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THERMAL DEAQUATION OF SOME 2-METHYL-8-QUINOLINOL CHELATE HYDRATES

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ABSTRACT

Chelate hydrates of Mg(II), Co(II), Ni(II), Cu(II), and Zn(II) with 2-methyl-8-quinolinol were studied by thermogravimetry, differential scanning calorimetry, and high temperature reflectance spectroscopy to determine the heats of deaquation and energy of activation of the reaction, and the changes in spectra upon deaquation. Heats of deaquation were found to be lower and energies of activation to be higher than for the corresponding 8-quinolinol chelate hydrates. The reflectance spectra of the anhydrous chelates of 8-quinolinol and 2-methyl-8-quinolinol were found to be very similar, but significant differences in the spectra of the corresponding chelate hydrates were noted. Differences in the thermal properties of the chelates were attributed to differences in bond strength, steric hindrance, and crystal structure.

INTRODUCTION

In earlier work done at this laboratory[1], the paucity of thermal data on the properties of 8-quinolinol chelate hydrates was noted. Data on the heats of deaquation, the energy of activation for the deaquation, and the changes in the high temperature reflectance spectra of the 8-quinolinol chelate hydrates of copper(II), cobalt(II), cadmium(II), nickel(II), manganese(II), zinc(II) and magnesium(II) were presented. In a related class of chelate hydrates, those of 2-methyl-8-quinolinol, there is also an absence of work on the thermal properties of the complexes. Borrel and Paris[2,3] studied the thermal properties of the 2-methyl-8-quinolinol complexes of copper(II), zinc(II), magnesium(II) and nickel(II) but their work was limited to a correlation of chelate structure with the procedural decomposition temperature.

The purpose of the present investigation is to study the thermal deaquation of the 2-methyl-8-quinolinol chelate hydrates of zinc(II), magnesium(II), copper(II), cobalt(II) and nickel(II). Data presented include the heats of deaquation, the kinetics of the deaquation reaction, and the high temperature reflectance spectra of the hydrated and anhydrous chelates.

EXPERIMENTAL

Preparation of complexes

The 2-methyl-8-quinolinol was obtained from the Aldrich Chemical Co. and was purified by recrystallization from water–ethanol solution, after treatment with decolorizing charcoal. All metal salts, solvents, and other materials were of reagent quality and were used without further purification. The general method of preparation of the complexes was by precipitation with ammonium hydroxide from a buffered water–ethanol solution of 2-methyl-8-quinolinol and the appropriate metal salt. The precipitated complexes were collected on a Buchner filter, washed three times with distilled water, and then air dried for 24 h at room temperature.

Analysis of complexes

Water content of the complexes was determined by mass-loss on the thermobalance. Metal content was determined by decomposition of the complexes with oxalic acid and then ignition to the metal oxide. The analytical data are given in Table I.

Instruments and technique

All TG work was done using a DuPont Model 950 thermogravimetric analyzer. A heating rate of 10°C/min and a dynamic nitrogen atmosphere were used for all analyses.

The techniques used for the collection of calorimetric and high temperature reflectance data were reported previously[1].

TABLE I

ANALYSIS OF COMPOUNDS

Compound	*%Metal*		*% Water*	
	Found	*Theor.*	*Found*	*Theor.*
$Co(MeOx)_2 \cdot H_2O$	14.7	14.99	5.0	4.58
$Ni(MeOx)_2 \cdot 1.5H_2O$	14.6	14.45	7.2	7.64
$Cu(MeOx)_2 \cdot 1.5H_2O$	15.5	15.62	6.4	6.64
$Zn(MeOx)_2 \cdot H_2O$	15.4	15.35	4.9	4.51
$Mg(MeOx)_2 \cdot 2H_2O$	6.4	6.46	10.7	9.57

MeOx, 2-methyl-8-quinolinol.

RESULTS AND DISCUSSION

Heats of deaquation

The heats of deaquation of the chelate hydrates are given in Table II.

Kinetics of deaquation

The activation energies, E_a, for the deaquation of the chelate hydrates were determined by the TG method proposed by Broido[4]. The activation energies are given in Table III, while the kinetics plots are shown in Fig. 1.

