Spectroscopic investigation of dichloro and hydrazido(2−) derivatives of bis(dithiocarbamato)dioxomolybdenum(VI) compounds. Crystal and molecular structure of bis(diisobutyldithiocarbamato)-(*N*,*N*-dimethylhydrazido(2−)-*N*′)oxomolybdenum(VI)

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Abstract

The reaction of bis(dithiocarbamato)dioxomolybdenum(VI) compounds, $MoO_2(S_2CNRR')_2$, with hydrochloric acid yields $MoOCl_2(S_2CNRR')_2$ in which molybdenum is seven-coordinated. An oxo ligand is also replaced when $MoO_2(S_2CNRR')_2$ is reacted with *N*,*N*-dimethylhydrazine, $HNNMe_2$. The products were characterised and their IR and electronic excitation spectra were measured and analysed. The spectra suggest that in these highly distorted octahedral compounds the *N*,*N*-dimethylhydrazido(2−) ligand is *cis* to the terminal oxo group. This was confirmed by the X-ray structure determination of bis(diisobutyldithiocarbamato)(*N*,*N*-dimethylhydrazido(2−)-*N*′)oxomolybdenum(VI). The unit cell of $MoO(NNMe_2)(S_2CN(i\text{-}Bu)_2)_2$ has dimensions $a = 19.641(5)$, $b = 10.317(2)$, $c = 17.702(5)$ Å, $\alpha = \gamma = 90$, $\beta = 109.69(2)°$, belongs to space group *Cc* and contains four molecules. Structure solution and refinement based on 344 unique reflections converged at a conventional discrepancy value of 0.038. Comparison with closely related compounds reveals that while alkyl and aryl groups in the hydrazido(2−) ligand have no appreciable effect on the metal–nitrogen bond and the linearity of the Mo–N–N fragment, substituents attached to the dithiocarbamato moieties exert strong influence on the electron distribution of the (*N*,*N*-dimethylhydrazido(2−) ligand thus affecting its more of interaction with the molybdenum centre. The O–Mo–N angle of 112.9° is wider than those observed in similar compounds while the N–N distance of 139 pm in the dimethylhydrazido(2−) group is the longest N–N bond encountered in this particular ligand.

Key words: Crystal structures; Molybdenum complexes; Oxo complexes; Dithiocarbamate complexes

Introduction

The recognition that molybdenum is an essential micronutrient for microorganisms, plants and animals and an indispensable constituent of enzymes that convert the atmospheric dinitrogen to ammonia has stimulated research in the coordination chemistry of this element [1–5]. Spectroscopic investigations and structural characterisation of metalloenzymes facilitating nitrogen fixation have also implicated sulfur and oxygen as ligand donor atoms while reactivity studies revealed involvement of the MoO_2^{2+} core and a single terminal oxo ligand in biological catalytic cycles [5]. The postulated involvement of molybdenum(VI)–hydrazido(2−) species as intermediates in the enzymatic activation of molecular nitrogen has directed the attention to chelates containing the MoS_xN_y and the $MoS_xN_yO_z$ chromophores [2]. The chromophores should be capable of participating in atom-transfer and electron-transfer reactions without disintegration. The ability of molybdenum to exist in a plethora of oxidation states constitutes a major stability factor and attainment of the highest of them, Mo(VI), demands for its stabilisation the presence of ligands that are not only good σ donors but also good π donors so that the requirements of Pauling's electroneutrality principle can be met. Organodithiocarbamates, $[(RR'NCSS)^-]$, upon coordination to metal ions impart sufficient electron density and stabilise the higher oxidation states with the substituents R,R′ exerting strong influence on the electron distribution within the dithiocarbamato moiety, on the mode of coordination and the field induced by these ligands [6, 7]. The remarkable reactivity of the resulting MoO_xS_y chromophores [8–14] has attracted considerable interest [4, 13–21]. However, the effect of substituents on spectroscopic and structural aspects has not been thoroughly

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investigated even though the stereochemistries of redox-related series are of fundamental interest for evaluating the consequences of electron transfer in molybdoenzymes.

In this paper, the first of a series, the influence of substituents R,R′ of the dithiocarbate moiety [(RR′NCSS)$^-$] on the electron distribution and the reactivity of the $Mo^{VI}O_2S_4$ chromophore towards organohydrazines and hydrochloric acid are investigated and the spectroscopic properties of the products are studied. For this purpose the synthesis of a series of molybdenum(VI) compounds was carried out and their vibrational and electronic excitation spectra were obtained and analysed. The crystal and molecular structure of bis(diisobutyldithiocarbamato)(*N*,*N*-dimethylhydrazido(2 −)-*N*′)oxomolybdenum(VI) was determined by X-ray diffraction methods. The compounds investigated are listed in Table 1.

Experimental

Reagents and synthesis of compounds

Na_2MoO_4 and $(NH_4)_2MoO_4$ were purchased from Riedel de Haen. Carbon disulfide (CS_2), and the secondary amines diisobutylamine ($(i\text{-}Bu)_2NH$), dibenzylamine ($Benz_2NH$), dicyclohexylamine (Cx_2NH), pyrrolidine (pyrrH), piperidine (pipH), 3-methylpiperidine (3-MepipH) and morpholine (MorH) were purchased from Merck. The non-symmetric organohydrazines *N*,*N*-dimethylhydrazine ($NNMe_2$) and *N*,*N*-diphenylhydrazine ($NNPh_2$) were purchased from Aldrich, the latter as hydrochloride. The sodium dithiocarbamates, RR′NCSSNa, (RR′dtcNa, where the R,R′ groups may be identical, non-identical or part of a cyclic structure) were prepared by methods already described [22]. Their isolation was not necessary. The bis(dithiocarbamato)dioxomolybdenum(VI) compounds, $[MoO_2(S_2CNRR')_2]$, were prepared by reacting Na_2MoO_4 with RR′NCSSNa according to standard literature procedures [8–11].

