Properties and *X*-Ray Crystal Structures of Copper(II) Mixed Complexes with Thiodiacetate and 2,2′-Bipyridyl or 2,2′:6′,2″-Terpyridyl

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Spectroscopic and structural investigations have been performed for two ternary complexes of copper(II), [Cu(bipy)(tda)(H_2O)]·4H_2O (1) and [Cu(terpy)(tda)] (2) (bipy = 2,2′-bipyridyl, terpy = 2,2′:6′,2″-terpyridyl, and tda = thiodiacetate). Crystals of (1) are monoclinic, space group $P2_1/c$, with a = 11.136(7), b = 21.13(1), c = 8.999(6) Å, β = 113.2(2)°, and R = 0.057. Crystals of (2) are also monoclinic, space group $C2/c$, with a = 10.551(6), b = 21.23(1), c = 8.633(5) Å, β = 112.0(2)°, and R = 0.035. Complex (1) consists of [Cu(bipy)(tda)(H_2O)] units connected by water molecules. The co-ordination polyhedron around the copper may be described as a distorted octahedron with the sulphur atom and the water molecule in axial positions. Complex (2) consists of polymeric chains of Cu(terpy) units bridged by the tda ligand *via* the oxygens of the carboxylate groups. Consequently, the co-ordination polyhedron around the copper atom may be described as a distorted trigonal-bipyramidal arrangement. E.s.r. spectra confirm the crystallographic results for (1) both in the solid state and in solution. For (2), however, different e.s.r. spectra are obtained of the microcrystalline powder and of the solution. Only the powder spectrum agrees with a distorted trigonal-bipyramidal structure.

RECENTLY, we investigated the structural characteristics of some ternary copper(II) complexes[1,2] containing heterocyclic di-imines or tri-imines and tridentate dicarboxylate dianions. The chromophoric groups CuN_3O_2 or CuN_2O_3 due to the co-ordination of *O*- and *N*-donor atoms gave rise to different stereochemical arrangements. This was rationalized by consideration of the different rigidities and binding abilities of the ligands.

Earlier, we reported studies on the thermodynamic and spectroscopic properties of copper(II) mixed complexes with 2,2′-bipyridine (bipy) or 2,2′:6′,2″-terpyridine (terpy) and some $X(CH_2COO)_2^{2-}$ ligands where X = O, S, or Se.[3-5] Pseudo-octahedral geometries were involved in the formation of these mixed species. The thermodynamic parameters ($\Delta G^\ominus$, $\Delta H^\ominus$, and $\Delta S^\ominus$), as well as the magnetic and optical results, showed no marked differences among the series of mixed complexes with oxydiacetate (oda), thiodiacetate (tda), and selenodiacetate (seda). In other words, the substitution of an ether oxygen atom by a sulphur or a selenium donor atom has little effect on the co-ordination features of these potentially tridentate ligands towards the metal ion in solution.

Despite the biological relevance of the sulphur atom in thioethers,[6,7] few reports on the co-ordinating properties of ligands containing this donor atom have appeared.[8-14] Therefore, we decided to extend our structural investigations to mixed copper(II) complexes containing the potential chromophores N_2O_2S or N_3O_2S.

We report here a spectroscopic investigation and the crystal and molecular structures of two mixed copper(II) complexes containing the thiodiacetate dianion as primary ligand and 2,2′-bipyridyl or 2,2′:6′,2″-terpyridyl as secondary ligands.

EXPERIMENTAL

Preparation of the Complexes.—Analytical-grade thiodiacetic acid, 2,2′-bipyridine, and 2,2′:6′,2″-terpyridine were employed to prepare the mixed complexes [Cu(bipy)(tda)(H_2O)]·4H_2O and [Cu(terpy)(tda)]. A stoicheiometric quantity of bipy or terpy in a water–methanol mixture was added to an aqueous solution in which the simple copper(II) complex with tda, the preparation and characterization of which is described elsewhere,[15] was dissolved. This solution was then evaporated to obtain a microcrystalline powder, the analytical results of which have already been reported.[16] The complex [Cu(bipy)(tda)(H_2O)]·4H_2O (1) was dissolved in hot water and, after slow evaporation of the solution at room temperature, light blue crystals were obtained a week later. The complex [Cu(terpy)(tda)] (2) was dissolved in a warm water–ethanol mixture to which n-butanol was added to prevent immediate precipitation. Bright green crystals could be collected in 3—4 d.

