Synthesis and Crystal Structures of Novel Copper(I) Co-ordination Polymers and a Hexacopper(I) Cluster of Quinoline-2-thione†

Susumu Kitagawa,[*,a] **Satoshi Kawata,**[a] **Youich Nozaka**[b] **and Megumu Munakata**[b]
[a] *Department of Chemistry, Tokyo Metropolitan University, Minami Ohsawa, 1-1, Hachiouji, Tokyo, 192-03, Japan*
[b] *Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, 577, Japan*

Quinoline-2-thione (C_9H_7NS) reacted with $[Cu(MeCN)_4]^+$ in tetrahydrofuran to give infinite-chain copper(I) complexes $[\{[Cu(C_9H_7NS)_2]X\}_\infty]$ (X = ClO_4 **1** or PO_2F_2 **2**) and $[Cu_6(C_9H_6NS)_6]$ **3**. The crystal structures of all three have been determined. Complexes **1** and **2** are isomorphous and crystallize in space group $P4_2/m$, $Z = 8$ with $a = 16.697(1)$, $c = 6.438(2)$ Å, and $a = 16.713(5)$, $c = 6.412(2)$ Å, respectively. Only the thione sulfur is involved in co-ordination to copper(I), in a bridging mode. Each copper has a distorted-tetrahedral geometry, resulting in an infinite linear-chain framework of $(CuS_2)_\infty$. Two types of chain–chain interactions exist, leading to a three-dimensional structure; stacking of the planar thione between the nearest neighbours with distances of 3.219(1) and 3.206(1) Å for **1** and **2**, respectively; hydrogen bonding between the counter anion X and the NH parts of the thione bridges the two ligands, and the neighbouring chains are linked. The visible spectra of the solids exhibited are different from those in solution, and are characteristic of the former. Complex **3** crystallizes in space group $P\bar{1}$, with $a = 13.524(3)$, $b = 13.547(2)$, $c = 8.2106(9)$ Å, $\alpha = 99.18(1)$, $\beta = 101.01(1)$, $\gamma = 118.26(1)$ and $Z = 2$. The copper core is a distorted octahedron, each copper having a trigonal geometry with two thionate sulfurs and a nitrogen donor from a μ_3-thionate ligand. With the quinoline-2-thione ligand, the polymeric complex is preferred to the hexanuclear complex.

We are currently studying the synthetic chemistry of crystalline co-ordination polymers of copper.[1] One aspect of this concerns the choice of linking ligands, which have at least two donor atoms or a donor atom with bridging capability. Sulfur-containing ligands are considered to be relevant because of the matching of hard–soft criteria and of their bridging ability. Although many polymeric copper compounds have so far been synthesised,[2] the linking ligands in the polymer backbone are simple ones such as S^{2-} and SCN^-.[3-6] To expand this chemistry it is of interest to use organic sulfur-containing ligands and to determine the factors which govern the electronic and geometric structures of the polymers, in order to facilitate their rational synthesis.

Ligands containing the thioamide structure have considerable co-ordination potential. Their flexibility based on the tautomerism thionate $[-N{=}C(S^-)-]$ $\longleftrightarrow$ thione $[-NHC({=}S)-]$ can afford various co-ordination modes.[7,8] Among copper(I) compounds a terminal or bridged thione form is common. Recently, a new μ_3-type co-ordination of a thioamide ligand has been found in polynuclear copper(I) compounds[9-11] of 1*H*-pyridine-2-thione (C_5H_5NS) and 1,4-imidazoline-2-thione which are present as the thionate form. To add an additional dimension to thioamidecopper(I) chemistry, it is proposed to find a route to co-ordination polymer chemistry. One choice is to reproduce the ability of pyridinethione to undergo intermolecular interaction. We have chosen quinoline-2-thione as a linking ligand, which has a larger aromatic part, and succeeded in the synthesis of multi-linked copper(I) co-ordination polymers. Here we describe the synthesis, structure determination, and some properties of these complexes.

Experimental

All operations were carried out under an atmosphere of purified argon. Solvents were dried by conventional methods and distilled under argon. The complexes $[Cu(MeCN)_4]X$ (X = PF_6 or ClO_4) were prepared according to the literature.[12,13] Quinoline-2-thione (C_9H_7NS) was purchased from Aldrich Chemicals.

Preparation of Complexes.—$[\{[Cu(C_9H_7NS)_2]ClO_4\}_\infty]$ **1**. A tetrahydrofuran (thf) solution (10 cm^3) of C_9H_7NS (6.4 mg, 0.04 mmol) was added to $[Cu(MeCN)_4]ClO_4$ (3.3 mg, 0.01 mmol) and stirred for 30 min. The clear orange solution (A) was transferred to a glass tube and kept at room temperature. Red plate crystals began to form by 10 d. One of these was used for X-ray crystallography. IR: ν(Cl–O) 1103, δ(O–Cl–O) 627 cm^{-1}.

$[\{[Cu(C_9H_7NS)_2]PO_2F_2\}_\infty]$ **2**. Red plate crystals of compound **2** were obtained from $[Cu(MeCN)_4]PF_6$ in a similar way to that described above. IR: ν(C=S) 1103, ν(P–F) 835 cm^{-1} (Found: C, 44.45; N, 5.65; H, 2.85. Calc. for $C_{18}H_{14}CuF_2N_2O_2PS_2$: C, 44.40; N, 5.75; H, 2.90%).

$[Cu_6(C_9H_6NS)_6]$ **3**. From the orange solution (A) mentioned above, yellow plate crystals were obtained by standing for 1 month after crystals of **1** had appeared. Yield 18%.

Physical Measurements.—The UV/VIS spectra were recorded with a Hitachi 150-20 spectrophotometer, IR spectra with a JASCO FT/IR-8000 spectrophotometer; KBr discs were used in each case.

