tain more than one band each. No splitting appears in the solution spectra, and, therefore, the splitting observed may be a consequence of the solid-state technique used.

The three absorption regions have been correlated with the transitions expected for tetragonally distorted cobalt(III). The splitting diagram in Figure 2 shows the allowed transitions for cobalt(III) upon descending from O_h to C_{4v} or D_{4h} symmetry.[26]

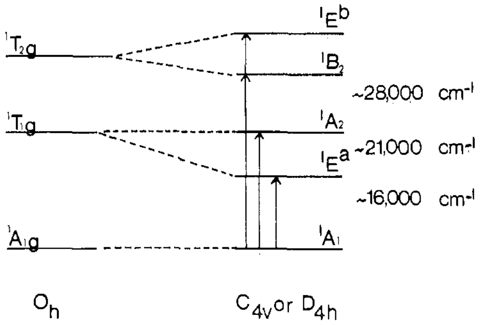

Figure 2.—Tetragonal splitting of the excited states of cobalt(III) and the energies associated with the allowed transitions.

The solid-state spectra are too poorly resolved to be used for the calculation of Dq^z values for the extraplanar anions by the method of Wentworth and Piper.[27] However, a value of the in-plane ligand field strength, Dq^{xy}, of TAAB has been calculated from the solution spectra. The average value of $\nu_A(^1A_2 \leftarrow {}^1A_1)$ is 21,830 ± 150 cm^{-1}. Since $10Dq^{xy} = \nu_A + C$, where C is the Racah parameter assumed to be constant at ~3800 cm^{-1} for cobalt(III), then Dq^{xy} is 2563 ± 15 cm^{-1} for octahedral TAAB. This value is almost the same as that reported for octahedral CR (2545 cm^{-1})[22] and slightly larger than that reported for *meso*-CRH (2500 cm^{-1}),[28] where CR is the macrocyclic, tetradentate, Schiff base ligand derived from 2,6-diacetylpyridine and 3,3'-diaminodipropylamine and CRH is the reduced form of this ligand. The trend observed in the analogous nickel(II) systems places the field strength of TAAB between those of the other two ligands.[1]

Acknowledgment.—This investigation was supported in part by U. S. Public Health Services Grant No. GM-10040 from the National Institute of General Medical Sciences.

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Complexes of Cobalt(II) Halides with Hydrazine Derivatives

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This paper describes novel complexes of cobalt(II) halides with hydrazine and hydrazine derivatives as well as some of their chemical properties. Compounds of the type $Co^{II}X_2(R{=}N{-}N{=}R)$ were obtained by direct reaction of cobalt(II) halides with ketazines and aldazines or by condensation of bis(hydrazinates) with ketones or aldehydes. Tris(hydrazino)-cobalt(II) halides of the type $Co^{II}X_2(N_2H_4)_3$ were prepared by ligand exchange of the azino complexes with hydrazine. The hydrochloride analogs, $Co^{II}X_2(N_2H_4 \cdot HCl)_3$, were the result of the reaction of cobalt(II) halides with hydrazones and hydroxylamine hydrochloride.

Introduction

The reaction of hydrazine with several transition metal ions has been the object of many publications since Franzen reported the preparation of various metal hydrazinates over half a century ago.[1] Most of these complexes were obtained by reactions in aqueous media[2] and the general structure of hydrazine complexes of cobalt(II) halides obtained by this method is limited to bidentate chelates the preparation and properties of which are well known and documented.[3] More recently, the reaction of anhydrous cobalt(II) chloride with anhydrous hydrazine at low temperature has led to the preparation of a hexahydrazinate complex of limited stability.[4] The tris(hydrazinates), however, to be expected as octahedral bidentate chelates of the hexacoordinated cobalt(II) halides, were never reported. Preparative work on complexes of substituted hydrazines and hydrazine derivatives is scarce[5,6] while the chemical properties of known hydrazine complexes of cobalt(II) halides have only been the object of insignificant investigations.[2,4,6] It has been generally observed in the past that reaction products between cobalt(II) halides and hydrazine, *i.e.*, $Co^{II}Cl_2(N_2H_4)_2$, are stable distorted octahedral complexes, insoluble in all solvents except those which destroy the compound.[4] The purpose of this investigation was to explore the possibility of preparing bidentate complexes of cobalt(II) halides with N-N ligands other than hydrazine, as well as isolating the probable tris(hydrazino)cobalt(II) halides. This was attempted by either direct reaction of cobalt(II) halides with azines and hydrazones or by

