Properties and Structural Characterization of the Mixed-ligand Complex Oxydiacetato(2,2′:6′,2″-terpyridyl)copper(II) Dihydrate †

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The crystal structure of the title complex has been determined by *X*-ray methods. Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 10.681(6)$, $b = 22.44(1)$, $c = 11.534(6)$ Å, and $\beta = 136.1(2)°$. The complex has a distorted octahedral stereochemistry with the two ligands co-ordinating in two approximately perpendicular planes.

Some years ago some of the present authors participated in a study of the spectral features of solid copper(II) mixed-ligand complexes with 2,2′-bipyridyl (bipy) or 2,2′:6′,2″-terpyridyl (terpy) and dicarboxylate ligands containing N, O, and S as donor atoms, *viz.* iminodiacetate (ida), oxydiacetate (oda), and thiodiacetate (tda) respectively.[1] Since peculiar differences were evident within this series of complexes we decided to investigate them more carefully.

Recently, we reported a spectroscopic and structural study [2] of the mixed-ligand complexes $[Cu(bipy)(tda)(H_2O)]\cdot4H_2O$ and [Cu(terpy)(tda)], in which the thiodiacetate ligand is tridentate in the former but bidentate in the latter. However, in aqueous solutions the same compounds did not reveal any peculiar feature, and pseudo-octahedral geometries can easily be attained by the copper(II) ion in the environments created by these ligands.[3] We report here a spectroscopic and structural study of $[Cu(terpy)(oda)]\cdot2H_2O$ to determine whether the oda ligand behaves in the same way as tda.

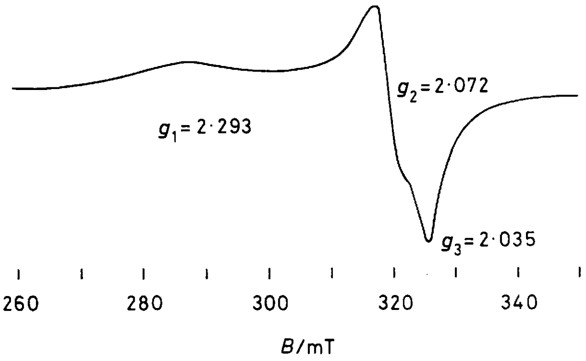

Figure 1. E.s.r. powder spectrum of $[Cu(terpy)(oda)]\cdot2H_2O$ at 77 K. The presumed error on the last decimal figure of *g* is ±0.005

Table 1. Values of *g* and electronic spectral maxima for copper(II) mixed-ligand complexes with 2,2′-bipyridyl or 2,2′:6′,2″-terpyridyl and oxydiacetate or thiodiacetate

Complex	$g_{\parallel}$	$g_{\perp}$		$10^{-3}\tilde{\nu}$/ cm^{-1}	Ref.
$[Cu(bipy)(oda)(H_2O)]\cdot4H_2O$	2.290	2.080		15.4	5
$[Cu(bipy)(tda)(H_2O)]\cdot4H_2O$	2.290	2.080		15.1	2
	g_1	g_2	g_3		
$[Cu(terpy)(oda)]\cdot2H_2O$	2.293	2.072	2.035	14.1	This work
[Cu(terpy)(tda)]	2.289	2.133	2.047	13.9, 10.0	2

Experimental

Suitable crystals of the [Cu(terpy)(oda)] complex were obtained by mixing [Cu(oda)] and terpy in water–ethanol in stoicheiometric ratios. After a week stable green crystals were collected.

E.s.r. spectra were recorded on a Varian E 9 spectrometer at 77 K. The magnetic field was calibrated using the free radical diphenylpicrylhydrazyl (dpph) as a marker.

