References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A27, 157–165.

BERRY, C. R. (1955). *Phys. Rev.* [2], **97**, 676–679.

BIRNSTOCK, R. & BRITTON, D. (1970). *Z. Kristallogr.* **132**, 87–98.

DANIELSSON, S., GRENTHE, I. & OSKARSSON, Å. (1976). *J. Appl. Cryst.* **9**, 14–17.

ELDING, I. (1976). *Acta Chem. Scand.* A30, 649–656.

GIBBONS, C. S. & TROTTER, J. (1971). *J. Chem. Soc.* (*A*), pp. 2058–2062.

HOLMBERG, B. (1976). *Acta Chem. Scand.* A30, 680–686.

HOLMBERG, B. & PERSSON, K. (1975). *Acta Cryst.* A31, S65.

IGLESIAS, J. E., PACHALI, K. E. & STEINFINK, H. (1974). *J. Solid State Chem.* **9**, 6–14.

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

KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969–975.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

SCHNERING, H. G. VON (1962). *Z. anorg. allgem. Chem.* **314**, 144–155.

STOMBERG, R. (1969). *Acta Chem. Scand.* **23**, 3498–3512.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

The Crystal and Molecular Structure of Tris(thiourea)copper(I) Hydrogen-*o*-phthalate. A Monomeric Trigonal Planar Copper(I) Complex

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$C_{11}H_{17}CuN_6O_4S_3$ is triclinic, space group $P\bar{1}$, with $a = 15.342$ (9), $b = 15.039$ (12), $c = 3.946$ (4) Å, $\alpha = 89.1$ (1), $\beta = 93.6$ (1), $\gamma = 95.6$ (1)°, $Z = 2$. The structure was refined to $R = 0.059$ for 2725 counter reflexions. It consists of discrete trigonal planar $\{Cu[SC(NH_2)_2]_3\}^+$ ions held in slices parallel to (100) by NH···S hydrogen bonds and of hydrogen-*o*-phthalate anions linked to the cations through NH···O hydrogen bonds. Coordination to Cu is through S atoms [Cu–S = 2.247 (4), 2.230 (4), 2.238 (3) Å]. One of these is involved in an intramolecular hydrogen bond (N–H···S = 3.390 Å, N–H–S = 154°). The geometry of the hydrogen-*o*-phthalate anion corresponds to that expected, with the carboxylic groups twisted on opposite sides of the phenyl ring and forming a particularly short intramolecular hydrogen bond (O–H···O = 2.351 Å, O–H–O = 156°).

Introduction

Cu^I complexes with ligands containing S as donor atom, such as thiourea and its *N*-substituted derivatives, exhibit a wide variety of stoichiometries and configurations. Tetrahedral Cu^I is found as discrete complexes in [Cu(tu)₄].½SiF₆ (tu = thiourea) (Hunt, Terry & Amma, 1974), [Cu(etu)₄]NO₃ (etu = ethylene-thiourea) (Battaglia, Bonamartini Corradi, Nardelli & Vidoni Tani, 1976) and [Cu(dmtu)₃Cl] (dmtu = *N,N'*-dimethylthiourea) (Girling & Amma, 1971), as S-bridged dimers in [Cu₂(tu)₆](BF₄)₂, [Cu₂(dmtu)₆]-(BF₄)₂ (Taylor, Weininger & Amma, 1974) and [Cu₂(tu)₆](ClO₄)₂ (Hanic & Durcanska, 1969), and as polymeric chains sharing corners in [Cu(tu)₃]Cl (Okaya & Knobler, 1964). Tetrahedral Cu^I alternating with S atoms form six-membered rings in [Cu₄(tu)₁₀]-

(SiF₆)₂.H₂O (Gash, Griffith, Spofford & Amma, 1973) and are arranged in polynuclear complexes in [Cu₄(tu)₉](NO₃)₄ (Vranka & Amma, 1966). Both tetrahedral and trigonal planar Cu^I are found as binuclear complexes in [Cu₂(etu)₄Cl₂] (Battaglia, Bonamartini Corradi, Nardelli & Vidoni Tani, 1976) and as S-bridged chains in [Cu₂(tu)₅]SO₄.2H₂O (Belicchi Ferrari & Fava Gasparri, 1976). Finally, trigonal planar Cu^I complexes are present as discrete ions in [Cu(etu)₃].½SO₄ and [Cu(tmtu)₃]BF₄ (tmtu = tetra-methylthiourea) (Weininger, Hunt & Amma, 1972), and linked in chains sharing vertices in [Cu(tu)₂]Cl (Spofford & Amma, 1970). The only example of trigonal planar coordination in Cu^I monomeric complexes involving unsubstituted thiourea is found in [Cu(tu)₃]Hpht (Hpht = hydrogen-*o*-phthalate), whose structure is reported in the present paper.

