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

Synthesis and Structure of Tetrabutylammonium *N*,*N*-Diethyldithiocarbamatobis(maleonitriledithiolato)molybdenate(IV) and -tungstate(IV)

W. P. BOSMAN* and A. NIEUWPOORT

Received August 5, 1975 AIC50586S

The compounds $(Bu_4N)[M(mnt)_2(dtc)]$ (M = Mo, W) have been synthesized by oxidative decarbonylation of $(Bu_4N)[M(CO)_5I]$ and characterized by conductivity, infrared, and magnetic susceptibility measurements. It is concluded that severe distortions from octahedral symmetry are present. This is confirmed by an x-ray structure determination for M = Mo. The compound forms crystals in the monoclinic space group $P2_1/c$. The cell dimensions are $a = 16.891$ (3) Å, $b = 12.611$ (2) Å, $c = 18.102$ (4) Å, $\beta = 93.13$ (1)°; $Z = 4$. The final R value is 0.07. The coordination polyhedron is close to a trigonal prism. The Mo–S distances for the dtc ligand are 2.456 (3) and 2.454 (3) Å and for the mnt ligands 2.355 (4), 2.353 (4), 2.358 (3), and 2.362 (3) Å. The interligand S–S distances between the two mnt ligands are 3.110 (5) and 3.116 (5) Å and between the dtc and mnt ligands are 3.240 (5), 3.276 (5), 3.219 (5), and 3.219 (5) Å.

Introduction

Two main reasons for the vast amounts of work performed on the complexes of the 1,2-dithiolato ligands $R_2C_2S_2{}^{2-}$ are their facile redox reactions and their unusual geometry.[1] Mostly, the compounds can be isolated in various oxidation states and often still more species can be shown to exist by voltammetric measurements. The coordination geometry is often strongly distorted from octahedral, e.g., as in $Mo(S_2C_2H_2)_3$[2] or $Mo(S_2C_6H_4)_3$,[3] where trigonal-prismatic coordination is found. The 1,1-dithiolato ligand diethyldithiocarbamate (abbreviated as dtc) can be isolated in complexes $[Mo(dtc)_4]^{0,1+}$.[4–7] This type of complexes shows also an interesting redox behavior. As a continuation of research on the dtc complexes of molybdenum and tungsten, we have tried to prepare complexes with both mnt (mnt = maleonitriledithiolate) and dtc ligands coordinated to the metal ion, to investigate the number of ligands present (3 or 4), the redox properties, and the structure of this type of complexes. In this paper we describe the synthesis of $(Bu_4N)[M(mnt)_2(dtc)]$ (M = Mo, W) and the structure of the molybdenum complex. In these complexes the coordination sphere of the metal is in good approximation a trigonal prism. Optical and voltammetric data on these compounds will be published elsewhere.[7]

Experimental Part

Synthesis of the Complexes. To a solution of 3 mmol of $(Bu_4N)[M(CO)_5I]$, prepared according to ref 8, in 100 ml of acetone that was freshly distilled from calcium hydride in a nitrogen atmosphere, 3 mmol of $NH_4(dtc)$ was added and refluxed 5 min. When the evolution of CO stopped, 3 mmol of $Na_2(mnt)$, prepared according to ref 9, was added, resulting again in the evolution of CO. After this reaction was finished, 3 mmol of I_2 and then 6 mmol of $NH_4(dtc)$ were added and finally the solution was refluxed for 30 min. The solvent was now evaporated and the residue was extracted with 50 ml of dichloromethane. After filtration, 50 ml ethanol was added and the solution was concentrated to a volume of 40 ml. After cooling of the mixture to −5 °C, crystals separated consisting of the product mixed with some $(Bu_4N)_2[M(mnt)_3]$. This last compound can be removed by recrystallization from 2-propanol. The presence of this impurity can be determined from the ir spectrum by an absorption at 324 cm^{-1}. The yield was around 40%, based on metal carbonyl.

$(Bu_4N)[Mo(mnt)_2(dtc)]$, mp 194–196 °C (uncor), is stable in the solid state as well as in solution. The dark violet crystals are soluble in acetone, chloroform, and ethanol forming violet solutions. Anal. Calcd for $C_{29}H_{46}MoN_6S_6$: C, 45.41; H, 6.04; N, 10.96. Found: C, 45.56; H, 6.13; N, 11.00.

The stable, dark brown crystals of $(Bu_4N)[W(mnt)_2(dtc)]$, mp 192–194 °C, show the same solubility as the molybdenum complex forming red-brown solutions. Anal. Calcd for $C_{29}H_{46}WN_6S_6$: C, 40.74; H, 5.42; N, 9.83. Found: C, 41.35; H, 5.46; N, 9.77.

Physical Measurements. Ir spectra were taken on a Perkin-Elmer 257 spectrometer and a Hitachi EPI-1 spectrometer. Electrical conductivities were measured in nitrobenzene solution with a Metrohm Konduktoskop E 365. Magnetic susceptibilities were measured on a Gouy balance.

