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Comparison of the Structures and Aqueous Solutions of [*o*-Phenylenediaminetetraacetato(4−)]cobalt(II) and [Ethylenediaminetetraacetato(4−)]cobalt(II) Ions

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The crystal structure of $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2{\cdot}4H_2O$ (I), where $PhDTA^{4-}$ is the anion *o*-phenylenediaminetetraacetate, has been determined and refined. The crystal structure of the previously known $[Co^{II}(H_2O)_4Co^{II}EDTA]{\cdot}2H_2O$ (II) has been refined. Crystal data: I, a = 14.1258 (8) Å, b = 9.3649 (6) Å, c = 8.5014 (6) Å, α = 98.760 (6)°, β = 100.649 (6)°, γ = 111.223 (6)°, space group $P\bar{1}$, Z = 1, R = 0.032; II, a = 14.504 (4) Å, b = 9.719 (3) Å, c = 13.280 (4) Å, space group $Pna2_1$, Z = 4, R = 0.032. For the coordination polyhedra of both $Co^{II}EDTA^{2-}$ and $Co^{II}PhDTA^{2-}$ there is *significant* distortion from an octahedron. In the case of $Co^{II}EDTA^{2-}$ the polyhedron is twisted much more away from a trigonal-prismatic and toward an antiprismatic configuration (octahedron) than is $Co^{II}PhDTA^{2-}$. This smaller twist of $Co^{II}PhDTA^{2-}$ is due to several factors, among which are the nearly planar N–C–C–N linkages in $PhDTA^{4-}$ and the changes in the interligand atom repulsions caused by the shorter N–N bite in $Co^{II}PhDTA^{2-}$. Evidence is presented which indicates that $PhDTA^{4-}$ serves as a hexadentate ligand over a wider pH range than does $EDTA^{4-}$. This observation is accounted for in terms of the stereochemistry of $PhDTA^{4-}$.

Introduction

The gauche character of the ethylenic backbone is thought to be a significant factor in determining the nature of the coordination polyhedron of complexes containing $EDTA^{4-}$ and $EDTA^{4-}$-like ligands.[1] For $EDTA^{4-}$ the staggered ethylenic backbone, with an N–C–C–N dihedral angle of approximately 55°, together with the sp^3 hybridization of the two nitrogen atoms, tends to cause the six donor atoms to adopt a pseudooctahedral configuration when the metal–donor atom bonds are shorter than approximately 2.05 Å.[2] Although longer bond distances favor the formation of structures twisted toward a trigonal prism, it is unlikely that a truly trigonal-prismatic configuration can be attained in $EDTA^{4-}$ complexes because this "would require the ethylenediamine ring system to be planar".[1]

In an effort to study further the influence of the staggered N–C–C–N backbone in determining the properties of complexes containing $EDTA^{4-}$-like ligands, we have investigated complexes of the *o*-phenylenediaminetetraacetate anion, $PhDTA^{4-}$.[3,4] In this ligand the carbon atoms of the N–C–C–N moiety are a part of the benzene ring and thus, unlike $EDTA^{4-}$, the N–C–C–N linkage of $PhDTA^{4-}$ is constrained to be nearly planar. An examination of molecular models revealed that when $PhDTA^{4-}$ acts as an hexadentate ligand, the six donor atoms tend to describe a trigonal prism (Figure 1) rather than a trigonal antiprism. In order to test this notion, salts of hexadentate $PhDTA^{4-}$ complexes of Co(II) were prepared, studied, and compared (where possible) with the corresponding $EDTA^{4-}$ complexes of Co(II). We report here the determination and refinement of the crystal structure of $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2{\cdot}4H_2O$,[4] the refinement of the crystal structure of the previously known substance $[Co^{II}(H_2O)_4Co^{II}EDTA]{\cdot}2H_2O$,[6] and spectral studies of $Co^{II}EDTA^{2-}$ and $Co^{II}PhDTA^{2-}$ in aqueous solution.

Experimental Section

All solvents and chemicals used in the experiments were obtained commercially and were of reagent grade, except for *o*-phenylenediamine which was practical grade. All were used without further purification. Electronic spectra were recorded at room temperature in 1- or 10-cm quartz cells using a Cary Model 14 spectrophotometer. The solution for obtaining the visible spectrum of $Co^{II}EDTA^{2-}$ was prepared by a method similar to that of Jorgensen[7] as follows. $Na_2H_2EDTA{\cdot}2H_2O$ (1.30 g, 3.49 × 10^{-3} mol), Na_2CO_3 (0.371 g, 3.49 × 10^{-3} mol), and $CoSO_4{\cdot}7H_2O$ (0.984 g, 3.49 × 10^{-3} mol) were added to a 50 mL volumetric flask which was then filled with distilled water. Infrared absorption spectra of Nujol, Fluorolube, and Kel-F mulls were recorded on a Beckman Model 10 spectrophotometer. Solution infrared spectra were taken in D_2O in cells with IR-Trans windows from the Barnes Engineering Co. with a 0.0014-cm spacer. Solutions suitable for obtaining the infrared spectra of $Co^{II}EDTA$ complexes were prepared by adding equimolar amounts of $[Co^{II}(H_2O)_4Co^{II}EDTA]{\cdot}2H_2O$ and $Na_2H_2EDTA{\cdot}2H_2O$ to enough D_2O to make an approximately 30% solution by weight of $Co^{II}EDTA^{2-}$. The pD was adjusted by adding Na_2CO_3. The pD measurements were made on a Corning Model 7 pH meter with a Corning semimicro combination electrode. All pD measurements reported in this work were computed by adding 0.40 pH unit to the "pH" reading on the meter.[8] ^1H NMR spectra were recorded using a Varian Model A-60 instrument with *tert*-butyl alcohol as the internal standard. Magnetic susceptibility measurements were performed as described previously.[9]

Analyses for carbon, hydrogen, and nitrogen were performed by Chemalytics, Inc., Tempe, Ariz., and by the Materials Chemistry Section, Washington State University, Pullman, Wash. Analyses for cobalt and/or sodium were performed at the Georgia Pacific Corp, Bellingham, Wash., or were obtained through the courtesy of Dr. L. J. Wilson or J. A. Johnson.

Preparation of *N*,*N*′-1,2-Phenylenebis(*N*-carboxymethyl)glycine-*o*-phenylenediaminetetraacetic Acid, $PhDTAH_4$. $PhDTAH_4$ was prepared by a modification of the method of Otozai and Kato.[10] A 1-L round-bottom flask was fitted with an efficient paddle-type stirrer and placed in an ice–salt bath at −15 °C. The stirrer was turned on and bromoacetic acid (77.5 g, 0.66 mol) was added to the flask with

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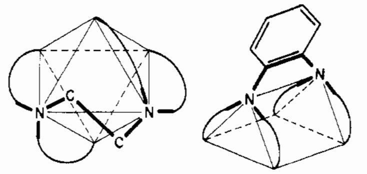

Figure 1. Idealized representations of the stereochemistry[5] of $Co^{III}EDTA^-$ and the expected stereochemistry of hexadentate $PhDTA^{4-}$ complexes.

enough water (approximately 50 mL) so that it was easily stirred. Throughout this preparation efficient stirring is essential. Sodium hydroxide (22.4 g, 0.66 mol) in 190 mL of water was added dropwise over a period of $1^1/_2$–2 h. The temperature was maintained between −5 and 0 °C until half the base was added and then no higher than 5 °C for the addition of the remainder of the base. Then *o*-phenylenediamine (7.5 g, 0.07 mol) was added and the solution was heated over about 1 h to 92 °C. While the brown solution was being heated to 92 °C, sodium hydroxide (22.4–27.4 g, 0.66–0.69 mol) as a 30% solution was added as necessary to keep the pH between 10 and 11. After about 2 h the reaction stopped as indicated by the pH remaining constant for 15 min. At this point the brown solution was maintained at 92 °C for an additional hour. It was then cooled to about 30 °C, filtered, and acidified to pH 1 with 12 M HCl (10–30 mL). The dark brown solution was allowed to evaporate in the dark for 24–48 h. [Note: light accelerates the decomposition of $PhDTAH_4$, especially in solution. Generally, decomposition is indicated by a purple color.] When the white prisms or needles appeared, they were collected, dried over P_4O_{10} for 8 h at 1 Torr, washed twice with small portions of acetone (at room temperature), and recrystallized from boiling acetone (yield 4 g, 15%). [Note: care should be taken to employ acetone with a reasonably low water content because the yield is diminished by the presence of water.]

The ^1H NMR spectrum of $PhDTAH_4$ in D_2O consists of a singlet at 4.0 ppm and an AA′BB′ pattern at 7.06 ppm downfield from *tert*-butyl alcohol with relative intensities 2:1. The infrared spectrum is shown in Figure 2. Anal. Calcd for $C_{14}O_8N_2H_{16}$: C, 49.42; H, 4.74; N, 8.23. Found: C, 49.52; H, 4.98; N, 8.45. No evidence of Cl^- ion was found via a sodium fusion test, further indicating (along with the analysis) that a hydrochloride salt had not formed.

Preparation of $Na_2[Co^{II}PhDTA]\cdot 3H_2O$. Sodium hydroxide (0.723 g, 1.81×10^{-2} mol) was dissolved in 20 mL of methanol, $PhDTAH_4$ (3.07 g, 9.04×10^{-3} mol) was added, and the resulting mixture was stirred into a uniform slurry. To this mixture was added cobalt(II) acetate tetrahydrate (2.25 g, 9.04×10^{-3} mol) dissolved in 30 mL of methanol. Within 2 h, with continuous stirring, a light orange solid appeared in the dark pink solution. The orange solid was collected and washed twice with cold methanol (yield 2.84 g, 62%). Recrystallization was accomplished from hot water. At room temperature the solubility of $Na_2[Co^{II}PhDTA]\cdot 3H_2O$ is about $^1/_2$ g/mL. The crystals which grow are (1) pink needles when the solution is cooled rapidly in a freezer to −15 °C, (2) orange prisms when the solution is allowed to cool to room temperature and evaporate, or (3) mixtures of pink and orange crystals when the solution is cooled to a temperature of 0 °C. When taken out of the mother liquor, both pink and orange crystals turn to an orange powder of composition $Na_2[Co^{II}PhDTA]\cdot 3H_2O$. Anal. Calcd for $Na_2[Co^{II}PhDTA]\cdot 3H_2O$: C, 33.94; H, 3.64; N, 5.66; Co, 11.92; Na, 9.29. Found (orange powder from pink needles): C, 33.95; H, 3.61; N, 5.71; Co, 11.99; Na, 9.12. Found (orange powder from orange prisms): C, 34.08; H, 4.04; N, 5.83; Co, 11.89; Na, 9.05.

Preparation of $[Co^{II}(H_2O)_6][Co^{II}PhDTA]$. $PhDTAH_4$ (1 g, 2.94×10^{-3} mol) was suspended in 20 mL of water. To this was added cobalt(II) acetate tetrahydrate (1.46 g, 5.88×10^{-3} mol) dissolved in 20 mL of water. Immediately a clear red solution formed. After 1 min of stirring a pink precipitate appeared. The pink product is readily recrystallized from hot water, in which it is slightly soluble. The solubility is approximately 3 g/100 mL at room temperature (yield from the first crop 0.3 g, 16%). It is to be noted that $[Co^{II}(H_2O)_6][Co^{II}PhDTA]$ will also form when $Co^{II}(H_2O)_6{}^{2+}$ ion is added to an aqueous solution of $Na_2[Co^{II}PhDTA]\cdot 3H_2O$. Anal. Calcd for $[Co(H_2O)_6][Co^{II}PhDTA]$: C, 29.90; H, 4.27; N, 4.98; Co, 20.96. Found: C, 30.02; H, 4.33; N, 5.00; Co, 20.81.

