Compounds with Symmetrical Tricobalt Chains Wrapped by Dipyridylamide Ligands and Cyanide or Isothiocyanate Ions as Terminal Ligands

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Received September 21, 2000

Three new linear compounds of the type $Co_3(dpa)_4X_2$, where dpa is the anion of di(2-pyridyl)amine and X is NCS^- (**5**), CN^- (**6**), and $N(CN)_2^-$ (**7**), have been prepared, and their structures and magnetic behavior have been studied. In all of them, including three different solvates of **5**, the Co_3 chains are symmetrical with Co−Co distances of ca. 2.31−2.32 Å. The appearance of four lines in the ^{1}H NMR spectra of the three compounds is also consistent with a symmetrical structure in solution. For all compounds, the magnetic behavior is quite similar with μ_{eff} of ca. 1.9−2.0 μ_B at temperatures between 1.8 and 200 K. As the temperature increases, the effective moments increase gradually, but since saturation is not reached, even at 400 K, the high-spin state cannot be assigned.

Introduction

The compound $Co_3(dpa)_4Cl_2$ (**1**), first reported in 1994,[1] has been carefully studied because of its ability to vary its internal dimensions and symmetry, especially the Co−Co distances, as a function of its crystal environment[2] and also with temperature.[3] This curious, and as far as we know unprecedented,[4] behavior is now well established but not yet satisfactorily explained although theoretical studies have been made[5] and are continuing.[6]

In the hope of throwing more light on this problem, it seemed reasonable to prepare and characterize analogous compounds having terminal ligands other than chloride ions. We have already reported the compounds $[Co_3(dpa)_4(CH_3CN)_2](PF_6)_2$ (**2**)[7] and $[Co_3(dpa)_4](BF_4)_2$ (**3**),[2b] and we have also studied $Co_3(dpa)_4Br_2$ (**4**).[8] In crystals of **2** and **3** we have so far found only symmetrical Co_3 chains, but the behavior of **4** is very similar to that of **1**.

In this paper we report the preparation and characterization of three new compounds of the type $Co_3(dpa)_4X_2$ in which X $= NCS^-$ (**5**), CN^- (**6**), and $N(CN)_2^-$ (**7**). Compound **5** has been obtained in three crystalline forms depending on the solvent used. These structures as well as those for **6** and **7** are reported here along with other physical properties.

Experimental Section

General. Manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified by conventional methods and were freshly distilled under nitrogen prior to use. Anhydrous $CoCl_2$ was purchased from Strem Chemicals, Inc. Di(2-pyridyl)amine was purchased from Aldrich and sublimed prior to use; $Co_3(dpa)_4Cl_2$ and $[Co_3(dpa)_4](BF_4)_2$ were prepared according to a published procedure.[2b]

Physical Measurements. ^{1}H NMR spectra were recorded on a Varian UNITY Plus 300 instrument at 300 MHz, with chemical shifts being referenced to CD_2Cl_2 (δ, 5.32 ppm) for **1** and MeOD (4.78 ppm) for **3**. The electronic absorption spectra were measured on a Cary 17 spectrophotometer. Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL (housed in the Department of Chemistry at Texas A&M University). Data were collected from 1.8 to 400 K at 1000 G on finely divided polycrystalline samples (26.05 mg for $\mathbf{5}\cdot 1.5CH_2Cl_2$, 19.70 mg for $\mathbf{6}\cdot CH_2Cl_2$, 29.97 mg for $\mathbf{7}\cdot 2CH_2Cl_2$). The magnetic susceptibility data were corrected for the sample holder and for the diamagnetic contribution which was estimated from Pascal's constants.[9] Cyclic voltammetry was performed in dichloromethane solution with a BAS model 100 scanning potentiostat using Pt working and auxiliary electrodes and 0.1 M TBAH, $(Bu^n{}_4N)(PF_6)$, as the supporting electrolyte. Potentials are referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple which occurs at $E_{1/2} = +0.44$ V versus Ag/AgCl. The values of $E_{1/2}$ were taken as $(E_{pa} + E_{pc})/2$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

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10.1021/ic001069a CCC: \$20.00

Table 1. Crystal Data and Structural Refinement for **5**·1.5CH$_2$Cl$_2$, **5**·5THF, **5**·2Toluene, **6**·CH$_2$Cl$_2$, and **7**·2CH$_2$Cl$_2$

	5·1.5CH$_2$Cl$_2$	**5**·5THF	**5**·2toluene	**6**·CH$_2$Cl$_2$	**7**·2CH$_2$Cl$_2$
formula	$C_{43.5}H_{35}N_{14}S_2Co_3Cl_3$	$C_{62}H_{72}O_5N_{14}S_2Co_3$	$C_{56}H_{48}N_{14}S_2Co_3$	$C_{43}H_{34}N_{14}Cl_2Co_3$	$C_{46}H_{36}N_{18}Cl_4Co_3$
fw	1101.12	1334.25	1157.99	994.53	1159.52
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Fdd*2 (No. 43)	*Pnn*2 (No. 34)	$P2_1/c$ (No. 14)
a, Å	16.920(1)	12.168(1)	14.1627(7)	12.9990(6)	18.585(2)
b, Å	17.621(1)	13.900(1)	24.299(1)	13.9720(7)	13.632(2)
c, Å	16.2104(9)	19.917(2)	30.991(2)	11.2270(6)	19.62292)
α, deg	90	71.803(2)	90	90	90
β, deg	106.782(5)	81.739(2)	90	90	105.08(1)
γ, deg	90	77.295(2)	90	90	90
V, Å^3	4627.2(5)	3111.7(5)	10665(1)	2039.1(2)	4799(20
Z	4	2	8	2	4
D_{calc}, g cm^{-3}	1.581	1.424	1.442	1.390	1.605
R indices [$I > 2\sigma(I)$], R1,[a] wR2[b]	0.045, 0.108	0.082, 0.186	0.055, 0.130	0.027, 0.067	0.052, 0.128
R indices (all data), R1,[a] wR2[b]	0.055, 0.116	0.121, 0.201	0.82, 0.145	0.030, 0.069	0.063, 0.141

