Mixed-Valent Oligooxocobaltates

Na$_{10}$Co$_4$O$_{10}$, an Oligooxocobaltate(II, III) with Unusual Magnetic Properties**

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The study of magnetic clusters of transition-metal ions is a very active area of research. There are two independent driving forces: one is based on the unusual behavior of so-called spin-ladder compounds, such as KCuCl$_3$ or Sr$_{14}$Cu$_{24}$O$_{41}$, which result from an interplay of strong and weak intra and interdimer interactions, respectively.[1,2] The dominant antiferromagnetic coupling within the dimers leads to a singlet ground state and a triplet excited state. Singlet–triplet excitations become delocalized, thus leading to dispersion, by the presence of weak interdimer interactions. The application of an external magnetic field leads to a crossing of the $M_s = -1$ component of the triplet with the singlet state (M_s = electron spin angular momentum), thus creating a quantum critical point. The other driving force is based on the observation, about 10 years ago, of slow magnetic relaxation in molecular spin clusters.[3] These so-called single molecule magnets (SMM) constitute a very interesting class of materials. Besides the slow relaxation of the magnetization, they exhibit quantum tunneling phenomena at low temperatures. Typical SMM are composed of 3d transition-metal ions and organic or inorganic bridging and coordinating ligands.

Alkalioxometallates of the transition elements can consist of oligomeric complex oxoanions which contain magnetic centers of diverse spin moments. Unlike molecular spin clusters the oligomeric complexes in these compounds are not magnetically shielded from each other, and we can expect an interesting interplay of intra and intercluster interactions leading to novel magnetic properties. Such compounds are only accessible through conventional solid-state reactions, in general, and this high-temperature route lacks sufficient control for a directed synthesis of a targeted compound. In particular, fixing mixed valence states of the transition element components is an intricate task. As a rather efficient approach to overcoming such difficulties, we have developed the azide/nitrate route.[4] In this route, all starting materials used are solid, and the composition of the product, including the oxygen content, can be fixed by weighing out the respective alkali azide, nitrate (or nitrite), and transition

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metal oxide in appropriate ratios. By employing this technique, we synthesized the new mixed valent, oligomeric oxocobaltate Na$_{10}$Co$_4$O$_{10}$.

Thoroughly ground starting materials were reacted in a specially designed vessel,[4b] according to Equation (1).

$$76\,NaN_3 + 14\,NaNO_3 + 12\,Co_3O_4 \rightarrow 9\,Na_{10}Co_4O_{10} + 121\,N_2 \qquad (1)$$
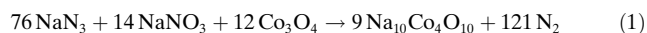
The as-obtained single-phase samples are sensitive to air, and are black. They decompose at 600°C, leaving CoO and NaCoO$_2$ as the only solid residues.

X-ray single crystal structure analysis[5] reveals a novel tetrameric oxoanion to be the prominent structural feature (Figure 1). Two edge sharing tetrahedra form the central unit, to which two CoO$_3$ triangles are attached by sharing a vertex with each one of the two tetrahedra. An inversion center is
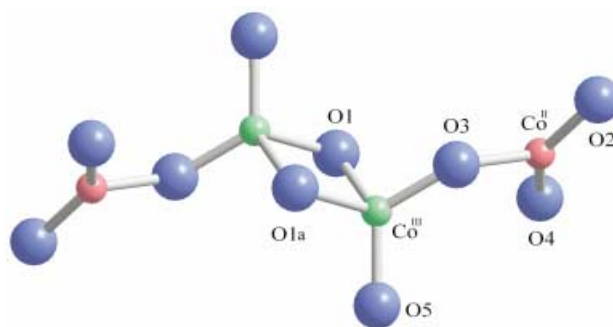

Figure 1. Crystal structure of the Co$_4$O$_{10}^{10-}$ anion. Bond lengths (Å): Co^{II}–O2 1.798, Co^{II}–O3 1.958, Co^{II}–O4 1.802, Co^{III}–O1 1.927, Co^{III}–O1a 1.951, Co^{III}–O3 1.823, Co^{III}–O5 1.777. Angles (°): Co^{II}-O3-Co^{III}: 124°, Co^{III}-O1-Co^{III}: 92°.

