Properties and Structural † Characterization of Copper(II) Mixed Complexes with 2,2':6',2''-Terpyridyl and Iminodiacetate or Pyridine-2,6-dicarboxylate

Nevenka Bresciani-Pahor and Giorgio Nardin
Istituto di Chimica, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy
Raffaele P. Bonomo * and Enrico Rizzarelli
Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, V. le A. Doria, 95125 Catania, Italy

The crystal structure and a visible optical and e.s.r. spectroscopic study of the two mixed complexes of copper(II), [Cu(terpy)(pydca)] (1) and [Cu(terpy)(ida)] (2) (pydca = pyridine-2,6-dicarboxylate, ida = iminodiacetate, and terpy = 2,2' : 6',2'' terpyridyl) are reported. Crystals of (1) are triclinic, space group $P\bar{1}$, with a = 10.964(7), b = 13.209(8), c = 9.724(6) Å, α = 98.3(1), β = 112.9(1), γ = 102.2(1)°, and R = 0.041. Crystals of (2) are monoclinic, space group $P2_1/n$, with a = 23.41(1), b = 10.538(7), c = 8.372(6) Å, β = 91.3(1)°, and R = 0.044. Complex (1) consists of [Cu(terpy)(pydca)] units linked together by water molecules. The copper atom is co-ordinated by terpy and pydca units which act as tridentate ligands in a distorted octahedral environment. The e.s.r. and visible spectra indicate that the solid-state stereochemistry is preserved in solution. In crystals of (2) Cu(terpy) units are bridged by ida units which act as unidentate ligands. The polymeric configuration in (2) is similar to that found for the analogous [Cu(terpy)(tda)] (tda = thiodiacetate). The copper atom is found to be in a distorted trigonal-bipyramidal geometry. It is significant that this stereochemistry is not preserved in solution. In fact the frozen solution e.s.r. (130 K) and visible absorption spectra of (2) agree with a six-co-ordinated environment about the copper(II) ion.

Recently we studied the structural features of two ternary complexes containing copper(II) ions, 2,2'-bipyridyl (bipy) and pyridine-2,6-dicarboxylate (pydca) or iminodiacetate (ida).[1] Despite the similarity of the ligand donor atoms, these ternary complexes displayed two different stereochemistries. In particular, the co-ordination polyhedron of [Cu(bipy)(ida)]·6H_2O was described as a distorted square pyramid, while [Cu_2(bipy)$_2$(pydca)$_2$]·4H_2O consisted of binuclear units formed by [Cu(bipy)$_2$]$^{2+}$ and [Cu(pydca)$_2$]$^{2-}$ linked together through the oxygen of carboxylate groups. A rather anomalous dimer was found to exist, with [Cu(bipy)$_2$]$^{2+}$ having a trigonal-bipyramidal geometry and [Cu(pydca)$_2$]$^{2+}$ being in a distorted octahedral environment. Differences were also present in solution, since visible and e.s.r. spectra of these compounds revealed different arrangements of the above ligands about the copper(II) ion.[2] The geometry of [Cu(bipy)(ida)] was preserved on going from solid state to solution, while [Cu(bipy)(pydca)] was found to be a monomer species having a pseudo-octahedral geometry.

A potentiometric study in this laboratory on the mixed complex formation among copper(II) ions, 2,2' : 6',2''-terpyridyl (terpy) and pydca or ida dianions has been reported.[3] [Cu(terpy)(pydca)] species formed easily, reaching 95% formation at pH 5, while the analogous complex with ida showed a low degree of formation (*ca.* 45% at pH 7). Moreover, both systems showed the presence of a certain amount of protonated mixed species. We thought to extend the structural investigation to the mixed complexes [Cu(terpy)(pydca)] and [Cu(terpy)(ida)] in order to see whether by imposing a more rigid situation, due to the planar co-ordinating mode of the terpy ligand, those differences are repeated. We also report a visible and e.s.r. spectroscopic study of these mixed complexes in solution. This investigation has been carried out with the specific purpose of finding evidence for particular differences in the co-ordination properties of these ligands in solution.

Experimental

Chemicals.—2,2' : 6',2''-Terpyridyl (Merck) was recrystallized from a water–methanol mixture. Iminodiacetic (BDH) and pyridine-2,6-dicarboxylic acid (Fluka) were recrystallized from water. The complex [Cu(terpy)(pydca)] was prepared by mixing together the reagents in stoicheiometric ratios, adding sodium hydroxide to obtain the dianion, and adding methanol to dissolve terpy. The solution obtained this way was slowly concentrated and n-butanol added to induce precipitation. After a few days, small light green crystals could be collected. [Cu(terpy)(ida)] was prepared in a slightly different way. The reagents in stoicheiometric ratios were dissolved in water and the solution neutralized with sodium hydroxide. Then it was concentrated to a small volume and acetone added, thereby avoiding precipitation. After two days, blue-green crystals separated from the solution. Analytical data for both complexes showed that water and in the latter case also a molecule of acetone were present in the molecular formulae of these complexes.

