Tuning the Metal−Metal Bonds in the Linear Tricobalt Compound $Co_3(dpa)_4Cl_2$: Bond-Stretch and Spin-State Isomers

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Sixteen crystal structures have been determined for the $Co_3(dpa)_4Cl_2$ (**1**) molecule in the following five crystalline solvates: **1**·0.85$(C_2H_5)_2O$·0.15CH_2Cl_2 (at 120, 213, 296 K); **1**·C_4H_8O (at 120, 295 K); **1**·C_6H_6 (at 170, 213, 260, 316 K); **1**·C_6H_{12} (at 120, 213, 295 K); and **1**·1.75C_7H_8·0.5C_6H_{14} (at 90, 110, 170, 298 K). For **1**·0.85-$(C_2H_5)_2O$·0.15CH_2Cl_2 the molecule of **1** is almost symmetrical at 120 K (Co−Co distances of 2.3191(3) and 2.3304(3) Å) and remains so at 296 K (2.2320(3) and 2.3667(4) Å). For **1**·C_4H_8O the Co_3 chain is precisely symmetric at both 120 and 295 K though the Co−Co distances increase from 2.3111(4) to 2.3484(4) Å as the temperature rises. Compound **1**·C_6H_6 is isomorphous with **1**·C_4H_8O at 213 and 295 K and has rigorously symmetrical molecules at these two temperatures. Between 213 and 120 K the space group changes from *Pccn* to *P2$_1$/c*, so that a symmetrical arrangement is no longer required and the two Co−Co distances then differ slightly (by 0.013 Å). For **1**·C_6H_6 there is a phase change between 316 K (*Pca2$_1$*) and 260 K (*Pna2$_1$*). At all four temperatures, however, the molecule is almost symmetrical, with the two independent Co−Co distances never differing by more than 0.026 Å. **1**·1.75C_7H_8·0.5C_6H_{14} contains, at all temperatures between 90 and 298 K, two crystallographically independent molecules, each of which is distinctly unsymmetrical at 298 K (Co−Co distances of 2.312(2) and 2.442(2) Å for one and 2.310(2) and 2.471(2) for the other). In the first of these the distances converge to a much smaller separation (0.056 Å) at 90 K while in the second the difference decreases to only 0.006 Å at 90 K. Magnetic susceptibility measurements from 1.8 to 350 K indicate in each case that a gradual spin crossover, from a doublet to a quartet state, occurs over this temperature range.

Introduction

The first $M_3(dpa)_4X_2$ molecule (dpa is the anion of di(2-pyridyl)amine) to be structurally characterized, about a decade ago, was $Ni_3(dpa)_4Cl_2$.[1] Subsequently, analogous compounds containing Cu,[2] Co,[3] Rh,[4] Ru,[4] and Cr[5] have also been reported, and for several of these metals, compounds containing axial ligands other than Cl have also been described.[6] The most fascinating of these compounds are those containing the $Co_3(dpa)_4Cl_2$ molecule, **1**.

This molecule displays the extraordinary property (shared to a lesser extent by its chromium analogue[5]) of being able to exist with either a symmetrical (*s*-) Co_3 chain or an unsymmetrical

Chart 1

s-$Co_3(dpa)_4Cl_2$ *u*-$Co_3(dpa)_4Cl_2$
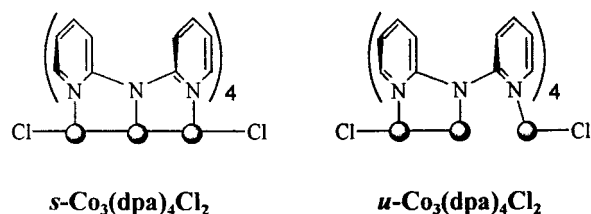
(*u*-) one, depending only on the crystal form in which it is found.[3,7] These two forms of the molecule are illustrated in Chart 1. For example, in *s*-**1**·CH_2Cl_2 (orthorhombic) the Co_3 chain is symmetrical, with both Co−Co distances equal to 2.3369(4) Å, whereas in *u*-**1**·2CH_2Cl_2 (tetragonal) the Co_3 chain is very unsymmetrical, with Co−Co distances of 2.299(1) Å and 2.471-(1) Å at 298 K. In the latter, at lower temperatures these two distances converge to become 2.3035(7) and 2.3847(8) Å at 20 K.[7] Both of these solvates are formed simultaneously from a CH_2Cl_2 solution at room temperature.

Though symmetrical and unsymmetrical molecules of **1** are clearly distinguishable in the solid state, solutions made from either *s*-**1**·CH_2Cl_2 or *u*-**1**·2CH_2Cl_2 are identical and appear to

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(1) Aduldecha, S.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1991**, 993.
(2) (a) Pyrka, G. J.; El-Mekki, M.; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1991**, 84. (b) Wu, L.-P.; Field, P.; Morrissey, T.; Murphy, C.; Nagle, P.; Hathaway, B. J.; Simmons, C.; Thornton, P. J. *J. Chem. Soc., Dalton Trans.* **1991**, 993.
(3) (a) Yang, E.-C.; Cheng, M.-C.; Tsai, M.-S.; Peng, S.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2377. (b) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV. *Chem. Commun.* **1997**, 421. (c) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV; Murillo, C. A. *J. Am. Chem. Soc.* **1997**, *119*, 10377. (d) Cotton, F. A.; Murillo, C. A.; Wang, X. *J. Chem. Soc., Dalton Trans.* **1999**, 3327.
(4) Sheu, J.-T.; Lin, C.-C.; Chao, I.; Wang, C.-C.; Peng, S.-M. *Chem. Commun.* **1996**, 315.
(5) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Murillo C. A.; Pascual, I. *Inorg. Chem.* **2000**, *39*, 748.
(6) See, for example, the following paper in this issue: Clérac, R.; Cotton, F. A.; Jeffery, S. P.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2001**, *40*, 1254.
(7) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Kirschbaum, K.; Murillo, C. A.; Pinkerton, A. A.; Schultz, A. J.; Wang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6226.

Table 1. Crystal Data and Structure Refinement for Co₃(dpa)₄Cl₂·0.85(C₂H₅)₂O·0.15CH₂Cl₂ (**1**·0.85(C₂H₅)₂O·0.15CH₂Cl₂)

formula	C₄₃.₅₅H₄₀.₈N₁₂O₀.₈₅Co₃Cl₂.₃		
fw	1004.21		
T, K	120	213	296
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	15.804(1)	15.8872(7)	15.9573(8)
b, Å	15.684(1)	15.7455(7)	15.8174(8)
c, Å	16.929(1)	16.9897(7)	17.0569(9)
α, deg	90	90	90
β, deg	98.933(1)	98.725(1)	98.303(1)
γ, deg	90	90	90
V, Å³	4145.2(5)	4200.8(3)	4260.1(4)
Z	4	4	4
d_{calcd}, g cm⁻³	1.609	1.588	1.566
μ (Mo Kα), mm⁻¹	1.387	1.369	1.350
R indices [$I > 2\sigma(I)$], R1,[a] wR2[b]	0.027, 0.065	0.027, 0.065	0.030, 0.070
R indices (all data), R1,[a] wR2[b]	0.032, 0.068	0.037, 0.070	0.041, 0.079

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

contain only symmetrical molecules.[8] Thus the pair of *s*-**1** and *u*-**1** molecules fall into the category of "bond-stretch isomers", according to the empirical definition employed by Hoffmann and Parkin.[9,10] This definition states that bond-stretch isomers are "molecules that differ only in the length of one or more bonds".

It is, of course, generally recognized that slightly different bond lengths (ca. 0.01 Å) may be found for the same molecule in different polymorphic crystal forms or even in the two (or more) molecules that, on rare occasions, are not crystallographically equivalent in the same crystal form. Such slight changes, which result from differing packing forces, are not to be regarded as constituting "bond-stretch isomerism". It could also be argued that if "bond-stretch isomerism" does not persist in solution, it is not genuine. If the latter be true, then there are no known examples of this phenomenon.

It is not our contention that the *s* and *u* forms of Co₃(dpa)₄-Cl₂ (or Cr₃(dpa)₄Cl₂) are necessarily entitled to be described as "bond-stretch isomers". Nevertheless, whatever they may, or may not, be called, their behavior is a fascinating and unique phenomenon and we are engaged in an effort to determine what underlies it. The work reported here is an attempt to explore the structural and magnetic behavior of a greater range of solvated crystals of Co₃(dpa)₄Cl₂, including the temperature dependences of both structures and magnetism.

