Inorganic Chemistry

The First Cobalt Metallacrowns: Preparation and Characterization of Mixed-Valence Cobalt(II/III), Inverse 12-Metallacrown-4 Complexes

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Aerobic reactions of $Co(O_2CMe)_2 \cdot 4H_2O$ with di-2-pyridyl ketone oxime (Hpko) in the presence of counterions (ClO_4^-, PF_6^-) give the tetranuclear, mixed-valence cobalt(II/III) clusters $[Co^{II}_2\text{-}Co^{III}_2(OR)_2(O_2CMe)_2(pko)_4S_2]X_2$ [R = H, S = MeOH, X = ClO_4 (**1**); R = Me, S = EtOH, X = PF_6 (**2**)] depending on the solvent mixture. Complexes **1** and **2** are the first Co members in the family of metallacrowns adopting the extremely rare inverse 12-metallacrown-4 motif.

Metallacrowns (MCs)[1] are the inorganic structural and functional analogues to crown ethers. The conceptual basis underlying these compounds is the metallacrown analogy,[1] which has demonstrated that cyclic structures generally analogous to crown ethers are accessible by substituting a transition metal ion and a nitrogen atom for the methylene carbons of a standard crown ether. Metallacrown nomenclature has been given in refs 1 and 2. There are now examples of [9-MC$_{M(ox)N(ligand)}$-3], [12-MC$_{M(ox)N(ligand)}$-4], [15-MC$_{M(ox)N(ligand)}$-5], and [24-MC$_{M(ox)N(ligand)}$-8] structural types, as well as fused and mixed-metal MCs.[1–3] For 12-MC-4 complexes, two structural motifs have been reported: classical or regular[1,4] and inverse;[1,2a,5] most 12-MC-4 species belong to the former type. In the classical motif, the two chelate rings formed allow for a N−O−M−N−O−M linkage, i.e., for an $[M-N-O]_n$ repeat unit, that forms a cyclic structure orienting oxygen donors toward the center of a cavity that is capable of binding cations. In the inverse motif, the ring metal ions, rather than anionic oxygen atoms, are oriented toward the center of the cavity that is capable of encapsulating anions, and the connectivity is transposed to N−O−M−O−N−M.

Pecoraro and co-workers have proposed[1] a "periodic table" of the MCs. There are nine metals in four oxidation states (II−V) that have been incorporated into the MC ring, and more than 20 metal ions, i.e., lanthanide, actinide, alkali, and alkaline earth, and transition metal ions have been captured in the central cavity of classical MCs. *It is astonishing that MCs have not yet been synthesized utilizing Co in the MC ring.* Incorporation of this redox-active and magnetic (in its Co^{II} form) 3d metal into the ring positions as well as the exploration of different binding modes might enhance the selectivity of MCs and bring about a wider variety of molecular recognition applications. We are now pleased to be able to fill in the empty Co position in the periodic table of the MCs. Herein, we report the first Co members in the MC family. The compounds are mixed-valent ($Co^{II/III}$) and adopt the inverse 12-MC-4 structural motif. Moreover, these complexes are the first mixed-valent inverse

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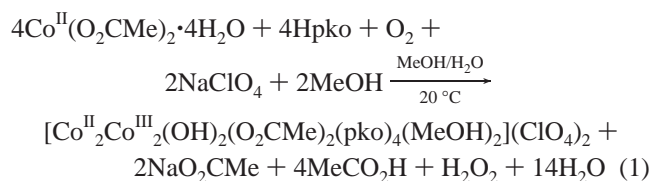
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MCs of any metal and constitute extremely rare examples of (i) inverse MCs[2a,5] and (ii) MCs containing a given ring metal in more than one oxidation state.[3a] It should be mentioned that aza 18-MC-6[6] and aza 16-MC-4[7] compounds containing the [Co^{III}−N−N]$_n$ and [Co^{III}−N−C−N]$_n$ repeat units, respectively, have been reported.

