transformation of VCoSb and VFeSb involves an increase of coordination number.

Interatomic distances between the constituent atoms of both MgCuSb- and Ni_2In-type structures are shown in Table V. From these, it is seen that the nearest-neighbor distance between the transition metal and Sb shrinks from D(Co–Sb) = 0.2511 nm to $D(M_d$–Sb) = 0.2425 nm, while that between the transition metals expands from D(V–Co) = 0.2511 nm to $D(M_a$–$M_a)$ = 0.2699 nm in the transformation.

In discussing interatomic distances in metal and intermetallic compounds, Pearson pointed out that Pauling's bond-order rule appears to be most reliable[6]

$$D(n) - D(1) = 0.060 \log n \text{ (Pauling's rule)}$$

In this equation n is the number of valence electrons per ligand, $D(1)$ represents the single-bond distance calculated by using Pauling's single-bond radii[7], and $D(n)$ is the observed bond distance.

In VCoSb-I with the MgCuSb-type structure ($C1_b$), D(Co–Sb) = 0.2511 nm is comparable with the sums of Co and Sb single-bond radii ($D(1)$ = 0.2533 nm), while D(Co–V) = 0.2511 nm is larger than the sums of Co and V single-bond radii ($D(1)$ = 0.2386 nm). The bond orders are calculated to be 1.17 for the Co–Sb bond and 0.62 for the Co–V bond. These values of bond order indicate that the Co–Sb bond is much stronger than the Co–V bond. Consequently, the Co atom is coordinated substantially by the four Sb atoms forming a tetrahedron due to the strong Co–Sb bond, although it is surrounded apparently by four Sb and four V atoms. That the bond order is 1.17 for the Co–Sb bond and that there is a tetrahedral bond directionality indicate that covalency between Co and Sb atoms occurs.

In VCoSb-II with the Ni_2In-type structure ($B8_2$), $D(M_d$–Sb) = 0.2425 nm is much smaller than the sums of M_d and Sb single-bond radii ($D(1)$ = 0.2584 nm), but $D(M_a$–$M_a)$ = 0.2425 nm is larger than the single-bond separation between M_a atoms ($D(1)$ = 0.2386 nm). The bond orders are calculated to be 1.84 for the M_d–Sb bond and 0.30 for the M_a–M_a bond. Considering the calculated value of n and the triangular bond directionality for the M_d–Sb bond, a strong covalency between M_d and Sb atoms is expected. It is concluded that the metal atom forms the covalent bond with the Sb atom in both MgCuSb- and Ni_2In-type structures and that the strength of the covalent bond increases in the transformation from the MgCuSb- to Ni_2In-type structure.

Registry No. VCoSb, 12526-55-5; VFeSb, 66590-17-8.

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Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80309

Reactions of Metal–Disulfur Complexes with Nucleophiles and Electrophiles[1]

K. LEONARD, K. PLUTE, R. C. HALTIWANGER, and M. RAKOWSKI DuBOIS*

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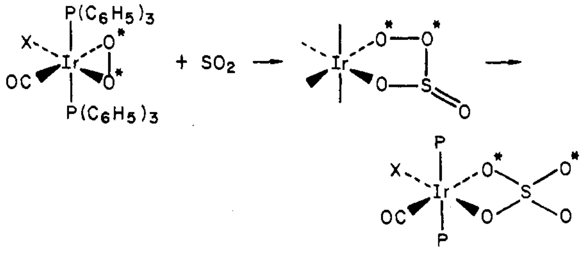
New synthetic methods for the preparation of the disulfur complexes of molybdenum $MoOS_2(S_2CNR_2)_2$ (where R = CH_3, C_2H_5, and n-C_3H_7) are described. The reactions of these disulfur complexes with a series of nucleophiles, N (N = $P(OC_2H_5)_3$, $P(C_6H_5)_3$, CH_3NC, CN^-, and SO_3^{2-}), have been characterized, and in each case the sulfur-substituted nucleophile ($\mathrm{S}\underset{\cdot\;\cdot}{-}\mathrm{N}$) and $MoO(S_2CNR_2)_2$ are produced. Reaction of $MoOS_2(S_2CNR_2)_2$ with C_6H_5SH or $C_6H_5S^-$ yields the dimeric molybdenum(V) complex $Mo_2O_2S_2(S_2CNR_2)_2$. The molybdenum–disulfur complexes do not react with the electrophile CH_3I, but reaction with CH_3SO_3F produces a new complex containing a persulfide ligand, $[MoO(SSCH_3)(S_2CNR_2)_2]^+$. Characteristics of the synthetic molybdenum complexes are compared to those of certain molybdoenzymes which have been found to contain labile sulfur atoms. Reactions of the coordinated disulfur ligand in $IrS_2(dppe)_2Cl$ (where dppe = bis(diphenylphosphino)ethane) have also been studied. In contrast to the molybdenum systems, no reactions occur with the common thiophiles $P(C_6H_5)_3$, $P(OC_2H_5)_3$, and CN^-. Methyl fluorosulfonate reacts to form a persulfide complex of Ir(III), $[Ir(SSCH_3)(dppe)_2]^{2+}$ which has been characterized by ^1H and ^{31}P NMR, conductivity studies, and analytical data.

