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# Bidentate Chelate Compounds. 3.[1] Cobalt(III) Chemistry of 2,2′-Dipyridylamine

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A cobalt(III) chemistry of the bidentate ligand 2,2′-dipyridylamine and its deprotonated form is established. The 3:1 cobalt(III) complex and its deprotonated forms have been resolved into enantiomers and the CD spectra recorded. These complexes have been shown to be asymmetric and not merely dissymmetric by $^{13}C$ NMR spectroscopy. The spectra of these complexes show unusually intense transitions in the visible region, and the rotational strengths in the CD spectra are correspondingly large. An interpretation of the origin of the transitions is given and is based on ligand repulsions. Some 2:1 cobalt(III) complexes and some new cobalt(II) complexes are also reported, together with tables of their IR and diffuse reflectance spectra.

## Introduction

The bidentate ligand 2,2′-dipyridylamine (HDPA) and its coordination complexes with such metal ions as nickel(II),[3] copper(II),[4] iron(II),[5] cobalt(II),[6] palladium(II),[7] and rhodium(III) and iridium(III)[8] have been studied extensively. Curiously enough, no cobalt(III) complexes had been reported until recently, when as a result of the attempted oxidation of $Co(HDPA)_3(ClO_4)_2$ by hydrogen peroxide, we were able to isolate the first known cobalt(III) complex, $Co(HDPA)_2O_2(ClO_4)$.[9]

Because of our interest in the application of exciton theory to the interpretation of the CD spectra of coordination complexes, we undertook the preparation of $Co(HDPA)_3^{3+}$ ion and its resolution. This complex provides an interesting test of this use of exciton theory because the ligands are nonplanar. Interligand interactions, negligible in such complex ions as $Ni(o\text{-phen})_3^{2+}$, $Ni(bpy)_3^{2+}$, $Os(bpy)_3^{3+}$,[10] $Ru(bpy)_3^{3+}$, and $Ru(o\text{-phen})_3^{3+}$[11] (*o*-phen = 1,10-phenanthroline; bpy = 2,2′-bipyridyl), could be considerable in $Co(HDPA)_3^{3+}$ because of the proximity of the ligands. The electron exchange terms would then make a significant contribution to the energies of the exciton states and would preclude the description of the exciton states as simple product functions of localized ligand states.

In this paper, we describe some new cobalt(II) complexes of HDPA and establish a cobalt(III) chemistry for HDPA. We conclude that the unusually high intensities of the visible region transitions of $Co(HDPA)_3^{3+}$ and related species are due to ligand transitions that are moved from the ultraviolet to the visible region by strong interligand repulsions and that are mixed with the d–d transitions of cobalt(III) ion usually observed in this region.

## Experimental Section

**Analytical and Physical Measurements.** All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Magnetic susceptibilities were measured by the Faraday method in a helium atmosphere at room temperature. Conductivities were measured using a YSI Model 31 conductivity bridge.

A Cary 14 recording spectrophotometer was used to record the unpolarized electronic absorption spectra. The diffuse reflectance spectra were recorded using a Varian Model 1411 diffuse reflectance accessory with type 1 illumination. The circular dichroism spectra were obtained using a Jasco ORD/UV-5/CD-1 spectropolarimeter.

Infrared spectra were recorded using a Perkin-Elmer 137 Infracord spectrophotometer and a Perkin-Elmer 621 spectrophotometer. The samples were prepared as Nujol mulls and as KBr disks.

**Reagents and Syntheses.** The following materials were used without purification, the supplier being shown in parentheses: *o*-phen monohydrate, bpy, $PbO_2$, 30% aqueous $H_2O_2$, $NaClO_4·H_2O$ (Fisher Scientific); en (Matheson Coleman and Bell); $Co(ClO_4)_2·6H_2O$ (G. Frederick Smith Co.); $Co(NO_3)_2·6H_2O$ (Allied Chemical Co.); Dowex 1-X8, 20–50 mesh (J. T. Baker Chemical Co.). The ligand HDPA was obtained from Aldrich Chemical Co. and recrystallized before use.

The salt $Na_3Co(CO_3)_3·3H_2O$ was prepared by Drinkard's method,[12] $Co(HDPA)_3(ClO_4)_2$ by Goodgame's method,[6] and the resolving agent potassium (+)-tris[*l*-cysteinesulfinato-*S*,*N*(2−)]cobaltate(III) (abbreviation (+)-$K_3(CYSU)_3Co$) by Gillard's method.[13]

**Nitratobis(2,2′-dipyridylamine)cobalt(II) Nitrate.** A solution of $Co(NO_3)_2·6H_2O$ (2.91 g, 0.01 mol) in 5 mL of warm absolute ethanol was prepared and added to a solution of HDPA (3.42 g, 0.02 mol) dissolved in 30 mL of absolute ethanol. An orange precipitate formed and was collected by filtration. The powder was washed with 30 mL of absolute ethanol and 30 mL of diethyl ether; yield 4.21 g (80.2%). Anal. Calcd for $CoC_{20}N_8H_{18}O_6$: C, 45.72; H, 3.46; Co, 11.22; N, 21.33. Found: C, 45.69; H, 3.43; Co, 11.08; N, 21.17. $\mu_{eff}$ 5.20 $\mu_B$.

**Bis(2,2′-dipyridylamine)(1,10-phenanthroline)cobalt(II) Nitrate; Bis(2,2′-dipyridylamine)(1,10-phenanthroline)cobalt(II) Perchlorate; Bis(2,2′-dipyridylamine)(2,2′-bipyridyl)cobalt(II) Perchlorate; Bis(2,2′-dipyridylamine)(ethylenediamine)cobalt(II) Perchlorate.** The appropriate cobalt(II) salt (3.66 g perchlorate, 2.91 g nitrate, 0.01 mol) and HDPA (3.42 g, 0.02 mol) were dissolved in hot absolute ethanol (15–20 mL). The second ligand (1.98 g *o*-phen, 1.56 g bpy, 0.6 g en, 0.01 mol) was dissolved in hot ethanol (20 mL) and the two solutions were mixed. Cooling of the mixture yielded yellow crystals that were collected by filtration and washed with 20 mL of water, 20 mL of absolute ethanol, and 20 mL of diethyl ether.

For $[Co(HDPA)_2\text{-}o\text{-phen}][NO_3]_2$, yield 2.75 g (39%). Anal. Calcd for $CoC_{32}N_{10}H_{26}O_6$: C, 54.47; H, 3.72; Co, 8.35; N, 19.86. Found: C, 54.21; H, 3.90; Co, 8.19; N, 19.73. $\mu_{eff}$ 5.13 $\mu_B$.