Preparation of dichlorobis(dithiocarbamato)-oxomolybdenum(VI) compounds

The compounds $[MoOCl_2(dtc)_2]$ were prepared by adding an excess of the stoichiometric amount of concentrated hydrochloric acid to a suspension of $[MoO_2(S_2CNRR')_2]$ in acetone and stirring the solution for one hour [13, 15, 17]. Recrystallisation under refrigeration was effected from dichloromethane–diethyl ether.

Preparation of bis(dithiocarbamato)(N,N-organohydrazido(2 −)-N′)oxomolybdenum(VI) compounds

The activation of the organohydrazines was accomplished by reacting them with the bis(dithiocarbamato)dioxomolybdenum(VI) compounds [13, 16–21]. To a 50 ml spherical flask equipped with reflux condenser were added 5 mmol of $MoO_2(dtc)_2$, methanol (sufficient to effect dissolution), and an equimolar amount of *N*,*N*-organohydrazine. The mixture was heated under reflux for 3 h. The solution was allowed to cool to room temperature, and the precipitate was separated by filtration. The product $[MoO(NNR^1R^2)(dtc)_2]$ was dissolved to a minimum volume of dichloromethane and diethyl ether was added gradually. The crystals formed by slow evaporation under refrigeration were filtered off. In the case of *N*,*N*-dimethylhydrazine, Me_2NNH_2, the reaction time was diminished to 1 h by a threefold increase in the amount

TABLE 1. Yield, melting points and elemental analysis of bis(dithiocarbamato)oxomolybdenum(VI) compounds containing chloro or *N*,*N*-dimethylhydrazido(2 −) groups

No.	Compound	R^1	R^2	Yield (%)	m.p. (°C)	C (%)	N (%)	H (%)
1	$MoOCl_2(i\text{-}Bu_2dtc)_2$	$(CH_3)_2CHCH_2$	$(CH_3)_2CHCH_2$	88	105–108	36.7(36.5)	4.8(4.74)	6.2(6.13)
2	$MoO(NNMe_2)(i\text{-}Bu_2dtc)_2$	$(CH_3)_2CHCH_2$	$(CH_3)_2CHCH_2$	91	98–100	41.4(41.5)	9.6(9.68)	7.4(7.32)
3	$MoOCl_2(Cx_2dtc)_2$	C_6H_{11}	C_6H_{11}	77	260–265	45.1(44.9)	3.9(4.03)	6.3(6.37)
4	$MoO(NNMe_2)(Cx_2dtc)_2$	C_6H_{11}	C_6H_{11}	87	145–147	48.8(49.2)	8.3(8.20)	7.4(7.38)
5	$MoOCl_2(Benz_2dtc)_2$	$C_6H_5CH_2$	$C_6H_5CH_2$	75	182–185	49.7(49.5)	3.8(3.85)	4.0(3.88)
6	$MoO(NNMe_2)(Benz_2dtc)_2$	$C_6H_5CH_2$	$C_6H_5CH_2$	90	165–167	54.1(53 8)	7.8(7.84)	4.8(4.79)
7	$MoOCl_2(Pyrrdtc)_2$	$(CH_2)_4$		81	120–123	25.5(25.3)	6.0(5.89)	3.3(3 39)
8	$MoO(NNMe_2)(Pyrrdtc)_2$	$(CH_2)_4$		85	130–133	31.5(31.2)	11.8(12.1)	4.7(4.80)
9	$MoOCl_2(Pipdtc)_2$	$(CH_2)_5$		79	135–138	28.5(28.6)	5.7(5.57)	3.9(4.00)
10	$MoO(NNMe_2)(Pipdtc)_2$	$(CH_2)_5$		85	196–198[a]	34.5(34.3)	11.2(11.4)	5.2(5.34)
11	$MoOCl_2(Mepipdtc)_2$	$CH_3CH(CH_2CH_2)_2$		82	160–165	32.0(31.6)	5.4(5.27)	4.7(4.55)
12	$MoO(NNMe_2)(Mepipdtc)_2$	$CH_3CH(CH_2CH_2)_2$		87	170–173	37.2(37.0)	10.7(10.8)	6.0(5.83)
13	$MoOCl_2(Morphdtc)_2$	$O(CH_2CH_2)_2$		73	152–155	24.1(23.7)	5.6(5.52)	3.1(3.18)
14	$MoO(NNMe_2)(Morphdtc)_2$	$O(CH_2CH_2)_2$		86	134–136	28.7(29.1)	11.4(11.3)	4.5(4.48)

[a] Ref. 16.

added. An excess of N,N-diphenylhydrazine, Ph_2NNH_2, resulted in replacement of both oxo groups and the synthesis of the bis[diphenylhydrazido(2 −] compounds [19].

