unit cell contains a deep-lying $z^2 - y^2$ orbital with two electrons to fill it. Here we calculate virtually no change in $N(E_f)$. Parts a and b of Figure 1 show a computed density of states and their orbital composition for the parent with $\delta = 0$ and a periodic solid for case A (with $\delta = 0.5$). Although the structure at $\delta = 0.5$ is disordered,[7] we find case B, with its linear $\mathrm{Cu^I}$ atoms, to be the more attractive from a chemical point of view.

These ideas then suggested that the real situation is much more complex than that suggested earlier by using a rigid-band model with the $y = 7$ parent. Since the exact location of the $z^2 - y^2$ band relative to $x^2 - y^2$ is open to question (a small parameter change would drop its energy enough to be partially filled at $\delta = 0$), the extent of filling of this band, probably crucial for the superconducting properties, will depend very much on the nature of these defects.

There are other sites that in principle may be associated with the defects. Analysis of these generates pictures that are is very similar for both the $\mathrm{YBa_2Cu_3O_{7-\delta}}$ and $\mathrm{(La,Sr)_2CuO_{4-\delta}}$ systems. Removing a single oxygen atom (O(2) or O(3)) associated with the copper atoms in one of the $\mathrm{CuO_2}$ planes in a $\mathrm{YBa_2Cu_3O_7}$ cell, which is doubled along either *a* or *b* respectively (Case C), will result in a marked drop of the half-full $x^2 - y^2$ orbitals associated with the two atoms to which the oxygen is coordinated (see 3). Since loss of this oxygen atom gives rise to a T-shaped geometry at two copper atoms, with deeper lying and now doubly filled $x^2 - y^2$ and z^2 orbitals there is no change (unless we let the geometry relax) of the Fermi level of the material. (We calculate −11.095eV). Two half-filled orbitals drop below the Fermi level and two extra electrons come via the defect to fill them completely, and from the calculation, $N(E_f)$ is halved. Two $\mathrm{Cu^{II}}$ atoms have now become $\mathrm{Cu^I}$. Removal of every O(2) or O(3) atom along either *a* or *b* respectively in one of the $\mathrm{CuO_2}$ sheets (case D) leads to a single two-coordinate copper atom per doubled cell. Since the $x^2 - y^2$ orbital associated with it drops in energy (3), and is now doubly filled, an extra electron gets added at the Fermi level, which should rise. The effect is half as large as expected on the rigid band model. The Fermi level is computed to lie at −11.787eV for this case. Here is no change in $N(E_f)$. This result is directly applicable to $\mathrm{La_2CuO_{4-\delta}}$. Although it is not exactly clear where the loss of oxygen atoms occurs here, removal of an in-plane oxygen leads to an analysis similar to the one we have just shown. For case A′ (the equivalent of case A above) for $\delta = 0.5$ we show in Figure 1c,d the change in the shape and location of the density of states at the Fermi level. In this arrangement all the copper atoms (now $\mathrm{Cu^I}$) are T-shaped, $x^2 - y^2$ has dropped dramatically as a result (see 3), and the Fermi level has dropped by about 0.5 eV to the top of this band. Thus the presence of in-plane defects in concentrations smaller than those used here just removes levels from the $x^2 - y^2$ band with a corresponding decrease in $N(E_f)$.

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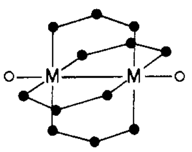
Synthesis and Molecular Structure of a Dinuclear Quadruply Bridged Cobalt(II) Compound with a Short Metal–Metal Bond, $\mathrm{Co_2[(\textit{p}\text{-}CH_3C_6H_4)NNN(\textit{p}\text{-}C_6H_4CH_3)]_4}$

Sir:

There are many environments of ligand atoms in which M–M bonds of order 1–4 may exist,[1] but undoubtedly the type of most general importance is that shown schematically in I. The $\mathrm{M_2}$ 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, $\mathrm{RNC(R')O^-}$, amidinato ions, $\mathrm{RNC(R')NR''^-}$, triazenato ions, which are usually of the symmetrical type, $\mathrm{RNNNR^-}$, and yet others.



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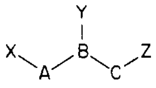

II

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 $\mathrm{M_2}$ unit they encapsulate. As a generalization, the more basic ligands, viz. $\mathrm{RNNNR^-} \approx \mathrm{RNC(R')NR^-} > \mathrm{RNC(R')O^-} > \mathrm{OC(R)O^-}$, seem to lend greater stability to a given $\mathrm{M_2^{4+}}$ unit; i.e., they strengthen the metal–metal interaction and also stabilize it in higher oxidation states.[2]

In recent work from this laboratory, we have exploited this property to obtain new $\mathrm{M_2}$ compounds of the type $\mathrm{M_2[(\textit{p}\text{-}CH_3C_6H_4)NCHN(\textit{p}\text{-}C_6H_4CH_3)]_4^{\textit{n}+}}$, with M = Ni, Pd, 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 $\mathrm{(\textit{p}\text{-}CH_3C_6H_4)NNN(\textit{p}\text{-}C_6H_4CH_3)^-}$ ligand the dicobalt(II) compound has been prepared and characterized chemically and structurally.