Spectroscopic Measurements.—Powder and solution spectra were recorded at 130 K in water–methanol (1 : 1) using a Varian E 12 *X*-band spectrometer equipped with a standard low-temperature control unit. A simulation procedure, based essentially on the computer program of Pilbrow and Wienfield,[4] was employed to obtain the spin-Hamiltonian perpendicular parameters of the frozen solution spectra. In all the other cases g values were evaluated directly from the experimental spectra. Diphenylpicrylhydrazyl (dpph) free radical was used as a g marker.

Visible reflectance and aqueous-methanolic solution spectra were obtained with a Perkin-Elmer 330 double-beam spectrophotometer equipped with a 60-mm diameter integrating sphere, at room temperature. Experiments were carried out

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† *Supplementary data available* (No. SUP 56034, 22 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

starting both from the reagents in stoicheiometric ratios and from the powders dissolved in the solvent mixtures.

Crystal Data for [Cu(terpy)(pydca)]·6H$_2$O (1).—C$_{22}$H$_{26}$CuN$_4$O$_{10}$, $M = 569.9$, triclinic, space group $P\bar{1}$ (from the final refinement), $a = 10.964(7)$, $b = 13.209(8)$, $c = 9.724(6)$ Å, $\alpha = 98.3(1)$, $\beta = 112.9(1)$, $\gamma = 102.2(1)°$, $U = 1\,227.5$ Å^3, $D_m = 1.55$, $Z = 2$, $F(000) = 578$, $D_c = 1.54$ g cm^{-3}, μ(Mo-K_α) = 9.93 cm^{-1}, $\lambda = 0.7107$ Å.

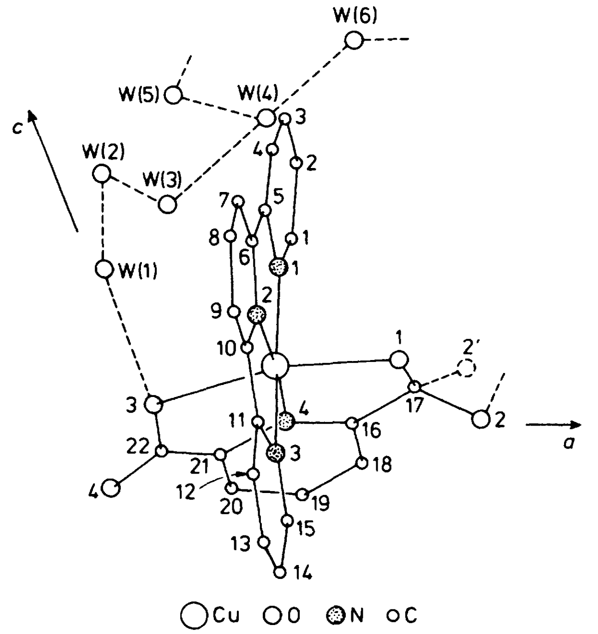

Figure 1. View of (1) along the b axis with the atom numbering scheme

Crystal Data for [Cu(terpy)(ida)]·Me$_2$CO·H$_2$O (2).—C$_{22}$H$_{24}$CuN$_4$O$_5$, $M = 504.1$, monoclinic, space group $P2_1/n$, $a = 23.41(1)$, $b = 10.538(7)$, $c = 8.372(6)$ Å, $\beta = 91.3(1)°$, $U = 2\,064.7$ Å^3, $D_m = 1.64$, $Z = 4$, $F(000) = 1\,044$, $D_c = 1.62$ g cm^{-3}, μ(Mo-K_α) = 11.4 cm^{-1}, $\lambda = 0.7107$ Å.

Structure Determination and Refinement.—Cell parameters for both (1) and (2) were determined from Weissenberg and precession photographs and refined with an on-line automated single-crystal Siemens diffractometer using Mo-K_α radiation. Intensities for both structures were collected using the $\theta-2\theta$ scan technique in the range $3.5 \leqslant \theta \leqslant 28°$. A total of 3 706, for (1), and 1 714 independent reflections, for (2), with $I \geqslant 3\sigma(I)$ were used and corrected for Lorentz and polarization effects. No correction for absorption was applied, since the crystals were approximately parallelepipeds with nearly equal edges [0.5, (1), and 0.3 mm, (2)].

Both structures were solved by conventional Patterson and Fourier methods. After the anisotropic refinement, a three-dimensional difference-Fourier synthesis was calculated to locate the H atoms. Calculated positions of all these occurred in positive regions of the electron-density map. The final anisotropic block-diagonal matrix least-squares refinement for all atoms, excluding the molecules of crystallization for (2) (H$_2$O and acetone) which were treated isotropically and including the fixed contribution of hydrogen atoms ($B = 5$ Å^2), gave $R = 0.041$ for (1) and $R = 0.044$ for (2). The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where $A = 18.0$ and $B = 0.013$ for (1) and $A = 30.0$ and $B = 0.009$ for (2) were chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta)/\lambda$.

