

A Dielectric Study of *Bis*-(2'-hydroxyacetophenonato)Copper(II)

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Abstract

The dielectric properties of dioxane solutions of the title compound were studied as a function of temperature. The differences between the total polarization and the molar refraction were found to be independent of temperature. This difference was attributed to atomic polarization, which might be caused by unusual freedom of bending and twisting of the chelate rings in the electric field. The dielectric properties and visible absorption spectrum of the title compound are similar to those of *bis*-salicylaldehyde-Cu(II) which has a symmetrical trans-planar structure in the solid state.

Molecules in an electromagnetic field in the radio frequency range exhibit a total dielectric polarization which is assumed to be composed of three additive components, each caused by a particular kind of induced motion: 1) orientation polarization due to motion of the molecule as a whole, 2) electronic polarization due to induced electron motion, and 3) atomic polarization, which is ascribed to field-induced bond length or bond angle distortion within the molecule. The orientation component P_o is absent if the molecule has no net dipole moment. The electron polarization P_E (or molar refraction) is obtained from refractive index measurements usually at visible light frequencies. Electron polarization is assumed to be temperature independent. The existence of atomic polarization P_A has been postulated because of a non-zero difference between the total polarization P_t as measured at radio frequencies and P_E for many symmetrical molecules. The atomic polarization component must be neglected or approximated for the calculation of a molecular dipole from P_T .

Many supposedly symmetrical molecules are known (3), however, in which the difference ($P_T - P_E$) is not negligible. Typical of such molecules is *bis*-(salicylaldehyde)Cu(II) (Fig. 1). In the present work we have studied the above compound for comparison purposes and also the related substance, *bis*-(2'-hydroxyacetophenonato)Cu(II) (Fig. 1), whose dielectric properties and structure have not been reported.

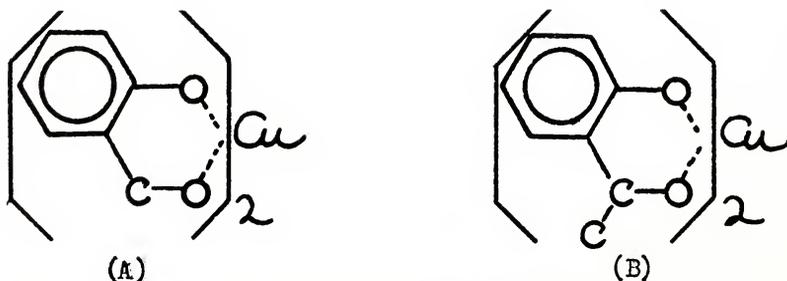


FIGURE 1. Skeletal structures of (A) *bis*-(salicylaldehyde)Cu(II) and (B) *bis*-(2'-hydroxyacetophenonato)Cu(II). No particular isomeric form of the complexes is implied here.

Experimental Procedures

Bis-(salicylaldehydato)Cu(II) and *bis*-(2'-hydroxyacetophenonato)Cu(II) were prepared by mixing the requisite amount of salicylaldehyde or 2'-hydroxyacetophenone, respectively, with aqueous cupric nitrate solution and titrating with vigorous stirring to pH 7 with aqueous sodium hydroxide solution. The crude complexes were re-crystallized from chloroform. Purity determinations were made by electrogravimetric copper analysis.

Reagent grade dioxane, chloroform, and benzene were purified by standard techniques.

Dielectric constant measurements in the radio frequency range were made with a heterodyne beat apparatus operating at 197 kc. The apparatus consisted of a precision air capacitor (General Radio 1422-D), beat frequency generator (General Radio 1304 B), fixed-frequency generator (Hewlett-Packard 201C), and dielectric cell (Kahl Scientific Company). Refractive indices were measured on a Bausch and Lomb type 33-45-58 refractometer. Specific volumes were determined with a pycnometer. Temperature control was estimated to be $\pm 0.1^\circ\text{C}$.

Calculations of the polarizations were made using the procedure of Halverstadt and Kumler (2).