Introduction

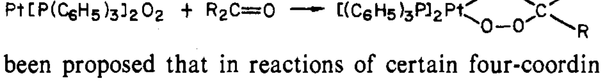
Although examples of mononuclear complexes containing the dioxygen ligand are known for most transition metal ions,[2] few monomeric complexes containing the analogous disulfur ligands have been characterized.[3-10] The latter have been prepared principally by two methods: by the reaction of elemental sulfur with coordinatively unsaturated compounds[4-6a] or by the reaction of hydrogen sulfide with compounds containing basic ligands.[3,6] Two disulfur complexes which have been characterized by X-ray diffraction studies are $[IrS_2(dppe)_2]^+$ (where dppe = bis(diphenylphosphino)ethane)[4b] and $MoOS_2[S_2CN(C_3H_7)_2]_2$.[6] The S_2 ligand is bonded to the metal ion in a side-on orientation in each case, and the S–S bond distances in the molecules are similar (2.066 (6) Å in the former complex and 2.018 (8) Å in the latter).[4b,6]

Studies of analogous side-on bonded dioxygen complexes have revealed no correlation between O–O bond distance and reactivity,[2,11] but a variety of reactions of the coordinated O_2 ligand have been characterized.[11] Labeling studies with ^{18}O have helped to characterize reactions of certain group 8 dioxygen complexes (e.g., reaction 1).[12] In some reactions the



(1)

peroxy linkage remains intact (e.g., reaction 2).[13,14] It has



(2)

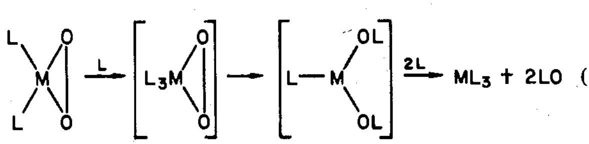
been proposed that in reactions of certain four-coordinate

Table I. Spectral Data for $MoOS_2(S_2CNR_2)_2$ Complexes

compd	IR data,[a] cm^{-1}			^1H NMR data,[b] ppm		visible spectral data[c]	
	$\nu_{C=N}$	$\nu_{Mo=O}$	ν_{S-S}	δ_{CH_3}	δ_{-CH_2-}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$MoOS_2[S_2CN(CH_3)_2]_2$	1555	920	556	3.07 s		578	1200
	1525			3.41 s		391	3400
				3.47 s			
				3.51 s			
$MoOS_2[S_2CN(C_2H_5)_2]_2$	1540	925[d]	556	1.45 t	4.02 q	576	1100
	1498	912		1.41 t	3.97 q	393	3200
				1.13 t	3.60 q		
$MoOS_2[S_2CN(C_3N_7)_2]_2$	1530	925	556	0.92 m	1.74 m	577	1000
	1490				3.63 m	394	2900

[a] Nujol mulls. [b] NMR spectra were recorded in $CDCl_3$; chemical shifts are with reference to Me_4Si. [c] Recorded on acetonitrile solutions at concentrations ranging from 1×10^{-4} to 1×10^{-3} M. [d] In CH_2Cl_2 solution one band is observed at 925 cm^{-1}.

dioxygen complexes, the reactant interacts with the π-bonded O_2 ligand after coordinating to the metal ion (reaction 3).[15]



(3)

Many of these examples result in a complete oxygen transfer while excess reactant fills the coordination sites vacated by the O_2 ligand (e.g., reactions 4 and 5).[15,16] Several dioxygen

$$Pt[P(C_6H_5)_3]_2O_2 + 3P(C_6H_5)_3 \rightarrow Pt[P(C_6H_5)_3]_3 + 2(C_6H_5)_3PO \quad (4)$$

$$Ni(RNC)_2O_2 + 4RNC \rightarrow Ni(RNC)_4 + 2RNCO \quad (5)$$

complexes have been studied as catalysts for the oxidation of hydrocarbons.[17-24] Some of these complexes have also been studied as models for more complex biological oxidizing systems.[25,26]

In contrast to the extensive investigations of dioxygen complexes, very few studies of the reactivity patterns of coordinated disulfur ligands have been reported.[3,27,28] The study of the disulfur complexes is of interest because they may serve as useful sulfur-transferring agents. These systems may also provide a basis for understanding important structural features of those metalloenzymes for which sulfur transfer reactions have been observed. The molybdoenzyme xanthine oxidase[29] and several other metalloproteins[30-33] have been found to contain labile sulfur atoms which can be abstracted by cyanide ion (reaction 6) and other nucleophiles. These labile sulfur

$$\text{enzyme–S} + CN^- \rightarrow \text{enzyme} + SCN^- \quad (6)$$

atoms are distinct from those which have been classified as acid labile; that is, the former do not react with acid to liberate hydrogen sulfide.[29,31] In some cases, the labile sulfur moiety plays a role in the enzyme mechanism. The activity of xanthine oxidase, for example, is inhibited by cyanide abstraction of sulfur, but the reactive sulfur site can be partially restored by the addition of sodium sulfide.[34]

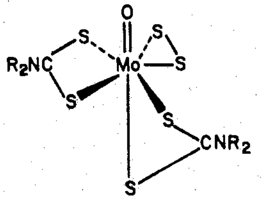
The nature of the labile sulfur moiety in the enzymes has not been established. The spectral features associated with the reactive sulfur linkage in several enzymes[29-34] are similar to those of organic persulfides (RSS^-), but many of the enzyme sulfur moieties are stable over a much greater pH range (pH 3–12) than are the organic models.[35] It has been proposed for xanthine oxidase that the nature of the labile sulfur is a stabilized persulfide molecule and that the means of stabilization may be by association with the molybdenum ion.[29] Other postulates on the nature of the labile sulfur linkage have also been proposed.[36-39]

We report in this paper a study of the lability characteristics of the disulfur ligand in two synthetic disulfur complexes. We have found that the S_2 ligand in $MoOS_2(S_2CNR_2)_2$ reacts readily with nucleophiles with thiophilic character in a sulfur transfer reaction. Most often the products are the sulfur-substituted nucleophile and $MoO(S_2CNR_2)_2$. The S_2 ligand in $IrS_2(dppe)_2^+$ does not react readily with nucleophiles, and no simple sulfur transfer reactions analogous to those observed for the molybdenum complex have been characterized. Reactions of the disulfur complexes with electrophiles have also been investigated. Reactions with methyl fluorosulfonate have led to characterized examples of metal–persulfide complexes. These studies indicate that the reactivity of the disulfur ligand can change significantly as the electronic environment, provided by the metal ion and other ligands, is varied.

