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New Linear Tricobalt Complex of Di(2-pyridyl)amide (dpa), $[Co_3(dpa)_4(CH_3CN)_2][PF_6]_2$[†]

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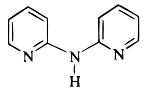
Reaction of the linear tricobalt compound $Co_3(dpa)_4Cl_2$ (**1**) (dpa = di(2-pyridyl)amide) with silver hexafluorophosphate in acetonitrile yields $[Co_3(dpa)_4(CH_3CN)_2][PF_6]_2$ (**2**). Two crystalline forms are obtained from the same solution, namely, a monoclinic ($P2_1$) form $\mathbf{2}\cdot CH_3CN\cdot 2Et_2O$ and a triclinic ($P\bar{1}$) form, $\mathbf{2}\cdot 3CH_3CN$. The tricobalt units in both crystals are essentially symmetrical, though this is not required by crystal symmetry, with Co−Co distances in the range 2.298−2.304 Å. Each of the two terminal Co atoms is coordinated to an acetonitrile molecule with Co−N distances in the range 2.068−2.111 Å at 213 K. The spiral arrangement of ligands gives an overall idealized D_4 point group symmetry for the cation $[Co_3(dpa)_4(CH_3CN)_2]^{2+}$. Chiral crystals of both Δ and Λ configurations in the $P2_1$ form have been isolated. The absolute configurations were determined by X-ray crystallography and their mirror-image circular dichroism spectra measured. The D_4 symmetry of the cation appears to be preserved in solution as judged by the presence of only five proton resonance signals in the ^1H NMR spectrum. Magnetic susceptibility measurements in the solid state indicates that **2** has a doublet ground state and exhibits an increase of the effective moment at high temperature (∼160 K) due to a spin crossover process.

Introduction

The versatile chemical and physical properties of polynuclear transition metal complexes have generated interest in the areas of molecule-based electronic,[1] photochemical,[2] and magnetic[3] materials. Understanding the metal to metal interactions in these polynuclear complexes is pivotal for the rational design and synthesis of molecules with intended properties. We are especially interested in a class of linear trinuclear complexes supported by the anion of di(2-pyridyl)amine, dpa (**I**). In the early 1990s, it was reported that the dpa ligand could organize divalent metal atoms, especially Cu(II) [4] and Ni(II),[5] into linear trimetallic units within a spiral arrangement of the ligands. Since then, many compounds of the type $M_3(dpa)_4X_2$, where X is a monoanion and M = Co,[6,7] Cr,[8] Rh,[9] and Ru,[7] have been synthesized and their structures have been determined by X-ray crystallography.



Hdpa (**I**)

One remarkable feature of this class of compounds is the tunable metal to metal interactions within the linear trinuclear unit.[10] In most cases, the $M_3(dpa)_4X_2$ molecule has a symmetrical arrangement of metal atoms. Molecules with a tricobalt[6,7] or trichromium[8] core may be symmetrical or unsymmetrical depending on the composition of the crystal, the nature of the axial ligands, and the crystallization conditions. The tendency of the chromium chains to form unsymmetrical molecules has been attributed to the favorable formation of a quadruple bond between two adjacent d^4 Cr^{2+} atoms, which leaves the third Cr^{2+} atom in a five-coordinate square-pyramidal environment. The one-electron oxidation of the Cr_3^{6+} core to Cr_3^{7+} produces only unsymmetrical $[Cr_3(dpa)_4Cl_2]^+$ species[8d] in which a terminal Cr^{3+} ion is isolated from the metal−metal bonded Cr_2^{4+} unit. For the tricobalt compound $Co_3(dpa)_4Cl_2$ (**1**) there are "bond stretch" isomers[11] that can be isolated from the same solution as crystals in either symmetrical *s*-$Co_3(dpa)_4Cl_2$ or unsymmetrical *u*-$Co_3(dpa)_4Cl_2$ forms (Chart 1).[12] The

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[†] Dedicated to the memory of Professor Olivier Kahn.

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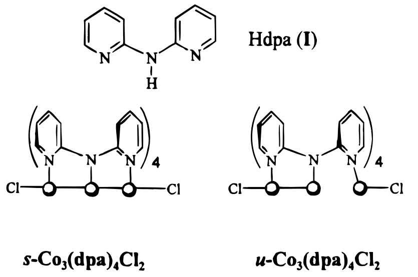
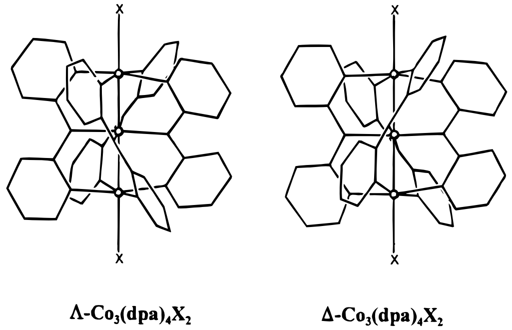
Chart 1