For $[Co(HDPA)_2\text{-}o\text{-phen}][ClO_4]_2$, yield 5.32 g (68.3%). Anal. Calcd for $CoC_{32}N_8H_{26}Cl_2O_8$: C, 49.40; H, 3.91; Cl, 8.58; Co, 7.13; N, 13.56. Found: C, 49.66; H, 3.66; Cl, 9.23; Co, 6.95; N, 13.54. $\mu_{eff}$ 5.01 $\mu_B$.

For $[Co(HDPA)_2bpy][ClO_4]_2$, yield 5.12 g (67.8%). Anal. Calcd for $CoC_{30}N_8H_{26}Cl_2O_8$: C, 47.63; H, 3.47; Cl, 9.37; Co, 7.79; N, 14.82. Found: C, 47.72; H, 3.43; Cl, 9.50; Co, 7.87; N, 14.84. $\mu_{eff}$ 5.09 $\mu_B$.

For $[Co(HDPA)_2en][ClO_4]_2$, yield 2.65 g (40.2%). Anal. Calcd for $CoC_{22}N_8H_{26}Cl_2O_8$: C, 40.01; H, 3.98; Cl, 10.74; Co, 8.92; N, 16.97. Found: C, 39.59; H, 4.01; Cl, 10.80; Co, 8.67; N, 16.65. $\mu_{eff}$ 4.06 $\mu_B$.

**Tris(2,2′-dipyridylamine)cobalt(II) Perchlorate Dihydrate.** A slurry of $Co(HDPA)_2O_2ClO_4$ (0.532 g, 0.001 mol, prepared as in ref 9) in 30 mL of absolute ethanol and a solution of HDPA (0.17 g, 0.001 mol) dissolved in 30 mL of absolute ethanol were mixed and then HCl (0.2 g, 38%) was added to the solution. The solution was treated with $NaClO_4·H_2O$ (1.00 g, 0.007 mol) to precipitate the perchlorate salt. The pea green solid was collected by filtration and was washed with 30 mL of water, 30 mL of ethanol, and 30 mL of diethyl ether. Anal. Calcd for $CoC_{30}N_9H_{31}Cl_2O_{10}$: C, 44.61; H, 3.87; Cl, 8.78; Co, 7.30; N, 15.61. Found: C, 44.54; H, 3.71; Cl, 9.01; Co, 6.91; N, 15.80. $\mu_{eff}$ 4.40 $\mu_B$.

**Carbonatodiaquo(2,2′-dipyridylamine)cobalt(II) Hemihydrate.** A solution of HDPA (3.42 g, 0.020 mol) in 20 mL of water was prepared by the addition of concentrated HCl (2 mL, 38%). To this aqueous solution was added $Na_3(Co(CO_3)_3)·3H_2O$ (3.62 g, 0.010 mol). A red solution resulted immediately. Bubbles of $CO_2$ were rapidly evolved. The reaction mixture was stirred and then heated on a hot water bath for 5 min. A violet solid began to crystallize while heating. More crystals were formed upon cooling in an ice bath. The crystals were collected by filtration and were washed with 20 mL of water, 20 mL of ethanol, and 20 mL of diethyl ether. Anal. Calcd for $CoC_{11}N_3H_{14}O_{5.5}$: C, 39.39; H, 4.22; Co, 17.59; N, 12.54. Found:

C, 39.87; H, 4.20; Co, 17.56; N, 12.53. $\mu_{eff}$ 5.23 $\mu_B$.

**Carbonatobis(2,2′-dipyridylamine)cobalt(III) Perchlorate.** The mother liquor from the $Co(HDPA)CO_3(H_2O)_2 \cdot {}^1/_2H_2O$ preparation was treated with $NaClO_4 \cdot H_2O$ (1.0 g, 0.007 mol) to yield a red powder. The solid was washed with 60 mL of water, 30 mL of absolute ethanol, and 20 mL of diethyl ether. Anal. Calcd for $CoC_{21}N_6H_{18}ClO_7$: C, 44.97; H, 3.24; Cl, 6.32; Co, 10.51; N, 14.99. Found: C, 45.12; H, 3.08; Cl, 6.42; Co, 10.41; N, 14.93. $\mu_{eff} \simeq 0\ \mu_B$.

**(2,2′-Dipyridylaminato)bis(2,2′-dipyridylamine)cobalt(III) Perchlorate. Method I.** A dry mixture containing $Co(HDPA)_3(ClO_4)_2$ (1.5 g, 0.002 mol) and $PbO_2$ (0.234 g, 0.001 mol) was prepared. An HCl solution was prepared by dissolving concentrated HCl (0.3 g, 38%) in 50 mL of water and adding the solution to the dry mixture. The mixture was heated for a total of 2 h with additional $PbO_2$ (0.234 g, 0.001 mol) being added after heating for 1 h. Upon the completion of the reaction, the mixture was treated with chloride resin to dissolve the tris complex. Filtration yielded a dark green solution. The dark green solution was treated with $NaClO_4$ (1.0 g, 0.0082 mol) to precipitate a green solid. The solid was redissolved and precipitated three times. The resulting green solid was recrystallized from boiling water to yield green needles of $Co(HDPA)_2(DPA)(ClO_4)_2$. Anal. Calcd for $CoC_{30}N_9H_{26}Cl_2O_8$: C, 46.76; H, 3.41; Cl, 9.20; Co, 7.65; N, 16.37. Found: C, 46.82; H, 3.52; Cl, 9.27; Co, 7.66; N, 16.42. $\mu_{eff} \simeq 0\ \mu_B$; $\Lambda_M$ 240.00 $\Omega^{-1}$ cm$^{-1}$ M$^{-1}$ ($H_2O$, 27 °C).

**Method II.** A slurry of $Co(HDPA)_3(ClO_4)_2$ (1.00 g, 0.0013 mol) with 500 mL of distilled water was prepared. Air was bubbled through the slurry for 5 min, and then the slurry was heated on a steam bath for 24 h. The steam of air bubbles was maintained throughout. The slurry changed from orange to dark green as the cobalt(III) complex formed. At the completion of the reaction, saturated aqueous $NaClO_4$ was added to precipitate the product. Starting material was removed by redissolving in ethanol–water using chloride resin and then heating the solution to decompose the cobalt(II) complex. The solution was treated with saturated aqueous $NaClO_4$ to reprecipitate the product. This process was repeated until the mother liquid was no longer red (a red-orange color is characteristic of the decomposed cobalt(II) complex). This complex was characterized by infrared, ultraviolet, and visible spectroscopy.

