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Structure changes of compounds with complex octahedral cluster anions and Co cations after annealing in vacuum

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Abstract

Dehydration process in recently synthesized porous inorganic salts containing water molecules and formed by large cluster anions $[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$ ($\text{X} = \text{S}, \text{Se}$) and transition metal cations has been investigated. Desolvation process of the complex $\text{Co}(\text{DMF})_6[\text{Mo}_6\text{Br}_8(\text{NCS})_6]$ containing cluster Mo anions and cations with dimethylformamide (DMF) molecules has been studied. Co K, Mo K and Re L₃ XAFS measurements of these new complicated compounds, before and after annealing in vacuum at the temperature of up to 250°C, were performed. Changes of electronic and spatial structure of these compounds after the heat treatment have been established, and adequate structural models of the amorphous compounds obtained are suggested and discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: EXAFS; Cluster anions; Annealing

1. Introduction

In recent years, a number of polynuclear cluster compounds of different nuclearity, containing chalcogen atoms and terminal cyanide ligands, were obtained. Such compounds usually have a complex composition and structure, and show an amazing diversity of coordination modes of elements, a large variety of spatial structures, and unique sorption, magnetic and optical properties [1]. Recently, novel synthetic approaches to obtainment of such compounds were developed, and a series of compounds containing chalcocyanide cluster anions and cations

of different types (alkali, alkali earth metals and 3d transition elements) were obtained for the first time [2–4]. Solvent removal from such compounds at low (< 100°C) temperatures gives rise to poorly crystallized compounds, with large unfilled cavities [5], leading to a coordination unsaturation of the metal centers, unusual coordination numbers and creation of conditions for an interaction between the paramagnetic ions.

In the present work, the structural changes are studied, which take place upon the formation of new complexes of such type (poorly crystallized amorphous), as a result of annealing and dehydration of the initial crystals. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy, which are capable of studying the local environment of atoms and

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characterizing noncrystalline objects with no long-range ordering, provide a unique possibility to solve such problems [6]. However, we do not know any other studies in which these methods were used to investigate such similar objects.

In recent-years, these methods were successfully employed, in particular, by the authors of this paper, to determine the structure of different coordination compounds in solutions [7,8] and in the solid state at different temperature [9].

In this work, the EXAFS and XANES spectroscopy are employed to study the structural changes in complex compounds containing octahedral cluster anions of rhenium $\{[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}, \text{X} = \text{S}, \text{Se}\}$, or molybdenum $\{[\text{Mo}_6\text{Br}_8(\text{NCS})_6]^{2-}\}$ and cobalt cations, which take place when the compounds are annealed under vacuum at temperatures of up to 250°C.

2. Experimental

2.1. Synthesis of the compounds

The compound $(\text{H}_3\text{O})_2\text{Co}_3[\text{Re}_6(\text{Se}_8(\text{CN})_6)_2] \cdot 14.5\text{H}_2\text{O}$ (Compound 1) was prepared by the interaction of aqueous solutions of $\text{K}_4[\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 3.5\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ by the procedure described elsewhere [4]. The compound $\text{Cs}_2\text{Co}[\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (Compound 2) was obtained by the interaction of aqueous solutions of $\text{Cs}_3\text{K}[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ and CoCl_2 . The compound $\text{Co}(\text{DMF})_6[\text{Mo}_6\text{Br}_8(\text{NCS})_6]$ (Compound 3) was prepared by the interaction of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8(\text{NCS})_6]$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in a solution of dimethyl formamide.

For the desolvation, a weighed amount (200 mg) of the material was ground in an agate mortar and pressed into tablets ($d = 12$ mm, $P = 50$ atm). The tablet was fixed inside a specially fabricated cell with beryllium windows and heated under vacuum for 2 h; after which, the cell was slowly cooled down, and the EXAFS and XANES spectra were measured without exposing the sample to the air. Conducting the experiment under such conditions helps to avoid water vapor absorption by the desolvated samples. The annealing temperatures for the samples were determined from the decomposition

curves of the materials in a vacuum under the conditions of a DTA experiment. The annealing temperatures were: for Sample 1—200°C, Sample 2—200°C, Sample 3—250°C.

