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Reactivity of Dithiocarbamates of Dimolybdenum. 3.[1] Crystal and Molecular Structure of Oxobis[(diethylcarbamodithioato)(tetrahydrofuran)iodooxomolybdenum(V)]

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The molybdenum(V) compound $Mo_2O_3(dtc)_2(THF)_2I_2$ has been synthesized by iodine oxidation of $Mo_2(dtc)_4$, which is obtained from reaction of 4 equiv of sodium diethyldithiocarbamate trihydrate with 1 equiv of molybdenum acetate. The green $Mo_2(dtc)_4$ complex has the molybdenum acetate structure with four bridging dithiocarbamates. The molecular structure of the Mo(V) compound has been determined: The crystalline compound belongs to triclinic space group $P\bar{1}$ with a = 8.055 (2) Å, b = 9.136 (3) Å, c = 11.551 (5) Å, α = 109.91 (2)°, β = 95.47 (2)°, and γ = 98.24 (2)°. The volume of the unit cell is 781.4 (6) Å^3 with Z = 1. The structure was refined to R_F = 4.33%. The complex exhibits a planar *trans*-O=Mo—O—Mo=O unit. In addition, the coordination sphere contains one THF per molybdenum, which exhibits an unusually long Mo-O(THF) bond.

Introduction

The syntheses and structures of numerous complexes containing multiple bonds between metal atoms have appeared in the literature in the last 25 years.[2] Currently, research efforts are turning to attempts at understanding the reactivity of these compounds.[3] For example, some groups are now trying to develop chemistry by considering the multiple metal–metal bond to be a center of unsaturation and therefore capable of undergoing addition reactions similar to those exhibited by carbon–carbon multiple bonds.[4] We have chosen to investigate the redox reactions of dithiocarbamates of dimolybdenum since this group of compounds shows particular promise for possessing a rich and important redox chemistry based on the reactions reported thus far. For example, when $Mo_2(dtc)_4$ is allowed to react with oxygen, $Mo_2O_3(dtc)_4$ results.[5] In addition, if $Mo_2(dtc)_4$ is left in methanol or THF solution, $Mo_2S_2(dtc)_2(tca)_2$ is formed where tca is a thiocarboxamide ligand[6] (see Figure 1). These two examples suggest that $Mo_2(dtc)_4$ is easily oxidized.

In particular we have initiated a study of the reactions of $Mo_2(dtc)_4$ with reducing agents. The structure of the product obtained from reaction of this complex with iodine, $Mo_2O_3(dtc)_2(THF)_2I_2$, is reported herein. The compound is found to possess a planar *trans*-O=Mo—O—Mo=O metal core. While this general structural type has been reported before, the present compound is of interest since there has been a lack of concensus in the literature over the correct assignment of infrared absorption bands to various molybdenum–oxygen stretching vibrations, particularly those of oxo-bridged dinuclear molybdenum(V) complexes.[7-9] At least in part, the lack of $Mo_2O_3^{4+}$ complexes that contain simple ligands other than bidentate sulfur ligands has contributed to the confusion. Chen et al.[10] have reported that ν(Mo=O) for $Mo_2O_3^{4+}$ complexes of the type $Mo_2O_3(LL)_2$, where LL represents bidentate sulfur ligands, should occur at 945 ± 16 cm^{-1}. $Mo_2O_3(dtc)_2(THF)_2I_2$ has a molybdenum-terminal oxygen stretching frequency of 970 cm^{-1}. This is the first example of a dithiolate-containing $Mo_2O_3^{4+}$ compound in which LL is replaced by monodentate ligands. The relationship between the structure and the high value of ν(Mo=O) for this compound is also discussed in this paper.

Experimental Section

Materials. Molybdenum acetate was prepared by the method of Wilkinson.[11] Sodium diethyldithiocarbamate trihydrate was purchased from Fisher Chemical Co. and was used as received. Diethylammonium diethyldithiocarbamate was prepared by addition of carbon disulfide to dry degassed diethylamine and filtration under argon of the colorless crystalline precipitate. All reactions were performed under an Ar atmosphere by using standard Schlenk techniques. Methanol was dried by refluxing over calcium sulfate for 2 h. It was then distilled onto fresh calcium sulfate where it was stored. Tetrahydrofuran was dried and stored over sodium and benzophenone and was distilled just prior to use.

