

were carried out using the XRAY76 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(C₄H₁₃N₃O₃)] 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 MoO₃-dien in aqueous solution various compounds have been found; one is the diethylenetriaminetrioxomolybdenum(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 MLO₃ (where M = Mo, W, L = cyclic triamine) have been reported by Roy & Wiegardt (1987) and Schreiber, Wiegardt, Nuber & Weiss (1989).

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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 XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1991). **C47**, 190–192

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

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Abstract. κ -Di[3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium] bromo(dicyanamido)cuprate(I) (2/1), C₂₂H₁₆BrCuN₃S₁₆, $M_r = 978.8$, orthorhombic, *Pnma*, $a = 12.871$ (5), $b = 29.548$ (9), $c = 8.466$ (6) Å, $V = 3220$ (3) Å³, $Z = 4$, $D_x = 2.019$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ 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.

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† The abbreviation BEDT-TTF is used for 3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene, C₁₀H₈S₈. 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-

Table 1. Atomic coordinates and equivalent isotropic thermal parameters ($\times 10^4$) in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Cu	0.37866 (8)	0.2500	0.56238 (12)	120 (3)
Br	0.36329 (7)	0.2500	0.83741 (10)	136 (3)
N0	0.0619 (6)	0.2500	0.3588 (8)	141 (24)
N1	0.2418 (6)	0.2500	0.4598 (8)	115 (23)
N2	-0.0086 (6)	0.2500	0.0898 (9)	127 (24)
C11	0.1587 (7)	0.2500	0.4053 (10)	104 (26)
C12	0.0319 (7)	0.2500	0.2188 (11)	116 (28)
S1	-0.02913 (12)	0.52113 (5)	0.2672 (2)	101 (4)
S2	0.09551 (11)	0.56588 (5)	0.0206 (2)	100 (4)
S3	0.11732 (12)	0.43666 (5)	0.2668 (2)	97 (4)
S4	0.24801 (11)	0.47512 (5)	0.0156 (2)	94 (4)
S5	-0.15799 (12)	0.59979 (5)	0.3415 (2)	117 (4)
S6	-0.01103 (13)	0.65393 (5)	0.0425 (2)	129 (5)
S7	0.24048 (12)	0.35347 (5)	0.3092 (2)	103 (4)
S8	0.39469 (12)	0.39913 (5)	0.0019 (2)	135 (5)
C1	0.0774 (5)	0.5187 (2)	0.1403 (7)	93 (18)
C2	0.1410 (5)	0.4816 (2)	0.1389 (7)	108 (18)
C3	-0.0582 (5)	0.5779 (2)	0.2234 (7)	99 (18)
C4	-0.0027 (5)	0.5983 (2)	0.1114 (7)	90 (18)
C5	0.2252 (4)	0.4050 (2)	0.2093 (7)	93 (17)
C6	0.2848 (4)	0.4221 (2)	0.0914 (7)	83 (17)
C7	-0.1859 (5)	0.6525 (2)	0.2431 (8)	203 (21)
C8	-0.0912 (5)	0.6793 (2)	0.1977 (8)	207 (21)
C9	0.3230 (5)	0.3233 (2)	0.1699 (7)	158 (19)
C10	0.4196 (5)	0.3497 (2)	0.1233 (7)	130 (19)

Nonius Diffractis 583 X-ray generator system, graphite monochromator, and UCLA automation system (Strouse, 1985) driven from a MicroVAX II computer. ω -scan data, 1.3° width, $1.5^\circ \text{ min}^{-1}$, $2\theta < 50^\circ$, $(\sin\theta/\lambda) < 0.595 \text{ \AA}^{-1}$, h : 0 to 15, k : 0 to 35, l : 0 to 10; lattice parameters from 38 centered reflections $18 < 2\theta < 26^\circ$. 3442 reflections collected (3 standards); 184 duplicates (mostly standards) averaged, $R_{\text{int}} = 0.005$ (on F); 2898 unique and allowed by space group; 2400 observed with $F_o > 3\sigma(F_o)$; corrected for Lorentz-polarization and absorption (Gaussian integration; min., max. transmission factors 0.715, 0.767). Computer programs supplied by Strouse (1985), scattering factors (including anomalous-dispersion contributions) from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Structure solved from room-temperature data (Kini, Geiser, Wang, Carlson, Williams, Kwok, Vandervoort, Thompson, Stupka, Jung & Whangbo, 1990) by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and completed by Fourier methods. Full-matrix least-squares refinement of 205 variable parameters, based on $|F_o|$. All non-H atoms refined with anisotropic thermal parameters. H atoms located on difference map and included at calculated positions with $U_{\text{iso}} = 0.0317 \text{ \AA}^2$. $(\Delta/\sigma)_{\text{max}} = 0.05$ in final cycle, with $R = 0.049$, $wR = 0.048$, $S = 1.71$. $w = 1/\sigma^2(F_o)$ and $\sigma(F_o) = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{1/2}/(2F_o)$, with $\sigma(F_o^2)$ based on counting statistics. Largest peaks ($+1.2$ and -0.6 e \AA^{-3}) on difference Fourier map in the vicin-

