Studies in Eight-Co-ordination. Part 5.† Crystal and Molecular Structure and Electron Spin Resonance Spectra of Tetrakis(diethyldithiocarbamato)molybdenum(V) Hexamolybdate and Chloride

By **C. David Garner, Nepal C. Howlader,** and **Frank E. Mabbs,*** Chemistry Department, University of Manchester, Manchester M13 9PL

Andrew T. McPhail, Richard W. Miller, and **Kay D. Onan,** Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, U.S.A.

The crystal structures of $[Mo(S_2CNEt_2)_4]_2[Mo_6O_{19}]$ (1) and $[Mo(S_2CNEt_2)_4]Cl$ (2) have been determined from diffractometer data by direct methods and refined by full-matrix least-squares calculations to R 0.050 and 0.083 over 2 893(1) and 3 079(2) statistically significant reflections. Both are monoclinic: (1), space group $C2/c$, a = 23.54(1), b = 12.72(1), c = 26.94(1) Å, β = 102.60(5)°, Z = 4; (2), space group $P2_1/c$, a = 10.67(1), b = 27.96(1), c = 11.13(1) Å, β = 93.06(5)°, Z = 4. The dimensions and configurations of the $[Mo(S_2CNEt_2)_4]^+$ ions are very similar in both crystals, with highly significant differences occurring only in the methyl-group orientations. The sulphur atoms from four bidentate ligands span the m edges of a D_{2d} dodecahedron with mean Mo–S_A 2.536(15) and Mo–S_B 2.491(8) Å in (1), and corresponding values of 2.531(9) and 2.505(12) Å in (2). Dimensions of the $[Mo_6O_{19}]^{2-}$ ion accord well with those determined in an earlier study: Mo–O(terminal) 1.673(13)—1.698(10), M–O(bridging), 1.881(10)—1.948(11), and Mo–O(central) 2.303(1)—2.323(1) Å. The single-crystal e.s.r. spectra of (1) and (2) are reported, and the molecular g values discussed in terms of the molecular structures and the electronic-absorption spectra of these complexes.

ALTHOUGH tetrakis(dithiocarbamato)molybdenum(V) complexes have been known for a number of years, the study of their electronic and molecular structures has been confimed to polycrystalline and solution measurements.[1] As part of our studies on the electronic and molecular structures of both eight-co-ordinate and molybdenum(V) complexes, we report the results of some single-crystal X-ray and e.s.r. studies of two tetrakis(diethyldithiocarbamato)molybdenum(V) complexes.

EXPERIMENTAL

Preparation.—The salt $[Mo(S_2CNEt_2)_4]_2[Mo_6O_{19}]$ was obtained as deep brown crystals by the slow evaporation of methyl cyanide solutions of $MoCl_3O$ and $Na[S_2CNEt_2]$ (in the mol ratio 1 : 2) in a dry-box under dinitrogen (Found: C, 21.4; H, 3.6; Mo, 32.1; N, 4.9; S, 23.1. Calc. for $C_{40}H_{80}Mo_8N_8O_{19}S_{16}$: C, 21.3; H, 3.6; Mo, 34.0; N, 5.0; S, 22.7%). The samples often contained small amounts of chloride (<1%) which were shown subsequently by the X-ray investigation to be due to $[Mo(S_2CNEt_2)_4]Cl$ as a minor constituent. The salt $[Mo(S_2CNEt_2)_4]Cl$ was also prepared by the method of Nieuwpoort[1] (Found: C, 33.0; H, 5.4; Cl, 4.8; Mo, 13.2; N, 7.7; S, 35.3. Calc. for $C_{20}H_{40}ClMoN_4S_8$: C, 33.2; H, 5.5; Cl, 4.9; Mo, 13.3; N, 7.7; S, 35.4%).

Crystal Data.—(1) $[C_{20}H_{40}MoN_4S_8]_2[Mo_6O_{19}]$, M = 2 257.7, Monoclinic, $a = 23.54(1)$, $b = 12.72(1)$, c = 26.94(1) Å, $\beta = 102.60(5)°$, U = 7 872 Å^3, $D_m = 1.92$ g cm^{-3}, $Z = 4$, $D_c = 1.905$ g cm^{-3}, $F(000)$ = 4 480, Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 149 cm^{-1}. Space group either $C2/c(C^6_{2h})$ or $Cc(C^4_s)$ from systematic absences: hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$; shown to be the former group by structure refinement.

(2) $[C_{20}H_{40}MoN_4S_8]Cl$, M = 724.5, Monoclinic, a = 10.67(1), b = 27.96(1), c = 11.13(1) Å, $\beta = 93.06(5)°$, U = 3 316 Å^3, D_m (not determined), $Z = 4$, $D_c = 1.451$ g cm^3, $F(000)$ = 1 500, μ(Cu-K_α) = 87.6 cm^{-1}. Space group $P2_1/c(C^5_{2h})$ uniquely from systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$.

Crystallographic Measurements.—Initial unit-cell dimensions for (1) were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation; corresponding information for (2) was obtained from precession photographs taken with Mo-K_α radiation (λ 0.710 7 Å). Single crystals of dimensions *ca.* 0.14 × 0.26 × 0.40 mm for (1) and *ca.* 0.22 × 0.28 × 0.30 mm for (2) were orientated on glass fibres so that their b and a^* directions were parallel to the ϕ axis of an Enraf–Nonius CAD3 diffractometer (nickel-filtered Cu-K_α radiation, 3° take-off angle). Refined unit-cell parameters were calculated by least-squares treatment of the θ, χ, and ϕ angles for 40(1) and 48(2) high-order reflections widely separated in reciprocal space. All the unique data in the range $4 < \theta < 67°$ were collected from each crystal by use of the θ—2θ scanning technique. From a total of 7 071 reflections measured for (1) and 6 251 reflections for (2), only 2 893(1) and 3 079(2) for which $I > 2.0\sigma(I)$ [where $\sigma^2(I)$ = scan count + total background count] were corrected for the usual Lorentz and polarization effects and used in the structure analyses and refinements. Absorption corrections, established by monitoring the ϕ dependence of the intensity of a reflection measured at χ 90° for each of (1) and (2), were also made to both data sets.

Structure Analyses.—Both structures were solved by the use of MULTAN[2] and successive E_0 and difference syntheses to give approximate positions for the non-hydrogen atoms. After several rounds of isotropic full-matrix least-squares refinement of both structure models, hydrogen atoms were included in the structure-factor calculations at their calculated positions with B 4.0 Å^2 for (1) and 3.5 Å^2 for (2). Several more least-squares iterations, during which positional and anisotropic thermal parameters for the non-hydrogen atoms were refined, led to convergence at R 0.050 for (1) and 0.083 for (2).