Experimental Section

Materials. Manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were purified by conventional methods and were freshly distilled under nitrogen prior to use. Anhydrous cobalt dichloride was purchased from Strem Chemicals, Inc.; 2,2′-dipyridylamine was purchased from Aldrich and sublimed prior to use. The compound Co₃(dpa)₄Cl₂ was made according to a previously published procedure.[3]

Physical Measurements. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer using KBr pellets. The magnetic susceptibility data were collected on a Quantum Design, model MPMS, SQUID housed in the Department of Chemistry at Texas A&M University; data were collected from 1.8 to 350 K at a field of 1000 G on finely divided polycrystalline samples (39.20 mg for **1**·0.85-(C₂H₅)₂O·0.15CH₂Cl₂, 58.05 mg for **1**·C₆H₁₂, 22.29 mg for **1**·C₄H₈O, 17.74 mg for **1**·C₆H₆, and 71.08 mg for **1**·1.75C₇H₈·0.5C₆H₁₄). The

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**·0.85(C₂H₅)₂O·0.15CH₂Cl₂

	120 K	213 K	296 K
Co(1)−Co(2)	2.3191(3)	2.3193(3)	2.3230(3)
Co(2)−Co(3)	2.3304(3)	2.3352(3)	2.3667(4)
Co(1)−Cl(1)	2.4430(4)	2.4559(5)	2.4463(6)
Co(3)−Cl(2)	2.4804(4)	2.4893(5)	2.4558(6)
Co(1)−N(1)	1.9763(14)	1.9795(15)	1.988(2)
Co(1)−N(4)	1.9933(14)	1.9961(14)	1.999(2)
Co(1)−N(7)	1.9676(14)	1.9698(15)	1.977(2)
Co(1)−N(10)	1.9738(14)	1.9761(15)	1.984(2)
Co(2)−N(2)	1.9097(14)	1.9132(14)	1.912(2)
Co(2)−N(5)	1.8996(13)	1.9029(14)	1.906(2)
Co(2)−N(8)	1.9020(14)	1.9070(14)	1.911(2)
Co(2)−N(11)	1.9051(13)	1.9062(14)	1.910(2)
Co(3)−N(3)	1.9825(14)	1.9921(15)	2.022(2)
Co(3)−N(6)	1.9787(14)	1.986(2)	2.020(2)
Co(3)−N(9)	1.9877(14)	1.9950(15)	2.021(2)
Co(3)−N(12)	1.9863(14)	1.9949(15)	2.022(2)
Co(1)−Co(2)−Co(3)	177.630(13)	178.037(13)	178.39(2)
Co(2)−Co(1)−Cl(1)	177.176(15)	177.41(2)	177.79(2)
Co(2)−Co(3)−Cl(2)	178.525(15)	178.64(2)	178.85(2)
N(1)−Co(1)−N(4)	89.88(5)	89.82(6)	89.88(7)
N(1)−Co(1)−N(7)	170.76(6)	170.60(6)	170.11(7)
N(1)−Co(1)−N(10)	91.39(5)	91.20(6)	91.13(7)
N(4)−Co(1)−N(7)	89.83(6)	89.92(6)	89.72(7)
N(4)−Co(1)−N(10)	171.02(6)	171.07(6)	170.75(7)
N(7)−Co(1)−N(10)	87.49(6)	87.62(6)	87.71(7)
N(2)−Co(2)−N(5)	89.44(6)	89.44(6)	89.55(7)
N(2)−Co(2)−N(8)	179.63(6)	179.51(6)	179.48(7)
N(2)−Co(2)−N(11)	89.55(6)	89.70(6)	89.76(7)
N(5)−Co(2)−N(8)	90.50(6)	90.28(6)	90.11(7)
N(5)−Co(2)−N(11)	178.98(6)	179.13(6)	179.22(7)
N(8)−Co(2)−N(11)	90.51(6)	90.58(6)	90.58(7)
N(3)−Co(3)−N(6)	87.95(6)	87.84(6)	87.45(7)
N(3)−Co(3)−N(9)	171.40(6)	171.06(6)	169.06(7)
N(3)−Co(3)−N(12)	92.24(6)	92.29(6)	92.42(7)
N(6)−Co(3)−N(9)	89.73(6)	89.63(6)	89.25(7)
N(6)−Co(3)−N(12)	170.62(6)	170.24(6)	168.07(7)
N(9)−Co(3)−N(12)	88.71(6)	88.77(6)	88.66(7)
N(1)−Co(1)−Cl(1)	94.64(4)	94.70(4)	94.88(5)
N(4)−Co(1)−Cl(1)	92.67(4)	92.75(4)	93.05(5)
N(7)−Co(1)−Cl(1)	94.60(4)	94.69(4)	95.02(5)
N(10)−Co(1)−Cl(1)	96.08(4)	96.01(4)	96.03(5)
N(3)−Co(3)−Cl(2)	93.95(4)	94.15(4)	95.12(5)
N(6)−Co(3)−Cl(2)	95.55(4)	95.73(4)	96.88(5)
N(9)−Co(3)−Cl(2)	94.51(4)	94.63(4)	95.63(5)
N(12)−Co(3)−Cl(2)	93.79(4)	94.00(4)	95.01(5)

data were corrected for the sample holder and for the diamagnetic contribution calculated from Pascal's constants.[11]

Preparation of 1·0.85(C₂H₅)₂O·0.15CH₂Cl₂. Ether (30 mL) was layered onto a solution of **1** (0.094 g, 0.10 mmol) in CH₂Cl₂ (15 mL). Crystals of **1**·0.85(C₂H₅)₂O·0.15CH₂Cl₂ grew over a period of 2 weeks. Yield: 0.079 g, 84%. IR (cm⁻¹): 1604 (s), 1593 (s), 1547 (w), 1470 (s), 1458 (s), 1425 (s), 1367 (s), 1314 (m), 1280 (m), 1263 (w), 1155 (m), 1105 (m), 1042 (w), 1021 (m), 932 (w), 885 (w), 844 (vw), 805 (vw), 782 (sh), 764 (s), 740 (m), 648 (vw), 638 (vw), 542 (w), 522 (w), 462 (w), 426 (w).

Preparation of 1·C₄H₈O. Hexanes (30 mL) were layered onto a solution of **1** (0.047 g, 0.050 mmol) in C₄H₈O (20 mL). Crystals of **1**·C₄H₈O were obtained in about 10 days. Yield: 0.048 g, 95%. IR (cm⁻¹): 1605 (s), 1593 (s), 1547 (w), 1470 (s), 1456 (s), 1428 (s), 1371 (s), 1313 (m), 1284 (m), 1252 (vw), 1242 (vw), 1154 (m), 1148 (sh), 1120 (vw), 1065 (vw), 1055 (vw), 1021 (m), 1009 (sh), 980 (w), 912 (vw), 884(w), 760 (s), 738 (m), 648 (vw), 638 (vw), 541 (w), 518 (w), 463 (w), 427 (w).

Preparation of 1·C₆H₁₂. Cyclohexane (25 mL) was layered onto a solution of **1** (0.046 g, 0.050 mmol) in toluene (25 mL). Crystals of

(8) Cotton, F. A.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **1999**, *38*, 6294.

(9) (a) Parkin, G.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1462. (b) Parkin, G. *Chem. Rev.* **1993**, *93*, 887. (c) Parkin, G. *Acc. Chem. Res.* **1992**, *25*, 455.

(10) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 4506.

(11) Boudreaux, E. A., Mulay, L. N., Eds. *Theory and Applications of Molecular Paramagnetism*; John Wiley & Sons: New York, 1976.
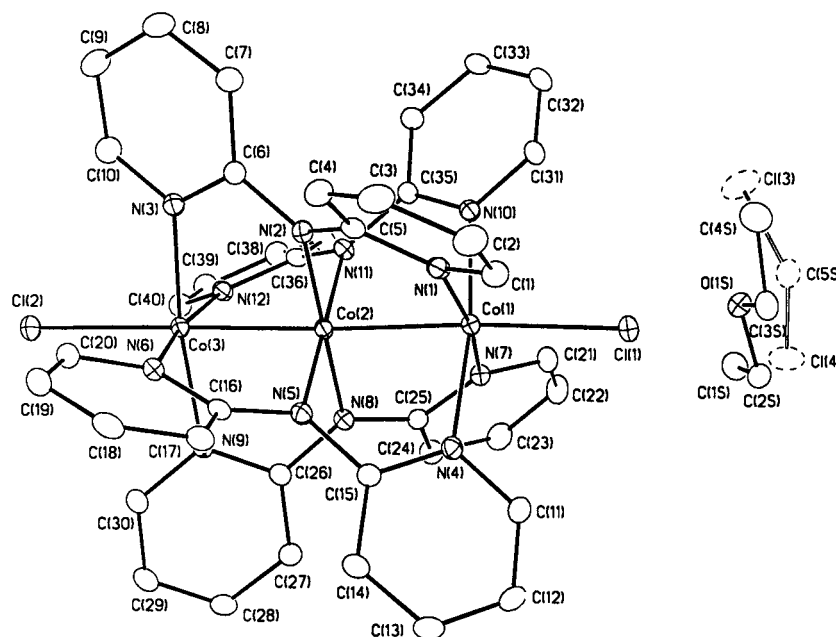
Figure 1. Perspective view of **1**·0.85(C₂H₅)₂O·0.15CH₂Cl₂ at 120 K. Atoms are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

Table 3. Crystal Data and Structure Refinement for Co₃(dpa)₄Cl₂·C₄H₈O (**1**·C₄H₈O)

formula	C₄₄H₄₀N₁₂OCo₃Cl₂	
fw	1000.57	
T, K	120	295
space group	*Pccn*	*Pccn*
a, Å	12.7212(8)	12.8698(6)
b, Å	14.1167(9)	14.1466(6)
c, Å	23.498(2)	23.812(1)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å³	4219.7(5)	4335.3(3)
Z	4	4
*d*calcd, g cm⁻³	1.575	1.533
μ(Mo Kα), mm⁻¹	1.345	1.309
R indices [*I* > 2σ(*I*)], R1,ᵃ wR2ᵇ	0.038, 0.098	0.038, 0.097
R indices (all data), R1,ᵃ wR2ᵇ	0.060, 0.106	0.062, 0.110

ᵃ R1 = Σ||*F*ₒ| − |*F*c||/Σ|*F*ₒ|. ᵇ wR2 = [Σ[*w*(*F*ₒ² − *F*c²)²]/Σ[*w*(*F*ₒ²)²]]¹ᐟ².

