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The Dependence of the Visible Absorption Spectrum of $B_{10}H_{13}py^-$ upon Solvent Polarity and Temperature

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The occurrence of a visible absorption band in the electronic spectra of $B_{10}H_{12}py_2$ and $B_9H_{13}py$ derivatives (py = substituted pyridine ligands) has been attributed to intramolecular charge-transfer transitions.[2,3] These transitions could be described as electron excitation from a filled orbital of π-symmetry contained in the boron framework and centered at boron 6 to an unfilled antibonding π-orbital of the attached ligand. Substituents placed in the 4-position of the pyridine ligand demonstrated that the ligand was the electron acceptor.[2,3] Such a model for the donor–acceptor system requires strong overlap of the donor–acceptor π-orbital system. Since overlap of this type is probably best described as a $\cos^2 \theta$ function, a considerable distortion from a coplanar conformation would nevertheless allow effective overlap. The planes of reference used here are the ligand ring and a plane described by boron atoms 5, 6, and 7 in $B_{10}H_{12}py_2$ derivatives. Indeed, the 2-bromopyridine derivative of $B_{10}H_{14}^{-2}$ contains ligand rings which are tilted[4] 45° from ideal planarity in the crystalline state. Such a value of θ would allow about 50% of the overlap possible in an idealized system. However, similar distortions do not destroy conjugation in molecules such as substituted diphenyls.[5]

In connection with other work we have had occasion to prepare the cesium and tetramethylammonium salts of the $B_{10}H_{13}py$ anion. Visual observations suggested that the long wave length band associated with this ion was dramatically shifted by changes in solvent polarity. Other qualitative observations indicated a pronounced temperature effect upon the color of $B_{10}H_{13}py$ anion solutions. These two effects were briefly explored and the results obtained are reported in this note.

The recent work of Kosower[6] and co-workers has provided a useful empirical correlation of transition energy with solvent polarity. The parameter, Z, devised by Kosower[6] provides a measure of solvent polarity, the value of which increases with increasing effective solvent polarity. The anion $B_{10}H_{13}py$ was examined in eleven solvents for which Z values were available. Figure 1 presents a plot of Z values *vs.* the observed transition energy, E_T. Table I contains these data and the observed extinction coefficients. The best estimated straight line of Fig. 1 may be expressed as $Z = 0.556E_T + 21.8$ which may be compared with the equation $Z = 0.330E_T + 81.7$ obtained by Kosower[6] for pyridine 1-oxide. Thus the direction of change of E_T with a change in Z is the same for the $B_{10}H_{13}py$ anion and pyridine 1-oxide, with the former species being more sensitive to solvent environment by a factor of 1.68. These results may be taken as further evidence that intramolecular charge transfer is responsible for the visible absorption band in $B_{10}H_{12}py_2$, $B_{10}H_{13}py^-$, and $B_9H_{13}py$.

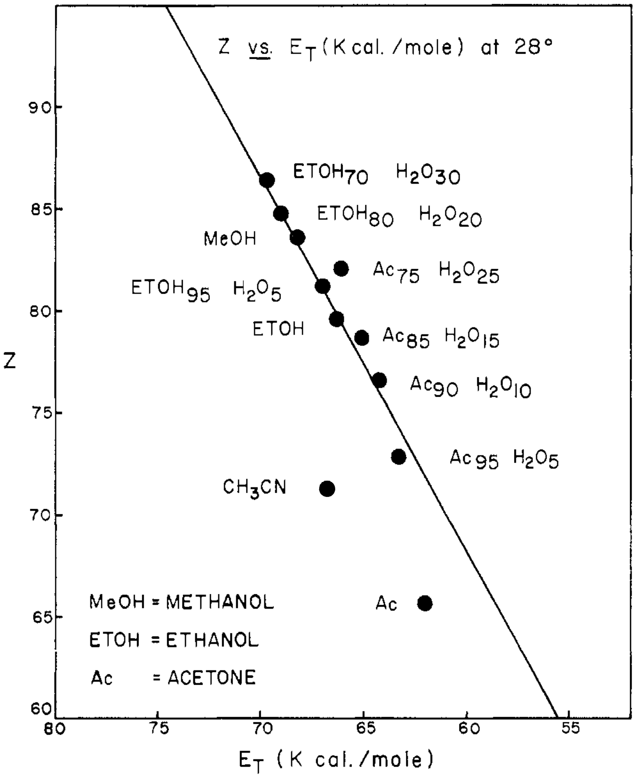

Fig. 1.—Plot of Z *vs.* transition energy.

Table I

Absorption Spectra of $B_{10}H_{13}py^-$ in Solvents of Varying Z Value, 28°

Solvent	E_T, kcal./mole	Z	$\epsilon \times 10^{-3}$
Acetone	62.0	65.7	3.10
Acetonitrile	66.8	71.3	2.97
Methanol	68.2	83.6	2.83
Ethanol	66.3	79.6	2.20
Water–acetone			
5 + 95	63.3	72.9	2.96
10 + 90	64.2	76.6	3.10
15 + 85	65.1	78.7	3.05
27 + 75	66.1	82.1	3.06
Water–ethanol			
5 + 95	67.0	81.2	2.14
20 + 80	69.0	84.8	2.75
30 + 70	69.7	86.4	2.78

In acetone solution the position of the λ_{max} associated with an internal charge-transfer transition varies from 462 mμ at 28° to 436 mμ at −70°. This result is in accord with the effect of temperature upon the spectrum

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[1] Alfred P. Sloan Research Fellow.