**Tris(2,2′-dipyridylamine)cobalt(III) Perchlorate.** $Co(HDPA)_2(DPA)(ClO_4)_2$ was prepared by method I. Chloride resin was used to dissolve the complex in 50 mL of water. The solution was made slightly acidic with 10% aqueous $HClO_4$ and then was treated with $NaClO_4$ (1.0 g, 0.0082 mol) to yield a dark blue precipitate of $Co(HDPA)_3(ClO_4)_3$. Anal. Calcd for $CoC_{30}N_9H_{27}Cl_3O_{12}$: C, 41.37; H, 3.13; Cl, 12.21; Co, 6.77; N, 14.48. Found: C, 41.10; H, 3.33; Cl, 12.04; Co, 6.66; N, 14.34. $\mu_{eff} \simeq 0\ \mu_B$.

**Tris(2,2′-dipyridylaminato)cobalt(III)–0.6-Chloroform.** The complex $Co(HDPA)_3(ClO_4)_3$ (1.0 g, 0.001 mol) was slurried with 50 mL of 0.5 M aqueous NaOH. The dark brown solid was dissolved by the addition of 100 mL of $CHCl_3$. The brown $CHCl_3$ layer was separated from the aqueous layer using a separatory funnel and was evaporated to dryness on a steam bath to yield $Co(DPA)_3$ as a brown solid. Anal. Calcd for $CoC_{30.6}N_9H_{24.6}Cl_{1.8}$: C, 57.33; H, 3.88; Co, 9.19; N, 19.67. Found: C, 57.00; H, 3.68; Co, 9.28; N, 19.88. $\mu_{eff} \simeq 0$; $\Lambda_M \simeq 0\ \Omega^{-1}$ cm$^{-1}$ M$^{-1}$ ($CHCl_3$), 27 °C; mol wt 621 ($CHCl_3$).

**Resolution of the Tris-Chelated Complexes of Cobalt(III). Method I.** A solution of $Co(HDPA)_3(ClO_4)_3$ was prepared by treating $Co(HDPA)_3(ClO_4)_3$ (0.5 g, 0.000 57 mol) with 5 mL of 10% aqueous HCl and chloride resin. The mixture was filtered with repeated washing of the remaining chloride resin with distilled water (5 mL). A concentrated solution of the resolving agent was prepared by dissolving (+)-$K_3(CYSU)_3Co$ (0.44 g, 0.000 66 mol) in 1 mL of distilled water. The solutions of the complex and resolving agent were mixed resulting in a thick precipitate. Aqueous NaOH (0.05 M) was added dropwise to dissolve all of the precipitate. Once dissolved, precipitation was induced by the addition of 1 drop of 5% aqueous HCl along with rapid mixing. (If precipitation did not occur, then additional drops of 5% aqueous HCl were added. When the step is complete, there should be a green mother liquor.) The mixture is allowed to digest at room temperature with rapid stirring for a period of 3 h, and then the precipitate was collected by centrifugation. The mother liquor was decanted into a test tube and was kept for reuse of the resolving agent. The solid was washed with 1 mL of distilled water. Optical purity was tested by converting the complex to the fully deprotonated form, extracting it into chloroform, and measuring the CD of the chloroform solution at 480 nm. This solution is saved for reuse. After measurement of the $\Delta\epsilon$, the sample was converted back to the fully protonated form by extracting the complex into 1% aqueous HCl and the solution was treated with the mother liquor containing the resolving agent. The cycle was repeated until maximum $\Delta\epsilon$ was obtained. The maximum value of $\Delta\epsilon$ obtained by this method was −20.0 L mol$^{-1}$ cm$^{-1}$ after 4 cycles.

**Method II.** The solutions were prepared as in method I. Once the resolving agent has been added to the solution of $Co(HDPA)_3^{3+}$ ion, a thick green precipitate results. The precipitate was separated from the mother liquor by centrifugation. Then the green solid was extracted repetitively by stirring with distilled water for a period of 30 min to remove the more soluble antipode. Each extract was decanted off from the mixture. The optical activity of selected extracts was determined by the method outline above. The maximum value of $\Delta\epsilon$ obtained by this method was −15.9 L mol$^{-1}$ cm$^{-1}$ after 29 cycles.

The antipode, which could not be purified by this method, gave a CD spectrum that was the exact opposite of the enantiomer isolated by methods I and II.

## Results and Discussion

**1. Preamble.** We summarize below some pertinent information about the properties and chelating ability of HDPA.

HDPA is a good bidentate ligand, not as good as *o*-phen or bpy (the iron(II) complex is paramagnetic) but not much worse (for $Ni(HDPA)_3^{2+}$, $Dq$ is 1120 cm$^{-1}$[3] compared to 1270 cm$^{-1}$ for $Ni(o\text{-phen})_3^{2+}$;[14] for $Fe(HDPA)_3^{2+}$, $Dq$ is 1200 cm$^{-1}$[5] compared 1310 cm$^{-1}$ for $Fe(o\text{-phen})_3^{2+}$[15]). There are important differences between HDPA and a ligand like bpy or *o*-phen. The latter is planar, or very nearly so in its complexes, whereas the former is not; the angle subtended by vectors normal to each pyridine ring varies from 9.8° in $Cu(HDPA)_2(ClO_4)_2$[16] to 38.2° in $Pd(DPA)_2$[17].

A ligand like *o*-phen or bpy forms five-membered chelate rings whereas HDPA forms six-membered ones. Were HDPA planar, the angle subtended at a metal ion by the donor nitrogen atoms would vary from about 68° at a bond distance of 2.0 Å to 120° at 1.3 Å and would be 90° at 1.6 Å. For planar *o*-phen or bpy the corresponding variation would be from 80° at 2 Å to 140° at 1.3 Å and is 90° at 1.8 Å.

In the complexes of HDPA, a subtended angle of 68° at 2 Å apparently does not lead to favorable bonding. A rotation of the pyridine rings around their amino nitrogen bonds allows much better overlap between the ligand and metal orbitals. Thus in $Pd(DPA)_2$, the dihedral angle 38.2° permits a subtended angle of 85.6° at 2.02 Å, and in $Cu(HDPA)_2(ClO_4)_2$, the angle 9.8° permits a subtended angle of 94.6° at 1.96 Å.

A consequence of such rotation, however, is the closer approach of the ligands to one another in 3:1 complexes. The symmetry of a 3:1 complex is lowered from the $D_3$ to the $C_3$ point group by the bending of the ligands. In those cases where the metal ion is small, this closer approach of the ligands necessitates a configuration that has no symmetry at all. Molecular models indicate severe crowding of the ligands in 3:1 complexes. Thus, although no unusual properties have been reported for the Ni(II), Co(II), Fe(II), Rh(III), and Ir(III) complexes of HDPA, we now report that the visible spectra of the 3:1 Co(III) complexes exhibit bands with intensities ($\epsilon \sim 1500$ L cm$^{-1}$ mol$^{-1}$) that are not characteristic of the usual d–d transitions of cobalt(III) ion. In contrast, the observed bands in the visible spectra of the 2:1 cobalt(III) complexes are characteristic of cobalt(III) d–d transitions.

