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[17] As suggested by a referee, this hypothesis can be tested by addition of oxalate to the heterogenized Mn catalyst. This completely stops the dihydroxylation, while some epoxidation still goes on.

# The *gem*-Diol Form of $(py)_2CO$ as a Ligand in Cobalt(II) Carboxylate Clusters: A Cubane Complex and a Novel Nonanuclear Species with a Vertex-Sharing Double Square Pyramidal Structure

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The study of polynuclear complexes of metals in moderate oxidation states has recently begun to lead not only to novel metal polyhedra but also to interesting physical properties. For example, nanosized polyiron and polymanganese complexes with high-spin ground states afford single-domain magnetic particles, which may display hysteresis effects of purely molecular origin.[1] To understand and exploit such phenomena, further examples of high-nuclearity clusters are required, and this is a challenge for the synthetic chemist. Several groups are pursuing routes to such complexes.[2]

We have developed the reaction of metal carboxylates with di-2-pyridyl ketone, $(py)_2CO$, which leads to incomplete replacement of the carboxylate ligands and the formation of large polynuclear arrays of copper[3] and manganese.[4] The structural diversity of these complexes stems from the ability of the singly and doubly deprotonated anions of the *gem*-diol form of $(py)_2CO$ and its derivatives to exhibit a variety of coordination modes, and sometimes two different modes occur in the same complex. We hoped that this strategy would prove to be generally applicable to the 3d metals, and this proved to be the case for cobalt(II). Here we report the cobalt(II) complexes **1** and **2**, which have unusual structures and interesting magnetic properties.

$[Co_9\{(py)_2CO_2\}_4(O_2CMe)_8(OH)_2]\cdot 14.6\,H_2O$ **1**

$[Co_4\{(py)_2C(OH)O\}_4(O_2CMe)_4]\cdot H_2O$ **2**

The course of the reaction between $Co(O_2CMe)_2\cdot 4\,H_2O$ and $(py)_2CO$ in MeCN under reflux depends on the molar ratio. Treatment of $Co(O_2CMe)_2\cdot 4\,H_2O$ with $(py)_2CO$ in a 2:1 molar ratio led to a pale purple solution and subsequent isolation of the nonanuclear complex **1** with doubly deprotonated ions of $(py)_2C(OH)_2$ as ligands; this is a consequence of the high $MeCO_2^-$ to $(py)_2C(OH)_2$ ratio (4:1) used in the reaction. Treatment of cobalt(II) acetate with one equivalent of $(py)_2CO$ led to crystals of the tetranuclear complex **2**, which contains singly deprotonated ions of $(py)_2C(OH)_2$ as ligands.

Complex **1** (Figure 1)[5] has a twofold axis passing through Co1 and is held together by two $\mu_4$-$OH^-$ ions, eight *syn,syn*-$\mu_2$:$\eta^1$:$\eta^1$-$MeCO_2^-$ groups, and four $(py)_2CO_2^{2-}$ ligands, which adopt the unprecedented $\mu_5$:$\eta^1$:$\eta^3$:$\eta^3$:$\eta^1$ coordination mode (**A**). The central Co site (Co1) is the shared apex of two square pyramids. An alternative description of **1** is as a square prism centered by an additional interstitial cobalt(II) ion (Co1). Each metal···metal edge of

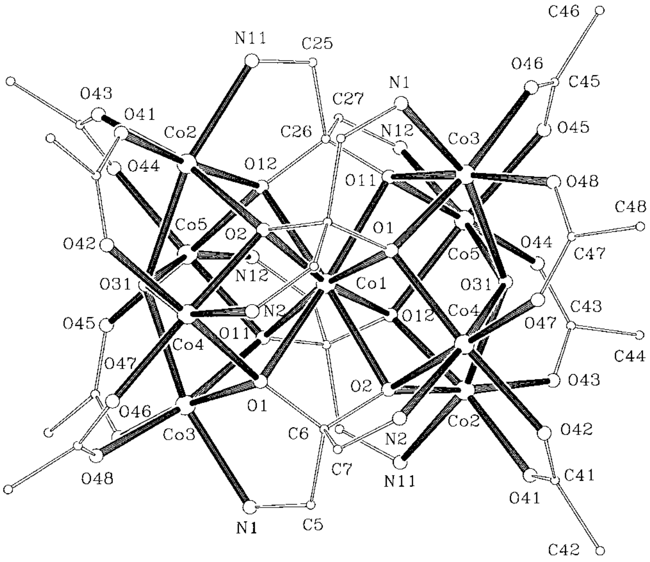
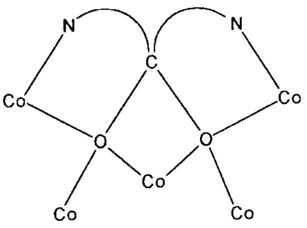