Crystal Structure Determinations of Compounds **1**–**3**.—*Data collection and refinement.* Suitable crystals were chosen and mounted on glass fibres with epoxy resin. Cell constants and the orientation matrix for intensity data collection for each crystal were based on the setting angles of 25 carefully centred reflections in the ranges $45 < 2\theta < 55$ and $25 < 2\theta < 39°$ for **1**

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Atomic positional parameters for $[\{[Cu(C_9H_7NS)_2]ClO_4\}_\infty]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.5000	0.5000	0.2500
Cu(2)	1.0000	0.0000	0.2500
Cl(1)	0.3824(1)	0.1106(1)	0.5000
S(1)	0.4479(1)	0.4064(1)	0.5000
S(2)	1.1061(1)	0.0133(1)	0.5000
O(1)	0.3061(5)	0.0769(5)	0.5000
O(2)	0.3807(6)	0.1864(5)	0.5000
O(3)	0.4257(9)	0.082(1)	0.350(3)
N(1)	0.3056(4)	0.3387(4)	0.5000
N(2)	1.2346(4)	−0.0782(4)	0.5000
C(11)	0.3445(5)	0.4082(5)	0.5000
C(12)	0.2992(5)	0.4806(5)	0.5000
C(13)	0.2169(6)	0.4755(6)	0.5000
C(14)	0.1761(6)	0.4014(6)	0.5000
C(15)	0.0934(6)	0.3942(7)	0.5000
C(16)	0.0588(6)	0.3201(9)	0.5000
C(17)	0.1056(6)	0.2511(7)	0.5000
C(18)	0.1871(5)	0.2557(6)	0.5000
C(19)	0.2231(5)	0.3318(6)	0.5000
C(21)	1.1546(5)	−0.0781(5)	0.5000
C(22)	1.1141(6)	−0.1522(6)	0.5000
C(23)	1.1555(6)	−0.2209(6)	0.5000
C(24)	1.2405(5)	−0.2225(5)	0.5000
C(25)	1.2871(6)	−0.2926(6)	0.5000
C(26)	1.3684(6)	−0.2885(6)	0.5000
C(27)	1.4069(5)	−0.2147(6)	0.5000
C(28)	1.3650(5)	−0.1435(6)	0.5000
C(29)	1.2804(5)	−0.1486(5)	0.5000

Table 2 Atomic positional parameters for $[\{[Cu(C_9H_7NS)_2]PO_2F_2\}_\infty]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.5000	0.5000	0.2500
Cu(2)	1.0000	0.0000	0.2500
S(1)	0.4523(2)	0.4042(2)	0.5000
S(2)	1.1062(2)	0.0100(2)	0.5000
P(1)	0.3889(3)	0.1034(3)	0.5000
F(1)	0.4432(7)	0.0747(6)	0.331(2)
O(1)	0.3200(7)	0.0543(7)	0.5000
O(2)	0.3877(7)	0.1868(7)	0.5000
N(1)	0.3122(7)	0.3329(6)	0.5000
N(2)	1.2332(7)	−0.0853(7)	0.5000
C(11)	0.3509(8)	0.4032(8)	0.5000
C(12)	0.3012(8)	0.4717(8)	0.5000
C(13)	0.2225(9)	0.4671(8)	0.5000
C(14)	0.1833(9)	0.392(1)	0.5000
C(15)	0.099(1)	0.383(1)	0.5000
C(16)	0.0664(8)	0.307(1)	0.5000
C(17)	0.117(1)	0.239(1)	0.5000
C(18)	0.198(1)	0.246(1)	0.5000
C(19)	0.230(1)	0.3219(8)	0.5000
C(21)	1.153(1)	−0.0833(8)	0.5000
C(22)	1.1120(8)	−0.156(1)	0.5000
C(23)	1.152(1)	−0.224(1)	0.5000
C(24)	1.236(1)	−0.228(1)	0.5000
C(25)	1.280(1)	−0.298(1)	0.5000
C(26)	1.362(1)	−0.295(1)	0.5000
C(27)	1.4029(9)	−0.223(1)	0.5000
C(28)	1.13582(9)	−0.153(1)	0.5000
C(29)	1.2762(8)	−0.156(1)	0.5000

Table 3 Atomic positional parameters for $[Cu_6(C_9H_6NS)_6]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	−0.0716(1)	0.0724(1)	−0.1583(2)
Cu(2)	−0.1229(1)	−0.0054(1)	0.1264(2)
Cu(3)	0.1330(1)	0.1759(1)	0.1278(2)
S(1)	−0.0023(2)	0.1896(2)	0.2385(3)
S(2)	−0.2316(2)	−0.1077(2)	−0.2801(3)
S(3)	0.0737(2)	0.1081(2)	−0.2792(3)
N(1)	−0.0839(6)	0.2129(6)	−0.063(1)
N(2)	−0.2974(6)	−0.0755(6)	−0.0022(9)
N(3)	0.2175(6)	0.2908(6)	−0.0021(9)
C(11)	−0.0573(7)	0.2531(7)	0.106(1)
C(12)	−0.0706(8)	0.3459(8)	0.182(1)
C(13)	−0.1129(8)	0.3943(8)	0.076(2)
C(14)	−0.1427(7)	0.3547(8)	−0.103(1)
C(15)	−0.1872(9)	0.401(1)	−0.221(2)
C(16)	−0.209(1)	0.360(1)	−0.393(2)
C(17)	−0.1886(9)	0.274(1)	−0.458(1)
C(18)	−0.1476(8)	0.224(1)	−0.350(1)
C(19)	−0.1248(7)	0.2635(8)	−0.170(1)
C(21)	−0.3341(7)	−0.1164(7)	−0.169(1)
C(22)	−0.4550(8)	−0.1695(8)	−0.268(1)
C(23)	−0.5327(7)	−0.1741(8)	−0.182(1)
C(24)	−0.4977(8)	−0.1311(7)	−0.003(1)
C(25)	−0.5743(8)	−0.1376(8)	0.094(2)
C(26)	−0.537(1)	−0.100(1)	0.267(2)
C(27)	−0.417(1)	−0.051(1)	0.358(1)
C(28)	−0.3386(8)	−0.0423(8)	0.268(1)
C(29)	−0.3763(7)	−0.0821(7)	0.089(1)
C(31)	0.1784(8)	0.2550(8)	−0.173(1)
C(32)	0.2221(9)	0.334(1)	−0.273(1)
C(33)	0.308(1)	0.446(1)	−0.192(2)
C(34)	0.3554(9)	0.4868(9)	−0.011(1)
C(35)	0.449(1)	0.601(1)	0.080(2)
C(36)	0.490(1)	0.634(1)	0.256(2)
C(37)	0.439(1)	0.554(1)	0.347(2)
C(38)	0.3510(9)	0.4424(8)	0.265(1)
C(39)	0.3069(8)	0.4069(8)	0.084(1)

