ZUSAMMENFASSUNG

Eisen-(3) kann mit einer Lösung von Äthylendiamin-di-(*o*-hydroxyphenylessigsäure) titriert werden. Der Endpunkt wird photometrisch bestimmt. Die Fehler liegen meistens unter 1%. Eine Reihe von Metallen zeigt keine Störung der Titration.

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U.V. ABSORPTION SPECTRA OF 8-OXYQUINOLINE AND ITS COPPER CHELATE

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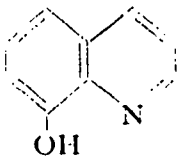
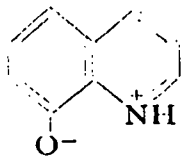
A comparative study of the absorption spectra of an organic ligand and its metal chelate can provide useful information regarding the nature of binding of the metal atom in the chelate. This has been shown by BASU AND CHATTERJEE[1,2] for chelates of acetyl acetone and quinoline 8-carboxylic acid. In the present communication the same method has been applied to secure information regarding the structure of the copper complex of 8-oxyquinoline.

In solution, 8-oxyquinoline should exist as I; despite the presence of the basic N atom in the molecule a zwitterion structure II is less probable in view of the weakly acidic character of the phenolic group.

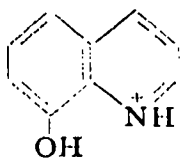


I

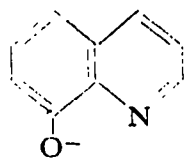


II

In acidic and alkaline media the molecule in all probability acquires the structures III and IV respectively.



III



IV

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In 95% ethyl alcoholic solution the free ligand has two absorption maxima at 242 mμ and 310 mμ (Fig. 1). In 0.1*N* KOH in 95% alcohol, the band at 242 mμ shifts to 256 mμ. The second band is broad and diffuse and may be looked upon as made up of two overlapping bands with maxima at 340 mμ and 370 mμ respectively (Fig. 1). In 0.1*N* perchloric acid the ligand band shows absorption maxima at 255 mμ, 310 mμ, 320 mμ and 370 mμ (Fig. 2). The copper chelate of 8-oxyquinoline shows two absorption maxima at 258 mμ and 395 mμ respectively (Fig. 2). The nature of the absorption curve is similar to that of the ligand itself but the 310-mμ ligand band is shifted to 395 mμ.

The chelate cannot be ionic, for the characteristic absorption band of the ligand in the alkaline medium is absent in the chelate. It cannot have a simple covalent structure (V) for this will put a positive charge on the N atom and the characteristic band of the ligand in the acid solution should be present in the chelate, while contrary is the case.

It is also important to account for the shift of the ligand absorption band at 310 mμ to 395 mμ in the chelate. Obviously this indicates a larger resonating path of the

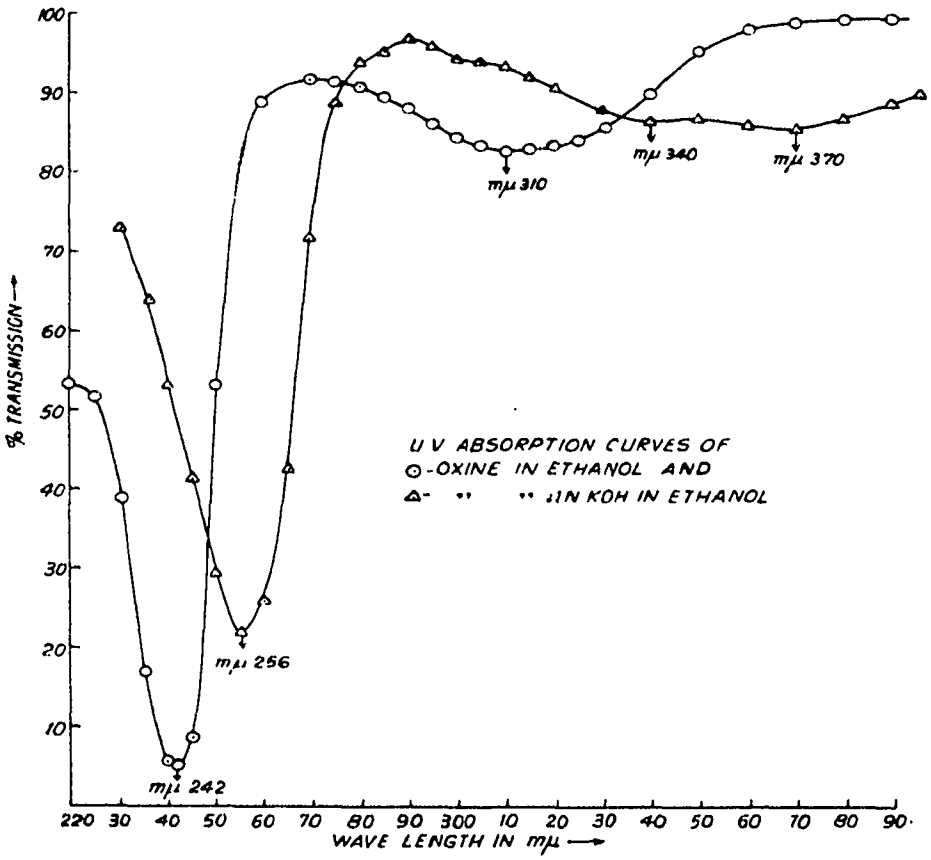

Fig. 1.