1·C₆H₁₂ were obtained in about 2 weeks. Yield: 0.045 g, 90%. IR (cm⁻¹): 1604 (s), 1593 (s), 1468 (s), 1457 (s, sh), 1427 (s, br), 1379 (sh), 1369 (s), 1313 (m), 1284 (m), 1264 (w), 1252 (w), 1242 (w), 1153 (m), 1148 (sh), 1108 (vw), 1054 (w), 1021 (m), 1009 (w), 977 (vw), 959 (vw), 924 (vw), 884 (w), 760 (s), 738 (m), 638 (vw), 541 (w), 518 (w), 463 (w), 427 (w).

**Preparation of 1·C₆H₆.** Hexanes (30 mL) were layered onto a solution of **1** (0.047 g, 0.050 mmol) in benzene (25 mL). Crystals of **1**·C₆H₆ were obtained in about 2 weeks. Yield: 0.046 g, 91%. IR (cm⁻¹): 1605 (s), 1594 (s), 1547 (w), 1470(s), 1457 (s), 1429 (s), 1366 (m), 1315 (m), 1280 (w), 1263 (w), 1152 (m), 1107 (vw), 1052 (vw), 1020 (w), 886 (w), 804 (vw), 760 (m), 740 (m), 684 (w), 638 (vw), 542 (w), 520 (w), 457 (w), 430 (w).

Preparation of 1·1.75C₇H₈·0.5C₆H₁₄. Hexanes (30 mL) were layered onto a solution of **1** (0.046 g, 0.050 mmol) in toluene (25 mL). Crystals were grown as thin plates in about 2 weeks. Yield: 0.049 g, 89%. IR (cm⁻¹): 1604 (s), 1593 (s), 1547 (w), 1469 (s), 1457 (s), 1424 (s, br), 1368 (s), 1313 (m), 1281 (m), 1252 (w), 1153 (s), 1107 (vw), 1052 (vw), 1021 (m), 1008 (m), 925 (vw), 886 (w), 760 (s), 738 (m), 694 (w), 637 (vw), 540 (vw), 518 (w), 464 (w), 426 (w).

X-ray Crystallography. In each case, a suitable crystal was attached to the end of a quartz fiber with a small amount of silicone grease and transferred to a goniometer head. Geometric and intensity data sets for **1**·C₆H₆ at 170, 213, 260, and 316 K were gathered on a Nonius FAST

Table 4. Selected Bond Distances (Å) and Angles (deg) for **1**·C₄H₈O

	120 K	295 K
Co(1)−Co(2)	2.3111(4)	2.3484(4)
Co(1)−Cl(1)	2.4402(7)	2.4234(8)
Co(1)−N(1)	1.983(2)	2.019(2)
Co(1)−N(3A)ᵃ	1.985(2)	2.026(2)
Co(1)−N(4)	1.983(2)	2.024(2)
Co(1)−N(6A)	1.976(2)	2.009(2)
Co(2)−N(2)	1.898(2)	1.908(2)
Co(2)−N(5)	1.898(2)	1.906(2)
Co(1A)−Co(2)−Co(1)	177.75(3)	177.48(3)
Co(2)−Co(1)−Cl(1)	179.20(2)	179.38(2)
N(1)−Co(1)−N(3A)	86.82(9)	86.24(8)
N(4)−Co(1)−N(1)	90.89(9)	90.81(9)
N(6A)−Co(1)−N(1)	170.72(9)	168.39(9)
N(4)−Co(1)−N(3A)	169.23(9)	166.72(9)
N(6A)−Co(1)−N(3A)	89.36(9)	88.95(9)
N(6A)−Co(1)−N(4)	91.30(9)	91.46(9)
N(1)−Co(1)−Cl(1)	95.32(7)	96.41(7)
N(3A)−Co(1)−Cl(1)	96.67(6)	97.76(6)
N(4)−Co(1)−Cl(1)	94.01(7)	95.43(6)
N(6A)−Co(1)−Cl(1)	93.53(7)	94.70(7)
N(2)−Co(2)−N(2A)	89.88(13)	89.97(12)
N(5)−Co(2)−N(2)	89.47(9)	89.51(9)
N(5A)−Co(2)−N(2)	179.29(9)	179.29(9)
N(5A)−Co(2)−N(2A)	89.47(9)	89.51(9)
N(5)−Co(2)−N(5A)	91.18(13)	91.01(13)

ᵃ Symm. op. A = ¹/₂ − *x*, ¹/₂ − *y*, *z*.

area detector system, utilizing the program MADNES.[12] Cell parameters were obtained from an autoindexing routine and were refined with 250 strong reflections in the 2θ range 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. Intensity data were transferred into SHELX format using the program PRO-COR.[13]

(12) Pflugrath, J.; Messerschmitt, A. *MADNES*, Munich Area Detector (New EEC) System, Version EEC 11/1/89, with enhancements by Enraf-Nonius Corp., Delft, The Netherlands. A description of MADNES appears in the following: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306−315.

(13) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21,* 67. (b) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 916.
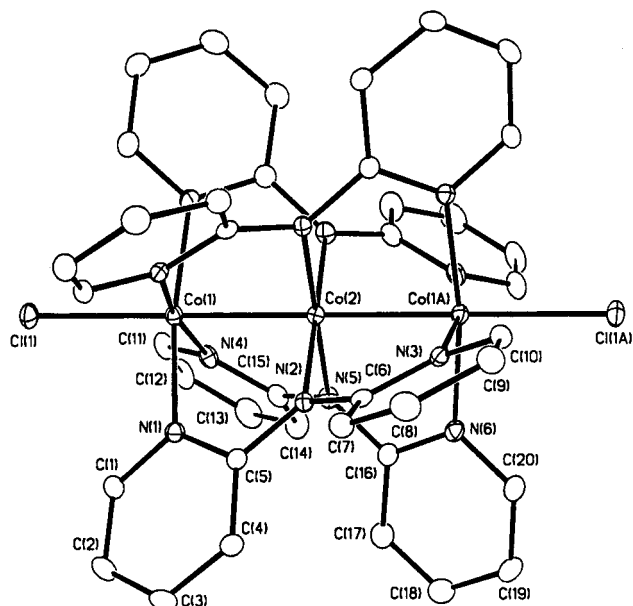
Figure 2. Perspective view of Co$_3$(dpa)$_4$Cl$_2$ (**1**) in **1**·C$_4$H$_8$O at 120 K. Atoms are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity. The same atomic labeling scheme is used for **1** in the orthorhombic form of **1**·C$_6$H$_{12}$.

Table 5. Crystal Data and Structure Refinement for Co$_3$(dpa)$_4$Cl$_2$·C$_6$H$_{12}$ (**1**·C$_6$H$_{12}$)

formula		C$_{46}$H$_{44}$N$_{12}$Co$_3$Cl$_2$	
fw		1012.62	
T, K	120	213	295
space group	*P*2$_1$/*c*	*Pccn*	*Pccn*
a, Å	14.309(2)	12.968(5)	13.092(1)
b, Å	12.805(2)	14.247(1)	14.269(2)
c, Å	23.560(3)	23.704(1)	23.928(2)
α, deg	90	90	90
β, deg	90.046(2)	90	90
γ, deg	90	90	90
V, Å^3	4317(1)	4379.5(5)	4469.6(8)
Z	4	4	4
d$_{calcd}$, g cm^{-3}	1.558	1.536	1.505
μ (Mo Kα), mm^{-1}	1.314	1.295	1.269
R indices [*I* > 2σ(*I*)], R1,^{a} wR2^b	0.027, 0.062	0.054, 0.149	0.039, 0.116
R indices (all data), R1,^{a} wR2^b	0.035, 0.065	0.062, 0.154	0.049, 0.131

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Data for **1**·0.85(C$_2$H$_5$)$_2$O·0.15CH$_2$Cl$_2$, **1**·C$_4$H$_8$O, **1**·C$_6$H$_{12}$, and **1**·1.75C$_7$H$_8$·0.5C$_6$H$_{14}$ were collected on a Bruker SMART 1000 CCD detector system equipped with a liquid nitrogen low-temperature controller. Cell parameters were obtained using SMART[14] software. Data were corrected for Lorentz and polarization effects using the program SAINTPLUS.[15] Absorption corrections were applied using SADABS.[16]

For each of the data sets the positions of the heavy atoms were found by the direct methods program in SHELXTL.[17] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. The interstitial solvent molecules were found to be disordered in the

(14) *SMART V5.05 Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.
(15) *SAINTPLUS, V5.00 Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.
(16) *SADABS*. Program for absorption correction using SMART CCD data based on the method of Blessing: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.
(17) *SHELXTL*, version 5.03; Siemens Industrial Automation Inc.: Madison, WI, 1994.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for **1**·C$_6$H$_{12}$ at 213 and 295 K

	213 K	295 K
Co(1)−Co(2)	2.3311(5)	2.3620(5)
Co(1)−Cl(1)	2.4362(11)	2.4218(10)
Co(1)−N(1)	2.003(3)	2.041(2)
Co(1)−N(3)	1.997(3)	2.030(3)
Co(1)−N(4)	2.012(3)	2.038(3)
Co(1)−N(6)	1.990(3)	2.019(3)
Co(2)−N(2)	1.903(3)	1.911(2)
Co(2)−N(5)	1.902(3)	1.912(2)
Co(1)−Co(2)−Co(1)#1^a	177.56(4)	177.15(3)
Co(2)−Co(1)−Cl(1)	178.95(4)	179.17(3)
N(1)−Co(1)−N(3)	86.60(13)	86.07(10)
N(1)−Co(1)−N(4)	168.26(14)	166.26(10)
N(1)−Co(1)−N(6)	88.41(13)	88.05(10)
N(3)−Co(1)−N(4)	91.09(13)	91.18(10)
N(3)−Co(1)−N(6)	169.51(14)	167.79(10)
N(4)−Co(1)−N(6)	91.94(13)	92.02(10)
N(2)#1−Co(2)−N(2)	90.1(2)	90.04(15)
N(2)−Co(2)−N(5)	89.63(14)	89.64(11)
N(2)−Co(2)−N(5)#1	179.14(14)	179.10(11)
N(5)−Co(2)−N(5)#1	90.7(2)	90.7(2)
N(1)−Co(1)−Cl(1)	97.13(10)	98.10(7)
N(3)−Co(1)−Cl(1)	96.02(10)	96.75(8)
N(4)−Co(1)−Cl(1)	94.55(10)	95.59(8)
N(6)−Co(1)−Cl(1)	93.76(10)	94.66(8)

^{a} Symm. op. #1 = $-^1/_2 - x$, $^3/_2 - y$, z.

