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Inorganica Chimica Acta 229 (1995) 77–80

Inorganica Chimica Acta

Synthesis and structure of $\{Cu_2(EBPYT)_3(PF_6)_2\}_n$ (where EBPYT = *N,N′*-ethylenebis(pyridin-2-thione)); a novel polymeric complex containing 4-, 18- and 36-membered rings [☆]

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Received 15 April 1994

Abstract

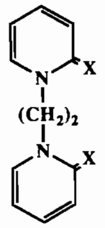
Reaction of *N,N′*-ethylenebis(pyridin-2-thione) (EBPYT) with $[Cu(MeCN)_4]PF_6$ in acetonitrile/ethanol yields the complex $\{Cu_2(EBPYT)_3(PF_6)_2\}_n$ which has been characterised by single crystal X-ray diffraction studies. The crystals are triclinic, space group $P\bar{1}$, $a=7.552(2)$, $b=10.936(3)$, $c=15.039(4)$ Å, $\alpha=110.93(2)$, $\beta=95.40(2)$, $\gamma=100.72(2)°$, $Z=2$. Each Cu(I) ion is tetrahedrally coordinated by four sulfur atoms, one from each of four different EBPYT ligands. Two of the sulfur atoms bridge pairs of copper atoms to form Cu_2S_2 units. These are further linked by the EBPYT ligands to form novel chains of contiguous 18- and 36-membered rings.

Keywords: Crystal structures; Copper complexes; Polydentate ligand complexes; Polymeric complexes

1. Introduction

We have recently shown that *N,N′*-ethylenebis(pyridin-2-one) (**Ia**) and related ligands with other organic 'spacer' units between the pyridine-2-one rings are able to generate a wide range of unusual polymeric complexes [1–4]. A particularly interesting feature of these materials is their propensity for forming large rings in which the metal ions form part of the ring framework. These can take the form of individual rings, chains of rings, sheets of rings or three-dimensional networks of rings, and a range of ring sizes up to 66-membered has been observed [4,5].

In view of the diverse behaviour of these O-donor ligands, we have initiated parallel studies with their S-donor counterparts (e.g. **Ib** and related ligands) as the change in the donor atom offers entry into large-ring 'framework-type' materials incorporating metals favouring sulfur coordination. Our initial results appear to justify this conclusion, and we report here, as an example, the structure of the complex $\{Cu_2(EBPYT)_3(PF_6)_2\}_n$ (**1**) formed by **Ib** (EBPYT).



I **a** X = O; **b** X = S

2. Experimental

2.1. Preparations

2.1.1. *N,N′-Ethylenebis(pyridin-2-thione) (**Ib**)*

This was obtained by reacting *N,N′*-ethylenebis(pyridine-2-one) (**Ia**) [1] with Lawesson's reagent in equimolar amounts in dry toluene, under nitrogen, at 100 °C for 5 h. The crude product crystallised on concentration of the reaction solution and was recrystallised from ethanol. The yields were 40–50% of yellow crystals, m.p. 219.5–220.5 (dec.). *Anal.* Calc. for $C_{12}H_{12}N_2S_2$: C, 58.0; H, 4.9; N, 11.3. Found: C, 58.3;

[☆] This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

SSDI 0020-1693(94)04228-N

H, 4.1; N, 11.4%. NMR, δ_H ($CDCl_3$): 5.15 (4H, s), 6.58 (2H, t), 7.20 (2H, t), 7.65 (4H, m). MS: 248 (M^+). (The constitution of the ligand is also confirmed by the structure of complex **1**.)

2.1.2. $\{Cu_2(EBPYT)_3(PF_6)_2\}_n$ (*1*)

A solution of **Ib** (0.02 g) in warm ethanol (15 cm^3) was mixed with one of $[Cu(MeCN)_4]PF_6$ (0.03 g) in acetonitrile (2 cm^3) to give an immediate precipitate of a bright yellow–orange complex. This was collected, washed with ethanol and ether and then recrystallised from acetonitrile/butan-1-ol (10:2) to yield orange prisms, which were characterised by single crystal X-ray diffraction measurements.

2.2. X-ray studies

A summary of the crystal data and of the data collection and refinement parameters for compound **1** is given in Table 1. Data were collected on a Siemens P4/PC diffractometer, using ω-scans ($3 < 2\theta < 116°$) and graphite monochromated Cu Kα radiation. The data were corrected for Lorentz and polarisation factors but not for absorption.

