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# New $\mu$-Oxo Octanuclear Complexes of 3d Elements Stabilized by Dialkylcarbamato Ligands. Synthesis and X-ray Crystal and Molecular Structures[†]

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The octanuclear aggregates $M_8(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}$ [M = Mn(II) **1**, Co(II) **2**, Ni(II) **3**] have been prepared in good yields by controlled hydrolysis of the corresponding metal carbamate precursors $[M(O_2CN^iPr_2)_2]_n$. X-ray analysis has shown compounds **1**–**3** to be isostructural. The core of **2** contains two distorted $\{M_4O\}$ tetrahedra related by an inversion center. The hexanuclear carbamates $M_6(O_2CNEt_2)_{12}$ in toluene undergo a metal redistribution process with formation of the hexanuclear carbamates $M'_xM''_{6-x}(O_2CNEt_2)_{12}$, M′ = Co, M″ = Mn, as evidenced by mass-spectrometric data. In the presence of moisture, the mixed octanuclear carbamates $Co_xMn_{6-x}(MnO)(CoO)(O_2CNEt_2)_{12}$ were promptly formed and detected by DCI/MS measurements. Mass spectral data of $Co_8(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}$ are also reported.

The number of polynuclear aggregates of 3d metals has increased enormously in recent years.[1] Interest in such inorganic complexes is due to a variety of applications which include molecular electronics,[2] photochemically driven electron transfer,[3] liquid crystalline materials,[4] and host−guest chemistry.[5]

The study of nanometer-sized transition metal aggregates is fundamental in understanding nucleation phenomena[6] or in the development of molecular magnets.[1,7] Polynuclear systems often contain $\mu$-oxo ligands bridging two or three metals, less commonly four, rarely six.[8] Uncharged systems of this type are of particular interest, but rational, high-yielding and reproducible syntheses of these species still represent a rather difficult target.

*N*,*N*-Dialkylcarbamato ligands are versatile from a structural viewpoint[9] and react with protic reagents, such as water, under mild conditions,[10] to give $\mu$-oxo metal complexes, a contribution to the driving force of the reaction coming from the formation of carbon dioxide. This reactivity has been exploited for (i) controlled hydrolysis to $\mu$-oxo molecular derivatives,[11] (ii) exhaustive hydrolysis to metal oxides; and (iii) implantation of metal cations on inorganic hydroxylated surfaces.[12]

We now want to communicate the synthesis of the isostructural derivatives of manganese(II), cobalt(II), and nickel(II), of formula $M_8(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}$ by hydrolysis of the carbamato precursors. Moreover, it has been found that the previously described isostructural[13] ethyl derivatives of manganese and cobalt, of formula $M_6(O_2CNEt_2)_{12}$, easily undergo metal exchange in solution, as established by mass

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spectral data (vide infra). A preliminary account of part of this work was recently reported.[14]

The $\mu$-oxo derivatives of manganese(II), cobalt(II), and nickel(II) were prepared according to eq 1, by hydrolysis of the homoleptic precursors, with a stoichiometric amount of water in toluene solution.[15] The cobalt complex $Co_8O_2(O_2CN^iPr_2)_{12}$ was prepared from the preformed species $[Co(O_2CN^iPr_2)_2]_n$, while the manganese(II) and nickel(II) derivatives were obtained starting from the appropriate anhydrous metal chloride upon addition of a stoichiometric amount of water, without isolation of the intermediate species. All $\mu$-oxo products were recrystallized from heptane by heating at 70 °C under dinitrogen and then cooling to room temperature.

$$(24/n)[M(O_2CN^iPr_2)_2]_n + 6H_2O \rightarrow 3M_8(\mu\text{-}O)_2(O_2CN\,^iPr_2)_{12} + 12NH\,^iPr_2 + 12CO_2 \quad (1a)$$

$$4M_6(O_2CNEt_2)_{12} + 6H_2O \rightarrow 3M_8(\mu\text{-}O)_2(O_2CNEt_2)_{12} + 12NHEt_2 + 12CO_2 \quad (1b)$$

The molecular structure[16] of the cobalt derivative $Co_8(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}$ was solved by X-ray diffractometric methods.[17] The molecule (Figure 1) consists of two $\{Co_4O\}$ pseudotetrahedra related by the $\bar{3}$ axis.

