Reactivity of Co-ordination Compounds in the Solid State. Part 1. Mixed-ligand Complexes of Oxalate and 2,2′-Bipyridyl with Copper(II), their Preparation, Interconversion, and Novel Solid-state Reactivity

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Mixed-ligand complexes of oxalate and 2,2′-bipyridyl with copper(II) have been prepared and characterized. Polymorphism has unequivocally been shown to occur. One form of the complex is correctly described as a mixed chelate; another modification is possibly a double salt or more likely a polymeric structure involving bridging oxalates. The complexes have been characterized by their electronic, e.s.r., and i.r. spectra and *X*-ray diffraction patterns. Unusually, interconversion of the various forms occurs in the solid state. The solid-state reactivity of these complexes and their diverse nature has not been appreciated in earlier studies.

THE importance of mixed-ligand complexes in biological systems has led to their study becoming a major area of contemporary research.[1,2] In solution, copper(II) forms stable complexes of approximately square-planar geometry; with two different bidentate chelating ligands, ternary complexes (the simplest mixed-ligand complexes) are readily formed and have been extensively studied. Most work on mixed-ligand systems has been carried out with copper(II) complexes, with an emphasis on stability-constant determinations.[1]

The thermodynamic stability of mixed-ligand complexes in solution is often much greater than would be predicted on a purely statistical basis. Suggested reasons for this include steric, electronic (*e.g.* π bonding) charge neutralization,[2] and recently hydrophobic [3] effects. The possibility of strong intramolecular hydrogen bonding seems to have been overlooked. The factors determining which complex precipitates from a solution containing copper(II) species are complicated.[4] The work presented here demonstrates the polymorphism of a mixed-ligand copper(II) complex and the surprising result that the thermodynamic product in the *solid* state is not the simple mixed chelate.

Complexes with π-acceptor ligands, *e.g.* 2,2′-bipyridyl (bipy), often form extremely stable ternary complexes in solution; such systems have been extensively studied.[5,6] There have also been several studies of solid mixed-ligand copper(II) bipy complexes with carboxylic or amino-acids [7-11] (see below).

The mixed-ligand complexes of the oxalate anion ($C_2O_4^{2-}$) and bipy with copper(II) have been prepared by a number of groups. Sone *et al.*[12] prepared a dark blue dihydrate which they believed to be the mixed chelate $[Cu(bipy)(O_4C_2)]\cdot 2H_2O$; over a number of days this compound turned green and finally dehydrated to give an anhydrous product postulated as $[Cu(bipy)_2][Cu(O_4C_2)_2]$. Sigel and co-workers [13] prepared a blue-green anhydrous mixed-ligand complex by a different method and noted no solid-state reactivity. Hathaway and co-workers [14] prepared an anhydrous blue complex which again showed no solid-state reactivity. In a recent survey of such complexes [15] only the results of Hathaway were cited.

It appears that the chemistry of mixed oxalate–bipy complexes of copper(II) is more complex than appreciated by some workers. Since we are developing an interest in the reactivity of co-ordination compounds in the solid state [16] and Sone's work suggests that a unique solid-state rearrangement is occurring, the mixed chelates of bipy and oxalate with copper(II) have now been prepared and studied by a wide range of physical methods. A preliminary communication of this work has already appeared.[17]