The structure was solved by the heavy atom method and the non-hydrogen atoms refined anisotropically. The hydrogen atoms were placed at idealised positions C–H = 0.96 Å, assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$ and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least-squares. The mean and maximum shift/errors in the final refinement were 0.000 and 0.001, respectively, and the maximum and minimum residual electron densities in the final ΔF map were 0.69 and -0.53 e Å^{-3}, respectively.

Table 1
Summary of crystal data and intensity collection

Formula	$C_{18}H_{18}CuF_6N_3PS_3$
M_r	581.0
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.552(2)
b (Å)	10.936(3)
c (Å)	15.039(4)
α (°)	110.93(2)
β (°)	95.40(2)
γ (°)	100.72(2)
Cell volume (Å^3)	1122.2(5)
Z	2
Crystal dimensions (mm)	0.06×0.06×0.3
ρ (calc.) (g cm^{-3})	1.72
μ (calc.) (mm^{-1})	5.239
Radiation	Cu Kα
Unique reflections measured	3080
Reflections considered observed $\|F_o\| > 3\sigma(\|F_o\|)$	2449
Weight (G) [a]	0.0005
No. parameters varied	308
R	0.053
R_w	0.073

[a] $w^{-1} = \sigma^2(F) + GF^2$.

Computations were performed on a 33 MHz 486 PC using the Siemens SHELXTL PLUS (PC version) [6]. Fractional coordinates for the non-hydrogen atoms are given in Table 2. Table 3 gives selected bond lengths and angles. See also Section 4.

3. Results and discussion

The X-ray measurements show that compound **1** has the stoichiometric formula $Cu_2(EBPYT)_3(PF_6)_2$. Each copper atom is tetrahedrally coordinated to four sulfur atoms, one from each of four different EBPYT ligands (Fig. 1). Two of the sulfur atoms act as unidentate donors whilst each of the other two form μ-S bridges linking pairs of copper centres. Sulfur bridges of this type are well-established, e.g. in linking pairs of copper

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3)

	x	y	z	U_{eq} [a]
Cu(1)	162(1)	3692(1)	4539(1)	39(1)
S(10)	−2197(2)	2106(2)	4612(1)	41(1)
C(11)	−1461(9)	1486(6)	5430(4)	27(3)
C(12)	397(9)	1647(7)	5786(5)	34(3)
C(13)	934(10)	1181(7)	6459(5)	43(3)
C(14)	−389(12)	493(8)	6813(6)	51(4)
C(15)	−2147(11)	311(8)	6471(5)	46(3)
N(16)	−2701(7)	798(5)	5795(4)	32(2)
C(17)	−4667(9)	607(7)	5498(5)	36(3)
S(20)	2043(2)	5246(2)	6016(1)	34(1)
C(21)	1455(8)	4901(6)	6985(4)	27(3)
C(22)	−366(9)	4494(7)	7100(5)	34(3)
C(23)	−726(10)	4221(7)	7885(5)	40(3)
C(24)	692(11)	4328(8)	8592(5)	52(4)
C(25)	2428(10)	4734(8)	8484(5)	44(3)
N(26)	2816(7)	5016(5)	7703(4)	30(2)
C(27)	4762(9)	5438(7)	7649(5)	36(3)
C(28)	5382(8)	6953(7)	7942(5)	35(3)
S(30)	2474(2)	3260(2)	3669(1)	39(1)
C(31)	1538(9)	2607(7)	2481(4)	31(3)
C(32)	−372(9)	2035(7)	2121(5)	40(3)
C(33)	−1069(10)	1612(8)	1170(5)	48(3)
C(34)	67(11)	1693(9)	509(6)	55(4)
C(35)	8134(10)	7821(8)	9170(5)	51(4)
N(36)	7391(7)	7414(6)	8207(4)	33(2)
P(1)	4765(3)	8192(3)	1253(2)	58(1)
F(1)	4500(16)	6672(8)	609(6)	194(6)
F(2)	5162(15)	9682(7)	1930(7)	181(6)
F(3)	2680(8)	8019(10)	1213(5)	140(6)
F(4)	6861(8)	8336(10)	1291(5)	139(5)
F(5)	4668(9)	8544(10)	328(5)	137(5)
F(6)	4852(7)	7810(7)	2168(4)	94(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3
Bond lengths (Å) and angles (°) for compound **1** with e.s.d.s in parentheses