Final atomic positional parameters for the non-hydrogen atoms are in Table 1. Anisotropic temperature-factor parameters for the non-hydrogen atoms and calculated hydrogen-atom positions have been deposited, together

---

† Part 4 is ref. 26.

[1] A. Nieuwpoort, J. H. E. Monnen, and J. A. Cras, *Rec. Trav. chim.*, 1973, **92**, 1086; A. Nieuwpoort, *J. Less-Common Metals*, 1974, **36**, 271; C. A. McAuliffe and B. J. Sayle, *Inorg. Chim. Acta*, 1975, L7; A. Nieuwpoort, H. M. Claessen, and J. G. M. Van der Linden, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 869.

[2] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

with Tables of observed and calculated structure amplitudes, equations of least-square planes through groups of atoms, and interionic distances <3.70 Å, in Supplementary Publication No. SUP 22329 (44 pp.).*

Atomic scattering factors used in all the structure-factor calculations were taken from ref. 3, except for hydrogen (ref. 4). In the least-squares calculations $\Sigma w\Delta^2$ minimized with weights being assigned according to the scheme $w^{\frac{1}{2}} = 1$ for $|F_o| < K$ and $w^{\frac{1}{2}} = K/|F_o|$ for $|F_o| > K$ [K = 190 for (1) and 38 for (2)].

E.S.R. Spectra.—*E.s.r. spectra of single crystals of the* complexes were recorded at room temperature and *Q*-band frequencies on equipment and by methods previously described.[5] The crystals were mounted such that the magnetic field could be orientated in the *ab*, *bc**, and *ac** crystallographic planes. The results are given in Tables 2 and 3.

Electronic Spectral Measurements.—The single-crystal unpolarized electronic-absorption spectra in the crystallographic *ac** plane for (1) and for poly(dimethylsiloxane) mulls of (2) were recorded at room temperature and 80 K as described previously.[6] Spectra were also recorded for solutions of both complexes. The results of these measurements are summarized in Table 4.

TABLE 1

Fractional atomic co-ordinates ($\times$ 10^4), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) For (1)			
Mo(1)	1 310.8(4)	745(1)	1 850.2(4)
S(A1)	1 662(1)	1 732(3)	1 159(1)
C(A2)	1 958(6)	583(12)	993(5)
S(A3)	1 769(2)	−439(3)	1 312(2)
N(A4)	2 309(5)	559(10)	675(4)
C(A5)	2 503(6)	1 505(14)	451(5)
C(A6)	3 059(7)	1 911(15)	791(6)
C(A7)	2 564(7)	−449(15)	549(7)
C(A8)	2 193(11)	−1 001(17)	91(8)
S(B1)	1 851(2)	−531(3)	2 518(2)
C(B2)	2 379(5)	430(12)	2 712(5)
S(B3)	2 262(2)	1 468(3)	2 320(2)
N(B4)	2 802(5)	311(12)	3 120(5)
C(B5)	3 244(8)	1 136(16)	3 256(8)
C(B6)	3 183(12)	1 762(18)	3 628(11)
C(B7)	2 806(7)	−594(13)	3 468(6)
C(B8)	2 414(9)	−440(18)	3 828(8)
S(C1)	1 063(1)	2 683(3)	1 919(1)
C(C2)	880(5)	2 414(12)	2 497(4)
S(C3)	855(2)	1 086(3)	2 581(1)
N(C4)	787(5)	3 116(9)	2 813(4)
C(C5)	641(6)	2 779(15)	3 304(5)
C(C6)	1 164(9)	2 523(17)	3 698(5)
C(C7)	824(7)	4 247(14)	2 716(5)
C(C8)	1 389(13)	4 699(19)	2 990(9)
S(D1)	709(2)	−894(4)	1 839(2)
C(D2)	181(6)	−365(13)	1 352(6)
S(D3)	378(2)	840(4)	1 199(2)
N(D4)	−300(5)	−877(11)	1 144(5)
C(D5)	−393(7)	−1 975(13)	1 306(7)
C(D6)	−724(8)	−1 931(18)	1 741(8)
C(D7)	−739(7)	−361(15)	785(8)
C(D8)	−713(10)	−696(19)	235(7)
Mo(2)	62.8(4)	5 150(1)	868.2(4)
Mo(3)	441.3(5)	6 633(1)	−4.2(4)
Mo(4)	901.5(4)	4 209(1)	155.4(4)
O(1)	0(−)	5 000(−)	0(−)
O(2)	391(4)	6 448(8)	689(3)
O(3)	784(4)	4 533(9)	827(3)
O(4)	−675(4)	5 769(8)	582(3)
O(5)	1 084(4)	5 694(9)	109(3)
O(6)	114(5)	5 281(11)	1 504(4)
O(7)	737(6)	7 822(10)	−29(5)
O(8)	1 567(4)	3 650(9)	263(4)
O(9)	−286(4)	3 827(8)	709(3)
O(10)	386(4)	3 066(8)	142(4)
(*b*) For (2)			
Mo	7 602.2(11)	949.4(4)	3 241.7(10)
Cl	2 411(3)	1 811(1)	9 034(3)
S(A1)	6 682(4)	1 555(1)	1 755(3)
C(A2)	5 438(12)	1 646(5)	2 648(14)
S(A3)	5 544(4)	1 274(1)	3 855(4)
N(A4)	4 569(12)	1 956(4)	2 401(12)
C(A5)	3 502(17)	2 006(6)	3 267(20)
C(A6)	2 305(21)	1 741(9)	2 737(25)
C(A7)	4 570(18)	2 287(18)	1 386(17)
C(A8)	5 217(28)	2 762(8)	1 747(25)
S(B1)	6 743(4)	211(1)	4 215(3)
C(B2)	6 365(13)	−29(4)	2 817(13)
S(B3)	6 578(4)	385(1)	1 726(3)
N(B4)	6 041(12)	−483(4)	2 663(11)
C(B5)	6 030(18)	−821(6)	3 685(16)
C(B6)	7 332(24)	−1 041(8)	3 939(19)
C(B7)	5 751(18)	−687(6)	1 464(15)
C(B8)	4 462(24)	−875(10)	1 348(23)
S(C1)	9 026(4)	1 072(1)	1 527(3)
C(C2)	10 032(14)	644(6)	2 127(14)
S(C3)	9 520(4)	429(2)	3 422(4)
N(C4)	11 084(11)	523(4)	1 616(11)
C(C5)	11 463(15)	766(6)	507(15)
C(C6)	10 943(19)	500(8)	−647(17)
C(C7)	11 831(16)	127(7)	2 099(17)
C(C8)	13 045(16)	317(9)	2 785(19)
S(D1)	8 034(4)	970(1)	5 511(3)
C(D2)	8 808(17)	1 496(6)	5 392(14)
S(D3)	8 750(5)	1 684(1)	3 926(4)
N(D4)	9 387(16)	1 720(5)	6 272(12)
C(D5)	9 392(23)	1 536(8)	7 514(18)
C(D6)	8 367(31)	1 740(13)	8 265(22)
C(D7)	10 309(30)	2 151(9)	6 023(22)
C(D8)	9 423(30)	2 516(12)	6 081(23)

RESULTS AND DISCUSSION

Crystal Structure.—The *X*-ray analyses establish that the major crystalline product we obtained from the reaction of $MoCl_3O$ and $Na[S_2CNEt_2]$ (1 : 2) in methyl cyanide was $[Mo(S_2CNEt_2)_4]_2[Mo_6O_{19}]$ (1) and the minor product was $[Mo(S_2CNEt_2)_4]Cl$ (2). Figures 1—3 show the atom-numbering schemes and geometries of the complex ions in (1) and (2). Interatomic distances and angles in these ions are in Tables 5 and 6.