The compounds $[MoOCl_2(SSCNRR')_2]$ and $[MoO(NNMe_2)(SSCNRR')_2]$ are obtained as coloured powders or crystalline solids. The stoichiometry and some physical constants are given in Table 1. The synthesis of $[MoO(NNMe_2)\{SSCN(CH_2)_5\}_2]$ has been previously reported [16]. Regarding its spectroscopic properties, the information supplied by those investigators was not extensive and therefore the preparation was repeated.

Physical measurements and determinations

Carbon, hydrogen and nitrogen were determined by microanalysis using a Perkin-Elmer 240B elemental analyser. The metal content of the chelates was determined employing a Perkin-Elmer 2100 atomic absorption spectrometer. Melting points were determined on a Reichert heated plate apparatus and are uncorrected (Table 1). Relative molecular masses were determined with a Knauer osmometer on dichloromethane solutions of the compounds. Molar conductivities were measured on a Metrohm 660 conductometer employing a calibrated dip type cell. The measurements were performed in a series of solutions of analytical grade nitrobenzene and nitromethane and concentrations ranging from 10^{-4} to 10^{-2} M were employed in order to examine the likelihood of concentration dependence. Magnetic susceptibility measurements in powdered samples were performed at 25 °C employing the Faraday method on a home-build balance calibrated against $Hg[Co(SCN)_4]$. Diamagnetic corrections were estimated from Pascal's constants. The effective magnetic moments, μ_{eff}, were calculated using the expression

$$\mu_{eff}/m_B = 48.98(\chi_M^{corr})^{1/2} \quad (T = 298\ K)$$

IR spectra, obtained by the KBr disc technique, were recorded on a Perkin-Elmer 1430 spectrophotometer with a range 4000–200 cm^{-1} calibrated against polystyrene. Electronic spectra in solution were measured on a Shimadzu UV-1202 spectrophotometer using 10 mm teflon stoppered quartz cells. The solid state electronic spectra were obtained from nujol mulls.

Crystal structure determination of $[MoO(NNMe_2)(i\text{-}Bu_2dtc)_2]$

Bright orange prismatic crystals suitable for X-ray analysis were grown by evaporation under refrigeration of a dichloromethane–diethyl ether solution of the compound. The crystal survey, unit cell dimension determination and measurement of reflections and their intensities at ambient temperature, were accomplished on a Phillips PW 1100 diffractometer (Table 2). Cell dimensions were determined by measuring 45 strong reflections with large θ values directly on the diffractometer. The intensities of three standard reflections measured every 90 reflections revealed no unexpected variation in intensity. The diffractometer output was processed with the CELREF program [23]. The data processing included corrections for background absorption, anomalous dispersion, Lorentz and polarisation effects.

TABLE 2. Crystal data and experimental details for the structural study of $[MoO(NNMe_2)(i\text{-}Bu_2dtc)_2]$

Formula	$MoC_{20}H_{42}N_4OS_4$
Molecular mass, M_r	578.78
Measurement of intensity data	
Crystal shape	bright orange needles
Crystal size (mm)	0.23×0.40×0.04
Instrument	Phillips PW 1100 as transformed by STOE
Radiation, λ (Å)	Mo Kα, 0.71069
Monochromator	graphite
Scan mode	coupled θ(crystal)–2θ(counter)
θ Range (°)	2 202–24
Measured reflections	4799→3255 reflected ($I \geqslant 2.8\sigma(I)$)
Unique reflections	344
Crystal parameters	
a (Å)	19.641(5)
b (Å)	10.317(2)
c (Å)	17.702(5)
α (°)	90
β (°)	109.69(2)
γ (°)	90
V_c (Å^3)	3377.41
D_m (Mg m^{-3})	1.138 (calculated)
Space group	Cc monoclinic
Molecules per cell	$Z = 4$
Absorption coefficient, μ (cm^{-1})	6.349
$F(000)$	1216
Final discrepancy factor	
R[a]	0.038
R_w[b]	0.038

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)]^{1/2}$; $w = 1/\sigma F_o$.

The position of the molybdenum ion was determined from a three-dimensional Patterson synthesis. A part of the structure was solved by introducing a known fragment and by examination of the Patterson map. Fourier maps allowed the location of all carbon, nitrogen, oxygen and sulfur atoms. Hydrogen positions were calculated wherever required. The positional parameters were refined employing the SHELX-76 program [24a]. The trial structure was refined routinely to an acceptable R index of 0.038. The refinement was concluded with a full-matrix least-squares procedure using a modification of the SHELX-86 program [24b]. The quantity minimised by the least-squares procedure was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed

