Symmetrical and Unsymmetrical Compounds Having a Linear Co₃⁶⁺ Chain Ligated by a Spiral Set of Dipyridyl Anions

F. Albert Cotton,*,† Lee M. Daniels,† Glenn T. Jordan, IV,† and Carlos A. Murillo*,†,‡

Contribution from the Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, and the Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

Abstract: Four compounds of the type $Co_3(dpa)_4XY$—where X and Y are Cl or BF_4 and dpa is the anion of dipyridylamine—have been prepared and structurally characterized. For X = Y = Cl, two significantly different types of complexes are formed. In one of them, $Co_3(dpa)_4Cl_2 \cdot CH_2Cl_2$, **1**, there is only one crystallographically independent Co−Co distance (2.3178(9) Å). In the second type of crystal, a mononuclear $Co(dpa)_2$ molecule is also found in the interstices of the crystal to give $Co_3(dpa)_4Cl_2 \cdot Co(dpa)_2$, **2**. Compound **2** has two independent and highly unsymmetrical Co−Co separations (2.285(1) and 2.459(1) Å) corresponding to a bonding and a nonbonding interaction. Reaction of **1** with 1 or 2 equiv of $AgBF_4$ yields $Co_3(dpa)_4Cl(BF_4) \cdot 2CH_2Cl_2$, **3**, and $Co_3(dpa)_4(BF_4)_2 \cdot 2CH_2Cl_2$, **4**, respectively. Similarly to **2**, compound **3** has a short and a long Co−Co separation (2.277 and 2.504(2) Å, respectively). However, **4** has independent but equal Co−Co distances of 2.253[2] Å, which are similar to that of **1**. We propose that since compounds of **1** and **2** differ only in the composition of the interstitial molecules (CH_2Cl_2 and $Co(dpa)_2$, respectively) but the Co−Co bonding is so different, then the $Co_3(dpa)_4Cl_2$ species should be considered as "stretch isomers".

Introduction

The discovery in 1990−1991 that the anion of dipyridylamine (dpa⁻) can serve to stabilize linear chains of three metal atoms with metal to metal distances[1] that clearly suggest the presence of bonding interactions between them was clearly, *by hindsight*, a very important one. Similar compounds containing the metallic elements Co,[2] Ru,[3] and Rh[3] were reported later. In four of the five compounds, the two M−M distances were equal, but in the case of cobalt they were reported to be very different. In very recent work[4] we have found the analogous chromium compound to also have the symmetrical arrangement.

We were intrigued, and puzzled, by the anomalous structure of the cobalt compound and also disturbed by the extremely poor yield (2−5%) reported. We thus set out to prepare the compound in better yield and to examine more closely the surprising unsymmetrical structure. It was more or less routine to find a preparative procedure that gave excellent yields, but it was far from routine to find that *our* $Co_3(dpa)_4Cl_2$ had a symmetrical structure. In our preliminary report on this work[5] we raised the question of whether the unsymmetrical compound (assuming that it was correctly identified, since severely disordered "solvent" molecules were said to be present) and our symmetrical one were "bond stretch isomers". We ventured

to suggest that in view of the unhappy history of previous claims of bond stretch isomers,[6] they probably were not and that some other explanation of the apparently conflicting results was to be sought.

Before proceeding to report our further studies, it is pertinent to recall what the term "bond stretch isomer" means. We accept Parkin's definition:[6] "...the unusual phenomenon whereby molecules differ only in the length of one or more bonds."

Experimental Section

General Methods. All manipulations were carried out by employing standard Schlenk techniques under an atmosphere of nitrogen. Solvents were distilled under nitrogen from appropriate drying agents. Anhydrous $CoCl_2$ was purchased from Alfa and stored in the drybox. 2,2′-Dipyridylamine was purchased from Aldrich and sublimed prior to use. Infrared spectral data were recorded as KBr pellets using a Perkin-Elmer 16PC FT-IR spectrophotometer at 2 cm⁻¹ resolution. Electronic absorption spectra were measured on a Cary 17 spectrophotometer. Elemental analyses for **1**, **3**, and **4** were satisfactory.