Table I. Crystal, Data Collection, and Refinement Parameters for $[Mo(I)(O)(S_2CNEt_2)(THF)]_2O$

(a) Crystal Parameters

formula	$C_{18}H_{36}I_2Mo_2N_2O_5S_4$	γ, deg	98.24 (2)
cryst syst	triclinic	V, Å^3	781.4 (6)
space group	$P\bar{1}$	Z	1
a, Å	8.055 (2)	μ, cm^{-1}	30.3
b, Å	9.136 (3)	size, mm	0.15 × 0.25 × 0.39
c, Å	11.551 (5)	color	yellow
α, deg	109.91 (2)	D(calcd), g cm^{-3}	2.02
β, deg	95.47 (2)	temp, °C	24

(b) Data Collection

diffractometer	Nicolet P3	data collcd	$\pm h,\pm k,+l$
radiation (λ, Å)	Mo Kα (0.71073)	scan method	ω
monochromator	graphite	rflns collcd	4840
scan range, deg	$4 \leq 2\theta \leq 60$	no. of unique rflns	4552
scan speed, deg min^{-1}	var, 5–20	no. of unique reflns with $F_o \geq 4\sigma(F_o)$	3627
std/rflns	9/97 (3% linear decay)		

(c) Structure Refinement

R_F, %	4.33	Δ/esd max	0.001
R_{wF},%	4.90	highest peak, e Å^{-3}	1.51 (0.78 Å from I(1))
g	0.001	slope, normal prob plot	1.176
data/param	24.0		

Reactions Using Hydrated Sodium Diethyldithiocarbamate. In a typical reaction 1.0 g (2.3 mmol) of molybdenum acetate was reacted with 0.94 g (9.3 mmol) of sodium diethyldithiocarbamate trihydrate in about 75 mL of dry degassed methanol. Almost immediately a green precipitate formed. After the mixture was stirred for 1 h, the green material, $Mo_2(dtc)_4$, was filtered. This was then immediately dissolved in dry THF, and 0.58 g (6.9 mmol) of iodine was added. The solution turned dark red over about 30–45 s. After being stirred for 1 h, the solution was refrigerated at −20 °C overnight. Filtration afforded the dark green microcrystalline product. Further refrigeration of the filtrate for several days yielded X-ray quality crystals. Anal. Calcd for $C_{18}H_{36}N_2S_4O_5Mo_2I_2$: C, 23.14; H, 3.88; N, 2.99; S, 13.72. Found: C, 23.12; H, 3.87; N, 2.83; S, 12.88.

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(1) Part 2: Baird, D. M.; Croll, S. D. *Polyhedron*, in press.

(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, NY, 1982.

(3) Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982**, *29*, 1.

(4) Cotton, F. A.; Diebold, M. D.; O'Connor, C. J.; Powell, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7438.

(5) Steele, D. F.; Stephenson, T. A. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 777.

(6) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 2745.

(7) Newton, W. E.; Corbin, J. L.; McDonald, J. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1044.

(8) Cotton, F. A.; Hunter, D. L.; Ricard, L.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 259.

(9) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594.

(10) Chen, G. J.-J.; McDonald, J. W.; Bravard, D. C.; Newton, W. E. *Inorg. Chem.* **1985**, *24*, 2327.

(11) Wilkinson, G.; Dori, Z. *Inorg. Synth.* **1969**, 87.