Preparation of $[Co^{II}(H_2O)_4Co^{II}EDTA]\cdot 2H_2O$. $Na_2H_2EDTA\cdot 2H_2O$ (12.0 g, 0.0323 mol) and cobalt(II) acetate tetrahydrate (16.1 g, 0.0646 mol) were dissolved in 50 mL of boiling water. Both solids dissolved immediately. The thick purple solution was filtered; the flask was stoppered and cooled to approximately 4 °C. Usually crystals formed after several hours although 1 or 2 days was sometimes required. Recrystallization was easily achieved from boiling water. Approximately 1 g of $[Co^{II}(H_2O)_4Co^{II}EDTA]\cdot 2H_2O$ will dissolve in 10 mL of boiling water. Note: boiling a solution of $[Co^{II}(H_2O)_4Co^{II}EDTA]\cdot 2H_2O$ in air for 10–15 min only slightly increases the very small peak due to $Co^{III}EDTA^-$ which appears in the $Co^{II}EDTA^{2-}$ visible spectrum. Anal. Calcd for $[Co^{II}(H_2O)_4Co^{II}EDTA]\cdot 2H_2O$: C, 23.2; H, 4.67; N, 5.45; Co, 23.0. Found: C, 23.6; H, 4.51; N, 5.42; Co, 23.0.

X-Ray Experimental Data for $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2\cdot 4H_2O$. The crystal selected for study was a plate on (100), bounded by ($\bar{1}$01) and (1$\bar{1}$0), with dimensions $0.1 \times 0.4 \times 0.3$ mm. This crystal turned out to have the composition $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2\cdot 4H_2O$ while the batch of crystals from which it was chosen had the bulk composition $Na_2[Co^{II}PhDTA]\cdot 3H_2O$. Further details of the crystal selection are given in the Results and Discussion. The crystal was coated with silicone oil and sealed in a capillary tube to prevent decomposition in the air. Oscillation and Weissenberg photographs showed the crystal to be triclinic. Examination of intensity statistics suggested the crystal was centric and the structure determination was successfully completed for space group $P\bar{1}$.

The cell dimensions are a = 14.1258 (8) Å, b = 9.3649 (6) Å, c = 8.5014 (6) Å, α = 98.760 (6)°, β = 100.649 (6)°, γ = 111.223 (6)°. Cell dimensions were determined at 18 °C with Ni-filtered Cu $K\bar{\alpha}$ radiation (λ 1.541 80 Å) on a computer-controlled Picker FACS-1 four-circle diffractometer controlled by programs derived from those of Lenhert and Henry.[11] The calculated density for Z = 1 is 1.7848 g/cm^3.

Intensity data were collected with Nb-filtered Mo $K\bar{\alpha}$ radiation (λ 0.710 69 Å) on a Picker automated four-circle diffractometer equipped with a scintillation counter and a pulse-height discriminator. The takeoff angle was 3.5°. Diffractometer settings for the θ–2θ scan method were calculated using the formula[12] scan range = $A + B \tan \theta$ with A = 1.2° and B = 1.0°. Background counts were measured at each end of the scan for 20 s. Data were collected to 2θ = 55°. Ten standard reflections were measured every 200 reflections on the average. These measurements were used to put all the intensity data on a common scale. The standard reflections decreased in intensity about 10% during 2 days of data collection due, we speculate, to very hot weather. When the temperature dropped, the intensities returned to their previous levels. The intensity of each reflection and its standard deviation were calculated by the formulas

$$I = C[S/(1 - TS) - (10t_s/2t_B)(B_1 + B_2 + 0.9)]$$

$$S = 10(S' + 0.45)$$

$$\sigma_I{}^2 = A_1 + A_2 + A_3 + A_4 + A_5$$

$$A_1 = SC^2/(1 - TS)^4$$

$$A_2 = 10(t_s/2t_B)^2(B_1 + B_2 + 0.9)$$

$$A_3 = 0.825[1 + 2(t_s/2t_B)^2]$$

$$A_4 = K^2[S/(1 - TS) + (10t_s/2t_B)(B_1 + B_2 + 0.9)]^2$$

$$A_5 = \sigma_T{}^2[CS^2/(1 - TS)^2]^2$$

where S' = decacounts recorded during scan time t_s, B_i = decacounts recorded during background time t_B, T = a correction parameter (6.625 $\times 10^{-8}$) for the apparent dead time of the detector, σ_T = standard deviation of T (0.64×10^{-8}), C = the scale factor, and K = an empirical stability constant (0.019) determined by analysis of standard reflections.

Of the 4590 reflections measured, 764 had intensities less than twice the estimated standard deviation. These reflections were assigned intensities equal to 2σ and each was included in a least-squares cycle only when F_c was greater than F_o. Lorentz and polarization factors were included in structure factor calculations. The linear absorption coefficient is 1.4 mm^{-1}. No absorption corrections were made, but anomalous dispersion corrections were made for cobalt.[13] All calculations were carried out on a CDC 6400 computer using a set of programs edited by Stewart et al.[14] The atomic scattering factors were from Doyle and Turner[15] for oxygen, sodium, carbon, cobalt, and nitrogen and from Stewart, Davidson, and Simpson[16] for hydrogen.

Table I. Parameters for $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2 \cdot 2H_2O \times 10^4$ [a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)[b]	24263 (2)	13375 (3)	5851 (3)	185 (1)	190 (1)	161 (1)	64 (1)	61 (1)	29 (1)
Co(2)	0	1/2	0	195 (2)	181 (2)	228 (2)	72 (2)	85 (1)	43 (1)
Na	941 (1)	2731 (1)	3780 (1)	335 (6)	418 (7)	281 (5)	193 (5)	120 (5)	88 (5)
N(10)	4085 (1)	2481 (2)	1875 (2)	215 (11)	191 (11)	169 (9)	97 (9)	87 (8)	42 (8)
N(20)	3125 (1)	1200 (2)	−1506 (2)	174 (10)	155 (10)	184 (9)	65 (8)	63 (8)	34 (8)
O(1)	377 (2)	3143 (2)	670 (2)	248 (11)	228 (11)	398 (11)	111 (9)	169 (9)	97 (8)
O(2)	656 (2)	4984 (3)	−1979 (2)	551 (15)	400 (14)	362 (11)	330 (12)	303 (11)	196 (10)
O(3)	1446 (2)	6524(2)	1525 (3)	316 (12)	253 (12)	324 (11)	−1 (9)	−4 (9)	75 (9)
O(4)	742 (2)	22 (3)	3392 (5)	503 (19)	444 (19)	1132 (27)	108 (16)	352 (19)	69 (17)
O(5)	1619 (2)	5605 (2)	4465 (3)	382 (14)	372 (14)	316 (11)	173 (11)	79 (10)	41 (9)
O(11)	2414 (1)	2869 (2)	2668 (2)	250 (10)	319 (11)	223 (8)	118 (9)	97 (7)	8 (8)
O(12)	3436 (2)	5118 (2)	4538 (2)	370 (13)	477 (14)	321 (10)	198 (11)	50 (9)	−153 (10)
O(21)	1240 (1)	−680 (2)	−1137 (2)	227 (10)	249 (10)	257 (9)	28 (8)	107 (7)	0 (7)
O(22)	936 (1)	−2460 (2)	−3429 (2)	288 (11)	249 (10)	251 (9)	11 (9)	66 (8)	−26 (8)
O(31)	2494 (1)	−235 (2)	1982 (2)	302 (11)	226 (10)	289 (9)	40 (8)	33 (8)	104 (8)
O(32)	3387 (2)	−420 (2)	4325 (2)	518 (14)	360 (13)	229 (9)	90 (11)	92 (9)	152 (9)
O(41)	1851 (1)	2656 (2)	−738 (2)	356 (11)	377 (12)	198 (8)	252 (10)	125 (8)	93 (8)
O(42)	1379 (2)	2911 (2)	−3288 (2)	538 (14)	606 (16)	237 (9)	450 (13)	122 (9)	148 (10)
C(10)	4745 (2)	2539 (2)	741 (3)	195 (12)	179 (12)	209 (11)	85 (10)	82 (9)	45 (9)
C(11)	4207 (2)	4092 (3)	2651 (3)	249 (14)	195 (13)	258 (13)	68 (11)	83 (11)	−14 (10)
C(12)	3286 (2)	4028 (3)	3363 (3)	267 (14)	300 (15)	190 (11)	149 (12)	57 (10)	24 (10)
C(20)	4265 (2)	1863 (2)	−932 (3)	174 (12)	162 (12)	232 (11)	67 (10)	78 (9)	42 (9)
C(21)	2687 (2)	−517 (3)	−2257 (3)	231 (13)	189 (13)	264 (13)	63 (11)	98 (10)	−3 (10)
C(22)	1529 (2)	−1279 (3)	−2305 (3)	348 (13)	182 (13)	207 (11)	69 (11)	74 (10)	67 (9)
C(30)	4892 (2)	1863 (3)	−2025 (3)	250 (13)	246 (14)	198 (12)	113 (11)	102 (10)	40 (10)
C(31)	4283 (2)	1620 (3)	3145 (3)	257 (14)	320 (16)	246 (13)	92 (13)	42 (11)	116 (12)
C(32)	3315 (2)	221 (3)	3184 (3)	320 (15)	212 (13)	192 (11)	102 (11)	104 (10)	47 (10)
C(40)	5974 (2)	2571 (3)	−1464 (3)	245 (14)	264 (15)	320 (13)	117 (12)	151 (11)	82 (11)
C(41)	2747 (2)	2031 (3)	−2674 (3)	283 (15)	320 (16)	212 (12)	164 (13)	114 (11)	132 (11)
C(42)	1920 (2)	2558 (3)	−2216 (3)	266 (14)	231 (14)	200 (11)	129 (11)	72 (10)	53 (10)
C(50)	6452 (2)	3282 (3)	193 (3)	158 (14)	267 (15)	379 (15)	70 (12)	79 (11)	62 (12)
C(60)	5835 (2)	3254 (3)	1297 (3)	205 (13)	274 (15)	240 (13)	81 (11)	37 (10)	16 (11)
Atom[c]	x/a	y/b	z/c	U, Å^2	Atom[c]	x/a	y/b	z/c	U, Å^2
H(1)	−10 (3)	233 (4)	55 (4)	42 (9)	H(14)	420 (2)	466 (3)	176 (3)	28 (6)
H(2)	83 (3)	307 (4)	25 (4)	42 (8)	H(23)	276 (2)	−76 (3)	−336 (4)	33 (7)
H(3)	83 (3)	432 (4)	−241 (4)	54 (10)	H(24)	308 (2)	−96 (3)	−155 (4)	36 (7)
H(4)	66 (3)	562 (5)	−254 (5)	65 (11)	H(31)	458 (2)	143 (3)	−309 (4)	34 (7)
H(5)	158 (3)	632 (5)	235 (5)	66 (12)	H(33)	460 (2)	229 (4)	414 (4)	39 (8)
H(6)	168 (3)	745 (4)	160 (4)	53 (10)	H(34)	479 (3)	122 (4)	297 (4)	47 (8)
H(7)	25 (4)	−72 (6)	343 (6)	101 (18)	H(41)	640 (2)	261 (3)	−219 (3)	32 (7)
H(8)	115 (4)	−15 (6)	289 (6)	100 (18)	H(43)	250 (3)	143 (4)	−370 (4)	54 (9)
H(9)	226 (3)	573 (4)	468 (4)	47 (9)	H(44)	333 (2)	295 (4)	−266 (4)	37 (7)
H(10)	151 (3)	619 (4)	501 (4)	56 (11)	H(51)	714 (2)	371 (3)	58 (3)	16 (5)
H(13)	487 (2)	465 (3)	348 (3)	26 (6)	H(61)	613 (2)	366 (3)	243 (4)	36 (7)

[a] Except as noted. [b] Coordinates for this atom are multiplied by 10^5. [c] Parameters for all H atoms are multiplied by 10^3.

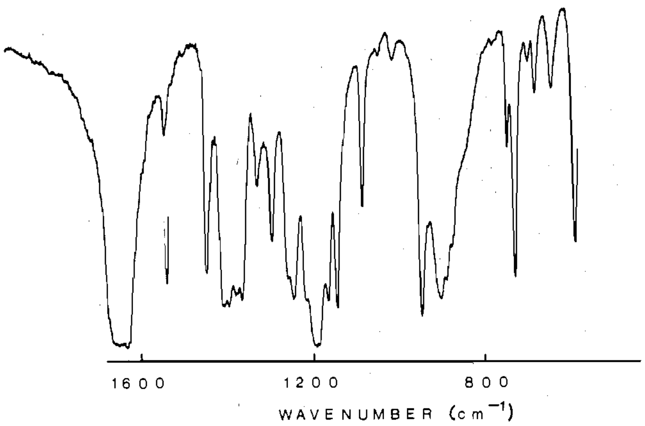

Figure 2. Infrared spectrum of $PhDTAH_4$ in a Nujol mull.