TABLE 3. Fractional atomic coordinates for $MoO(NNMe_2)(SSCNCH_2CH(Me)_2)$ with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Mo	−1.1325	0.5651(3)	0.1319(3)	C(6)	0.0983(9)	0.3053(11)	0.1724(10)
O	−0.1861(8)	0.5069(9)	0.0418(7)	C(7)	0.1356(9)	0.3475(9)	0.2614(8)
S(1)	−0.0265(7)	0.4199(8)	0.1838(7)	C(8)	0.1719(9)	0.2171(10)	0.2968(8)
S(2)	−0.0342(7)	0.6102(8)	0.0661(8)	C(9)	0.2017(8)	0.4261(10)	0.2581(8)
S(3)	−0.1823(7)	0.7856(8)	0.0940(8)	C(10)	−0.1062(7)	0.8647(8)	0.1591(6)
S(4)	−0.0610(7)	0.7532(7)	0.2345(8)	C(11)	−0.0352(7)	0.0353(10)	0.2378(9)
N(1)	−0.1708(9)	0.5390(10)	0.2123(8)	C(12)	−0.0517(8)	0.0371(12)	0.3177(9)
N(2)	−0.1893(8)	0.4832(12)	0.2743(8)	C(13)	−0.1128(9)	0.1299(12)	0.3198(11)
N(3)	0.0695(8)	0.4120(10)	0.1120(9)	C(14)	0.0193(11)	0.0849(14)	0.3816(12)
N(4)	−0.1101(9)	0.9923(10)	0.1860(8)	C(15)	−0.1540(10)	0.0875(13)	0.1240(9)
C(1)	0.0134(8)	0.4845(9)	0.1207(7)	C(16)	−0.1230(9)	0.0871(12)	0.0544(11)
C(2)	0.1081(10)	0.4649(13)	0.0590(9)	C(17)	−0.1700(10)	0.1828(11)	−0.0107(12)
C(3)	0.0777(10)	0.4306(9)	−0.0319(11)	C(18)	−0.0622(11)	0.0124(14)	0.0357(10)
C(4)	0.0800(9)	0.2808(13)	−0.0201(10)	C(19)	0.8658(8)	0.5379(8)	0.3528(10)
C(5)	0.1142(8)	0.5059(13)	−0.0838(7)	C(20)	0.7441(8)	0.4005(10)	0.2723(8)

TABLE 4. Selected bond lengths (Å) and angles (°) for $MoO(NNMe_2)(SSCNCH_2CH(Me)_2)_2$

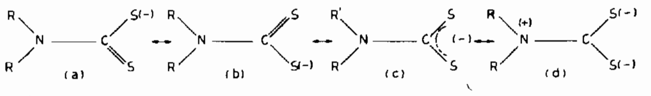
Mo–O	1.697(16)			Mo–N(1)–N(2)	162.6(16)
Mo–S(1)	2.477(12)	N(3)–C(6)	1.505(19)	O–Mo–N(1)	112.9(8)
Mo–S(2)	2.611(16)	C(6)–C(7)	1.560(19)	O–Mo–S(1)	108.2(6)
Mo–S(3)	2.478(11)	C(7)–C(8)	1.552(15)	O–Mo–S(2)	87.8(7)
Mo–S(4)	2.705(9)	C(7)–C(9)	1.547(19)	O–Mo–S(3)	90.4(6)
Mo–N(1)	1.841(18)	S(3)–C(10)	1.752(16)	O–Mo–S(4)	154.4(8)
N(1)–N(2)	1.390(18)	S(4)–C(10)	1.752(16)	N(1)–Mo–S(1)	97.8(6)
N(2)–C(19)	1.552(18)	C(10)–N(4)	1.410(17)	N(1)–Mo–S(2)	158.1(7)
N(2)–C(20)	1.552(19)	N(4)–C(11)	1.514(17)	Mo–S(1)–C(1)	92.0(7)
S(1)–C(1)	1.703(19)	C(11)–C(12)	1.554(17)	S(1)–Mo–S(2)	67.5(4)
S(2)–C(1)	1.698(17)	C(12)–C(13)	1.546(19)	S(1)–Mo–S(3)	149.5(4)
C(1)–N(3)	1.382(19)	C(12)–C(14)	1.551(18)	S(3)–Mo–S(4)	65.9(2)
N(3)–C(2)	1.495(19)	N(4)–C(15)	1.508(18)	S(1)–C(1)–S(2)	112.7(8)
C(2)–C(3)	1.558(19)	C(15)–C(16)	1.548(20)	S(1)–C(1)–N(3)	114.9(10)
C(3)–C(4)	1.558(19)	C(16)–C(17)	1.561(19)	S(3)–C(10)–S(4)	107.2(8)
C(3)–C(5)	1.551(19)	C(16)–C(18)	1.548(20)	N(3)–C(2)–C(3)	117.8(16)
				C(4)–C(3)–C(5)	125.2(17)
				N(1)–N(2)–C(19)	105.6(17)
				N(1)–N(2)–C(20)	130.7(14)
				C(19)–N(2)–C(20)	107.2(8)

Non-bonded atom–atom distance: O–N(1) 2.949(20)

and calculated structure amplitudes and where the weights, *w*, are taken as $w = 1/\sigma^2(F_o)$. The refinement terminated when the shifts calculated for the parameters in the least-squares cycles were all zero. Crystal data as well as details of data collection and structure refinement are listed in Table 2. Fractional atomic coordinates are listed in Table 3, while bond angles and distances are given in Table 4.

Results and discussion

The reaction of molybdenum(VI) with dithiocarbamates affords a series of compounds, the composition of which depends on the nature of the ligands, their concentration and the acidity of the reaction mixture [8–13]. The bis(dithiocarbamato)dioxomolybdenum(VI) compounds, $[MoO_2(S_2CNRR')_2]$, are readily obtained under the appropriate experimental conditions [9, 10]. In addition to the MoO_2^{2+} core, their coordination geometry involves the dithiocarbamato moieties bound to molybdenum(VI) ion through the four sulfur atoms and forming four-membered chelate rings [25]. The coordinating behaviour of these uninegative bidentate 1,1-dithioligands may be explained by the resonance structures (a)–(d) (Scheme 1). The necessity of maximum utilisation of the metal orbitals of π symmetry precludes *trans* configuration of the MoO_2^{2+} core since the oxygen pπ orbitals would, as required by symmetry, share the same metal d orbitals. The existence of the



Scheme 1.

two oxo ligands in the $[MoO_2(S_2CNRR')_2]$ compounds in a *cis* configuration is revealed by the two strong bands that occur in the IR spectra in the 935–880 cm^{-1} region [26–28]. The stability of the $[MoO_2(S_2CNRR')_2]$ species in the air and benzene solutions was found to depend on the groups R,R′. While alkyl groups gave stable compounds, incorporation of entities $-N(RR')$ resulting from aryl or methylene groups that are part of a cyclic structure afforded compounds that deteriorated with time. The morpholine derivative, $[MoO_2(morphdtc)_2]$, that turned dark purple, was found to be the least stable.