**2. Cobalt(II) Complexes.** The cobalt(II) compounds reported here were obtained either as precursors to, or as byproducts from, the preparation of cobalt(III) complexes, and are all formulated as six-coordinate, pseudooctahedral complexes.

The compound $[Co(HDPA)(H_2O)_2CO_3] \cdot 0.5H_2O$ was obtained as a byproduct in the attempted preparation of $Co(HDPA)_3^{3+}$ from Drinkard's salt. Ions of the type $[Co(HDPA)_2A]^{2+}$ (A = *o*-phen, bpy, and en) were prepared as potential precursors to the corresponding Co(III) complexes,

**Table I.** Diffuse Reflectance Spectra of the Cobalt(II) Complexes

| complex | $\bar{\nu}_{max}$[a] (transition assignment[b]) | | | | | | $Dq$[a] |
|---|---|---|---|---|---|---|---|
| $[Co(HDPA)(H_2O)_2CO_3]\cdot{}^1/_2H_2O$ | 7580 (2) | 9 010 (1) | 18 690 (4) | 20 510[c] (5) | 25 320[c] (L) | 28 780 (L) | 800 |
| $[Co(HDPA)_2NO_3]NO_3$ | 7580[c] (1) | 8 470 (2) | 18 180[c] (3) | 20 410[c] (4) | 24 540[c] (L) | 28 580 (L) | 950 |
| $[Co(HDPA)_3(H_2O)_2](ClO_4)_2$ | | | 14 800 (4) | 21 700[c] (L) | 25 300 (L) | 28 900 (L) | 300 |
| $[Co(HDPA)_2$-*o*-phen$](ClO_4)_2$ | | 10 300 (2) | 18 520[c] (6) | 20 830[c] (4) | 24 390 (L) | 28 570 (L) | 1100 |
| $[Co(HDPA)_2$-*o*-phen$](NO_3)_2$ | | 10 400 (2) | 18 700[c] (6) | 21 000[c] (4) | 24 400 (L) | 28 200 (L) | 1100 |
| $[Co(HDPA)_2bpy](ClO_4)_2$ | | 10 300 (2) | 18 300[c] (6) | 20 400[c] (4) | 24 400 (L) | 31 700 (L) | 1100 |
| $[Co(HDPA)_2en](ClO_4)_2$ | | 10 400 (2) | *d* | 20 800[c] (4) | 26 100[c] (L) | 31 700 (L) | 1100 |
| $[Co(HDPA)_3](ClO_4)_2$ | | 10 400 (2) | 18 500 (6) | 21 000 (4) | 23 800 (L) | | 1100 |

[a] In units of $cm^{-1}$. [b] Transition assignments are designated as follows: from the ground state, ${}^4\Gamma_6$, to (1) ${}^2\Gamma_8$; (2) ${}^4\Gamma_6$, ${}^4\Gamma_7$, ${}^4\Gamma_8$, ${}^4\Gamma_8$; (3) ${}^4\Gamma_8$; (4) ${}^4\Gamma_6$, ${}^4\Gamma_7$, ${}^4\Gamma_8$, ${}^4\Gamma_8$; (5) ${}^2\Gamma_7$; (6) ${}^2\Gamma_6$, ${}^2\Gamma_8$ (see ref 18); L = ligand transition. [c] Shoulder. [d] Undefined absorption.

but so far, the appropriate oxidations have failed. Treatment of $[Co(HDPA)_2NO_3]NO_3$ with $H_2O_2$ and $NaClO_4$ yields $[Co(HDPA)_2O_2]ClO_4$.

The complex $[Co(HDPA)_3(H_2O)_2](ClO_4)_2$ was obtained when the peroxo complex was treated with HDPA in hydrochloric acid solution in the hope of preparing $Co(HDPA)_3{}^{3+}$. This complex differs from that of Goodgame by containing two molecules of water that appear to be coordinated (see below).

All the cobalt(II) compounds are high-spin complexes indicating a ${}^4T_1$ ground state before taking account of any lowering of symmetry.

**Diffuse Reflectance Spectra.** The band maxima and shoulders in the diffuse reflectance spectra of these cobalt(II) complexes are shown in Table I.

For those complexes that contain the $CoN_6$ chromophore, the assignments have been made as follows: $({}^4\Gamma_6, {}^4\Gamma_7, {}^4\Gamma_8, {}^4\Gamma_8) \leftarrow {}^4\Gamma_6$, 10 000-$cm^{-1}$ band; $({}^4\Gamma_6, {}^4\Gamma_7, {}^4\Gamma_8, {}^4\Gamma_8) \leftarrow {}^4\Gamma_6$, 20 500-$cm^{-1}$ band. These assignments follow those of Goodgame.[6,18] In general, the band at 18 500 $cm^{-1}$ occurs as a very weak shoulder on the higher energy transition and is assigned to the transition $({}^2\Gamma_6, {}^2\Gamma_8) \leftarrow {}^4\Gamma_6$. The transition ${}^4\Gamma_8 \leftarrow {}^4\Gamma_6$ is not observed.

The spectra of the complexes that contain both oxygen and nitrogen donor ligands are more difficult to interpret. The IR evidence presented below indicates that $[Co(HDPA)_2NO_3]NO_3$ contains a $CoN_4O_2$ chromophore and that $[Co(HDPA)(H_2O)_2CO_3]\cdot 0.5H_2O$ contains a $CoN_2O_4$ one. The spectra of the two complexes appear similar and resemble closely the spectra reported for cobalt(II) complexes that also contain $CoN_2O_4$ chromophores.[19] For example, the complex $[Co(2\text{-picoline})_2(NO_3)_2]$, which contains two bidentate nitrate groups, exhibits bands at 18 250 and 21 020 $cm^{-1}$ in its diffuse reflectance spectrum and at 7425, 8850, and 18 540 $cm^{-1}$ in its solution spectrum (it is not clear if the near-IR diffuse reflectance spectra of this complex and the others reported by Lever was measured, but we assume that they were not).