located at the middle of the edge common to the tetrahedra. The threefold triangular planar coordination, which is the one strongly preferred by Co^{2+} in alkali oxocobaltates (II),[6] justifies the assignment of the oxidation state of +2 of cobalt to this unit. This interpretation is backed by the Co–O bondlengths which, on average, agree well with data reported in the literature.[6] As a consequence Co^{3+} is assigned to the tetrahedral sites. This is rare, but not without precedent. We are aware of five examples: RbCoO$_2$,[7] β-KCoO$_2$,[8] Na$_5$CoO$_4$,[9] Li$_3$Na$_2$CoO$_4$[10] and K$_5$CoW$_{12}$O$_{40}$·20H$_2$O[11] are known to contain Co^{3+} in a tetrahedral coordination. Again, the bond lengths observed comply with published data,[9, 10] and with the sums of the respective ionic radii.[12] Considering the Co–O separations in detail, one notices significant variations, thus reflecting strong disturbances of the ideal geometries of the coordination polyhedra (Figure 1). However, all deviations can be understood in terms of the different functionalities of the oxygen atoms involved. As a rule, edges shared by two polyhedra are contracted, while the centering cations repel each other. Furthermore, the distances from cobalt centers to bridging ligands are longer than those to terminal ones. With these qualitative rules in mind, the distances Co^{3+}–O1 (common edge) as well as Co^{2+}–O3 (bridging oxygen) being longest, and Co^{3+}–O5, Co^{2+}–O2 and Co^{2+}–O4 (all terminal) being shortest, appear reasonable.

Also, the O-Co^{3+}-O angles varying from 88.4° to 118.8° are consistent with this view. The complex anions are "isolated" from each other by sodium ions which on their part have irregular oxygen coordination numbers ranging from 4 to 6 with bond lengths from 2.32 to 2.97 Å (Figure 2), which is again in the expected range.

The magnetic properties of $Na_{10}Co_4O_{10}$, represented as χ versus T and χT versus T, are shown in Figure 3 (χ = magnetic susceptibility). The behavior is most unusual, with a very low χT value of 5.4 emu K per Co_4 unit at 330 K and a sharp increase of χ around 40 K. Below 35 K the zero-field cooled and field-cooled data diverge, which indicates the onset of magnetic order. We can clearly distinguish two different temperature regimes reflecting different magnitudes of exchange interactions. The smooth part of the curve obtained between 330 K and 50 K is characteristic of dominant antiferromagnetic (AF) interactions within the cluster. The discontinuity at 38 K is attributed to cooperative intercluster interactions. Both, the increase and the divergence of χ, point to a magnetic ordering with a nonvanishing magnetic moment.

We can identify and roughly quantify the dominant exchange coupling by comparing the present results with magnetic data obtained for systems containing the constituents of our cluster as isolated units. From the data on Na_4CoO_3[13] for Co^{2+} in triangular oxo coordination, we deduce a χT value of 2 emu K per Co^{2+}, which is essentially independent on T between 300 K and 100 K. Figure 4 shows a comparison of χT versus T values of the title compound and $Na_6Co_2O_6$.[14] The latter was prepared by a similar route to $Na_{10}Co_4O_{10}$, and the crystal structure reveals the presence of dimers of tetrahedrally coordinated Co^{3+} ions sharing an edge, that is, exactly the inner part of the tetramer. The χT values in Figure 4 are given per $Co_4O_{10}^{10-}$ tetramer and $Co_2O_6^{6-}$ dimer, respectively. The two compounds have distinctly different magnetic properties. The dimer χT values are significantly higher and essentially temperature independent between 300 K and 100 K. We conclude that in our Co_4 cluster, showing Co^{2+}–Co^{3+} and Co^{3+}–Co^{3+} separation of 3.33 Å and 2.78 Å respectively, there are dominant antiferromagnetic interactions between the terminal Co^{2+} ions and their nearest Co^{3+} neighbors. These significantly reduce χT from about 12 to 5.4 emu K per tetramer at 330 K and lead to the observed continuous decrease down to about 50 K. We use the simplest possible model to obtain an estimate of this coupling strength. The magnetic moments of Co^{2+} and Co^{3+} are assumed isotropic with $S = 3/2$ and $S = 2$ values, respectively (S = spin angular momentum). The Co^{2+}–Co^{3+} interactions are expressed in terms of a Heisenberg exchange Hamiltonian: [Eq. (2)]

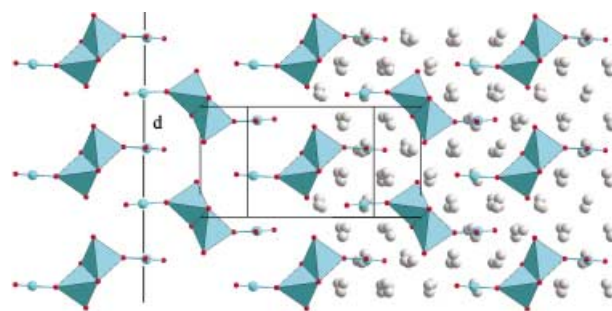$$\mathcal{H} = -2J(\vec{S}_1 \vec{S}_2 + \vec{S}_3 \vec{S}_4) \qquad (2)$$