A Varian E-12 spectrometer equipped with a standard low-temperature apparatus was used to record the e.s.r. powder spectra of these complexes. The free radical diphenylpicrylhydrazyl (g = 2.0036) was used as a field marker. Experimental data were collected at 120 K.

Crystal Data.—(1). $C_{14}H_{14}CuN_2O_5S{\cdot}4H_2O$, M = 457.98, Monoclinic, space group $P2_1/c$, a = 11.136(7), b = 21.13(1), c = 8.999(6) Å, β = 113.2(2)°, U = 1 946 Å^3, D_m = 1.58, Z = 4, D_c = 1.56 g cm^{-3}, $F(000)$ = 948, μ(Mo-K_α) = 13.2 cm^{-1}, λ = 0.7107 Å.

(2). $C_{19}H_{15}CuN_3O_4S$, M = 444.97, Monoclinic, space group $C2/c$ (from structure determination), a = 10.551(6), b = 21.23(1), c = 8.633(5) Å, β = 112.0(2)°, U = 1 793 Å^3, D_m = 1.68, Z = 4, D_c = 1.65 g cm^{-3}, $F(000)$ = 908, μ(Mo-K_α) = 14.1 cm^{-1}, λ = 0.7107 Å.

Crystals of (1) rapidly become opaque and lose crystallinity when removed from the mother-liquor, probably due to the loss of water molecules. Therefore it was necessary to mount the crystals in glass capillaries completely filled with vaseline oil.

Cell parameters for both (1) and (2) were determined from Weissenberg and precession photographs using Cu-K_α radiation and refined by a least-squares fit of 2 θ, χ, and φ setting angles of the Siemens AED diffractometer for 25 and 20 accurately centred reflections respectively. Intensity data for both structures were collected with Mo-K_α filtered radiation using the θ—2θ scan technique in the range $3.5 \leqslant \theta \leqslant 28°$. A total of 3 130 (1) and 1 241 (2) independent reflections with $I \geqslant 3\sigma(I)$ were used and corrected for Lorentz and polarization effects. No correction for absorption was applied in view of the small dimensions of the crystals [0.4 × 0.3 × 0.8 mm for (1) and 0.4 × 0.25 × 0.7 mm for (2)].

Structure Determination and Refinement.—Both structures were solved by Patterson and Fourier methods. For compound (2) the space group *Cc* was assumed during the preliminary calculations. However, the resultant atomic arrangement around the copper atom (see below) strongly suggested the possibility of locating the crystallographically independent unit around the two-fold axes assuming the *C*2/*c* space group. Least-squares refinement for the two space groups led to the same *R* index and very similar atomic parameters, although with larger estimated standard deviations for the *Cc* space group as would be expected. A statistical test on *E* values was then carried out and clearly suggested a centric space group. The subsequent calculations were then performed using the *C*2/*c* space group. After least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms, a three-dimensional Fourier difference synthesis was calculated to locate the H atoms of both (1) and (2). Final anisotropic least-squares refinement, including fixed contributions for hydrogen atoms (B = 5 Å^2), gave R values of 0.057 for (1) and 0.035 for (2). The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$ where A = 14.0 and B = 0.013 for (1) and A = 24.4 and B = 0.006 for (2) were chosen such that $w(|F_o| - |F_c|)^2$ remained essentially constant over all ranges of $|F_o|$ and $(\sin \theta)/\lambda$.