The spectrum of the nitrato complex can be interpreted using Liehr's energy level diagram[18] as follows. The transition at 18 180 $cm^{-1}$ is very weak and the ratio of this energy to the energy of the second transition is 2.15.[20] For a value of $Dq$ of about 950 $cm^{-1}$, the following transitions are then predicted ${}^2\Gamma_8 \leftarrow {}^4\Gamma_6$, 7500 $cm^{-1}$; $({}^4\Gamma_6, {}^4\Gamma_7, {}^4\Gamma_8, {}^4\Gamma_8) \leftarrow {}^4\Gamma_6$, 8500 $cm^{-1}$; ${}^4\Gamma_8 \leftarrow {}^4\Gamma_6$, 18 100 $cm^{-1}$; $({}^4\Gamma_6, {}^4\Gamma_7, {}^4\Gamma_8, {}^4\Gamma_8) \leftarrow {}^4\Gamma_6$, 20 100 $cm^{-1}$. An additional transition $({}^2\Gamma_6, {}^2\Gamma_7, {}^2\Gamma_8, {}^2\Gamma_8) \leftarrow {}^4\Gamma_6$ at 15 000 $cm^{-1}$ is predicted but is not observed.

The spectrum of the carbonato complex differs from that of the nitrate by having an intense transition at 18 690 $cm^{-1}$ and a weak transition at 20 510 $cm^{-1}$. Although the positions of the band maxima appear the same, the interpretations of the transitions must be different, because the intensity of the ${}^4\Gamma_8 \leftarrow {}^4\Gamma_6$ transition is known to be very weak. For a value of $Dq$ of 800 $cm^{-1}$, the following predictions obtain: $({}^4\Gamma_6, {}^4\Gamma_7, {}^4\Gamma_8, {}^4\Gamma_8) \leftarrow {}^4\Gamma_6$, 7600 $cm^{-1}$; ${}^2\Gamma_8 \leftarrow {}^4\Gamma_6$, 8800 $cm^{-1}$; $({}^4\Gamma_6, {}^4\Gamma_7, {}^4\Gamma_8, {}^4\Gamma_8) \leftarrow {}^4\Gamma_6$, 18 600; ${}^2\Gamma_7 \leftarrow {}^4\Gamma_6$, 22 700 $cm^{-1}$. This interpretation is not wholly satisfactory but is forced by the intensity of the band at 18 690 $cm^{-1}$. The transition ${}^4\Gamma_8 \leftarrow {}^4\Gamma_6$ is predicted to fall at 15 400 $cm^{-1}$.

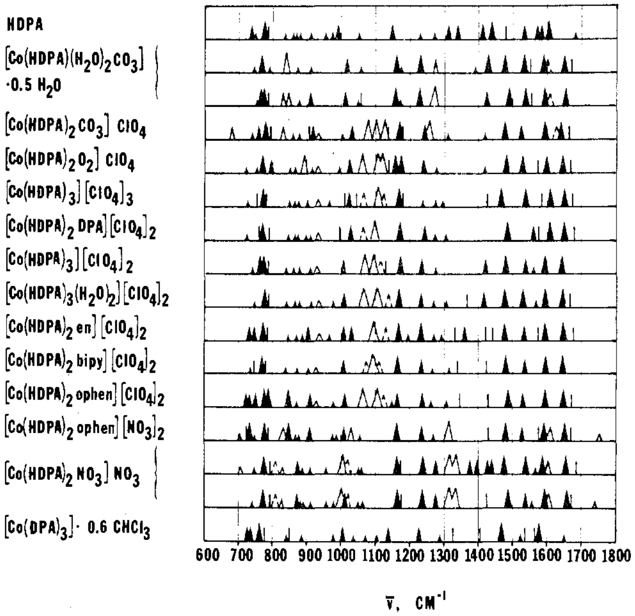

**Figure 1.** Representations of the IR spectra of all cobalt(II) and cobalt(III) complexes reported in this paper. All spectra were measured as Nujol mulls except for the second and the third last, which were measured as KBr disks. See the text for a discussion (organic ligand vibrations, black triangles; shoulders, black lines; inorganic ligands and anions, open triangles; shoulders, broken open triangles; triangle size reflects intensity s, m, w). The range 600–1800 $cm^{-1}$ is shown.

Finally, the complex $[Co(HDPA)_3(H_2O)_2](ClO_4)_2$ has been formulated as such, and not as $[Co(HDPA)_3](ClO_4)_2\cdot 2H_2O$, because of the difference between its diffuse reflectance spectrum and that of Goodgame's complex. As can be seen in Figure 1, the two complexes have very similar IR spectra, but whereas the visible spectrum of Goodgame's complex is characteristic of cobalt(II) complexes, the spectrum of $[Co(HDPA)_3(H_2O)_2](ClO_4)_2$ is not. A single weak transition is observed at 14 800 $cm^{-1}$. We have rationalized the spectrum in terms of a very weak ligand field, arising from what must be an unusual environment for the cobalt ion. Two HDPA ligands act as monodentate, one is bidentate and the two water molecules complete the coordination number of six. This rationalization is not satisfactory but no other explanation can reasonably be advanced.

The spectrum resembles that of a low-spin cobalt(III) complex, but the complex is paramagnetic and no paramagnetic cobalt(III) complexes, that contain four nitrogen donor atoms, are known. It might be supposed that the HDPA is oxidized during the decomposition of the peroxo complex to a pyridine *N*-oxide type ligand, HDPA·O. There is no

**Table II.** Diffuse Reflectance Spectra of the Cobalt(III) Complexes

| complex | $\bar{\nu}_{\max}$[a] | | | | | $Dq/B$[a] |
|---|---|---|---|---|---|---|
| $[Co(HDPA)_2CO_3]ClO_4$ | | 19 610 | 25 000[b] | 29 200 | | 2200/600 |
| $[Co(HDPA)_2O_2]ClO_4$ | | 19 230 | 23 250[b] | 27 030 | | 2120/488 |
| $[Co(HDPA)_3](ClO_4)_3$ | 16 000 | 20 000 | | 28 900[b] | 31 800 | |
| $[Co(HDPA)_2DPA](ClO_4)_2$ | 14 600 | 20 800 | | 27 800[b] | | |
| $[Co(DPA)_3]\cdot 0.6CHCl_3$ | 15 900[b] | 18 500 | 24 700 | 27 400 | | |

[a] In units of $cm^{-1}$. [b] Shoulder.

evidence to support this contention because pyridine *N*-oxide complexes have characteristic, strong bands at 830 $cm^{-1}$ (N–O bend) and 1250 $cm^{-1}$ (N–O stretch).[27] These are absent in the IR spectrum of this complex (see Figure 1).

A final possibility is that the complex is tetrahedral, containing one bidentate and two monodentate HDPA ligands, the water being hydrates. Tetrahedral cobalt(II) complexes usually exhibit two d–d bands.[20] If the higher energy band lies at 14 500–15 000 $cm^{-1}$, the low energy one falls near 6000 $cm^{-1}$. This complex has no absorption from 5500 $cm^{-1}$ up until the band at 14 800 $cm^{-1}$ is observed. The absence of a band at 6000 $cm^{-1}$ does not preclude a tetrahedral structure. On the balance of available evidence, however, we have assigned an octahedral structure to the complex.

