angles in Table 3,* the numbering schemes are shown in Figs. 1 and 2, Figs. 3 and 4 are packing diagrams for compounds (I) and (II) respectively.

Related literature. The bis copper(II) complex of unprotonated daes, $Cu(daes)_2(NO_3)_2$, has been reported by Boeyens, Dobson & Hancock, (1985). In compound (I), the Cu—S bond length of 2·300 (2) Å is similar to the mean Cu—S bond length of 2·303 Å found in the structure of bis(3,6-dithiaoctane)copper-(I) tetrafluoroborate and falls in the range found for Cu^I—S bond lengths in tetrahedral complexes (2·30–2·34 Å) (Baker & Norris, 1977).

The compound $Cu(dien)(SCN)_2$ (Cannas, Carta & Marongiu, 1974) is square pyramidal with dien having a meridional coordination and the Cu—N bond lengths are about 0·03 Å longer than the corresponding Cu—N bond lengths in compound (II) which is a square planar complex. The tetrasubstituted Et_4dien coordinates via one axial and two equatorial sites to the Cu atom in the trigonal bi-

pyramidal $Cu(Br)N_3(Et_4dien)$ complex (Ziolo, Allen, Titus, Gray & Dori, 1972). In this complex the Cu—Br bond length [2·586 (1) Å] is longer than the Cu—Br(1) bond length of 2·395 (2) Å found in compound (II). The distance between Br(2) and Cu, 3·12 Å, is similar to the Cu···Br distance [3·130 (5) Å] found in Cu(1,11-diamino-3,6,9-trithiaundecane)Br by Drew, Rice & Richards (1980).

References

BAKER, E. N. & NORRIS, G. E. (1977). *J. Chem. Soc. Dalton Trans.* pp. 877–882.

BOEYENS, J. C. A., DOBSON, S. M. & HANCOCK, R. D. (1985). *Inorg. Chem.* **24**, 3073–3076.

CANNAS, M., CARTA, G. & MARONGIU, G. (1974). *J. Chem. Soc. Dalton Trans.* pp. 553–555.

DREW, M. G. B., RICE, D. A. & RICHARDS, K. M. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2503–2508.

HAMILTON, W. C. & IBERS, J. A. (1974). Editors. *International Tables for X-ray Crystallography*, Vol. IV, pp. 99, 140. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

NORTH, A. C. T., PHILIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

TAYLOR, L. T. & BAREFIELD, E. K. (1969). *J. Inorg. Nucl. Chem.* **31**, 3831–3839.

ZIOLO, R. F., ALLEN, M., TITUS, D. D., GRAY, H. B. & DORI, Z. (1972). *Inorg. Chem.* **11**, 3044–3050.

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53315 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A Redetermination of the Structure of Diethylenetriaminetrioxomolybdenum(VI)

By Pascual Román,* Antonio Luque and Juan M. Gutiérrez-Zorrilla

Departamento de Química Inorgánica, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

Abstract. $[Mo(C_4H_{13}N_3)O_3]$, $M_r = 247·11$, orthorhombic, *Pbcm*, $a = 6·890$ (1), $b = 10·248$ (2), $c = 11·691$ (2) Å, $V = 825·5$ (3) Å^3, $Z = 4$, $D_m = 1·99$ (1), $D_x = 1·99$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 15·19$ cm^{-1}, $T = 295$ K, $F(000) = 496$, $R = 0·026$, $wR = 0·031$ for 2203 observed unique reflections with $I > 3\sigma(I)$. The Mo atom has a distorted octahedral coordination geometry and it is bonded strongly to three O atoms [mean Mo—O = 1·75 (1) Å], but only weakly to the diethylenetriamine N atoms [mean Mo—N = 2·32 (1) Å]. The structure consists of $[Mo(C_4H_{13}N_3)O_3]$ units linked by hydrogen bonds of type N—H···O.