and **2** respectively. Crystals **1** and **2** are isomorphous. Preliminary photographic data revealed Laue symmetry $4/m$. Systematic absences ($00l$ for $l = 2n + 1$) characteristic of the space groups $P4_2$ and $P4_2/m$ were observed. The latter centrosymmetric group subsequently shown to be correct by successful refinement and reasonable positional and thermal parameters. The unique data set was measured to a 2θ limit predetermined by the scope of the data, using a Rigaku AFC5R automated diffractometer fitted with monochromatic Cu-Kα and Mo-Kα radiation sources for **1** and **2**, respectively, and operating in conventional ω–2θ scan mode at 23 °C. The intensities of three representative reflections, measured after every 150, remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction was applied. The data were also corrected for Lorentz and polarization effects. N Independent reflections were obtained, N_o with $I > 3.00\sigma(I)$ being considered 'observed' and used in the least-squares refinement.

The structures were solved by direct methods.[14] Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were located in a Fourier difference map, but their parameters were not refined. The final cycle of full-matrix least-squares refinement was based on N_o and n variable parameters and converged at values of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, where $w = 4F_o^2/\sigma^2(F_o^2)$, as given below.

For compound **3**, the cell constants and orientation matrix, obtained from a least-squares refinement using the setting angles of 24 carefully centred reflections, corresponded to a triclinic cell. Based on packing considerations, and the successful solution and refinement of the structure, the space group was determined to $P\bar{1}$. ω–2θ Scans at 2θ range < 120.1° were used for data collection. The structure was solved by direct methods as above.

The positional parameters for complexes **1**–**3** are listed in Tables 1–3.

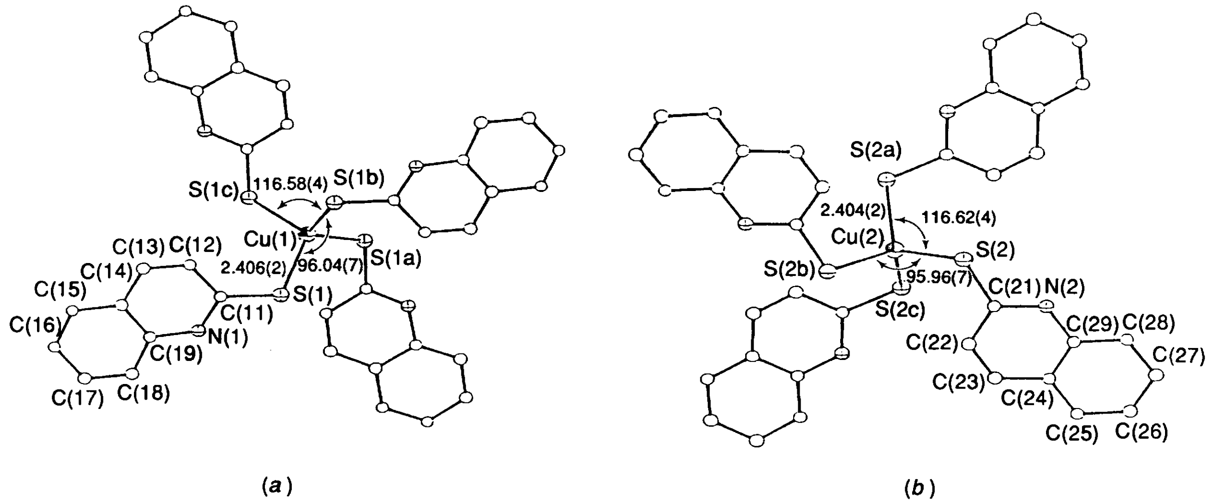

Fig. 1 Crystal structure of compound **1** projected down the *c* axis. Two asymmetric units are shown in (*a*) and (*b*) with thermal ellipsoids at the 50% probability level for Cu, S and N atoms. Ellipsoids of the carbon atoms in the quinoline rings have been arbitrarily reduced

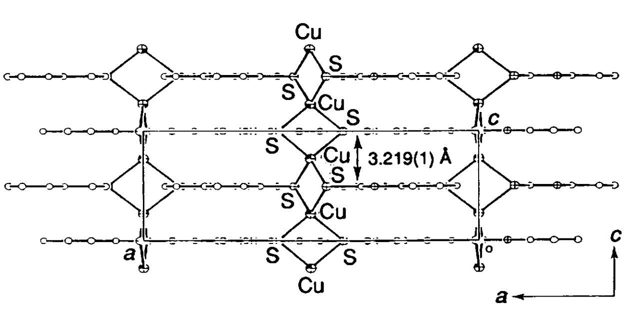

Fig. 2 Crystal structure of compound **1** without counter anions, projected down the *b* axis. The ligand sits on the mirror plane. The shortest interplanar distance is 3.219(1) Å as displayed

Crystal data. **1**, $C_9H_7Cl_{0.5}Cu_{0.5}NO_2S$, $M = 242.72$, tetragonal, space group $P4_2/m$, $a = 16.697(1)$, $c = 6.438(2)$ Å, $U = 1794.8(8)$ Å^3, $Z = 8$, $D_c = 1.796$ g cm^{-3}, λ(Cu-Kα) = 1.541 78 Å, $F(000) = 984$, $\mu = 55.15$ cm^{-1}, T = 23 °C. Specimen size: 0.10 × 0.15 × 0.10 mm. $2\theta_{max} = 55.15°$; N_o, N = 1281, 1481; n = 160, R,R' = 0.065, 0.089; $\Delta/\sigma = 0.09$.

