Synthesis, Structures, Magnetic Properties, and Absorption Spectra of the Alkaline Oxocobaltates(II): Li_6CoO_4, Na_4CoO_3, and $Na_{10}Co_4O_9$

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Received April 17, 1998. Revised Manuscript Received August 13, 1998

The synthesis of Li_6CoO_4, Na_4CoO_3, and $Na_{10}Co_4O_9$ and the refinements of the crystal structures of the two sodium compounds are reported. The physical properties of these materials have been studied by measuring the absorption spectra and the susceptibility. An interpretation of these data is presented for the tetrahedral $[CoO_4]^{6-}$ and trigonal planar $[CoO_3]^{4-}$ complexes in terms of the angular-overlap model.

Introduction

There has been considerable interest in, for example, "Manganese Blue", i.e., compounds that contain Mn^{5+} in tetrahedral coordination with oxygen, as a material for industrial purposes. Reinen and co-workers also extensively studied the spectroscopic properties of related compounds.[1] Their results include studies of how doped materials in different hosts effect the site symmetry of the transition metal cation and allow access to "tuneable" shifts in the absorption bands. Egyptian Blue, $CaCuSi_4O_{10}$, used in the old Egyptian culture for dying purposes, has been studied in terms of the characterization of the square planar Cu^{2+} connected by oxygen[2] and compared to $K_6CuSi_2O_8$ and $A_4CuSi_2O_7$ (A = Rb, Cs) recently.[3] The change of the counterions from Ca^{2+} to alkaline cations has again some influence on the copper site.

The main aspect of this study is to present the cobalt compounds Li_6CoO_4, Na_4CoO_3, and $Na_{10}Co_4O_9$ and their properties in order to make experimental data accessible for future applications.

Alkaline-rich oxometalates have been of considerable interest in the past. The synthesis of these highly moisture sensitive compounds requires special precautions, so their properties were excluded from further investigation. Therefore, knowledge is still limited to the characterization of new phases and the determination of their crystal structures. In the past, ligands such as O^{2-} were considered to stabilize higher oxidation states, as for example in $KMnO_4$, K_2FeO_4, or K_3FeO_4 with the transition metal ion in a tetrahedral coordination.[4] More recent investigations clearly show that under certain conditions the lower valent oxometalates with alkaline counterions can be obtained. However, these "low"-valent oxometalates exhibit unusually low coordination numbers (CN) for the transition metal ion. The crystal data of these compounds reveal a decreasing coordination of the transition metal ion, for example CN = 3 for Co^{2+} and Fe^{2+} or CN = 2 for Ni^{2+}, Fe^{+}, Co^{+}, and Ni^{+}, respectively.[5,6] The properties of K_2NiO_2, KNa_2NiO_2, and K_3NiO_2 have been investigated.[7,8] Most of these compounds do show a ratio of alkaline to transition metal of 3:1. Therefore, these compounds can be considered as alkaline-rich materials with the transition metalate complexes "diluted" in the solid state of A_2O. Proceeding in this way, the structure of Li_6CoO_4 [9] and the refined one of Na_4CoO_3 fit the model. Both compounds have been studied in terms of their magnetic and spectroscopic properties. The magnetic behavior of $Na_{10}Co_4O_9$ is compared to Na_4CoO_3 in the further discussion.

Experimental Section

Li_6CoO_4, Na_4CoO_3, and $Na_{10}Co_4O_9$ can be obtained by reaction of Li_2O (Aldrich, 98%) or Na_2O [reaction of NaOH (Merck, p.a.) with Na (Riedel-de Häen, 98%)], respectively, with CoO [from thermal decomposition of the carbonate] in sealed Ag containers at 450−550 °C. To synthesize pure highly crystalline phases it is necessary to use a small excess of the alkaline oxide. All reactions were carried out in an Ar atmosphere for handling these compounds as well as sealing them to prevent them from reacting with air and moisture. Furthermore, the Ag containers were enclosed under inert gas in glass ampules.

Another route to prepare these compounds is via redox reactions. For example, one may oxidize Co metal with Na_2O_2

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10.1021/cm9802907 CCC: $15.00

in the presence of Na_2O, or one may use CuO as an oxidizing agent; metallic copper is then formed. Both reactions occur at approximately 300 °C (DSC, Netzsch STA 409, 10 K/min, closed Ag containers, Ar atmosphere) to form CoO in the first step and Cu (XRD, Stoe, Ag crucible, N_2 atmosphere). The formation of the ternary phases takes place at higher temperatures.

The purity of the samples was checked by X-ray diffractometry (Guinier technique).

The crystal structures of Na_4CoO_3 and $Na_{10}Co_4O_9$ were redetermined from intensity data collected on a IPDS (Stoe) and AED2 four-circle diffractometer (Siemens), respectively.