Experimental

Crystals of the compound were prepared by adding a thiourea solution to a warm aqueous solution of cupric phthalate. Thiourea reduces Cu^{II} to Cu^{I} and long, white needles of the compound formed.

Crystal data

$C_{11}H_{17}CuN_6O_4S_3$, M_r = 457·02, triclinic, a = 15·342 (9), b = 15·039 (12), c = 3·946 (4) Å, α = 89·1 (1), β = 93·6 (1), γ = 95·6 (1)°, V = 904 (1) Å³, D_o = 1·68, D_c = 1·68 g cm⁻³, Z = 2, $F(000)$ = 468, Cu $K\alpha$ radiation, λ = 1·54178 Å, μ(Cu $K\alpha$) = 51·6 cm⁻¹. Space group $P\bar{1}$ from the structure determination. Cell parameters were determined from rotation and Weissenberg photographs and refined from diffractometer data.

Intensities were collected on a Siemens AED single-crystal diffractometer with Ni-filtered Cu $K\alpha$ radiation and the ω–2θ scan technique. An elongated prism, 0·035 × 0·100 × 0·300 mm, was aligned with **c** along the φ axis of the diffractometer and all reflexions with 2θ < 140° were measured. Of 3436 independent reflexions, 2725 with I > $2\sigma(I)$ were used in the analysis. Corrections were made for Lorentz and polarization factors but not for absorption. Scale and overall isotropic temperature factors were obtained by Wilson's method.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares, first with isotropic, then with anisotropic thermal parameters. The H atoms were located from a ΔF synthesis. Further refinement included the H atoms with isotropic thermal parameters. Unit weights were used. The final R was 0·059 (observed reflexions only). Scattering factors for non-hydrogen atoms were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Final atomic parameters are given in Tables 1 and 2.*

All calculations were carried out on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna) with programs written by Immirzi (1967).

Table 1. *Final atomic coordinates for non-hydrogen atoms* ($\times 10^4$), *with e.s.d.'s in parentheses*

	x	y	z
Cu	1415 (1)	2689 (1)	816 (2)
S(1)	679 (1)	3848 (1)	−956 (4)
S(2)	695 (1)	1339 (1)	1380 (4)
S(3)	2867 (1)	2957 (1)	1858 (4)
O(1)	5763 (4)	4035 (3)	2317 (15)
O(2)	7104 (3)	3653 (3)	2406 (15)
O(3)	7762 (3)	2304 (4)	2517 (15)
O(4)	7390 (4)	859 (4)	2501 (15)
N(11)	−999 (3)	3996 (4)	−2442 (15)
N(12)	−537 (3)	2654 (3)	−3817 (13)
N(21)	2164 (3)	888 (3)	4704 (14)
N(22)	1096 (3)	−236 (3)	3553 (15)
N(31)	3935 (3)	4351 (3)	3868 (15)
N(32)	2497 (3)	4476 (3)	4664 (13)
C(1)	−356 (3)	3463 (4)	−2520 (13)
C(2)	1371 (4)	614 (4)	3351 (14)
C(3)	3112 (3)	3994 (4)	3574 (14)
C(4)	5926 (4)	2590 (4)	287 (13)
C(5)	5079 (4)	2594 (4)	−1297 (16)
C(6)	4635 (4)	1846 (4)	−2701 (16)
C(7)	5009 (4)	1059 (4)	−2622 (16)
C(8)	5840 (4)	1029 (4)	−1125 (16)
C(9)	6315 (3)	1753 (4)	339 (14)
C(10)	7222 (4)	1622 (5)	1946 (17)
C(11)	6275 (4)	3477 (5)	1792 (17)

