Crystal and Molecular Structure of Diaquahydrogen(I) μ-Oxo-[bis(diethyldithiocarbamato)oxomolybdate(IV)][bis(diethyldithiocarbamato)oxomolybdenum(V)] Bis{μ-oxo-bis[bis(diethyldithiocarbamato)oxomolybdenum(V)]} (1), and μ-Oxo-bis[bis(diethyldithiocarbamato)oxomolybdenum(V)] (2), and the Single-crystal Electron Spin Resonance Spectrum of (1)

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Monoclinic crystals of form (1) belong to space group $C2/c$, with a = 31.340(10), b = 9.671(3), c = 38.027(10) Å, β = 110.72(5)°; the unit cell contains eight molecules of $[MoO(S_2CNEt_2)_2]_2O$ oxo-bridged dimers (four with approximate C_2 symmetry, four with crystallographic C_i symmetry), four $[Mo_2O_3(S_2CNEt_2)_4]^-$ anions, and four $[H_5O_2]^+$ ions. The structure has been solved with the aid of direct methods and refined by full-matrix least-squares calculations to R 0.074 using 5 508 reflections. Triclinic crystals of compound (2) belong to space group $P\bar{1}$, with a = 8.493(3), b = 12.232(4), c = 9.775(3) Å, α = 107.52(5), β = 114.40(5), and γ = 95.82(5)°; the unit cell contains one centrosymmetric $[MoO(S_2CNEt_2)_2]_2O$ oxo-bridged dimer. The structure has been solved by the heavy-atom method and refined by full-matrix least-squares calculations to R 0.052 using 2 340 reflections. The distorted-octahedral geometries around the molybdenum atoms in both compounds are similar; the respective mean dimensions are Mo–O(terminal) 1.686(13), 1.680(14) Å, and Mo–O(bridging) 1.875(14), 1.859(1) Å. The Mo–S lengths range from 2.436(2) to 2.694(2) Å depending upon the nature of the *trans* ligand. The single-crystal e.s.r. behaviour of (1) shows the presence of two distinct paramagnetic molybdenum centres in the crystal which have been assigned to the $[Mo_2O_3(S_2CNEt_2)_4]^-$ ion. The principal molecular g values for these two centres are 1.976, 1.978, 1.984, and 1.978, 1.981, and 1.984.

THERE has been considerable interest in dimeric molybdenum(V) compounds since they were suggested as models for certain molybdoenzyme systems.[1] This interest has lead to the structural characterisation of compounds containing the Mo_2O_4,[2] Mo_2O_3,[2,3] $Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)$,[4] $Mo_2O_2(\mu\text{-}S)_2$,[5] Mo_2S_4,[6] and $Mo_2O_2(\mu\text{-}SPh)_2(\mu\text{-}Cl)$ [7] units. All of these dimeric compounds have been reported to be diamagnetic in the solid state, except for $[Mo_2O_3(tpp)_2]$ (tpp = tetraphenylporphinate) which has a nearly linear O=Mo–O–Mo=O arrangement, as opposed to the other compounds which have the Mo=O group *cis* to the bridged moiety. However, some measurements [8] on solutions of the diamagnetic dimers have been interpreted in terms of paramagnetic dimers existing in the solutions, and in one case this has been confirmed by e.s.r. measurements using isotopically enriched molybdenum.[9] Nevertheless, none of the paramagnetic species observed in these solutions has been isolated in the solid state. The possibility of paramagnetism in Mo_2O_3-type dimers has been discussed by Cotton and his co-workers.[3b] It was considered that twisting of the Mo_2O_3 bridging unit so that the terminal oxygen atoms were no longer eclipsed could give rise to a (thermally accessible) spin-triplet state.

Despite $[Mo_2O_3(S_2CNEt_2)_4]$ being a commonly formed and used compound, it has not been previously structurally characterised, although the structure of the propyl analogue has been reported.[3c] As part of our studies of molybdenum(V) diethyldithiocarbamate complexes we now report the single-crystal structures of two forms of this dimer, $[H_5O_2][Mo_2O_3(S_2CNEt_2)_4]_3$ and $[Mo_2O_3(S_2CNEt_2)_4]$ (2), in addition to the single-crystal e.s.r. behaviour of (1).

EXPERIMENTAL

Preparation.—Small needle-shaped crystals of $[H_5O_2][Mo_2O_3(S_2CNEt_2)_4]_3$ (1) and $[Mo_2O_3(S_2CNEt_2)_4]$ (2) were obtained in small quantities during attempts to grow large crystals of $[MoO(S_2CNEt_2)_3]$ by slow evaporation in a dry-box of a solution of $MoCl_3O$ and $Na[S_2CNEt_2]$ (1 : 3 mol ratio) in dried CH_2Cl_2. Both (1) and (2) were initially identified from the crystal-structure determination, the remainder of the sample being subsequently confirmed by analysis [Found: C, 28.5; H, 4.6; Mo, 23.0; N, 6.6; S, 30.5. Calc. for (1): C, 28.4; H, 5.0; Mo, 22.7; N, 6.6; S, 30.4%].

Crystal Data.—(1), $C_{30}H_{60}Mo_3N_6O_{4\cdot5}S_{12}\cdot0.5H_5O_2$, M = 1 268.0, Monoclinic, a = 31.340(10), b = 9.671(3), c = 38.027(10) Å, β = 110.72(5)°, U = 10 780 Å^3, D_m(flotation) = 1.59 g cm^{-3}, Z = 8, D_c = 1.562 g cm^{-3}, $F(000)$ = 517 2, Cu-K_α radiation, λ = 1 541 8 Å, μ(Cu-K_α) = 104.0 cm^{-1}. [A possible alternative formulation for (1) is $C_{30}H_{60}Mo_3N_6O_{4.5}S_{12}\cdot0.5H_3O_2$, M = 1 267.0, D_c = 1.561 g cm^{-3}, $F(000)$ = 516 4.] Space group either $Cc(C_s^4)$ or $C2/c(C_{2h}^6)$ from systematic absences: hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$; concluded to be the latter from structure solution and refinement.