TABLE II

HEATS OF DEAQUATION OF CHELATE HYDRATES

Compound	*ΔH, kcal*	
	per mole of complex	*per mole of H_2O*
$Co(MeOx)_2 \cdot H_2O$	15.8 ±0.8	15.8 ±0.8
$Ni(MeOx)_2 \cdot 1.5H_2O$	14.0 ±0.7	9.4 ±0.5
$Cu(MeOx)_2 \cdot 1.5H_2O$	14.4 ±0.7	9.6 ±0.5
$Zn(MeOx)_2 \cdot H_2O$	17.9 ±0.9	17.9 ±0.9
$Mg(MeOx)_2 \cdot 2H_2O$	24.4 ±1.0	12.2 ±0.6

TABLE III

DEAQUATION ACTIVATION ENERGIES OF CHELATE HYDRATES

Compound	*E_a, kcal/mole*
$Co(MeOx)_2 \cdot H_2O$	32 ±3
$Ni(McOx)_2 \cdot 1.5H_2O$	35 ±4
$Cu(MeOx)_2 \cdot 1.5H_2O$	34 ±3
$Zn(MeOx)_2 \cdot H_2O$	40 ±4
$Mg(MeOx)_2 \cdot 2H_2O$	23 ±2

HTRS and DRS data

The HTRS and DRS curves of $Zn(MeOx)_2 \cdot H_2O$ are shown in Figs. 2 and 3, respectively. All of the compounds were studied by this technique, but these data will not be reproduced here.

GENERAL

There appears to be some correlation between the heats of deaquation and general coordination theory, but it does not seem as apparent as it was in the case of the 8-quinolinol chelate hydrates. When the comparison is made on the basis of the heats of deaquation of the complexes, the only correlation is between the magnesium complexes; the heats of deaquation of the other 2-methyl-8-quinolinol complexes are much lower than the corresponding 8-quinolinol complexes. A similarity is seen when the basis of comparison is that of the heats of deaquation in kcal/mole of water for the 8-quinolinol complexes with similar data for the 2-methyl-8-quinolinol complexes. Here the notable exception is that of the magnesium complexes. The selection of such a basis seems justifiable in that the comparison is then between complexes containing about the same amount of water of hydration.

The slightly lower heats of deaquation for the 2-methyl-8-quinolinol derivative can be explained on the basis of difference in the ligands. In the case of the 2-methyl derivative, the presence of the methyl group *ortho* to the ring nitrogen atom allows for an inductive effect which can increase electron density at the ring nitrogen. Therefore, the increased charge density there should allow a stronger coordinate bond to be formed with the metal ion. If the coordinate bond is stronger, then there

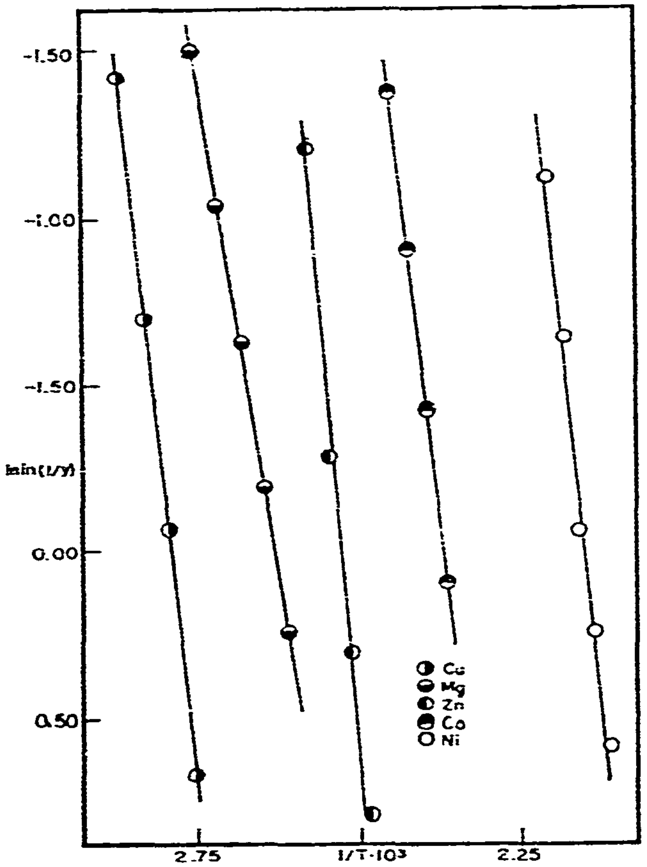

Fig. 1. Deaquation kinetics curves of chelate hydrates.

