molecules can readily be made on the grounds of their interactions with the rest of the structure: those with their O atom directly bonded to the heavy atoms [*W*(1) and *W*(2)], presumably more strongly attached, and those which only interact through H bonds. This correlates nicely with TGA data, which show a two-step dehydration process in the ranges 338–345 K, and 349–375 K, with weight losses of 11 and 12% (expected values, 11% each).

Formate groups are very active in coordinating the structure. Both formate (I) and formate (II) ions have a rather symmetrical coordination pattern, and the sharing of the acidic character between both O atoms is evidenced by the very similar C—O distances [C(1)—O(11) 1·26 (1), C(1)—O(12) 1·25 (1), C(2)—O(21) 1·25 (1), C(2)—O(22) 1·26 (1) Å]. Formate (III), instead, has only one O atom involved in direct coordination to a heavy ion [Sr—O(31) 2·63 (1) Å]. The other O atom is a double acceptor of H bonds and, through this, the only link between layers. This asymmetrical nature is clearly revealed in the C—O distances [C(3)—O(31) 1·27 (1), C(3)—O(32) 1·20 (1) Å].

Thermal parameters show relative values in fair agreement with the vibrational behaviour expected from coordination considerations. Thus, there is a clear distinction between doubly coordinated water molecules and H-bonded ones, as well as between formate O atoms shared by two heavy-atom c.p. and those involved only once.

The authors are indebted to Miss Graciela Nievas for technical assistance.

References

FAVAS, M. C. & KEPERT, D. L. (1981). *Progress in Inorganic Chemistry*, Vol. 28, edited by S. J. LIPPARD, pp. 309–367. New York: John Wiley.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MARTINEZ-RIPOLL, M., HAASE, A. & BRAUER, G. (1973). *Acta Cryst.* B**29**, 1715–1717.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

WINCHELL, A. (1954). *The Optical Properties of Organic Compounds*, p. 15. New York: Academic Press.

Acta Cryst. (1985). C**41**, 197–199

Structure of the 2/1 Complex Dibenzotetrathiafulvalenium Hexachlorocuprate(II),* $2C_{14}H_8S_4^+.Cu_2Cl_6^{2-}$

BY MASAKO HONDA, CHUJI KATAYAMA AND JIRO TANAKA

Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464, *Japan*

AND MASASHI TANAKA†

Department of Chemistry, College of General Education, Nagoya University, Nagoya 464, *Japan*

(*Received* 9 *July* 1984; *accepted* 8 *October* 1984)

Abstract. $M_r = 948{\cdot}54$, monoclinic, $C2/m$, $a = 9{\cdot}224\,(1)$, $b = 24{\cdot}976\,(3)$, $c = 7{\cdot}317\,(2)$ Å, $\beta = 108{\cdot}28\,(1)^\circ$, $V = 1600{\cdot}7\,(6)$ Å^3, $Z = 2$, $D_m = 1{\cdot}96$, $D_x = 1{\cdot}97$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 109{\cdot}54$ cm^{-1}, $F(000) = 944$, $T = 293$ K, $R = 0{\cdot}053$ for 1337 observed reflections. The central C=C bond in the cation is longer than that found in the neutral compound, but agrees with that of other dibenzotetrathiafulvalenium cations. The structure contains stacking columns of the dibenzotetrathiafulvalenium cation along the *c* axis. The $Cu_2Cl_6^{2-}$ anion has normal bond lengths and angles.

Introduction. Organic charge-transfer radical salts consisting of the electron donor TTF (tetrathiafulvalene) and an electron acceptor such as TCNQ (tetracyano-*p*-quinodimethane) display high electric conductivities (Cohen, Coleman, Garito & Heeger, 1974). The crystal structures of the organic conductors are composed of characteristic columns in which the donor cation and acceptor anion radicals are stacked separately. Electrons and holes are delocalized in the respective columns. This causes high anisotropy in the solid-state properties of the organic conductors, such as electric, optical and magnetic ones. Many compounds analogous to TTF have been synthesized to obtain radical salts with high electric conductivity. Dibenzotetrathiafulvalene (DBTTF) is one of them and the direct oxidation of DBTTF by halogens and metal

---

* Alternative nomenclature: bis(2,2′-bi-1,3-benzodithiolyldenium) hexachlorodicuprate.