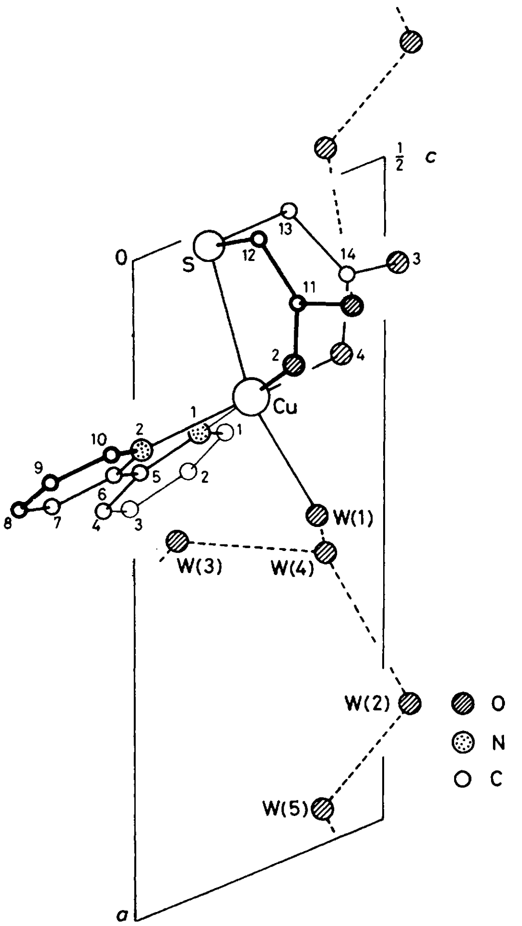

FIGURE 1 Side view of (1) along the *b* axis, together with the atom-numbering scheme

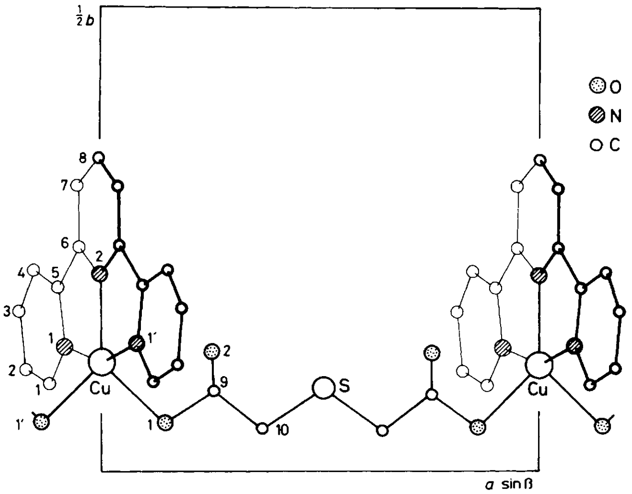

FIGURE 2 A view of (2) along the *c* axis, showing the atom-numbering scheme

TABLE 1

Atomic fractional co-ordinates (× 10^3 for H atoms; × 10^4 for others) for (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	2 790(1)	445(0)	2 271(1)
S	187(1)	566(1)	1 369(1)
O(1)	1 866(3)	2 053(2)	4 103(4)
O(2)	2 710(3)	1 299(2)	3 115(4)
O(3)	1 518(4)	−624(2)	5 105(5)
O(4)	2 594(3)	20(2)	4 120(4)
W(1)	5 054(3)	578(2)	3 708(5)
N(1)	3 083(4)	−391(2)	1 369(4)
N(2)	2 914(4)	761(2)	219(4)
C(1)	3 069(5)	−971(2)	1 968(6)
C(2)	3 178(6)	−1 520(2)	1 215(7)
C(3)	3 338(6)	−1 465(3)	−255(7)
C(4)	3 368(5)	−875(2)	−881(6)
C(5)	3 233(4)	−341(2)	−55(5)
C(6)	3 192(4)	303(2)	−663(5)
C(7)	3 381(5)	454(2)	−2 069(6)
C(8)	3 250(6)	1 071(3)	−2 580(6)
C(9)	2 917(7)	1 535(3)	−1 730(7)
C(10)	2 777(6)	1 358(2)	−304(6)
C(11)	1 752(4)	1 561(2)	3 302(5)
C(12)	383(5)	1 291(3)	2 509(8)
C(13)	215(5)	−30(3)	2 813(6)
C(14)	1 543(5)	−219(2)	4 112(5)
W(2)	1 569(5)	−1 936(2)	4 526(6)
W(3)	4 550(4)	2 690(2)	857(5)
W(4)	5 668(4)	1 891(2)	3 776(6)
W(5)	−337(5)	2 705(2)	3 958(6)
H(1)	297	−100	301
H(2)	314	−194	169
H(3)	343	−185	−83
H(4)	350	−83	−190
H(7)	359	12	−269
H(8)	341	119	−355
H(9)	277	198	−212
H(10)	257	169	34
H(121)	6	121	339
H(122)	−18	162	176
H(131)	−19	−42	219
H(132)	−34	12	338