Table 7. Selected Bond Distances (Å) and Angles (deg) for **1**·C$_6$H$_{12}$ at 120 K

Co(1)−Co(2)	2.3127(5)	Co(2)−Co(3)	2.3253(5)
Co(1)−Cl(1)	2.4381(6)	Co(3)−Cl(2)	2.4462(6)
Co(1)−N(1)	1.976(2)	Co(1)−N(4)	1.993(2)
Co(1)−N(7)	1.992(2)	Co(1)−N(10)	1.972(2)
Co(2)−N(2)	1.897(2)	Co(2)−N(5)	1.906(2)
Co(2)−N(8)	1.882(2)	Co(2)−N(11)	1.913(2)
Co(3)−N(3)	1.975(2)	Co(3)−N(6)	1.996(2)
Co(3)−N(9)	1.985(2)	Co(3)−N(12)	2.003(2)
Co(1)−Co(2)−Co(3)	177.31(2)	Co(2)−Co(1)−Cl(1)	178.47(2)
Co(2)−Co(3)−Cl(2)	178.92(2)	N(1)−Co(1)−N(4)	86.20(8)
N(1)−Co(1)−N(7)	169.15(7)	N(1)−Co(1)−N(10)	89.47(8)
N(4)−Co(1)−N(7)	91.99(8)	N(4)−Co(1)−N(10)	170.99(8)
N(7)−Co(1)−N(10)	90.78(8)	N(2)−Co(2)−N(5)	90.26(7)
N(2)−Co(2)−N(8)	179.44(7)	N(2)−Co(2)−N(11)	89.76(8)
N(5)−Co(2)−N(8)	89.58(8)	N(5)−Co(2)−N(11)	179.18(8)
N(8)−Co(2)−N(11)	90.40(8)	N(3)−Co(3)−N(6)	87.31(8)
N(3)−Co(3)−N(9)	170.17(8)	N(3)−Co(3)−N(12)	90.07(8)
N(6)−Co(3)−N(9)	88.56(8)	N(6)−Co(3)−N(12)	168.95(8)
N(9)−Co(3)−N(12)	92.30(8)	N(1)−Co(1)−Cl(1)	96.43(6)
N(4)−Co(1)−Cl(1)	95.41(6)	N(7)−Co(1)−Cl(1)	94.39(6)
N(10)−Co(1)−Cl(1)	92.92(6)	N(3)−Co(3)−Cl(2)	95.68(6)
N(6)−Co(3)−Cl(2)	96.95(6)	N(9)−Co(3)−Cl(2)	93.68(5)
N(12)−Co(3)−Cl(2)	93.98(6)		

orthorhombic forms of **1**·C$_4$H$_8$O, **1**·C$_6$H$_{12}$, and also in **1**·1.75C$_7$H$_8$· 0.5C$_6$H$_{14}$. There are two different solvent molecules occupying the same site in **1**·0.85(C$_2$H$_5$)$_2$O·0.15CH$_2$Cl$_2$. The ratio of the interstitial (C$_2$H$_5$)$_2$O and CH$_2$Cl$_2$ molecules was found to be 0.85:0.15 from structural analysis. All non-hydrogen atoms, including the solvent molecules in **1**·0.85(C$_2$H$_5$)$_2$O·0.15CH$_2$Cl$_2$, were refined anisotropically. The mono- clinic form of **1**·C$_6$H$_{12}$ was twinned on the [100] direction with a refined ratio of twin components close to 1:1. Details of data collection and refinement are given in CIF format as Supporting Information.

Results and Discussion

Crystallization. The starting material Co$_3$(dpa)$_4$Cl$_2$ (**1**) was prepared on a gram scale as *s*-**1**·CH$_2$Cl$_2$ according to published procedures.[3] Crystals of **1**·0.85(C$_2$H$_5$)$_2$O·0.15CH$_2$Cl$_2$ were isolated by layering a dichloromethane solution of **1** with diethyl ether. Crystals of **1**·C$_4$H$_8$O and **1**·C$_6$H$_6$ were obtained by

Table 8. Crystal Data and Structure Refinement for Co$_3$(dpa)$_4$Cl$_2$·C$_6$H$_6$ (**1**·C$_6$H$_6$)

formula		C$_{46}$H$_{38}$N$_{12}$Co$_3$Cl$_2$		
fw		1006.57		
T, K	170	213	260	316
space group	*Pna*2$_1$	*Pna*2$_1$	*Pna*2$_1$	*Pca*2$_1$
a, Å	18.4767(7)	18.358(2)	18.521(2)	18.5460(7)
b, Å	29.031(2)	29.14(1)	29.046(3)	14.5527(8)
c, Å	15.9276(5)	16.00593)	16.068(1)	16.2431(6)
α, deg	90	90	90	90
β, deg	90	90	90	90
γ, deg	90	90	90	90
V, Å^3	8543.5(7)	8646(4)	8644(1)	4383.9(3)
Z	8	8	8	4
d_{calcd}, g cm^{-3}	1.565	1.547	1.547	1.525
μ(Mo Kα), mm^{-1}	1.327	1.312	1.312	1.293
R indices [$I > 2\sigma(I)$], R1,^{a} wR2^b	0.038, 0.098	0.055, 0.132	0.063, 0.160	0.045, 0.104
R indices (all data), R1,^{a} wR2^b	0.043, 0.104	0.068, 0.155	0.074, 0.177	0.053, 0.112

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 9. Selected Interatomic Distances (Å) and Angles (deg) for **1**·C$_6$H$_6$