Results and Discussion

Synthesis of $MoOS_2(S_2CNR_2)_2$. Since the reported syntheses of the molybdenum–disulfur complexes are limited by low yields,[6] new synthetic methods have been devised for their efficient preparation. The complexes $MoOS_2(S_2CNR_2)_2$, where R = CH_3, C_2H_5, or n-C_3H_7, can be prepared in relatively high yields by the reaction of the oxo-bridged molybdenum(V) dimer $Mo_2O_3(S_2CNR_2)_4$ with sodium tetrasulfide in a polar solvent. The tetrasulfide anion has been proposed to dissociate into disulfur radical anions in polar solvents,[40] and this radical may be the reacting species which cleaves the molybdenum–oxygen bridge. The complexes can also be formed by the reaction of $MoO_2(S_2CNR_2)_2$ with sodium sulfide or by the reaction of $Mo_2O_3(S_2CNR_2)_4$ with elemental sulfur.

The crystalline disulfur derivative $MoOS_2[S_2CN(C_3H_7)_2]_2$ prepared from sodium tetrasulfide was identified by comparison of its unit cell dimensions with those reported for the complex previously.[6,41] The other disulfur complexes of the dithiocarbamate series are very similar to the N,N-dipropyl derivative in chemical and physical characteristics and are presumed to have the same basic structure (structure I).



I

Spectral data which have not been reported previously for these complexes are included in Table I.

Reactions of $MoOS_2(S_2CNR_2)_2$ with Nucleophiles. A series of several nucleophiles which are known to show a high reactivity toward the S–S bond, such as phosphites, phosphines, isocyanides, and cyanide and sulfite ions, react with the disulfur ligand of $MoOS_2(S_2CNR_2)_2$ in a single type of reaction pathway: the S–S and Mo–S bonds are cleaved and sulfur atom transfer to the nucleophile is effected (eq 7). The

$$MoOS_2(S_2CNR_2)_2 + 2\text{nucleophile} \rightarrow MoO(S_2CNR_2)_2 + 2\text{S=nucleophile} \quad (7)$$

Table II. Products of the Reactions of $MoOS_2(S_2CNR_2)_2$ with Nucleophiles[a]

nucleophile[b]	products	% yield of Mo product
$P(OC_2H_5)_3$	$S{=}P(OC_2H_5)_3$, $MoO(S_2CNR_2)_2$	70
$P(C_6H_5)_3$	$S{=}P(C_6H_5)_3$, $MoO(S_2CNR_2)_2$	37
CH_3NC	CH_3NCS, $MoO(S_2CNR_2)_2$	65
CN^-	SCN^-, $MoO(S_2CNR_2)_2$	71
SO_3^{2-}	$S_2O_3^{2-}$, $MoO(S_2CNR_2)_2$	32
$C_6H_5S^-$	$C_6H_5SSC_6H_5$, $Mo_2O_2S_2(S_2CNR_2)_2$, $C_6H_5SSSC_6H_5$	72
C_6H_5SH	$C_6H_5SSC_6H_5$, $Mo_2O_2S_2(S_2CNR_2)_2$, $C_6H_5SSSC_6H_5$	81

[a] In most of the reactivity studies, the *N*-diethyl ligand derivative was used. The disulfur complexes with *N*-dimethyl and *N*-dipropyl ligand derivatives show similar characteristics. [b] 2 equiv of nucleophile/equiv of $MoOS_2(S_2CNR_2)_2$ was used.

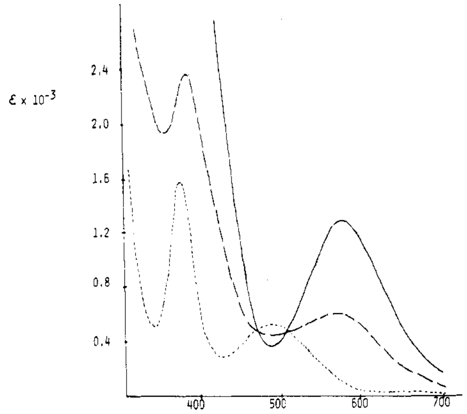


Figure 1. Visible spectra in acetonitrile: —, $MoOS_2[S_2CN(C_2H_5)_2]_2$; ···, $MoO[S_2CN(C_2H_5)_2]_2$ formed in the reaction $MoOS_2[S_2CN(C_2H_5)_2]_2 + 2P(C_6H_5)_3$; ---, equimolar amounts of $MoO[S_2CN(C_2H_5)_2]_2$ and $MoOS_2[S_2CN(C_2H_5)_2]_2$ present after the reaction $MoOS_2[S_2CN(C_2H_5)_2]_2 + P(C_6H_5)_3$.

products of several reactions of this type are given in Table II. The resulting molybdenum(IV) product was isolated from each reaction and characterized spectrally by comparison with reported data.[42] The substituted nucleophiles have been identified by their infrared spectra and/or mass spectra. The visible spectrum of a solution containing 2 equiv of phosphine/equiv of $MoOS_2(S_2CNR_2)_2$ indicates that the molybdenum(IV) complex is formed nearly quantitatively in this reaction (Figure 1). Although the yields of the molybdenum(IV) complex in the sulfur transfer reactions listed in Table II vary depending on crystallization and isolation techniques, no other molybdenum-containing products have been detected in significant amounts in these reactions.