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nondestructive condensation of bis(hydrazino)cobalt(II) halides with ketones or aldehydes.

Experimental Section

Magnetic susceptibility was measured by the Gouy method and the electronic spectra of the solid complexes were determined on a Beckman DB-GT spectrometer fitted with its reflectance attachment. Infrared spectra were obtained from potassium bromide wafers on a Perkin-Elmer 337 grating spectrometer. X-Ray powder diffraction patterns were obtained with a Philips 12045 diffraction unit, with chromium diffraction tube, vanadium β filter, and a General Electric 10-cm diameter camera. The Kodak NS-54T film was developed for 8 min upon sample exposures of 15–30 hr. Each film was measured twice on a GE linear comparator. Molecular weights were determined by melting point depression in β-naphthol.

(Cyclohexanone azino)cobalt(II) Bromide.—A solution of 21.9 g (0.1 mol) of anhydrous cobalt(II) bromide in 50 ml of dry acetone was added slowly under agitation to a solution of 19.2 g (0.1 mol) of freshly prepared cyclohexanone azine in 50 ml of dry acetone, at room temperature. After maintaining the agitation for 20 min, the resulting blue precipitate was filtered, washed with acetone, and dried. The 51 g of dry blue powder represented a quantitative yield of (cyclohexanone azino)cobalt(II) bromide decomposing above 250°. *Anal.* Calcd for $Co^{II}Br_2(C_6H_{10}{=}N{-}N{=}C_6H_{10})$: C, 35.06; H, 4.90; N, 6.81; Br, 38.88; Co, 14.33. Found: C, 35.08; H, 4.99; N, 6.79; Br, 39.10; Co, 14.15. Infrared spectrum (in cm^{-1}): 2910 vs, 2850 vs, 1590 vs, 1445 s, 1350 m, 1315 m, 1280 w, 1250 m, 1140 w, 1030 w, 995 s, 915 w, 865 m, 665 w. Molecular weight: calcd, 411; found, 439.

(Propionaldazino)cobalt(II) Chloride.—An anhydrous methanolic solution of 11.2 g (0.1 mol) of propionaldazine and 12.9 g (0.1 mol) of cobalt(II) chloride was slowly evaporated under vacuum at room temperature. The resulting amorphous dark blue solid was washed with petroleum ether (bp 36–57°) and vacuum dried. A quantitative yield of (propionaldazino)cobalt(II) chloride, melting with decomposition above 150°, was obtained. *Anal.* Calcd for $Co^{II}Cl_2(C_3H_6{=}N{-}N{=}C_3H_6)$: C, 29.77; H, 4.99; N, 11.57; Cl, 29.30; Co, 24.35. Found: C, 30.02; H, 5.10; N, 11.48; Cl, 28.97; Co, 24.44. Molecular weight: calcd, 242; found, 233.

(Benzophenone azino)cobalt(II) Bromide.—Twenty-seven grams (0.1 mol) of anhydrous bis(hydrazino)cobalt(II) bromide, prepared from cobaltous bromide and hydrazine, was treated with 100 g of recrystallized benzophenone at 300° for 1 hr or until the green reaction mixture appeared homogeneous. After cooling, the reaction product was thoroughly washed with dry methyl ethyl ketone to eliminate the excess of benzophenone. The resulting 34.4 g of blue powder represented a 62% yield of (benzophenone azino)cobalt(II) bromide, melting with decomposition at 165°. *Anal.* Calcd for $Co^{II}Br_2(C_{13}H_{10}{=}N{-}N{=}C_{13}H_{10})$: C, 53.91; H, 3.48; N, 4.83; Br, 27.59; Co, 10.17. Found: C, 52.90; H, 3.92; N, 4.80; Br, 28.62; Co, 10.81. Molecular weight: calcd, 579; found, 558.

