added. The resultant mauve precipitate was filtered off and washed with ether. It may be recrystallized by adding ether to the saturated solution in methanol; yield 0.25 g.

Anal. Calcd. for $C_{10}H_{24}N_4Cl_2Ni$: C, 36.3; H, 7.3; N, 17.0; Cl, 21.5. Found: C, 36.3; H, 7.4; N, 16.9; Cl, 21.5.

Dibromo(1,4,8,11-tetraazacyclotetradecane)nickel(II) was prepared from nickel(II) bromide hexahydrate in an analogous way.

Anal. Calcd. for $C_{10}H_{24}N_4Br_2Ni$: C, 28.7; H, 5.7; N, 13.3; Br, 38.2. Found: C, 28.9; H, 6.0; N, 13.3; Br, 38.3.

Diiodo(1,4,8,11-tetraazacyclotetradecane)nickel(II).—Nickel(II) iodide (0.39 g.) was dissolved in hot 1-butanol (200 ml.) and added to a solution of the ligand (0.25 g.) in ethanol (10 ml.). The brown solution was heated for 2 min. at 100°, filtered while hot, and allowed to cool. Brown crystals were deposited (0.4 g.), filtered off, and washed with ether.

Anal. Calcd. for $C_{10}H_{24}N_4I_2Ni$: C, 23.4; H, 4.7; N, 10.9; I, 49.5. Found: C, 23.5; H, 4.8; N, 10.9; I, 49.7.

(1,4,8,11-Tetraazacyclotetradecane)nickel (II) Perchlorate.—Nickel(II) perchlorate (0.45 g.) dissolved in ethanol (20 ml.) was added to a solution of the ligand (0.25 g.) in ethanol (10 ml.). The solution turned brown and golden yellow crystals began to separate. The solution was evaporated to a small volume (5 ml.), and the crystals were dissolved by adding acetone (20 ml.) and reprecipitated by adding ether. The complex (0.4 g.) was filtered off and washed with ether.

Anal. Calcd. for $C_{10}H_{24}N_4Cl_2O_8Ni$: C, 26.2; H, 5.3; N, 12.2; Cl, 15.5. Found: C, 26.2; H, 6.0; N, 12.2; Cl, 15.5.

Visible absorption spectra were measured with a Unicam SP-500 quartz spectrophotometer; infrared spectra of Nujol and hexachlorobutadiene mulls between rock salt plates were measured with a Perkin-Elmer PE 137 spectrometer. Magnetic susceptibility measurements were made by the Gouy method and conductivities were measured with a Wayne-Kerr universal bridge, the solutions being contained in a cell fitted with shiny platinum electrodes.

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Preparations and Properties of Chromium(II) Complexes. II. Complexes with Pyridine[1]

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Reactions between pyridine and chromium(II) halides have resulted in the isolation of the complexes $CrCl_2 \cdot 2py$, $CrBr_2 \cdot 2py$, $CrBr_2 \cdot 6py$, $CrI_2 \cdot 4py$, and $CrI_2 \cdot 6py$ (where py = pyridine), which are all relatively stable in air. The room temperature magnetic susceptibilities indicate the presence of four unpaired electrons. Low-temperature reflectance spectra show two bands, one near 10,000–12,000 cm.$^{-1}$ and another at ~17,000 cm.$^{-1}$. X-Ray powder patterns have been compared, where possible, with those of the corresponding copper(II) complexes. These data all indicate that the complexes are extensively distorted from octahedral symmetry.

Introduction

Pyridine forms a very large number of complexes with many divalent first-row transition metal salts,[2] particularly the simple halides.[2,3] Many of these compounds date back to the very early literature.[4] As expected, information on chromium(II)–pyridine systems is scarce, with few definite and well-characterized complexes having been reported. Relatively stable complexes are formed with the formate[5] and acetate,[6] $[Cr(HCOO)_2py]_2$ and $[Cr(CH_3CO_2)_2py]_2$, the pyridine probably occupying the same position as water in[7] the well-known $[Cr(CH_3CO_2)_2H_2O]_2$. This type of structure is found[8] in $[Cu(CH_3CO_2)_2py]_2$.

