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Induced Redox Reactions Between Molybdenum Dialkyldithiocarbamates and Chloroform, and X-ray Crystal Structure of $[Mo((C_2H_5)_2NCS_2)_4](Cl \cdot H_2O) \cdot xCHCl_3$ ($x = 0.88$)

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Abstract

Chloroform solutions of molybdenum(III or IV) dithiocarbamate (dtc) are stable when kept in an inert atmosphere, but the following redox reactions take place when they are exposed to air: $10Mo_2(dtc)_6 + 8CHCl_3 + 8H_2O + 21O_2 \rightarrow 14tds + 4HCl + 2H_2O_2 + 4HOC(O)Cl + 2[Mo(dtc)_4]_2Mo_6O_{19} + 4[Mo(dtc)_4](Cl \cdot H_2O) \cdot CHCl_3$ (tds = tetraethylthiuram disulfide, $[(C_2H_5)_2NCS_2]_2$; and $2Mo(dtc)_4 + 4CHCl_3 + 4H_2O + 2O_2 \rightarrow 2[Mo(dtc)_4](Cl \cdot H_2O) \cdot CHCl_3 + 2HOC(O)Cl + 2HCl + H_2O_2$. Although the well known slow oxidation of $CHCl_3$ by air is similar to those given above, the presence of the Mo-compounds increases the rate by a factor of many orders of magnitude. The crystals of the common product, $[Mo(dtc)_4](Cl \cdot H_2O) \cdot xCHCl_3$, are triclinic, space group $P\bar{1}$, $a = 12.206(3)$, $b = 13.314(4)$, $c = 14.786(3)$ Å, $\alpha = 116.68(2)$, $\beta = 110.76(2)$, $\gamma = 92.42(2)°$, and $Z = 2$. The structure, which was determined from 5690 observed reflections to an R factor of 0.056, consists of a packing of $Mo(dtc)_4^+$ ions, centrosymmetric hydrogen-bonded dimeric $[Cl^- \cdot H_2O]_2$ anions, and $CHCl_3$ molecules of fractional occupancy ($x = 0.88$). A very broad medium intensity IR band for the water molecule was observed between 3200–3600 cm^{-1}. For the cation, the Mo–S distances range from 2.508(2) to 2.533(2) Å with a mean of 2.522(10) Å, which is the same as that found in anhydrous $Mo(dtc)_4Cl$.

Introduction

Reactions between common solvents such as chloroform and metal complexes of dithiocarbamate have attracted little attention. Tamminen and Hjelt [1] mentioned that copper(I) diethyldithiocarbamate (dtc) was oxidized in boiling chloroform to give $Cu(dtc)_2$ and a sparingly soluble salt, $[Cu(dtc)] \cdot CuCl$. However, the reaction of chloroform and the role of oxygen from the air has not been investigated. Nieuwpoort [2] reported the formation of adducts when $Mo(dtc)_4X$ (X = Br, I) were dissolved in chloroform and the excess solvent allowed to slowly evaporate. Later, he [3] suggested that an oxidation reaction resulted in the formation of $Mo(dtc)_4Cl$ when $Mo(dtc)_4$ is dissolved in chloroform under a nitrogen atmosphere. In contrast, Brown *et al.* [4] reported that under a strictly inert atmosphere molybdenum(III) or molybdenum(IV) dialkyldithiocarbamates formed adducts when dissolved in haloforms with no apparent oxidation. Recently, we found that air-oxidation of $Mo_2(dtc)_6$ in chloroform gave $[Mo(dtc)_4]_2Mo_6O_{19}$ [5], and yet another product was subsequently identified as $[Mo(dtc)_4](Cl \cdot H_2O) \cdot xCHCl_3$ which contains a hydrogen-bonded cyclic dimeric anion $(Cl^- \cdot H_2O)_2$ in its crystal structure [6]. We now report details of the X-ray crystallographic results of the latter complex, and the interesting redox reaction between chloroform and molybdenum(III or IV) diethyldithiocarbamates via routes involving free radicals.

