The stronger the fifth ligand the higher the energy of the d_{z^2} orbital becomes. This model requires that the shift in energy be inversely proportional to the axial donor strength.

For the complexes reported here (Table I) the differences in band positions are small; however, it appears that nickel may respond to changes in axial donor strength as predicted. The band maxima are in the order $I^- \sim ClO_4^- > Br^- > Cl^-$, which is, of course, opposite to the spectrochemical series. As previously stated, the chloride and bromide exist as hydrates and data available on these complexes are not sufficient to tell whether the water molecules or halide ions are coordinated. The fact that there is a light shift in absorption maximum between the Cl^- and Br^- complexes indicates that the fifth ligand is probably not the same for the two. The halide ions are assumed to be coordinated.

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Cobalt(III) Complexes Containing the Macrocyclic, Tetradentate, Schiff Base Ligand Tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine

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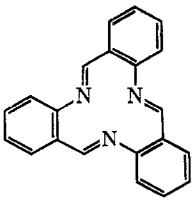
Cobalt(III) compounds of the stoichiometries $Co(TAAB)X_3$ and $Co(TAAB)XY_2$, where TAAB is tetrabenzo[*b,f,j,n*]-[1,5,9,13]tetraazacyclohexadecine, X^- is Br^-, Cl^-, NO_3^-, NCS^-, or N_3^-, and Y^- is ClO_4^- or NO_2^-, have been prepared *via* the metal ion directed self-condensation of *o*-aminobenzaldehyde. By means of a variety of physical methods the compounds have been characterized as pseudooctahedral cobalt(III) complexes. The geometry of the complexes is discussed with respect to the usual stereochemistry of the cobalt ion and its role as a template in the ring-forming reaction.

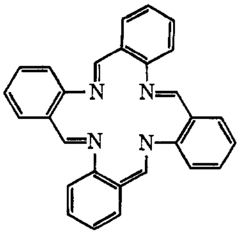
Introduction

In recent years the synthesis of many new macrocyclic ligands has been facilitated by the use of transition metal ions serving as templates.[1] Extensive studies of *o*-aminobenzaldehyde in the presence of a variety of metal ions have demonstrated that this reaction is governed by template effects.[2-9]

Depending upon the particular metal ion used, this reaction yields two types of macrocyclic Schiff base ligands which can be isolated only in the form of their metal complexes. These are a closed tridentate, tribenzo[*b,f,j*][1,5,9]triazacycloduodecine, abbreviated TRI, structure I, and a closed tetradentate, tetrabenzo-[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine, abbreviated TAAB, structure II.



I



II

Because two ligands of different multidentate character can be formed and since a variety of metal ions can be used in this condensation reaction, this system affords a unique opportunity for studying the stereoselectivity of the metal ion acting as a template in the ring-forming reaction. To illustrate, in the presence of nickel(II) ions, both TRI and TAAB are formed and complexes of either square-planar geometry, $Ni(TAAB)^{2+}$, or pseudooctahedral geometry, $Ni(TAAB)X_2$, $Ni(TRI)X_2 \cdot H_2O$, and $Ni(TRI)_2^{2+}$, have been isolated and characterized.[2-7] However, in the presence of copper(II) ions, only TAAB is formed and only complexes of square-planar geometry, $Cu(TAAB)^{2+}$, have been isolated.[6]

In view of the usual stereochemistry of cobalt ions, the self-condensation of *o*-aminobenzaldehyde in the presence of cobalt(II), with subsequent oxidation of the metal ion to cobalt(III), is expected to result in the template synthesis of both ligands which could then be isolated as the pseudooctahedral cobalt(III) complexes. Investigations of the cobalt reactions have confirmed these expectations.[10,11]

In an earlier paper, the synthesis and characterization of two diastereoisomers of the bis-tridentate complex, $Co(TRI)_2^{3+}$, structure III, were reported.[12] No evidence for a complex containing only 1 mol of TRI per cobalt(III) ion was found. The structure of $Co(TRI)_2^{3+}$ was first established by a single-crystal X-ray structure determination.[13]