Low-temperature (−78 °C) interaction of anhydrous $\mathrm{CoCl_2}$ with 2 equiv of $\mathrm{Li^+triaz^-}$, where triaz = $\mathrm{(\textit{p}\text{-}CH_3C_6H_4)NNN(\textit{p}\text{-}C_6H_4CH_3)}$, prepared in situ from Htriaz and *n*-BuLi, in THF as solvent, immediately afforded $\mathrm{Co_2(triaz)_4}$ (eq 1) as a brown microcrystalline solid that contains interstitial THF molecules.

$$2\mathrm{CoCl_2} + 4\mathrm{Li^+triaz^-} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Co_2(triaz)_4} + 4\mathrm{LiCl} \tag{1}$$

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}H NMR spectrum taken on a vacuum-dried sample indicates that this is a diamagnetic compound with a formula close to $\mathrm{Co_2(triaz)_4{\cdot}7THF}$.[5] 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 $\mathrm{Co(triaz)_2}$ containing tetrahedrally coordinated cobalt(II) ions. It is extremely sensitive to moisture, with decomposition to Htriaz and $\mathrm{Co(OH)_2}$, as shown by IR spectroscopy. Recrystallization

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(5) Spectral data for $\mathrm{Co_2(triaz)_4{\cdot}7THF}$ is as follows. ^{1}H NMR ($\mathrm{C_6D_6}$, δ): 6.86 (dd, $\mathrm{C_6\textit{H}_4}$, 32 H), 3.46 (s, br, ca. 30 H), 1.97 (s, $\mathrm{C\textit{H}_3}$, 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, 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.

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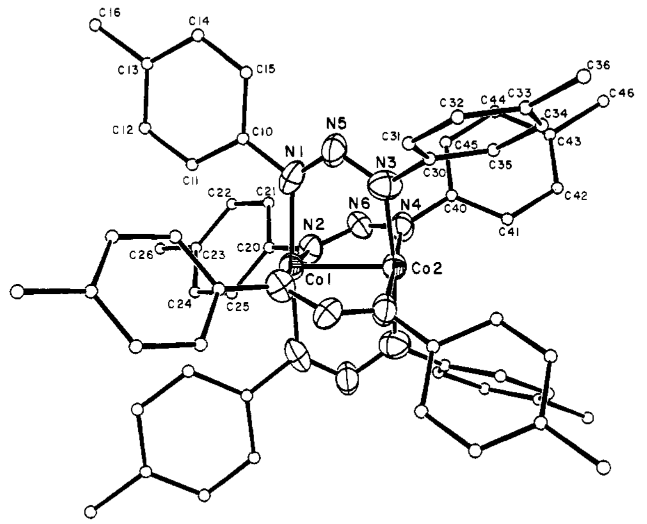

Figure 1. ORTEP view of the $Co_2(triaz)_4$ molecule in $Co_2(triaz)_4 \cdot 2C_6H_5CH_3$. The tolyl carbon atoms have been drawn with arbitrary radii, and hydrogen atoms have been omitted for the sake of clarity. Relevent structural parameters are as follows: Co1-Co2, 2.265 (2) Å; N1-Co1-Co2-N3, 17.7 (4)°; N2-Co1-Co2-N4, 16.2 (4)°.

from concentrated toluene solutions afforded X-ray-quality crystals of $Co_2(triaz)_4 \cdot 2C_6H_5CH_3$.[6]

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 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 $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ MO scheme, as expected on a qualitative basis.[1] A carboxylato compound, $Co_2(O_2CPh)_4(NC_9H_9)$, 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.[7] This and other related carboxylato compounds show magnetic properties consistent with through-the-bridge antiferromagnetic exchange.[8,9] Another ion that can be considered as having a metal–metal interaction between Co(II) centers, although of a different structure, is $[Co_2(CN)_{10}]^{6-}$, with a metal–metal separation reported as 2.798 (2)[10] and 2.794 (2) Å[11] in the salt $Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$.

A recent theoretical analysis of $M_2(form)_4$ (M = Ni, Pd; form = $(p\text{-}CH_3C_6H_4)NCHN(p\text{-}C_6H_4CH_3)$] suggests[4] 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 $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ relative ordering. A theoretical investigation of the $Co_2(triaz)_4$ compound with the Xα-SCF MO treatment is now in progress and will be reported later.

The molecule of $Co_2(triaz)_4$ 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. $M_2(form)_4$ (M = Ni, Pd,[4] Rh,[12] Ir[3]) and $M_2(triaz)_4$ (M = Ni, Pd).[13]

In conclusion, we wish to observe that $Co_2(triaz)_4$, because of the lack of axial ligands, exhibits a coordination geometry previously unknown to cobalt(II).

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: For the compound $Co_2(triaz)_4 \cdot 2C_6H_5CH_3$, 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 $Co_2(triaz)_4 \cdot 2C_6H_5CH_3$: 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^3, Z = 2, d_{calcd} = 1.274 g·cm^{-3}; R = 0.0605, R_w = 0.0792 for 1554 data with $F_o^2 > 3\sigma(F_o^2)$.

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Characterization of $YBa_2(Cu,Ag)_3O_7$ Superconductors

Sir:

The recently discovered Y-Ba-Cu-O superconductor,[1] identified as $YBa_2Cu_3O_{7-x}$ (x < 0.5),[2] has a structure with two distinct types of Cu, formally Cu^{2+} and Cu^{3+}. The Cu is found in CuO_5 pyramids, with Cu slightly displaced from the basal plane (Cu^{2+}), and in CuO_4 squares (Cu^{3+}). The former give rise to Cu–O planes and the latter to Cu–O chains.[3] The idea that this arrangement of planes and chains is crucial for superconducting (SC) behavior finds some support in measurements of electrical anisotropy on single crystals.[4] Indeed, only minor effects have been reported, in terms of SC character, when Y or up to half the Ba was substituted by similar ions.[5] Subsequent work by Veal et al. did, however, show a systematic decrease in T_c in the solid solution $YBa_{2-x}Sr_xCu_3O_7$, with increasing Sr content, and they ascribed this decrease to lattice distortions around the Ba, Sr site, which affect the adjacent Cu–O chains.[6] Also, $YBa_2Cu_3O_6$ was found

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