RESULTS AND DISCUSSION

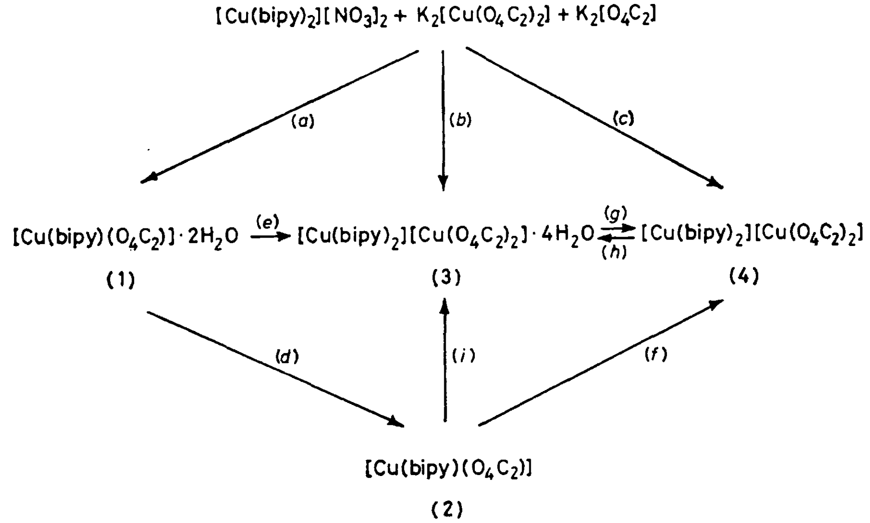
Preparations and Interconversions.—As the methods of preparation are critical to this work and previous methods seem unreliable, a *brief* discussion of the preparation and interconversion of the complexes is given here, full details being provided in the Experimental section. The mixed-ligand complexes were initially prepared by the method of Sone *et al.*[12] Warm aqueous solutions of $[Cu(bipy)_2][NO_3]_2$ and $K_2[Cu(O_4C_2)_2]\cdot 2H_2O$ (dissolved in potassium oxalate) were mixed. The blue crystalline solid thus obtained was often contaminated with a green powder. A detailed study of the effect of the reaction conditions on the product was undertaken.

On mixing cold dilute solutions of the oxalate and bipy complexes a clear blue crystalline precipitate of empirical formula $[Cu(bipy)(O_4C_2)]\cdot 2H_2O$ (1) was obtained. The product was dried in air and could be converted into a stable blue anhydrous complex $[Cu(bipy)(O_4C_2)]$ (2) by vacuum desiccation or drying in an oven at 60—80 °C.

On mixing hot solutions (*ca.* 80 °C) of the bipy and oxalate complexes a green microcrystalline product of empirical formula $[Cu(bipy)(O_4C_2)]$ (4) precipitated almost immediately. If hot solutions were mixed and the product allowed to precipitate at a somewhat lower temperature (*ca.* 40 °C) a green hydrate complex $[Cu(bipy)(O_4C_2)]\cdot 2H_2O$ (3) was obtained. This could be converted into the anhydrous complex by desiccation or storage in an oven (60—80 °C).

The complexes could be interconverted in a number of ways. On standing in the open laboratory the blue hydrate (1) changed over a period of days to the green hydrate (3); this process appeared to be accelerated in a humidifier. After a further 1 or 2 d this compound effloresced to give the green anhydrous modification (4).

Thoroughly air-dried samples of the blue monohydrate could be dehydrated in an oven (60—80 °C) or on a thermal balance to give the blue anhydrous complex (2). This form appears indefinitely stable in the absence of water vapour, one sample was kept for 3 months in a drying oven. In contrast, if a damp sample of (1) was heated in an oven (60—80 °C) it was totally and rapidly converted into the anhydrous green modification (4).



SCHEME Transformations observed: (*a*) on mixing cold dilute solutions, 5—15 °C, *ca.* 0.02 mol dm^{-3}, immediate precipitate; (*b*) hot dilute solutions, *ca.* 0.005 mol dm^{-3}, mixed at 80—90 °C, then allowed to crystallize at 40 °C; (*c*) on mixing hot concentrated solutions, 80—90 °C, *ca,* 0.1 mol dm^{-3}, immediate precipitate; (*d*) heating air-dried sample in an oven at *ca.* 60 °C or vacuum desiccation; (*e*) standing in open air or under water; (*f*) standing under hot (70—80 °C) water; (*g*) standing in air, oven drying, or desiccation; (*h*) standing under water for 3—4 d at 50 °C; (*i*) standing under water

The green hydrate could be prepared by stirring forms (1) or (2) under water overnight. Form (4) could be converted with difficulty into form (3) by prolonged storage (several days) under water at 40—50 °C. The interconversion and preparations of the complexes are summarized in the Scheme.