Experimental

(a) Measurements and Starting Material

Infrared spectra in the 4000–300 cm^{-1} region were recorded as 2% KBr and CsBr disks on a Perkin-Elmer 983 spectrophotometer. Electronic spectra were obtained in dichloromethane and chloroform solutions in the range 50.0–13.0 kK on a Perkin-Elmer Lambda-5 UV–Vis spectrophotometer. Proton NMR spectra were measured in deuterated chloroform and acetone on a Bruker WP-80 spectrometer. Elemental analyses were carried out by Guelph Chemical Laboratories Ltd. Reagent grade chemicals were used without further purification except where specified. $Mo_2(dtc)_6$ and $Mo(dtc)_4$ were

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prepared by previously reported methods [4, 7]. Styrene was purified by washing three times with equal volumes of 10% NaOH followed by three times with equal volumes of deionized water. The wet styrene was then fractionally distilled under vacuum at 313–315 K.

(b) Reaction of $Mo_2(dtc)_6$ with Chloroform in Air

Two grams (1.85 mmol) of $Mo_2(dtc)_6$ in 100 ml chloroform was left to oxidize in air at 298 K for 48 h. The reddish-brown crystals formed were filtered off and characterized as $[Mo(dtc)_4]_2Mo_6O_{19}$ [5]. The filtrate was dried by evaporation under vacuum. The residue was then dissolved in 20 ml each of acetone and chloroform, and after filtration to remove any insoluble material, the clear solution was allowed to crystallize in a slow stream of nitrogen to remove the solvent. The brown crystals so formed were collected by filtration. Another crop was obtained by recrystallization from a chloroform/hexane mixture. After the crystals were collected, the filtrate was then chromatographed over silica gel and eluted with chloroform to give a yellowish layer which when evaporated gave pale yellow crystals of tetraethylthiuram disulfide (tds). The yield of the brown crystals was 60–65%. *Anal.* Calc. for $[Mo(dtc)_4(Cl\cdot H_2O)\cdot CHCl_3$, $MoC_{21}H_{43}N_4S_8OCl_4$: C, 29.27; H, 4.99; N, 6.50. Found: C, 29.85; H, 5.01; N, 6.44%. NMR in $CDCl_3$: $\delta(CH_3) = 1.33$ ppm, $J = 3.68$ Hz; $\delta(CHCl_3) = 7.2$ ppm (compared to 7.3 ppm of pure solvent; this peak was also observed when d_6-acetone was used as solvent).

(c) Reaction of $Mo(dtc)_4$ with Chloroform in Air

A procedure similar to that outlined above was used. After a chloroform solution of $Mo(dtc)_4$ was left in air for 48 h, its volume was reduced to 20 ml under vacuum and then chromatographed over silica gel. The column was washed with chloroform to remove the decomposition products. The brown product did not descend along the column. The silica gel was therefore removed, and the compound was washed off by 250 ml each of chloroform and acetonitrile. The mixture was filtered and the solvent was removed under vacuum to leave a brown product which was confirmed as $Mo(dtc)_4\,Cl\cdot H_2O)\cdot CHCl_3$.

(d) Testing for Radicals in Solution

The experiment was performed in parallel with a control to confirm the presence of free radicals in the reaction between $Mo_2(dtc)_6$ and chloroform. Two solutions were prepared by mixing 60 ml chloroform and 5 ml styrene; and 0.54 g (0.5 mmol) of $Mo_2(dtc)_6$ was added to one of them. The mixtures were then stirred in air for 48 h. They were then fractionally distilled under vacuum at 313–318 K. The colorless distillate was then tested for the presence of Cl^- ions and of the carbonyl group by measuring the μ(CO) band at 1715 cm^{-1}. The residues were washed with methanol and acetone, and at this point, the wall of the flask with $Mo_2(dtc)_6$ added showed a thin white layer of polystyrene which was insoluble in methanol and water, slightly soluble in acetone, and soluble in chloroform. The control or blank flask had no trace of polymer.

(e) Crystallographic Studies

The title compound rapidly loses $CHCl_3$ upon exposure to air, but a single crystal coated with clear nail polish and mounted inside a 0.5 mm Lindemann glass capillary remained sufficiently stable for diffraction study. Cell constants and intensities of the reflection were measured on a Nicolet R3m automated four-circle diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å), a scintillation counter, and a pulse-height analyser. Stability of the crystal was monitored by repeated measurements of three standard reflections. The raw data were processed with a learnt-profile procedure [8], and absorption corrections were applied using an empirical method based on a pseudo-ellipsoidal analysis of azimuthal (ψ) scans of selected strong reflections [9]. Relevant parameters and crystal data are given in Table I.