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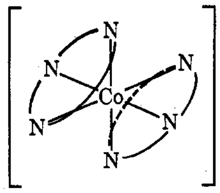
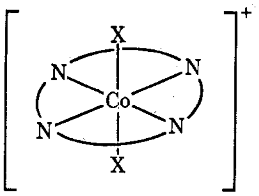


III



IV

We now report the template synthesis of cobalt(III) complexes containing the macrocyclic TAAB ligand. These new compounds, with general formulas Co(TAAB)X_3, structure III, and Co(TAAB)XY_2 again reflect the preference of cobalt ions toward formation of octahedral complexes.

Experimental Section

Materials.—*o*-Aminobenzaldehyde was freshly prepared by the method of Smith and Opie.[14] All other chemicals were obtained commercially and were reagent grade or equivalent.

Reaction of Cobalt(II) Bromide with *o*-Aminobenzaldehyde.—Freshly prepared *o*-aminobenzaldehyde (10.0 g, 0.083 mol) was dissolved in 40 ml of absolute ethanol and brought under reflux. A solution of 4.53 g (0.021 mol) of $CoBr_2$ in 10 ml of ethanol, containing 2 drops of HBr, was added. The color of the solution changed immediately from yellow to green. Solid material began to deposit after about 20 min. Refluxing was continued for 8 hr and then the mixture was chilled overnight. A dark green powder (A) was collected, washed with chilled ethanol and ether, and dried overnight, *in vacuo*, at 100°, yield ~40%.

Isolation of Dibromotetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinecobalt(III) Bromide, [Co(TAAB)Br_2]Br.—A 0.65-g sample of A was stirred overnight at room temperature in 650 ml of water or ethanol which had been strongly acidified with 65 ml of concentrated HBr. Air was simultaneously bubbled through the solution. The red-brown precipitate which formed was collected and purified by washing with methanol until the filtrate was colorless. The maroon product was dried overnight, *in vacuo*, at 100°; yield ~20%. The material is very insoluble and was not recrystallized. *Anal.* Calcd for $CoC_{28}H_{20}N_4Br_3$: C, 47.30; H, 2.84; N, 7.88; Br, 33.75; Co, 8.30. Found: C, 46.93; H, 3.18; N, 7.83; Br, 33.87; Co, 8.11.

Synthesis of Dinitratotetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinecobalt(III) Nitrate, [Co(TAAB)$(NO_3)_2$]NO_3.—A 2.72-g sample (0.0038 mol) of [Co(TAAB)Br_2]Br was ground in a mortar with a pestle with 4.02 g (0.012 mol) of $AgNO_3$ which had been dissolved in 5 ml of water containing 2 drops of concentrated HNO_3. During the grinding, the color of the paste changed from red to brownish yellow. The mixture was washed into a beaker with 400 ml of water which had been acidified to a pH of 2 with HNO_3. After removal of AgBr, the red-brown aqueous solution was evaporated to dryness and the residue was dissolved in acidic methanol. A stream of air was passed across the solution to induce crystallization. The red-brown crystals which formed were collected, washed with ether, and dried overnight, *in vacuo*, at 100°; yield ~50%. *Anal.* Calcd for $CoC_{28}H_{20}N_7O_9$: C, 51.20; H, 3.08; N, 14.92; Co, 8.97. Found: C, 51.46; H, 3.15; N, 15.08; Co, 8.88.

Synthesis of Dichlorotetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinecobalt(III) Chloride, [Co(TAAB)Cl_2]Cl.—A 2.72-g sample (0.0038 mol) of [Co(TAAB)Br_2]Br was ground in a mortar with a pestle with 1.65 g (0.012 mol) of freshly prepared AgCl. During the grinding, the color of the paste changed from red to brownish yellow. The mixture was washed into a beaker with 2 l. of water which had been adjusted to a pH of 2 with concentrated HCl. The AgBr was removed and the resulting solution was evaporated nearly to dryness. The ochre solid which precipitated was collected, washed with ethanol and ether, and dried overnight, *in vacuo*, at 100°; yield ~45%. The compound was very insoluble and was not recrystallized. *Anal.* Calcd for $CoC_{28}H_{20}N_4Cl_3$: C, 58.20; H, 3.46; N, 9.70; Cl, 18.40; Co, 10.18. Found: C, 58.16; H, 3.63; N, 9.93; Cl, 18.65; Co, 9.87.