Experimental Results

The experimental plots of dielectric constant as a function of concentration of complex at 30°C are reproduced in Figures 2 and 3. The lines on the graphs represent an estimated error of about ± 0.5 molecules here exist in a *trans*-configuration with planar ligand rings. specific volume / concentration and refractive index / concentration graphs are shown in Figures 4 and 5, respectively. Polarizations calculated from these experiments at 30°C are shown in Table 1. The result for the salicylaldehyde complex is in agreement within experimental error with the literature value (3). The 2'-hydroxyacetophenone complex has not previously been studied, but the result for $(P_T - P_E)$ is not unreasonable in that the addition of a methyl group to a molecule has been found to increase the $(P_T - P_E)$ difference by some 5 to 15 cc (4).

Estimates of the $(P_T - P_E)$ difference for *bis*-(2'-hydroxyacetophenonato)Cu(II) as a function of temperature from 10 to 50°C were made as follows. The dielectric constants for one intermediate concentration of the complex in dioxane were obtained over the temperature range. Because the determination of the polarization from a single dielectric constant measurement is subject to some error, the resulting curve of dielectric constant *versus* temperature was displaced slightly so that the value of the polarization calculated from it at 30°C agreed approximately with the more precise result reported above from dielectric constant / concentration experiments. The temperature dependence of the refractive indices of the complex solutions was as-

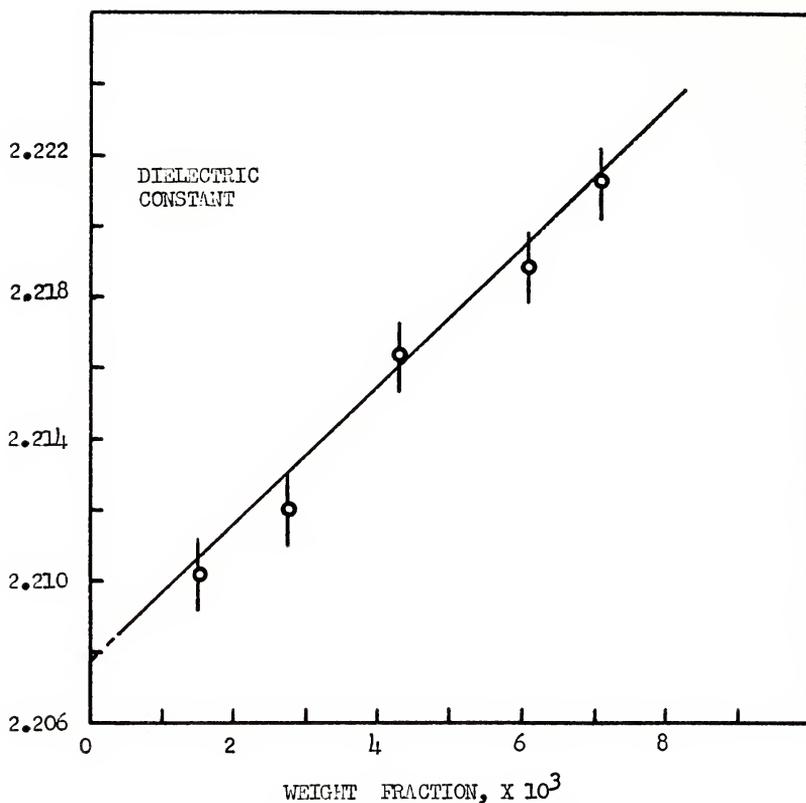


FIGURE 2. Dielectric constant versus weight fraction of bis-(salicylaldehyde)Cu(II) in dioxane at 30°C.

sumed to be that of the parent 2'-hydroxyacetophenone. The temperature dependence of the specific volumes for both the complex and the solution were assumed to be identical, and were taken from Smyth (5). The dependence of the specific volume on concentration was taken to be that reported above for 30°C. Polarizations calculated from this temperature dependence study are summarized in Table 2.

Discussion

The ($P_T - P_E$) difference reported in Table 1 for the salicylaldehyde complex is in agreement with the literature value (3). These workers assumed the molecule to be symmetrical in solution and hence identified this difference with atomic polarization. Since that time the structure of this complex has been determined in the solid state (1). The molecules here exist in a *trans*-configuration with planar ligand rings, but with the ligand rings slightly displaced relative to each other. If the molecule has this same configuration in solution then the high