Recent work has shown pyridine to coordinate with chromium(II) phthalocyanine[9] and bis(benzoylacetonato)chromium(II).[10] The little information which is available on chromium(II) halide complexes with pyridine is contradictive and inaccurate. The complex $CrCl_2 \cdot 2py \cdot 2H_2O$ was obtained from the reaction between aqueous chromium(II) chloride solution and pyridine,[5] and later[3,11] $CrCl_2 \cdot 2py$ was obtained from the same reaction and also from the reaction between anhydrous chromium(II) chloride and pyridine.[12,13] The latter complex is high-spin[3] and isomorphous[13] with the corresponding copper(II) complex, the crystal structure of which is known.[14,15] Attempts to prepare $CrBr_2 \cdot 2py$ have also been made,[3] but no analytical data were reported. Magnetic measurements on the sample indicated that the complex was in a very impure state. To our knowledge, no spectral studies have been carried out on any of these complexes.

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[1] Part I: J. P. Fackler, Jr., and D. G. Holah, *Inorg. Chem.*, **4**, 954 (1965).

[2] See, for example, the articles by N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961), and P. C. H. Mitchell, *ibid.*, **18**, 382 (1961), which list a number of such complexes.

[3] N. S. Gill, R. S. Nyholm, and (in part) G. A. Barclay, T. I. Christie, and P. J. Pauling, *ibid.*, **18**, 88 (1961).

[4] For example, F. Reitzenstein, *Z. anorg. allgem. Chem.*, **11**, 254 (1895); **18**, 253 (1898).

[5] W. Traube, E. Burmeister, and R. Stahn, *ibid.*, **147**, 50 (1925).

[6] D. N. Hume and H. W. Stone, *J. Am. Chem. Soc.*, **63**, 1200 (1941).

[7] J. N. Van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 501 (1953).

[8] J. Hanic, D. Stempelova, and K. Hanicova, *ibid.*, **17**, 633 (1964).

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[10] R. Nast and H. Rückemann, *Chem. Ber.*, **93**, 2329 (1960).

[11] J. H. Balthis, Jr., and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **58**, 1474 (1936).

[12] M. Chatelet, *Compt. rend.*, **199**, 290 (1934).

[13] H. Lux, L. Eberle, and D. Sarre, *Chem. Ber.*, **97**, 503 (1964).

[14] E. G. Cox, E. Sharratt, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 129 (1936).

[15] J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

As part of a systematic examination of chromium(II) chemistry, we have investigated various reactions between pyridine and chromium(II) halides and report here several new complexes together with some of their physical properties.

Experimental

Preparations.—All preparations, reactions, and analyses were carried out using the closed, ground-glass equipment described in part I,[1] in conjunction with the nitrogen-filled glove box, also described previously.[1] All solvents were purged of oxygen by boiling and flushing with nitrogen before entry into the box.

Dichlorobis(pyridine)chromium(II).—An excess of pyridine is slowly added with shaking to a solution of $CrCl_2 \cdot 4H_2O$[1] in water. The reaction, which is strongly exothermic, produces a bright green precipitate. This can be recrystallized from ethanol,[13] but is more soluble and much more easily recrystallized from dimethylformamide, from which light green needles are obtained. These are washed with ethanol and dried under vacuum at room temperature.

Anal. Calcd. for $CrCl_2 \cdot 2py$: C, 42.72; H, 3.59; Cr, 18.50; Cl, 25.25. Found: C, 42.5; H, 3.6; Cr, 18.6; Cl, 25.2.

Dibromobis(pyridine)chromium(II).—The procedure, using $CrBr_2 \cdot 6H_2O$,[1] is similar to that for $CrCl_2 \cdot 2py$, except that an excess of pyridine is avoided. The bright green precipitate is recrystallized from ethanol.

Anal. Calcd. for $CrBr_2 \cdot 2py$: C, 32.46; H, 2.72; Cr, 14.05; Br, 43.19. Found: C, 32.3; H, 2.8; Cr, 14.0; Br, 43.1.

Dibromohexakis(pyridine)chromium(II).—$CrBr_2 \cdot 2py$ reacts with an excess of pyridine to give a dark green product which is recrystallized from an ethanol–pyridine mixture.