An alternate procedure for synthesis of [Co(TAAB)Cl_2]Cl involved the direct reaction of $CoCl_2$ with *o*-aminobenzaldehyde followed by air oxidation of the product in the presence of HCl.

Synthesis of Dithiocyanatotetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinecobalt(III) Thiocyanate, [Co(TAAB)$(NCS)_2$]NCS.—A 1.18-g sample (2.05×10^{-3} mol) of [Co(TAAB)Cl_2]Cl was ground in a mortar with a pestle with 1.05 g (6.15×10^{-3} mol) of $AgNO_3$ which had been dissolved in 10 ml of water. The mixture was taken up in 300 ml of water and the AgCl was removed. The red-brown filtrate was added to a solution of 1.0 g (1.23×10^{-2} mol) of NaSCN which had been dissolved in 25 ml of water. The brown solid which precipitated immediately was collected and recrystallized from methanol; yield ~30%. *Anal.* Calcd for $CoC_{31}H_{20}N_7S_3$: C, 57.70; H, 3.13; N, 15.20; S, 14.88; Co, 9.13. Found: C, 57.50; H, 3.40; N, 15.22; S, 15.07; Co, 8.87.

Synthesis of Diazidotetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinecobalt(III) Azide, [Co(TAAB)$(N_3)_2$]N_3.—A 1.08-g sample (1.64×10^{-3} mol) of [Co(TAAB)$(NO_3)_2$]NO_3 was dissolved in 250 ml of a 4:1 methanol–water mixture. This was added to a solution containing 1.0 g (4.9×10^{-3} mol) of NaN_3 in 20 ml of water. A dark, crystalline material precipitated. After concentration of the solution under an air stream, the product was collected, washed with chilled methanol and ether, and dried overnight, *in vacuo*, at 100°; yield ~75%. *Anal.* Calcd for $CoC_{28}H_{20}N_{13}$: C, 56.25; H, 3.35; N, 30.50; Co, 9.87. Found: C, 55.64; H, 3.54; N, 29.72; Co, 10.22.

Synthesis of Nitratoperchloratotetrabenzo[*b,f,j,n*][1,5,9,13]-tetraazacyclohexadecinecobalt(III) Perchlorate, [Co(TAAB)-$(NO_3)(ClO_4)$]ClO_4.—A 1.18-g sample (2.05×10^{-3} mol) of [Co(TAAB)Cl_2]Cl was ground in a mortar with a pestle with 1.05 g (6.15×10^{-3} mol) of $AgNO_3$ which had been dissolved in 10 ml of water. The mixture was taken up in 300 ml of water and the AgCl was removed. The red-brown filtrate was added to 1.5 g (1.23×10^{-2} mol) of $NaClO_4$ which had been dissolved in 25 ml of water containing 5 drops of $HClO_4$. Upon concentration of solution, dark red crystals formed. The product was collected, recrystallized from methanol containing a few drops of $HClO_4$, and dried overnight, *in vacuo*, at room temperature; yield ~100%. *Anal.* Calcd for $CoC_{28}H_{20}N_5Cl_2O_{11}$: C, 45.90; H, 2.73; N, 9.57; Cl, 9.70; Co, 8.05. Found: C, 45.82; H, 2.95; N, 9.40; Cl, 9.65; Co, 8.22.

