Trinuclear Complexes M[Co(en)$_2$(SO$_3$)$_2$]$_2$(H$_2$O)$_2$·4H$_2$O (M=Mn, Fe, Co, Ni, Cu, Zn): Their Utilization for Stoichiometric Spinel Oxides and the Crystal Structure of Ni[Co(en)$_2$(SO$_3$)$_2$]$_2$(H$_2$O)$_2$·4H$_2$O

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Trinuclear complexes of the general formula M[Co(en)$_2$(SO$_3$)$_2$]$_2$(H$_2$O)$_2$·4H$_2$O (M=Mn, Fe, Co, Ni, Cu, Zn) were synthesized. The crystal structure of one of the compounds in the series, Ni[Co(en)$_2$(SO$_3$)$_2$]$_2$(H$_2$O)$_2$·4H$_2$O were determined by single crystal X-ray diffraction studies. It crystallizes in a monoclinic unit cell (a=10.079(1), b=11.560(1), c=12.699(1) Å, β=101.8(1)°, V=1448.4(2) Å^3). In the structure, a nickel atoms is bonded to two [Co(en)$_2$(SO$_3$)$_2$]$^{-1}$ through the oxygen atoms of the sulfite ligands that have Co-S bonds. Thermolysis of the complexes for M=Mn, Co, Cu, Zn in air at as low as 750 °C resulted in spinel oxides while the M=Ni compound resulted in a solid solution of rock salt type CoO and NiO. The Fe complex did not produce a single phase oxide but a mixture of M$_2$O$_3$ (M=Fe, Co) and spinel type compound.

Introduction

Single source precursors for solid state materials are of great interest not only for the thin film processes but also for low temperature synthesis of bulk materials.[1] Single source routes for solid state oxides also benefit from the stoichiometry control of metal atoms. However, there are quite a few examples of precursor molecules for spinel oxides in the literature. MFe(C$_2$O$_4$)$_3$·6H$_2$O (M=Mn, Co, Ni, Zn)[2] and M$_3$Fe$_6$(CH$_3$CO$_2$)$_{17}$O$_3$ OH·12C$_5$H$_5$N (M=Mg, Mn, Co, Ni)[3] compounds could be converted into MFe$_2$O$_4$ spinel compounds when pyrolyzed at 1000-1300 °C. Pyrolysis of some ammonium chromate salts of various formula at relatively low temperatures (< 1200 °C) reportedly produced nearly stoichiometric MCr$_2$O$_4$ (M=Mg, Ni, Mn, Co, Cu, Zn, Fe) spinel oxides.[4]

Coordination compounds of sulfite groups have been studied widely mainly because of its ability to choose different bonding modes of metal-sulfur and metal-oxygen depending on the nature of the transition metal atom.[5] Sulfite ion is classified as an intermediary base in the hard-soft acid and base theory,[6] although this classification neglects its ability to bind through both sulfur and oxygen sides. The bonding properties of sulfite ligand are extensively studied depending on the metal atoms.[5] In general, metal-sulfur bonding mode is preferred for noble metals while metal-oxygen mode is predominant for the other transition metal atoms.

In this study, we sought the possibility of making sulfite complexes that hold more than one type of metal atoms so that their thermolysis would result in stoichiometric metal compounds. We have synthesized and characterized a series of compounds that have two trivalent cobalt and one divalent transition metals. The thermolysis reactions of these yielded stoichiometric spinel oxides for most of the cases.

Experimental

Synthesis. The title compounds were obtained from reactions of corresponding divalent metal and [Co(en)$_2$(SO$_3$)$_2$]$^{-1}$ ions in aqueous solutions. Na$_2$[Co(en)$_2$(SO$_3$)$_2$]ClO$_4$ salt was obtained according to the literature procedure.[7] The crystalline powder was recrystallized before use. This was dissolved in distilled water to make a 0.33M solution based on cobalt metal. 1M aqueous solutions of divalent metal ions (M=Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd) were prepared by dissolving metal nitrates or sulfates in distilled water. The solutions of the cobalt complex and divalent metal ion were combined in M : Co ratio of 1 : 2 to make a clear solution. After standing one or two days, there formed brown crystalline precipitates except for the Ca reaction. These were recovered by filtration and washing with ethanol and air drying. Typical yields were over 70% regardless the type of M ion.