2.2. Measurements and processing of X-ray absorption spectra

The Co K, Mo K and Re L₃ EXAFS and XANES spectra were measured using the synchrotron radiation of the VEPP-3 storage ring of the Budker Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk. A channel-cut Si(111) single crystal was used as the two-crystal monochromator.

The obtained data were processed using the EXCURV92 package of program [10]. In the data processing, the phase and amplitude characteristics were calculated in the X_α -DW approximation using the procedures of the package [10]. For the analysis of the local environment of Co atoms, the fitting of Fourier-filtered data with k^2 weighing in the interval of photoelectron wave vectors from 3 to 12 Å⁻¹ was used. The error of determination of the interatomic distances in the fitting procedure was ~ 0.01 Å. The value of the amplitude damping factor, S_0^2 , due to the many body effects, was fixed to be equal to 0.8, and was checked against the results of data fitting for the initial complex $(\text{H}_3\text{O})_2\text{Co}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 14.5\text{H}_2\text{O}$.

3. Results and discussions

The ligand environment of the cobalt atoms in the initial compounds as determined by X-ray structural analyses are shown in Fig. 1. The coordination environments of cobalt atoms in Compounds 1 and 2 are similar, and are formed by the four nitrogens of the cyano groups and two oxygen atoms of the water molecules in the *cis*- and *trans*- positions (Table 1). The cobalt atoms bridge the $[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$ anions to form a polymer framework. Compound 2 has a close-packed layered structure, whereas Compound 1 has a rather loose covalently bonded framework $\{\text{Co}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2\}^{2-}$, with cavities filled by water molecules. The environment of the cobalt atoms in Compound 3 consists of six oxygen atoms of the

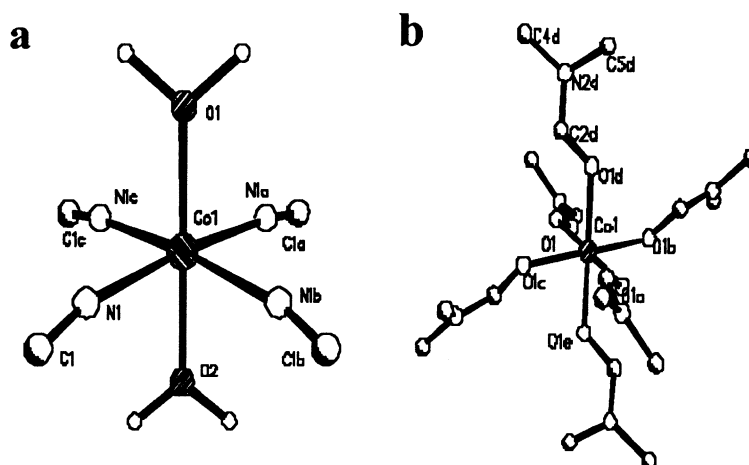


Fig. 1. The structure of the Co atom coordination site in initial compounds: (a) $(\text{H}_3\text{O})_2\text{Co}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 14.5\text{H}_2\text{O}$ (1), $\text{Cs}_2\text{Co}[\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (2); (b) $\text{Co}(\text{DMF})_6[\text{Mo}_6\text{Br}_8(\text{NCS})_6]$ (3) ($\text{O}-\text{Co}-\text{O}$ and $\text{O}-\text{Co}-\text{N}$ angles $\sim 90^\circ$).

dimethyl formamide ligands, at a distance of 2.086 Å. Such complex cations $[\text{Co}(\text{DMF})_6]^{2+}$ are packed into a unit cell with the cluster anions $[\text{Mo}_6\text{Br}_8(\text{NCS})_6]^{2-}$.

