the compound. In order to resolve this ambiguity, a stereospecific synthesis was carried out by utilizing the two-dimensional interlayer spaces of clay mineral.[5] In that case, however, only the monomeric complex was formed, because the interatomic distance between the Cu(II) ions in the interlayer of montmorillonite was too large to bridge the distance between Cu(II) ions with rubeanic acid molecules. In order to solve this problem, it is necessary to find another suitable layered compound as a host material in which the amounts of exchangeable cation could be easily controlled. Fortunately, it was reported that $MoO_3$ can take up hydrated sodium ions and those ions are easily exchanged by various kinds of cations.[6] This behavior of hydrated sodium molybdenum trioxide is quite similar to that of clay minerals. $MoO_3$ is known to crystallize in a layer lattice in which two-dimensional metal oxide sheets are separated by a van der Waals gap.[7] In the present investigation, synthesis of nickel(II)–rubeanic acid coordination polymer in the interlayer space of $MoO_3$ was carried out and the structure of the complex was investigated by chemical analysis, X-ray diffraction, thermogravimetric analysis, infrared spectra, and magnetic susceptibility.

## Experimental Section

**Materials and Preparations.** Rubeanic acid (dithiooxamide) $NH_2C(S)C(S)NH_2$ was obtained from Mallinckrodt Chemical Works, and it was recrystallized from ethanol. Nickel chloride and molybdenum trioxide (Special Grade Reagent, Nakarai Chemicals, Ltd.) were used without further purification. Single crystals of $MoO_3$ were prepared by vapor-phase transport with $I_2$. $MoO_3$ can easily take up hydrated sodium cations between the interlayer space according to the procedure given below. Powders or single crystals of $MoO_3$ were suspended in aqueous solutions of 1 M $Na_2S_2O_4$ at room temperature for a few hours. The chemical formula of the material prepared in this way was determined to be $Na_{0.5}(H_2O)_nMoO_3$ by atomic absorption analysis. The intercalated sodium ions are easily replaced by Ni(II) ions by treating with 1 M aqueous solutions of nickel chloride at 100 °C for 1 day. The product was washed several times with acetone until a negative chloride ion test with $AgNO_3$ was obtained, and then it was dried in air. It was determined by conventional wet methods that this compound had a chemical formula of $Ni_{0.25}(H_2O)_nMoO_3$. The product was soaked in an acetone solution saturated with rubeanic acid at 60 °C for a few days, washed several times with acetone to remove free ligand molecules, and dried in vacuo. This product is denoted RA–Ni–$MoO_3$ in this paper.

**Measurements.** The X-ray diffraction patterns of $Na_{0.5}(H_2O)_nMoO_3$, $Ni_{0.25}(H_2O)_nMoO_3$, and its rubeanic acid complex RA–Ni–$MoO_3$ were obtained using a Rigaku-Denki diffractometer with Ni-filtered Cu K$\alpha$ radiation.

Differential thermogravimetric analysis was made up to 700 °C using a Rigaku-Denki unit programmed for a heating rate of 10 °C/min.

The infrared spectra in the region 4000–700 $cm^{-1}$ were obtained on a Hitachi Perkin-Elmer spectrophotometer fitted with a sodium chloride prism. Samples were dispersed in potassium bromide disks. Calibration of the spectrophotometer was made using polystyrene bands.

The magnetic susceptibilities were determined by the Faraday method using a magnetic field of about 10 000 G. The measurement was conducted in the temperature region between 80 and 300 K. The temperature calibration of the equipment was obtained by the measurement of the magnetic susceptibility of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$.

The electrical resistivity measurements were carried out on a pressed body of powdered specimens with a four-probe technique in about $10^{-2}$ Torr at room temperature.

## Results and Discussion

The X-ray diffraction data of $MoO_3$, $Na_{0.5}(H_2O)_nMoO_3$, and $Ni_{0.25}(H_2O)_nMoO_3$ and its rubeanic acid complex are tabulated in Table I. In the Na ion uptake reaction, the basal spacing of $MoO_3$ increased from 6.9 to 11.4 Å at 25 °C and 70% humidity. In the case when the Na ion was exchanged by Ni(II) ion, the value of the basal spacing increased to 14.6

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