Phosphate coordination in copper(II) complexes

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Abstract. The structural aspects of phosphate coordination in $Cu(bipy)_2 (H_2PO_4)_2 \sim 0.25$ H_3PO_4 (1) and $Cu(phen)_2(H_2PO_4)_2 \sim 0.25$ H_3PO_4 (2) (bipy = 2,2' bipyridyl; phen = 1,10 phenanthroline) have been investigated by IR, electronic and ESR spectra. In both complexes bidentate coordination from $H_2PO_4^-$ ion is suggested. The complexes have been assigned *cis*-distorted octahedral stereochemistry. It is interesting that the stereochemistry is essentially of a static nature in (1) while it is fluxional in (2).

1. Introduction

Coordination compounds of transition metal ions containing orthophosphate ion have not been studied extensively as compared to those containing other common anions. The multivalent nature of the orthophosphate ion and its potential for multidentate coordination were expected to show an interesting variety of coordination modes. Some of the early studies reported on phosphate-coordinated complexes were on cobalt(III)-ammonia complexes containing orthophosphate and substituted ortho-phosphate ions (Siebert 1958; Schmidt and Taube 1963). The structural aspects of cobalt(III) and copper(II) complexes containing ammonia/other co-ligands and orthophosphate ions have been investigated by IR spectra, and both mono- and bidentate orthophosphate ions have been observed (Lincoln and Stranks 1968; Ojima and Nonoyama 1973). Studies on the hydrolytic behaviour of some of these complexes have also been reported (Lincoln and Stranks 1968).

The present work reports some of the structural aspects of phosphate ion coordination in the complexes $Cu(bipy)_2(H_2PO_4)_2 \sim 0.25$ H_3PO_4 and $Cu(phen)_2$-$(H_2PO_4)_2 \sim 0.25$ H_3PO_4.

2. Experimental

2.1 *Chemicals*

Commercially available AnalaR grade 2,2' bipyridyl, 1,10 phenanthroline, ortho-phosphoric acid and $CuCl_2 \cdot 2H_2O$ were used without further purification. Ethyl alcohol was dehydrated over molecular sieve (type 5A, Union carbide) and distilled under dry nitrogen before use.

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2.2 *Preparation of complexes*

The complexes were prepared by reaction between $CuCl_2 \cdot 2H_2O$, orthophosphoric acid and the neutral ligand in dry alcohol to minimise the water content of the medium and thereby prevent coordination of water.

2.2a $Cu(bipy)_2(H_2PO_4)_2 \sim 0.25\ H_3PO_4$: Alcoholic solutions of bipy (10 mmol in 20 ml) and H_3PO_4 (10 mmol in 20 ml) were gradually added to an alcoholic solution of $CuCl_2 \cdot 2H_2O$ (5 mmol in 20 ml) simultaneously. The original yellowish green colour of the copper(II) chloride solution changed to green and a green precipitate (which was found to be $Cu(bipy)Cl_2$) was formed in the initial stages of addition of reactants. The addition of bipy and H_3PO_4 was continued until the green colour of the supernatant solution turned pale blue. The precipitation of the green compound was complete at this stage and it was removed by filtration. To the filtrate the remaining bipy and H_3PO_4 were added when a blue compound precipitated out, which was filtered, washed and dried *in vacuo*. Yield, 0.8 g, Anal. Found: Cu, 10.6; P, 11.6; N, 8.9, H_3PO_4, 4%; Calc. for $Cu(bipy)_2(H_2PO_4)_2 \sim 0.25\ H_3PO_4$; Cu, 10.7; P, 11.7; N, 9.4; H_3PO_4, 4.1%.

2.2b $Cu(phen)_2(H_2PO_4)_2 \sim 0.25\ H_3PO_4$. The preparation of this complex (greenish blue) is analogous to that of $Cu(bipy)_2(H_2PO_4)_2 \sim 0.25\ H_3PO_4$. Yield, 0.8 g, Anal. Found: Cu, 10.0; P, 10.4; N, 9.1; H_3PO_4, 3.5%; Calc. for $Cu(phen)_2(H_2PO_4)_2 \sim 0.25$ H_3PO_4: Cu, 9.9; P, 10.8; N, 8.7; H_3PO_4, 3.8%.

