Copper(II)-promoted Oxidation of Mercaptocarboxylic Acids. The Characterization of Disulphide- and Oxalate-containing Products. Crystal Structures of $[\{Cu(bipy)(2,2'\text{-}dtdp)\}_n]\cdot 3nH_2O$ and $[\{Cu(bipy)(3,3'\text{-}dtdp)\}_n]\cdot 2nH_2O$ (bipy = 2,2'-bipyridine, dtdp = dithiodipropanoate) *

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The reaction of 2- and 3-mercaptopropanoic acids with an aqueous solution of 2,2'-bipyridine (bipy) and copper(II) acetate dihydrate (molar ratio 1 : 2 : 1) under aerobic conditions yields the copper(II) disulphide complexes $[\{Cu(bipy)(2,2'\text{-}dtdp)\}_n]\cdot 3nH_2O$ (2,2'-dtdp = 2,2'-dithiodipropanoate) and $[\{Cu(bipy)(3,3'\text{-}dtdp)\}_n]\cdot 2nH_2O$ (3,3'-dtdp = 3,3'-dithiodipropanoate). Both complexes have been structurally characterized by single-crystal *X*-ray crystallography. Crystals of the complex $[\{Cu(bipy)(2,2'\text{-}dtdp)\}_n]\cdot 3nH_2O$ are triclinic, space group $P\bar{1}$, with a = 8.598(5), b = 10.378(6), c = 11.205(6) Å, α = 96.43(5), β = 94.34(4), γ = 91.16(5)°, and Z = 2. The structure consists of crystallographically equivalent $Cu(bipy)^{2+}$ units linked by 2,2'-dtdp ligands into infinite chains. The lattice water molecules participate in a hydrogen-bonding network that connects the 2,2'-dtdp ligands in adjacent chains. Each copper atom has a distorted square-pyramidal co-ordination geometry with the two bipy nitrogen and two carboxylate oxygen atoms in equatorial positions [Cu–N(1) 1.998(6), Cu–N(2) 2.008(6), Cu–O(1) 1.925(5), and Cu–O(3) 1.981(5) Å]. An apically bound disulphide sulphur completes the co-ordination sphere. The Cu–S distance [2.678(2) Å] is considered to be at the short end of the range expected for axial Cu–S (disulphide) bond lengths. Crystals of the complex $[\{Cu(bipy)(3,3'\text{-}dtdp)\}_n]\cdot 2nH_2O$ are monoclinic, space group $P2_1/n$, with a = 9.686(4), b = 9.409(3), c = 21.231(4) Å, β = 102.0(2)°, and Z = 4. The structure consists of crystallographically equivalent $Cu(bipy)^{2+}$ centres linked by 3,3'-dtdp ligands into infinite zigzag chains. The chains are connected into sheets *via* carboxylate oxygen atoms which asymmetrically bridge adjacent copper atoms from neighbouring chains. The sheets are connected *via* a network of hydrogen bonds involving the lattice water molecules and carboxylate oxygen atoms. The copper atoms are in an irregular six-co-ordinate environment. The bipy nitrogens and two carboxylate oxygens occupy an approximate square plane [Cu–N(1) 1.988(3), Cu–N(2) 1.995(4) Cu–O(1) 1.934(3), and Cu–O(3) 1.961(3) Å]. Axial bonding is achieved by a bridging carboxylate oxygen [Cu–O(3') 2.231(4) Å], which is also linked equatorially to an adjacent copper atom, and a weakly bound carboxylate oxygen [Cu–O(4) 2.826(5) Å]. In contrast to the above results, the reaction of sodium mercaptoacetate with 2,2'-bipyridine and copper(II) acetate dihydrate results in desulphurization of the mercaptoacetate and formation of a ternary oxalate (ox) complex $[Cu(bipy)(ox)]\cdot 2H_2O$.

Interest in the interaction of thiols with copper(II) has gained considerable impetus from the identification, by *X*-ray crystallography, of Cu^{II}–S(cysteine) bonds in the blue copper proteins azurin[1–4] pseudoazurin,[5] and plastocyanin.[6,7] Structurally characterized small molecule copper(II)–thiolate complexes are limited to a few examples with aromatic[8–11] and aliphatic thiolates.[12,13] Normally the interaction of thiols with copper(II) leads to the reduction of the metal to copper(I) and formation of the appropriate disulphide.[14] Mechanistic studies have identified a variety of redox decay pathways dependent upon the solvent and pH used, the composition of the coligands attached to the copper, and the nature of the substituents on the thiol.[15–17] Of particular interest was the identification of the persulphide copper(II) complex, $[CuL(SSCH_2CO_2)]\cdot 2MeOH$ (L = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) isolated from the reaction of mercaptoacetate with $[CuL]^{2+}$.[18]

In this paper we report the results of an investigation of the reaction of three mercaptocarboxylic acids, *viz.* mercaptoacetic and 2- and 3-mercaptopropanoic acids, with the 2,2'-bipyridine–copper(II) system under aerobic conditions. The 2- and 3-mercaptopropanoic acids are oxidized to their respective disulphides which co-ordinate to the copper. The resulting polymeric copper(II) disulphide complexes, $[\{Cu(bipy)(2,2'\text{-}dtdp)\}_n]\cdot 3nH_2O$ (bipy = 2,2'-bipyridine, 2,2'-dtdp = 2,2'-dithiodipropanoate) and $[\{Cu(bipy)(3,3'\text{-}dtdp)\}_n]\cdot 2nH_2O$ (3,3'-dtbp = 3,3'-dithiodipropanoate), have been characterized by *X*-ray crystallography. The latter complex does not contain a Cu–S bonding interaction. The former, however, provides a rare example of a relatively strong copper(II)–disulphide bond. This is relevant to one proposal for the metal-binding site in the blue copper protein stellacyanin, for which it has been suggested one ligand is a cystine disulphide.[19] In contrast to the results for the 2- and 3-mercaptopropanoic acids, the oxidation of mercaptoacetate does not give a disulphide complex, but instead affords the oxalate ion, identified in the ternary complex $[Cu(bipy)(ox)]\cdot 2H_2O$ (ox = oxalate).

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Experimental

Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer. Magnetic susceptibilities were determined by the Faraday method using a Cahn balance no. 7550. Infrared spectra were obtained on a Pye Unicam SP3-300 instrument. The thiols were purchased from the Aldrich Chemical Co. Microanalyses were by Professor A. D. Campbell, University of Otago.