The atom-numbering schemes for (1) and (2) are shown in Figures 1 and 2 respectively. The atomic co-ordinates for the

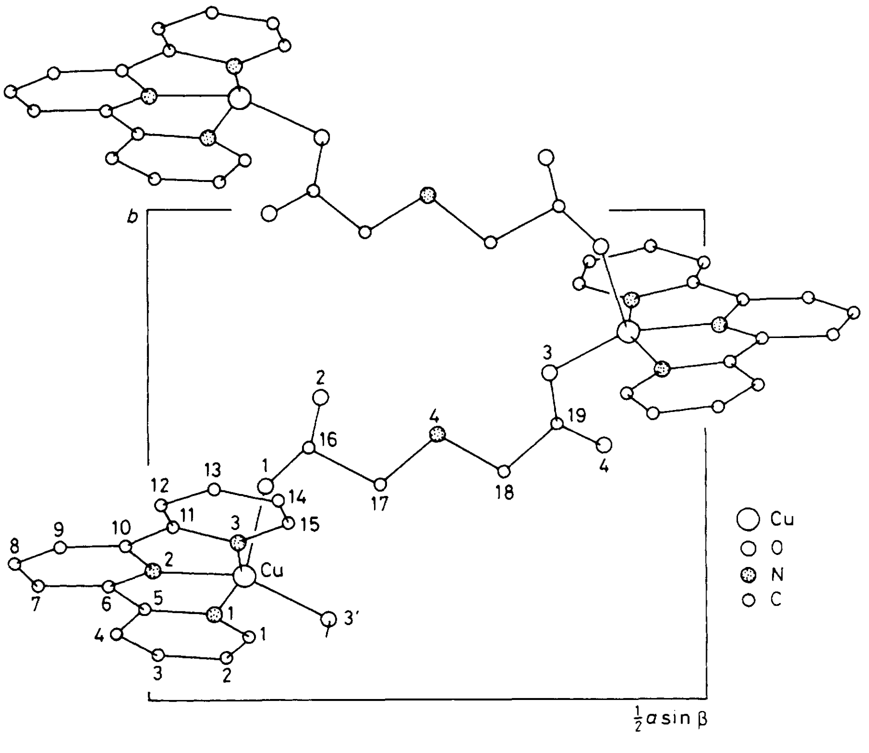

Figure 2. View of (2) along the c axis with the atom numbering scheme. The molecules of crystallization have been omitted for clarity

Table 1. Fractional atomic co-ordinates ($\times 10^4$) of the non-hydrogen atoms, with estimated standard deviations in parentheses, for (1)

Atom	x	y	z	Atom	x	y	z
Cu	2 468(1)	3 364(0)	1 269(1)	C(4)	3 938(5)	4 041(4)	6 126(5)
O(1)	4 644(3)	3 492(3)	1 379(4)	C(5)	3 369(4)	4 005(4)	4 565(5)
O(2)	5 602(7)	2 584(6)	166(9)	C(6)	2 938(4)	4 898(3)	3 936(5)
O(2′)	5 834(7)	2 268(6)	1 295(10)	C(7)	2 947(5)	5 853(4)	4 761(5)
O(3)	86(3)	2 353(2)	464(4)	C(8)	2 515(5)	6 601(4)	3 968(6)
O(4)	−1 400(3)	983(3)	−1 551(4)	C(9)	2 081(5)	6 395(4)	2 379(6)
W(1)	98(4)	2 690(3)	3 423(4)	C(10)	2 109(4)	5 435(3)	1 619(5)
W(2)	845(4)	1 415(3)	5 467(4)	C(11)	1 735(4)	5 086(3)	−53(5)
W(3)	1 757(4)	−390(3)	4 603(4)	C(12)	1 324(5)	5 700(4)	−1 088(6)
W(4)	2 824(8)	−2 329(6)	7 165(9)	C(13)	1 021(6)	5 288(4)	−2 632(6)
W(5)	3 887(4)	−1 178(4)	1 617(6)	C(14)	1 112(5)	4 277(4)	−3 088(5)
W(6)	4 136(5)	−787(4)	6 588(6)	C(15)	1 530(5)	3 707(4)	−1 984(5)
N(1)	3 170(4)	3 143(3)	3 468(4)	C(16)	3 351(5)	1 718(4)	−43(6)
N(2)	2 518(3)	4 713(3)	2 407(4)	C(17)	4 689(6)	2 627(5)	751(9)
N(3)	1 835(4)	4 091(3)	−488(4)	C(18)	3 262(5)	724(4)	−804(7)
N(4)	2 235(3)	1 942(3)	42(4)	C(19)	1 994(5)	−60(4)	−1 525(6)
C(1)	3 533(5)	2 297(4)	3 937(6)	C(20)	832(5)	186(3)	−1 488(5)
C(2)	4 096(6)	2 273(5)	5 476(7)	C(21)	1 002(4)	1 201(3)	−682(4)
C(3)	4 302(5)	3 190(5)	6 573(6)	C(22)	−216(4)	1 546(3)	−584(5)

