DEJČMAN, E. N. & RODIČEVA, G. V. (1964). Zh. Neorg. Khim. 9, 807–812.

HAMILTON, W. C. (1959). Acta Cryst. 12, 609–610.

HARITONOV, J. J. & DEJČMAN, E. N. (1965). Zh. Neorg. Khim. 10, 853–860.

LARSON, A. C. (1967). Acta Cryst. 23, 664–665.

LINDEL, W. & HUBER, F. (1974). Z. Anorg. Allg. Chem. 408, 167–174.

PREUT, H. & HUBER, F. (1979). Z. Anorg. Allg. Chem. 450, 120–130.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system–version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

Structure of Tris[2(1H)-pyridinethione-S]copper(I) Nitrate (TPTCN), [Cu(C5H5NS)3]NO3

BY S. C. KOKKOU, S. FORTIER* AND P. J. RENTZEPERIS

Applied Physics Laboratory, Aristotle University of Thessaloniki, Thessaloniki, Greece

AND P. KARAGIANNIDIS

Laboratory of Inorganic Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

Abstract. $M_r = 459.055$, triclinic, $P\bar{1}$, $a = 7.187$ (1), $b = 10.436$ (2), $c = 13.835$ (3) Å, $\alpha = 109.56$ (1), $\beta = 85.15$ (1), $\gamma = 107.91$ (1)°, $Z = 2$, $V = 930.2$ (6) Å^3, $F(000) = 462$, $D_c = 1.639$, $D_m = 1.630$ Mg m^{-3} (by flotation), m.p. $= 425$–427 K, μ(Mo $K\alpha$, $\lambda = 0.71069$ Å) $= 1.56$ mm^{-1}; $R = 0.059$ for 1162 independent non-zero reflexions. The structure consists of isolated Cu(SC5H5N)$_3^+$ ions connected to the NO$_3^-$ ions through O···H—N hydrogen bonds. The Cu atom in the complex ion is surrounded by three S atoms in a planar, distorted trigonal coordination.

Introduction. Copper–sulphur coordination compounds have been of considerable interest, mainly because of their stereochemistry and its relevance to certain oxidation–reduction reactions in biological systems. Of particular importance are Cu^I compounds with the metal atom in the rather rare planar trigonal coordination. We report here the crystal and molecular structure of tris[2(1H)-pyridinethione]copper(I) nitrate (TPTCN hereafter), which was prepared for the first time by one of us (PK). Magnetic measurements showed the compound to be diamagnetic, indicating thus that copper is in the +1 oxidation state.

Experimental. Pure bright-orange needle-like crystals, aqueous solution of copper(II) nitrate added to 2-mercaptopyridine in ethanol, 0.42 × 0.10 ×

0.07 mm, computer-controlled Philips PW 1100 four-circle single-crystal diffractometer, cell constants and standard deviations by least-squares analysis of θ angles of 150 strong reflexions, intensity statistics indicated $P\bar{1}$, 3D data, graphite-monochromated Mo $K\alpha$, ω-scan mode, 3235 unique reflexions, $\theta = 3$–25°, 1162 with $I > 2\sigma(I)$, no absorption correction, direct methods with MULTAN (Main, Woolfson, Lessinger, Germain & Declercq, 1977), phases of 220 strong reflexions determined, 16 non-hydrogen atoms, i.e. MS$_3$ core and two of the pyridine rings, located on E map, remaining atoms with Fourier syntheses, full-matrix least squares, XRAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1976), atomic scattering factors and anomalous dispersion corrections for Cu and S from International Tables for X-ray Crystallography (1974), H atoms, at calculated positions, with isotropic temperature coefficients, not refined, $w = 1/\sigma^2(F)$, $R = 0.059$ ($R_w = 0.048$), mean shift/error ratio 0.18.

Discussion. The final positional parameters and equivalent isotropic temperature coefficients for the non-hydrogen atoms are given in Table 1.† Interatomic distances and angles are given in Table 2.

---

* Present address: Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, New York 14203, USA.