Aerobic reaction of Co^{II}(O$_2$CMe)$_2$·4H$_2$O with di-2-pyridyl ketone oxime (Hpko), in the presence of NaClO$_4$ (1:1:1 molar ratio), in a solvent mixture comprising MeOH and H$_2$O (5:1, v/v) at room temperature led to a dark red solution, from which were subsequently obtained crystals of [Co$^{II}_2$-Co$^{III}_2$(OH)$_2$(O$_2$CMe)$_2$(pko)$_4$(MeOH)$_2$](ClO$_4$)$_2$·4MeOH·3.08H$_2$O (**1**·4MeOH·3.08H$_2$O) in 70% yield. The formation of **1** can be represented by eq 1.

$$4\text{Co}^{II}(\text{O}_2\text{CMe})_2\cdot4\text{H}_2\text{O} + 4\text{Hpko} + \text{O}_2 +$$
$$2\text{NaClO}_4 + 2\text{MeOH} \xrightarrow[\text{20 °C}]{\text{MeOH/H}_2\text{O}}$$
$$[\text{Co}^{II}_2\text{Co}^{III}_2(\text{OH})_2(\text{O}_2\text{CMe})_2(\text{pko})_4(\text{MeOH})_2](\text{ClO}_4)_2 +$$
$$2\text{NaO}_2\text{CMe} + 4\text{MeCO}_2\text{H} + \text{H}_2\text{O}_2 + 14\text{H}_2\text{O} \quad (1)$$

Using metallacrown nomenclature, the formula of the complex is {(OH)$_2$[inv12-MC$_{Co(II/III)N(pko)}$-4](O$_2$CMe)$_2$(MeOH)$_2$}-(ClO$_4$)$_2$·4MeOH·3.08H$_2$O. The isolation of an inverse MC is a consequence[5] of the substitution of the pko$^-$ ligand for the previously employed hydroxamate or mixed hydroxamate/pko$^-$ ligand systems. The tetranuclear cation of 1 (Figure 1)[8] lies on a crystallographic inversion center with a rectangular arrangement of the metal centers. The rectangle is defined by Co1···Co2 and Co1···Co2′ dimensions of 3.213(1) and 4.441(1) Å, respectively; the Co1···Co2···Co1′ and Co2···Co1···Co2′ angles are 97.1° and 82.9°, respectively.

The cobalt centers are bridged along each short side (edge) of the rectangle by one hydroxide [O21, O21′], one syn,syn-η^1:η^1:μ_2 MeCO$_2^-$ ligand, and one oximato(−1) group, while bridging along each long side occurs through one oximato(−1) group only. Charge considerations require a 2Co^{II}, 2Co^{III} oxidation-state description (mixed-valent complex). Cobalt−ligand distances fall into two well-separated groups with all distances from Co1 being <1.95 Å and those from Co2 being >2.03 Å; thus, Co1 and its symmetry-related Co1′ are assigned as the Co^{III} atoms. The pko$^-$ ligands (Chart 1) comprise two pairs arranged along the edges and the sides

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(8) Crystal structure data for **1**·4MeOH·3.08H$_2$O: C$_{54}$H$_{70.16}$Cl$_2$Co$_4$N$_{12}$O$_{27.08}$, M_w = 1627.28, triclinic, space group $P1$· with a = 10.523(5) Å, b = 13.556(5) Å, c = 12.465(5) Å, α = 110.15(1)°, β = 95.25(2)°, γ = 92.05(2)°, V = 1658(2) Å^3, Z = 1, ρ_{calc} = 1.630 g cm^{-3}, T = 298 K, $F(000)$ = 837, μ(Mo Kα) = 1.157 mm^{-1}, $2\theta_{max}$ = 49.5°, 5936 reflections collected, 5654 unique (R_{int} = 0.0220), 530 refined parameters, R1(F) = 0.0545 and wR2(F^2) = 0.1379 using 4454 reflections with $I > 2\sigma(I)$. Crystal structure data for **2**·5.6MeOH: C$_{59.6}$H$_{78.4}$F$_{12}$Co$_4$N$_{12}$O$_{17.6}$P$_2$, M_w = 1770.20, triclinic, space group $P1$· with a = 11.867(4) Å, b = 14.534(6) Å, c = 12.289(5) Å, α = 70.09(1)°, β = 80.60(1)°, γ = 69.86(1)°, V = 1868(2) Å^3, Z = 1, ρ_{calc} = 1.575 g cm^{-3}, T = 298 K, $F(000)$ = 907, μ(Mo kα) = 1.018 mm^{-1}, $2\theta_{max}$ = 48.5°, 6360 reflections collected, 6043 unique (R_{int} = 0.0174), 547 refined parameters, R1(F) = 0.0531 and wR2(F^2) = 0.1327 using 4373 reflections with $I > 2\sigma(I)$.
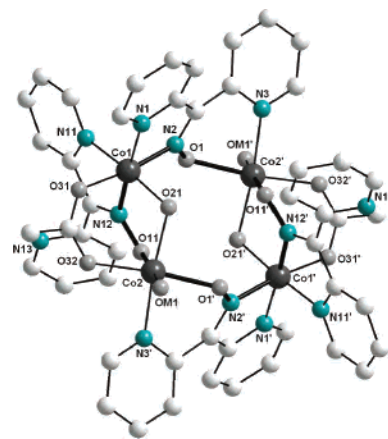
Figure 1. Partially labeled ball-and-stick presentation of the cation of **1**. H atoms are omitted for clarity. Primed and unprimed atoms are related by the crystallographic inversion center. O21 and O21′ are the hydroxo oxygen atoms, and OM1 and OM1′ are the oxygen atoms of the methanol ligands. The metallacrown ring is outlined in bold.

