Inorg. Chem. **2000,** *39,* 1039−1041 **1039**

A Dinuclear Cation with Both Four- and Five-Coordinate Cobalt(II)

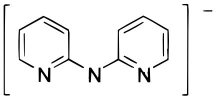
F. Albert Cotton,*,[†] Carlos A. Murillo,*,[†,‡] and Hong-Cai Zhou[†]

The Laboratory for Molecular Structure and Bonding,
Department of Chemistry, P.O. Box 30012,
Texas A&M University, College Station, Texas 77842-3012,
and Escuela de Química, Universidad de Costa Rica,
Ciudad Universitaria, Costa Rica

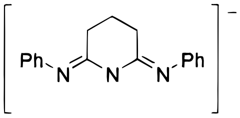
Received October 8, 1999

Introduction

As described in many other publications[1] from this laboratory we are exploring the use of suitable polydentate ligands to cause the formation of linear chains of metal atoms wherein direct contact between the metal atoms is facilitated. Most of our recent work has focused on chains of three metal atoms, and the ligand we have used most is the anion of di(2-pyridyl)amine, dpa$^-$ (**I**). However, we have also been exploring the use of other tridentate ligands, one of which is the anion of 2,6-(diphenylimino)piperidine, DPhIP$^-$ (**II**). Several dichromium compounds of this ligand have already been reported,[2] and reports on a number of other metals are in preparation. In attempting to employ this ligand to form complexes containing two or three Co^{II} atoms, we obtained some unexpected and novel results, which are presented here.



I



II

Experimental Section

General Procedures. All syntheses and sample manipulations were carried out under an atmosphere of nitrogen with standard Schlenk and glovebox techniques. The compound HDPhIP (2,6-diphenyliminopiperidine) was synthesized according to a literature method.[3] Methyllithium (1.0 M solution in THF/cumene) was purchased from Aldrich Chemical Co. Anhydrous $CoCl_2$ and $TlPF_6$ were purchased from Strem Chemicals. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

Preparation of $[Co_2(DPhIP)_3][Co(HDPhIP)Cl_3]\cdot CH_3CN$, 1. The compound H(DPhIP) (0.53 g, 2.0 mmol) was dissolved in THF (15 mL) and cooled to −78 °C, and $^3/_4$ of it was deprotonated by BuLi (1.6 M in hexanes, 0.9 mL, 1.4 mmol). The resulting pale-yellow solution was evacuated to dryness and mixed with anhydrous $CoCl_2$ (0.20 g, 1.54 mmol) in a drybox. Acetonitrile (15 mL) was then added to the mixture under nitrogen; the suspension became blue first, and then green while being stirred at room temperature. The green suspension was heated at reflux temperature for 2 h; the dark green solution obtained was filtered while hot, and the filtrate was cooled to room temperature and layered with diethyl ether. Dark-green prismatic crystals of **1** were obtained. Yield: 0.28 g (41%). IR (KBr, cm^{-1}): 1636 (w), 1617 (w), 1577 (w), 1566 (w), 1534 (vs), 1510 (m), 1445 (s), 1412 (m), 1355 (m), 1319 (w), 1262 (w), 1223 (m), 1190 (m), 1151 (w), 1077 (w), 1027 (w), 969 (w), 933 (w), 908 (w), 857 (w), 795 (m), 759 (m), 713 (m), 694 (m), 676 (w), 657 (w), 605 (w), 507 (w), 473 (w). Anal. Found: C, 59.36; H, 4.83; N, 12.18. Calcd: C, 61.17; H, 4.99; N, 13.25.