Crystals of (1) and (2) both contain discrete monomeric $[Mo(S_2CNEt_2)_4]^+$ cations having very similar co-ordination geometries in which the molybdenum atom is surrounded by eight approximately equidistant sulphur atoms from the bidentate S_2CNEt_2 ligands. The angles between the S(A1)S(A3)S(Cl)S(C3) and S(B1)S(B3)-S(D1)S(D3) trapezoids [89.4 in (1) and 89.3° in (2)] are only slightly different from 90° and thus indicate[7] that the co-ordination is close to a $D_{2d}(\bar{4}2m)$ dodecahedral arrangement in which the ligands span the *m* edges.[8]

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[3] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[4] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1975, **42**, 3175.

[5] C. D. Garner, P. Lambert, F. E. Mabbs, and J. K. Porter, *J.C.S. Dalton*, 1972, 320.

[6] D. L. McFadden, A. T. McPhail, C. D. Garner, and F. E. Mabbs, *J.C.S. Dalton*, 1975, 263.

[7] S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 1968, **7**, 1686.

[8] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

Other shape parameters (see Table 7) also accord well with the 'most favourable' arrangement within this geometry. Although quite similar, the Mo–S bond lengths in the cations of complexes (1) and (2) display a slight non-equivalence according to whether or not the sulphur atoms occupy dodecahedral A or B sites [means are Mo–S_A 2.536(15) in (1), 2.531(9) Å in (2); Mo–S_B 2.491(8) in (1), 2.505(12) Å in (2)]. These dimensions are similar to the corresponding values [Mo–S_A 2.543(1), Mo–S_B 2.475(1) Å] in neutral [$Mo(S_2CPh)_4$] [9] which is constrained to have $\bar{4}$ crystallographic symmetry and the W–S_A and W–S_B values of 2.524(8) and 2.494(12) Å respectively in [$W(S_2CNEt_2)_4$]Br.[10] The last complex is isomorphous with (2). Such inequalities are common in D_{2d} dodecahedral complexes containing bidentate sulphur ligands,[9-13] and it has been suggested that they arise from differences in ligand–ligand repulsions [8,14] and/or from differences in ligand-to-metal p_π–d_π bonding.[13] However, if the latter effect were important, then small differences in the C–S_A and C–S_B bond lengths might be expected. Evidence for such differences has not been obtained from any crystallographic determination reported to date, including the data described herein. Moreover, a recent survey of the results of several *X*-ray structural studies on eight-co-ordinate complexes, which included variations in the electronic configuration of the

TABLE 2

Observed and calculated angular variation of the e.s.r. spectrum of [$Mo(S_2CNEt_2)_4]_2[Mo_6O_{19}$] at room temperature ($\nu$ = 34 970 MHz)

	10H/T						
	*ac** plane, *c** = 0			*ab* plane, *a* = 0		*bc** plane, *b* = 0	
		Calc.					
θ/°	Obs.	Alternative (1)	Alternative (2)	Obs.	Calc. Alternatives (1) and (2)	Obs.	Calc. Alternatives (1) and (2)
0	12.620	12.621	12.612	12.614	12.612	12.626	12.626
15	12.621	12.626	12.629	12.613	12.613	12.626	12.626
30	12.622	12.628	12.633	12.617	12.616	12.625	12.615
45	12.621	12.628	12.633	12.620	12.619	12.624	12.624
60	12.619	12.624	12.629	12.623	12.623	12.623	12.622
75	12.616	12.618	12.621	12.625	12.625	12.622	12.621
90	12.613	12.612	12.612	12.626	12.626	12.622	12.621
105	12.611	12.607	12.604	12.625	12.625	12.622	12.621
120	12.610	12.605	12.600	12.623	12.623	12.623	12.622
135	12.611	12.606	12.600	11.620	12.619	12.624	12.624
150	12.614	12.609	12.605	12.617	12.616	12.625	12.625
165	12.617	12.615	12.612	12.615	12.613	12.626	12.626
180	12.620	12.621	12.621	12.614	12.612	12.626	12.626

Alternative 1: g_z = 1.962, g_y = 1.977, and g_x = 2.000. The directions corresponding to these *g* values are from Mo to the midpoints of S(A1)–S(C1) (*z*) S(B3)–S(A3) (*y*), and S(A3)–S(D3) (*x*). Alternative 2: g_z = 1.978, g_y = 1.972, and g_x = 1.989. The directions corresponding to these *g* values are from Mo to the midpoints of S(A1)–S(C1) (*z*), S(C3)–S(D3) (*y*), and S(C3)–S(B3) (*x*).

TABLE 3

Observed and calculated angular variation of the e.s.r. spectrum of [$Mo(S_2CNEt_2)_4$]Cl at room temperature (ν = 35 090 MHz)

	10H/T					
	*ac** plane, *c** = 0		*ab* plane, *a* = 0		*bc** plane, *b* = 0	
θ/°	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	12.674	12.675	12.659	12.660	12.669	12.670
15	12.680	12.683	12.660	12.661	12.670	12.670
30	12.682	12.687	12.663	12.662	12.672	12.671
45	12.678	12.686	12.666	12.665	12.674	12.673
60	12.673	12.679	12.668	12.668	12.675	12.674
75	12.667	12.670	12.669	12.669	12.676	12.675
90	12.659	12.660	12.670	12.670	12.676	12.675
105	12.654	12.652	12.669	12.669	12.676	12.675
120	12.652	12.648	12.668	12.668	12.675	12.674
135	12.654	12.650	12.666	12.665	12.673	12.673
150	12.660	12.656	12.663	12.662	12.672	12.671
165	12.666	12.665	12.660	12.661	12.670	12.670
180	12.674	12.675	12.659	12.660	12.669	12.670

The calculated values are for g_z = 1.980, g_y = 1.974, and g_x = 1.984. The directions corresponding to these *g* values are from Mo to the midpoints of S(D1)–S(B1) (*z*), S(D3)–S(C3) (*y*), and S(A3)–S(D3) (*x*). All the other alternative directions tested gave too large an anisotropy in the *ac** plane.