Table 2. *Final atomic coordinates for hydrogen atoms* ($\times 10^3$) *and isotropic thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses*

	x	y	z	B
H(1)	752 (4)	314 (4)	275 (14)	3·7 (1·3)
H(5)	479 (4)	322 (4)	−126 (15)	4·6 (1·4)
H(6)	407 (4)	189 (4)	−388 (16)	5·4 (1·5)
H(7)	470 (4)	49 (4)	−359 (14)	4·0 (1·3)
H(8)	612 (4)	44 (4)	−53 (15)	4·9 (1·4)
H(111)	−86 (4)	457 (4)	−163 (15)	5·1 (1·5)
H(112)	−157 (4)	378 (4)	−288 (15)	5·0 (1·4)
H(121)	−106 (4)	248 (4)	−468 (16)	5·4 (1·5)
H(122)	−6 (4)	233 (4)	−450 (17)	6·4 (1·6)
H(211)	241 (4)	150 (4)	468 (14)	4·0 (1·3)
H(212)	251 (4)	48 (4)	579 (15)	5·1 (1·5)
H(221)	60 (4)	−54 (4)	224 (16)	6·1 (1·6)
H(222)	145 (4)	−63 (4)	433 (16)	5·7 (1·6)
H(311)	410 (4)	492 (4)	459 (16)	5·4 (1·5)
H(312)	430 (4)	404 (4)	287 (12)	5·3 (1·5)
H(321)	267 (4)	503 (4)	559 (14)	4·0 (1·3)
H(322)	196 (4)	414 (4)	517 (14)	3·9 (1·3)

Discussion

The structure consists of discrete $[Cu(tu)_3]^+$ cations and hydrogen-o-phthalate anions. Coordination around Cu is trigonal planar and involves the S atoms of three independent tu molecules (Fig. 1), with Cu—S distances (Table 3) in good agreement with those in

[Cu(tmtu)₃]BF₄ (Weininger, Hunt & Amma, 1972) and S—Cu—S angles close to 120°.

All the tu ligands are planar (Table 4) and form dihedral angles of 33·1 [S(1)C(1)N(11)N(12)], 14·6 [S(2)C(2)N(21)N(22)], and 40·8° [S(3)C(3)N(31)-N(32)]with the coordination plane. The geometries of the three tu ligands are not significantly different and are close to that of uncomplexed thiourea (Truter, 1967), except the S—C—N angles which are significantly different in each ligand: the S—C—N angle involving C—N bent toward Cuᴵ is greater than the other. N(21) is involved in an intramolecular hydrogen bond with S(3) [N(21)—H(211)···S(3) = 3·390 (8) Å] while N(12)—H(122)···S(2ᵛ), 3·518 (6), and N(32)—H(322)···S(1ᵛⁱⁱ), 3·420 (5) Å, hydrogen bonds join the complexes in chains running along [001]. These chains are linked in slices parallel to (100) (Fig. 2) by centrosymmetric hydrogen bonds, N(11)—H(111)···S(1ᶦᶦᶦ) 3·507 (9) and N(22)—H(221)···S(2ᶦᶦ) 3·544 (6) Å, which involve pairs of thiourea molecules belonging to adjacent complexes. This hydrogen bonding is of the same type as in other uncomplexed molecules containing the −C(S)NHR group (Manotti Lanfredi, Tiripicchio, Tiripicchio Camellini, Monaci & Tarli, 1977; Belicchi Ferrari, Gasparri Fava & Pelizzi, 1976).
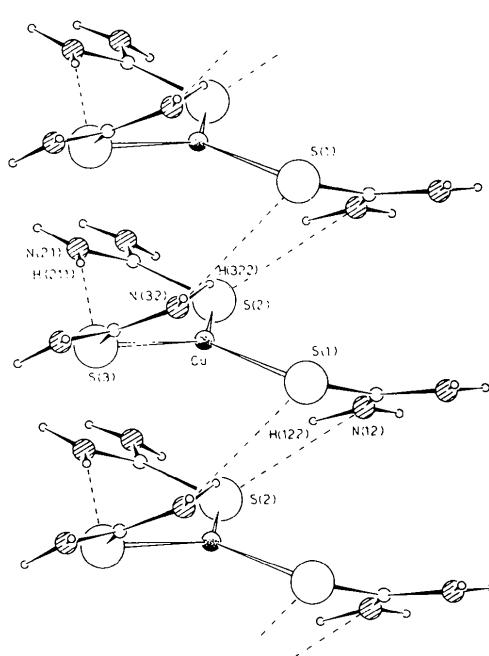

Fig. 1. Clinographic projection showing the linkage of the coordination polyhedra along c.