is less attraction for the electron pair of the water molecule; consequently, the water should be held less strongly than it would be in the absence of a methyl group, *i.e.*, as in the 8-quinolinol complexes. This argument could also be applied to the transition metals, the Co(II)- -Ni(II)- -Cu(II) compounds, where *d*-orbitals are available for bonding, but not to the complexes of magnesium(II), where such orbitals are not available, or to Zn(II), where *d*-orbitals are completely filled. For the magnesium(II) complex, it might be suggested that the relatively high charge density of the Mg^{2+} ion was not offset enough by the increase in electron density to decrease the attraction of the water molecules. There is also the possibility that the presence of the methyl group introduces a steric hindrance that limits the close approach of the ligand to the metal ion, and thereby offsets the advantage gained by the inductive effect of such an electron-donating group. The slightly higher heat of deaquation of the zinc(II) complex of 2-methyl-8-quinolinol, compared to that of the 8-quinolinol complex, can be accounted for on the basis of such a steric hindrance. Since Zn^{2+} is the largest ion of the first transition series, the close approach of the ligand would be limited by the methyl group; therefore, the bond could be weaker than expected, perhaps weaker even than that of the 8-quinolinol, and the water molecule could then approach more closely and thereby form a stronger bond.

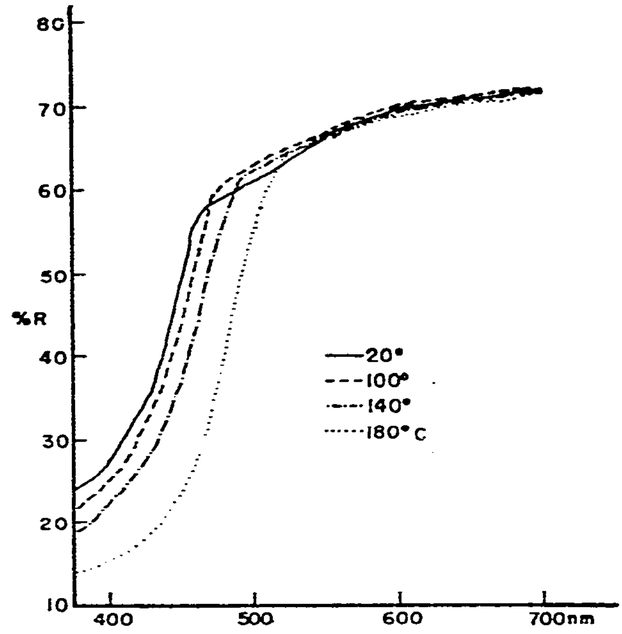

Fig. 2. HTRS curves of $Zn(MeOx)_2 \cdot H_2O$.

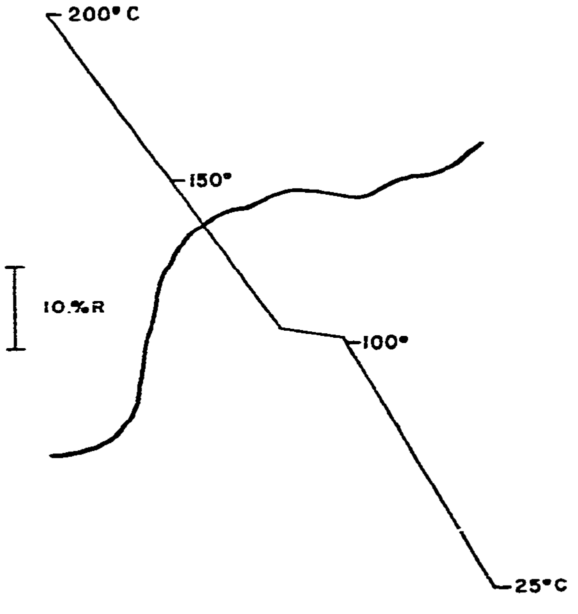

Fig. 3. DRS curve of $Zn(MeOx)_2 \cdot H_2O$ at 470 nm.

In all of the cases of the 2-methyl-8-quinolinol complexes which were studied, the activation energies for the deaquation reaction were found to be higher than those obtained for the corresponding 8-quinolinol complexes. The magnitude of the increase ranges from about 20% for the nickel(II) complex to about 70% for the zinc(II) complex.