Pyrolysis of precursor molecules. Each molecular precursor was pyrolyzed in air at 750 °C with a heating rate of 1 °C/min and a two hour hold in an alumina boat to get black powder. The final weight of the black powder corresponded to the complete loss of all organic and sulfite parts of the molecule.

Single crystal X-ray structure determination. A brown rhombus crystal of Ni[Co(en)$_2$(SO$_3$)$_2$]$_2$(H$_2$O)$_2$·4H$_2$O of approximate dimension 0.4 x 0.3 x 0.2 mm glued on a glass fiber was mounted on a Enraf Nonius CAD4 diffractometer equipped with monochromated Mo Ka radiation (λ=0.71079 A). Initial random search on the crystal resulted in twenty five peaks that could be indexed with a monoclinic unit cell (a=10.079(1), b=11.560(1), c=12.699(1) Å, β=101.8(1)°, V=1448.4(2) Å^3). Data collection was performed accordingly on a hemisphere (hkl and hk-l). The systematic extinction condition 0k0 (k=2n+1), h0l (h+l=2n+1) uniquely indicated that the space group was P2$_1$/n (No. 14) which was confirmed by the crystal structure refinement results.

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Table 1. Crystal data and structure refinement for $Ni[Co(en)_2(SO_3)_2]_2(H_2O)_2 \cdot 4H_2O$

Empirical formula	C4 H11 Co N4 Ni0.50 O7 S2
Formula weight	379.57
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2₁/n (No. 14)
Unit cell dimensions	a=11.5600(10) Å
	b=12.6990(10) Å beta=101.79(10)°
	c=10.0790(10) Å
Volume	1448.4(2) Å³
Z	4
Density (calculated)	1.741 Mg/m³
Absorption coefficient	2.131 mm⁻¹
F(000)	768
Crystal size	0.4×0.3×0.2 mm
Theta range for data collection	2.41 to 22.98°
Index ranges	0<=h<=12, -13<=k<=13, 0<=l<=10
Reflections collected	1938
Independent reflections	997 [R(int)=0.0440]
Refinement method	Full-matrix least-squares on F²
Data / restraints / parameters	997 / 0 / 187
Goodness-of-fit on F^2	1.192
Final R indices [I>2sigma(I)]	R₁=0.0353, wR₂=0.0998
R indices (all data)	R₁=0.0368, wR₂=0.1018
Largest diff. peak and hole	0.378 and -0.309 e.Å⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$) for $Ni[Co(en)_2(SO_3)_2]_2(H_2O)_2 \cdot 4H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Co	8265(1)	8378(1)	1623(1)	16(1)
Ni	10000	10000	5000	20(1)
S(1)	10120(2)	8098(1)	2691(2)	20(1)
S(2)	8391(2)	10077(1)	2085(2)	20(1)
O(1)	7265(5)	10618(4)	1442(6)	26(3)
O(2)	9387(6)	10559(4)	1612(7)	29(3)
O(3)	8525(6)	10263(4)	3593(6)	21(3)
O(4)	10247(6)	6981(5)	3031(7)	50(3)
O(5)	10925(7)	8369(5)	1788(9)	50(3)
O(6)	10438(6)	8691(4)	3988(6)	34(3)
O(7)	11000(6)	10917(5)	3934(9)	30(3)
N(1)	8178(8)	6878(5)	1022(8)	25(4)
N(2)	8713(7)	8673(5)	-97(8)	27(4)
N(3)	6514(8)	8538(6)	860(10)	29(4)
N(4)	7767(7)	8001(5)	3293(8)	25(4)
C(1)	8760(11)	6766(6)	-157(11)	34(6)
C(2)	8491(8)	7731(6)	-1014(9)	29(4)
C(3)	5855(9)	8047(6)	1809(12)	29(5)
C(4)	6507(11)	8293(7)	3236(13)	41(6)
O(1)	1739(10)	5708(7)	1586(15)	72(6)
O(1)	2934(13)	9190(10)	1386(11)	81(5)

The direct methods on SHELXS-86[8] resulted in atomic positions of all of the metal and sulfur atoms and most of C, N, O atoms. Refinements with SHELXL-93 program[9] including these atoms and subsequent difference Fourier map calculations resulted in the remaining C, N, and O atoms. Hydrogen positions were program generated and included in the refinements as a riding model except for those on water molecules which could not be located. The final cycles of full-matrix refinements including the anisotropic thermal parameters for all non-hydrogen atoms resulted in a good convergence of R=0.0368 for all reflections.