Crystallography.—The crystals of $[Cu(terpy)(oda)]\cdot2H_2O$ were elongated along the *c* axis and one of dimensions 0.3 × 0.5 × 0.8 mm was chosen for the crystallographic study. Cell parameters were determined from Weissenberg and precession photographs and refined using diffractometer setting angles. Intensity data were collected with Mo-K_α filtered radiation on a Siemens AED diffractometer using the θ–2θ scan technique in the range $3.5 \leqslant \theta \leqslant 28°$.

The structure was solved *via* the heavy-atom method and refined by full-matrix least squares. All computations were made using the *X*-RAY system.[4]

Crystal data. $C_{19}H_{15}CuN_3O_5\cdot2H_2O$, $M = 464.9$, Monoclinic, $a = 10.681(6)$, $b = 22.44(1)$, $c = 11.534(6)$ Å, $\beta = 136.1(2)°$, $U = 1\,916.9$ Å^3, $D_m = 1.62$, $Z = 4$, $D_c = 1.61$ g cm^{-3}, $F(000) = 956$, space group $P2_1/c$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 12.4 cm^{-1}.

A total of 2 127 independent reflections with $I \geqslant 3\sigma(I)$ were used and corrected for Lorentz and polarization effects. No correction for absorption was applied. Final anisotropic least-squares refinement, including fixed contributions for hydrogen atoms ($B = 5$ Å^2), gave a *R* value of = 0.033.

Final atomic fractional co-ordinates are given in Table 2, selected bond lengths and angles in Table 3.

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† *Supplementary data available* (No. SUP 23607, 14 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Atomic fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Cu	3 819(1)	1 371(0)	1 759(1)	C(7)	2 395(6)	3 101(2)	−101(5)
O(1)	1 481(6)	2(2)	2 212(6)	C(8)	3 383(6)	3 442(2)	1 348(6)
O(2)	1 995(4)	888(1)	1 721(4)	C(9)	4 453(6)	3 177(2)	2 902(5)
O(3)	4 478(4)	479(1)	2 024(4)	C(10)	4 519(5)	2 556(2)	2 978(5)
O(4)	6 082(4)	1 301(1)	1 894(4)	C(11)	5 565(5)	2 184(2)	4 490(5)
O(5)	7 406(5)	656(2)	1 577(5)	C(12)	6 558(5)	2 408(2)	6 084(5)
N(1)	2 059(4)	1 464(1)	−763(4)	C(13)	7 490(6)	2 060(2)	7 401(5)
N(2)	3 554(4)	2 232(1)	1 566(4)	C(14)	7 428(6)	1 407(2)	7 121(5)
N(3)	5 482(4)	1 591(1)	4 202(4)	C(15)	6 416(6)	1 211(2)	5 508(5)
C(1)	1 348(6)	1 026(2)	−1 881(5)	C(16)	2 226(6)	338(2)	1 990(6)
C(2)	200(6)	1 141(2)	−3 569(5)	C(17)	3 537(6)	32(2)	2 048(6)
C(3)	−226(6)	1 725(2)	−4 115(5)	C(18)	5 693(6)	258(2)	1 970(5)
C(4)	501(6)	2 182(2)	−2 978(5)	C(19)	6 449(5)	787(2)	1 801(5)
C(5)	1 649(5)	2 036(2)	−1 297(5)	W(1)	8 996(4)	1 390(1)	890(4)
C(6)	2 536(5)	2 483(2)	66(5)	W(2)	1 070(5)	321(2)	4 218(5)