The preparation method of Sigel and co-workers[13] seemed to give mixtures or form (4); the product of Hathaway and co-workers[14] is uncertain. The method used here is a modification of that of Sone *et al.*;[12] however, careful control of reaction conditions is necessary for the preparation of pure complexes.

Electronic and E.S.R. Spectra.—The results of this study together with three of earlier workers are reported in Table 1. A straightforward comparison of the results leads us to assign the complex prepared by Sigel as (4), that by Hathaway as (2), and those prepared by Sone as (1) and (4). The observed g values for all the polycrystalline samples lie in the range 2.04—2.30 with no absorption at low or high fields. They are consistent with magnetically dilute copper(II) complexes having no strong copper–copper interactions; the complexes may thus be considered as monomeric copper(II) species.[14,18] All the complexes have spectra with lowest $g > 2.04$, consistent with a $d_{x^2-y^2}$ or d_{xy} ground state, as expected.

The electronic spectra of bis(bipyridyl)copper(II) complexes are well documented.[18-20] In general, the absorption due to the *d–d* transitions occurs at much greater wavelength than would be expected from a simple consideration of the position of bipy in the spectrochemical series. This is due to distortion of the CuN_4 chromophore from the square plane, partly caused by the steric interaction of the 6,6′ protons of bipy. The absorptions of complexes (1) and (2) occur in the region of the spectrum expected for square-planar CuN_2O chromophores (from a simple consideration of the spectrochemical series[12]). Further, the spectrum occurs at similar energy to that of solutions containing the mixed-ligand complex; in solution the simple mixed chelate $[Cu(bipy)(O_4C_2)]$ is known to be the dominant form.[1,6]

TABLE 1

Electronic and e.s.r. spectra of the complexes

Complex	Ref.	$10^{-3}\tilde{\nu}_{max.}$/cm^{-1}	E.s.r. g_1	g_2	g_3
(1) $[Cu(bipy)(O_4C_2)]\cdot 2H_2O$	12	17.1			
	*	17.1	2.050	2.211	
(2) $[Cu(bipy)(O_4C_2)]$	14	17.0, 9.0 (sh)	2.061	2.233	
	*	17.1	2.050	2.188	
(3) $[Cu(bipy)(O_4C_2)]\cdot 2H_2O$	*	15.3	2.065	2.388	
(4) $[Cu(bipy)(O_4C_2)]$	13	14.1	2.066	2.126	2.228
	12	14.3			
	*	15.1	2.070	2.138	2.235

* This work.

Although the e.s.r. spectra observed for mixed chelates need not be of axial character they are often found to be so.[21] The two-g-value spectra recorded for forms (1) and (2) are typical of such spectra. Sigel has recorded the e.s.r. spectra of the mixed-ligand species in solution; his molecular g values (2.063 and 2.258) are remarkably similar to the crystal g values of complexes (1) and (2) and seem to bear little relation to his solid species. The electronic and e.s.r. spectra are thus consistent with assigning complexes (1) and (2) as mixed chelates with approximately square-planar geometries; the fifth and sixth co-ordination positions may be occupied by a distant ligator, *e.g.* co-ordinated water, in the hydrated form.

The spectra of complexes (3) and (4) are less easy to interpret. The reflectance spectra have maxima which are almost the mean of those of the parent complex, making it tempting to assign them as double salts. However, an increase in co-ordination number to five or even six could lead to an absorption at lower energy, particularly as a non-square-planar complex will not have the possibility of the synergic bonding[13] available in the square-planar mixed chelate. The e.s.r. spectra are also more complicated, and whereas complex (3) has an axial spectrum that of complex (4) is rhombic.[18] This could reflect only a minor shift in the position of the copper atom or ligand between these two complexes, but suggests a non-square-planar geometry for complex (4).[18]

Infrared Spectra.—Infrared spectra are reported between 4 000 and 250 cm^{-1}. Many bands attributed to bipy are little altered on co-ordination; these are listed, together with powder *X*-ray diffraction results and elemental analyses, in Supplementary Publication No. SUP 23046 (6 pp.).* Certain i.r. bands in complexes of this kind may be tentatively used to assign the mode of co-ordination; these are listed in Table 2.