(f) Structure Solution and Refinement

The structure was solved by Patterson and Fourier methods, and refined by blocked-cascade least-squares [10] using the SHELXTL program package [11] on a Data General Corporation Nova 3/12 minicomputer. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [12]. Anisotropic temperature factors were given to all non-hydrogen atoms except C(1) of the chloroform molecule, whose site occupancy factor x was treated as a variable in refinement. The final atomic parameters are given in Table II, see also 'Supplementary Material'.

Results and Discussion

Air oxidation of $Mo_2(dtc)_6$ in a chloroform solution resulted in the formation of $[Mo(dtc)_4]_2Mo_6O_{19}$ [5] and $[Mo(dtc)_4](Cl\cdot H_2O)\cdot CHCl_3$ according to the reaction:

$$\begin{aligned}10Mo_2(dtc)_6 + 8CHCl_3 + 8H_2O + 21O_2 &\longrightarrow \\ 14tds + 4HCl + 2H_2O_2 + 4HOC(O)Cl \\ + 2[Mo(dtc)_4]_2Mo_6O_{19} \\ + 4[Mo(dtc)_4](Cl\cdot H_2O)\cdot CHCl_3\end{aligned}$$

Under the same condition $Mo(dtc)_4$ gave only one Mo-compound according to the reaction:

TABLE I. Crystal Data and Parameters Used in X-ray Structural Determination

Molecular formula	$[Mo(Et_2dtc)_4](Cl{\cdot}H_2O){\cdot}xCHCl_3$
Molecular weight	861.87 ($x = 1$)
Cell constants	
a	12.206(3) Å
b	13.314(4) Å
c	14.786(3) Å
α	116.68(2)°
β	110.76(2)°
γ	92.42(2)°
V	1948.5(8) $Å^3$
Z	2
Density (calc.)	1.469 g cm^{-3}
Space group	$P\bar{1}$
Radiation	graphite-monochromatized Mo Kα, $\lambda = 0.71069$ Å
Absorption coefficient	10.40 cm^{-1}
Crystal size	0.32 × 0.36 × 0.40 mm
Mean μr	0.25
Transmission factors	0.752 to 0.844
Scan type and speed	$\omega-2\theta$; 2.02–8.37 deg min^{-1}
Scan range	1° below Kα_1 to 1° above Kα_2
Backgroung counting	stationary counts for one-half of scan time at each end of scan
Collection range	$h, \pm k, \pm l; 2\theta_{max} = 50°$
Unique data measured	6761
Observed data with $|F_o|3\sigma(|F_o|), n$	5690
Number of variables, p	348
Site occupancy factor of $CHCl_3, x$	0.881(5)
$R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$	0.056
Weighting scheme	$w = [\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$
$R_w = |\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$	0.0078
$S = [\Sigma w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$	1.926

$$2Mo(dtc)_4 + 4CHCl_3 + 4H_2O + 2O_2 \longrightarrow 2[Mo(dtc)_4](Cl{\cdot}H_2O){\cdot}CHCl_3 + 2HOC(O)Cl + 2HCl + H_2O_2$$

The common product $[Mo(dtc)_4](Cl{\cdot}H_2O){\cdot}CHCl_3$ in the two reactions is a stable brown crystalline material, the water molecule being derived from either the atmosphere humidity or the moisture in the solvents. The chloroform of crystallization is easily lost if the sample is left under vacuum for several hours. The compound is very soluble in chloroform and ethanol, less soluble in acetone and insoluble in hexane, benzene, and diethyl ether. When dissolved in a mixture of acetone and H_2O, the chloride ions gave a precipitate upon addition of Ag^+ ions.