Table 2. Fractional atomic co-ordinates ($\times 10^4$) of the non-hydrogen atoms, with estimated standard deviations in parentheses, for (2)

Atom	x	y	z	Atom	x	y	z
Cu	789(0)	2 547(1)	2 803(1)	C(9)	−826(3)	3 114(6)	4 689(10)
N(1)	527(2)	1 839(6)	675(7)	C(10)	−235(3)	3 108(7)	4 421(9)
N(2)	−32(2)	2 717(5)	3 018(7)	C(11)	215(3)	3 479(7)	5 587(9)
N(3)	754(2)	3 247(6)	5 062(7)	C(12)	111(4)	4 032(7)	7 064(9)
N(4)	2 525(2)	5 280(6)	1 718(8)	C(13)	585(4)	4 339(8)	8 051(9)
O(1)	1 026(2)	4 389(5)	1 851(7)	C(14)	1 130(4)	4 098(8)	7 533(10)
O(2)	1 475(3)	6 238(6)	1 977(9)	C(15)	1 201(4)	3 545(8)	6 041(10)
O(3)	3 479(2)	6 635(5)	2 049(6)	C(16)	1 464(3)	5 076(8)	1 849(9)
O(4)	4 030(2)	5 234(6)	796(7)	C(17)	2 031(3)	4 357(8)	1 675(10)
C(1)	864(3)	1 393(7)	−486(9)	C(18)	3 087(3)	4 662(8)	1 199(9)
C(2)	645(4)	935(7)	−1 942(9)	C(19)	3 569(3)	5 579(8)	1 355(8)
C(3)	59(4)	954(8)	−2 204(9)	C(20)	2 292(5)	226(11)	9 034(12)
C(4)	−299(3)	1 432(8)	−1 016(10)	C(21)	2 334(5)	−205(12)	7 702(16)
C(5)	−53(3)	1 871(7)	413(9)	C(22)	2 405(5)	1 226(12)	9 414(15)
C(6)	−377(3)	2 341(8)	1 795(8)	O(5)	2 119(5)	−545(10)	10 031(12)
C(7)	−971(3)	2 343(8)	1 939(10)	W(1)	2 576(4)	1 966(9)	5 792(10)
C(8)	−1 185(3)	2 742(8)	3 412(11)				

non-hydrogen atoms are listed in Tables 1 and 2 respectively. A list of interatomic distances and angles of interest is reported in Table 3. Atomic scattering factors were those of Moore.[5]

Results and Discussion

Spectroscopic Results.—In the case of [Cu(terpy)(pydca)] the frozen solution e.s.r. spectra obtained both from the reagents in stoicheiometric ratios or from the microcrystalline powder dissolved in 1 : 3 methanol–water are identical. The spin-Hamiltonian parameters deduced for this complex are reported in Table 4 together with those obtained in a previous study for the analogous complex with bipy.[2] The difference between these two sets of parameters clearly indicates the co-ordination of the third nitrogen of terpy to the copper(II) ion. The value of A_z for [Cu(terpy)(pydca)] does not undergo the expected enhancement with respect to that for [Cu(bipy)(pydca)] and this can be explained by taking into account a more distorted polyhedron of co-ordination forms in the case of the former complex.

In the case of [Cu(terpy)(ida)] the frozen solution e.s.r. spectrum obtained from the reagents showed the presence of two absorbing species. A careful analysis of their parallel and perpendicular peaks revealed they were $[Cu(ida)_2]^{2-}$ (ref. 2) and $[Cu(terpy)_2]^{2+}$.[6] In methanol–water it is probable that a disproportionation reaction (i) takes place at low temperature. A spectrum run in a solution where acid was added up

$$2[Cu(terpy)(ida)] \rightleftharpoons [Cu(ida)_2]^{2-} + [Cu(terpy)_2]^{2+} \qquad (i)$$

to pH 2 showed the presence of a single species. Upon running a spectrum of the supernatant acetone–water solution used for the preparation of the solid complex, it was possible to observe a spectrum due to the mixed species. All these spectra are reported in Figures 3 and 4. The spectrum of [Cu(terpy)(ida)] at pH 2 refers to a species where the ida dianion is probably protonated or not co-ordinated [Figure 3(*a*)], while the complicated pattern obtained by the overlap of the two $[Cu(ida)_2]^{2-}$ and $[Cu(terpy)_2]^{2+}$ spectra can be seen in Figure 3(*b*). In Table 4 the spin-Hamiltonian parameters concerning these spectra are reported together with those of the analogous complex of bipy. These differences cannot be used as a diagnostic aid since the complex [Cu(bipy)(ida)] was found to be five-co-ordinate, having a square-pyramidal geometry.[1,2]