Table I. Crystal Data of the Molybdenum Complex

$C_{29}H_{46}N_6S_6Mo$	Monoclinic
Fw = 767.04	Space group $P2_1/c$
$a = 16.891$ (3) Å	$F(000) = 376$
$b = 12.611$ (2) Å	$\mu = 7.0$ cm^{-1}
$c = 18.102$ (4) Å	λ(Mo Kα) = 0.71069 Å
$\beta = 93.13$ (1)°	$d_{found} = 1.32$ g cm^{-3} ($Z = 4$)
$V = 3850$ Å^3	$d_{calcd} = 1.32$ g cm^{-3}

Collection of X-Ray Data. A single crystal of the molybdenum compound was mounted on a glass fiber, normal to the (010) plane. The dimensions of the crystal were 0.17 × 0.33 × 0.10 mm. The x-ray examination of the crystal and data collection were performed at 20 °C on a Nonius CAD3 single-crystal diffractometer using Zr-filtered Mo Kα radiation. The systematic extinctions are, for $h0l$, $l = 2n + 1$, and for $0k0$, $k = 2n + 1$, which are compatible with the space group $P2_1/c$ (No. 14). Twenty-two reflections were carefully centered and their setting angles were refined by least squares to obtain unit cell dimensions and an orientation matrix for data collection. The crystal data are given in Table I. The density was measured by flotation in a mixture of CCl_4 and acetyl acetate. Intensity data were collected up to $\theta = 20°$ using the θ–2θ scan technique with a scan speed of 10° θ/min. One standard reflection was remeasured after every 15 reflections and used for long-range fluctuation correction. No evidence was found for crystal movement or crystal decomposition. The net intensities I and their standard deviations σ_I were given by $I = C - (B_1 + B_2)$ and $\sigma_I = [C + B_1 + B_2]^{-1/2}$ where C is scan count and B_1 and B_2 are the two background counts each measured in half of the total scan time. Of the 3570 independent reflections, 2548 reflections had $I > 3\sigma_I$ and were marked as observed. No absorption correction was made in view of the low absorption coefficient; transmission coefficients were calculated for selected reflections and found in the range 0.82–0.84. Lorentz and polarization corrections were applied.

Structure Determination and Refinement. The molybdenum atom was found from a three-dimensional Patterson map. The remaining part of the structure was found by applying direct methods on normalyzed difference Fourier coefficients using the program DIRDIF.B.[10] The resulting Fourier synthesis showed all of the nonhydrogen atoms of the anion and part of the cation. The remaining atoms were located on a difference Fourier map.

The reflections with $I > 3\sigma_I$ were used in the refinement by full-matrix least-squares methods allowing anisotropic vibration for Mo and S. The quantity minimized was $\sum w(|F_o| - K|F_c|)^2$ with $w = [\sigma_F{}^2 + (0.05F_o)^2]^{-1}$ and $\sigma_F = (F/2I)\sigma_I$.

All parameter shifts in the final cycle were smaller than their esd's. The final conventional R value was 0.07 (on 2548 reflections). No search was made for hydrogen atoms. The atomic scattering factors were those of the neutral atoms, corrected for anomalous scattering ($\Delta f'$), using data from ref 30. All calculations were carried out on an IBM 370/158 computer with the X-Ray system of crystallographic programs.[11]

Table II. Atomic Parameters for Mo with Standard Deviations[a]

A. The Anion

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.1465 (1)	0.0159 (1)	0.1968 (1)	0.0254 (6)	0.0650 (10)	0.0217 (5)	−0.0001 (4)	0.0025 (4)	−0.0023 (4)
S(1)	0.2444 (2)	0.1336 (3)	0.2451 (2)	0.029 (2)	0.096 (3)	0.042 (2)	−0.006 (3)	0.000 (2)	−0.020 (2)
S(2)	0.2380 (2)	−0.1149 (3)	0.2380 (2)	0.032 (2)	0.093 (3)	0.038 (2)	0.012 (3)	0.001 (2)	0.010 (2)
S(3)	0.0606 (2)	0.1401 (3)	0.2479 (2)	0.030 (2)	0.053 (3)	0.033 (2)	−0.002 (2)	0.009 (2)	−0.001 (2)
S(4)	0.0538 (2)	−0.1066 (3)	0.2399 (2)	0.029 (2)	0.055 (3)	0.030 (2)	0.001 (2)	0.006 (2)	−0.003 (2)
S(5)	0.1393 (2)	0.1361 (3)	0.0899 (2)	0.050 (2)	0.075 (3)	0.027 (2)	−0.007 (2)	0.005 (2)	0.005 (2)
S(6)	0.1319 (2)	−0.0877 (3)	0.0822 (2)	0.048 (2)	0.075 (3)	0.021 (1)	−0.000 (2)	0.004 (2)	−0.004 (2)

	x	y	z	B, Å²		x	y	z	B, Å²
N(1)	0.4351 (11)	0.1572 (16)	0.3550 (11)	11.3 (5)	C(5)	−0.0160 (6)	0.0696 (9)	0.2843 (6)	3.5 (3)
N(2)	0.4289 (13)	−0.1632 (17)	0.3450 (12)	12.6 (5)	C(6)	−0.0786 (7)	0.1290 (9)	0.3156 (7)	4.2 (3)
N(3)	−0.1284 (7)	0.1736 (9)	0.3437 (7)	5.9 (3)	C(7)	−0.0207 (7)	−0.0348 (8)	0.2805 (6)	3.3 (3)
N(4)	−0.1408 (7)	−0.1343 (10)	0.3266 (7)	6.5 (3)	C(8)	−0.0857 (7)	−0.0912 (9)	0.3061 (6)	3.7 (3)
N(5)	0.1063 (7)	0.0356 (9)	−0.0385 (6)	5.4 (3)	C(9)	0.1252 (7)	0.0284 (9)	0.0338 (7)	3.8 (4)
C(1)	0.3203 (7)	0.0559 (10)	0.2838 (7)	4.7 (3)	C(10)	0.0889 (9)	−0.0587 (13)	−0.0848 (9)	6.6 (5)
C(2)	0.3859 (11)	0.1053 (14)	0.3195 (10)	7.8 (4)	C(11)	0.1613 (12)	−0.0998 (17)	−0.1224 (11)	9.9 (4)
C(3)	0.3174 (7)	−0.0464 (10)	0.2800 (7)	4.6 (3)	C(12)	0.0997 (9)	0.1440 (12)	−0.0764 (9)	6.9 (5)
C(4)	0.3802 (11)	−0.1071 (15)	0.3148 (10)	7.9 (4)	C(13)	0.1789 (12)	0.1813 (16)	−0.0997 (11)	9.7 (4)