Anal. Calcd. for $CrBr_2 \cdot 6py$: C, 52.59; H, 4.40; Cr, 7.58; Br, 23.29. Found: C, 52.3; H, 4.5; Cr, 7.6; Br, 23.5.

Diiodotetrakis(pyridine)chromium(II).—Pyridine is slowly added to an aqueous solution[1] of $CrI_2 \cdot 6H_2O$ until a green precipitate is formed. The reaction is strongly exothermic and the resultant green precipitate is difficult to filter. Recrystallization from a dimethylformamide–ethanol mixture gives brown crystals.

Anal. Calcd. for $CrI_2 \cdot 4py$: C, 38.60; H, 3.24; Cr, 8.36; I, 40.79. Found: C, 38.6; H, 3.2; Cr, 8.3; I, 40.6.

Diiodohexakis(pyridine)chromium(II).—The green product from the $CrI_2 \cdot 6H_2O$–pyridine reaction or the brown $CrI_2 \cdot 4py$ reacts with excess pyridine to form a dark green material which is recrystallized from an ethanol–pyridine mixture. If ethanol alone is used, a mixture of $CrI_2 \cdot 4py$ and $CrI_2 \cdot 6py$ is obtained.

Anal. Calcd. for $CrI_2 \cdot 6py$: C, 46.17; H, 3.87; Cr, 6.66; I, 32.52. Found: C, 46.2; H, 3.9; Cr, 6.1; I, 31.7.

The complexes $CuCl_2 \cdot 2py$,[3] $CuBr_2 \cdot 2py$,[3] and $CuBr_2 \cdot 6py$[16] were prepared as previously described, the first two being recrystallized from dimethylformamide.

Physical Measurements.—Reflectance spectra, at room and liquid nitrogen temperatures, and room temperature magnetic moments were measured, maintaining oxygen-free conditions as described previously.[1] X-Ray powder patterns of samples, sealed in glass capillaries, were measured with a Debye–Scherrer camera using copper Kα radiation with appropriate filters. Thermogravimetric analyses were conducted on a Stanton thermobalance while a slow stream of argon gas was passed through the furnace chamber. The samples, covered with a wad of steel wool, were weighed in small plastic-capped glass vials and transferred onto the thermobalance pan. The plastic stopper was removed and the furnace which had been previously flushed with argon was immediately lowered into position, thus preventing entry of air into the sample vial. A heating rate of 1°/min. was used.

TABLE I

SPECTRAL AND MAGNETIC DATA

		Reflectance spectra, cm.$^{-1}$		Magnetic moments: χ_g (uncor.) $\times 10^6$	Magnetic moments: μ_{eff} (cor.), B.M.^{d}
$CrCl_2 \cdot 2py$	*a*	10,520 sh^c	14,600	34.4	4.84 ± 0.05
	b	10,800	15,050		
$CrBr_2 \cdot 2py$	*a*	10,500 sh	14,000	25.8	4.81 ± 0.05
	b	10,300	14,300		
$CrBr_2 \cdot 6py$	*a*	12,100 sh	17,150	14.5	4.94 ± 0.05
	b	11,600	17,000		
$CrI_2 \cdot 6py$	*a*	12,500 sh	17,100	13.2	5.03 ± 0.05
	b	12,750	17,000		
$CrI_2 \cdot 4py$	*a*	12,500 sh	C.t.^{c}	16.9	5.03 ± 0.05
	b	12,100	C.t.		

^{a} Room temperature. ^{b} Liquid nitrogen temperature. ^{c} sh = shoulder, c.t. = charge transfer. ^{d} Measurements at 20°. See part I for diamagnetic corrections.