Comparing the magnetic parameters of the mixed species (1) and (2), the only difference is the A_z value, which is larger for (2), due to the stronger donor ability of the amine nitrogen of

Table 3. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) [Cu(terpy)(pydca)]·6H_2O (1)

Cu–O(1)	2.314(4)	Cu–N(2)	1.935(4)	C(22)–O(3)	1.250(5)	C(17)–O(1)	1.236(8)
Cu–O(3)	2.419(3)	Cu–N(3)	2.038(4)	C(22)–O(4)	1.250(4)	C(17)–O(2)	1.34(1)
Cu–N(1)	2.060(4)	Cu–N(4)	1.983(3)	C(22)–C(21)	1.530(7)	C(17)–O(2′)	1.37(1)
						C(17)–C(16)	1.515(6)

O(1)–Cu–O(3)	151.0(3)	O(3)–Cu–N(2)	100.3(1)	N(2)–Cu–N(3)	80.5(2)	O(1)–C(17)–O(2)	121.1(6)
O(1)–Cu–N(1)	89.1(2)	O(3)–Cu–N(3)	89.6(1)	N(2)–Cu–N(4)	174.9(2)	O(1)–C(17)–C(16)	117.5(6)
O(1)–Cu–N(2)	108.7(1)	O(3)–Cu–N(4)	74.7(1)	N(3)–Cu–N(4)	98.5(2)	O(2)–C(17)–C(16)	114.9(6
O(1)–Cu–N(3)	96.1(2)	N(1)–Cu–N(2)	79.6(2)	O(3)–C(22)–O(4)	127.3(5)	O(2)–C(17)–O(2′)	123.3(3)
O(1)–Cu–N(4)	76.4(1)	N(1)–Cu–N(3)	160.0(2)	O(3)–C(22)–C(21)	116.3(2)	O(2′)–C(17)–C(16)	112.3(6)
O(3)–Cu–N(1)	95.2(1)	N(1)–Cu–N(4)	101.5(2)	O(4)–C(22)–C(21)	116.5(4)		

(*b*) [Cu(terpy)(ida)]·Me_2CO·H_2O (2)

Cu–O(1)	2.175(6)	Cu–N(3)	2.034(6)	O(3)–C(19)	1.274(9)	N(4)–C(18)	1.500(9)
Cu–O(3′)	1.966(5)	O(1)–C(16)	1.253(9)	O(4)–C(19)	1.241(9)	C(16)–C(17)	1.54(1)
Cu–N(1)	2.015(6)	O(2)–C(16)	1.23(1)	N(4)–C(17)	1.51(1)	C(18)–C(19)	1.52(1)
Cu–N(2)	1.943(5)						

O(1)–Cu–O(3′)	103.3(2)	O(3′)–Cu–N(2)	154.4(2)	O(1)–C(16)–O(2)	126.3(7)	N(4)–C(18)–C(19)	110.9(6)
O(1)–Cu–N(1)	94.7(2)	O(3′)–Cu–N(3)	99.9(2)	O(1)–C(16)–C(17)	115.0(7)	O(3)–C(19)–O(4)	125.6(7)
O(1)–Cu–N(2)	102.3(2)	N(1)–Cu–N(2)	80.4(2)	O(2)–C(16)–C(17)	118.8(7)	O(3)–C(19)–C(18)	117.3(6)
O(1)–Cu–N(3)	91.9(2)	N(1)–Cu–N(3)	159.9(2)	N(4)–C(17)–C(16)	110.1(6)	O(4)–C(19)–C(19)	117.2(7)
O(3′)–Cu–N(1)	97.0(2)	N(2)–Cu–N(3)	79.6(2)	C(17)–N(4)–C(18)	111.5(6)		

Table 4. Visible absorption and e.s.r.[a] spectroscopic data for the mixed complexes [Cu(terpy)(pydca)] and [Cu(terpy)(ida)] in solution and in the solid state

