COPPER(II) PHOSPHATE AND ARSENATE COMPLEXES WITH ETHYLENEDIAMINE AND PROPYLENEDIAMINE*

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Coordination complexes of copper(II) phosphate and arsenate with ethylenediamine and propylenediamine have been prepared. The general molecular formulae are shown to be $[CuL_2]_3(PO_4)_2$ and $[CuL_2]_3(AsO_4)_2$. Infrared and visible absorption spectra show bands in the vicinity of 3300 cm^{-1} and 16000 cm^{-1}, respectively.

Experimental

The complexes were prepared by the following method: 1 g of powdered copper(II) phosphate or arsenate was suspended in 10 ml of acetone (A.R.). A little more than the calculated quantity of diamine was added. The reaction mixture was shaken for two days, kept overnight in a refrigerator, filtered, and washed several times with acetone and dried over P_4O_{10}.

(i) *Bis(ethylenediamine)copper(II) Phosphate*, $[Cu\ en_2]_3(PO_4)_2$

The complex is blue-violet in colour and soluble in water, nitrobenzene, and formamide (Found: Cu, 25·4; N, 22·6; base, 48·8; PO_4, 25·3. Calc. for $C_{12}H_{48}Cu_3N_{12}O_8P_2$: Cu, 25·7; N, 22·7; base, 48·6; PO_4, 25·7%).

(ii) *Bis(propylenediamine)copper(II) Phosphate*, $[Cu\ pn_2]_3(PO_4)_2$

The complex is violet in colour and soluble in water, nitrobenzene, and formamide (Found: Cu, 22·9; N, 20·1; base, 53·5; PO_4, 23·2. Calc. for $C_{18}H_{60}Cu_3N_{12}O_8P_2$: Cu, 23·1; N, 20·4; base, 53·85; PO_4, 23·05%).

(iii) *Bis(ethylenediamine)copper(II) Arsenate*, $[Cu\ en_2]_3(AsO_4)_2$

The complex is blue in colour and soluble in water and formamide (Found: Cu, 23·0; N, 20·1; base, 43·2; AsO_4, 33·3. Calc. for $C_{12}H_{48}As_2Cu_3N_{12}O_8$: Cu, 23·0; N, 20·3; base, 43·5; AsO_4, 33·55%).

(iv) *Bis(propylenediamine)copper(II) Arsenate*, $[Cu\ pn_2]_3(AsO_4)_2$

The complex is similar to that of the ethylenediamine complex (Found: Cu, 20·6; N, 18·2; base, 48·7; AsO_4, 30·3. Calc. for $C_{18}H_{60}As_2Cu_3N_{12}O_8$: Cu, 20·9; N, 18·4; base, 48·7; AsO_4, 30·45%).

The total base was determined as outlined previously.[1] Infrared spectra were recorded on a Perkin–Elmer 137B spectrophotometer. Spectra were recorded in the NaCl region (4000–650 cm^{-1}). The KBr disk technique was used with the solid complexes. The visible absorption spectra were obtained from aqueous solutions with a Unicam SP500 instrument.

On the basis of analyses and conductance values (Table 1), the general molecular formulae are shown to be $[CuL_2]_3(PO_4)_2$ and $[CuL_2]_3(AsO_4)_2$ where L is ethylenediamine or propylenediamine.

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[1] Narain, G., *Can. J. Chem.*, 1966, **44**(8), 895.

Discussion

All complexes show a sharp absorption band in the vicinity of 3300 cm^{-1}, which is assigned to the NH-stretching vibration. In free aliphatic amines the band occurs at 3400 cm^{-1}. This negative shift of frequency is because of the coordination of the amine to the metal atom, thus resulting in the formation of a highly covalent M–N bond, which weakens the NH bond order.[2]

The arrangement of any four groups around a copper(II) ion has usually been found to be planar. The stabilizing energy as calculated by the energy level diagram is greater for a square planar than a tetrahedral structure, and hence it is

TABLE 1
CONDUCTANCES AND SPECTRAL DATA

	$[Cu\ en_2]_3(PO_4)_2$	$[Cu\ pn_2]_3(PO_4)_2$	$[Cu\ en_2]_3(AsO_4)_2$	$[Cu\ pn_2]_3(AsO_4)_2$
Conductance (mho)	430	433	460	428
NH stretching frequency (cm^{-1})	3290	3300	3295	3300
Negative shift with respect to amines (cm^{-1})	110	100	105	100
ν_{max} (cm^{-1})	16000	15870	16000	16000
Molar extinction coefficient	120	115	120	125

evident that unless ligands possess sufficient steric repulsions which can balance the decrease in crystal field stabilization energy, the tetracoordinated complex will not take a tetrahedral configuration. However, although such an arrangement is known[3] to occur in the case of $CuCl_4^{2-}$, the planar configuration is the usual one.

These complexes which are blue-violet in colour, dissolve in water to give blue solutions, which exhibit a single maximum in the vicinity of 16000 cm^{-1}. The position of this maximum depends on the intensity of the ligand field around the metal. Thus for $[Cu(H_2O)_4]^{2+}$ ion the maximum is observed at 12500 cm^{-1}. The successive replacement of water ligands by amines shifts the maximum from 12500 cm^{-1} to 16660 cm^{-1} for $[Cu\ amine_4]^{2+}$. This hypsochromic effect is due to the stronger ligand field environment produced around the metal which causes the absorption maximum to shift from far red to the middle of the red region of the spectrum.

[2] Svatos, G. F., Sweeny, D. M., Mizushima, S., Curran, C., and Quagliano, J. V., *J. Am. chem. Soc.*, 1957, **79**, 3313.

[3] Felsenfeld, G., *Proc. R. Soc.* A, 1956, **236**, 506.