† To whom correspondence should be addressed.

0108-2701/85/020197-03$01.50

halides was reported to yield radical salts such as $DBTTF_2.I_3$ (Shibaeva, Rozenberg, Aldoshina, Lubovskaya & Khidekel, 1979), $DBTTF_8.(SnCl_6)_3$ and $DBTTF_3.SnBr_6$ (Shibaeva, Rozenberg & Lubovskaya, 1980). In this paper, we report the crystal structure of the complex of DBTTF with cupric chloride.

Experimental. Crystal prepared by diffusion of DBTTF and $CuCl_2$ in acetonitrile solution. Dark-red plate-like crystal 0·35 × 0·008 × 0·60 mm. D_m by flotation. Rigaku automated four-circle diffractometer. Cell dimensions from 20 selected reflections with $29 < \theta < 31°$. 1455 measured reflections, $2\theta_{\max} = 126°$, $-10 \le h \le 10$, $0 \le k \le 28$, $0 \le l \le 8$, $R_{\text{int}} = 0{\cdot}024$. Three standard reflections after every 100 reflections (decay less than 2%). Structure solved by the Monte-Carlo direct method (Furusaki, 1979) with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) using 1337 non-zero unique reflections, refined on F^2 by full-matrix least-squares program with absorption correction by analytical method (Katayama, Sakabe & Sakabe, 1972). Transmission factors 0·02 to 0·42. Non-H atoms given anisotropic temperature factors. All H atoms located from difference Fourier map and refined with isotropic temperature factors equivalent to that for bonded carbon atom. $R = 0{\cdot}053$, $S = [\sum w(|F_o|^2 - |F_c|^2)^2/(m-n)]^{1/2} = 4{\cdot}87$, $w = 1/\sigma^2(F^2)$, $(\Delta/\sigma)_{\max} = 0{\cdot}165$ for z of H(7) atom, $\Delta\rho_{\max} = 1{\cdot}0$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *ORTEP* (Johnson, 1965) employed for drawing molecular structure and *PLUTO*78 (Motherwell, 1978) for crystal structure projection. All calculations made on FACOM M-382 computer at the computer center of Nagoya University.

Discussion. The atomic parameters are given in Table 1.* The projection of the structure along the c axis is shown in Fig. 1. The cation radicals are stacked to form columns along the c axis with an interplanar distance of about 3·6 (1) Å. Shortest contacts between adjacent cations in a column are found between S(1) and S(3) with a distance of 3·443 (1) Å (see Table 2). Fig. 2 shows the bond lengths and bond angles of the DBTTF cation and $Cu_2Cl_6^{2-}$ anion. The length of the central C=C bond in the DBTTF cation is longer than that of the neutral DBTTF molecule [$R_{C=C} = 1{\cdot}336$ (2) Å] (Emge, Wiygul, Chappell, Bloch, Ferrais, Cowan & Kistenmacher, 1982) and is comparable with those of other DBTTF cations (Shibaeva, Rozenberg, Aldoshina, Lubovskaya & Khidekel, 1979; Shibaeva,

