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The Stability of Bis(8-quinolinolato)copper(II)

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Synopsis. The IR spectra of the titled and related compounds have been measured, and the stabilities of the chelates characterized by the relative strengths of the metal-nitrogen bonds. An explanation has been made by comparing the extraction behavior of Cu(II) and Fe(III) chelates.

The stability constants for several metal complexes of 8-quinolinol and related substances have been determined by Irving and Rossotti, and the contribution of the metal-nitrogen bonds to the stability of the copper(II) complex of 8-quinolinol demonstrated although no experimental evidence was presented.[1)]

In the work described below, the stability of the metal chelate has been characterized through the effect of the methyl group of the 8-quinolinol skeleton on the metal-nitrogen bonds.

Experimental

Reagents and Apparatus. 8-Quinolinol was obtained from Wako Pure Chemicals. The methyl derivatives of 8-quinolinol were prepared as described by Phillips and Merritt,[2)] and the purity confirmed through melting point measurements, elemental analysis, IR, and NMR spectra.

The IR spectra were measured by a Nippon Bunko IR-F type spectrophotometer. Samples were in the form of Nujol mulls between polyethylene sheets.

Determination of Acid Exponents for the Reagents. The distribution ratios of 8-quinolinol and the methyl derivatives between chloroform and the aqueous phase of $\mu=0.2$ ($NaClO_4$) were measured at 20 °C as a function of pH, and the distribution data analysed according to Dyrssen.[3)]

Synthesis of Copper(II) Complexes. An ethanolic solution of 8-quinolinol and an aqueous solution of copper(II) acetate were mixed in a molar ratio of 2 to 1, and the mixture allowed to stand for two days. The resulting precipitate was filtered, washed with ethanol and dried over a steam bath. The anhydrous copper(II) complexes of the methyl-substituted 8-quinolinols were obtained according to the above procedure.

Extraction Curves. An aqueous solution ($\mu=1.0$: $NaClO_4$) of copper(II) or iron(III) was equilibrated with an equal volume of chloroform containing the reagent (5.0×10^{-3} mol dm^{-3}), the pH of the aqueous phase and the absorbance of the organic phase being measured after separation.

Results and Discussion

The values of the partition coefficients D_R, acid exponents pK_{OH} and pK_{NH} for 8-quinolinol and the methyl-derivatives are given in Table 1, the data of which are in good agreement with the literature values.[4)] The pK_{HO} values for the methyl derivatives are similar whereas the pK_{NH} values increase in the order; 8-quinolinol <5-methyl-8-quinolinol <4-methyl-8-quinolinol. The inductive and resonance effects due to the methyl-group are reflected in the above trend, and thus the stability of a metal complex can be predicted by choosing an appropriate derivative.

Table 1. Equilibrium constants for 8-quinolinol and its derivatives

Reagent	log D_R	pK_{OH}	pK_{NH}
8-Quinolinol	2.37±0.02	9.77±0.10	4.67±0.14
4-Methyl-8-quinolinol	2.65±0.05	10.28±0.19	5.23±0.17
5-Methyl-8-quinolinol	2.83±0.02	10.10±0.21	5.05±0.09

Table 2. Most important IR absorption bands for copper(II) complexes

Ligand	$\bar{\nu}$/cm^{-1} Cu–O	$\bar{\nu}$/cm^{-1} Cu–N
8-Quinolinol	325	290
4-Methyl-8-quinolinol	326	310
5-Methyl-8-quinolinol	321	300

The assignments of the $\bar{\nu}$(Cu–O) and $\bar{\nu}$(Cu–N) frequencies were conducted according to the work of Ohkaku and Nakamoto,[5)] and the results are summarized in Table 2. It should be noted that the bis(8-quinolinolato)copper(II) obtained by the above procedure was of the β-type, which is known to be a dimer having bridged oxygen atoms. As seen from Table 2, the effect of substitution is negligible on the $\bar{\nu}$(Cu–O) frequency indicating that the stability of bis(8-quinolinolato)copper(II) may depend on the strength of the metal-nitrogen bonds. The increasing order of the pK_{NH} values supports the increasing order of the $\bar{\nu}$(Cu–N), strongly suggesting that the stability for the copper(II) complex is mainly due to the metal-nitrogen bonds.

In order to examine the stability of the copper(II) complex in solution, solvent extraction studies were conducted and the extraction behavior of copper(II) compared with that of iron(III) which is a harder acid than copper(II). The extraction curves for iron(III) obtained by using 8-quinolinol and the methyl derivatives were almost identical, which were shown by a single curve having a $pH_{1/2}$ of 1.54±0.05. A notable effect of the substituent on the extraction of copper(II) was however, observed, and $pH_{1/2}$ values decreased in the following order; 8-quinolinol ($pH_{1/2}=2.0$)>5-methyl-8-quinolinol(1.90)>4-methyl-8-quinolinol(1.76).

The above differences in extraction behavior of the metals may be caused by a difference in the acid strength between the ions. The metal-oxygen bonds in tris(8-quinolinolato)iron(III) play an important role in stabilizing the complex. In contrast, the stability for the copper(II) complex depends mainly upon the metal-nitrogen bonds, as is shown by the present IR studies.

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