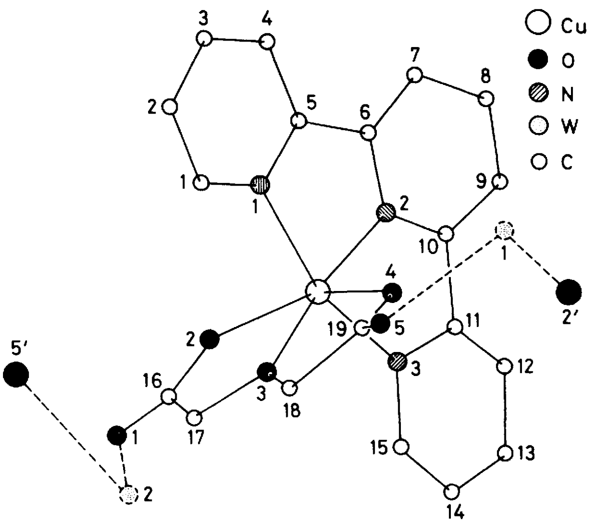

Figure 2. A view of [Cu(terpy)(oda)]·$2H_2O$ with the atom-numbering scheme. The primed oxygen atoms are related by translation along the *a* axis

Table 3. Selected bond lengths (Å) and angles (°)

Cu–N(1)	2.039(3)	Cu–O(2)	2.202(5)
Cu–N(2)	1.942(3)	Cu–O(3)	2.070(5)
Cu–N(3)	2.031(4)	Cu–O(4)	2.312(5)
N(1)–Cu–N(2)	80.0(1)	O(2)–Cu–O(3)	74.3(2)
N(1)–Cu–N(3)	160.0(1)	O(2)–Cu–O(4)	146.6(1)
N(1)–Cu–O(2)	97.4(2)	O(3)–Cu–O(4)	72.4(2)
N(1)–Cu–O(3)	100.1(1)	Cu–O(2)–C(16)	117.8(5)
N(1)–Cu–O(4)	87.0(2)	O(2)–C(16)–C(17)	117.9(7)
N(2)–Cu–N(3)	80.0(1)	C(16)–C(17)–O(3)	108.7(4)
N(2)–Cu–O(2)	115.7(2)	Cu–O(3)–C(17)	120.7(4)
N(2)–Cu–O(3)	170.0(2)	C(17)–O(3)–C(18)	115.4(4)
N(2)–Cu–O(4)	97.7(2)	Cu–O(3)–C(18)	123.4(3)
N(3)–Cu–O(2)	91.4(2)	O(3)–C(18)–C(19)	108.4(4)
N(3)–Cu–O(3)	99.6(1)	C(18)–C(19)–O(4)	118.7(6)
N(3)–Cu–O(4)	95.5(2)	Cu–O(4)–C(19)	115.8(4)

Results and Discussion

A powdered sample of the complex dissolved in water–methanol solution gives an e.s.r. spectrum identical to that observed starting from a mixture of the reagents in the same solvent.[3] Unfortunately the crystals were not suitable for a detailed e.s.r. single-crystal study. The powder e.s.r. spectrum of [Cu(terpy)(oda)]·$2H_2O$ is shown in Figure 1 together with its *g* values taken directly from the experimental spectrum.

It is interesting to compare these data with those previously obtained (Table 1) for [Cu(bipy)(oda)(H_2O)]·$4H_2O$, [Cu(bipy)(tda)(H_2O)]·$4H_2O$, and [Cu(terpy)(tda)]. While the first two sets of data clearly indicate similar copper(II) environments, as already confirmed by the molecular structure of these complexes,[2,5] the magnetic parameters of the two complexes with terpy show a peculiar trend. Both exhibit an anisotropic e.s.r. spectrum. Moreover, the rhombic component is more pronounced in the complex [Cu(terpy)(tda)] which is five-co-ordinated in a distorted trigonal bipyramid,[2] the sulphur atom being unco-ordinated. The three *g* values found from the spectrum of [Cu(terpy)(oda)]·$2H_2O$ surely reflect a rather distorted polyhedron of nitrogen and oxygen atoms around the copper atom, and also indicate that a different co-ordination geometry is involved in this complex with respect to [Cu(terpy)(tda)]. Even if the lowest *g* value is smaller than 2.04,[6,7] the *g* values together with the intensity ratios of the lines found in the e.s.r. spectrum of this compound probably suggest that the ground-state orbital of the copper(II) ion in this environment is essentially $|x^2 - y^2\rangle$. The anisotropy experimentally determined is probably due to a small degree of mixing of $|xy\rangle$ and $|3z^2 - r^2\rangle$ into the ground-state orbital because of the low symmetry of this site. The visible reflectance spectra seem to confirm this assignment. The shift of $\nu_{max.}$ towards lower frequencies in the case of [Cu(terpy)(oda)]·$2H_2O$ relative to [Cu(bipy)(oda)(H_2O)]·$4H_2O$ and [Cu(bipy)(tda)(H_2O)]·$4H_2O$ reflects the co-ordination of another nitrogen atom to the copper(II) ion, thus forming a substantially different chromophore in a more distorted polyhedron. In the case of [Cu(terpy)(tda)] two distinct peaks were found, again reflecting the different geometry [2] adopted by the copper(II) ion in this environment.