The symmetry relations result in only two independent sets of metal atoms, namely, Co(2) in the apical position on the $\bar{3}$ axis and Co(1). Three equivalent carbamates connect Co(2) to the three equivalent Co(1)'s within the same tetrahedron, while six other crystallographically equivalent carbamates interconnect the Co(1) atoms of the facing tetrahedra. The Co(2) atoms are four-coordinated with a pseudotetrahedral geometry, while Co(1) are five-coordinated in a trigonal bipyramidal geometry. The molecule has an ellipsoidal shape of approximate dimensions 16.5 × 15 Å. The molecules are packed according to a trigonal lattice leaving channels occupied by heptane, which is heavily disordered.

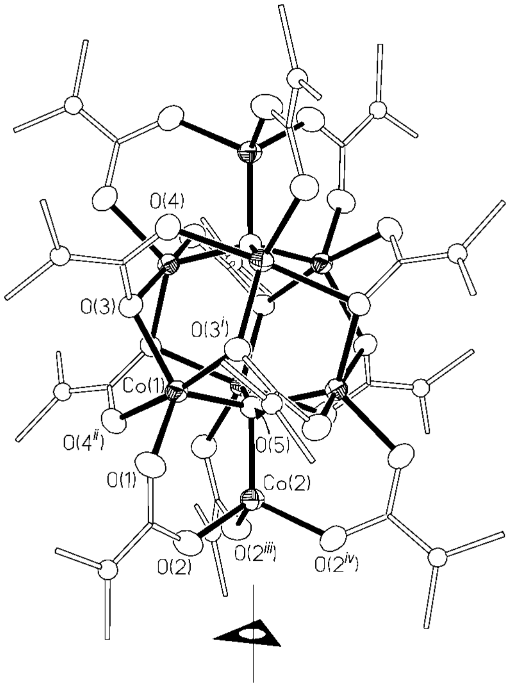

**Figure 1.** Core of $Co_8(\mu_4\text{-}O)_2(O_2CN^iPr_2)_{12}$. Cobalt and oxygen atoms are represented by 30% probability ellipsoids, nitrogen atoms by small circles, and carbon atoms are omitted for clarity. The symbol below the drawing marks the position of the $\bar{3}$ operator, the inversion center being the middle point of the molecule. Co−O bond distances (Å) and angles (deg): Co(1)−O(5), 1.972(1); Co(1)−O(1), 1.985(4); Co(1)−O(3), 2.022(3); Co(1)−O(4$^{ii}$), 2.071(4); Co(1)−O(3$^i$), 2.209(4); Co(2)−O(2), 1.963(4); Co(2)−O(5), 1.972(5); O(5)−Co(1)−O(1), 115.4(2); O(5)−Co(1)−O(3), 122.1(2); O(1)−Co(1)−O(3), 122.4(2); O(5)−Co(1)−O(4$^{ii}$), 94.8(1); O(1)−Co(1)−O(4$^{ii}$), 91.3(2); O(3)−Co(1)−O(4$^{ii}$), 88.0(2); O(5)−Co(1)−O(3$^i$), 92.3(1); O(1)−Co(1)−O(3$^i$), 88.7(2); O(3)−Co(1)−O(3$^i$), 85.39(7); O(4$^{ii}$)−Co(1)−O(3$^i$), 172.2(2); O(2)−Co(2)−O(2$^{iii}$), 104.8(2); O(2)−Co(2)−O(5), 113.8(1). i = $-z+1, -x+1, -y$; ii = $-y+1, -z, -x+1$; iii = $z+1, x-1, y$; iv = $y+1, z, x-1$.

