Interaction between CO_2 and Copper(II) Ephedrinates

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Summary The reaction of CO_2 with different Cu^{II} ephedrinates leads to incorporation of carbon dioxide into the ligand without formation of a metal–CO_2 bond.

RECENT work on transition-metal complexes containing small molecules has led to the discovery of a number of CO_2-carrier compounds.[1] The stability of these complexes is due almost entirely to back-donation from metal to ligand and it is clear from a theoretical point of view that the metal ion in these complexes must be in a lower oxidation state surrounded by highly basic ligands.

Vlčková and Bartoň have reported the formation of carbon dioxide complexes of several Cu^{II} ephedrine derivatives.[2] We feel, however, that their observations must be re-interpreted in accordance with the general requirements mentioned above, especially since their explanation was not totally convincing. Their reported hypsochromic shift (visible spectrum), for example, is too large compared with other CO_2-complexes, and the i.r. absorption maxima are identical with those of dissolved CO_2.

There are several further explanations for the incorporation of carbon dioxide into Cu^{II} ephedrine derivatives.

(a) Földi *et al.* have shown that in aqueous solutions $(\pm)$-ψ-ephedrine forms cationic, hydroxo complexes with the copper(II) ion.[3] These compounds easily react with CO_2 forming carbonates.

(b) In the presence of traces of water carbon dioxide can act as an acid causing the protonation of the ligand. Violet to green colour changes can be observed on the addition of acids to ethanolic solutions of Cu^{II} $(+)$-ψ-ephedrinate and can be reversed by bases.

(c) Carbon dioxide reacts with the ligand itself. The reaction of $(+)$-ψ-ephedrine with CO_2 was found to give a colourless oil containing 1 mole CO_2 per mole ephedrine. This compound is stable only under a carbon dioxide atmosphere and releases CO_2 quickly while standing in air. This observation is in accordance with the known fact that amines and amino-alcohols form carbamates with CO_2.[4] The carbamates are rather unstable, though co-ordination to a metal ion can stabilize them to a certain extent.

We conclude therefore, that there is no interaction between the Cu^{II} central ion of Cu^{II} ephedrinates and CO_2. Reaction of the amine group of the ephedrine ligands can account for all the observed phenomena, including the large hypsochromic shift in the visible spectrum. Owing to electronic requirements Cu^{II}-containing carbon dioxide carriers are unlikely to be discovered.

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