Table 1. *Positional parameters* (×10^5) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2 ×10^2)
Cu(1)	100000	93154 (2)	50000	271 (8)
Cl(2)	101203 (16)	100000	29572 (19)	349 (8)
Cl(3)	100683 (11)	87101 (3)	72546 (15)	372 (8)
S(1)	29809 (9)	6532 (2)	11628 (13)	260 (8)
S(3)	62757 (10)	6290 (2)	31635 (14)	279 (8)
C(2)	46067 (34)	2811 (14)	21510 (44)	238 (11)
C(4)	62736 (41)	17304 (15)	33517 (56)	292 (11)
C(5)	54978 (43)	22117 (15)	29706 (53)	306 (12)
C(6)	39192 (44)	22247 (14)	20228 (54)	305 (12)
C(7)	30947 (41)	17578 (15)	14400 (53)	288 (11)
C(8)	38630 (38)	12722 (13)	18092 (47)	236 (11)
C(9)	54562 (37)	12623 (14)	27722 (49)	249 (11)

Table 2. *Selected intermolecular distances* (Å)

S(1)–S(3$^{\text{i}}$)	3·990 (1)	Cu(1)–S(3$^{\text{iii}}$)	3·276 (1)
S(1)–S(3$^{\text{ii}}$)	3·443 (1)	Cu(1)–S(1$^{\text{iv}}$)	4·505 (1)
		Cu(1)–S(1$^{\text{v}}$)	4·486 (1)

Symmetry code:
(i) $1-x, y, 1-z$
(ii) $1-x, y, -z$
(iii) $x, 1-y, z$
(iv) $1-x, 1-y, 1-z$
(v) $1-x, 1-y, -z$

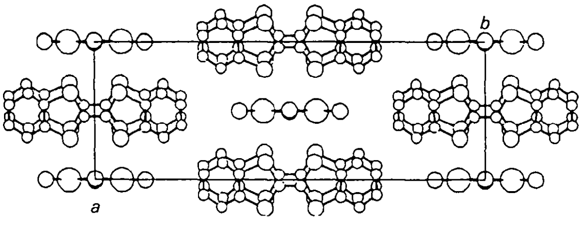

Fig. 1. Projection of the structure along the c axis.

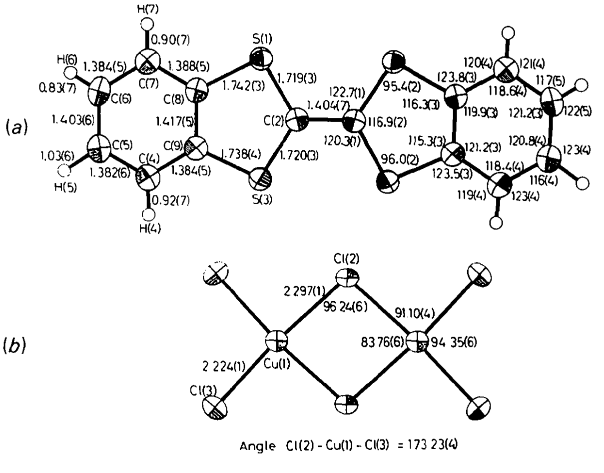

Fig. 2. Molecular dimensions for (*a*) the DBTTF cation and (*b*) the $Cu_2Cl_6^{2-}$ anion (Å and deg).

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39815 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Rozenberg & Lubovskaya, 1980). Furthermore, the S(1)—C(8) and S(3)—C(9) bonds are slightly longer than S(1)—C(2) and S(3)—C(2) as predicted theoretically (Haddon, 1975). The $Cu_2Cl_6^{2-}$ anion has two types of Cu—Cl bond, 2·224 (1) and 2·297 (1) Å, which are comparable with those [2·267 (3) and 2·314 (3) Å] of $K_2Cu_2Cl_6$ (Willett, Dwiggins, Kruh & Rundle, 1963).

References

Cohen, M. J., Coleman, L. B., Garito, A. F. & Heeger, A. J. (1974). *Phys. Rev. B*, **10**, 1298–1307.

Emge, T. J., Wiygul, F. M., Chappell, J. S., Bloch, A. N., Ferrais, J. P., Cowan, D. O. & Kistenmacher, T. J. (1982). *Mol. Cryst. Liq. Cryst.* **87**, 137–161.