s-$Co_3(dpa)_4Cl_2$ *u*-$Co_3(dpa)_4Cl_2$

Chart 2



Λ-$Co_3(dpa)_4X_2$ Δ-$Co_3(dpa)_4X_2$

former has metal−metal bonding delocalized over the three cobalt atoms,[13] whereas the latter has a singly bonded Co_2^{4+} unit and a separated Co^{2+} ion. In the solid state, these isomers exhibit a doublet ground state at low temperatures. When the temperature is increased, the two forms undergo gradual one-step spin crossover processes to higher spin states. Because the spin crossover process is incomplete when the sample begins to lose solvent molecules at 350 K, it is difficult to assign unambiguously the nature of the high-spin state ($S = {}^3/_2$ or $S = {}^5/_2$).[14] Chemical oxidation of **1** produced the cation $[Co_3(dpa)_4Cl_2]^+$ that has a ground state with $S = 0$. This undergoes a two-step spin crossover in which the spin state changes from $S = 0$ to $S = 1$ and then to $S = 2$ in the temperature range 1.8−350 K.[15]

An important feature in the class of $M_3(dpa)_4X_2$ compounds is their typical helical arrangement of the four dpa ligands about the M_3 unit. While the set of four ligands has the capacity to organize a linear chain of metal atoms, it is also forced by the internal nonbonded (H···H) contacts to form an overall molecular structure with a helical configuration having right- or left-handed helicity (designated Δ or Λ, respectively), as shown in Chart 2. Up to now, the isolated products have been racemic mixtures of right- and left-handed species, and crystal structures have shown an equal number of molecules of each enantiomer.

We report here the preparation a new tricobalt compound $[Co_3(dpa)_4(CH_3CN)_2][PF_6]_2$ (**2**) in which the terminal ligands are neutral. Both Λ and Δ enantiomers with the composition **2**·CH_3CN·Et_2O have been isolated as single crystals, and their absolute configurations have been determined by X-ray crystallography. It has been possible to measure the CD spectra of both enantiomers and to assign each one to the correct enantiomers. This new linear tricobalt compound has also been characterized by other spectroscopic as well as electrochemical methods in solution. Results from magnetic susceptibility measurements have provided additional information on the nature of the spin crossover process of **2** in the solid state.

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. Silver hexafluorophosphate was purchased from Strem Chemicals, Inc. Di(2-pyridyl)amine was purchased from Aldrich and sublimed prior to use; $Co_3(dpa)_4Cl_2$ (**1**) was prepared according to a previously published procedure.[6]

Physical Measurements. ^{1}H NMR spectra of **2** were recorded on a Varian UnityPlus 300 instrument at 300 MHz, with chemical shifts being referenced to CD_3CN (1.95 ppm). The electronic absorption spectra were measured on a Cary 17 spectrophotometer. Circular dichroism (CD) spectra were recorded at ambient temperature on an AVIV model 62A DS spectropolarimeter. X-band EPR spectra in frozen dichloromethane solution were recorded on a Bruker model ESP 300 spectrometer equipped with an Oxford Instruments ESR 900 cryostat (4.2−300 K). Cyclic voltammetry was performed in acetonitrile solution with a BAS model 100 scanning potentiostat using Pt working and auxiliary electrodes and 0.1 M $[n\text{-}Bu_4N][PF_6]$ 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 $E_{1/2}$ are taken as $(E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

The magnetic susceptibility data were obtained on a polycrystalline sample (60.3 mg) with the use of a Quantum Design, model MPMS-5, superconducting quantum interference device (SQUID) magnetometer housed in the Department of Physics and Astronomy at Michigan State University; data were collected from 1.8 to 350 K at a field of 1000 G. The magnetic susceptibility data were corrected for the sample holder contribution and for the intrinsic diamagnetic contribution, which was estimated experimentally at -5×10^{-4} emu mol^{-1}. This value is in excellent agreement with the value of -7×10^{-4} calculated from Pascal's constants.[16]