0020-1669/86/1325-3458$01.50/0

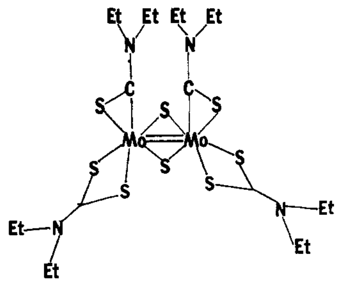

Figure 1. Structure of $Mo_2S_2(dtc)_2(tca)_2$.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	y	z	U^a
Mo(1)	617 (1)	512 (1)	1715 (1)	33 (1)*
I(1)	3179 (1)	3003 (1)	1979 (1)	56 (1)*
S(1)	1909 (2)	241 (1)	3663 (1)	42 (1)*
S(2)	−642 (2)	−2086 (2)	1736 (1)	48 (1)*
O(1)	0	0	0	36 (2)*
O(2)	2789 (4)	−1003 (4)	889 (3)	46 (1)*
O(3)	−806 (5)	1583 (5)	2320 (3)	54 (2)*
N(1)	713 (5)	−2605 (5)	3743 (4)	40 (1)*
C(1)	664 (6)	−1606 (6)	3154 (4)	38 (2)*
C(2)	−362 (7)	−4219 (6)	3246 (5)	50 (2)*
C(3)	−2019 (9)	−4263 (8)	3725 (7)	71 (3)*
C(4)	1799 (8)	−2175 (7)	4955 (4)	50 (2)*
C(5)	3547 (8)	−2548 (8)	4828 (6)	66 (3)*
C(6)	4504 (7)	−938 (7)	1447 (6)	58 (2)*
C(7)	4569 (9)	−2610 (8)	1339 (7)	72 (3)*
C(8)	3212 (10)	−3648 (7)	282 (7)	72 (3)*
C(9)	2392 (8)	−2513 (6)	−155 (5)	54 (2)*

[a] Values marked with an asterisk indicate that the equivalent isotropic U is defined as one-third of the trace of the orthoganalized $\mathbf{U}_{ij}$ tensor.

Spectroscopic Measurements. Electronic absorption spectra were recorded on a Hitachi 100A or a Perkin-Elmer 552 spectrophotometer in methylene chloride solutions. Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer as KBr pellets that were prepared under inert conditions. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

Crystal Structure Determination. Preliminary photographic work revealed no symmetry higher than triclinic. The centrosymmetric space group $P\bar{1}$ was initially assumed and later proved correct by the resulting chemically reasonable structure. The unit cell parameters and the details of data collection and refinement may be found in Table I; the parameters were obtained from the least-squares fit of the angular settings of 25 reflections, $23° < 2\theta < 28°$, which included Friedel pairs to validate optical and diffractometer alignment. Corrections for a 3% linear decay and for absorption (ψ-scan, maximum transmission 0.164, minimun transmission 0.142) were applied to the intensity data.

The structure was solved by an interpreted Patterson routine that provided Mo, I, and S atom positions; the remaining non-hydrogen atoms were located by difference Fourier methods. The crystallographic asymmetric unit consists of half of the complex with O(1) residing at the origin. The final cycles of refinement included anisotropic temperature factors for all non-hydrogen atoms as fixed, idealized, isotropic contributions (d(C–H) = 0.96 Å).

Atomic coordinates are listed in Table II, and selected bond distances and angles are given in Table III. Additional crystallographic data are available as supplementary data.

Results and Discussion

Table III. Selected Bond Distances and Angles for $Mo_2O_3(dtc)_2(THF)_2I_2$

(a) Bond Distances (Å)

Mo(1)–O(1)	1.872 (4)	Mo(1)–S(2)	2.452 (2)
Mo(1)–O(2)	2.448 (4)	S(1)–C(1)	1.711 (5)
Mo(1)–O(3)	1.664 (4)	S(2)–C(1)	1.742 (5)
Mo(1)–I(1)	2.755 (1)	C(1)–N(1)	1.313 (8)
Mo(1)–S(1)	2.493 (1)		

(b) Bond Angles (deg)