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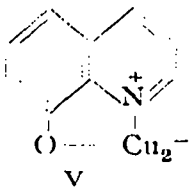
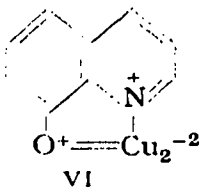
electrons in the chelate than in that of the ligand itself. All these characteristics can however be explained if the structure VI be accepted for the chelate.



V



VI

In this structure Cu is doubly bonded to oxygen and since the double bond is in conjugation with the double bonds in the ring system, the structure shows characteristic absorption of its own which we attribute to the 295-mμ band.

The structure, however, presupposes a planar configuration, in which copper is in dsp^2-hybridised state; the additional pπ–dπ bond possibly confers further stability to the planar structure.

MERRITT, CADY AND MUNDY[3] have cited X-ray evidence in favour of a tetrahedral configuration of anhydrous copper oxinate. The space group P $2_1/a$ reported by the last named authors apparently indicates that the molecule is non-centrosymmetric but this is not quite conclusive. Also an outer level sp^3-configuration for the copper complex should have considerable contribution from the ionic structure and the characteristic absorption band of the oxinate ion should be present in the chelate which is not actually the case.

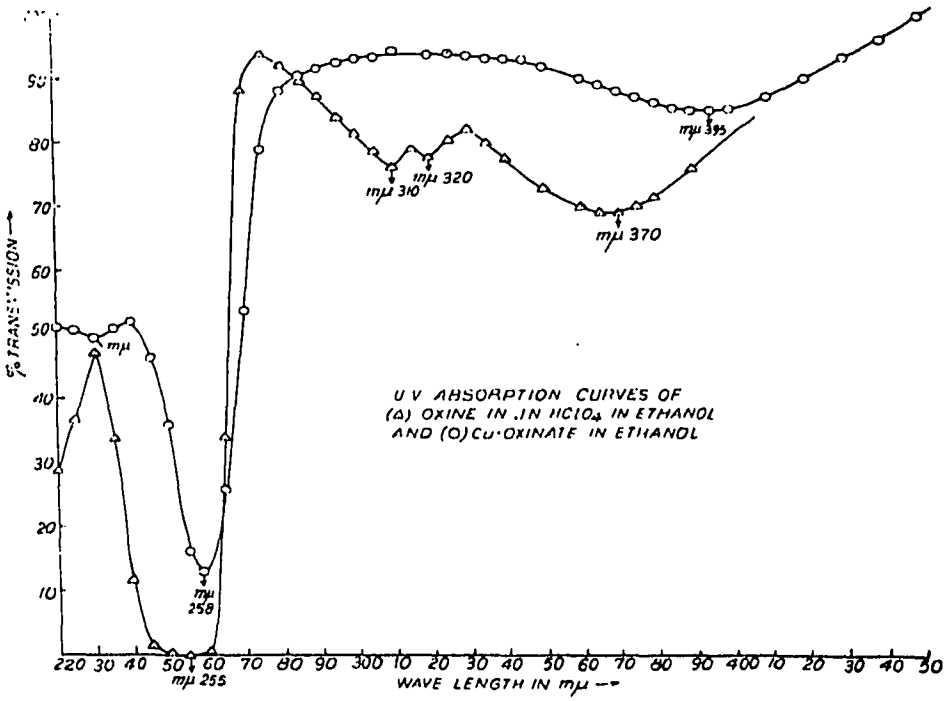


Fig. 2.

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The structural analogy of zinc oxinate dihydrate and copper oxinate dihydrate as implied by the above workers is not tenable. In the zinc compound itself for which sp^3–d^2-configuration has been suggested there is considerable difference between the polar and equatorial Zn–O bond distances, indicating the non equivalence of these bonds. Such octahedral sp^3–d^2-structure for the hydrated copper complex will be still less probable, since in this case the water molecules are more loosely bound than that of the zinc complex. This is indicated by the fact that whereas the zinc compound loses water at 135°, the copper complex is completely dihydrated at 105°. Further, it has recently been shown by JONES *et al.*[4] that in all probability there is π-bonding between metal and ligand in nickel-8-oxyquinoline chelate, which evidently presupposes a planar structure for the chelate. The possibility for such a planar structure is even greater in copper chelates.

Ultraviolet absorption measurements were carried out with the help of Beckman model D.U. quartz spectrophotometer using 1-cm quartz absorption cells. The alcohol used was refluxed for 6–8 h with solid caustic soda and distilled. It showed complete transmission down to 220 mμ. The concentrations of the solutions employed were 10^{-4}–$10^{-5}M$.

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SUMMARY

From a comparison of the U.V. absorption spectra of the copper chelate of 8-oxyquinoline in ethyl alcoholic solution with those of the ligand itself in the same medium and in the presence of 0.1*N* $HClO_4$ and 0.1*N* NaOH respectively, a probable structure for the former has been suggested. The structure presupposes a planar configuration for the complex and a metal–ligand double bonding.

RÉSUMÉ

Une étude a été effectuée en vue de déterminer la structure probable du chélate cuivre–hydroxy-8-quinoléine.

ZUSAMMENFASSUNG

Es wird eine Untersuchung zur Ermittlung der wahrscheinlichen Struktur des Kupfer–8-oxychinolats beschrieben.

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