Preparation of 2·CH_3CN·2Et_2O and 2·3CH_3CN. Acetonitrile (25 mL) was added to a solid mixture of $Co_3(dpa)_4Cl_2$·CH_2Cl_2 (0.31 g, 0.30 mmol) and $AgPF_6$ (0.16 g, 0.62 mmol) in a 100 mL flask. The suspended solids slowly dissolved, giving a brown solution. The mixture was stirred for 2 h during which time a white precipitate, presumably AgCl, had formed. This was removed by filtration through Celite to give a dark-brown solution. Slow diffusion of Et_2O into the CH_3CN solution yielded crystals of **2**·CH_3CN·2Et_2O and **2**·3CH_3CN. From the bottom of the tube, a large number of block-shaped crystals of **2**·3CH_3CN were isolated. Along the wall of the tube, a small number of rectangular platelets of **2**·CH_3CN·2Et_2O were collected. The combined yield for **2** is ca. 90%. Samples for spectroscopic studies were dried under vacuum to remove interstitial solvent molecules. No difference between the two forms was detected by any of the spectroscopic methods employed. IR (KBr, cm^{-1}): 2270 (w), 1603 (s), 1554 (w), 1473 (s), 1431 (s), 1373 (s), 1314 (m), 1283 (m), 1246 (w), 1157 (s), 1113 (w), 1021 (m), 839 (br, s), 761 (m), 738 (m), 557 (m), 518 (w), 459 (w), 428 (w). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 10.47 (s, 8H), 3.51 (d, 8H, $^2J_{HH} = 6.6$ Hz), 2.89 (s, 6H, CH_3CN), −2.87 (t, 8H). UV/vis (CH_3CN), λ (nm): 312 ($\epsilon = 57\,700$ M^{-1} cm^{-1}), 369 (sh) ($\epsilon = 14\,720$ M^{-1} cm^{-1}), 442 ($\epsilon = 4865$ M^{-1} cm^{-1}), 544 ($\epsilon = 2432$ M^{-1} cm^{-1}).

X-ray Crystallography. Each crystal was mounted on the top of a quartz fiber with a small amount of silicone grease and transferred to a goniometer head for data collection. Geometric and intensity data for Λ-**2**·CH_3CN·2Et_2O and **2**·3CH_3CN and were gathered on a Nonius FAST area detector system at 213 K, utilizing the program MADNES.[17]

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Table 1. Crystal Data and Structure Refinement for *rac*-**2**·$3CH_3CN$, Λ-**2**·CH_3CN·$2Et_2O$, and Δ-**2**·CH_3CN·$2Et_2O$

compound	*rac*-**2**·$3CH_3CN$	Λ-**2**·CH_3CN·$2Et_2O$	Δ-**2**·CH_3CN·$2Et_2O$
empirical formula	$C_{50}H_{47}Co_3F_{12}N_{17}P_2$	$C_{50}H_{61}Co_3F_{12}N_{15}O_2P_2$	$C_{50}H_{61}Co_3F_{12}N_{15}O_2P_2$
fw	1352.78	1370.87	1370.87
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	$P2_1$ (No. 4)
a, Å	12.498(2)	11.7576(7)	11.721(2)
b, Å	12.5101(5)	21.9059(6)	21.801(3)
c, Å	19.913(1)	12.0621(5)	12.027(5)
α, deg	99.072(4)	90	90
β, deg	104.152(7)	111.883(3)	111.93(2)
γ, deg	101.106(7)	90	90
V, Å^3	2893.0(5)	2882.9(2)	2851(1)
Z	2	2	2
temp (K)	213	213	163
d_{calcd}, g cm^{-3}	1.553	1.579	1.597
R indices [$I > 2\sigma(I)$], R1,[a] wR2[b]	0.061, 0.152	0.043, 0.114	0.043, 0.110
R indices (all data), R1,[a] wR2[b]	0.068, 0.159	0.044, 0.116	0.055, 0.117

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

Cell parameters were obtained from an autoindexing routine and were refined with 250 strong reflections within a 2θ range of 18.1−41.6°. Single-crystal X-ray work of Δ-**2**·CH_3CN·$2Et_2O$ was performed on a Nonius CAD4 diffractometer at 163 K. Detailed procedures have previously been described.[18] Unit-cell refinement for Δ-**2**·CH_3CN·$2Et_2O$ utilized 25 strong reflections in the 2θ range of 30.2°− 40.0°. Cell dimensions and Laue symmetry for all crystals were confirmed from axial photographs. All data were corrected for Lorentz and polarization effects.

For each of the three data sets the positions of the heavy atoms were found using the direct methods program in SHELXTL.[19] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Details of data collection and refinement are given in Table 1. Selected distances and angles are listed in Table 2. Other crystallographic data are given as Supporting Information.

Results and Discussion

Synthesis and Crystal Structures. The reaction of $Co_3(dpa)_4Cl_2$ (**1**) with silver hexafluorophosphate in acetonitrile solution yields $[Co_3(dpa)_4(CH_3CN)_2][PF_6]_2$ in which the axially coordinated halide atoms are replaced by acetonitrile molecules, the charge being compensated by PF_6^- anions:

$$Co_3(dpa)_4Cl_2 + 2AgPF_6 + 2CH_3CN = [Co_3(dpa)_4(CH_3CN)_2][PF_6]_2 + 2AgCl \quad (1)$$

It is noteworthy that the silver ions do not oxidize the tricobalt unit under the reaction conditions used here, although oxidation of a Co_2(benzamidinate)$_4$ complex by $AgPF_6$ is known to occur.[20] The coordination of acetonitrile molecules is consistent with the IR band observed at 2270 cm^{-1}. Compound **2** crystallizes from the same solution as two different solvates, namely, a chiral $P2_1$ form, **2**·CH_3CN·$2Et_2O$, and a centrosymmetric $P\bar{1}$ form, **2**·$3CH_3CN$. Long plate-shaped crystals of the chiral monoclinic form in either Δ or Λ configurations were isolated as minor products. Structures of the Δ and Λ enantiomers were determined by single-crystal X-ray crystallography at 163 and 213 K, respectively. A triclinic form **2**·$3CH_3CN$ crystallizes as block-shaped crystals in large quantity, and its structure was determined at 213 K.