Preparation of $[Co_2(DPhIP)_3](PF_6)Li(THF)_3(PF_6)$, 2. A solution of Li(DPhIP) prepared by neutralizing a THF solution of H(DPhIP) (0.53 g, 2.0 mmol) with MeLi in THF (1.0 M, 2.2 mL, 2.2 mmol) was added to a mixture of $CoCl_2$ (0.23 g, 1.8 mmol) and $TlPF_6$ (1.4 g, 4.0 mmol), and a dark gray suspension was obtained. It was heated at reflux temperature for 3 h and allowed to stand overnight. After filtration, the dark green filtrate was layered with hexanes, and a crop of green prismatic crystals of **2** was obtained after 5 days of diffusion. Yield: 0.63 g (67%). IR (KBr, cm^{-1}): 1578 (w), 1537 (vs), 1498 (w), 1450 (s), 1412 (m), 1359 (m), 1324 (w), 1260 (w), 1227 (m), 1191 (m), 1154 (w), 1072 (w), 1046 (w), 1028 (w), 1003 (w), 972 (w), 842 (vs), 796 (m), 760 (m), 713 (m), 694 (w), 604 (w), 558 (m), 504 (w), 405 (w). Anal. Found: C, 51.20; H, 4.87; N, 8.68. Calcd: C, 53.36; H, 5.12; N, 8.89.

Preparation of $[Co_2(DPhIP)_3]_2(CoCl_4)\cdot 2CH_2Cl_2$, 3. The compound H(DPhIP) (0.53 g, 2.0 mmol) in THF (10 mL) was deprotonated with an equivalent amount of MeLi (1.0 M in THF), and anhydrous $CoCl_2$ (0.20 g, 1.5 mmol) was added. The blue green suspension was heated at reflux temperature for 14 h, and the color of the mixture turned to dark green. The resulting green solid was then collected by filtration, washed with 2 × 5 mL of THF, and dissolved in CH_2Cl_2 (15 mL). The green solution obtained was then layered with hexanes. Green prismatic crystals of **3** were obtained after 1 week. Yield: 0.15 g (23%). IR (KBr, cm^{-1}): 1686 (w), 1672 (w), 1655 (w), 1638 (w), 1618 (w), 1578 (w), 1533 (br, vs), 1452 (br, s), 1411 (m), 1355 (s), 1262 (m), 1227 (s), 1191 (s), 1152 (w), 1073 (w), 1026 (w), 970 (w), 933 (w), 908 (w), 856 (w), 794 (br, vs), 760 (m), 714 (s), 694 (vs), 622 (w), 603 (w), 507 (w). Anal. Found: C, 57.06; H, 4.63; N, 11.59. Calcd: C, 57.29; H, 4.62; N, 11.56.

Crystallographic Studies. Data collection for compounds **1** and **3** was carried out on a Nonius Fast area detector diffractometer with each crystal mounted on the tip of a glass fiber under a stream of nitrogen at −60 °C. Cell parameters were obtained by least-squares refinement of 250 reflections ranging in 2θ from 15° to 41°. Laue groups and centering conditions were confirmed by axial images. Data were collected using 0.2° intervals in ϕ for the range $0° < \phi < 220°$ and 0.2° intervals in ω for two different regions in the range $0° < \omega < 72°$. In this way, nearly a full sphere of data was collected. The highly redundant data sets were corrected for Lorentz and polarization effects. For compound **1**, the program SORTAV[4] was used to correct for absorption.

Data collection for compound **2** was performed on a Nonius CAD4 diffractometer at −115 °C, and an empirical absorption correction based on ψ-scans was applied.

[†] Texas A&M University.

[‡] University of Costa Rica.

(1) (a) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV. *Chem. Commun.* **1997**, 421. (b) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *J. Am. Chem. Soc.* **1997**, *119*, 10223. (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.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Chem. Commun.* **1998**, 39. (e) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *Inorg. Chem. Commun.* **1998**, *1*, 1. (f) Cotton, F. A.; Murillo, C. A.; Wang, X. *Inorg. Chem. Commun.* **1998**, *1*, 281. (g) Cotton, F. A.; Daniels, L. M.; Lu, T.; Murillo, C. A.; Wang, X. *J. Chem. Soc., Dalton Trans.* **1999**, 517. (h) Clérac, R.; Cotton, F. A.; Dunbar, K. R.; Murillo, C. A.; Pascual, I.; Wang, X. *Inorg. Chem.* **1999**, *38*, 2655.

(2) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I.; Zhou, H.-C. *J. Am. Chem. Soc.* **1999**, *121*, 6856.

