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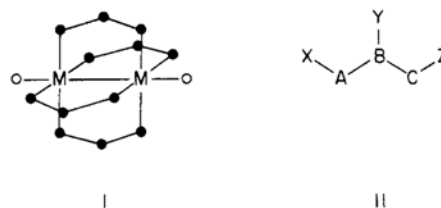
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**Synthesis and Molecular Structure of a Dinuclear  
Quadruply Bridged Cobalt(II) Compound with a Short  
Metal–Metal Bond,  $\text{Co}_2[(p\text{-CH}_3\text{C}_6\text{H}_4)\text{NNN}(p\text{-C}_6\text{H}_4\text{CH}_3)]_4$**

Sir:

There are many environments of ligand atoms in which M–M bonds of order 1–4 may exist,<sup>1</sup> but undoubtedly the type of most

general importance is that shown schematically in I. The  $\text{M}_2$

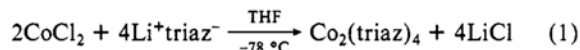


unit is embraced by a set of four bent, triatomic, bidentate ligands, usually carrying a charge of –1 (or –2), arranged in a paddle-wheel or lantern pattern. There may also be two additional ligands in axial positions, but not necessarily. A more detailed but general representation of the bidentate ligand is II. The commonest ligands are carboxylate ions, but other important ones include amido anions,  $\text{RNC}(\text{R}')\text{O}^-$ , amidinato ions,  $\text{RNC}(\text{R}')\text{NR}'^-$ , triazenato ions, which are usually of the symmetrical type,  $\text{RNNNR}^-$ , and yet others.

It is well-known that because of the different electronic properties of these ligands they have quite different effects on the stabilities, oxidation potentials, spectra, etc. of the  $\text{M}_2$  unit they encapsulate. As a generalization, the more basic ligands, viz.  $\text{RNNNR}^- \approx \text{RNC}(\text{R}')\text{NR}^- > \text{RNC}(\text{R}')\text{O}^- > \text{OC}(\text{R})\text{O}^-$ , seem to lend greater stability to a given  $\text{M}_2^{4+}$  unit; i.e., they strengthen the metal–metal interaction and also stabilize it in higher oxidation states.<sup>2</sup>

In recent work from this laboratory, we have exploited this property to obtain new  $\text{M}_2$  compounds of the type  $\text{M}_2[(p\text{-CH}_3\text{C}_6\text{H}_4)\text{NCHN}(p\text{-C}_6\text{H}_4\text{CH}_3)]_4^{n+}$ , with  $\text{M} = \text{Ni}, \text{Pd}, \text{Ir}$  and  $n = 0, 1, 3, 4$ . We have attempted to employ the same ligand to synthesize the corresponding cobalt compound, but without success. However, we can now report that with the  $(p\text{-CH}_3\text{C}_6\text{H}_4)\text{-NNN}(p\text{-C}_6\text{H}_4\text{CH}_3)^-$  ligand the dicobalt(II) compound has been prepared and characterized chemically and structurally.

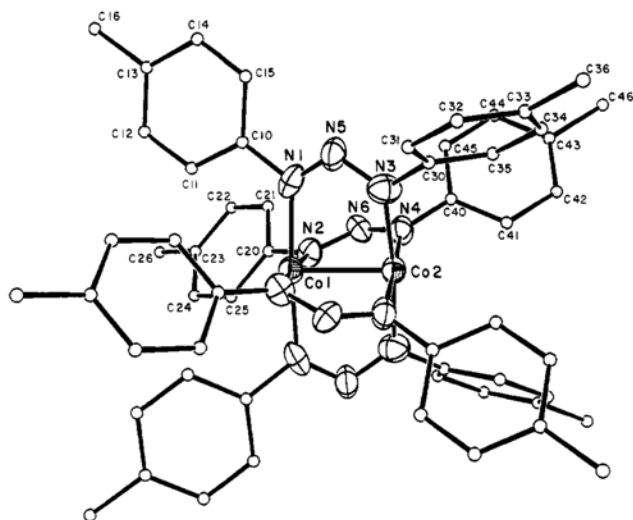
Low-temperature (–78 °C) interaction of anhydrous  $\text{CoCl}_2$  with 2 equiv of  $\text{Li}^+\text{triaz}^-$ , where  $\text{triaz}^- = (p\text{-CH}_3\text{C}_6\text{H}_4)\text{NNN}(p\text{-C}_6\text{H}_4\text{CH}_3)^-$ , prepared in situ from Htriaz and  $n\text{-BuLi}$ , in THF as solvent, immediately afforded  $\text{Co}_2(\text{triaz})_4$  (eq 1) as a brown microcrystalline solid that contains interstitial THF molecules.



These are easily lost (at least partially) upon separation of the solid from its mother liquor, and an accurate elemental analysis could not therefore be obtained.