On the basis of chemical information the crystal was initially assumed to have the composition $Na_2[Co^{II}PhDTA] \cdot xH_2O$. A Patterson map implied the presence of more heavy atoms. Using trial and error to find the cobalt position, Fourier maps were calculated which revealed the composition as $Na_2[Co^{II}(H_2O)_6]$-$[Co^{II}PhDTA]_2 \cdot 4H_2O$, and on this basis the structure was refined.

Refinement was by full-matrix least squares minimizing $\sum w(F_o - F_c)^2$. The discrepancy factors used were $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. In the final cycle of refinement the weights used were the reciprocals of the variances of the F_o. Hydrogen positions and isotropic temperature factors were refined along with heavy-atom positions and anisotropic temperature factors. The last cycle gave $R = 0.032$ and $R_w = 0.036$. The average and maximum parameter shifts were 0.015σ and 0.31σ, respectively. A final difference-Fourier synthesis showed no regions of electron density greater than 0.4 e Å^{-3}.

Thermal parameters and atom positions for $Na_2[Co^{II}(H_2O)_6]$-$[Co^{II}PhDTA]_2 \cdot 4H_2O$ can be found in Table I.

X-ray Experimental Data for $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$. The crystal studied was a needle along [001] with dimensions 0.2 × 0.4 × 0.7 mm. Oscillation and Weissenberg photographs were taken and reflections $0kl$ ($k + l = 2n + 1$) and $h0l$ ($h = 2n + 1$) were systematically absent. These confirmed that the crystal at hand was probably the same space group, $Pna2_1$, as reported by Porai-Koshits.[6]

Cell dimensions were determined and intensity data collected at 18 °C with Nb-filtered Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å) on a computer-controlled Picker FACS-1 four-circle diffractometer controlled by programs derived from those of Lenhert and Henry.[11] The cell dimensions are $a = 14.504$ (4) Å, $b = 9.719$ (3) Å, $c = 13.280$ (4) Å, $V = 1871.9$ Å^3. The calculated density is 1.824 g/cm^3 on the basis of $Z = 4$. The experimental density as determined by Porai-Koshits is 1.75 g/cm^3.[6]

Intensity data were taken by a θ–2θ scan with 10-s backgrounds at each end of the scan. The scan speed was 2°/min. Data were collected to $2\theta = 60°$. Three standard reflections were measured every

Table II. Parameters for $[Co^{II}(H_2O)_4Co^{II}EDTA]\cdot 2H_2O \times 10^4$ [a]

Atom	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)[b]	6769 (3)	18037 (4)	25014[c]	135 (1)	170 (2)	205 (2)	0 (1)	−4 (1)	−1 (1)
Co(2)[b]	23957 (3)	69313 (5)	22604 (6)	175 (2)	168 (2)	233 (2)	14 (1)	−4 (2)	−3 (1)
N(10)	−721 (2)	2426 (3)	2824 (3)	137 (12)	179 (13)	272 (15)	11 (10)	−19 (12)	−25 (12)
N(20)	348 (2)	2418 (3)	979 (3)	166 (14)	179 (14)	232 (15)	−5 (11)	−35 (12)	−15 (12)
O(1)	1865 (2)	5977 (3)	3580 (3)	256 (14)	297 (14)	260 (14)	−12 (11)	−2 (12)	11 (12)
O(2)	2613 (2)	8844 (3)	2983 (3)	327 (16)	241 (14)	406 (20)	9 (11)	−31 (14)	−93 (13)
O(3)	2973 (2)	7798 (4)	964 (3)	252 (14)	369 (16)	366 (18)	41 (12)	92 (14)	129 (14)
O(4)	1085 (2)	7664 (4)	1852 (3)	231 (14)	341 (16)	436 (19)	108 (12)	−114 (14)	−115 (14)
O(5)	4776 (4)	8614 (5)	3414 (5)	556 (26)	656 (29)	906 (40)	−91 (23)	165 (28)	−241 (30)
O(6)	3076 (3)	4884 (4)	−303 (3)	588 (26)	402 (19)	373 (21)	−116 (18)	140 (18)	−88 (16)
O(11)	738 (2)	1905 (3)	4033 (3)	246 (15)	401 (18)	221 (15)	82 (12)	−17 (11)	−7 (12)
O(12)	135 (3)	2987 (4)	5352 (3)	314 (16)	571 (22)	237 (16)	41 (15)	35 (13)	−46 (15)
O(21)	1747 (2)	865 (3)	1714 (2)	162 (11)	274 (14)	258 (14)	30 (10)	2 (10)	9 (11)
O(22)	2122 (3)	81 (4)	189 (3)	413 (19)	388 (19)	259 (16)	165 (14)	111 (14)	57 (13)
O(31)	51 (2)	−129 (3)	2485 (3)	174 (11)	160 (10)	453 (17)	−11 (8)	61 (13)	−33 (13)
O(32)	−1274 (2)	−1243 (3)	2576 (3)	199 (12)	210 (12)	480 (19)	−65 (9)	−14 (13)	5 (14)
O(41)	1311 (2)	3773 (3)	2466 (3)	304 (13)	258 (12)	221 (13)	−108 (10)	−13 (12)	−11 (12)
O(42)	1965 (2)	5232 (3)	1397 (3)	301 (15)	200 (13)	287 (15)	−79 (11)	33 (12)	−28 (11)
C(11)	−662 (3)	3185 (4)	3779 (4)	214 (18)	264 (19)	283 (21)	54 (14)	0 (15)	−60 (15)
C(12)	120 (3)	2643 (5)	4451 (4)	209 (18)	285 (20)	262 (20)	−23 (15)	30 (15)	4 (16)
C(21)	675 (3)	1230 (4)	367 (3)	285 (20)	246 (18)	246 (19)	36 (15)	−17 (16)	−55 (15)
C(22)	1593 (3)	693 (4)	779 (3)	204 (17)	204 (17)	274 (19)	28 (14)	48 (15)	37 (14)
C(31)	−1301 (3)	1154 (4)	2916 (4)	155 (16)	204 (17)	457 (25)	−23 (13)	63 (17)	−46 (17)
C(32)	−809 (3)	−165 (4)	2625 (3)	202 (16)	160 (13)	271 (20)	−18 (11)	−2 (15)	−13 (14)
C(41)	866 (3)	3705 (4)	731 (3)	325 (21)	239 (18)	263 (20)	−85 (15)	−69 (17)	45 (15)
C(42)	1424 (3)	4270 (4)	1603 (3)	207 (16)	154 (16)	250 (18)	1 (13)	−20 (14)	−16 (14)
C(10)	−986 (3)	3296 (4)	1950 (4)	221 (17)	256 (20)	328 (22)	68 (15)	−53 (17)	−27 (16)
C(20)	−676 (3)	2623 (5)	968 (4)	196 (17)	345 (22)	280 (20)	60 (16)	−95 (16)	−25 (17)

Atom[d]	*x/a*	*y/b*	*z/c*	*U*, Å²	Atom[d]	*x/a*	*y/b*	*z/c*	*U*, Å²
H(13)	−130 (3)	325 (5)	414 (4)	55 (12)	H(43)	38 (3)	463 (4)	58 (4)	40 (11)
H(14)	−52 (2)	415 (4)	365 (3)	24 (8)	H(44)	126 (3)	379 (4)	18 (4)	30 (11)
H(23)	21[e]	50[e]	38[e]	26[e]	H(96)	−167[e]	341[e]	194[e]	26[e]
H(24)	76[e]	155[e]	−35[e]	26[e]	H(97)	−69[e]	422[e]	201[e]	26[e]
H(33)	−187 (3)	111 (4)	233 (4)	46 (11)	H(98)	−85[e]	323[e]	39[e]	27[e]
H(34)	−152 (4)	91 (5)	348 (5)	62 (15)	H(99)	−99[e]	171[e]	89[e]	27[e]

[a] Except as noted. [b] Coordinates for this atom are multiplied by 10^5. [c] Not refined to fix origin in polar space group. [d] Parameters for all H atoms are multiplied by 10^3. [e] Atom in calculated position.

250 reflections and four others were measured every 500 reflections. These measurements were used to put all the intensities on a common scale. There were no systematic changes in the intensities of the standards during the data collection. The intensity of each reflection and its standard deviation were calculated by the formulas

$$I = C[S/(1 - TS) - [B_1/(1 - TB_1) + B_2/(1 - TB_2)]\,(t_s/2t_B)]$$

$$\sigma_I^2 = C^2\{(S/(1 - TS))(1 + K^2S/(1 - TS)) + (t_s/2t_B)^2\,[B_1/(1 - TB_1) + B_2/(1 - TB_2)]\}$$

where S = peak counts recorded during scan time t_s, B_1 = low 2θ background counts, B_2 = high 2θ background counts, t_B = background time, T = an empirical constant to compensate for the dead time of the detector (6.0×10^{-8}), K = an empirical stability constant (0.03) determined by analysis of standard reflections, and C = the scale factor.

Of the 2852 reflections which were not systematically absent, 72 had intensities less than 2.0 times the estimated standard deviation. These reflections were included in a least-squares cycle only when F_c was greater than F_o. Lorentz and polarization factors were included in the structure factor calculations. The absorption coefficient is 1.9 mm^{-1}. No absorption correction was made but anomalous dispersion corrections were made for cobalt.[13] All calculations were carried out on a CDC 6400 computer using a set of programs edited by Stewart et al.[14] The atomic scattering factors were taken from Doyle and Turner[15] for oxygen, cobalt, carbon, and nitrogen and from Stewart, Davidson, and Simpson for hydrogen.[16]

Because $[Co^{II}(H_2O)_4Co^{II}EDTA]\cdot 2H_2O$ is isostructural with the corresponding zinc compound,[6] the atomic positions from the zinc compound[17] were used as a starting model. The refinement was by full-matrix least squares minimizing $\sum w(F_o - F_c)^2$. The discrepancy factors used were $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. Twenty of the twenty-four hydrogen atoms were found in a ΔF Fourier map. These atoms were refined with isotropic temperature factors, but only six hydrogen atoms converged to reasonable positions (bond distances 0.8–1.2 Å, bond angles 90–115°). The positions of the hydrogen atoms of the water molecules were difficult to calculate reliably, so they were deleted from the model entirely. Of the hydrogen atoms on the ligand, H(96), H(97), H(99), H(23), and H(24) were put in calculated positions. H(13), H(14), H(33), H(34), H(43), and H(44) were left unchanged, and none of the hydrogen parameters were refined further. In the final cycle of refinement, R = 0.032, R_w = 0.046, and the mean and maximum parameter shifts were 0.03σ and 0.3σ, respectively.

Refinement of the structure (excluding the hydrogen atoms) given in Table II gave R = 0.036 and R_w = 0.051. Refinement of the inverted structure gave R = 0.039 and R_w = 0.055. Application of Hamilton's R-factor ratio test[18] gave 0.055/0.051 = 0.039/0.036 = 1.08 and $R_{225,2569,0.005}$ = 1.05. Therefore the hypothesis that the inverted structure is correct can be rejected at the 0.5% significance level. The anomalous scattering factors used[13] for cobalt were $\Delta f'$ = 0.4 and $\Delta f''$ = +1.1.

Thermal parameters and atom positions for $[Co^{II}(H_2O)_4Co^{II}EDTA]\cdot 2H_2O$ can be found in Table II.

Results and Discussion

As is noted in the Experimental Section two salts of $Co^{II}PhDTA^{2-}$ are readily synthesized, the Na^+ salt and the $Co^{II}(H_2O)_6^{2+}$ salt.[19] By controlling the rate of cooling and the final temperature during the recrystallization of the sodium salt it is possible to produce two crystalline substances (one orange and one pink). (See the Experimental Section for details.) When the crystals are removed from the mother liquor and dried in air, both samples become pinkish orange powders. The powders have (1) the identical composition $Na_2[Co^{II}PhDTA]\cdot 3H_2O$, (2) the same visible and infrared spectra in aqueous solution, and (3) the same infrared mull spectra. Crystals of $[Co^{II}(H_2O)_6][Co^{II}PhDTA]$[19] are also pink and, in contrast to the two sodium salts, are sparingly soluble

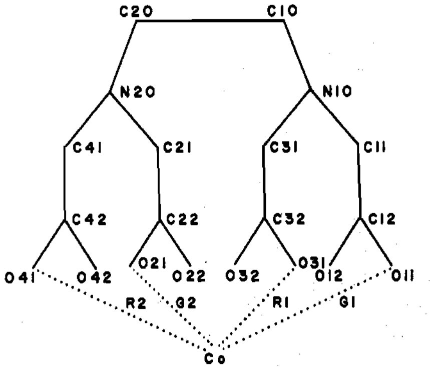

Figure 3. Numbering scheme for $EDTA^{4-}$-class ligands.

in water. They retain their crystallinity when exposed to the air at room temperature but lose weight and turn dark purple upon drying at approximately 1 Torr for 8 h over P_4O_{10} at about 25 °C.