The crystal data are summarized in Table 1. Atomic positions and important bond angles and distances are listed in Table 2 and Table 3, respectively.

Characterization. Thermogravimetric analyses of the complex precursors were performed with a SDT-2960 (TA instruments) thermal analysis system in air and N_2 atmosphere from room temperature up to 900 °C with a heating rate of 10 °C /min.

Infrared spectra of the complex precursors were recorded on a Nicolet 205 spectrometer on KBr pressed pellets.

Results and Discussion

The molecular structure of the precursor complex $Ni[Co(en)_2(SO_3)_2](H_2O)_2$ is shown in Figure 1. The crystal has four lattice water molecules per formula unit. The two

$[Co(en)_2(SO_3)_2]^{-1}$ complex ligands are bonded to the central Ni atom via O-bridges of the sulfite ligands. The Ni atom is also ligated by two water molecules to complete an octahedral coordination. The complex ligand of this compound is unique in that the sulfite group is bonded to trivalent cobalt via S-atom while the rest of 3d transition metal sulfite compounds in the literature have M-O-S linkages. This is a remarkable exception in view of the hard-soft acid-base theory. Sulfur, being a soft base, tends to bind to soft acids such as platinum group metals. To our knowledge, trivalent cobalt is the only 3d transition metal that can bond through sulfur of sulfite group probably due to its low spin configuration. Once Co-S bond is formed, the three terminal O atoms of each sulfite group may be able to function as ligands to form bridges between cobalt and other metal atoms.

In order to make a neutral precursor molecules out of this negatively charged cobalt complex, we have tried some reactions with divalent metal atoms (Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd). Except for the Ca reaction which did not form any compound, the reactions produced similarly looking crystalline precipitates in high yields (70%).
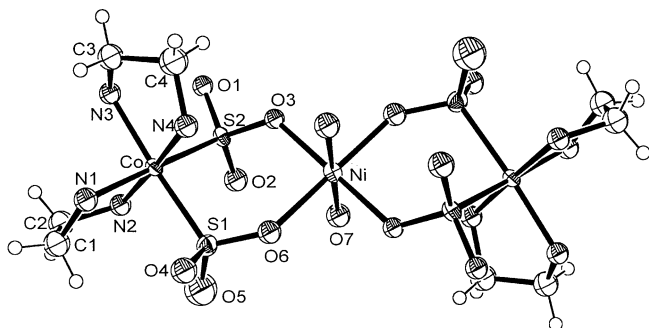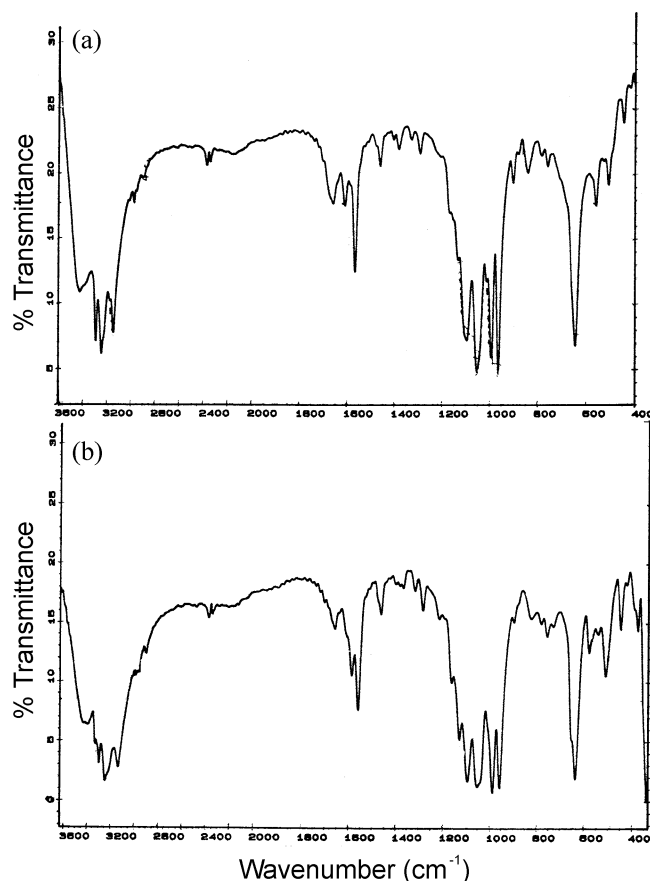
The X-ray powder patterns of the precipitates were similar to one another indicating that the precipitates had the similar crystal structures. However, the calculated powder pattern with the atomic positions from the single crystal structure data did not agree with those from the precipitates. The morphology of the precipitate was rather a needle-like, different from the rhombic single crystals. This is true even for the precipitate from the Ni reactions which also yielded single