Complex	g_z	g_y	g_x	g_{iso}	10^4A_z	10^4A_y	10^4A_x	10^4A^{N}	$10^4A_{\perp}^{N}$	$10^3\nu_{max}/cm^{-1}$ (ε)[b]	Ref.
[Cu(terpy)(pydca)]	2.255(1)	2.070(5)	2.055(5)	2.126(5)	168(1)	8(3)	5(3)	15(2)	—	15.3 (69), 10.3 (37)	*c*
[Cu(bipy)(pydca)]	2.282(1)	2.075(5)	2.055(5)	2.137(5)	165(1)	3(2)	5(2)	14(2)	—	13.9 (41), 10.1 (25)	2
[Cu(terpy)(ida)] [d]	2.286(2)	2.075(5)		2.145(5)	172(2)	10(3)		—	—	—	*c*
[Cu(terpy)(ida)] [e]	2.251(1)	2.065(5)	2.052(5)	2.122(5)	176(1)	8(3)	5(3)	—	—	14.6 (69)	*c*
[Cu(bipy)(ida)]	2.256(1)	2.068(5)	2.040(5)	2.121(5)	179(1)	10(2)	7(2)	—	—	15.1 (46), 12.3 (sh)	2
	g_1	g_2	g_3	$g_{iso.}$							
[Cu(terpy)(pydca)] [f]	2.251(5)	2.070(5)		2.130(5)						15.1, 9.3	*c*
[Cu(terpy)(ida)] [f]				2.121(5)						14.0, 10.5	*c*

[a] The values in parentheses are the presumed errors on the last figure. All hyperfine coupling constants are in cm^{-1}. [b] The values in parentheses are the molar absorption coefficients (dm^3 mol^{-1} cm^{-1}). [c] This work. [d] In a methanol–water (1 : 1) solution of pH *ca.* 2 before the addition of methanol. [e] In an acetone–water (saturated) solution of pH *ca.* 7 before the addition of acetone. [f] Solid state.

ida with respect to the pyridine N of pydca. These *g* and *A* values are characteristic of copper(II) ions in a $d_{x^2-y^2}$ or d_{xy} ground state[7] in pseudo-octahedral geometries. In particular, they agree quite well with the expected values for CuN_4 or CuN_4O_2 chromophores.[8] The low rhombic anisotropy found for both complexes by the simulation of the perpendicular parts of their spectra is probably over-estimated. On the other hand, it reflects that these complexes possess rather distorted polyhedra even in solution.

These data seem to suggest that both complexes are six-co-ordinate. A distorted octahedron should be the preferential stereochemistry in solution. In fact, owing to the planarity of the terpy ligand, which can occupy three equatorial sites or two apical and one equatorial positions, both ida and pydca should approach the copper(II) ion co-ordination sphere lying in a plane approximately perpendicular to that of the terpy molecule. The spectrum in Figure 4 also shows the $\frac{3}{2}$ line on an enlarged scale (lower trace) in order to evaluate a possible nitrogen superhyperfine pattern. Unfortunately the quality of this spectrum is not good enough to allow the assignment to a specific number of interacting nitrogen atoms to be made.

The powder e.s.r. spectrum of the undiluted compound [Cu(terpy)(pydca)] showed two peaks. The spectrum is clearly axial with the highest *g* value very similar to the g_z of the same compound in solution. An isotropic e.s.r. spectrum was obtained in the case of the solid [Cu(terpy)(ida)] complex. Because of probable misalignment, these spectra are uninformative and no conclusions can be deduced from them.[7]

The solution visible and powder reflectance optical spectra for both complexes are reported in Figure 5. A clear similarity can be seen between the solid and solution spectra of [Cu(terpy)(pydca)]. In fact, both spectra present two bands the maxima of which fall approximately at the same frequencies. These spectra are consistent with an octahedral geometry undergoing a tetragonal elongation.[9] It is a clear indication that apart from packing considerations the solid stereochemistry is substantially preserved on going from the solid state to solution, as already found by Murtha and Walton.[10]

In the case of [Cu(terpy)(ida)] a quite symmetrical band was found in solution, while a maximum centred at a slightly different frequency with some shoulder at lower frequency was seen in the spectrum of the solid compound. The spectra are

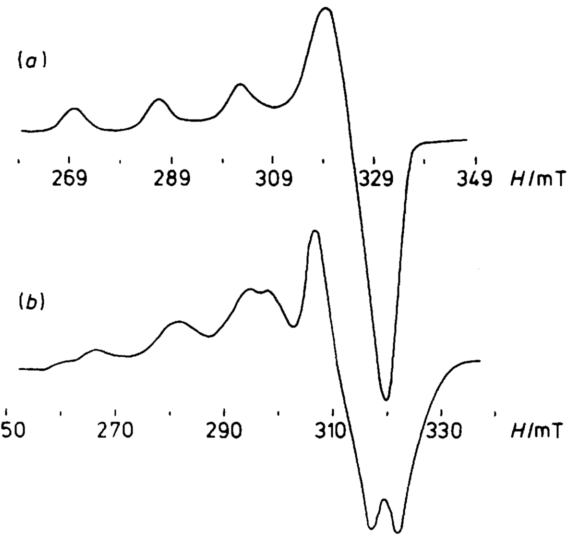

Figure 3. Frozen solution e.s.r. spectra (130 K) of the copper(II)–terpy–ida system in water–methanol (1 : 1): (*a*) pH 2 and (*b*) pH 5, before the addition of methanol