3.1. XANES spectra

For Compound 1, Fig. 2 shows radical changes in the X-ray absorption spectrum in the Co K edge region (XANES Co K) after annealing in vacuum at 200°C . The amplitude of the after-edge resonance, the relative intensity of the maximum B , in the absorption spectrum corresponding to the electron transition from the $1s$ level to the p -states, is decreased by a factor of two. This may indicate a substantially reduced symmetry for the first sphere

of the Co environment, and a nonuniformity of the sample. The noticeable increase of the intensity of the pre-edge resonance A , associated with the increasing probability of the quadrupole $1s-3d$ transition, also indicates a decreased symmetry of the Co environment. Such changes in the spectrum appear to be due to the fact that annealing leads to the removal of the water molecules, which are chemically bound to the Co atoms. Exposing the annealed sample to the air for several hours leads to a slight increase in the after-edge maximum B intensity.

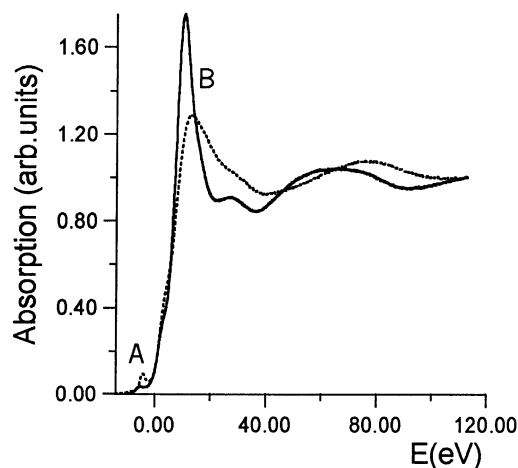


Fig. 2. Experimental Co K XANFS spectra for Sample 1 before annealing—solid line; after annealing—dashed line.

Table 1

Interatomic distances between cobalt and oxygen atoms $R(\text{Co}-\text{O})$, cobalt and nitrogen atoms $R(\text{Co}-\text{N})$ from X-ray structural analyses

Compound	$R(\text{Co}-\text{O})$, Å	$R(\text{Co}-\text{N})$, Å
$(\text{H}_3\text{O})_2\text{Co}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 14.5\text{H}_2\text{O}$ (1)	2.157, 2.279	2.054, 2.058, 2.077, 2.089
$\text{Cs}_2\text{Co}[\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (2)	2.036, 2.092	2.161
$\text{Co}(\text{DMF})_6[\text{Mo}_6\text{Br}_8(\text{NCS})_6]$ (3)	2.086	—

The changes in the CoK XANES spectrum for Compound 2 annealed under the same conditions, are similar, although they are much less pronounced.

For Compound 3, noticeable changes in the CoK XANES spectrum were observed only at annealing temperatures above 200°C. Annealing this compound at 250°C leads to a three-fold decrease of the amplitude in the region of the edge resonance, while the intensity of the pre-edge resonance *A* is noticeably increased. Such changes in the spectrum indicate a substantially decreased symmetry of the first coordination sphere of the Co environment, and can be explained only by the removal of the dimethyl formamide from the sample, which was found at the same temperature in the thermal analysis experiments.

3.2. EXAFS spectra

The results for different structural models of the studied compounds are given in Table 2. For the Fourier filtration of the experimental radial structural functions of Co, the interval of interatomic distances $0.75 \text{ \AA} < R < 2.35 \text{ \AA}$, corresponding to the first coordination sphere of Co atoms, was used in most of

the cases. This allowed a simplification of the fitting procedure and made possible to obtain true data about the nearest environments. For Compound 3 after annealing, the first coordination sphere could not be isolated, probably because of a chemical reaction that took place during annealing, as a result of the appearance of additional atoms at rather short distances of about 3.0 \AA and shorter.

