Electronic Properties and Crystal Structure of (2,2′-Bipyridyl)-*catena*-μ-(oxalato-O^1O^2:$O^{1'}O^{2'}$)-copper(II) Dihydrate and Aqua(2,2′-bipyridyl)-(oxalato-O^1O^2)copper(II) Dihydrate

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The crystal structure of the title compounds $[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ (1) and $[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$ (2) have been determined by *X*-ray analysis. Compound (1) crystallises in the triclinic space group $P\bar{1}$ with a = 9.673(3), b = 8.940(3), c = 9.103(3) Å, α = 105.718(3), β = 110.347(3), γ = 97.539(3)°, and Z = 2. The six-co-ordinate $CuN_2O_2O'_2$ chromophore of (1) involves an elongated rhombic octahedral stereochemistry involving a symmetrically co-ordinated bipy ligand (mean Cu-N 2.007 Å) and unsymmetrically co-ordinated bridging oxalate groups (mean Cu-O 1.988 and 2.320 Å). Compound (2) crystallises in the triclinic space group $P\bar{1}$ with a = 10.565(3), b = 7.246(3), c = 10.806(3) Å, α = 102.467(3), β = 62.119(3), γ = 98.134(3)°, and Z = 2. The CuN_2O_2O' chromophore of (2) is basically square pyramidal with a symmetrically co-ordinated bipy ligand (mean Cu-N 1.989 Å), and a symmetrically co-ordinated oxalate group (mean Cu-O 1.953 Å) in the plane of the square pyramid, and a water molecule at 2.341 Å out of the plane. The electronic reflectance spectrum of (1) involves a main band at 14 500 cm⁻¹ with a resolved broad band at 9 300 cm⁻¹, while that of (2) involves a single broad band at 15 600 cm⁻¹, a difference that is consistent with the structures and suggests an ' electronic criterion of stereochemistry ' to distinguish these two structures.

TERNARY complexes of the copper(II) ion with 2,2′-bipyridyl (bipy) ligands and the oxalate ion have been reported [1,2] to involve the anhydrous and dihydrated 2,2′-bipyridyl(oxalato)copper(II) complexes. A more recent re-examination of this system has shown that they are subject to polymorphism, characterised by marked colour changes, along with changes in the electronic and e.s.r. spectra. As the complexes were formulated [1-3] as either rhombic coplanar isomers, as double salts $[Cu(bipy)_2][Cu(C_2O_4)_2]$, or as structures involving bridging oxalate groups, the system has been re-examined to obtain some *X*-ray crystallographic structural evidence for the polymorphic phases. The present paper reports the structure determination of $[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ (1), and $[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$ (2), and compares their electronic properties.

EXPERIMENTAL

Preparations.—Complex (1). A hot solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.24 g, 1 mmol) in water (25 cm³) and bipy (0.31 g, 2 mmol) in ethanol (25 cm³) were added to a hot solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.24 g, 1 mmol) in water (25 cm³) and $K_2(C_2O_4)\cdot H_2O$ (0.37 g, 2 mmol) in water (25 cm³); the mixture was heated to boiling, filtered, and allowed to stand. A mixture of blue and violet crystals was deposited after a few days. The blue crystals of (1) were separated by hand (Found: Cu, 41.9; H, 2.45; N, 8.15. $C_{12}H_{12}CuN_2O_6$ requires C, 41.9; H, 3.5; N, 8.15%).

Complex (2). A solution of bipy (0.4 g, 2.5 mmol) in CH_3CN (20 cm³) was added to a suspension of $Cu(C_2O_4)\cdot 0.5H_2O$ (0.136 g, 0.85 mmol) in CH_3CN (20 cm³) and the suspension warmed and stirred while water (20 cm³) was added. The hot solution was filtered and the dark blue filtrate allowed to evaporate yielding green microcrystals