(3) Elvidge, J. A.; Linstead, R. P.; Salaman, A. M. *J. Chem. Soc.* **1959**, 208.

(4) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

10.1021/ic991186+ CCC: $19.00

Table 1. Crystal Data and Structure Refinement

	1	**2**	**3**
chemical formula	$C_{70}H_{68}N_{13}Cl_3Co_3$	$C_{63}H_{72}N_9O_3F_{12}P_2Co_2Li$	$C_{104}H_{100}N_{18}Cl_8Co_5$
fw	1375.51	1418.04	2180.27
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	15.8538(8)	16.904(3)	19.2680(7)
b, Å	13.4781(4)	17.328(4)	20.562(7)
c, Å	31.912(2)	23.828(5)	27.777(7)
α, deg	90	98.21(3)	74.784(6)
β, deg	103.044(3)	99.91(3)	76.97(1)
γ, deg	90	105.84(3)	75.95(2)
V, Å^3	6642.9(5)	6480(2)	10146(4)
Z	4	4	4
T, °C	−60(2)	−115(2)	−60(2)
radiation λ, Å	0.71073	0.71073	0.71073
ρ(calcd), g cm^{-3}	1.374	1.453	1.427
μ(Mo Kα), cm^{-1}	9.13	6.48	10.68
R1[a]	0.044	0.061	0.117
wR2[b]	0.110	0.165	0.327

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. Denotes value of the residual considering only the reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. Denotes value of the residual considering all the reflections.

Table 2. Bond Distances and Angles for Three Crystallographically Independent $[Co_2(DPhIP)_3]^+$ Units

1		**2**			
four-coordinate Co−N (Å)	1.972(3)	Co(1)−N(1)	1.963(5)	four-coordinate Co−N (Å)	1.960(5)
	1.974(3)	Co(1)−N(9)	1.977(5)		1.969(5)
	2.028(3)	Co(1)−N(5)	2.031(5)		2.038(5)
	2.108(3)	Co(1)−N(4)	2.099(5)		2.082(5)
five-coordinate Co−N (Å)	2.027(3)	Co(2)−N(6)	1.997(6)	five-coordinate Co−N (Å)	2.009(5)
	2.032(3)	Co(2)−N(8)	2.007(5)		2.030(6)
	2.063(3)	Co(2)−N(3)	2.029(5)		2.034(5)
	2.168(3)	Co(2)−N(2)	2.210(5)		2.196(5)
	2.347(3)	Co(2)−N(7)	2.254(6)		2.224(5)
four-coordinate N−Co−N (deg)	64.3(1)	N(5)−Co(1)−N(4)	64.4(2)	four-coordinate N−Co−N (deg)	64.5(2)
	110.7(1)	N(1)−Co(1)−N(9)	110.7(2)		112.1 (2)
	110.8(1)	N(9)−Co(1)−N(4)	113.7(2)		112.7(2)
	117.3(1)	N(1)−Co(1)−N(4)	116.5(2)		114.4(2)
	118.2(1)	N(1)−Co(1)−N(5)	117.9(2)		116.1(2)
	121.4(1)	N(9)−Co(1)−N(5)	125.5(2)		126.8(2)
five-coordinate N−Co−N (deg)	60.4(1)	N(8)−Co(2)−N(7)	62.2(2)	five-coordinate N−Co−N (deg)	62.3(2)
	62.9(1)	N(3)−Co(2)−N(2)	62.7(2)		62.8(2)
	102.5(1)	N(6)−Co(2)−N(7)	99.3(2)		101.8(2)
	106.3(1)	N(3)−Co(2)−N(7)	103.0(2)		103.9(2)
	106.4(1)	N(8)−Co(2)−N(2)	104.6(2)		104.5(2)
	109.0(1)	N(6)−Co(2)−N(2)	106.7(2)		104.8(2)
	111.3(1)	N(6)−Co(2)−N(3)	115.3(2)		110.9(2)
	112.3(1)	N(8)−Co(2)−N(3)	121.5(2)		124.4(2)
	136.4(1)	N(6)−Co(2)−N(8)	122.7(2)		124.5(2)
	144.4(1)	N(2)−Co(2)−N(7)	153.8(2)		153.2(2)

The positions of the cobalt atoms and their first coordination spheres were determined by direct methods and refined by using the program SHELXL-93. All non-hydrogen atoms were found by successive iterations of least-squares refinement followed by Fourier syntheses and, during the final cycles, were refined anisotropically. Hydrogen atoms were placed in idealized positions, and a common thermal parameter was refined.

