

structure of the compound and Fig. 2 a stereo-diagram of the unit-cell packing.*

Related literature. The title compound is obtained as a ubiquitous, low-yield product in oxidation reactions of W₂{η⁵-C₅(CH₃)₅}₂(CO)₄ with methylarsaoxane, *cyclo*-(CH₃AsO)₄, in sealed tubes in which the CO eliminated produces autoprressurizations of 2.5–5 MPa; under these conditions a portion of the W

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and further bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53240 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Di-μ-bromo-(4-thia-1,7-diazoniaheptane)bis[bromocopper(I)] and Bromo(1,4,7-triazaheptane)copper(II) Bromide

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Abstract. (I) [Cu₂Br₄(C₄H₁₄N₂S)], *M_r* = 568.94, monoclinic, *C*2/*c*, *a* = 14.104 (2), *b* = 7.414 (1), *c* = 13.025 (4) Å, β = 93.54 (2)°, *V* = 1359.5 Å³, *Z* = 4, *D_x* = 2.780 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 149.0 cm⁻¹, *F*(000) = 1064, room temperature, final *R* = 0.0393 for 1377 unique reflections. (II) [CuBr(C₄H₁₃N₃)]Br, *M_r* = 326.52, orthorhombic, *Pmn*2₁, *a* = 8.716 (1), *b* = 8.588 (1), *c* = 6.337 (1) Å, *V* = 474.33 Å³, *Z* = 2, *D_x* = 2.286 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 106.0 cm⁻¹, *F*(000) = 314, room temperature, final *R* = 0.0394 for 1271 unique reflections. In (I) the S atom lies on a twofold axis and is coordinated to two Cu atoms. Each Cu atom is tetrahedrally coordinated with one S and three Br atoms in its coordination sphere. Two Br atoms are bridging, giving rise to a polymeric structure. In (II) the Cu atom, both Br atoms and one N atom lie in a mirror plane and the geometry around the Cu atom is best described as square planar with one Br and three N donor atoms in the plane. The Br ion lies above and below the plane of the complex with a Cu...Br distance of 3.12 Å.

Experimental. Crystals of (I) were obtained as follows. Methanol solutions of 4-thia-1,7-diazheptane (daes) and copper dibromide were reacted according to the method of Taylor & Barefield (1969) and the

starting material is carbonylated (Harper & Rheingold, 1990). The title compound is isomorphous with its Mo analogue (Clegg, Compton, Ewington & Norman, 1988).

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expected yellow-green precipitate of Cu(daes)Br₂ was obtained. The precipitate was redissolved in water and drops of dilute HBr acid were added to prevent copper hydroxide precipitation. The solution was evaporated partially, filtered and then evaporated further until a solid started to appear. On standing, olive-green crystals formed in the brown-green solution, these were decanted and washed with ethanol. Crystals of (II) were grown by slow diffusion in a U-tube. Methanol was placed in the U-tube and on either side, separated by glass frits, were placed equimolar solutions of copper dibromide and 1,4,7-triazaheptane (dien). The system was stoppered and allowed to stand. The two solutions diffused to give a green mother liquor and from this dark-blue crystals of Cu(dien)Br₂ were obtained.

Intensities measured at room temperature on an Enraf-Nonius CAD-4 diffractometer (graphite-monochromated Mo *K*α radiation). Cell dimensions determined from least-squares refinement of 25 reflections (14 ≤ θ ≤ 21°). Reflections measured in the ω:2θ scan mode [scan width (0.6 + 0.35tanθ)° and variable scan speed]. Three standard reflections showed no significant variation over the data collection. Lp and absorption corrections (North, Phillips & Mathews, 1968) applied to the data. Additional experimental details are given in Table 1.