---

[9] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1975, 2079.

[10] J. G. Wijnhoven, *Crystal Struct. Comm.*, 1973, **2**, 637.

[11] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1974, 1258.

[12] L. Fanfani, A. Nunzi, P. F. Zanazzi, and A. R. Zanzari, *Acta Cryst.*, 1972, **B28**, 1298.

[13] M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse, and I. F. Rendell, *J.C.S. Dalton*, 1972, 1052.

[14] D. G. Blight and D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1556.

metal and the extent of π conjugation within the ligand, suggested that these differences produced no significant or systematic structural changes in the metal's primary co-ordination sphere. Accordingly, it therefore appears that ligand–ligand repulsions are the predominant influence in determining the variation in M–S_A and M–S_B bond lengths in these nearly D_{2d} dodecahedral complexes.

TABLE 4

Electronic-absorption spectra (10^3 cm^{-1}) with molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) for solution spectra in parentheses

(*a*) Spectra of (1) and (2) in $CHCl_3$ solution

13.25 (sh) (*ca.* 15), 13.95 (98), 16.18 (196), 19.09 (1 770), 21.78 (sh) (*ca.* 4 121), 22.21 (4 538), 25.00 (sh) (*ca.* 4 153), 25.98 (sh) (*ca.* 5 077), 32.54 (sh) (*ca.* 25 000), 38.89 (16 346)

(*b*) Poly(dimethylsiloxane) mull of (2) at 80 K

12.0 (sh), 14.0 (sh), 16.2 (sh), 18.6, 20.0 (sh), 21.0, 24.9 (sh)

(*c*) Unpolarized single crystal of (1) in the *ac** plane

Room temperature	80 K
12.9 (sh)	[a]
14.7 (sh)	14.6 (sh)
15.9 (sh)	16.0 (sh)
[b]	17.0
[b]	19.2
[b]	20.4
[b]	21.4 (sh)
[b]	21.9

sh = Shoulder.

[a] Spectrum too intense to measure at >16 000 cm^{-1}.
[b] Band too weak to observe.

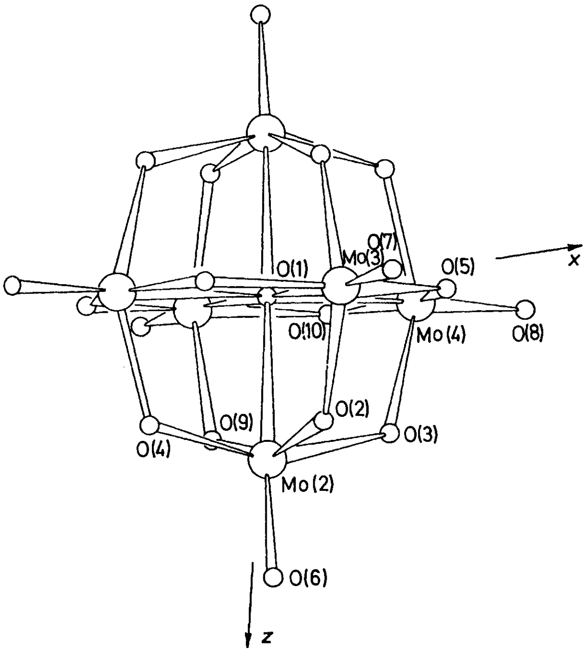

FIGURE 1 Atom-numbering scheme and geometry of the $[Mo_6O_{19}]^2$ anion in (1)

π Delocalization over the S_2CN group would be expected to produce a planar $S_2CN(C)_2$ system. Although the latter moieties are indeed close to being planar in complexes (1) and (2) they do exhibit small unsystematic deformations. Moreover, there are considerable variations in the displacement of the molybdenum atom from the least-squares planes: in (1) these range from 0.022 to 0.419 Å while in (2) the range is from 0.057 to 0.490 Å. These ' distortions ' are typical for such systems and almost certainly originate in the differences in crystal-packing forces experienced by the different S_2CNEt_2 groups of these cations. The results of many crystallographic studies show that the preferred conformation of S_2CNEt_2 ligands is that in which the two terminal methyl groups are orientated *trans* with respect to the S_2CNEt_2 plane.[15] In the crystals of complexes (1) and (2), however, two ligands of the former and one of the latter have their methyl groups in the *cis* conformation, presumably as a result of non-bonding interactions between neighbouring ions. The dimensions of the S_2CNEt_2 ligands in (1) and (2) are presented in Table 5. Apparent differences between chemically equivalent bond lengths and valency angles at the ethyl groups should not be regarded as significant since these parameters are not corrected for the effects of thermal motion and, in the case of the unusually short C(5)–C(6) bond in ligand B of (1), where a *cis* methyl orientation exists, may even involve some slight disordering of the methyl groups. Other bond lengths are in good agreement with those from other studies of S_2CNEt_2 ligands: means S–C 1.71(2), C–N 1.31(2), N–C 1.48(4), and C–C 1.57(7) Å.

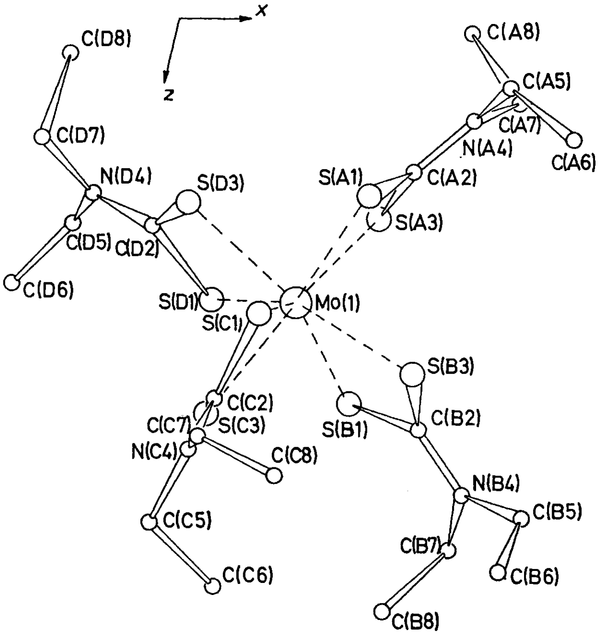

FIGURE 2 Atom-numbering scheme and geometry of the $[Mo(S_2CNEt_2)_4]^+$ cation in crystals of $[Mo(S_2CNEt_2)_4]_2[Mo_6O_{19}]$ (1)

This study of salt (1) represents the second complete

---

[15] See, for example, D. Prown, D. G. Holah, and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, 786; J. C. Dewan, D. L. Kepert, C. L. Kepert, C. L. Raston, D. Taylor, A. H. White, and E. N. Maslen, *J.C.S. Dalton*, 1973, 2082; K. Henrick, C. L. Raston, and A. H. White, *ibid.*, 1976, 26; K. Dymock, G. J. Palenik, J. Slezak, C. L. Raston, and A. H. White, *ibid.*, p. 28.