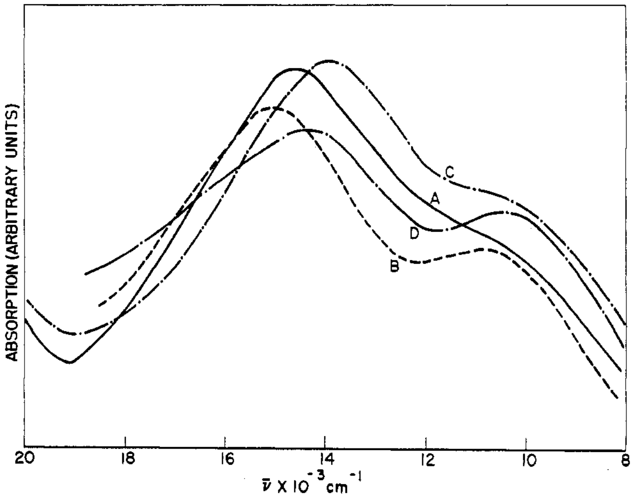

Figure 1.—Reflectance spectra: A, $CrCl_2 \cdot 2py$ at room temperature; B, $CrCl_2 \cdot 2py$ at liquid nitrogen temperature; C, $CrBr_2 \cdot 2py$ at room temperature; D, $CrBr_2 \cdot 2py$ at liquid nitrogen temperature.

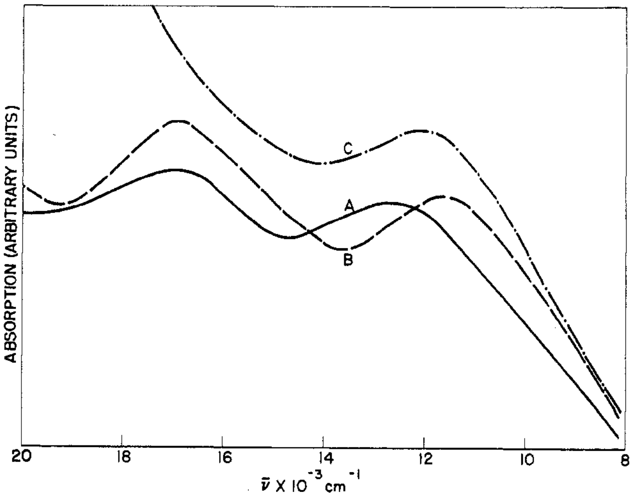

Figure 2.—Reflectance spectra at liquid nitrogen temperature: A, $CrI_2 \cdot 6py$; B, $CrBr_2 \cdot 6py$; C, $CrI_2 \cdot 4py$.

Results

In the series of complexes obtained, $CrCl_2 \cdot 2py$, $CrBr_2 \cdot 2py$, $CrBr_2 \cdot 6py$, $CrI_2 \cdot 4py$, and $CrI_2 \cdot 6py$, there are several apparent gaps. For example, although the bulk of the product from the aqueous chromium(II) iodide–pyridine reaction was light green, suggesting

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[16] P. Pfeiffer and V. Pimmer, *Z. anorg. allgem. Chem.*, **48**, 98 (1906).

TABLE II

d SPACINGS (Å.) CALCULATED FROM X-RAY POWDER PATTERNS[a]

$CrCl_2 \cdot 2py$	$CuCl_2 \cdot 2py$	$CrBr_2 \cdot 2py$	$CuBr_2 \cdot 2py$	$CrBr_2 \cdot 6py$	$CuBr_2 \cdot 6py$	$CrI_2 \cdot 6py$	$CrI_2 \cdot 4py$
8.80 s	8.59 s	9.04 s	8.89 s	8.31 s	8.31 s	8.35 s	8.42 m
7.82 s	7.68 s	7.75 s	7.62 s	7.49 s	7.49 s	7.68 w	7.03 s
6.15 m	6.07 m	6.17 vw	6.09 vw	5.62 s	5.57 m	5.65 m	5.81 s
4.84 s	4.79 s	4.93 s	4.82 m	4.25 m	4.21 m	4.53 m	4.97 w
4.22 m	4.17 m	4.06 w	4.02 w	4.09 s	4.10 s	4.12 s	4.74 w
3.91 m	3.93 w	3.99 s	3.92 s	3.75 s	3.71 s	3.78 w	4.48 w
3.80 m	3.81 s	3.66 s	3.75 m	3.10 m	3.12 m	3.13 w	4.08 s
3.46 s	3.46 s	3.47 s	3.40 s	2.98 m	2.96 w	3.01 w	3.78 w

[a] Visual intensities: s, strong; m, medium; w, weak; v, very.

the formation of $CrI_2 \cdot 2py$, analysis showed its composition to be nonreproducible. Recrystallization from ethanol or dimethylformamide resulted in the formation of brown $CrI_2 \cdot 4py$. The complex $CrBr_2 \cdot 4py$ was not obtained, although some brown crystals, perhaps the complex, were observed during the recrystallization of $CrBr_2 \cdot 2py$ from dimethylformamide. $CrCl_2 \cdot 2py$ did not react further with pyridine, either in the solid state or in ethanol or dimethylformamide solutions. On exposure to air it is several minutes before any of these complexes shows visible signs of decomposition; the two hexakis(pyridine) complexes smell strongly of pyridine. All complexes, however, are stable indefinitely when stored under nitrogen.