Table 3. Bond distances (Å) and angles (°)

(a) In the tris(thiourea)copper(I) cation

Cu—S(1)	2·247 (4)	N(11)—H(111)	0·93 (6)
Cu—S(2)	2·230 (4)	N(11)—H(112)	0·91 (6)
Cu—S(3)	2·238 (3)	N(12)—H(121)	0·87 (6)
S(1)—C(1)	1·717 (5)	N(12)—H(122)	0·97 (6)
S(2)—C(2)	1·721 (6)	N(21)—H(211)	0·96 (6)
S(3)—C(3)	1·708 (7)	N(21)—H(212)	0·93 (6)
C(1)—N(11)	1·333 (8)	N(22)—H(221)	0·97 (6)
C(1)—N(12)	1·325 (8)	N(22)—H(222)	0·88 (6)
C(2)—N(21)	1·328 (8)	N(31)—H(311)	0·91 (6)
C(2)—N(22)	1·309 (8)	N(31)—H(312)	0·88 (6)
C(3)—N(31)	1·322 (7)	N(32)—H(321)	0·92 (6)
C(3)—N(32)	1·340 (7)	N(32)—H(322)	0·95 (6)

S(1)—Cu·S(2)	119·8 (1)	H(111)—N(11)—H(112)	120 (5)
S(1)—Cu—S(3)	117·2 (1)	H(121)—N(12)—C(1)	121 (4)
S(2)—Cu—S(3)	123·0 (1)	H(122)—N(12)—C(1)	119 (4)
Cu—S(1)—C(1)	109·7 (2)	H(121)—N(12)—H(122)	117 (6)
Cu—S(2)—C(2)	110·4 (2)	H(211)—N(21)—C(2)	124 (4)
Cu—S(3)—C(3)	109·9 (2)	H(212)—N(21)—C(2)	120 (4)
S(1)—C(1)—N(11)	119·0 (5)	H(211)—N(21)—H(212)	116 (5)
S(1)—C(1)—N(12)	122·2 (4)	H(221)—N(22)—C(2)	126 (4)
N(11)—C(1)—N(12)	118·8 (5)	H(222)—N(22)—C(2)	121 (4)
S(2)—C(2)—N(21)	122·2 (5)	H(221)—N(22)—H(222)	110 (5)
S(2)—C(2)—N(22)	119·2 (5)	H(311)—N(31)—C(3)	124 (4)
N(21)—C(2)—N(22)	118·6 (5)	H(312)—N(31)—C(3)	113 (4)
S(3)—C(3)—N(31)	120·0 (4)	H(311)—N(31)—H(312)	121 (6)
S(3)—C(3)—N(32)	122·6 (4)	H(321)—N(32)—C(3)	119 (4)
N(31)—C(3)—N(32)	117·4 (5)	H(322)—N(32)—C(3)	115 (4)
H(111)—N(11)—C(1)	118 (4)	H(321)—N(32)—H(322)	122 (5)
H(112)—N(11)—C(1)	121 (4)		

(b) In the hydrogen-o-phthalate anion

C(4)—C(5)	1·407 (9)	C(4)—C(11)	1·505 (10)
C(5)—C(6)	1·364 (9)	C(11)—O(1)	1·232 (9)
C(6)—C(7)	1·364 (9)	C(11)—O(2)	1·282 (8)
C(7)—C(8)	1·376 (9)	O(2)—H(1)	1·05 (6)
C(8)—C(9)	1·388 (9)	C(5)—H(5)	1·08 (6)
C(9)—C(4)	1·417 (9)	C(6)—H(6)	0·97 (6)
C(9)—C(10)	1·529 (8)	C(7)—H(7)	1·01 (6)
C(10)—O(3)	1·268 (9)	C(8)—H(8)	1·04 (6)
C(10)—O(4)	1·214 (10)		

