Adducts of Copper(II) Complexes with Carbon Dioxide

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Summary The reaction of carbon dioxide with the copper(II) chelates of (—)-ephedrine, ψ-ephedrine, *N*-ethylnorephedrine, and *N*-n-butylnorephedrine was studied; on the basis of spectrophotometric data and gravimetric and elemental analysis the formation of 1 : 1 adducts between carbon dioxide and these chelates is shown.

THE adducts of transition-metal complexes of Ru, Rh, Pt, and Ir[1] with carbon dioxide are known and a synthesis of Co–CO_2 complexes was recently reported.[2] The reactions of carbon dioxide with organometallic compounds of titanium[3] have also been described, but the adducts of carbon dioxide with copper(II) complexes have not been reported. We have found that the violet benzene solutions of the copper(II) chelates of (—)-ephedrine, ψ-ephedrine, *N*-ethylnorephedrine, and *N*-n-butylnorephedrine turn green on treatment with carbon dioxide. If the temperature is raised or nitrogen is passed into the solution, the violet colour is restored, a process which can be repeated several times. The spectral data on the copper(II) chelates and their adducts with carbon dioxide in the visible region are shown in the Table.

In the u.v., λ_{max} shifts from 260 to 250 nm when the methanolic solutions of the chelates are treated with carbon dioxide. The observed wavelengths of the absorption maximum are also reversible and this returns to 260 nm if the solutions are treated with argon.

In the i.r. spectrum of the adduct of copper(II) ephedrinate with carbon dioxide in benzene there is a medium-strong doublet at 2350 and 2380 cm^{-1} assignable to the ν_3 vibration of the carbon dioxide[4] molecule. The observed splitting of the band frequency ν_3 can be explained by the existence of a co-ordination bond between copper and carbon dioxide causing the equality of the bonds between carbon and oxygen in the molecule of carbon dioxide to be impaired.

Treatment of the copper(II) chelates in iso-octane or cyclohexane with carbon dioxide causes formation of a crystalline precipitate of the adducts of the chelates with carbon dioxide. The adducts of the copper(II) chelates with carbon dioxide in solution or in the crystalline form are stable in a carbon dioxide atmosphere. On standing in air carbon dioxide is released. The benzene solution of the copper(II) chelate of *N*-n-butylnorephedrine is sensitive even to the carbon dioxide of the air.

The equilibrium constant, *K*, for the formation of the adduct of carbon dioxide with copper(II) ephedrinate was determined spectrophotometrically in methanol at 500 nm. Using the modified equation of Benesi and Hildebrand[5] it was found that K is 198 lmol^{-1} at 10° and 38 lmol^{-1} at 18°. The results of elemental analysis of the crystalline product of the reaction between carbon dioxide and copper(II) ephedrinate are in agreement with the existence of a 1:1 adduct. Similarly, gravimetric estimation of the carbon dioxide liberated from the adduct with copper(II) ephedrinate has shown that carbon dioxide and chelate are bound in the molar ratio 1:1.

Table

Visible spectra of copper(II) *chelates in benzene at* 20°

Copper(II) chelate of	λ_{max}/nm[a]	ϵ/(l mol^{-1} cm^{-1})	λ_{max}/nm[b]	ϵ/(l mol^{-1} cm^{-1})
(−)-Ephedrine ..	514	155	700	74
ψ-Ephedrine ..	500	121	700	82
N-Ethylnorephedrine	518	98	690	48
N-n-Butylnorphedrine	525	60[c]	660	41[c]

[a] For [Cu^{2+}] = 5 × 10^{-3} M. [b] In the presence of CO$_2$. [c] Approximate value since the chelate could not be prepared in crystalline form.

The copper(II) chelates of (−)-ephedrine, ψ-ephedrine, N-ethylnorephedrine, and N-n-butylnorephedrine are soluble in non-polar solvents such as benzene, cyclohexane, and iso-octane in spite of the fact that they contain lyophilic groups. It has been proved that copper(II) ephedrinate in the crystalline form as well as in non-polar solvents associates with itself to form a trimer.[6] The equilibrium trimer $\rightleftharpoons$ monomer shifts with increasing polarity of the solvent to the right. For the methanolic solutions of copper(II) ephedrinate the Lambert–Beer law is valid (the chelate is in the monomeric form) and is also valid for iso-octane and cyclohexane solutions (the chelate is in the trimeric form). The Lambert–Beer law holds for the adducts of these chelates with carbon dioxide in benzene and methanol solution.

On the basis of these phenomena it may be assumed that the formation of the adduct is possible only with the monomeric form of copper(II) ephedrinate. The prior dissociation of the trimeric form is therefore necessary for adduct formation.

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