The room temperature reflectance spectra presented in Table I and Figures 1 and 2 each show a band in the visible region with a shoulder on the low-energy side. At low temperatures this shoulder is resolved into a distinct maximum. The similarity between these spectra and those reported previously[1] is to be noted. Since the complexes are considerably less susceptible to oxidation then the simple hydrates, there is no difficulty avoiding contamination with traces of chromium(III). The spectra of $CrCl_2 \cdot 2py$ and $CrBr_2 \cdot 2py$ are almost identical. A surprising difference exists between the spectra of $CrBr_2 \cdot 6py$ and $CrI_2 \cdot 6py$ in the low-energy region, the former having a maximum at 11,600 cm.$^{-1}$ while the latter displays a maximum at 12,750 cm.$^{-1}$. In the higher energy region the two spectra are nearly identical. A charge-transfer band in the spectrum of $CrI_2 \cdot 4py$ masks the visible region, leaving only the 12,500 cm.$^{-1}$ shoulder. Low-temperature measurements at 77°K., apart from resolving the low-energy shoulder, lead to no apparent resolution of the visible band, as had been observed in the hydrate spectra.[1]

Room temperature magnetic susceptibilities of the complexes recorded in Table I show the presence of four unpaired electrons per chromium(II). All the complexes have moments[17] close to the spin-only value of 4.9 B.M.

X-Ray powder patterns of all these chromium(II) complexes have been recorded and *d* spacings for the first eight lines (except for those which are too weak to measure accurately) are shown in Table II. It has been reported previously that the patterns of $CrCl_2 \cdot 2py$ and $CuCl_2 \cdot 2py$ are "very similar."[3,13] Table II confirms the fact that these two complexes are isomorphous. The data also show that $CrBr_2 \cdot 2py$ and $CuBr_2 \cdot 2py$ are isomorphous, as are $CrBr_2 \cdot 6py$, $CuBr_2 \cdot 6py$, and $CrI_2 \cdot 6py$. It is also apparent that $CrCl_2 \cdot 2py$ and $CrBr_2 \cdot 2py$ have similar patterns and do in fact have quite similar crystal structures (see Discussion).

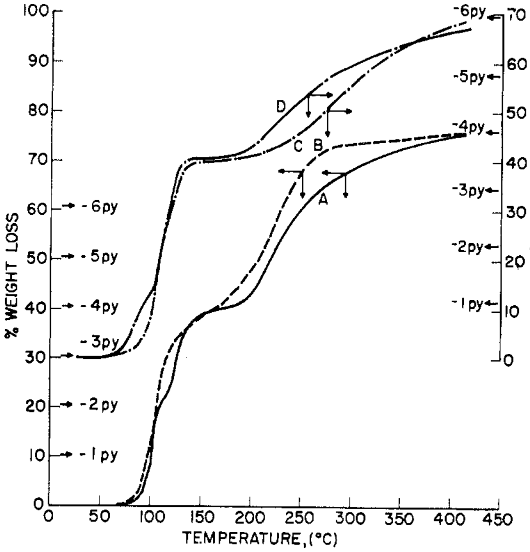

Figure 3.—Thermogravimetric analyses: A and B, $CrI_2 \cdot 6py$; C and D, $CrBr_2 \cdot 6py$.

In view of the possible existence of three (or more) pyridine complexes of the bromide and iodide of chromium(II), namely $CrX_2 \cdot x py$, where $x = 2$, 4, or 6, thermogravimetric analyses of $CrI_2 \cdot 6py$ and $CrBr_2 \cdot 6py$ were performed. While the results from several experiments on one complex are not completely reproducible, the important features remain fairly constant and typical curves are shown in Figure 3. The iodide shows a clear break when four pyridine molecules have been lost at ~150°, implying that the compound $CrI_2 \cdot 2py$ is formed. At higher temperatures considerably more weight is lost than is required for the removal of six pyridine molecules and it is concluded that after the loss of four pyridines, decomposition occurs. In fact iodine vapors can be seen above the residue if the furnace is raised while above 350°. In an effort to obtain $CrI_2 \cdot 2py$, the complex $CrI_2 \cdot 4py$ was heated carefully under vacuum, but this led only to decomposition.