2, $C_9H_7Cu_{0.5}FNOP_{0.5}S$, $M = 243.48$, tetragonal, space group $P4_2/m$, $a = 16.713(5)$, $c = 6.412(2)$ Å, $U = 1791(1)$ Å^3, $Z = 8$, $D_c = 1.806$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, $F(000) = 984$, $\mu = 15.71$ cm^{-1}, T = 23 °C. Specimen size: 0.20 × 0.30 × 0.25 mm; $2\theta_{max} = 55.0°$; N_o, N = 985, 2247; n = 160; R,R' = 0.061, 0.073; $\Delta/\sigma = 0.03$.

3, $C_{27}H_{18}Cu_3N_3S_3$, $M = 671.28$, triclinic, space group $P\bar{1}$, $a = 13.524(3)$, $b = 13.547(2)$, $c = 8.2106(1)$ Å, $\alpha = 99.18(1)$, $\beta = 101.01(1)$, $\gamma = 118.26(1)°$, $U = 1245(1)$ Å^3, $Z = 2$, $D_c = 1.791$ g cm^{-3}, λ(Cu-Kα) = 1.541 78 Å, $F(000) = 672$, $\mu = 54.42$ cm^{-1}, T = 23 °C. Specimen size: 0.15 × 0.20 × 0.10 mm; $2\theta_{max} = 120.1°$; N_o, N = 2301, 3704; n = 325; R,R' = 0.049, 0.055; $\Delta/\sigma = 0.03$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

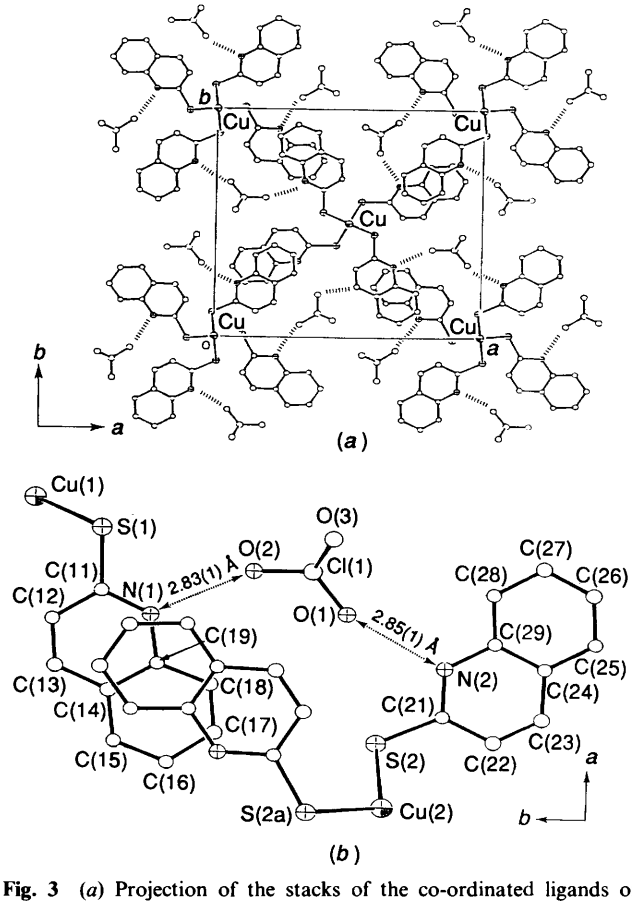

Fig. 3 (*a*) Projection of the stacks of the co-ordinated ligands of compound **1** along the *c* axis. (*b*) A view of portions of the macrocations and anions. The broken lines indicate the sites of hydrogen bonding between the perchlorate anion and the NH moiety of the ligand

Results and Discussion

Structures of Compounds **1** *and* **2**.—The molecular structures of the two crystallographic asymmetric copper units of **1** are shown in Fig. 1 and selected bond distances and angles are listed in Table 4. Both copper atoms bind to the sulfur atom of neutral quinolinethione, forming a distorted tetrahedron. The Cu–S distances [average 2.405(2) Å] fall within the range previously reported for copper(I) complexes.[7,15] The angles S–Cu(1)–S are 116.58(4) and 96.04(7)°, and S–Cu(2)–S 116.62(4) and 95.96(7)°, dissimilar to those (110°) involving four-co-ordinate geometry such as $[Cu(py)_4]^+$ (py = pyridine).[16] Fig. 2 shows that each copper is involved in a one-dimensional polymeric structure, whose backbone, $(CuS_2)_\infty$, develops along the *c* axis. The nearest-neighbour Cu ··· Cu distance is 3.219(1) Å, indicative of no direct metal–metal interaction. The line connecting all the Cu atoms in the backbone coincides with the crystallographic four-fold screw axis (4_2) and all the thione ligands sit on the crystallographic mirror plane.