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

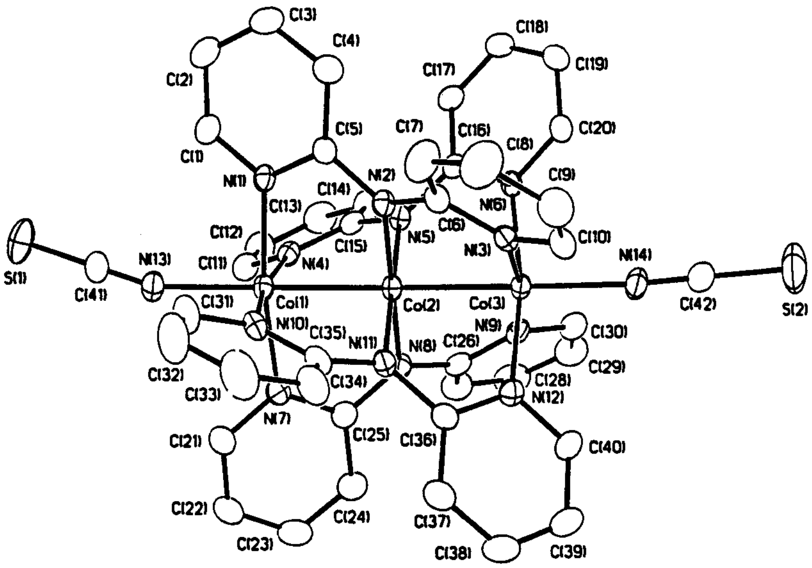

Figure 1. Perspective view of Co$_3$(dpa)$_4$(NCS)$_2$ in **5**·1.5CH$_2$Cl$_2$. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. The same labeling scheme is also used for **1**·5THF.

Preparation of Co$_3$(dpa)$_4$(NCS)$_2$·1.5CH$_2$Cl$_2$ (5·1.5CH$_2$Cl$_2$). Acetone (15 mL) was added to a reaction flask containing a mixture of green [Co$_3$(dpa)$_4$](BF$_4$)$_2$·2CH$_2$Cl$_2$ (0.124 mg, 0.100 mmol) and KSCN (0.020 g, 0.21 mmol). A dark red color appeared immediately. After stirring for 1.5 h at room temperature, the solvent was removed under vacuum. The remaining solid was extracted with CH$_2$Cl$_2$ (15 mL) and filtered. The filtrate was then layered with hexanes (30 mL). Reddish-brown crystals formed after standing for 1 week at room temperature. Yield: 0.096 g (87%). ^{1}H NMR (CD$_2$Cl$_2$, rt): δ 11.49 (8H), 9.16 (8H), 8.54 (8H), 0.10 (8H). IR (KBr, cm^{-1}): 2057 (s), 1607 (m), 1593 (m), 1470 (s), 1432 (s), 1369 (m), 1315 (m), 1283 (w), 1246 (w), 1157 (m), 1025 (m), 885 (w), 761 (m), 741 (m), 457 (w). UV/vis nm (ϵ, M^{-1} cm^{-1}): 318 (98300), 390 (18900), 445 (7700), 552 (3630). $E_{1/2}$ (ox)$_1$ 441 mV. Anal. Calcd for $C_{42}H_{32}N_{14}S_2Co_3$: C, 51.81; H, 3.31; N, 20.14. Found: C, 52.03; H, 3.33; N, 20.22.

Preparation of Co$_3$(dpa)$_4$(NCS)$_2$·5THF (5·5THF). It was prepared as above but using THF to extract the solid residue. Crystals were obtained by slow diffusion of hexanes into a THF solution at −15 °C. IR (KBr, cm^{-1}): 2063 (s), 1607 (s), 1593 (s), 1547 (s), 1470 (s), 1429 (s), 1375 (m), 1309 (m), 1277 (w), 1249 (w), 1154 (m), 1108 (w), 1051 (w), 1022 (m), 887 (w), 761 (s), 741 (m), 520 (w), 457 (w).

Preparation of Co$_3$(dpa)$_4$(NCS)$_2$·2C$_6$H$_5$CH$_3$ (5·2C$_6$H$_5$CH$_3$). It was prepared as above but using toluene to extract the solid residue. The product is only slightly soluble in toluene. Crystals were obtained by slow diffusion of hexanes into a toluene solution at room temperature. IR (KBr, cm^{-1}): 2055 (s), 1606 (m), 1594 (m), 1548 (w), 1468 (s), 1427 (s), 1372 (m), 1313 (m), 1261 (w), 1154 (m), 1094 (w), 1022 (m), 886 (w), 801 (w), 738 (m), 758 (m), 456 (sh).

