

SOME STUDIES IN INORGANIC COMPLEXES

VII. COPPER(II) WITH 2-PICOLYLAMINE

By G. J. SUTTON*

[Manuscript received January 5, 1960]

Summary

A study has been made of the bis(2-picolylamine) copper(II) complex in association with various anions. Of the salts investigated, the chloride, bromide, and nitrate are blue, the iodide is green, and the perchlorate and tetraiodomercurate are purple. Blue solutions are obtained in water, and the molecular absorption spectra are identical and are characteristic of bispicolylamine copper(II) ion. However, conductance measurements in methanol and nitromethane show that there is some metal halogen bonding for the iodide, and this is also indicated by a slight shift in the absorption spectrum to longer wavelengths in the same solvents. The mean magnetic moment of the copper atom in the complexes was found to be 1.93 B.M.

I. INTRODUCTION

The violet-blue chelate bis(2-picolylamine) copper(II) ion is formed instantaneously in aqueous solution by allowing the base to react with copper salt. On shaking and allowing to stand, the complexes are precipitated as crystalline plates even in the case of the nitrate, at semimolar concentration. The salts are less soluble than the corresponding ethylenediamine complexes and the purple perchlorate and tetraiodomercurate may be of analytical value. The chloride, bromide, and nitrate are bright blue, whilst the iodide is green. With the exception of the very insoluble tetraiodomercurate, the salts at millimolar concentration in water give an identical blue colour and absorption spectra (Table 1), and conductances in water show that under these conditions the anions are free (Table 2). However, since the iodide only was found to be sparingly soluble in methanol and nitromethane, it was decided to carry out conductance measurements and measurements of absorption spectra in the visible spectrum in these solvents. Even at the necessarily low concentrations ($4 \times 10^{-4}M$), there is incomplete ionization of halogen (Table 2) and a shift of absorption to longer wavelength (Table 1). Although X-ray information is not available, the results indicate that an octahedral arrangement may exist in the solid state for the iodide. This has also been proposed by Figgis and Harris (1959) for an analogous copper(II) bromide complex of *o*-phenanthroline. It is interesting to observe that when the complex cation is coupled with perchlorate or tetraiodomercurate anions the salts are purple in colour. Since it is unlikely that any coordination by the anions takes place, the cation is probably a tetravalent

* School of Chemistry, University of New South Wales, Granville College, Sydney.

square complex which can be octahedral in aqueous solution by solvent molecules. It is also noteworthy that none of the complexes investigated contains water molecules in the crystal state. Magnetic measurements were carried out, since Ray and Sen (1948) observed that red-yellow copper(II) complexes have a magnetic moment of 1.7–1.9 B.M., whilst those which are green-blue have moments of 1.9–2.0 B.M. It was found that even with the magnetically dilute

TABLE 1
ABSORPTION SPECTRA OF COPPER(II) COMPLEXES AT $2.00 \times 10^{-4}M$

Substance	Maxima	Minima	Solvent
Cu pic ₂ ⁺⁺	595	450	Water
Cu pic ₂ I ₂	595	450	Water
Cu pic ₂ I ₂	610	475	Methanol
Cu pic ₂ I ₂	615	475	Nitromethane

TABLE 2
MOLECULAR CONDUCTANCES OF COPPER(II) COMPLEXES AT $10^{-3}M$ AT 25 °C

Substance	Ω^{-1}	Solvent	Substance	Ω^{-1}	Solvent
Cu pic ₂ Cl ₂ ..	258	Water	Cu pic ₂ I ₂ ..	216	Water
Cu pic ₂ Br ₂ ..	239	Water	Cu pic ₂ I ₂ ..	73	Methanol*
Cu pic ₂ (NO ₃) ₂ ..	242	Water	Cu pic ₂ I ₂	36.9	Nitromethane*

* $4 \times 10^{-4}M$ concentration.