Cu(1)–S(10)	2.284(2)	Cu(1)–S(20)	2.377(2)
Cu(1)–S(30)	2.298(2)	Cu(1)–Cu(1A)	2.768(2)
Cu(1)–S(20A)	2.443(2)	S(10)–C(11)	1.699(8)
C(11)–C(12)	1.409(9)	C(11)–N(16)	1.369(9)
C(12)–C(13)	1.347(12)	C(13)–C(14)	1.399(12)
C(14)–C(15)	1.329(12)	C(15)–N(16)	1.372(11)
N(16)–C(17)	1.463(8)	C(17)–C(17A)	1.564(11)
S(20)–C(21)	1.708(8)	S(20)–Cu(1A)	2.443(2)
C(21)–C(22)	1.411(9)	C(21)–N(26)	1.373(8)
C(22)–C(23)	1.355(12)	C(23)–C(24)	1.394(11)
C(24)–C(25)	1.348(11)	C(25)–N(26)	1.360(11)
N(26)–C(27)	1.476(8)	C(27)–C(28)	1.520(10)
C(28)–N(36)	1.474(8)	S(30)–C(31)	1.692(6)
C(31)–C(32)	1.429(9)	C(31)–N(36A)	1.368(9)
C(32)–C(33)	1.354(11)	C(33)–C(34)	1.388(12)
C(34)–C(35A)	1.336(10)	C(35)–N(36)	1.379(9)
C(35)–C(34A)	1.336(10)	N(36)–C(31A)	1.368(9)
S(10)–Cu(1)–S(20)	117.9(1)	S(10)–Cu(1)–S(30)	125.7(1)
S(20)–Cu(1)–S(30)	97.1(1)	S(10)–Cu(1)–Cu(1A)	113.5(1)
S(20)–Cu(1)–Cu(1A)	56.1(1)	S(30)–Cu(1)–Cu(1A)	120.5(1)
S(10)–Cu(1)–S(20A)	89.8(1)	S(20)–Cu(1)–S(20A)	109.9(1)
S(30)–Cu(1)–S(20A)	117.1(1)	Cu(1A)–Cu(1)–S(20A)	53.8(1)
Cu(1)–S(10)–C(11)	109.0(2)	S(10)–C(11)–C(12)	124.0(6)
S(10)–C(11)–N(16)	120.1(5)	C(12)–C(11)–N(16)	115.9(7)
C(11)–C(12)–C(13)	122.5(7)	C(12)–C(13)–C(14)	119.4(7)
C(13)–C(14)–C(15)	118.8(9)	C(14)–C(15)–N(16)	122.0(8)
C(11)–N(16)–C(15)	121.4(6)	C(11)–N(16)–C(17)	120.5(6)
C(15)–N(16)–C(17)	118.1(6)	N(16)–C(17)–C(17A)	109.2(7)
Cu(1)–S(20)–C(21)	112.0(2)	Cu(1)–S(20)–Cu(1A)	70.1(1)
C(21)–S(20)–Cu(1A)	110.5(3)	S(20)–C(21)–C(22)	124.0(5)
S(20)–C(21)–N(26)	119.0(5)	C(22)–C(21)–N(26)	117.0(6)
C(21)–C(22)–C(23)	120.7(7)	C(22)–C(23)–C(24)	120.8(7)
C(23)–C(24)–C(25)	118.3(8)	C(24)–C(25)–N(26)	121.8(7)
C(21)–N(26)–C(25)	121.6(6)	C(21)–N(26)–C(27)	121.0(6)
C(25)–N(26)–C(27)	117.5(6)	N(26)–C(27)–C(28)	112.0(6)
C(27)–C(28)–N(36)	111.3(6)	Cu(1)–S(30)–C(31)	107.7(2)
S(30)–C(31)–C(32)	123.7(6)	S(30)–C(31)–N(36A)	120.8(4)
C(32)–C(31)–N(36A)	115.4(6)	C(31)–C(32)–C(33)	121.4(7)
C(32)–C(33)–C(34)	120.7(6)	C(33)–C(34)–C(35A)	118.6(7)
N(36)–C(35)–C(34A)	121.7(8)	C(28)–N(36)–C(35)	117.0(6)
C(28)–N(36)–C(31A)	121.1(5)	C(35)–N(36)–C(31A)	121.9(5)

atoms, as in $(Ph_3P)_2Cu(\mu\text{-}SPh)_2Cu(PPh_3)_2$ (**2**) [7], or in the formation of more extensive copper arrays, e.g. the $Cu_4(\mu\text{-}S)_6$ unit in $Cu_4[SC(NH_2)_2]_9(NO_3)_4 \cdot 4H_2O$ [8].

