Local Coordination of Co²⁺ and Ni²⁺ Cations in Polyacrylate Matrices

N. N. Trofimova[a], Ya. V. Zubavichus[b, c], O. I. Titova[a], E. A. Karpyuk[a], V. A. Ivanov[a], A. D. Pomogailo[d], and Yu. L. Slovokhotov[a, c]

[a] *Moscow State University, Moscow, 119991 Russia*

[b] *National Research Center Kurchatov Institute, Moscow, 123182 Russia*

[c] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*

[d] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

e-mail: slov@phys.chem.msu.ru

Abstract—Parameters of the local coordination of Co^{2+} and Ni^{2+} cations in polymer matrices are determined by XAFS spectroscopy at the K edges of the corresponding elements. Ion-exchange complexes of Ni^{2+} and polymethacrylate, low-molecular acrylamide complexes $[M(CH_2=CHC(O)NH_2)_6](NO_3)_2$ (M = Co or Ni), and products of their thermal polymerization are investigated. The final results are in agreement with the octahedral coordination of M atoms (average distances, 2.10–2.11 (Co–O) and 2.05–2.06 Å (Ni–O).

INTRODUCTION

X-ray amorphous complexes of metals and polymer matrices with coordinating functional groups are formed during polymerization, ion exchange, and heterogeneous catalysis. The structure of these complexes can be determined using a set of physical methods that includes optical, magnetic resonance, X-ray absorption fine-structure (XAFS) spectroscopy, and small-angle X-ray scattering (SAXS) [1, 2]. The XAFS data for polymer complexes of 3d metals [3, 4] and lanthanides [5] reveal typical local coordinations of cations that. according to the SAXS data, can closely approach one another (to distances of 4–5 Å) at high concentrations, thus forming heterogeneous nanoregions. Inorganic [6] and combined [7] matrices allow both the statistical coordination of guest cations and their chemical modification; e.g., layered nanocomposites $M(OH)_{2-y}(H_2O)_y^{y+}/MoS_2^{y-}$ can form after adding hydrated cations of 3d metals to an aqueous monolayer dispersion of molybdenum disulfide [8].

In this work, we report the results from a synchrotron XAFS study of the local coordination of Co^{2+} and Ni^{2+} cations in polymer matrices of two types: cross-linked polymethacrylate (PMA) [9] and products of thermal polymerization of low-molecular acrylamide complexes $[M(CH_2=CHC(O)NH_2)_6](NO_3)_2$ (M = Co and Ni) [10]. If acid polymer $[H^+]$-PMA is an ionite and forms X-ray amorphous complexes with metal cations, the second type of compounds are convenient model objects that allow us to study changes in the coordination of metal cations as a result of cross-linking a polymer network from complexes with known structures.

EXPERIMENTAL

Ni–PMA samples (Ia–Id) were prepared according to the technique in [9] by passing a 1.8-M aqueous solution of nickel(2+) chloride through a column with ionite Na⁺–PMA at room temperature. The preparation of low-molecular complexes $[M(CH_2=CHC(O)NH_2)_6](NO_3)_2$ (M = Co (IIa) or Ni (IIIa)) and products of their thermal polymerization at 50–60°C (II and III, respectively) was described in [10, 11]. According to X-ray diffraction data, all of our polymer complexes were amorphous and contained no crystalline impurities.

The XAFS spectra for the series of Ni–PMA samples (I) and reference samples were recorded on the STM station of the Kurchatov Center for Synchrotron Radiation and Nanotechnology using radiation from the bending magnet of the Sibir'-2 storage ring (electron-beam energy, 2.5 GeV; current 100 mA; slit Si(111) monochromator). The spectra were recorded at room temperature at the K edge of Ni in the transmission geometry using three ionization chambers; exact energy calibration was performed using a reference nickel foil. The XAFS spectra for samples II and IIa (III and IIIà) at the K edges of Co (Ni) were measured at room temperature on the EXAFS station of the Siberian Synchrotron Radiation Centre (storage ring electron-beam energy, 2.0 GeV; current 60–120 mA; wiggler channel; slit Si(111) monochromator; transmission geometry with two ionization chambers). The spectra were conventionally processed and simulated using the IFEFFIT software package [12]. The model parameters were fitted with the oscillatory function $k^3\chi(k)$ in the ranges k 2–13 Å⁻¹ (for Co) and
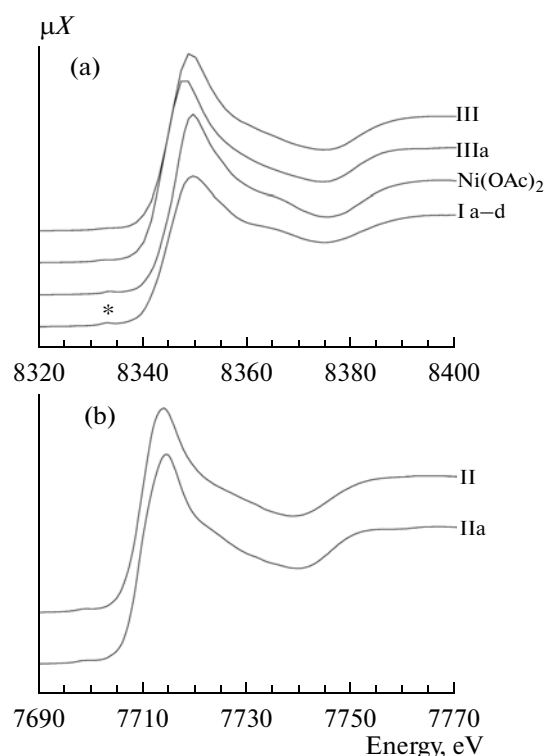
Fig. 1. (a) K-edge XANES of Ni in the samples of Ni–PMA (I), $(CH_3COO)_2Ni \cdot 4H_2O$, low-molecular $[Ni(CH_2=CH(O)NH_2)_6](NO_3)_2$ complex (IIIa), and its thermal polymerization product (III); the pre-edge feature is indicated by the asterisk. (b) K-edge XANES of Co in low-molecular $[Co(CH_2=CH(O)NH_2)_6](NO_3)_2$ complex (IIa) and its thermal polymerization product (II).