Because the single crystal which was selected for the x-ray structure determination does not have the composition of either of the two readily prepared $Co^{II}PhDTA^{4-}$ compounds previously mentioned, the provenance of this single crystal bears mention. An aqueous solution of $Na_2[Co^{II}PhDTA]\cdot 3H_2O$ was allowed to evaporate until crystals appeared. A well-formed orange crystal was chosen and sealed in a capillary. The remaining crystals were collected and dried in the air. The elemental analyses and the visible and infrared spectra of this dried substance showed it to be $Na_2[Co^{II}PhDTA]\cdot 3H_2O$. However, when the structure determination was completed, the single crystal was found to have the composition $Na_2[Co(H_2O)_6][CoPhDTA]_2\cdot 4H_2O$. Before the completion of the structure determination there had been no evidence that such a mixed sodium hexaaquocobalt(II) salt had formed in any of our preparations. Furthermore, after the completion of the structure determination several attempts were made to prepare the mixed salt. Without exception these efforts led to the isolation of either orange crystals, which when dry have the composition $Na_2[Co^{II}PhDTA]\cdot 3H_2O$, or the pink $[Co^{II}(H_2O)_6][Co^{II}PhDTA]$, or a mixture of the two. Thus, the selection of a crystal of $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2\cdot 4H_2O$ for the x-ray study was fortuitous. Clearly, the preparation of more such crystals is possible. However, our experience leads us to the conclusion that substantial difficulties will be associated with finding those specific conditions (e.g., the correct ranges for the $Na^+(aq)$, $[Co^{II}(H_2O)_6]^{2+}(aq)$, $[Co^{II}PhDTA]^{2-}(aq)$ and $H^+(aq)$ ion concentrations) which are appropriate for the formation of significant amounts of the mixed species.

Nomenclature and Numbering of Atoms. Hoard[5] has pointed out that the "glycine" chelate rings in EDTA and EDTA-like complexes can be divided into two classes. G rings are those rings whose mean planes are more nearly parallel to the N–M–N plane and R rings are those rings whose mean planes are more nearly perpendicular to the N–M–N plane. For all of the complexes discussed in this paper, mean planes have been determined for all "glycine" chelate rings and the G and R rings identified. Then the atoms have been numbered (see Figure 3) so that the "backbone" consists of N(10)–C(10)–C(20)–N(20), the G "arms" are N(10)–C(11)–C(12)–O(11) and O(12) and N(20)–C(21)–C(22)–O(21) and O(22), and the R arms are N(10)–C(31)–C(32)–O(31) and O(32) and N(20)–C(41)–C(42)–O(41) and O(42). The oxygen atoms bound to the chelated metal ion are O(*j*1). Further, the metal ion of the complex is numbered M(1), and oxygen atoms of water molecules are numbered O(1), etc. Use is also made of the notation suggested by Porai-Koshits[20] in which a complex having, for example, C(11) and C(10) on the same side of the N–M–N plane is called E, G/R and a complex having C(31) and C(10) on the same side of the N–M–N plane is called E, R/G.

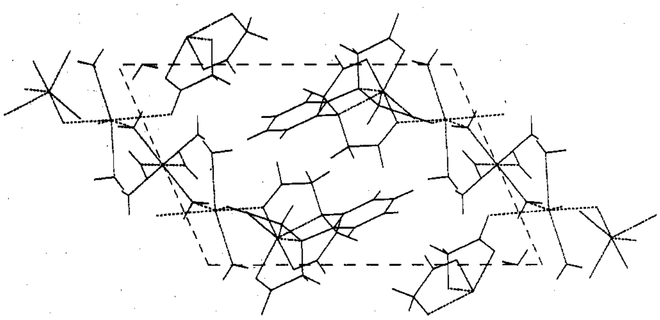

Figure 4. A projection of the unit cell of $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2\cdot 4H_2O$ down the *c* axis.

Table III. Hydrogen Bonds Found in $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2\cdot 4H_2O$

A-H-B[a]	A-H, Å	H-B, Å	A-B, Å	A-H-B, deg
O(1)-H(1)-O(21) (ii)	0.79 (3)	1.99 (3)	2.737 (2)	158 (3)
O(1)-H(2)-O(41) (i)	0.80 (4)	1.92 (4)	2.724 (3)	173 (3)
O(2)-H(3)-O(42) (i)	0.81 (4)	1.88 (4)	2.692 (3)	174 (3)
O(2)-H(4)-O(22) (iii)	0.81 (5)	2.00 (4)	2.793 (3)	166 (3)
O(3)-H(5)-O(5) (i)	0.77 (4)	2.01 (4)	2.762 (3)	168 (4)
O(3)-H(6)-O(31) (iii)	0.80 (4)	1.99 (4)	2.780 (3)	170 (4)
O(4)-H(7)-O(42) (ii)	0.80 (5)	2.44 (5)	3.224 (3)	173 (5)
O(4)-H(8)-O(31) (i)	0.82 (7)	2.20 (6)	3.010 (4)	168 (4)
O(5)-H(9)-O(12) (i)	0.85 (4)	1.96 (4)	2.756 (4)	155 (3)
O(5)-H(10)-O(22) (iv)	0.75 (4)	2.15 (4)	2.888 (3)	170 (4)

[a] For each hydrogen bond the second oxygen atom (atom B) is related to the atom given in Table I by the symmetry operation given in parentheses: (i) x, y, z; (ii) $-x, -y, -z$; (iii) $x, y + 1, z$; (iv) $x, y + 1, z + 1$.

The Structures of $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2\cdot 4H_2O$ and $[Co^{II}(H_2O)_4Co^{II}EDTA]\cdot 2H_2O$. The structure of $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2\cdot 4H_2O$ consists of sheets parallel to (100), with the sodium ions and the two types of cobalt(II) ions joined within the sheets by bridging oxygen atoms and by O–H···O hydrogen bonds (Figure 4). Adjacent sheets interact only through van der Waals contacts. The shortest intersheet contacts are H···H = 2.5 Å, H···O = 2.5 Å, and H···C = 2.7 Å. From the $Co^{II}PhDTA^{2-}$ anion, O(11), O(22), and O(42) are coordinated to three different sodium ions, and O(12), O(21), O(22), O(31), O(41), and O(42) are receptors in hydrogen bonds from water molecules. From the $Co^{II}(H_2O)_6{}^{2+}$ cation, O(1) is coordinated to a sodium ion and forms two hydrogen bonds, and O(2) and O(3) each form two hydrogen bonds. Of the six oxygen atoms coordinated to the sodium ion, three are carboxylate oxygen atoms: one is from a water molecule of a $Co^{II}(H_2O)_6{}^{2+}$ ion, and two are from other water molecules. One of the lattice water oxygen atoms, O(4), forms hydrogen bonds to two carboxylate oxygen atoms while the other, O(5), forms hydrogen bonds to two carboxylate oxygen atoms and also acts as receptor for a hydrogen bond from a water molecule of a $Co^{II}(H_2O)_6{}^{2+}$ cation.

As shown in Table III, all of the hydrogen atoms of all five water molecules are involved in hydrogen bonds. Except for those involving O(4), the O···O distances range from 2.692 to 2.888 Å. The two O(4)···O distances are both above 3 Å, and this is reflected in the large thermal parameters of all three atoms of the water molecule.

The NaO_6 polyhedron may be described as a markedly distorted octahedron. Examination of 33 NaO_6 polyhedra described in the recent literature shows that the present octahedron is within the reported range. The Na–O distances are listed in Table IV, showing a mean distance of 2.492 Å and a range of 0.334 Å. The polyhedra from the literature

Table IV. Sodium-Oxygen Distances (Å) Found in $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2 \cdot 4H_2O$[a]

Na-O(11) (i)	2.410 (2)	Na-O(4) (i)	2.413 (3)
Na-O(22) (ii)	2.526 (2)	Na-O(5) (i)	2.439 (2)
Na-O(42) (iii)	2.419 (2)	Mean	2.492
Na-O(1) (i)	2.744 (2)		

[a] The oxygen atom for each sodium-oxygen bond is related to the atom given in Table I by the symmetry operation given in parentheses: (i) x, y, z; (ii) $-x, -y, -z$; (iii) $x, y, z + 1$.

Table V. Hydrogen Bonds in $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$

A-B[a]	Value, Å	B[a]-A-C[a]	Value, deg
O(1)-O(41)(i)	2.725 (4)	O(41)(i)-O(1)-O(22)(v)	109.4 (1)
O(1)-O(22)(v)	2.735 (5)		
O(2)-O(6)(v)	2.683 (6)	O(6)(v)-O(2)-O(21)(ii)	94.4 (1)
O(2)-O(21)(ii)	2.876 (5)		
O(3)-O(22)(ii)	2.740 (5)	O(22)(ii)-O(3)-O(12)(vi)	105.8 (2)
O(3)-O(12)(vi)	2.868 (5)		
O(4)-O(12)(viii)	2.739 (5)	O(12)(viii)-O(4)-O(31)(ii)	92.9 (1)
O(4)-O(31)(ii)	2.749 (6)		
O(5)-O(32)(iii)	2.978 (6)	O(32)(iii)-O(5)-O(1)(iv)	129.3 (2)
		O(32)(iii)-O(5)-O(4)(iv)	75.6 (1)
O(5)-O(1)(iv)	3.064 (6)		
O(5)-O(4)(iv)	3.074 (7)		
O(6)-O(11)(vi)	2.755 (5)	O(11)(ii)-O(6)-O(42)(i)	122.1 (2)
O(6)-O(42)(i)	2.795 (5)		

[a] The second atom (atom B or C) is related to the atom listed in Table II by the symmetry operation given in parentheses: (i) x, y, z; (ii) $x, 1 + y, z$; (iii) $^1/_2 + x, ^1/_2 - y, z$; (iv) $^1/_2 + x, ^3/_2 - y, z$; (v) $^1/_2 - x, ^1/_2 + y, ^1/_2 + z$; (vi) $^1/_2 - x, ^1/_2 + y, -^1/_2 + z$; (vii) $^1/_2 - x, -^1/_2 + y, -^1/_2 + z$; (viii) $-x, 1 - y, -^1/_2 + z$.

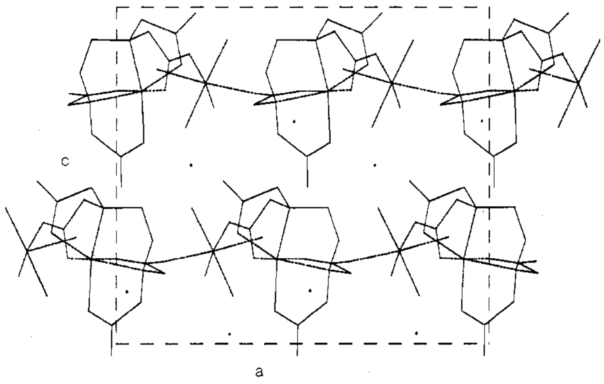

Figure 5. A projection of the unit cell of $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$ down the *b* axis.

