chemistry

Structure of new porous compounds after annealing in vacuum

S.B. Erenburg*, N.V. Bausk, N.G. Naumov, V.A. Chutornoi, V.E. Fedorov, L.N. Mazalov

Institute of Inorganic Chemistry RAS, Lavrentiev av.3, Novosibirsk 630090, RUSSIA, Email: simon@che.nsk.su

Dehydration process in recently synthesized porous inorganic salts formed by large cluster anions $[Re_6X_8(CN)_6]^{4-}$ (X= S, Se), transition metal cations and water molecules has been investigated. Desolvation process of the complex $Co(DMF)_6[Mo_6Br_8(NCS)_6]$, where DMF – dimethylformamide, has been studied. CoK, MoK and ReL_3 XAFS measurements of these new complicated compounds before and after annealing in vacuum at temperature up to 250°C were performed. Changes of electronic and spatial structure of these compounds under the heating process have been established and adequate structural models of the amorphous compounds obtained are suggested and discussed.

Keywords: XAFS; cluster anions; annealing

1. Introduction

In the 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 (Dunbar and Heintz, 1997). 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 (Naumov *et al.*, 1997; Naumov *et al.*, 1998). Solvent removal from such compounds at low (<100°C) temperatures gives rise to poorly crystallized compounds with large unfilled cavities 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. EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near-edge structure) spectroscopy which are capable of studying the local environment of atoms and characterizing noncrystalline objects with no long-range ordering provide a unique possibility to solve such problems (Koninsberger and Prins, 1988). However, we do not know any other studies in which these methods were used to investigate such and 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 (Mazalov *et al.*, 1997; Erenburg *et al.*, 1999) and in solid state at different temperatures (Erenburg, Bausk, Lavrenova and Mazalov, 1999).

In this work, the EXAFS and XANES spectroscopy are employed to study the structural changes in complex compounds containing octahedral cluster anions of rhenium, $[Re_6X_8(CN)_6]^{4-}$, X=S, Se, or molybdenum, $[Mo_6Br_8(NCS)_6]^{2-}$, and cations of

cobalt which take place when the compounds are annealed under vacuum at temperatures up to 250°C.

2. Experimental

The compound $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5H_2O$ (Compound 1) was prepared by the interaction of aqueous solutions of $K_4[Re_6Se_8(CN)_6] \cdot 3.5H_2O$ and $CoCl_2 \cdot 6H_2O$ by the procedure described elsewhere (Naumov *et al.*, 1998). The compound $Cs_2Co[Re_6S_8(CN)_6] \cdot 2H_2O$ (Compound 2) was obtained by the interaction of aqueous solutions of $Cs_3K[Re_6S_8(CN)_6] \cdot 2H_2O$ and $CoCl_2$. The compound $Co(DMF)_6[Mo_6Br_8(NCS)_6]$ (Compound 3) was prepared by the interaction of $(Bu_4N)_2[Mo_6Br_8(NCS)_6]$ and $CoCl_2 \cdot 6H_2O$ in a solution of dimethyl formamide (DMF).

The samples were fixed inside a specially fabricated cell with beryllium windows and heated under vacuum for 2 hr after which the cell was slowly cooled down and the EXAFS and XANES spectra were measured without sample contact with air. The annealing temperatures were found to be equal to: for Samples 1,2 – 200°C, for Sample 3 – 250°C from the decomposition curves of the materials in a vacuum under the conditions of a differential thermal analysis (DTA) experiment.

The CoK, MoK and ReL_3 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) monochromator was used.

The obtained data were processed using the EXCURV92 package (Binsted *et al.*, 1991). In the data processing the phase and amplitude characteristics were calculated in the X_α-DW approximation (Binsted *et al.*, 1991). For the analysis of the local environment of Ge atoms the fitting of Fourier-filtered data with the k^2 weighing in the interval of photoelectron wave vectors from 3 Å^{-1} 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 $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5H_2O$.

3. Results and discussion

3.1. *XRD data*

The coordination environments of cobalt atoms in compounds 1 and 2 are similar and are formed by four nitrogen atoms of the cyano groups and two oxygen atoms of the water molecules in the cis- and trans-position (Table 1).