TABLE 2

Significant i.r. bands (cm^{-1}) and assignment

Complex	ν_{sym}(COO)	ν_{asym}(COO)	M–O	M–N
(1) $[Cu(bipy)(O_4C_2)]\cdot 2H_2O$	1 670, 1 640	1 410, 1 320	795, 550, 425	340
(2) $[Cu(bipy)(O_4C_2)]$	1 670, 1 645	1 380, 1 318	795, 542, 418	338
(3) $[Cu(bipy)(O_4C_2)]\cdot 2H_2O$	1 665, 1 610	1 355, 1 295	795— 420	310, 285
(4) $[Cu(bipy)(O_4C_2)]$	1 660, 1 600	1 360, 1 295	795— 420	310, 280
$K_2[Cu(O_4C_2)_2]\cdot 2H_2O$	1 672, 1 645	1 411, 1 277	795, 541, 420	
$[Cu(bipy)_2][NO_3]_2$				315, 290

The situation is again least ambiguous for complexes (1) and (2); for these the symmetric (ν_{sym}) and antisymmetric (ν_{asym}) stretches of the carboxylate group occur at similar frequencies to those of $[Cu(O_4C_2)_2]^{2-}$.[22] The separation of these bands (*ca.* 262 cm^{-1}) is typical of a unidentate carboxylic acid.[23] The metal–oxygen stretches (Table 2) also occur at a similar frequency to those of the oxalate complex. The metal–nitrogen stretches of $[Cu(bipy)_2]^{2+}$ have been assigned to a band in the region of 300 cm^{-1};[21,24] no such band is observed for complex (1) or (2). A new strong band is observed at 340 cm^{-1}, attributed to the M–N stretch shifted to higher energy by the stronger bonding in the mixed chelate.

The spectra of complexes (3) and (4) are more difficult to assign; more bands are observed in the region of ν_{asym} and ν_{sym} of the carboxylate group and there is a slightly greater separation of ν_{sym} and ν_{asym}. This has been used to suggest the presence of bridging oxalates.[15,25] A band at 310 cm^{-1} appears in the spectrum of both (3) and (4); this could suggest a shift in the mode of co-ordination of the bipy group to one similar to that in $[Cu(bipy)_2][NO_3]_2$ (a distorted octahedron?) with removal of the synergic π bonding in the coplanar mixed chelate.

Other Techniques.—All complexes were examined by *X*-ray diffraction (powder method). The four modifications are confirmed as being crystallographically distinct both from each other and the ' parent ' chelates (see SUP 23046). Isomorphous compounds were obtained by all methods of preparation and interconversion; in particular, it should be noted that compounds prepared by the solid-state reactions were crystalline.

Thermogravimetric analysis revealed the loss of water from the complexes. Water was easily lost from complex (3) (11.8% at 52—86 °C). Complex (1) showed slightly more complicated behaviour, losing 9.2% at 46—65 °C (10 °C min^{-1}) equivalent to 1.5 mol of H_2O per mol of complex and 2.5% at 65—105 °C. This could suggest the co-ordination of one water molecule per two atoms of copper(II). As water of crystallization is fairly easily lost this may explain previous reports of anhydrous complexes.

Conclusions.—The results presented show that mixed oxalate–bipy complexes of copper(II) exist in at least two modifications with drastically different first co-ordination spheres at copper(II). Earlier workers failed to appreciate this; thus earlier spectroscopic parameters may be suspect.

Complexes (1) and (2) are mixed chelates, the co-ordination geometry at copper closely approximating a square plane of CuN_2O_2; two distant ligands (bond length *ca.* 3 Å) are possibly present. It is more difficult to assign a geometry to complexes (3) and (4); undoubtedly they are not simple mixed chelates. It is tempting to suggest that disproportionation to the double salt $[Cu(bipy)_2][Cu(O_4C_2)_2]$ has occurred, however, the i.r. results run contrary to this. A structure involving bridging oxalates is a strong possibility with a co-ordination number greater than four. Mixed-ligand complexes of copper(II) with N-heterocycles and carboxylic acids similar to both kinds of complex prepared in this study are known.[15] However, this is the first occasion that both kinds of compound have been prepared from a single system; this appears to be a unique case of polymorphism.