The increase in activation energy is in accord with the increased thermal stability of the 2-methyl-8-quinolinol chelates. This increase, however, seems paradoxical when it is noted that the heats of deaquation for these complexes are lower than those found for the 8-quinolinol complexes. The implication of the increased activation energy is that the water is harder to remove from the 2-methyl-8-quinolinol chelate than from the 8-quinolinol chelate. This apparent contradiction might be accounted for in two ways. First, consider the difference in the composition of the complexes: the 8-quinolinol chelates, except for that of magnesium, are dihydrates. For the 2-methyl derivatives, the zinc(II) and cobalt(II) complexes are monohydrates, those of nickel(II) and copper(II) are one-and-a-half-hydrates, and the magnesium compound is a dihydrate. If the structural difference in the ligands is not considered, then the main difference between the two series of compounds is that of water content. Assuming that the lattice forces are about the same, then it is not unexpected that the attractions for a single molecule, or one-and-a-half molecules, of water would be greater than on two or more water molecules. Considering this, the lattice would require more thermal agitation (*i.e.*, a higher temperature) to open it up and allow the water to be removed. Second, there is the possibility that upon deaquation, the 2-methyl derivatives rearrange to a lower lattice energy configuration than do the 8-quinolinol chelates, and the energy difference then contributes to an apparent lowering of the heat of deaquation. It is also possible that some combination of these two hypothetical processes also occur. The difference in the activation energy could then be attributed to the different environments which the water molecules occupy in the complex. In the complexes of magnesium(II), cobalt(II) and zinc(II), which contain less water per mole of complex than do their 8-quinolinol complexes, the increased forces on the lesser number of water molecules then results in an increased activation energy. This is also true in the case of the complexes of copper(II) and nickel(II), but, since they contain more water relative to the 8-quinolinol complexes, the magnitude of the increase is less. For the copper(II) complex, the distortion produced by the Jahn–Teller effect is not sufficient to lower the activation energy.

The HTRS and DRS curves of the chelates studied are similar to those of the corresponding 8-quinolinol complexes. For the cobalt(II), nickel(II), and copper(II) complexes, the decrease in reflectance at the red end of the spectrum observed in the 8-quinolinol chelates is again present; however, the decrease in the copper(II) reflectance is greater, covering all of the red region and not merely involving the small band centered at 520 nm, as was observed in the 8-quinolinol chelate. The complexes of magnesium(II) and zinc(II), like their 8-quinolinol counterparts, do not exhibit a decrease in the red region of the spectrum but instead show a shift to longer wavelengths of the large absorption shoulder found in the blue end of the spectrum. The presence of the methyl group does not appear to have a major effect upon the position of absorption peak at the blue end of the spectra; however, there are noticeable changes in other portions of the spectra. In the magnesium(II) complex, the shoulder of the curve moves to longer wavelengths, from 475 nm in the 8-quinolinol complex to ~530 nm. There is also a slight dip in the curve at about 600 nm which is absent from the complex of the unsubstituted ligand. The zinc(II) complex, on the other hand, shows a blue shift; the shoulder is displaced from 500 nm to 475 nm in the 2-methyl-8-quinolinol complex. Copper(II) complex on the other hand shows a very large difference. The strong reflectance band at 520 nm is absent, and instead there is a slight hump in the curve centered at about 630 nm. This difference is striking even to the eye; the 8-quinolinol complex is a bright green, while the 2-methyl-8-quinolinol chelate is dull bronze color looking very much like powdered copper metal. There is also a marked difference in the spectrum of the cobalt(II) complexes. A fairly sharp peak at 620 nm occurs in the spectrum of the 2-methyl derivative, while no such artifact occurs in the spectrum of the 8-quinolinol complex. Again, a difference is readily apparent to the eye; the unsubstituted ligand complex is a dull yellow, while the other is a lustrous copper-bronze. The nickel(II) complex also exhibits a marked difference in the red region of the spectra. Again, a fairly sharp peak centered at ~575 nm is observed, that is absent from the spectrum of the complex of the unsubstituted ligand.

The spectra of the anhydrous complexes are very similar. It is the spectra of the hydrates species that show the differences mentioned above. The most notable difference is in the comparison of the spectra of the hydrated chelates of copper(II), nickel(II) and cobalt(II). Since these ions have *d*-orbitals available for bonding, a variation in the number of molecules of water may result in a change in type of bonding or coordination, or both. Changes in spectra commonly occur when there is a variation in the type of bonding or coordination. It has not been determined whether or not the spectra of the complexes arise from *d*–*d* transitions, from charge transfer, or both, nor has the structure of the complexes been determined. Exact assignment of the spectral artifacts must await the determination of these things.

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