Fig. 2. Moduli of the EXAFS Fourier transforms for the samples under study (from bottom to top): Ni–PMA complex (I, spectrum averaged over four samples), $(CH_3COO)_2Ni \cdot 4H_2O$ $(Ni(OAc)_2)$, amorphous nickel hydroxide $Ni(OH)_2$, low-molecular $[Ni(CH_2=CH(O)NH_2)_6](NO_3)_2$ complex (IIIa), its thermal polymerization product (III), low-molecular $[Co(CH_2CH(O)NH_2)_6](NO_3)_2$ complex (IIa), and its thermal polymerization product (II).

2–12 Å^{-1} (for Ni) at $R = 1$–2.3 Å for the first coordination sphere and 1–3.5 Å for the two-sphere model in the cases of NiO and $Ni(OH)_2$.

RESULTS AND DISCUSSION

The XAFS spectra of four samples of Ni–PMA complex (Ia–Id), differing in preparation time and the storage time in air before recording (from one week to two months), coincided in both the near-edge (XANES) and extended (EXAFS) regions. The parameters of the first coordination sphere (radius $R_{Ni–O} = 2.051(6)$, $2.051(6)$, $2.056(8)$, and $2.049(5)$ Å and Debye–Waller factor $\sigma^2 = 0.0065(7)$, $0.0065(7)$, $0.0069(10)$, and $0.0072(6)$ Å^2 for samples Ia–Id, respectively), obtained by fitting the EXAFS function at a fixed coordination number $N = 6$, differ within the experimental error, demonstrating the good reproducibility of Ni–PMA complex preparing the according to the technique in [9] with saturation of all coordinating carboxyl groups (controlled with complexometric titration). Below, we analyze the XAFS function of complex I averaged over all four samples.

The shape of the near-edge XANES region (Fig. 1a) in the spectrum of complex I is very similar to
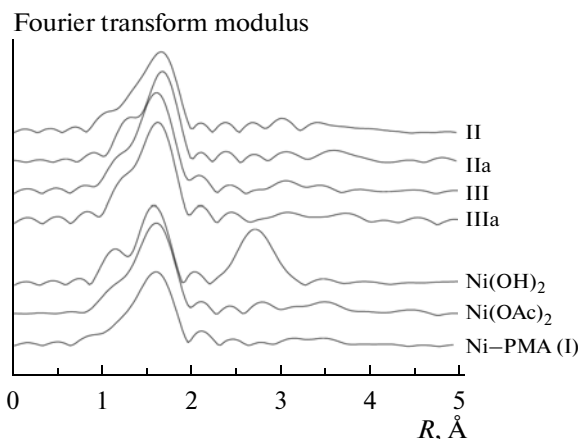
that for tetrahydrates of nickel acetate and nitrate, where Ni^{2+} ions are octahedrally coordinated by acido ligands and H_2O molecules in the first coordination sphere [13]. A pre-edge feature observed in all these spectra at 8333–8334 eV corresponds to the forbidden (within the dipole approximation) electronic transition $1s \rightarrow 3d$, whose intensity correlates with the degree of distortion of the coordination polyhedron. This feature could indicate mixed coordination of the Ni^{2+} cation by carboxyl fragments and water molecules in the Ni^{2+}–PMA polymer complex. The shapes of the K absorption edges of Co (Ni) for polymerized samples II (III) and low-molecular complexes IIa (IIIa), where the coordination of M^{2+} cations by six O atoms of acrylamide ligands is close to an ideal octahedral [14], virtually coincide; the pre-edge feature $(1s \rightarrow 3d)$ is very weakly pronounced (Figs. 1a, 1b). The symmetric octahedral coordination of M^{2+} cations is likely retained in polymerized complexes II and III.