Preparation of Co$_3$(dpa)$_4$(CN)$_2$·CH$_2$Cl$_2$ (6·CH$_2$Cl$_2$). Methanol (15 mL) was added to a reaction flask containing a mixture of [Co$_3$(dpa)$_4$](BF$_4$)$_2$·2CH$_2$Cl$_2$ (0.23 g, 0.19 mmol) and KCN (0.031 g, 0.48 mmol). A dark red solution was formed immediately. After it was stirred for 20 min at room temperature, the solvent was removed under vacuum. The remaining solid was extracted with CH$_2$Cl$_2$ (15 mL) and filtered. The filtrate was then layered with hexanes (30 mL). Dark brown crystals of **6**·CH$_2$Cl$_2$ were obtained in 10 days. These were collected and washed with hexanes. Yield: 0.14 g, 74%. ^{1}H NMR (CD$_2$Cl$_2$, rt): δ 14.01 (8H), 11.20 (8H), 7.82 (8H), 2.56 (8H). IR (KBr, cm^{-1}): 2091 (w), 1607 (s), 1594 (s), 1468 (s), 1458 (sh, s), 1432 (s), 1370 (s), 1317 (m), 1281 (m), 1167 (m), 1152 (m), 1116 (w), 1020 (m), 883 (w), 758 (m), 736 (m), 541 (w), 520 (w), 456 (w), 432 (w). UV/vis nm (ϵ, M^{-1} cm^{-1}): 320 (195000), 410 (30500), 454 (7200), 556 (4890). $E_{1/2}$(ox)$_1$: 276 mV. $E_{1/2}$(ox)$_2$: 1008 mV. Anal. Calcd for $C_{43}H_{34}N_{14}Cl_2Co_3$: C, 51.93; H, 3.45; N, 19.72. Found: C, 51.41; H, 3.44; N, 19.31.

Preparation of Co$_3$(dpa)$_4$(N(CN)$_2$)$_2$·2CH$_2$Cl$_2$ (7·2CH$_2$Cl$_2$). Methanol (15 mL) was added to a reaction flask containing a mixture of [Co$_3$(dpa)$_4$](BF$_4$)$_2$·2CH$_2$Cl$_2$ (0.24 g, 0.20 mmol) and NaN(CN)$_2$ (0.045 g, 0.50 mmol). A dark brown solution formed immediately. After it was stirred for 20 min at room temperature, the solvent was removed under vacuum. The remaining solid was extracted with CH$_2$Cl$_2$ (15 mL) and filtered. The filtrate was then layered with hexanes (30 mL). Dark brown crystals of **7**·2CH$_2$Cl$_2$ were obtained in 5 days. These were collected and washed with hexanes. Yield: 0.19 g, 82%. ^{1}H NMR (CD$_2$Cl$_2$, rt): δ 11.15 (8H), 7.08 (8H), 6.29 (8H), −1.09 (8H). IR (KBr, cm^{-1}): 2261 (m), 2214 (w), 2156 (s), 1599 (m), 1546 (w), 1470 (s), 1428 (s), 1373 (m), 1342 (w), 1314 (m), 1278 (w), 1155 (m), 1113

Table 2. Selected Bond Distances (Å) and Angles (deg) for **5**·1.5CH_2Cl_2 and **5**·5THF

	5·1.5CH_2Cl_2	**5**·5THF
Co(1)−Co(2)	2.3223(6)	2.313(2)
Co(2)−Co(3)	2.3087(6)	2.309(2)
Co(1)−N(1)	1.995(3)	1.998(6)
Co(1)−N(4)	1.988(3)	1.961(6)
Co(1)−N(7)	1.971(3)	1.983(6)
Co(1)−N(10)	1.985(3)	1.990(6)
Co(2)−N(2)	1.895(2)	1.890(4)
Co(2)−N(5)	1.895(3)	1.889(6)
Co(2)−N(8)	1.890(3)	1.898(5)
Co(2)−N(11)	1.902(3)	1.900(6)
Co(3)−N(3)	1.968(3)	1.966(5)
Co(3)−N(6)	1.972(3)	1.980(6)
Co(3)−N(9)	1.989(3)	1.997(5)
Co(3)−N(12)	1.958(3)	1.983(6)
Co(1)−N(13)	2.059(3)	2.047(8)
Co(3)−N(14)	2.042(3)	2.051(6)
N(13)−C(41)	1.157(4)	1.154(9)
N(14)−C(42)	1.158(5)	1.155(9)
S(1)−C(41)	1.624(4)	1.615(8)
S(2)−C(42)	1.622(4)	1.619(8)
Co(3)−Co(2)−Co(1)	179.07(2)	179.20(6)
N(1)−Co(1)−N(4)	90.67(11)	88.8(2)
N(1)−Co(1)−N(7)	171.46(11)	170.5(2)
N(1)−Co(1)−N(10)	89.34(11)	91.1(2)
N(1)−Co(1)−N(13)	93.99(11)	94.8(3)
N(4)−Co(1)−N(7)	88.83(11)	90.3(2)
N(4)−Co(1)−N(13)	93.84(11)	94.2(3)
N(4)−Co(1)−N(10)	170.31(11)	171.1(2)
N(7)−Co(1)−N(10)	89.73(11)	88.32(3)
N(7)−Co(1)−N(13)	94.54(11)	94.7(2)
N(10)−Co(1)−N(13)	95.82(12)	94.6(3)
N(2)−Co(2)−N(5)	89.69(12)	90.2(2)
N(2)−Co(2)−N(8)	179.35(12)	179.8(2)
N(2)−Co(2)−N(11)	89.93(12)	90.2(2)
N(5)−Co(2)−N(8)	89.68(12)	89.7(2)
N(5)−Co(2)−N(11)	179.22(11)	179.7(3)
N(8)−Co(2)−N(11)	90.70(12)	90.0(3)
N(3)−Co(3)−N(6)	88.25(11)	89.3(2)
N(3)−Co(3)−N(9)	171.09(11)	170.7(2)
N(3)−Co(3)−N(12)	89.99(11)	90.4(2)
N(3)−Co(3)−N(14)	94.10(12)	94.6(2)
N(6)−Co(3)−N(9)	91.44(11)	89.6(2)
N(6)−Co(3)−N(12)	170.43(11)	170.1(2)
N(6)−Co(3)−N(14)	94.41(11)	94.6(2)
N(9)−Co(3)−N(12)	88.84(11)	89.1(2)
N(9)−Co(3)−N(14)	94.80(12)	94.6(2)
N(12)−Co(3)−N(14)	95.10(12)	95.3(3)
N(13)−Co(1)−Co(2)	178.88(9)	179.8(2)
N(14)−Co(3)−Co(2)	179.07(8)	179.7(2)
N(13)−C(41)−S(1)	178.3(3)	178.6(7)
N(14)−C(42)−S(2)	178.6(4)	178.5(7)