TABLE 1

Crystal and refinement data

Compound	$[Cu(bipy)(C_2O_4)]\cdot 2H_2O$	$[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$
M	343.54	361.54
Stoicheiometry	$C_{12}H_{12}CuN_2O_6$	$C_{12}H_{14}CuN_2O_7$
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.673(3)	10.565(3)
b/Å	8.940(3)	7.246(3)
c/Å	9.103(3)	10.806(3)
α/°	105.718(3)	102.467(3)
β/°	110.347(3)	62.119(3)
γ/°	97.539(3)	98.134(3)
Z	2	2
U/Å³	688.0	713.1
D_m/g cm⁻³ (flotation)	1.52(2)	1.52(2)
D_c/g cm⁻³	1.45	1.48
F(000)	346.00	370.00
No. of unique reflections (no. measured)	3 606(3 668)	2 111(2 420)
$R = (\Sigma\Delta/\Sigma\|F_o\|)$	0.0378	0.0383
$R' = (\Sigma\Delta w^{\frac{1}{2}}/\Sigma\|F_o\|w^{\frac{1}{2}})$	Fixed weight	0.0466
Max. final shift/e.s.d.	0.003	0.0016
Residual electron density/e Å⁻³	0.51	0.46

and blue-violet crystals of (2), which were separated by hand (Found: C, 40.3; H, 3.35; N, 7.65. $C_{12}H_{14}CuN_2O_7$ requires C, 39.8; H, 3.85; N, 7.75%).

Crystal Data.—The crystal and refinement data for (1) and (2) are summarised in Table 1. The preliminary unit-cell and space-group data were determined from precession photographs and refined by diffractomer. The intensity data for (1) were collected on a Philips PW1100 four-circle diffractometer using Mo-K_α radiation ($\lambda = 0.7107$ Å),[4] and that for (2) on a Enraf Nonius CAD4 diffractometer using Cu-K_α radiation ($\lambda = 1.5418$ Å).[5] The data for (1) were not corrected for absorption ($\mu = 15.6$ cm^{-1}), but the data for (2) were corrected ($\mu = 23.3$ cm^{-1}).

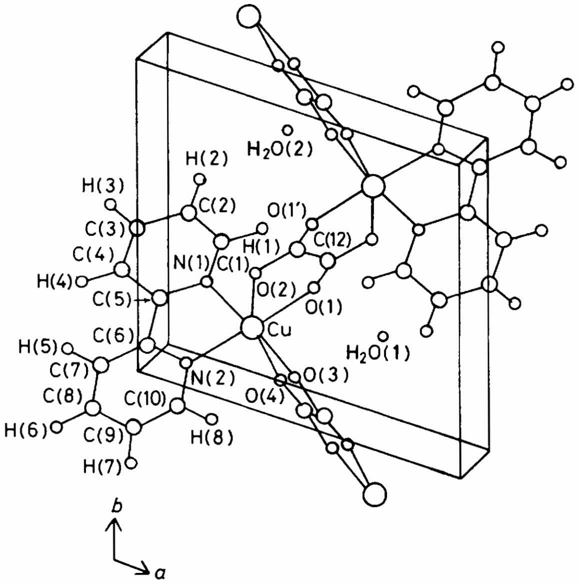

FIGURE 1 Local molecular structure, atom numbering scheme, and molecular packing viewed down the approximate *c* axis for $[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ (1)

The structures of (1) and (2) were solved using Patterson and Fourier techniques and refined by blocked-matrix least squares with anisotropic temperature factors for all of the non-hydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and floated on the associated carbon or oxygen atoms, assuming C–H or O–H = 1.08 Å, and a fixed temperature factor of 0.07 Å^2. All calculations were carried out using SHELX-76 [6] and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and XPUB (R. Taylor) on an IBM 4341 computer. The final atomic co-ordinates are given in Table 2, some selected bond-length and bond-angle data in Table 3, and selected mean-plane data in Table 4. The final structure factors, isotropic and anisotropic temperature factors, calculated hydrogen atom positions, full bond-length and bond-angle data, and full mean-plane data are given in Supplementary Publication No. SUP 23249 (47 pp.).*

Figure 1 illustrates the local molecular structure of (1) and the polymerisation in the *b* axis direction, viewed down the approximate *c* axis direction, and Figure 2 illustrates that of (2) with the packing in the unit cell viewed down the approximate *a* axis.

Electronic Properties.—Electronic spectra were recorded as previously described [7] and are illustrated in Figure 3. Both e.s.r. spectra are axial and only differ significantly in the value of the highest *g*, namely 2.328 for (1) and 2.286 for (2). The single-crystal *g* factors for (1) (2.063, 2.084, and 2.328) indicate a small rhombic component. Both complexes are blue or blue-violet in colour, but involve significantly different electronic spectra; (1) has a main peak at 14 500 cm^{-1}, with a medium-strong shoulder at 9 300 cm^{-1}, while (2) has a single broad peak at 15 600 cm^{-1}.