[2] B. M. Graybill and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2673 (1961).

[3] B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962).

[4] E. W. Hughes and C. Fritchie, Jr., private communication, Sept., 1963.

[5] For many examples of this effect, see H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 384.

[6] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

of 1-ethyl-4-carbomethoxypyridinium iodide in chloroform solution.[6] The latter solution was red-orange at 25° and became pale yellow at $-75°$. Such changes were reasonably attributed to an increase in Z value for solvent as the temperature is decreased.

Experimental

Materials.—Reagent grade solvents were dried by the usual procedures and used in the preparation of spectrophotometric solutions.

The $B_{10}H_{13}py$ anion was prepared as previously described[7] and converted to the corresponding cesium and tetramethylammonium salts. These salts were employed interchangeably since no evidence for a cation effect in the spectra was obtained.

Spectrophotometric Method.—Accurately weighed samples of the $B_{10}H_{13}py^-$ salt were made up to a predetermined volume at 28° and their spectra recorded with a Cary Model 14 spectrophotometer.

The spectrum determined at $-70°$ in acetone solution was obtained with a jacketed cell compartment cooled by Dry Ice.

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(7) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 622 (1962).

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
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Structure of Tris(pyridine N-oxide)cobalt(II) Chloride and Bromide

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Previous reports of tris(pyridine N-oxide)cobalt(II) halides either did not attempt to assign a structure[1] or assigned a tentative structure based on very limited data.[2] The chloride complex[1] has an infrared absorption at 1220 cm.$^{-1}$ which appears to be a characteristic frequency of the N–O group in complexes containing only pyridine N-oxide as ligand in the first coordination sphere of the central ion; the same complex has a low conductivity (30.2 ohm^{-1} cm.^{2} mole^{-1}) in dimethylformamide, which suggests that some chloride coordination persists even at the dilution used for the conductivity measurements. The bromide[2] was found to have an apparent molecular weight of 247 (calculated, 504) in phenol and a conductivity of 19 to 29 ohm^{-1} cm.^{2} mole^{-1}, depending on concentration, in acetonitrile. These data, plus a magnetic moment of 4.67 B.M. and the green color of the complex, were taken as evidence of a tetrahedral structure for a 1:1 electrolyte and the complex was formulated[2] as $[CoL_3X]X$ (where L represents the ligand, pyridine N-oxide, and X represents a halide ion).

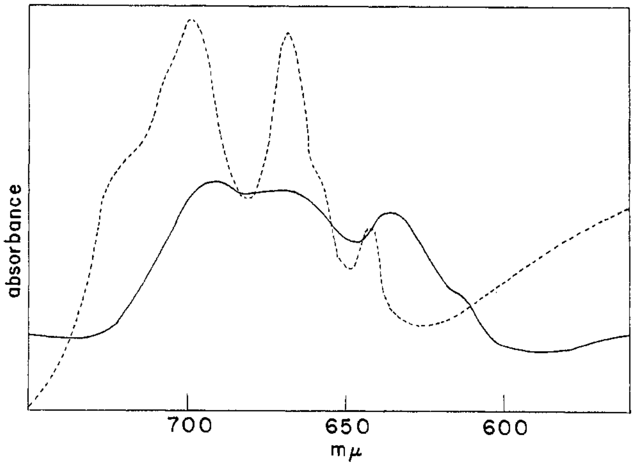

Fig. 1.—Spectra of the CoL_3X_2 compounds as mulls in hexachlorobutadiene: --------, X = Br; ———, X = Cl.

Since the two complexes have similar colors and similar magnetic moments (4.75 B.M. for the chloride[1]), it seems likely that the two have the same type of structure. The additional observations that: (1) the conductivity data seem somewhat low for a 1:1 electrolyte (values up to 85 were assigned as 1:1 electrolytes in dimethylformamide[1]); (2) the magnetic moment of the octahedral complex, $CoL_6(ClO_4)_2$, was reported to be 4.69 B.M.,[1] and the moment cannot, therefore, be used as evidence of tetrahedral coordination; and (3) the suggested structure does not agree with the infrared observation led us to investigate the structure of these complexes.

Results and Discussion

Tris(pyridine N-oxide)cobalt(II) chloride and bromide were prepared and visible spectra were obtained for the solids and for solutions in both dimethylformamide and acetonitrile. The spectra of the solids, Fig. 1, were found to be almost identical with those of the corresponding tetrahalocobaltate(II) anions.[3] There is some variation in the relative intensities of the ν_3 components of the bromide complex as compared to the tetrabromocobaltate(II) anion. The same type of variation was reported[4] recently for the tetrachlorocobaltate(II) anion with different cations in crystal spectra.

The spectral results suggest that the solid contains the tetrahalocobaltate(II) anion and that the compound should be formulated as the mixed complex, $[CoL_6][CoX_4]$. To check such a possibility, cadmium was substituted for the tetrahedral cobalt[5] to give $[CoL_6][CdX_4]$. Attempted preparations using chloride salts gave a green substance, presumably CoL_3Cl_2, mixed with a lighter-colored substance; the same preparation using the bromide salts gave an orange-red substance,

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