A drawing of the dication Δ-$[Co_3(dpa)_4(CH_3CN)_2]^{2+}$ in **2**·CH_3CN·$2Et_2O$ is shown in Figure 1; selected bond distances and angles are listed in Table 2. The dication resides on a crystallographic general position with two independent Co(1)−Co(2), Co(2)−Co(3) distances of 2.301(1), 2.299(1) Å for the Δ isomer at 163 K and 2.300(1), 2.298(1) Å for the Λ isomer at 213 K. These very similar distances confirm the symmetrical arrangement of the three cobalt atoms in the cation. The exact equality cannot be expected because the site of the central atom does not demand it. The terminal Co atoms are also coordinated to acetonitrile molecules at the axial positions. The averaged Co−N_{axial} distances of 2.087 Å for Δ-**2** and 2.107 Å for Λ-**2** are consistent with a single bond between the terminal Co and N atoms.

In the centrosymmetric $P\bar{1}$ form, compound **2** is found as a racemate, *rac*-**2**, with an equal amount of Δ and Λ isomers, as shown in Figure 2. The tricobalt unit is again effectively symmetrical with distances between the Co atoms of 2.301(1) and 2.304(1) Å, and distances of 2.068(5), 2.090(5) Å for the two terminal Co−N bonds (Table 2). In summary, all three data sets for compound **2** show essentially symmetrical arrangements of the three cobalt atoms (with averaged Co−Co distances of 2.301 Å). These values are only about 0.017 Å shorter than those observed in *s*-$Co_3(dpa)_4Cl_2$ (averaged 2.318 Å).[6,12,14] It appears that the change of axial coordination from chloride ions to acetonitrile molecules has very little effect on the bonding interactions among the metal atoms.

NMR Spectra. As for **1**, the acetonitrile-substituted product **2** is paramagnetic in solution and in the solid state. The existence of "bond stretch isomers" of **1** in the solid state[12,14] suggests that the difference in energy between the symmetrical and unsymmetrical molecules is small. A small change in the crystallization conditions may lead to a significant variation of metal-to-metal distances. If the "bond stretch isomers" exist in solution, more than one species could perhaps be observed by methods such as ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **2** is shown in Figure 3. It consists of only five signals centered at 10.47, 3.52, 2.91, 2.14, −2.86 ppm that are shifted significantly upfield compared to those of the chloride compound **1**, which were found at 47.96, 33.21, 15.96, and 16.78 ppm.[21] The

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Table 2. Selected Bond Distances (Å) and Angles (deg) for *rac*-**2**·3CH$_3$CN, Λ-**2**·CH$_3$CN·2Et$_2$O, and Δ-**2**·CH$_3$CN·2Et$_2$O