B. The Cation

	x	y	z	B, Å²		x	y	z	B, Å²
N(6)	0.3225 (6)	0.5174 (8)	0.0825 (6)	4.7 (2)	C(22)	0.3667 (8)	0.6174 (11)	0.0567 (8)	5.8 (3)
C(14)	0.2365 (8)	0.5112 (9)	0.0498 (8)	4.9 (3)	C(23)	0.3261 (12)	0.7236 (16)	0.0780 (12)	9.2 (5)
C(15)	0.2293 (10)	0.5114 (11)	−0.0359 (9)	6.5 (4)	C(24)	0.3812 (18)	0.8188 (25)	0.0655 (18)	14.2 (9)
C(16)	0.1406 (14)	0.5075 (16)	−0.0600 (13)	10.1 (6)	C(25)	0.3705 (27)	0.8387 (39)	−0.0071 (30)	23.7 (17)
C(17)	0.0981 (18)	0.6123 (26)	−0.0439 (17)	15.0 (8)	C(26)	0.3139 (9)	0.5169 (10)	0.1670 (8)	5.4 (3)
C(18)	0.3707 (8)	0.4225 (11)	0.0554 (8)	5.7 (3)	C(27)	0.3951 (11)	0.5179 (13)	0.2116 (10)	7.5 (4)
C(19)	0.3397 (12)	0.3163 (16)	0.0779 (11)	9.1 (5)	C(28)	0.3787 (17)	0.5047 (16)	0.2957 (15)	11.1 (6)
C(20)	0.3958 (12)	0.2320 (18)	0.0409 (12)	10.0 (5)	C(29)	0.4499 (36)	0.4951 (37)	0.3441 (33)	26.4 (20)
C(21)	0.3797 (18)	0.1231 (27)	0.0677 (18)	16.7 (10)					

[a] The key to the atomic numbering is given in Figure 3. The expression used for the temperature factors of the anisotropic refined atoms is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Interligand Contact Distances Less Than 3.6 Å

C(6)-S(4)	3.51 (2)	C(8)-S(3)	3.56 (2)
N(3)-S(2)	3.53 (2)	N(4)-S(3)	3.46 (2)
N(3)-S(4)	3.43 (2)	N(4)-S(5)	3.27 (2)
N(3)-S(6)	3.30 (2)	N(4)-C(14)	3.37 (2)
N(3)-C(14)	3.41 (2)	N(4)-C(26)	3.50 (2)

The final atomic coordinates and anisotropic thermal parameters are given in Table II. The estimated standard deviations that are given in parentheses are the result of the least-squares refinement. The thermal parameters of one mnt ligand are higher than those of the second one. This is explained by the loose packing for the first ligand. The nitrile atoms C(2), N(1), C(4), and N(2) have no interligand contact distances less than 3.6 Å, while the corresponding atoms of the second ligand have ten distances in the range 3.3–3.6 Å (see Table III).

A survey of thermal parameters and estimated standard deviations of the butyl atoms suggest ill-defined positions of these atoms, especially the end atoms. We did not spend more time on this problem, as we did not expect significant improvement of the structure data by further investigations.

Results

The synthesis is based on the oxidative decarbonylation of $[M(CO)_5I]^-$ with I_2 in the presence of the ligands mnt^{2-} and dtc^-. Though we looked for an eight-coordinated mixed-ligand complex, we only succeeded in the isolation of the six-coordinated mixed-ligand complexes and compounds containing one type of ligand. Slight changes in the procedure, as replacing I_2 and dtc^- by tetraethylthiuram disulfide, result in the formation of only $(Bu_4N)_2[Mo(mnt)_3]$ and $[Mo(Et_2dtc)_4]I$. We did not succeed in isolating intermediate reaction products; only oily products could be obtained. Until now, no simpler synthetic route has been found.

Conductivity measurements of the compounds in nitrobenzene solution at 25°C showed that the compounds behave as 1:1 electrolytes. Λ could be calculated from the Onsager plots of Λ vs. $c^{1/2}$ and is 20.9 and 22.1 cm² Ω^{-1} equiv⁻¹ for the Mo and W complexes, respectively. With $\lambda^+ = 11.55$ for Bu_4N^+;[12] λ^- for the anions is 9.3 and 10.6, respectively. Magnetic susceptibility measurements showed that the compounds are diamagnetic.

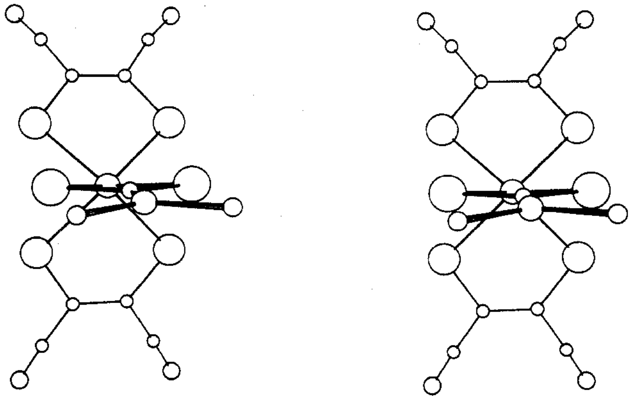

Figure 1. Stereoview of the complex ion along the c^* axis.

