

Stereochemistry and structural phase transition of Cu(II) complexes containing orthophosphate ions and pyridine/picoline

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Abstract. Copper complexes of the type $\text{Cu}(L)_4(\text{H}_2\text{PO}_4)_2$ designated as complex (I), and $\text{Cu}(L)_4\text{HPO}_4$ designated as complex (II), (where $L = \text{pyridine (py) or } \gamma\text{-picoline (pic)}$) have been synthesised, characterised by chemical analyses, IR, and electronic and magnetic susceptibility data. From ESR studies it is concluded that complexes (I) have elongated *trans* octahedral stereochemistry. The temperature dependence of the ESR spectrum of $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ suggests a fluxional behaviour in the immediate coordination of Cu(II), whereas very little variation of the ESR spectrum of the $\text{Cu}(\text{pic})_4(\text{H}_2\text{PO}_4)_2$ complex indicates that the stereochemistry of this complex is essentially static in nature. The differential scanning calorimetric studies in the case of $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ complex have given clear evidence for the occurrence of a structural phase transition at 147 K. The absence of any abrupt changes in the ESR spectrum at that temperature excludes the possibility of any changes in the immediate environment of Cu(II).

Keywords. Copper(II) complexes; octahedral stereochemistry; differential scanning calorimetric studies; structural phase transition.

1. Introduction

Structural studies of transition metal complexes with phosphate coordination have been reported by a number of investigators (Siebert 1958; Schmidt and Taube 1963; Lincoln and Stranks 1968; Ojima and Nonoyama 1973). Recently we have reported ESR and electronic spectral studies of some copper (II) bipyridyl/1, 10-phenanthroline complexes containing orthophosphate ions (Sastri *et al* 1984). Some of these complexes were found to exhibit temperature dependent fluxional behaviour. The present work is aimed at extending these investigations to Cu(II) phosphate complexes containing unidentate ligands such as pyridine and substituted pyridines. This paper describes the preparation and structural elucidation of $\text{Cu}(L)_4(\text{H}_2\text{PO}_4)_2$ and $\text{Cu}(L)_4\text{HPO}_4$ complexes from IR, electronic spectral, ESR and magnetic susceptibility data. Differential scanning calorimetric (DSC) studies were also conducted to see if any structural phase change occurs in these compounds.

2. Experimental

2.1 Chemicals

All chemicals were of reagent grade and were used without further purification.

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2.2 Preparation of complexes

The complexes were prepared by reaction between $\text{Cu}(\text{H}_2\text{PO}_4)_2/\text{Cu}(\text{HPO}_4)$ and the neutral ligand (*L*) in dry methanol-2,2'-dimethoxy propane medium.

2.2a $\text{Cu}(\text{py}/\text{pic})_4(\text{H}_2\text{PO}_4)_2$: $\text{Cu}(\text{H}_2\text{PO}_4)_2$ was prepared by dissolving CuCO_3 (2.0 g 10 mM) in the minimum amount of 85% orthophosphoric acid by warming and stirring. Green coloured $\text{Cu}(\text{H}_2\text{PO}_4)_2$ (identified by chemical analysis) was precipitated from the clear green coloured solution by the addition of dry methanol. To the slurry of this compound in dry methanol-2,2'-dimethoxy propane mixture (1:1 ratio, 20 ml), freshly distilled dry pyridine/gamma-picoline (50.0 mM) was added drop by drop with constant stirring for about five hours with occasional warming. The green coloured slurry changed to greenish blue colour slowly and same coloured compound was precipitated out. The precipitate was filtered, washed with 1% py in methanol-dimethoxypropane mixture and dried in a vacuum desiccator. Yield, $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$, 3.00 gm. Analysis: Found – Cu, 11.02; P, 10.56; N, 9.52; Calc. for $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ Cu, 11.07; P, 10.80; N, 9.75. Yield, $\text{Cu}(\text{pic})_4(\text{H}_2\text{PO}_4)_2$ 3.50 g. Analysis: Found – Cu, 9.98; P, 9.65; N, 8.45; Calc. for $\text{Cu}(\text{pic})_4(\text{H}_2\text{PO}_4)_2$; Cu, 10.08; P, 9.98; N, 8.89.