Experimental. Diethylenetriaminetrioxomolybdenum(VI), $Mo(dien)O_3$, was obtained by mixing aqueous solutions of diethylenetriammonium heptamolybdate trihydrate (Román, Luque, Gutiérrez-Zorrilla & Zúñiga, 1990) and molybdenum trioxide to a final pH of 5·5. After three weeks at room temperature, pale yellow plate crystals were isolated; they were washed with water and ether and stored in a desiccator with calcium chloride. The density was measured by flotation in $CHBr_3/CCl_4$ (Román & Gutiérrez-Zorrilla, 1985). A crystal with approximate dimensions $0·30 \times 0·20 \times 0·15$ mm was analyzed at 295 K with an Enraf–Nonius CAD-4 diffractometer, utilizing graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters were obtained from a least-

---

* To whom correspondence should be addressed.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Mo	0·05680 (2)	0·01971 (1)	0·25000	0·0169 (1)
O(1)	0·2224 (2)	0·1480 (2)	0·2500	0·0302 (9)
O(2)	0·1097 (2)	-0·0780 (1)	0·3688 (1)	0·0277 (6)
N(1)	-0·2517 (2)	-0·0714 (1)	0·2500	0·0227 (7)
C(2)	-0·3582 (2)	-0·0406 (2)	0·3562 (1)	0·0299 (8)
C(3)	-0·3369 (2)	0·1025 (2)	0·3876 (1)	0·0310 (8)
N(4)	-0·1308 (2)	0·1395 (1)	0·3776 (1)	0·0233 (5)
H(11)	-0·232 (7)	-0·160 (4)	0·250	0·011 (7)
H(21)	-0·490 (7)	-0·062 (4)	0·345 (4)	0·025 (8)
H(22)	-0·303 (7)	-0·092 (5)	0·411 (5)	0·030 (9)
H(31)	-0·382 (8)	0·118 (5)	0·460 (5)	0·033 (9)
H(32)	-0·415 (6)	0·144 (4)	0·339 (4)	0·023 (8)
H(41)	-0·082 (6)	0·119 (4)	0·445 (3)	0·018 (7)
H(42)	-0·123 (5)	0·221 (3)	0·367 (3)	0·016 (6)

Table 2. *Selected bond distances (Å) and angles (°), and hydrogen contacts for* Mo(dien)O_3

Mo—O(1)	1·741 (2)	N(1)—H(11)	0·91 (4)
Mo—O(2)	1·750 (1)	C(2)—H(21)	0·94 (5)
Mo—N(1)	2·321 (2)	C(2)—H(22)	0·91 (5)
Mo—N(4)	2·325 (1)	C(3)—H(31)	0·92 (5)
N(1)—C(2)	1·476 (2)	C(3)—H(32)	0·89 (4)
C(2)—C(3)	1·519 (2)	N(4)—H(41)	0·88 (4)
C(3)—N(4)	1·475 (2)	N(4)—H(42)	0·85 (3)

O(1)—Mo—O(2)	107·20 (4)	O(2)—Mo—N(4)	84·75 (4)
O(2)—Mo—O(2')*	105·04 (3)	O(2)—Mo—N(1)	87·73 (4)
N(1)—Mo—N(4)	72·75 (3)	N(1)—C(2)—C(3)	111·2 (1)
N(4)—Mo—N(4')	79·93 (4)	N(4)—C(3)—C(2)	108·8 (1)
O(1)—Mo—N(4)	88·02 (3)	C(2)—N(1)—C(2')	114·5 (1)

A—H···O	Site of O	A—H	A···O	H···O	∠A—H···O
N(1)—H(11)···O(1)	$-x, -\frac{1}{2}+y, z$	0·91 (5)	2·883 (2)	1·97 (4)	174 (3)
N(1)—H(11)···O(1)	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$	0·91 (5)	2·883 (2)	1·97 (4)	174 (3)
N(4)—H(41)···O(2)	$-x, -y, 1-z$	0·88 (4)	3·034 (1)	2·23 (4)	152 (3)
N(4)—H(42)···O(2)	$-x, \frac{1}{2}+y, z$	0·85 (3)	2·901 (2)	2·06 (3)	170 (3)

* Primed atoms are related to their unprimed equivalents by the symmetry operation: $x, y, \frac{1}{2} - z$.