(w), 1020 (m), 886 (w), 760 (m), 739 (sh, w), 520 (w), 459 (w), 433 (w). UV/vis nm (ϵ, M^{-1} cm^{-1}): 316 (70400), 388 (12300), 448 (3850), 554 (1880). $E_{1/2}(ox)_1$: 466 mV. $E_{1/2}(ox)_2$: 1242 mV. Anal. Calcd for $C_{44}H_{32}N_{18}Co_3$: C, 53.40; H, 3.23; N, 25.48. Found: C, 53.03; H, 3.26; N, 25.38.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **5**·2Toluene

Co(1)−Co(2)	2.3140(8)	Co(2)−Co(1A)[a]	2.3140(8)
Co(1)−N(1)	1.977(7)	Co(1)−N(3)	1.995(6)
Co(1)−N(4)	1.966(7)	Co(1)−N(6)	1.976(6)
Co(1)−N(7)	2.051(6)	Co(2)−N(2)	1.898(6)
Co(2)−N(5)	1.900(6)	S(1)−C(21)	1.622(7)
N(7)−C(21)	1.174(9)		

N(4)−Co(1)−N(1)	171.0(2)	N(4)−Co(1)−N(6)	89.5(3)
N(4)−Co(1)−N(3)	91.1(3)	N(6)−Co(1)−N(1)	88.4(3)
N(1)−Co(1)−N(3)	89.5(3)	N(6)−Co(1)−N(3)	170.2(2)
N(6)−Co(1)−N(7)	95.3(3)	N(4)−Co(1)−N(7)	94.0(3)
N(3)−Co(1)−N(7)	94.4(3)	N(1)−Co(1)−N(7)	94.9(3)
N(2)−Co(2)−N(5A)	89.9(2)	N(2)−Co(2)−N(2A)	90.7(4)
N(2)−Co(2)−N(5)	179.3(3)	N(2A)−Co(2)−N(5A)	179.3(3)
N(5A)−Co(2)−N(5)	89.5(4)	N(2A)−Co(2)−N(5)	89.9(2)
N(7)−C(21)−S(1)	178.0(6)	Co(1)−Co(2)−Co(1A)	176.07(9)

[a] Atoms labeled “A” are symmetry generated by a crystallographic 2-fold axis.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **6**·CH_2Cl_2

Co(1)−Co(2)	2.3392(2)	Co(2)−Co(1A)[a]	2.3392(2)
Co(1)−N(1)	1.985(2)	Co(2)−N(5)	1.901(2)
Co(1)−N(2)	1.981(2)	Co(2)−N(6)	1.906(2)
Co(1)−N(3)	1.959(2)	Co(1)−C(21)	2.040(2)
Co(1)−N(4)	2.004(2)	N(7)−C(21)	1.138(3)

Co(1)−Co(2)−Co(1A)	178.35(3)	C(21)−Co(1)−Co(2)	178.58(6)
N(7)−C(21)−Co(1)	177.1(3)	N(3)−Co(1)−C(21)	94.79(8)
N(1)−Co(1)−N(2)	89.86(8)	N(4)−Co(1)−C(21)	96.63(10)
N(1)−Co(1)−N(3)	89.35(8)	N(5)−Co(2)−N(5A)	89.48(13)
N(1)−Co(1)−N(4)	168.90(7)	N(5)−Co(2)−N(6A)	178.81(11)
N(2)−Co(1)−N(3)	170.82(7)	N(5A)−Co(2)−N(6A)	89.85(7)
N(2)−Co(1)−N(4)	90.23(8)	N(5)−Co(2)−N(6)	89.85(7)
N(3)−Co(1)−N(4)	88.79(8)	N(5A)−Co(2)−N(6)	178.81(11)
N(1)−Co(1)−C(21)	94.42(10)	N(6A)−Co(2)−N(6)	90.84(13)
N(2)−Co(1)−C(21)	94.38(8)		

[a] Atoms labeled “A” are symmetry generated by a crystallographic 2-fold axis.