2.2b $\text{Cu}(\text{py})/(\text{pic})_4(\text{HPO}_4)$: The preparation of this complex (dark blue) is similar to that of $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ complexes, except that CuHPO_4 was prepared by dissolving cupric oxide in 85% orthophosphoric acid, always keeping CuO in excess while dissolving in the acid. Yield, $\text{Cu}(\text{py})_4(\text{HPO}_4)$, 2.00 g. Analysis: Found – Cu, 13.20; P, 6.9; N, 11.65; Calc. for $\text{Cu}(\text{py})_4(\text{HPO}_4)$; Cu, 13.35; P, 6.5; N, 11.76. Yield, $\text{Cu}(\text{pic})_4(\text{HPO}_4)$, 2.40 g. Analysis: Found – Cu, 11.77; P, 5.89; N, 10.55; Calc. for $\text{Cu}(\text{pic})_4(\text{HPO}_4)$ Cu, 11.94; P, 5.83; N, 10.52.

2.3 Instrumental methods

IR spectra of the complexes were recorded on a Perkin Elmer 577 spectrophotometer using nujol and hexachlorobutadiene (HCBT) mulls. Electronic absorption spectra of nujol mulls were recorded on a Cary-14 spectrophotometer. ESR spectra of powdered samples were recorded on a Varian V-4502 spectrometer operating at X-band frequency. 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 $\text{Hg}[\text{Co}(\text{CNS})_4]$ as standard. DSC experiments were carried out on a Perkin Elmer 2-C instrument.

3. Results and discussion

3.1 Results

The ESR spectrum of polycrystalline $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ at room temperature was isotropic with the *g* value ($g = 2.010 \pm 0.001$), while at 77 K, the spectrum was anisotropic with $g_{\parallel} = 2.18 \pm 0.001$ and $g_{\perp} = 2.008 \pm 0.001$ (figures 1a, b). The ESR spectrum of $\text{Cu}(\text{py})_4(\text{HPO}_4)$ and $\text{Cu}(\text{pic})_4(\text{HPO}_4)$ were isotropic at room temperature and at 77 K, with $g = 2.006 \pm 0.001$. The ESR spectrum of $\text{Cu}(\text{pic})_4(\text{H}_2\text{PO}_4)_2$ (figures 2a, b) showed an axial spectrum both at room temperature and at 77 K,

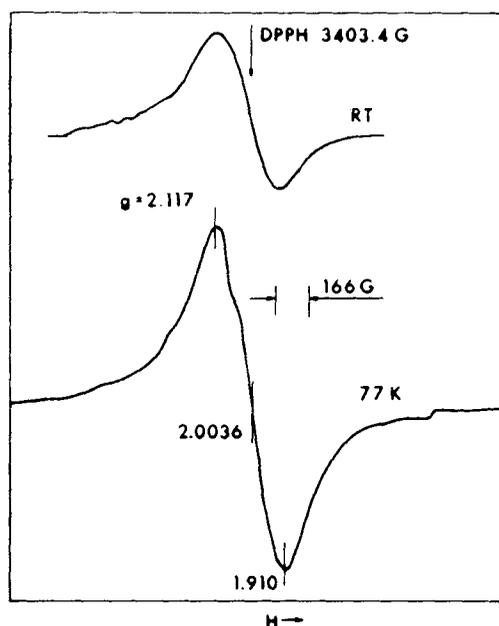


Figure 1. EPR spectrum of $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ at room temperature (A) and at 77 K (B). The anisotropic features, with parallel components on the lower field side, can be observed at 77 K.

with partially resolved hyperfine structure. The spectrum yielded the values $g_{\parallel} = 2.19 \pm 0.001$, $g_{\perp} = 2.010 \pm 0.001$, $A_{\parallel} = 181 \pm 1\text{G}$ and $A_{\perp} < 25\text{G} \pm 1\text{G}$. The room temperature magnetic moments of $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ and $\text{Cu}(\text{pic})_4(\text{H}_2\text{PO}_4)_2$ were 1.85 and 1.83 B.M. respectively, while the values for the corresponding HPO_4^{2-} complexes were 1.80 and 1.90 B.M.

The IR spectra obtained for the compounds investigated in the region $600\text{--}4000\text{ cm}^{-1}$ are consistent with the reported values for the internal modes of all constituent groups (Chapman and Thirlwell 1964; Gill *et al* 1961; Choca *et al* 1972; Saito *et al* 1973; Biagetti *et al* 1966). Further, the IR spectra have provided evidence for the metal (copper) – oxygen, and metal – nitrogen vibration suggesting the coordination of neutral ligand and phosphate ions to the metal. The frequencies for these vibrations are:

(a) Cu – N stretching; 270 cm^{-1} ($\text{Cu py}_4(\text{H}_2\text{PO}_4)_2$) 295, 285, 258, 250 cm^{-1} ($\text{Cu py}_4(\text{H}_2\text{PO}_4)_2$), 260 cm^{-1} ($\text{Cu pic}_4\text{ HPO}_4$) and 290, 275, 265, 260 cm^{-1} ($\text{Cu pic}_4\text{ HPO}_4$).