(Biacetyl cyclohexanone diazino)cobalt(II) Bromide.—(A) Twenty-two grams (0.1 mol) of anhydrous cobalt(II) bromide was intimately blended with 27.4 g (0.1 mol) of biacetyl cyclohexanone diazine, prepared by condensation of cyclohexanone and biacetyl dihydrazone. The mixture was heated to 150–200° for 15 min in a well-ventilated hood and behind adequate shield protection. After cooling, the reaction mixture was dissolved in a minimum amount of methyl ethyl ketone and the complex was precipitated with *n*-hexane. Twenty-seven grams of (biacetyl cyclohexanone diazino)cobalt(II) bromide, a light green powder melting with decomposition at 210°, was filtered and dried (55% yield). *Anal.* Calcd for $Co^{II}Br(C_6H_{10}{=}N{-}N{=}C(CH_3)C(CH_3){=}N{-}N{=}C_6H_{10})$: C, 38.96; H, 5.31; N, 11.36; Br, 32.40; Co, 11.95. Found: C, 37.88; H, 5.12; N, 11.19; Br, 32.62; Co, 11.50.

(B) Forty-five grams of bis(biacetyl dihydrazono)cobalt(II) bromide, prepared from biacetyl dihydrazone and cobalt(II) bromide,[7] was suspended in 500 ml of cyclohexanone. The reaction mixture was refluxed until the complex dissolved and the water of condensation was eliminated by azeotropic distillation. Upon cooling, 56.2 g of (biacetyl cyclohexanone diazino)cobalt(II) bromide was obtained by precipitation with *n*-hexane (83% yield). *Anal.* Found: C, 38.95; H, 5.55; N, 9.88; Br, 33.53; Co, 11.74.

Tris(hydrazino)cobalt(II) Chloride.—In a drybox, under nitrogen atmosphere, 6.4 g (0.02 mol) of (cyclohexanone azino)cobalt(II) chloride, prepared following the procedure described above for the bromide, was dissolved in 50 ml of dimethylformamide. To this solution was added, under vigorous agitation, a solution of 3.0 g of anhydrous hydrazine in 50 ml of dimethylformamide. The immediately precipitated pale orange tris(hydrazino)cobalt(II) chloride was filtered and washed with anhydrous ether (100% yield). When dry, this complex is unstable in air and decomposes violently at room temperature. It can nevertheless be stored for several days under refrigeration in ampoules under nitrogen. *Anal.* Calcd for $Co^{II}Cl_2(N_2H_4)_3$: H, 5.34; N, 37.18; Cl, 31.37; Co, 26.07. Found: H, 5.01; N, 38.00; Cl, 31.41; Co, 26.04. Infrared spectrum (in cm^{-1}): 3195 vs, 3090 vs, 2175 w, 1620 vs, 1590 vs, 1400 s, 1325 s, 1310 s, 1220 s, 1160 vs, 970 s, 620 m, 565 vs, 518 m.

Tris(phenylhydrazino)cobalt(II) Chloride.—Following the general procedure outlined above for the preparation of tris(hydrazino)cobalt(II) chloride, the tris(phenylhydrazine) analog was obtained in quantitative yields by treating a solution of 6.4 g (0.02 mol) of (cyclohexanone azino)cobalt(II) chloride in 50 ml of dimethylformamide with 9.1 g of phenylhydrazine. The salmon pink complex is unstable in air although less explosive than the tris hydrazinate. *Anal.* Calcd for $Co^{II}Cl_2(C_6H_5N_2H_3)_3$: C, 47.58; H, 5.32; N, 18.50; Cl, 15.61; Co, 12.97. Found: C, 46.99; H, 5.33; N, 18.88; Cl, 15.60; Co, 13.01.