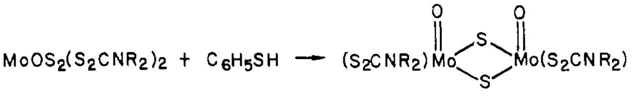
The products resulting from the addition of 1 equiv of a nucleophile (triphenylphosphine) to the disulfur complex have also been studied spectrally (Figure 1). The absorption of $MoOS_2(S_2CNR_2)_2$ at 575 nm decreases to 45–50% of its original intensity while the absorption characteristic of $MoO(S_2CNR_2)_2$ at 490 nm indicates that ~50% of the molybdenum–disulfur complex has been reduced to this molybdenum(IV) species. The results indicate that both sulfur atoms are ultimately abstracted from the same molecule (eq 8) and that

$$MoOS_2(S_2CNR_2)_2 + P(C_6H_5)_3 \rightarrow {}^1/_2MoOS_2(S_2CNR)_2 + {}^1/_2MoO(S_2CNR_2)_2 + S{=}P(C_6H_5)_3 \quad (8)$$

a molybdenum complex with a terminal sulfido ligand in addition to the terminal oxo ligand is not produced in significant amounts in this reaction (eq 9). A different molybdenum

$$MoOS_2(S_2CNR_2)_2 + P(C_6H_5)_3 \not\rightarrow MoO(S)(S_2CNR_2)_2 + S{=}P(C_6H_5)_3 \quad (9)$$

complex is isolated from reactions of $MoOS_2(S_2CNR_2)_2$ with the nucleophiles thiophenol and thiophenolate ion, which have been used previously as reducing agents for molybdenum(VI) and certain molybdenum(V) dithiocarbamate complexes.[43] In these reactions it is likely that only one sulfur atom is abstracted from the coordinated disulfur ligand;[44] the isolated product has been characterized by spectral and analytical data as a molybdenum(V) dimer with bridging sulfur atoms (eq 10). Diphenyl disulfide and diphenyl trisulfide have also been



(10)

identified by mass spectroscopy as products in the reaction (Table II).

Reactions of $MoOS_2(S_2CNR_2)_2$ with Electrophiles. The coordinated disulfur ligand does not react readily with mild electrophiles. While reactions with nucleophiles often occur within minutes, no significant reaction is observed with $MoOS_2(S_2CNR_2)_2$ and excess methyl iodide or with 2–4 equiv of 1 N HCl after stirring for 24 h.[59] However, the addition of 1 equiv of methyl fluorosulfonate to the molybdenum–disulfur complex does result in a color change from green to orange. The product, where R of the dithiocarbamate ligands is $-CH_3$, has been isolated and characterized; spectral data and elemental analyses are consistent with the formulation of a molybdenum(VI) persulfide complex, $MoO(SSCH_3)[S_2CN(CH_3)_2]_2SO_3F$. The analogous persulfide derivative with ethyl dithiocarbamate ligands has not been crystallized, but it has been characterized by NMR studies.

In the infrared spectrum of $MoO(SSCH_3)[S_2CN(CH_3)_2]_2SO_3F$, a strong band assigned to the molybdenum–oxygen stretch occurs at 920 cm^{-1}. Absorbances at 1280 and 575 cm^{-1} are associated with the fluorosulfonate ion. The complex has a molar conductivity of 76 Ω^{-1} cm^2 mol^{-1} in nitromethane, which is in the range typically observed for a 1:1 electrolyte.[45] In the NMR spectrum of the product a singlet at 3.05 ppm (relative intensity 3) is assigned to the methylated disulfur ligand. Two dithiocarbamate methyl resonances (each of relative intensity 6) occur at 3.40 and 3.57 ppm. Low-temperature NMR studies in the range from +30 to ca. −60 °C reveal no fluxional behavior for the methylated disulfur ligand. The spectral data do not establish whether the $SSCH_3$ ligand is coordinated in a side-on orientation to form a seven-coordinate species or in an end-on orientation to form a six-coordinate cation.

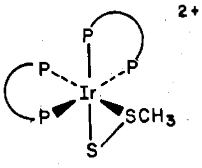
Evidence that the disulfur ligand rather than a dithiocarbamate is the site of methylation is provided by a study of the decomposition of the persulfide complexes. The complexes are unstable in solution, particularly in the presence of trace amounts of moisture. The same sulfur-containing products are observed by NMR in the decomposition of both $MoO(SSCH_3)[S_2CN(CH_3)_2]_2^+$ and $MoO(SSCH_3)[S_2CN(C_2H_5)_2]_2^+$. The resonance at 3.05 ppm in the NMR spectrum disappears and three new singlets appear at 2.56, 2.49, and 2.35 ppm in $CDCl_3$ (total relative intensity 3). These coincide with the resonances of added samples of dimethyl tetrasulfide, dimethyl trisulfide, and dimethyl disulfide, respectively.[46] Workup of the persulfide complex with ammonium hexafluorophosphate in alcohol also results in loss of the persulfide ligand. The complex $MoO(S_2CNR_2)_3PF_6$ is isolated in low yields.