Reaction of the Mercaptocarboxylic Acids with the 2,2′-*Bipyridine–Copper*(II) *Acetate System.—Synthesis of* $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$. To a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) and bipy (0.31 g, 2 mmol) in water (15 cm^3) was added dropwise a solution of 2-mercaptopropanoic acid (0.36 cm^3, 4 mmol) in water (5 cm^3). The resulting dark green solution was filtered and upon standing for a few days deposited dark blue needle-like crystals of the product. These were washed with water and dried in air. Yield: 0.31 g (30%). The trihydrate was established by *X*-ray crystallography but the complex loses lattice water so that analytical data were obtained on the monohydrate, $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot nH_2O$ (Found: C, 43.5; H, 3.9; N, 6.3. $C_{16}H_{18}CuN_2O_5S_2$ requires C, 43.1; H, 4.1; N, 6.3%); $\lambda_{max.}$(Nujol) 664 nm, $\mu_{eff.} = 1.81$.

Synthesis of $[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]\cdot 2nH_2O$. This complex was prepared in a manner similar to that described above but using 3- rather than 2-mercaptopropanoic acid. Yield 0.44 g (50%). The dihydrate form was identified from *X*-ray crystallography. Analytical data were obtained on an anhydrous sample (dried *in vacuo*), $[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]$ (Found: C, 45.0; H, 4.0; N, 6.1. $C_{16}H_{16}CuN_2O_4S_2$ requires C, 44.9; H, 3.7; N, 6.5%); $\lambda_{max.}$(Nujol) 631 nm, $\mu_{eff.}$ 1.85.

Oxalate formation from mercaptoacetate. To a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) and 2,2′-bipyridine (0.31 g, 2 mmol) in water (15 cm^3) was added dropwise a solution of sodium mercaptoacetate (0.23 g, 2 mmol) in water (5 cm^3). The resulting intense green solution was filtered, and upon standing overnight deposited dark blue needle-shaped crystals (0.32 g). These were removed from solution, and after 1 week dark green rhombic crystals (0.10 g) were also obtained. Recrystallizations of the green crystals from hot water yielded the blue form. Tests for sulphur[20] proved negative for both forms, indicating the absence of mercaptoacetate. I.r. spectral data and microanalyses suggested the compounds were ternary 2,2′-bipyridine–oxalate complexes, *e.g.* $[Cu(bipy)(ox)]\cdot 2H_2O$ (Found: C, 41.7; H, 2.55; N, 8.1. Calc. for $C_{12}H_{12}CuN_2O_6$ C, 41.7; H, 3.5; N, 8.2%). An authentic sample,[21] with an identical i.r. spectrum, was prepared from an aqueous solution of an equimolar mixture of sodium oxalate, copper(II) acetate monohydrate, and 2,2′-bipyridine.

Crystallography.—A similar procedure was used for the data collection and structure solution for both complexes $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$ and $[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]\cdot 2nH_2O$.

Crystal data for $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$. $C_{16}H_{22}CuN_2O_7S_2$, $M = 481.5$, triclinic, $a = 8.598(5)$, $b = 10.378(6)$, $c = 11.205(6)$ Å, $\alpha = 96.43(5)$, $\beta = 94.34(4)$, $\gamma = 91.16(5)°$, $U = 990(1)$ Å^3 (by least-squares refinement on diffractometer angles of 16 automatically centred reflections), space group $P\bar{1}$, $D_m = 1.60$ g cm^{-3}, $Z = 2$, $D_c = 1.62$ g cm^{-3}, $F(000) = 494$, $\mu(\text{Mo-}K_\alpha) = 12.82$ cm^{-1}. Deep blue prisms. Crystal dimensions (distance from centroid) 0.09, 0.13, 0.12, 0.09 mm.

Crystal data for $[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]\cdot 2nH_2O$. $C_{16}H_{20}CuN_2O_6S_2$, $M = 463.5$, monoclinic, $a = 9.686(4)$, $b = 9.409(3)$, $c = 21.231(4)$ Å, $\beta = 102.0(2)°$, $U = 1\,893(1)$ Å^3 (by least-squares refinement on diffractometer angles of 20 automatically centred reflections), space group $P2_1/n$, $D_m = 1.61$ g cm^{-3}, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $F(000) = 948$, $\mu(\text{Mo-}K_\alpha) = 13.36$ cm^{-1}. Deep blue parallelepiped-shaped crystals. Dimensions $0.70 \times 0.10 \times 0.08$ mm.

Data collection and processing. Nicolet R3m diffractometer at 153 K, ω—2θ mode ($5° \leqslant 2\theta \leqslant 45°$), graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å). Data corrected for Lorentz and polarization effects; empirical absorption corrections applied.

$[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$. Scan range 2.0°, scan speed 5.86° min^{-1}, 2 674 reflections measured (h, $\pm k$, $\pm l$), 1 935 unique with $I > 3\sigma(I)$ (maximum, minimum transmission factors = 0.794, 0.771).

$[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]\cdot 2nH_2O$. Scan range 1.4°, scan speed 5.86° min^{-1}, 3 356 reflections measured (h, k, $\pm l$), 2 248 unique with $I > 3\sigma(I)$ (maximum, minimum transmission factors = 0.777, 0.762).

Structure analysis and refinement. Patterson and Fourier methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions for $[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]\cdot 2nH_2O$ giving final R and R' values of 0.0376 and 0.0377 with the weighting scheme $w = 1.2342/(\sigma^2 F_o + 0.000\,619 F_o^2)$. For $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$ the C(2), O(2), and C(3) atoms of the disulphide ligand were found to possess a two-fold disorder along with three lattice water molecules. Since site occupancy values were found to be close to 0.75 for the atoms associated with more intense peaks and 0.25 for the remaining atoms, these values were used in the refinement. All non-hydrogen atom positions were refined with anisotropic thermal parameters (except those with site occupancy factors of 0.25) and C–H hydrogen atoms were included in calculated positions. The hydrogen atoms of the water molecules were not located unambiguously. Final R and R' values were 0.0553 and 0.0566, the weighting scheme being $w = 2.9332/(\sigma^2 F_o + 0.000\,296 F_o^2)$. Computations were performed with SHELXTL 86[22] and SHELX 76[23] programs, atomic scattering factors being as defined therein except those for copper which were taken from ref. 24. Fractional atomic co-ordinates are given in Tables 1 and 2 and selected bond lengths and angles in Tables 3 and 4.