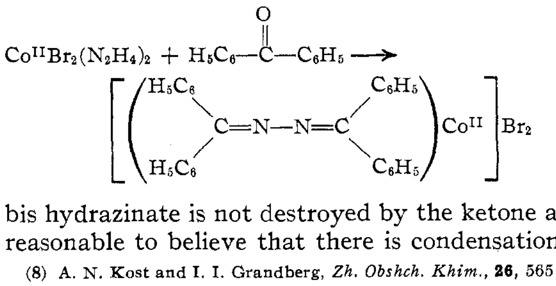
Tris(hydrazine hydrochloride)cobalt(II) Chloride.—Sixty-nine grams (0.6 mol) of freshly distilled benzal hydrazone was added dropwise, under agitation and at room temperature, to a solution of 41.4 g (0.6 mol) of hydroxylamine hydrochloride and 13 g (0.1 mol) of cobalt(II) chloride in 250 ml of anhydrous methanol. The agitation was maintained for 30 min and the precipitated purple complex was filtered, washed with ether, and air dried. Thirty-three grams of tris(hydrazine hydrochloride)cobalt(II) chloride was obtained (99% yield). The compound is infusible, stable in air, and very soluble in water. Quantitative amounts of benzaldoxime and residual hydrazine hydrochloride can be further isolated by distillation of the methanol filtrate. *Anal.* Calcd for $Co^{II}Cl_2(N_2H_4{\cdot}HCl)_3$: H, 4.51; N, 25.05; Cl, 52.85; Co, 17.57. Found: H, 4.48; N, 24.99; Cl, 52.53; Co, 17.60.

Discussion of Results

Cyclohexanone azine has been reported to form with $ZnCl_2$ a not fully characterized white complex.[8] We found that this same ketazine reacts easily, at room temperature, with alcoholic solutions of anhydrous cobalt(II) halides to form 1:1 complexes of bright colors (deep blue for the chloride, pale blue for the bromide, green for the iodide) (see eq 1). Other similar ligands

$$H_{10}C_6{=}N{-}N{=}C_6H_{10} + Co^{II}X_2 \longrightarrow [(H_{10}C_6{=}N{-}N{=}C_6H_{10})Co^{II}]X_2 \quad (1)$$

such as acetone azine, cyclopentanone azine, propionaldazine, or benzaldazine react similarly but sometimes at slightly higher temperatures. The cobalt(II) halide azinates are all soluble in dimethylformamide and conductometric titrations in that solvent indicate the formation of the 2:1 electrolyte as formulated in eq 1. A benzophenone azino complex of cobalt(II) bromide was obtained by refluxing a suspension of the bis hydrazinate in benzophenone (eq 2). In this case, the



(2)

bis hydrazinate is not destroyed by the ketone and it is reasonable to believe that there is condensation of the

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[7] R. C. Stoufer and D. H. Bush, *J. Amer. Chem. Soc.*, **78**, 6016 (1956).

[8] A. N. Kost and I. I. Grandberg, *Zh. Obshch. Khim.*, **26**, 565 (1956).

TABLE I

Complexes	Color	μ(18°), BM	X-Ray powder pattern, d (I/I_1)			
(Cyclohexanone azino)cobalt(II) bromide	Dark blue	4.49	8.94 (1.0)	6.06 (0.8)	4.76 (0.9)	4.24 (0.9)
(Cyclohexanone azino)cobalt(II) chloride	Pale blue	4.52	9.85 (1.0)	8.22 (0.6)	4.31 (0.8)	4.14 (0.8)
(Cyclopentanone azino)cobalt(II) chloride	Pale blue	4.61	9.14 (1.0)	7.86 (0.4)	4.22 (0.8)	3.72 (0.8)
(Propionaldazino)cobalt(II) chloride	Dark blue	4.69	5.48 (1.0)	4.26 (0.8)	2.70 (0.4)	2.48 (0.3)
Tris(hydrazino)cobalt(II) chloride	Pale orange	4.80	6.38 (1.0)	5.76 (0.5)	4.47 (0.7)	4.34 (0.4)
Tris(phenylhydrazino)cobalt(II) chloride	Salmon pink	4.96	12.80 (1.0)	6.62 (0.3)	5.90 (0.8)	5.32 (0.5)
Tris(hydrazine hydrochloride)cobalt(II) chloride	Pale violet	5.06	6.88 (1.0)	4.85 (0.5)	3.09 (0.4)	3.07 (0.4)