Each CuS_4 tetrahedron is appreciably distorted with angles at Cu in the range 89.74(7)–125.65(8)°. The terminal Cu–S bonds (2.284(2) and 2.298(2) Å) are significantly shorter than those formed by the bridging sulfur atoms (2.377(2) and 2.443(2) Å). The terminal Cu–S bond lengths may be compared with those of 2.319(5)–2.362(6) Å found in $[Cu(thiourea)_4]_2(SiF_6)$ [9], and the values for the bridge bonds with those of 2.344(4) and 2.415(4) Å reported for **2** [7]. The Cu···Cu distance within the planar Cu_2S_2 ring (2.768(2) Å) is well toward the lower end of the range reported for other dinuclear Cu(I) systems with bridging S-donor ligands [10], but shorter Cu···Cu distances are known (e.g. 2.613 Å in $[Cu(SC_6H_4CH_3\text{-}o)(C_{12}H_8N_2)]_2 \cdot CH_3CN$ [11]); it is too long for any significant metal–metal bonding. Whereas the S–Cu–S ring angle (109.9(1)°) does not depart from tetrahedral, the Cu–(μ-S)–Cu bond angle (70.1(1)°) is appreciably contracted.

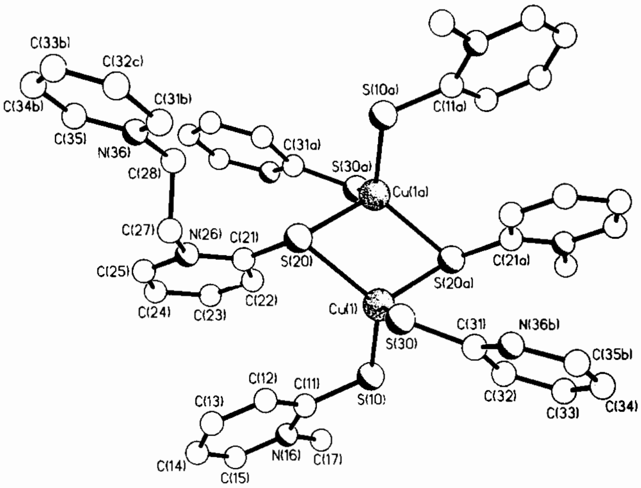


Fig. 1. View of the copper atom environment in **1**, showing the crystallographic numbering scheme.

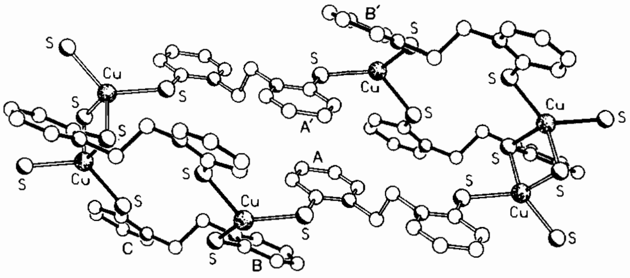


Fig. 2. View of part of the structure of **1** showing the contiguous, linked 18- and 36-membered rings.

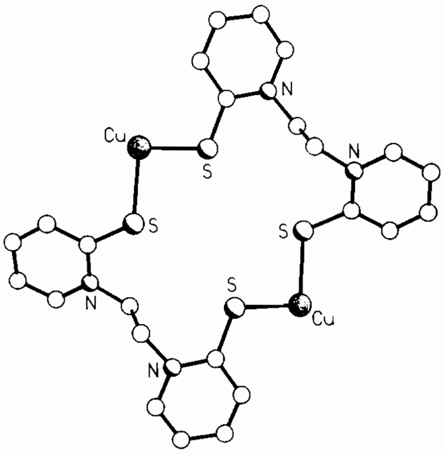


Fig. 3. The 18-membered ring system present in **1**.

The particularly novel feature of the structure of compound **1** is the way in which the Cu_2S_2 units are bridged by EBPYT ligands to form linked 18- and 36-membered rings (Fig. 2). Both macrocyclic rings are centrosymmetric. In the 18-membered ring (Fig. 3) the

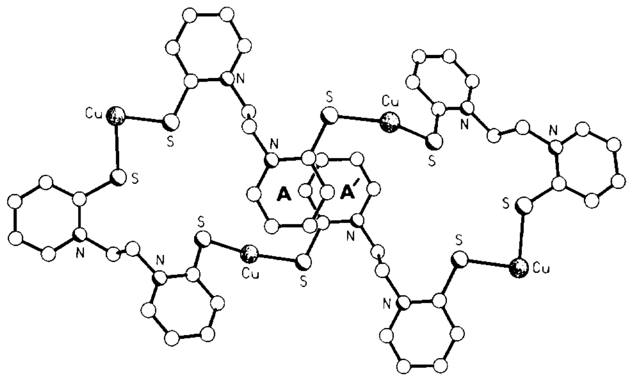


Fig. 4. The folded 36-membered ring system in 1, showing the stacking of two of the pyridyl rings.