As seen from Table 2, for Compound 1 before annealing, the use of two rounded interatomic distances to nitrogen, $R(\text{Co-N})$, and two distances to oxygen, $R(\text{Co-O})$, taken from Ref. [4] and reasonable Debye–Waller factors ($\sigma^2 = 0.005 \text{ \AA}^2$), gives a satisfactory value of the index *F* ($F = 4$, Table 2) characterizing the fitting quality. For Compound 1 after annealing, the fitting of the analogous model with fixed coordination numbers, n_1 , and Debye–Waller factors, σ^2 , but without oxygen in the first coordination sphere, gives four equal distances $R(\text{Co-N})$ and the index $F = 2.1$.

For Compound 2 in the initial state, the use of interatomic distances to oxygen atom $R(\text{Co-O})$ and nitrogen atom $R(\text{Co-N})$, taken from X-ray structural analysis, gives reasonable values of the Debye–Waller factors and an acceptable value of the fitting quality ($F = 2.8$). For Compound 2 after annealing, fitting of the analogous model with fixed coordination numbers, n_1 , and Debye–Waller factors, σ^2 , with one oxygen ($n_2 = 1$) and without oxygen in the first sphere of the Co environment, gives four equal distances $R(\text{Co-N})$ and acceptable values of $F = 2.3$.

To study the possible changes in the spatial structure of the complex anions $[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$, ($\text{X} = \text{S}, \text{Se}$), in Samples 1 and 2 during their annealing in vacuum, $\text{Re}L_3$ were measured for these samples. Comparing the experimental functions $k^2\chi(k)$ of $\text{Re}L_3$ for Samples 1 and 2, before and after annealing, shows that they are practically similar, whereas the amplitude of the main maximum of the radial structural function $F(R)$ was decreased by 5–8% after annealing. Such changes may be explained by small distortions of the Re–CN bond upon removal of oxygen from the first sphere of the Co environment.

For Compound 3 before annealing, the use of the interatomic distance to oxygen $R(\text{Co-O})$ and the coordination number $n_1 = 6$, taken from X-ray struc-

Table 2

Structure parameters obtained by fitting procedure for models of compounds: $(\text{H}_3\text{O})_2\text{Co}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 14.5\text{H}_2\text{O}$ (1), $\text{Cs}_2\text{Co}[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ (2), $\text{Co}(\text{DMF})_6[\text{Mo}_6\text{Br}_8(\text{NCS})_6]$ (3) after annealing in vacuum

Sample	$R(\text{N})$	n_1	σ^2	$R(\text{O})$	n_2	σ^2	<i>F</i>
(1) Before annealing	2.06	2	0.005	2.16	1	0.005	4.0
	2.08	2	0.005	2.28	1	0.005	
(1) After annealing	1.98	2	0.005				2.1
	1.98	2	0.005				
(2) Before annealing	2.16	4	0.005	2.04	1	0.003	2.8
				2.09	1	0.005	
(2) After annealing	2.07	4	0.005				2.3
(2) After annealing	2.09	4	0.005	2.04	1	0.003	2.3
(3) Before annealing				2.08	6	0.005	0.9
Sample	$R(\text{S})$	n_3	σ^2	$R(\text{C})$	n_4	σ^2	<i>F</i>
(3) After annealing	2.14	2	0.07	3.23	2	0.005	4.6
	2.33	2	0.06	3.23	2	0.005	

$R(\text{N}, \text{O}, \text{S}, \text{C})$ (\AA)—interatomic distances between Co atoms and N, O, S, C atoms; n_1, n_2, n_3, n_4 —coordination numbers of N, O, S and C atoms by Co; σ^2 —Debye–Waller factors (\AA^2). *F*—value of the fitting quality [10].

tural analysis, gives a reasonable value of the Debye–Waller factor σ^2 and a good value of the fitting index $F = 0.9$ (Table 2). After annealing at 250°C, the experimental functions $k^2\chi(k)$ of CoK and the form of the radial structural function $F(R)$ for Compound 3 were radically changed: there appeared an additional maximum (shoulder), corresponding to the distance of the order of 3 Å. For the larger distances, the function had faint features and became practically unchanged. Such changes may be interpreted by the appearance of additional atoms at the corresponding distances (3 Å) and the absence of a well ordered structure at larger distances.