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[17] Values of 4.66 and 4.98 B.M. have been reported[3] for $CrCl_2 \cdot 2py$ and 4.43 B.M. for $CrBr_2 \cdot 2py$, but the samples contained considerable quantities (we estimate up to ~40%) of chromium(III).

A sharp and consistent break in the curve of $CrBr_2 \cdot 6py$ is obtained when ~3.5 pyridine molecules have been lost. Between 300 and 400° the weight loss levels off to the expected value for the removal of all six pyridines, indicating the formation of $CrBr_2$. Similar results have been observed in the thermogravimetric analysis of many cobalt(II) and nickel(II) pyridine complexes.[18-20]

Discussion

The structures of $CuCl_2 \cdot 2py$[3,14,15] and $CuBr_2 \cdot 2py$[21] consist basically of *trans*, planar $MX_2 \cdot 2py$ units connected together in such a way that each copper(II) atom has halides from adjacent $MX_2 \cdot 2py$ units coordinated to the axial positions. Unlike the class A $MX_2 \cdot 2py$ complexes[3] which have essentially equal M–X bond lengths, these class B tetragonal complexes have two very different M–X distances. These distances are 2.28 and 3.05 Å. in the chloride and 2.46 and 3.17 Å. in the bromide. Cu–N distances are 2.02 Å. in the former and 1.99 Å. in the latter. X-Ray powder patterns indicate that $CrCl_2 \cdot 2py$[22] and $CrBr_2 \cdot 2py$ have very similar structures to their copper(II) analogs.

Reflectance spectra of the two $CrX_2 \cdot 2py$ species are shown in Figure 1. A detailed discussion of the susceptibility of systems having $3d^4$ electron configurations to Jahn–Teller distortions and the influence such distortions have on the energy level diagram was given[1] in part I. The same qualitative assignments suggested for the interpretation of the spectra of the hydrates are considered to apply in these cases. Thus the low-energy band in the 10,500 $cm.^{-1}$ region is thought to be the transition between the split ground-state components, $^5A_g \leftarrow {}^5B_g$ (in a rhombic field), with the broad band in the visible (half-width ~5000 $cm.^{-1}$) being made up of transitions to the three components arising from the split $^5T_{2g}$ term. In view of the rather large distortions from octahedral symmetry present in the $CrX_2 \cdot 2py$ molecules, it is somewhat surprising that no further resolution of the 14,000–15,000 $cm.^{-1}$ bands is observed, especially in view of the resolution obtained in rhombic $CrCl_2 \cdot 4H_2O$.[1] The transition corresponding to $10Dq$ probably lies slightly on the low-energy side of the broad band in the visible region, *i.e.*, close to 15,000 $cm.^{-1}$ in the chloride and near 14,000 $cm.^{-1}$ in the bromide. The shift is consistent with the relative positions of chloride and bromide in the spectrochemical series.[23]

Whereas the polymeric $CrX_2 \cdot 2py$ species are fairly insoluble in ethanol, the $CrX_2 \cdot 6py$ complexes are comparatively more soluble and dissociate readily with loss of pyridine, thus