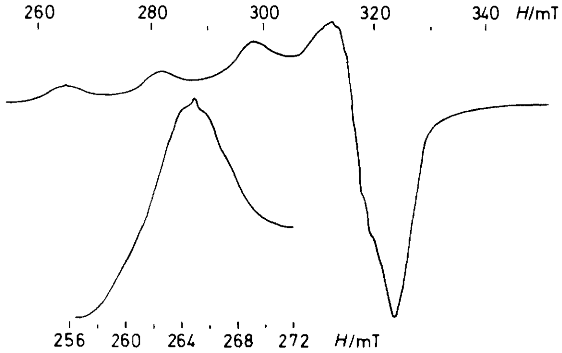

Figure 4. Frozen solution e.s.r. spectrum (130 K) of the saturated water–acetone solution containing (2)

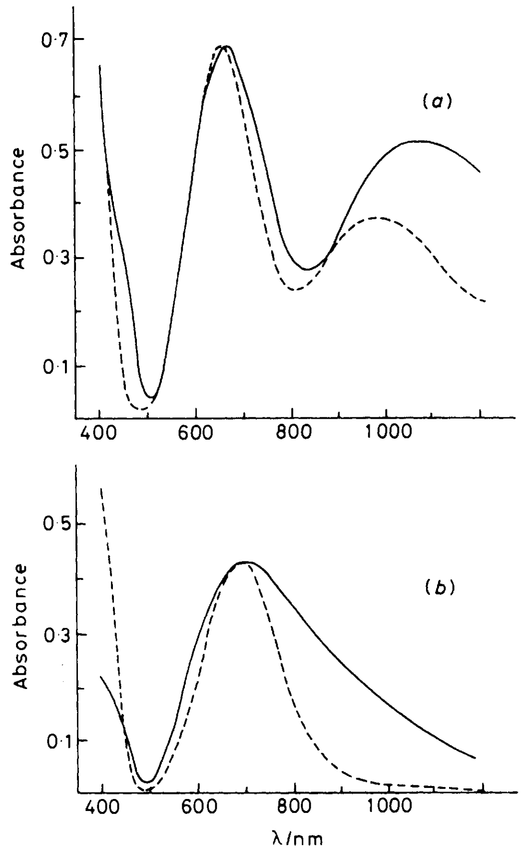

Figure 5. Visible solution (——) and reflectance (— — —) spectra of (*a*) [Cu(terpy)(pydca)] (5 mmol $\mathrm{dm^{-3}}$) and (*b*) [Cu(terpy)(ida)] (3.08 mmol $\mathrm{dm^{-3}}$). Reflectance spectrum absorption curves were normalized to the solution spectrum heights

clearly different and this could be associated with dissimilar environments about the copper(II) ion. It is difficult to draw definite conclusions about the particular stereochemistry adopted by the copper(II) ion in this mixed complex with terpy and ida in the solid state on the basis of its visible and powder e.s.r. spectra. The *X*-ray structure was therefore determined (below) to clarify this.

X-Ray Structure Determination.—Crystals of (1) consist of [Cu(terpy)(pydca)] units linked by water molecules which stabilize the crystal by forming a net of hydrogen bonds (Figure 1) as already observed in other similar complexes.[1,11,12] The copper atom is co-ordinated by terpy and pydca units which act as tridentate ligands in a distorted octahedral environment. The equatorial positions are occupied by the nitrogen donors [Cu–N(1) 2.060(4), Cu–N(2) 1.935(4), Cu–N(3) 2.038(4), Cu–N(4) 1.983(3) Å], while the axial sites are occupied by two oxygen atoms of the carboxylate groups of the pydca ligand [Cu–O(1) 2.314(4), Cu–O(3) 2.419(3) Å]. This considerable difference of 0.1 Å is probably due to the hydrogen bond between W(1) (W = water) and O(3) [O(3)–W(1) 2.841(6) Å]. The nitrogens of the basal plane are coplanar within ±0.5 Å and the copper atom is displaced only 0.04 Å from their mean plane. The whole terpy ligand is planar within ±0.1 Å and makes dihedral angles of 97.1 and 101.6° with the mean planes of the pydca ligand including O(2) and O(2′) respectively. A statistical location of the oxygen atom O(2′) was hypothesized.