compound	*rac*-**2** (213 K)	Λ-**2** (213 K)	Δ-**2** (163 K)
Co(1)−Co(2)	2.301(1)	2.300(1)	2.301(1)
Co(2)−Co(3)	2.304(1)	2.298(1)	2.299(1)
Co(1)−N(1)	1.984(5)	1.985(5)	1.977(5)
Co(1)−N(4)	1.971(5)	1.966(5)	1.962(5)
Co(1)−N(7)	1.992(5)	1.984(5)	1.976(5)
Co(1)−N(10)	1.960(5)	1.980(5)	1.985(5)
Co(2)−N(2)	1.895(5)	1.892(5)	1.891(5)
Co(2)−N(5)	1.898(5)	1.902(4)	1.898(5)
Co(2)−N(8)	1.894(5)	1.897(4)	1.885(5)
Co(2)−N(11)	1.899(5)	1.891(5)	1.895(5)
Co(1)−N(13)	2.068(5)	2.111(5)	2.099(6)
Co(3)−N(3)	1.985(5)	1.978(5)	1.982(5)
Co(3)−N(6)	1.978(5)	1.980(5)	1.979(5)
Co(3)−N(9)	1.986(5)	1.966(4)	1.961(5)
Co(3)−N(12)	1.972(5)	1.973(5)	1.982(5)
Co(3)−N(14)	2.090(5)	2.089(5)	2.076(5)
N(13)−C(41)	1.131(7)	1.118(8)	1.100(9)
N(14)−C(43)	1.104(8)	1.133(8)	1.141(9)
C(41)−C(42)	1.460(9)	1.46(1)	1.47(1)
C(43)−C(44)	1.46(1)	1.46(1)	1.47(1)
Co(3)−Co(2)−Co(1)	179.25(4)	179.24(5)	179.25(4)
N(13)−Co(1)−Co(2)	177.5(1)	179.3(2)	179.2(2)
N(14)−Co(3)−Co(2)	179.8(1)	178.9(2)	178.3(2)
N(4)−Co(1)−N(1)	88.7(2)	88.4(2)	88.4(2)
N(1)−Co(1)−N(7)	90.6(2)	91.2(2)	91.6(2)
N(10)−Co(1)−N(1)	170.9(2)	170.7(2)	170.5(2)
N(1)−Co(1)−N(13)	92.8(2)	94.2(2)	94.3(2)
N(4)−Co(1)−N(7)	171.3(2)	170.7(2)	170.2(2)
N(10)−Co(1)−N(4)	89.9(2)	89.2(2)	89.1(2)
N(4)−Co(1)−N(13)	94.9(2)	95.3(2)	95.6(2)
N(10)−Co(1)−N(7)	89.4(2)	89.6(2)	89.2(2)
N(10)−Co(1)−N(13)	96.3(2)	95.0(2)	95.0(2)
N(8)−Co(2)−N(2)	89.2(2)	89.8(2)	90.0(2)
N(2)−Co(2)−N(5)	90.5(2)	90.2(2)	90.1(2)
N(2)−Co(2)−N(11)	179.4(2)	179.9(2)	179.4(2)
N(8)−Co(2)−N(5)	179.6(2)	179.7(2)	179.8(3)
N(5)−Co(2)−N(11)	90.1(2)	89.8(2)	90.1(2)
N(7)−Co(1)−N(13)	93.8(2)	93.9(2)	94.1(2)
N(8)−Co(2)−N(11)	90.2(2)	90.1(2)	89.8(2)
N(6)−Co(3)−N(3)	89.6(2)	88.9(2)	89.5(2)
N(3)−Co(3)−N(9)	89.2(2)	89.8(2)	89.6(2)
N(12)−Co(3)−N(3)	170.7(2)	170.7(2)	170.4(2)
N(6)−Co(3)−N(9)	171.1(2)	170.8(2)	170.7(2)
N(12)−Co(3)−N(6)	89.6(2)	90.7(2)	90.4(2)
N(12)−Co(3)−N(9)	90.2(2)	89.1(2)	89.1(2)
N(3)−Co(3)−N(14)	94.7(2)	95.6(2)	96.4(2)
N(6)−Co(3)−N(14)	94.2(2)	94.3(2)	94.2(2)
N(9)−Co(3)−N(14)	94.7(2)	95.0(2)	95.0(2)
N(12)−Co(3)−N(14)	94.6(2)	93.7(2)	93.1(2)
Co(1)−N(1)−N(3)−Co(3)	50.1(2)	−49.4(2)	49.4(2)
Co(1)−N(4)−N(6)−Co(3)	49.1(2)	−50.1(2)	50.6(2)
Co(1)−N(7)−N(9)−Co(3)	48.7(2)	−51.1(2)	51.6(2)
Co(1)−N(10)−N(12)−Co(3)	49.5(2)	−51.7(2)	51.9(2)

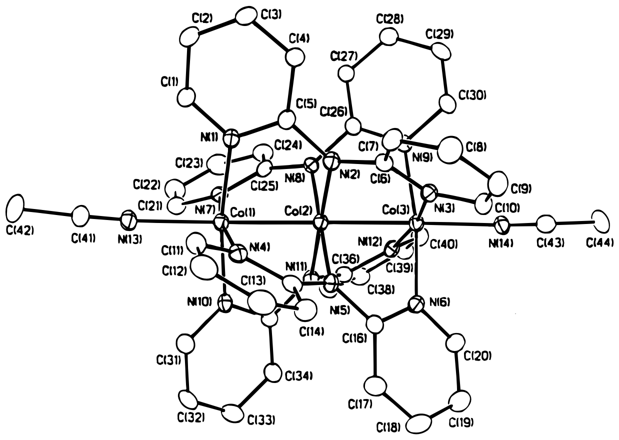

Figure 1. Perspective view of the [Co$_3$(dpa)$_4$(CH$_3$CN)$_2$]$^{2+}$ cation in Δ-**2**·CH$_3$CN·2Et$_2$O at 163 K. Atoms are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

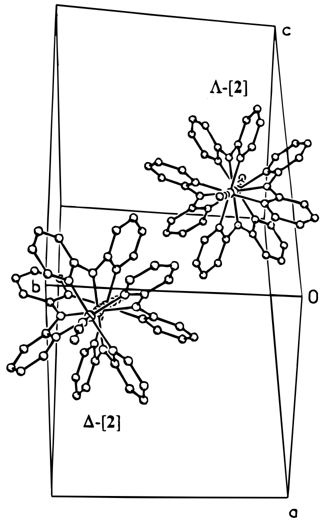

Figure 2. Disposition of the cations Δ- and Λ-[Co$_3$(dpa)$_4$(CH$_3$CN)$_2$]$^{2+}$ in the unit cell of the centrosymmetric space group *P*1 for *rac*-**2**·3CH$_3$CN.