(b) Cu – O stretching: 255 cm^{-1} ($\text{Cu py}_4(\text{H}_2\text{PO}_4)_2$), 310 cm^{-1} ($\text{Cu py}_4\text{ HPO}_4$), 250 cm^{-1} ($\text{Cu pic}_4(\text{H}_2\text{PO}_4)_2$) and 300 cm^{-1} ($\text{Cu pic}_4\text{ HPO}_4$).

The electronic absorption (mull) spectra of all these complexes were found to be similar, with broad absorption peaks in 650–950 nm. Whereas the spectrum of $\text{Cu py}_4(\text{H}_2\text{PO}_4)_2$ and $\text{Cu pic}_4(\text{H}_2\text{PO}_4)_2$ contained a dominant absorption at 650 nm with an unresolved shoulder at 800 nm, the corresponding complexes of type II (with HPO_4) have the dominant absorption at 700 nm with the shoulder shifting towards longer wavelengths. This suggests a greater axial distortion in the later complexes.

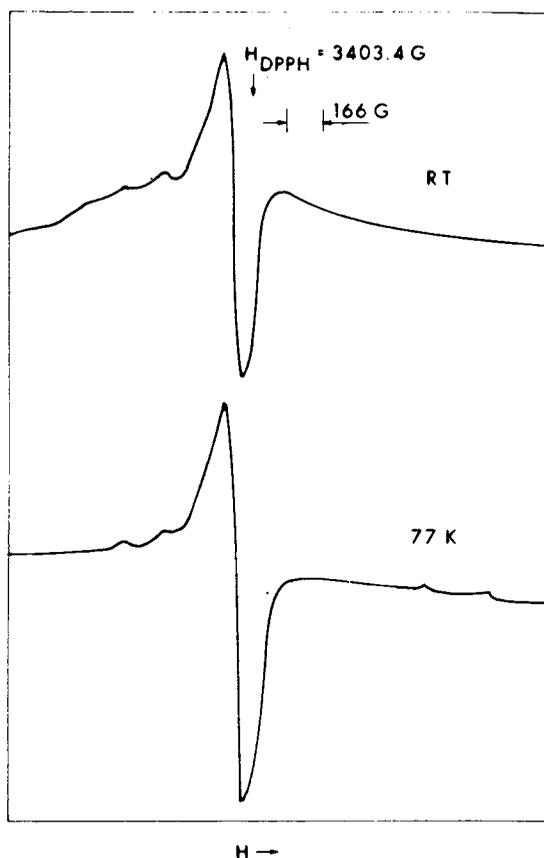


Figure 2. EPR spectrum of $\text{pic}_4(\text{H}_2\text{PO}_4)_2$ at room temperature and at 77 K.

3.2 Discussion

From the ESR spectra of $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ complexes, the g values observed for the $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ complex at 77 K ($g_{\parallel} > g_{\perp} > 2.0$) shows that the unpaired electron has predominant $(x^2 - y^2)$ character. This suggests that the Cu(II) ion in the complex has *trans* octahedral geometry with elongation along the z -axis. The dynamic behaviour at room temperature resulting in an isotropic spectrum and the anisotropy at 77 K were interpreted as being due to temperature dependent motional effects of CuL_4O_2 chromophore resulting in averaging of anisotropies at room temperature. This can be visualised either as temperature dependent hindered motion or temperature dependent vibronic coupling (Hathaway *et al* 1981). Lowering the temperature of such complexes leads to the freezing out of the dynamical distortions and, in certain cases, such a process is accompanied by first-order structural phase transition (Hathaway *et al* 1981). DSC experiments indicated phase transition at 147 K with a sharp peak, in the case of $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ (figure 3), but the ESR spectra taken at this temperature have not shown any changes. Therefore the structural phase transition observed at 147 K from DSC does not appear to result in the distortion in the immediate coordination

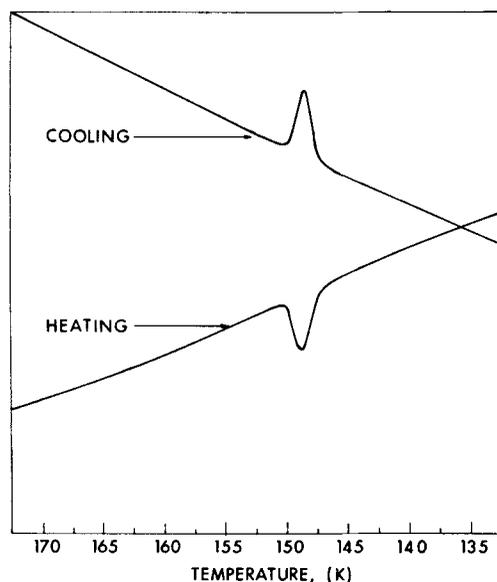


Figure 3. DSC scan of $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ below room temperature.