	molecule 1					molecule 2		
	170 K	213 K	260 K	316 K		170 K	213 K	260 K
Co(1)−Co(2)	2.3135(8)	2.3229(14)	2.3244(13)	2.3417(9)	Co(4)−Co(5)	2.3189(8)	2.3261(15)	2.3230(14)
Co(2)−Co(3)	2.3280(8)	2.3444(15)	2.3500(14)	2.3665(9)	Co(5)−Co(6)	2.3283(8)	2.3378(15)	2.3454(14)
Co(1)−Cl(1)	2.4583(12)	2.468(2)	2.458(2)	2.4608(14)	Co(4)−Cl(3)	2.4792(12)	2.487(2)	2.473(2)
Co(3)−Cl(2)	2.4785(13)	2.477(2)	2.460(2)	2.450(2)	Co(6)−Cl(4)	2.4899(12)	2.493(2)	2.475(2)
Co(1)−N(1)	1.983(4)	1.991(6)	1.990(6)	2.009(4)	Co(4)−N(13)	1.980(4)	1.988(6)	1.985(6)
Co(1)−N(4)	1.987(4)	1.977(6)	2.002(6)	2.000(4)	Co(4)−N(16)	1.960(4)	1.967(7)	1.975(6)
Co(1)−N(7)	1.973(4)	1.980(6)	1.998(6)	2.010(4)	Co(4)−N(19)	1.995(4)	1.997(6)	2.003(6)
Co(1)−N(10)	1.988(3)	1.993(6)	1.994(6)	2.004(4)	Co(4)−N(22)	1.980(4)	1.982(7)	1.995(6)
Co(2)−N(2)	1.909(4)	1.905(7)	1.903(6)	1.895(4)	Co(5)−N(14)	1.895(4)	1.897(6)	1.908(6)
Co(2)−N(5)	1.906(4)	1.897(6)	1.909(6)	1.914(4)	Co(5)−N(17)	1.911(4)	1.912(6)	1.897(6)
Co(2)−N(8)	1.914(4)	1.912(6)	1.918(6)	1.901(4)	Co(5)−N(20)	1.908(4)	1.898(6)	1.912(6)
Co(2)−N(11)	1.892(4)	1.892(6)	1.893(6)	1.915(4)	Co(5)−N(23)	1.897(4)	1.897(6)	1.914(6)
Co(3)−N(3)	2.003(4)	2.013(7)	2.020(7)	2.023(4)	Co(6)−N(15)	1.987(4)	1.993(6)	1.994(6)
Co(3)−N(6)	1.974(4)	1.977(7)	2.003(8)	2.022(4)	Co(6)−N(18)	1.982(4)	1.984(7)	2.007(7)
Co(3)−N(9)	1.982(4)	1.992(7)	2.004(6)	2.000(4)	Co(6)−N(21)	1.975(4)	1.987(6)	1.990(7)
Co(3)−N(12)	1.991(4)	2.001(6)	2.019(7)	2.018(4)	Co(6)−N(24)	1.991(4)	2.005(7)	2.008(7)
Co(1)−Co(2)−Co(3)	176.81(3)	177.16(6)	177.51(6)	178.41(4)	Co(4)−Co(5)−Co(6)	178.81(4)	178.89(6)	178.87(6)
Co(2)−Co(1)−Cl(1)	178.87(4)	178.80(7)	178.82(7)	179.03(5)	Co(5)−Co(4)−Cl(3)	178.15(4)	178.32(7)	178.50(7)
Co(2)−Co(3)−Cl(2)	177.33(4)	177.49(8)	177.94(8)	179.02(5)	Co(5)−Co(6)−Cl(4)	179.65(4)	179.77(7)	179.69(7)
N(1)−Co(1)−N(4)	91.2(2)	91.0(3)	91.8(3)	88.7(2)	N(13)−Co(4)−N(16)	89.2(2)	89.2(3)	88.9(3)
N(1)−Co(1)−N(7)	171.18(15)	170.7(3)	170.8(2)	168.9(2)	N(13)−Co(4)−N(19)	170.78(15)	170.8(2)	170.3(3)
N(1)−Co(1)−N(10)	89.0(2)	88.8(3)	88.4(3)	88.8(2)	N(13)−Co(4)−N(22)	89.2(2)	89.3(3)	89.5(3)
N(4)−Co(1)−N(7)	89.4(2)	89.9(3)	89.0(2)	90.5(2)	N(16)−Co(4)−N(19)	89.5(2)	89.6(3)	89.9(3)
N(4)−Co(1)−N(10)	170.76(15)	170.7(2)	170.4(2)	169.3(2)	N(16)−Co(4)−N(22)	170.8(2)	170.3(3)	170.3(3)
N(7)−Co(1)−N(10)	88.9(2)	88.8(3)	89.3(2)	90.0(2)	N(19)−Co(4)−N(22)	90.7(2)	90.3(3)	90.1(3)
N(2)−Co(2)−N(5)	89.7(2)	90.4(3)	89.4(3)	90.4(2)	N(14)−Co(5)−N(17)	90.3(2)	90.7(3)	90.7(3)
N(2)−Co(2)−N(8)	179.2(2)	179.0(3)	178.9(3)	179.1(2)	N(14)−Co(5)−N(20)	179.2(2)	178.8(3)	179.0(3)
N(2)−Co(2)−N(11)	90.7(2)	91.0(3)	90.8(3)	89.8(2)	N(14)−Co(5)−N(23)	90.0(2)	90.1(3)	89.5(3)
N(5)−Co(2)−N(8)	89.5(2)	88.9(3)	89.8(3)	90.5(2)	N(17)−Co(5)−N(20)	90.5(2)	90.5(3)	90.4(3)
N(5)−Co(2)−N(11)	179.5(2)	178.6(3)	179.1(3)	179.7(2)	N(17)−Co(5)−N(23)	179.7(2)	179.1(3)	179.7(3)
N(8)−Co(2)−N(11)	90.1(2)	89.8(3)	90.0(3)	89.3(2)	N(20)−Co(5)−N(23)	89.3(2)	88.6(3)	89.5(3)
N(3)−Co(3)−N(6)	89.8(2)	89.6(3)	89.1(3)	91.4(2)	N(15)−Co(6)−N(18)	90.3(2)	90.3(3)	90.2(3)
N(3)−Co(3)−N(9)	170.8(2)	170.0(3)	169.1(3)	167.8(2)	N(15)−Co(6)−N(21)	170.7(2)	170.9(3)	169.7(3)
N(3)−Co(3)−N(12)	91.6(2)	91.4(3)	91.4(3)	88.1(2)	N(15)−Co(6)−N(24)	88.6(2)	88.3(3)	88.1(3)
N(6)−Co(3)−N(9)	89.1(2)	89.2(3)	89.2(3)	88.5(2)	N(18)−Co(6)−N(21)	89.1(2)	89.1(3)	89.1(3)
N(6)−Co(3)−N(12)	169.5(2)	169.1(3)	168.0(3)	168.3(2)	N(18)−Co(6)−N(24)	171.0(2)	170.5(3)	169.8(3)
N(9)−Co(3)−N(12)	88.0(2)	87.9(3)	88.0(3)	89.6(2)	N(21)−Co(6)−N(24)	90.6(2)	90.8(3)	90.8(3)
N(1)−Co(1)−Cl(1)	95.73(11)	96.0(2)	95.7(2)	95.87(12)	N(13)−Co(4)−Cl(3)	94.24(11)	94.2(2)	94.9(2)
N(4)−Co(1)−Cl(1)	93.92(11)	94.4(2)	93.4(2)	96.37(12)	N(16)−Co(4)−Cl(3)	95.42(12)	95.6(2)	95.7(2)
N(7)−Co(1)−Cl(1)	93.00(11)	93.2(2)	94.0(2)	95.17(11)	N(19)−Co(4)−Cl(3)	94.96(11)	95.0(2)	94.7(2)
N(10)−Co(1)−Cl(1)	95.25(11)	94.9(2)	95.4(2)	94.24(11)	N(22)−Co(4)−Cl(3)	93.69(11)	94.1(2)	93.9(2)
N(3)−Co(3)−Cl(2)	85.03(11)	94.9(2)	84.3(2)	95.81(12)	N(15)−Co(6)−Cl(4)	95.17(11)	94.9(2)	95.7(2)
N(6)−Co(3)−Cl(2)	95.65(11)	96.1(2)	96.3(2)	96.07(12)	N(18)−Co(6)−Cl(4)	94.53(11)	94.6(2)	95.5(2)
N(9)−Co(3)−Cl(2)	94.82(11)	95.1(2)	95.5(2)	96.32(13)	N(21)−Co(6)−Cl(4)	94.13(12)	94.2(2)	94.6(2)
N(12)−Co(3)−Cl(2)	94.60(12)	94.6(2)	95.6(2)	95.61(12)	N(24)−Co(6)−Cl(4)	94.43(11)	94.9(2)	94.6(2)

layering the corresponding THF and benzene solutions with hexanes. Slow diffusion of cyclohexane onto a toluene solution of **1** gave **1**·C$_6$H$_{12}$. However, when the same solution was layered with hexanes, crystals of **1**·1.75C$_7$H$_8$·0.5C$_6$H$_{14}$ were produced. Here we witnessed a remarkable impact on the

crystallization processes of **1** by changing only the solvents used in layering from cyclohexane to the commercially available mixture of hexanes.

Structural Studies. For **1**·0.85(C$_2$H$_5$)$_2$O·0.15CH$_2$Cl$_2$ crystal data at 120, 213, and 296 K are listed in Tables 1 and 2. It
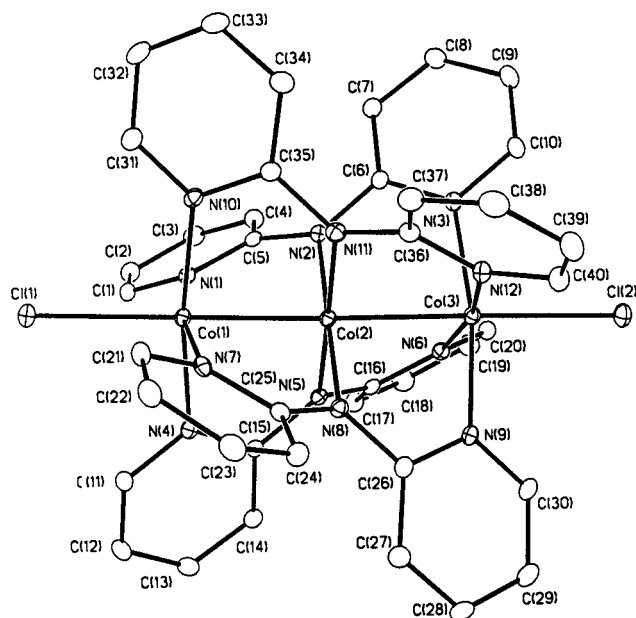
Figure 3. Perspective view of Co$_3$(dpa)$_4$Cl$_2$ (**1**) in the monoclinic form of **1**·C$_6$H$_{12}$ at 120 K. Atoms are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

crystallizes in the centrosymmetric space group $P2_1/c$ where the molecule of **1** resides on a general position. The interstices are occupied by (C$_2$H$_5$)$_2$O and CH$_2$Cl$_2$ molecules in a ratio of about 0.85:0.15. A drawing of the Co$_3$(dpa)$_4$Cl$_2$ molecule is shown in Figure 1. At 120 K the two Co−Co distances are 2.3191(3) and 2.3304(3) Å, but the discrepancy increases with increasing temperature so that at 296 K the distances are 2.3230-(3) and 2.3667(4) Å. Without doubt the discrepancy at 120 K is so small (ca. 0.01 Å) that the molecule can be considered symmetric, but a difference of 0.044 Å raises a question. There is also an increase of 0.020 Å in the average Co−Co distance from 120 to 296 K.

For **1**·C$_4$H$_8$O the structure (see Tables 3 and 4 and Figure 2) is truly symmetrical at both 120 and 295 K although there is a significant increase in the Co−Co distances, from 2.3111(4) to 2.3484(4) Å, namely, 0.037 Å.