**IR Spectra.** Figure 1 contains representations of the IR spectra of all cobalt complexes reported here plus that of Goodgame and the free ligand for comparison. Although these IR spectra are dominated by ligand vibrations, these vibrations are rather constant from one complex to the next, enabling the identification of vibrations that are characteristic of the other groups. A complete table of vibrational assignments and band positions is available as supplementary material.

The complex $[Co(HDPA)_2\text{-}o\text{-phen}][NO_3]_2$ shows the usual vibrations of nitrate ion at 1754 (w), 1312 (s), 1032 (m), 827 (m), and 702 (w) $cm^{-1}$. There appears an additional weak shoulder at 1608 $cm^{-1}$. In $[Co(HDPA)_2NO_3]NO_3$, the nitrate ion absorbs at essentially the same frequencies. The bidentate nitrato group has its absorptions[21] at 1603 $cm^{-1}$ (m, $\nu_1(A_1)$, NO stretch), 1332 $cm^{-1}$ (s, $\nu_4(B_1)$, $NO_2$ asymmetric stretch), 1011 $cm^{-1}$ (s, $\nu_2(A_1)$, $NO_2$ symmetric stretch), 806 $cm^{-1}$ (m, $\nu_3(A_1)$, $NO_2$ symmetric bend), 705 $cm^{-1}$ (w, $\nu_6(B_2)$, out-of-plane rocking). The asymmetric bend, $\nu_5(B_1)$, is obscured by an intense ligand vibration at 750 $cm^{-1}$.

In $[Co(HDPA)(H_2O)_2CO_3]\cdot 0.5H_2O$, the bidentate carbonato group shows vibrations[22] as follows: 1605 $cm^{-1}$ (sh, $\nu_1(A_1)$; C–O stretch), 1277 $cm^{-1}$ (m, $\nu_5(B_2)$, asymmetric $CO_2$ stretch), 842 $cm^{-1}$ (s, $\nu_8(B_1)$, out-of-plane rocking).

**3. Cobalt(III) Complexes.** The oxidation of $Co(HDPA)_3^{2+}$ to $Co(HDPA)_3^{3+}$ was not easily accomplished and several different procedures and oxidants were used in the original attempts to prepare it. It was prepared by an oxidation using $PbO_2$ in HCl solution and subsequently by passing air through a solution of $Co(HDPA)_3^{2+}$ for 24 h at 100 °C. The other oxidants employed seemed to destroy the ligand rather than oxidize the complex. Treatment of $Co(HDPA)_3^{2+}$ with $H_2O_2$ leads to the formation of the cobalt(III) complex $[Co(HDPA)_2O_2]ClO_4$.[9]

Once prepared, the tris complex is relatively stable and can exist in four forms:

$$Co(HDPA)_3^{3+} \rightleftarrows [Co(HDPA)_2DPA]^{2+} + H^+$$

$$[Co(HDPA)_2DPA]^{2+} \rightleftarrows [Co(HDPA)(DPA)_2]^+ + H^+$$

$$[Co(HDPA)(DPA)_2]^+ \rightleftarrows Co(DPA)_3 + H^+$$

Dark blue $Co(HDPA)_3^{3+}$ exists only in strongly acidic conditions (pH ~2), indicating the enhanced acidity of these protons after coordination. This behavior is similar to the acidity of the cobalt(III) complexes of pyridine-2-carbaldehyde-2-pyridyl hydrazone[23] and related ligands.[24] At pH ~6, the equilibria favor the formation of deep green $Co(HDPA)_2(DPA)^{2+}$. Treatment of this ion with base yields the dark brown neutral complex $Co(DPA)_3$. We did not attempt to isolate the monoprotonated form $Co(HDPA)(DPA)_2^+$.

When $[Co(HDPA)_3](ClO_4)_3$ is dissolved in water, the complex cation partially dissociates to $[Co(HDPA)_2DPA]^{2+}$, and the perchlorate salt of this dark green ion precipitates from the solution. The color of the mother liquor can be blue to green, depending on the amount dissolved.

$Co(DPA)_3$ is very soluble in chloroform and crystallizes from this solvent with 0.6 mol of chloroform/mol of complex. This parallels the behavior of other neutral complexes containing ligands where a negative charge is localized on the periphery of the molecule.[25]

Two other cobalt(III) complexes have been prepared, the peroxo complex already reported and $[Co(HDPA)_2CO_3]ClO_4$. This latter complex is obtained when Drinkard's salt is treated with HDPA; a cobalt(II) complex is also isolated (see above). The carbonato and peroxo complexes have very similar properties, both being red, insoluble substances. All the cobalt(III) complexes are diamagnetic.

**IR Spectra.** The IR spectra (see Figure 1) of the various 3:1 complexes require no comment, except to note that a strong N–H bending mode is present between 1645 and 1653 $cm^{-1}$ in the spectra of all cobalt(II) and cobalt(III) complexes containing protonated ligands. This band is absent in the spectrum of $Co(DPA)_3$. The free ligand is dimeric in the solid state,[26] the N–H being hydrogen bonded to a ring nitrogen; the band is observed at 1603 $cm^{-1}$.

The carbonato and peroxo complexes have IR spectra that are virtually identical except for the vibrations that are characteristic of the respective anionic ligands. The carbonato complex shows the characteristic bidentate modes at 1626 $cm^{-1}$ (sh, $\nu_1(A_1)$, C–O stretch), 1259 $cm^{-1}$ (s, $\nu_5(B_2)$, asymmetric $CO_2$ stretch), 830 $cm^{-1}$ (m, $\nu_8(B_1)$, out-of-plane rocking), and at 678 $cm^{-1}$ (m, $\nu_6(B_2)$, $\delta(O_ICO_{II})$).

**Diffuse Reflectance and Solution Spectra.** Table II contains the positions of band maxima and shoulders in the diffuse reflectance spectra. Table III contains the data for solution spectra. The carbonato and peroxo complexes are too insoluble to enable the measurement of their solution spectra. In their solid-state spectra, the peak near 19 000 $cm^{-1}$ can be assigned to the ${}^1T_1 \leftarrow {}^1A_1$ transition. The origin of the other visible peaks is not clear. A satisfactory explanation obtains if the bands at 27 030 and 29 200 $cm^{-1}$ in the peroxo and carbonato complexes, respectively, are assigned to the ${}^1T_2 \leftarrow {}^1A_1$ transition. This assignment leads to values of $Dq$ and $B$ for the two complexes of 2120 and 488 $cm^{-1}$ and 2200 and 600 $cm^{-1}$, respectively. The two bands at 23 260 and 25 000 $cm^{-1}$ must then be assigned to a ligand transition since there are no singlet–triplet spin-forbidden transitions for low-spin $d^6$ configurations that lie between the two spin-allowed transitions. If these bands are assumed to be the ${}^1T_2 \leftarrow {}^1A_1$ transition, then values for $B$ obtain that are too small (252 and 337 $cm^{-1}$). Normally, the degeneracies of the ${}^1T_1$ and ${}^1T_2$ terms are not lifted in *cis*-$Co(aa)_2x_2$ complexes.

