Complexes of Copper(II) with *o*-Carboxyphenyldiarylarsines

By S. S. SANDHU* and S. S. PARMAR

(*Department of Chemistry, Punjabi University, Patiala, India*)

ATTEMPTS to prepare copper(II) complexes with tertiary arsines have resulted in the formation of either copper(I) complexes with the tertiary arsines or copper(II) complexes with their oxides, owing to the easy reduction of copper(II) to copper(I) by arsenic(III).[1,2] We report the stabilization of copper(II) with the novel ligands, *o*-carboxyphenyldiphenylarsine and *o*-carboxyphenyldi-(*p*-tolyl)arsine. The reactions of copper(II)acetate monohydrate and these two ligands (alcohol, reflux) resulted in the separation of light green and bright green solids, respectively. Under similar conditions another ligand, *o*-carboxyphenyldimethylarsine gave a white crystalline solid. Efforts to obtain complexes of the oxides of these three ligands with copper(II) under similar conditions ended in failure. The complex of copper(II) with *o*-carboxyphenyldiphenylphosphine oxide was used to prepare the corresponding arsine oxide[3] complex. The elemental analyses for copper and arsenic(III), i.r. spectra, reflectance spectra, and magnetic measurements on the three complexes are consistent with the formulae:

$[Ph_2As{\cdot}C_6H_4{\cdot}CO_2]_2Cu$ (I),

$[(p\text{-}MeC_6H_4)_2As{\cdot}C_6H_4{\cdot}CO_2]_2Cu$ (II),

and $[Me_2As{\cdot}C_6H_4{\cdot}CO_2]Cu,2H_2O$ (III).

Distinction between complexes of ligands containing arsenic(III) and arsenic(V) was made by decomposing each complex in glacial acetic acid. Dilution with sufficient water precipitated, quantitatively, the ligand containing arsenic(III), which was separated, redissolved in acetic acid, and titrated against standard iodine solution. Millimolar solutions of copper(II) complexes in nitrobenzene behave as non-electrolytes. In order to establish the co-ordination of arsenic(III) with copper(II), solutions of both the complexes as well as the ligands in nitrobenzene were titrated with methyl iodide by a conductometric method. The conductance of the complexes did not show any increase while the conductance of solutions of the ligands did increase significantly (*cf.* ref. 4).

The complexes of copper(II) are paramagnetic with effective magnetic moments; (I), 1·64 and (II), 1·91 B.M. while the copper(I) complex (III) is diamagnetic. The absorption band for As–C$_{\text{aromatic}}$ lies between 1060—1100 cm.$^{-1}$ in the i.r. spectra of triphenylarsine and phenylarsonic acid.[5] For the ligands, *o*-carboxyphenyldiphenylarsine and *o*-carboxyphenyldi-(*p*-tolyl)arsine, the As–C$_{\text{aromatic}}$ stretching frequency has been observed at 1067 and 1066 cm.$^{-1}$, while bands at 1065 and 1064 cm.$^{-1}$ have been recorded in the spectra of the sodium salts of these ligands. For the copper(II) complexes these bands are shifted to 1080 and 1078 cm.$^{-1}$, probably owing to co-ordination of arsenic(III) with copper(II).[6] Similar shifts have been observed for the complexes of these ligands with cobalt(II), nickel(II), *etc.*, which have been shown to be octahedral by various physical methods such as reflectance spectra and magnetic susceptibility measurements at different temperatures.[7] The i.r. spectra of all these three complexes showed shifts in the antisymmetric and symmetric stretching frequencies of the carboxylate ion observed in the spectra of sodium salts of the three ligands. These shifts, together with the slight solubility of these complexes in various organic solvents, suggest a polymeric structure with distorted octahedral environments. This is supported by reflectance spectra of the copper(II) complexes (I) and (II), which are exactly similar. The spectra show a broad band around 800 mμ (820—780 mμ) which is comparable with the band at 833 mμ observed in the spectrum of ion $[Cu(H_2O)_6]^{2+}$ and is assigned to the electronic transition $^2T_{2g} \leftarrow E_g$.[8] The presence of water molecules in complex (III) has also been confirmed by i.r. spectra.

One of us (S. S. P.) thanks the Council of Scientific and Industrial Research, New Delhi, for financial support.

(*Received, May 6th*, 1968; *Com.* 562.)

---

[1] G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 47.
[2] R. S. Nyholm, *J. Chem. Soc.*, 1951, 1767, and references therein.
[3] K. Issleib and H. Zimmermann, *Z. anorg. Chem.*, 1967, **353**, 197.
[4] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 1961, 4433.
[5] N. B. Colthup, L. H. Daly, and S. E. Wiberlly, "Introduction to Infrared and Raman Spectroscopy", Academic Press, 1964, 413.
[6] G. B. Dacon and J. H. S. Green, *Chem. and Ind.*, 1965, 1031.
[7] S. S. Sandhu and S. S. Parmar, unpublished work.
[8] B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, 1966, 312.