The data for **1**·C$_6$H$_{12}$ are given in Tables 5−7, and the molecule at 120 K is shown in Figure 3. There is a phase change between 213 K (*Pccn*) and 120 K (*P2$_1$/c*). In *Pccn* the two Co−Co distances are crystallographically equivalent while in *P2$_1$/c* they are not. At 295 K the (equal) Co−Co distances are 2.3620-(5) Å while at 120 K the two slightly different Co−Co distances are 2.3127(5) and 2.3253(5) Å. The increase from the average of the two low-temperature distances to the distance at 295 K is 0.043 Å.

The data for **1**·C$_6$H$_6$ are given in Tables 8 and 9, and a drawing of the molecule at 316 K is presented in Figure 4 along with a drawing of the two molecules that make up the asymmetric unit in the low-temperature space group *Pna2$_1$* at 170 K. The phase change occurs between 316 and 260 K, but we have not attempted to determine the transition temperature exactly. In space group *Pna2$_1$* there are two crystallographically independent molecules on general positions, both of which are nearly but not exactly symmetrical. The average of the differences between the two Co−Co distances in each molecule is only 0.012 Å at 170 K. At 316 K, in space group *Pca2*, there is only one molecule on a general position which is slightly unsymmetrical, with the two Co−Co distances differing by 0.025 Å. Here again there is a significant increase in the average Co−Co distance, namely, 0.032 Å from 170 to 316 K.

(a)

(b)
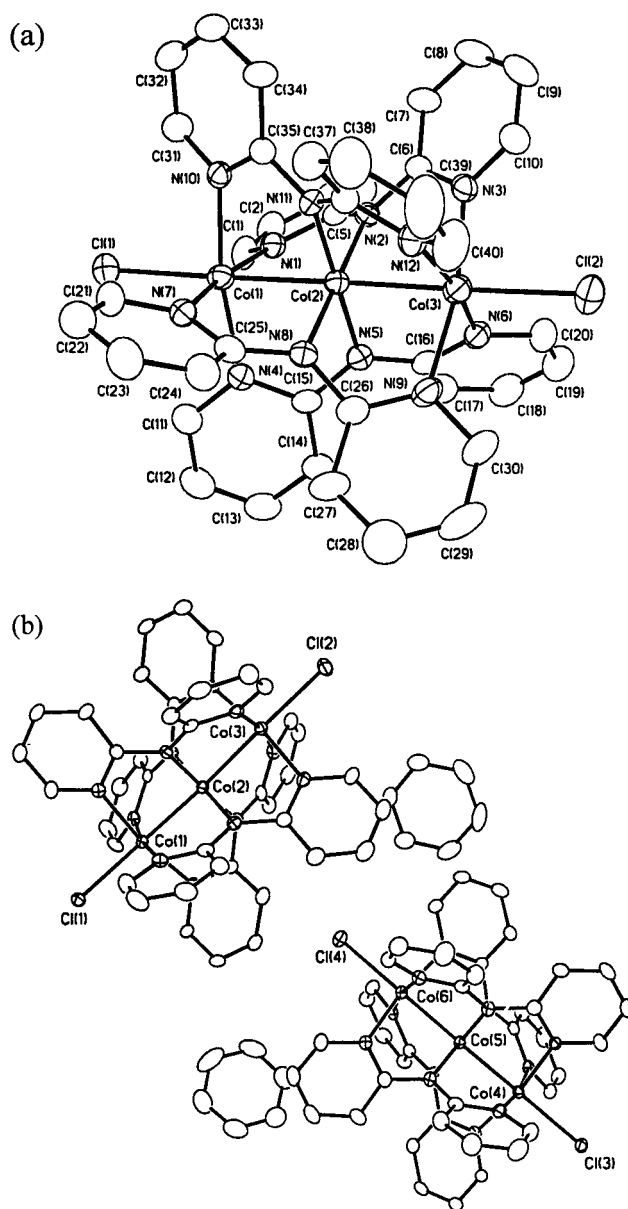
Figure 4. (a) Perspective view of Co$_3$(dpa)$_4$Cl$_2$ (**1**) in **1**·C$_6$H$_6$ at 316 K. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. (b) The asymmetric unit in the low-temperature form of **1**·C$_6$H$_6$ at 170 K.

The data for **1**·1.75C$_7$H$_8$·0.5C$_6$H$_{14}$ are presented in Tables 10 and 11. There are two molecules in the asymmetric unit (as shown in Figure 5), and they behave somewhat differently as a function of temperature (Figure 6). Molecule **A** is significantly unsymmetrical even at 90 K (the two Co−Co distances differ by 0.056 Å) and becomes much more so as the temperature rises, until at 298 K the difference is 0.161 Å. At 298 K, this molecule is typical of what we have previously designated *u*-Co$_3$(dpa)$_4$Cl$_2$.[7] The second molecule, **B**, is symmetrical at 90 K (the two Co−Co distances differ by only 0.006 Å), but by 298 K it has become essentially a *u*-Co$_3$(dpa)$_4$Cl$_2$ molecule, with the two Co−Co distances differing by 0.130 Å. Since in this case both molecules undergo such an extreme change in symmetry, it is not clear what significance can be attached to the change in mean Co−Co distance from the lowest to the highest temperature. However, for whatever they mean the results are 0.062 and 0.060 Å for molecules **A** and **B**, respectively.

Table 10. Crystal Data and Structure Refinement for **1**·1.75C$_7$H$_8$·0.5C$_6$H$_{14}$

formula		$C_{55.25}H_{53}N_{12}Co_3Cl_2$		
fw		1132.79		
T, K	90	110	170	298
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	16.738(1)	16.774(2)	16.849(1)	17.056(1)
b, Å	17.851(1)	17.913(2)	17.959(1)	18.250(1)
c, Å	19.134(1)	19.195(2)	19.176(1)	19.297(2)
α, deg	80.729(1)	80.925(2)	80.424(1)	80.266(1)
β, deg	81.710(1)	81.633(2)	81.250(1)	80.797(1)
γ, deg	63.384(1)	63.389(2)	63.330(1)	63.217(1)
V, Å^3	5027.6(5)	5073(1)	5093.1(5)	5261.0(7)
Z	4	4	4	4
d_{calcd}, g cm^{-3}	1.497	1.483	1.477	1.430
μ(Mo Kα), mm^{-1}	1.137	1.127	1.122	1.086
R indices [$I > 2\sigma(I)$], R1,^{a} wR2^b	0.045, 0.119	0.047, 0.119	0.048, 0.128	0.060, 0.175
R indices (all data), R1,^{a} wR2^b	0.078, 0.132	0.072, 0.136	0.074, 0.144	0.107, 0.197

^{a} R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 $= [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 11. Selected Interatomic Distances (Å) and Angles (deg) for **1**·1.75C$_7$H$_8$·0.5C$_6$H$_{14}$