Table 5. Selected Bond Distances (Å) and Angles (deg) for (**7**·2CH_2Cl_2)

Co(1)−Co(2)	2.3194(8)	Co(2)−Co(3)	2.3184(8)
Co(1)−N(1)	1.981(3)	Co(1)−N(4)	1.977(3)
Co(1)−N(7)	1.997(3)	Co(1)−N(10)	1.977(3)
Co(1)−N(13)	2.084(3)	Co(2)−N(2)	1.907(3)
Co(2)−N(5)	1.910(3)	Co(2)−N(8)	1.896(3)
Co(2)−N(11)	1.897(3)	Co(3)−N(3)	1.982(3)
Co(3)−N(6)	1.971(3)	Co(3)−N(9)	1.983(3)
Co(3)−N(12)	1.985(3)	Co(3)−N(16)	2.090(3)

Co(1)−Co(2)−Co(2)	178.48(3)	N(1)−Co(1)−N(4)	90.55(12)
N(1)−Co(1)−N(7)	169.71(11)	N(1)−Co(1)−N(10)	87.96(12)
N(4)−Co(1)−N(7)	91.28(12)	N(4)−Co(1)−N(10)	171.04(11)
N(7)−Co(1)−N(10)	88.67(12)	N(2)−Co(2)−N(5)	91.48(12)
N(2)−Co(2)−N(8)	178.47(12)	N(2)−Co(2)−N(11)	89.22(12)
N(5)−Co(2)−N(8)	90.05(12)	N(5)−Co(2)−N(11)	179.29(12)
N(8)−Co(2)−N(11)	89.25(12)	N(6)−Co(3)−N(3)	92.47(12)
N(3)−Co(3)−N(9)	170.45(11)	N(3)−Co(3)−N(12)	87.36(12)
N(6)−Co(3)−N(9)	87.46(12)	N(6)−Co(3)−N(12)	171.21(12)
N(9)−Co(3)−N(12)	91.26(12)	N(1)−Co(1)−N(13)	95.73(12)
N(4)−Co(1)−N(13)	94.49(12)	N(7)−Co(1)−N(13)	94.22(12)
N(10)−Co(1)−N(13)	94.45(12)	N(3)−Co(3)−N(16)	95.37(12)
N(6)−Co(3)−N(16)	93.91(13)	N(9)−Co(3)−N(16)	94.16(12)
N(12)−Co(3)−N(16)	94.85(12)	C(41)−N(13)−Co(1)	172.1(3)
C(41)−N(14)−C(42)	121.9(3)	C(43)−N(16)−Co(3)	176.1(3)
C(43)−N(17)−C(44)	123.1(4)		

X-ray Crystallography. Each crystal was mounted on a quartz fiber with a small amount of silicone grease and transferred to a goniometer head. Geometric and intensity data for **5**·1.5CH_2Cl_2 and **7**·2CH_2Cl_2 at 213 K were gathered on a Nonius FAST area detector system, utilizing the software program MADNES.[10] Cell parameters were obtained from an auto indexing 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 PROCOR.[11]

Data for **5**·5THF, **5**·2toluene, and **6**·CH_2Cl_2 at 213 K were collected on a Bruker SMART 1000 CCD detector system. Cell parameters were

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(10) 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.

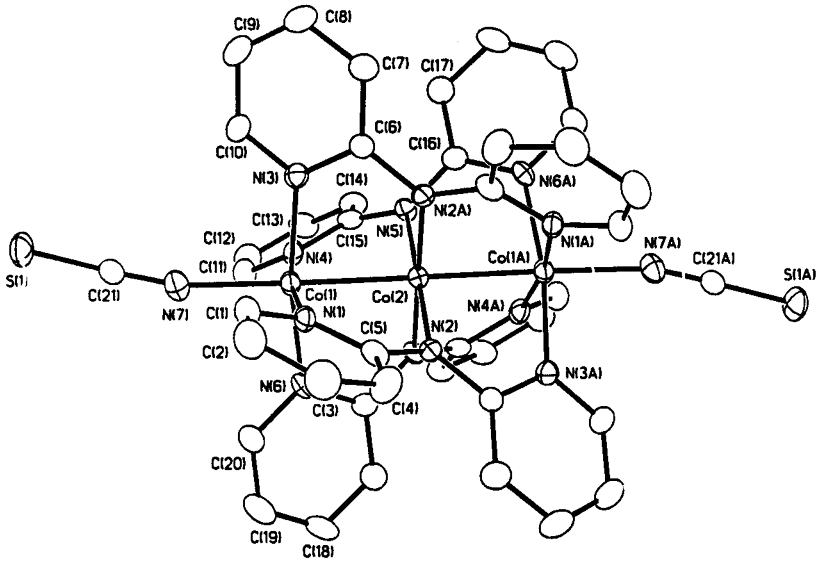

Figure 2. Perspective view of $Co_3(dpa)_4(NCS)_2$ in **5**·2toluene. A 2-fold axis comprising Co(2) relates the two halves of the molecules. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

obtained using SMART[12] software. Data were corrected for Lorentz and polarization effects using the program SAINT.[13] Absorption corrections were applied using SADABS.[14]

For each of the five data sets the positions of the heavy atoms were found by the direct methods program in SHELXTL.[15] 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 partially disordered in all five compounds, and they were refined isotropically. Other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed on calculated positions in the final refinement. Details of crystal data and structural refinement are given in Table 1. Selected distances and angles for **5**·$1.5CH_2Cl_2$ and **5**·5THF, **5**·2toluene**,** **6**·CH_2Cl_2, and **7**·$2CH_2Cl_2$ are listed in Tables 2−5.