Table 3. Selected bond lengths [A] and angles [°] for $Ni[Co(en)_2(SO_3)_2]_2(H_2O)_2 \cdot 4H_2O$

Co-N(2)	1.944(8)	Co-N(4)	1.955(9)
Co-N(1)	1.993(5)	Co-N(3)	2.030(6)
Co-S(2)	2.206(2)	Co-S(1)	2.228(2)
Ni-O(3) x2	2.011(4)	Ni-O(6) x2	2.075(5)
Ni-O(7) x2	2.084(7)		
S(1)-O(4)	1.468(5)	S(1)-O(5)	1.493(10)
S(1)-O(6)	1.489(5)	S(2)-O(2)	1.463(8)
S(2)-O(1)	1.495(5)	S(2)-O(3)	1.513(6)
N(2)-Co-N(4)	176.4(2)	N(2)-Co-N(1)	85.1(3)
N(4)-Co-N(1)	91.5(3)	N(2)-Co-N(3)	94.0(3)
N(4)-Co-N(3)	84.8(3)	N(1)-Co-N(3)	90.1(3)
N(2)-Co-S(2)	89.0(2)	N(4)-Co-S(2)	94.4(2)
N(1)-Co-S(2)	174.1(3)	N(3)-Co-S(2)	89.8(2)
N(2)-Co-S(1)	92.6(2)	N(4)-Co-S(1)	88.5(2)
N(1)-Co-S(1)	88.7(2)	N(3)-Co-S(1)	173.2(3)
S(2)-Co-S(1)	92.08(7)		
O(3)-Ni-O(3)	180.0	O(3)-Ni-O(6)	92.7(2)
O(3)-Ni-O(6)	87.3(2)	O(6)-Ni-O(6)	180.0
O(3)-Ni-O(7)	91.3(2)	O(3)-Ni-O(7)	88.7(2)
O(6)-Ni-O(7)	91.2(2)	O(7)-Ni-O(7)	180.0
O(4)-S(1)-O(5)	109.8(5)	O(4)-S(1)-O(6)	105.8(3)
O(5)-S(1)-O(6)	110.8(4)	O(4)-S(1)-Co	107.6(2)
O(5)-S(1)-Co	110.1(2)	O(6)-S(1)-Co	112.6(3)
O(2)-S(2)-O(1)	110.0(3)	O(2)-S(2)-O(3)	109.6(3)
O(1)-S(2)-O(3)	105.2(3)	O(2)-S(2)-Co	111.1(3)
O(1)-S(2)-Co	110.0(2)	O(3)-S(2)-Co	110.8(2)

Figure 2. Infrared spectra for a) $Ni[Co(en)_2(SO_3)_2]_2(H_2O)_2 \cdot 4H_2O$ and b) $Zn[Co(en)_2(SO_3)_2]_2(H_2O)_2 \cdot 4H_2O$.

crystals. However, the IR spectra and TG data for the single crystals and the precipitate from the Ni reactions were identical which implied that they had the identical compounds and compositions but with different packing modes.