The MoO_2^{2+} core in the $[MoO_2(S_2CNRR')_2]$ compounds exhibits interesting reactivity. Addition of concentrated hydrochloric acid changes the pattern of peaks in the 935–880 cm^{-1} region and a strong absorption is observed at higher frequencies (~ 950 cm^{-1}) attributable to the stretching vibration of the Mo=O bond [29]. The stoichiometry of the compounds (Table 1) indicates displacement of one oxo ligand. The implication is that despite their functioning as strong π donors, the terminal oxo groups retain sufficient electron density to render one of them susceptible to electrophilic attack. The absence of electrical conductivity suggests heptacoordinated molybdenum(VI). Previous studies revealed that molybdenum is roughly at the centre of a distorted pentagonal bipyramid. Steric interactions compel one of the chlorine atoms and the oxygen to occupy the apices of the polyhedron [15]. The two strongly electron-withdrawing chloride anions remove π electron density from the Mo=O unit to such an extent that the metal–oxygen bond becomes extremely labile to facilitate smooth oxo abstraction [13].

The MoO_2^{2+} core in the $[MoO_2(S_2CNRR')_2]$ species additionally exhibits behaviour akin to organic carbonyl compounds since it reacts with the H_2N group to form products analogous to Schiff bases. The reaction of $[MoO_2(S_2CNRR')_2]$ with N-substituted hydrazines affords products the composition of which depends on the concentration, the extent of N-substitution of the hydrazine molecule and, more important, on the nature of the substituents. For example, when $[MoO_2(S_2CN(i\text{-}Bu)_2)_2]$ was reacted with *N,N*-dimethylhydrazine (H_2NNMe_2), the product $[Mo(N_2Me_2)O\{S_2CN(i\text{-}Bu)_2\}_2]$ was obtained even when excess of *N,N*-dimethylhydrazine was employed and the reaction was carried out in inert solvents at elevated temperature for prolonged time. In the IR spectrum of the product, the pattern of the bands associated with the symmetric and asymmetric vibrations of the MoO_2^{2+} core changes as expected and a sharp band emerged at 1590 cm^{-1} having approximately the same oscillator strength with the Mo=O stretching vibration (Fig. 1). The new band is attributed to the stretching vibration of the N–N bond of the N-substituted hydrazine [28]. The organohydrazido ligand may coordinate in a variety of modes (Scheme 2). The frequency of the N–N bond precludes 'isodiazene' type of bonding and is inconsistent with 'side-on' coordination. The 'linear' and the 'bent' configurations of the hydrazido(2−) ligand (Scheme 2(b) and (c)) are interconvertible and depend on factors influencing the metal–nitrogen bond order and the extent of localisation of a lone pair on the nitrogen atom [30].

The oxo–hydrazido(2−) compounds were also exclusively obtained when the other bis(dithiocarbamato)dioxomolybdenum(VI) compounds were reacted with H_2NNMe_2, as the elemental analyses and the absorption band at ~ 1590 cm^{-1} disclosed (Table 1). However,

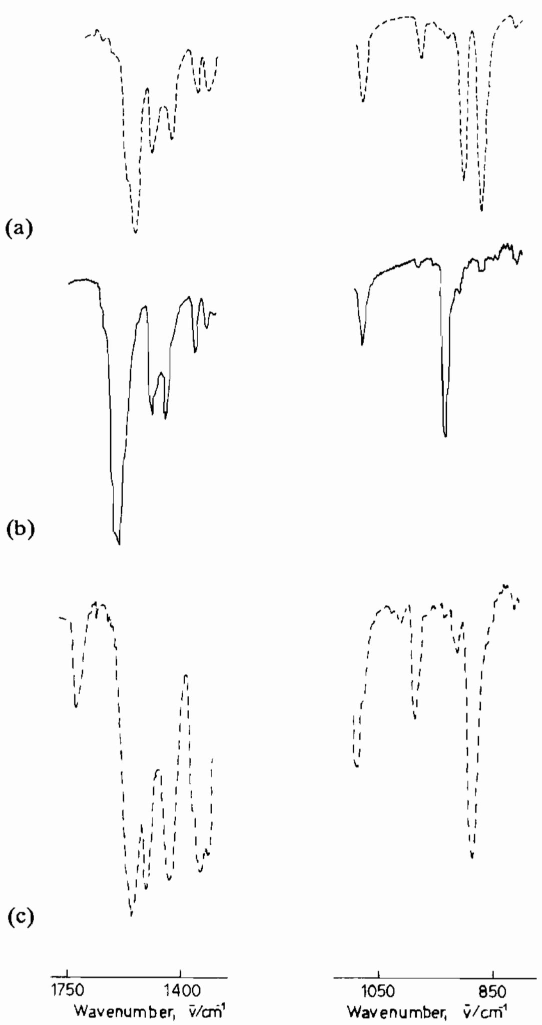
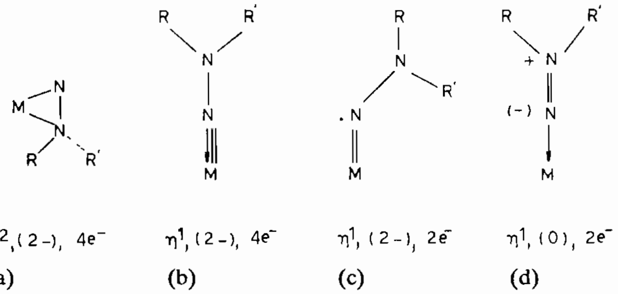
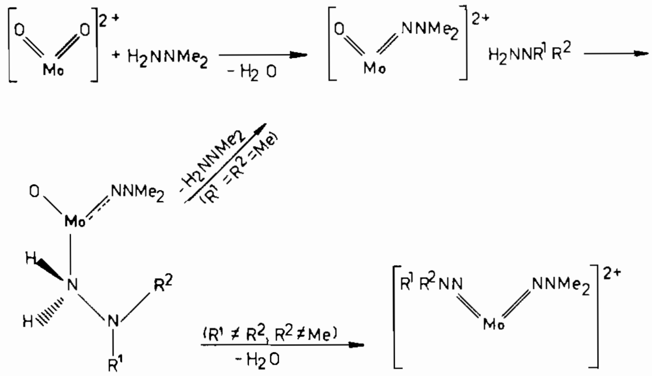