The atom-numbering schemes for (1) and (2) are shown in Figures 1 and 2 respectively. Tables 1 and 2 give the final values of the refined atomic parameters together with their standard deviations derived from the inverse matrix of the least-squares refinement. Observed and calculated structure factors, anisotropic thermal parameters, and least-squares planes are given in Supplementary Publication No. SUP 23212 (27 pp.).* Atomic scattering factors were those of Moore.[17] The majority of the calculation was performed using the *X*-Ray system.[18]

TABLE 2

Atomic fractional co-ordinates ($\times 10^3$ for H atoms; $\times 10^4$ for others) for (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	0	1 176(0)	2 500
S	5 000	925(1)	2 500
O(1)	1 437(2)	490(1)	2 532(3)
O(2)	2 487(3)	1 363(1)	2 304(4)
N(1)	−803(3)	1 356(1)	4(3)
N(2)	0	2 100(2)	2 500
C(1)	−1 173(4)	919(2)	−1 215(5)
C(2)	−1 735(4)	1 084(2)	−2 897(5)
C(3)	−1 913(4)	1 712(2)	−3 325(5)
C(4)	−1 524(4)	2 164(2)	−2 084(4)
C(5)	−963(3)	1 972(2)	−422(4)
C(6)	−486(3)	2 405(2)	1 031(4)
C(7)	−501(4)	3 063(2)	982(5)
C(8)	0	3 383(2)	2 500
C(9)	2 438(3)	784(2)	2 432(4)
C(10)	3 663(4)	390(2)	2 460(5)
H(1)	−104	47	−90
H(2)	−201	75	−377
H(3)	−232	184	−451
H(4)	−164	262	−237
H(7)	−86	329	−9
H(8)	0	385	250
H(110)	399	11	348
H(210)	339	12	144

RESULTS AND DISCUSSION

Spectroscopic Results.—Powdered samples of the mixed complexes dissolved in water–methanol give identical e.s.r. spectra to those obtained from a mixture of the reagents in the same solvent. The solution spectra have already been reported and discussed.[5] The e.s.r. powder spectra of $[Cu(bipy)(tda)(H_2O)]\cdot 4H_2O$ and [Cu(terpy)(tda)] are shown in Figure 3 together with the *g* values measured directly from the experimental spectra. In the case of the mixed complex with bipy, the *g* values correlate fairly well with those derived from the simulation procedure used to analyze the solution spectra.[5] They are typical of the copper(II) ion with oxygen and nitrogen donor atoms in a six-co-ordinate environment. A minor discrepancy is found in the $g_\perp$ value, probably due to weak exchange interactions between neighbouring sites. As in the case of the analogous complex $[Cu(bipy)(oda)(H_2O)]\cdot 4H_2O$,[2] the data suggest that the environment around the copper(II) ion is preserved on going from the solid state to solution.

The e.s.r. powder spectrum of [Cu(terpy)(tda)], however, is completely different from that of the solution. The spectrum is similar to that reported by Wasson *et al.*[19] for $[Cu(dqp)X_2]$ [dqp = 2,6-di(2′-quinolyl)-pyridine, X = Cl or Br] in which the copper(II) ion was found in a distorted trigonal-bipyramidal geometry of approximate symmetry C_{2v}, although the *g* values of the two complexes are different due to different chromophores. On the basis of a theoretical calculation using the crystal-field approach, the ground state was postulated to be a mixture of $d_{x^2-y^2}$ (60%) and d_{z^2} (40%).