Reaction Studies of $IrS_2(dppe)_2Cl$. The disulfur ligand in $IrS_2(dppe)_2Cl$ does not react with common thiophiles under conditions similar to those used in the reactions of the molybdenum–disulfur complex. For example, $IrS_2(dppe)_2Cl$ was recovered unchanged after stirring with triphenylphosphine, triethyl phosphite, or cyanide ion for 24 h. The reaction of $IrS_2(dppe)_2Cl$ with phenyl isocyanate has been investigated. It was thought that reaction with the S_2 ligand may produce a five-membered metallocyclic complex, $[(dppe)_2\overline{IrSSC(O)N}(R)]^+$. However, an X-ray diffraction study of the product isolated from this reaction reveals that the cation $IrS_2(dppe)_2^+$ remains intact and is basically the same as the structure determined for the acetonitrile solvate by Ibers.[4b] The reaction which occurs is the hydrolysis of PhNCO by trace moisture; a subsequent reaction of the resulting amine with PhNCO forms *sym*-diphenylurea. The urea is associated with the iridium complex through hydrogen bonding with the chloride ion. The urea solvate causes the complex to crystallize in space group $P\bar{1}$ in contrast to $P\bar{4}2_1c$ for the previously determined structure. The bond lengths in the iridium coordination sphere are, within error, the same as those determined by Ibers. However, the Ir–S bonds in this determination are equivalent while those in the acetonitrile adduct are significantly different. Details of the X-ray analysis are included as supplementary material.

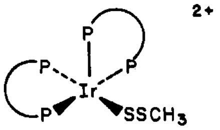
Over a period of 48 h a gradual color change is observed in the reaction of $IrS_2(dppe)_2Cl$ with methyl fluorosulfonate. The yellow product has been isolated as a hexafluorophosphate salt. Characterization of the complex by several methods suggests that the S_2 ligand is the site of methylation according to reaction 11. Analytical data confirm the proposed com-

$$IrS_2(dppe)_2^+ + CH_3SO_3F \xrightarrow{NH_4PF_6} [Ir(SSCH_3)(dppe)_2](PF_6)_2 \quad (11)$$

position of the product, and conductivity measurements are consistent with the formulation of a 2:1 electrolyte; $\Lambda = 220$ Ω^{-1} cm^2 mol^{-1} in acetone.[45] The ^{1}H NMR spectrum of the product in $(CD_3)_2CO$ has a doublet at 2.40 ppm ($J = 5.5$ Hz), which collapses to a singlet with ^{31}P decoupling. This resonance is assigned to a methylated sulfur ligand in a position trans to a phosphorus donor.[49] A methyl ligand coordinated directly to Ir(III) would be expected to have a more complex splitting pattern involving coupling with both cis and trans phosphine ligands.[51] The ^{31}P NMR spectrum of the complex indicates that there are four inequivalent phosphorus atoms in the molecule (see Experimental Section).[52] The spectral data are consistent with structures II and III.[54] However we believe that the preference of Ir(III) for six-coordination, the observed trans phosphorus coupling with the methyl protons, and the rigid nature of the molecule are considerations which favor structure II.[60]



II



III

Conclusion

The molybdenum compounds $MoOS_2(S_2CNR_2)_2$ provide examples of well-characterized metal sulfur complexes with ligands which have lability characteristics similar to the reactive sulfur moiety in certain molybdoenzymes.[39] The following similarities to the enzymes are noted: the complexes undergo sulfur transfer reactions with a variety of nucleophiles; after sulfur abstraction, the S_2 complex can be regenerated by the addition of sodium sulfide to the oxidized molybdenum dithiocarbamate derivative; the disulfur ligand is not labile in reactions with 1 N HCl.[59] Electronic environment appears to be important in determining the reactivity of the disulfur ligand since $IrS_2(dppe)_2Cl$ does not participate in sulfur transfer reactions.

Table III. Crystallographic Data for $[Ir(S_2)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl\cdot 2(C_6H_5NH)_2CO$

a, Å	13.055 (3)	fw	1513.14
b, Å	17.398 (5)	d(calcd), g/mL	1.41
c, Å	17.430 (4)	d(obsd), g/mL	1.43
α, deg	90.35 (2)	Z	2
β, deg	106.89 (2)	F(000)	1540
γ, deg	109.17 (2)	ν, cm^{-1}	22.2
vol, Å^3	3556 (1)	λ, Å	0.71069
space group	$P\bar{1}$		

Experimental Section

Materials. Sodium diethyldithiocarbamate dihydrate was purchased from Fisher. The sodium salts of dimethyl- and dipropyldithiocarbamic acids were prepared by reported procedures.[55] The molybdenum complexes $Mo_2O_3(S_2CNR_2)_4$, $MoO_2(S_2CNR_2)_2$, and $MoO(S_2CNR_2)_2$ were prepared as reported previously.[55-57] Sodium tetrasulfide (96%) and anhydrous sodium sulfide were purchased from Alfa. Chlorocarbonylbis(triphenylphosphine)iridium(I) and bis(diphenylphosphino)ethane were purchased from Strem Chemicals. Methyl fluorosulfonate was purchased from Aldrich. $IrS_2(dppe)_2Cl$ was prepared by reported procedures.[4]