Table VI. Metal-Oxygen Distances (Å) and Oxygen-Metal-Oxygen Angles (deg) of $[CoO_6]^{2+}$ Groups Found in $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2 \cdot 4H_2O$ and $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$

$[Co^{II}(H_2O)_6]^{2+}$ in $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2 \cdot 4H_2O$			
Co(2)-O(1)	2.119 (2)	O(1)-Co(2)-O(2)	93.00 (9)
Co(2)-O(2)	2.066 (2)	O(1)-Co(2)-O(3)	86.97 (8)
Co(2)-O(3)	2.058 (2)	O(2)-Co(2)-O(3)	89.93 (8)
Av[a]	2.081 (2, 38)		
$[Co^{II}(H_2O)_4O_2]^{2+}$ in $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$			
Co(2)-O(1)	2.126 (3)	O(1)-Co(2)-O(42)	89.9 (1)
Co(2)-O(2)	2.116 (3)	O(2)-Co(2)-O(3)	87.7 (1)
Co(2)-O(3)	2.092 (4)	O(2)-Co(2)-O(4)	87.3 (1)
Co(2)-O(4)	2.101 (3)	O(2)-Co(2)-O(32)	93.1 (1)
Co(2)-O(42)	2.105 (3)	O(2)-Co(2)-O(42)	168.6 (1)
Co(2)-O(32)	2.085 (3)	O(3)-Co(2)-O(4)	90.8 (1)
Av[a]	2.104 (3, 32)	O(3)-Co(2)-O(32)	85.7 (1)
		O(3)-Co(2)-O(42)	89.2 (1)
O(1)-Co(2)-O(2)	93.7 (1)	O(4)-Co(2)-O(32)	176.4 (1)
O(1)-Co(2)-O(3)	177.1 (1)	O(4)-Co(2)-O(42)	81.8 (1)
O(1)-Co(2)-O(4)	91.9 (1)	O(32)-Co(2)-O(42)	97.6 (1)
O(1)-Co(2)-O(32)	91.7 (1)		

[a] For the averages, the first number in parentheses is the average of the standard deviations and the second is the maximum deviation from the mean.

Table VII. Bond Distances (Å) in the Ligand Moiety of $Co^{II}PhDTA^{2-}$ and $Co^{II}EDTA^{2-}$ [a]

Bond	$Co^{II}PhDTA^{2-}$	$Co^{II}EDTA^{2-}$
C(10)-C(20)	1.393 (3)	1.527 (7)
C(20)-N(20)	1.453 (3)	1.498 (5)
C(10)-N(10)	1.454 (3)	1.486 (6)
N(10)-C(11)	1.486 (3)	1.470 (6)
N(10)-C(31)	1.487 (4)	1.500 (5)
N(20)-C(21)	1.483 (3)	1.490 (6)
N(20)-C(41)	1.489 (4)	1.495 (5)
C(11)-C(12)	1.520 (4)	1.536 (6)
C(31)-C(32)	1.523 (3)	1.517 (5)
C(21)-C(22)	1.520 (3)	1.531 (6)
C(41)-C(42)	1.512 (4)	1.516 (6)
C(12)-O(11)	1.270 (2)	1.275 (5)
C(12)-O(12)	1.240 (3)	1.242 (6)
C(32)-O(31)	1.282 (3)	1.261 (5)
C(32)-O(32)	1.224 (3)	1.248 (4)
C(22)-O(21)	1.271 (3)	1.273 (5)
C(22)-O(22)	1.244 (2)	1.248 (6)
C(42)-O(41)	1.271 (3)	1.254 (5)
C(42)-O(42)	1.241 (3)	1.251 (5)

[a] The number in parentheses is the standard deviation.

have mean Na–O distances from 2.371 to 2.511 Å, only three having mean distances greater than 2.492 Å. The mean of the 183 individual reported Na–O distances is 2.438 Å. The O–Na–O angles have a mean deviation from 90° of 9.3°, while the mean for the 33 polyhedra from the literature is 7.2°.

The crystal structure of $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$ consists of zigzag chains along *a* with the plane of the zigzag parallel to (001) (Figure 5). In the approximate center of each segment is a Co(1) ion coordinated by the two nitrogen atoms and four oxygen atoms (one from each carboxylate group) of an $EDTA^{4-}$ ion. Two of the other oxygen atoms of the $EDTA^{4-}$ ion, on opposite sides of the Co(1) ion, are coordinated to Co(2) ions which form the ends of the segment. The Co(2) ions are also coordinated by four water molecules. These chains are linked together in both the *b* and *c* directions by hydrogen bonds. Oxygen–oxygen contacts which are short enough to be considered to correspond to hydrogen bonds are listed in Table V. Again, all of the hydrogen atoms of all six water molecules appear to be involved in hydrogen bonds. Except for those involving O(5), the O···O distances range from 2.683 to 2.876 Å. The O(5)···O distances are longer, with one of the hydrogen atoms forming a bifurcated hydrogen bond, and this is reflected in the observation that O(5) has the largest thermal parameters of any atom in the structure.

The $Co^{II}(H_2O)_6^{2+}$ ion in $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2 \cdot 4H_2O$ and the $Co^{II}(H_2O)_4O_2^{2+}$ moiety in $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$ are quite comparable even though the latter (see above) is not a discrete cation. The pertinent interatomic distances and angles are listed in Table VI. The $Co^{II}(H_2O)_6^{2+}$ coordination polyhedron is a slightly distorted octahedron residing at a center of symmetry. The Co–O(1) distance is longer than the others and may arise from the interaction of O(1) with the Na^+ ion. The $Co^{II}(H_2O)_4O_2^{2+}$ coordination polyhedron in $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$ is more distorted from octahedral geometry and slightly larger than the $Co^{II}(H_2O)_6^{2+}$ coordination polyhedron. The greatest divergence from regular octahedral bond angles is found in those angles involving O(42) and O(32), the oxygen atoms from the bridging carboxylate groups.

Interatomic distances and angles within the chelating ligand moieties are listed in Tables VII–IX for both $Na_2[Co^{II}(H_2O)_6][Co^{II}PhDTA]_2 \cdot 4H_2O$ and $[Co^{II}(H_2O)_4Co^{II}EDTA] \cdot 2H_2O$. All of these distances and angles are normal. Only

Table VIII. Bond Angles (deg) Found in $Co^{II}PhDTA^{2-}$ and $Co^{II}EDTA^{2-}$ [a]

Angle	$Co^{II}PhDTA^{2-}$	$Co^{II}EDTA^{2-}$
Co(1)-N(10)-C(11)	102.8 (1)	104.9 (2)
Co(1)-N(10)-C(31)	107.8 (2)	108.1 (2)
Co(1)-N(10)-C(10)	111.4 (1)	104.3 (2)
C(11)-N(10)-C(31)	111.1 (2)	112.1 (3)
C(11)-N(10)-C(10)	110.9 (2)	113.8 (3)
C(31)-N(10)-C(10)	112.3 (2)	112.8 (3)
Co(1)-N(20)-C(21)	103.2 (1)	103.1 (2)
Co(1)-N(20)-C(41)	108.4 (2)	109.0 (3)
Co(1)-N(20)-C(20)	110.4 (1)	105.3 (3)
C(21)-N(20)-C(41)	110.4 (2)	111.7 (3)
C(21)-N(20)-C(20)	111.9 (2)	114.4 (3)
C(41)-N(20)-C(20)	112.2 (2)	112.6 (3)
C(10)-C(20)-N(20)	119.3 (2)	109.9 (4)
C(20)-C(10)-N(10)	118.8 (2)	110.3 (3)
N(10)-C(11)-C(12)	110.9 (2)	111.9 (3)
N(10)-C(31)-C(32)	114.3 (2)	114.3 (3)
N(20)-C(21)-C(22)	110.7 (2)	110.2 (3)
N(20)-C(41)-C(42)	113.5 (2)	113.8 (3)
C(11)-C(12)-O(11)	116.5 (2)	117.4 (4)
C(11)-C(12)-O(12)	118.0 (2)	118.7 (4)
O(11)-C(12)-O(12)	125.5 (3)	123.9 (4)
C(31)-C(32)-O(31)	117.4 (2)	118.6 (3)
C(31)-C(32)-O(32)	117.9 (2)	117.9 (3)
O(31)-C(32)-O(32)	124.7 (2)	123.4 (3)
C(21)-C(22)-O(21)	116.6 (2)	117.2 (4)
C(21)-C(22)-O(22)	119.2 (2)	118.2 (4)
O(21)-C(22)-O(22)	124.2 (2)	124.6 (4)
C(41)-C(42)-O(41)	117.4 (2)	119.2 (3)
C(41)-C(42)-O(42)	118.1 (2)	116.0 (4)
O(41)-C(42)-O(42)	124.4 (3)	124.8 (4)
C(12)-O(11)-Co(1)	114.9 (2)	115.5 (3)
C(32)-O(31)-Co(1)	116.7 (1)	117.0 (2)
C(22)-O(21)-Co(1)	115.5 (1)	114.6 (2)
C(42)-O(41)-Co(1)	117.3 (2)	115.1 (3)

[a] The number in parentheses is the standard deviation.

Table IX. Bond Distances (Å) and Angles (deg) of the 1,2-Diazaphenyl Portion of $Co^{II}PhDTA^{2-}$

	Distances		
C(20)-N(20)	1.453 (3)	C(30)-C(40)	1.380 (3)
C(10)-N(10)	1.454 (3)	C(40)-C(50)	1.386 (3)
C(10)-C(20)	1.393 (3)	C(50)-C(60)	1.390 (4)
C(20)-C(30)	1.398 (4)	C(60)-C(10)	1.390 (3)
	Angles		
N(10)-C(10)-C(60)	121.2 (2)	C(10)-C(20)-C(30)	119.2 (2)
N(10)-C(10)-C(20)	118.8 (2)	C(20)-C(30)-C(40)	120.4 (2)
N(20)-C(20)-C(10)	119.3 (2)	C(30)-C(40)-C(50)	120.4 (2)
N(20)-C(20)-C(30)	121.4 (2)	C(40)-C(50)-C(60)	119.6 (2)
C(20)-C(10)-C(60)	120.0 (2)	C(50)-C(60)-C(10)	120.3 (2)

the C–O bond distances in the carboxyl groups deserve comment. The eight carboxyl groups in the two structures may be divided into three classes. Carboxyl group 3 in $PhDTA^{4-}$ has O(31) coordinated to Co(1) and accepting two hydrogen bonds, while O(32) is bonded only to C(32). This group has the longest (1.282 (3) Å) C–O(*j*1) bond and the shortest (1.224 (3) Å) C–O(*j*2) bond. Carboxyl groups 1, 2, and 4 in $PhDTA^{4-}$ and groups 1 and 2 in $EDTA^{4-}$ have O(*j*1) coordinated to Co(1) and either a hydrogen atom or a sodium ion, while O(*j*2) interacts only with hydrogen atoms or sodium ions. These groups have intermediate C–O bond lengths (C–O(*j*1) = 1.270–1.275 Å; C–O(*j*2) = 1.240–1.248 Å). Carboxyl groups 3 and 4 in $EDTA^{4-}$ have O(*j*1) coordinated to (Co(1) and a hydrogen atom, while O(*j*2) is coordinated to Co(2)) and a hydrogen atom. These groups have the shortest C–O(*j*1) bonds (1.254 (5) and 1.261 (4) Å) and the longest C–O(*j*2) bonds (1.251 (5) and 1.248 (4) Å) and are essentially symmetrical as expected for an M–O–C–O–M unit.

As observed in the Introduction, an EDTA-like complex is restricted from adopting a trigonal-prismatic coordination polyhedron by the N–C–C–N dihedral angle of about 55°. Since the N–C–C–N dihedral angle in $Co^{II}PhDTA^{2-}$ is approximately zero, a conformation much closer to trigonal prismatic is possible. For these reasons, and because both complexes involve the same metal ion in the same formal oxidation state and spin state,[22] a comparison of the coordination polyhedra of $Co^{II}EDTA^{2-}$ and $Co^{II}PhDTA^{2-}$ is of particular interest.

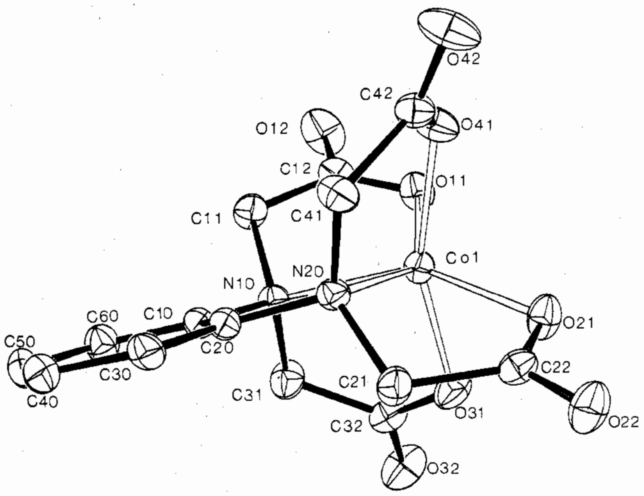

Figure 6. ORTEP[21] drawing of $[Co^{II}PhDTA]^{2-}$ showing 50% probability thermal ellipsoids.