TABLE II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å × 10^3)

Atom	x	y	z	U_{eq}[a]
Mo	1561.8(4)	1709.1(4)	3075.0(4)	31.1(2)
S(1)	2153(1)	2684(1)	5150(1)	41.9(7)
S(2)	3572(1)	3141(1)	4186(1)	45.9(8)
S(3)	368(2)	3231(1)	3234(1)	46.9(9)
S(4)	1511(1)	2476(1)	1782(1)	40.8(8)
S(5)	−25(1)	946(1)	3492(1)	41.8(7)
S(6)	−178(1)	204(1)	1330(1)	44.9(8)
S(7)	2396(2)	159(1)	3431(1)	45.9(8)
S(8)	2679(1)	717(1)	1896(1)	42.0(8)
Cl(4)	7126(1)	5057(1)	−154(1)	34.6(6)
C(11)	3497(5)	3466(5)	5418(5)	36(3)
N(1)	4313(4)	4179(4)	6403(4)	41(3)
C(12)	4173(6)	4381(6)	7427(5)	54(4)
C(13)	5443(6)	4833(6)	6568(6)	57(4)
C(14)	3651(9)	5398(8)	7871(7)	86(6)
C(15)	6477(6)	4240(7)	6733(7)	72(5)
C(21)	626(5)	3362(5)	2225(5)	38(3)
N(2)	215(5)	4041(4)	1823(4)	46(3)
C(22)	539(6)	4090(6)	966(6)	56(4)
C(23)	−590(7)	4761(7)	2200(7)	71(5)
C(24)	−318(7)	3254(7)	−214(6)	71(5)
C(25)	183(11)	5996(8)	3174(9)	115(7)
C(31)	−819(5)	−45(5)	2088(5)	37(3)
N(3)	−1761(4)	−878(4)	1703(4)	41(2)
C(32)	−2169(6)	−1071(6)	2443(5)	53(3)
C(33)	−2392(6)	−1704(6)	508(6)	59(4)
C(34)	−1499(8)	−1886(8)	2804(8)	85(6)
C(35)	−3559(7)	−1432(9)	−45(7)	83(5)
C(41)	2948(5)	−182(5)	2446(5)	39(3)
N(4)	3517(4)	−1019(4)	2125(4)	43(3)
C(42)	3972(6)	−1205(6)	1285(6)	55(4)
C(43)	3728(7)	−1778(6)	2605(6)	61(4)
C(44)	3041(8)	−1986(7)	96(7)	74(5)
C(45)	5023(8)	−1359(8)	3548(8)	88(6)
C(1)	6544(18)	2259(18)	3564(18)	193(8)
Cl(1)	7119(4)	3733(3)	4313(3)	131(3)
Cl(2)	6567(4)	1604(3)	2304(3)	139(3)
Cl(3)	6795(6)	1585(3)	4269(4)	170(4)
Ow	5400(5)	6661(4)	811(5)	69(3)
Hwa	592	622	630	80
Hwb	469	620	580	80

[a] U_{eq} defined as one-third of the trace of the orthogonalized U tensor.

It is interesting, but not surprising, that chloroform solutions of $Mo_2(dtc)_6$ and $Mo(dtc)_4$ remain stable when kept under an inert N_2 atmosphere; their interaction with $CHCl_3$ may be described by the formation of adducts [4]. The strong interaction between these compounds and $CHCl_3$ promoted their reaction with air or moisture or both. Till now, we have not been able to grow suitable crystals of the adducts to study the nature of their interactions with $CHCl_3$, but the present study has clearly shown that there exist synergetic effects in the oxidation of $Mo_2(dtc)_6$ and $Mo(dtc)_4$ by air and chloroform. The overall reaction may be described as a reduction of chloroform by Mo(III) or Mo(IV) complexes, and the process is induced by oxygen from the air.

TABLE III. Infrared Spectra (cm^{-1})[a] of [Mo(dtc)$_4$](Cl·H$_2$O)·CHCl$_3$ and Related Compounds

Compound	μ(RNC)	μ_s(CN)	μ_{as}(CS)	μ(MoS)	μ(OH)	μ(C–Cl)	Reference
Mo(dtc)$_4$	1500vs	1002s	580s	355s			20
Mo(dtc)$_4$I$_3$	1507vs	1000s	565w	350m			19
Mo(dtc)$_4$·CHCl$_3$	1510vs	1000s	580m	355s			[b]
Mo(dtc)$_4$(Cl·H$_2$O)·CHCl$_3$	1508vs	1018s 1008w	580s	358s 365sh	3200–3600m	742	[b]
(Mo(dtc)$_4$)$_2$Mo$_6$O$_{19}$	1515vs	1008vs 990vw	550m	355s 365sh			5

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] This work.