X-ray determination of the hexamolybdate(2−) anion geometry; the results accord very well with those of the previous study.[16] Although the anion is constrained to possess only crystallographic $\bar{1}(C_i)$ symmetry and thus there are three crystallographically independent molybdenum atoms, departures from strict octahedral symmetry are small. The cage-like structure of the anion may be viewed as being comprised of six distorted MoO_6 octahedra, in each of which four faces are shared at a common vertex. Within each of these octahedra the molybdenum atom is involved in three distinct types of bonding. One bond is to a multiply bonded oxo-type oxygen atom [mean Mo–O(terminal) 1.686 Å], four are to oxygen atoms which are shared by one other

TABLE 5

Interatomic distances (Å) and angles (°) in the $[Mo(S_2CNEt_2)_4]^+$ cation of (1) and (2); estimated standard deviations are in parenthese

(*a*) Dodecahedral dimensions

	A sites	
	(1)	(2)
Mo–S(A1)	2.530(4)	2.530(4)
Mo–S(B1)	2.548(4)	2.526(4)
Mo–S(C1)	2.549(4)	2.525(4)
Mo–S(D1)	2.518(5)	2.544(4)
Mean	2.536	2.531
	Type *g* edges	
S(A1)–S(B3)	3.157(5)	3.273(5)
S(A1)–S(D3)	3.252(5)	3.204(6)
S(A3)–S(B1)	3.214(6)	3.250(5)
S(A3)–S(D1)	3.182(6)	3.264(6)
S(B1)–S(C3)	3.152(6)	3.195(6)
S(B3)–S(C1)	3.191(5)	3.259(5)
S(C1)–S(D3)	3.240(6)	3.198(6)
S(C3)–S(D1)	3.187(6)	3.257(6)
Mean	3.197	3.238
	Type *a* edges	
S(A1)–S(C1)	2.983(5)	2.867(5)
S(B1)–S(D1)	2.941(6)	2.876(5)
Mean	2.962	2.872
	(1)	(2)
S(A1)–Mo–S(A3)	67.7(1)	67.7(1)
S(A1)–Mo–S(B1)	130.1(1)	133.7(1)
S(A1)–Mo–S(B3)	77.9(1)	80.9(1)
S(A1)–Mo–S(C1)	71.9(1)	69.1(1)
S(A1)–Mo–S(C3)	140.0(1)	136.6(1)
S(A1)–Mo–S(D1)	132.5(1)	132.7(1)
S(A1)–Mo–S(D3)	80.6(1)	79.3(1)
S(A3)–Mo–S(B1)	79.2(1)	80.5(1)
S(A3)–Mo–S(B3)	93.6(1)	93.1(1)
S(A3)–Mo–S(C1)	139.6(1)	136.8(1)
S(A3)–Mo–S(C3)	152.3(1)	155.7(1)
S(A3)–Mo–S(D1)	78.9(1)	80.6(1)
S(A3)–Mo–S(D3)	92.7(1)	92.4(1)
S(B1)–Mo–S(B3)	67.8(1)	67.7(1)

	B sites	
	(1)	(2)
Mo–S(A3)	2.492(4)	2.504(4)
Mo–S(B3)	2.494(4)	2.516(4)
Mo–S(C3)	2.479(4)	2.511(4)
Mo–S(D3)	2.497(4)	2.489(5)
Mean	2.491	2.505
	Type *m* edges	
S(A1)–S(A3)	2.796(6)	2.804(5)
S(B1)–S(B3)	2.812(6)	2.809(5)
S(C1)–S(C3)	2.817(5)	2.800(5)
S(D1)–S(D3)	2.803(6)	2.797(6)
Mean	2.807	2.803
	Type *b* edges	
S(A3)–S(B3)	3.636(6)	3.644(5)
S(A3)–S(D3)	3.610(6)	3.604(6)
S(B3)–S(C3)	3.566(5)	3.577(6)
S(C3)–S(D3)	3.661(5)	3.655(6)
Mean	3.618	3.620
	(1)	(2)
S(B1)–Mo–S(C1)	130.6(1)	133.0(1)
S(B1)–Mo–S(C3)	77.7(1)	78.7(1)
S(B1)–Mo–S(D1)	71.0(1)	69.1(1)
S(B1)–Mo–S(D3)	139.0(1)	136.6(1)
S(B3)–Mo–S(C1)	78.5(1)	80.5(1)
S(B3)–Mo–S(C3)	91.6(1)	90.7(1)
S(B3)–Mo–S(D1)	138.8(1)	136.8(1)
S(B3)–Mo–S(D3)	153.3(2)	155.7(1)
S(C1)–Mo–S(C3)	68.1(1)	67.5(1)
S(C1)–Mo–S(D1)	131.6(1)	131.5(1)
S(C1)–Mo–S(D3)	79.9(1)	79.3(1)
S(C3)–Mo–S(D1)	79.3(1)	80.2(1)
S(C3)–Mo–S(D3)	94.7(1)	93.9(2)
S(D1)–Mo–S(D3)	68.0(1)	67.5(1)