Table 4 Selected bond distances (Å) and angles (°) *

(*a*) $[\{[Cu(C_9H_7NS)_2]ClO_4\}_\infty]$							
Cu(1)–S(1)	2.406(2)	C(14)–C(15)	1.39(1)	N(1)–C(11)	1.33(1)	C(23)–C(24)	1.42(1)
Cu(2)–S(2)	2.404(2)	C(15)–C(16)	1.37(2)	N(1)–C(19)	1.38(1)	C(24)–C(25)	1.40(1)
Cl(1)–O(1)	1.393(9)	C(16)–C(17)	1.39(2)	N(2)–C(21)	1.34(1)	C(24)–C(29)	1.40(1)
Cl(1)–O(2)	1.266(9)	C(17)–C(18)	1.36(1)	N(2)–C(29)	1.40(1)	C(25)–C(26)	1.36(1)
Cl(1)–O(3)	1.30(1)	C(18)–C(19)	1.41(1)	C(11)–C(12)	1.43(1)	C(26)–C(27)	1.39(1)
S(1)–C(11)	1.727(8)	C(21)–C(22)	1.41(1)	C(12)–C(13)	1.38(1)	C(27)–C(28)	1.38(1)
S(2)–C(21)	1.727(9)	C(22)–C(23)	1.34(1)	C(13)–C(14)	1.41(1)	C(38)–C(29)	1.42(1)
S(1)–Cu(1)–S(1a)	116.58(4)	C(13)–C(14)–C(19)	117.1(8)	C(25)–C(24)–C(29)	118.0(8)	C(21)–C(22)–C(23)	120.3(9)
S(1)–Cu(1)–S(1b)	96.04(7)	C(15)–C(14)–C(19)	119.1(9)	C(24)–C(25)–C(26)	120.8(9)	C(22)–C(23)–C(24)	122.2(9)
S(2)–Cu(2)–S(2a)	116.62(4)	C(14)–C(15)–C(16)	120(1)	C(25)–C(26)–C(27)	120.4(8)	C(23)–C(24)–C(25)	124.8(9)
S(2)–Cu(2)–S(2b)	95.96(7)	C(15)–C(16)–C(17)	121(1)	C(26)–C(27)–C(28)	121.9(8)	C(23)–C(24)–C(29)	117.3(8)
O(1)–Cl(1)–O(2)	112.6(7)	C(16)–C(17)–C(18)	121(1)	C(11)–N(1)–C(19)	124.0(7)	C(25)–C(24)–C(29)	118.0(8)
O(1)–Cl(1)–O(3)	111.2(6)	C(17)–C(18)–C(19)	119(1)	C(21)–N(2)–C(29)	123.2(7)	C(24)–C(25)–C(26)	120.8(9)
O(2)–Cl(1)–O(3)	112.1(8)	N(1)–C(19)–C(14)	119.3(8)	S(1)–C(11)–N(1)	118.3(6)	C(25)–C(26)–C(27)	120.4(8)
O(3)–Cl(1)–O(3′)	96(2)	N(1)–C(19)–C(18)	120.2(8)	S(1)–C(11)–C(12)	123.0(6)	C(26)–C(27)–C(28)	121.9(8)
Cu(1)–S(1)–Cu(1′)	83.96(7)	C(14)–C(19)–C(18)	120.6(8)	N(1)–C(11)–C(12)	118.7(7)	C(27)–C(28)–C(29)	117.0(8)
Cu(1)–S(1)–C(11)	110.5(2)	S(2)–C(21)–N(2)	118.0(7)	C(11)–C(12)–C(13)	118.5(8)	N(2)–C(29)–C(24)	118.6(7)
Cu(2)–S(2)–Cu(2′)	84.04(7)	S(2)–C(21)–C(22)	123.4(7)	C(12)–C(13)–C(14)	122.4(9)	N(2)–C(29)–C(28)	119.6(8)
Cu(2)–S(2)–C(21)	105.3(2)	N(2)–C(21)–C(22)	118.5(8)	C(13)–C(14)–C(15)	124(1)	C(24)–C(29)–C(28)	121.9(8)
(*b*) $[\{[Cu(C_9H_7NS)_2]PO_2F_2\}_\infty]$							
Cu(1)–S(1)	2.402(3)	C(26)–C(27)	1.37(2)	N(1)–C(19)	1.38(2)	C(15)–C(16)	1.37(2)
Cu(2)–S(2)	2.398(3)	C(27)–C(28)	1.39(2)	N(2)–C(21)	1.34(2)	C(16)–C(17)	1.43(2)
S(1)–C(11)	1.70(1)	C(28)–C(29)	1.37(2)	N(2)–C(29)	1.38(2)	C(17)–C(18)	1.35(2)
S(2)–C(21)	1.74(1)	C(11)–C(12)	1.41(2)	C(23)–C(24)	1.41(2)	C(18)–C(19)	1.39(2)
P(1)–F(1)	1.49(1)	C(12)–C(13)	1.32(2)	C(24)–C(25)	1.39(2)	C(21)–C(22)	1.40(2)
P(1)–O(1)	1.41(1)	C(13)–C(14)	1.42(2)	C(24)–C(29)	1.38(2)	C(22)–C(23)	1.31(2)
P(1)–O(2)	1.39(1)	C(14)–C(15)	1.42(2)	C(25)–C(26)	1.38(2)		
N(1)–C(11)	1.34(2)	C(14)–C(19)	1.40(2)				
S(1)–Cu(1)–S(1a)	116.45(6)	C(14)–C(15)–C(16)	119(1)	O(1)–P(1)–O(2)	124.6(8)	C(22)–C(23)–C(24)	123(2)
S(1)–Cu(1)–S(1b)	96.3(1)	C(15)–C(16)–C(17)	120(1)	C(11)–N(1)–C(19)	126(1)	C(23)–C(24)–C(25)	124(2)
S(2)–Cu(2)–S(2a)	116.55(7)	C(16)–C(17)–C(18)	122(2)	C(21)–N(2)–C(29)	123(1)	C(23)–C(24)–C(29)	117(1)
S(2)–Cu(2)–S(2b)	96.1(1)	C(17)–C(18)–C(19)	118(1)	S(1)–C(11)–N(1)	119(1)	C(27)–C(28)–C(29)	120(1)
Cu(1)–S(1)–Cu(1′)	83.7(1)	N(1)–C(19)–C(14)	116(1)	S(2)–C(11)–C(12)	125(1)	N(2)–C(29)–C(24)	119(1)
Cu(1)–S(1)–C(11)	109.8(4)	N(1)–C(19)–C(18)	121(1)	N(1)–C(11)–C(12)	115(1)	N(2)–C(29)–C(28)	119(1)
Cu(2)–S(2)–Cu(2)	83.9(1)	C(14)–C(19)–C(18)	123(1)	C(11)–C(12)–C(13)	123(1)	C(24)–C(29)–C(28)	122(1)
Cu(2)–S(2)–C(2′)	105.7(4)	S(2)–C(21)–N(2)	118(1)	C(12)–C(13)–C(14)	121(1)	C(25)–C(24)–C(29)	119(1)
F(1)–P(1)–F(1′)	93(1)	S(2)–C(21)–C(22)	124(1)	C(13)–C(14)–C(15)	123(1)	C(25)–C(26)–C(27)	122(1)
F(1)–P(1)–O(1)	107.9(6)	N(2)–C(21)–C(22)	118(1)	C(13)–C(14)–C(19)	119(1)	C(26)–C(27)–C(28)	118(1)
F(1′)–P(1)–O(2)	109.3(5)	C(21)–C(22)–C(23)	120(1)	C(15)–C(14)–C(19)	118(1)		

