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"DIELECTRIC POLARIZATION STUDIES OF METALLIC CHELATES"

by

Robert G. Charles and Henry Freiser

UNIVERSITY OF PITTSBURGH

CONTRACT NO. AT(30-1)-860

UNCLASSIFIED

17-71
MFC-24395

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4/25/51

The dielectric polarizations of dioxane solutions of lead 8-hydroxyquinolinate and disalicylidene-methylamine copper have been measured at 30° C. These compounds, as do the acetylacetonates, are found to have abnormally high atomic polarizations. It is possible that most metallic chelates exhibit this phenomenon. The solubilities of some metallic 8-hydroxyquinolates in benzene and dioxane at 25° C have also been measured.

This study was undertaken as part of an overall program designed to relate the structure of chelating reagents with their analytical behavior. It was decided to apply the dipole moment technique in order to correlate the charge distribution within the molecules of metallic chelates with their structures and stabilities. To be suitable for the present work, a metallic compound must have the following characteristics: 1) Definite composition. 2) It must be anhydrous and have no solvent of crystallization, with the possible exception of the solvent used in the measurement of polarization. 3) Sufficient solubility in such solvents as dioxane or benzene to permit accurate dielectric constant measurements.

Because of its analytical importance and the number of metals with which it combines, 8-hydroxyquinoline was first investigated. The limited solubilities of metallic 8-hydroxyquinolates in benzene and dioxane prevented the full use of these chelates and the metal salts of Schiff bases, which give similarly constructed chelates, were also investigated.

EXPERIMENTAL

Preparation and Purification of Materials. - Jones and Laughlin reagent-grade benzene was used after careful fractionation as described previously.¹ Car-

1. Keswani and Freiser, This Journal, 71, 218 (1949)

bide and Carbon Co. dioxane was purified by the procedure outlined in Weiss-
sodium before use.
berger and Proskauer² and distilled from/Lemke Co. 8-hydroxyquinoline was re-

2. Weissberger and Proskauer, ORGANIC SOLVENTS, The Clarendon Press (1935)

crystallized from alcohol and water and melted at 72.4° C. The metallic hydroxyquinolates were prepared by precipitation with oxine from an aqueous solution of the metal ion in the manner described by Welcher³ and were dried at the

3. Welcher, ORGANIC ANALYTICAL REAGENTS, Vol. 1, p. 265ff, D. VanNostrand Co., Inc., New York, 1947.

recommended temperature in a constant temperature oven. Salicylidene-methylamine copper was prepared from salicylaldehyde and methylamine as described by Pfeiffer⁴ and purified by recrystallization from alcohol and from dilute dioxane.

4. Pfeiffer, J. prakt. Chem. 153, 270 (1939)

The corrected melting point of the salt was found to be $158.4 - 159.2^{\circ}$ C. The purity of this compound was also established by the electrolytic determination of copper. The salt was decomposed by evaporation with a mixture of hydrochloric, nitric and sulfuric acids to fumes of sulfur trioxide and then diluted to a volume of 200 ml. and electrolyzed in the usual manner. Anal. Calculated for $C_{16}H_{16}O_2N_2Cu$; Cu, 19.15% Found: Cu, 19.15, 19.16, 19.08

Solubility of Metallic 8-Hydroxyquinolates.- The solubilities of a number of metallic 8-hydroxyquinolates in benzene and dioxane were determined by weighing the residue obtained from the evaporation of a weighed portion of the saturated solution. The solution was prepared by extracting the solid compound in a Soxhlet extractor, and allowing the solution to cool to room temperature. The results are summarized in Table I, where the solubilities are given in terms of mole fractions.

Dipole Moment Measurements and Calculations.- The dielectric polarizations of lead 8-hydroxyquinolate and of disalicylidene-methylamine copper were measur-

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ed in the manner previously described. The results are summarized in Table II where the dielectric constants, ϵ , and the densities, \underline{d} , of dioxane solutions containing mole fraction, f_2 , of the chelate are given along with the molar polarization and molar refraction. Because the solutions were colored no direct measurement of molar refraction was made. Calculation of molar refractions were made from appropriate group refractions.

Table I

Solubilities of Some 8-Hydroxyquinolates at 25° C

<u>Metal</u>	<u>Solvent</u>	
	<u>Benzene</u>	<u>Dioxane</u>
Lead	0.00013	0.0016
Cadmium	negligible	negligible
Uranium	-----	0.00051
Iron (III)	0.00028	-----
Copper (II)	0.000032	-----
Bismuth	-----	0.000428

The concentrations are given in terms of mole fractions.

Table II

Dielectric Polarization Data at 30° C

f_2	ϵ	d	P_2	MR_D	μ_{app}
Lead 8-Hydroxyquinolate					
0.0000	2.2310 ^a	1.0204			
0.0016 ^b	2.2363	1.0204	187	105.	2.0
Disalicylidene-methylamine Copper					
0.00000	2.2310	1.02039	-		
0.003453	2.2523	1.02406	158.		
0.006913	2.2700	1.02773	150		
0.008798	2.2839	1.02973	155		
0.01044	2.2905	1.03145	151	104.	1.22

a) determined by comparison with benzene

b) only one measurement was made due to the limited solubility of this compound

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DISCUSSION

The high degree of symmetry possessed by the structures of the two chelates whose dielectric polarization were determined make it unlikely that they should have significant dipole moments. While it would be possible that the lead compound has a tetrahedral arrangement around the lead, as is commonly found in lead compounds, and thus make a polar molecule, compounds of copper similar to the one studied have been shown to be planar.⁵ It would be possible

5. Cox, Wardlaw and Webster, J. Chem. Soc., 1936, 775

for a planar copper salt to have a moment if the molecule were of cis configuration (both nitrogen atoms on the same side) and indeed, disalicylidenemethylamine copper is known to exist in two crystalline forms. Of these two forms, the green modification (the one used) is the more stable and therefore is probably the trans.

It would appear from this discussion that the results might be reasonably interpreted in terms of the presence of abnormally high atomic polarization as has been observed by Finn, Hampson and Sutton⁶ for metallic acetylac-

6. Finn, Hampson and Sutton, J. Chem. Soc., 1938, 1254

tonates. The measurements reported here and those of Sutton and coworkers lead to the doubt of the existence of any metallic chelates which do not have any abnormally large atomic polarization. This unfortunately obscures the useful application of the technique of dipole moments to the evaluation of charge distribution in these interesting molecules. There does exist a possibility of evaluation of the dipole moment from the atomic polarization if the latter is viewed as arising from molecular oscillation as described by Coop and Sutton.⁷ Coop and Sutton propose an equation relating the atomic polarization to the dipole moment of half of the molecule and to the force constant associated with

the corresponding bending of the molecule. If the force constant could be evaluated from infrared absorption data then it should be possible to apply the Coop and Sutton⁷ equation to solve the dipole moment of half the chelate molecule. Without a knowledge of the force constants, atomic polarization

7. Coop and Sutton, *ibid.*, 1269

data could not give more than the qualitative order of the ring to metal moments of a series of salts of a given chelating agent or of a series of chelates of a given metal and this, only if it could be assumed that the force constants were of approximately of the same magnitude.

ACKNOWLEDGEMENT: The authors are grateful for the support of the Atomic Energy Commission, under whose grant this work was performed.

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