C(9)—C(4)—C(5)	117·3 (5)	C(9)—C(10)—O(3)	117·6 (6)
C(4)—C(5)—C(6)	122·2 (6)	C(9)—C(10)—O(4)	118·2 (6)
C(5)—C(6)—C(7)	120·3 (6)	O(3)—C(10)—O(4)	124·1 (6)
C(6)—C(7)—C(8)	119·3 (6)	C(11)—O(2)—H(1)	121 (3)
C(7)—C(8)—C(9)	122·3 (6)	H(5)—C(5)—C(4)	116 (3)
C(8)—C(9)—C(4)	118·5 (5)	H(5)—C(5)—C(6)	122 (3)
C(5)—C(4)—C(11)	113·2 (5)	H(6)—C(6)—C(5)	119 (4)
C(9)—C(4)—C(11)	129·5 (5)	H(6)—C(6)—C(7)	120 (4)
C(4)—C(9)—C(10)	125·7 (5)	H(7)—C(7)—C(6)	123 (4)
C(8)—C(9)—C(10)	115·7 (5)	H(7)—C(7)—C(8)	118 (3)
C(4)—C(11)—O(1)	119·6 (6)	H(8)—C(8)—C(7)	124 (3)
C(4)—C(11)—O(2)	119·5 (6)	H(8)—C(8)—C(9)	113 (3)
O(1)—C(11)—O(2)	120·9 (7)		

Table 4. *Least-squares planes and atom deviations*

Equations of least-squares planes are in the form: $AX + BY + CZ = D$, where X, Y and Z are coordinates in Å referred to orthogonal axes, obtained from fractional coordinates by applying the matrix:

$$
\begin{matrix}
a \sin \gamma & 0 & -c \sin \alpha \cos \beta^* \\
a \cos \gamma & b & c \cos \alpha \\
0 & 0 & c \sin \alpha \sin \beta^*
\end{matrix}
$$

Deviations (Å) of relevant atoms from the planes are in square brackets.

	A	B	C	D
Plane(I): Cu, S(1), S(2), S(3)	0·2038	−0·2344	−0·9505	−0·7598
[Cu −0·009 (1), S(1) 0·003 (2), S(2) 0·003 (2), S(3) 0·003 (2)]				
Plane (II): S(1), C(1), N(11), N(12)	0·2699	0·3290	−0·9049	2·4953
[S(1) 0·001 (2), C(1) −0·002 (5), N(11) 0·001 (6), N(12) 0·001 (5)]				
Plane (III): S(2), C(2), N(21), N(22)	0·4440	−0·2056	−0·8721	−0·4120
[S(2) 0·001 (2), C(2) 0·003 (6), N(21) −0·001 (5), N(22) −0·001 (6)]				
Plane (IV): S(3), C(3), N(31), N(32)	−0·0527	0·4122	−0·9096	0·7669
[S(3) 0·001 (2), C(3) 0·001 (6), N(31) 0·001 (6), N(32) 0·001 (5)]				
Plane (V): C(4), C(5), C(6), C(7), C(8), C(9)	0·4468	0·1867	−0·8750	4·5067
[C(4) −0·004 (5), C(5) 0·004 (6), C(6) 0·001 (6), C(7) −0·004 (6), C(8) 0·001 (6), C(9) 0·002 (5), C(10) −0·016 (7), C(11) −0·060 (7), O(1) −0·424 (6), O(2) 0·314 (6), O(3) 0·326 (6), O(4) −0·317 (6), H(1) 0·32 (6)]				
Plane (VI): C(4), C(11), O(1), O(2)	0·1500	0·3546	−0·9229	2·3165
[C(4) 0·003 (5), C(11) −0·012 (7), O(1) 0·004 (6), O(2) 0·004 (6), H(1) −0·32 (6)]				
Plane (VII): C(9), C(10), O(3), O(4)	0·3924	−0·1027	−0·9140	3·4785
[C(9) 0·003 (5), C(10) −0·011 (7), O(3) 0·004 (6), O(4) 0·004 (6)]				
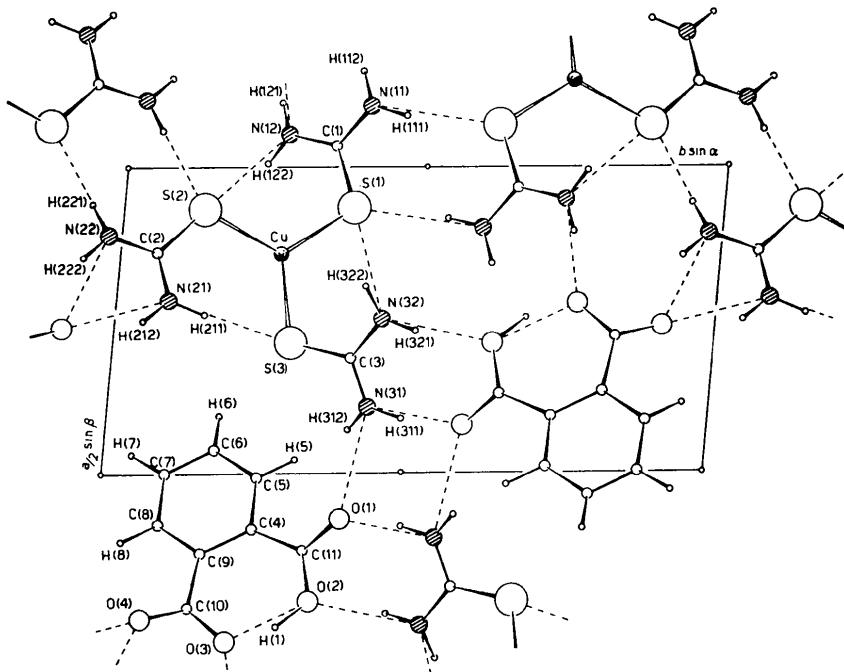
Fig. 2. Projection of the structure along |001|.