Preparation of $Co_3(dpa)_4Cl_2 \cdot 2CH_2Cl_2$ (1). In a 100 mL round-bottom flask, 0.480 g (2.80 mmol) of Hdpa was dissolved in 16 mL of THF. The solution was cooled to −78 °C, and then 2.0 mL of 1.4 M CH_3Li was added. The solution immediately turned milky white, but quickly became a clear pale yellow solution upon warming to room temperature. Anhydrous $CoCl_2$ (0.275 g, 2.12 mmol) was then added to the reaction mixture from a solid addition tube. The resulting brown solution was refluxed for 5.5 h and then stirred overnight. After filtration of the mixture, a dark red powder was collected and washed several times with small portions of THF. The powder was dissolved in CH_2Cl_2 and layered with hexanes to yield a large crop of dark green crystals. Additional product was obtained from workup of the filtrate. The solvent was removed from the filtrate under vacuum, leaving behind a dark residue. The residue was dissolved in 10 mL of CH_2Cl_2, filtered to remove LiCl, and layered with hexanes. Crystals from both solutions were collected, washed with hexanes, and dried under vacuum. Yield: 0.300 g (0.296 mmol, 42.3%). IR (KBr, cm⁻¹): 3102 (w), 3072

† Texas A&M University.
‡ University of Costa Rica.
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10378   *J. Am. Chem. Soc., Vol. 119, No. 43, 1997*

Cotton et al.

Table 1.   Crystal and Structure Refinement Data for Compounds **1**, **2**, **3**, and **4**

	1	2	3	4
formula	$Co_3(N_3C_{10}H_8)_4Cl_2\cdot$ $2CH_2Cl_2$	$Co_3(N_3C_{10}H_8)_4Cl_2\cdot$ $Co(N_3C_{10}H_8)_2$	$Co_3(N_3C_{10}H_8)_4ClBF_4\cdot$ $2CH_2Cl_2$	$Co_3(N_3C_{10}H_8)_4(BF_4)_2\cdot$ $2CH_2Cl_2$
formula weight	1098.3	1327.8	1149.7	1201.0
crystal system	orthorhombic	tetragonal	monoclinic	monoclinic
space group	*Pnn2*	*P4/n*	*C2/c*	*P2₁/c*
color	dark green	brown	black	dark green
a, Å	12.8145(9)	13.803(4)	18.777(7)	20.594(2)
b, Å	13.955(1)	13.803(4)	16.538(2)	13.754(4)
c, Å	11.1660(9)	14.9460(3)	15.455(6)	18.937(4)
β, deg	90	90	109.73(2)	114.76(2)
volume, Å³	1996.8(3)	2848(2)	4518(3)	4871(2)
Z	2	2	4	4
R1,[a] wR2[b]	0.032, 0.078	0.039, 0.091	0.042, 0.095	0.070, 0.148
R1, wR2	0.047, 0.084	0.050, 0.099	0.101, 0.114	0.095, 0.169
goodness-of-fit[c]	1.035	1.11	1.14	1.07

[a] $R1 = [\sum w(F_o - F_c)^2/\sum wF_o2]^{1/2}$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0623P)^2]$, where $P = [\max(F_o^2 \text{ or } 0) + 2(F_c)^2]/3$. [c] Quality-of-fit $=[\sum w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

(w), 3030 (w), 1636 (vw), 1607 (s), 1593 (s), 1547 (m), 1469 (vs), 1423 (vs), 1369 (s), 1318 (m), 1282 (m), 1268 (m), 1167 (m), 1152 (s), 1116 (w), 1057 (w), 1023 (s), 884 (m), 759 (s), 736 (s), 539 (w), 519 (w), 456 (w), 428 (w). $\lambda = 565$ nm (ϵ 1.97 × 10³ M⁻¹ cm⁻¹); 390 (sh) nm (ϵ 1.77 × 10⁴ M⁻¹ cm⁻¹); 320 nm (ϵ 5.83 × 10⁴ M⁻¹ cm⁻¹).