H_3PO_4 in the complexes was determined by the method described for solvent extraction and estimation of H_2SO_4 (Allen 1956). Both the above Cu(II) complexes were insoluble in common organic solvents. They were stable in air and melted with decomposition at 463–498 K.

2.3 *Physical methods used for characterisation of complexes*

IR spectra of the complexes were recorded on Perkin Elmer 577 spectrophotometer using nujol mulls. Electronic absorption spectra of nujol mulls were recorded on Cary-14 spectrophotometer. ESR spectra of powdered samples were obtained on a Varian V-4502 spectrometer operating at X-band frequencies. DPPH was used as a *g*-marker and the magnetic field was measured using an NMR gaussmeter. Magnetic susceptibilities of the compounds were measured by the Gouy method on powdered samples using $Hg[Co(CNS)_4]$ as standard.

3. Results and discussion

The electronic absorption spectrum of $Cu(bipy)_2(H_2PO_4)_2 \sim 0.25\ H_3PO_4$ showed two bands due to $d–d$ transitions at $13700\ cm^{-1}$ and $10400\ cm^{-1}$ while in $Cu(phen)_2$-$(H_2PO_4)_2 \sim 0.25\ H_3PO_4$ the spectrum showed a band at $12900\ cm^{-1}$ and a shoulder at $10200\ cm^{-1}$ (figure 1). The frequencies of the two absorption bands and the energy difference between the two transitions giving rise to these bands are closely similar to those observed for *bis*-bipy complexes of Cu(II) with *cis*-distorted octahedral stereochemistry (Hathaway *et al* 1969; Hathaway and Billing 1970; Fitzgerald *et al* 1981). This indicates that in addition to the two bidentate bipy/phen ligands the orthophosphate ion is also coordinated to the metal ion. The higher and lower energy bands observed for *cis*-distorted octahedral complexes of the type $[Cu(bipy)_2X]X(X = NO_2^-$, $CH_3CO_2^-$ etc) have been attributed to $d_{yz}, d_{xz}, d_{x^2-y^2} \to d_{z^2}$ and $d_{xy} \to d_{z^2}$
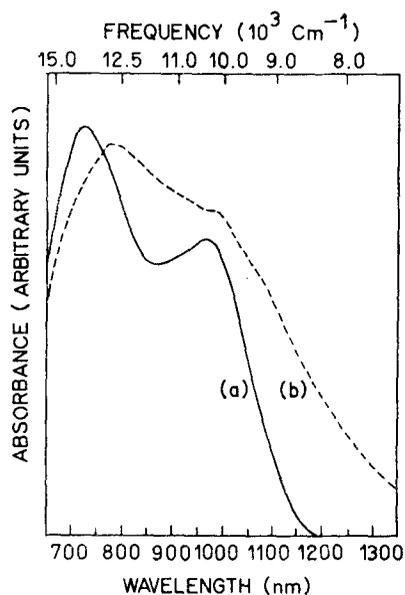
Figure 1. Electronic spectra (nujol mulls) **a.** Cu(bipy)$_2$(H$_2$PO$_4$)$_2$ ∼ 0·25 H$_3$PO$_4$; **b.** Cu(phen)$_2$(H$_2$PO$_4$)$_2$ ∼ 0·25 H$_3$PO$_4$.

transitions respectively (Hathaway *et al* 1969). Therefore similar assignments may be made also in Cu(bipy)$_2$(H$_2$PO$_4$)$_2$ ∼ 0·25 H$_3$PO$_4$ and Cu(phen)$_2$(H$_2$PO$_4$)$_2$ ∼ 0·25 H$_3$PO$_4$.