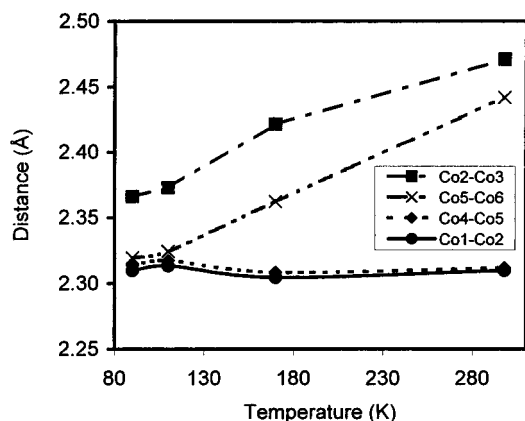|	molecule 1					molecule 2			
	90 K	110 K	170 K	298 K		90 K	110 K	170 K	298 K
Co(1)−Co(2)	2.3098(6)	2.3135(6)	2.3046(6)	2.310(2)	Co(4)−Co(5)	2.3139(6)	2.3174(6)	2.3084(6)	2.312(2)
Co(2)−Co(3)	2.3660(6)	2.3728(6)	2.4216(6)	2.471(2)	Co(5)−Co(6)	2.3196(6)	2.3245(6)	2.3622(6)	2.442(2)
Co(1)−Cl(1)	2.4081(9)	2.4100(10)	2.4067(10)	2.408(4)	Co(4)−Cl(3)	2.4333(10)	2.4369(9)	2.4267(9)	2.419(4)
Co(3)−Cl(2)	2.4467(9)	2.4483(9)	2.4029(9)	2.367(4)	Co(6)−Cl(4)	2.4212(10)	2.4207(9)	2.3960(9)	2.346(4)
Co(1)−N(1)	1.981(3)	1.985(3)	1.979(3)	1.974(11)	Co(4)−N(13)	1.959(3)	1.961(3)	1.960(3)	1.997(10)
Co(1)−N(4)	1.971(3)	1.972(3)	1.971(3)	1.980(11)	Co(4)−N(16)	1.996(3)	2.001(3)	1.994(3)	1.973(10)
Co(1)−N(7)	1.972(3)	1.973(3)	1.973(3)	1.975(12)	Co(4)−N(19)	1.972(3)	1.976(3)	1.970(3)	1.990(10)
Co(1)−N(10)	1.991(3)	1.991(3)	1.979(3)	1.976(12)	Co(4)−N(22)	1.976(3)	1.980(3)	1.974(3)	1.966(10)
Co(2)−N(2)	1.894(3)	1.899(3)	1.900(3)	1.908(10)	Co(5)−N(14)	1.904(3)	1.904(2)	1.906(2)	1.904(10)
Co(2)−N(5)	1.901(3)	1.899(3)	1.902(3)	1.908(9)	Co(5)−N(17)	1.893(3)	1.897(3)	1.898(3)	1.906(9)
Co(2)−N(8)	1.911(3)	1.910(3)	1.913(3)	1.919(10)	Co(5)−N(20)	1.897(3)	1.899(2)	1.901(2)	1.895(10)
Co(2)−N(11)	1.900(3)	1.900(3)	1.899(3)	1.906(10)	Co(5)−N(23)	1.891(3)	1.889(3)	1.893(3)	1.907(9)
Co(3)−N(3)	2.025(3)	2.032(3)	2.070(3)	2.120(10)	Co(6)−N(15)	1.973(3)	1.983(3)	2.015(3)	2.094(10)
Co(3)−N(6)	2.018(3)	2.024(3)	2.073(3)	2.120(10)	Co(6)−N(18)	1.982(3)	1.985(3)	2.017(3)	2.093(10)
Co(3)−N(9)	2.019(3)	2.027(3)	2.063(3)	2.097(10)	Co(6)−N(21)	2.023(3)	2.026(3)	2.057(3)	2.094(11)
Co(3)−N(12)	2.010(3)	2.018(3)	2.065(3)	2.115(10)	Co(6)−N(24)	1.989(3)	1.995(3)	2.025(3)	2.129(10)
Co(1)−Co(2)−Co(3)	178.72(3)	178.70(3)	178.13(2)	178.03(9)	Co(4)−Co(5)−Co(6)	177.05(3)	177.13(2)	177.44(2)	177.99(9)
Co(2)−Co(1)−Cl(1)	179.76(4)	179.63(3)	179.74(4)	179.8(2)	Co(5)−Co(4)−Cl(3)	177.82(3)	177.91(3)	178.12(3)	178.57(12)
Co(2)−Co(3)−Cl(2)	179.19(3)	179.27(3)	179.82(3)	179.85(11)	Co(5)−Co(6)−Cl(4)	178.34(3)	178.39(3)	178.50(3)	179.09(13)
N(1)−Co(1)−N(4)	90.04(11)	90.13(11)	89.88(11)	90.5(4)	N(13)−Co(4)−N(16)	89.15(11)	89.09(10)	89.23(10)	89.0(4)
N(1)−Co(1)−N(7)	89.56(12)	89.66(12)	89.42(12)	89.3(5)	N(13)−Co(4)−N(19)	170.29(11)	170.34(11)	170.69(11)	169.8(4)
N(1)−Co(1)−N(10)	170.84(11)	170.98(11)	170.98(11)	171.0(5)	N(13)−Co(4)−N(22)	90.20(11)	90.03(11)	89.94(11)	90.4(4)
N(4)−Co(1)−N(7)	171.17(11)	170.97(12)	171.35(12)	170.9(5)	N(16)−Co(4)−N(19)	90.48(11)	90.44(11)	90.35(11)	90.0(4)
N(4)−Co(1)−N(10)	88.95(12)	88.80(11)	89.18(11)	89.0(5)	N(16)−Co(4)−N(22)	169.62(12)	169.51(11)	169.92(11)	170.2(4)
N(7)−Co(1)−N(10)	90.04(12)	89.99(12)	90.16(12)	89.8(5)	N(19)−Co(4)−N(22)	88.42(11)	88.67(11)	88.85(11)	88.8(4)
N(2)−Co(2)−N(5)	89.80(12)	89.76(11)	89.83(11)	89.6(4)	N(14)−Co(5)−N(17)	89.67(11)	89.77(11)	89.68(11)	89.7(4)
N(2)−Co(2)−N(8)	90.26(12)	90.25(11)	90.26(12)	90.3(4)	N(14)−Co(5)−N(20)	178.95(11)	178.99(11)	178.70(11)	179.9(4)
N(2)−Co(2)−N(11)	179.68(12)	179.68(12)	179.53(12)	179.3(4)	N(14)−Co(5)−N(23)	90.20(11)	90.04(11)	90.25(11)	89.5(4)
N(5)−Co(2)−N(8)	179.25(11)	179.32(12)	178.92(12)	178.7(4)	N(17)−Co(5)−N(20)	89.84(11)	89.92(11)	89.87(11)	90.3(4)
N(5)−Co(2)−N(11)	89.88(12)	89.93(11)	89.82(11)	90.2(4)	N(17)−Co(5)−N(23)	179.53(12)	179.46(11)	179.67(11)	178.1(4)
N(8)−Co(2)−N(11)	90.06(12)	90.06(11)	90.09(11)	90.0(4)	N(20)−Co(5)−N(23)	90.30(11)	90.28(11)	90.20(11)	90.4(4)
N(3)−Co(3)−N(6)	90.20(11)	90.03(10)	89.49(10)	88.5(4)	N(15)−Co(6)−N(18)	89.42(11)	89.24(11)	89.25(11)	88.6(4)
N(3)−Co(3)−N(9)	91.78(11)	91.99(10)	92.29(10)	92.0(4)	N(15)−Co(6)−N(21)	169.46(12)	169.28(11)	167.06(11)	163.6(4)
N(3)−Co(3)−N(12)	168.65(11)	168.35(11)	165.03(11)	162.2(4)	N(15)−Co(6)−N(24)	88.22(11)	88.35(11)	88.06(11)	90.5(4)
N(6)−Co(3)−N(9)	168.23(11)	168.03(11)	165.29(11)	162.7(4)	N(18)−Co(6)−N(21)	90.86(11)	91.02(11)	90.83(11)	87.6(4)
N(6)−Co(3)−N(12)	85.71(11)	85.68(10)	84.66(10)	84.2(4)	N(18)−Co(6)−N(24)	170.81(11)	170.58(11)	168.36(11)	162.3(4)
N(9)−Co(3)−N(12)	90.14(11)	90.05(10)	89.98(10)	90.2(4)	N(21)−Co(6)−N(24)	89.84(11)	89.66(11)	89.27(11)	88.4(4)
N(1)−Co(1)−Cl(1)	93.93(8)	93.92(8)	94.16(8)	94.1(3)	N(13)−Co(4)−Cl(3)	95.69(8)	95.60(8)	95.37(8)	94.3(3)
N(4)−Co(1)−Cl(1)	94.70(8)	94.72(8)	94.64(9)	94.9(3)	N(16)−Co(4)−Cl(3)	94.31(8)	94.29(8)	94.18(8)	95.7(3)
N(7)−Co(1)−Cl(1)	94.12(9)	94.30(9)	94.01(9)	94.2(4)	N(19)−Co(4)−Cl(3)	94.02(8)	94.05(8)	93.94(8)	95.9(4)
N(10)−Co(1)−Cl(1)	95.23(8)	95.10(8)	94.86(8)	94.9(4)	N(22)−Co(4)−Cl(3)	96.07(9)	96.19(8)	95.91(8)	94.1(3)
N(3)−Co(3)−Cl(2)	95.02(8)	95.14(8)	96.80(8)	98.3(3)	N(15)−Co(6)−Cl(4)	95.01(9)	95.11(8)	96.14(8)	97.7(3)
N(6)−Co(3)−Cl(2)	96.61(8)	96.62(8)	97.84(8)	99.2(3)	N(18)−Co(6)−Cl(4)	93.35(8)	93.45(8)	94.78(8)	98.6(3)
N(9)−Co(3)−Cl(2)	94.77(8)	94.95(8)	96.44(8)	97.8(3)	N(21)−Co(6)−Cl(4)	95.71(9)	95.57(8)	96.76(8)	98.7(3)
N(12)−Co(3)−Cl(2)	95.96(8)	96.12(8)	97.64(8)	98.9(3)	N(24)−Co(6)−Cl(4)	95.49(8)	95.83(8)	96.75(8)	99.0(3)

Over and above all of the other interesting structural details just enumerated, the main point arising from all of these data is that, in each compound, there is a rather large increase in the mean Co−Co distance as the temperature increases from ca. 170 K to ca. 300 K. For the five compounds, in the same order they have been discussed, these changes are 0.020, 0.037, 0.043, 0.032, and 0.061 Å. Changes of this magnitude are not normal for a compound in which the electronic state is unchanged over the same temperature range.[18] What is the explanation?
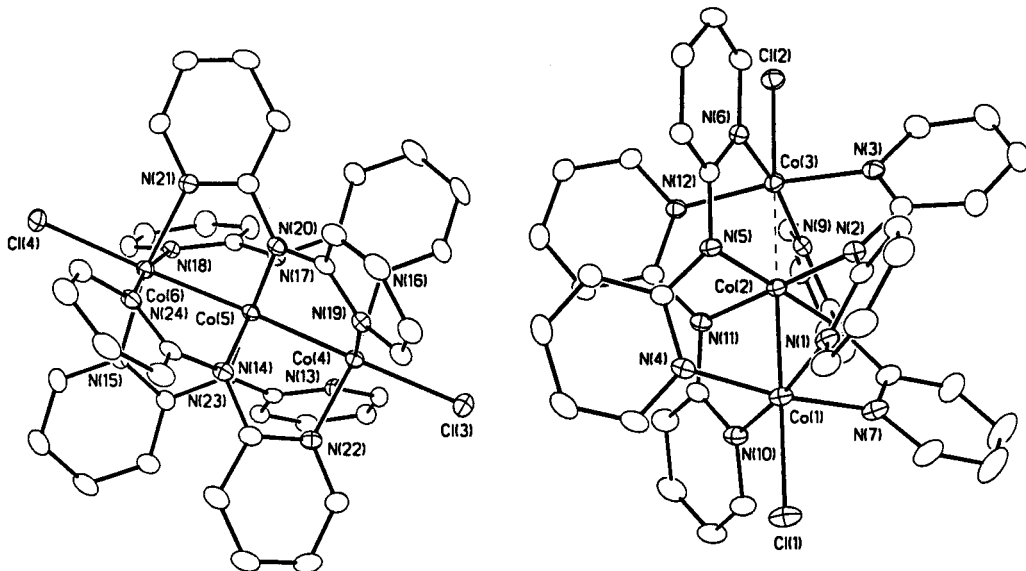
Figure 5. Perspective view of the two independent molecules of $Co_3(dpa)_4Cl_2$ (**1**) in $1 \cdot 1.75C_7H_8 \cdot 0.5C_6H_{14}$ at 90 K. Atoms are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity. The same atomic labeling scheme is used for data collected at other temperatures.