Preparation of Co₃(dpa)₄Cl₂·Co(dpa)₂ (2). In a 100 mL round bottom flask, 0.480 g (2.80 mmol) of Hdpa was dissolved in 20 mL of toluene. The solution was cooled to −78 °C, and 2.0 mL of 1.4 M CH₃Li was added with stirring. The milky white mixture was warmed to room temperature, and 0.278 g (2.14 mmol) of anhydrous CoCl₂ was added from a solids addition tube. After the mixture was stirred for several minutes, 15 mL of THF was added. The solution immediately turned dark green-brown. After being stirred overnight at room temperature, the mixture was a dark brown solution with a brown precipitate. The brown solid was collected by filtration and washed with 10 mL of 1:1 mixture of Et₂O and toluene. The solid was dissolved in 20 mL of CH₂Cl₂ and layered with 40 mL of hexanes. After 10 days of diffusion, several large brown crystals (0.4 mm) had grown. IR (KBr, cm⁻¹): 3084 (w), 3054 (w), 3012 (w), 1605 (s), 1593 (s), 1546 (w), 1533 (m), 1469 (vs), 1459 (vs), 1436 (vs), 1369 (m), 1313 (m), 1279 (m), 1248 (w), 1152 (m), 1024 (w), 1006 (m), 886 (w), 789 (m), 757 (m), 736 (m), 519 (w), 427 (w). This preparation was repeated many times, and several crystals were examined by diffraction methods (see below). They all had the same composition but the yields were consistently low. Dark green crystals of **1** were also formed from this solution after longer periods of diffusion (3−4 weeks).

Preparation of Co₃(dpa)₄ClBF₄·2CH₂Cl₂ (3). In a 50 mL Schlenk flask, 0.296 g (0.319 mmol) of Co₃(dpa)₄Cl₂ was dissolved in 15 mL of CH₂Cl₂ to give a dark red-green solution. In a separate flask, 0.065 g (0.33 mmol) of AgBF₄ was suspended in 10 mL of CH₂Cl₂. While the AgBF₄ was stirred vigorously, the Co₃(dpa)₄Cl₂ solution was added via cannula. There was no noticeable color change. After 45 min of stirring, a light precipitate had formed, presumably AgCl. Stirring was continued for 1.25 h at room temperature, and the reaction mixture was filtered with the aid of Celite to give a dark solution. This solution was concentrated to 13 mL and layered with hexanes. Large black crystals formed within 1 week of diffusion. The crystals were collected, washed with small portions of hexanes, and dried under vacuum. Yield: 0.249 g (0.254 mmol, 79.6%). IR (KBr, cm⁻¹): 3104 (w), 3071 (w), 3033 (w), 1635 (w), 1605 (s), 1595 (s), 1549 (m), 1470 (vs), 1429 (vs), 1371 (s), 1314 (m), 1286 (m), 1156 (s), 1109 (br, m), 1022 (m), 920 (m), 886 (m), 759 (s), 739 (m), 540 (w), 519 (w), 458 (w) 427 (w). UV/vis (CH₂Cl₂): $\lambda = 563$ nm (ϵ 1.65 × 10³ M⁻¹ cm⁻¹); 380 (sh) nm; 318 nm (ϵ 5.77 × 10⁴ M⁻¹ cm⁻¹).

Preparation of Co₃(dpa)₄(BF₄)₂·2CH₂Cl₂ (4). In a Schlenk tube, 0.140 g (0.151 mmol) of Co₃(dpa)₄Cl₂ was dissolved in 15 mL of CH₂-Cl₂ to give a dark red-green solution. In a separate flask, 0.70 g (0.36 mmol) of AgBF₄ was suspended in 10 mL of CH₂Cl₂. While the AgBF₄ was stirred vigorously, the Co₃(dpa)₄Cl₂ solution was added via cannula. After several minutes, the color of the solution changed to dark green

and a grayish-white precipitate lined the bottom of the flask. The reaction was stirred for 2.5 h at room temperature and then filtered with the aid of Celite to give a dark green solution. This solution was concentrated to 18 mL and layered with 30 mL of hexanes. Dark green crystals formed within 1 week of diffusion. The crystals were collected, washed with a small amount of hexanes, and dried under vacuum. Yield: 0.0935 g (0.0907 mmol, 60.0%). IR (KBr, cm⁻¹): 3099 (w), 3075 (w), 3032 (w), 1635 (m), 1597 (s), 1549 (m), 1471 (vs), 1428 (vs), 1371 (s), 1310 (m), 1285 (m), 1228 (m), 1157 (s), 1055 (br, s), 1027 (s), 929 (m), 886 (m), 865 (m), 760 (s), 739 (s), 533 (w), 521 (m), 458 (w), 427 (w). UV/vis (CH₂Cl₂): $\lambda = 705$ nm (ϵ 9.48 × 10² M⁻¹ cm⁻¹); 600 nm (ϵ 1.01 × 10³ M⁻¹ cm⁻¹); 535 nm (ϵ 1.10 × 10³ M⁻¹ cm⁻¹); 311 nm (ϵ 5.34 × 10⁴ M⁻¹ cm⁻¹).