TABLE 3
MAGNETIC SUSCEPTIBILITIES OF COPPER(II) COMPLEXES CORRECTED TO 20 °C

Substance	$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	$\chi_M \times 10^{-6}$	μ (B.M.)
Cu pic ₂ Cl ₂	4.18	1465	1587	1.94
Cu pic ₂ Br ₂	3.26	1435	1578	1.93
Cu pic ₂ I ₂	2.56	1368	1551	1.92
Cu pic ₂ (NO ₃) ₂ ..	3.65	1473	1585	1.93
Cu pic ₂ HgI ₄	1.29	1277	1570	1.92

tetraiodomercurate the magnetic moment for the copper atom was 1.93 ± 0.02 B.M., indicating considerable orbital contribution (Table 3). The salts of the complex were readily decomposed by dilute strong acids, and by boiling with strong alkali reduction to cuprous oxide resulted. Attempts to prepare pure copper(I) complexes directly or by reduction with hydroxylamine, hydrazine, or cyanide were unsuccessful, owing to the formation of cuprous oxide.

II. EXPERIMENTAL

The physical measurements were made in accordance with the methods outlined in previous papers of this series.

(a) *Bis(2-picolyamine) Copper(II) Chloride*.—Cupric chloride (1.35 g; 10mm) in water (10 ml) was treated with 2-picolyamine (2.16 g; 20mm) with shaking. The violet-blue crystalline powder which settled out from the blue solution was separated by centrifuging, washed with ethanol and ether, and dried at 105 °C (yield 3.28 g, m.p. 196 °C) (Found: Cl, 20.2; Cu, 18.0%. Calc. for $C_{12}H_{16}N_4Cl_2Cu$: Cl, 20.2; Cu, 18.2%).

(b) *Bis(2-picolyamine) Copper(II) Bromide*.—Cupric bromide (2.23 g; 10mm) in water (10 ml) was treated with 2-picolyamine (2.16 g; 20mm) and the above procedure repeated. Violet-blue crystals resulted (yield 4.05 g; m.p. 200 °C) (Found: Br, 36.1; Cu, 14.4%. Calc. for $C_{12}H_{16}N_4Br_2Cu$: Br, 36.4; Cu, 14.5%).

(c) *Bis(2-picolyamine) Copper(II) Iodide*.—Cupric chloride (1.35 g; 10mm) in water (10 ml) was treated with a mixture of lithium iodide (2.7 g) and 2-picolyamine (2.16 g; 20mm) in water (10 ml) and the green microcrystalline precipitate which formed treated as in (a) (yield 5.30 g, m.p. 208 °C) (Found: C, 27.1; H, 2.9; I, 47.1; Cu, 12.0%. Calc. for $C_{12}H_{16}N_4I_2Cu$: C, 27.0; H, 3.0; I, 47.5; Cu, 11.9%).

(d) *Bis(2-picolyamine) Copper(II) Nitrate*.—A solution of copper(II) nitrate (1.88 g; 10mm) in water was treated with 2-picolyamine (2.16 g; 10mm) as in (a). Violet-blue cubic crystals were obtained (yield 3.14 g, m.p. 256 °C (decomp.)) (Found: C, 35.4; H, 4.0; Cu, 15.7%. Calc. for $C_{12}H_{16}N_6O_8Cu$: C, 35.7; H, 4.0; Cu, 15.7%).

(e) *Bis(2-picolyamine) Copper(II) Perchlorate*.—Procedure (a) was repeated with the addition of sodium perchlorate (3.0 g) together with picolyamine (2.16 g) in water (10 ml). The purple microcrystalline powder which resulted was found to be almost insoluble in common organic solvents (yield 4.18 g) (Found: C, 30.3; H, 3.4; Cu, 13.2%. Calc. for $C_{12}H_{16}N_4Cl_2O_8Cu$: C, 30.1; H, 3.4; Cu, 13.8%).

(f) *Bis(2-picolyamine) Copper(II) Tetraiodomercurate*.—Copper nitrate (1.88 g; 10mm) in water (20 ml) was treated with 2-picolyamine (2.16 g; 10mm) and a solution of potassium tetraiodomercurate (7.9 g) in water (20 ml) added with stirring. The purple precipitate which formed was treated as in (a) (yield 9.8 g, m.p. 248 °C) (Found: Cu, 6.4; I, 51.0%. Calc. for $C_{12}H_{16}N_4I_4HgCu$: Cu, 6.5; I, 51.4%).

III. ACKNOWLEDGMENT

The author wishes to thank Dr. E. Challen of the Microanalytical Laboratory for carbon and hydrogen analyses.

IV. REFERENCES

- FIGGIS, B. N., and HARRIS, C. M. (1959).—*J. Chem. Soc.* **1959**: 855.
 RAY, P., and SEN, D. N. (1948).—*J. Indian Chem. Soc.* **25**: 473.