squares fitting of the setting angles for 25 reflections with $8 \le \theta \le 13°$. The $\omega/2\theta$ scan mode was used, data were collected for $2\theta \le 80°$; index range $0 \le h \le 12$, $0 \le k < 18$, $0 \le l \le 21$. Two control reflections ($\bar{1}13$, $\bar{2}12$) were monitored every 100 reflections. No crystal decay was observed. 2651 unique reflections were measured, 2203 with $I > 3\sigma(I)$ were used in the refinement. Data were corrected for Lorentz and polarization effects. The position of the molybdenum atom was located in a Patterson map, the remaining non-H atoms of the structure were located in subsequent Fourier syntheses. An empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to data refined with isotropic displacement parameters; the min./max. corrections were 0·74/1·21. The structure was then refined anisotropically on F. H atoms were located from $\Delta\rho$ maps and were refined isotropically. A weighting scheme of the type $w = w_1.w_2$ with $w_1 =$

$k_1/(a + b|F_o|)^2$ and $w_2 = k_2/[c + d\sin\theta/\lambda + e\sin^2\theta/\lambda]^2$ was used to obtain flat dependence in $\langle w\Delta^2F \rangle$ vs $\langle F_o \rangle$ and vs $\langle \sin\theta/\lambda \rangle$ (Martínez-Ripoll & Cano, 1975); the coefficients used were $k_1 = 0·40$; $k_2 = 1·01$; $a = 1·02$; $b = -0·17$ for $|F_o| < 8$; $a = 0·22$; $b = 0·02$ for $8 < |F_o| < 34$; $a = 1·49$; $b = -0·05$ for $|F_o| > 34$; $c = 35·25$; $d = -136·93$; $e = -134·93$ for $\sin\theta/\lambda < 0·56$; $c = 0·34$; $d = 0·16$; $e = 0·00$ for $\sin\theta/\lambda > 0·56 \text{ Å}^{-1}$. Final refinement with 82 parameters gave the discrepancy indices $R = 0·026$, $wR = 0·031$, $S = 1·45$, $(\Delta/\sigma)_{max} = 0·04$, $\Delta\rho_{max} = 0·89$, $\Delta\rho_{min} = -0·70 \text{ e Å}^{-3}$. Neutral atoms scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Most calculations
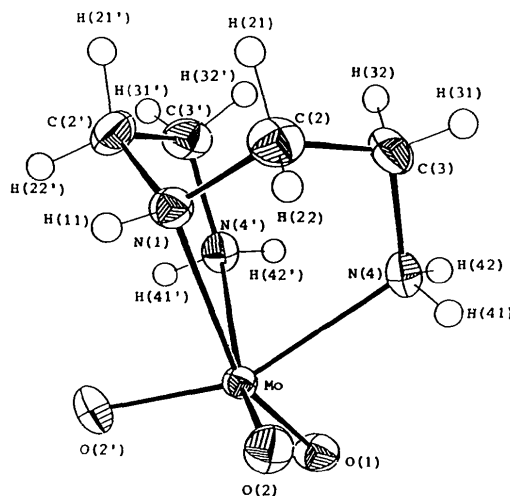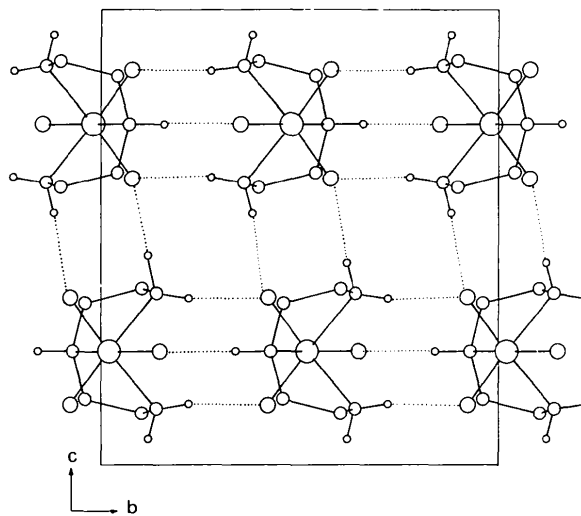

Fig. 1. View of diethylenetriaminetrioxomolybdenum(VI) with atom labelling.