Figure 2. Crystal structure of $Na_{10}Co_4O_{10}$. Viewed along $\bar{4}01$. Co_4O_{10}-clusters are given in cyan with oxygen atoms in red (for detailed structure of the oxoanion see Figure 1). Sodium atoms (gray balls) are drawn only on the right hand part. The dashed line corresponds to a possible interaction pathway between clusters (with Co^{II}-Co^{II} distances $d = 4.1$ Å) leading to cooperative effects below 38 K.
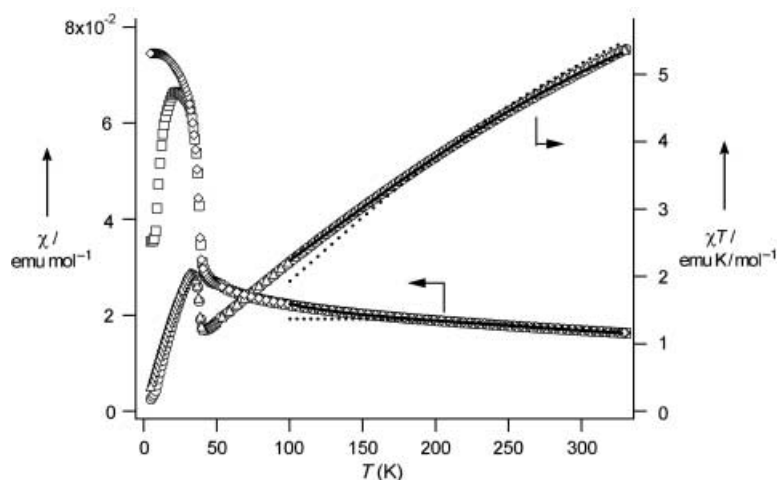

Figure 3. Magnetic susceptibility of $Na_{10}Co_4O_{10}$ represented as χ versus T and χT verus T. The applied field was 1 Tesla, and ZFC ($\square$, $\circ$) and FC ($\diamond$, $\triangle$) refer to zero-field cooled and field-cooled, respectively. The dotted and full lines correspond to least-squares fits using equation (1) and the van Vleck equation. Dotted lines: $g_{Co^{2+}} = g_{Co^{3+}}$ set to 2.0, best fit $2J = -70$ cm^{-1}. Full lines: Best fit with $g_{Co^{2+}} = 1.71$, $g_{Co^{3+}} = 2.15$, $2J = -81$ cm^{-1}.

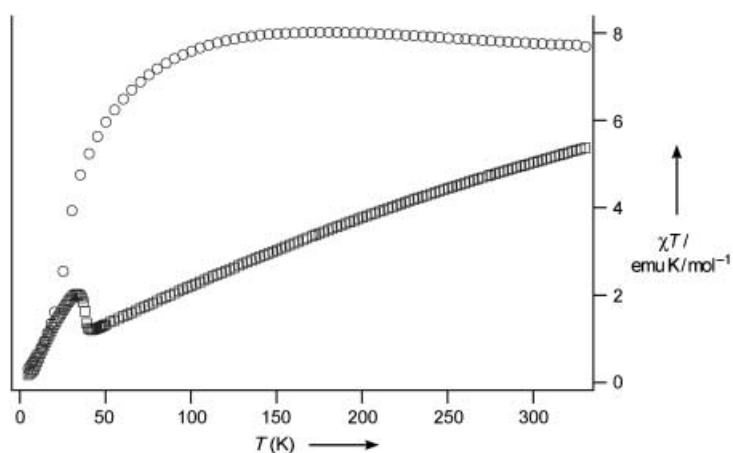**Figure 4.** Magnetic susceptibility of $Na_{10}Co_4O_{10}$ ($\square$) and $Na_6Co_2O_6$ ($\circ$) represented as χT per tetramer and dimer, respectively, versus T. The applied field was 1 Tesla.

in which $S_1 = S_4 = 3/2$ and $S_2 = S_3 = 2$, and the Co^{3+}–Co^{3+} interaction is neglected (J = spin coupling constant). A least-squares fit of χT calculated on the basis of Equation (2) and the van Vleck equation[15] with $g = 2.0$ (g = g-factor) for all the ions to the data between 330 K and 100 K yields $2J = -70$ cm^{-1} and the broken line in Figure 3. The full line corresponds to a fit with the g values as additional fit parameters: $g_1 = g_4 = 1.71$, $g_2 = g_3 = 2.15$ and $2J = -81$ cm^{-1}. Considering the very approximate character of our model the fits are surprisingly good. Anisotropy, which is expected to be important for both Co^{2+} and Co^{3+} in distorted triangular and T_d coordination, respectively, does not significantly affect the magnetic properties above 100 K.