For this system I favour assigning complexes (3) and (4) as polymeric species involving bridging oxalates, a structure which might exploit the unusual electronic properties of the d^9 copper(II) configuration. The final

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

product of all the reaction steps is compound (4); hence, in the solid state, this is the thermodynamically most stable form of these mixed-ligand complexes. In marked contrast to what is found in solution, this complex is not correctly described as a simple monomeric mixed-ligand species of approximate square-planar geometry.[6]

Work is in progress to survey other mixed-ligand complexes of copper(II) for polymorphism. The situation will not be unequivocally resolved until crystal structures are available for such polymorphs, and work of this kind is anticipated.

EXPERIMENTAL

Copper(II) nitrate trihydrate and potassium oxalate monohydrate were BDH AnalaR grade; 2,2′-bipyridyl was supplied by Aldrich.

Methods.—Diffuse-reflectance spectra were recorded with a Beckman DK2a spectrophotometer. Infrared spectra were obtained for Nujol mulls between caesium iodide plates or for potassium bromide pellets (1% 100-mg discs) on Perkin-Elmer 457 and 257 spectrophotometers. Thermogravimetric analysis was performed using a Stanton Redcroft TG 750 instrument at a rate of 10 °C min^{-1} under dry nitrogen (10 cm^3 min^{-1}), the sample size lying between 3 and 8 mg. Diffraction patterns were measured with a Philips diffractomer using Cu-*K* radiation of 1.5418 Å. E.s.r. spectra were recorded with a Varian E4 spectrometer, substantially the same results being obtained at *ca.* 77 K as at room temperature (*ca.* 293 K). Crystal *g* values were calculated by the method of Kneubuhl.[18,26]

Preparations.—The mixed-ligand complexes were prepared as outlined below; all gave satisfactory microanalysis [17] (C, H, N, Cu, and H_2O). Dipotassium bis(oxalato)cuprate(II) dihydrate and bis(2,2′-bipyridyl)copper(II) dinitrate were prepared by literature [21,27,28] methods. In all preparations the oxalate complex was dissolved in potassium oxalate solution (0.01—0.1 mol dm^{-3}); the concentration of potassium oxalate did not effect the reaction product, but the rate of crystallization may have been marginally effected.

[Cu(bipy)(O_4C_2)]·H_2O (1). Equivalent amounts of cold (*ca.* 5—15 °C) dilute (0.02 mol dm^{-3}) solutions of the parent complexes were mixed. An almost immediate precipitate of small blue lustrous crystals was obtained.

[Cu(bipy)(O_4C_2)] (2). Form (1) was heated in an oven (60—80 °C) or allowed to stand in a vacuum desiccator, readily losing its water of crystallization to give (2). Form (2) appears indefinitely stable in the absence of water vapour.

[Cu(bipy)(O_4C_2)]·$2H_2O$ (3). Equivalent amounts of hot (80—90 °C) dilute ($<5 \times 10^{-3}$ mol dm^{-3}) solutions of the parent complexes were mixed. The solution was then allowed to slowly crystallize at temperatures >40 °C, giving the compound as small green rhombs. Form (3) could easily be prepared by stirring forms (1) or (2) under water overnight. If form (4) was heated under water at 50 °C for 3—4 d it was eventually converted into form (3).

[Cu(bipy)(O_4C_2)] (4). Equivalent amounts of hot (80—90 °C) concentrated (0.02—0.1 mol dm^{-3}) solutions of the parent complexes were mixed; form (4) was almost immediately obtained as a microcrystalline precipitate. It could also be prepared from (3) by dehydration in an oven (60—80 °C) or vacuum desiccator.

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