Fig. 1. Selected absorption bands in the IR spectra of $[MoO_2(S_2CN(i\text{-}Bu)_2)_2]$ (a), $[MoOCl_2(S_2CN(i\text{-}Bu)_2)_2]$ (b), and $[Mo(NNMe_2)O(S_2CN(i\text{-}Bu)_2)_2]$ (c).



Scheme 2.



Scheme 3.

reduction of the basicity of the substituted hydrazine resulted in replacement of the second oxo ligand. Actually, employment of H_2NNPh_2 led to partial replacement of the oxo ligands only when the concentration of the hydrazine was inadequate to replace the second oxo group. Excess of H_2NNPh_2 readily afforded $[Mo(NNPh_2)(S_2CN(i\text{-}Bu)_2)_2]$ under relatively mild conditions. These observations indicate that the reaction pathway is dictated by the extent of N-substitution and the electron distribution in the hydrazine molecule. The behaviour of the *cis*-MoO_2^{2+} core may be explained by the mechanism proposed by Chatt *et al.* [19]. It is presumed that the incoming hydrazine interacts covalently with the metal centre and proton transfer to the most basic site is facilitated. Depending on the N-substituents, that site may be either the oxo ligand or the coordinated hydrazide (Scheme 3).

Infrared spectra

The position and the shape of certain bands in the IR spectra of the bis(dithiocarbamato)dioxomolybdenum(VI) compounds are indicative of the mode of coordination of the dithiocarbamate group and the occurrence of coligands. A pair of strong bands in the 935–880 cm^{-1} region are attributed to the MoO_2^{2+} core and are considered as indicative of the *cis* configuration of the oxo ligands and adoption of C_{2v} symmetry. Group theoretical considerations indicate the existence of two stretching vibrations, the symmetric (a_1) and the antisymmetric (b_1), that are both IR and Raman active. Raman polarisation measurements revealed that the symmetric stretching vibrations v_s are higher in energy than the antisymmetric ones [26–28]. Previous studies on compounds containing the MoO_2^{2+} core have disclosed that the frequencies of the stretching vibrations, v_s and v_{as}, depend on the coligands [26–28]. This is amply demonstrated in the present case since groups far away from the coordination sites induce spectral shifts. In $[MoO_2\{S_2CN(C_2H_5)_2\}_2]$ the vibrations v_s and v_{as} occur at 912.3 and 881.2 cm^{-1}, respectively. Replacement of the ethyl groups by isobutyl ones shifts the bands towards higher frequencies while cyclisation with the $-(CH_2)_5-$ group has the opposite effect. This suggests that the substituents alter the electron density in the MoO_2^{2+} core by induction. Replacement of one oxo ligand results in replacement of the pair of bands by a single band that is attributed to the Mo=O strecth.

The replacement of the oxo ligand additionally culminates in shifts and changes in the shape of other bands that in the IR spectra of the bis(dithiocarbamato)dioxomolybdenum compounds are associated with the dithiocarbamato moiety and its mode of coordination. For instance, the strong band observed at 995 ± 15 cm^{-1} and attributed to the C$\overset{...}{-}$S stretching vibration, is considered as indicative of bidentate coordination [33]. The frequency of the δ(SCS) mode and that of the C$\overset{...}{-}$N stretching vibration (thioureide band) are affected by the charge of the central metal ion, the stereochemistry of the chelates and by the substituents attached to the nitrogen atom demonstrating the well-documented receptiveness of the dithiocarbamato moiety to mass and electronic effects [34]. The changes may be reasonably accounted for by the resonance forms of the dithiocarbamato ligand (Scheme 1) and reaffirm previous observations that the coligands also exert strong influence. The influence of the coligands is highlighted when one oxo group is replaced by two chloride ions. While the double band due to the MoO_2^{2+} core disappears and a strong band emerges at ~950 cm^{-1}, the intense band at ~1490 cm^{-1} attributable to the C$\overset{...}{-}$N stretching vibration is shifted by about 40 cm^{-1} to higher frequencies (Fig. 1).