Physical Measurements. Infrared spectra of Nujol mulls and of solutions were recorded on a Perkin-Elmer 337 grating spectrophotometer. Visible spectra were recorded on a Cary 17 spectrophotometer. Proton NMR spectra were obtained at 90 MHz by using a Varian 390 spectrometer. Phosphorus-31 NMR spectra were obtained on a JEOL-PFT 100 spectrometer equipped with standard probe and radio-frequency unit accessories. Mass spectra were obtained by using a Varian MAT CH-5 spectrometer. Conductivities were measured for 10^{-3} M solutions by using a Serfass bridge from Industrial Instruments. Molecular weight measurements were made with a Wescan Model 233 molecular weight apparatus. Elemental analyses and some of the molecular weight measurements were performed by Spang Microanalytical Laboratories. The cell parameters for a crystal of $MoOS_2[S_2CN(C_3H_7)_2]_2$ were determined on a Syntex $P\bar{1}$ autodiffractometer and were refined by a least-squares fit to 15 carefully centered reflections using programs supplied by Syntex. Details of the structural determination of $IrS_2(dppe)_2Cl\cdot HN(Ph)CON(Ph)H$ are available in the supplementary material. Some crystallographic data are given in Table III.

Syntheses of $MoOS_2[S_2CNR_2]_2$. From Na_2S_4. (I) The dimeric complex $Mo_2O_3(S_2CNR_2)_4$ (5.0 mmol) was slurried in 60 mL of acetone. Powdered sodium tetrasulfide (5.0 mmol) was added, and the solution was stirred for 4–6 h. The acetone was evaporated to ~15 mL. The resulting dark green precipitate was filtered and washed with two or three 20-mL portions of water until the washings were colorless. The *N,N*-dimethyl and *N,N*-diethyl derivatives were recrystallized from dichloromethane/cyclohexane (1:1 v/v). The *N,N*-dipropyl derivative was recrystallized from acetone; yields 40–50%. Anal. Calcd for $MoOS_2[S_2CN(CH_3)]_2$: C, 17.31; H, 2.88; S, 46.15. Found: C, 17.44; H, 2.76; S, 46.29. Calcd for $MoOS_2[S_2CN(C_2H_5)_2]_2$: C, 25.42; H, 4.24; S, 40.68; mol wt, 472. Found: C, 25.50; H, 4.23; S, 40.64; mol wt, 480 ($CHCl_3$). Calcd for $MoOS_2[S_2CN(C_3H_7)_2]_2$: C, 31.82; H, 5.30; S, 36.36. Found: C, 31.73; H, 5.22; S, 36.32.

(II) $MoO(S_2CNR_2)_2$ (0.8 mmol) was slurried in 50 mL of acetonitrile under a nitrogen atmosphere, and sodium tetrasulfide (0.4 mmol) was added. After being stirred for 15 h the green solution was filtered to remove a yellow precipitate. The filtrate was evaporated to 5 mL to crystallize a deep green product. This was identified as $MoOS_2(S_2CNR_2)_2$ from spectral comparisons with known samples; yield 32%. The yellow product was recrystallized from dichloromethane and identified from analytical data as $Mo_2O_2S_2(S_2CNR_2)_2$, yield 24%. Anal. Calcd ($R = C_2H_5$): C, 20.55; H, 3.42; S, 32.88. Found: C, 20.59; H, 3.43; S, 32.98.

From Na_2S. $MoO_2(S_2CNR_2)_2$ (1.4 mmol) was dissolved in 100 mL of acetone/benzene (1:1 v/v). Sodium sulfide (1.4 mmol) in 10 mL of water was added. After 6 h, the solvent was evaporated and the remaining deep green solid was dissolved in dichloromethane and extracted with four 50-mL portions of water. The dichloromethane solution was dried over molecular sieves. Subsequent addition of an equal volume of cyclohexane and slow evaporation resulted in the precipitation of the dark green product; yield 27% based on sulfide. (When 2 equiv of Na_2S was used, the dimer $Mo_2O_2S_2(S_2CNR_2)_2$ was isolated.)

From S_8. $Mo_2O_3(S_2CNR_2)_4$ (4.8 mmol) was dissolved in benzene/acetone (1:1 v/v) and sulfur (4.8 mmol) was added. After being stirred for 16 h, the solution was filtered. The crude products were recrystallized as outlined above; yield 60%.

Reactions of $MoOS_2[S_2CNR_2]_2$ with Nucleophiles. The following reactions were done under a nitrogen atmosphere.

(a) $P(C_6H_5)_3$, $P(OC_2H_5)_3$, CH_3NC. $MoOS_2(S_2CNR_2)_2$ (1.0 mmol) was dissolved in dichloromethane (20 mL)/benzene (20 mL) and 2 equiv of nucleophile was added. The solution was stirred for 1 h with $P(C_6H_5)_3$ and $P(OC_2H_5)_3$ and for 15 h with CH_3NC. Evaporation of solvent to ~10 mL resulted in the crystallization of $MoO(S_2CNR_2)_2$. This was filtered and the filtrate was evaporated to isolate the sulfur-substituted nucleophile. See Table II for yields.

(b) CN^-, SO_3^{2-}. $MoOS_2(S_2CNR_2)_2$ (1.0 mmol) was dissolved in dichloromethane (30 mL), and the ionic nucleophile was dissolved in water (10 mL)/ethanol (10 mL). The two solutions were mixed and stirred vigorously for 3 h. Partial evaporation of solvent resulted in crystallization of $MoO(S_2CNR_2)_2$. This was filtered and the filtrate was evaporated to dryness. The remaining solid was extracted with water which was evaporated to produce the sulfur-substituted nucleophile.