† Lists of structure factors, anisotropic thermal parameters of the non-hydrogen atoms, H-atom parameters, bond lengths involving H atoms and various least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38150 (14 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for the non-hydrogen atoms*

Here and throughout this paper e.s.d's are given in parentheses and refer to the last digit.

	x	y	z	B_{eq}*
Cu(1)	−0·1055 (3)	−0·5047 (2)	0·2160 (1)	4·0
S(1)	0·1641 (6)	−0·5338 (4)	0·1316 (3)	4·0
S(2)	−0·2185 (6)	−0·3183 (4)	0·2697 (3)	4·8
S(3)	−0·2636 (6)	−0·7020 (4)	0·2530 (3)	5·1
O(1)	−0·2243 (18)	−0·9524 (12)	0·5711 (9)	7·3
O(2)	−0·2743 (16)	−0·9069 (12)	0·4385 (9)	5·8
O(3)	−0·2979 (17)	−0·7657 (12)	0·5859 (7)	6·3
N(1)	0·3494 (16)	−0·2534 (14)	0·2041 (8)	3·2
N(2)	−0·0715 (14)	−0·0506 (11)	0·2761 (8)	2·9
N(3)	−0·4982 (15)	−0·7330 (10)	0·4066 (8)	3·8
N(4)	−0·2633 (18)	−0·8738 (14)	0·5342 (11)	3·7
C(1)	0·3014 (20)	−0·3770 (17)	0·1211 (12)	3·8
C(2)	0·3830 (20)	−0·3601 (16)	0·0269 (11)	3·5
C(3)	0·4891 (24)	−0·2315 (20)	0·0216 (12)	4·6
C(4)	0·5317 (21)	−0·1080 (19)	0·1100 (15)	5·5
C(5)	0·4552 (22)	−0·1209 (17)	0·2045 (12)	3·9
C(6)	−0·0960 (18)	−0·1909 (14)	0·2166 (11)	2·8
C(7)	−0·0178 (20)	−0·2127 (16)	0·1159 (10)	3·4
C(8)	0·0675 (22)	−0·0969 (20)	0·0836 (11)	4·9
C(9)	0·0885 (21)	0·0461 (17)	0·1497 (12)	5·0
C(10)	0·0131 (19)	0·0628 (13)	0·2427 (10)	3·8
C(11)	−0·4578 (19)	−0·6771 (14)	0·3280 (10)	3·3
C(12)	−0·5793 (23)	−0·5984 (15)	0·3185 (11)	4·0
C(13)	−0·7249 (24)	−0·5803 (15)	0·3856 (14)	4·7
C(14)	−0·7629 (22)	−0·6444 (15)	0·4648 (11)	3·6
C(15)	−0·6453 (21)	−0·7219 (16)	0·4716 (10)	4·6

*$B_{eq} = \frac{8}{3}\pi^2$ trace $\tilde{U}$.

Fig. 1. Clinographic projection of the TPTCN molecule.

Table 2. *Interatomic distances* (Å) *and angles* (°)

(*a*) Bond lengths

Cu−S(1)	2·225 (5)	N(4)−O(1)	1·21 (2)
Cu−S(2)	2·213 (5)	N(4)−O(3)	1·20 (2)
Cu−S(3)	2·228 (5)	N(4)−O(2)	1·26 (2)
S(1)−C(1)	1·68 (2)	S(2)−C(6)	1·70 (2)
C(1)−C(2)	1·43 (2)	C(6)−C(7)	1·43 (2)
C(2)−C(3)	1·35 (2)	C(7)−C(8)	1·38 (3)
C(3)−C(4)	1·42 (2)	C(8)−C(9)	1·43 (2)
C(4)−C(5)	1·41 (3)	C(9)−C(10)	1·33 (2)
C(5)−N(1)	1·36 (2)	C(10)−N(2)	1·36 (2)
N(1)−C(1)	1·38 (2)	N(2)−C(6)	1·38 (2)
S(3)−C(11)	1·70 (1)		
C(11)−C(12)	1·41 (3)		
C(12)−C(13)	1·35 (2)		
C(13)−C(14)	1·43 (3)		
C(14)−C(15)	1·36 (3)		
C(15)−N(3)	1·34 (2)		
N(3)−C(11)	1·37 (2)		