(2), $C_{20}H_{40}Mo_2N_4O_3S_8$, M = 833.0, Triclinic, a = 8.493(3), b = 12.232(4), c = 9.775(3) Å, α = 107.52(5), β = 114.40(5), γ = 95.82(5)°, U = 851.6 Å^3, D_m (not measured), Z = 1, D_c = 1.624 g cm^{-3}, $F(000)$ = 424, Cu-K_α radiation, μ(Cu-K_α) = 109.4 cm^{-1}. Space group $P1(C_1^1)$ or $P\bar{1}(C_i^1)$; deduced to be the latter by structure solution and refinement.

Crystallographic Measurements.—Preliminary unit-cell dimensions and space-group information for forms (1) and (2) were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation and precession photographs taken with Mo-K_α radiation (λ 0.710 7 Å). Refined unit-cell dimensions were obtained later by least-squares treatment of the θ, χ, and ϕ angles for 40 reflections, widely separated in reciprocal space, from crystals of dimensions *ca.* 0.12 × 0.15 × 0.50 (1) and *ca.* 0.18 × 0.32 × 0.70 mm (2) which were orientated on an Enraf–Nonius CAD 3 automated diffractometer (nickel-filtered Cu-K_α radiation; 3° take-off angle). All unique data in the range $4 < \theta < 67°$ were recorded by use of the θ—2θ scanning technique. From these measurements, only those 5 508(1) and 2 340(2) reflections for which $I > 2.0\sigma(I)$, where $\sigma^2(I)$ = scan count + total background count, were corrected for Lorentz and polarisation effects for use in the structure analyses and refinements. Absorption corrections, established from the dependence on ϕ of the intensities of the 0 6 0(1) and 4 0 $\bar{2}$(2) reflections measured at $\chi = 90°$, were also made to these data sets.

TABLE 1

Fractional atomic co-ordinates (× 10^4) for the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z
(*a*) Compound (1)			
Mo(1)	176.8(4)	180.7(15)	4 583.3(4)
Mo(2)	1 339.1(4)	1 669.5(16)	3 239.4(3)
Mo(2′)	2 592.2(4)	1 936.3(17)	3 777.3(3)
μ-O(1)	0(—)	0(—)	5 000(—)
O(2)	−165(4)	1 427(14)	4 316(3)
μ-O(3)	1 964(4)	1 696(15)	3 528(4)
O(4)	1 133(4)	426(14)	3 446(3)
O(4′)	2 727(4)	892(14)	4 156(3)
S(A1)	495(2)	−2 405(5)	4 768(1)
C(A2)	−6(5)	−2 903(17)	4 442(4)
S(A3)	−355(2)	−1 591(5)	4 193(1)
N(A4)	−133(5)	−4 216(17)	4 377(4)
C(A5)	178(6)	−5 349(21)	4 561(5)
C(A6)	457(8)	−5 743(28)	4 320(7)
C(A7)	−586(9)	−4 622(30)	4 124(7)
C(A8)	−930(8)	−4 810(28)	4 334(7)
S(B1)	736(1)	130(6)	4 246(1)
C(B2)	1 112(5)	937(17)	4 643(4)
S(B3)	895(1)	1 185(5)	4 991(1)
N(B4)	1 527(5)	1 308(16)	4 662(4)
C(B5)	1 835(7)	2 106(24)	4 995(6)
C(B6)	1 818(10)	3 596(34)	4 896(8)
C(B7)	1 708(7)	994(22)	4 365(5)
C(B8)	1 926(9)	−406(29)	4 436(7)
S(C1)	1 467(1)	4 227(5)	3 026(1)
C(C2)	1 242(7)	4 780(22)	3 351(5)
S(C3)	1 098(1)	3 483(5)	3 597(1)
N(C4)	1 207(6)	6 096(21)	3 419(5)
C(C5)	1 039(9)	6 571(30)	3 725(7)
C(C6)	547(12)	6 873(41)	3 567(10)
C(C7)	1 351(8)	7 201(27)	3 224(7)
C(C8)	1 843(9)	7 652(30)	3 415(7)
S(D1)	624(1)	1 807(6)	2 668(1)
C(D2)	916(7)	951(22)	2 434(5)
S(D3)	1 491(1)	700(6)	2 699(1)
N(D4)	728(6)	511(21)	2 076(5)
C(D5)	225(9)	719(29)	1 854(7)
C(D6)	155(10)	2 043(32)	1 644(8)
C(D7)	1 003(7)	−202(23)	1 883(6)
C(D8)	968(11)	−1 750(36)	1 932(9)
S(C′1)	2 580(2)	2 696(5)	3 098(1)
C(C′2)	2 838(5)	1 150(18)	3 084(4)
S(C′3)	2 901(2)	114(5)	3 468(1)
N(C′4)	2 978(5)	769(17)	2 816(4)
C(C′5)	2 908(7)	1 678(23)	2 484(6)
C(C′6)	2 474(8)	1 352(27)	2 176(6)
C(C′7)	3 186(7)	−583(23)	2 813(6)
C(C′8)	3 712(8)	−545(28)	2 998(7)
S(D′1)	3 328(1)	3 239(6)	3 970(1)
C(D′2)	3 050(6)	4 616(20)	4 059(5)
S(D′3)	2 463(1)	4 264(6)	3 971(2)
N(D′4)	3 227(5)	5 838(16)	4 166(4)
C(D′5)	2 972(7)	7 005(25)	4 251(6)
C(D′6)	3 083(10)	7 215(34)	4 652(8)
C(D′7)	3 697(6)	6 158(21)	4 184(5)
C(D′8)	3 689(8)	6 736(26)	3 807(6)
O(W1) *	4 741(11)	511(36)	2 534(9)
O(W2)	5 000(—)	2 855(39)	2 500(—)
(*b*) Compound (2)			
Mo(1)	−116.8(7)	1 563.7(4)	412.4(6)
μ-O(1)	0(—)	0(—)	0(—)
O(2)	−1 534(7)	1 550(5)	−1 392(6)
S(A1)	1 227(2)	1 769(2)	3 529(2)
C(A2)	−941(9)	1 503(6)	3 161(8)
S(A3)	−2 492(2)	1 346(2)	1 236(2)
N(A4)	−1 448(8)	1 425(6)	4 258(7)
C(A5)	−3 329(10)	1 154(8)	3 880(9)
C(A6)	−4 095(14)	−155(11)	3 369(13)
C(A7)	−125(11)	1 643(7)	5 936(9)
C(A8)	411(15)	2 931(9)	7 022(10)
S(B1)	992(2)	3 801(2)	1 716(2)
C(B2)	2 972(9)	3 617(6)	1 719(7)
S(B3)	2 943(2)	2 142(1)	867(2)
N(B4)	4 386(8)	4 492(5)	2 283(7)
C(B5)	4 387(13)	5 750(7)	3 046(10)
C(B6)	3 969(16)	6 362(9)	1 921(15)
C(B7)	6 016(11)	4 300(7)	2 193(10)
C(B8)	7 473(13)	4 332(9)	3 738(12)