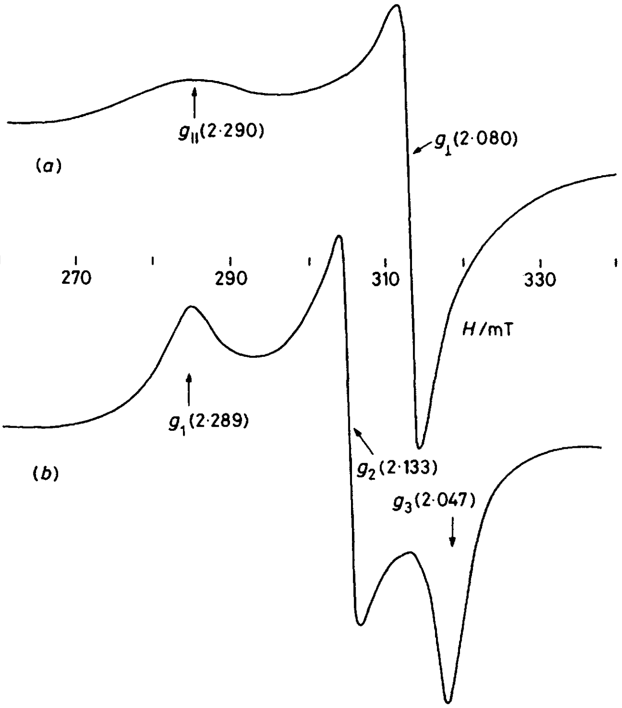

FIGURE 3 E.s.r. powder spectra of $[Cu(bipy)(tda)(H_2O)]\cdot 4H_2O$ (*a*) and [Cu(terpy)(tda)] (*b*) at 120 K. The presumed error of the last decimal place of *g* is ±0.005. The magnetic parameters obtained from the solution spectrum of (*b*) were: $g_z = 2.253 \pm 0.001$, $g_y = 2.070 \pm 0.005$, $g_x = 2.064 \pm 0.005$; $A_z = 0.0175 \pm 0.0001$, $A_y = 0.0008 \pm 0.0003$, $A_x = 0.0005 \pm 0.0003$ cm^{-1}

The reflectance absorption spectrum of (2) in the visible region also shows a marked difference from that of the solution. A symmetric band centred at 14 600 cm^{-1} (ε = 142 dm^3 mol^{-1} cm^{-1}) was observed for the aqueous methanolic solution, while a peak at 13 900 and a shoulder at 10 000 cm^{-1} were obtained for the solid state.[16] The combined spectral data suggest that the environment about the copper(II) ion in the crystal is different from that in solution in which a pseudo-octahedral geometry was assumed.

Structure of (1).—Crystals of (1) consist of $[Cu(bipy)(tda)(H_2O)]$ units connected by water molecules which stabilize the crystal by forming a net of hydrogen bonds. The overall arrangement is very similar to that found in the analogue $[Cu(bipy)(oda)(H_2O)]\cdot 4H_2O$.[2] The co-ordination sphere around the copper atom may be described as a distorted octahedron with the sulphur atom and the water molecule, W(1), in axial positions

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

[Cu–S 2.697(1), Cu–W(1) 2.353(3) Å, Table 3]. The equatorial positions are occupied by the nitrogen donors of bipy[Cu–N(1) 2.024(4), Cu–N(2) 2.019(4) Å] and by two oxygen atoms of the tda ligand [Cu–O(2) 1.973(4), Cu–O(4) 1.977(4) Å]. The copper atom is nearly coplanar (0.03 Å) with the equatorial donor atoms displaced by ±0.08 Å from their mean plane in a slight tetrahedral distortion. The complex shows the typical Jahn–Teller distorted co-ordination sphere of the copper(II) ion. On the other hand, the Cu–S bond distance of 2.697(1) Å is in the range [2.609(6)—2.824(5) Å] observed in similar complexes, *e.g.* CuLCl(ClO_4) {L = 3,4-bis(2-aminoethylthio)toluene}[9] and bis[1,3-bis(5′-phenylimidazol-2′-yl)-2-thioxopropane]copper(II) diperchlorate,[14] and confirms the suggested poor affinity of thioethers for copper(II). The two pyridine rings of bipy appear nearly planar with a torsion angle around the C(5)–C(6) bond of 7.7°, while in the complexes [Cu(bipy)(oda)(H_2O)] and [Cu(bipy)(ida)] (ida = iminodiacetate)[1,2] the entire bipy ligand is almost planar, the torsion angles being 1.7 and 1.2° respectively. The three donor atoms of the terdentate ligand tda are mutually *cis* as already reported for the zinc(II), cadmium(II), and nickel(II) complexes, [Zn(tda)(H_2O)$_3$],[20] [Cd(tda)(H_2O)],[21] and K_2[Ni(tda)$_2$]·3H_2O.[22] The two halves of the tda ligand are planar within ±0.02 Å and the CSC angle of 102.6(3)° is comparable with that of 101.8(3)° in the zinc(II) complex,[20] 103.1(4)° in the cadmium(II) compound,[21] and 103.2(11) and 104.2(14)° in the nickel(II) bis complex.[22]