Mo(1)–O(1)–Mo(1a)	180	O(3)–Mo(1)–S(1)	97.8 (1)
O(1)–Mo(1)–O(2)	78.9 (1)	O(3)–Mo(1)–S(2)	100.8 (1)
O(1)–Mo(1)–O(3)	102.8 (1)	O(3)–Mo(1)–I(1)	97.4 (1)
O(1)–Mo(1)–S(1)	157.6 (0)	S(1)–Mo(1)–S(2)	71.5 (0)
O(1)–Mo(1)–S(2)	95.7 (0)	S(1)–Mo(1)–I(1)	91.5 (0)
O(1)–Mo(1)–I(1)	94.5 (0)	S(2)–Mo(1)–I(1)	156.6 (0)
O(2)–Mo(1)–O(3)	177.9 (1)	S(1)–C(1)–S(2)	113.6 (3)
O(2)–Mo(1)–S(1)	80.7 (1)	S(1)–C(1)–N(1)	124.0 (3)
O(2)–Mo(1)–S(2)	80.2 (1)	S(2)–C(1)–N(2)	122.4 (3)
O(2)–Mo(1)–I(1)	81.2 (1)		

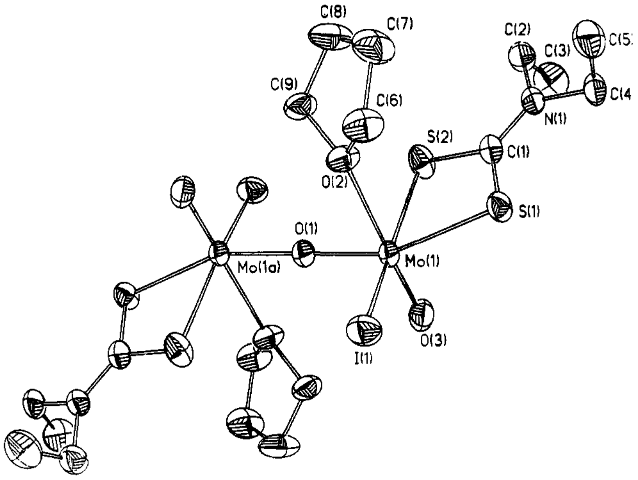

Figure 2. Labeling Scheme for $Mo_2O_3(dtc)_2(THF)_2I_2$.

The synthesis of the title compound was accomplished by first forming $Mo_2(dtc)_4$ by reaction of molybdenum acetate with 4 equiv of sodium diethyldithiocarbamate trihydrate. Early reports indicate that the initial product is transformed to a Mo(IV) thiocarboxamide species if allowed to sit in solution for some time.[5,12] The thiocarboxamide species is an unusual complex in which each molybdenum is oxidized by two electrons through reduction of two of the dithiocarbamate ligands, producing a complex that has two sulfides which bridge the two molybdenum atoms had a thiocarboxamide ligand on each molybdenum (Figure 1). As a result, $Mo_2(dtc)_4$ was reacted with iodine immediately after it was isolated to prevent rearrangement to the thiocarboxamide complex, $Mo_2S_2(dtc)_2(tca)_2$. The actual product obtained is a Mo(V) complex with the formula $Mo_2O_3(dtc)_2(THF)_2I_2$. There is an example of a very similar reaction involving the product formed from molybdenum acetate and the lithium salt of 2-thiopyridine (tp).[13] The initially formed green product reacts rapidly with even extremely small quantities of oxygen to give the Mo(V) compound $Mo_2O_3(tp)_4$.

The structure of the present compound has several interesting features. The labeling scheme for the atoms is shown in Figure 2. The O=Mo—O—Mo=O unit is in a strictly trans planar arrangement. This is only the fourth example with this sort of arrangement in a $Mo_2O_3^{4+}$ complex to be structurally characterized but the first that contains a dithiocarbamate and monodentate ligands. Either a cis or trans arrangement is expected as opposed to a structure in which the metal–terminal oxygen bonds are at 90° to one another. This is because the cis and trans structures maximize π-bonding between each molybdenum and the bridging oxygen.[14] The other three complexes with the trans arrangement are the thiopyridine complex mentioned before, the diethyldithiophosphinate complex, $Mo_2O_3(dtp)_4$,[15] and $[Mo_2O_3(NCS)_8]^{2+}$.[16] The ethyl xanthate complex, $Mo_2O_3(ext)_4$,[17] and

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[12] Vella, P.; Zubieta, J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 477.