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

Results and Discussion

(*a*) *Disulphide Complexes.*—The reactions of 2- and 3-mercaptopropanoic acids with aqueous solutions of 2,2′-bipyridine and copper(II) acetate (molar ratio 1:2:1) afford deep blue crystalline complexes. Magnetic moments, just above the spin-only value for copper(II), and *d–d* bands in the 600—700 nm range (see Experimental section) point to the divalent nature of the metal ions.[25] I.r. spectra indicated the presence of co-ordinated carboxylate groups and 2,2′-bipyridine ligands but it was the single-crystal *X*-ray structure determinations (see below) that showed the thiols had in fact been oxidized to disulphides, and that the complexes were polymeric, *viz.* $[\{Cu(bipy)(2,2'\text{-dtdp})_n\}]\cdot 3nH_2O$ and $[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]\cdot 2nH_2O$.

Crystal structure of catena-2,2′-*bipyridine*-μ-(2,2′-*dithiodipropanoato*-O,S;O′) *copper*(II) *trihydrate*, $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$. The complex is polymeric, consisting of equivalent $Cu(bipy)^{2+}$ units linked by the 2,2′-dtdp ligands to give an infinite structure. A view of part of the polymer is shown in Figure 1 and selected bond lengths and angles are given in Table 3.

Each copper atom has a distorted square-pyramidal co-ordination geometry. The 2,2′-bipyridine nitrogen atoms, N(1) and N(2), and the carboxylate oxygen atoms O(1) and O(3) lie in an approximate square plane with Cu–N(1) 1.998(6), Cu–N(2) 2.008(6), Cu–O(1) 1.925(5), and Cu–O(3) 1.981(5) Å. The co-ordination sphere is completed by a more weakly bound

Table 1. Atomic co-ordinates (× 10^4) for non-hydrogen atoms of $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$, with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	9 218(1)	2 663(1)	1 967(1)	C(2)	8 003(14)	5 000(11)	3 642(9)
S(1)	7 111(2)	4 527(2)	2 137(2)	C(2a)	7 520	4 697	3 888
S(2)	5 201(2)	3 333(2)	2 170(2)	C(3)	7 081(15)	5 940(11)	4 357(10)
O(1)	9 050(6)	2 841(5)	3 682(4)	C(3a)	8 511	5 965	4 260
O(2)	8 174(16)	3 697(9)	5 361(6)	C(4)	3 599(9)	4 498(8)	2 318(10)
O(2a)	7 582	3 449	5 268	C(5)	3 539(10)	5 428(10)	1 470(11)
O(3)	810(5)	4 081(5)	2 036(5)	C(6)	2 110(9)	3 541(9)	2 205(7)
O(4)	2 257(6)	2 381(5)	2 311(5)	C(7)	10 060(8)	2 939(8)	−531(7)
O(5)	3 599(10)	984(10)	4 116(8)	C(8)	10 085(10)	2 550(8)	−1 717(7)
O(5a)	3 007	1 019	4 452	C(11)	8 519(8)	1 142(7)	−291(6)
O(6)	699(14)	1 162(10)	5 099(7)	C(10)	8 485(9)	715(8)	−1 501(7)
O(6a)	945	868	4 821	C(9)	9 295(11)	1 451(9)	−2 225(7)
O(7)	6 092(12)	1 599(11)	5 731(8)	C(12)	7 711(8)	448(7)	593(7)
O(7a)	5 386	2 850	6 097	C(13)	6 819(8)	−673(7)	273(7)
N(1)	9 298(6)	2 229(5)	190(5)	C(14)	6 112(9)	−1 235(8)	1 173(8)
N(2)	7 903(6)	1 019(6)	1 740(5)	C(15)	6 301(9)	−665(8)	2 322(8)
C(1)	8 342(11)	3 693(8)	4 293(8)	C(16)	7 205(9)	457(8)	2 583(7)

Table 2. Atomic co-ordinates (× 10^4) for non-hydrogen atoms of $[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]\cdot 2nH_2O$, with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	1 491(1)	4 162(1)	4 939(1)	C(4)	−4 094(5)	842(6)	2 383(2)
S(1)	−956(2)	1 539(2)	2 830(1)	C(5)	−3 916(5)	908(6)	1 696(2)
S(2)	−2 944(2)	2 034(2)	2 926(1)	C(6)	−5 133(5)	245(5)	1 222(2)
O(1)	458(3)	2 405(3)	4 731(2)	C(7)	3 205(5)	1 949(5)	5 747(2)
O(2)	1 946(3)	1 468(4)	4 171(2)	C(8)	4 337(5)	1 453(5)	6 194(2)
O(3)	−4 957(3)	175(3)	635(1)	C(9)	5 424(5)	2 379(6)	6 442(2)
O(4)	−6 221(3)	−148(4)	1 378(2)	C(10)	5 354(5)	3 766(5)	6 235(2)
O(5)	2 676(4)	3 829(4)	2 754(2)	C(11)	4 182(4)	4 201(5)	5 780(2)
O(6)	1 890(4)	5 997(4)	1 873(2)	C(12)	3 990(5)	5 656(5)	5 523(2)
N(1)	3 118(4)	3 312(4)	5 547(2)	C(13)	4 970(5)	6 737(5)	5 675(2)
N(2)	2 722(4)	5 876(4)	5 115(2)	C(14)	4 669(5)	8 066(5)	5 407(2)
C(1)	793(5)	1 519(5)	4 328(2)	C(15)	3 368(5)	8 296(5)	4 995(2)
C(2)	−354(5)	432(5)	4 077(2)	C(16)	2 430(5)	7 168(5)	4 867(2)
C(3)	−479(6)	60(6)	3 377(3)				