(c) C_6H_5SH. $MoOS_2(S_2CNR_2)_2$ (0.5 mmol) was dissolved in dichloromethane and C_6H_5SH (1.0 mmol) was added. The solution was stirred for 15 h. The yellow crystals which formed were filtered and recrystallized from CH_2Cl_2/CH_3OH. Anal. Calcd for $Mo_2O_2S_2[S_2CN(C_2H_5)_2]_2$: C, 20.55; H, 3.42; S, 32.88. Found: C, 20.64; H, 3.46; S, 32.82. The filtrate was evaporated, and the remaining solid was recrystallized from ether and identified by mass spectral analysis as $C_6H_5(S)_3C_6H_5$.

Reaction of $MoOS_2(S_2CNR_2)_2$ with CH_3SO_3F. $MoOS_2[S_2CN(CH_3)_2]_2$ (0.5 mmol) was dissolved in dry CH_2Cl_2 (15 mL) and CH_3SO_3F (0.5 mmol) was added. After the mixture was stirred for 1 h, the solvent was evaporated to ~5 mL and the resulting yellow compound was filtered. The product was recrystallized from CH_2Cl_2; yield 40%. Anal. Calcd for $MoO(SSCH_3)[S_2CN(CH_3)_2]_2SO_3F\cdot CH_2Cl_2$: C, 15.61; H, 2.76; S, 36.42. Found: C, 15.77; H, 2.82; S, 36.39. The presence of 1 mol of CH_2Cl_2 is confirmed by NMR: $\delta = 5.25$ (s, relative area 2, CH_2Cl_2), $\delta = 3.57$ (s, 6, $-N(CH_3)$), $\delta = 3.40$ (s, 6, $-N(CH_3)$), $\delta = 3.06$ (s, 3, $-SSCH_3$).

$MoO(SSCH_3)[S_2CN(C_2H_5)_2]_2SO_3F$: NMR in $CDCl_3$: $\delta = 1.30$ (mult, 12, NCH_2CH_3), $\delta = 3.05$ (s, 3, $-SSCH_3$), $\delta = 3.85$ (mult, 8, $-NCH_2$).

Attempted Metathesis Reaction with $MoO(SSCH_3)(S_2CNR_2)_2SO_3F$. The persulfide complex was prepared as described above. The product was dissolved in ethanol and 2 equiv of NH_4PF_6 in ethanol was added. A dark insoluble product was filtered and the filtrate was partially evaporated to give a mixture of green and orange crystals. The orange product was recrystallized from acetone and identified as $MoO(S_2CNR_2)_3PF_6$[58] by comparison of spectral data with that of a known sample of the complex.

Attempted Reactions of $IrS_2(dppe)_2Cl$ with Nucleophiles. $P(C_6H_5)_3$. Under a nitrogen atmosphere, $IrS_2(dppe)_2Cl\cdot CH_3CN$ (0.17 g, 0.15 mmol) and $P(C_6H_5)_3$ (0.09 g, 0.33 mmol) were dissolved in dichloromethane/benzene (40/20 mL) and refluxed for 20 h. No reaction occurred and both reactants were recovered.

NaCN. $IrS_2(dppe)_2Cl\cdot CH_3CN$ (0.11 g, 0.10 mmol) was dissolved in 20 mL of CH_2Cl_2. An ethanolic solution (~20 mL) of NaCN (0.014 g, 0.29 mmol) was added. The homogeneous solution was stirred for 24 h. No reaction occurred; the iridium complex was recovered by evaporation of solvent. The orange residue was washed with water and then recrystallized from CH_2Cl_2/CH_3CN and dried in vacuo. Anal. Calcd for $IrS_2dppe_2Cl\cdot CH_3CN$: C, 57.40; H, 4.52; S, 5.67. Found: C, 57.38; H, 4.52; S, 5.71.

C_6H_5NCO. Under a nitrogen atmosphere $IrS_2(dppe)_2Cl\cdot CH_3CN$ (0.10 g, ~0.10 mmol) was dissolved in CH_2Cl_2 and C_6H_5NCO (~0.11 mmol) was added. After being stirred for 24 h the solution was evaporated to dryness, and the resulting orange solid was recrystallized from acetonitrile; IR $\nu_{C=O}$ 1700 cm^{-1}. The product was characterized by X-ray diffraction as $IrS_2(dppe)_2Cl\cdot 2(C_6H_5NH)_2CO$.

Reaction of $IrS_2(dppe)_2Cl$ with CH_3SO_3F. Under a nitrogen atmosphere $IrS_2(dppe)_2Cl$ (0.20 g, 0.18 mmol) was dissolved in CH_2Cl_2 (20 mL) and CH_3SO_3F (0.03 mL, 0.35 mmol) was added. After stirring of the mixture for 48 h, the yellow product was filtered and redissolved in acetone. Ammonium hexafluorophosphate (0.06 g, 0.36 mmol) was dissolved in ethanol and added to the acetone solution. Partial evaporation of solvent produced yellow crystals, which were recrystallized from acetone/ethanol; yield 66%. Anal. Calcd for $Ir(SSCH_3)(dppe)_2(PF_6)_2$: C, 46.86; H, 3.76; S, 4.72. Found: C, 46.93; H, 3.90; S, 4.72. ^1H NMR (CD_3COCD_3): $\delta = 2.40$ (d, relative area 3, $-SSCH_3$), $\delta = 2.8$ (br, 8, $-PCH_2CH_2P-$), $\delta = 7.5$ (br, 40, $-P(C_6H_5)_2$). ^{31}P NMR in CD_3COCD_3: $\nu_1 = -11.3$ (referenced to phosphoric acid, $J_{P_1-P_2} = 0$, $J_{P_1-P_3} = 0$, $J_{P_1-P_4} = 13.4$ Hz), $\nu_2 = -14.4$ ($J_{P_2-P_3} = 9.8$, $J_{P_2-P_4} = 0$ Hz), $\nu_3 = -17.4$ ($J_{P_3-P_4} = 3.7$ Hz), $\nu_4 = -18.1$.