Crystallographic Procedures. Single-crystal X-ray work of **1** and **3** was performed on a Nonius CAD4 diffractometer at −105 °C, and that of **2** and **4** was done on a Nonius FAST diffractometer at −60 °C utilizing the program MADNES.[7] Suitable crystals were mounted on the top of a quartz fiber with a small amount of silicone grease and transferred to a goniometer head. Unit-cell refinement for **1** and **3** utilized 25 strong reflections in the range of $30 \leq 2\theta \leq 40°$ for **1** and $18 \leq 2\theta \leq 34°$ for **3**. Cell parameters for **2** and **4** were obtained from an autoindexing routine and were refined with 250 strong reflections within a 2θ range of 18.1−41.6°. Cell dimensions and Laue symmetry for all crystals were confirmed from axial photographs. All data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ-scans was applied for **1** and **3**. For compound **4**, the program SORTAV[8] was used to correct for absorption. Data were processed into SHELX format using the programs XCAD for data collected from the CAD4 diffractometer and PROCOR[9] for data collected from the FAST diffractometer.

In structures **1**, **2**, and **4**, the positions of the heavy atoms were found in direct methods by the way of the program package SHELXTL.[10] In structure **3**, the metal atoms were located by the Patterson method. For all structures, subsequent cycles of least-squares refinement followed by difference-Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms for structures **1**, **3**, and **4** were placed in idealized calculated positions. For structure **2**, hydrogen atoms were located in difference Fourier maps and then refined isotropically. Other details of data collection and refinement are given in Table 1. Selected atomic distances and angles for **1**, **2**, **3**, and **4** are provided in Tables 2, 3, 4, and 5, respectively. Other crystallographic data are given as Supporting Information.

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Table 2. Selected Bond Lengths (Å) and Angles [deg] for **1**[a]

Co(1)-N(1)	1.985(7)	Co(1)-Cl(1)	2.520(2)
Co(1)-N(2)	1.984(7)	Co(2)-N(5)	1.903(8)
Co(1)-N(3)	1.971(7)	Co(2)-N(6)	1.902(8)
Co(1)-N(4)	2.022(7)	N(1)-C(1)	1.35(1)
Co(1)-Co(2)	2.3178(9)	N(1)-C(5)	1.35(1)
N(3)-Co(1)-N(2)	172.2(3)	N(2)-Co(1)-Cl(1)	93.6(2)
N(3)-Co(1)-N(1)	90.2(3)	N(1)-Co(1)-Cl(1)	94.8(2)
N(2)-Co(1)-N(1)	89.8(3)	N(4)-Co(1)-Cl(1)	95.5(2)
N(3)-Co(1)-N(4)	88.4(3)	Co(2)-Co(1)-Cl(1)	178.44(8)
N(2)-Co(1)-N(4)	90.1(3)	N(6)-Co(2)-N(5)	89.5(2)
N(1)-Co(1)-N(4)	169.6(3)	N(6)'-Co(2)-N(5)	178.5(4)
N(3)-Co(1)-Co(2)	87.3(2)	N(5)'-Co(2)-N(5)	89.9(5)
N(2)-Co(1)-Co(2)	84.9(2)	N(6)-Co(2)-Co(1)	88.1(2)
N(1)-Co(1)-Co(2)	85.5(2)	N(5)-Co(2)-Co(1)	91.6(3)
N(4)-Co(1)-Co(2)	84.2(2)	Co(1)-Co(2)-Co(1)'	177.04(13)
N(3)-Co(1)-Cl(1)	94.2(2)	C(1)-N(1)-C(5)	119.3(8)

[a] Primed atoms generated by $-x, -y + 2, z$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