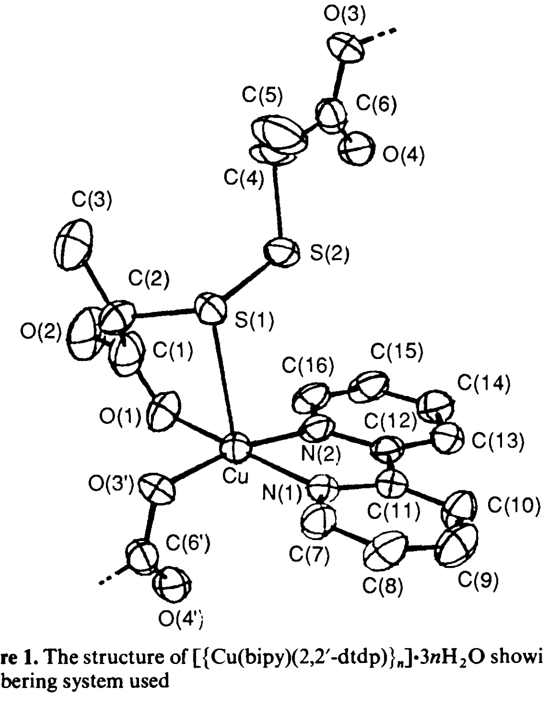

Figure 1. The structure of $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$ showing the numbering system used

sulphur atom from the disulphide moiety [Cu–S(1) 2.678(2) Å]. The copper to nitrogen distances are normal for copper(II)–bipyridine co-ordination. The copper to carboxylate oxygen distances are significantly different from each other (by 0.056 Å) but both fall within the 'short range' (1.9—2.1 Å) expected for equatorial Cu–O bonds.[25] The basal plane is distorted by a slight tetrahedral twist [deviations N(1) 0.05, N(2) −0.06, O(1) 0.05, and O(3) −0.05 Å from the least-squares plane through these basal donor atoms] with the copper atom displaced 0.1 Å towards the apical sulphur. The Cu–S(1) bond deviates by 13.9° from the normal to the basal plane. Deviations from a regular square-pyramidal geometry are to be expected for copper(II) although restraints introduced by the polymeric nature of the complex and the formation of the five-membered chelate ring [involving atoms Cu, O(1), C(1), C(2), and S(1)] will limit the plasticity effect.[25]

The axial Cu–S(disulphide) distance at 2.678(2) Å indicates a significant interaction of the disulphide sulphur with the copper(II) atom. To our knowledge only three examples of disulphide complexation to copper(II) have been previously characterized by *X*-ray crystallography and two of these contain much longer axial Cu–S bonds, *viz.* $Na_4[Cu_2L]\cdot 6H_2O$ ($L = [\{SCH_2CH[C(O)NCH_2CO_2][C(O)CH_2CH_2CHNH_2CO_2]\}_2]^{8-}$) with Cu–S 3.16(1) and 3.28(1) Å[26] and $[(CuL)_2]\cdot 9H_2O$ (L = 3,3′-dithiodivalinate) with Cu–S 3.057(10) and 3.138(9) Å.[27] For the third complex, $[\{Cu_2L(H_2O)_2\}_n]\cdot 4nH_2O$ [H_4L = *NNN′N′*-tetrakis(carboxymethyl)-2,2′-dithiobis(ethylamine)][28] the Cu–S(disulphide) distance of 2.721(3) Å is very close to that found in the present complex. Other copper(II) complexes which contain disulphides do not display Cu–S co-ordination.[29,30] Axial Cu–S(thioether) bond lengths have been

Table 3. Selected distances (Å) and angles (°) for [{Cu(bipy)(2,2′-dtdp)}$_n$]·3$n$$H_2O$ with standard deviations in parentheses*

Cu–O(1)	1.925(5)	C(1)–C(2)	1.635(15)
Cu–O($3^{\rm I}$)	1.981(5)	C(1)–C(2a)	1.374(11)
Cu–N(1)	1.998(6)	C(2)–C(3)	1.466(16)
Cu–N(2)	2.008(6)	C(2a)–C(3a)	1.552(10)
Cu–S(1)	2.678(2)	C(2)–S(1)	1.811(11)
S(1)–S(2)	2.043(3)	C(2a)–S(1)	1.954(10)
S(2)–C(4)	1.856(9)	C(4)–C(5)	1.427(13)
C(1)–O(1)	1.253(11)	C(4)–C(6)	1.591(11)
C(1)–O(2)	1.213(11)	C(6)–O(3)	1.271(10)
C(1)–O(2a)	1.358(9)	C(6)–O(4)	1.233(10)
O(5) ··· O(7)	2.715	O(6) ··· O($1^{\rm III}$)	2.820
O(5) ··· O($7^{\rm II}$)	2.722	O(6) ··· O($6^{\rm IV}$)	2.652
O(5) ··· O(6)	2.808	O(7) ··· O(2)	2.880
O(5) ··· O(4)	2.809		
O(1)–Cu–O($3^{\rm I}$)	94.4(2)	C(1)–C(2)–C(3)	112.9(1.0)
O(1)–Cu–S(1)	80.6(2)	C(1)–C(2a)–C(3a)	107.8(4)
O(1)–Cu–N(1)	172.2(2)	C(1)–C(2)–S(1)	108.6(7)
O(1)–Cu–N(2)	91.6(2)	C(1)–C(2a)–S(1)	113.5(4)
O($3^{\rm I}$)–Cu–S(1)	86.5(2)	C(3)–C(2)–S(1)	113.4(8)
O($3^{\rm I}$)–Cu–N(1)	92.6(2)	C(3a)–C(2a)–S(1)	107.3(1)
O($3^{\rm I}$)–Cu–N(2)	169.2(2)	C(2)–S(1)–S(2)	111.2(4)
S(1)–Cu–N(1)	103.3(6)	C(2a)–S(1)–S(2)	92.8(1)
S(1)–Cu–N(2)	103.4(2)	C(2)–S(1)–Cu	86.6(4)
N(1)–Cu–N(2)	81.0(2)	C(2a)–S(1)–Cu	89.0(1)
O(1)–C(1)–O(2)	124.5(1.0)	S(2)–S(1)–Cu	96.8(1)
O(1)–C(1)–O(2a)	123.2(8)	S(1)–S(2)–C(4)	102.5(3)
O(1)–C(1)–C(2)	114.3(8)	S(2)–C(4)–C(5)	114.8(7)
O(1)–C(1)–C(2a)	127.3(8)	S(2)–C(4)–C(6)	101.4(6)
O(2)–C(1)–C(2)	119.7(1.0)	C(5)–C(4)–C(6)	114.2(8)
O(2a)–C(1)–C(2a)	102.1(7)	C(4)–C(6)–O(3)	114.8(8)
Cu–O(1)–C(1)	127.6(6)	C(4)–C(6)–O(4)	120.6(8)
Cu–O($3^{\rm I}$)–C($6^{\rm I}$)	105.0(5)	O(3)–C(6)–O(4)	124.5(7)

* Atoms labelled O(2), C(2), and C(3) have site occupancy values of 0.75, O(2a), C(2a), and C(3a) have values of 0.25 (see text). Superscripts refer to atoms at the following positions: I $1 + x, y, z$; II $1 - x, -y, 1 - z$; III $x - 1, y, z$; IV $-x, -y, 1 - z$.

found in the range 2.56—2.82 Å,[31,32] which coupled with the data given above for the disulphide complexes would indicate a possible range of 2.56—3.28 Å for axial Cu–S(disulphide) distances. The observed Cu–S distance of 2.678(2) Å lies towards the shorter end of this range and points to a moderately strong axial Cu–S(disulphide) interaction in the complex [{Cu(bipy)(2,2′-dtdp)}$_n$]·3$n$$H_2O$.