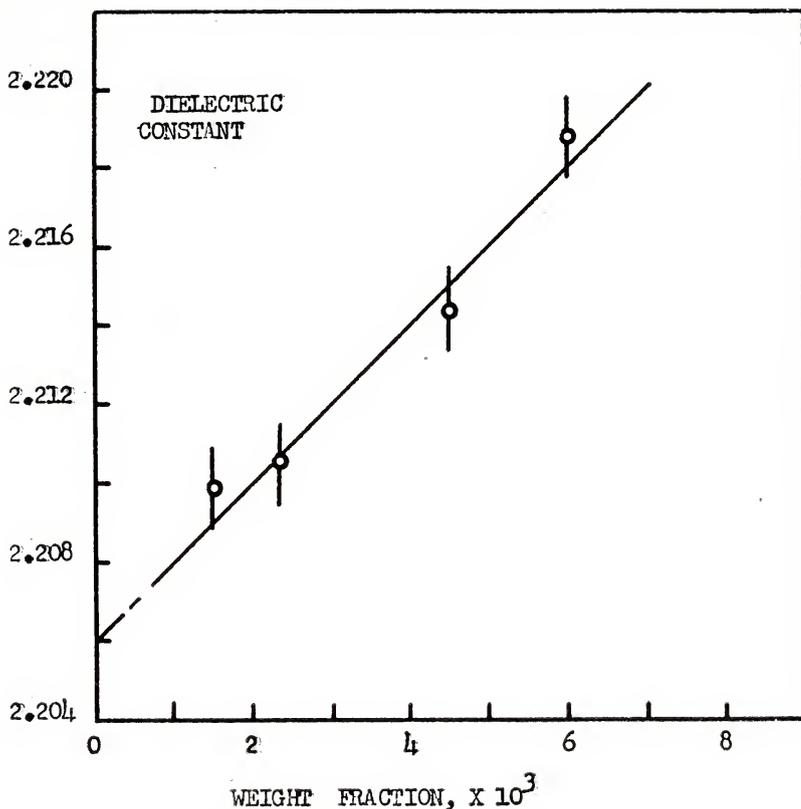


FIGURE 3. Dielectric constant versus weight fraction of bis-(2'-hydroxyacetophenonato)Cu(II) in dioxane at 30°C.

value of $(P_T - P_E)$ must be assigned to atomic polarization. The same should be true for the title compound in that it exhibits similar dielectric properties. However, a determination of the structure for the title compound has yet to be made. Nevertheless, the possibility that these molecules might possess distinctly different configurations in the solid and in solution must be recognized.

TABLE 1. Polarization results at 30°C in dioxane.

| <i>bis</i> -(salicylaldehydato)Cu(II) | <i>bis</i> -(2'-hydroxyacetophenonato)Cu(II) |
|---------------------------------------|--|
| $P_T = 149$ cc | $P_T = 170$ cc |
| $P_E = 77$ cc | $P_E = 85$ cc |
| $(P_T - P_E) = 72 \pm 4$ cc | $(P_T - P_E) = 85 \pm 5$ cc |

Additional evidence for a symmetrical structure of these molecules in solution comes from the temperature dependence of the polarization

reported in Table 2. From this it is seen that the electronic polarization is independent of temperature as would be predicted, but the difference ($P_T - P_E$) increases somewhat as the temperature increases. If this difference had an appreciable orientation polarization component the trend would be the reverse of this. Hence we conclude that the ($P_T - P_E$) difference does represent atomic polarization and that the slight increase with temperature is due to the approximations made in the calculations.

TABLE 2. Effect of temperature on ($P_T - P_E$) for bis-(2'-hydroxyacetophenonato)Cu(II) in dioxane.

| T, °C | P_T cc | P_E cc | ($P_T - P_E$), cc |
|-------|----------|----------|---------------------|
| 10 | 167 | 85 | 82 |
| 20 | 171 | 85 | 86 |
| 30 | 173 | 85 | 88 |
| 40 | 175 | 85 | 90 |
| 50 | 178 | 85 | 93 |