Table 1
Interatomic distances between cobalt and oxygen atoms R(Co-O), cobalt and nitrogen atoms R(Co-N) from X-ray structural analyses.

Compound		R(Co-O), Å	R(Co-N), Å
$(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5H_2O$	(1)	2.157, 2.279	2.054, 2.058 2.077, 2.089
$Cs_2Co[Re_6S_8(CN)_6] \cdot 2H_2O$	(2)	2.036, 2.092	2.161
$Co(DMF)_6[Mo_6Br_8(NCS)_6]$	(3)	2.086	-

The cobalt atoms bridge the $[Re_6X_8(CN)_6]^{4-}$ anions to form a polymer framework. Compound 2 has a close-packed layered structure whereas Compound 1 has a rather loose covalently bonded framework $\{Co_3[Re_6Se_8(CN)_6]_2\}^{2-}$, with cavities are filled by water molecules. The environment of the cobalt atoms in Compound 3 consists of six oxygen atoms of the dimethyl formamide ligands at a distance of 2.086 Å. Such complex cations $[Co(DMF)_6]^{2+}$ are packed into a unit cell with the cluster anions $[Mo_6Br_8(NCS)_6]^{2-}$.
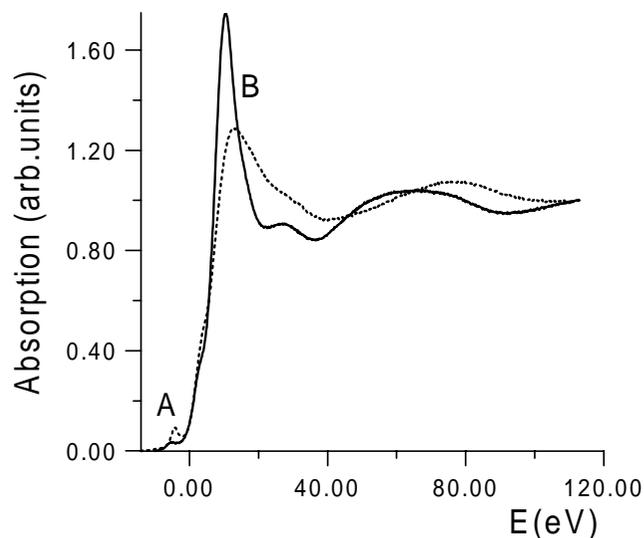
Figure 1
Experimental Co*K* XANFS spectra for the Compound 1 before annealing - solid line, after annealing - dashed line.

3.2. *XANES spectra*

For Compound 1 Fig. 1 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 white line *B*, in the absorption spectrum corresponding to the electron transition from the 1*s* 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 1*s* – 3*d* 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 chemically bound to the Co atoms. Exposing the annealed sample to the air for several hours leads to a slightly increase in the after-edge maximum *B* intensity.

The changes in the Co*K* XANES spectrum for Compound 2 annealed under the same conditions are analogous although they are much less pronounced.

Annealing Compound 3 at 250°C leads to a three-fold decrease of the amplitude in the region of the after-edge resonance *B* of the Co*K* XANES spectrum 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 from the sample of the dimethyl formamide which was found at the same temperature in the thermal analysis experiments.

3.2. *EXAFS spectra*

After annealing at 200°C the experimental functions $k^2\chi(k)$ of Co*K* and the form of the radial structural function F(R) for Compounds 1,2 were changed (Fig. 2). 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 for Co the interval of interatomic distances corresponding to the first coordination sphere of Co atoms was used in most of the cases: 0.75 Å <R< 2.35 Å. This allowed a simplification of the fitting procedure and made possible to obtain true data about the nearest environments. For Compound 3
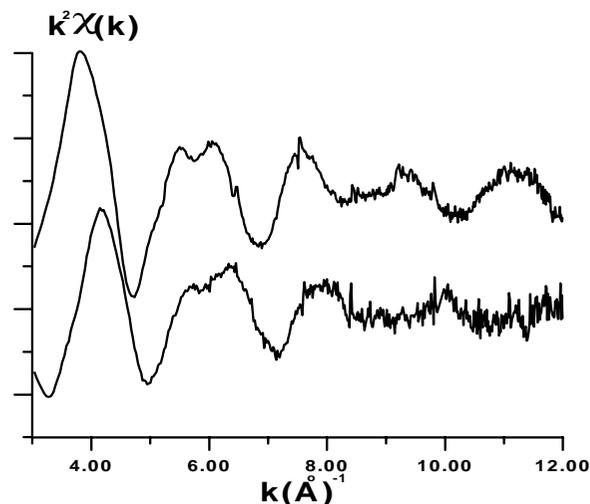