It is appropriate to discuss the behavior of the ligand transition upon complexation to metal ions. The manifolds

**Table III.** The Electronic Absorption Spectra and the CD Spectra of Cobalt(III) Complexes, Measured in Solution

| $[Co(HDPA)_3](ClO_4)_3$ | | $[Co(HDPA)_2DPA]$-$(ClO_4)_2$ | $[Co(DPA)_3]\cdot 0.6CHCl_3$ | |
|---|---|---|---|---|
| $\bar{\nu}$ ($\epsilon$)[a] | $\bar{\nu}$ ($\Delta\epsilon$)[b] | $\bar{\nu}$ ($\epsilon$)[c] | $\bar{\nu}$ ($\epsilon$)[d] | $\bar{\nu}$ ($\Delta\epsilon$)[d] |
| 15.94 (1301) | 16.64 (+10.40) | 15.15 (1210) | 16.26[e] (924) | 15.62 (+6.10) |
| 20.30 (1537) | 20.00 (−28.00) | 20.83 (1083) | 18.86 (1364) | 18.80 (−10.70) |
| | 26.12 (+4.80) | | | 21.10 (−16.10) |
| 27.93[e] (10220) | 27.96 (+24.80) | | 24.84[e] (18410) | 24.68 (+64.80) |
| 30.30 (20320) | 29.48 (+51.20) | | 25.47 (19190) | |
| 33.61 (21070) | 31.88 (+28.80) | 31.44 (22610) | 28.36 (15780) | 28.16 (+34.80) |
| 35.71[e] (19830) | | 34.84 (25960) | 29.62[e] (16550) | 29.36 (+30.00) |
| 39.60[e] (28500) | | 41.15 (44260) | 33.30 (30190) | 31.64 (+9.60) |
| 42.55 (49260) | | | 38.09[e] (30810) | |

[a] Band maxima in $10^3 \times cm^{-1}$ and molar extinction coefficient ($L\ cm^{-1}\ mol^{-1}$) for the absorption spectrum measured in 5% aqueous HCl. [b] Band maxima in $10^3 \times cm^{-1}$ and differential dichroic absorption ($\epsilon_l - \epsilon_r$) for the CD spectrum measured in 5% aqueous HCl. [c] Absorption spectrum measured in water. [d] Absorption and CD spectra measured in chloroform. [e] Shoulder.

of ligand transitions are unaffected by complexation to metal ions that have totally symmetric ground states arising from inert gas or completely filled d-orbital configurations, e.g., $Hg^{2+}$. Upon complexation of the ligand with metal ions having some empty d orbitals, the manifolds exhibit resolution and substantial red shifts. In the cobalt(II) complexes, the first ligand transitions are seen at about 25 000 $cm^{-1}$, whereas in the free ligand, the first transitions occur near 32 000 $cm^{-1}$. Likewise, the copper(II) complex, although pseudotetrahedral, exhibits ligand transitions as low as 18 000–19 000 $cm^{-1}$. Thus the appearance of ligand transitions at 23 000–25 000 $cm^{-1}$ is not unusual, and the spectra of the two complexes can be interpreted satisfactorily in terms of an octahedral *cis*-$CoN_4O_2$ chromophore.

The spectra of the three forms of the 3:1 complex show bands in the visible region that are far too intense to be ascribed to the usual d–d transitions associated with the octahedral $CoN_6$ chromophore (see Table III). This fact raises the question of the disposition of the six nitrogen donor atoms around the cobalt ion—is it trigonal prismatic, or octahedral, or some intermediate configuration?

An examination of molecular models, using an octahedral disposition of the $CoN_6$ chromophore, shows that there is only one way the molecule can be put together (not including the enantiomer). Two ligands are bonded cis to one another and are related by a $C_2$ operation. The third ligand can then be bonded in only one way, related by a $C_2$ operation to one of the two ligands already in place. The final arrangement is asymmetric and shows severe crowding of the ligands.

This structure is consistent with the $^{13}C$ NMR spectrum of $Co(DPA)_3\cdot 0.6CHCl_3$. The proton-decoupled spectrum shows a single resonance due to the 0.6 mol of $CHCl_3$/mol of $Co(DPA)_3$ and 24 resonances in the aromatic region. This latter region is shown in Figure 2 (see Acknowledgments). The positions of these resonances in $\delta_{Me_4Si}$ ppm (intensities in parentheses) are the following: 159.87 (26), 159.07 (20), 158.88 (11), 158.67 (13), 152.77 (26), 150.15 (74), 149.07 (28), 148.11 (42), 145.33 (35), 138.89 (40), 138.08 (47), 137.86 (48), 137.50 (63), 137.40 (77), 120.05 (50), 119.85 (51), 119.29 (46), 118.67 (47), 117.65 (42), 115.96 (61), 115.66 (109), 114.58 (51), 111.19 (47), and 109.52 (47). The $CHCl_3$ resonance occurs at $\delta$ 77.77 (185).

Any $C_3$ axis or $C_2$ axis of symmetry would require a maximum of 10 or 15 different carbon resonances, respectively. Thus, the molecule is asymmetric, not merely dissymmetric.

Molecular models indicate that a trigonal-prismatic structure for the complex may have a plane of symmetry; the resolution of the complex into enantiomers eliminates this possibility. The models also indicate that a configuration of the $CoN_6$ chromophore that is intermediate between a trigonal prism and octahedron may have a threefold axis of rotation; the $^{13}C$ NMR evidence indicates that such symmetry is not present.

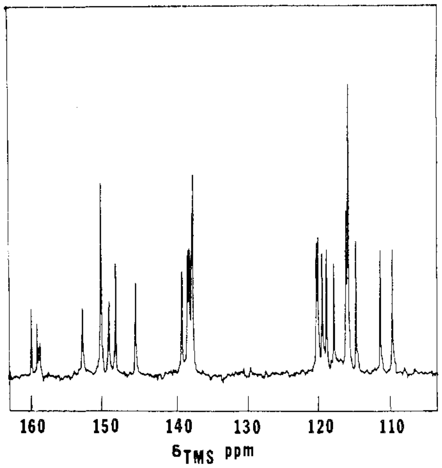

**Figure 2.** The proton-decoupled $^{13}C$ NMR spectrum of $Co(DPA)_3\cdot 0.6CHCl_3$ measured in deuteriochloroform. Only the 24 resonances in the aromatic region are shown (see Acknowledgement).