The infrared spectra of the complexes showed absorptions that are due to both ligands and the cation. Some ligand frequencies are given in Table IV. The assignment of the absorptions of the mnt ligands is made according to Schrauzer and Mayweg[13] and Adams and Cornell.[14] The assignment of the dtc ligands is made in agreement with the assignment of Jensen for $Ni(Me_2dtc)_2$[15] (see also ref 7).

Description of the Crystal Structure of the Molybdenum Complex

Figure 1 is a stereoview of the anion along the c^* axis and Figure 2 is a stereoview along the a^* axis showing the trigonal prism. These figures are obtained by the program ORTEP.[16] Bond distances and angles are given for the mnt ligands in Figure 3a, for the dtc ligand in Figure 3b, and for the tet-

Table IV. Infrared Frequencies of the Compounds

	mnt vib				dtc vib					
	ν(C≡N)	ν(C=C)		ν(C–C≡N)	ν(C=N)				ν(C–S)	
mnt^{2-}	2190 s	1424 s		522 m						
$(Bu_4N)_2[Mo(mnt)_3]$	2205 s	1492 sh	1485 s	507 s						
$(Bu_4N)_2[W(mnt)_3]$	2204 s	1500 m	1487 s	507 s						
$(Bu_4N)[Mo(mnt)_2(Et_2dtc)]$	2205 s		1488 s	511 s	1512 s		1004 w	609 w		
$(Bu_4N)[W(mnt)_2(Et_2dtc)]$	2205 s	1488 m	1482 s	509 s	1515 s		1004 w	609 w		
$Mo(Et_2dtc)_4$					1493 vs		1003 w			
$W(Et_2dtc)_4I$					1518 vs	1014 sh	1002 w	611 m	578 m	558 m
$Mo(Et_2dtc)_4I$					1518 vs	1014 sh	1002 w	611 m	578 m	558 m

	Metal–sulfur vib caused by					
	dtc		mnt	mnt	mnt	Ref
$(Bu_4N)_2[Mo(mnt)_3]$			324 s	277 w		14
$(Bu_4N)_2[W(mnt)_3]$			331 s	317 m		This work
$(Bu_4N)[Mo(mnt)_2(Et_2dtc)]$	369 m	355 m	340 m	283 w	214 m	This work
$(Bu_4N)[W(mnt)_2(Et_2dtc)]$		356 m	350 m	312 m	249 m	This work
$Mo(Et_2dtc)_4$		352 m				5
$Mo(Et_2dtc)_4I$		358 m				4
$W(Et_2dtc)_4I$		354 m				7

Table V. Bond Distances (Å) and Angles (deg) in the Tetrabutylammonium Ion

Distances			
N(6)–C(14)	1.54 (2)	C(19)–C(20)	1.60 (3)
N(6)–C(18)	1.54 (2)	C(20)–C(21)	1.49 (4)
N(6)–C(22)	1.55 (2)	C(22)–C(23)	1.56 (3)
N(6)–C(26)	1.54 (2)	C(23)–C(24)	1.54 (4)
C(14)–C(15)	1.55 (2)	C(24)–C(25)	1.34 (7)
C(15)–C(16)	1.54 (3)	C(26)–C(27)	1.55 (3)
C(16)–C(17)	1.54 (3)	C(27)–C(28)	1.57 (4)
C(18)–C(19)	1.50 (3)	C(28)–C(29)	1.45 (7)
Angles			
C(14)–N(6)–C(18)	110.0 (9)	N(6)–C(26)–C(27)	113 (2)
C(14)–N(6)–C(22)	112.6 (9)	C(14)–C(15)–C(16)	108 (2)
C(14)–N(6)–C(26)	104 (1)	C(15)–C(16)–C(17)	112 (2)
C(18)–N(6)–C(22)	105 (1)	C(18)–C(19)–C(20)	105 (2)
C(18)–N(6)–C(26)	113.1 (9)	C(19)–C(20)–C(21)	111 (2)
C(18)–N(6)–C(26)	112.0 (9)	C(22)–C(23)–C(24)	111 (2)
N(6)–C(14)–C(15)	114 (2)	C(23)–C(24)–C(25)	104 (3)
N(6)–C(18)–C(19)	114 (2)	C(26)–C(27)–C(28)	108 (2)
N(6)–C(22)–C(23)	113 (2)	C(27)–C(28)–C(29)	114 (4)

rabutylammonium ion in Table V. The interligand S–S distances are given in Table VI.

The MoS_6 polyhedron is a nearly perfect trigonal prism. The polyhedron consists of two approximately equilateral S_3 triangles (dihedral angle 6.0°). The triangles are not twisted with respect to the threefold axis. The distances of the molybdenum atom to the three lateral faces are 0.830 (1) Å to the plane formed by S(1), S(2), S(3), and S(4), 0.941 (1) Å to the plane formed by S(1), S(2), S(5), and S(6), and 0.999 (1) Å to the plane formed by S(3), S(4), S(5), and S(6).

Table VII gives the weighted least-squares planes through the sulfur atoms and the adjacent carbon atoms and the distances of the molybdenum atom to these planes. The molybdenum atom lies significantly out of the planes of the dtc ligand and one mnt ligand. The angle between the plane of the ligand and the plane of the metal and sulfur atoms is for the first mnt ligand 2.4°, for the second mnt ligand 0.8°, and for the dtc ligand 5.3°. The ligands have the expected geometry. There are no unusual contact distances.