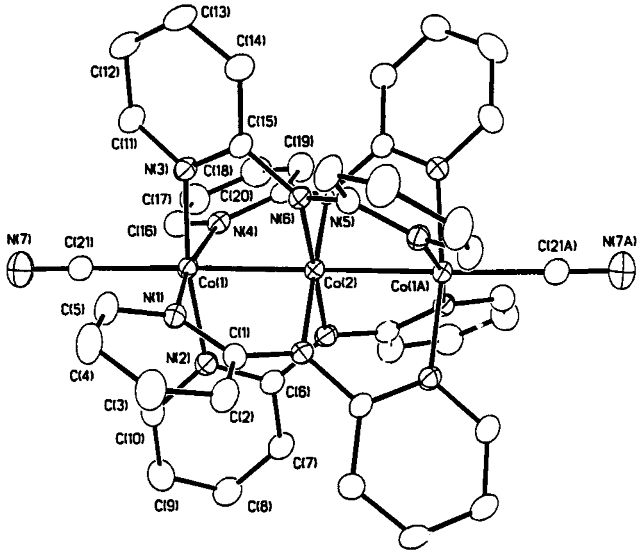

Figure 3. Perspective view of $Co_3(dpa)_4(CN)_2$ in **6**·CH_2Cl_2. A 2-fold axis comprising Co(2) relates the two halves of the molecules. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

Results and Discussion

Compound **3** is particularly important because it serves as a good starting material for the preparation of other $Co_3(dpa)_4X_2$ compounds. It appears that the BF_4^- ions are not strongly held and they are therefore easily replaced by many other ligands. Thus, the reaction used to prepare each of the new compounds (where X represents the new ligand) can be written generally as

$$Co_3(dpa)_4(BF_4)_2 + 2X^- \rightarrow Co_3(dpa)_4X_2 + 2BF_4^-$$

$Co_3(dpa)_4(NCS)_2$, 5. This compound has been obtained in three solvated crystalline forms, **5**·$1.5CH_2Cl_2$, **5**·5THF, and **5**·2toluene. The structures of the $Co_3(dpa)_4(NCS)_2$ molecule found in the first and third of these are shown in Figures 1 and 2, respectively. The structure found in **5**·5THF is not significantly different, and the atom-numbering scheme is the same as that in Figure 1. The entire chain of nine atoms from S to S is not strictly linear, but the only significant deviations occur where the −NCS groups join the Co_3 chain. Each NCS ion is linear, as is the Co_3 chain. The most important feature of all these structures is that the Co_3 chain is symmetrical, that is, either the two Co−Co distances are identical by crystallographic symmetry, as in **5**·2toluene (2.3140(8) Å), or they are almost identical even though there is no crystallographic constraint. Thus in **5**·$1.5CH_2Cl_2$ the distances are 2.3223(6) and 2.3087(6) Å and in **5**·5THF they are 2.313(2) and 2.309(2) Å. The grand average of all five independent distances, with the one that is required to be identical to its neighbor weighted twice, is 2.314 Å, and no individual distance differs from this by more than 0.008 Å.

The isothiocyanate ligand has been present in two previous cases where metal atom chains are enveloped in ligands that are extensions of the dpa motif, namely, $Co_5(tpda)_4(NCS)_2$[16] and $Ni_5(tpda)_4(NCS)_2$.[17] In the former, the Co−NCS distances

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(11) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 67. (b) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 916.

(12) *SMART V5.05 Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(13) *SAINTPLUS, V5.00 Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(14) *SADABS*. Program for absorption correction using SMART CCD based on the method of Blessing: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.

(15) *SHELXTL*, version 5.03; Siemens Industrial Automation Inc.: Madison, WI, 1994.

(16) Shieh, S.-J.; Chou, C.-C.; Lee, G.-H.; Wang, C.-C.; Peng, S.-M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 56.

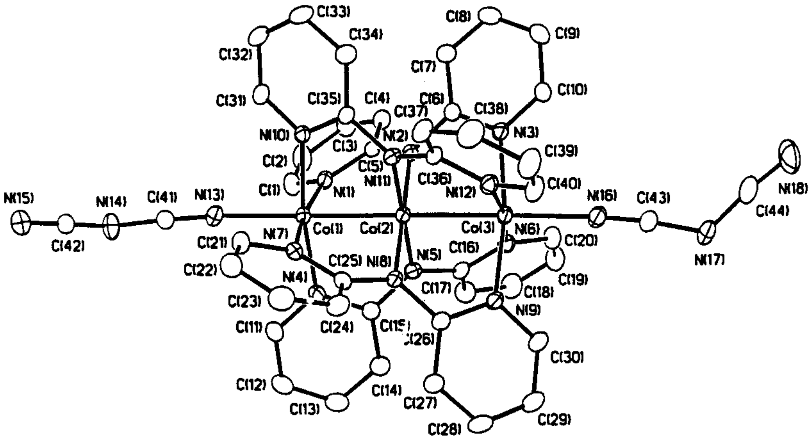

Figure 4. Perspective view of $Co_3(dpa)_4(N(CN)_2)_2$ in $7{\cdot}2CH_2Cl_2$. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