[13] Cotton, F. A.; Fanwick, P. E.; Fitch, J. W. *Inorg. Chem.* **1978**, *17*, 3254.

[14] Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

[15] Knox, J. R.; Prout, C. K. *Acta Crystallogr.* **1965**, *4*, 1377.

[16] Bino, A.; Cohen, S.; Tsimiiering, L. *Inorg. Chim. Acta* **1983**, *77*, L79.

[17] Blake, A. B.; Cotton, F. A.; Wood, J. S. *J. Am. Chem. Soc.* **1964**, *86*, 3024.

the dipropyldithiocarbamate complex, $Mo_2O_3(Prdtc)_4$,[18] have the cis arrangement.

As in other structures of this type, a strong trans effect is observed for the bond across from the terminal Mo=O bond. In each of the dithiolate complexes the Mo–S bond trans to the terminal oxygen is longer than the other Mo–S bonds in the complex. For example, in the dipropyldithiocarbamate case the metal–sulfur bond trans to the terminal oxygen is 2.67 Å while the other Mo–S bonds are about 0.2 Å shorter. In the present case the Mo–O(THF) bond is exceptionally long, even considering that it is trans to the terminal oxygen, with the bond being about 0.45 Å longer than expected for a simple Mo–O single bond.[19,20] With a length of 2.46 Å it is much longer than the equivalent bond found in other molybdenum complexes that contain a Mo–O(THF) bond. In the compound $MoOCl_4(THF)$, in which the THF is trans to a terminal Mo=O bond, the bond length is 2.33 Å.[21] In the imido complex $MoCl_4(tolN)(THF)$, in which the THF is trans to the imido group, the Mo–O(THF) distance is 2.234 Å.[22] It would be interesting to make the bromide and chloride analogues of $Mo_2O_3(dtc)_2(THF)_2I_2$ and determine the Mo–O(THF) distance in these compounds. In fact, we are pursuing these compounds.

The electronic absorption spectrum of the complex was studied. Three absorbances characterize the spectrum of this compound. Bands appear at 619 ($\epsilon = 4400$) and 492 nm ($\epsilon = 10\,100$), and a shoulder appears at 360 nm ($\epsilon = 4800$). $Mo_2O_3(dtc)_4$ has similar absorbances at 512 and 378 nm. It has been suggested that the band near 500 nm must be due to a transition involving the Mo–O–Mo bridge.[23] We believe, by analogy, that the band at 492 nm in the spectrum of $Mo_2O_3(dtc)_2(THF)_2I_2$ must involve electronic transitions from the three-center Mo–O–Mo π-bonding orbital to the corresponding antibonding orbital. The shoulder at 360 nm would then be due to a similar transition involving the terminal oxygen. However, it is interesting that the Mo–O–Mo band has been shifted to a higher energy. Other workers have considered the absorbance near 526 nm to be indicative of the linear Mo–O–Mo moiety and have considered assignment of this structure to complexes that do not possess this band to be suspect. A recent report of the tris(pyrazolyl)borate complex suggests that a band at 460 nm can be assigned to this transition.

Unlike $Mo_2O_3(dtc)_4$, the 492-nm band in the spectrum of $Mo_2O_3(dtc)_2(THF)_2I_2$ does not change in intensity upon dilution of a methylene chloride solution over a range of 0.5×10^{-4}–1.9×10^{-4} M. $Mo_2O_3(dtc)_4$ complexes have been shown to equilibrate in solution with their Mo(IV) and Mo(VI)[24] counterparts as shown in reaction 1. It has been believed for some time that oxygen

$$Mo_2O_3(dtc)_4 \rightleftarrows MoO(dtc)_2 + MoO_2(dtc)_2 \qquad (1)$$

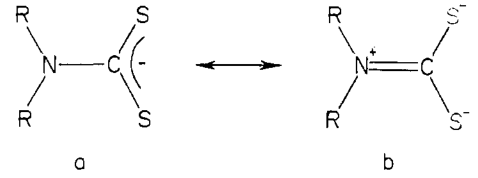
atom transfer enzymes such as the nitrate reductases act through a MoO_2^{2+} to MoO^{2+} to MoO_2^{2+} cycle. Model studies of this cycle have been hindered by reaction 1.[25] The present compound is the first dithiocarbamate-containing oxo-bridged molybdenum(V) species reported that does not readily undergo this process.