(*b*) Bond angles

S(1)−Cu−S(2)	131·0 (0·2)	S(1)−C(1)−C(2)	123·3 (1·1)
S(1)−Cu−S(3)	109·0 (0·2)	S(1)−C(1)−N(1)	122·5 (1·2)
S(2)−Cu−S(3)	120·0 (0·2)	S(2)−C(6)−C(7)	127·2 (1·0)
Cu−S(1)−C(1)	108·8 (0·6)	S(2)−C(6)−N(2)	117·1 (1·0)
Cu−S(2)−C(6)	111·5 (0·5)	S(3)−C(11)−C(12)	125·3 (1·2)
Cu−S(3)−C(11)	110·1 (0·6)	S(3)−C(11)−N(3)	118·4 (1·2)
N(1)−C(1)−C(2)	114·1 (1·4)	N(2)−C(6)−C(7)	115·7 (1·3)
C(1)−C(2)−C(3)	121·3 (1·3)	C(6)−C(7)−C(8)	119·2 (1·3)
C(2)−C(3)−C(4)	121·6 (1·6)	C(7)−C(8)−C(9)	122·0 (1·4)
C(3)−C(4)−C(5)	118·6 (1·6)	C(8)−C(9)−C(10)	117·3 (1·5)
C(4)−C(5)−N(1)	116·6 (1·3)	C(9)−C(10)−N(2)	121·5 (1·2)
C(5)−N(1)−C(1)	127·7 (1·3)	C(10)−N(2)−C(6)	124·1 (1·1)
N(3)−C(11)−C(12)	116·2 (1·2)		
C(11)−C(12)−C(13)	120·2 (1·7)		
C(12)−C(13)−C(14)	120·9 (1·8)		
C(13)−C(14)−C(15)	117·9 (1·4)		
C(14)−C(15)−N(3)	119·6 (1·5)		
C(15)−N(3)−C(11)	125·1 (1·4)		

(*c*) Hydrogen-bond distances

N(1)−H(13)···O(1ⁱ)	3·37 (2)
N(2)−H(14)···O(2ⁱⁱ)	2·82 (2)
N(3)−H(15)···O(3)	3·13 (2)

Symmetry code
(i) $2-x, -1-y, 1-z$
(ii) $x, 1+y, z$

A clinographic projection of the TPTCN molecule is shown in Fig. 1. The characteristic feature in the $\text{Cu}(\text{SC}_5\text{H}_5\text{N})_3^+$ ion is that the Cu atom is surrounded by the three S atoms in a planar, distorted trigonal coordination. The same was observed in the case of tris(tetramethylthiourea)copper(I) tetrafluoroborate (Weininger, Hunt & Amma, 1972) and bis(tetraphenyl-phosphonium) tris(thiophenolato)cuprate(I) (Cou-couvanis, Murphy & Kanodia, 1980). The dis-

tance of the Cu atom from the plane of the S atoms is 0·034 (2) Å. Whereas the angle S(2)−Cu−S(3) is ideal [120·0 (2)°], the other two deviate considerably from 120°, being 109·0 (2) and 131·0 (2)°. This deviation may be attributed to steric hindrance caused by the adjacent pyridine rings $P1$ and $P2$ (Fig. 1). These rings are roughly parallel to each other [$P1 \wedge P2 = 15·01$ (3)°] and their angles with the plane of the S atoms are 51·74 (2) and 39·95 (6)°, respectively. This conformation causes the deviation of the two S−Cu−S angles from their ideal value. The third pyridine ring $P3$ makes an angle of 37·87 (10)° with the plane of the S atoms.