The insertion of the dimethylhydrazido(2−) group, probably a four-electron donor, is accompanied by spectral shifts, too. Also a multitude of bands emerge in the region in which the thioureide absorption is observed. A notable feature is the band of medium intensity that appears at ~1590 cm^{-1} due to the N$\overset{...}{-}$N bond (Fig. 1). No bands assignable to metal–nitrogen stretching could be identified in the range 1000–1200 cm^{-1} probably because of the intervening ligand bands.

Description of the structure of [Mo(N$_2$Me$_2$)O{S$_2$CN(i-Bu)$_2$}$_2$]

The structure of [Mo(N$_2$Me$_2$)O{S$_2$CN(i-Bu)$_2$}$_2$] comprises well-separated monomers. The relatively small dithiocarbamate chelates make the compound sterically unencumbered. Unusual intramolecular contacts were not observed and there are no significant intermolecular non-bonded contacts in the unit cell, and it is therefore most unlikely that packing forces have any influence on the molecular geometry. The crystallographic analysis showed that both dithiocarbamates are chelating. It also revealed that only one nitrogen atom of the hydrazido(2−) group interacts covalently with molybdenum(VI). The monohapto hydrazido(2−) group and the remaining oxo ligand assume the anticipated *cis* configuration about the molybdenum centre with an angle of 112.9(8)°. The strong σ and π donor nature of the oxo ligand and the nitrogen atom of the hydrazido(2−) group makes it favourable for them to avoid competing for the same p and d orbitals. *Trans* coordination of the oxo groups would have forced them to share two d orbitals and one p orbital. Adoption of the *cis* configuration enables them to share only a single d orbital. Idealised octahedral geometry requires bond angles around the metal of 90 or 180°. The observed values suggest a highly distorted octahedral structure (see Tables 3 and 4). The arrangement of the atoms in the molecule is shown in Fig. 2.

In the [Mo(N$_2$Me$_2$)O{S$_2$CN(i-Bu)$_2$}$_2$] molecule the dithiocarbamate ligands form four-membered chelate rings and adopt the usual geometry seen for these ligands in this mode of coordination. The small bite angles at 67.5(4) and 65.9(2)° are partly responsible for the observed distortion from octahedral arrangement of the donor atoms. The Mo–S distances are within the range of the bond lengths observed in molybdenum dithiocarbamates [4]. The Mo–S distances with S *trans* to S are virtually equal so the observed lengthening of the other two Mo–S bonds reflects the influence of the coligands (the oxo and dimethylhydrazido(2−) groups). The effect of the more strongly bonded oxo group is demonstrated by the greater *trans* influence exerted by this ligand relative to the monohapto hydrazido(2−) group and in many other structural parameters. For example, while the dithiocarbamato chelate ring containing the sulfur *trans* to the hydrazido(2−) group is nearly planar, the deviation from planarity of the other chelate ring is quite significant with C(10) protruding. The perturbation induced by the hydrazido(2−) group is also transmitted to the nitrogen atom bonded to the chelate ring and the N(4)–C(10) distance of only 138 pm is shorter than that of the N(3)–C(1) bond (Table 4). The other N–R (R = i-Bu) distances are much longer and exceed the distance of a standard C–N single bond (147 pm). Recourse to the resonance structures within the ligand itself makes it immediately clear that the forms (c) and (d) are the main contributors (Scheme 1). The terminal methyl groups all seem to be well behaved and there is no sign of any disorder.

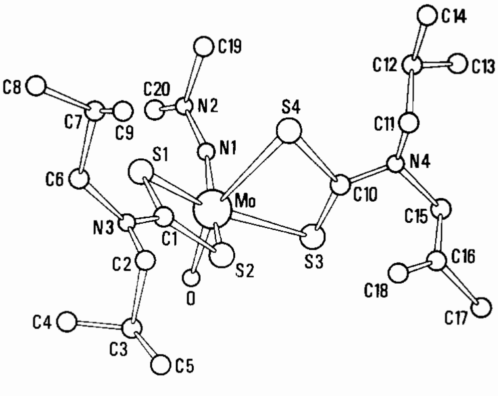


Fig. 2. Perspective view of the molecule [Mo(NNMe$_2$)O(S$_2$CN(i-Bu)$_2$)$_2$] showing the atom-labelling scheme.

The hydrazido(2−) group is close to being planar with N(2) protruding only 6.5 pm from the plane defined by the remaining sceletal atoms. It is nearly linearly bonded to molybdenum, in a manner similar to that observed in most other Mo–hydrazido(2−) compounds. The N(1)–N(2) distance is 139 pm being appreciably longer than the average N=N double bond (124 pm in PhNNPh) but substantially shorter than the single N–N bond in *N,N*-dimethylhydrazine (145 pm in Me$_2$NNH$_2$). The contraction relative to H$_2$NNMe$_2$ suggests delocalisation of electron density. The Mo–N(1)–N(2) angle of 162.6(16)° suggests, in valence-bond terminology, predominance of sp hybridisation about N(1) while the planarity of the hydrazido(2−) group implicates sp^2 hybridisation about N(2), even though the relevant angles deviate from 120° (Table 4). The Mo–N(1) distance is 184.1 pm, the longest yet observed in similar hydrazido and diazenido compounds where substantial degree of multiple-bond character has been postulated (Table 5). The bent tilts the hydrazido(2−) group slightly towards the oxo ligand as observed in most oxo–hydrazido(2−) compounds (Table 5). The lower bond order of the Mo–N linkage and the less obtuse Mo–N(1)–N(2) angle suggest enhanced contributions from forms (c) and (d) (Scheme 2).