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Registry No. $MoOS_2[S_2CN(CH_3)_2]_2$, 71393-29-8; $MoOS_2[S_2CN(C_2H_5)_2]_2$, 64525-55-9; $MoOS_2[S_2CN(C_3H_7)_2]_2$, 64525-54-8; $Mo_2O_3[S_2CN(CH_3)_2]_4$, 20023-85-2; $Mo_2O_3[S_2CN(C_2H_5)_2]_4$, 20023-86-3; $Mo_2O_3[S_2CN(C_3H_7)_2]_4$, 53426-41-8; $MoO[S_2CN(CH_3)_2]_2$, 39587-09-2; $MoO[S_2CN(C_2H_5)_2]_2$, 25395-92-0; $MoO[S_2CN(C_3H_7)_2]_2$, 38702-66-8; $MoO_2[S_2CN(CH_3)_2]_2$, 53585-31-2; $MoO_2[S_2CN(C_2H_5)_2]_2$, 19680-83-2; $MoO_2[S_2CN(C_3H_7)_2]_2$, 17476-41-4; Na_2S_4, 12034-39-8; Na_2S, 1313-82-2; S_8, 10544-50-0; $Mo_2O_2S_2[S_2CN(C_2H_5)_2]_2$, 55723-33-6; $MoO(SSCH_3)[S_2CN(CH_3)_2]_2SO_3F$, 71393-31-2; $InS_2(dppe)_2Cl$, 31603-13-1; $Ir(SSCH_3)(dppe)_2(PF_6)_2$, 71393-33-4; $IrS_2(dppe)_2Cl\cdot 2(C_6H_5NH)_2CO$, 71393-34-5.

Supplementary Material Available: A listing of experimental parameters for the structure determination of $IrS_2(dppe)_2Cl\cdot 2(C_6H_5NH)_2CO$, a table of bond distances and angles for the iridium coordination sphere, and tables of positional and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Inorganic Chemistry,
Catholic University, Toernooiveld, Nijmegen, The Netherlands

^{13}C NMR Spectra of Dithiocarbamates. Chemical Shifts, Carbon–Nitrogen Stretching Vibration Frequencies, and π Bonding in the NCS_2 Fragment

H. L. M. VAN GAAL, J. W. DIESVELD, F. W. PIJPERS,[1] and J. G. M. VAN DER LINDEN*

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From the ^{13}C NMR spectra of 71 dithiocarbamates, the chemical shifts of the carbon atom of the NCS_2 moiety are correlated to the π bonding in the NCS_2 fragment. With the aid of pattern recognition techniques, the dithiocarbamates are divided into five classes: (i) the free ligands; (ii) "normal" oxidation state transition metal dtc's; (iii) "normal" coordination number main group dtc's and organic dtc's; (iv) "high" oxidation state transition metal dtc's; (v) "low" coordination number main group dtc's. Normal, high, and low refer to the fractional oxidation number (FON), a useful quantity, defined as the ratio between oxidation number and coordination number. "Normal" is FON = $^1/_2$. A high FON refers to a high oxidation state or a low coordination number and correlates with a high $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ and a low $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$. As such, the FON is a characteristic property distinguishing classes ii and iii from classes iv and v. It is not the difference between transition metals and main group element but rather the difference between symmetric and asymmetric dithiocarbamate bonding that distinguishes classes ii and iv from classes iii and v. In a semiempirical way $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$ could be expressed as a linear function of the sum of the CN, CS1, and CS2 π-bond orders, and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ of the CN π-bond order. The sum of the π-bond orders is derived to be maximal for equal π bonds and to decrease with increasing inequality of the three π bonds. Therefore, the free ligands (class i), with nearly equal π bonds, are located at the upper limit of δ values; the compounds with high $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ (classes iv and v) have low CS and low total π-bond orders, thus low δ values; and the compounds with asymmetrically bonded dtc (classes iii and iv) have low total π-bond orders and low δ values. For the various classes estimates of mean CN and CS π-bond orders, calculated from $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ values, are given. Other effects, which influence $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$, are the substituent on nitrogen and the period to which the central metal belongs.

Introduction

^{13}C NMR spectroscopy is a valuable analytical technique for the determination of the structures of organometallic and coordination compounds. As such it has been applied to transition metal dithiocarbamates in several cases. From our own results[2] and those of others[3–9] we observed that the chemical shift of the carbon atom in the NCS_2 fragment of the dithiocarbamate ligand varies with the coordinated atom and with changes in the molecular framework. Up to now, no attention was paid to the factors which influence these shift variations, and the information contained herein was not made explicit. In order to unravel the various influences, we have undertaken a systematic investigation of a large number of diamagnetic dithiocarbamates, covering nearly all features expected to play a possible role.

Application of pattern recognition techniques proved to be very helpful in classifying the measured compounds into distinct groups and in relating on empirical grounds the $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$ with the bonding modes and with the carbon–nitrogen stretching vibration frequencies. This permitted an

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