The IR spectra of the precipitates all consisted of the fingerprints of the expected structure as shown in Figure 2. Since the other compounds show essentially the same spectra, we show only two of them in this figure. All of the absorption peaks in the spectrum can be assigned to the typical vibrational frequencies of the functional groups; peaks at 3200-3400 cm^{-1} to H_2O, peaks at 3188, 2743, 2520, 1601, 1511, 1086, 1034 cm^{-1} to $NH_2(CH_2)_2NH_2$, peaks at 950-

Figure 1. Molecular structure and labeling scheme of $Ni[Co(en)_2(SO_3)_2]_2(H_2O)_2 \cdot 4H_2O$.

1150 cm^{-1} to S-O, M-O, and CH_2 rocking modes, 630 cm^{-1} to $M-SO_3$, and 610 cm^{-1} to M-N stretching modes.

Thermogravimetric data of the present compounds are also almost the same (Figure 3). There are generally four steps of weight losses. The first step peaked at 100 °C corresponds to the loss of both the ligand and lattice water molecules. The origins of the other following steps are not clear, but the second and the third ones seem from the loss of ethylendiamine ligands and the fourth one mostly from the loss of sulfite groups. The fourth steps of weight losses are completed at 800-850 °C depending on the nature of the M atoms. The final weights of M=Mn, Co, Cu, Zn compounds were very closed to those expected for MCo_2O_4 spinel formation. The M=Fe, Ni compounds show further complications after the fourth step of weight loss. In the Ni case, there is a gradual weight loss starting from the end of the fourth step by a very small amount which can be attributed to the loss of oxygen atoms from the reduction reaction of Co^{3+} to Co^{2+}. This is confirmed by that the final oxide product of this compound is a solid solution of rock salt type CoO and NiO (see below). The final weight from the Fe complex was 29.12% when TG was run in air which was slightly larger than the theoretical value of 28.22%. In fact, the final weight can be explained with the solid solution formation of Co_2O_3 and Fe_2O_3. In order to control the final oxygen content, TG was run under a flow of N_2 for this compound to get 28.04%
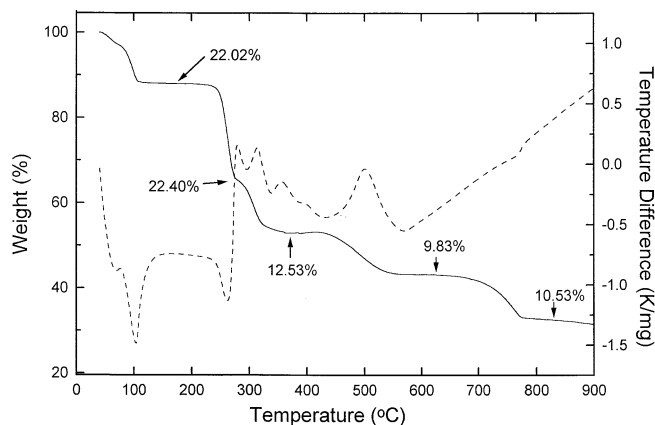
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Figure 3. Thermogravimetric data for $Mn[Co(en)_2(SO_3)_2]_2(H_2O)_2$ $\cdot 4H_2O$.

Table 4. Thermolysis spinel products of $M[Co(en)_2(SO_3)_2]_2$ $(H_2O)_2 \cdot 4H_2O$ at 750 °C for 2 hours in air

M	results	lattice parameters (Å)		references	remarks
		this study	literature		
Mn	spinel	8.256(2)	8.269	23-1237[a]	
Fe	spinel	8.363(1)	8.3919 ($CoFe_2O_4$)	22-1086[a]	two phases
		8.144(1)	8.254 ($FeCo_2O_4$)	10	
Co	spinel	8.077(1)	8.084		9-418[a]
Ni	rock salt				
Cu[b]	spinel	8.064(5)	8.054	11	
			($Cu_{0.92}Co_{2.08}O_4$)		
Zn[b]	spinel	8.0921(8)	8.0946(2)	23-1390[a]	

[a]JCPDS File number. [b]Mixed with impurity peaks (see text).