Chart 1 Crystallographically Established Coordination Modes of pko$^-$ in Complexes **1** and **2** and Harris Notation[9] That Describes These Modes

2.1110   2.1111
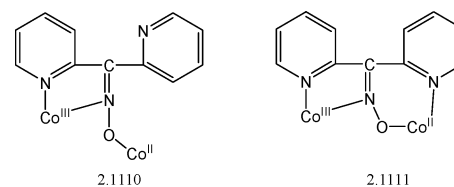
of the rectangle. Edge pko$^-$ ions function as η^1:η^1:η^1:μ_2 ligands (or as 2.1110 ligands using Harris notation[9]). Long-side pko$^-$ ions adopt the η^1:η^1:η^1:η^1:μ_2 (or 2.1111[9]) coordination mode. A terminal MeOH molecule fills the sixth coordination site at each Co^{II} atom.

Compound **1** realizes an inverse 12-MC-4 structural type and can accommodate two OH$^-$ ions within the metallacrown ring. Previous examples of inverse 12-MC-4 complexes involve {(OH)$_2$[inv12-MC$_{Zn(II)N(pko)}$-4](O$_2$CMe)$_2$},[5a] {(OH)$_2$-[inv12-MC$_{Zn(II)N(pko)}$-4]Cl$_2$},[2a] and {(OH)$_2$[inv12-MC$_{Zn(II)N(paO)}$-4]Cl$_2$},[5b] where paO is the monoanion of *syn*-2-pyridyl-aldoxime.

Compound **1** is unique to the small group of inverse 12-MC-4 complexes in several ways. First and foremost, this compound is mixed-valent, and this provides a different opportunity for site differentiation. In the Zn inverse 12-MC-4 complexes,[2a,5] the Zn^{II} atoms are site-differentiated because two metal centers are octahedral and two are tetrahedral; in **1**, the Co ions are site-differentiated because two are divalent and two are trivalent. Second, **1** is a cationic species, whereas the zinc(II) complexes are neutral. And third, in the inverse Zn 12-MC-4 complexes with pko$^-$,[2a,5a] only three of the heteroatoms of the pko$^-$ ligands are bound (2.1110), leaving one of the 2-pyridyl nitrogens unbound, whereas in **1**, the pko$^-$ ligands adopt two different coordination modes (2.1110, 2.1111).

The access to the OH$^-$-bridged cluster **1** suggested that the Co^{II}/MeCO$_2^-$/Hpko reaction system might be capable of

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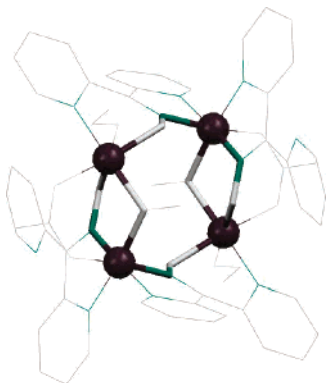
Figure 2. Stereoview of the cation of **2** highlighting the inverse metallacrown ring and the methoxo bridges.

extension to RO^--bridged analogues of **1**. The above-described procedure, but using a 10:1 v/v MeOH/EtOH solvent mixture (i.e., significantly decreasing the concentration of H_2O in the system) and PF_6^- counterions (instead of ClO_4^- ions), was found to successfully give complex $[Co^{II}_2Co^{III}_2(OMe)_2(O_2CMe)_2(pko)_4(EtOH)_2](PF_6)_2 \cdot$ 5.6MeOH (**2**·5.6MeOH) in good overall yield. The isolation of **1** in preference to a MeO^--bridged cluster from MeOH/H_2O, even in the presence of a volume excess of MeOH, seems to be a consequence of the weaker acidity of MeOH ($pK_a \approx 15.5$) compared to that of H_2O. The cation of **2** was found to have a structure (Figure 2)[8] analogous to that of the hydroxide-containing cation of **1** but with MeO^- and EtOH ligands in place of OH^- and MeOH groups, respectively.