$$CrI_2 \cdot 4py \xrightleftharpoons[C_2H_5OH]{py-C_2H_5OH} CrI_2 \cdot 6py$$

$$CrBr_2 \cdot 2py \xrightleftharpoons[C_2H_5OH]{C_2H_5OH-py} CrBr_2 \cdot 6py$$

In the solid state, however, the complexes appear perfectly stable to loss of pyridine. The bromide presents one of the very rare examples of a chromium(II) complex being more stable than its copper(II) counterpart $CuBr_2 \cdot 6py$, which loses pyridine very rapidly in air to form $CuBr_2 \cdot 2py$. In fact these hexapyridinechromium(II) complexes appear to be among the few examples of divalent metal ions surrounded by six pyridine molecules which do not rapidly lose pyridine. Hieber and Floss[24] report the magnetic susceptibility of $FeI_2 \cdot 6py$ and $[Fe(py)_6][Fe_4(CO)_{13}]$. The early literature contains several articles in which attempts were made to prepare compounds of the type $MX_2 \cdot 6py$. Besides $CuBr_2 \cdot 6py$ which is mentioned above,[4,16] the complexes $CdI_2 \cdot 6py$,[4] $CdBr_2 \cdot 6py$,[4] $Cu(NO_3)_2 \cdot 6py$,[16] $MnBr_2 \cdot 6py$,[25] and $CoI_2 \cdot 6py$[26] have been made, but all appear to lose pyridine very quickly. Very recent work[27] on the copper(II)–pyridine system suggests that a *maximum* of four pyridine molecules can be coordinated to a copper(II) ion in methanol. This corroborates our observation of the instability of $CuBr_2 \cdot 6py$. The size difference between the Cr^{2+} and Cu^{2+} ions presumably is responsible for these significant chemical differences. Size differences also appear to be of critical importance when considering[28] tetrahedral chromium(II).

The spectra of $CrBr_2 \cdot 6py$ and $CrI_2 \cdot 6py$ are shown in Figure 2. In the visible region the two spectra are identical, both showing a band at 17,000 $cm.^{-1}$. As in the $CrX_2 \cdot 2py$ species, the transition corresponding to $10Dq$ probably occurs at slightly lower energies than the main visible absorption. Thus the $10Dq$ value of ~16,000 $cm.^{-1}$ is compared with a $10Dq$ value[1] of ~13,900 $cm.^{-1}$ for $Cr(H_2O)_6{}^{2+}$. Observation of splitting on the high-energy side of this band (if any occurs) is difficult due to the presence of a charge-transfer band which appears just above 20,000 $cm.^{-1}$. However, the two spectra differ in the positions of the low-energy bands, which occur at 11,600 $cm.^{-1}$ in the bromide and at 12,750 $cm.^{-1}$ in the iodide. If both lattices contain the $Cr(py)_6{}^{2+}$ ion, as is likely (*vide infra*), the spectra suggest the cation is more highly distorted in the iodide than in the bromide. The X-ray powder patterns of the two compounds (and $CuBr_2 \cdot 6py$) indicate that the salts have similar structures. Hence the transition responsible for the low-energy band apparently is more sensitive to the small

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[18] D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **25**, 1067 (1963).

[19] J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *ibid.*, **26**, 1895 (1964).

[20] A. K. Majumdar, A. K. Mukherjee, and A. K. Mukherjee, *ibid.*, **26**, 2177 (1964).

[21] V. Kupick and S. Durovic, *Nature*, **184**, 1060 (1959); *Czech. J. Phys.*, **10**, 182 (1960).

[22] This point about the chlorides has been discussed in ref. 3 and 13. In ref. 3, Table 2, $CrCl_2 \cdot 2py$, $CuCl_2 \cdot 2py$, $CrBr_2 \cdot 2py$, and $CuBr_2 \cdot 2py$ are all incorrectly listed as being tetrahedral, even though the text discusses the correct structures.

[23] T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1961, p. 266.

[24] W. Hieber and J. G. Floss, *Z. anorg. allgem. Chem.*, **291**, 314 (1957).

[25] H. Grossmann, *Ber.*, **37**, 564 (1904).

[26] A. Hantzsch, *Z. anorg. allgem. Chem.*, **159**, 273 (1927).

[27] H. C. Volger and W. Breckman, "Proceedings of the Eighth International Conference on Coordination Chemistry," V. Gutman, Ed., Springer-Verlag, New York and Vienna, 1964, p. 38.

[28] D. G. Holah and J. P. Fackler, Jr., to be published.

structural differences produced by replacing bromide by iodide than is the higher energy band. Another difference in the behavior of these two complexes is seen in their thermogravimetric analyses (Figure 3). The iodide shows a clear break when four pyridine molecules are lost, while the bromide curve consistently breaks when ~3.5 pyridine molecules are removed. This also may reflect structural and bonding differences.