The IR spectra showed Cu–N stretching modes at 285 cm^{-1} (s) and 275 cm^{-1} (sh) for the copper(II)-bipy complex and at 265 cm^{-1} (sh) and 240 cm^{-1} (s) for copper(II)-phen complex as observed for tris-bipy and phen complexes of copper(II) (Saito *et al* 1972). No bands attributable to Cu–O stretching modes which are expected in the region 250–350 cm^{-1} (Nuttal *et al* 1971; Contreras and Seguel 1976) were observed although electronic spectra indicated coordination of H$_2$PO$_4^-$. It is possible that Cu–O stretching modes are either obscured by the Cu–N stretching/ligand modes, or may appear only at much lower frequencies since long Cu–O bonds have been observed in related complexes (Hathaway *et al* 1969). The different P–O stretching modes formed two broad bands, at 1050–1200 cm^{-1} and around 970 cm^{-1}. The in-plane bending mode characteristic of H$_2$PO$_4^-$/H$_3$PO$_4$ was observed at 1240 cm^{-1} which showed a downward shift of ∼ 40 cm^{-1} with respect to the corresponding band for H$_2$PO$_4^-$ in NaH$_2$PO$_4$ (Chapman and Thirlwell 1964). This is indicative of slight weakening of the hydrogen bonds in the complexes (Chapman and Thirlwell 1964). Other bands due to H$_2$PO$_4^-$ and H$_3$PO$_4$ were observed in the expected region (Chapman and Thirlwell 1964). The bipy and phen bands in the region 1050–1200 cm^{-1} were found superimposed on the broad bands due to H$_2$PO$_4^-$ and H$_3$PO$_4$ referred to above. The remaining bands due to bipy and phen were observed in the expected region (Inskeep 1962; Saito *et al* 1972).

The ESR spectrum of polycrystalline Cu(bipy)$_2$(H$_2$PO$_4$)$_2$ ∼ 0·25 H$_3$PO$_4$ at room temperature was anisotropic with the g values 2·106 ± 0.001 ($g_\perp$) and 2·173 ± 0·001 ($g_\parallel$). At liquid nitrogen temperature the ESR spectrum contained prominent peaks with g

values $2 \cdot 187 \pm 0 \cdot 001$ (g_z), $2 \cdot 109 \pm 0 \cdot 001$ (g_y) and a shoulder with g value $2 \cdot 028 \pm 0 \cdot 001$ (g_x) suggesting a small non-axial distortion of the complex at 77° K. On the other hand the room temperature ESR spectrum of $Cu(phen)_2(H_2PO_4)_2 \sim 0.25$ H_2PO_4 was isotropic with a g value of $2 \cdot 125 \pm 0 \cdot 001$ whereas at liquid nitrogen temperature the spectrum became anisotropic with g values $2 \cdot 079 \pm 0 \cdot 001$ $(g_\perp)$ and $2 \cdot 182 \pm 0 \cdot 001$ $(g_\parallel)$. The spectra exhibiting these features are shown in figure 2a–d. The g values observed for the copper(II)-bipy complex at 77 K $(g_z > (g_x + g_y)/2 > 2)$ and copper(II)-phen complex $(g_\parallel > g_\perp > 2)$ suggest *trans* octahedral structures (Hathaway and Billing 1970), but such structures are highly unlikely for *bis*-bipy and phen complexes of Cu(II) (Hathaway *et al* 1969) and other first row transition metal ions in $+2$ oxidation state (McKenzie 1971). This has been attributed to strong steric repulsions that may occur in such structures between the α-hydrogen atoms of the two ligand molecules. ESR spectral features similar to those for the above phosphatocomplexes of copper(II) have also been observed for *cis*-distorted octahedral *bis*-bipy and phen complexes of copper(II) containing other bidentate oxyanions (Fitzgerald *et al* 1981; Clifford *et al* 1982). These complexes have been assigned pseudo *cis*-distorted octahedral structures (I) arising from pseudodynamic Jahn-Teller effect in some cases, and square pyramidal distorted octahedral structures (II) of an essentially static nature in other cases. In addition,
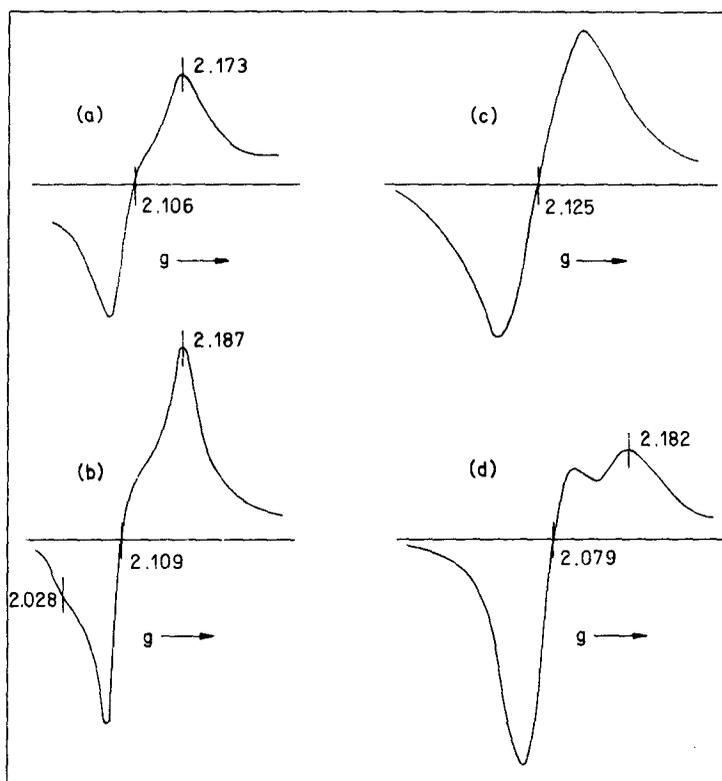
Figure 2. ESR spectra: $Cu(bipy)_2(H_2PO_4)_2 \sim 0 \cdot 25$ H_2PO_4 at a. room temperature b. liquid nitrogen temperature; $Cu(phen)_2(H_2PO_4)_2 \sim 0 \cdot 25$ H_3PO_4 at c. room temperature d. liquid nitrogen temperature.