Ligands containing only disulphide groups as donors exhibit weak ligation towards copper(II) (for example log $K^{\mathrm{Cu}^{2+}}_{\mathrm{CuL}}$ is 0.49 in 50% aqueous ethanol for the case where L = Me_2S_2[33]) unless the disulphide moiety is brought into contact with copper by chelation. For the complex [{Cu(bipy)(2,2′-dtdp)}$_n$]·3$n$$H_2O$, as well as for the previously reported co-ordinated disulphide complexes of copper(II),[26–28] this is achieved with five-membered chelate rings which include the disulphide S-donor atoms. In metalloproteins, disulphide co-ordination would be achieved by the appropriate conformation of the polypeptide chain. For the 'blue' copper protein stellacyanin, it has been suggested, from a consideration of amino acid sequence and spectroscopic data, that one of the ligands co-ordinated to the copper is an axially bound cystine disulphide[19,33–35] (athough recently this has been questioned[36]). Attempts to synthesize small-molecule copper(II) complexes with strong Cu–S(disulphide) interactions can face problems of S–S cleavage or metal reduction.[37–39] However the present study indicates that axial Cu–S(disulphide) bond lengths as short as 2.7 Å are possible, and that this kind of interaction could occur in stellacyanin or other copper proteins.

Table 4. Selected distances (Å) and angles (°) for [{Cu(bipy)(3,3′-dtdp)}$_n$]·2$n$$H_2O$ with standard deviations in parentheses*

Cu–O(1)	1.934(3)	C(1)–O(2)	1.230(5)
Cu–O($3^{\rm I}$)	1.961(3)	C(1)–C(2)	1.519(6)
Cu–N(1)	1.988(3)	C(2)–C(3)	1.510(7)
Cu–N(2)	1.995(4)	C(3)–S(1)	1.808(5)
Cu–O($3^{\rm II}$)	2.231(4)	C(4)–C(5)	1.506(6)
Cu–O($4^{\rm I}$)	2.826(5)	C(5)–C(6)	1.513(6)
S(1)–S(2)	2.032(5)	C(6)–O(3)	1.294(5)
S(2)–C(4)	1.814(5)	C(6)–O(4)	1.225(5)
C(1)–O(1)	1.286(5)	Cu ··· $\mathrm{Cu^{III}}$	3.348(3)
O(5) ··· O($4^{\rm I}$)	2.720	O(5) ··· O($6^{\rm IV}$)	2.781
O(5) ··· O(6)	2.768	O(6) ··· O($2^{\rm V}$)	2.722
O(1)–Cu–N(1)	96.0(1)	C(1)–O(1)–Cu	121.1(3)
O(1)–Cu–N(2)	173.8(1)	C($6^{\rm I}$)–O($3^{\rm I}$)–Cu	112.9(3)
O(1)–Cu–O($3^{\rm I}$)	89.1(1)	Cu–O($3^{\rm I}$)–$\mathrm{Cu^{II}}$	102.5(3)
O(1)–Cu–O($3^{\rm II}$)	91.3(1)	C($6^{\rm I}$)–O($3^{\rm I}$)–$\mathrm{Cu^{II}}$	144.7(3)
O(1)–Cu–O($4^{\rm I}$)	92.0(1)	C($6^{\rm I}$)–O($4^{\rm I}$)–Cu	73.0(3)
O($3^{\rm I}$)–Cu–N(1)	174.8(1)	O(1)–C(1)–O(2)	125.1(4)
O($3^{\rm I}$)–Cu–N(2)	94.1(1)	O(1)–C(1)–C(2)	113.6(4)
O($3^{\rm I}$)–Cu–O($3^{\rm II}$)	77.5(1)	O(2)–C(1)–C(2)	121.2(4)
O($3^{\rm I}$)–Cu–O($4^{\rm I}$)	51.3(1)	C(1)–C(2)–C(3)	113.8(4)
N(1)–Cu–N(2)	80.9(1)	C(2)–C(3)–S(1)	114.1(4)
N(1)–Cu–O($4^{\rm I}$)	129.2(1)	S(2)–C(4)–C(5)	114.3(4)
N(1)–Cu–O($3^{\rm II}$)	101.4(1)	C(4)–C(5)–C(6)	113.6(4)
N(2)–Cu–O($4^{\rm I}$)	85.9(1)	C(5)–C(6)–O(3)	115.0(4)
N(2)–Cu–O($3^{\rm II}$)	94.6(1)	C(5)–C(6)–O(4)	122.6(4)
O($4^{\rm I}$)–Cu–O($3^{\rm II}$)	128.5(1)	O(3)–C(6)–O(4)	122.4(4)
C(3)–S(1)–S(2)	103.6(3)		

* Superscripts refer to atoms at the following positions: I $-0.5 - x, 0.5 + y, 0.5 - z$; II $0.5 + x, 0.5 - y, 0.5 + z$; III $-x, 1 - y, 1 - z$; IV $0.5 - x, y - 0.5, 0.5 - z$; V $0.5 - x, 0.5 + y, 0.5 - z$.