Table 1. *Experimental details*

Crystal dimensions	0.16 × 0.21 × 0.26 mm	0.20 × 0.18 × 0.15 mm
θ range	$3 \leq \theta \leq 27^\circ$	$2 \leq \theta \leq 30^\circ$
Range of h, k, l	-18 → 18, 0 → 9, 0 → 16	0 → 12, 0 → 12, -8 → 8
Scan speed, ° min ⁻¹	1.1-5.5	0.9-5.5
Transmission factors	48.0-99.7%	50.9-99.7%
Standard reflections	066 460 932	271 404 800
Refls. measured	2460	1549
unique	1377	1271
R_{int}	0.0153	-
observed [$F > 4\sigma F$]	1161	905
No. of parameters	70	52
Final R	0.0393	0.0394
$(\Delta/\sigma)_{\text{max}}$	1.36	1.48
$(\Delta\rho)_{\text{min}}/(\Delta\rho)_{\text{max}}, \text{e } \text{Å}^{-3}$	0.97, -1.38	1.76, -1.99

Table 2. *Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^3$, Cu and Br $\times 10^4$) for (I) and (II)*

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	U_{eq}
(I)				
Cu	5305 (1)	4264 (2)	1037 (1)	324 (3)
Br(1)	3791 (1)	3610 (1)	97 (1)	281 (2)
Br(2)	6409 (1)	1817 (1)	1477 (1)	308 (2)
S	5000	5843 (4)	2500	19 (1)
C(1)	6007 (6)	7333 (12)	2745 (7)	22 (2)
C(2)	5877 (7)	8592 (14)	3665 (7)	29 (2)
N	6755 (5)	9706 (11)	3826 (7)	31 (2)
(II)				
Cu	0	-1181 (2)	95 (20)	516 (5)
Br(1)	0	1606 (1)	0	501 (3)
Br(2)	0	-1693 (2)	4969 (12)	415 (3)
N(1)	0	-3467 (13)	-280 (40)	44 (4)
N(2)	2273 (9)	-1447 (9)	361 (49)	70 (5)
C(1)	1462 (9)	-4141 (11)	499 (36)	63 (5)
C(2)	2721 (11)	-3054 (10)	-264 (38)	44 (3)

Table 3. *Distances (Å) and angles (°) for (I) and (II)*

(I)			
Cu—Br(1)	2.444 (1)	Cu—Br(2)	2.436 (2)
Cu—S	2.300 (2)	Cu—Cu	2.990 (3)
Cu—Br(1')	2.554 (1)	S—C(1)	1.812 (9)
C(1)—C(2)	1.540 (12)	C(2)—N	1.492 (11)
Br(1)—Cu—Br(2)	119.7 (1)	Br(1)—Cu—S	108.3 (1)
Br(2)—Cu—S	109.5 (1)	Br(1)—Cu—Br(1')	106.6 (1)
Br(2)—Cu—Br(1')	105.1 (1)	S—Cu—Br(1')	106.9 (1)
Cu—S—S(1)	105.7 (3)	Cu—S—Cu(1'')	118.8 (1)
C(1)—S—C(1'')	104.8 (6)	Cu—S—C(1'')	110.5 (3)
S—C(1)—C(2)	112.2 (6)	C(1)—C(2)—N	107.9 (7)
(II)			
Cu—Br(1)	2.395 (2)	Cu—Br(2)	3.120
Cu—N(1)	1.977 (12)	Cu—N(2)	2.002 (9)
N(1)—C(1)	1.484 (5)	N(2)—C(2)	1.488 (5)
C(1)—C(2)	1.520 (5)		
Br(1)—Cu—N(1)	171.7 (9)	Br(1)—Cu—N(2)	96.7 (2)
Br(1)—Cu—Br(2)	99.5	Br(2)—Cu—N(1)	88.8
Br(2)—Cu—N(2)	84.3	N(1)—Cu—N(2)	84.1 (3)
N(2)—Cu—N(2'')	163.7	Cu—N(1)—C(1)	110.3 (7)
Cu—N(2)—C(2)	110.1 (8)	N(1)—C(1)—C(2)	105.9 (7)
C(1)—N(1)—C(1'')	118.3 (12)	N(2)—C(2)—C(1)	107.2 (8)

Symmetry code: (i) $1-x, 1-y, -z$; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $-x, y, z$.