Figure 1. Crystal structure of **1**. Water molecules are omitted for clarity. Most carbon atoms of the pyridine rings have been omitted. Distances [Å]: Co–Co 3.10–6.52, Co1–O 2.24–2.27, Co2,3,4,5–O 2.02–2.31, Co–N 2.12–2.13.



**A**

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the bases is bridged by one acetate, one hydroxo oxygen atom, and one oxygen atom of a $(py)_2CO_2^{2-}$ ligand. Of the five crystallographically independent Co sites, four (Co2–Co5) have a coordination geometry close to a distorted octahedron ($CoNO_5$ chromophore). The most salient feature of the structure is the coordination number of eight around Co1, which is extremely rare.[6] The average Co1–O bond length to the $(py)_2CO_2^{2-}$ ligands is 2.26 Å, which is about 0.2 Å larger than the average Co2,3,4,5–O bond length (2.07 Å), as expected for a higher coordination number. The coordination geometry around Co1 is best described as a square antiprism; the O1-Co1-O11 and O2-Co1-O12 angles are 47.3 and 46.4°, respectively (the value for a perfect square antiprism is 45°). Another unexpected feature of **1** is the two $\mu_4$-$OH^-$ ligands at the center of each base of the double square pyramid. Each hydroxo group is displaced by 0.70 Å out of the best mean plane described by the four metal atoms to which it is bound on the side opposite to Co1. Such $\mu_4$-hydroxo units are very unusual in 3d metal chemistry.[7] To the best of our knowledge, only one other nonorganometallic, discrete homometallic nonanuclear $Co^{II}$ aggregate with O and/or N ligation is known.[8a] Of relevance also is the structure of the anion $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$, in which a nonanuclear $Co^{II}$ cluster is encapsulated in a polyoxometalate;[8b] the large anion contains nine $CoO_6$ octahedra, which share oxygen atoms with one another, three $\alpha$-B $PW_9O_{34}$ moieties, and two $PO_4$ groups.

X-ray analysis of **2**[5] revealed a tetranuclear cubane assembly (Figure 2). The alternating nonmetal vertices of the cube are occupied by four deprotonated oxygen atoms of the $\mu_3$:$\eta^1$:$\eta^3$:$\eta^1$-$(py)_2C(OH)O^-$ ligands (**B**). A monodentate acetate group completes a distorted octahedral $N_2O_4$ coordination environment at each metal center. Complex **2** joins a very small family of $Co^{II}$ cubane complexes.[9]

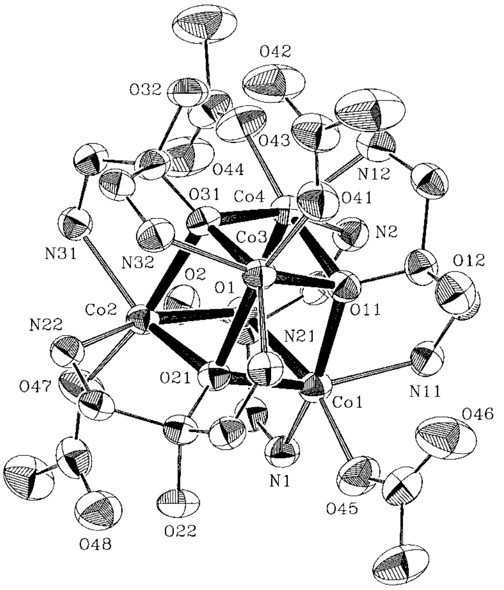
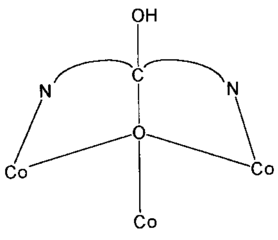


Figure 2. Crystal structure of **2**. The water molecule is omitted. Most carbon atoms of the pyridine rings have been omitted for clarity. Distances [Å]: Co–Co 3.22–3.25, Co–O 1.99–2.27, Co–N 2.10–2.18.

