Isomerism of Mixed Ligand Copper(II) Complexes Containing 1,10-Phenanthroline and Oxalate

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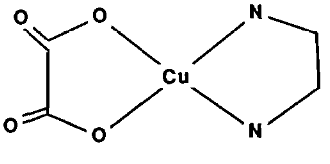
We have demonstrated the polymorphism of the mixed oxalato, 2,2'-bipyridyl (bipy) complexes of copper(II) [1–3]. At least five different complexes [4] have been isolated, but crystallography combined with spectral studies [3] suggests coordination at copper to fall into only two distinct classes. The first an approximately N_2O_2 chromophore of one oxalate and one bipyridyl coordinated in a square plane at copper(II) (form I); axially coordinated water may or may not be present depending on the modification. The second an axially elongated N_2O_4 chromophore consisting of one bipyridyl and two catena bridging oxalates (form II).

There have been two recent reports [4, 5] of mixed complexes of copper(II) with oxalate and 1,10-phenanthroline (phen). These workers did not appreciate that polymorphism of the kind we have described for the bipyridyl systems [1–3] also occurs for the 1,10-phenanthroline complexes. This prompts us to publish details of the synthesis and electronic properties of two complexes of formula $[Cu(C_2O_4)(phen)]\cdot nH_2O$ ($n = 0$ and 2); which were first characterised some years ago in our laboratory [6].

In our later study [3] of the oxalate/bipyridyl system we noted the extreme sensitivity of the electronic spectra of these complexes to the above two modes of coordination (I *versus* II). The simple mixed chelates (I) are characterised by a single broad absorption in the visible/near infrared ($\lambda_{max} \sim 15.5 \times 10^3$ cm^{-1}), the bridged N_2O_6 chromophores by two bands at ~9.3 and ~14.5 $\times 10^3$ cm^{-1}; as in the structurally related bis-hexafluoroacetanato mono-bipyridyl copper(II) complex [7]. This criterion is now used to consider literature reports of mixed $[Cu(C_2O_4)(phen)]$ complexes. Kwik and Ang reported [8] a complex $[Cu(C_2O_4)(phen)]$, $\lambda_{max} = 15.5 \times 10$ cm^{-1}; Sone *et al.* [9] $[Cu(C_2O_4)(phen)]\cdot 2H_2O$, $\lambda_{max} = 15.4 \times 10^3$ cm^{-1}; both results consistent with an approximately square planar N_2O_2 chromophore. A recent crystallographic study of a blue complex confirms this general conclusion [4]; copper has distorted square pyramidal coordination [4], the fifth position being occupied by a water molecule at 2.24 Å in the blue complex $[Cu(C_2O_4)(phen)]\cdot 2H_2O$. However, both Seminara *et al.* [10] and Kwik and co-workers [5] have reported a complex $[Cu(C_2O_4)(phen)]$ with bands in the electronic



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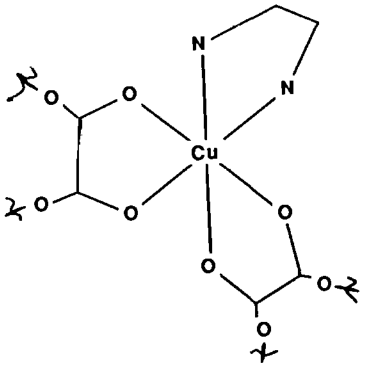

II

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TABLE I. Analytical Results and Spectroscopic Parameters

Sample	Analysis (%)				Electronic spectrum[b]	ESR	Notes
	C	H	N	H_2O[a]			
$[Cu(C_2O_4)(phen)]\cdot 2H_2O$	45.72	3.29	7.62	9.80			calculated
$[Cu(C_2O_4)(phen)]\cdot 2H_2O$	45.91	3.61	7.37	9.50	15.38	2.22, 2.06	I
$[Cu(C_2O_4)(phen)]$	50.68	2.43	8.44				calculated
$[Cu(C_2O_4)(phen)]$	50.36	2.48	8.66		13.9, 8.6	2.156[d]	II

[a] By thermogravimetry. [b] 10^3/cm^{-1} measured between 4.0 and 20 $\times 10^3$ cm^{-1}. [c] Estimated by method Kneubuhl [1], highest g value a broad signal. [d] Isotropic or near isotropic ESR g_{av}.

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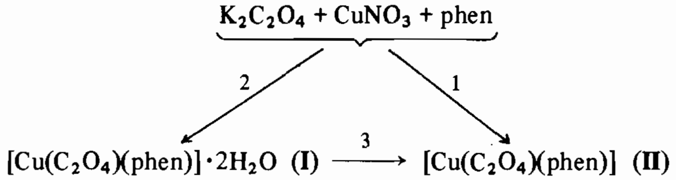

Scheme 1. The preparation of mixed 1,10-phenanthroline oxalato copper(II) complexes. 1. Hot, 80–90 °C, solutions in water, immediate precipitate, $[Cu(II)] = [phen] = [C_2O_4{}^{2-}] \sim 1 \times 10^{-2}$ mol dm^{-3}. 2. Hot, 80–90 °C, solutions in water, slow crystallisation, $[Cu(II)] = [phen] = [C_2O_4{}^{2-}] \sim 1$–$5 \times 10^{-4}$ mol dm^{-3} or from solutions used to prepare II; complex II filtered off. 3. Reflux the solid under water for ~10 min.