Crystallographic data for **1**−**3** are given in Table 1. Selected bond distances and angles for three crystallographically independent $Co_2(DPhIP)_3^+$ cations (one in **1**, two in **2**) are found in Table 2.

Structural Details

The $[Co_2(DPhIP)_3]^+$ ion has an uncommon structure in which there are one four-coordinate Co^{II} and one five-coordinate Co^{II} held in proximity, but not close enough for any bonding interaction between the two (Figure 1). Neither coordination sphere is very regular, but the four-coordinate one is much closer to tetrahedral than to planar, and the five-coordinate one is closer to trigonal bipyramidal than to square pyramidal. Major distortions are unavoidable because of the four-membered chelate rings that are incorporated into each coordination sphere. In each of these there must be N−Co−N angles of only 60−65°.

The structural studies have provided details of seven crystallographically independent $Co_2(DPhIP)_3^+$ cations, one in **1**, two in **2**, and four in **3**. All are essentially congruent, and for purposes of explicit discussion we chose one of them (the one with Co(1) and Co(2)) in **2**. While the N−Co(1)−N angles range from 64.4(2)° to 125.5(2)°, it is still reasonable to describe the coordination polyhedron as a distorted tetrahedron. The most extreme deviations from the ideal tetrahedral angle can be traced to the extremely small angle within the four-membered chelate ring. The critical distinction favoring the tetrahedron as the ideal structure of reference is the fact that there are two N−Co−N planes that are approximately perpendicular; dihedral angle N(4)−Co(1)−N(5)/N(1)−Co(1)−N(9) = 95(1)°.

As for the geometry about Co(2), there are three essentially equal Co−N bond lengths (1.997(6), 2.007(5), and 2.029(5) Å) that are coplanar with angles of 115.3(2)°, 121.5(2)°, and 122.7(2)°. These bonds define the equatorial plane of a trigonal

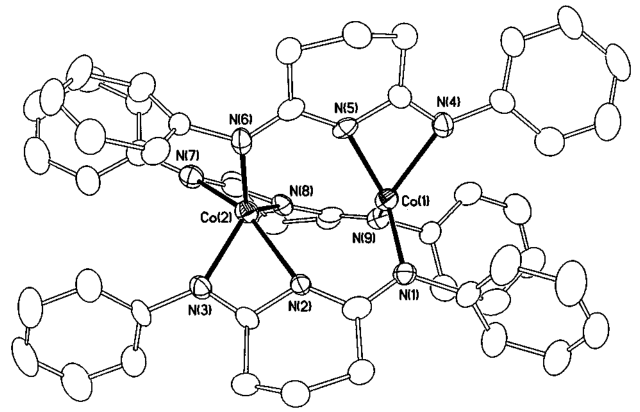


Figure 1. Drawing of the molecular structure of one of the two $[Co_2(DPhIP)_3]^+$ units in **2**. Displacement ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

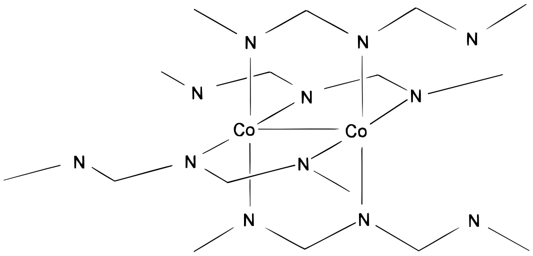
bipyramid. The other two Co(2)−N bonds are much longer (2.21 and 2.25 Å) and make an angle of 153.8(2)°. The major distortions from idealized D_{3h} symmetry are again caused by the small (62−63°) angles within the two chelate rings.