Synthesis of Dinitrotetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinecobalt(III) Nitrate, [Co(TAAB)$(NO_2)_2$]NO_3.—A 0.2-g sample (3.04×10^{-4} mol) of [Co(TAAB)$(NO_3)_2$]NO_3 was dissolved in 200 ml of water and the solution was deaerated for 30 min. The solution was chilled to 5° and nitric oxide was bubbled into it for 1 hr. After about 10 min, the color of the solution changed from cherry red to yellow-orange. After 30 min, a brick red precipitate formed. The product was collected, washed with ether, and dried overnight, *in vacuo*, at 100°; yield ~75%. *Anal.* Calcd for $CoC_{28}H_{20}N_7O_7$: C, 52.30; H, 3.45; N, 15.25. Found: C, 52.95; H, 3.32; N, 15.29.

Physical Measurements.—Infrared absorption spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. Both KBr and Nujol mull techniques were utilized and polystyrene was used for calibration. Electronic spectra were obtained with a Cary Model 14 recording spectrophotometer. Solution spectra were run in 1-cm quartz cells. Spectra of solid samples were measured in Nujol mulls using the diffuse-transmittance technique.[15] Molar conductivities were calculated from electrical resistance of solutions (10^{-3} *M* in complex) measured with an Industrial Instruments, Inc., Model RC-16B conductivity bridge. Magnetic susceptibilities were measured using both the Gouy and Faraday methods. Susceptibilities of ligands and anions were calculated from Pascal's constants.[16] Mass spectra of solid samples were obtained at 250° using an MS-9 mass spectrometer. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by A Bernhardt Mikroanalytisches Laboratorium, Engelskirchen, West Germany.

Results and Discussion

A mixture of two cobalt(III) complexes containing the cations Co(TRI)$_2^{3+}$, structure III, and Co(TAAB)-X_2^+, structure IV, results from air oxidation of the crude material obtained from self-condensation of *o*-aminobenzaldehyde in the presence of various co-

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(15) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1279 (1964).

(16) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

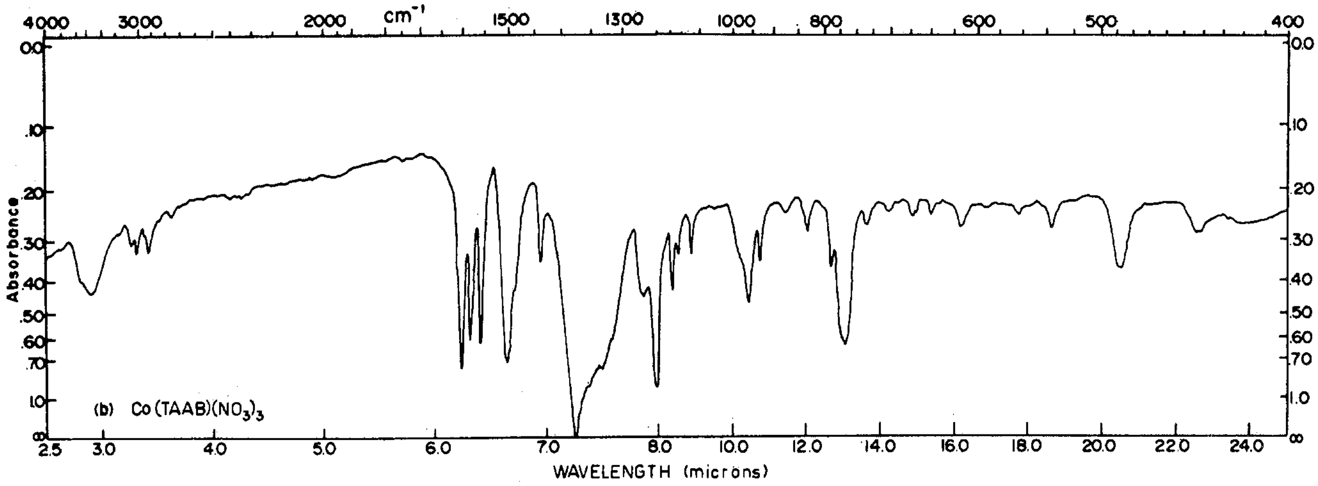

Figure 1.—Infrared spectrum of $[Co(TAAB)(NO_3)_2]NO_3$.