TABLE 3

Relevant bond lengths (Å) and angles (°) for [Cu(bipy)(tda)(H_2O)]·4H_2O

(*a*) Bond lengths

Cu–S	2.697(1)	N(1)–C(1)	1.342(6)
Cu–O(2)	1.973(4)	N(1)–C(5)	1.360(7)
Cu–O(4)	1.977(4)	C(1)–C(2)	1.372(8)
Cu–W(1)	2.353(3)	C(2)–C(3)	1.409(10)
Cu–N(1)	2.024(4)	C(3)–C(4)	1.373(8)
Cu–N(2)	2.019(4)	C(4)–C(5)	1.392(7)
O(2)–C(11)	1.271(6)	C(5)–C(6)	1.460(6)
O(1)–C(11)	1.242(6)	C(6)–C(7)	1.399(8)
C(11)–C(12)	1.518(7)	C(7)–C(8)	1.372(8)
C(12)–S	1.808(6)	C(8)–C(9)	1.381(9)
S–C(13)	1.801(6)	C(9)–C(10)	1.403(9)
C(13)–C(14)	1.533(6)	N(2)–C(10)	1.333(6)
O(4)–C(14)	1.273(7)	N(2)–C(6)	1.363(6)
O(3)–C(14)	1.244(7)		

(*b*) Angles

N(1)–Cu–O(2)	172.6(2)	O(2)–Cu–S	79.8(1)
N(1)–Cu–S	106.6(1)	O(2)–Cu–O(4)	93.1(2)
N(1)–Cu–O(4)	91.7(2)	O(2)–Cu–W(1)	83.1(1)
N(1)–Cu–N(2)	80.9(2)	S–Cu–O(4)	80.5(1)
N(1)–Cu–W(1)	91.0(1)	S–Cu–W(1)	161.0(1)
N(2)–Cu–O(2)	94.6(2)	O(4)–Cu–W(1)	92.4(1)
N(2)–Cu–S	98.4(1)	C(12)–S–C(13)	102.6(3)
N(2)–Cu–O(4)	171.9(1)	Cu–S–C(12)	92.0(2)
N(2)–Cu–W(1)	91.1(2)	Cu–S–C(13)	90.3(2)

Structure of (2).—Crystals of [Cu(terpy)(tda)] comprise polymeric chains nearly parallel to the [100] direction, in which Cu(terpy) units are bridged by the thiodiacetate ligand through the oxygens of the carboxylate groups, as shown in Figure 2. The co-ordination polyhedron around the copper atom, located on the two-fold axis at $0, y, \frac{1}{4}$, can be described as a distorted trigonal bipyramid. The axial sites are occupied by the two lateral nitrogen atoms of terpy [Cu–N(1) = Cu–N′(1) 2.034(3) Å, Table 4], while the equatorial sites are occupied by the central terpy nitrogen [Cu–N(2) 1.962(4) Å] and by the oxygen atoms of two tda units [Cu–O(1) = Cu–O′(1) 2.095(3) Å] (see Figure 2). The terpy ligand, arranged around the two-fold symmetry axis at $0, y, \frac{1}{4}$, is planar within ±0.04 Å and nearly perpendicular (92.4°) to the polymeric chain. The tda acts as a bidentate ligand between two subsequent copper atoms, the sulphur being located on the two-fold axis at $\frac{1}{2}, y, \frac{1}{4}$. It assumes a zigzag approximately planar conformation, similar to that found in thiodiacetic acid[23] which has crystallographically imposed *m* symmetry.