(*b*) Diethyldithiocarbamate ligands

	ligand A		ligand B		ligand C		ligand D	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
S(1)–C(2)	1.72(2)	1.72(1)	1.74(2)	1.72(1)	1.74(1)	1.72(2)	1.74(2)	1.70(2)
C(2)–S(3)	1.67(2)	1.70(2)	1.68(2)	1.70(1)	1.71(2)	1.68(2)	1.68(2)	1.71(2)
C(2)–N(4)	1.31(2)	1.29(2)	1.32(2)	1.32(2)	1.29(2)	1.33(2)	1.32(2)	1.29(2)
N(4)–C(5)	1.46(2)	1.54(2)	1.47(3)	1.48(2)	1.50(2)	1.48(2)	1.49(2)	1.47(2)
N(4)–C(7)	1.49(2)	1.46(2)	1.48(2)	1.47(2)	1.47(2)	1.45(2)	1.45(2)	1.59(3)
C(5)–C(6)	1.52(2)	1.57(3)	1.31(3)	1.53(3)	1.48(2)	1.56(3)	1.54(3)	1.52(4)
C(7)–C(8)	1.52(3)	1.54(3)	1.49(3)	1.47(3)	1.49(3)	1.56(3)	1.49(3)	1.40(4)
Mo–S(1)–C(2)	89.2(5)	90.3(5)	88.8(5)	90.2(5)	88.8(5)	90.0(5)	89.8(5)	90.3(6)
Mo–S(3)–C(2)	91.6(5)	91.7(5)	92.1(5)	91.1(5)	91.9(4)	91.4(5)	91.8(5)	91.8(5)
S(1)–C(2)–S(3)	110.9(8)	110.2(8)	110.8(8)	110.2(7)	109.7(7)	111.0(8)	110.5(8)	110.3(9)
S(1)–C(2)–N(4)	122.6(12)	123.1(12)	122.0(12)	122.5(11)	124.6(11)	122.4(12)	122.4(12)	125.2(13)
S(3)–C(2)–N(4)	126.4(12)	126.8(12)	127.2(12)	127.2(11)	125.7(10)	126.6(12)	127.1(12)	124.4(14)
C(2)–N(4)–C(5)	123.1(13)	118.5(13)	119.5(14)	121.8(12)	119.3(13)	120.8(13)	120.3(13)	121.4(16)
C(2)–N(4)–C(7)	120.8(13)	124.1(14)	120.9(13)	122.0(12)	122.6(12)	119.7(13)	119.4(14)	120.7(15)
C(5)–N(4)–C(7)	115.9(12)	117.3(13)	119.4(14)	116.1(12)	118.1(12)	119.3(13)	120.3(13)	117.1(16)
N(4)–C(5)–C(6)	109.7(12)	109.7(17)	115.9(19)	110.7(15)	112.4(12)	111.5(14)	108.6(14)	114.7(19)
N(4)–C(7)–C(8)	113.3(15)	111.4(16)	112.9(15)	111.7(16)	111.8(15)	110.3(16)	112.3(16)	96.9(24)

---

[16] H. R. Allcock, E. C. Bissell, and E. T. Shawl, *Inorg. Chem.*, 1973, **12**, 2963.

TABLE 6

Interatomic distances (Å) and angles (°) in the hexamolybdate anion of (1); * estimated standard deviations are in parentheses

(*a*) Bond lengths			
Mo–O (central)			
Mo(2)–O(1)	2.319(1)	Mo(4)–O(1)	2.303(1)
Mo(3)–O(1)	2.323(1)	Mean	2.315
Mo–O (terminal)			
Mo(2)–O(6)	1.698(9)	Mo(4)–O(8)	1.686(10)
Mo(3)–O(7)	1.673(13)	Mean	1.686
Mo–O (bridging)			
Mo(2)–O(2)	1.928(10)	Mo(3)–O(9′)	1.943(9)
Mo(2)–O(3)	1.896(10)	Mo(3)–O(10′)	1.938(10)
Mo(2)–O(4)	1.909(9)	Mo(4)–O(3)	1.933(9)
Mo(2)–O(9)	1.881(10)	Mo(4)–O(5)	1.948(11)
Mo(3)–O(2)	1.912(9)	Mo(4)–O(10)	1.889(10)
Mo(3)–O(5)	1.899(10)	Mo(4)–O(4′)	1.942(8)
		Mean	1.916
(*b*) O–Mo–O valency angles			
Central-terminal			
O(1)–Mo(2)–O(6)	179.0(4)	O(1)–Mo(4)–O(8)	178.8(4)
O(1)–Mo(3)–O(7)	177.5(4)	Mean	178.4
Terminal-bridging			
O(6)–Mo(2)–O(2)	102.9(5)	O(7)–Mo(3)–O(9′)	103.0(5)
O(6)–Mo(2)–O(3)	103.4(5)	O(7)–Mo(3)–O(10′)	102.9(5)
O(6)–Mo(2)–O(4)	103.0(5)	O(8)–Mo(4)–O(3)	104.2(5)
O(6)–Mo(2)–O(9)	104.4(5)	O(8)–Mo(4)–O(5)	102.1(5)
O(7)–Mo(3)–O(2)	105.4(5)	O(8)–Mo(4)–O(10)	104.4(5)
O(7)–Mo(3)–O(5)	104.5(5)	O(8)–Mo(4)–O(4′)	102.7(5)
		Mean	103.6
Bridging-central			
O(2)–Mo(2)–O(1)	76.1(3)	O(9′)–Mo(3)–O(1)	75.3(3)
O(3)–Mo(2)–O(1)	76.6(3)	O(10′)–Mo(3)–O(1)	75.3(3)
O(4)–Mo(2)–O(1)	77.0(3)	O(3)–Mo(4)–O(1)	76.3(3)
O(9)–Mo(2)–O(1)	76.5(3)	O(5)–Mo(4)–O(1)	76.8(3)
O(2)–Mo(3)–O(1)	76.3(3)	O(10)–Mo(4)–O(1)	76.7(3)
O(5)–Mo(3)–O(1)	77.2(3)	O(4′)–Mo(4)–O(1)	76.8(3)
		Mean	76.4
Bridging-bridging			
O(2)–Mo(2)–O(3)	85.8(4)	O(5)–Mo(3)–O(9′)	86.6(4)
O(2)–Mo(2)–O(4)	85.7(4)	O(9′)–Mo(3)–O(10′)	84.6(4)
O(3)–Mo(2)–O(9)	88.2(4)	O(3)–Mo(4)–O(5)	86.1(4)
O(4)–Mo(2)–O(9)	87.9(4)	O(3)–Mo(4)–O(10)	87.7(4)
O(2)–Mo(3)–O(5)	89.1(4)	O(5)–Mo(4)–O(4′)	86.3(4)
O(2)–Mo(3)–O(10′)	86.4(4)	O(10)–Mo(4)–O(4′)	87.7(4)
		Mean	86.8
O(2)–Mo(2)–O(9)	152.6(4)	O(5)–Mo(3)–O(10′)	152.4(4)
O(3)–Mo(2)–O(4)	153.4(4)	O(3)–Mo(4)–O(4′)	153.0(4)
O(2)–Mo(3)–O(9′)	151.5(4)	O(5)–Mo(4)–O(10)	153.5(4)
		Mean	152.7
(*c*) Mo–O–Mo valency angles			
Mo(2)–O(1)–Mo(3)	90.06(4)	Mo(2)–O(1)–Mo(4′)	90.05(4)
Mo(2)–O(1)–Mo(3′)	89.94(4)	Mo(3)–O(1)–Mo(4)	89.79(5)
Mo(2)–O(1)–Mo(4)	89.95(4)	Mo(3)–O(1)–Mo(4′)	90.21(5)
		Mean	90.00
Mo(2)–O(2)–Mo(3)	117.6(5)	Mo(3)–O(5)–Mo(4)	116.1(5)
Mo(2)–O(3)–Mo(4)	117.1(5)	Mo(2)–O(9)–Mo(3′)	118.2(5)
Mo(2)–O(4)–Mo(4′)	116.2(4)	Mo(4)–O(10)–Mo(3′)	117.8(5)
		Mean	117.2

* Primed atoms are related to the unprimed atoms by the centre of symmetry at 0, ½, 0.

molybdenum atom [mean Mo–O(bridging) 1.918 Å], and one is to an oxygen atom which is shared by all the six molybdenum atoms [mean Mo–O(central) 2.315 Å]. These distances are all in excellent agreement with the corresponding values from the previous study,[16] 1.677, 1.928, 2.319, and 3.274 Å. The variations in the individual Mo–O(bridging) bonds in that study [range 1.855(4)—2.005(4) Å] were slightly greater than in the present case [range 1.881(10)—1.948(11) Å], probably as a consequence of the involvement in the former of a pair of bridging oxygen atoms in N–H · · · O hydrogen bonds which could perturb slightly the equivalence of the Mo–O bonds.