Magnetic measurements were carried out with a SQUID, Quantum Design, and Faraday balance, respectively. The data were corrected for diamagnetic contributions.[10] Room-temperature absorption spectra were recorded with a Cary 05E (Varian) spectrometer. Unfortunately, the single crystals were too small and too dark in color so that no single-crystal measurement could be carried out. Therefore, only powder samples of ground crystals were used. IR spectra were obtained on a Nicolet 5PC spectrometer.

Results and Discussion

Crystal Structures. Li_6CoO_4 has been previously characterized by Hoppe and Luge.[9] The structure can be described as a derivative of the Li_2O type of structure with one-eighth of the tetrahedral sites unoccupied according to $4Li_2O \equiv Li_8O_4 \rightarrow Li_6Co\square O_4$. The Co−O distances are 199.6 pm and the O−Co−O angles 104.5° (4×) and 119.9° (2×), respectively. Therefore, the isolated $[CoO_4]^{6-}$ complex is not of T_d symmetry but has the point symmetry D_{2d}. Shortest interatomic Co−Co distances are 465.4 pm. Li_6CoO_4 crystalizes in the space group $P4_2/nmc$ and the lattice constants were refined within this work to $a = 654.40(5)$ pm and $c = 465.14(5)$ pm, in good agreement with the literature data.[9]

Previous structure determinations of Na_4CoO_3 and $Na_{10}Co_4O_9$ reveal some controversy with respect to differences in Co−O distances and O−Co−O angles.[11,12] Also, the space group *Cc* for Na_4CoO_3 led to some discussion. While the structure determination was first carried out in $P1$ [13] and almost at the same time in *Cc*,[11] there was a comment referring to the corrected space group, *Cc*, later on.[14] An investigation related to the acentric space group, *Cc*, was to look at the SHG effect (second harmonic generation), which could be observed using a powder sample of Na_4CoO_3. Therefore, a redetermination of the crystal structure seemed to be advisable as these data were also used for the input to carry out the calculations in terms of the AOM (angular-overlap model) with respect to the measured magnetic and spectroscopic properties. Results of the crystal structure redetermination for Na_4CoO_3 and $Na_{10}Co_4O_9$ are presented in Tables 1−4. In comparison with previous results, it could be confirmed that only one crystallographic site for Co^{2+} is present in Na_4CoO_3 (*Cc*). A better refinement in this space group also gave more consistent interatomic distances and angles for the $[CoO_3]^{4-}$ complex (Table 5). Specially the latter ones were important for the calculation and assignment of the spectrum. For example, interatomic distances of $d(Co-O) = 172$, 187, and 205 pm were given in the literature.[11] In the case of $Na_{10}Co_4O_9$, the previous obtained results could be confirmed.[11,12b]

Table 1. Crystallographic Data for Na_4CoO_3

space group, *Cc* (No. 9); crystal system, monoclinic, $Z = 4$
$a = 1103.7(2)$ pm, $b = 576.42(7)$ pm, $c = 814.9(1)$ pm, $\beta = 114.06(1)°$
IPDS data: $-14 < h < 14$, $-7 < k < 7$, $-10 < l < 10$, $2\Theta_{max} = 56.05°$
1050 unique reflections of 4483 measured
$\lambda = 71.069$ pm, Kα(Mo), $\mu = 3.69$ mm^{-1}, $F(000) = 380$
$R_{int} = 3.07\%$, $R_1 = 2.36\%$ for 1004 $F_o > 4\sigma(F_o)$, 2.52% for all data
$wR_2 = 6.02\%$, GOOF = 1.097, $w = 0.042$, refinement[15]
powder data: $a = 1103.71(7)$ pm, $b = 576.39(5)$ pm, $c = 814.81(5)$ pm, $\beta = 114.058(4)°$

Table 2. Atomic Parameters and Coefficients of the Equivalent Temperature Factors[16] (in pm^2) for Na_4CoO_3

atom	site	*x*	*y*	*z*	U_{eq}
Co	4a	0.85544(3)	0.15091(6)	0.68630(4)	111(1)
Na1	4a	0.9891(2)	−0.3400(2)	0.8835(3)	221(4)
Na2	4a	0.7684(3)	−0.3314(3)	0.4765(3)	234(4)
Na3	4a	0.6844(2)	−0.2115(2)	0.7867(2)	170(3)
Na4	4a	0.0850(1)	0.1585(2)	0.0651(2)	144(3)
O1	4a	0.6890(2)	0.0033(5)	0.5456(3)	134(5)
O2	4a	0.0154(3)	0.0088(4)	0.7680(4)	150(6)
O3	4a	0.8104(2)	0.4487(4)	0.7332(3)	128(5)