The band at 619 nm is of unknown origin. Jowitt and Mitchell have reported a similar band in the spectra of $Mo_2O_3(dtc)_4$ complexes near 620 nm ($\epsilon = 2900$) and suggested that the source of the band is a d–d transition.[26] On the other hand, this band was not observed at all for the same compounds in a study by Chen.[10] The large molar extinction coefficient in the present case seems to rule out assignment to a d–d transition.

Table IV. Mo=O Stretching Frequencies for Selected $Mo_2O_3^{4+}$ Compounds

compd	ν, cm^{-1}	compd	ν, cm^{-1}
$Mo_2O_3(Me_2dtc)_4$	933	$Mo_2O_3(Me_2dtp)_4$	960
$Mo_2O_3(Et_2dtc)_4$	932	$Mo_2O_3(Et_2dtp)_4$	961
$Mo_2O_3(n\text{-}Pr_2dtc)_4$	929	$Mo_2O_3(Et_2dtc)_2(THF)_2I_2$	970

Scheme I



Like other oxomolybdenum systems, $Mo_2O_3(dtc)_2(THF)_2I_2$ exhibits a very strong band in its infrared spectrum due to ν(M=O). In the present case this band appears at 970 cm^{-1}. This is quite high for an $Mo_2O_3^{4+}$ dithiocarbamate species. As mentioned, Chen and co-workers have shown by ^{18}O isotope studies, that terminal Mo=O bands should be found in the range of 945 ± 16 cm^{-1} for $Mo_2O_3(LL)_4$ systems when LL is dithiocarbamates, dithiophosphinates, or xanthates.[10] The ν(Mo=O) frequency in oxomolybdenum compounds has been correlated with the number of oxygen atoms competing for π-accepting orbitals on the molybdenum.[26] That is, for a given ligand the following sequence should be observed for ν(Mo=O):

$$MoO(LL)_2 > Mo_2O_3(LL)_4 > MoO_2(LL)_2$$

The band in the infrared spectrum of $Mo_2O_3(dtc)_2(THF)_2I_2$ is more in the range expected for MoO_2^{2+} compounds, 965 ± 8 cm^{-1}. This suggests that the O(THF) and I ligand atoms in this compound are less effective π-donating ligands than the dithiocarbamate that they have replaced, in turn making the π-accepting orbitals on molybdenum more readily available to the terminal oxygen. This seems consistent with the fact that dithiophosphinate complexes of $Mo_2O_3^{4+}$ have high values of ν(Mo=O) in comparison with the equivalent dithiocarbamate complexes (Table IV).[14] Dithiocarbamates should be much better at competing with the terminal oxygens for π-accepting orbitals on the molybdenum because of the predominance of resonance form b in Scheme I.[27] Dithiophosphinates are not capable of adopting an equivalent form. As a result, in the dithiophosphinate complexes the terminal oxygen can form a stronger π-bond with the molybdenum. The notion that a stronger π-interaction is occurring between the molybdenum and the terminal oxygen in the present compound also seems to be supported by the exceptionally long bond to THF, which is trans to the Mo=O bond. Weak bands located at 780 and 760 cm^{-1} and a shoulder at 785 cm^{-1} all fall in the region where bridging ν(Mo–O–Mo) vibrations are found. It is therefore difficult to assign one of these bands to that vibration.

Conclusions

It seems clear, on the basis of results reported here and reported recently by Lincoln and Koch,[9] that assignment of a linear oxo-bridged dimolybdenum(V) structure may not be ruled out by the frequency of the molybdenum–terminal oxygen stretching vibration or by the lack of a strong absorbance in the electronic spectrum very near 526 cm^{-1}. It appears that more $Mo_2O_3^{4+}$ compounds containing a dithiocarbamate and other ligands need to be studied before infrared and electronic absorption characteristics may be assigned with confidence.