Synthetic chemistry in progress supports the view that the formation of **1** and **2** is an anion (OH^-, MeO^-)-directed assembly,[10] i.e., the OH^- or MeO^- ions formed during the synthesis of these materials act as templates around which the clusters form.

Both complexes show intact ions and molecular ions via ESI-MS in MeCN, suggesting that the structure is present in solution.

The cyclic voltammograms of **1** and **2** in MeCN in the presence of 0.1 M $^nBu_4NPF_6$ as the supporting electrolyte (Pt disk working electrode, Pr wire auxiliary, Ag/AgCl reference, saturated LiCl in EtOH; under these conditions, the redox transition for ferrocene was at $+0.525$ V) both exhibit a quasireversible reduction process at -1.13 to -1.14 V, assigned as the conversion of the Co^{III} atoms to Co^{II} centers. The presence of four N atoms in the coordination sphere of each Co^{III} is expected to stabilize the $3+$ oxidation state and, consequently, to lower the potential of the Co^{III}/Co^{II} conversion. On the other hand, the O-rich coordination sphere of the Co^{II} atoms would preferably render these centers at the $2+$ oxidation state. The lack of obvious redox waves at more positive potentials supports this hypothesis, clearly demonstrating a resistance to oxidation of the Co^{II} atoms.

Solid-state dc magnetic susceptibility measurements were performed for a very fresh sample of the representative compound **1**·4MeOH·3.08H$_2$O in the range of $2-300$ K under a field of 0.4 T. On the basis of the structure of **1**, the only unpaired electrons will be on the Co^{II} centers, as the Co^{III} ions are low-spin (t_{2g}^6, $S = 0$). Thus, from the magnetic viewpoint, the complex is effectively dinuclear. The $\chi_m T$ product ($\chi_m = $ molar magnetic susceptibility) decreases gradually from the room-temperature value of 6.58 cm^3 mol^{-1} K to 3.70 cm^3 mol^{-1} K at 2 K. The room-temperature value is larger than the spin-only value for two noninteracting $S = {}^3/_2$ ions (3.75 cm^3 mol^{-1} K), but close to the value expected (6.76 cm^3 mol^{-1} K) for two free Co^{II} ions with negligible spin$-$orbit coupling, indicating a significant contribution from the orbital momentum, typical of the Co^{II} ion in an octahedral field ($^4T_{1g}$ ground state). Magnetization measurements at 2 K show saturation at 5 T, with an MN/β value of 4.7. Because the paramagnetic metal ions alternate with the diamagnetic ones in the ring of **1**, superexchange between the Co^{II} atoms should be negligible, if any. The observed decrease of $\chi_m T$ can be attributed to the zero-field splitting of the quartet ground state, which for high-spin, six-coordinate Co^{II} complexes is relatively large. Room- and low-temperature $\chi_m T$ and magnetization values are in the normal range for systems containing isolated Co^{II} ions.[11]

In summary, we have developed access to the first members of the subfamily of Co metallacrowns. Moreover, this work emphasizes further the coordinative flexibility and versatility of the ligand pko$^-$ and its synthetic utility in polynuclear 3d-metal chemistry. The $-[O-Co-O-N-Co-N]^-$ repeat unit observed in the $Co^{II}_2Co^{III}_2$ clusters is perfectly acceptable for inverse metallacrown structures but should not sustain a regular metallacrown (with an encapsulated fifth metal ion), as this connectivity would require adjacent six- and four-membered chelate rings.[1] This repeat unit also assists the creation of a nitrogen-rich environment around the two Co^{III} ions; such an environment stabilizes the $3+$ oxidation state of Co in the mixed-valent clusters.

Supporting Information Available: Ball-and-stick presentation of the inverse metallacrown ring of complex **1**, M vs H and $\chi_m T$ vs T data for the same complex, analytical data for **1**·4MeOH·3.08H$_2$O, and crystallographic data for **1**·4MeOH·3.08H$_2$O (CCDC 249267) and **2**·5.6MeOH (CCDC 249268) in CIF format. This material is available free of charge via the Internet at http:/pubs.acs.org.

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