* Occupation factor 0.50.

Structure Analyses.—The space group of form (1) was assumed to be $C2/c$ and the structure was solved by a combination of direct methods using MULTAN [10] and F_o Fourier syntheses to give approximate positions for the non-hydrogen atoms. Refinement of atomic positional and isotropic thermal parameters by full-matrix least-squares calculations reduced R to 0.097. A difference-Fourier synthesis confirmed not only that the majority of calculated hydrogen-atom positions coincided with regions of positive electron density but also revealed the presence of two large peaks in the region of the crystallographic two-fold axis. These peaks were ascribed to oxygen atoms, one of which was placed on the two-fold axis while the other lay close to this axis but was disordered since the distance from its symmetry-related molecule was short (*ca.* 1.7 Å). These oxygen atoms were initially assumed to belong to water molecules. An ordered pair of water molecules occupying general positions of the non-centric space group Cc would also satisfy the electron-density distribution. However, this would necessitate removal of the centre of symmetry which would consequently double the number of parameters required to define the $[MoO(S_2CNEt_2)_2]_2O$ dimers. Since the results of the refinement in the centrosymmetric space group provided good agreement between chemically equivalent bond lengths in the dimers and no unreasonable thermal parameters were noted, we conclude that relaxation of the symmetry constraints is unnecessary and that $C2/c$ is the correct space group. Both the extra oxygen atoms were then included (one with 50% occupation) together with the hydrogen atoms in the next structure-factor calculation for which R was 0.094. All non-hydrogen atoms were then allowed to assume anisotropic thermal parameters during several further rounds of least-squares calculations which brought the refinement to convergence at R 0.074.

The structure of form (2) was solved by the heavy-atom method. Atomic positional and thermal parameters, at first isotropic and subsequently anisotropic, were then refined by full-matrix least-squares calculations to R 0.099. Inclusion of hydrogen atoms at their calculated positions further reduced R to 0.096. After several additional rounds of least-squares calculations, during which only the parameters of the non-hydrogen atoms were varied, the refinement converged at R 0.052. A difference electron-density distribution showed no unusual features.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths

	C_i molecular symmetry		
	(1)	(2)	mean [a]
Mo(1)–S(A1)	2.692(5)	2.694(2)	2.693(5)
Mo(1)–S(A3)	2.483(5)	2.480(2)	2.482(5)
Mo(1)–S(B1)	2.513(4)	2.527(2)	2.520(4)
Mo(1)–S(B3)	2.438(5)	2.436(2)	2.437(2)
Mo(1)–μ-O(1)	1.863(1)	1.854(1)	1.859(1)
Mo(1)–O(2)	1.691(14)	1.669(6)	1.680(14)
	C_2 molecular symmetry		
	(1) unprimed	(2) primed	mean [a]
Mo(2)–S(C1)	2.678(5)	2.673(5)	2.676(5)
Mo(2)–S(C3)	2.494(4)	2.496(5)	2.495(5)
Mo(2)–S(D1)	2.514(5)	2.499(5)	2.507(5)
Mo(2)–S(D3)	2.453(4)	2.446(6)	2.450(6)
Mo(2)–μ-O(3)	1.875(14)	1.874(14)	1.875(14)
Mo(2)–O(4)	1.686(13)	1.685(13)	1.686(13)