Co(1)-Co(2)	2.459(1)	Co(1)-N(1)	2.125(3)
Co(2)-Co(3)	2.285(1)	Co(2)-N(2)	1.907(3)
Co(1)-Cl(1)	2.353(2)	Co(3)-N(3)	1.965(3)
Co(3)-Cl(2)	2.386(2)	Co(4)-N(4)	1.973(3)
N(1)-Co(1)-N(1a)	88.48(2)	Co(3)-Co(2)-Co(1)	180.0
N(1)-Co(1)-N(1b)	161.27(13)	N(3a)-Co(3)-N(3)	89.70(3)
N(1)-Co(1)-Cl(1)	99.36(7)	N(3b)-Co(3)-N(3)	171.77(13)
N(1)-Co(1)-Co(2)	80.64(7)	N(3)-Co(3)-Co(2)	85.89(7)
N(2a)-Co(2)-N(2)	89.996(12)	N(3)-Co(3)-Cl(2)	94.11(7)
N(2b)-Co(2)-N(2)	179.00(14)	N(4c)-Co(4)-N(4)	94.0(2)
N(2)-Co(2)-Co(3)	89.50(7)	N(4)-Co(4)-N(4d)	117.69(8)
N(2)-Co(2)-Co(1)	90.50(7)		

[a] Symmetry transformations used to generate equivalent atoms: a, $-y + 1/2, x, z$; b, $-x + 1/2, -y + 1/2, z$; c, $-x + 3/2, -y + 1/2, z$; d, $y + 1/2, -x + 1, -z + 1$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**[a]

Co(1)-Co(2)	2.504(2)	Co(3)-N(3)	1.943(4)
Co(2)-Co(3)	2.277(2)	Co(3)-N(6)	1.948(4)
Co(1)-Cl(1)	2.371(2)	Co(3)-F(1)	2.223(5)
Co(1)-N(4)	2.097(4)	B(1)-F(1)	1.44(2)
Co(1)-N(1)	2.155(4)	B(1)-F(2)	1.32(2)
Co(2)-N(5)	1.908(4)	B(1)-F(3)	1.33(2)
Co(2)-N(2)	1.912(4)	B(1)-F(4)	1.32(2)
Co(3)-Co(2)-Co(1)	180.0	N(5)-Co(2)-Co(1)	90.2(1)
Cl(1)-Co(1)-Co(2)	180.0	N(2)-Co(2)-Co(1)	91.5(1)
Co(2)-Co(3)-F(1)	180.0	N(3)-Co(3)-N(3)'	174.9(3)
Co(3)-F(1)-B(1)	173.2(8)	N(3)-Co(3)-N(6)	87.2(2)
N(1)-Co(1)-N(1)'	163.2(2)	N(3)-Co(3)-N(6)'	92.6(2)
N(4)-Co(1)-N(4)'	163.8(3)	N(6)-Co(3)-N(6)'	175.3(3)
N(4)-Co(1)-N(1)	86.8(2)	N(3)-Co(3)-F(1)	92.6(1)
N(4)-Co(1)-N(1)'	90.8(2)	N(6)-Co(3)-F(1)	92.4(1)
N(4)-Co(1)-Cl(1)	98.1(1)	N(3)-Co(3)-Co(2)	87.4(1)
N(1)-Co(1)-Cl(1)	98.4(1)	N(6)-Co(3)-Co(2)	87.6(1)
N(4)-Co(1)-Co(2)	81.9(1)	F(2)-B(1)-F(4)	111(2)
N(1)-Co(1)-Co(2)	81.6(1)	F(2)-B(1)-F(3)	113(2)
N(5)-Co(2)-N(5)'	179.6(3)	F(4)-B(1)-F(3)	111(2)
N(5)-Co(2)-N(2)	90.4(2)	F(2)-B(1)-F(1)	109(1)
N(5)-Co(2)-N(2)'	89.6(2)	F(4)-B(1)-F(1)	106(1)
N(2)-Co(2)-N(2)'	177.0(3)	F(3)-B(1)-F(1)	107(2)
N(2)-Co(2)-Co(3)	88.5(1)		

[a] Primed atoms generated by $-x + 1, y, -z + 1/2$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