Table 3. Crystallographic Data for $Na_{10}Co_4O_9$

space group, *P*-1 (No. 2); $Z = 2$
$a = 836.3(2)$ pm, $b = 846.8(2)$ pm, $c = 1137.2(2)$ pm
$\alpha = 86.552(9)°$, $\beta = 70.26(1)°$, $\gamma = 61.260(9)°$
four-circle-diffractometer data: $-9 < h < 6$, $-9 < k < 9$, $-12 < l < 12$; $2\Theta_{max} = 45.07°$
1724 unique reflections of 3556 measured
$\lambda = 71.069$ pm, Kα(Mo), $\mu = 5.09$ mm^{-1}, $F(000) = 580$
$R_{int} = 3.17\%$, $R_1 = 3.41\%$ for 1063 $F_o > 4\sigma(F_o)$, 7.91% for all data
$wR_2 = 8.19\%$, GOOF = 0.985, $w = 0.0302$, refinement[15]
powder data: $a = 835.6(2)$ pm, $b = 846.5(2)$ pm, $c = 1142.6(3)$ pm
$\alpha = 86.73(2)°$, $\beta = 70.15(2)°$, $\gamma = 61.23(2)°$

Table 4. Atomic parameters and Coefficients of the Equivaltent Temperature Factors[16] (in pm^2) for $Na_{10}Co_4O_9$

atom	*x*	*y*	*z*	U_{eq}
Co1	0.0639(2)	0.0322(2)	0.6431(1)	164(3)
Co2	−0.4239(2)	0.7536(2)	0.8509(1)	174(3)
Co3	−0.7079(2)	0.1865(2)	0.8579(1)	163(3)
Co4	−0.2406(2)	0.4609(2)	0.6500(1)	176(3)
Na1	0.3476(5)	−0.4200(5)	0.6268(3)	239(9)
Na2	−0.1420(5)	0.3257(5)	0.8834(3)	243(9)
Na3	0.4985(5)	−0.1157(5)	0.6076(3)	215(8)
Na4	0.0063(4)	0.6311(5)	0.8561(3)	204(8)
Na5	0.1543(5)	−0.1132(5)	0.8864(3)	217(8)
Na6	0.1708(5)	0.3431(5)	0.6299(3)	219(8)
Na7	−0.5241(4)	0.4250(5)	0.8783(3)	211(8)
Na8	0.3735(5)	−0.1637(5)	0.3640(3)	253(9)
Na9	0.1016(5)	0.2247(5)	0.3803(3)	262(9)
Na10	−0.2620(5)	0.0258(5)	0.8841(3)	230(8)
O1	−0.4499(7)	0.9691(7)	0.7884(5)	214(14)
O2	−0.1977(7)	0.2428(7)	0.7144(5)	224(14)
O3	0.2509(7)	0.0667(8)	0.5272(5)	224(15)
O4	0.0617(7)	−0.1576(7)	0.7247(5)	202(13)
O5	−0.6005(7)	0.7084(7)	0.9658(5)	179(13)
O6	−0.6915(7)	0.3720(7)	0.7736(5)	216(13)
O7	−0.9080(7)	0.1674(7)	0.9721(4)	165(13)
O8	−0.1625(7)	0.5653(7)	0.7528(5)	176(12)
O9	−0.3497(7)	0.5695(7)	0.5386(5)	214(13)

The main features of the structures are shown in Figures 1 and 2. Isolated $[CoO_3]^{4-}$ complexes are present in Na_4CoO_3. The structure can also be described as a member of the (distorted) Li_2O type of

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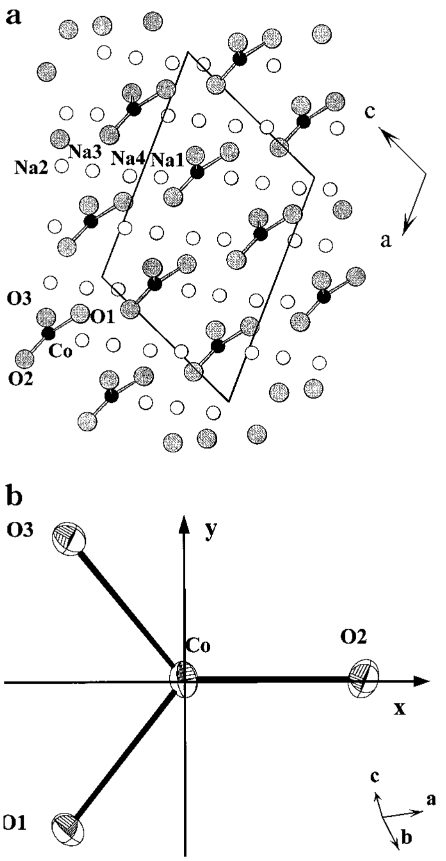

Figure 1. (a) Crystal structure of Na_4CoO_3. (b) Part of the structure of Na_4CoO_3 illustrating the $[CoO_3]^{4-}$ complex (thermal vibration ellipsoids of 50% probability) with respect to the crystal coordinates (*a, b, c*) and the axis (*x, y,* and *z*; *z* is perpendicular to the plane defined by *x* and *y*) used for the assignment of the spectroscopic data.