Table III lists the IR spectra of [Mo(dtc)$_4$]$_2$-Mo$_6$O$_{19}$, [Mo(dtc)$_4$](Cl·H$_2$O)·CHCl$_3$ and other related compounds. The IR spectra of the typically bidentate dithiocarbamate ligand have μ(RNC), μ_s(CS), and μ_{as}(CS) as shown [13, 14]. It is known that the μ(RNC) bands steadily shift to higher frequencies as the oxidation number of Mo in the complexes increases, and the observed band at 1508 cm^{-1} is consistent with data for other Mo(VI) compounds [15]. The μ(MoS) and μ_s(CS) bands exhibit shoulders, perhaps suggesting a slight assymetric bonding of –CS$_2$ to Mo in [Mo(dtc)$_4$](Cl·H$_2$O)·CHCl$_3$. These observations are in agreement with the bond distances obtained from X-ray diffraction (Table IV). In the μ(OH) region, its spectrum exhibits a very broad (from 3200 to 3600 cm^{-1}), medium intensity band with a half width of about 220 cm^{-1}. This band, slightly lower than that of pure water, is attributable to the water molecules hydrogen-bonded to Cl$^-$ forming a cyclic (Cl$^-$·H$_2$O)$_2$ anion, thus weakening the OH bonds [6]. It is also noteworthy to point out that the strong peak at 742 cm^{-1} is due to μ(C–Cl) of chloroform.

The electronic spectrum of [Mo(dtc)$_4$](Cl·H$_2$O)·CHCl$_3$ consists of ten bands in the range 13–50 kK, their positions (intensities ϵ) being 13.2 (vw), 14.1 (50), 15.9 (128), 19.1 (1923), 21.7 (5338), 22.3 (5389), 25.2 (5738), 29.4 (10 512), 33.3 (19 435), 38.8 kK (20 487). The first three weak bands in the visible region may be due to ligand field transitions, whereas the strong ones may be assigned to metal-to-ligand charge transfers [16]. The observed band with the highest energy and intensity is a π–π^* transition [17]. The observed electronic spectrum is in excellent agreement with those of other compounds containing the Mo(dtc)$_4^+$ ion [18].

It is well known that in the presence of light and humidity, oxygen in the air decomposes pure chloroform slowly to, *inter alia*, COCl$_2$ and HCl by a free radical mechanism. The present study demonstrated that dissolution of Mo(III) and Mo(IV) diethyldithiocarbamates in CHCl$_3$ increased the latter's reaction rate with air by many orders of magnitude, leading to the formation of [Mo(dtc)$_4$]-

TABLE IV. Selected Bond Lengths (Å) and Bond Angles (°)