It is possible that the inability of $Mo_2O_3(dtc)_2(THF)_2I_2$ to dissociate in solution stems from the same source as the high frequency observed for Mo=O stretching. That is, the replacement of a dithiocarbamate with an iodide and THF, which are not good π-donating groups, may increase the strength of the

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(18) Ricard, L.; Estienne, J.; Karagiannidis, P.; Toledana, P.; Mitchell, A.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 277.

(19) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *6*, 867.

(20) Schroder, F. A. *Acta Crystallogr. Sect. B*: *Struct. Crystallogr. Cryst. Chem.* **1975**, *31*, 2294.

(21) Bird, P. H.; Wickramasinghe, W. A. *Can. J. Chem.* **1981**, *5*, 2879.

(22) Chou, C. Y.; Huffman, J. C.; Maata, E. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1184.

(23) Newton, W. E.; Corbin, J. L.; Bravard, D. E.; Searles, J. E.; McDonald, J. W. *Inorg. Chem.* **1974**, *13*, 1100.

(24) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 925.

(25) Tanaka, T.; Tanaka, K.; Matsuda, T.; Hashi, K. In *Molybdenum Chemistry of Biological Significance*; Newton, W. E., Otsuka, S., Eds.; Plenum: New York, NY, 1980; p 361.

(26) Mitchell, P. C. H.; Jowitt, R. N. *J. Chem. Soc. A* **1970**, 1702.

(27) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301.

molybdenum–bridging oxygen bond just as it strengthens the molybdenum–terminal oxygen bond. The tris(pyrazolyl)borate complex reported by Lincoln and Koch[9] does not dissociate in solution either, and it has a reported Mo=O stretching frequency of 966 cm^{-1}.

In addition, a significant beginning has been made toward characterizing the reactivity of the molybdenum–molybdenum quadruply bonded dithiocarbamates.

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Registry No. $Mo_2O_3(dtc)_2(THF)_2I_2$, 103817-70-5; $Mo_2(dtc)_4$, 68026-97-1.

Supplementary Material Available: Tables of complete bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (4 pages); a table of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Medicinal Chemistry, Hiroshima University, School of Medicine,
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Hiroshima University, Higashi-Senda, Naka-ku, Hiroshima 730, Japan

Coordination of Pentadentate Macrocycles, Doubly Deprotonated 1,4,7,10,13-Pentaazacyclohexadecane-14,16-dione, to High-Spin Nickel(II) and Low-Spin Nickel(III). X-ray Study of a Novel Redox System