balt(II) salts, CoX_2. Separation of the mixture into its components is most easily accomplished for the Br^- derivatives since $[Co(TRI)_2]Br_3$ and $[Co(TAAB)Br_2]Br$ show marked differences in solubility. For this reason, $CoBr_2$ is conveniently used as the cobalt(II) salt in the template synthesis, and the oxidation is carried out in the presence of high concentrations of HBr. The separation of the soluble bis-tridentate complex from the relatively insoluble complex of the tetradentate ligand is achieved by washing the mixture several times with hot, acidic methanol. $[Co(TAAB)Br_2]Br$ is isolated by filtration as an insoluble, microcrystalline maroon solid, while $[Co(TRI)_2]Br_3$ is obtained as a yellow-orange solid by concentration of the yellow methanol filtrate. The characterization of $[Co(TRI)_2]Br_3$ is described elsewhere.[12]

Metathetical reactions of $[Co(TAAB)Br_2]Br$ have been used to prepare six additional cobalt(III) complexes of the general formulas $[Co(TAAB)X_2]X$, where X^- is Cl^-, NCS^-, NO_3^-, or N_3^-, and $Co(TAAB)XY_2$, where X^- is NO_3^- and Y^- is ClO_4^- or NO_2^-. These cobalt(III) complexes have been characterized by elemental analyses, infrared, electronic, and mass spectra, and magnetic susceptibility and conductivity measurements. The insolubilities of some of the derivatives precluded a thorough investigation of their properties in solution.

Analytical data for the cobalt complexes (Experimental Section) indicate their formulation as cobalt(III) derivatives containing one TAAB ligand and three anions per cobalt.

The presence of the tetradentate ligand has been confirmed by measuring the mass spectra of $[Co(TAAB)(NO_3)_2]NO_3$ and $[Co(TAAB)(NCS)_2]NCS$. In both cases, relatively intense *m/e* peaks at 412, corresponding to $(TAAB)^+$, were present, while *m/e* peaks at 309 or 308 corresponding to $(TRI)^+$ or $(TRI\text{-}H)^+$ were absent or very weak. In addition, a peak at 472 corresponding to $Co(TAAB)^+$ was observed in the spectrum of the nitrate derivative.

The cyclic nature of the ligand is inferred from infrared spectra of the derivatives. The ir spectrum of $[Co(TAAB)Br_2]Br$, which is typical of all of the cobalt derivatives, is reported in Table I along with the spectrum of $Ni(TAAB)Br_2$ for comparison. The similarity of the spectra, including the absence of any bands attributable to –NH or >C=O stretching frequencies, and the appearance of a strong band at ~1570 cm⁻¹ which has been assigned to the >C=N stretching vibration, establishes the presence of the completely condensed TAAB macrocycle. Strong bands at 1610 and 1592 cm⁻¹ and medium peaks at 1499 and 1449 cm⁻¹ are also observed. These are assigned to the usual modes of ortho-disubstituted benzene.[17]

TABLE I

INFRARED SPECTRA OF $[Co(TAAB)Br_2]Br^a$ AND $[Ni(TAAB)Br_2^a$

$[Co(TAAB)Br_2]Br^b$	Assignments^c	$Ni(TAAB)Br_2$
3448 w	H_2O	3400 w
3077 vw		
3030 w	CH str	3020 vw
2933 m	CH str	2890 vw
2786 vw		
1610 vs	C_6, ring I	1615 vs
1592 s	C_6, ring II	1590 s
1572 vs	C=N str	1562 vs
1499 w	C_6, ring III	1490 m
1449 m	C_6, ring IV	1440 m
1397 s		1391 m
1325 s		
1285 w		1280 m
1250 m		1240 vw, b
1218 vw		
1190 s		1194 s
1170 m		1168 w
1124 m		1120 m
992 w		981 m
952 vw		
927 w		922 m
869 vw		870 vw
830 vw		824 m
795 m	CH def	775 s
765 vs	CH def	764 s
730 w		730 vw
675 vw		670 vw
650 vw		
618 w		600 vw
594 vw		595 w
537 w		532 w
489 s		494 w, b
413 w, b		472 w, b

[a] KBr disks. [b] Values given in cm⁻¹. [c] Abbreviations: m, medium; w, weak; vw, very weak; s, strong; vs, very strong; b, broad.