(*b*) Valency angles

	C_i molecular symmetry		
	(1)	(2)	mean [a]
S(A1)–Mo(1)–S(A3)	67.9(2)	67.9(1)	67.9(2)
S(A1)–Mo(1)–S(B1)	81.7(2)	82.3(1)	82.0(2)
S(A1)–Mo(1)–S(B3)	91.8(2)	88.4(1)	90.1(2)
S(A1)–Mo(1)–μ-O(1)	83.4(1)	84.6(1)	84.0(1)
S(A1)–Mo(1)–O(2)	156.3(5)	160.0(2)	158.2(5)
S(A3)–Mo(1)–S(B1)	97.0(2)	97.6(1)	97.3(2)
S(A3)–Mo(1)–S(B3)	158.2(2)	155.3(1)	156.8(2)
S(A3)–Mo(1)–μ-O(1)	96.1(1)	94.3(1)	95.2(1)
S(A3)–Mo(1)–O(2)	89.1(5)	93.2(2)	91.2(5)
S(B1)–Mo(1)–S(B3)	71.3(1)	71.2(2)	71.3(2)
S(B1)–Mo(1)–μ-O(1)	154.7(1)	157.5(1)	156.1(1)
S(B1)–Mo(1)–O(2)	96.6(5)	94.3(2)	95.5(5)
S(B3)–Mo(1)–μ-O(1)	89.0(1)	90.3(1)	89.7(1)
S(B3)–Mo(1)–O(2)	110.1(5)	109.3(2)	109.7(5)
μ-O(1)–Mo(1)–O(2)	105.2(5)	104.1(2)	104.7(5)
Mo(1)–S(A1)–C(A2)	84.9(6)	85.2(3)	85.1(6)
Mo(1)–S(A3)–C(A2)	91.1(6)	91.6(3)	91.4(6)
Mo(1)–S(B1)–C(B2)	85.9(5)	86.4(2)	86.2(5)
Mo(1)–S(B3)–C(B2)	89.1(6)	88.9(3)	89.0(6)
Mo(1)–μ-O(1)–Mo(1″) [b]	180.0(—)	180.0(—)	180.0(—)
	C_2 molecular symmetry		
	(1) unprimed	(1) primed	mean [a]
S(C1)–Mo(2)–S(C3)	67.8(1)	67.3(1)	67.6(1)
S(C1)–Mo(2)–S(D1)	82.7(2)	80.9(2)	81.8(2)
S(C1)–Mo(2)–S(D3)	90.2(2)	95.2(2)	92.7(2)
S(C1)–Mo(2)–μ-O(3)	85.8(4)	83.8(4)	84.8(4)
S(C1)–Mo(2)–O(4)	157.5(5)	154.7(4)	156.1(5)
S(C3)–Mo(2)–S(D1)	94.8(2)	91.3(2)	93.1(2)
S(C3)–Mo(2)–S(D3)	155.6(2)	157.6(2)	156.6(2)
S(C3)–Mo(2)–μ-O(3)	97.3(4)	100.8(4)	99.1(4)
S(C3)–Mo(2)–O(4)	90.4(5)	87.6(4)	89.0(5)
S(D1)–Mo(2)–S(D3)	71.0(1)	71.4(2)	71.2(2)
S(D1)–Mo(2)–μO(3)	158.8(4)	155.0(5)	156.9(5)
S(D1)–Mo(2)–O(4)	93.9(5)	97.2(4)	95.6(5)
S(D3)–Mo(2)–μ-O(3)	91.3(4)	90.6(4)	91.0(4)
S(D3)–Mo(2)–O(4)	109.8(5)	108.2(5)	109.0(5)
μ-O(3)–Mo(2)–O(4)	103.3(6)	105.0(6)	104.2(6)
Mo(3)–S(C1)–C(C2)	85.7(7)	86.9(6)	86.3(7)
Mo(3)–S(C3)–C(C2)	91.7(7)	92.4(6)	92.1(7)
Mo(3)–S(D1)–C(D2)	86.9(7)	88.2(6)	87.6(7)
Mo(3)–S(D3)–C(D2)	88.0(6)	87.9(6)	88.0(7)
Mo(2)–μ-O(3)–Mo(2′)		172.2(9)	

TABLE 2 (*Continued*)

(*c*) Intermolecular separations <3.70 Å between the non-hydrogen atoms

(*i*) Compound (1)

O(W1) · · · O(W2$^{\mathrm{I}}$)	2.43	C(C8) · · · O(4$^{\mathrm{II}}$)	3.51
O(4′) · · · C(B8$^{\mathrm{I}}$)	3.30	O(4′) · · · C(B7$^{\mathrm{I}}$)	3.56
O(2) · · · C(A5$^{\mathrm{II}}$)	3.32	O(4′) · · · C(B5$^{\mathrm{IV}}$)	3.60
O(2) · · · C(A6$^{\mathrm{II}}$)	3.36	C(C′6) · · · C(C′7$^{\mathrm{III}}$)	3.62
O(4) · · · C(B7$^{\mathrm{I}}$)	3.36	C(D′8) · · · C(D7$^{\mathrm{III}}$)	3.62
C(C7) · · · O(4$^{\mathrm{II}}$)	3.37	S(D1) · · · S(D1$^{\mathrm{VI}}$)	3.66
O(4′) · · · C(B6$^{\mathrm{IV}}$)	3.41	S(C′1) · · · C(C′6$^{\mathrm{III}}$)	3.67
C(D′7) · · · O(2$^{\mathrm{V}}$)	3.43	O(4) · · · S(B1$^{\mathrm{III}}$)	3.68
C(D′8) · · · O(2$^{\mathrm{V}}$)	3.44		

(*ii*) Compound (2)

C(A7) · · · O(2$^{\mathrm{VII}}$)	3.32	O(2) · · · C(B6$^{\mathrm{II}}$)	3.47
C(A8) · · · O(2$^{\mathrm{VII}}$)	3.33		

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

I	x, y, z	V	$\frac{1}{2} + x, \frac{1}{2} + y, z$
II	$x, 1 + y, z$	VI	$-x, y, \frac{1}{2} - z$
III	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	VII	$x, y, 1 + z$
IV	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$	VIII	$-x, 1 - y, -z$

[a] Estimated standard deviations (e.s.d.s) quoted in parentheses for the mean of two dimensions are the larger of those for the individual values. Estimated standard deviations quoted in parentheses for the mean of several values are given by e.s.d. = $[\sum_{i=1}^{n}(x_i - \bar{x})^2/(n - 1)]^{\frac{1}{2}}$, where n = number of values of x_i and $\bar{x}$ is the mean. [b] Mo(1″) is related to Mo(1) by the centre of symmetry.

Final atomic positional parameters for the non-hydrogen atoms of forms (1) and (2) are in Table 1. Calculated hydrogen-atom positions and anisotropic thermal parameters for the non-hydrogen atoms, with Tables of observed and calculated structure amplitudes, ligand dimensions, and selected least-squares planes, are available as Supplementary Publication No. SUP 22463 (53 pp.).†

Neutral-atom scattering factors used in all the structure-factor calculations were taken from ref. 11 for the non-hydrogen atoms, and from ref. 12 for hydrogen; those of Mo and S were corrected for the effects of anomalous dispersion.[13] In the least-squares calculations, $\Sigma w\Delta^2$ was minimised with weights, w, being assigned according to the scheme $w^{\frac{1}{2}} = 1$ for $|F_o| \leqslant K$ and $K/|F_o|$ for $|F_o| > K$ [K = 190.0 for form (1) and 28.0 for (2)]. The adequacy of these weighting schemes was demonstrated by the fact that they gave no systematic dependence of $\langle w\Delta^2 \rangle$ on $|F_o|$.