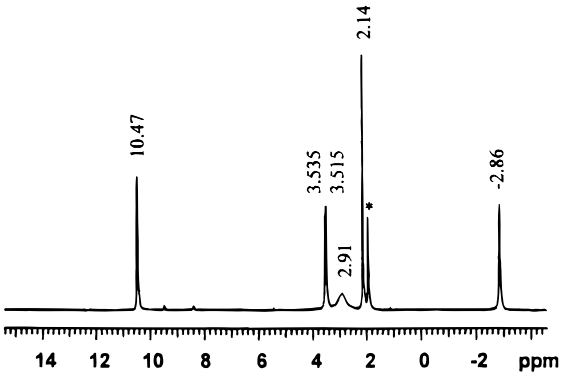

Figure 3. ^{1}H NMR spectrum of **2** in CD$_3$CN at ambient temperature. The starred peak corresponds to the solvent.

upfield shifts of the NMR signals for **2** are probably due to the cationic nature of the tricobalt unit. The peak for the coordinated acetonitrile molecules at 2.14 ppm is clearly separated from the solvent signal at 1.95 ppm, indicating that if there is exchange of acetonitrile molecules between the cation [Co$_3$(dpa)$_4$(CH$_3$CN)$_2$]$^{2+}$ and free acetonitrile molecules in solution, it is slow on the NMR time scale. The other four signals are from the pyridyl groups of the dpa ligands. There are a total of 32 protons on the ligands that coordinate to the tricobalt core. The fact that only four peaks of the ligands are observed in the ^{1}H NMR spectrum is consistent with the D_4 symmetry of the cation [Co$_3$(dpa)$_4$(CH$_3$CN)$_2$]$^{2+}$ in solution, though oscillation between unsymmetrical structures that is fast on the NMR time scale cannot be ruled out.

EPR Spectroscopy. Figure 4 shows the X-band EPR spectrum of compound **2** in acetonitrile glass at 5 K. It shows one isotropic resonance with a g factor of 2.31, which is consistent with the expected $S = {}^1/_2$ ground state for the [Co$_3$(dpa)$_4$(CH$_3$CN)$_2$]$^{2+}$ core. This g value is very close to that of 2.35 observed for **1** in a dichloromethane glass,[21] and it is

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

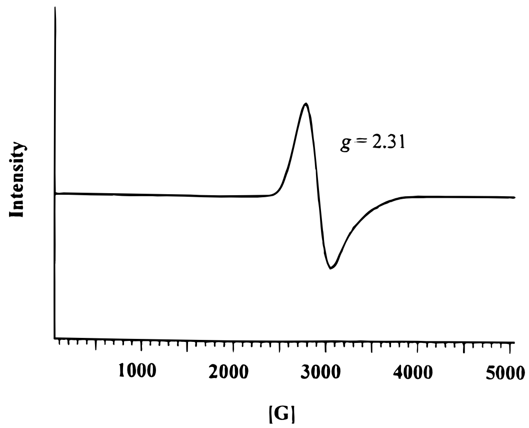

Figure 4. X-band EPR spectrum of **2** in CH_3CN at 5 K.

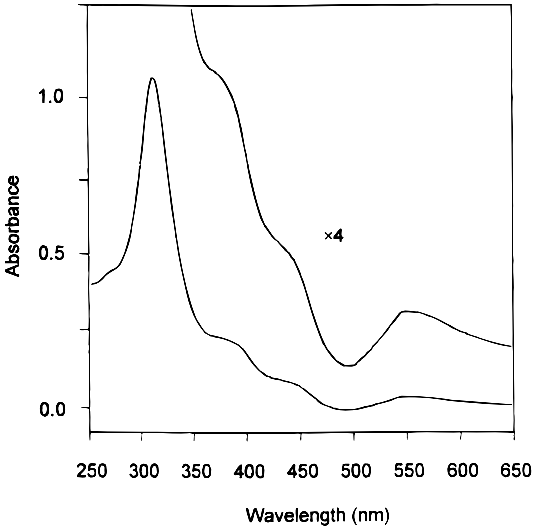

Figure 5. Electronic spectrum of **2** in CH_3CN at room temperature.

also in agreement with that obtained from SQUID measurements in which a doublet ground state is found (vide infra). The similarity of the EPR spectra of **1** and **2** is also consistent with the symmetrical structure observed in the solid state in both cases.