Discussion

The Coordination Polyhedron. From the magnetic susceptibility data it could be concluded that the coordination

Table VI. Sulfur–Sulfur Contacts (Å) and the Twist Angle (deg) in Some Tris-Bidentate Dithio Ligand Complexes

		Twist angle, 2φ		S–S dist					
				Intraligand dist of		Interligand dist between			
	Normalized bite[b]	Predicted[c]	Exptl	Dithiolene	dtc	Dithiolene	dtc	Dithiolene and dtc	Ref
$Mo(S_2C_2H_2)_3$	1.33	49	0	3.10		3.11			2
$Mo(S_2C_6H_4)_3$	1.31	48	0	3.11		3.09			3
$[Mo(mnt)_2(dtc)]^-$	1.27[a]	44	0	3.08	2.83	3.12		3.24	This work
$[Mo(mnt)_3]^{2-}$	1.31	48	28	3.11		3.19			18
$Fe(dtc)_2(S_2C_2(CF_3)_2)$	1.27[a]	44	38	3.05	2.80		3.20	3.14, 3.22	19
$Fe(dtc)_3$	1.21	39	38		2.85		3.44		20

[a] Mean value. [b] Ratio of the M–S distance to the intraligand S–S distance. [c] According to Kepert.[17]

Table VII. Equations of Least-Squares Planes for the Ligands and the Distances (in Å) of the Atoms from Their Respective Planes ($AX + BY + CZ - D = 0$)

	A	B	C	D	Dist from plane
S(1)–S(2)–C(1)–C(3)	0.4982	0.0195	−0.8668	−1.8705	Mo, −0.0735 (9); S(1), 0.000 (3); S(3), 0.000 (3); C(1), −0.01 (2); C(3), 0.01 (2)
S(3)–S(4)–C(5)–C(7)	−0.4670	0.0576	−0.8824	−4.2165	Mo, 0.0243 (9); S(3), 0.000 (3); S(4), 0.000 (3); C(3), −0.01 (1); C(4), 0.01 (1)
S(4)–S(5)–C(9)	0.9907	−0.0346	−0.1317	1.9696	Mo, −0.1868 (9)

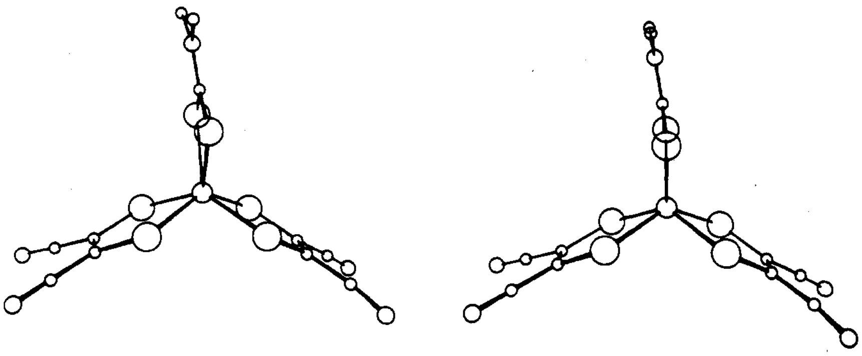

Figure 2. Stereoview of the complex ion along the *a* axis.