E.S.R. Spectra.—E.s.r. spectra at room temperature and 150 K were recorded as previously described [14] on single crystals of (1). The crystallographic axes of crystals (*ca.* 0.2 × 0.2 × 0.7 mm) were located by X-ray techniques and the crystals mounted such that the magnetic field could be orientated in the crystallographic a^*b, bc, and a^*c planes. The e.s.r. spectrum of a solution of (1) in dry chloroform was also recorded at room temperature.

RESULTS AND DISCUSSION

The results of the single-crystal X-ray determinations indicate (see below) that the major component, of the sample formed by allowing a mixture of $MoCl_3O$ and $Na[S_2CNEt_2]$ (1 : 3) in dry CH_2Cl_2 to evaporate in a dry-box, has the (probable) composition $[H_5O_2]^+[Mo_2O_3(S_2CNEt_2)_4]^-\cdot 2[Mo_2O_3(S_2CNEt_2)_4]$. The minor con-

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

stituent is [$Mo_2O_3(S_2CNEt_2)_4$]. Interatomic distances and angles are listed in Table 2.

Crystal and Molecular Structure.—Crystals of (1) contain two crystallographically distinct types of discrete [$MoO(S_2CNEt_2)_2]_2O$ units. The co-ordination geometry about the molybdenum atoms in these dimers is shown in Figure 1 and the packing of these units in the crystal is illustrated in Figure 2. Each unit cell contains twelve [$MoO(S_2CNEt_2)_2]_2O$ moieties; for four of these (C_i type) the bridging oxygen atom is situated on a crystallographic centre of symmetry and the other eight (C_2 type) have an approximate two-fold axis which passes through the bridging oxygen atom [μ-O(3)] and bisects the O(4) • • • O(4′) line joining the terminal oxygen atoms. The central portions of these dimers closely resemble that in the diamagnetic compounds [$Mo_2O_3L_4$] [L = $S_2P(OEt)$,[3a] S_2COEt,[3b] or S_2CNPr_2 [3c]]. In the C_2-type dimers the Mo(2)–O(3)–Mo(2′) angle [172.4(9)°] clearly departs significantly from linearity, whereas the high estimated standard deviation associated with the results of the [$Mo_2O_3(S_2COEt)_4$] investigation [178(4)°] precluded such a conclusion. This folding of the Mo–O–Mo bridging angle within the [$MoO(S_2CNEt_2)_2]_2O$ molecules is accompanied by a small, but possibly significant, lengthening of the Mo–O bridging bonds and by a small rotation of the terminal oxygen atoms away from an exactly eclipsed conformation, the O(4)–Mo(2)–Mo(2′)–O(4′) torsion angle being −5.5(7)°. All of these effects serve to increase the distance between the terminal oxygen atoms in these dimers.