Recourse to the bonding parameters of similarly structured octahedral molybdenum(VI) compounds reveals striking differences between the [Mo(N$_2$Me$_2$)O(S$_2$CN(i-Bu)$_2$)$_2$] and [Mo(N$_2$Me$_2$)O(S$_2$CNMe$_2$)$_2$] molecules that highlight the influence of the isobutyl group (Table 5). For example, the Mo–N distance increases from 179.9 to 184.1 pm and the O–Mo–N angle gets more obtuse since it changes from 104.4 to 112.9(8)° even though no change in the constitution of the

TABLE 5. Pertinent parameters for $MoO(NNMe_2)_2(i\text{-}Bu_2dtc)_2$ and related six-coordinated molybdenum(VI) compounds

No.	Compound	X	Mo–X	Mo–S(Y)		N_h–N_h	C–N	X–Mo–X	Mo–N–N	S–C–S	Ref.
1	$MoO_2(S_2CNEt_2)_2$	O O	1 703 1.703	2.450 2.450	2.639[a] 2.639	na na	1.315 1.315	105.81	na[i]	113 7[b] 113.7[b]	25
2	$MoO_2(oxine)_2$[c]	O O	1.71 1.71	1.98[d] 1.98[d]	2.32[e] 2.32[e]	na	na	104	na	na	31
3	$MoO(NNMe_2)(S_2CNMe_2)_2$	O N	1.708 1.799	2.433 2.519	2.576 2.720	1.288	1.349 1.300	104.40	168.0	115.7 113.1	16
4	$MoO(NNMe_2)(oxine)_2$	O N	1.671 1.800	2.250[d] 2.019[e]	2.123[e] 2.302[d]	1 28	na	100.8	155.5	na	17
5	$MoO(NNMe_2)(i\text{-}Bu_2dtc)_2$	O N	1.697 1.841	2.478 2.477	2.705 2 611	1.390	1.410 1.382	112.9	162.6	107.2 112.7	this work
6	$MoO(NNPh_2)(S_2N_2)$[g]	O N	1.696 1.778	2 478 2.408	2.464[e] 2.359[e]	1.309	1.382 1.410	105.9	172.9	na na	18
7	$MoO(NNPh_2)(OSL)_2$[h]	O N	1.703 1.779	2.420 2.534	2.148[e] 2.199[e]	1.309	na	102.6	176.2	na	21
8	$Mo(NNMePh)_2(S_2CNMe_2)_2$	N N	1.790 1.790	2.488 2.488	2.662 2.662	1.30 1.30	1.30 1.30	107.2	172 6 172.6	113.8 113.8	19
9	$Mo(NNPh_2)_2(S_2CNMe_2)_2$	N N	1.790 1.790	2.493 2.493	2.680 2.680	1.31 1.31	1.34 1.34	107 5	169.9 169 9	115 6 115.6	19
10	$Mo(NPh)_2(S_2CNEt_2)_2$	N N[f]	1.754 1.789	2.453 2.461	2.602 2.755	na na	1.327 1.330	103.5	169.4 139.4	114.0 115.6	32

[a]S(Y) atom *trans* to X. [b]Calculated from the data in ref. 29. [c]Oxine = hydroxyquinoline. [d]Oxygen atom. [e]Nitrogen atom. [f]Bent nitrene. [g]Tetradentate ligand. [h]Benzothiohydroxamato ligand. [i]na = not applicable.

coligands took place. The distance between the hydrazido(2 −) nitrogens also increases from 128.8 to 139.0 pm suggesting appreciable diminution of the double-bond character. The Mo–N–N angle decreases from 168 to 162.6° and at the same time the hydrazido(2 −) group changes orientation with the N(2) atom facing towards the oxo ligand as happens with the vast majority of the oxo–hydrazido(2 −), bis(hydrazido(2 −)) and bis(diazenido(2 −)) compounds (Table 5). The observed structural changes clearly indicate that although the substituents are not linked to the central metal ion they engender electronic effects that are transmitted to the coligands.

Conclusions

In this study a number of interesting results have been presented. It has been shown that in bis(dithiocarbamato)dioxomolybdenum(VI) chelates the oxo ligands exhibit behaviour akin to the carbonyl oxygen and are susceptible to electrophilic attack. Hydrohalogenic acids react and form heptacoordinated oxo compounds while simple *N*,*N*-dialkylhydrazines displace the oxo ligands and coordinate 'head-on'. The extent of displacement is dictated by the basicity of the *N*,*N*-dialkylhydrazines. Spectral shifts suggest that substituents within the dithiocarbamato moiety influence the electron distribution about the molybdenum(VI) cation even though the reactivity pattern of these compounds does not change. The effects of the substituents on the dithiocarbamato chelate rings and the coligands are illustrated in the crystal and molecular structure of $[Mo(N_2Me_2)O\{S_2CN(i\text{-}Bu)_2\}_2]$. Replacing a methyl group by an isobutyl one alters the orientation of the *N*,*N*-dimethylhydrazido(2 −) ligand, reduces the bond order of the N–N bond, causes elongation of the Mo–N bond and enhances the bend in the Mo–N–N segment.

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