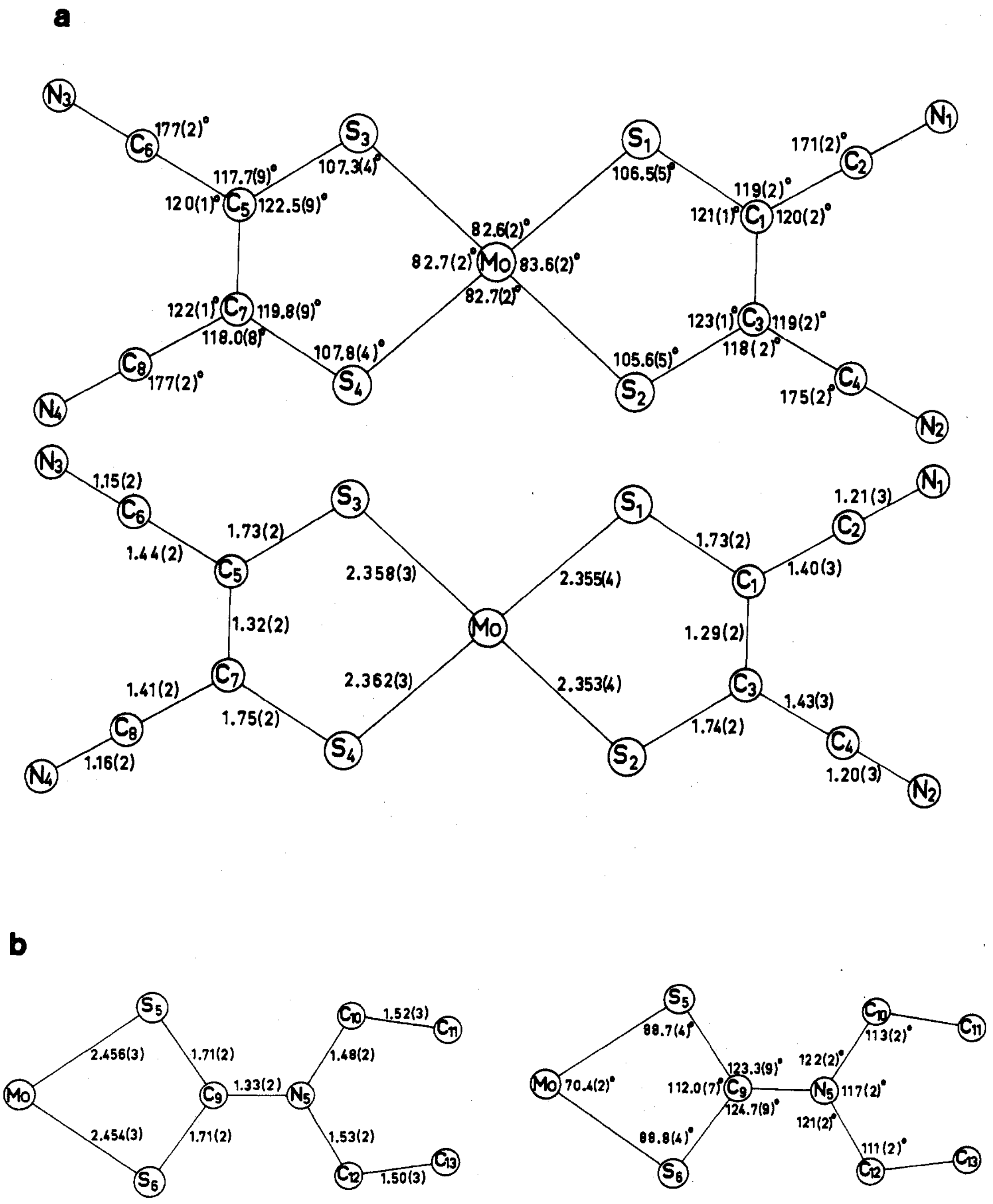

Figure 3. Bond distances and angles for (a) mnt ligands and (b) dtc ligands.

geometry is strongly distorted from octahedral symmetry, because otherwise two unpaired electrons would be found. The distortion can be described by the twist angle between the upper and lower triangle relative to the threefold axis that is present in the idealized octahedron and trigonal prism where this angle is 60 and 0°, respectively (see ref 17).

Table VIII. Metal-Sulfur Distances (Å) and Bite Angles (deg) for Some Complexes

	M–S dist		Bite angle		
	mnt	dtc	mnt	dtc	Ref
$[(Mo(mnt)_2(dtc)]^-$	2.357	2.455	83.1	70.4	This work
$[Mo(mnt)_3]^{2-}$	2.374		82.4		18
$Mo(dtc)_4$		2.53		67.3	6

As was shown by Kepert[17] on the basis of arguments concerning the interligand repulsion energy, the form of the coordination polyhedron of tris-bidentate chelate complexes depends on the normalized bite. Here normalized bite is defined as the ratio of the metal–donor atom distance to the intraligand donor atom distance. With smaller bite, more distortion of the polyhedron toward a trigonal prism can be expected and is indeed observed. The only exception to this rule is found for complexes of 1,2-dithiolate ligands as, for instance, mnt. However, dtc complexes follow this rule closely. In Table VI the experimental distortion angle 2ϕ in several complexes is compared with the predicted value. Obviously, the value of the new complex deviates much from the calculated value.

From Table VI it can be concluded that all complexes deviating from the expected geometry have interligand sulfur–sulfur distances that are 0.6–0.7 Å shorter than the van der Waals distance of 3.7 Å. It has been suggested that interligand sulfur–sulfur interactions play an important role in 1,2-dithiolato complexes.[21] In the highly oxidized complexes the trigonal prism was thought to be stabilized by sulfur–sulfur bonding in the direction of the metal z^2 orbital. When electrons are added to the complex, these occupy this metal orbital destabilizing the sulfur–sulfur bonding: distortion toward an octahedron is expected, and in $[Mo(mnt)_3]^{2-}$ this is observed.[18] However, the recent work of Takats[3,22] is not in agreement with this argument: the structures of $[Zr(S_2C_6H_4)_4]^{2-}$ and $[Ta(S_2C_6H_4)_3]^-$ show strong distortions from a trigonal–prismatic structure. The efficient mixing of metal and ligand orbitals is considered nowadays as being more important for the stabilization of prismatic coordination.[22] On the basis of arguments concerning σ bonding, Huisman et al.[23] have shown that trigonal-prismatic coordination may be more stable than octahedral coordination for highly covalent 4d and 5d transition metal complexes when the electron configuration of the metal ion is d^0, d^1, or d^2. For our compound, the replacement of an mnt ligand by a dtc ligand which is less covalently bonded to the metal ion may result in a more covalent bonding of the remaining two mnt ligands to the metal ion, thus stabilizing a prismatic geometry. We are currently investigating this explanation by extended Hückel MO calculations.

The Metal–Sulfur Distances and Vibrations. The explanation given above for the stabilization of the prism is in agreement with the metal–sulfur vibrations of the mnt ligands. As Table IV shows, these vibrations are shifted about 18 cm^{-1} to higher energy when the $[M(mnt)_3]^{3-}$ complexes and the mixed-ligand complexes are compared. A stronger bond between the mnt ligands and the metal ion is also suggested by the metal–sulfur distance, which is significantly shorter in $[Mo(mnt)_2(dtc)]^-$ than in $[Mo(mnt)_3]^{2-}$ (Table VIII). This is still more significant upon considering that on going from an octahedron to an ideal trigonal prism (ideal prism: prism with all edges equal), without changing the bite, the metal–sulfur distances must increase. The increase of the metal–sulfur frequency as the structure of the complex deviates less from a trigonal prism is also noted in other complexes.[24]

The metal–sulfur frequency of the dtc ligand is close to the value found in $Mo(dtc)_4$ and $[Mo(dtc)_4]I$ though the metal–sulfur distance is significantly longer than in $Mo(dtc)_4$. However, it is difficult to compare vibrations and distances from complexes with a different coordination number.