The ethyl derivatives $M_6(O_2CNEt_2)_{12}$ of well-established[13] crystal structure were subjected to a mass-spectrometric study, which led us to detect a metal redistribution phenom-

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(15) Under a dinitrogen atmosphere, to a toluene (500 mL) solution of the *N,N*-diisopropylcarbamato derivative $Co(O_2CN^iPr_2)_2$ (7.44 g; 21.4 mmol) was added dropwise a solution of water (0.096 mL; 5.3 mmol) in THF (200 mL), the resulting solution being stirred for 24 h. After evaporation to dryness in vacuo, the solid residue was suspended in heptane (200 mL). Large blue crystals of $Co_8O_2(O_2CN^iPr_2)_{12}$ (79% yield) were obtained by slow cooling of the hot solution down to room temperature. Anal. Calcd for $C_{84}H_{168}Co_8N_{12}O_{26}$, MW 2233.8: C, 45.2; H, 7.6; N, 7.5; Co, 21.1; $CO_2$, 23.6. Found: C, 41.3; H, 7.1; N, 6.6; Co, 20.9; $CO_2$, 23.4, corresponding to a $CO_2$/Co molar ratio of 1.50. IR (Nujol, KBr; 1700−1300 cm$^{-1}$): 1623 w, 1568 s, 1520 s, 1461 s, 1379 s, 1354 s. Mass-spectral data (vide infra) showed a molecular anion cluster consisting of $[M]^-$ at *m/z* 2233 (90%) and $[M+1]^-$ at *m/z* 2234 (90%), together with a singly charged fragment anion at *m/z* 1116 (100%). No other fragments were detected. Mass spectra were obtained by desorption chemical ionization (DCI/MS) with isobutane as the reagent gas by using a Finnigan 8400 double-focusing instrument operated at 2000 resolution. MS spectra were recorded in the profile mode, and both positive and negative ions were detected. The corresponding $\mu$-oxo ethyl derivative was similarly prepared (52% yield) from the bis(*N,N*-diethylcarbamato)cobalt(II) precursor upon reaction with a stoichiometric amount of a $1.06 \times 10^{-2}$ M solution of water in toluene. Anal. Calcd for $Co_8O_2(O_2CNEt_2)_{12}$, $C_{60}H_{120}Co_8N_{12}O_{26}$, MW, 1897.1: C, 38.0; H, 6.4; N, 8.9; Co, 24.8; $CO_2$, 27.8. Found: C, 36.9; H, 6.3; N, 8.7; Co, 23.3; $CO_2$, 25.5, corresponding to a $CO_2$/Co molar ratio of 1.50. IR (Nujol, KBr; 1700−1300 cm$^{-1}$): 1558 s, 1510 s, 1461 m, 1433 s, 1377 s, 1349 m, 1317 s.

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(17) A single crystal of $Co_8O_2(O_2CN^iPr_2)_{12}\cdot C_7H_{16}$ of dimensions 0.46 × 0.42 × 0.35 mm$^3$ was sealed in a glass capillary under an atmosphere of dinitrogen saturated with heptane vapors and mounted on a Bruker-AXS P4 diffractometer. Crystallographic data for $C_{91}H_{184}Co_8N_{12}O_{26}$, FW = 2333.94: $T = 293$ K, $\lambda = 0.71073$ Å, trigonal, rhombohedral cell, space group $R\bar{3}$, $a = 16.078(1)$ Å, $\alpha = 76.176(7)°$, $V = 3845.0(5)$ Å$^3$, $Z = 1$, $D_c = 1.008$ g·cm$^{-3}$, $\mu = 0.893$ mm$^{-1}$. 7501 collected reflections ($\theta_{max}$ 23°) were merged, giving 3557 independent reflections (2671 $I > 2\sigma(I)$). Residual maxima of electron density were considered as disordered solvent molecules statistically placed on one of the six symmetry-related positions. The lattice heptane was refined in a constrained geometry by adjusting its dihedral angles. The calculated density is 1.008 g·cm$^{-3}$, a low value for a substance containing 23% of cobalt. We believe that some of the lattice heptane can leave the solid with no collapse of the structure. The final refinement cycle on $F^2$ for 219 parameters with 11 constraints gave $R(F_o) = 0.0514$, $R_w(F_o^2) = 0.1920$, $S = 1.134$.