RESULTS AND DISCUSSION

Crystal Structures.—The structure of (1) consists of neutral $Cu(bipy)(C_2O_4)$ units involving bridging oxalate anions to give a ' zigzag ' polymeric structure parallel to the *b* axis; the two water molecules are not co-ordinated to the copper atom, but are present as lattice water. The copper atom involves a six-co-ordinate $CuN_2O_2O'_2$ chromophore with an elongated rhombic octahedral structure, Figure 1. The bipy ligand is symmetrically co-ordinated in the plane [8] and the two oxalate ligands are asymmetrically co-ordinated [9] with one short copper–oxygen bond (mean Cu–O 1.988 Å), and one long Cu–O bond (mean 2.320 Å) to yield a tetragonality,[10] *T* (mean in-plane bond distance divided by mean out-of-plane bond distance) of 0.863. The oxalate groups are centrosymmetric and involved in an asymmetric bridging role between centre-related copper atoms, staggered along the *b* axis direction, Figure 1. There are no unusual bond lengths or angles in the oxalate,[9] and bipy groups [9,11] (see SUP 23249); the bipy ligand is planar, Table 4, and the dihedral angle between the pyridine rings is only 1.9°. The bite angles at the copper atom are normal,[8,9] that of the bipy ligand is 80.9°, and those of the two oxalates are 77.4 and 77.9°, which are not significantly different. The N(1), N(2), O(1), O(3) atoms are reasonably planar, with only a slight tetrahedral distortion [12] (Table 4 and SUP 23249), and the O(2) $\cdots$ O(4) direction makes an angle of 84° to this plane, but with the O(2)–Cu–O(4) angle (159.5°) significantly reduced from 180° due to the small bite angles of the oxalate groups.[9] The elongated rhombic octahedral stereochemistry of the $CuN_2O_2O'_2$ chromophore, with an elongation restricted by the bite of the chelate oxalate ligands to a tetragonality of 0.863, is closely comparable to the structure [13] of [Cu(bipy)-(hfacac)$_2$] (3) (hfacac = 1,1,1,6,6,6-hexafluoroacetylacetonate), which has *T* = 0.864.

The oxygen atoms of the water molecules are reasonably close together (2.708 Å) with no evidence for a calculated hydrogen bond between them, but $H_2O(1)$ and $H_2O(2)$ form non-bonding contacts of 2.894 and 2.882 Å to O(3) and O(1) respectively, Table 3, to form a potential hydrogen bonding chain approximately parallel to the *c* axis.

The crystal structure of (2) consists of neutral Cu-(bipy)$(C_2O_4)(OH_2)$ units and two unco-ordinated water molecules in the unit cell. The copper atom involves a five-co-ordinate CuN_2O_2O' chromophore, with a square-pyramidal structure [as previously suggested for (1) and

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

(2), see ref. 3]. The bipy ligand[8] and oxalate anion[14] are both symmetrically co-ordinated to the copper atom (mean Cu–N 1.989 Å, mean Cu–O 1.953 Å) in the plane of the square pyramid with a water molecule occupying the fifth co-ordinate position at a distance of 2.341 Å. An O(2′) atom from a symmetry-related oxalate ion occupies the sixth co-ordinate position at a distance of 3.019 Å, which is long even for weak semi-co-ordination. Both the bipy ligand[11] and the oxalate ion are reasonably planar, Table 4, with the dihedral angle between the pyridine rings of 6.3° comparable to angles of up to 11° previously observed[11] for the co-ordinated bipy ligand. The mean planes of the bipy and oxalate ligands involve a dihedral angle of 13.5° due to a slight trigonal distortion[12] of the N(1),N(2),O(1),O(2) plane (see SUP 23249), with N(1)–Cu–O(1) and N(2)–Cu–O(2) angles of 178.9 and 166.2° respectively. The Cu atom lies 0.115 Å above the N(1),N(2),O(1),O(2) mean plane towards the co-ordinated water molecule. All the angles at the Cu atom are predictable, 90 ± 10°, and there are no unusual bond lengths or bond angles in the bipy[11] or oxalate[9] ligands.