Crystals of [Cu(terpy)(oda)]·$2H_2O$ consist of monomeric [Cu(terpy)(oda)] units linked by water molecules as depicted in Figure 2. The co-ordination polyhedron around the copper atom can be described as a distorted octahedron with the nitrogen atoms of the terpy ligand and the ether oxygen atom of oda in the equatorial sites, the two axial positions being occupied by the oxygens of the carboxylate groups [Cu–O(2) 2.202(5), Cu–O(4) 2.312(5) Å].

The planarity of the terpy ligand and the achievement of a strongly chelated structure by the oda ligand impose a nearly planar configuration on the latter as in [Ca(oda)(H_2O)$_5$] [8] and

Table 4. Mean internal angles (°) of the two equivalent five-membered rings of oxydiacetate in planar and *cis* conformation; an asterisk indicates an ether oxygen atom

	Complex			
Angle	[Cu(terpy)(oda)] [a]	[Ca(oda)] [b]	[Cu(bipy)(oda)] [b]	[Cu(oda)] [b]
CuO*C	122.1	123.8	103.7	104.3
O*CC	108.5	109.1	114.5	112.8
CCO	118.3	119.0	119.5	121.5
COCu	116.8	123.7	123.0	124.9
OCuO*	73.4	64.2	76.0	74.3
	539.1	539.8	536.7	537.8
CO*C	115.4	112.4	114.7	114.3

[a] oda in planar conformation. [b] oda in *cis* conformation.

[Cd(oda)(H_2O)$_3$].[9] In contrast, in other copper(II) complexes the oxydiacetate ligand always appeared in a *cis* conformation.[5,10] The present structure is the first example of a copper complex where the oda is nearly planar. The dihedral angle between the two halves of oda is 3.8° and the overall ligand is planar within ±0.08 Å. This situation is very similar to that found in [Ca(oda)(H_2O)$_5$] [6] where the tridentate ligand is planar within ±0.07 Å, with a dihedral angle of 2.9°. In the *cis* conformation the angle between the two halves of the ligand is 103.2° in [Cu(bipy)(oda)(H_2O)]·4H_2O [5] and 101.9° in [Cu(oda)]·0.5H_2O.[10]

In Table 4 are reported the mean internal angles of the two equivalent five-membered rings of the oda ligand in planar and *cis* conformation respectively. It is interesting that the COC angle and the sum of the internal angles in the rings are nearly constant. On the contrary, a large variation is observed for the CuOC angles so that the ether oxygen atom appears to be *sp*^{2} hybridized for the planar and *sp*^{3} for the *cis* conformation. This ' flexibility ' of the ether oxygen and the strong chelating ability of the oxydiacetate ligand may result in the different geometries of oda in copper complexes.

As already mentioned, on the basis of the e.s.r. results and the *X*-ray diffraction study, the analogous [Cu(terpy)(tda)] complex consists of polymeric chains and the sulphur is not co-ordinated to the copper atom. This can be attributed to the suggested poor affinity of thioethers for copper(II) [11] and to the inability of sulphur to widen its angles within the tda rings,[2] in contrast with what is observed for the oda ligand in planar configuration.

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