The 2,2′-dtdp disulphide ligand, which links the copper(II) atoms, is involved in a hydrogen-bonding network with the lattice water molecules, of which there are three per copper. A portion of the disulphide ligand, involving the chelate ring carbons, C(2) and C(3), and the non-co-ordinated carboxylate oxygen, O(2), are disordered over two positions. The site occupancies are 0.75 and 0.25. (The latter sites are identified with the postscript 'a' in Table 3.) In addition, the three lattice water molecules [with oxygens in sites O(5) and O(5a), O(6) and O(6a), and O(7) and O(7a)] are similarly disordered. Each of the two models corresponds to a different hydrogen-bonding network within the crystal lattice. The molecular orientation which includes the atoms with site occupancies of 0.25 is poorly defined and will not be considered in detail. The contact distances for the lattice water molecules (2.65—2.88 Å, see also Table 3) are typical for hydrogen-bonding interactions.[40]

Co-ordination of the disulphide unit does not appear to have introduced any marked strain into the 2,2′-dtdp ligand. For instance the bond lengths and angles in the half of the molecule which is involved in the chelate ring show no unusual differences when compared to the remainder. The C–S distances are comparable with those in other disulphides.[41] The S–S bond distance at 2.043(3) Å lies in the range reported for aliphatic disulphides (2.00—2.05 Å), which when coupled with the observed S–S torsion angle of 90.07° is consistent with an unconstrained disulphide.[42,43] The bond lengths and angles in the bipy ligand are normal[44–46] with the two rings individually planar and virtually coplanar with each other, but for a twist of 1.30° about the C(11)–C(12) bond.

*Crystal structure of catena-*2,2′*-bipyridine-*μ-(3,3′*-dithiodipropanoato-O,O*′;*O*″*)copper*(II) *dihydrate*, [{Cu(bipy)(3,3′-dtdp)}$_n$]·2$n$$H_2O$. This complex is also polymeric and consists of equivalent $Cu(bipy)^{2+}$ units linked by 3,3′-dtdp ligands into

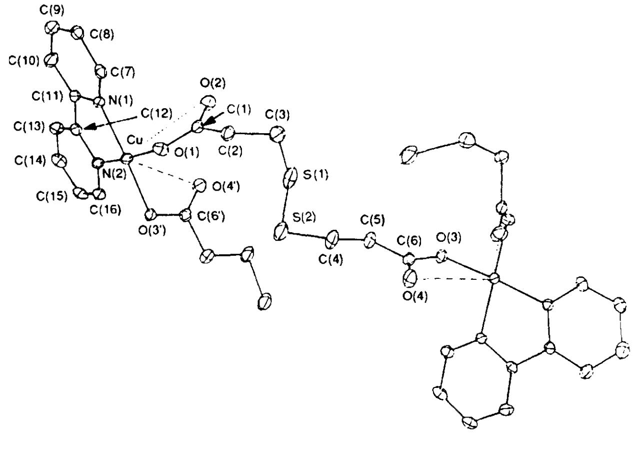

Figure 2. The structure of $[\{Cu(bipy)(3,3'\text{-}dtdp)\}_n]\cdot 2nH_2O$ showing the numbering system used

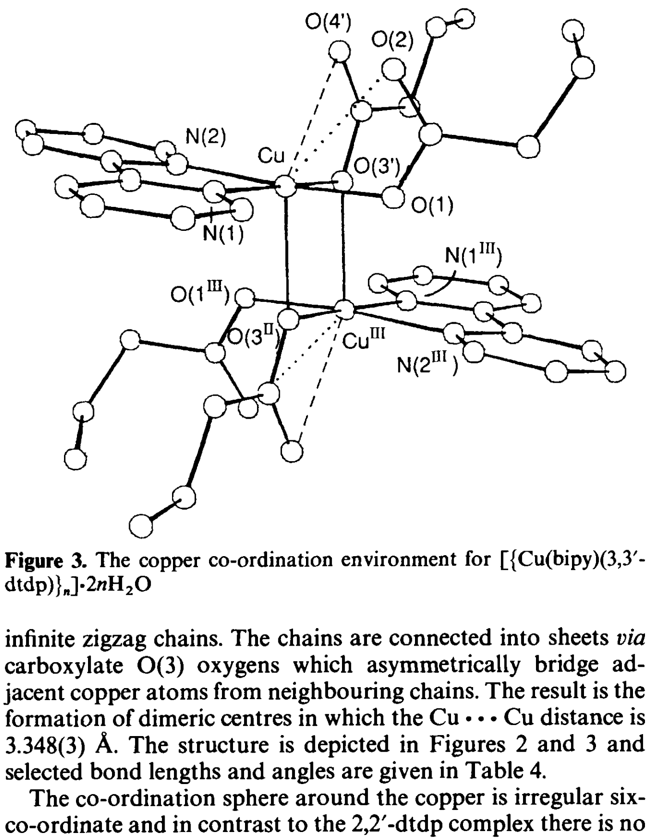

Figure 3. The copper co-ordination environment for $[\{Cu(bipy)(3,3'\text{-}dtdp)\}_n]\cdot 2nH_2O$

infinite zigzag chains. The chains are connected into sheets *via* carboxylate O(3) oxygens which asymmetrically bridge adjacent copper atoms from neighbouring chains. The result is the formation of dimeric centres in which the Cu ··· Cu distance is 3.348(3) Å. The structure is depicted in Figures 2 and 3 and selected bond lengths and angles are given in Table 4.

The co-ordination sphere around the copper is irregular six-co-ordinate and in contrast to the 2,2′-dtdp complex there is no copper–disulphide sulphur bonding. Two bipy nitrogens, N(1) and N(2), and the carboxylate oxygens, O(1) and O(3), co-ordinate to the copper in an approximate square plane [Cu–N(1) 1.988(3), Cu–N(2) 1.995(4), Cu–O(1) 1.934(3), and Cu–O(3) 1.961(3) Å]. Axial bonding is established by the bridging carboxylate oxygen, O(3′), which simultaneously occupies an equatorial position in one half of the dimer and an apical position [Cu–O(3′) 2.231(4) Å] in the other half. The co-ordination is completed by the carboxylate oxygen atom O(4) from the same carboxylate group as the equatorial ligand O(3). This forms a weak pseudo-axial bond to the copper, with the Cu–O(4) distance being 2.826(5) Å. There is also a weak seventh contact between the bridging ligand and the copper atom [Cu–O(2) 3.11 Å] but, for reasons discussed below, this seems less significant. Overall the geometry could be described as square pyramidal, defined by the atoms Cu, N(1), N(2), O(1), O(3), and O(3′) with an additional weakly co-ordinated sixth ligand, O(4), which deviates by approximately 40° from the axial position of an octahedron. The geometry does possess features which suggest that a description in terms of six- rather than five-co-ordination is more appropriate. The four atoms O(1), O(3), N(1) and N(2) exhibit poor planarity (deviations 0.05—0.06 Å from their mean plane), but the copper atom is not significantly displaced from this basal plane (deviation 0.04 Å). In most distorted square-pyramidal copper(II) complexes the metal atom is displaced from the basal plane, by around 0.1—0.5 Å towards the apical ligand.[25] The absence of this type of distortion suggests that the weakly co-ordinated O(4) atom influences the copper atom to be coplanar with the basal ligand atoms. The apical Cu–O(3′) bond deviates by 12.0° from the normal to the basal plane. These features suggest that the copper co-ordination environment approximates a tetragonally distorted octahedron, further distorted by the geometrical constraints of the four-membered Cu–O(3)–C(6)–O(4) chelate ring.