hydrazine with the solvent, followed by the displacement of one of the ligands, probably caused by steric crowding. This compound could not be obtained by direct reaction of benzophenone azine with cobalt(II) bromide, which seems to preclude a two-step reaction involving, first, a decomposition of the bis hydrazinate, followed by a chelation of the metal halide with the benzophenone azine formed subsequently by condensation of the ketone with free hydrazine. The total reflectance spectrum and room-temperature magnetic susceptibility of the azinates are characteristic of tetrahedral cobalt(II) complexes (Figure 1 and Table I).

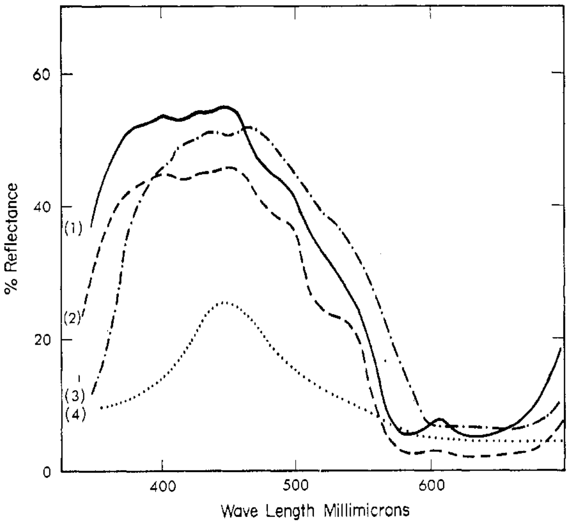
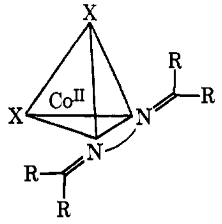


Figure 1.—Electronic spectra of cobalt azinates: (1) (cyclohexanone azino)cobalt(II) chloride; (2) (cyclopentanone azino)cobalt(II) chloride; (3) (cyclohexanone azino)cobalt(II) bromide; (4) (propionaldazino)cobalt(II) chloride.

The intense absorption in the red part of the spectrum is due to the $^4A_2 \rightarrow {}^4T_1(P)$ state transition and accounts for the characteristic blue color of the compounds. The magnetic moments in the range 4.4–4.8 BM are also consistent with a tetrahedral structure. All the azine complexes prepared showed a characteristic N–N stretching absorption lying in the 980–995-cm^{-1} region of their infrared spectrum. Prior observations made with polymeric metal halide complexes containing bidentate hydrazine groups have led to the identification of the N–N stretching vibration of such compounds as lying in the 960–985-cm^{-1} region.[9] Several complexes containing unidentate hydrazines have also been investigated and their N–N stretching frequency was observed to move consistently to lower frequencies, *e.g.*, 952 cm^{-1} for $[Hg(N_2H_4)_2]Cl_2$[10] and 956 cm^{-1} for BF_3-(N_2H_4).[11] Thus, the N–N stretching frequency appears to be useful for determining the presence of uni- or bidentate types of hydrazine derivatives.