The EXAFS Fourier transforms for the Ni^{2+}–PMA and tetrahydrates $(CH_3COO)_2Ni \cdot 4H_2O$ and $Ni(NO_3)_2 \cdot 4H_2O$ used as reference samples contain a single coordination sphere (Fig. 2) that consists of four water molecules and two acido ligands in low-molecular aqua complexes. Since there is no second coordination sphere, the formation of nickel hydroxide in grains of polymer I can be excluded from consideration. The Fourier transform moduli for monomer (IIa and IIIa) and polymer (II and III) acrylamide complexes are very close and also contain a single coordination sphere. A similar coordination was observed earlier in other transition-metal complexes with polymer carboxyl ligands [1, 5, 7].

Parameters of the local environment of Co²⁺ and Ni²⁺ cations: coordination-sphere radii R, coordination numbers N, and the Debye–Waller factor σ^2 according to EXAFS data (X-ray diffraction data are given for comparison)

Sample	R, Å	N	σ^2, Å²
Ni-PMA* (**I**)	2.05(1) Ni–O	5.8	0.0078(10)
[Co(CH₂=CH(O)NH₂)₆](NO₃)₂			
polymer (**II**)	2.10(2) Co–O	6.3	0.0078(6)
monomer (**IIa**)	2.11(1) Co–O	6.1	0.0068(13)
[Ni(CH₂=CH(O)NH₂)₆](NO₃)₂			
polymer (**III**)	2.06(1) Ni–O	6.9	0.0060(9)
monomer (**IIIa**)	2.06(1) Ni–O	7.8	0.0071(10)
NiO	2.08(1) Ni–O	6**	0.0059(10)
	2.95(2) Ni–Ni	12**	
Ni(OAc)₂ · 4H₂O	2.00(1) Ni–O	2**	0.0059 (15)
	2.09(1) Ni–O	4**	0.0046(10)
Ni(NO₃)₂ · 4H₂O	2.06(1)	6**	0.0069(15)
Ni(OH)₂	2.03(1) Ni–O	6**	0.0055(11)
	3.09(2) Ni–Ni	6**	0.0097(20)
Ni(OAc)₂ · 4H₂O NIAQACO₃*** [13]	2.048 – 2.092, averaged 2.071	6	–
[Co(CH₂CH(O)NH₂)₆](NO₃)₂ WARRIR*** [14]	2.075 – 2.117, averaged 2.090	6	–
[Ni(CH₂CH(O)NH₂)₆](NO₃)₂ WARROX*** [14]	2.045 – 2.078, averaged 2.058	6	–

Notes: * Spectrum averaged over four samples Ia–Id.

     ** Fixed parameter.

      *** Reference codes of the corresponding crystal structures in the Cambridge Structural Database (CSD) are given along with the references.

CONCLUSIONS

X-ray diffraction (XRD) analysis showed that the lengths of the M–O bonds for aqua and acido ligands in the complexes differ slightly and are generally within 2.04–2.08 (Ni²⁺) [13] and 2.08–2.13 Å (Co²⁺) [14]. The EXAFS data for polymer samples were thus simulated by one coordination sphere of oxygen atoms. The obtained structural parameters are given in the table; the quality of fitting is demonstrated in Fig. 3 (from the example of complex I).

According to the simulated EXAFS spectra, the Ni–O distance is 2.053(10) (I) and 2.06(1) Å (III and IIIa), which is in good agreement with the XRD data. The Co–O distances for II (2.10(2) Å) and IIa (2.11(1) Å) coincide within the experimental error and are also in good agreement with the XRD data (see table). The coordination numbers N determined with a rather high degree of error correspond to octahedral or octahedrally distorted coordination of Co²⁺ and Ni²⁺ cations in polymer complexes.
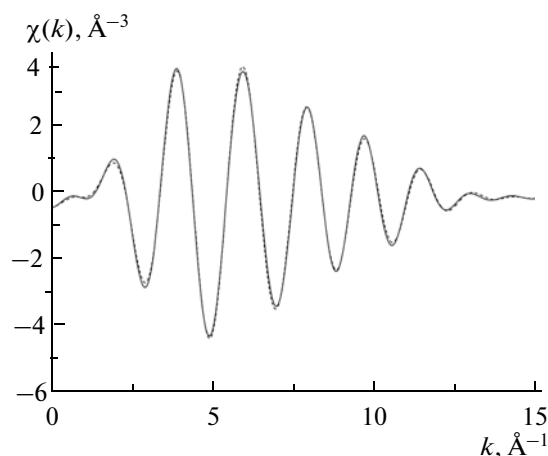
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Fig. 3. Contribution from the first sphere in Ni–PMA sample (I) to the weighting oscillatory EXAFS function $k^3\chi(k)$. The simulation results are indicated by the dotted line.

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