Table 5. *Hydrogen bonds*

N(21)–H(211)···S(3)	3·390 (8) Å		N(21)–H(211)–S(3)	154 (4)°
H(211)···S(3)	2·50 (6)		H(211)–N(21)–S(3)	19 (3)
O(2)–H(1)···O(3)	2·351 (9)		O(2)–H(1)–O(3)	156 (6)
H(1)···O(3)	1·35 (6)		H(1)–O(2)–O(3)	13 (3)
N(21)–H(212)···O(4^i)	2·959 (9)		N(21)–H(212)–O(4^i)	147 (5)
H(212)···O(4^i)	2·13 (6)		H(212)–N(21)–O(4^i)	23 (4)
N(22)–H(222)···O(4^i)	2·936 (8)		N(22)–H(222)–O(4^i)	146 (5)
H(222)···O(4^i)	2·16 (6)		H(222)–N(22)–O(4^i)	24 (4)
N(22)–H(221)···S(2^{ii})	3·554 (6)		N(22)–H(221)–S(2^{ii})	179 (5)
H(221)···S(2^{ii})	2·58 (6)		H(221)–N(22)–S(2^{ii})	1 (4)
N(11)–H(111)···S(1^{iii})	3·507 (9)		N(11)–H(111)–S(1^{iii})	172 (5)
H(111)···S(1^{iii})	2·59 (6)		H(111)–N(11)–S(1^{iii})	6 (4)
N(12)–H(121)···O(3^{iv})	2·909 (7)		N(12)–H(121)–O(3^{iv})	167 (6)
H(121)···O(3^{iv})	2·06 (6)		H(121)–N(12)–O(3^{iv})	9 (4)
N(12)–H(122)···S(2^v)	3·518 (6)		N(12)–H(122)–S(2^v)	154 (5)
H(122)···S(2^v)	2·62 (6)		H(122)–N(12)–S(2^v)	19 (4)
N(31)–H(311)···O(1^{vi})	2·860 (8)		N(31)–H(311)–O(1^{vi})	158 (6)
H(311)···O(1^{vi})	1·99 (6)		H(311)–N(31)–O(1^{vi})	15 (4)
N(31)–H(312)···O(1)	2·992 (8)		N(31)–H(312)–O(1)	139 (5)
H(312)···O(1)	2·27 (6)		H(312)–N(31)–O(1)	30 (4)
N(32)–H(321)···O(2^{vi})	3·051 (9)		N(32)–H(321)–O(2^{vi})	172 (5)
H(321)···O(2^{vi})	2·13 (6)		H(321)–N(32)–O(2^{vi})	5 (4)
N(32)–H(322)···S(1^{vii})	3·420 (5)		N(32)–H(322)–S(1^{vii})	149 (5)
H(322)···S(1^{vii})	2·57 (6)		H(322)–N(32)–S(1^{vii})	23 (3)