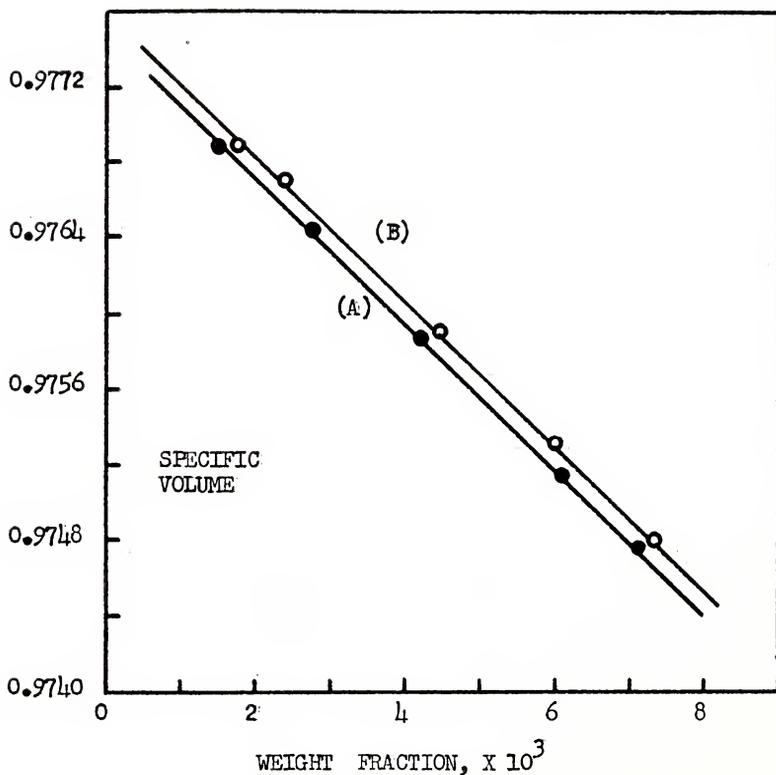


FIGURE 4. Specific volume versus weight fraction for (A) bis-(salicylaldehydato)Cu(II) and (B) bis-(2'-hydroxyacetophenonato)Cu(II) in dioxane at 30°C.

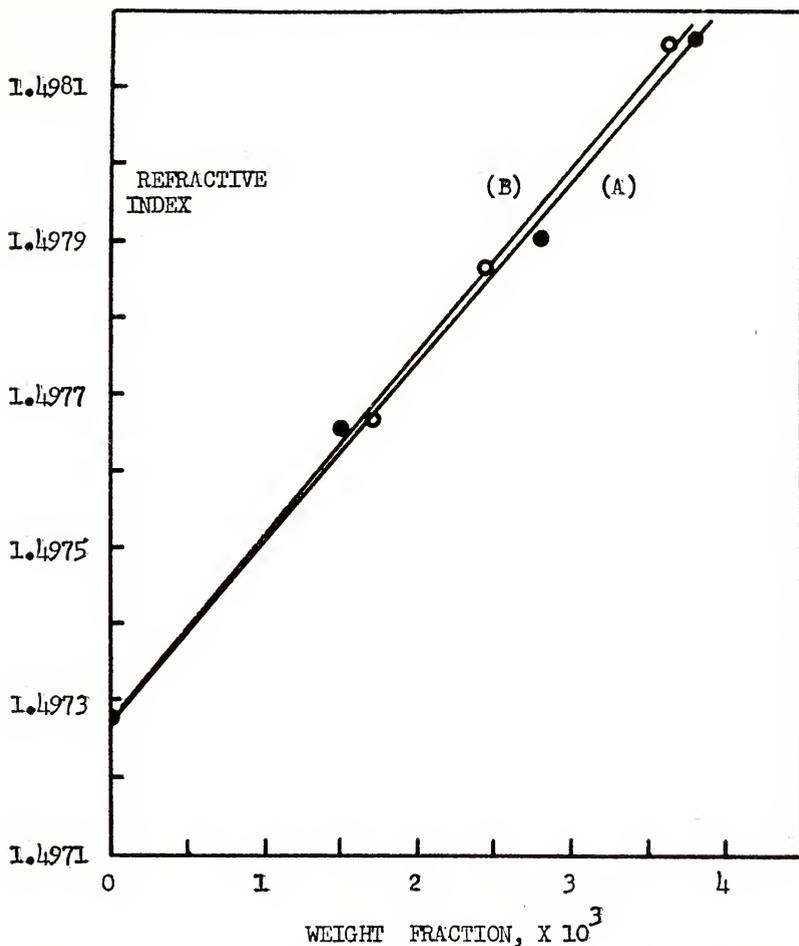


FIGURE 5. Refractive index versus weight fraction for (A) *bis*-(salicylaldehydato)Cu(II) and (B) *bis*-(2'-hydroxyacetophenonato)Cu(II) in dioxane at 30°C.

