

New Cu(I) Ethylenediamine Carbonyl Complex

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Summary Preparation of the mononuclear complex $[\text{Cu}(\text{en})\text{CO}]\text{Cl}$ and the binuclear complex $[(\text{en})\text{Cu}(\text{CO})_2\text{-Cu}(\text{en})]\text{Cl}_2$ is reported.

WELL characterized carbonyl complexes of copper(I) are not common, although it is known that copper(I) can bind carbon monoxide under various conditions.^{1,2} Brackman³ suggested that carbon monoxide co-ordinates to copper(I)-amine complexes in the Cu^I-catalysed oxidative coupling reactions of CO with certain amines. In view of the interest in reactions of this type we have attempted to isolate complexes of copper(I) with amines and carbon monoxide. Here we report the preparation of complexes of the type $[\text{Cu}(\text{en})\text{CO}]\text{Cl}$.

On mixing CuCOCl (1 mol) suspended in methanol in a closed vessel at 0 °C with ethylenediamine (0.5 mol) quantitative evolution of carbon monoxide takes place and a white solid compound is obtained which analyses as $\text{Cu}_2(\text{en})\text{Cl}_2$.

The i.r. spectrum of this solid shows bands in the region 1000–1200 cm^{-1} due to complexed ethylenediamine. Strong absorption at 1010 cm^{-1} suggests that the ethylenediamine molecule is a bridge between two metal atoms, and probably has a symmetrical *trans*-configuration.⁴

With CuCOCl (1 mol), partially dissolved in methanol, and of ethylenediamine (1 mol) at -30 °C, the solid dissolves and the original CO stretching vibration at 2090 cm^{-1} of the CuCOCl solution is replaced by a new strong band at 2080 cm^{-1} . A white precipitate which analyses as $\text{Cu}(\text{en})(\text{CO})\text{Cl}$

can be obtained by addition of light petroleum and diethyl ether to the solution at -30 °C. The i.r. spectrum of the compound (Nujol mull) shows a strong band at 2080 cm^{-1} , and the bands at 1000–1200 cm^{-1} typical of chelated ethylenediamine.⁵

Conductivity measurements in methanol at -25 °C indicate that the compound is a 1:1 electrolyte, and therefore must be formulated as the ionic complex $[\text{Cu}(\text{en})\text{-CO}]\text{Cl}$ (I).

When a methanolic solution containing CuCOCl and ethylenediamine in the mol ratio 1:1 was evaporated to dryness at -20 °C a white solid was obtained which again analysed as $\text{Cu}(\text{en})(\text{CO})\text{Cl}$. However, the i.r. spectrum of this compound showed a strong band at 1905 cm^{-1} which was attributed to bridging CO groups. Elemental analyses and i.r. spectra suggested that the compound can be formulated as a binuclear complex: $[(\text{en})\text{Cu}(\text{CO})_2\text{Cu}(\text{en})]\text{Cl}_2$ (II). If this compound is dissolved in methanol at temperatures higher than -30 °C, the band at 1905 cm^{-1} disappears and is replaced by a band at 2080 cm^{-1} as shown in the spectrum of (I). These data indicate that (I) and (II) exist in equilibrium in methanol solution, (I) prevailing at temperatures above -30 °C.

Work is in progress to elucidate the structures and reactivities of these compounds which we believe are the first well characterised copper(I) carbonyl complexes.

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