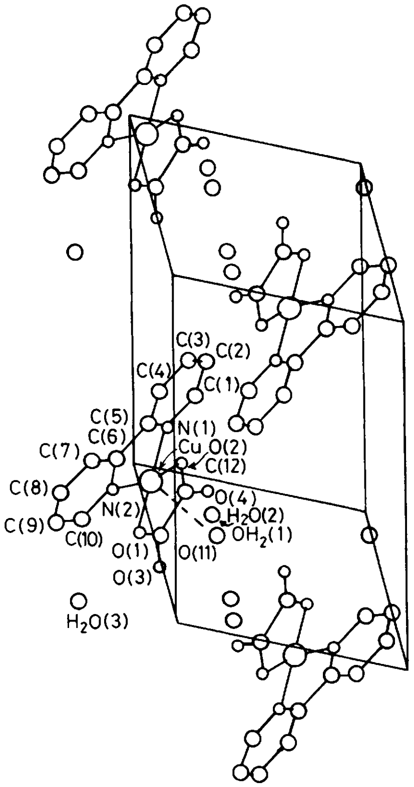

FIGURE 2 Local molecular structure, atom numbering scheme, and atom packing viewed down the approximate *a* axis for $[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$ (2)

The two unco-ordinated water molecules involve a relatively short $H_2O(2) \cdots H_2O(3)$ contact of 2.866 Å (Table 3) suggesting hydrogen bonding, but also to the co-ordinated $OH_2(1)$, and O(1) of the oxalate group. Further non-bonding contacts (1 − *x*, 1 − *y*, − *z*), Table 3, yield a weak dimer with a Cu–Cu distance of 3.69 Å, but as the hydrogen positions reported are calculated rather than observed, the hydrogen-bonding network has not been developed.

TABLE 2

Atom co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
$[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ (1)			
Cu	3 139	2 090	4 480
N(1)	1 633(2)	2 910(2)	5 327(2)
C(1)	1 952(3)	4 219(3)	6 641(3)
C(2)	846(3)	4 701(3)	7 154(4)
C(3)	−639(3)	3 801(3)	6 275(4)
C(4)	−987(3)	2 440(3)	4 909(3)
C(5)	179(2)	2 009(2)	4 460(3)
C(6)	−42(2)	593(2)	3 043(3)
C(7)	−1 440(3)	−499(3)	2 035(3)
C(8)	−1 522(3)	−1 794(3)	722(3)
C(9)	−219(3)	−1 961(3)	455(3)
C(10)	1 147(3)	−838(3)	1 518(3)
N(2)	1 232(2)	425(2)	2 793(2)
O(1)	4 931(2)	3 812(2)	6 234(2)
O(2)	3 329(2)	3 990(2)	3 212(2)
C(11)	4 814(2)	−139(2)	5 727(2)
C(12)	4 532(2)	5 038(2)	4 129(2)
O(3)	4 493(2)	1 038(2)	3 573(2)
O(4)	3 883(2)	513(2)	6 115(2)
$H_2O(1)$	5 564(3)	1 581(3)	1 117(4)
$H_2O(2)$	5 645(7)	3 764(4)	−432(3)
$[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$ (2)			
Cu	1 380	1 333(1)	3 649
N(1)	2 415(2)	2 157(3)	4 825(2)
C(1)	1 914(3)	3 309(4)	6 078(3)
C(2)	2 755(3)	3 985(4)	6 766(3)
C(3)	4 153(4)	3 434(4)	6 116(3)
C(4)	4 679(3)	2 239(4)	4 809(3)
C(5)	3 766(3)	1 614(3)	4 203(3)
C(6)	4 174(3)	280(3)	2 832(3)
C(7)	5 470(3)	560(4)	2 068(3)
C(8)	5 686(3)	−1 889(4)	853(3)
C(9)	4 600(3)	−2 321(4)	462(3)
C(10)	3 361(3)	−1 400(4)	1 236(3)
N(2)	3 134(2)	−116(3)	2 412(2)
$OH_2(1)$	2 355(2)	4 014(3)	2 572(2)
O(1)	321(2)	531(3)	2 517(2)
O(2)	−438(2)	2 281(3)	5 130(2)
C(11)	−900(3)	1 199(4)	3 124(3)
C(12)	−1 353(3)	2 286(3)	4 682(3)
O(3)	−1 730(2)	1 081(3)	2 608(2)
O(4)	−2 531(2)	2 996(3)	5 370(2)
$H_2O(2)$	694(3)	−2 078(3)	36(2)
$H_2O(3)$	1 248(3)	4 621(3)	723(3)