Table 5. Selected Interatomic Distances (in pm) and Angles (in grd) for Na_4CoO_3

Co−O2	180.9(3)	O3−Co−O2	129.9(1)	Na3−O1	234.0(3)
Co−O3	186.9(2)	O1−Co−O2	124.8(1)	Na3−O1	241.0 (3)
Co−O1	192.3(2)	O1−Co−O3	105.0(1)	Na3−O2	242.2(3)
Na1−O3	221.4(3)	O1−Na1−O3	122.0(1)	Na3−O3	254.1(3)
Na1−O1	226.3(3)	O2−Na1−O3	119.3(1)	Na4−O2	230.0(3)
Na1−O2	228.8(3)	O2−Na1−O1	110.4(1)	Na4−O1	230.0 (3)
Na2−O1	228.2(4)			Na4−O3	238.1(3)
Na2−O3	231.4(3)			Na4−O2	238.3(3)
Na2−O3	232.5(3)				
Na2−O2	280.3(4)				

structure with partially empty cation and anion sites according to $[Na_3\square_3(NaCo)]O_3\square$. One O^{2-} site is unoccupied, so the coordination number of $Na(1)^+$ and Co^{2+} is reduced from four (tetrahedral) to three (distorted trigonal planar); for interatomic distances and angles, see Table 5. Co^{2+} is located about 3 pm out of the plane defined by the three coordinating oxygen atoms. Shortest Co−Co interatomic distances are about 443 pm, forming zigzag chains parallel to [001].

A special feature of the structure of $Na_{10}Co_4O_9$ is that the $[CoO_3]$ units are connected via corners to yield $[Co_4O_9]^{10-}$ tetramers (Figure 2); for interatomic distances and angles, see Table 6. The mean interatomic Co−Co distance within the tetramer is 325 pm and it is 400 pm to Co belonging to neighboring tetramers, so that if one only accounts for these distances, a layer results, neglecting the next sphere with Co−Co distances of 480 pm. Na−O distances are observed within the range 230−248 pm for Na1 to Na8 (CN = 4). Na9 has three distances to oxygen atoms between 235 and 240 pm and a longer one of 262 pm. For Na10, a coordination of 4 + 1 is observed with Na10−O distances of 241−253 pm and one of 268 pm.

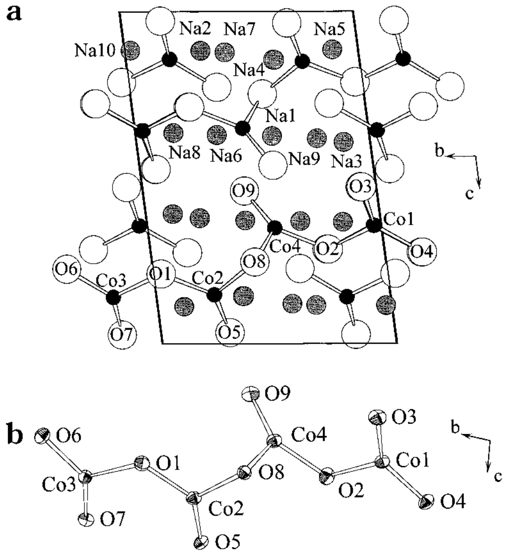

Figure 2. (a) Crystal structure of $Na_{10}Co_4O_9$. (b) The tetramer unit $[Co_4O_9]^{10-}$ in $Na_{10}Co_4O_9$ (thermal vibration ellipsoids of 50% probability).

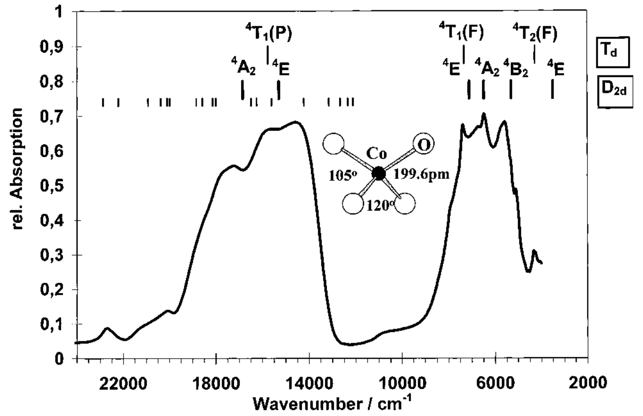

Figure 3. Absorption spectrum of Li_6CoO_4 with assigned calculated transitions in T_d ($^4A_2$ ground state) and D_{2d} ($^4B_1$ ground state). The unlabeled ones represent the calculated spin-forbidden transitions in D_{2d}. The insert shows the $[CoO_4]^{6-}$ complex in Li_6CoO_4 with interatomic distances and angles.