Moreover, molecules of the type studied here have been found (6) to exhibit molar extinction coefficients of about 350 in chloroform at about 600 nm if the molecule has fixed into it a *cis*-arrangement of the ligands, as in N — N' — disalicylidene ethylenediamine copper(II), but an extinction coefficient of only about 60 for *bis*-(salicylaldehydato)Cu(II) at this wavelength. In Figure 6 we report the visible absorption spectra for *bis*-(salicylaldehydato)Cu(II) and for *bis*-(2'-hydroxyacetophenonato)Cu(II) in chloroform. The former is in agreement with literature; the latter has not been reported. The two spectra of Figure 6 are quite similar, which lends additional support to the argument that the configuration of the title compound is completely analogous to that of the salicylaldehyde complex which has been shown to be symmetrical in the solid state.

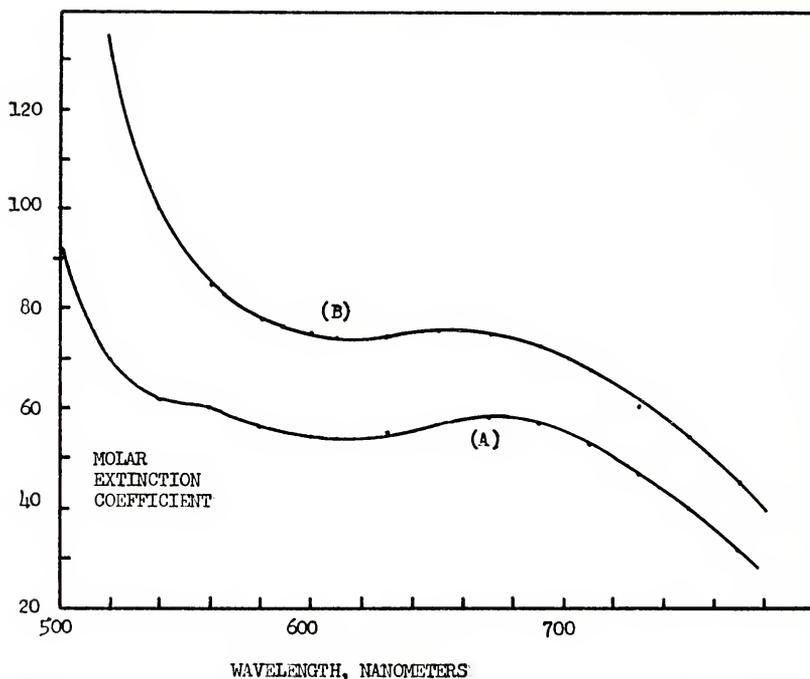


FIGURE 6. Molar extinction coefficients versus wavelength for (A) bis-(salicylaldehydato)Cu(II) and (B) bis-(2-hydroxyacetophenonato)Cu(II) in chloroform.

Acknowledgment

The authors acknowledge the financial assistance of an Undergraduate Research Participation Grant to one of us (JRH).

Literature Cited

- HALL, D., A. J. MCKINNON, and T. N. WATERS. 1965. The colour isomerism and structure of copper co-ordination compounds. Part VIII. The crystal structure of a second crystalline form of bis-salicylaldehydato-copper(II). *J. Chem. Soc.* 1965:425-430.
- HALVERSTADT, I. F., and W. D. KUMLER. 1942. Solvent polarization error and its elimination in calculating dipole moments. *J. Amer. Chem. Soc.* 64:2988-2992.
- MACQUEEN, J., and J. W. SMITH. 1965. The atom polarization of some co-ordination compounds of metals. *J. Chem. Soc.* 1956:1821-1827.
- SACCONI, L., M. CIAMPOLINI, F. MAGGIO, and G. DEL RE. 1960. Studies in coordination chemistry. VI. The dielectric polarization of some metal chelates of N-alkylsalicylaldimines. *J. Amer. Chem. Soc.* 82:815-818.
- SMYTH, C. P., and W. S. WALLS. 1931. Electric moment and molecular structure. IV. The glycols. *J. Amer. Chem. Soc.* 53:2115-2122.
- WATERS, J. M., and T. N. WATERS. 1964. The colour isomerism and structure of some copper co-ordination compounds. Part VI. The visible absorption spectra of copper complexes. *J. Chem. Soc.* 1964:2489-2492.