In addition, the ir spectra of the NCS^- and NO_3^- derivatives exhibit absorptions due to the anions which indicate that both ionic and coordinated anions are

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[17] A. R. Katritzky and R. A. Jones, *J. Chem. Soc.*, 3670 (1959).

present.[18–20] The ir spectrum of $[Co(TAAB)(NO_3)_2]NO_3$ is shown in Figure 1. A comparison of the nitrate absorptions in $Ni(TAAB)(NO_3)_2$ and $[Co(TAAB)(NO_3)_2]NO_3$ along with the band assignments is reported in Table II. The strong, sharp bands at 1380 cm^{-1} and strong shoulder at 1338 cm^{-1} have been attributed to ionic nitrate. The remaining three bands occurring at 1510, 1256, and 961 cm^{-1} are due to the coordinated anion. These bands are also observed in the spectrum of $Co(TAAB)(NO_3)(ClO_4)_2$. On the assumption that the molecule has C_{2v} symmetry, these bands have been assigned to the asymmetric stretching vibration and the symmetric stretching vibration. It can be seen that the splitting of the asymmetric stretching mode is ~150 cm^{-1} larger in the cobalt(III) complex than in the nickel(II) complex. While in certain cases, large splittings of this band have been correlated with the presence of bidentate nitrate in macrocyclic metal complexes,[21,22] it is felt that a folding of the conjugated TAAB ligand in $[Co(TAAB)(NO_3)_2]NO_3$ is unlikely. Such a conclusion is in accord with X-ray data which have shown that both $Ni(TAAB)I_2 \cdot H_2O$ and $Ni(TAAB)(BF_4)_2$ contain essentially planar donors[23] and with the electronic spectrum of $[Co(TAAB)(NO_3)_2]NO_3$ which can be interpreted on the basis of a trans-cobalt(III) geometry (*vide infra*).

TABLE II

ASSIGNMENTS OF NITRATE ABSORPTIONS IN THE IR SPECTRA OF $[Co(TAAB)(NO_3)_2]NO_3$ AND $Ni(TAAB)(NO_3)_2$[a]

$[Co(TAAB)(NO_3)_2]NO_3$[b]	$Ni(TAAB)(NO_3)_2$[b]	Assignment[c]
1510 s	1410 s	Asym str (coord)
1380 s	. . .	Asym str (ionic)
1338 sh	. . .	Asym str (ionic)
1256 s	1310 s	Asym str (coord)
961 m, b	1065 m	Sym str (coord–ionic)

[a] Nujol mulls. [b] Values given in cm^{-1}. [c] Assumed C_{2v} symmetry for coordinated NO_3^-.

TABLE V

ELECTRONIC SPECTRA OF $Co(TAAB)X_3$ AND $Co(TAAB)XY_2$ COMPLEXES[a]

Complex	Medium[b]	ν_{IE}	ν_{IA}	ν_{II}
$[Co(TAAB)Br_2]Br$	Solid	14.4	18.9, 20.0	23.6, 27.0
	DMF	15.2	21.7	28.0
$[Co(TAAB)Cl_2]Cl$	Solid	15.6	20.2, 21.3	26.3, 28.2
$[Co(TAAB)(NO_3)_2]NO_3$	Solid	16.3	19.3, 22.2	27.8
	H_2O	16.3 (350)	22.0 (2500)	28.6 (24,000)
$[Co(TAAB)(N_3)_2]N_3$	Solid	15.6	18.5, 22.2	26.3
$[Co(TAAB)(NCS)_2]NCS$	Solid	16.6	19.7	29.0
$[Co(TAAB)(NO_3)(ClO_4)]ClO_4$	Solid	16.4	22.7	28.6
	H_2O	16.2 (385)	21.8 (1280)	29.4 (14,000)
$[Co(TAAB)(NO_2)_2]NO_3$	Solid	20.0	24.4	28.6

[a] In kK (ε). [b] Diffuse-transmittance technique was used for solid-state spectra.