Metal–ligand bond lengths			
Mo–S(2)	2.508(2)	Mo–S(6)	2.509(1)
Mo–S(7)	2.519(2)	Mo–S(3)	2.519(2)
Mo–S(4)	2.525(2)	Mo–S(1)	2.529(2)
Mo–S(5)	2.531(2)	Mo–S(8)	2.533(2)
Bond lengths of dithiocarbamate ligands			
S(1)–C(11)	1.720(7)	S(2)–C(11)	1.711(8)
S(3)–C(21)	1.708(8)	S(4)–C(21)	1.704(7)
S(5)–C(31)	1.731(5)	S(6)–C(31)	1.707(8)
S(7)–C(41)	1.705(8)	S(8)–C(41)	1.709(8)
N(1)–C(11)	1.291(6)	N(2)–C(21)	1.315(10)
N(3)–C(31)	1.318(8)	N(4)–C(41)	1.331(8)
Interatomic distances within the water–chloride dimer			
Ow–Hwa	0.911(6)	Ow–Hwb	0.895(6)
Ow··Cl(4)	3.287(8)	O··Cl(4)′	3.311(8)
Bond lengths of the chloroform molecule			
C(1)–Cl(1)	1.72(2)	C(1)–Cl(2)	1.68(3)
C(1)–Cl(3)	1.62(3)		
Bond angles within the coordination sphere			
S(1)–Mo–S(2)	67.5(1)	S(3)–Mo–S(4)	67.6(1)
S(5)–Mo–S(6)	68.1(1)	S(7)–Mo–S(8)	67.5(1)
S(1)–Mo–S(5)	68.9(1)	S(4)–Mo–S(8)	68.1(1)
S(5)–Mo–S(7)	78.5(1)	S(5)–Mo–S(3)	80.6(1)
S(1)–Mo–S(3)	81.8(1)	S(1)–Mo–S(7)	81.2(1)
S(2)–Mo–S(4)	79.7(1)	S(2)–Mo–S(8)	79.3(1)
S(6)–Mo–S(4)	80.3(1)	S(6)–Mo–S(8)	80.2(1)
S(6)–Mo–S(3)	91.0(1)	S(6)–Mo–S(7)	90.7(1)
S(2)–Mo–S(3)	94.3(1)	S(2)–Mo–S(7)	93.8(1)
S(1)–Mo–S(4)	132.9(1)	S(1)–Mo–S(8)	132.4(1)
S(5)–Mo–S(4)	134.4(1)	S(5)–Mo–S(8)	132.7(1)
S(3)–Mo–S(8)	135.6(1)	S(4)–Mo–S(7)	135.5(1)
S(1)–Mo–S(6)	137.0(1)	S(2)–Mo–S(5)	136.5(1)
S(2)–Mo–S(6)	155.5(1)	S(3)–Mo–S(7)	156.7(1)
Other angles			
Mo–S(1)–C(11)	91.0(2)	Mo–S(2)–C(11)	92.0(2)
Mo–S(3)–C(21)	91.0(2)	Mo–S(4)–C(21)	90.8(3)
Mo–S(5)–C(31)	89.9(3)	Mo–S(6)–C(31)	91.2(2)
Mo–S(7)–C(41)	91.3(3)	Mo–S(8)–C(41)	90.7(2)
Angles within the water–chloride dimer			
Ow–Cl(4)–Ow′	71.4(4)	Cl(4)–Ow–Cl(4)′	108.9(4)
Hwa–Ow–Hwb	109.5(5)		

Symmetry information: ′1 – x, 1 – y, 1 – z.

$(Cl{\cdot}H_2O){\cdot}CHCl_3$ and $[Mo(dtc)_4]_2Mo_6O_{19}$, also via free radical routes. In fact, so many free radicals were present in the system that polymerization of styrene had been observed (see 'Experimental'). The mechanism may be the same for $Mo(dtc)_4$ and $Mo_2(dtc)_6$, and we illustrate how such a pathway may progress ($x = 1, y = 4$; and $x = 2, y = 6$; respectively):

$$Mo_x(dtc)_y + CHCl_3 \longrightarrow Mo_x(dtc)_y{\cdot}CHCl_3$$

$$Mo_x(dtc)_y{\cdot}CHCl_3 \xrightarrow[O_2]{h\nu} Mo_x(dtc)_yH^* + \underset{\nearrow\, O_2}{CCl_3O_2^*}$$

$$CCl_3O_2^* + CHCl_3 \longrightarrow CCl_3OOH + CCl_3^*$$

$$CCl_3OOH \longrightarrow CCl_3O^* + HO^*$$

$$CCl_3O^* \longrightarrow COCl_2 + Cl^*$$

$$COCl_2 + H_2O \longrightarrow HOC(O)Cl + HCl$$

$$2HO^* \longrightarrow H_2O_2$$

$$HO^* + {}^*Cl \longrightarrow HOCl$$

$$2Cl^* \longrightarrow Cl_2 \xrightarrow{H_2O} HOCl + HCl$$

$$HOCl + H_2O \longrightarrow H_2O_2 + HCl$$

$$Mo_x(dtc)_yH^* + H_2O_2 + HCl \xrightarrow{CHCl_3} [Mo(dtc)_4](Cl{\cdot}H_2O){\cdot}CHCl_3 + Mo_{x-1}(dtc)_{y-4}$$

Therefore, when $x = 1$ and $y = 4$, only $[Mo(dtc)_4]$-$(Cl{\cdot}H_2O){\cdot}CHCl_3$ is produced; whereas when $x = 2$ and $y = 6$, the remaining species may be subjected to further oxidation leading to the formation of $[Mo(dtc)_4]_2Mo_6O_{19}$. Further chemical evidence for the proposed reaction route is the presence of chloride ions (precipitated as AgCl), and of the μ(CO) IR band at 1715 cm^{-1}.

