The Structure of a Chelate of Copper(II) with 1-(2-Pyridylazo)-2-naphthol

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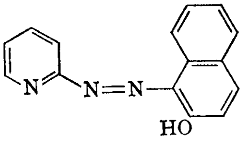
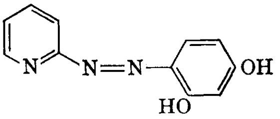
TERDENTATE complexing agents containing an azo-group, a heterocyclic nitrogen atom, and a hydroxy-group *ortho* to the azo-group, are used in the spectrophotometric and titrimetric determination of metal ions as well as in their separation by solvent-extraction techniques. Two of the most widely used reagents that belong to this class of compounds are 1-(2-pyridylazo)-2-naphthol (PAN) (I) and 4-(2-pyridylazo)resorcinol (PAR) (II).

It has been predicted that when chelation occurs between PAN and a metal ion such as copper(II), two five-membered chelate rings are formed.[1] The heterocyclic nitrogen, the hydroxy-group and the nitrogen atom farthest from the pyridine ring are involved in chelate formation. It has been suggested that PAR, on the other hand, may form a copper(II) chelate in which "the azo-group as a whole rather than one of the component nitrogen atoms," is co-ordinated to the copper(II).[2]

In potentiometric[3] and solvent-extraction studies[4] of the metal chelates of PAN and PAR it was found that the formation constant of the 1 : 1 copper–PAN chelate differed considerably from the formation constant that was obtained by a spectrophotometric method.[5] In the absence of a satisfactory explanation of this anomaly and in view of the lack of information on the structures of metal chelates of *o*-hydroxy-azo-dyes of analytical importance, we have begun a systematic investigation of the structures of these compounds. We report here the structure of the 1 : 1 copper–PAN chelate.

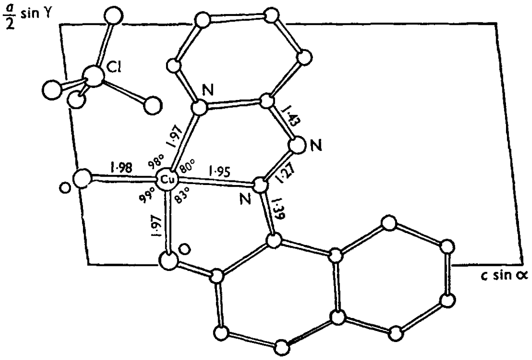


(I)



(II)

The reaction of copper(II) perchlorate with PAN in an ethanol–water medium gives a 1 : 1 as well as a 1 : 2 complex.[6] Single crystals of the 1 : 1 copper–PAN complex having the composition, $Cu(PAN),H_2O,ClO_4$ were isolated from an ethanol-water mixture. The compound crystallizes in the space group $P\bar{1}$; $a = 10{\cdot}38$, $b = 8{\cdot}22$, $c = 9{\cdot}35$ Å, $\alpha = 85° 20'$, $\beta = 96° 48'$, $\gamma = 93° 19'$ and $Z = 2$. The relative intensities of 2076 independent reflections were estimated visually from equi-inclination Weissenberg photographs obtained with nickel-filtered Cu-K_α radiation, and the multiple film technique. The structure was solved in projection down the *a* and *b* axes by the heavy-atom method. All the atomic co-ordinates were refined with individual isotropic temperature factors by successive three-dimensional differential Fourier syntheses. The *R*-factor for the observed reflections is 13% at the present stage of the refinement. The structure of the molecule viewed down the *b* axis is shown in the Figure. The bond lengths and bond angles in the chelate rings are shown; their approximate standard deviations are 0·01 Å. The bond lengths and bond angles that are not shown have the expected values.



FIGURE

It is apparent that the ligand is terdentate, the pyridine nitrogen, the phenolic oxygen, and the nitrogen atom farthest from the heterocyclic ring being co-ordinated to the copper ion to form two five-membered chelate rings. The fourth co-ordination position is occupied by a water molecule. All the Cu–N and Cu–O distances are normal. The molecule is very nearly planar and this is undoubtedly why the 1 : 1 chelate is very stable.[5] The angles around the copper ion deviate considerably from 90° and consequently the chelate cannot be considered to be a square-planar chelate. It is significant that the double-bond character of the azo-group is preserved in the chelate ring and that there is essentially no delocalization of electrons in this chelate ring.

It is of interest to compare the stepwise formation constants that have been reported for the chelates of PAN with metal ions in the first transition series.[3] The stepwise formation constants of the manganese(II), nickel(II), and zinc(II) chelates are separated by less than a factor of ten. The second stepwise formation constant of the copper(II) chelate however, is smaller than the first formation constant by a factor of 10^7. If the reported stepwise formation constants for the copper chelates are valid,[7] the greatly reduced stability of the 1 : 2 copper–PAN chelate must be attributed to the molecule of PAN acting as a bidentate rather than a terdentate ligand.

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