We conclude that the $CoN_6$ chromophore is octahedral and that probably all the 3:1 complexes of other metal ions are asymmetric. No unusual properties have been reported for them and the spectra of the Rh(III) and Ir(III) complexes have bands in the range 26 000–34 000 $cm^{-1}$ that show intensities characteristic of octahedral d–d transitions. Furthermore, the 2:1 cobalt(III) complexes reported here also show no unusual properties. The molecular models show that the introduction of the third HDPA ligand is responsible for substantial crowding together of the ligands. Introduction of a carbonato or peroxo bidentate ligand does not cause this crowding.

States that have closed-shell configurations interact repulsively at van der Waals distances. If a stable entity still results because of some other interaction (in this case complexation with the metal ion), there can be two results. Firstly, the occupied levels are destabilized relative to the free states while some of the unoccupied levels are stabilized. The net effect is substantial lowering of the transition energies in the new set of states. Secondly, charge-transfer transitions from ligand to metal can also be shifted to much lower energies.

The bands observed in the visible region are most probably due to mixing of perturbed ligand transitions with the usual d–d transitions of the cobalt(III) ion, with complete lifting of the degeneracy of the $^1T_1$ state (see CD spectra below). We suggest this because the intensities of CT transitions are usually much higher. The electronic absorption and the CD spectra of $CoDPA_3\cdot 0.6CHCl_3$ are shown in Figure 3.

This unusual behavior of these 3:1 cobalt(III) complexes must be due to the marginal shortness of the Co(III)–N bond distance relative to other metal–nitrogen distances. The steric interactions between ligands is sufficient to cause the 3:1 iron(II) complex to be paramagnetic even though Fe-

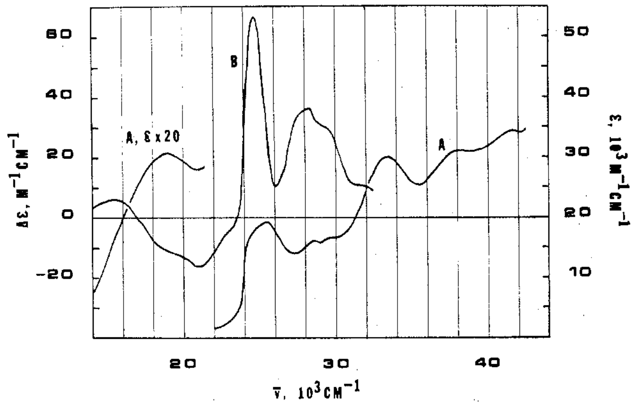

**Figure 3.** The electronic absorption spectrum (curve A) and the CD spectrum (curve B) of $Co(DPA)_3{\cdot}0.6CHCl_3$, measured in chloroform.

$(HDPA)_2(CN)_2$ is diamagnetic, again illustrating that the third ligand is responsible for the crowding.

Finally, the spectrum of $Co(DPA)_3{\cdot}0.6CHCl_3$ in chloroform solution obeys Beer's law at concentrations around $10^{-4}$ M. The spectrum of $[Co(HDPA)_3](ClO_4)_3$ obeys it in 5% aqueous HCl, as does that of $[Co(HDPA)_2DPA](ClO_4)_2$ in water, both at concentrations of $10^{-4}$ M. The spectrum of the fully protonated complex does not follow the law in aqueous solution, and the complex completely equilibrates to the monodeprotonated ion in DMF and $Me_2SO$ solutions.

The spectrum of $[Co(HDPA)_2DPA]^{2+}$ does not follow Beer's law in either DMF or $Me_2SO$ solutions, and at concentrations of $10^{-5}$ M equilibrates to the completely deprotonated form.

**Resolution and CD Spectra.** The resolution of $Co(HDPA)_3^{3+}$, or of $Co(DPA)_3$, into enantiomers was only partially achieved, and the values of $\Delta\epsilon$ reported in Table III are the maximum values that have been obtained so far. Nevertheless, these values are significantly larger than the values usually observed for the pure d–d transitions of cobalt(III) ion in chiral environments. Typically, such d–d transitions have molar extinction coefficients of 50–300 units, and differential dichroic absorptions that lie in the range −4 to +4 units. These higher values of $\Delta\epsilon$ are consistent with the assertion that the transitions involved contain considerable contributions from perturbed ligand transitions.

Because we hope this to be a preliminary report on the resolution and the interpretation of the CD spectra of the cobalt(III) complexes of HDPA, we conclude this discussion by noting the following. If one accepts that strong interactions between ligands are responsible for the observed properties of the 3:1 complexes, then one must also accept that there should be considerable exchange of electrons between ligands. As a result, a theory of optical activity, such as the exciton theory, that ignores electron exchange, should fail to rationalize the CD spectra of these complexes. This seems to be the case. The sum rule

$$\sum_j R_{j\leftarrow o} = 0$$

where the sum is over coupled free ligand transitions, is clearly not obeyed.

It would thus seem that we achieved a little more success than we bargained for in testing the concept of exciton coupling in complexes containing suitable nonplanar ligands.

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**Registry No.** $[Co(HDPA)_2NO_3]NO_3$, 68238-19-7; $[Co(HDPA)_2$-*o*-phen$][NO_3]_2$, 68238-21-1; $[Co(HDPA)_2$-*o*-phen$][ClO_4]_2$, 68238-22-2; $[Co(HDPA)_2bpy][ClO_4]_2$, 68238-24-4; $[Co(HDPA)_2en][ClO_4]_2$, 68238-26-6; $[Co(HDPA)_3(H_2O)_2][ClO_4]_2$, 68238-28-8; $Co(HDPA)(H_2O)_2CO_3$, 68238-29-9; $[Co(HDPA)_2CO_3]ClO_4$, 68238-31-3; $[Co(HDPA)_2DPA][ClO_4]_2$, 68238-33-5; $[Co(HDPA)_3][ClO_4]_3$, 63890-07-3; $Co(DPA)_3$, 68238-34-6; $[Co(HDPA)_2O_2]ClO_4$, 65956-93-6; $[Co(HDPA)_3][ClO_4]_2$, 15412-27-8; $Na_3(Co(CO_3)_3)$, 23311-39-9.

**Supplementary Material Available:** A table of vibrational frequencies of all cobalt(II) and cobalt(III) complexes, with assignments (2 pages). Ordering information is given on any current masthead page.

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