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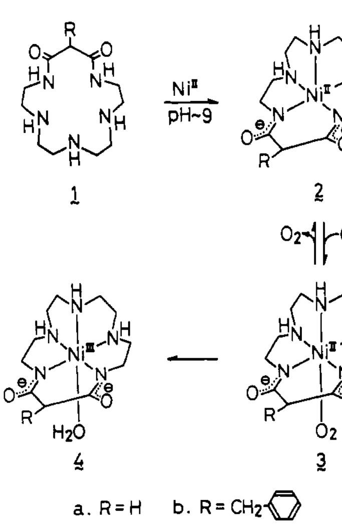
A novel nickel redox system with peptide-mimic macrocyclic pentaamines has been structurally characterized. Compound **2a**, a high-spin Ni(II) complex of the unsubstituted title ligand, $[Ni^{II}H_{-2}L]\cdot H_2O$, crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 8.670$ (1) Å, $b = 11.896$ (2) Å, $c = 14.054$ (3) Å, $\beta = 99.22$ (1)°, and $R = 0.048$. Compound **4b**, a low-spin nickel(III) complex of 15-benzyl-substituted dioxo[16]aneN_5, $[Ni^{III}(H_{-2}L')(H_2O)]ClO_4\cdot 2H_2O$, crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 9.379$ (3) Å, $b = 9.486$ (2) Å, $c = 15.280$ (5) Å, $\alpha = 75.80$ (2)°, $\beta = 83.04$ (3)°, $\gamma = 61.65$ (2)°, and $R = 0.044$. The high-spin Ni(II) complex has a distinct five-coordinate, square-pyramidal geometry with the two deprotonated amide nitrogens coordinating at the basal plane. The Ni(II) ion lies 0.22 Å from the mean basal plane toward the apical nitrogen, and the apical Ni–N bond is bent by 18.4° from the perpendicular. The average equatorial bond lengths Ni(II)–N and Ni(II)–N^- (imide anion) are 2.096 (4) and 1.977 (4) Å, respectively, while the Ni(II)–apical N bond is very short, 2.049 (4) Å. The water molecules form hydrogen bonds with the electron-rich amide oxygen atoms. The low-spin Ni(III) complex, which is formed by air oxidation or electrochemical oxidation of the corresponding high-spin Ni(II) complex, has a six-coordinate, octahedral geometry with a H_2O molecule occupying the sixth position. The nickel(III) ion moves into the mean plane of the four equatorial nitrogens (only 0.044 Å above) with shortened bond distances for the equatorial Ni(III)–N bond, 1.963 (5) Å, and Ni(III)–N^-, 1.890 (4) Å, and an elongated apical Ni(III)–N bond, 2.067 (4) Å. The steric strain around the nickel(III) is reduced. The present structural comparison for the Ni(II)- and Ni(III)-dioxo[16]aneN_5 complexes provides a rationale for the earlier observed 1:1 O_2 adduct formation and facile inner-sphere electron transfer from Ni(II) to O_2.

Introduction

A number of trivalent nickel complexes with nitrogen donors have been prepared by chemical and electrochemical oxidation in nonaqueous solution[2-7] or in the solid state.[8] However, in water or basic solvents, the Ni(III) state tends to rapidly decompose.[8,9] Recently, however, Ni(III) in 14-membered macrocyclic tetraamine (cyclam) ligands have been found to be stabilized by acidic aqueous solutions in the presence of excess SO_4^{2-} ion; the redox potential for Ni(III)/Ni(II) with unsubstituted cyclam is +0.51 V vs. SCE.[10] Deprotonated oligopeptides were also found as ligands appropriate for Ni(III) in aqueous solution.[11] However, few Ni(II)–peptide systems undergo air oxidation to the Ni(III) species. Obviously, their oxidation potentials ranging from 0.72 to 0.55 V vs. SCE[12] are not low enough to induce reduction of O_2. Only one example was reported, Ni(II)–tetraglycine ($E° = 0.57$ V vs. SCE at pH 8.6), that is considered to autocatalytically form the Ni(III) species as a transient intermediate for the subsequent oxidation of the peptide ligand.[13]



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[1] (a) Department of Medicinal Chemistry. (b) Department of Chemistry.

[2] Review article: Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.

[3] Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611.

[4] Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

[5] Takvoryan, N.; Farmey, K.; Katovis, V.; Lovecchio, F.; Gore, E. S.; Anderson, L. B.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 711.

[6] Sen, D.; Saha, C. *J. Chem. Soc., Dalton Trans.* **1976**, 776.

[7] Desideri, A.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1977**, 205.

[8] Gore, E. S.; Busch, D. H. *Inorg. Chem.* **1973**, *12*, 1.

[9] Barefield, E. K.; Mocella, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4238.

[10] Zeigerson, E.; Ginzburg, G.; Schwartz, N.; Luz, Z.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1979**, 241.

[11] Bossu, F. P.; Margerum, D. W. *J. Am. Chem. Soc.* **1976**, *98*, 4003.

[12] Bossu, F. P.; Margerum, D. W. *Inorg. Chem.* **1977**, *16*, 1210.

[13] Bossu, F. P.; Paniago, E. B.; Margerum, D. W.; Kirksey, S. T. *Inorg. Chem.* **1978**, *17*, 1034.

0020-1669/86/1325-3461$01.50/0