The three Cu−S bond lengths 2·225 (5), 2·228 (5) and 2·213 (5) Å are normal and fall within the range of values found in other Cu−S complexes [see references mentioned above and especially the literature cited in Coucouvanis, Murphy & Kanodia (1980)]. Once again
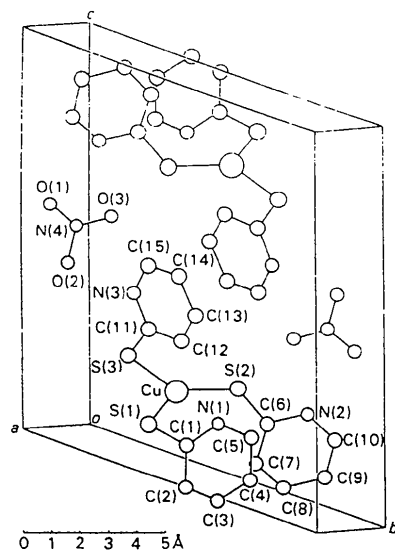
Fig. 2. Clinographic projection of the molecular packing in the unit cell.

it is found that the Cu—S distances in trigonal coordination are considerably shorter than the sum of the corresponding tetrahedral covalent radii, *i.e.* 2·39 Å (Pauling, 1960). However, this fact may not be considered as sufficient evidence for the existence of partial multiple bonding.

The S—C bond distances are normal and the Cu—S—C bond angles are less than the value of 120° expected for *sp²*-hybridized atoms, in good agreement with what has been so far reported (Spofford & Amma, 1970; Girling & Amma, 1971; Weininger *et al.*, 1972; Coucouvanis *et al.*, 1980).

The geometrical features of the pyridine rings are close to those of an aromatic ring. The mean C—C and C—N distances in rings *P*1, *P*2 and *P*3 are 1·40 (2) and 1·37 (2), 1·39 (2) and 1·37 (2), 1·39 (2) and 1·35 (2) Å, respectively. These values and the corresponding bond angles are in agreement with the values found in most pyridine compounds (Fletcher & Skapski, 1972; Downie Harrison & Raper, 1972; Le

Borgne & Grandjean, 1975; Cotton, Fanwick & Fitch, 1978).

The molecular packing is illustrated in Fig. 2. The isolated $Cu(SC_5H_5N)_3^+$ ions are connected to the planar nitrate ions through hydrogen bonds O···H—N, the presence of which is shown also from IR spectra [presence of v(NH) at 3185 cm^{-1} and absence of v(SH) at 2500 cm^{-1}]. The three hydrogen bridging bonds 3·37 (2), 2·82 (2) and 3·13 (2) Å (Table 2) are within the range of acceptable values. In the nitrate ion the N(4)—O(2) distance [1·26 (2) Å] is longer than the other two. This slight asymmetry may be attributed to the corresponding shortest hydrogen-bridge distance, namely O(2)···H(14)—N(2) = 2·82 (2) Å.

References

COTTON, F. A., FANWICK, P. E. & FITCH, J. W. (1978). *Inorg. Chem.* **17**, 3254–3257.
COUCOUVANIS, D., MURPHY, C. N. & KANODIA, S. K. (1980). *Inorg. Chem.* **19**, 2993–2998.
DOWNIE, T. C., HARRISON, W. & RAPER, E. S. (1972). *Acta Cryst.* **B28**, 283–290.
FLETCHER, S. R. & SKAPSKI, A. C. (1972). *J. Chem. Soc. Dalton Trans.* pp. 635–639.
GIRLING, R. L. & AMMA, E. L. (1971). *Inorg. Chem.* **10**, 335–340.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press.
LE BORGNE, G. & GRANDJEAN, D. (1975). *J. Organomet. Chem.* **92**, 381–392.
MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
SPOFFORD, W. A. III & AMMA, E. L. (1970). *Acta Cryst.* **B26**, 1474–1483.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1976). The XRAY system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WEININGER, M. S., HUNT, G. W. & AMMA, E. L. (1972). *J. Chem. Soc. Chem. Commun.* pp. 1140–1141.