which was smaller than the desired value. The difficulty of getting the desired final weight from this Fe-compound appears to stem from our inability of obtaining $FeCo_2O_4$ spinel compound. (see below)

Supported by the TG data, these molecular precursors were pyrolyzed at 750 °C for two hours. The results are summarized and compared with the literature data from high temperature solid state reactions in Table 4. X-ray powder patterns of the final products from M=Mn and Co composed of single phases of spinel oxides (Figure 4). The Cu and Zn complexes also produced spinel oxides but with some impurity peaks. The Cu compound listed in the JCPDS file (37-878) has the composition $Cu_{0.92}Co_{2.08}O_4$ implying that the stoichiometric phase is not stable. The impurities in the Zn compounds may be due to the loss of ZnO during the pyrolysis reaction. The stoichiometric $ZnCo_2O_4$ is reported to be synthesized at 450 °C, much lower than our reaction temperature. The Ni compound resulted in a solid solution of rock salt CoO and NiO. The pyrolysis reaction of Fe compound appears to be dependent on many unknown factors. Some reactions resulted in a mixture of two spinel phases of about the same amounts probably with different Fe and Co compositions and the other a mixture of a spinel and M_2O_3 phases. The lattice parameters of the two spinel phases in the first case were 8.363(1) and 8.144(1) Å. The lattice parameters of stoichiometric $FeCo_2O_4$ and $CoFe_2O_4$ compounds are reported to be 8.254 and 8.3919 Å, respectively, implying that the one with the larger unit cell has a composition close to $CoFe_2O_4$. We can rationalize the above observations as the following. The metal atoms whose complexes produced single phase spinel oxides are stable in their divalent states and there is no redox reactions during the pyrolysis reactions. Divalent Mn and Zn do not have crystal field stabilization energies for octahedral sites. Divalent Cu is more stable than trivalent state and this does not seem to cause any redox reaction with trivalent Co. Contrarily, in the Fe-case, all of Fe^{2+} ions will undergo redox reactions with Co^{3+} in the precursor molecule to make Fe^{3+} and Co^{2+} and, thus, complicating the reaction mechanism. The 750 °C reaction may too low to complete the conversion reaction into single phase

Figure 4. X-ray powder diffraction patterns of the thermolized products of $M[Co(en)_2(SO_3)_2]_2(H_2O)_2 \cdot 4H_2O$. Indices are given based on the cubic spinel structure. Peaks marked with *are from impurities.

spinel oxide. However, higher temperature reactions do not seem to help because of the reduction of Co^{3+} at 800-850 °C as indicated by the TG data. Both $CoFe_2O_4$ and $FeCo_2O_4$ are reported to have Fe^{3+} ions.[10,11] For Ni, there may not be any redox reactions but the strong tendency for both divalent Ni and trivalent Co for octahedral sites does not allow the spinel formation at all with some of the metals in the tetrahedral sites. Instead, it apparently chooses to crystallize in rock-salt structure with all the metal atoms in octahedral sites.

Our successful conversions of some of the precursor complexes into spinel oxides at much lower temperatures than

those in the literature appear to be related with the oxidation states of the metal ions in addition to other benefits of single source precursors, that is, the oxidation states of the metal ions in the precursors are preserved in the final spinel oxides. As discussed above, the successful conversion reactions (M=Mn, Co, and partly Cu, Zn) do not undergo redox reactions between and M^{2+} and Co^{3+}. By contrast, in the Fe case, Fe^{2+} in the precursor has to be oxidized into Fe^{3+} to form either $CoFe_2O_4$ and $FeCo_2O_4$ which apparently requires higher thermal energy than 750 °C.

In summary, we have demonstrated a possible strategy to make a molecular precursor by utilizing the bifuctional nature of sulfite ligand. This idea can be extended to other ligands that can function as a bridging ligand. The key of the stoichiometry control partly lies on the use of ethylenediamine groups that limit the size of the molecules in trinulcear complexes. The 750 °C/2hr condition of pyrolysis is much milder than the literature single source methods typically of 1000 °C or higher and much lower than the conventional solid state reaction methods of 1200-1500 °C.

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