Variable-temperature magnetic susceptibility data were collected for **1** and **2** (SQUID magnetometer, 1.0 and 6.0 kG field, Figure 3). The decrease in the product $\chi_M T$ of **1** ($\chi_M$ is the molar magnetic susceptibility per formula unit) from 27.0 emu mol$^{-1}$ K at 300 K to 6.0 emu mol$^{-1}$ K at 5 K indicates antiferromagnetic interactions. It is not possible to fit the behavior of an array of nine or four (vide infra) orbitally degenerate $Co^{II}$ centers given current theory.



**B**

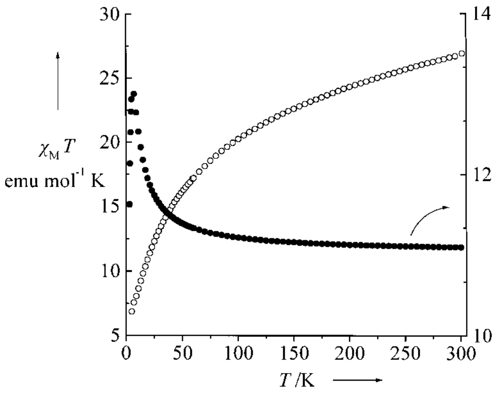


Figure 3. Plots of $\chi_M T$ versus $T$ for **1** (○) and **2** (●).

For **2** $\chi_M T$ increases from 11.2 emu mol$^{-1}$ K at 300 K to 13.1 emu mol$^{-1}$ K at 7.0 K and then falls to 11.6 emu mol$^{-1}$ K at 3 K, consistent with a ferrimagnetically coupled $S = 3$ ground state. Smit et al.[10] reported high-field magnetization data on the cubane complex $[Co_4(OMe)_4(acac)_4(MeOH)_4]$ which were consistent with a ferromagnetically coupled $Co^{II}$ cluster.

The results on cobalt(II) complexes reported here again illustrate the extraordinary structural flexibility of mixed $RCO_2^-/(py)_2CO$ systems.

## *Experimental Section*

**1**: MeCN (45 mL) was added to a mixture of $Co(O_2CMe)_2 \cdot 4H_2O$ (0.27 g, 1.08 mmol) and $(py)_2CO$ (0.10 g, 0.54 mmol). The solids dissolved on stirring under reflux for 2 h to give a pale purple solution, which was allowed to stand undisturbed at room temperature overnight. Well-formed, X-ray quality crystals of **1** appeared slowly. The purple crystals were collected by filtration, washed with a little cold EtOH, and dried in air. Yield 30%. Elemental analysis calcd for $C_{60}H_{87.2}N_8O_{40.6}Co_9$ (%): C 34.3, H 4.2, N 5.3, Co 25.3; found: C 34.4, H 4.1, N 5.5, Co 25.7.

**2**: Solid $Co(O_2CMe)_2 \cdot 4H_2O$ (0.24 g, 0.95 mmol) was dissolved with stirring in a solution of $(py)_2CO$ (0.17 g, 0.92 mmol) in MeCN (40 mL) under reflux. The resulting purple solution was layered with $Et_2O$/*n*-hexane (1/1, 45 mL). Slow mixing yielded large red prismatic crystals of **2**, which were collected, washed with a little cold EtOH and $Et_2O$, and dried in air. Yield 35%. Elemental analysis calcd for $C_{52}H_{50}N_8O_{17}Co_4$ (%): C 48.2, H 3.9, N 8.7, Co 18.2; found : C 48.0, H 4.0, N 8.5, Co 18.4.