The bond distances within the copper co-ordination sphere all appear to be normal. The Cu–N and Cu–O distances in the basal plane are within the accepted ranges for such bonds and the value of 2.231(4) Å for Cu–O(3′) is at the short end of the range (2.22—2.89 Å) expected for axial interactions.[25] The off-axis co-ordination and the longer Cu–O(4) distance exhibited by the O(4) carboxylate oxygen are typical features of chelated carboxylates.[25]

The two carboxylate groups in the structure have very similar orientations (Figure 3) but although the differences are small one can be considered chelating and the other monodentate. For the non-chelating carboxylate the Cu–O(2) distance at 3.11 Å is outside the range ($\leqslant 2.9$ Å) generally accepted for the more weakly bound second carboxylate oxygen to copper distances.[25] It is also noted that the equatorial Cu–O(carboxylate) distance [Cu–O(3)] for the chelated carboxylate is 1.961(3) Å whereas that for the non-chelated carboxylate [Cu–O(1)] is 1.934(3) Å. The carboxylate which has the stronger axial interaction has the weaker equatorial bond.

The 3,3′-dtdp ligand exhibits no unusual structural features. The disulphide S–S bond length is 2.032(5) Å and the S–S torsion angle is 84.5°. Both are typical for aliphatic disulphides[42,43] and not markedly different from the values found in the co-ordinated disulphide ligand 2,2′-dtdp described earlier. Similarly the bond parameters for bipy are normal.[44—46] The pyridine rings are individually planar but do not lie in the same plane due to a 4.39° twist about the C(11)–C(12) bond.

There are two non-co-ordinated water molecules [$H_2O(5)$ and $H_2O(6)$] associated with each asymmetric unit of the structure. These are involved in a hydrogen-bonding scheme which links the polymeric sheets together through interactions with the non-equatorially bound carboxylate oxygen atoms, O(2) and O(4). The O ··· O distances (2.72—2.78 Å, see also Table 4) are within the range expected for such interactions.[40]

(*b*) *Oxalate Formation from Mercaptoacetate*.—The interaction of sodium mercaptoacetate with the bipy–Cu^{II} system in water gave a 2,2′-bipyridine–oxalate complex rather than a ternary complex containing a disulphide. A number of ternary copper(II) complexes containing bipy and oxalate are known and they can be interconverted with changes in both colour and spectral properties.[21,47] The blue and green oxalate complexes isolated in this study are in fact different hydrates with the blue one, $[Cu(bipy)(ox)]\cdot 2H_2O$, predominating. The reaction did not occur when carried out in the absence of oxygen.

While the facile oxidative desulphurization of mercaptoacetate by copper(II) is somewhat unexpected, oxalate formation from mercaptoacetate is not unprecedented. Over 50 years ago it was reported that mercaptoacetic acid (as well as 2,2′-dithiodiacetic acid) when heated in the presence of sodium or barium hydroxide, in a reaction catalysed by Cu^{2+} ions, gave oxalate ions.[48] Possible mechanisms for this alkaline decomposition reaction have been discussed.[49] More recently, it was shown that chelated mercaptoacetate in the complex $[Cr(en)_2(SCH_2CO_2)]^+$ (en = ethylenediamine) when oxidised by Np^{VI} or Ce^{IV} affords a monothio-oxalate complex $[Cr(en)_2(SOCCO_2)]^+$, and this when heated in perchloric acid decomposes to free oxalic acid and H_2S.[50] Spectroscopic and kinetic evidence indicate the neptunium(VI) oxidation of the cobalt(III)–mercaptoacetate analogue to be more complicated but one of the proposed products was the monoprotonated oxalate ligand complex, $[Co(en)_2(H_2O)(Hox)]^{2+}$.[51]

Presumably the initial step in the reaction of mercaptoacetate with the bipy–Cu^{II} system is the formation of a transient ternary complex of the type $[Cu(bipy)(SCH_2CO_2)]$, which is then oxidized at the thiolate carbon. A similar intermediate, $[CuL(SCH_2CO_2)]$(L = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane), has been postulated, on the basis of spectroscopic evidence, in the formation of the persulphide complex $[CuL(SSCH_2CO_2)]\cdot 2MeOH$.[17] Analogous $Cu^{II}L$ complexes with 3-mercaptopropanoate[12] and 2-mercaptobenzoate[8] can be isolated and have been shown by *X*-ray crystallography to contain Cu–S bonds. The oxidation of mercaptoacetate in the presence of transition-metal ions is clearly complex, with not only oxalate being produced. The isolation of the above-mentioned persulphidoacetate complex[18] as well as production of succinic acid from the mercaptoacetate–vanadium(II) reaction[52] illustrate this point.

In contrast, the mercaptocarboxylic acids 2- and 3-mercaptopropanoic acids, when oxidized in the presence of bipy–Cu^{II}, give well defined disulphide complexes. Presumably initial reduction of the metal to copper(I) occurs with concomitant oxidation of the co-ordinated thiolate to the disulphide. Subsequent oxidation of copper(I) would give the isolated complexes, $[\{Cu(bipy)(2,2'\text{-dtdp})\}_n]\cdot 3nH_2O$ and $[\{Cu(bipy)(3,3'\text{-dtdp})\}_n]\cdot 2nH_2O$, with five-membered chelate-ring formation being possible only in the former case to achieve disulphide sulphur co-ordination to the copper(II). Further studies are being carried out on these reactions.

Acknowledgements

We thank the New Zealand University Grants Committee for support and the award of a postgraduate scholarship (to M. L. B.), and Dr W. T. Robinson (University of Canterbury) for assistance in the collection of *X*-ray crystallographic data.