* Cu(1′) and Cu(2′) are related to Cu(1) and Cu(2) by the symmetry operation $x, -y, \frac{1}{2} + z$. S(*n*a), S(*n*b) and S(*n*c) are related to the corresponding S(*n*) atom by the operations $x, -y, \frac{1}{2} + z$, $-x, -y, z$ and $-x, y, \frac{1}{2} + z$, respectively. F(1′) and O(3′) are related to F(1) and O(3) by the operation $x, y, -z$.

It is worth noting that there are two types of interchain interactions. First, stacks of the aromatic moieties of the thione ligands in the nearest-neighbour chains are formed with interplanar distances of 3.219(1) Å. This interplanar distance is shorter than that in graphite, contributing to the stabilization of this crystalline form. Comparable distances (3.26–3.35 Å)[5] have been found in $[\{CuL(CN)\}_\infty]$ [L = 2,9-dimethyl-1,10-phenanthroline (dmphen) and 2,2′-biquinoline (bq)], where the stacks exist for only one co-ordinated ligand L of each copper moiety. In contrast to $[\{CuL(CN)\}_\infty]$ all the co-ordinated thiones of **1** are involved in the stacking interaction so that each chain can interact tightly with the four surrounding nearest neighbours [Fig. 3(*a*)]. Secondly, there is hydrogen bonding between the chains. The role of the ClO_4 anion is not only as a counter anion of copper(I) but also as a bridge joining two chains with hydrogen bonding. Fig. 3(*b*) shows the hydrogen bonding between the unco-ordinated NH sites and the anion, O(1) ··· H–N(2) and O(2) ··· H–N(1), the distances being 2.85(1) and 2.83(1) Å, respectively, in accord with literature values.[17,18] It is concluded that complex **1** is a three-dimensional polymer having an eclipsed conjugated π system and a hydrogen-bonding network in the crystal which arises from the unique thione ligand.

The crystal structure of **2** is essentially isomorphic to that of **1**. The Cu–S distance is 2.40 Å (average) and the angles S–Cu(1)–S are 116.45(6) and 96.3(1), and S–Cu(2)–S 116.55(7) and 96.1(1)°, very similar to those of **1**. The stacking distance of 3.206(1) Å is also similar. Interestingly, a tetrahedral monovalent anion is introduced in the unit cell although an octahedral PF_6^- anion is used in the synthesis. This feature was unexpected. The structure of the anion was not satisfactorily confirmed by IR spectroscopy: ν(P–O) was not found while ν(P–F) was observed. Elemental analysis implied the presence of $PO_2F_2^-$, which is likely produced by partial hydrolysis of PF_6^- by water present in the starting materials or solvent.[19] In the case of the hydrogen bonding the distance O ··· H–N is 2.74(1) Å, slightly shorter than in the case of **1**. These results show that the crystalline form obtained from the copper–thione system prefers a tetrahedral monovalent anion having hydrogen-bonding capability.

Structure of Compound **3**.—The entire molecule of **3** having C_i symmetry is shown in Fig. 4. Table 5 provides a list of important bond distances and angles. The molecule displays an octahedral core of copper atoms, each having a trigonal geometry involving a nitrogen and two thionate sulfur atoms. The geometries of the

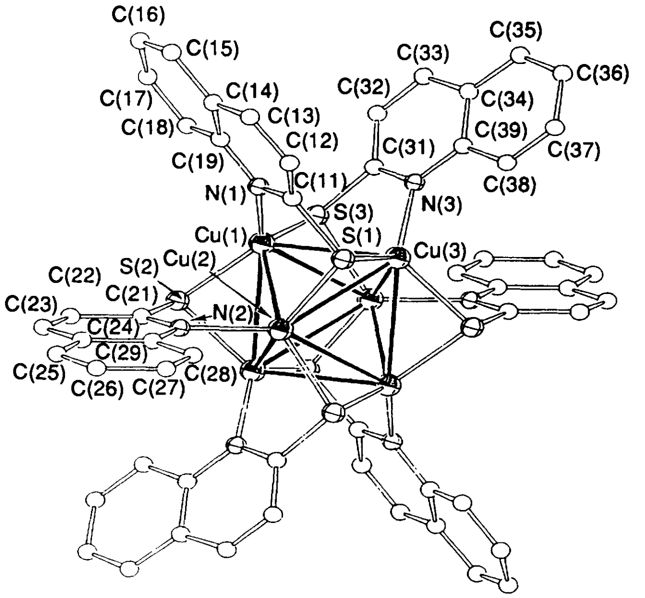

Fig. 4 Molecular structure of compound **3** showing the 50% probability thermal ellipsoids. Ellipsoids of the carbon atoms in the quinoline rings have been arbitrarily reduced. Only half the atoms are labelled; others are related by a centre of inversion