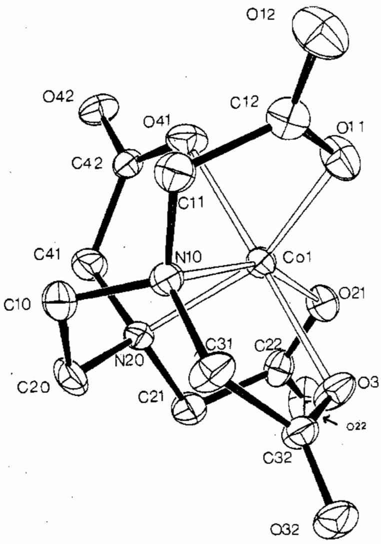

Figure 7. ORTEP[21] drawing of $[Co^{II}EDTA]^{2-}$ showing 50% probability thermal ellipsoids.

Metal–ligand bond distances and angles are listed in Table X. The average metal–oxygen distances in $Co^{II}EDTA^{2-}$ and $Co^{II}PhDTA^{2-}$ are identical. The Co–N distances are larger in the $PhDTA^{4-}$ complex than in the $EDTA^{4-}$ complex, perhaps due to the weaker electron-donor properties of nitrogen atoms attached to a benzene ring relative to those attached to an aliphatic group.

Examination of the bond angles shows that the $PhDTA^{4-}$ complex is more distorted from octahedral geometry than the $EDTA^{4-}$ complex (mean deviations from octahedral angles are 16.7° and 10.1°, respectively). The coordination polyhedra are shown in Figures 6 and 7. Both complexes may be described as intermediate between a trigonal antiprism and a trigonal prism. The two triangular faces, N(10)–O(11)–O(31) and N(20)–O(21)–O(41), are nearly parallel in both complexes, are about 2.73 Å apart in the $PhDTA^{4-}$ complex and about 2.63 Å apart in the $EDTA^{4-}$ complex, and

Table X. Distances (Å) and Angles (deg) in the Coordination Polyhedra of Co^{II}PhDTA^{2-} and Co^{II}EDTA^{2-}

Atoms	Co^{II}PhDTA^{2-}	Co^{II}EDTA^{2-}
	Bond Distances	
M-O(11)	2.109 (2)	2.039 (4)
M-O(31)	2.045 (2)	2.087 (3)
M-N(10)	2.171 (2)	2.158 (3)
M-O(21)	2.117 (1)	2.082 (3)
M-O(41)	2.065 (2)	2.123 (3)
M-N(20)	2.196 (2)	2.161 (4)
Av^a	2.117 (2, 80)	2.108 (3, 70)
$\overline{\text{M-O}}$	2.084 (2, 39)	2.083 (3, 44)
$\overline{\text{M-N}}$	2.184 (2, 13)	2.160 (4, 2)
	Contact Distances	
N(10)-O(11)	2.700 (3)	2.705 (5)
N(10)-O(31)	2.745 (2)	2.761 (4)
N(20)-O(21)	2.715 (2)	2.711 (4)
N(20)-O(41)	2.733 (3)	2.753 (5)
N(10)-N(20)	2.805 (2)	2.900 (5)
O(11)-O(21)	3.874 (2)	3.556 (5)
O(11)-O(31)	2.924 (3)	3.021 (5)
O(11)-O(41)	2.811 (3)	2.884 (5)
O(21)-O(31)	2.781 (2)	2.835 (4)
O(21)-O(41)	2.870 (3)	3.063 (4)
O(31)-O(41)	4.052 (3)	4.209 (4)
N(20)-O(11)	4.099 (3)	4.126 (5)
N(20)-O(31)	3.566 (3)	3.212 (5)
N(10)-O(21)	4.092 (2)	4.158 (5)
N(10)-O(41)	3.580 (3)	3.259 (5)
	Angles	
N(10)-M-O(11)	78.21 (7)	80.2 (1)
N(10)-M-O(31)	81.20 (7)	81.1 (1)
N(10)-M-O(21)	145.25 (8)	157.3 (1)
N(10)-M-O(41)	115.35 (7)	99.1 (1)
N(10)-M-N(20)	79.96 (7)	84.3 (1)
N(20)-M-O(11)	144.46 (6)	158.4 (1)
N(20)-M-O(31)	114.44 (8)	98.2 (1)
N(20)-M-O(41)	79.72 (8)	80.0 (1)
N(20)-M-O(21)	78.01 (6)	79.4 (1)
O(11)-M-O(21)	132.94 (7)	119.3 (1)
O(11)-M-O(31)	89.48 (7)	94.2 (1)
O(11)-M-O(41)	84.74 (7)	87.7 (1)
O(21)-M-O(31)	83.86 (6)	85.7 (1)
O(21)-M-O(41)	86.67 (7)	93.5 (1)
O(31)-M-O(41)	160.73 (7)	178.1 (1)

[a] For the averages, the first number in parentheses is the average of the standard deviations and the second is the maximum deviation from the mean.

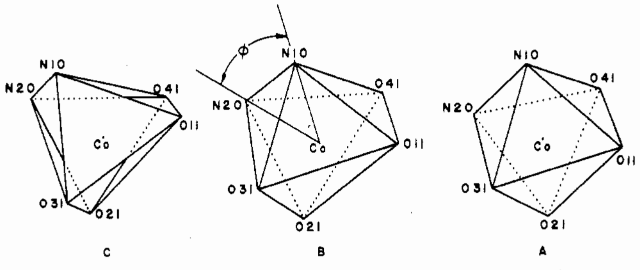

Figure 8. Projection drawings of coordination polyhedra: A, Co^{III}EDTA$^-$;[5] B, Co^{II}EDTA^{2-}; C, Co^{II}PhDTA^{2-}. The twist angle Φ is approximately the angle shown measured in the plane of the paper.

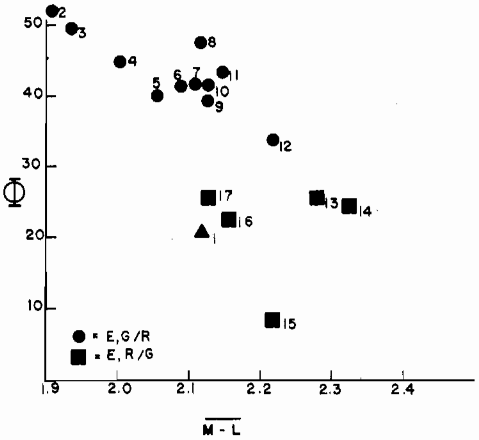

Figure 9. Twist angle, Φ, vs. mean metal–ligand atom distance: **1**, Co^{II}PhDTA^{2-} in Na$_2$[Co^{II}(H$_2$O)$_6$][Co^{II}PhDTA]$_2$·4H$_2$O; **2**, Co^{III}EDTA$^-$ in NH$_4$[Co^{III}EDTA]·2H$_2$O;[5] **3**, Al^{III}EDTA$^-$ in K-[Al^{III}EDTA]·2H$_2$O;[24] **4**, Fe^{III}EDTA$^-$ in Li[Fe^{III}EDTA]·3H$_2$O;[25] **5**, Mn^{III}CDTA$^-$ in K[Mn^{III}CDTA]·H$_2$O;[26] **6**, Zn^{II}EDTA^{2-} in [Zn^{II}-(H$_2$O)$_4$Zn^{II}EDTA]·2H$_2$O;[27] **7**, Co^{II}EDTA^{2-} in [Co^{II}-(H$_2$O)$_4$Co^{II}EDTA]·2H$_2$O; **8**, Cu^{II}EDTA^{2-} in K$_2$[Cu^{II}EDTA]·3H$_2$O;[28] **9**, Fe^{III}(H$_2$O)EDTA$^-$ in Li[Fe^{III}(H$_2$O)EDTA]·2H$_2$O;[29] **10**, Fe^{III}-(H$_2$O)EDTA$^-$ in Rb[Fe^{III}(H$_2$O)EDTA]·H$_2$O;[29] **11**, Fe^{III}(H$_2$O)EDTA$^-$ in [C(NH$_2$)$_3$][Fe^{III}(H$_2$O)EDTA]·2H$_2$O;[30] **12**, Mg^{II}(H$_2$O)EDTA^{2-} in [Mg^{II}(H$_2$O)$_6$][Mg^{II}(H$_2$O)EDTA]·2H$_2$O;[31] **13**, Mn^{II}(H$_2$O)EDTA^{2-} in [Mn^{II}(H$_2$O)$_4$][Mn^{II}(H$_2$O)HEDTA]$_2$·4H$_2$O;[2,32] **14**, Mn^{II}(H$_2$O)-EDTA^{2-} in Li$_2$[Mn^{II}(H$_2$O)EDTA]·4H$_2$O;[33] **15**, Mg^{II}(H$_2$O)EDTA^{2-} in Na$_2$[Mg^{II}(H$_2$O)EDTA]·5H$_2$O;[1] **16**, Sn^{IV}(H$_2$O)EDTA in [Sn^{IV}-(H$_2$O)EDTA];[34] **17**, Fe^{III}(H$_2$O)CDTA$^-$ in Ca[Fe(H$_2$O)CDTA]$_2$·8H$_2$O.[35] The twist angle was calculated as described in ref 23.

are twisted[23] relative to each other by 19° in the PhDTA^{4-} complex and by 38° in the EDTA^{4-} complex. (See Figure 8 and compare Co^{III}EDTA$^-$ with the two Co(II) complexes.) Thus, as expected for a complex in which the N–C–C–N angle is approximately zero, Co^{II}PhDTA^{2-} is more nearly trigonal prismatic by about 20° than any MEDTA^{n-} six-coordinate complex. [In fact, the only six- or seven-coordinate hexadentate EDTA^{4-}-like complex known to the authors which has a smaller twist angle is the monocapped trigonal-prismatic Mg(EDTA)(H$_2$O)$^{2-}$ in Na$_2$[Mg(EDTA)(H$_2$O)]·5H$_2$O[1] with a twist angle (Φ) of 8° (Figure 9).[36]]

In spite of the apparent success of predicting the smaller Φ for Co^{II}PhDTA^{2-} than for Co^{II}EDTA^{2-} based on the stereochemistry of the N–C–C–N linkage, it was of interest to question how other differences between the PhDTA^{4-} and EDTA^{4-} Co(II) complexes might affect Φ. Accordingly, repulsion-model calculations patterned after those done by Kepert[37] for tris(bidentate) complexes were performed. For each model complex defined by a particular set of metal–ligand atom bond distances and N–N and "glycine" bite distances, we have calculated the twist angle Φ (defined by the N atoms) corresponding to the minimum in ligand–ligand repulsion energy.

The model complex is defined in a polar coordinate system to consist of a metal ion at the origin and two triangles, N(10), O(31), O(11) and N(20), O(21), O(41) (cf. Figure 8), related by a twofold axis passing through the metal ion and the midpoint of the N(10)–N(20) line and both constrained to remain perpendicular to the polar axis as the model is twisted. The interligand Coulombic repulsion energy ($=\sum 1/d_{\text{L-L}}$) is calculated for a series of values of the twist angle, and the angle for minimum energy is found empirically. Some of the principal results from these calculations are shown in Table XI. As can be seen, the Coulombic repulsion model predicts the twist angle within 6°. Some insight into the functionality of the Coulombic repulsion model was gained by selecting values for the distances and "bites" characteristic of Co^{II}EDTA^{2-} and Co^{II}PhDTA^{2-} and then performing a series of calculations in which a single variable was systematically changed (e.g., the N(10)–N(20) distance). We were thus able to estimate the values of the derivatives

$$d\Phi/d(\text{Co-N}) \approx -138°/\text{Å}$$

$$d\Phi/d(\text{N(10)-N(20)}) \approx +111°/\text{Å}$$

$$d\Phi/d(\text{Co-O}) \approx -70°/\text{Å}$$

$$d\Phi/d(\text{N-O bites}) \approx +43°/\text{Å}$$

Table XI. Comparison of Calculated (Repulsion Model) and Observed Φ's for Hexacoordinate, Hexadentate $EDTA^{4-}$-Class Complexes

	Φ, deg		Distances, Å		
Complex	Obsd[a]	Calcd	N(10)-N(20)	M-N[b]	M-O[b]
$Co^{II}PhDTA^{2-}$	19.4	24.3	2.806	2.184	2.084
$Co^{III}EDTA^-$	52.7	55.3	2.72	1.924	1.900
$Al^{III}EDTA^-$	44.4	48.5	2.76	2.04	1.89
$Zn^{II}EDTA^{2-}$	35.5	32.9	2.84	2.14	2.06
$Co^{II}EDTA^{2-}$	38.2	37.8	2.900	2.160	2.083
$Fe^{III}EDTA^-$	37.4	43.6	2.95	2.20	1.94

[a] Based on N(10)-N(20) only; see Figure 8. [b] Average value.