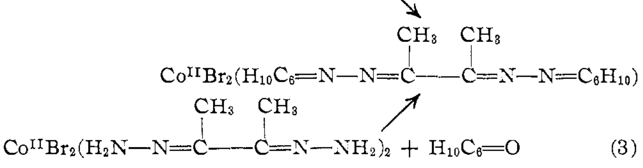
In the case of the azinocobalt(II) halides these N–N vibrations regularly occur at frequencies higher than those reported for bidentate hydrazinates (970 cm^{-1}) or unidentate hexahydrazinates,[4] and since they were found to exist in monomeric form, it is reasonable to believe that the azinates can adopt the bidentate chelate structure of type I. Only closely related analogs exhibit some isomorphous characters, as indicated by the X-ray powder diffraction patterns (Table I). Although polydentate metal complexes with ligands containing azine[12] or hydrazone[13] groups have been reported, there is little indication that the different nitrogen atoms of such ligands show bonding preferences depending upon their position in the ligand, or even that bonding actually occurs between the metal and the N–N groups.



I

If, as we think, azines tend to form bidentate chelates with cobalt(II) halides, the investigation of ligands containing nitrogen atoms common to an azino group as well as to a strong and better known chelating group could be of interest to show possible bonding preferences.

As an example, biacetyl(cyclohexanone diazine) was treated with cobalt(II) halides and the corresponding 1:1 complexes, generally green powders, were obtained. Alternatively, the same complexes were prepared by condensation of bis(biacetyl dihydrazono)cobalt(II) halides of known structure[7] with cyclohexanone (eq 3).



$$H_{10}C_6{=}N{-}N{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}N{-}N{=}C_6H_{10} + Co^{II}Br_2 \searrow Co^{II}Br_2(H_{10}C_6{=}N{-}N{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}N{-}N{=}C_6H_{10}) \nearrow Co^{II}Br_2(H_2N{-}N{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}N{-}NH_2)_2 + H_{10}C_6{=}O \qquad (3)$$

Here again, the condensation reaction is followed by the displacement of one ligand. It seems well accepted that biacetyl dihydrazone forms stable bidentate chelates with cobalt(II) halides, in which coordination

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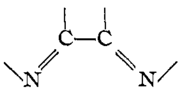
bonding is ensured by the lone pair electrons of the two nitrogen atoms next to the alkane group, not by the terminal $-NH_2$ groups of the hydrazone.[14] It is therefore reasonable to propose a similar structure for the biacetyl(cyclohexanone diazino)cobalt(II) halides where the



group appears to be favored over the more labile $=N—N=$ ligand. This is further reinforced by the fact that monohydrazones do not seem to form stable complexes with cobalt(II) halides. Instead, the reaction of cobalt(II) chloride with benzal hydrazone at room temperature leads to the cleavage of the hydrazone and the formation of bis(hydrazino)cobalt(II) chloride and free benzaldazine (eq 4). The azine complexes of cobalt(II) halides are stable compounds which can be stored for several months without decomposition, but at high temperature they decompose, generally into pyrroles or pyrazolines, according to the structure of the azine.[15] The azine ligand is easily displaced by anhydrous hydrazine or phenyl hydrazine to yield quantitative amounts of the corresponding tris(hydrazino)cobalt(II) halides by ligand exchange (eq 5). The tris hydrazinates of cobalt(II) chloride, bromide, and iodide were prepared but only the chloride complex could be investigated properly. The chloride can be stored in ampoules under nitrogen for a few days below 0° but the bromide and iodide analogs decompose violently. They are readily soluble in anhydrous hydrazine and yield, upon evaporation, the reported hexahydrazinates.[4] Freshly prepared tris hydrazinates and phenylhydrazinates are crystalline light orange or pink solids exhibiting a strong N–N stretching vibration in the 970-cm^{-1} region of the infrared spectrum, indicative of a probable bidentate bridging or chelating hydrazine.[9] Magnetic moments above 4.8 BM at room temperature are characteristic of high-spin octahedrally coordinated d^7 ions. In the visible spectrum, the absorption bands which are seen in the blue part of the spectrum, thus accounting for the pink color of the tris hydrazinates, are most likely due to the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition (450 mμ) and, at a lower energy, to the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition (500–550 mμ) (Figure 2). Such electronic spectra are to be expected for octahedrally coordinated cobalt(II) complexes and one would be tempted to speculate that the tris hydrazinates might adopt the form of monomeric three-membered chelates. The instability of the complexes, however, made any further attempt to elucidate their structure fruitless. It then became possible to prepare the tris(hydrazine hydrochloride)cobalt(II) chloride by hydrazone cleavage in the presence of hydroxylamine hydrochloride. This reaction led to quantitative amounts of the hydrazinate and of benzaldoxime (eq 6). In order to obtain quantitative yields, the stoichiometry indicated in (6) is necessary and points to the formation of the unstable hexa(hydrazine hydrochloride)cobalt(II) chloride as a possible intermediate unidentate complex. The tris hydrazinate is a stable infusible pale violet crystalline solid, insoluble in most organic solvents but very soluble in water in which it dissociates quantitatively into $Co^{II}Cl_2$ and $N_2H_4\cdot HCl$. Conductivity measurements reveal that a similar dissociation occurs in methanol. Its physical properties are similar to those of the known bis(hydrazine hydrochloride)cobalt(II) chloride[16] and its high effective magnetic moment (5.06 BM) at room temperature as well as its electronic spectrum (Figure 2) strongly indicates an octahedral environment. $Co^{II}Cl_2(N_2H_4\cdot HCl)_3$ was the only compound of this study which could yield stable single crystals and a structure resolution of this complex is the object of a separate investigation.

