

The effect of solvent on the structure of the transition metal complexes in solution

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CdK EXAFS, ZnK and CuK EXAFS and XANES spectra were measured for solutions of cadmium, zinc and copper dialkyldithiocarbamates in organic solvents with varying donating abilities: benzene, pyridine, tributylphosphine and for some model compounds. The parameters of the local surroundings of the Cd, Zn and Cu atoms for complex forms in solutions were determined using EXAFS spectroscopy. Spatial structure models of the complex forms in a metal chelate - nonaqueous solvent system are suggested.

Keywords: X-ray absorption; structure of solution; chelate compounds

1. Introduction

Conventional description of physicochemical properties of metal complexes in solutions are based on model of two types of interactions: 1) chemical interaction of the metal atom with ligands of the first coordination sphere and 2) nonspecific interaction of the inner sphere of the metal complex with medium (solvent) as dielectric continuum. For electroneutral complexes, the interaction inside the complex (in the inner sphere) is much greater than that with the medium (solvent). There are cases when organic solvent molecules are directly coordinated by the metal atoms of a molecular compound in solutions, for example: alkylbenzenes by antimony of antimony trichloride (Schmidbaur *et al.*, 1987) or benzene by palladium of palladium chloride (Erenburg *et al.*, 1995). EXAFS spectroscopy study of metal chelate complexes formation in series of nonaqueous solvents with varying donating abilities is of obvious chemical interest.

2. Experimental

The chelates: Cd[(n-C₄H₉)₂NCS₂]₂ (below CdL₂), Cd[(C₂H₅)₂NCS₂]₂ (below CdL₂), Zn[(n-C₄H₉)₂NCS₂]₂ (below ZnL₂) and Cu[(C₂H₅)₂NCS₂]₂ (below CuL₂) were prepared according to the standard procedure (Coucovanis, 1970).

The CdK EXAFS, ZnK and CuK EXAFS and XANES spectra were recorded using synchrotron radiation of the VEPP-3 storage ring at the G.Budker Institute of Nuclear Physics in Novosibirsk. Ring settings during the measurements: energy 2 GeV, current 100 mA. The CdK, ZnK and CuK absorption spectra were measured in the transmission mode using Ar/He and Xe ionization chambers as monitoring and final detectors, respectively. A channel-cut Si(111) single crystal was used as a monochromator.

The data obtained were processed with the EXCURV-92 package (Binsted *et al.*, 1991). The phase and amplitude characteristics were calculated in the $X\alpha$ approximation using the package procedures. For analyzing the local surroundings of Cd and Zn atoms, Fourier-filtered data were fitted with k^2 weighing in the range of photoelectron wave vectors from 3 to 10 Å⁻¹. In the fitting procedure, the error of determination of interatomic distances was not higher than 0.02 Å in all cases. Solid complexes

Table 1

Parameters obtained by the fitting procedure for solutions of cadmium dialkyldithiocarbamates CdL and CdL^I in organic solvents (3 Å⁻¹ < χ < 10 Å⁻¹). Interatomic distances R(Å), Debye-Waller factors σ^2 (Å²) and quality of fit factor R_{EXAFS}(%) were extracted using EXCURV92 package procedure (Binsted *et al.*, 1991).

Lig	Sol vent	Model	R, Å Cd-S	R, Å Cd-N,P	σ^2 , Å ² Cd-S	σ^2 , Å ² Cd-N,P	R _E (%)
L	C ₆ H ₆	4S	2.58		0.008		18.0
L	C ₆ H ₆	4S	2.60		0.008		11.5
		S	2.77		0.006		
L	Py	4S	2.59		0.008		20.8
L	Py	4S+N	2.62	2.36	0.011	0.003	14.1
L	Py	4S+2N	2.62	2.40	0.012	0.009	13.8
L ^I	Py	4S	2.60		0.007		18.2
L ^I	Py	4S+N	2.63	2.36	0.010	0.0001	9.7
L ^I	Py	4S+2N	2.63	2.41	0.012	0.006	8.9
L ^I	TBP	4S	2.58		0.007		19.5
L ^I	TBP	4S+P	2.58	2.73	0.005	0.001	14.7
L ^I	TBP	4S+2P	2.58	2.73	0.007	0.011	15.4

CdL₂, CdL₂(2,2'-Bipy), CdL₂(1,10-phenanthroline) and ZnL₂, ZnL₂(1,10-phenanthroline) were used as model compounds. The factors of amplitude damping S_0^2 determined by the fitting procedure for solid model complexes are equal to 0.74 for Zn and Cu atoms and to 0.81 for Cd atoms. Various models of local surroundings with fixed coordination numbers of Cd, Zn and Cu atoms were checked during the fitting procedure to examine the possibility of further coordination of solvent molecules by metal.