References

1 G. E. Norris, B. F. Anderson, and E. N. Baker, *J. Mol. Biol.*, 1983, **165**, 501.
2 G. E. Norris, B. F. Anderson, and E. N. Baker, *J. Am. Chem. Soc.*, 1986, **108**, 2784.
3 E. W. Ainscough, A. G. Bingham, A. M. Brodie, W. R. Ellis, H. B. Gray, T. M. Loehr, J. E. Plowman, G. E. Norris, and E. N. Baker, *Biochemistry*, 1987, **26**, 71.
4 E. T. Adman, R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, *J. Mol. Biol.*, 1978, **123**, 35.
5 K. Petratos, D. W. Banner, T. Beppu, K. S. Wilson, and D. Tsernoglou, *FEBS Lett.*, 1987, **218**, 209.
6 J. M. Guss and H. C. Freeman, *J. Mol. Biol.*, 1983, **169**, 521.
7 J. M. Guss, P. R. Harrowell, M. Murata, V. A. Norris, and H. C. Freeman, *J. Mol. Biol.*, 1986, **192**, 361.
8 J. L. Hughey, T. G. Fawcett, S. M. Rudich, R. A. Lalancette, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, 1979, **101**, 2617.
9 O. P. Anderson, C. M. Perkins, and K. K. Brito, *Inorg. Chem.*, 1983, **22**, 1267.
10 N. Aoi, Y. Takano, H. Ogino, G. Matsubayashi, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1985, 703.
11 A. A. Addison and E. Sinn, *Inorg. Chem.*, 1983, **22**, 1225.
12 E. John, P. K. Bharadwaj, J. A. Potenza, and H. J. Schugar, *Inorg. Chem.*, 1986, **25**, 3065.
13 P. K. Bharadwaj, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, 1986, **108**, 1351.
14 J. Whelan and B. Bosnich, *Inorg. Chem.*, 1986, **25**, 3671.
15 A. G. Lappin and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 1978, 1606.
16 D. Cavallini, C. DeMarco, S. Dupre, and G. Rotilio, *Arch. Biochem. Biophys.*, 1969, **130**, 354.
17 R. Holwerda, *J. Inorg. Biochem.*, 1988, **33**, 131 and refs. therein.
18 E. John, P. K. Bharadwaj, K. Krogh-Jespersen, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, 1986, **108**, 5015.
19 A. G. Lappin, 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1981, vol. 13, p. 15.
20 B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith, and A. R. Tatchell, 'Vogel's Textbook of Practical Organic Chemistry,' Longman, London, 1978, p. 934.
21 P. O'Brien, *J. Chem. Soc., Dalton Trans.*, 1981, 1540.
22 G. M. Sheldrick, SHELXTL 86, Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, University of Gottingen, 1986.
23 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, Cambridge University, 1976.
24 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
25 B. J. Hathaway, in 'Comprehensive Coordination Chemistry,' vol. 5, eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, pp. 596—662.
26 K. Miyoshi, Y. Sugiura, K. Ishizu, Y. Iitaka, and H. Nakamura, *J. Am. Chem. Soc.*, 1980, **102**, 6130.
27 J. A. Thich, D. Mastropaolo, J. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, 1974, **96**, 726.
28 N-H, Dung, B. Viossat, A. Busnot, J. M. Gonzalez-Perez, and J. Niclos-Gutierrez, *Acta Crystallogr., Sect. C*, 1985, **41**, 1739.
29 J. A. Thich, R. A. Lalancette, J. A. Potenza, and H. J. Schugar, *Inorg. Chem.*, 1976, **15**, 2731.
30 M. C. Brianso, J. L. Brianso, W. Gaete, and J. Ros, *Inorg. Chim. Acta*, 1981, **49**, 263.
31 J. C. A. Boyens, S. M. Dobson, and R. D. Hancock, *Inorg. Chem.*, 1985, **24**, 3073.
32 D. G. Fortier and A. McAuley, *Inorg. Chem.*, 1989, **28**, 655.
33 H. Sigel, K. H. Scheller, V. M. Rheinberger, and B. E. Fischer, *J. Chem. Soc., Dalton Trans.*, 1980, 1022.
34 O. Farver, A. Licht, and I. Pecht, *Biochemistry*, 1987, **26**, 7317.
35 H. R. Engeseth, M. A. Hermodson, and D. R. McMillin, *FEBS Lett.*, 1984, **171**, 257.
36 J. M. Guss, E. A. Merritt, R. P. Phizackerley, B. Hedman, M. Murata, K. O. Hodgson, and H. C. Freeman, *Science*, 1988, **241**, 806.
37 J. M. Downes, J. Whelan, and B. Bosnich, *Inorg. Chem.*, 1981, **20**, 1081.
38 L. S. Higashi, M. Lundeen, E. Hilti, and K. Seff, *Inorg. Chem.*, 1977, **16**, 310.
39 A. Odani, T. Maruyama, O. Yamauchi, T. Fujiwara, and K. Tomita, *J. Chem. Soc., Chem. Commun.*, 1982, 646.
40 M. D. Joesten, 'Hydrogen Bonding,' Marcel Dekker, New York, 1974.
41 A. Senning, 'Sulphur in Organic and Inorganic Chemistry,' Marcel Dekker, New York, 1972, vol. 3, p. 113.
42 D. D. Jones, I. Bernal, M. N. Frey, and T. F. Koetzle, *Acta Crystallogr., Sect. B*, 1974, **30**, 1974.
43 G. Rindorf, F. S. Jorgensen, and J. P. Snyder, *J. Org. Chem.*, 1980, **45**, 5343.
44 F. S. Stephens, *J. Chem. Soc. A*, 1969, 2081.
45 R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 1970, **74**, 3497.
46 G. W. Bushnell and M. A. Khan, *Can. J. Chem.*, 1972, **50**, 315.
47 P. O'Brien, W. Fitzgerald, J. Foley, D. McSweeney, N. Ray, D. Sheahan, S. Tyagi, and B. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1982, 1117.
48 A. Schöberl, *Liebigs Ann. Chem.*, 1933, **507**, 111.
49 J. P. Danehy, 'The Chemistry of Organic Sulfur Compounds,' eds. N. Kharasch and C. Y. Meyers, Pergamon, Oxford, 1966, vol. 2, p. 337.
50 C. J. Weschler, J. C. Sullivan, and E. Deutsch, *J. Am. Chem. Soc.*, 1973, **95**, 2720.
51 C. J. Weschler, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 1974, **13**, 2360.
52 J. Konstantatos, G. Kalatzis, E. Vrachnou-Astra, and D. Katakis, *Inorg. Chem.*, 1983, **22**, 1924.

Received 21st September 1989; *Paper* 9/04022F