Furusaki, A. (1979). *Acta Cryst.* A**35**, 220–224.

Haddon, R. C. (1975). *Aust. J. Chem.* **28**, 2333–2342.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Katayama, C., Sakabe, N. & Sakabe, K. (1972). *Acta Cryst.* A**28**, S207.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Motherwell, S. (1978). *PLUTO78*. Program for drawing molecular and crystal structures. Univ. of Cambridge, England.

Shibaeva, R. P., Rozenberg, L. P., Aldoshina, M. Z., Lubovskaya, R. N. & Khidekel, M. L. (1979). *Zh. Strukt. Khim.* **20**, 485–490.

Shibaeva, R. P., Rozenberg, L. P. & Lubovskaya, R. N. (1980). *Kristallografiya*, **25**, 507–513.

Willett, R. D., Dwiggins, C., Kruh, R. F. & Rundle, R. E. (1963). *J. Chem. Phys.* **38**, 2429–2436.

Acta Cryst. (1985). C**41**, 199–200

Bis(3-aminopropanol-*O*,*N*)bis(isothiocyanato)nickel(II), $[Ni(NCS)_2(C_3H_9NO)_2]$

By S. B. Sanni* and A. T. H. Lenstra†

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, *B*-2610 *Wilrijk, Belgium*

and V. C. Patel

Department of Chemistry, Fourah Bay College, University of Sierra Leone, Freetown, Sierra Leone

(*Received* 10 *July* 1984; *accepted* 11 *October* 1984)

Abstract. $M_r = 325{\cdot}1$, monoclinic, $P2_1/n$, $a = 8{\cdot}869\,(2)$, $b = 8{\cdot}857\,(3)$, $c = 9{\cdot}163\,(3)$ Å, $\beta = 107{\cdot}05\,(4)°$, $V = 688{\cdot}2\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}569$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}69$ mm^{-1}, $F(000) = 340$, $T = 300$ K. Final $R = 0{\cdot}026$ for 1474 observed reflections. The complex is centrosymmetric with Ni^{II} octahedrally coordinated by N of the NCS^- ions, and by O and N of the 3-aminopropanol bidentate ligands. The moiety Ni—N(1)—C(3)—C(2)—C(1)—O forms a chair conformation flattened at the Ni side. There is an OH···S internal hydrogen bond of 3·25 Å.

Introduction. In pursuance of our studies of metal complexes of aminoalcohols, we have prepared a series of novel nickel complexes using various such ligands. The title compound was prepared using a procedure in which nickel(II) acetate was treated with hot 3-aminopropanol and sodium thiocyanate (dissolved in methanol) was added to the resultant bluish-green viscous liquid. Blue crystals of the title compound separated out after a few days. Crystallization was from hot methanol. Elemental analysis confirmed the identity of the complex (found: Ni 18·09, S 19·85, H 5·55, N 17·30, C 29·44; calculated for $C_8H_{18}N_4NiO_2S_2$: Ni 18·06, S 19·73, H 5·58, N 17·23, C 29·56%).

We undertook the X-ray analysis in order to confirm low-temperature magnetic-measurement results which revealed the presence of a six-membered ring (in the nickel coordination) in the chair form and to establish the possibility of internal hydrogen bonding.

Experimental. Crystal 0·2 × 0·1 × 0·15 mm. Cell dimensions determined from setting angles of 25 high-order reflections. Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo radiation, ω/θ scan, range $0 < \theta \leq 27°$, $0 \leq h \leq 11$, $0 \leq k \leq 11$, $-11 \leq l \leq 11$. Three intensity- and orientation-control reflections measured every 120 min and 200 reflections respectively, no significant drift noted. Intensities not corrected for absorption because of small crystal size and low linear absorption coefficient. 1735 independent

---

* On leave from the University of Benin, Department of Chemistry, Benin City, Nigeria.

† Author to whom correspondence should be addressed.

0108-2701/85/020199-02$01.50