$$4H_5C_6—CH{=}N—NH_2 + Co^{II}Cl_2 \longrightarrow Co^{II}Cl_2(N_2H_4)_2 + 2H_5C_6—CH{=}N—N{=}CH—C_6H_5 \quad (4)$$

$$(H_{10}C_6{=}N—N{=}C_6H_{10})Co^{II}X_2 + 3N_2H_4 \longrightarrow Co^{II}X_2(N_2H_4)_3 + H_{10}C_6{=}N—N{=}C_6H_{10} \quad (5)$$

$$6H_5C_6—CH{=}N—NH_2 + 6NH_2OH\cdot HCl + Co^{II}Cl_2 \longrightarrow Co^{II}Cl_2(N_2H_4\cdot HCl)_3 + 6H_5C_6—CH{=}NOH + 3N_2H_4\cdot HCl \quad (6)$$

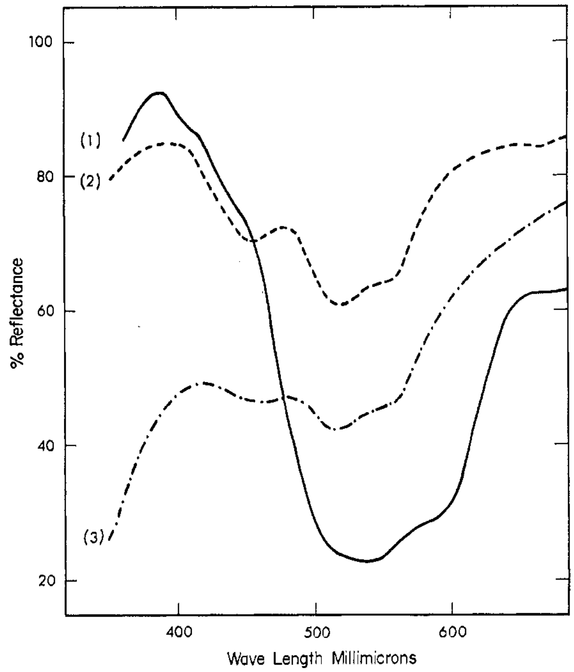


Figure 2.—Electronic spectra of cobalt tris hydrazinates: (1) tris(hydrazine hydrochloride)cobalt(II) chloride; (2) tris(hydrazino)cobalt(II) chloride; (3) tris(phenylhydrazino)cobalt(II) chloride.

Acknowledgment.—The authors wish to thank Mr. M. Paliobagis for conducting the X-ray diffraction experiments.

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