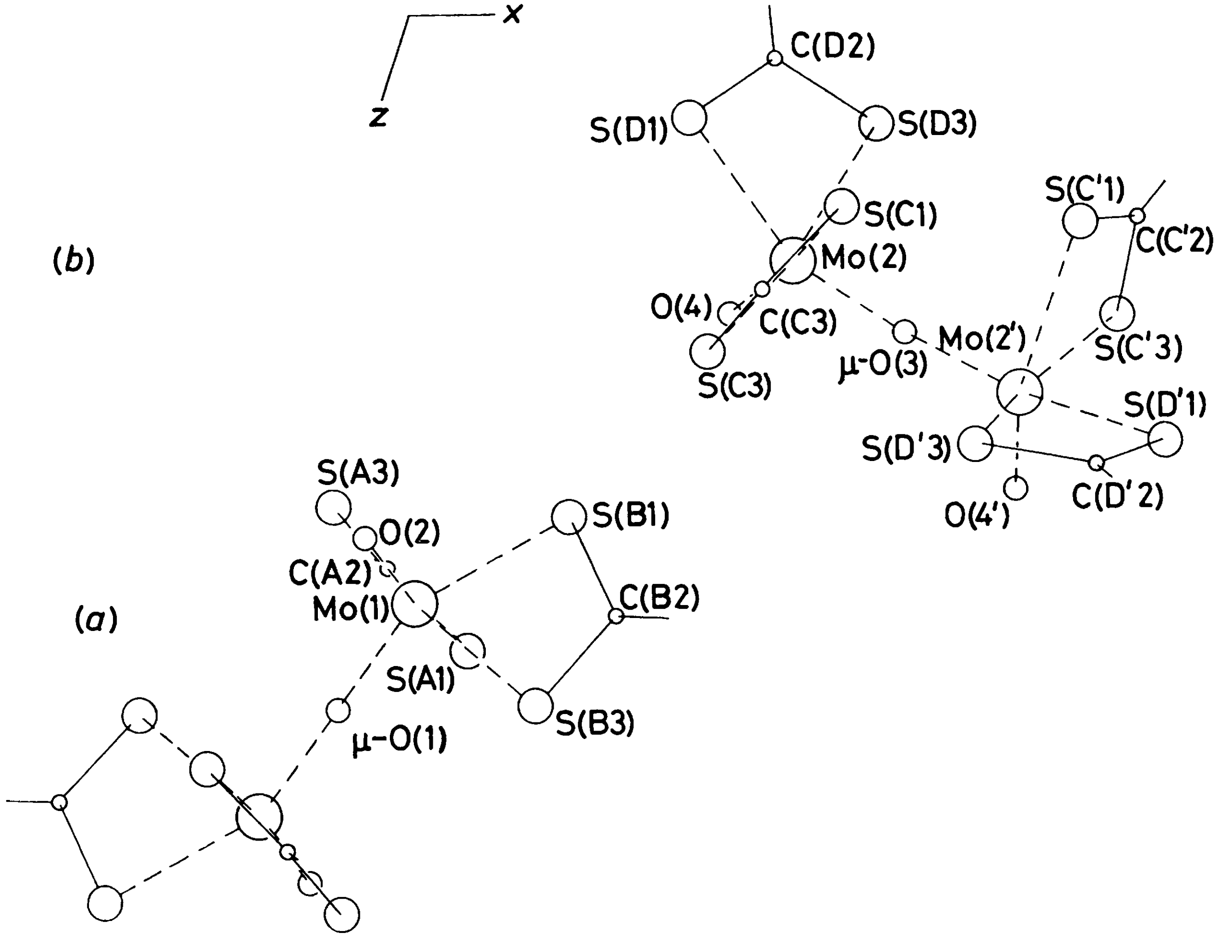

FIGURE 1 Molybdenum atom co-ordination in (*a*) the C_i-type, and (*b*) the C_2-type [$MoO(S_2CNEt_2)_2]_2O$ dimers in crystals of form (1)

Each unit cell of (1) also contains four pairs of oxygen atoms, O(W2) being placed on a crystallographic two-fold axis, whilst O(W1) is disordered over two crystallographically related sites (see Experimental section). The O(W1) • • • O(W2) separation was calculated to be 2.43 Å, although a separation in the range 2.30—2.65 Å would be compatible with the observed data. The maximum separation is shorter than the oxygen–oxygen distance in hydrogen-bonded water molecules (range 2.70—2.80 Å),[15] suggesting that these oxygen atoms do not belong to a pair of hydrogen-bonded water molecules. We have considered two alternative assignments for O(W1) and O(W2), namely that they could belong to either [H_3O_2]$^-$ or [H_5O_2]$^+$. The [H_5O_2]$^+$ ion has been characterised in a number of systems, and the observed oxygen–oxygen separations (range 2.414—2.60 Å) [15,16] are comparable with those found in the present study. On the other hand, $[H_3O_2]^-$ has not been structurally characterised in the solid state, the best approximation being water molecules hydrogen bonded to hydroxide ions which are co-ordinated to metal ions. Such systems give oxygen–oxygen separations (range 2.64—2.80 Å)[17] that are greater than those in the present study. For these reasons we formulate (1) as $[H_5O_2]^+[Mo_2O_3(S_2CNEt_2)_4]^-\cdot 2[Mo_2O_3(S_2CNEt_2)_4]$. Half of the C_2-type dimers are then presumed to be the dimeric anion, since the $[H_5O_2]^+$ ion is closer to these sites than to those of the C_i-type dimers. Any lack of distinction in structural dimensions between $[Mo_2O_3(S_2CNEt_2)_4]$ and $[Mo_2O_3(S_2CNEt_2)_4]^-$ is consistent with the general similarity in the structural details observed for equivalent units of molybdenum-(IV), -(V), and -(VI) compounds.[18]

Triclinic crystals of (2) comprise only discrete C_i-type $[MoO(S_2CNEt_2)_2]_2O$ dimers which are arranged crystallographically as shown in Figure 3.

The co-ordination geometries about the three crystallographically independent molybdenum atoms in form (1) and the molybdenum in form (2) are very similar. The sulphur atoms from two bidentate S_2CNEt_2 ligands and two *cis* oxygen atoms (one terminal and one bridging) are arranged in a distorted octahedral manner around the molybdenum so that all the X–Mo–Y angles involving *trans*-related X and Y ligand atoms lie in the range 154.7(1)—160.0(2)°. A comparison of the deviations of atoms from least-squares planes through the two most nearly coplanar groups of four atoms in the molybdenum co-ordination sphere reveals significant differences between corresponding individual displacements in both halves of the C_2-type dimers; a similar situation exists in the C_i-type dimers of forms (1) and (2). Electronic factors could be responsible for these variations within the dimer types, but they may also arise from differences in crystal-packing forces which produce slightly different mutual orientations of the pairs of $SCNEt_2$ ligands associated with each molybdenum atom.

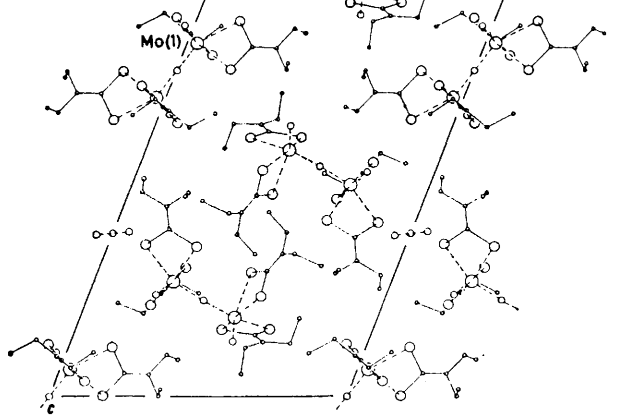

FIGURE 2 Packing arrangement in crystals of form (1), viewed in projection along the *b* axis

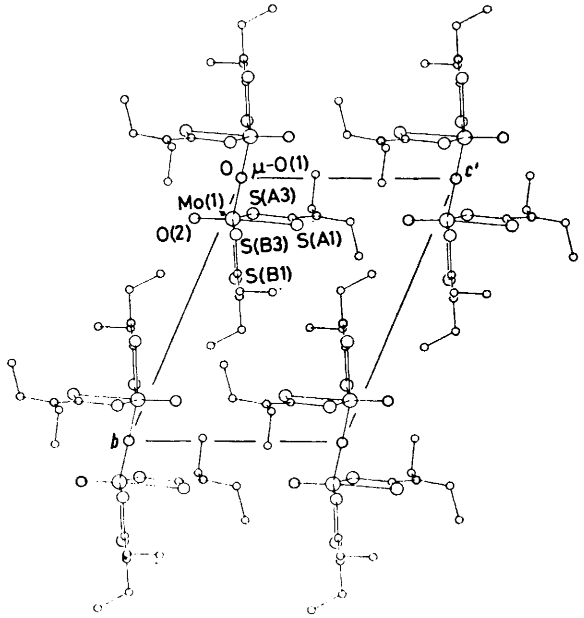

FIGURE 3 Packing of $[MoO(S_2CNEt_2)_2]_2O$ C_i-type dimers in crystals of form (2), viewed in projection along the *a* axis