Figure 2
Experimental Co*K* EXAFS spectra for the Compound 2 before annealing – upper curve, after annealing – lower curve.

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 which there additionally appeared atoms at rather short distances of about 3.0 Å and shorter.

Table 2
Structure parameters obtained by fitting procedure for models of compounds 1, 2 and 3 after annealing in vacuum. R(N, O, S, C) (Å) – 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 by Co; σ^2 – Debye-Wallers factors (Å^2), F – value of the fitting quality (Binsted *et al*., 1991).

Sample	R(N)	n_1	σ^2	R(O)	n_2	σ^2	F
(1) before	2.06	2	0.005	2.16	1	0.005	4.0
annealing	2.08	2	0.005	2.28	1	0.005	
(1) after	1.98	2	0.005				2.1
annealing	1.98	2	0.005				
(2) before	2.16	4	0.005	2.04	1	0.003	2.8
annealing				2.09	1	0.005	
(2) after	2.07	4	0.005				2.3
annealing							
(2) after	2.09	4	0.005	2.04	1	0.003	2.3
annealing							
(3) before				2.08	6	0.005	0.9
annealing							
Sample	R(S)	n_3	σ^2	R(C)	n_4	σ^2	F
(3) after	2.14	2	0.07	3.23	2	0.005	4.6
annealing	2.33	2	0.06	3.23	2	0.005	

As is seen from Table 1 and Table 2, for Compounds 1 and 2 in the initial state the use of interatomic distances from Co to oxygen atoms R(Co-O) and nitrogen atoms R(Co-N) taken from X-ray structural analysis gives reasonable values of the Debye-Waller factor and an acceptable values of the fitting quality F. For Compounds 1 and 2 after annealing fitting of the analogous model with fixed coordination numbers (n_1) and Debye-Waller factor values (σ^2) without oxygen (for Compounds 1 and 2) and with one oxygen atom (n_2=1 for Compound 2) in the first sphere of the Co environment gives four equal distances R(Co-N) and acceptable values of F.

To study the possible changes in the spatial structure of the complex anions $[Re_6X_8(CN)_6]^{4-}$, (X=S, Se), in Compounds 1 and 2 during their annealing, Re*L₃* were measured for these samples. Comparing the experimental functions $k^2\chi(k)$ of Re*L₃* for Sample 1 and 2 before and after annealing shows that they are practically identical whereas the amplitude of the main maximum of the radial structural function F(R) was decreased by 5-8% after
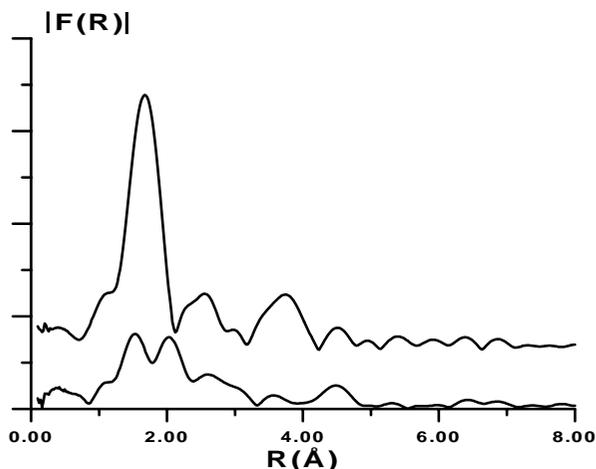
Figure 3

Fourier transform magnitude |F(R)| of $k^3\chi(k)$ CoK EXAFS data for Compound 3: before annealing – upper curve, after annealing – lower curve.