Consideration of these terms clearly indicates that the functionality is a complicated one and that in the case of the $Co^{II}PhDTA^{2-}$ and $Co^{II}EDTA^{2-}$ complexes the "reason" the model predicts a lower Φ for the former is that it contains the shorter N(10)–N(20) bite. Thus 72% of the difference in Φ between the two species may be accounted for by a model which takes no cognizance of the stereochemistry of the N(10)–C(10)–C(20)–N(20) linkage. One is still tempted to conclude that the planar N–C–C–N backbone of $PhDTA^{4-}$ does tend to give smaller twist angles than the gauche backbone of $EDTA^{4-}$ but that at least one other effect must be important, namely, interligand atom Coulombic repulsion. The influence of other factors such as variation of CFSE with Φ and variations of the stereochemistry of the rest of the ligand also will merit closer examination. For instance crystal field calculations at various Φ's using the Co–N, Co–O, and bite distances of $Co^{II}PhDTA^{2-}$ indicate that the smaller the value of Φ the more favorable the CFSE.[38] Examination of Figure 9 reveals that the detailed stereochemistry of the chelate rings also influences the twist angle. The set of hexadentate (six- or seven-coordinate) $EDTA^{4-}$ (and $CDTA^{4-}$, cyclohexanediaminetetraacetate) complexes having the E, G/R conformation generally shows a decrease in twist angle with increasing mean metal–ligand distance.[2] However, three out of five complexes with E, R/G ring patterns have smaller Φ's than comparable complexes with E, G/R patterns. It is not the seven-coordinate nature of the three (**15–17**) that accounts for the difference because **9–12** are also seven-coordinate hexadentate $EDTA^{4-}$ complexes. It is noteworthy (1) that the two remaining complexes with E, R/G ring patterns seem to "fit in" with the E, G/R set and (2) that a complex with a planar N–C–C–N backbone cannot even be classified in the E, G/R or E, R/G patterns.

Clearly there is a great deal more to do to understand and appropriately weigh the several factors involved in determining the detailed stereochemistry of $EDTA^{4-}$-class complexes. Specifically a more quantitative evaluation of the role of the planar backbone in determining the structure of $PhDTA^{4-}$ and $EDTA^{4-}$ complexes must await the collection of precise structural data of more complexes, particularly those of $PhDTA^{4-}$. Nevertheless, it is still reasonable to anticipate that some hexadentate $PhDTA^{4-}$ complex will be found with $\Phi = 0°$ because $PhDTA^{4-}$, unlike $EDTA^{4-}$, is not absolutely restricted[1] from forming a trigonal-prismatic array of donor atoms.

When the G and R rings of $Co^{II}PhDTA^{2-}$ and $Co^{II}EDTA^{2-}$ are compared to those of other EDTA-like complexes found in the literature, a number of interesting phenomena are observed. For example, the mean Co–O bond distances are longer in the G rings than in the R rings of the $PhDTA^{4-}$ complex, whereas they are shorter in the G rings than in the R rings of the $EDTA^{4-}$ complex. An examination of all of the published structures of hexadentate (and six- and seven-coordinate) $EDTA^{4-}$ and $EDTA^{4-}$-like complexes shows that within experimental error the only other structures in which the M–O distances are shorter in the G rings are the $Cu^{II}EDTA^{2-}$ complex[28] and $ZnEDTA^{2-}$ in $[Zn(H_2O)_4ZnEDTA]\cdot 2H_2O$. It should be noted that it is the carboxylate groups on the R rings of the isostructural $Co^{II}EDTA^{2-}$ and $ZnEDTA^{2-}$ which bridge the two metal ions and this is probably the cause of the relatively long metal–oxygen distances. Thus, in solution or in other crystals this unusual R–G reversal may well not hold.

The published structures of $EDTA^{4-}$ and $CDTA^{4-}$ hexadentate, six- or seven-coordinate complexes show a mean angle of 17° between G rings and E rings and 84° between R rings and E rings for the E, G/R conformation. The corresponding angles for $Co^{II}EDTA^{2-}$ are 20 and 82°. For the E, R/G conformation the angles are 48° for G rings and 65° for R rings. (It is interesting to note that for $Mg^{II}(EDTA)(H_2O)^{2-}$ in $Na_2[Mg^{II}(EDTA)(H_2O)]\cdot 5H_2O$ these angles are 54 and 56° and, as mentioned above, the twist angle is 8°). These angles are 35 and 58° for $Co^{II}PhDTA^{2-}$, which may therefore be described as having G rings intermediate between those of E, G/R and E, R/G conformations, while its R rings are tipped farther from perpendicular to the $\overline{N-C-C-N-M}$ rings than for any other complex (except $Mg^{II}(EDTA)(H_2O)^{2-}$).

Distortions of chelate rings from planarity may be measured in several different ways. We have selected the mean deviation of the five atoms of the ring from its least-squares plane. We find the mean deviation of G rings to be 0.18 Å for E, G/R complexes, 0.20 Å for E, R/G complexes, 0.16 Å for $Co^{II}EDTA^{2-}$, and 0.18 Å for $Co^{II}PhDTA^{2-}$. For the R rings we find 0.08 Å for E, G/R complexes, 0.14 Å for E, R/G complexes, 0.05 Å for $Co^{II}EDTA^{2-}$, and 0.06 Å for $Co^{II}PhDTA^{2-}$. The above noted differences between complexes with the E, G/R and E, R/G conformations are not due merely to an accumulation of angle distortions or to packing considerations. The differences are due to the fact that the E, R/G and E, G/R conformations are different in principle and cannot be interconverted (when all four acetate arms are bonded to the metal) except through the barrier of a planar conformation of the ethylenediamine ring.[20]

The Co(II)–EDTA–H_2O and Co(II)–PhDTA–H_2O Systems. Several investigations have provided insight into the nature of the various equilibria involved in the Co(II)–EDTA–H_2O system.[39–41] The reactions of interest (eq 1 and 2) involve the

$$Co^{II}(H_2O)EDTA^{2-}(aq) \rightleftarrows Co^{II}EDTA^{2-}(aq) \qquad K_{65} \tag{1}$$

$$Co^{II}(H_2O)HEDTA^{-}(aq) \rightleftarrows H^{+}(aq) + Co^{II}(H_2O)EDTA^{2-}(aq) \qquad K_1 \tag{2}$$

six-coordinate hexadentate complex $Co^{II}EDTA^{2-}$ as well as the two six-coordinate complexes $Co^{II}(H_2O)EDTA^{2-}$ and $Co^{II}(H_2O)HEDTA^-$, both of which contain one uncoordinated carboxylate group. In the latter case, the uncoordinated carboxyl group is protonated. Taking $K_{65} \approx 4$[39,41] and $K_1 \approx 10^{-3}$,[39] eq 1 and 2 can be combined to give two ratios particularly useful when considering the gross electronic and infrared spectral changes occurring in the Co(II)–EDTA–H_2O system as the pH is lowered from an initial value near 7 (eq 3 and 4).

$$R_1 = \frac{[Co^{II}EDTA^{2-}]}{[Co^{II}(H_2O)EDTA^{2-}] + [Co^{II}(H_2O)HEDTA^-]} = \frac{K_1K_{65}}{[H^+] + K_1} = \frac{4 \times 10^{-3}}{[H^+] + 10^{-3}} \tag{3}$$

$$R_2 = \frac{[Co^{II}EDTA^{2-}] + [Co^{II}(H_2O)EDTA^{2-}]}{[Co^{II}(H_2O)HEDTA^-]} = \frac{K_1K_{65} + K_1}{[H^+]} = \frac{5 \times 10^{-3}}{[H^+]} \tag{4}$$

Equation 3 is most appropriate to consider when discussing

Table XII. Selected Characteristic Bands[a] from Infrared Spectra (cm^{-1})

$Na_2[Co^{II}$-PhDTA]$\cdot 3H_2O$	$[Co^{II}(H_2O)_6]$-$[Co^{II}$PhDTA]	Co(II)-PhDTA-D_2O system[c]		$[Co^{II}(H_2O)_4$-Co^{II}EDTA]$\cdot 2H_2O$	Co(II)-EDTA-D_2O system[c]	
		pD 6	pD 1		pD 8.4	pD 3.4
1609 vs	1600 vs	1602 vs	1723	1594 vs	1598 vs	1719
1495 w	1494 w	1495	1603 vs	1450[b]	1436 sh	1600 vs
1445 w	1447 w[b]	1462 sh	1495	1405 s[b]	1402 s	1441
1400 s[b]	1408 s	1447 sh	1462 sh	1390 s[b]	1322	1402
1339	1341	1409 s	1448 sh	1339 m	1272 w	1325
1317	1318	1335	1407 s	1275 w	1116 w	1105
1302 w	1304 sh	1322	1333	1115 sh	1100	1000 w
1235	1279	1289 w		1100	1000 w	968 w
1211	1246	1117	1114	1010 w	966 w	925
1181	1209	1102	1103	994 w	922	861 w
1100	1125	1037 w	982 w	963 w	866 w	
1033	1092	987 w	958 w	922		
913 s	1036	962 w	918	870		
790	1000	917		715		
709	966					
	934					
	913					
	705					

[a] Spectra taken with Nujol mulls except where noted; vs = very strong, s = strong, sh = shoulder, w = weak. [b] Spectra taken with Kel-F or Fluorolube mull. [c] Spectra taken with D_2O solution.

the electronic spectral changes. Since the only difference between $Co^{II}(H_2O)HEDTA^-$ and $Co^{II}(H_2O)EDTA^{2-}$ involves the protonation of an uncoordinated carboxyl group, the electronic spectra of these two are expected to be *very similar*.[41] Consequently, the denominator of R_1 is the concentration of species giving rise to one characteristic spectrum, whereas the numerator is the concentration of the species giving rise to the other characteristic spectrum. At a pH of 7, where $R_1 \approx 4$, the spectral characteristics are due primarily to the presence of $Co^{II}EDTA^{2-}$, whereas at a pH of 2, where $R_1 = 0.36$, the characteristics are due primarily to $Co^{II}(H_2O)HEDTA^-$. It is to be noted that a rapid change[40] occurs in the spectrum between pH values of 4 and 3 where R_1 is changing from 3.6 to 2, respectively.

In the infrared experiment it is the appearance of a band at ~1700 cm^{-1} (due to the presence of a COOD or COOH group)[42] that becomes apparent as the pH (pD) is lowered from an initial value of ~7. A band arising from the asymmetric stretching mode of both coordinated and uncoordinated COO^- groups[42,43] is also present in the spectra. It is, of course, present over a wide range of pH (pD) values and is not nearly as diagnostic as the band near 1700 cm^{-1}. Using eq 4 we note that R_2, the ratio of concentrations of species containing no protonated carboxylate groups to those containing a COOH (or COOD) group, changes from a value of 50 at a pH of 4 to a value of 5 at a pH of 3. Since the results of electronic spectra studies have shown[39,40] that the reactions represented by eq 1 and 2 are proceeding significantly to the right in this pH range, we wished to see whether the infrared spectra of D_2O solutions could also be used to detect the changes.[42] Accordingly, we examined the spectra of equimolar Co(II) and EDTA solutions at various pDs. Over the pD range of ~8.4–~5.4 no infrared band attributable to COOD could be found. However, at pD ~3.4 there is *clearly* present a peak at 1719 cm^{-1} (Figure 10), a reasonable position for the asymmetric stretching mode of a protonated carboxylate group.[42] Thus, the infrared experiments were shown to be useful in studying the equilibria and were also applied to the Co(II)–PhDTA–D_2O system (Figure 10 and Table XII).