Figure 6. Temperature dependence of metal−metal distances for the molecules of **1** in $1 \cdot 1.75C_7H_8 \cdot 0.5C_6H_{14}$.

Magnetic Susceptibility Measurements. The explanation is found when we examine the magnetic data. Plots of μ_{eff} vs temperature for each of the compounds are shown in Figure 7. In every case, below 100 K, the $Co_3(dpa)_4Cl_2$ molecule is in a spin-doublet ground state with a g value of about 2.4. The field dependence of the magnetic moment at 1.8 K can be fitted to the Brillouin function for an $S = \frac{1}{2}$ spin which allows us to evaluate more precisely the g value at 1.8 K in each case: 2.370-(5) for $1 \cdot 0.85(C_2H_5)_2O \cdot 0.15CH_2Cl_2$, 2.370(5) for $1 \cdot C_6H_{12}$, 2.350(5) for $1 \cdot C_4H_8O$, 2.353(5) for $1 \cdot C_6H_6$, and 2.349(5) for $1 \cdot 1.75C_7H_8 \cdot 0.5C_6H_{14}$. Above 100 K, the effective moments begin to increase gradually without reaching saturation even at 350 K. It is worth noting at this point that $1 \cdot C_6H_{12}$ exhibits at about 210 K a kink in the magnetic moment probably related to the structural phase transition observed in the X-ray study (vide supra*).* No such feature was observed for $1 \cdot C_6H_6$, although this also has a structural phase transition between 316 and 260 K as shown by the X-ray study. This typical spin-crossover process has been already observed in numerous compounds of
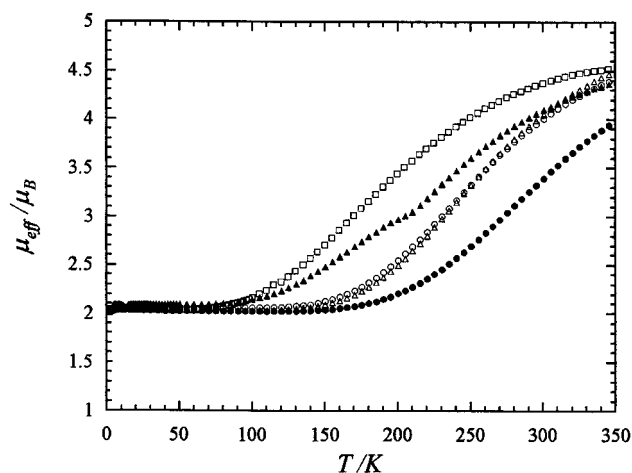
Figure 7. Temperature dependence of the effective magnetic moment at 1000 G for $1 \cdot 0.85(C_2H_5)_2O \cdot 0.15CH_2Cl_2$ (●), $1 \cdot C_6H_6$ (△), $1 \cdot C_4H_8O$ (○), $1 \cdot C_6H_{12}$ (▲), and $1 \cdot 1.75C_7H_8 \cdot 0.5C_6H_{14}$ (□)

this family where the high-spin state can be assigned to either an $S = \frac{3}{2}$ or $S = \frac{5}{2}$ state.[7] In these compounds, the spin-crossover can be modeled to a phenomenological model involving an equilibrium between the two magnetic states.[19] This led us to conclude that for each compound the higher magnetic state has $S = \frac{3}{2}$ with a g value of about 2.7(1).

The bonding in these Co_3 chains is not fully understood,[20] but the following things can be said with certainty. Over the chain, there are 12 more-or-less delocalized molecular orbitals made up of four 3d orbitals from each metal atom (one 3d orbital being strongly involved in Co−N bonding). Of these 12 MOs, roughly speaking there will be four that are bonding, four that are nonbonding, and four that will be antibonding. The three Co^{II} atoms contribute a total of 21 electrons, which must occupy these 12 MOs.

In the ground state, 16 electrons will fill the bonding and nonbonding orbitals and five will occupy antibonding orbitals so that two such orbitals are doubly occupied and one electron

(18) We could find no studies of this in the literature, but there have been several unpublished ones done in the laboratory. For example, for Cr_2-(2,6-dimethoxyphenyl)₄ the Cr−Cr distances at 90 and 295 K are 1.8473(4) and 1.847(1) Å, respectively.

(19) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

(20) Rohmer, M.; Bénard, M. *J. Am. Chem. Soc.* **1998**, *120*, 9372.

Table 12. Co-Co Distances (Å) in the $Co_3(dpa)_4Cl_2$ Molecule in Various Environments and at Various Temperatures

solvent of crystallization per $Co_3(dpa)_4Cl_2$	temp, K	Co(1)−Co(2)	Co(2)−Co(3)[a]	ref
$2CH_2Cl_2$, $1H_2O$	b	2.290(3)	2.472(3)	3a
$1CH_2Cl_2$	296	2.3369(4)	c	7
	168[d]	2.3178(9)	c	3c
	109	2.3214(8)	2.3224(8)	7
	20[e]	2.34(1)	2.34(1)	7
$2CH_2Cl_2$	298	2.299(1)	2.471(1)	7
	213	2.2943(9)	2.466(1)	3d, 7
	173	2.2958(9)	2.457(1)	7
	133	2.295(1)	2.440(1)	7
	20	2.3035(7)	2.3847(8)	7
$1Co(dpa)_2$[f]	213	2.285(1)	2.459(1)	3c
$0.85(C_2H_5)_2O$, $0.15CH_2Cl_2$	296	2.3230(3)	2.3667(4)	
	213	2.3193(3)	2.3352(3)	
	120	2.3191(3)	2.3304(3)	
$1C_4H_8O$	295	2.3484(4)	c	
	120	2.3111(4)	c	
$1C_6H_{12}$	295	2.3620(5)	c	
	213	2.3311(5)	c	
	120	2.3127(5)	2.3253(5)	
$1C_6H_6$	316	2.3417(9)	2.3665(9)	
	260[g]	2.324(1)	2.350(1)	
	260[g]	2.323(1)	2.345(1)	
	213[g]	2.323(1)	2.344(1)	this work
	213[g]	2.326(1)	2.338(1)	
	170[g]	2.3135(8)	2.3280(8)	
	170[g]	2.3189(8)	2.3283(8)	
$1.75C_7H_8$, $0.5C_6H_{14}$	298[g]	2.310(2)	2.471(2)	
	298[g]	2.312(2)	2.442(2)	
	170[g]	2.3046(6)	2.4216(6)	
	170[g]	2.3084(6)	2.3622(6)	
	110[g]	2.3135(6)	2.3728(6)	
	110[g]	2.3174(6)	2.3245(6)	
	90[g]	2.3098(6)	2.3660(6)	
	90[g]	2.3139(6)	2.3196(6)	

[a] Arbitrarily taken as the longer Co−Co separation. [b] Not reported. [c] Crystallographically equivalent to Co(1)−Co(2). [d] Original paper contains a typographical error; the correct number of solvent molecules per Co3 unit is one (not two). [e] Neutron data. [f] Not actually a "solvent" molecule. [g] There are two crystallographically independent molecules in the same crystal.

is left unpaired in an antibonding orbital. The most strongly antibonding orbital remains empty. Thus, as a rough approxima-

tion, the bond order of each Co−Co bond will be $(4 - 2.5)/2 = 0.75$ in the ground state. If the lowest quartet state is attained by the promotion of a nonbonding or less antibonding electron to the remaining unoccupied antibonding orbital, the bonding must be weakened and the bond order could drop to as low as $(4 - 3)/2 = 0.5$. Thus, as a spin crossover from the ground doublet state to the quartet state occurs, the bond length must increase by more than would be expected for a more ordinary molecule that remains in its ground state over the range of measurement.

Concluding Remarks

With the completion of the work reported in this paper, we have concluded, at least for the foreseeable future, our structural studies of the molecule $Co_3(dpa)_4Cl_2$. As shown in Table 12, a very extensive database concerning the structural variability of this molecule as a function of environment and temperature has been assembled. Along with the structural facts, the magnetic behavior has been thoroughly examined, and the nature of the molecule in solution has also been established by NMR spectroscopy and cyclic voltammetry. There are, perhaps, those who might question whether one molecule merits so much study. Obviously, we think it does, because its structural variability (which may or may not be properly called bond-stretch isomerism) is so unusual, if not unique. We have recently found that this extraordinary behavior is paralleled, in many ways, by the bromine analogue, but there are also minor differences that could provide interesting new clues.[21] Our understanding of metal−metal bonding cannot be considered complete until it is able to deal with a case like this, as well as with the normal examples. We think the facts are becoming clear and abundant. Can a satisfactory explanation be given?

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

(21) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Murillo, C. A.; Wang, X. *J. Chem. Soc., Dalton Trans.*, in press.