Figure 4

Experimental MoK EXAFS spectra for the Compound 3 before annealing – solid line, after annealing – dashed line.

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(Co-O) and the coordination number $n_1 = 6$ taken from X-ray structural 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 (Fig. 3).

Attempts to use different models of the first sphere of the Co atom environment only with sulfur or nitrogen atoms of SCN groups of $[Mo_6Br_8(NCS)_6]^{2-}$ cluster anions does not give a good value of the fitting index F. It appears reasonable to include into the model also carbon atoms of the SCN groups. In Table 2 are given the results of fitting of this model with the Fourier filtration interval of the experimental radial structural functions of 0.75 Å<R < 3.3 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 $[Mo_6Br_8(NCS)_6]^{2-}$ in Sample 3 upon its annealing under vacuum the MoK were measured for these samples (Fig. 4). Comparing the experimental and model F(R) for this sample before and after annealing indicated a 20% decrease of 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-NSC bond upon the removal of oxygen from the first sphere of the Co environment and the formation of Mo-NCS-Co bonds.

4. Conclusion

It was established that in Compounds 1, 2 the dehydration leads to 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
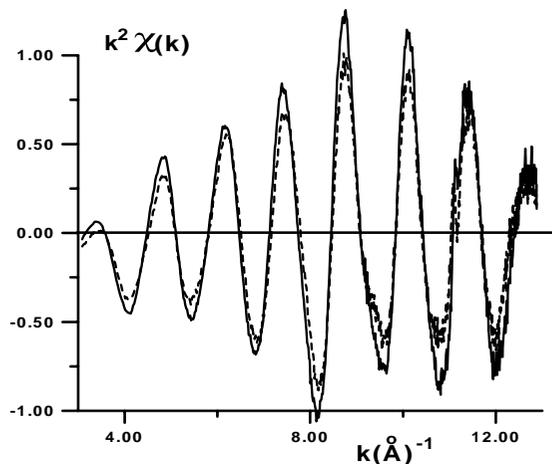
the initial complex. It is shown that the cluster anions $[Re_6X_8(CN)_6]^{4-}$, X = S, Se do not undergo any appreciable changes during dehydration.

For the complex $Co(DMF)_6[Mo_6Br_8(NCS)_6]$, which was synthesized and characterized for the first time, annealing under vacuum at 250°C was found to lead to 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 in which Co coordinates in pairs four sulfur atoms of the SCN group while the structure of the molybdenum bromide core of the complex anion was not changed in any appreciable way.

References

Binsted, N., Campbell, J.W., Gurman, S.J. and Stephenson, P.C. *SERC Daresbury Lab. Rep.* (1991).

Dunbar, K.R. and Heintz, R.A. *Progress in Inorg. Chem.* Ed. By K.D. Karlin, **45**,1997.

Erenburg, S.B., Bausk, N.V., Zemskova, S.M. and Mazalov, L.N. *Journal of Synchrotron Radiation*. **6**(3), 582-584 (1999).

Erenburg, S.B., Bausk, N.V., Lavrenova, L.G. and Mazalov, L.N. *Journal of Synchrotron Radiation*. **6**(3), 576-578 (1999).

Koninsberger, D.C and Prins, R. Eds. *X-ray Absorption: Principles Applications, Techniques of EXAFS, SEXAFS and XANES* / - New York, Wiley, 1988, p. 710.

Mazalov, L.N., Erenburg, S.B., Bausk, N.V., Tkachev, S.V., Zemskova, S.M. and Larionov, S.V. *Russian J. Struct. Chem*. **38**(4), 601-607 (1997).

Naumov, N.G.., Virovets, A.V., Podberezskaya, N.V. and Fedorov, V.E. *Russian J. Struct. Chem.* **38**(5), 898-914 (1997).

Naumov, N.G., Virovets, A.V., Sokolov, M.N., Artemkina, S.B. and Fedorov, V.E. *Angew. Chem. Int.Ed.Engl*. **37**(13/14), 1943-1945 (1998).