The complex $CrI_2 \cdot 4py$ probably has a structure similar to the structures of $NiI_2 \cdot 4py$ and $CoI_2 \cdot 4py$,[29] which are known to be tetragonal, containing four coplanar pyridines and halogens in *trans* axial positions. This molecule might be expected to have a spectrum characteristic of a tetragonal species, thus displaying at least two bands. However, due to the presence of a low-energy charge-transfer absorption, only the band near 12,000 cm.$^{-1}$ is observed. The presence of this charge-transfer band, not present at similar energies in $CrI_2 \cdot 6py$, is consistent with the expected metal-halogen bonding of the $CrI_2 \cdot 4py$ and the lack of such bonding in the $CrX_2 \cdot 6py$ complexes.

Acknowledgments.—The support of the National Science Foundation, GP-196, is gratefully acknowledged. We also wish to thank Prof. Louis Gordon for the use of the thermogravimetric balance.

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[29] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford, 1962, p. 915.

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High-Spin Hexa-, Penta-, and Tetracoordinated Complexes of Cobalt(II) with Schiff Bases Formed from Salicylaldehydes and N,N-Substituted Ethylenediamines

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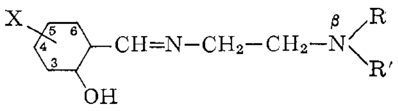
The Schiff bases formed from ring-substituted salicylaldehydes and N,N-substituted ethylenediamines react with cobalt(II) to give high-spin complexes with the generic formula $[X\text{-SALen-}(R)R']_2Co$ (I). When neither R nor R′ is an aryl group the solid complexes have either a *cis*-octahedral configuration or a five-coordinate distorted square-pyramidal configuration. The latter group of compounds is the first in which high-spin square-pyramidal cobalt(II) has been found. When R and R′ are both phenyl groups the complexes have a tetrahedral configuration. When R is hydrogen or a methyl group and R′ is an aryl group the stereochemistry of the complex is not known. In solution octahedral, pyramidal, and tetrahedral species exist in an equilibrium mixture.

Introduction

In previous papers[1,2] it was shown that complexes of nickel(II) with two molecules of Schiff bases of the general formula



can have octahedral, square-planar, or pentacoordinate configurations according to the nature of the substituents X, R, and R′.

We have now prepared various cobalt(II) complexes with analogous ligands, given the generic formula $[X\text{-SALen-}N(R)R']_2Co$ (I), and studied their properties by means of spectrophotometric, magnetic, and dipole moment measurements.

Experimental

Preparation of the Compounds.—All the compounds were prepared and collected under a nitrogen atmosphere in order to avoid oxidation by atmospheric oxygen. Two different preparative methods were used: (A) A solution of 0.025 mole of the appropriate N-substituted ethylenediamine in 15 ml. of ethanol was added to a suspension of 0.010 mole of bis(X-salicylaldehydato)-cobalt(II) dihydrate in 50 ml. of ethanol. (B) A solution of 0.010 mole of cobaltous acetate in 15 ml. of water was added to a solution of 0.020 mole of X-salicylaldehyde and 0.025 mole of N-substituted ethylenediamine in 50 ml. of ethanol.

In both cases the reaction mixture was then heated on a water bath until a clear red solution was obtained. Hot water (about 75 ml.) was then added and the solution was allowed to cool at room temperature. The resulting crystals were filtered, washed with aqueous ethanol and ether, and then dried under a nitrogen atmosphere. These compounds are soluble in chloroform, benzene, and pyridine, slightly soluble in ethanol, dioxane, and cyclohexane, and insoluble in diethyl ether and petroleum ether. The analytical data for these compounds are summarized in Table I.

Spectrophotometric Measurements.—The absorption spectra were recorded with a Beckman DK2 spectrophotometer. The solvents were purified by the standard procedures used for spectrophotometric measurements. The reflectance spectra were recorded using the standard Beckman reflectance attachment and magnesium oxide as a reference. Concentrations of the solutions were in the range 0.01–0.02 *M*.

Magnetic Susceptibility Measurements.—The magnetic susceptibility measurements were performed by the Gouy method, with the apparatus and the experimental technique described in a previous paper.[3] The sample tube was calibrated with Hg-

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[1] L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965).

[2] L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).

[3] L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).