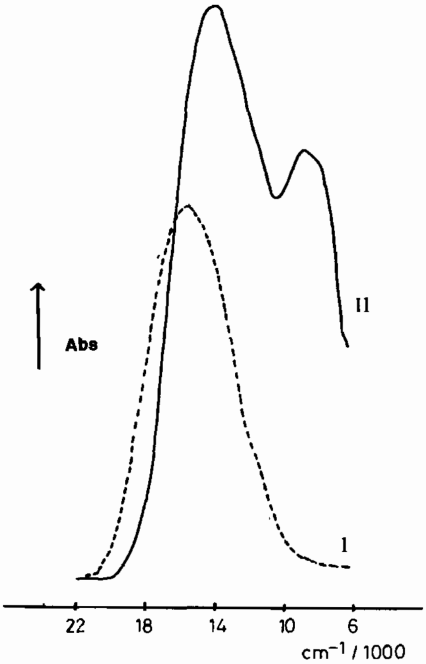

Fig. 1. Electronic spectra of mixed oxalate phenanthroline complexes.

spectrum at ~14.0 and ~9 × 10^3 cm^{-1}; results remarkably similar to ours for the polymeric form of the mixed oxalate bipyridyl complex. The above observations suggest similar polymerisation isomerism for the mixed oxalate phenanthroline complexes of copper to that we have [1–3] unequivocally established for the oxalate/bipyridyl system.

Results and Discussion

We rapidly confirmed that a blue complex of stoichiometry $[Cu(C_2O_4)(phen)]\cdot 2H_2O$ (I) separated from solutions of copper(II) salts, potassium oxalate and 1,10-phenanthroline in a 1:1:1 ratio. Analytical results together with spectral parameters are summarised in Table I. If this complex is refluxed under water for five to ten minutes it is rapidly and quantitatively converted to a blue–green complex $[Cu(C_2O_4)(phen)]$ (**II**). Conditions for the preparation and interconversion of these phases are summarized in Scheme 1. As outlined above the electronic spectra (Fig. 1) of these two complexes allow us to assign their first coordination spheres with some confidence. **I** is a simple mixed chelate with N_2O_2 occupying the square plane at copper(II); more distant ligation by axial water completing a square pyramid is now confirmed by the crystal structure [4] (single peak electronic spectrum). **II** is assigned as a polymeric structure of N_2O_6 chromophores probably involving catena bridging oxalates (two peak electronic spectrum).

The results presented in this note establish that the mixed oxalato 1,10-phenanthroline complexes of copper(II) exist in two main isomeric forms; monomeric complexes in which oxalate and 1,10-phenanthroline occupy a square plane and polymeric complexes with catena bridging oxalates. Polymorphism is apparently widespread for these systems; we believe that many other such examples may be obtained from this and related systems [12], and indeed have some evidence for hydrated forms of compound **II** [6]. It is hence extremely important that preparative details are provided in papers reporting studies of labile complexes of this type.

References

1 P. O'Brien, *Transition Met. Chem.*, *5*, 314 (1980).
2 P. O'Brien, *J. Chem. Soc., Dalton Trans.*, 1540 (1981).
3 W. Fitzgerald, J. Foley, D. McSweeney, N. Ray, D. Sheahan, S. Tyagi, B. Hathaway and P. O'Brien, *J. Chem. Soc., Dalton Trans.*, 1117 (1982).
4 A. C. Fabretti, G. Franchini, P. Zannini and M. Divaira, *Inorg. Chim. Acta*, *105*, 187 (1985).
5 W.-L. Kwik, K.-P. Ang, H. S.-O. Chan, V. Chebolu and S. A. Koch, *J. Chem. Soc., Dalton Trans.*, 2519 (1986).
6 P. O'Brien, unpublished results.
7 R. J. Dudley and B. Hathaway, *J. Chem. Soc. A*, 2794 (1970).
8 W.-L. Kwik and K. P. Ang, *Aust. J. Chem.*, *31*, 459 (1978).
9 K. Sone, S. Utsuno and T. Ogura, *J. Inorg. Nucl. Chem.*, *31*, 117 (1969).
10 S. Musumeci, E. Rizzarell, S. Sammartano and A. Seminara, *Z. Anorg. Allg. Chem.*, *433*, 297 (1977).
11 F. K. Kneubuhl, *J. Chem. Phys.*, *33*, 1074 (1960).
12 M. Jalve, J. Faus, M. Verdguer and A. Gleizes, *J. Am. Chem. Soc.*, *106*, 8306 (1984).