Table IX. Distances (in Å) between the Metal Ion and the Planes of the Ligands in Several Mixed-Ligand Complexes and Angles (deg) between the Planes of the Ligands

	dtc-plane	mnt-plane	∠(mnt)-(dtc)	∠(mnt)-(mnt)	Ref
Ni(mnt)(dtc)	0.11	0.04	158.1		27
$[Cu(mnt)(dtc)]^-$	0.11	0.02	164.1		26
Au(mnt)(dtc)	0.10	0.10	171.1		25
$[Mo(mnt)_2(dtc)]^-$	0.19	0.07, 0.02	127.4, 110.4	122.2	This work

In the compound under investigation the metal ion deviates significantly from the least-squares planes of the dtc and one of the mnt ligands: respectively 0.19 and 0.07 Å (Table VII). In the complex $[Mo(mnt)_3]^{2-}$ the metal is situated in these planes.[18] From the atom parameters for the compounds $[M(mnt)(dtc)]^a$ (M = Ni, Au, a = 0; M = Cu, a = 1−) it can be derived that in these complexes the metal is not located in one of the planes through the ligands[25–27] (see Table IX). For the gold complex, this effect was noted earlier.[25]

The Geometry of the Ligands and the Infrared Spectra. The geometries of the mnt ligands are equal within experimental uncertainty in $[Mo(mnt)_2(dtc)]^-$ and $[Mo(mnt)_3]^{2-}$.[18] The infrared absorptions of the ligands in both complexes show no significant differences, so in both compounds the ligands are close to the dithiolate form.

The geometries of the dtc ligands in $[Mo(mnt)_2(dtc)]^-$ and $Mo(dtc)_4$[6] are equal also. In the infrared spectra of these compounds, only the CN frequency is different: 1493 cm^{-1} in $Mo(dtc)_4$[5], and 1512 cm^{-1} in $(Bu_4N)[Mo(mnt)_2(dtc)]$. In the complexes $[M(dtc_4)]X$ (M = Mo, W) this value is 1518 cm^{-1}.[4,7] However, the influence on the CN frequency by removal or addition of a ligand may amount to 20 cm^{-1},[27,28] so the shift in the CN frequency allows no conclusion on the electron density of the ligands.

Acknowledgment. The authors wish to thank Mr. W. Peters for the preparation of the compounds, Dr. J. H. Noordik and Mr. J. M. M. Smits for the collection of the x-ray data, Professor Dr. Ir. J. J. Steggerda and Dr. P. T. Beurskens for helpful discussions, and the reviewer for some helpful remarks. The investigations were supported in part by the Netherlands Foundation for Chemical Research, SON.

Registry No. $(Bu_4N)[Mo(mnt)_2(Et_2dtc)]$, 57587-23-2; $(Bu_4N)[W(mnt)_2(Et_2dtc)]$, 57587-25-4; $(Bu_4N)_2[W(mnt)_3]$, 25595-46-4; $(Bu_4N)[Mo(CO)_5I]$, 57587-26-5; $(Bu_4N)[W(CO)_5I]$, 57587-27-6.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
(2) A. E. Smith, C. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **87**, 5798 (1965).
(3) M. J. Bennett, M. Cowie, J. L. Martin, and J. Takats, *J. Am. Chem. Soc.*, **95**, 7504 (1973).
(4) A. Nieuwpoort, *J. Less-Common Met.*, **36**, 271 (1974).
(5) Z. B. Varadi and A. Nieuwpoort, *Inorg. Nucl. Chem. Lett.*, **10**, 801 (1974).
(6) J. G. M. van der Aalsvoort and P. T. Beurskens, *Cryst. Struct. Commun.*, **3**, 653 (1974).
(7) A. Nieuwpoort, Thesis, Nijmegen, 1975.
(8) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2868 (1963).
(9) A. Davison and R. H. Holm, *Inorg. Synth.*, **10**, 11 (1967).
(10) R. O. Gould, Th. H. v. d. Hark, and P. T. Beurskens, *Acta Crystallogr., Sect. A*, **31**, 813 (1975).
(11) "The X-Ray System", Technical Report TR-192 of the Computer Science Center, University of Maryland, College Park, Md., June 1972.
(12) J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965).
(13) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **88**, 3223 (1966).

(14) D. M. Adams and J. B. Cornell, *J. Chem. Soc.*, 1299 (1968).
(15) K. A. Jensen, B. M. Dahl, P. H. Nielsen, and G. Borch, *Acta Chem. Scand.*, **26**, 2241 (1972).
(16) C. K. Johnson, "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(17) D. L. Kepert, *Inorg. Chem.*, **11**, 1561 (1972).
(18) G. F. Brown and E. I. Stiefel, *Inorg. Chem.*, **12**, 2140 (1973).
(19) D. L. Johnston, W. L. Rohrbangh, and W. D. Horrocks, Jr., *Inorg. Chem.*, **10**, 1474 (1971).
(20) J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973).
(21) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1956 (1966).
(22) J. L. Martin and J. Takats, *Inorg. Chem.*, **14**, 1358 (1975).
(23) R. Huisman, R. de Jonge, C. Haas, and F. Jellinek, *J. Solid State Chem.*, **3**, 56 (1971).
(24) J. L. Martin and J. Takats, *Inorg. Chem.*, **14**, 73 (1975).
(25) J. H. Noordik, Thesis, Nijmegen, 1971; J. H. Noordik, Th.W. Hummelink, and J. G. M. van der Linden, *J. Coord. Chem.*, **2**, 185 (1973).
(26) A. L. Spek, *Cryst. Struct. Commun.*, **3**, 463 (1974).
(27) H. M. Hendriks, W. P. Bosman, and P. T. Beurskens, *Cryst. Struct. Commun.*, **3**, 447 (1974).
(28) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suom. Kemistil. B*, 29, 75 (1956).
(29) K. A. Jensen and V. Krishnan, *Acta Chem. Scand.*, **24**, 1088 (1970).
(30) "International Tables for X-Ray Crystallography" Kynoch Press, Birmingham, England, 1962.

Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, and the Department of Geology and Minerology, University of Michigan, Ann Arbor, Michigan 48109

Crystal and Molecular Structure of Phosphorus Triiodide

EDWARD THEODORE LANCE, JOHN M. HASCHKE,* and D. R. PEACOR

Received August 11, 1975 AIC506001

The crystal structure of phosphorus triiodide has been reinvestigated using single-crystal x-ray diffraction techniques. The structure is hexagonal, space group $P6_3$, with $a = 7.133 \pm 0.002$ Å, $c = 7.414 \pm 0.002$ Å, and $Z = 2$. The structure consists of a nearly ideal hexagonal closest packing of iodine atoms with the phosphorus atoms above the plane of iodines, approximately halfway between trigonal and octahedral coordination. A close correspondence is found between the structure of phosphorus triiodide and triiodomethane, and the results suggest that the nonbonded electron pair on phosphorus is stereochemically important.

Introduction

The crystal structure of phosphorus triiodide was originally investigated by Braekken,[1] who determined the iodine atom positions and the space group as $P6_3/m$ or $P6_3$. However, the phosphorus positions were not determined. Wyckoff[2] has suggested that the phosphorus and iodine atoms are coplanar, but this assignment differs from that found in the molecular structure.[3] A redetermination of the structure has been initiated in an effort to redefine fully the structural parameters for the solid.

Experimental Section

Preparation. Crystals of red-orange phosphorus triiodide were prepared by vacuum sublimation. Samples of triiodide were obtained by the reaction of europium diiodide and europium phosphate with silicon dioxide at 900–950 °C.[4] In the crystal growth procedures, the triiodide was sealed in evacuated glass ampules and transported across a temperature gradient bounded by a maximum of 50 °C and a minimum of 20 °C. All manipulations of the triiodide were performed in a nitrogen-filled glovebox, and crystals were immersed in paraffin oil during examination in air. A single crystal (parallelepiped, $a \times a \sin 120° \times c$; corresponding dimensions $0.30 \times 0.20 \times 0.19$ mm) was selected and sealed in a thin-walled (0.01 mm) glass capillary.

Single-Crystal Analysis. Conventional Weissenberg and precession methods were employed for a-axis alignment of the crystal and for the confirmation of the space group assignment as $P6_3/m$ or $P6_3$. Lattice parameters ($a = 7.133$ (2) Å, $c = 7.414$ (2) Å) were refined from powder data obtained with a forward-focusing Guinier camera.[4] Intensity measurements were made using a Weissenberg-geometry single-crystal diffractometer with scintillation detection and pulse height analysis of graphite-monochromatized Mo Kα radiation. Reflections were scanned at 4° min^{-1} in the ω–2θ scan mode using 30-s background counts at both ends of the scan. Selected intensities from the first few levels were remeasured at the end of data collection, and there were no significant changes in their values. The intensities were corrected for Lorentz–polarization and absorption effects ($\mu = 146.6$ cm^{-1}). A total of 500 intensities were collected, and symmetry-equivalent values were averaged to yield a final set of 342 reflections (9 levels, $h = 0$–8); 76 of these were below the minimum observable value.[5]

Structure Determination

A three-dimensional Patterson function, generated from the corrected intensities, permitted location of the iodine atoms. Preliminary refinement of the iodine and phosphorus atom positions was made assuming space group $P6_3/m$ with the iodine atoms in special position 6h and the phosphorus atoms in special position 2c. This calculation gave convergence of the iodine atom positions at a very high R value (46%), but the phosphorus atom z coordinate did not converge in this space group. A difference electron density function was generated and showed the phosphorus atoms to be out of the plane of the iodine atoms. An ordered distribution of phosphorus atoms requires that the space group be $P6_3$, which was employed for subsequent refinement. The origin was fixed by arbitrarily setting the z coordinate of iodine at 0.0.

A full-matrix, least-squares refinement of the atomic parameters and isotropic temperature factors was carried to convergence using the scattering factors of Doyle and Turner[6] and anomalous dispersion corrections of Cromer and Liberman.[7] The weighting scheme of Cruickshank[8] was used throughout. Further refinement proceeded with anisotropic thermal parameters to a residual, R, of 6.5% ($R = 8.8$% including unobserved reflections; $R_w = 9.5$%, $R_w = 14.2$% including unobserved reflections). The final atom coordinates and anisotropic temperature factors are listed in Table I.

Discussion

Bond lengths and angles, of which selected values are presented in Table II, were calculated from the refined atom coordinates and lattice parameters with standard errors calculated using the full variance–covariance matrix of the atom coordinates and standard deviations of the lattice parameters. The values of the phosphorus to iodine nearest neighbor bond distance (2.463 ± 0.005 Å) and iodine–phosphorus–iodine bond angle (102.0 ± 0.3°) agree very well with those reported (2.43 ± 0.04 Å and 102 ± 2°) from electron diffraction studies of the gas-phase molecule.[3] A two-dimensional representation of the structure viewed along the c axis is shown in Figure 1 and a three-dimensional drawing of the asymmetric molecular unit showing the thermal ellipsoids is shown in Figure 2.

The structure consists of a nearly ideal hexagonal closest packing of iodine atoms, with the phosphorus atoms ($z = 0.146$) located between the octahedral ($z = 0.25$) and trigonal

* To whom correspondence should be addressed at the University of Michigan.