Co(1)-Co(2)	2.254(2)	Co(2)-N(5)	1.899(6)
Co(3)-Co(2)	2.252(2)	Co(2)-N(2)	1.899(6)
Co(1)-N(7)	1.953(7)	Co(2)-N(8)	1.900(6)
Co(1)-N(10)	1.958(6)	Co(3)-N(6)	1.946(6)
Co(1)-N(1)	1.958(6)	Co(3)-N(3)	1.954(6)
Co(1)-N(4)	1.965(6)	Co(3)-N(12)	1.965(6)
Co(1)-F(1)	2.250(5)	Co(3)-N(9)	1.968(7)
Co(2)-N(11)	1.889(6)	Co(3)-F(5)	2.230(5)
Co(3)-Co(2)-Co(1)	177.58(6)	N(5)-Co(2)-Co(3)	89.2(2)
N(7)-Co(1)-N(10)	89.9(3)	N(2)-Co(2)-Co(3)	89.0(2)
N(7)-Co(1)-N(1)	174.6(3)	N(8)-Co(2)-Co(3)	91.1(2)
N(10)-Co(1)-N(1)	91.2(3)	N(11)-Co(2)-Co(1)	91.3(2)
N(7)-Co(1)-N(4)	89.1(3)	N(5)-Co(2)-Co(1)	89.0(2)
N(10)-Co(1)-N(4)	174.8(3)	N(2)-Co(2)-Co(1)	89.3(2)
N(1)-Co(1)-N(4)	89.4(3)	N(8)-Co(2)-Co(1)	90.5(2)
N(7)-Co(1)-Co(2)	86.9(2)	N(6)-Co(3)-N(3)	89.7(3)
N(10)-Co(1)-Co(2)	86.4(2)	N(6)-Co(3)-N(12)	174.8(3)
N(1)-Co(1)-Co(2)	87.9(2)	N(3)-Co(3)-N(12)	89.8(3)
N(4)-Co(1)-Co(2)	88.4(2)	N(6)-Co(3)-N(9)	91.1(3)
F(1)-Co(1)-Co(2)	178.5(1)	N(3)-Co(3)-N(9)	174.7(3)
N(11)-Co(2)-N(5)	179.6(3)	N(12)-Co(3)-N(9)	88.9(3)
N(11)-Co(2)-N(2)	89.7(3)	N(6)-Co(3)-Co(2)	88.0(2)
N(5)-Co(2)-N(2)	90.1(3)	N(3)-Co(3)-Co(2)	88.1(2)
N(11)-Co(2)-N(8)	90.2(3)	N(12)-Co(3)-Co(2)	86.9(2)
N(5)-Co(2)-N(8)	90.0(3)	N(9)-Co(3)-Co(2)	86.7(2)
N(2)-Co(2)-N(8)	179.8(2)	F(5)-Co(3)-Co(2)	179.3(1)
N(11)-Co(2)-Co(3)	90.5(2)		
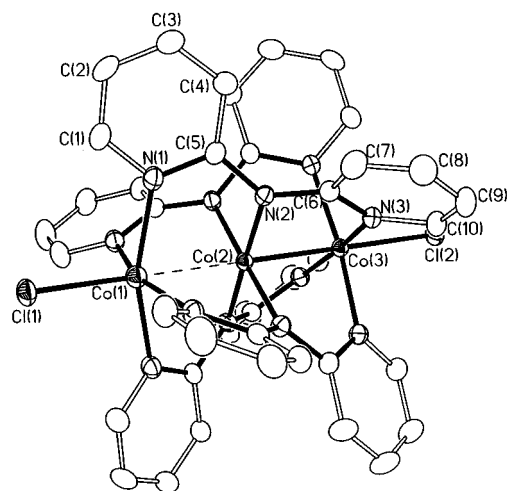
Figure 1. A drawing of the molecular structure of Co₃(dpa)₄Cl₂ in **2** showing the unsymmetrical Co–Co separations. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

Results and Discussion

Structural Results. For compounds **1**–**4** each structure consists of a linear chain of three cobalt atoms that are bridged by four dpa⁻ anions. The steric crowding of the hydrogen atoms on the pyridyl rings forces the molecules to adopt a helical twist around the metal centers. The axial coordination sites of the terminal cobalt atoms are occupied by either Cl⁻ anions (for **1** and **2**), a Cl⁻ anion, and a fluorine atom from a BF₄⁻ anion (in **3**), or by fluorine atoms from two BF₄⁻ anions (in **4**). Complex **1** crystallizes in space group *Pnn*2 with Co(2) residing on a crystallographic 2-fold axis. Compound **2**, which is shown in Figure 1, consists of the trinuclear Co₃(dpa)₄Cl₂ molecule and the tetrahedral complex Co(dpa)₂. The compound crystallizes in the tetragonal space group *P*4/*n* with the 4-fold axis collinear with the trinuclear metal axis. The tetrahedral Co atom resides on a $\bar{4}$ axis. The molecular dimensions of Co(dpa)₂ are essentially the same as those found in crystals of pure Co-(dpa)₂.[11] The C(15)-N(5)-C(15)' angle of 127.0(4)° is in the range expected for a cobalt(II) cation chelated by two dpa anions.[12] Compound **3** crystallizes in the monoclinic space group *C*2/*c*; the trinuclear metal axis is collinear with the 2-fold axis. The structural diagram of **4** is shown in Figure 2. It crystallizes in space group *P*2₁/*c* with the molecule residing on a general position.