Both structures solved by Patterson method, full-matrix least-squares refinement based on F (Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms located from difference map and refined, H atoms placed in calculated positions and refined with common isotropic temperature factor. At convergence $R = 0.039$ for (I) and 0.039 for (II). Scattering factors for C, H, N, S and Br given in *SHELX76* (Sheldrick, 1976) and those for Cu corrected for f' and f'' (Hamilton & Ibers, 1974). Atomic parameters are given in Table 2, bond distances and

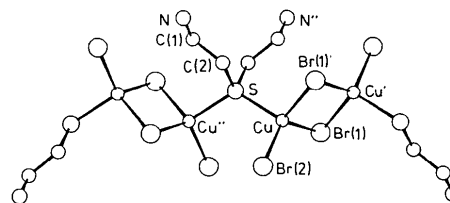


Fig. 1. Four asymmetric units of compound (I) showing the numbering scheme and the polymeric nature of the compound.

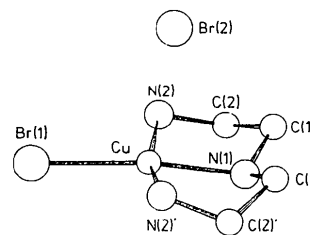


Fig. 2. One formula unit of compound (II) showing the atomic numbering scheme.

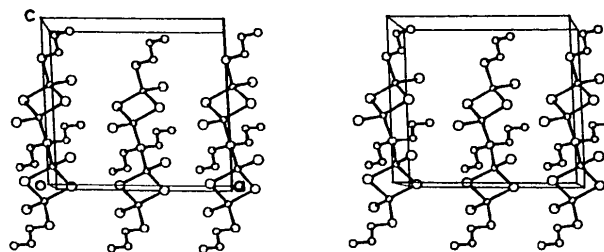


Fig. 3. Packing diagram for compound (I).

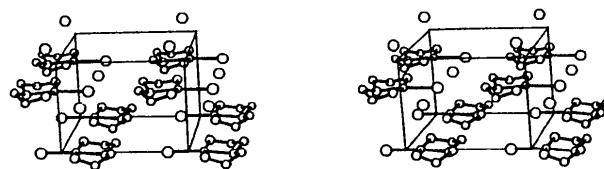


Fig. 4. Unit cell diagram for compound (II).

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(NO₃)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 Et₄dien coordinates *via* one axial and two equatorial sites to the Cu atom in the trigonal bi-

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pyramidal Cu(Br)N₃(Et₄dien) 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).

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A Redetermination of the Structure of Diethylenetriamnetrioxomolybdenum(VI)

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Abstract. [Mo(C₄H₁₃N₃)O₃], *M_r* = 247.11, orthorhombic, *Pbcm*, *a* = 6.890 (1), *b* = 10.248 (2), *c* = 11.691 (2) Å, *V* = 825.5 (3) Å³, *Z* = 4, *D_m* = 1.99 (1), *D_x* = 1.99 g cm⁻³, λ(Mo *Kα*) = 0.71069 Å, μ = 15.19 cm⁻¹, *T* = 295 K, *F*(000) = 496, *R* = 0.026, *wR* = 0.031 for 2203 observed unique reflections with *I* > 3σ(*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(C₄H₁₃N₃)O₃] units linked by hydrogen bonds of type N—H...O.

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Experimental. Diethylenetriamnetrioxomolybdenum(VI), Mo(dien)O₃, 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 CHBr₃/CCl₄ (Román & Gutiérrez-Zorrilla, 1985). A crystal with approximate dimensions 0.30 × 0.20 × 0.15 mm was analyzed at 295 K with an Enraf-Nonius CAD-4 diffractometer, utilizing graphite-monochromated Mo *Kα* radiation. Unit-cell parameters were obtained from a least-