Symmetry code

(i) $1 - x, -y, 1 - z$
(ii) $-x, -y, -z$
(iii) $-x, 1 - y, -z$
(iv) $-1 + x, y, -1 + z$

(v) $x, y, -1 + z$
(vi) $1 - x, 1 - y, 1 - z$
(vii) $x, y, 1 + z$

The slices of hydrogen-bonded complex cations are joined by a system of N—H···O hydrogen bonds involving the hydrogen-o-phthalate anions (Table 5). The geometry of the hydrogen-o-phthalate anion is as expected with the benzene ring planar (Table 4) and the carboxylic groups (both planar) rotated in opposite directions by nearly the same angles: 17·1 and −19·8° for the deprotonated and the protonated carboxyl groups respectively. H(1) attached to O(2) is out of the plane of its carboxylic group by 0·32 Å and is involved in a strong intramolecular hydrogen bond [O(2)–H(1)···O(3) = 2·351 (9) Å] which is responsible for the relative orientations of the carboxylic groups. Although this distance is shorter than in LiHpht.2H$_2$O (Gonschorek & Küppers, 1975) [O(2)···O(3) = 2·385 (2) Å] where the hydrogen bond is symmetric [O(2)–H(1) = 1·200 (29), O(3)–H(1) = 1·191 (29) Å] and the hydrogen-o-phthalate anion is planar, in the present structure the O(2)–H(1)···O(3) hydrogen bond is unsymmetrical and deviates appreciably from linearity, O(2)–H(1)–O(3) being 156 (6)° [172 (3)° in LiHpht.2H$_2$O]. Therefore, the short intramolecular distance O—H···O found now in the hydrogen-o-phthalate anion can be related neither to the planarity of the anion (as in LiHpht.2H$_2$O), nor to the symmetry of the hydrogen bonding. The non-planarity of the phthalate anion is probably due to the rather strong

N—H···O hydrogen bonds which the —NH$_2$ groups of the tu molecules form with the O atoms of the carboxylic groups. These last interactions probably produce a deformation of the C(9)C(10)O(3)O(4) group allowing a closer approach of O(3) to O(2).

References

BATTAGLIA, P., BONAMARTINI CORRADI, A., NARDELLI, M. & VIDONI TANI, M. E. (1976). *J. Chem. Soc. Dalton,* pp. 143–146.
BELICCHI FERRARI, M. & FAVA GASPARRI, G. (1976). *Cryst. Struct. Commun.* 5, 935–940.
BELICCHI FERRARI, M., GASPARRI FAVA, G. & PELIZZI, C. (1976). *Acta Cryst.* B32, 901–908.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
GASH, A. G., GRIFFITH, E. H., SPOFFORD, W. A. & AMMA, E. L. (1973). *Chem. Commun.* pp. 256–257.
GIRLING, R. L. & AMMA, E. L. (1971). *Inorg. Chem.* 10, 335–340.
GONSCHOREK, W. & KÜPPERS, H. (1975). *Acta Cryst.* B31, 1068–1072.
HANIC, F. & DURCANSKA, E. (1969). *Inorg. Chim. Acta,* 3, 293–298.

HUNT, G. W., TERRY, N. W. & AMMA, E. L. (1974). *Cryst. Struct. Commun.* **3**, 523–526.

IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743–749.

MANOTTI LANFREDI, A. M., TIRIPICCHIO, A., TIRIPICCHIO CAMELLINI, M., MONACI, A. & TARLI, F. (1977). *J. Chem. Soc. Dalton*, pp. 417–422.

OKAYA, Y. & KNOBLER, C. (1964). *Acta Cryst.* **17**, 928–930.