structures of intermediate character between (I) and (II) have also been observed. These structures show asymmetric coordination of bidentate anions like NO_2^- and CH_3COO^- with two Cu–O bonds of different bond lengths as determined by room temperature x-ray crystallography. The difference in the Cu–O bond length can be as high as 0·6 A (structure type II) or almost negligible in some cases (structure type I). The copper(II) dihydrogen phosphate complexes of bipy and phen are also expected to have similar structures in view of the evidence from electronic and ESR spectra and are therefore formulated as $[Cu(L)_2(H_2PO_4)][H_2PO_4] \sim 0·25 \ H_3PO_4$ (L = bipy or phen) in which bidentate coordination from $H_2PO_4^-$ ion has been assumed by analogy with their counterparts containing other oxyanions (Fitzgerald *et al* 1981; Clifford *et al* 1982). The room temperature magnetic moments of the bipy and phen complexes were 1.9 B.M. and 2.08 B.M. respectively and are in the expected range (Figgis and Lewis 1960).

The ESR spectra of $Cu(bipy)_2(H_2PO_4)_2 \sim 0·25 \ H_3PO_4$ showed very little variation with temperature and therefore it appears to have a stereochemistry which is essentially of a static nature. However, there is a significant variation of the ESR spectra of the phen analogue with temperature which shows the fluxional nature of the CuN_4O_2 chromophore in the molecule (Fitzgerald *et al* 1981; Clifford *et al* 1982). This can arise if the magnitudes of the energy barriers separating the three available potential energy wells (each corresponding to an elongated chromophore with the elongation axes misaligned in three mutually perpendicular directions) in the bipy complex are different from those of the phen complex (Fitzgerald *et al* 1981; Clifford *et al* 1982). The structures suggested for these complexes lack axial symmetry and three *g* values are expected. The ESR spectra at liquid nitrogen temperature appear to show a third *g* value (symptomatic of a further distortion to symmetry lower than axial) only in the bipy complex. It is perhaps possible that for such a transition (averaged non-axial → static non-axial) a still lower temperature is required in the phen analogue.

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