The  $^1\text{H}$  NMR spectrum taken on a vacuum-dried sample indicates that this is a diamagnetic compound with a formula close to  $\text{Co}_2(\text{triaz})_4 \cdot 7\text{THF}$ .<sup>3</sup> The product is fairly stable at room temperature, although long storage of solid samples and of its solutions under argon at the laboratory temperature resulted in the production of blue insoluble material, presumably oligomeric  $\text{Co}(\text{triaz})_2$  containing tetrahedrally coordinated cobalt(II) ions. It is extremely sensitive to moisture, with decomposition to Htriaz and  $\text{Co}(\text{OH})_2$ , as shown by IR spectroscopy. Recrystallization

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- (5) Spectral data for  $\text{Co}_2(\text{triaz})_4 \cdot 7\text{THF}$  is as follows.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 6.86 (dd,  $\text{C}_6\text{H}_4$ , 32 H), 3.46 (s, br, ca. 30 H), 1.97 (s,  $\text{CH}_3$ , 24 H), 1.32 (s, br, ca. 26 H). Weak peaks at 9.43 (s), 7.50 (s, br), and 2.19 (s) were also present and were attributed to free Htriaz. IR (Nujol mull,  $\text{cm}^{-1}$ ): 3020 m, 1605 m, 1500 s, 1410 w, 1380 w, 1300 vs, 1260 vs, 1165 w, 1110 w, 1045 m, 1010 w, 890 w, 825 ms, 755 w, 715 w, 660 m, 625 w, 525 m, 495 w.



**Figure 1.** ORTEP view of the  $\text{Co}_2(\text{triaz})_4$  molecule in  $\text{Co}_2(\text{triaz})_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ . The tolyl carbon atoms have been drawn with arbitrary radii, and hydrogen atoms have been omitted for the sake of clarity. Relevant structural parameters are as follows:  $\text{Co1-Co2}$ , 2.265 (2) Å;  $\text{N1-Co1-Co2-N3}$ , 17.7 (4)°;  $\text{N2-Co1-Co2-N4}$ , 16.2 (4)°.

from concentrated toluene solutions afforded X-ray-quality crystals of  $\text{Co}_2(\text{triaz})_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ .<sup>6</sup>

The dinuclear molecule has imposed  $C_2$  symmetry, with the two cobalt atoms lying on the crystallographic twofold axis. The geometry is that typical of the quadruply bridged  $\text{M}_2^{4+}$  dimers as represented in I. Because of the steric crowding caused by the tolyl groups around the axial positions, no axial ligation is observed. A view of the molecule is shown in Figure 1. The crystal structure is completed by interstitial toluene molecules that occupy general positions. The separation between the two  $d^7$  cobalt ions is 2.265 (2) Å and is consistent with full pairing of the electrons in a  $\sigma^2\pi^4\delta^2\delta^*\pi^*4$  MO scheme, as expected on a qualitative basis.<sup>1</sup> A carboxylato compound,  $\text{Co}_2(\text{O}_2\text{CPh})_4(\text{NC}_9\text{H}_9)$ , containing axial quinoline ligands, is the only other structurally characterized compound of cobalt with a structure of type I, and it has a metal-metal separation of 2.832 (2) Å.<sup>7</sup> This and other related carboxylato compounds show magnetic properties consistent with through-the-bridge antiferromagnetic exchange.<sup>8,9</sup> Another ion that can be considered as having a metal-metal interaction between  $\text{Co}(\text{II})$  centers, although of a different structure, is  $[\text{Co}_2(\text{CN})_{10}]^{6-}$ , with a metal-metal separation reported as 2.798 (2)<sup>10</sup> and 2.794 (2) Å<sup>11</sup> in the salt  $\text{Ba}_3[\text{Co}_2(\text{CN})_{10}] \cdot 13\text{H}_2\text{O}$ .

A recent theoretical analysis of  $\text{M}_2(\text{form})_4$  ( $\text{M} = \text{Ni}, \text{Pd}$ ;  $\text{form} = (p\text{-CH}_3\text{C}_6\text{H}_4)\text{NCHN}(p\text{-C}_6\text{H}_4\text{CH}_3)$ ) suggests<sup>4</sup> that the ligand-based orbitals interact extensively with the metal  $d$  orbitals that are involved in the metal-metal interaction and this may result for the cobalt compound in a pattern different from the expected  $\sigma^2\pi^4\delta^2\delta^*\pi^*4$  relative ordering. A theoretical investigation of the  $\text{Co}_2(\text{triaz})_4$  compound with the  $X\alpha$ -SCF MO treatment is now in progress and will be reported later.

The molecule of  $\text{Co}_2(\text{triaz})_4$  is twisted away from the eclipsed conformation by (average) 17.0°. The cobalt atoms are displaced from the least-squares planes determined by the nitrogen atoms of the corresponding coordination spheres by (average) 0.07 Å

in the outward direction. These features are common to other compounds of structure I, e.g.  $\text{M}_2(\text{form})_4$  ( $\text{M} = \text{Ni}, \text{Pd}$ ,<sup>4</sup>  $\text{Rh}$ ,<sup>12</sup>  $\text{Ir}^3$ ) and  $\text{M}_2(\text{triaz})_4$  ( $\text{M} = \text{Ni}, \text{Pd}$ ).<sup>13</sup>

In conclusion, we wish to observe that  $\text{Co}_2(\text{triaz})_4$ , because of the lack of axial ligands, exhibits a coordination geometry previously unknown to cobalt(II).

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**Supplementary Material Available:** For the compound  $\text{Co}_2(\text{triaz})_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ , an outline of data collection, structure solution, and refinement and tables of crystal data, atomic fractional coordinates, bond distances and angles, and temperature factors (9 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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- (6) Crystal data for  $\text{Co}_2(\text{triaz})_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ : orthorhombic, space group  $P2_12_12$ ,  $a = 14.977$  (5) Å,  $b = 17.392$  (6) Å,  $c = 11.999$  (2) Å,  $V = 3125$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calcd}} = 1.274$  g·cm<sup>-3</sup>;  $R = 0.0605$ ,  $R_w = 0.0792$  for 1554 data with  $F_o^2 > 3\sigma(F_o^2)$ .
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