(11) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV, Murillo, C. A. *J. Chem. Soc., Chem. Commun.* **1997**, 1673.
(12) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV; Murillo, C. A. *Polyhedron,* in press.
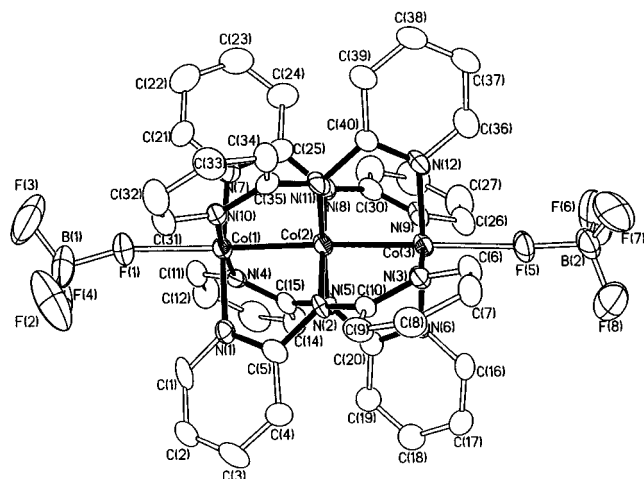
Figure 2. Structural representation of Co₃(dpa)₄(BF₄)₂ in **4** showing similar Co—Co distances. Non-hydrogen atoms are represented by their 40% probability ellipsoids.
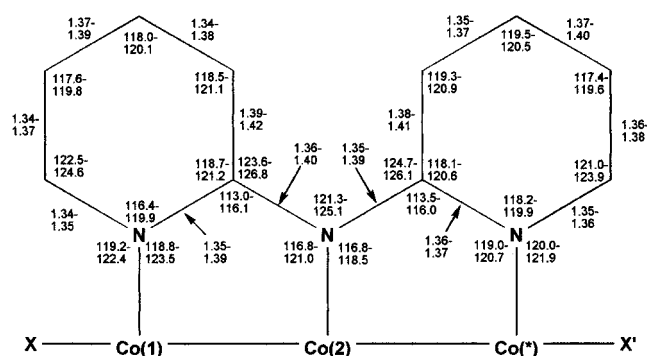

Figure 3. Ranges of the distances (angstroms) and angles (degrees) in the dpa⁻ ligands for all structures described in the text.

Because of the highly unusual nature of the results we are reporting here, we have been extremely careful to examine the crystallographic results for any signs, however subtle, of error. We have found none. Several phases of this careful examination will now be described.

For any structure that contains elements that are familiar and expected to be invariant, the quality and consistency of the dimensions of these elements affords a valuable indication of the quality and correctness of the structure as a whole. In the present case, the dimensions of the pyridyl rings afford this sort of indication. In Figure 3 we show the ranges of the distances and angles in the dpa⁻ ligands for all four structures. The C—C and C—N distances and the ring angles in each individual case have small esd's, and the entire range covered by each type over all four compounds is very small. For each given type of C—C and C—N distance, the entire range is 0.01−0.04 Å. For each type of angle within the pyridyl rings the range is as little as 1.0° and no more than 3.5°.