Corresponding bond lengths and valency angles at the molybdenum atoms in both types of dimer agree very well and they are also in accord with those derived for other molybdenum(V) dimers in earlier studies.[3] The mean Mo–O(terminal) bond lengths [1.686(13) in the C_2-type and 1.680(14) Å in the C_i-type dimers] do not differ significantly and are also comparable to those of 1.672(15) and 1.668(5) Å at six-co-ordinate molybdenum in the discrete $[MoOCl_4(OH_2)]^-$ (ref. 19) and $[MoO(OH_2)(CN)_4]^{2-}$ ions.[20] These short bond lengths imply extensive amounts of d_π–p_π Mo–O bonding in these species, giving rise to a multiple bond order which is diminished slightly from that in $[MoOCl_4]^-$ [1.610(10) Å][21] by the presence of *trans* ligands. The mean of the Mo–O bridging bonds in the C_2-type dimers [1.875(14) Å] may be slightly elongated over that in the C_i-type dimers [1.859(1) Å] as a consequence of the O(4) $\cdots$ O(4') eclipsing interaction in the former. These distances and the linearity or near linearity of the Mo–O–Mo bridging angles are consistent with a significant amount of multiple-bond character in these bridges.

The Mo–S distances vary according to the nature of the *trans* ligand. Thus, the longest Mo–S distances [mean 2.676(5) in the C_2-type and 2.693(5) Å in the C_i-type dimers] occur *trans* to the Mo–O(terminal) bond, a feature which is typical of oxomolybdenum compounds.[18] The next-to-longest Mo–S bond involves the sulphur atom which lies *trans* to the multiple Mo–O bridging bond, and the slightly shorter mean length [2.507(5) Å] in the C_2-type dimers compared with that [2.520(4) Å] in the C_i-type dimers may reflect the slight lengthening (and presumed weakening) of the bridging bond in the former due to the O(4) ··· O(4′) repulsions. The lengths of the remaining two mutually *trans* Mo–S bonds are unequal in each molecule [2.495(5) and 2.450(6) Å in the C_2-type dimers, and 2.482(5) and 2.437(2) Å in the C_i-type dimers].

The dimensions and conformations of the S_2CNEt_2 ligands show no unusual features. In all cases the molybdenum atom lies close (Δ 0.021 to 0.244 Å) to the least-squares planes through the approximately planar delocalised S_2CNC_2 moieties, and the methyl groups adopt the most favourable *trans* conformation.[22] Mean bond lengths in the ligands are in good agreement with those from other studies of dithiocarbamato-compounds: S–C 1.72(2), C–N 1.32(2), N–C 1.48(2), and C–C 1.50(3) Å.

E.S.R. Spectra.—E.s.r. measurements on single crystals of (1) and (2) showed (1) to have a well characterised spectrum whilst (2) exhibited only an extremely weak, ill defined, absorption, and it was therefore considered to be effectively e.s.r. inactive. The e.s.r. spectrum of crystallographically characterised single crystals of (1) showed two distinct signals, attributable to an electron associated with a molybdenum atom, at all orientations in the crystallographic *a*c* plane. In the *a*b* and *bc* planes the spectra showed four partially overlapping signals at certain orientations. At the *b* axis all of the signals became equivalent, whereas at each of the *a** and *c* axes there were two distinct sets of signals. The magnetic fields corresponding to the *g*-value resonances are given in Figure 4. Molybdenum hyperfine splittings were observed at some orientations, particularly when the magnetic field was parallel to the crystallographic axes and also in the *a*c* plane where the spectra were simplest. At the *b* axis the hyperfine splitting consisted of six equally spaced lines (Δ*H* 26 G),† characteristic of an electron interacting with a single molybdenum centre. Increasing the gain of our spectrometer did not reveal the characteristic hyperfine pattern attributable to an electron interacting with two equivalent molybdenum nuclei. Also, cooling the crystals to 150 K did not improve the resolution, the only change being an approximate four-fold increase in intensity compared with that at room temperature. When the magnetic field was parallel to the *a** or *c* axes again a six-line hyperfine splitting pattern on each of the *g*-value resonances was observed. At the *a** axis the hyperfine splitting was 29 G associated with the low-field line and 59 G associated with the high-field line. At the *c* axis the corresponding values were 28 and 58 G respectively. Because of the overlapping spectra we have been unable to measure a sufficient number of hyperfine splittings, particularly in the *bc* and *a*b* planes, to make a complete analysis.

In the light of the above e.s.r. behaviour and the crystallographic data, the e.s.r. spectra are assigned to a $[Mo_2O_3(S_2CNEt_2)_4]^-$ ion containing one unpaired electron. On this basis the e.s.r. data from Figure 4 have been treated by Schonland's method[23] to give the principal molecular *g* values and their direction cosines shown in Table 3. Unfortunately these direction cosines do not allow us to assign unambiguously the principal molecular *g* values to any particular molecular centre, since, as we have found in other molybdenum(V) compounds of low symmetry,[24] they do not coincide with any metal-ligand directions. This means that the e.s.r. data do not locate the $[Mo_2O_3(S_2CNEt_2)_4]^-$ ions in the unit cell. The observed angular variation of the e.s.r. spectrum and the hyperfine pattern due to the electron interacting with only a single molybdenum centre are compatible with the previous suggestion that the dimeric anion occupies the C_2-type sites, but only if the unpaired electron is *localised* on one molybdenum atom in the dimer. The dimeric anion must then be randomly distributed over all of the C_2-type sites. Alternatively, if, owing to the small size of the crystals obtained in this