The presence of cobalt(III) in these compounds has been established by measurement of magnetic susceptibilities, molar conductivities, and electronic spectra. Magnetic susceptibility measurements were obtained for five of the compounds and are reported in Table III.

TABLE III

MAGNETIC SUSCEPTIBILITIES (CGSU) OF $Co(TAAB)X_3$ AND $Co(TAAB)XY_2$ COMPLEXES

Complex	$10^6\chi_M$[a]	$10^6\chi_M(cor)$[b]	Temp, °K
$[Co(TAAB)Br_2]Br$	127	447	295
$[Co(TAAB)Cl_2]Cl$[c]	−29	258	295
$[Co(TAAB)(NO_3)_2NO_3$	51	324	296
$[Co(TAAB)(NCS)_2]NCS$	−176	133	297
$[Co(TAAB)(NO_3)(ClO_4)]ClO_4$	−36	263	295

[a] Uncorrected value. [b] The diamagnetic correction for $Co(TAAB)^{3+}$ was taken as 216.4×10^{-6}; corrections for the anions were obtained from ref 16. [c] Prepared by metathesis from $[Co(TAAB)(NO_3)_2]NO_3$.

These data show that the compounds are essentially diamagnetic, although the residual paramagnetisms are slightly larger than normally expected for spin-paired cobalt(III).

Molar conductances for the soluble derivatives have been calculated and are reported in Table IV. The NCS^-, Br^-, and NO_3^- derivatives exhibit typical 1:1 electrolyte behavior in CH_3NO_2[24] and DMF,[25] while the mixed derivative $Co(TAAB)(NO_3)(ClO_4)_2$ behaves as a 2:1 electrolyte. These data indicate that NO_3^-, Br^-, and NCS^- remain coordinated to cobalt in these solutions and support the conclusions drawn from the ir spectra of the NCS^- and NO_3^- derivatives. As expected, those derivatives which are soluble in water exhibit 3:1 electrolyte behavior.

TABLE IV

CONDUCTIVITY DATA FOR COBALT(III) TAAB COMPLEXES[a]

Complex	Λ_M, mhos/cm H_2O	 CH_3NO_2	 DMF
$[Co(TAAB)(NO_3)_2]NO_3$	452	78	. . .
$[Co(TAAB)Br_2]Br$	. . .	. . .	73
$[Co(TAAB)(NCS)_2]NCS$	. . .	75	. . .
$Co(TAAB)(NO_3)(ClO_4)_2$	480	132	. . .

[a] All measurements were made on ~10^{-3} *M* solutions at 25°.

The electronic spectra of these compounds are summarized in Table V. Solution spectra for $[Co(TAAB)Br_2]Br$ in DMF and $[Co(TAAB)(NO_3)_2]NO_3$ and $[Co(TAAB)(NO_3)(ClO_4)]ClO_4$ in water are reported. All other spectra were obtained by use of the diffuse-transmittance technique.[15] The solid-state spectra are, in general, poorly resolved. Three regions of absorption at 14,000–16,000, 19,000–21,000, and 25,000–29,000 cm^{-1} can be distinguished; however, the second and third bands are unsymmetrical and appear to con-

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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]

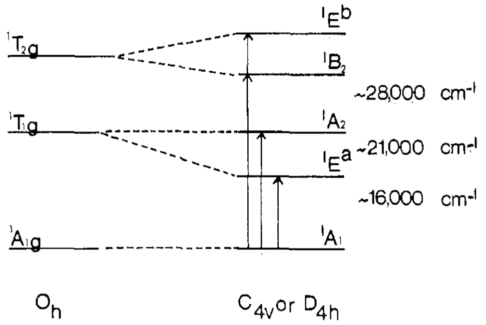

Figure 2.—Tetragonal splitting of the excited states of cobalt(III) and the energies associated with the allowed transitions.

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 $\sim$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]

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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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