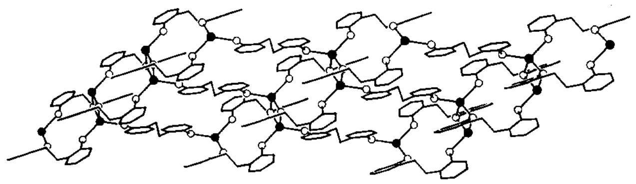


Fig. 5. Part of the polymeric sheet formed by 1.

geometry about the ethylene bridge in the EBPYT ligand is *anti*-disposed, with the two pyridyl rings inclined by 32°, and with the sulfur donor atoms it is *syn*-disposed. In the 36-membered ring one pair of EBPYT linking units is in common with the 18-membered ring (Fig. 2). The other pair again have an *anti*-geometry about their ethylene linkage (which lies on a centre of symmetry) but with an *anti*-disposition of the sulfur donor atoms.

Although the 18-membered ring is approximately planar (with a maximum deviation of 0.9 Å from the mean plane) it is still essentially self-filling with all four sulfur atoms directed inwards. The *trans*-annular S–S distances are in the range 4.07–5.64 Å.

The 36-membered ring is also self-filling but it is folded, forming two 'compartments' (Fig. 4) each with three sulfur atoms directed inwards and one outwards. The *trans*-annular distances between the inwardly directed sulfur atoms are 4.07 and 4.68 Å. The folding of the larger ring results in a parallel π-stacking of one pair of pyridyl rings (A and A′ in Fig. 2); their interplanar spacing is 3.34 Å and the centroid–centroid distance is 3.83 Å. This stacking arrangement extends to include one ring (B and B′) from each adjacently fused 18-membered ring. The A and B and A′ and B′ rings are, respectively, inclined by 17° and the A–B centroid–centroid separation is 3.77 Å. This motif is further extended via partial overlap between the pyridyl ring B and ring C of a symmetry-related macrocycle and hence throughout the structure. The rings B and C are inclined by 22° and their centroid–centroid separation is 3.89 Å.

The 4-, 18- and 36-membered rings are linked contiguously to form a polymeric sheet, part of which is illustrated in Fig. 5. The anions are positioned in the interstices between the polymeric sheets, with the shortest intermolecular contacts being between the pyridyl protons attached to C(13) and C(35) and fluorines F(6) and F(4) at 2.49 and 2.47 Å, respectively.

The present result demonstrates that extended reach sulfur donor ligands based on linked pyridine-thiones and related systems do, indeed, have appreciable potential for generating unusual molecular frameworks containing very large rings.

4. Supplementary material

Additional crystallographic data (including anisotropic thermal parameters and a complete list of bond lengths and angles) have been deposited at the Cambridge Crystallographic Data centre.

Acknowledgements

We thank the SERC for the diffractometer and the CEC for a Visiting Fellowship (to S.M.). We acknowledge Ripon College for granting D.A.K. sabbatical leave during the fall of 1993.

References

[1] G.A. Doyle, D.M.L. Goodgame, S.P.W. Hill and D.J. Williams, *J. Chem. Soc., Chem. Commun.*, (1993) 207.
[2] D.M.L. Goodgame, S.P.W. Hill and D.J. Williams, *J. Chem. Soc., Chem. Commun.*, (1993) 1019.
[3] G.A. Doyle, D.M.L. Goodgame, A. Sinden and D.J. Williams, *J. Chem. Soc., Chem. Commun.*, (1993) 1170.
[4] D.M.L. Goodgame, S.P.W. Hill and D.J. Williams, *Polyhedron, 12* (1993) 2933.
[5] S.P.W. Hill, *Ph.D. Thesis*, London University, UK, 1993.
[6] G.M. Sheldrick, *SHELXTL PLUS PC Version*, Siemens Analytical Instruments Inc., Madison, WI, 1992.
[7] I.G. Dance, P.J. Guerney, A.D. Rae and M.L. Scudder, *Inorg. Chem., 22* (1983) 2883.
[8] E.H. Griffith, G.W. Hunt and E.L. Amma, *J. Chem. Soc., Chem. Commun.*, (1976) 432.
[9] G.W. Hunt, N.W. Terry and E.L. Amma, *Acta Crystallogr., Sect. B, 35* (1979) 1235.
[10] B.J. Hathaway, *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon, Oxford, 1987, Ch. 53.
[11] R.K. Chadna, R. Kumar and D.G. Tuck, *Can. J. Chem., 65* (1988) 1336.