Because two of the compounds have the symmetrical Co₃ chain and two others have unsymmetrical Co₃ chains, it is necessary to examine the inner dimensions of these molecules, two by two, and this is done in Figure 4. In the symmetrical compounds, the Co—Co distances vary from 2.254 to 2.318 Å from one compound to the other. This cannot be considered too surprising since the nature of the terminal ligands (X,X′) changes significantly, from Cl⁻ in one case to BF₄⁻ in the other. Apart from this, however, the other dimensions are almost the same. The Co—N distances for the outer Co atoms are all in the narrow range 1.953−2.022 Å and the Co—N distances for the inner Co atoms are in the even narrower range 1.889−1.903 Å.
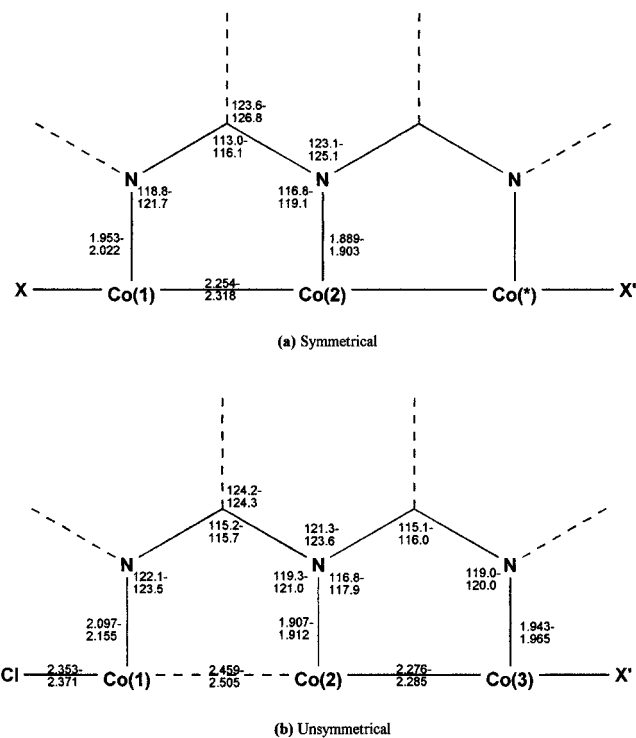

Figure 4. Inner dimensions (in angstroms or degrees) for the compounds containing (a) symmetrical and (b) unsymmetrical Co—Co distances.

For the two unsymmetrical structures the inner dimensions are again very similar for the two different compounds, as can be seen in the lower part of Figure 4. It is of considerable interest that for Co(1), which is at the outer end of the long Co—Co bond, the Co—N distances are considerably longer, 2.097−2.155 Å, than those to the two Co atoms that are linked by the short Co—Co bond, 1.907−1.965 Å. This looser bonding provides an explanation for the consistently larger displacement parameters of these Co(1) atoms.

Why the Co(1)—N distances are longer is not easy to say, but it may be noted that, in the unsymmetrical compounds, the Co(1)—Cl distances, 2.353 and 2.371 Å, are much shorter than the Co—Cl distances, 2.520 Å, in the symmetrical dichloro molecule. Evidently, the weaker Co—N bonding is compensated by the stronger Co—Cl bonding.

Another significant observation that adds credibility to these structures is the recent characterization of symmetrically and unsymmetrically Cr—Cr-bonded Cr₃(dpa)₄Cl₂ and Cr₃(dpa)₄Cl(BF₄), respectively, and also of an oxidized [(Cr₃(dpa)₄F(BF₄)]⁺ species.[4] The last two species clearly show the presence of a localized Cr—Cr quadruply bonded segment attached to a five-coordinate nonbonded XCrN₄ group. It is also important to point out that both **1** and **3** are essentially isostructural with the corresponding chromium analogues.

By analogy to the chromium complexes, we believe that the compounds containing unsymmetrical Co—Co bonding can be formally considered as composed of a Co—Co bonded fragment attached to a nonbonded XCoN₄ moiety while complexes with symmetrical Co—Co bonds must have delocalized metal-to-metal bonds. The appearance of both symmetrical and unsymmetrical Co—Co bonding in the Co₃(dpa)₄Cl₂ molecules in **1** and **3**, respectively, as well as the unsymmetrical bonding reported earlier[2] suggests that the difference in energy between the symmetrical and unsymmetrical molecules is small since small perturbations in the crystals—which are normally not

associated with drastic changes in intramolecular bond distances—have a very significant impact on the metal-to-metal distances.

As noted in the introduction, there is a rather straightforward definition of "bond stretch isomers". Authentic examples have not yet appeared. In the present case, if the interstitial solvent molecules are ignored, the three $Co_3(dpa)_4Cl_2$-containing species just mentioned satisfy the definition of "bond stretch isomers".

Supporting Information Available: Figures of compounds **1** and **3** and tables of crystallographic data including diffractometer and refinement data, final coordinates, bond lengths, bond angles, and anisotropic displacement parameters (28 pages). See any current masthead page for ordering and Internet access instructions.

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