Table 5 Bond distances (Å) and angles (°) for $[Cu_6(C_9H_6NS)_6]$

Cu(1)–Cu(2)	2.787(2)	Cu(2)–S(1)	2.249(3)
Cu(1)–Cu(2′)	3.144(2)	Cu(2)–S(3′)	2.252(3)
Cu(1)–Cu(3)	2.817(2)	Cu(2)–N(2)	2.047(7)
Cu(1)–Cu(3′)	3.125(2)	Cu(3)–S(1)	2.260(3)
Cu(2)–Cu(3)	3.151(2)	Cu(3)–S(2′)	2.257(3)
Cu(2)–Cu(3′)	2.786(2)	Cu(3)–N(3)	2.045(7)
Cu(1)–S(2)	2.243(3)	S(1)–C(11)	1.755(8)
Cu(1)–S(3)	2.253(3)	S(2)–C(21)	1.769(8)
Cu(1)–N(1)	2.034(7)	S(3)–C(31)	1.741(9)
Cu(2)–Cu(1)–Cu(2′)	89.97(5)	S(2)–Cu(1)–S(3)	113.5(1)
Cu(2)–Cu(1)–Cu(3)	68.43(5)	S(2)–Cu(1)–N(1)	121.9(2)
Cu(2)–Cu(1)–Cu(3′)	55.88(4)	S(3)–Cu(1)–N(1)	115.9(2)
Cu(2′)–Cu(1)–Cu(3)	55.40(4)	Cu(1)–Cu(2)–S(1)	75.99(7)
Cu(2′)–Cu(1)–Cu(3′)	60.34(4)	Cu(1)–Cu(2)–S(3′)	134.68(8)
Cu(3)–Cu(1)–Cu(3′)	90.12(5)	Cu(1)–Cu(2)–N(2)	87.7(2)
Cu(1)–Cu(2)–Cu(1′)	90.03(5)	Cu(3′)–Cu(2)–S(1)	134.59(9)
Cu(1)–Cu(2)–Cu(3)	56.24(4)	Cu(3′)–Cu(2)–S(3′)	76.73(7)
Cu(1)–Cu(2)–Cu(3′)	68.22(5)	Cu(3′)–Cu(2)–N(2)	85.9(2)
Cu(1′)–Cu(2)–Cu(3)	59.53(4)	S(1)–Cu(2)–S(3′)	113.6(1)
Cu(1′)–Cu(2)–Cu(3′)	56.33(4)	S(1)–Cu(2)–N(2)	120.2(2)
Cu(3)–Cu(2)–Cu(3′)	90.16(6)	S(3′)–Cu(2)–N(2)	118.1(2)
Cu(1)–Cu(3)–Cu(1′)	89.88(5)	Cu(2′)–Cu(3)–S(1)	133.99(9)
Cu(1)–Cu(3)–Cu(2)	55.34(4)	Cu(2′)–Cu(3)–S(2′)	76.60(7)
Cu(1)–Cu(3)–Cu(2′)	68.27(5)	Cu(2′)–Cu(3)–N(3)	86.2(2)
Cu(1′)–Cu(3)–Cu(2)	60.13(4)	S(1)–Cu(3)–S(2′)	114.2(1)
Cu(1′)–Cu(3)–Cu(2′)	55.90(4)	S(1)–Cu(3)–N(3)	119.6(2)
Cu(2)–Cu(3)–Cu(2′)	89.84(6)	S(2′)–Cu(3)–N(3)	118.5(2)
Cu(2)–Cu(1)–S(2)	76.80(7)	Cu(2)–S(1)–Cu(3)	88.67(9)
Cu(2)–Cu(1)–S(3)	134.57(8)	Cu(1)–S(2)–Cu(3′)	87.97(9)
Cu(2)–Cu(1)–N(1)	89.2(2)	Cu(1)–S(3)–Cu(2′)	88.53(9)

Cu(2) and Cu(3) have a regular Y shape with *ca.* 114 and 119° for S–Cu–S and S–Cu–N, respectively, whereas the apical Cu(1) has a distorted Y shape with angles of 113.5(1), 115.9(2), and 121.9(2)° for S(2)–Cu(1)–S(3), S(3)–Cu(1)–N(1), and S(2)–Cu(1)–N(1), respectively. The Cu_6 framework is characterized by the two types of triangular faces: two faces of regular triangles [A type, Cu(1′)–Cu(2)–Cu(3) and one related to the inversion centre] and six equilateral triangles (B type). The copper atoms of the A faces are all bridged by sulfur atoms, while those of the B faces are bridged by a μ_3-thionate anion. The Cu_6 core thus lacks octahedral symmetry, individual copper–copper distances ranging from 2.786(2) to 3.151(2) Å [average 2.968(2) Å]. The structure is close to that of $[Cu_6(C_5H_4NS)_6]$[9] indicating no apparent effect of the aromatic ring size on the molecular geometry.