Table 6. Selected Interatomic Distances (in pm) and Angles (in grd) for $Na_{10}Co_4O_9$

Co1−O3	180.8(5)	O2−Co1−O4	107.5(2)
Co1−O4	181.2(5)	O4−Co1−O3	134.4(3)
Co1−O2	196.2(5)	O2−Co1−O3	117.9(2)
Co2−O5	179.3(5)	O8−Co2−O1	106.2(2)
Co2−O1	185.7(5)	O1−Co2−O5	130.1(2)
Co2−O8	194.5(5)	O8−Co2−O5	123.5(2)
Co3−O7	181.0(5)	O1−Co3−O6	106.7(2)
Co3−O6	182.9(5)	O6−Co3−O7	133.3(2)
Co3−O1	196.8(5)	O1−Co3−O7	119.8(2)
Co4−O9	176.6(5)	O8−Co4−O2	102.1(2)
Co4−O2	185.9(5)	O2−Co4−O9	131.7(2)
Co4−O8	194.1(5)	O8−Co4−O9	125.8(2)

Spectroscopic Investigation of Li_6CoO_4. The absorption spectrum of Li_6CoO_4 shows two broad bands in the visible and the near-infrared region centered at ≈15 800 and ≈6500 cm^{-1}, respectively (Figure 3). These are the two spin-allowed transitions for a d^7 ion in a

Table 7. AOM Parameters (in cm^{-1}) for Li_6CoO_4 and Na_4CoO_3

	Li_6CoO_4	Na_4CoO_3
B	685	585
C	2750	2260
ξ	320	300
k	0.71	0.70
e_σ(O)	6400	(D_{3h}) 7100 (C_{2v}; C_s) 7200 (O2), 7000 (O1, O3)
e_π(O)	2400	(D_{3h}) 1600 (C_{2v}; C_s) 1700 (O2), 1500 (O1, O3)

Table 8. Observed and Calculated Transition Energies (in cm^{-1}) for Li_6CoO_4 and Na_4CoO_3

Li_6CoO_4			Na_4CoO_3		
observed (approx)	(D_{2d})	calcd	observed (approx)	(C_s)	calcd
5300	$^4B_2$	5290		$^4A''$	2370
6500	$^4A_2$	6475	5000	$^4A'$	4860
7200	^4E	7100	5750	$^4A'$	5710
15250	^4E	15290	7450	$^4A''$	7485
16900	$^4A_2$	16830	8100	$^4A'$	8075
			11050	$^4A''$	11025
			13000	$^4A'$	12905
			14600	$^4A''$	14750

tetrahedral coordination from the $^4A_2$(F) ground state to $^4T_1$ of the P and the F term, respectively. The transition to $^4T_2$(F) would be located at about 4000 cm^{-1}, almost in the MIR region of the spectrum, and could not be measured completely due to the splitting by reduced symmetry. Figure 3 shows the spectrum and assignment of these spin-allowed transitions from the $^4B_1$(F) ground state for D_{2d}, with the tetrahedral parent terms also given. The location of the assigned bands results from calculations using the AOM (CAMMAG[17]) for T_d and D_{2d} symmetry, respectively. Tables 7 and 8 give the parameters used for the calculations and the observed and calculated transition energies, respectively. Apart from that, the spectrum reveals considerable structure that can be derived from intensity-stealing processes by spin-forbidden transitions and possibly by vibrational fine structure as well. These features will be subject of further investigations.

The metal−ligand interaction can be described using the AOM relating to bonding in transition metal complexes.[24] The d-orbital energies may be expressed in terms of σ- and π-interactions, represented as antibonding parameters e_σ and e_π.