around the Cu(II) ion. The ESR spectra of $\text{Cu}(\text{L})_4(\text{HPO}_4)$ complexes were found to be essentially temperature independent. DSC experiments indicated the absence of any phase changes in the temperature range 300 to 77 K. The ESR spectrum of $\text{Cu}(\text{pic})_4(\text{H}_2\text{PO}_4)_2$ (figures 2a,b) showed an axial spectrum both at room temperature and at 77 K, with well-resolved hyperfine structure. DSC experiments have not shown any peaks in the range 300 to 77 K. The g values ($g_{\parallel} > g_{\perp} > 2$) indicate an elongated octahedron with $d(x^2 - y^2)$ as the ground state. The A_{\perp} and A_{\parallel} values obtained for this complex are in agreement with those reported for tetragonally distorted $\text{Cu}(\text{py})_4(\text{CF}_3\text{COO})_2$ complexes (Pradillas *et al* 1979). The very little variation of the ESR spectrum with temperature indicates that the coordination around Cu(II) in this complex is essentially static in nature. The room temperature magnetic moment values for all these $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ and $\text{Cu}(\text{L})_4(\text{HPO}_4)$ complexes are in the range expected for the octahedral complexes.

The far IR spectra of $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ complexes showed two bands in the region $350\text{--}200\text{ cm}^{-1}$, conforming to *trans* octahedral stereochemistry (D_{4h}), which is also consistent with the evidence from the ESR data, whereas the far IR spectra of $\text{Cu}(\text{L})_4(\text{HPO}_4)$ complexes showed a large number of bands conforming to *cis* octahedral stereochemistry. The metal-nitrogen and metal-oxygen stretching modes for these complexes have been assigned in accordance with the reported data. Although two copper-oxygen stretching bands are expected in the case of $\text{Cu}(\text{L})_4(\text{HPO}_4)$ complexes, only one broad band is observed in each case. It is perhaps possible that the other band might have been obscured in the broad envelope.

The broad electronic absorption band obtained in the case of $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ complexes, and the splitting of this band with a pronounced shoulder in the case of $\text{Cu}(\text{L})_4(\text{HPO}_4)$ complexes, indicating a greater distortion of the octahedral

geometry, are in accordance with the reported observations for this type of complexes (Pradillas *et al* 1979; Hathaway *et al* 1981).

4. Conclusions

ESR and IR have shown that the complexes $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ and $\text{Cu}(\text{pic})_4(\text{H}_2\text{PO}_4)_2$ have coordinating H_2PO_4 groups in the *trans* positions and py/pic molecules in the equatorial plane. The electronic and ESR spectral features similar to the above complexes have also been observed for the elongated *trans* octahedral $\text{Cu}(\text{py})_4(\text{CF}_3\text{COO})_2$ complex (Pradillas *et al* 1979), and thus the $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ complexes are also expected to have similar structures. It is interesting that the stereochemistry of $\text{Cu}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ is fluxional in nature, while that of $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ is essentially static. This is probably due to the presence of hydrogen-bonding between the hydrogen of the methyl group in picolene and phosphate ions. The differences in the IR and electronic spectral data of $\text{Cu}(\text{L})(\text{HPO}_4)$ complexes from that of $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ complexes have indicated a more distorted octahedron conforming to *cis* octahedral stereochemistry for the former complexes. Spectral features similar to $\text{Cu}(\text{L})_4(\text{HPO}_4)$ complexes have also been observed in the *cis* octahedral $\text{Cu}(\text{II})$ complexes (Hathaway *et al* 1981). Although axial spectra are expected for the *cis* octahedral $\text{Cu}(\text{II})$ complexes, only temperature independent isotropic spectra were observed for the $\text{Cu}(\text{L})(\text{HPO}_4)$ complexes. A similar observation was reported in the case of the $\text{Cu}(\text{L})_4(\text{H}_2\text{PO}_4)_2$ ($\text{L} = 1,10$, phenanthroline) complex at room temperature (Sastry *et al* 1984), although at 77 K the phen-complex gave an anisotropic spectrum. A temperature lower than 77 K might be required to observe the anisotropy in the ESR spectra of the py/pic analogue.

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