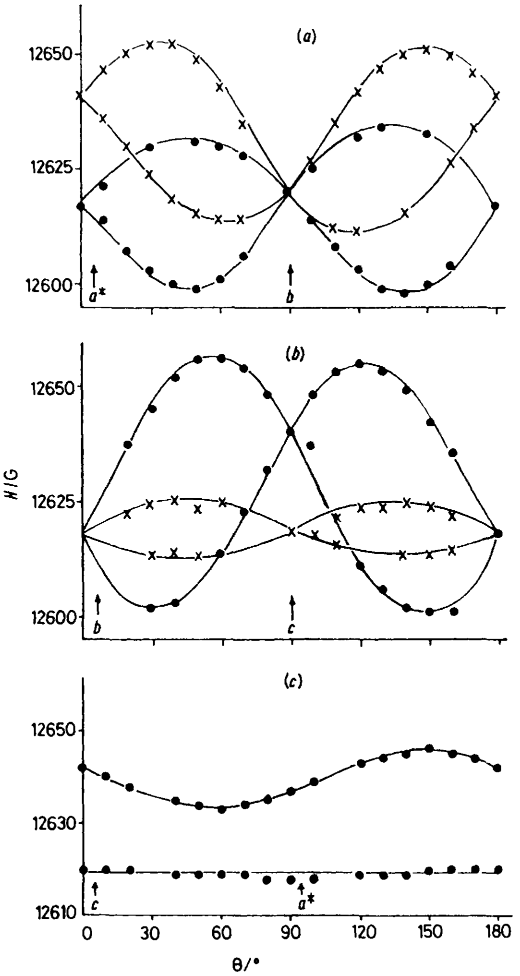

FIGURE 4 Angular variation of the *g*-value resonances for (1) at ν = 34 980 MHz: (*a*) *a*b*, (*b*) *bc*, and (*c*) *a*c* plane

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† Throughout this paper: 1 G = 10^{-4} T.

study, we have failed to detect the hyperfine pattern due to the electron interacting with the two equivalent molybdenum atoms, then the angular variation of the e.s.r. spectrum means that the dimeric anion must be randomly distributed over both the C_2- and C_i-type sites.

TABLE 3

Principal molecular *g* values and direction cosines of the two molybdenum centres

	Alternative (1)		
g	direction cosine with respect to		
	a *	*b*	*c*
Centre (1)			
1.975	−0.338 1	0.609 4	−0.717 2
1.977	0.863 4	−0.102 4	−0.494 1
1.984	−0.374 5	−0.786 2	−0.491 5
	Alternative (2)		
1.976	0.509 0	−0.553 1	0.659 0
1.978	−0.808 8	−0.469 3	0.586 3
0.984	−0.293 3	−0.831 8	−0.471 2
Centre (2) *			
1.978	0.668 9	−0.700 5	0.248 8
1.981	0.321 7	−0.028 9	−0.946 4
1.984	0.670 1	0.713 1	0.206 0

* Because of the invariance of the resonance position in the *a*c* plane, the method of interpretation gives only one set of *g* values and direction cosines for this centre.

We have also considered the possibility that the e.s.r. signals in this system could arise from the presence of a monomeric molybdenum(V) impurity. However, we rule this out for the following reasons. Given the method of preparation, the most probable impurities would be $[MoOCl(S_2CNEt_2)_2]$, $[MoO(S_2CNEt_2)_3]$, and $[Mo(S_2CNEt_2)_4]^+$. The first of these can be eliminated since separate single-crystal studies[25] give the principal molecular *g* values as 1.945, 1.958, and 1.984; two of these values are clearly different from those found in the present study. The other two systems cannot be eliminated by single-crystal studies, since their principal molecular *g* values are very similar to those found for the present system. However, their e.s.r. behaviour in $CHCl_3$ solution is different from that found for the present dimer system. For $[MoO(S_2CNEt_2)_3]$ we find a signal with $g_{iso.} = 1.980$ and $a_{iso.} = 34.8 \times 10^{-4}$ cm^{-1}, and for $[Mo(S_2CNEt_2)_4]^+$ a signal with $g_{iso.} = 1.980$ and $a_{iso.} = 34.5 \times 10^{-4}$ cm^{-1}. The present dimeric system upon dissolution in chloroform gave two sets of signals, $g_{iso.} = 1.967$ and $a_{iso.} = 42.1 \times 10^{-4}$ cm^{-1}, and $g_{iso.} = 1.964$ and $a_{iso.} = 38.3 \times 10^{-4}$ cm^{-1}. Initially, the latter signal is more intense than the former, but these relative intensities are reversed with time. Therefore, it would appear that the present dimeric system reacts with chloroform, whereas, over a similar period of time, no reaction was observed between chloroform and $[MoO(S_2CNEt_2)_3]$ or $[Mo(S_2CNEt_2)_4]^+$.

Although mixed-oxidation-state (Mo^V–Mo^{IV}) dimers have been proposed on the basis of electrochemical reduction of molybdenum(V) dimers,[26] this study appears to be the first case in which such a species has been isolated. These observations could have important implications for the state of molybdenum in certain molybdenum-containing enzymes such as xanthine oxidase, aldehyde oxidase, sulphite oxidase, and nitrate reductase. These enzymes are usually considered to contain two molybdenum atoms per active unit,[27] whereas e.s.r. signals obtained from them are usually interpreted in terms of mononuclear molybdenum centres.[28] The present study indicates that e.s.r. signals which appear to belong to a mononuclear molybdenum(V) centre may indeed be obtained from binuclear molybdenum centres containing one unpaired electron.

Crystallographic calculations were performed on an IBM 370/165 computer located at the Triangle Universities Computation Centre, Research Triangle Park, North Carolina, and were supported by a grant of computer time from Duke University. 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.

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