Attempts to use different models of the first sphere of the Co atom environment only with sulfur or nitrogen atoms of SCN groups of $[\text{Mo}_6\text{Br}_8(\text{NCS})_6]^{2-}$ cluster anions, does not give a good value of the fitting index F . It appears reasonable to also include into the model carbon atoms of the SCN groups. Table 2 and Fig. 3 give the results of fitting of this model with the Fourier filtration interval of the experimental radial structural functions of $0.75 \text{ Å} < R < 3.3 \text{ Å}$. The model gives acceptable value of F . Thus, SCN groups link the anions with the Co^{2+} cations after the removal of dimethyl formamide molecules. Carbon atoms are at a distance of 3.23 Å from Co atoms, which corresponds to SCN groups bending. The added inclusion into the model of two

bromine atoms makes for better value of $F = 2.8$, but this model with Co–Br distances are equal to 3.0 Å is unsuitable from geometrical consideration.

To study the possible changes in the spatial structure of the complex cluster anions $[\text{Mo}_6\text{Br}_8(\text{NCS})_6]^{2-}$ in Sample 3, upon its annealing under vacuum, MoK were measured for these samples. Comparing the experimental and model $F(R)$ for this sample before and after annealing indicated a 20% decrease in the amplitude of the main maximum of the radial structural function $F(R)$ after annealing. Such changes may be explained by distortions of the Mo–NCS–Co bonds upon the removal of oxygen from the first sphere of the Co environment and the formation of Mo–NCS–Co bonds.

4. Conclusion

For two model compounds, $(\text{H}_3\text{O})_2\text{Co}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 14.5\text{H}_2\text{O}$ (1) and $\text{Cs}_2\text{Co}[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ (2), having close coordination polyhedra of their Co atoms, the dehydration under vacuum at 200°C was studied, and structural models of the Co cation environments were constructed. It was established that in Complexes (1) and (2), dehydration leads to the removal of water molecules from the first coordination sphere of cobalt. The coordination environment of the Co atoms changes from the octahedral (4N + 2O) to distorted square-planar (4N). The Co–N distance is decreased by 0.1 Å as compared with the initial complex. The cobalt atoms in the dehydrated structures are coordinately unsaturated, and apparently are capable of coordinating different molecules. It is shown that the cluster anions $[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$, X = S, Se do not undergo any appreciable changes during dehydration.

For the complex $\text{Co}(\text{DMF})_6[\text{Mo}_6\text{Br}_8(\text{NCS})_6]$, which was synthesized and characterized for the first time, annealing under vacuum at 250°C was found to lead to the removal of oxygen from the first coordination sphere of Co, i.e. to the removal from the complex of the dimethyl formamide (DMF) molecules. The reaction gives rise to a compound with four sulfur atoms of the SCN group coordinated to Co, while the structure of the molybdenum bromide core of the complex anion was not changed in any appreciable way.

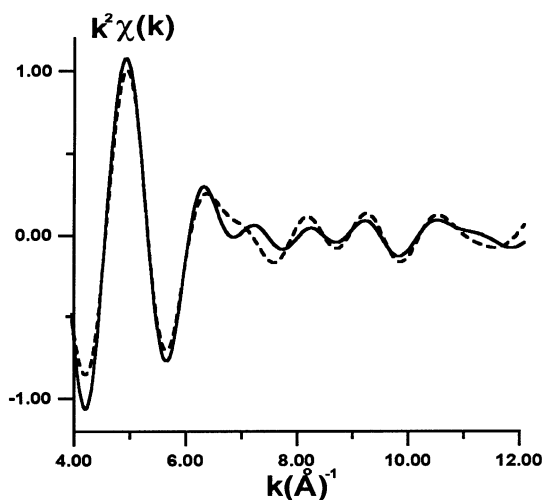


Fig. 3. Experimental CoK EXAFS spectra for the Compound 3 after annealing—solid line; for model with 2S, 2S, 4C atoms in the environment of Co atom—dashed line.

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