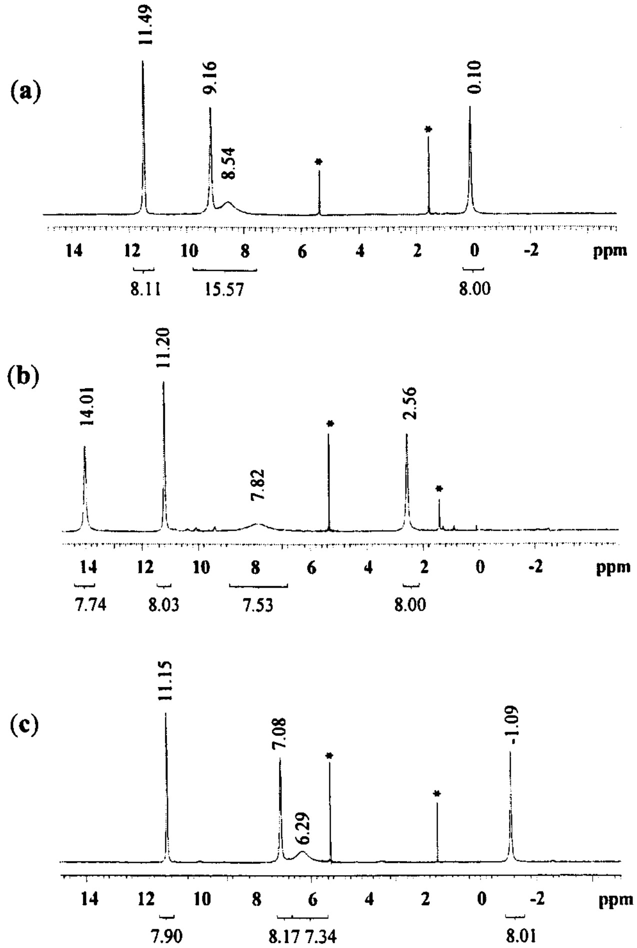

Figure 5. ^1H NMR spectra of (a) **5**, (b) **6**, and (c) **7** in CD_2Cl_2 at ambient temperature. The starred peaks correspond to the solvent.

were reported to be 2.06(1) and 2.07(1) Å, quite comparable to the present Co−NCS distances, which lie in the range 2.04−2.06 Å.

As noted briefly in the Introduction, the $Co_3(dpa)_4Cl_2$ molecule has shown a remarkable variability of structure, depending on temperature for a given solvate but also varying from one solvate to another. The range of this variability is shown by the data summarized in Table 12 of the preceding paper.[3b] In the case of $Co_3(dpa)_4(NCS)_2$ we have examined three differently solvated crystals and found them all to contain symmetrical molecules.

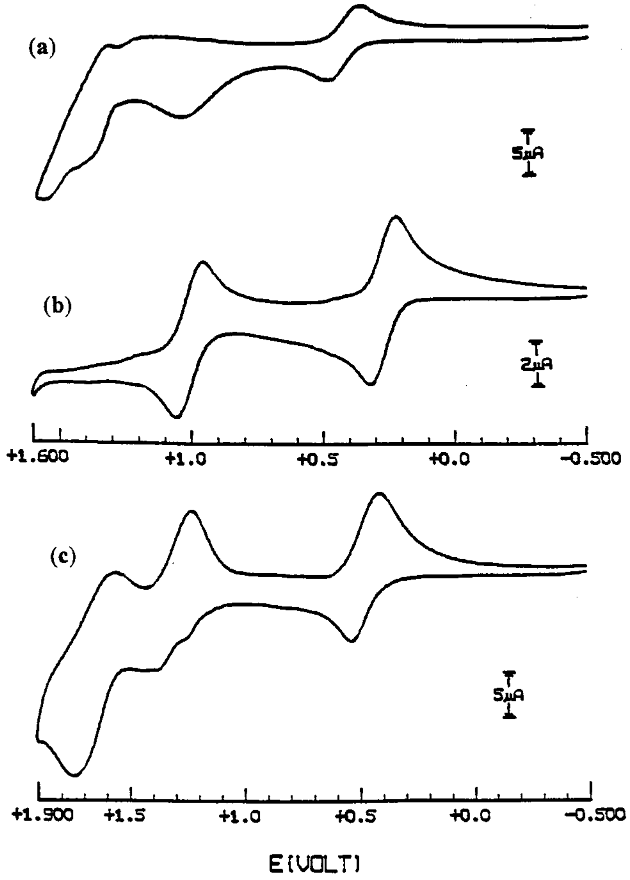

Figure 6. Cyclic voltammogram (CV) of (a) **5**, (b) **6**, and (c) **7** in CH_2Cl_2 solution.

The molecules of $Co_3(dpa)_4(CN)_2$, **6**, and $Co_3(dpa)_4(NCNCN)_2$, **7**, are shown in Figures 3 and 4 and metrical results given in Tables 4 and 5, respectively. Again, the molecules are symmetrical. For **6** the symmetrical character is crystallographically required and both Co−Co distances are 2.3392(2) Å. In **7**, equality is not imposed crystallographically and the two distances refined to slightly different values, 2.3194(8) and 2.3184(8) Å, but the apparent difference is not statistically significant.

On the basis of the structural results reported here, it appears that only the $Co_3(dpa)_4X_2$ compounds with X = Cl and Br have a tendency to display unsymmetrical Co_3 chains. Of course in

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(17) Wang, C.-C.; Lu, W.-C.; Chou, C.-C.; Lee, G.-H.; Chem, J.-M.; Peng, S.-M. *Inorg. Chem.* **1998**, *37*, 4059.