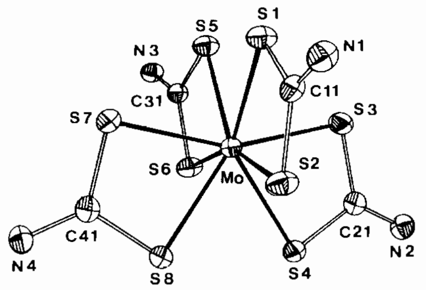

Fig. 1. ORTEP plot (ethyl groups omitted) showing the ligand coordination about the metal center in the $Mo(dtc)_4^+$ cation.

The crystal structure of $[Mo(dtc)_4](Cl{\cdot}H_2O){\cdot}xCHCl_3$ contains a packing of dimeric, hydrogen-bonded cyclic $(Cl{\cdot}H_2O^-)_2$ anions, $Mo(dtc)_4^+$ cations and $CHCl_3$ molecules. As shown in Fig. 1, the core of the $Mo(dtc)_4^+$ cation conforms closely to D_{2d} symmetry, with the S atoms arranged about the Mo(V) atom in the form of a triangulated dodecahedron. The measured Mo–S bonds in the range 2.508–2.533 Å may be divided into two bisphenoidal sets, such that the S atoms at the vertices of a flattened tetrahedron [S(2), S(3), S(6) and S(7)] lie closer to the metal center than the remaining S atoms which constitute an elongated tetrahedron. The Mo–S distances for anhydrous $Mo(dtc)_4Cl$ [18] and $Mo(dtc)_4I_3$ [19] lie in wider ranges, 2.489–2.544 Å, and 2.499–2.546 Å respectively, but the range is narrow for $Mo(dtc)_4$, 2.520–2.537 Å [20]. The overall average Mo–S distances for $Mo(dtc)_4$, $[Mo(dtc)_4](Cl{\cdot}H_2O){\cdot}xCHCl_3$, $Mo(dtc)_4Cl$, and $Mo(dtc)_4I_3$ are 2.529(8), 2.522(10), 2.518(17), and 2.522(26) Å (standard deviations indicate the spread of the data used in the average) respectively. An interesting dissimilarity between $Mo(dtc)_4$ and $[Mo(dtc)_4(Cl{\cdot}H_2O){\cdot}xCHCl_3$ is the orientation of their NCS_2 groups. From the stereo packing diagram

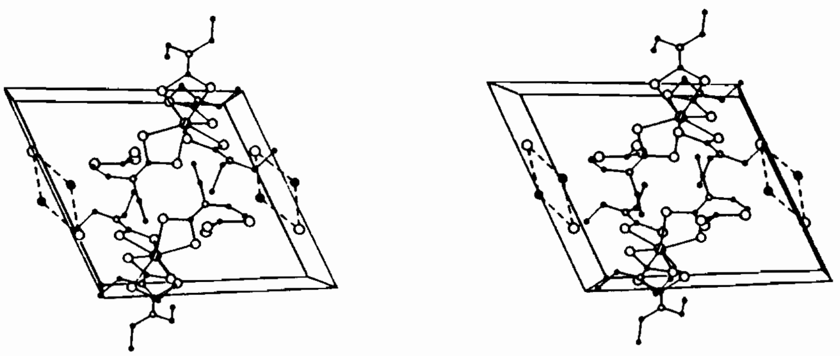

Fig. 2. Stereo diagram of the molecular packing in the crystal structure of $[Mo(dtc)_4](Cl{\cdot}H_2O){\cdot}CHCl_3$. Hydrogen atoms have been omitted for clarity, and O–H•••Cl hydrogen bonds are represented by broken lines. The unit-cell origin lies at the lower left corner, with *a* slanting upwards, *b* pointing towards the reader, and *c* from left to right.

(Fig. 2), it can be seen that the NCS_2 groups lie pairwise on two planes in the present structure, a conformation shared by $Mo(dtc)_4Cl$ [18] and $Mo(dtc)_4I_3$ [19]; in contrast to this, no two NCS_2 groups lie in the same plane in the $Mo(dtc)_4$ molecule [20].

Supplementary Material

Tables of hydrogen coordinates, anisotropic temperature factors, and measured and calculated structure factors are available from the authors.

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