Despite (1) and (2) both having a blue colour and molecular formula that differs by only one water molecule, they have entirely different Cu chromophore structures; (1) has a six-co-ordinate elongated rhombic octahedral $CuN_2O_2O'_2$ chromophore while (2) has a square-pyramidal CuN_2O_2O' chromophore. Neither has a rhombic coplanar $Cu(bipy)(C_2O_4)$ structure or a dimeric $[Cu(bipy)_2][Cu(C_2O_4)_2]$ structure as previously suggested,[1-3] but (1) does involve bridging oxalate ligands to give a polymeric structure as previously suggested.[3]

Electronic Properties.—The polycrystalline e.s.r. spectra of (1) and (2), Figure 3, are both clearly axial, but are distinguished by the numerical values of the high *g* factor of 2.328 and 2.286 respectively. As the Cu chromophores in both complexes are aligned, the crystal *g* factors equate with the local molecular *g* factors in both

TABLE 3

Selected bond lengths and non-bonded distances (Å) and bond angles (°), with estimated standard deviations in parentheses

$[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ (1)		$[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$ (2)	
(*a*) Bond lengths			
N(1)–Cu	2.002(4)	N(2)–Cu	1.988(4)
O(1)–Cu	1.992(3)	OH_2(1)–Cu	2.341(4)
O(3)–Cu	1.984(4)	O(2)–Cu	1.936(4)
N(2)–Cu	2.012(3)	N(1)–Cu	1.989(5)
O(2)–Cu	2.320(4)	O(1)–Cu	1.969(4)
O(4)–Cu	2.319(4)		
(*b*) Non-bonded distances			
$H_2O(1)\cdots O(3)$	2.894	$OH_2(1)\cdots H_2O(3)$	2.865
$H_2O(1)\cdots H_2O(2^{i})$	2.708	$OH_2(1)\cdots O(4^{i})$	2.805
$H_2O(2)\cdots O(1)$	2.882	$H_2O(2)\cdots O(1)$	2.820
$i = x,y,z - 1$		$H_2O(2)\cdots H_2O(3)$	2.866
		$H_2O(2)\cdots O(3^{i})$	2.761
		$H_2O(2)\cdots H_2O(3^{i})$	2.856
		$i = 1 - x,1 - y,-z$	
(*c*) Bond angles			
N(2)–Cu–N(1)	80.9(2)	N(1)–Cu–N(2)	81.5(2)
O(1)–Cu–N(2)	175.7(1)	OH_2(1)–Cu–N(1)	89.3(2)
O(2)–Cu–N(2)	103.0(2)	O(1)–Cu–OH_2(1)	91.0(2)
O(3)–Cu–N(1)	173.7(1)	O(2)–Cu–N(1)	94.7(2)
O(3)–Cu–O(1)	90.4(2)	O(2)–Cu–O(1)	84.2(2)
O(4)–Cu–N(1)	98.9(2)	O(1)–Cu–N(2)	99.6(2)
O(4)–Cu–O(1)	86.0(2)	OH_2(1)–Cu–N(2)	93.5(2)
O(4)–Cu–O(3)	77.9(2)	O(1)–Cu–N(1)	178.9(1)
O(1)–Cu–N(1)	94.8(2)	O(2)–Cu–N(2)	166.2(1)
O(2)–Cu–N(1)	94.5(2)	O(2)–Cu–OH_2(1)	99.7(2)
O(2)–Cu–O(1)	77.4(2)		
O(3)–Cu–N(2)	93.9(2)		
O(3)–Cu–O(2)	90.1(2)		
O(4)–Cu–N(2)	94.5(2)		
O(4)–Cu–O(2)	159.5(1)		

TABLE 4

Selected mean-plane data

$[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ (1)		r.m.s.d. (Å)
Plane 1:	O(1),O(2),O(1′),O(2′),C(12),C(12′)	0.0011
Plane 2:	N(1),C(1)—C(5)	0.0025
Plane 3:	N(2),C(6)—C(10)	0.0033
Plane 4:	N(1),N(2),C(1)—C(10)	0.0168
Plane 5:	N(1),N(2),O(1),O(3)	0.0283