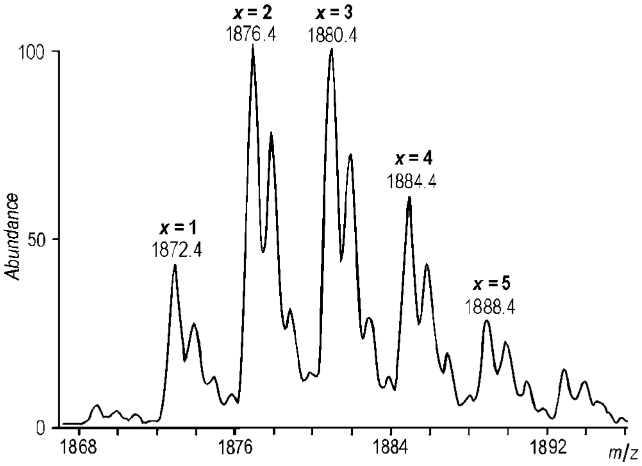

**Figure 2.** Negative ion mass spectrum of $[Co_xMn_{6-x}(MnO)(CoO)(O_2CNEt_2)_{12}]^-$ obtained by DCI/MS: molecular ion region. Intensity.

enon in solution leading to intermetallic (Mn/Co) hexanuclear complexes. Similar results were obtained by one of the following methods: (a) synthesis of the carbamato complexes from mixtures of the anhydrous metal chlorides in the appropriate molar ratio; (b) mixing the individual carbamato species in toluene solution. The redistributed hexanuclear complexes $M_6(O_2CNEt_2)_{12}$ of manganese and cobalt were detected. Moreover, the presence of adventitious water was sufficient to induce rapid hydrolysis in the hydrocarbon solutions of the mixed hexanuclear ethyl derivatives giving the corresponding octanuclear complexes of formula $M_8(O)_2(O_2CNEt_2)_{12}$, together with the corresponding fragmentation products. Thus, for example, toluene solutions containing the carbamates in Mn/Co nominal molar ratios ranging from 2.5 to 0.7 gave a set of molecular ions of the following compositions (both negative and positive ions were recorded): negative ions, $[Co_xMn_{6-x}(MnO)(CoO)(O_2CNEt_2)_{12}]^-$, $m/z$ 1868 ($x = 0$), 1872 ($x = 1$), 1876 ($x = 2$), 1880 ($x = 3$), 1884 ($x = 4$), 1888 ($x = 5$), 1892 ($x = 6$); positive ions, $[Co_xMn_{6-x}(MnO)_2(O_2CNEt_2)_{12} + H]^+$, $m/z$ 1865 ($x = 0$), 1869 ($x = 1$), 1873 ($x = 2$), 1877 ($x = 3$), 1881 ($x = 4$), 1885 ($x = 5$), 1889 ($x = 6$). The relative intensities within each set depend on the analytical Mn/Co ratio. Figure 2 shows the MS spectrum of a toluene solution containing the octanuclear species in the analytically established Mn/Co molar ratio of 0.7.

These results show the exceptional stability of the octanuclear $\mu$-oxo products. A study of metal redistribution phenomena within the preformed isostructural octanuclear $\mu$-oxo derivatives of the entire Mn → Ni sequence and on the corresponding lanthanide complexes $Ln_4(O_2CN^iPr_2)_{12}$,[18] using mass spectrometry as the analytical tool, is in progress.

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**Supporting Information Available:** Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Additionally, crystallographic data for the structure reported in this paper have been deposited with the Cambridge Data Centre (Dep. No. CCDC 175412).

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