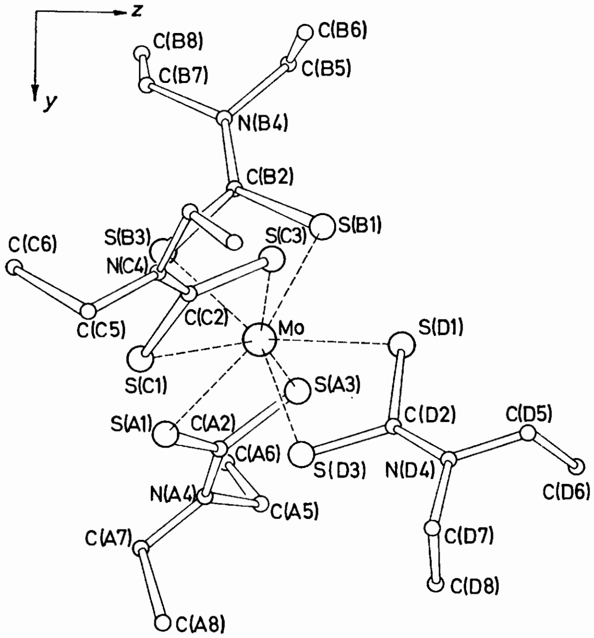

FIGURE 3 Atom-numbering scheme and geometry of the $[Mo(S_2CNEt_2)_4]^+$ cation in crystals of $[Mo(S_2CNEt_2)_4]Cl$ (2)

In addition to the excellent correspondence between the dimensions derived for the $[Mo_6O_{19}]^{2-}$ anion from these two studies, the geometries around the individual molybdenum atoms also accord well with those for other complexes involving a single multiply bonded oxygen atom. For example, the short Mo–O(terminal) multiple bond length is very similar to those of [1.672(15) and 1.668(5) Å] at six-co-ordinate molybdenum in the discrete $[MoCl_4O(OH_2)]^-$ (ref. 17) and $[Mo(CN)_4O(OH_2)]^{2-}$ ions.[18] The length of the Mo–O(central) bond, *trans* to the terminal multiply bonded oxo-group, is between that for the corresponding Mo–OH_2 distances [2.393(15)

TABLE 7

Shape parameters [a] for the D_{2d} S_8 co-ordination dodecahedron in (1) and (2)

	(1)	(2)	'Most favourable' [b]
Mo–S_A/Å	2.536(15)	2.5319(9)	
Mo–S_B/Å	2.491(8)	2.505(12)	
g	1.27	1.29	1.24
m	1.12	1.11	1.17
b	1.44	1.44	1.49
a	1.18	1.14	1.17
Mo–S_A/Mo–S_B	1.02	1.01	1.03
θ_A/°	35.7(1)	34.6(1)	35.2
θ_B/°	76.4(1)	77.8(1)	73.5

[a] The unit of length for the edges is the mean Mo–S bond distance. [b] Ref. 5.

---

[17] C. D. Garner, L. H. Hill, F. E. Mabbs, D. L. McFadden, and A. T. McPhail, *J.C.S. Dalton*, 1977, 1202.

[18] P. R. Robinson, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, 1975, **14**, 2035.

2.271(4) Å] in these two complexes. The Mo–O(bridging) bond assumes a value close to those [1.93(2) and 1.940(2) Å] in the [$Mo_2O_4(SO_2NC_5H_{10})_2$] [19] and [$Mo_2O_4(S_2CNEt_2)_2$] [20] di-μ-oxo-complexes. In agreement with the geometries at the molybdenum atoms in other six-co-ordinate complexes, the metal atom is displaced (mean Δ 0.45 Å) from the least-squares plane through the bridging oxygen atoms towards the multiply bonded oxygen atom, an arrangement which tends to equalize O · · · O separations.

Electronic-absorption Spectra.—The electronic-absorption spectra of salts containing the [$Mo(S_2CNEt_2)_4$]$^+$ ion consist of a background absorption, the intensity of which increases with increasing energy, upon which a number of features are apparent (see Table 4). These data are in good agreement with those reported by Nieuwpoort and is co-workers.[1] Since we have not observed any polarization in the spectra of single crystals of (1) and (2) we report only the unpolarized spectra. The crystal spectrum of (1) showed weak absorptions at 12 900, 14 700, and 15 900 cm^{-1} at room temperature, the spectrum at >16 000 cm^{-1} being too intense to measure. These features correspond to those observed at 13 300, 14 000, and 16 200 cm^{-1} for (1) and (2) in $CHCl_3$ solution, and in the less well defined mull spectrum of (2) at 80 K. On cooling the single crystal of (1) to 80 K the first absorption was too weak to be observed; however, a general improvement in resolution was achieved and features at 14 600, 16 000, 17 000, 19 200, 20 400, 21 400, and 21 900 cm^{-1} were observed.

The electronic structures of eight-co-ordinate complexes have been the subject of some theoretical and experimental studies,[1,21-26] most of which relate to oxygen-donor ligands. Simple crystal-field arguments suggest that the probable *d*-orbital ordering in these [$Mo(S_2CNEt_2)_4$]$^+$ cations is $d_{x^2-y^2} < d_{xz,yz} < d_{z^2} < d_{xy}$.[21] This sequence is in agreement with that deduced by Nieuwpoort using ligand-field and extended-Hückel LCAO calculations.[1] However, this latter calculation interspersed several empty ligand π orbitals between the metal d_{z^2} and d_{xy} levels. Thus the first two absorptions may be assigned to the $(d_{x^2-y^2})^1 \rightarrow (d_{xz,yz})^1$ promotion. The difference in energy between the first two bands of these complexes in $CHCl_3$ solution is *ca.* 700 cm^{-1}. In a D_{2d} system this represents the splitting of the d_{xz} and d_{yz} orbitals by the metal spin–orbit coupling constant appropriate to the complex. The separation observed is close to the spin–orbit coupling constant for free Mo^{2+} ion.[27] In the crystal spectrum of (1), and the less well defined mull spectrum of (2), the difference in energy between the first two bands is *ca.* 1 800 cm^{-1} which is greater than the spin–orbit coupling constant of free Mo^{5+} ion.[27] This splitting of the d_{xz} and d_{yz} orbitals is therefore attributed to a combination of spin–orbit coupling and a low-symmetry ligand-field component. The absorption coefficient of the third band (*ca.* 16 000 cm^{-1}) in the spectrum is consistent with the assignment to the promotion $(d_{x^2-y^2})^1 \rightarrow (d_{z^2})^1$. However, based on the magnitudes of their absorption coefficients, the bands at *ca.* >16 000 cm^{-1} appear to originate from charge-transfer transitions. Nieuwpoort's theoretical studies suggest that these are predominantly metal-to-ligand in nature.