Table 2. Interatomic distances (\AA) and angles ($^\circ$) in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br

Cu—N1	1.963 (7)	S4—C6	1.759 (6)
Cu—N2	1.941 (8)	S5—C3	1.752 (6)
Cu—Br	2.337 (2)	S5—C7	1.801 (6)
N0—C11	1.306 (11)	S6—C4	1.747 (6)
N0—C12	1.304 (11)	S6—C8	1.831 (6)
N1—C11	1.166 (11)	S7—C5	1.751 (6)
N2—C12	1.156 (11)	S7—C9	1.820 (6)
S1—C1	1.744 (6)	S8—C6	1.742 (6)
S1—C3	1.757 (6)	S8—C10	1.814 (6)
S2—C1	1.739 (6)	C1—C2	1.370 (8)
S2—C4	1.763 (6)	C3—C4	1.332 (8)
S3—C2	1.740 (6)	C5—C6	1.357 (8)
S3—C5	1.744 (6)	C7—C8	1.505 (9)
S4—C2	1.739 (6)	C9—C10	1.519 (8)
N1—Cu—N2	112.2 (3)	C1—C2—S3	120.1 (5)
N1—Cu—Br	111.4 (2)	C1—C2—S4	124.5 (5)
N2—Cu—Br	136.4 (2)	S3—C2—S4	115.4 (3)
C11—N0—C12	124.8 (8)	C4—C3—S1	118.0 (5)
C11—N1—Cu	177.1 (7)	C4—C3—S5	129.2 (5)
C12—N2—Cu	158.3 (7)	S1—C3—S5	112.9 (3)
N1—C11—N0	174.2 (9)	C3—C4—S2	116.6 (5)
N2—C12—N0	170.5 (9)	C3—C4—S6	129.2 (5)
C1—S1—C3	94.4 (3)	S2—C4—S6	114.2 (3)
C1—S2—C4	94.9 (3)	C6—C5—S3	117.1 (4)
C2—S3—C5	95.5 (3)	C6—C5—S7	128.0 (5)
C2—S4—C6	95.3 (3)	S3—C5—S7	114.9 (3)
C3—S5—C7	101.6 (3)	C5—C6—S4	116.7 (4)
C4—S6—C8	100.4 (3)	C5—C6—S8	129.3 (5)
C5—S7—C9	100.2 (3)	S4—C6—S8	114.0 (3)
C6—S8—C10	102.1 (3)	C8—C7—S5	114.3 (5)
C2—C1—S1	120.5 (5)	C7—C8—S6	115.1 (5)
C2—C1—S2	123.9 (5)	C10—C9—S7	113.3 (4)
S1—C1—S2	115.6 (3)	C9—C10—S8	114.5 (4)

ity of Br atom. No correction for extinction. Final atomic positions and isotropic thermal parameters are given in Table 1.* Relevant geometrical results are listed in Table 2, drawings of both the BEDT-TTF cation and the polymeric $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}^-$ anion are shown in Fig. 1, and a unit-cell packing diagram is depicted in Fig. 2.

The intramolecular distances and angles are essentially the same (albeit with lower e.s.d.'s) as at room temperature (Kini, Geiser, Wang, Carlson, Williams, Kwok, Vandervoort, Thompson, Stupka, Jung & Whangbo, 1990), except for those involving the ethylene end groups of the BEDT-TTF molecule. In particular, the ethylene group C7—C8 is disordered at room temperature, but ordered at 20 K, as reflected by longer C—C apparent bond lengths (1.51 vs 1.35 \AA), smaller S—C—C angles and smaller thermal parameters.

Related literature. The title compound is the organic superconductor with the highest ambient-pressure transition temperature reported to date, $T_c = 11.6 \text{ K}$

* 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 53382 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(inductive onset) or 12.5 K (resistive onset) (Kini, Geiser, Wang, Carlson, Williams, Kwok, Vandervoort, Thompson, Stupka, Jung & Whangbo, 1990).