Dihedral angles (°) between planes (2)—(3) 1.9(1); (1)—(4) 98.7(1)

$[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$ (2)		
Plane 1:	O(1),O(2),C(11),C(12),O(3),O(4)	0.0103
Plane 2:	N(1),C(1)—C(5)	0.0038
Plane 3:	N(2),C(6)—C(10)	0.0099
Plane 4:	N(1),N(2),C(1)—C(10)	0.0542
Plane 5:	N(1),N(2),O(1),O(2)	0.1107

Dihedral angles (°) between planes (2)—(3) 6.3; (1)—(4) 13.5.

TABLE 5

Tentative assignment of the electronic spectrum (cm^{-1}) of $[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ (1) by analogy with that of $[Cu(bipy)(hfacac)_2]$ (3)

Transition	Energy (3)	Energy (1)
$d_{z^2} \longrightarrow d_{xy}$	9 400	9 300
$d_{yz} \longrightarrow d_{xy}$	13 000	14 500
$d_{xz} \longrightarrow d_{xy}$	14 000	
$d_{x^2-y^2} \longrightarrow d_{xy}$	14 600	

complexes [7] and indicate a $d_{x^2-y^2}$ (or d_{xy}) ground state in both. The observation of two bands in the electronic spectrum of (1) is consistent with the restricted elongated tetragonal distortion [15] of (1), $T = 0.863$, and their energies are comparable to those of 9 500 and 13 700 cm^{-1} observed [16] for (3), which has $T = 0.864$. This suggests that the electronic spectrum of (1) may be assigned by analogy [16] to that of (3), see Table 5. The single broad peak for (2), Figure 3(*b*), is consistent [9] with a square-pyramidal structure, but as there is no evidence for shoulders in the spectrum, it is not possible to make a definite assignment from it. The unsymmetrical bidentate bridging role of the oxalate anion involving one short and one long Cu–O distance suggests a possible antiferromagnetic (or ferromagnetic) pathway for coupling of the copper(II) spins; these magnetic properties will be described elsewhere.

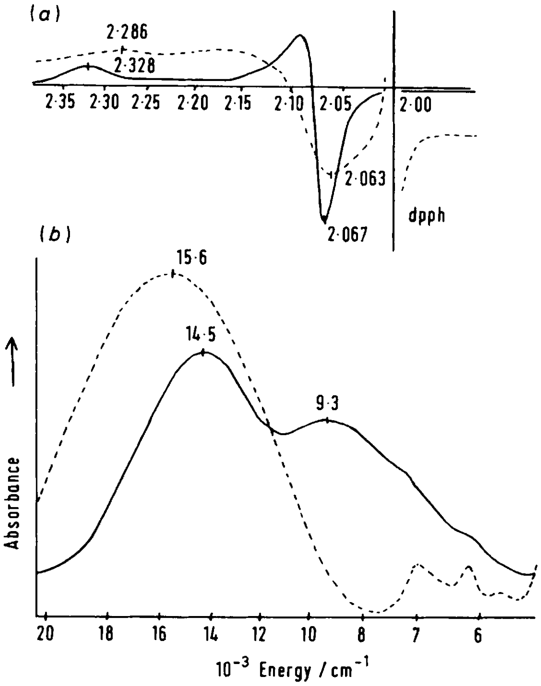

FIGURE 3 (*a*) Polycrystalline e.s.r. spectra (dpph = diphenylpicrylhydrazyl) and (*b*) electronic reflectance spectra of $[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ (——) and $[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$ (- - -)

The electronic reflectance spectra of (1) and (2) are clearly different (a difference that is not so apparent in the e.s.r. spectra), which is associated with the clear difference in the local molecular structure of (1) and (2), that is best revealed in the low-energy shoulder of (1). This emphasises not only the advantage of the use [17] of electronic reflectance spectra as an ' electronic criterion of stereochemistry ' of these comparable complexes of the copper(II) ion (over the corresponding use of the e.s.r. spectra), but equally the importance of recording the electronic spectra of copper(II) complexes, not just in the visible region, but down into the near-i.r. region (20 000—5 000 cm^{-1}). From a comparison of the properties of (1) and (2) with those reported for complexes (1)—(4) of ref. 3, structure (1) above corresponds with complex (3) in ref. 3.

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