The dominant antiferromagnetic Co^{2+}–Co^{3+} interaction with $2J = -81$ cm^{-1} is due to the superexchange through the oxygen ion. The Co^{3+} lies approximately in the triangular plane of the Co^{2+} coordination, and the Co^{2+}-O-Co^{3+} angle is 124°. The planar Co^{2+} coordination forces two unpaired electrons into the coordination plane. They will have significant overlap with oxygen 2s and 2p orbitals. On the Co^{3+} side all the t_2 orbitals are singly occupied in tetrahedral coordination. As a result of the overlap with the oxygen orbitals some spin density will be transferred also from Co^{3+} to oxygen. The situation thus bears some resemblance with dihydroxo-bridged Cu^{2+} dimers, in which the relevant orbital interactions occur in the Cu^{2+}-O-Cu^{2+} plane.[16] In these, the sign and the magnitude of J is a function of the angle at the bridging oxygen, and for an angle of 124° it is strongly antiferromagnetic. The interaction between the central Co^{3+} ions is much weaker, and we attribute this mainly to the much smaller Co^{3+}-O-Co^{3+} angle of 92°, which leads to a cancellation of ferro and antiferromagnetic contributions to J within Co^{3+}–O/O−Co^{3+} plane. This view is supported by comparison with $Na_6Co_2O_6$ where for a virtually identical geometry there is no manifestation of magnetic interactions down to about 100 K.

At 50 K in $Na_{10}Co_4O_{10}$ we thus have two strongly AF coupled Co^{2+}–Co^{3+} dimers, each with a $S = 1/2$ ground state. The coupling between these dimers is weak and cannot be quantified because of the onset of the ferromagnetic order at 38 K. This cooperative effect results from intercluster interactions. An inspection of the crystal structure (Figure 2) reveals unusually short Co^{2+}–Co^{2+} distances of $d = 4.1$ Å along the b axis between neighboring clusters, which may act as interaction pathways. From the small value of the ordered moment $M = 0.13$ μ_B per Co_4 at 10 K the order is more likely canted antiferromagnetic rather than ferromagnetic.

In conclusion, the unusual new structure of the title compound is accompanied by unusual magnetic properties. We can clearly determine a hierarchy of exchange effects. A strong antiferromagnetic intracluster exchange interaction between Co^{2+} and Co^{3+} ions dominates the high T magnetic behavior. Below 38 K cooperative effects become important. As a consequence, the intracluster Co^{3+}–Co^{3+} coupling and the intercluster interactions cannot be separated.

Experimental Section

Starting materials for the preparation of $Na_{10}Co_4O_{10}$ were NaN_3 (Sigma, 99.5%), $NaNO_3$ (Aldrich, 99%) and activated Co_3O_4.

Cobalt oxide was prepared by heating $Co(C_2O_4)\cdot 2H_2O$ (Alfa, Reagent Grade) in a stream of oxygen at 375°C for 24 h. Precursors (NaN_3, $NaNO_3$ and Co_3O_4) were mixed in the required ratio according to Equation (1), ground in a ball mill, pressed in pellets under 10^5 N, dried under vacuum (10^{-3} mbar) at 150°C for 12 h, and placed under argon in a tightly closed steel container provided with a silver inlay.[4b] In a flow of dry argon the following temperature treatment was applied: 25→260°C (100 K h^{-1}); 260→380°C (5 K h^{-1}); 380–500°C (20 K h^{-1}) followed by subsequent annealing for 50 h at 500°C. The obtained black powder is very sensitive to air and moisture and all following manipulation were performed in an inert atmosphere of purified argon.

Single crystals were grown by subsequent annealing of the as-prepared powder at 500°C for 2000 h in silver crucibles, which were sealed in glass ampoules under dry argon.

Magnetic measurements were performed on a SQUID-Magneto-meter (MPMS 5.5, Quantum Design) between 2 and 330 K in a magnetic field up to 5 T.

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[5] Crystal data: monoclinic, $C2/c$ (No. 15), $Z = 4$, $a = 14.9061(4)$, $b = 8.1008(2)$, $c = 11.4233(3)$ Å, $\beta = 104.6102(9)°$, $M_r = 625.62$, $\rho = 3.11$, Single crystal X-ray structure determination: intensities were measured at 293 K with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) on a Bruker AXS Diffraktometer with APEX Smart CCD; 3510 independent reflections (13458 total measured) were analysed by direct method. The refinement by full-matrix least squares gave final values $R_1(all) = 0.0294$, $R_w(all) = 0.0689$. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-413025.

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