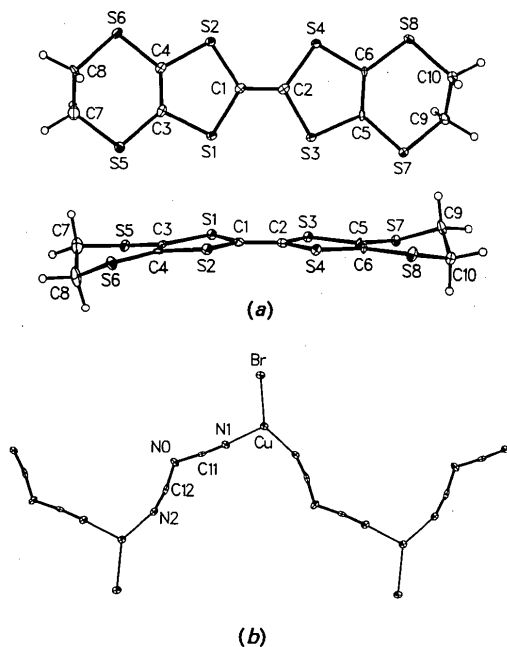


Fig. 1. (a) Top and side views of the BEDT-TTF radical cation, and (b) view of the polymeric anion chains in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, indicating the atomic numbering scheme used. All atoms (except hydrogen) are drawn with 50% probability ellipsoids.

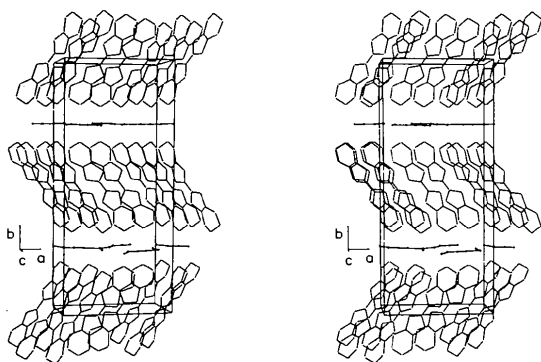


Fig. 2. Unit-cell packing stereo diagram of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br. H atoms are omitted for clarity.

The field of organic conductors and superconductors has recently been reviewed (Williams, Wang, Emge, Geiser, Beno, Leung, Carlson, Thorn, Schultz & Whangbo, 1987). The main interest in the current structure analysis was to determine if the crystal structure remained the same upon cooling, apart from the omnipresent effects of lattice contraction and reduction in thermal vibrations, or if a low-temperature transition occurred. The ordering of the ethylene group C7—C8 is the most noteworthy effect of cooling, whereas the structure remains essentially the same, and no low-temperature structural transitions are evident.

Note added in proof. After the submission of this manuscript, we discovered that the chlorine analogue of the title compound, κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl, is a superconductor with even higher transition temperature, $T_c = 12.8$ K (resistive midpoint) at 0.3 kbar applied pressure (Williams, Kini, Wang, Carlson, Geiser, Montgomery, Pyrka, Watkins, Kommers, Boryschuk, Strieby Crouch, Kwok, Schriber, Overmyer, Jung, & Whangbo, 1990).

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References

- KINI, A. M., GEISER, U., WANG, H. H., CARLSON, K. D., WILLIAMS, J. M., KWOK, W. K., VANDERVOORT, K. G., THOMPSON, J. E., STUPKA, D. L., JUNG, D. & WHANGBO, M.-H. (1990). *Inorg. Chem.* **29**, 2555–2557.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- STROUSE, C. (1985). *UCLA Crystallographic Package*. Univ. of California, Los Angeles, USA.
- WILLIAMS, J. M., KINI, A. M., WANG, H. H., CARLSON, K. D., GEISER, U., MONTGOMERY, L. K., PYRKA, G. J., WATKINS, D. M., KOMMERS, J. M., BORYSCHUK, S. J., STRIEBY CROUCH, A. V., KWOK, W. K., SCHIRBER, J. E., OVERMYER, D. L., JUNG, D. & WHANGBO, M.-H. (1990). *Inorg. Chem.* **29**, 3262–3274.
- WILLIAMS, J. M., WANG, H. H., EMGE, T. J., GEISER, U., BENO, M. A., LEUNG, P. C. W., CARLSON, K. D., THORN, R. J., SCHULTZ, A. J. & WHANGBO, M.-H. (1987). *Rational Design of Synthetic Metal Superconductors*, edited by S. J. LIPPARD. In *Prog. Inorg. Chem.* **35**, 51–218.