SPOFFORD, W. A. & AMMA, E. L. (1970). *Acta Cryst.* **B26**, 1474–1483.

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

TAYLOR, I. F., WEININGER, M. S. & AMMA, E. L. (1974). *Inorg. Chem.* **13**, 2835–2842.

TRUTER, M. R. (1967). *Acta Cryst.* **22**, 556–559.

VRANKA, R. G. & AMMA, E. L. (1966). *J. Amer. Chem. Soc.* **88**, 4270–4271.

WEININGER, M. S., HUNT, G. W. & AMMA, E. L. (1972). *Chem. Commun.* pp. 1140–1141.

The Crystal and Molecular Structure of 2,4,6-Tris(2'-pyridinio)-1,3,5-triazine Pentachloromanganate(III) Chloride Monohydrate

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$[C_{18}H_{15}N_6]^{3+}[MnCl_5]^{2-}.Cl^-.H_2O$ is monoclinic, space group $P2_1/n$, with $a = 13.27$ (2), $b = 15.31$ (1), $c = 12.10$ (1) Å, $\beta = 105.3$ (1)°, $Z = 4$. The structure was refined to $R = 0.082$ for 1339 diffractometer data. The $[MnCl_5]^{2-}$ anion is square-pyramidal, with a slight distortion towards a trigonal bipyramid, and has approximate mm symmetry. The longer axial Mn–Cl distance of 2.413 (6) Å compares with the two average equatorial distances of 2.250 (6) and 2.275 (7) Å; the Mn atom is 0.39 Å above the Cl equatorial plane. The closely planar cation contains the three pyridyl N atoms in protonated form, two of which are hydrogen-bonded to the free Cl^- ion and the third to the water molecule, which also hydrogen bonds the $[MnCl_5]^{2-}$ ion. The cations, the Cl atoms and the water molecules are contained in two sets of planes 3.18 Å apart and parallel to $(20\bar{1})$; the Mn atoms lie between these planes.

Introduction

2,4,6-Tris(2'-pyridyl)-1,3,5-triazine (tpt) has been well characterized in its interactions with transition-metal ions (Barclay, Vagg & Watton, 1977, and references therein). From acidic solutions salts have been isolated in which either the three pyridyl groups of the molecule are protonated or the molecule acts as a tridentate ligand in a protonated form (Vagg, Warrener & Watton, 1967; Barclay, Vagg & Watton, 1977).

Unrelated to that work several reports of the isolation of chloro complexes of Mn^{3+} have appeared. The $[MnCl_6]^{3-}$ ion is stabilized by the presence of large tervalent cations (Hatfield, Fay, Pfluger & Piper, 1963; Levason, McAuliffe & Murray, 1972) although such compounds have not been investigated structurally. A series of compounds have been studied (Levason & McAuliffe, 1973) in which the $[MnCl_5]^{2-}$ ion exists. An X-ray structural analysis (Bernal, Elliot & Lalancette, 1971) has shown this species to be a distorted square-pyramidal unit in $[bipyH_2][MnCl_5]$.

The corresponding salt of tpt and Mn^{3+} has been prepared (Vagg & Watton, unpublished) of general formula $(tptH_3)(H_2O)MnCl_6$. Its structure was investigated both to clarify the stereochemistry of the Mn atom and also as part of our overall investigations on the organic molecule.

Experimental

The compound was prepared by reaction of tpt and a 'brown solution' (Goodwin & Sylva, 1965) of $KMnO_4$ in 10 M HCl. Dark-green needles were obtained.

Over a period of days the unprotected crystals, like the bipyridine analogue (Bernal, Elliot & Lalancette, 1971), show signs of decomposition, which was arrested by mounting the crystals in a gelatin capsule prior to data collection.

Crystal data

$C_{18}H_{17}N_6Cl_6OMn$, $M_r = 601.0$, monoclinic, $a = 13.27$ (2), $b = 15.31$ (1), $c = 12.10$ (1) Å, $\beta = 105.3$ (1)°, $V = 2371.2$ Å^3, $D_m = 1.70$ (by flotation), $Z = 4$, $D_c = 1.67$ g cm^{-3}, $F(000) = 1208$, μ(Cu $K\alpha$) =