Discussion

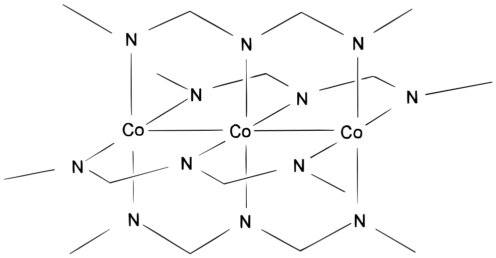
The motivation for this work was the hope of preparing either a compound with a pair of directly bonded Co^{II} atoms, **A**, or one with a chain of three Co^{II} atoms, **B**. In fact the only products we have been able to isolate and characterize are compounds containing the cation **C**.

Failure to obtain **B** is only moderately surprising in view of previous experience with other metals. In the case of chromium,[2] compounds of type **A** were obtained, with a quadruply bonded Cr_2 unit. However, there were significant interactions of the dangling nitrogen atoms with the π^* orbitals of the Cr_2^{4+} unit: not sufficient to break the Cr−Cr bond, but sufficient to weaken and hence lengthen it to 2.265(1) Å. In the case of $Mo_2(DPhIP)_4$ a structure of type **A** was also obtained,[5] but because of the great strength of the Mo to Mo quadruple bond, the four dangling nitrogen atoms simply dangle and have no significant effect on it. In these cases, the metal to metal bonds are strong enough to resist the possibility of being broken in order to allow the formation of four more metal to nitrogen bonds. We know that such a structural change is sterically possible because of the existence of $Cr_2(DPhIP)_4^{2+}$ containing compounds in which each chromium atom is in a distorted octahedron of nitrogen atoms.[6]

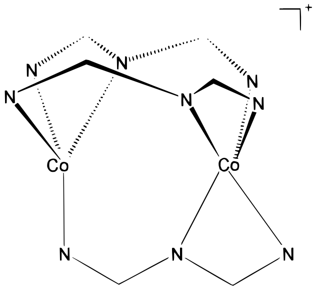
Moreover, in the case of cobalt, the two metal atoms simply forego the possibility of adding one more DPhIP ligand, which would allow the formation of three more Co−N bonds. It is not obvious why. Thus we have this very unusual cation, $Co_2(DPhIP)_3^+$, in which there are one Co^{II} in a distorted tetrahedron of nitrogen atoms and another Co^{II} in a very distorted trigonal bipyramid of nitrogen atoms. Occurrences like this are seldom easy to explain, especially because several paddlewheel compounds containing Co−Co singly bonded units surrounded by four amidinate ligands and metal to metal distances of 2.265(2)−2.3735(9) Å have been prepared.[7] These distances are similar to those found for the dichromium complex mentioned earlier.[2]



A



B



C

We have also shown that three amidinate groups are capable of sustaining metal to metal bonds in Co_2^+ units; the distances range from 2.3201(9) to 2.385(1) Å.[8] Oxidation of such complexes gave non-metal−metal-bonded dicobalt cations having three amidinate bridges and an acetonitrile molecule on each pseudotetrahedral cobalt atom.[8] The Co−N (amidinate) distances of 1.924(8)−1.989(7) Å in such types of complexes are very similar to those of the four-coordinate cobalt atoms of the cations reported here which are found to be ca. 2.0 Å (see Table 2). As expected, the Co−N distances for the five-coordinate Co atoms are longer.

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for support.

Supporting Information Available: Fully labeled figures of compounds **1**−**3** and one X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991186+

---

(5) Cotton, F. A.; Murillo, C. A.; Roy, L. E.; Zhou, H.-C. *Inorg. Chem.*, accepted.

(6) Cotton, F. A.; Murillo, C. A.; Zhou, H.-C. Unpublished results.

(7) Cotton, F. A.; Daniels, L. M.; Feng, X.; Maloney, D. J.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 291.

(8) Cotton, F. A.; Daniels, L. M.; Maloney, D. J.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 283.