E.S.R. Spectra.—In each of these monoclinic systems the expected signals from the two magnetically inequivalent molecules in the *ab* and *bc** planes were not observed, suggesting significant intermolecular magnetic interaction. The observed data are given in Tables 2 and 3. The method used to obtain the principal molecular *g* values uses the observed g_{aa}, g_{bb}, and g_{cc}** values and *assumes* a knowledge of the respective direction cosines of the principal molecular *g* values from the crystal structure.[28] The correctness of the choice of direction cosines and of the calculated molecular *g* values was tested by computing the angular variation of the e.s.r. spectrum in each crystallographic plane; that combination which best reproduced the experimental data was taken to be the appropriate set. The direction cosines were obtained from the crystallographic data, taking the *z* direction to be the bisector of the *a* edge of the dodecahedron [S(A1) and S(C1) or S(D1) and S(B1)] and the *x* and *y* axes as the midpoints of pairs of opposite *b* edges.[29] Because of the deviations from perfect D_{2d} symmetry this leads to eight possible sets of direction cosines. The molecular directions and their corresponding *g* values which best reproduce the experimental data are also summarized in Tables 2 and 3. This method of interpretation is very sensitive to changes in the assumed direction cosines and any sets of direction cosines other than those quoted lead to a poorer reproduction of the e.s.r. spectral data, particularly in the *ac** plane.

The molecular *g* values obtained for both systems show only relatively small anisotropies and also indicate that the symmetries of the [$Mo(S_2CNEt_2)_4$]$^+$ units are lower than D_{2d}. The *g* values for [$Mo(S_2CNEt_2)_4$]Cl are $g_z = 1.980$, $g_x = 1.974$, and $g_y = 1.984$. These values give the appearance of axial symmetry, but not in the conventional sense of $g_x = g_y$. The ambiguities in the interpretation of the e.s.r. behaviour of a magnetically concentrated system were previously [28] resolved by diluting the paramagnetic species in an amorphous diamagnetic host lattice. However, in the case of [$Mo(S_2CNEt_2)_4$]Cl this has not been possible since we

---

[19] M. G. B. Drew and A. Kay, *J. Chem. Soc.* (*A*), 1971, 1846.

[20] L. Ricard, C. Martin, R. Wiest, and R. Weiss, *Inorg. Chem.*, 1975, **14**, 2300.

[21] C. D. Garner and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1970, 1711.

[22] F. E. Mabbs and W. R. Smail, *J. Chem. Soc.* (*A*), 1970, 1716.

[23] C. D. Garner, P. Lambert, F. E. Mabbs, and J. K. Porter, *J.C.S. Dalton*, 1972, 320.

[24] D. E. Billing, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc.* (*A*), 1970, 1877.

[25] R. J. Dudley, B. J. Hathaway, and P. G. Hodgson, *J. Chem. Soc.* (*A*), 1971, 3355.

[26] C. D. Garner and F. E. Mabbs, *J.C.S. Dalton*, 1976, 525.

[27] T. M. Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.

[28] C. D. Garner, P. Lambert, F. E. Mabbs, and T. J. King, *J.C.S. Dalton*, 1977, 1191.

[29] J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Amer. Chem. Soc.*, 1968, **90**, 3177.

found that $[Nb(S_2CNEt_2)_4]Cl$ was not isomorphous with the molybdenum analogue.

Experimentally we cannot distinguish between the two sets of principal molecular g values and associated direction cosines obtained for (1), but by comparison with the $[Mo(S_2CNEt_2)_4]X$ complexes the values $g_z = 1.978$, $g_y = 1.972$, and $g_x = 1.989$ seem to be the most appropriate.

The molecular geometries, g values, and solid-state electronic spectra indicate that the $[Mo(S_2CNEt_2)_4]^+$ ions in these two systems are closer to D_2 than to D_{2d} symmetry. Mixing of the metal $d_{x^2-y^2}$ and d_{z^2} orbitals in this symmetry leads to the first-order g-value expressions (1) and (2), where $\phi(x^2 - y^2) = ad_{x^2-y^2} - bd_{z^2}$,

$$g_x = 2.002\,3 - \frac{2k_x^2\lambda(3b - a)^2}{E(d_{yz}) - E[\phi(x^2 - y^2)]} \qquad (1)$$

$$g_y = 2.002\,3 - \frac{2k_y^2\lambda[(3b)^{\frac{1}{2}} + a]^2}{E(d_{xz}) - E[\phi(x^2 - y^2)]} \qquad (2)$$

$a^2 + b^2 = 1$, λ is the metal spin–orbit coupling constant in the complex, and k_x and k_y are orbital angular-momentum reduction parameters. The experimental data do not allow an unambiguous determination of the parameters in equations (1) and (2). However, some approximate values may be obtained with the following assumptions. If we assume $k_x = k_y$, then the experimental data [alternative 2 for compound (1)] can be accounted for with $a^2 = 0.99$ and $k_x^2 = 0.21$—0.14 for λ ranging in value from that for Mo^{2+} to that for Mo^{5+}. Thus only a relatively small amount of metal d-orbital mixing is required to account for the anisotropy between g_x and g_y. Alternatively, if the metal d-orbital mixing is assumed to be negligible then the experimental data lead to anisotropic k values, namely k_x^2 in the range 0.13—0.09 and k_y^2 in the range 0.30—0.20 for λ ranging from that for Mo^{2+} to that for Mo^{5+}. The low values of k obtained from either of these two approaches are indicative of considerable covalency in the metal–ligand bonding.

C. D. G. and F. E. M. thank the S.R.C. for support, and N. C. H. thanks the Commission for Commonwealth Scholarships in the U.K. for a research grant. Crystallographic calculations were performed on an I.B.M. 370/165 computer located at the Triangle Universities Computation Centre, Research Triangle Park, North Carolina, and supported by a grant of computer time from Duke University.

[8/118 *Received, 24th January, 1978*]