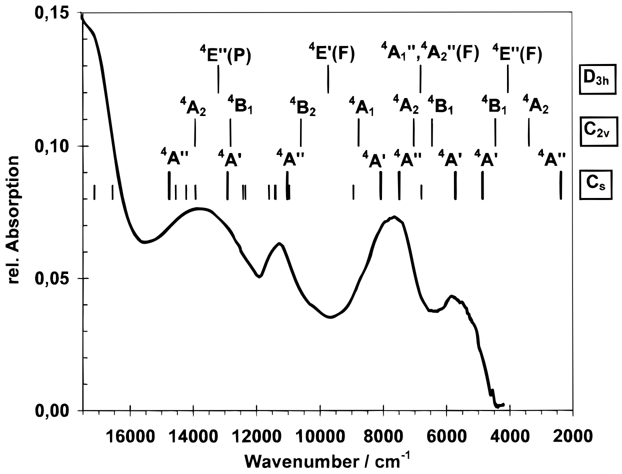

Figure 4. Absorption spectrum of Na_4CoO_3 with assigned calculated transitions in D_{3h} ($^4A_2'$ ground state), C_{2v} ($^4B_2$ ground state) and using the crystal data input of distorted reduced symmetry C_s ($^4A''$ ground state) (bold, spin-allowed transitions; the others represent the calculated spin-forbidden ones).

To compare these results for the tetrahedral complex in Li_6CoO_4 with octahedral complexes, one can roughly assume the simple relation $\Delta_t = -4/9\Delta_o$ with $10D_q = \Delta_o = 3e_\sigma - 4e_\pi$.[20,24] That gives in this case for $[CoO_4]^{6-}$ $\Delta_t = -4270$ cm^{-1} and $\Delta_o = 9600$ cm^{-1} (obtained with the e_σ and e_π values given in Table 7), respectively. For $[Co(H_2O)_6]^{2+}$ Δ_o is found to be 9300 cm^{-1},[18] and for NiO, Δ_o equals 8900 cm^{-1}.[19] The M−O distances are considerably longer with $d(Co-OH_2) = 215$ pm and $d(Ni-O) = 210$ pm compared to $d(Co-O) = 199.6$ pm for Li_6CoO_4. Δ_o tends to increase as the M−O distance shortens in a way related to the change in the bonding parameters, e_σ and e_π, by the power of 5−6 of the bond length.[20] This might account for the differences in Δ_o. As in Li_6CoO_4, Co^{2+} is tetrahedrally coordinated by oxygen; it is of some interest to also compare Δ_t with other compounds in such a coordination, which is difficult as there are almost no spectroscopic data of Co^{2+} coordinated by four oxygen available. In conclusion, one would roughly expect Δ_t to be ≈ -4100 cm^{-1} for the oxo complex, which is in good agreement with the calculated data derived from the above-mentioned equations for the given octahedral examples and the data of the CoN_4 T_d chromophore.[23] Recently, Bronger et al.[21] published magnetic data for Na_6CoS_4, K_6CoS_4, and Na_6CoSe_4 and referred to $\Delta_t = -2880$ cm^{-1} for Na_6CoS_4, obtained from spectroscopic investigations. This is even lower than observed for $[CoCl_4]^{2-}$ ($\Delta_t = -3200$ cm^{-1}),[18] but in agreement with the spectrochemical series.

Spectroscopic Investigation of Na_4CoO_3 and $Na_{10}Co_4O_9$. The absorption spectrum of Na_4CoO_3 is shown in Figure 4. The assignment was made according to the one-electron sequence of d-orbitals in D_{3h}: $d_{x^2-y^2}$, $d_{xy} \gg d_{z^2} > d_{xz}$, d_{yz} (see Figure 1b). Thereafter the symmetry was reduced to C_{2v}, which is close to the true site symmetry for Co^{2+} in the compound, and finally, the structural data (atomic parameters and lattice constants, Table 2) according to the C_s point symmetry were used for the input.

Changing to C_{2v}, and paying tribute to the different Co−O distances in reducing the e_σ and e_π parameters for the longer spacings [average distance (Co−O1 and

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Co−O3) and equal angles ∠O2−Co−O1 and ∠O2−Co−O3, respectively], introduces the splitting of the former degenerate E and (A_1,A_2) states. The site symmetry derived from the crystal data is lower, C_s, for which the calculated transitions are as well shown in Figure 4. Here it is assumed that the bonding Co−O1 and Co−O3 can be represented as an average environment, and therefore, the calculation in C_s symmetry accounts not only for the derivation of bond angles (O−Co−O) but also for the slightly aplanar geometry of the complex and the different interatomic distances *d*(Co−O2) and *d*(Co−O1, Co−O3), respectively. The e_π parameters are regarded to be isotropic and therefore represent average values, although the complex symmetry demands anisotropic interactions. The AOM parameters are included in Table 7.

Many publications have been devoted to the effect of d−s mixing, in particular for Cu^{2+} in square planar coordination, effectively decreasing the energy of the d_{z^2} orbital.[2,22] Therefore, one should also expect some contribution in this case. Actually, a rather good fit to the experimental spectrum is obtained without taking d−s mixing into account. On the contrary, a further e_{ds} value would bring the $^4A_2'$(F) and $^4E''$(F) (D_{3h}) states closer together, leaving the transition at 11 000 cm^{-1} in the spectra unassigned, and might even lead to a change of the ground state to $^4E''$(F). On the other hand, more states would then contribute to the magnetic properties, yielding much higher μ_{eff} than observed (see below). Therefore, it seems safe to assume that the contribution due to d−s mixing is small.