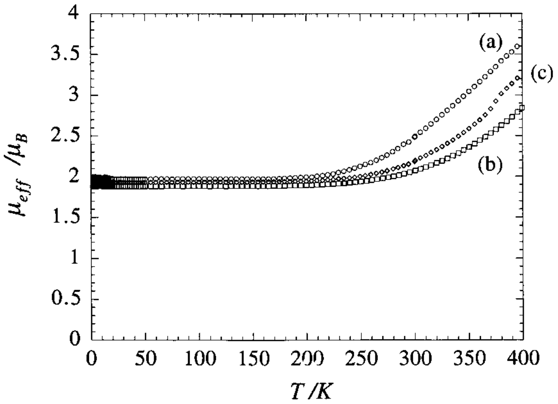

Figure 7. Temperature dependence of the effective magnetic moment measured in the solid state for (a) **5**·1.5CH_2Cl_2, (b) **6**·CH_2Cl_2, and (c) **7**·2CH_2Cl_2.

cases where the axial ligands are not identical, the Co_3 chains are always markedly unsymmetrical. It is interesting that, among the $Cr_3(dpa)_4X_2$ compounds, the *only* ones that are symmetrical are those with X = Cl.[18] The entire question of symmetrical versus unsymmetrical structures in this class of compounds remains very much open, and we plan to look into it further.

Turning now to other characteristics of **5**, **6**, and **7**, we discuss first their ^{1}H NMR spectra, which are shown in Figure 5. As in the case of $Co_3(dpa)_4Cl_2$,[2d] all three new compounds display spectra in which there are only four lines, consistent with their structures being symmetrical in solution. In none of the three are the lines shifted as far downfield as they were in the case of $Co_3(dpa)_4Cl_2$. In addition, the pattern of these spectra is quite different from that for $Co_3(dpa)_4Cl_2$, where, by means of a COSY spectrum, we were able to make an unambiguous assignment of the lines. It does not appear possible to do that here because no multiplet structure has been so far resolved on any of the lines.

As shown in Figure 6, all three new compounds are electrochemically active. Of primary interest is the fact that each one is easily subjected to a one-electron oxidation. This is particularly so for $Co_3(dpa)_4(CN)_2$, which also appears to have a second more or less reversible oxidation that might be achieveable chemically. In view of the interesting behavior of the $[Co_3(dpa)_4Cl_2]^+$ ion[19] we hope in the future to isolate and study a compound containing the $[Co_3(dpa)_4(CN)_2]^+$ ion, and perhaps even the $[Co_3(dpa)_4(CN)_2]^{2+}$ ion.

Magnetic Susceptibility Measurements. These were performed on a polycrystalline sample of each of the following: **5**·1.5CH_2Cl_2, **6**·CH_2Cl_2, and **7**·2CH_2Cl_2. As shown in Figure 7, the magnetic behavior for all three compounds is quite similar. The μ_{eff} is essentially constant between 1.8 and 200 K with values of 2.02, 1.87, and 1.93 μ_B for **5**·1.5CH_2Cl_2, **6**·CH_2Cl_2, and **7**·2CH_2Cl_2, respectively. These data are consistent with the presence of a doublet ground state with a *g* value between 2.2 and 2.3 as observed for similar compounds of this family.[3] Temperature dependence of the magnetization at 1.8 K can be fitted to the expected Brillouin equation, for an $S = \epsilon$ system, which allows us to evaluate more precisely the *g* values: 2.293(5), 2.212(5), and 2.205(5) for **5**·1.5CH_2Cl_2, **6**·CH_2Cl_2, and **7**·2CH_2Cl_2, respectively. At low temperature (between 1.8 and 10 K), the absence of a slight decrease of the effective moment indicates the absence of antiferromagnetic interactions between Co_3 units contrary to what was observed in **1**,[3] **2**,[7] and **4**.[8] Above 200 K, the magnetic behavior of all compounds in this series is again very similar: the effective moment increases gradually without reaching saturation even at 400 K. This temperature dependence has already been observed for a spin-crossover process in other compounds of this family.[3,7,8,19] It is worth noting that measurements done by decreasing or increasing the temperature did not reveal any hysteresis effect. The partial spin-crossover behavior observed up to 400 K (the thermal limit of our equipment) prevents us from assigning unambiguously the high-spin state of these materials, which could be ${}^{3}/_{2}$ or ${}^{5}/_{2}$. Nevertheless, these new series of linear trinuclear Co species with axially coordinated ligands open new possibilities for the design of cooperative spin-crossover systems. Our work is currently devoted to interconnecting these trinuclear units with di- or polycyanide linkers and thus to try to convert the often observed spin-crossover shown by numerous compounds of this family above 200 K into a tunable collective spin transition that may have a detectable memory effect around room temperature.

Acknowledgment. We thank the National Science Foundation for financial support and Prof. K. R. Dunbar for her assistance with the magnetic studies.

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

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[18] Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Murillo, C. A.; Pascual, I. *Inorg. Chem.* **2000**, *39*, 3065.

[19] Clérac, R.; Cotton, F. A.; Dunbar, K. R.; Lu, T.; Murillo, C. A.; Wang, X. *J. Am. Chem. Soc.* **2000**, *122*, 2272.