TABLE 4

Relevant bond lengths (Å) and angles (°) for [Cu(terpy)(tda)]

(*a*) Bond lengths

Cu–O(1)	2.095(3)	C(1)–C(2)	1.392(5)
Cu–N(1)	2.034(3)	C(2)–C(3)	1.378(6)
Cu–N(2)	1.962(4)	C(3)–C(4)	1.382(5)
O(1)–C(9)	1.257(5)	C(4)–C(5)	1.393(5)
C(9)–O(2)	1.237(4)	C(5)–C(6)	1.483(5)
C(9)–C(10)	1.531(5)	C(6)–C(7)	1.397(5)
C(10)–S	1.801(4)	C(6)–N(2)	1.342(4)
N(1)–C(1)	1.347(5)	C(7)–C(8)	1.393(4)
N(1)–C(5)	1.352(4)		

(*b*) Angles

O(1)–Cu–N(1)	99.0(1)	Cu–O(1)–C(9)	106.1(2)
O(1)–Cu–N(1′)	96.0(1)	O(1)–C(9)–C(10)	117.1(3)
O(1)–Cu–O(1′)	91.9(1)	O(1)–C(9)–O(2)	124.2(4)
O(1)–Cu–N(2)	134.0(1)	O(2)–C(9)–C(10)	118.7(3)
N(1)–Cu–N(2)	79.2(1)	C(9)–C(10)–S	107.9(3)
N(1)–Cu–N(1′)	158.4(1)	Cu(10)–S–C(10′)	101.8(2)

Despite the different conformations, the bond lengths and angles of tda are similar in both (1) and (2). The CSC angle of 101.8(2)° is similar to the corresponding angle of 102.6(3)° in (1) in which the tda ligand acts as a tridentate ligand. Both values are significantly greater than that [95.8(9)°] observed in free thiodiacetic acid, therefore the observed increase in the CSC angle after co-ordination of tda does not appear to be ascribable to the formation of five-membered rings, as suggested in the case of [Zn(tda)(H_2O)$_3$].[20] The crystal packing shows polymeric chains parallel to the [100] direction at $z = \frac{1}{4}$ and $\frac{3}{4}$. The terpy ligands, nearly perpendicular to the chain axis, allow effective van der Waals interactions between facing terpy units of adjacent chains. These appear sufficient to hold together the chains in the crystal, without any need for the hydrogen-bonded network of water molecules found in similar complexes.[1,2]

E.s.r., optical, and diffractometric data point to the similar configurations adopted by oda[2] and tda in mixed complexes involving the bipy ligand, both in the solid state and in solution. On the contrary, with the terpy ligand, a five-co-ordinate copper atom is found in [Cu(terpy)(tda)]. The non-co-ordination of the sulphur atom may be ascribed both to electronic and steric effects. It is well known that interactions between sulphur, a typical soft donor atom, and hard or borderline metal ions, such as copper(II), are rather weak. In fact very often other donor atoms, such as nitrogen or oxygen, have been added to sulphur-containing ligands in order to enhance the co-ordination tendency of the sulphur atom itself. Therefore, the strong binding ability of these other donors ' drags ' the sulphur atom into co-ordination with copper(II) ions, as is probably the case in the [Cu(bipy)(tda)(H_2O)] compound, (1). On the other hand, in the [Cu(terpy)(tda)] complex, (2), geometric effects seem to hinder the co-ordination of the sulphur atom. In this case, the planarity of the terpy ligand and consequently the availability of three co-ordination sites on a plane roughly perpendicular to the terpy molecule prevent the usual *fac* conformation of the tda ligand, which is therefore forced to assume the nearly planar conformation already observed in the [Ca(oda)$(H_2O)_5$] derivative.[24] The oda ligand in this conformation requires larger Ca–O–C and C–O–C angles [Ca–O(1)–C(2) 124.0(3), Ca–O(1)–C(3) 123.6(3), C(2)–O(1)–C(3) 112.4(3)°] than in the folded conformation,[2] however, a similar widening of the angles around sulphur is less likely, hence the planar arrangement of tda is not possible.

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