From IR investigations of Na_4CoO_3, one finds a wide region between 1600 and 4000 cm^{-1} of unstructured absorption (≈40% transmittance loss) and three sharp intense bands at 607, 560, and 470 cm^{-1}. The latter ones are part of further investigations.

Comparing these results with those of others is almost impossible because only spectroscopic investigations of more common coordination geometries of the 3d-transition metal ions is accessible. But relations to five-coordinate Co^{2+} complexes (D_{3h})[23,25] can be drawn by removing the contribution of the two axial ligands.

The absorption spectrum of $Na_{10}Co_4O_9$ revealed only two broad unstructured bands in the visible (≈14 000 cm^{-1}) and the near-infrared (≈10 000-6000 cm^{-1}, with a shoulder extending to 4000 cm^{-1}). The very broad one in the near-infrared can be looked at as the superimposed spectra of two different [CoO_3] complexes, one with two oxygen atoms connected via corners to neighboring Co^{2+} and the other one with two terminal oxygen atoms. Upon including the dependence of the bonding parameters on the Co−O distance and reducing the π-interaction for the bridging oxygen atoms, fits the observed spectrum quite closely. Because of the poorly resolved spectrum, no further details are presented.

Na_4CoO_3 is intensely red, like most of the oxometalates of iron, cobalt, and nickel with the transition metal in an environment of the low (“unsaturated”) coordination numbers of 2 or 3. $Na_{10}Co_4O_9$ is even darker in color. The more intense bands commencing from 16 000 cm^{-1} toward higher wavenumbers cannot be described in terms of the AOM and are most probably low-lying charge-transfer transitions. This region has to be considered in future studies.

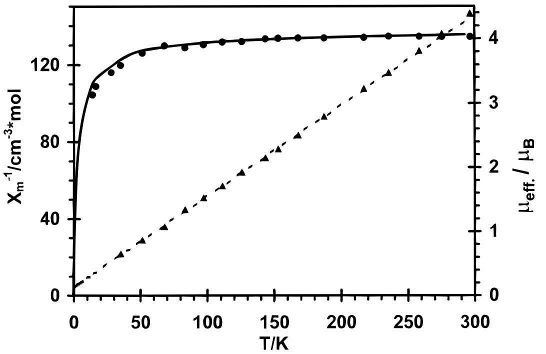

Figure 5. Observed and calculated (AOM parameter set) reciprocal susceptibility (▲, - - -) and μ_{eff}/μ_B (●, −) for Li_6CoO_4.

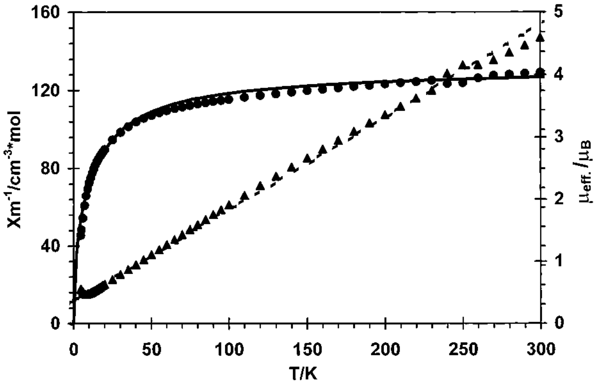

Figure 6. Observed and calculated (AOM parameter set) reciprocal susceptibility (▲, - - -) and μ_{eff}/μ_B (●, −) for Na_4CoO_3.

Magnetic Properties of Li_6CoO_4. Hoppe and Luge presented magnetic data of Li_6CoO_4 previously.[9] They found a much smaller value for μ_{eff} of 4.1μ_B compared to Cs_2CoCl_4 (μ_{eff} = 4.7μ_B)[18] at 300 K. A reinvestigation of the magnetic behavior was carried out, and within the experimental error, we observed the same value. These measurements were performed on a Faraday magnetometer. The Curie−Weiss law assumed for this data set yields $\Theta = -8$ K, and therefore, antiferromagnetic behavior is present for this compound. The calculation of the magnetic behavior includes corrections for antiferromagnetic interactions and the first- and second-order Zeeman effect (CAMMAG[17]). The orbital reduction parameter, *k*, was set to 0.71, matching the reduction of the Racah parameter, *B*, (B_o = 971 cm^{-1})[23] as well. The effective spin−orbit coupling parameter, ξ = 320 cm^{-1} (ξ_o = 515 cm^{-1}),[18] is used for the input. Figure 5 shows the measured and calculated reciprocal susceptibility and μ_{eff} values for Li_6CoO_4.