Electronic Spectra. The electronic absorption spectrum of **2** is shown in Figure 5. There are four bands in the UV/vis region. Although there is no rigorous theoretical treatment available at present for the electronic spectra of tricobalt compounds, the origin of the transitions can be assigned tentatively by comparing the spectra with that of the ligand and mononuclear dpa complexes. The high-intensity band at 312 nm is similar to that displayed by the free ligand[22] and is assigned as a spin-allowed $\pi-\pi^*$ transition. The shoulder at 369 nm is likely to be a charge-transfer band. The lower energy absorption bands at 442 and 544 nm are essentially the same for both **1** and **2** and can thus be assigned to metal-centered transitions in the Co_3^{6+} core.

Circular Dichroism Spectra. Enantiomerically pure crystals of **2** were isolated from solution as either Λ or Δ isomers, and their absolute configurations were determined by X-ray crystallography on individual crystals. Both isomers exhibit significant Cotton effects as evidenced by the strong signals obtained in the circular dichroism (CD) spectra shown in Figure 6. The ratio of circular dichroic to isotropic absorbance ($\Delta\epsilon/\epsilon$), also called anisotropy or dissymmetry factor,[23] is associated with the nature of transitions. For electric dipole allowed and magnetic dipole forbidden transitions (CT and ligand $\pi-\pi^*$ transitions), the $\Delta\epsilon/\epsilon$ factor is equal to or less than 5×10^{-3} ($\Delta\epsilon/\epsilon \leq 5 \times 10^{-3}$); for magnetic dipole allowed and electric dipole forbidden transitions (ligand field transitions, $n-\pi^*$ transitions), $\Delta\epsilon/\epsilon \geq 5 \times 10^{-3}$. The transition for the Λ isomer at 312 nm has a negative sign ($\Delta\epsilon/\epsilon = 8.2 \times 10^{-4}$) in the CD spectrum, while the bands at 369 nm ($\Delta\epsilon/\epsilon = 1.5 \times 10^{-3}$), 442 nm ($\Delta\epsilon/\epsilon = 8.25 \times 10^{-3}$), and 544 ($\Delta\epsilon/\epsilon = 5.0 \times 10^{-3}$) nm are positive. The CD spectrum for the Δ isomer has mirror symmetry relative to that of the Λ isomer, as expected for a pair of enantiomers. The CD bands at 312 and 369 nm have small $\Delta\epsilon/\epsilon$ values with the former corresponding to a ligand $\pi-\pi^*$ transition and the latter corresponding to a LMCT transition. Both are electric dipole allowed and magnetic dipole forbidden transitions. The greater dissymmetry factor $\Delta\epsilon/\epsilon$ for the bands at 442 and 544 nm indicates these two bands are magnetic dipole allowed and electric dipole forbidden metal-centered transitions. The fact that crystals of **2** with different absolute configurations exhibit CD spectra of essentially the same intensity but opposite signs indicates that the two enantiomers do not interconvert in solution.

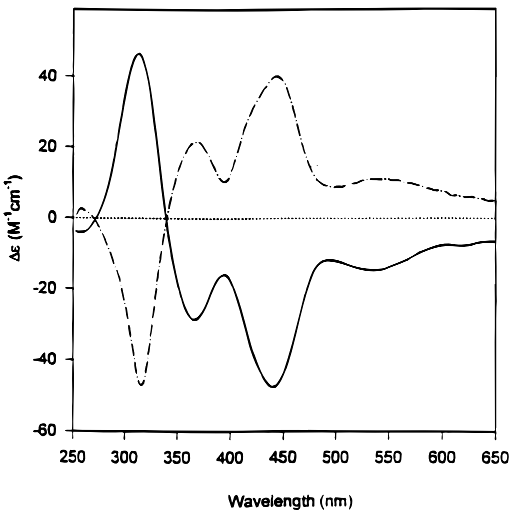

Figure 6. CD spectra of individual single crystals of Δ-**2** (solid line) and Λ-**2** (dashed line) in CH_3CN solution.

Electrochemical Properties. Compound **2** was investigated by cyclic voltammetry; the result is shown in Figure 7. The cyclic voltammogram of **2** displays a reversible one-electron wave at $E_{1/2}(\text{ox})_1 = +0.60$ V, which is about 0.28 V higher than that for **1**,[15] and an irreversible wave at $E_{1/2}(\text{ox})_2 = +1.40$ V in the range +1.6 to −0.2 V. The first $E_{1/2}$ value is unaffected in the scan-rate range 25−1000 mV s^{-1}, as judged by the fact that the peak current is proportional to the square root of the scan rate, as expected for a reversible process. Work is in progress in our laboratory to chemically oxidize **2** with the hope of isolating the one-electron-oxidized product.

Magnetic Susceptibility Measurements. These were performed on a polycrystalline sample of the racemic compound. As the plot in Figure 8 indicates, μ_{eff} is constant at 2.1 μ_B between 50 and 150 K. These data are consistent with the presence of a doublet ground state for the tricobalt unit with a g value of 2.4, as observed for similar compounds in this family.[14] At lower temperatures, the slight decrease of the

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(22) Huang, W.-L.; Segers, D. P.; DeArmond, M. K. *J. Phys. Chem.* **1981**, *85*, 2080.