Fig. 2. The crystal packing of $[\text{Mo(C}_4\text{H}_{13}\text{N}_3)\text{O}_3]$ along the a axis. Hydrogen bonds are indicated by dotted lines.

were carried out using the *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) running on a MicroVAX II computer. Atomic coordinates and equivalent isotropic temperature factors are given in Table 1,* selected bond lengths and angles and hydrogen contacts for Mo(dien)O₃ are listed in Table 2. The atomic arrangement is built up by [Mo(C₄H₁₃N₃)O₃] units. Fig. 1 shows the atomic numbering scheme used for diethylenetriamine-trioxomolybdenum(VI). A projection of the unit-cell content on (100) is given in Fig. 2. The Mo atom is octahedrally coordinated to three O atoms and three N atoms. Hydrogen bonds of type N—H···O connect neighbouring molecules.

Related literature. During the methodical study of the system MoO_3–dien in aqueous solution various compounds have been found; one is the diethylene-triaminetrioxomolybdenum(VI) (Luque, 1990). A different synthesis method for the title compound was reported by Marzluff (1964) and Cotton & Elder

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53217 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(1964) solved the crystal structure, but the H atoms were incorrectly positioned. They were not refined. Crystal structures containing MLO_3 (where M = Mo, W, L = cyclic triamine) have been reported by Roy & Wieghardt (1987) and Schreiber, Wieghardt, Nuber & Weiss (1989).

References

COTTON, F. A. & ELDER, R. C. (1964). *Inorg. Chem.* **3**, 397–401.
LUQUE, A. (1990). PhD Thesis, Univ. Pais Vasco, Spain.
MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS*. Program for the automatic treatment of weighting schemes for least-squares refinement. Instituto Rocasolano, CSIC, Serrano 119, 26006 Madrid, Spain.
MARZLUFF. W. F. (1964). *Inorg. Chem.* **3**, 395–397.
ROMÁN, P. & GUTIÉRREZ-ZORRILLA, J. M. (1985). *J. Chem. Educ.* **62**, 167–169.
ROMÁN, P., LUQUE, A., GUTIÉRREZ-ZORRILLA, J. M. & ZÚÑIGA, F. J. (1990). *Z. Kristallogr.* **190**, 249–258.
ROY, P. S. & WIEGHARDT, K. (1987). *Inorg. Chem.* **26**, 1885–1888.
SCHREIBER, P., WIEGHARDT, K., NUBER, B. & WEISS, J. (1989). *Polyhedron*, **8**, 1675–1682.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

Structure at 20 K of the Organic Superconductor κ-Di[3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalenium] Bromo(dicyanamido)cuprate(I), κ-(BEDT-TTF)₂Cu[N(CN)₂]Br

BY URS GEISER,* ARAVINDA M. KINI, HAU H. WANG, MARK A. BENO AND JACK M. WILLIAMS*

Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439, USA

Abstract. κ-Di[3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalenium] bromo(dicyanamido)-cuprate(I) (2/1), $C_{22}H_{16}BrCuN_3S_{16}$, $M_r = 978·8$, orthorhombic, *Pnma*, $a = 12·871$ (5), $b = 29·548$ (9), $c = 8·466$ (6) Å, $V = 3220$ (3) Å^3, $Z = 4$, $D_x = 2·019$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 2·93$ mm^{-1}, $F(000) = 1956$, $T = 20$ (1) K, final $R = 0·049$ for 2400 independent observed reflections with $F_o > 3\sigma(F_o)$. The structure contains molecular dimers of partially charged BEDT-TTF† radical cations.

---

* Authors to whom correspondence may be addressed.

† The abbreviation BEDT-TTF is used for 3,4;3′,4′-bis-(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene, $C_{10}H_8S_8$. The molecule is also known under the abbreviation 'ET'.

The dimers are arranged orthogonal to neighboring dimers and form conducting layers, separated by anion layers consisting of parallel, infinite zigzag ···dicyanamido—Cu(Br)—dicyanamido···chains.

Experimental. Black, rhombus-shaped crystals were grown by electrocrystallization. The same crystal that was used for the room-temperature structure determination (Kini, Geiser, Wang, Carlson, Williams, Kwok, Vandervoort, Thompson, Stupka, Jung & Whangbo, 1990) was mounted on a diffractometer consisting of Huber 4-circle goniostat, Air Products Displex® closed-cycle refrigeration system and temperature controller (Si diode thermometer), Enraf–