The situation with respect to the Co(II)–PhDTA–H_2O system is similar in kind to the EDTA case but different in degree. Our conclusions are drawn from pH measurements, electronic and infrared spectral studies, and the ^{17}O NMR studies of Hunt.[44]

When $Na_2[Co^{II}PhDTA]\cdot 3H_2O$ is dissolved in water, we observe no pH change. The visible spectrum of $[Co^{II}(H_2O)_6][Co^{II}PhDTA]$ (in a 5.4×10^{-3} M solution) consists of a simple superposition of the $Co^{II}(H_2O)_6^{2+}$ spectrum and the spectrum of $Na_2[Co^{II}PhDTA]\cdot 3H_2O$, both at concentrations of 5.4×10^{-3} M. The ^{17}O NMR studies[44] indicate that there are no appreciable concentrations of $Co^{II}PhDTA^{4-}$ complexes containing complexed water molecules (at a pH value of 7). Thus, the predominant $PhDTA^{4-}$-containing species in solution at pH ~7 is clearly $Co^{II}PhDTA^{2-}$, a six-coordinate complex containing hexadentate $PhDTA^{4-}$.

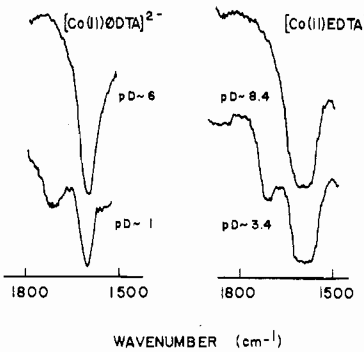

Figure 10. Portions of the infrared spectra of complexes present in D_2O solutions.

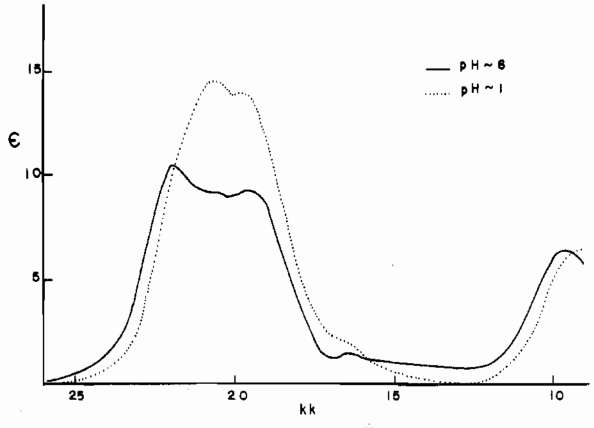

Figure 11. Electronic spectra of the Co^{II}–PhDTA–H_2O system at two pH values.

At pHs between 7 and 3, the visible spectrum of an aqueous solution of $Na_2[Co^{II}PhDTA]\cdot 3H_2O$ is essentially unchanged; however, at a pH of 1 the spectrum is significantly different

Table **XIII.** Electronic Spectra of Aqueous Solutions of Co(II) Complexes[a]

$Na_2[Co^{II}PhDTA]\cdot 3H_2O$ (pH 6)		$[Co^{II}EDTA]^{2-}$ [c]		$Na_2[Co^{II}PhDTA]\cdot 3H_2O$ (pH 1)		$[Co^{II}(H_2O)_6]^{2+}$ [d]		
ν, cm^{-1}	ϵ, M^{-1} cm^{-1}	ν, cm^{-1}	ϵ, M^{-1} cm^{-1}	ν, cm^{-1}	ϵ, M^{-1} cm^{-1}	ν, cm^{-1}	ϵ, M^{-1} cm^{-1}	Assignment
9 700	6.2	9 180	8.2	9 240	6.4	8 100	1.4	$^4T_{1g} \rightarrow {}^4T_{2g}$
16 300	1.7	16 200	2.6	16 700	1.8	16 000	0.3	$^4T_{1g} \rightarrow {}^4A_{2g}$
19 400	9.1	19 450	12.3	19 850	13.9	19 400	4.9	$^4T_{1g} \rightarrow {}^4T_{1g}$ (P)
20 600	9.1	20 600	13.3	20 600	14.5	21 600[b]		
21 900	10.4	21 400	14.1					

[a] Band maxima reported except as noted. [b] Shoulder; see Figure 9.4 of ref 45. [c] Solution from which spectrum was taken was prepared as indicated in the Experimental Section. This spectrum is essentially identical with that reported in ref 7 taken at pH 8. Note: the spectrum of "pure" $[Co^{II}EDTA]^{2-}$ is not obtainable by a direct measurement in aqueous solution because of the value of K_{65}. [d] See ref 45 and 46 for discussion and band assignments.

(Table XIII, Figure 11). The differences are independent of the acid used to adjust the pH in that identical results are obtained with aqueous HCl and $HClO_4$. Over a pD range of ~8.4–~3.4 the only band present in the infrared spectra (in the 1600–1830 cm^{-1} range) is at 1602 cm^{-1} (Table XII, Figure 10). At pD ~1 a second band appears at 1723 cm^{-1}, thus indicating the presence of a protonated carboxylate group.[42] We note that both the electronic and infrared spectral changes occur at lower pH values in the Co(II)–PhDTA system than in the Co(II)–EDTA case. Assuming that the equilibria shown in (1) and (2) can be applied to the Co(II)–PhDTA system, some estimate of both K_1 and K_{65} can be made. The value of K_1 for the singly charged $Co^{II}(H_2O)HPhDTA^-$ is expected to be $\sim 10^{-3}$ just as it is for other singly charged complexes with protonated carboxylate groups.[47] For instance, $Co^{II}(H_2O)HEDTA^-$ has a pK of ~3[39] as does $Co^{III}(X)HEDTA^-$ (where $X^- = Cl^-$ or Br^-).[48] Given that $K_1 \approx 10^{-3}$ and that the pH range (where dramatic changes are occurring in the spectra) is from 3 to 1, then $K_{65} \geq 40$. Assuming that the relative solvation parameters ($\Delta H°$ and $\Delta S°$) for the various complexes *are not* the factors determining K_{65}, then there is some reason to expect that this large K_{65} value for the PhDTA system may be ascribed to a relative instability of the proposed pentadentate complex $Co^{II}(H_2O)PhDTA^{2-}$. An examination of molecular models reveals that an approximately octahedral species (in terms of the donor atoms) is expected for $Co^{II}(H_2O)PhDTA^{2-}$. However, due to *the planar N–C–C–N backbone*, this pentadentate complex must feature *two* G rings and one R ring. According to Hoard et al.,[49] this arrangement is less stable than the alternative (two R rings and one G ring) expected for $Co^{II}(H_2O)EDTA^{2-}$ and found in a variety of similar complexes containing the ethylenediaminetriacetate moiety in pentadentate coordination.[49–51] Thus we propose that the right to left transformation represented in eq 1 involves, in the EDTA system, a change from a complex containing two R and two G rings to one containing two R rings and one G ring whereas, in the PhDTA system, it involves a relatively less favorable change from two R and two G rings to *one* R ring and two G rings. The consequences of these proposed changes are consistent with the considerations advanced in the preceding discussion of structure parameters. Thus, it would be expected that in solution the mean Co–O bond distances for G rings are larger than those for R rings for both $Co^{II}EDTA^{2-}$(aq) and $Co^{II}PhDTA^{2-}$(aq). Because of the constraints of the benzene backbone in $Co^{II}PhDTA^{2-}$ it must break one of the shorter bonds, a Co–O bond in an R ring, to become a pentadentate complex. This process, being relatively unfavorable (compared to breaking a Co–O bond in a G ring), "happens" at a lower pH.

As can be seen in Figure 11 and Table XIII, the electronic spectrum of $Co^{II}PhDTA^{2-}$ clearly exhibits a multiplicity beyond that expected for an octahedral species (such as $Co(H_2O)_6^{2+}$). Given the fact that $PhDTA^{4-}$ contains two kinds of donor atoms (N and O) and that there is a very large deviation from an octahedral coordination polyhedron, the increase in multiplicity is not surprising. In the case of the spectrum taken at pH 1 (Figure 11 and Table XIII) the absorption envelope is similar in apparent multiplicity and band position to $Co^{II}(H_2O)_6^{2+}$. However, if assignments are made directly analogous to $Co(H_2O)_6^{2+}$ (Table XIII) the ν_2/ν_1 ratio is somewhat low (at 1.81).[52] Thus, not unexpectedly it is probably inappropriate to apply the octahedral crystal-field formalism to the spectral interpretation of the species present at pH ~1.

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Registry No. I, 64813-41-8; II, 12785-79-4; $[Co^{II}EDTA]^{2-}$, 14931-83-0; $[Co^{II}PhDTA]^{2-}$, 64813-39-4; $PhDTAH_4$, 40774-59-2; bromoacetic acid, 79-08-3; *o*-phenylenediamine, 95-54-5; $[Al^{III}EDTA]^-$, 15009-37-7; $[Zn^{II}EDTA]^{2-}$, 12519-36-7; $[Co^{III}EDTA]^-$, 15136-66-0; $[Fe^{III}EDTA]^-$, 15275-07-7.

Supplementary Material Available: Listings of the structure factor amplitudes (33 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of *trans*-Tetrakis(pyridine)dichloroiron(II), -nickel(II), and -cobalt(II) and *trans*-Tetrakis(pyridine)dichloroiron(II) Monohydrate

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The crystal and molecular structures of $Fe(py)_4Cl_2$, $Co(py)_4Cl_2$, $Ni(py)_4Cl_2$, and $Fe(py)_4Cl_2 \cdot H_2O$ have been determined from three-dimensional x-ray diffraction data collected on a four-circle diffractometer. The first three compounds crystallize in the tetragonal $I4_1/acd$ space group with unit cell parameters of ca. 15.9 Å for a and ca. 17.1 Å for b and a volume of ca. 4350 Å^3. $Fe(py)_4Cl_2 \cdot H_2O$ crystallizes in the monoclinic $P2_1/c$ space group with $a = 9.384$ (6) Å, $b = 16.766$ (4) Å, $c = 16.342$ (9) Å, $\beta = 121.497$ (25)°, and $V = 2192.2$ (1.2) Å.^{3} The structures were solved by Patterson and Fourier methods and refined where feasible by full-matrix least-squares procedures. All nonhydrogen atoms were refined with anisotropic thermal parameters and all pyridine hydrogen atoms were located by electron difference methods although more accurate positions were derived through geometric considerations; the resulting conventional R factors are 4.77, 4.83, 4.98, and 3.88%, respectively. In each complex the metal is coordinated in a trans fashion to two chloride ions and four pyridine molecules. The molecules, which possess 222 but not $\bar{4}$ symmetry, are oriented with their pseudotetragonal (Cl–M–Cl) axis normal to the tetragonal axis of the crystals. The individual molecules of $M(py)_4Cl_2$ are well isolated from each other with essentially no intermolecular contact distances of less than the sum of van der Waals radii. The one exception to this is $Fe(py)_4Cl_2 \cdot H_2O$ where the water molecule serves as a presumably hydrogen-bonded bridge between two chloride ions in adjacent molecules. In the anhydrous iron, cobalt, and nickel complexes the M–Cl bond distances are 2.430 (3), 2.440 (2), and 2.437 (3) Å, and the M–N bond distances are 2.229 (6), 2.183 (4), and 2.133 (4) Å, respectively. The decrease in the M–N bond distance with increasing metal atomic number is attributed to the importance of the increasing number of t_{2g} π-bonding electrons in the metal ions. The relatively constant M–Cl bond distance is attributed to the constant number of σ-bonding electrons in these metal ions. The dihedral angle between the plane of the coordinate nitrogen atoms and the pyridine ring is ca. 51° in the anhydrous complexes. The increase of this dihedral angle above 45° is attributed either to a pyridine hydrogen to chlorine hydrogen-bonded interaction or to a hydrogen–carbon interaction on adjacent coordinated pyridine molecules.

Introduction

There have been many papers[1-8] which have dealt with the electronic and magnetic properties of tetrakis(pyridine)-metal(II) chloride complexes. In several of these papers it has been assumed that the molecule possesses tetragonal symmetry with trans chloride ligands in the axial coordination positions and pyridine in the four equatorial positions. This is a reasonable assumption in view of the preliminary x-ray structural results for $Ni(py)_4Cl_2$—based on a two dimensional

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