The carboxylate groups in the pydca ligand are twisted with respect to the pyridine ring, the torsion angle around C(21)–C(22) being 18.4°, and around C(16)–C(17), 16.9° [mean value for O(2) and O(2′)]. On the contrary, in $[\mathrm{Cu_2(bipy)_2(pydca)_2}]\cdot 4\mathrm{H_2O}$,[1] the whole pydca ligand is nearly planar. In the present case the conformation of the pydca ligand seems to be imposed by the mutual orientation of the pyridine ring and terpy ligand, with a dihedral angle 99.0°. Consequently the torsion of the carboxylate groups favours a more regular co-ordination around the copper atom. It is interesting that the sum of the angles around C(22) is 360.1° and also the C–O distances [C(22)–O(4) 1.250(4), C(22)–O(3) 1.250(5) Å] are indicative of a complete delocalization over the carboxylate group. This situation is not observed in the second carboxylate group where two distinct maxima are present in the Fourier map and interpreted as oxygen atoms, each with occupancy of 0.5, bonded to the C(17) atom. Analogous splitting of the other atoms involved in this carboxylate group is not observed. The relevant bond distances [C(17)–O(2) 1.34(1), C(17)–O(2′) 1.37(1) Å] are significantly longer than C(17)–O(1) [1.236(8) Å]. The sum of the angles around C(17) is 353.5° if we consider O(2) and 353.1° for O(2′). The poor planarity around C(17) seems, however, to be a consequence of the disorder of the carboxylate group which cannot be resolved by Fourier maps.

In crystals of (2) Cu(terpy) units, nearly perpendicular to the [010] direction, are bridged by iminodiacetate units which act as unidentate ligands. The polymeric chains are developed in the cell in a zig-zag manner around the screw axes parallel to the [010] direction (see Figure 2). Acetone and water molecules occupy the empty spaces between the polymeric chains. The configuration in (2) is similar to that found for the analogous [Cu(terpy)(tda)] (tda = thiodiacetate).[11] Nevertheless, in the latter the chains run in a linear and not in a zig-zag manner. The co-ordination polyhedron around the copper can be described as a distorted trigonal bipyramid with the axial sites occupied by two lateral nitrogens of the terpy molecule, while the equatorial sites are occupied by the central terpy nitrogen and by the oxygen atoms O(1) and O(3′) of the ida as depicted in Figure 2. In this complex, the particular behaviour of the ida ligand as found in the complex [Cu(bipy)-(ida)] is foreclosed in the presence of the terpy ligand which uses three coplanar sites in the copper co-ordination. Therefore in (2) a planar geometry should be expected for ida as previously found in the analogous [Cu(terpy)(oda)] complex (oda = oxydiacetate).[13] As already indicated [1,12-14] a planar conformation of the tridentate dicarboxylate dianion requires a widening of the angles around its central donor atom. The nitrogen in the ida ligand seems to be able to meet these steric conditions as confirmed by the planar conformation of the similar bpa ligand [bis(3-aminoproply)amine] found in $[\mathrm{Cu(bipy)(bpa)}][\mathrm{No_3}]_2$.[14] Consequently for the complex [Cu(terpy)(ida)] the observed behaviour of ida as a bidentate ligand cannot be explained with the same geometrical and electronic arguments invoked for the analogous [Cu(terpy)-(tda)].[11] Therefore other geometric factors have to be important in [Cu(terpy)(ida)], namely the steric interaction between terpy and the imino-group of the ida ligand. In fact, in $[\mathrm{Cu(terpy)(oda)}]\cdot 2\mathrm{H_2O}$ [13] with the oda ligand in a planar arrangement, the ether oxygen is 2.8 Å from the nearest hydrogen of the terpy ligand. If an NH group substitutes the ether oxygen, the expected H···H contact should be approximately 1.8 Å, well below the normal van der Waals distance. Since it is difficult to envisage a distortion to alleviate such a contact, a polymeric arrangement is favoured in the solid state.

Conclusions

The diffractomeric studies on single crystals of the mixed complexes [Cu(terpy)(pydca)] and [Cu(terpy)(ida)] confirm the interpretation of their e.s.r. and visible optical results. Two different geometries around the copper atom have been observed in the solid state according to the different mutual interactions between terpy and the two dianionic ligands. It is very important to point out that differences found in the solid state are not present in solution. The two mixed species showed a quite similar pattern in their frozen e.s.r. and visible absorption spectra. So, while in the solid state the ida dianion acts as unidentate ligand, the nitrogen atom not being co-ordinated, the e.s.r. spectrum of [Cu(terpy)(ida)] in frozen solution clearly indicated that the ida nitrogen is involved in co-ordination to copper(II). This means that, while in solution the only discriminating factor in determining the geometry of the two complexes is the planarity of the terpy molecule which prevents the *cis* co-ordination for the ida ligand and imposes a nearly planar co-ordination for both ida and pydca ligands, in the solid state further factors contribute in building up the molecular structures of these compounds. In the case of [Cu(terpy)(ida)] the steric interaction between the terpy ligand and the imino-group of the ida dianion appears to be the factor which precludes a planar co-ordination of the latter in the solid state. A greater flexibility of the ligands in solution, which alleviates this steric interaction, could explain the different behaviour of the ida ligand in the solid state and in solution.

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