Received: June 23, 1998
Revised version: December 22, 1998 [Z12037IE]
German version: *Angew. Chem.* **1999**, *111*, 1036–1038

**Keywords:** clusters · cobalt · magnetic properties · O ligands

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[5] Crystal data for **1**: $C_{60}H_{87.2}Co_9N_8O_{40.6}$, crystal dimensions $0.10 \times 0.10 \times 0.30$ mm, monoclinic, space group $C2/c$, $a = 14.37(1)$, $b = 39.28(3)$, $c = 16.62(1)$ Å, $\beta = 115.69(3)^\circ$, $V = 8451(1)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.651$ g cm$^{-3}$, $2\theta_{max} = 50^\circ$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\theta - 2\theta$ scan, $T = 298$ K, 7637 measured reflections, 7369 independent reflections ($R_{int} = 0.0384$) all included in the refinement. Lorentzian, polarization, and $\Psi$-scan absorption corrections were made, $\mu = 1.814$ mm$^{-1}$, $[\Delta/\sigma]_{max} = 0.075$, 560 parameters refined, $R1 = 0.0642$ (for 5734 reflections with $I > 2\sigma(I)$), $wR2 = 0.1712$ (on $|F^2|$). Max./min. residual peaks in the final difference map $0.840/-0.901$ e Å$^{-3}$. Crystal data for **2**: $C_{52}H_{50}Co_4N_8O_{17}$, crystal dimensions $0.15 \times 0.30 \times 0.50$ mm, monoclinic, space group $I2/a$, $a = 27.49(1)$, $b = 19.020(7)$, $c = 20.744(7)$ Å, $\beta = 91.31(1)^\circ$, $V = 10841.9(6)$ Å$^3$, $Z = 8$, $\rho_{calcd} = 1.586$ g cm$^{-3}$, $2\theta_{max} = 50^\circ$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\theta - 2\theta$ scan, $T = 298$ K, 9833 measured reflections, 9550 independent reflections ($R_{int} = 0.0221$) all included in the refinement. Lorentzian, polarization, and $\Psi$-scan absorption corrections were applied, $\mu = 1.282$ mm$^{-1}$, $[\Delta/\sigma]_{max} = 0.025$, 923 parameters refined, $R1 = 0.0404$ (for 6908 reflections with $I > 2\sigma(I)$), $wR2 = 0.1056$ (on $|F^2|$). Max./min. residual peaks in the final difference map $0.993/-0.349$ e Å$^{-3}$. Crystals of **1** and **2** were mounted in capillaries filled with drops of mother liquor and in air, respectively. The structures were solved by direct methods with SHELXS-86 and refined by full-matrix least-squares techniques on $F^2$ by using SHELXL-93. For both structures, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the ligands in **1** were introduced at calculated positions as riding on bonded atoms; no hydrogen atoms of $H_2O$ molecules were included in the refinement. All hydrogen atoms in **2** were located by difference maps and their positions refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-102038 and CCDC-102039. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# Isomerism and Blue Electroluminescence of a Novel Organoboron Compound: $B_2^{III}(O)(7\text{-azain})_2Ph_2$**

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Organic electroluminescent (EL) devices based on organic or organometallic materials have attracted much attention because of their high luminance, low driving voltage, and easy fabrication.[1–4] To achieve a full color display, the three basic color components red, green, and blue are required. Red and green emitters for organic EL devices have become readily available. Useful and efficient organic or organometallic blue emitters are however still very rare. Previously reported blue emitters of organometallic or coordination compounds in organic EL devices employed either derivatives of 8-hydroxyquinoline or azomethine as the emitting ligands.[3, 4] The common feature of those previously reported blue emitting ligands is that they are all chelating ligands and bind to the central atom through both nitrogen and oxygen donor atoms. We have been interested in the application of organometallic and coordination compounds in EL devices because the properties of this class of compounds such as volatility and stability can be modified readily by manipulating the coordination environment around the central atom.[5] We have discovered recently that 7-azaindole and di-2-pyridylamine ligands yield a strong blue luminescence when bound to an aluminum or boron center.[6] The 7-azaindole or di-2-pyridyl amine ligands contain nitrogen donor atoms only and can bind to the central atom by either a bridging mode or a chelating mode. They are therefore very different from the previously

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[**] This work was supported by the Natural Sciences and Engineering Research Council of Canada and Xerox Research Foundation. 7-azain = 7-azaindole anion.