Characteristics of the Aromatic Structure of the Ligand.— Although quinoline-2-thione is the ligand present in all three compounds, **1** and **2** form red crystals whereas **3** forms yellow crystals. Copper(I) compounds having thione sulfur atoms exhibit bands in the region of 280–310 nm.[20] When co-ordination to copper occurs, the intraligand band of the free thione undergoes a small red shift (10–20 nm) and exhibits metal-to-ligand charge-transfer (m.l.c.t.) character.[21] Crystals of the complexes are yellow or at most orange. For instance, orange crystals have been obtained for discrete copper(I) complexes of pyridine-2-thione, $[Cu(C_5H_5NS)_3]NO_3$[22] and $[Cu_2(\mu\text{-}C_5H_5NS)_2(C_5H_5NS)_4]X_2$ (X = Cl or Br).[14c] The UV/VIS spectra of KBr disc samples of metal-free quinoline-2-thione and the compounds **1** and **2** were measured. The intraligand transition band of the metal-free thione appears near 400 nm, while the copper(I) complexes exhibit a red shift of this band to 420 nm. This band has a shoulder near 500 nm, which exhibits m.l.c.t. character. This band profile is responsible for the red colour of the crystals. However, no red shift was observed for a solution of copper(I) and the thione. For the polymeric compound $[\{Cu(dmphen)(CN)\}_\infty]$,[5] the m.l.c.t. band is influenced by stacking of co-ordinated dmphen. The firm stacks of quinoline-2-thione also affect the spectroscopic properties of the intraligand and/or copper–ligand interactions in **1** and **2**.

It has been established[9] that a hexacopper(I) core is formed from a thioamide ligand by deprotonation and growth of low-molecular-weight species in solution. In the case of quinoline-2-thione the polymer species preferentially forms before crystallization of the hexanuclear species. Both the stacking and hydrogen-bonding ability of this ligand promote the formation of the polymeric structure because no other simple thioamide ligands give a similar structure. On this basis, the presence of a large aromatic ring in thioamide compounds is an important means of synthesising infinite-chain systems having $(CuS_2)_\infty$ backbones, making the quinoline-2-thione ligand quite unique.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 04650746) from the Ministry of Education, Science and Culture of Japan.

References

1 S. Kitagawa, M. Munakata and T. Tanimura, *Chem. Lett.*, 1991, 623; S. Kitagawa, S. Matsuyama, M. Munakata, N. Osawa and H. Masuda, *J. Chem. Soc., Dalton Trans.*, 1991, 1717; S. Kitagawa, S. Matsuyama, M. Munakata and T. Emori, *J. Chem. Soc., Dalton Trans.*, 1991, 2869; S. Kitagawa, M. Munakata and T. Tanimura, *Inorg. Chem.*, 1992, **31**, 1714.
2 B. J. Hathaway in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, London, 1988, vol. 15, p. 533.
3 C. L. Raston, B. Walter and A. H. White, *Aust. J. Chem.*, 1979, **32**, 2757.
4 D. K. Smith and V. I. Saunders, *Acta Crystallogr., Sect. B*, 1982, **38**, 907.
5 G. O. Morpurgo, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1984, 785; G. Dessy, V. Fares, P. Imperatori and G. O. Morpurgo, *J. Chem. Soc., Dalton Trans.*, 1985, 1285.
6 P. C. Healey, C. Pakawatchai, R. I. Papasergio, V. A. Patrick and A. H. White, *Inorg. Chem.*, 1984, **23**, 3769.
7 E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115.
8 E. Block, M. Gernon, H. Kang, G. O.-Okai and J. Zubieta, *Inorg. Chem.*, 1991, **30**, 1736; A. Deeming, K. I. Hardcastle, M. N. Meah, P. A. Bates, H. M. Dawes and M. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1988, 227.

9 S. Kitagawa, M. Munakata, H. Shimono, S. Matuyama and H. Masuda, *J. Chem. Soc., Dalton Trans.*, 1990, 2105.

10 E. Block, M. Gernon, H. Kang and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1342.

11 E. S. Raper, J. R. Creighton and W. Clegg, *Inorg. Chim. Acta*, 1991, **183**, 179.

12 P. Hemmerich and C. Sigwart, *Experientia*, 1963, **19**, 488.

13 D. F. Shriver, *Inorganic Syntheses*, Wiley-Interscience, New York, 1979, vol. 19, p. 90.

14 C. J. Gilmore, MITHRIL, *J. Appl. Crystallogr.*, 1984, **17**, 42; P. T. Beurskens, DIRDIF, Technical Report 1984/1, Crystallography Laboratory, Törnooiveld, Nijmegen, 1984.

15 (*a*) D. M. L. Goodgame, G. A. Leach, A. C. Skapski and K. A. Woode, *Inorg. Chim. Acta*, 1978, **31**, L375; (*b*) E. C. Constable and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1987, 2281; (*c*) G. A. Stergioudis, S. C. Kokkou, P. J. Rentzeperis and P. Karagiannidis, *Acta Crystallogr. Sect. C*, 1987, **43**, 1685.

16 A. H. Lewin, R. J. Michl, P. Ganis, U. Lepore and G. A. Avitabile, *Chem. Commun.*, 1971, 1400.

17 *Chemistry of the Elements*, eds. N. N. Greenwood and A. Earnshaw, Pergamon, Oxford, 1984, p. 65.

18 L. N. Kuleshova and P. M. Zorkii, *Acta Crystallogr., Sect. B*, 1981, **37**, 1363.

19 D. L. Reger, M. F. Huff and L. Lebioda, *Acta Crystallogr., Sect. C*, 1991, **47**, 1167; M. I. Bruce, M. P. Cifuentes, K. R. Grundy, M. J. Liddell, M. R. Snow and E. R. T. Tiekink, *Aust. J. Chem.*, 1988, **41**, 597; C. White, S. J. Thompson and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **134**, 319; H. R. Clark and M. M. Jones, *J. Am. Chem. Soc.*, 1970, **92**, 816.

20 P. Karagiannidis, P. D. Akrivos, D. Mentzafos and A. Terzis, *Inorg. Chim. Acta*, 1991, **181**, 263.

21 S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, M. Mentzafos and A. Terzis, *Polyhedron*, 1991, **9**, 935.

22 S. C. Koddou, S. Fortier and P. J. Rentzeperis, *Acta Crystallogr., Sect. C*, 1983, **39**, 178.

Received 30*th November* 1992; *Paper* 2/06386G