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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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).

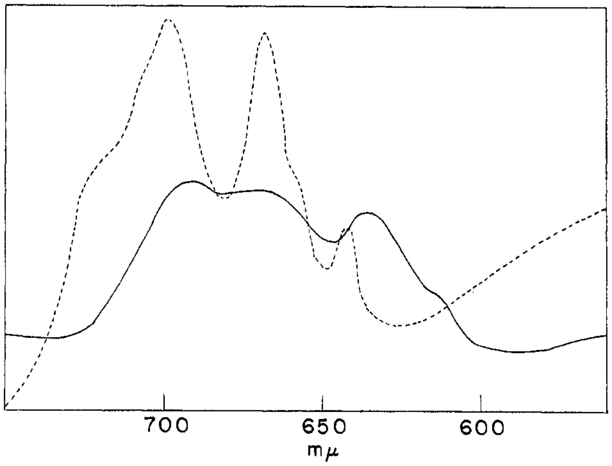

Fig. 1.—Spectra of the CoL_3X_2 compounds as mulls in hexachlorobutadiene: --------, X = Br; ———, X = Cl.

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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[2] K Issleib and A. Kreibich, *Z. anorg. allgem. Chem.*, **313**, 339 (1962).

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$[CoL_6][CdBr_4]$. X-Ray powder patterns (data presented in Table I) for CoL_3Br_2 and for $[CoL_6][CdBr_4]$ were found to be almost identical in both peak position and intensity, and the compounds thus appear to be isomorphous; the CoL_3X_2 compounds, therefore, contain both tetrahedral and octahedral cobalt(II) complexes.

Table I

X-Ray Powder Patterns[a]

$[CoL_6][CdBr_4]$ *d*, Å.	*I*	CoL_3Br_2 *d*, Å.	*I*
14.243	m	14.243	m
8.665	w	8.665	w
7.431	s	7.493	s
6.857	vs	6.857	vs
6.320	w	6.276	w
6.021	m	5.981	m
5.862	m	5.862	m
5.273	w	5.273	w
4.818	s	4.818	s
4.149	m	4.149	m
4.055	s	4.037	s
3.966	s	3.948	m
3.218	w	3.206	w
3.162	m	3.129	m
3.066	s	3.046	m

[a] The symbols used to designate intensities are: s, strong; m, medium; w, weak; and v, very.

A similar structure was recently assigned to the cobalt(II) halide complex of the chelate ligand, bis(diisopropoxyphosphinyl)methane, on the basis of its spectrum.[6]

Attempts were made to obtain the spectrum of $[CoL_6][CdBr_4]$ as a mull, but due to the low extinction coefficients of octahedral bands and the background noise encountered with the mull technique, very poor results were obtained. Attempts were also made to obtain the spectrum of this compound in dimethylformamide and in acetonitrile; in both solvents, the compound gave deep blue solutions and the spectra were identical, with respect to absorption positions, with the spectra of CoL_3Br_2 in the same solvents; molar extinction coefficients were much lower than those of CoL_3Br_2.

These spectral results indicate that the solution measurements previously reported, such as conductivity and molecular weight, are not directly related to the species present in the solid since reaction apparently occurs on dissolving. These results also raise the question as to what species are present in solution. In an attempt to answer this, we dissolved cobalt(II) bromide in dimethylformamide and observed the spectrum as the concentration of pyridine N-oxide was increased; no appreciable change in any visible band was noted although the tail of an ultraviolet band did increase in intensity. The only explanations are that: (1) there is no coordination by pyridine N-oxide in these solutions, or (2) pyridine N-oxide and dimethylformamide have identical ligand field parameters.

Studies of the octahedral nickel(II) complexes of these two ligands[7,8] support the latter explanation; the fact that the spectrum of the pyridine N-oxide complex of nickel(II) was obtained in dimethylformamide does not rule out the possibility of solvent exchange. The spectrum of the same complex in acetonitrile[9] is similar to, though not identical with, the spectrum in dimethylformamide.

Although we cannot identify the species present, the solution spectra of CoL_3X_2 and $[CoL_6][CdBr_4]$ indicate that the cobalt(II) is present predominantly as tetrahedral species in solution.

Experimental

Tris(pyridine N-oxide)cobalt(II) Halides.—The bromide and chloride were prepared by methods in the literature.[1,2]

Anal. Calcd. for $Co(C_5H_5NO)_3Cl_2$: C, 43.39; H, 3.64. Found: C, 43.45; H, 3.89. Calcd. for $Co(C_5H_5NO)_3Br_2$: C, 35.74; H, 3.00. Found: C, 35.98; H, 3.08.

Hexakis(pyridine N-oxide)cobalt(II) Tetrabromocadmiate.—A hot ethanol solution of anhydrous $CoBr_2$, anhydrous $CdBr_2$, and pyridine N-oxide, in mole ratios of 1:1:6, was prepared and allowed to cool. The blue solution yielded an orange-red solid on standing; the solid was filtered, washed, and dried.

Anal. Calcd. for $[Co(C_5H_5NO)_6][CdBr_4]$: C, 33.94; H, 2.85; Co, 5.55. Found: C, 33.88; H, 2.95; Co, 5.50.

Spectral Measurements.—All spectral measurements were made using a Bausch and Lomb Spectronic 505. Solid spectra were obtained by the mull technique, using hexachlorobutadiene as mulling liquid.

X-Ray Powder Patterns.—X-Ray powder patterns were obtained with a Phillips diffractometer, using Cu Kα radiation. Several packings were run, and some preferred orientation was observed. The results are presented in Table I.

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Ternary Perovskite Phases in Systems of Lithium Hydride with Barium, Strontium, and Calcium Hydrides

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As part of a series of studies on lithium hydride phase equilibria, these systems have been investigated by X-ray powder crystallography. No previous work has been reported on the systems lithium hydride–barium hydride and lithium hydride–strontium hydride.