(23) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994.

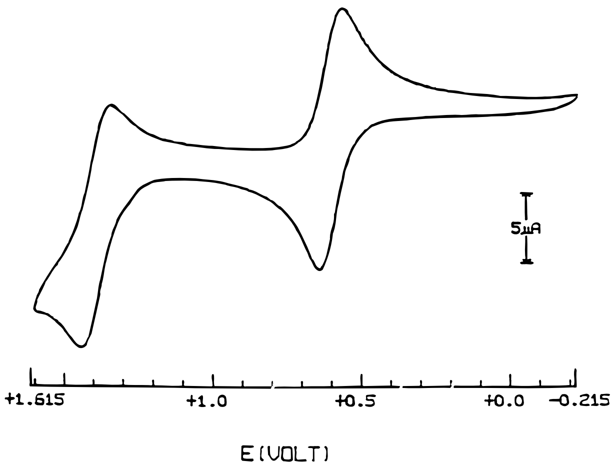

Figure 7. Cyclic voltammogram (CV) of **2** (5.0×10^{-4} M) in acetonitrile solution.

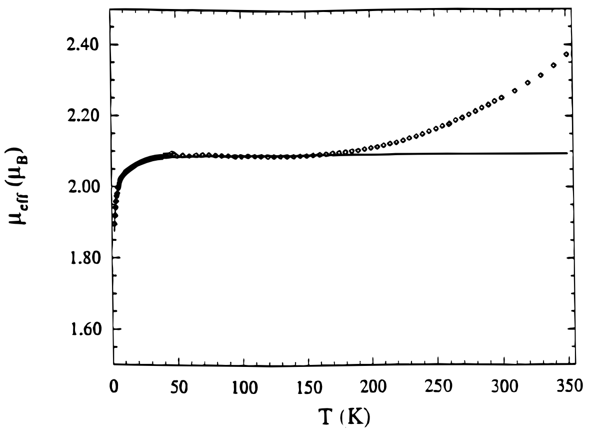

Figure 8. Temperature dependence of the effective magnetic moment measured in the solid state for **2** (○, experimental data; −, fitted results).

effective moment reveals the presence of weak antiferromagnetic interactions between the tricobalt cations. A Curie−Weiss fitting (Figure 8, solid line) of the experimental data between 1.8 and 160 K allows for an estimation of these magnetic interactions (J) of -0.3 K^{-1}.[24] Above 160 K, the effective magnetic moment increases gradually without any saturation at 350 K. This behavior, which is typical for a spin crossover process, has already been observed for **1**[14,21] and for other compounds in this family.[14] The lack of saturation at 350 K (the temperature limit of our equipment) for **2** prevents an evaluation of the high-temperature state.

Conclusions

Substitution of the axial chloride ligands of the linear tricobalt compound $Co_3(dpa)_4Cl_2$ (**1**) by acetonitrile molecules produces the corresponding dication $[Co_3(dpa)_4(CH_3CN)_2]^{2+}$ in high yield. Chiral crystals of the linear tricobalt compound $[Co_3(dpa)_4(CH_3CN)_2][PF_6]_2$ (**2**) in either Λ or Δ configuration were isolated, and their absolute structures were determined by X-ray crystallography. The chirality of the molecules of **2** was confirmed by measuring corresponding solution CD spectra. In addition, compound **2** also crystallizes as a racemic mixture containing both Λ and Δ isomers. In all cases, the isolated compound has a symmetrical arrangement of the tricobalt unit in solution and in the solid state. The symmetrical structure of the cation is consistent with delocalized bonding over the three Co atoms. The magnetic measurements on **2** in the solid state show that the ground state of the tricobalt unit is $S = {}^1/_2$, the same as that observed for **1**. They also show that for **2** there is a state of higher spin that is partially populated at higher temperatures. Unfortunately, even at 350 K, the extent of this population is too small to permit us to determine either the spin state or the energy above the ground state.

Acknowledgment. The authors thank the National Science Foundation for financial support.

Supporting Information Available: X-ray crystallographic data in CIF format for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Intermolecular interactions between the tricobalt units have been estimated from the spin Hamiltonian

$$H = -2J\sum_{i,j} S_i S_j$$

where J is the exchange parameter and S_i, S_j are the magnetic spin of the Co_3 unit ($S = {}^1/_2$). At low field and below 150 K, the temperature dependence of the susceptibility is very well described by the Curie−Weiss law $\chi = C/(T - \theta)$, where C is the Curie constant and θ the Weiss constant. The molecular field theory yields an estimation of the magnetic exchange J from θ: $J = 2\theta/z$, where z is the number of nearest neighbors, which is 3 from the crystal structure.