In comparison with the results obtained for Na_6CoS_4 (μ_{eff} = 4.6μ_B),[21] it is plausible, according to the lower value for Δ_t for the sulfide compound, which means that the first transition energies are found at lower wavenumbers and therefore these states contribute to the magnetic moment of the ground state in a more extended manner. This influence can be estimated from the equation approximately representing the first-order Zeeman effect on the magnetic moment, $\mu_{eff}^{spin-only}$, after corrections for the temperature-independent paramag-

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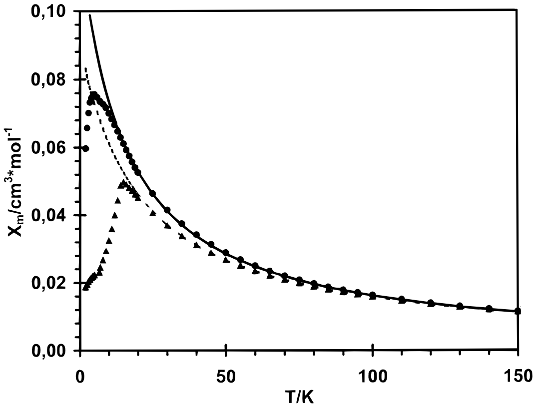

Figure 7. Observed and calculated (Curie−Weiss law) susceptibility for Na_4CoO_3 (●, −) and $Na_{10}Co_4O_9$ (▲, - - -).

netism (TIP) for A_2 terms: $\mu_{eff} = \mu_{eff}^{spin-only}(1-4k^2\lambda_o/|10D_q|)$ with $|10D_q| = |\Delta_t|$ and $\lambda_o = -\xi_o/3$ for Co^{2+} in a tetrahedral environment.[18] With the knowledge of the spectroscopic data for this compound now, see above, this can be explained as a result of Δ_t being much larger and the effective spin−orbit coupling parameter being smaller for Li_6CoO_4 than in the chloro and the sulfide compound, respectively.

Magnetic Properties of Na_4CoO_3 and $Na_{10}Co_4O_{10}$. Na_4CoO_3 and $Na_{10}Co_4O_9$ have both μ_{eff} values $\approx 4.0\mu_B$ at 300 K and show antiferromagnetic behavior according to the Curie−Weiss law with $\Theta \approx -15$ and -25 K, respectively. Again, the data for Na_4CoO_3 could be fit in the temperature region with the bonding parameters obtained from the interpretation of the spectra, with corrections for antiferromagnetic interactions and inclusion of a somewhat smaller value for $k = 0.70$ and $\xi = 300$ cm^{-1} (Figure 6). If one pronounces that the contribution of d−s mixing produces a $^4E''(F)$ ground state with the $^4A_2'$ within a few hundred wavenumbers, μ_{eff} is calculated including first and second Zeeman interaction to be $\approx 4.5\mu_B$. Therefore, the magnetic data provides some support for the above-discussed assignment. $Na_{10}Co_4O_9$ shows a very similar behavior to Na_4CoO_3 (Figure 7). The low-temperature region is of some interest for more detailed investigations. It appears that apart from the three-dimensional ordering in both compounds, a second effect (shoulder at $\approx$10 K) could be present for $Na_{10}Co_4O_9$, making it an interesting material to study low-dimensional cooperative effects.

Conclusions

Magnetic and spectroscopic properties of Li_6CoO_4 and Na_4CoO_3 are described in terms of the angular-overlap model. Comparing these two compounds, it seems that in terms of bonding the $[CoO_3]^{4-}$ is even more “covalent“ than the $[CoO_4]^{6-}$ complex as estimated from the B/B_o ratio. The derived Racah parameter, B, for Co^{2+} in Li_6CoO_4 is comparable with those reported in the literature for similar ligands (O, N) ($\approx$800 cm^{-1} for octahedral, $\approx$750 cm^{-1} for trigonal bipyramidal, and $\approx$700 cm^{-1} for tetrahedral environments).[23,25] For the trigonal planar complex in Na_4CoO_3, a much lower B value is found here. The e_π value is strongly reduced for the distorted trigonal planar complex. Similar e_π and k parameters have been used for the interpretation of square planar complexes.[2,3]

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft, Bonn, is gratefully acknowledged.

Supporting Information Available: Listings of atomic parameters, coefficients of the anisotropic and equivalent temperature factors, and interatomic distances and angles for Na_4CoO_3 and $Na_{10}Co_4O_9$ (6 pages). Ordering information is given on any masthead page.

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