3. Results and discussion

3.1. Cd dialkyldithiocarbamate molecules in solutions

CdK EXAFS spectra were measured for the complexes in the solid state and for their organic solutions. The experimental $k^2\chi(k)$ curve is presented in the Fig. 1 for CdL₂ in benzene. We checked whether the surroundings formed by the sulfur atoms separated by nonequivalent distances around the Cd atoms in the solid state are preserved in a pyridine (Py) solution of CdL₂ and CdL₂. As a result of the fitting procedure, it was established that the four sulfur atoms in the solution of the complexes lie at equal distances from the cadmium atoms.

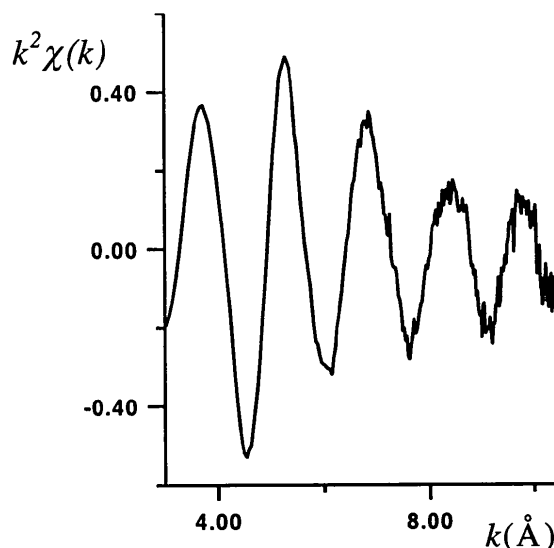


Figure 1
Experimental EXAFS spectra of CdL₂ in benzene.

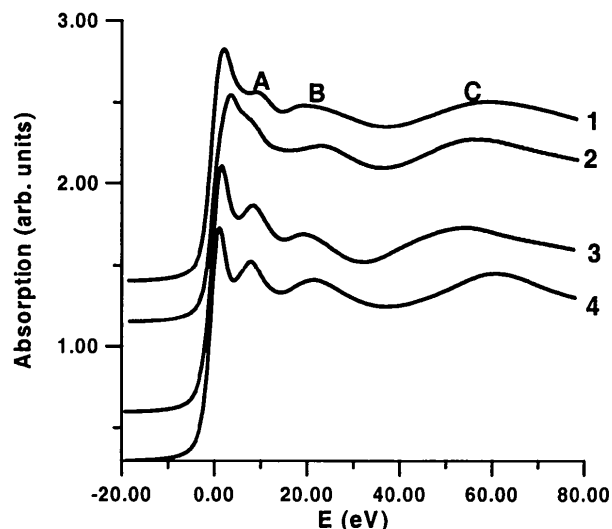


Figure 2
Zn K XANES spectra of ZnL_2 in solid state - 1, in tributylphosphine - 2, in pyridine - 3, in benzene - 4.

The results of the fitting procedure presented in the Table 1 are considerably improved (fit factor R_{EXAFS} decreased) when one or two nitrogen atoms, which may be coordinated to cadmium atoms in solution, are introduced in sequence into the model. It should be emphasized that 4S+1N model gives unreasonable values of Debye-Waller factors and 4S+2N model is preferable. Cd-S and Cd-N interatomic distances presented in the Table 1 for the complexes solutions in Py are close to XRD data for solid complexes in which Cd atoms have 4S+2N surrounding (Glinskaya *et al.*, 1992). For example, for solid $CdL_2(2,2'-Bipy)$ XRD analysis gave around Cd atoms two pairs of S atoms lying at 2.68 Å and 2.65 Å as well as two N atoms lying at 2.43 Å. The data obtained indicate that coordination of nitrogen atoms by cadmium atoms in a pyridine solution is realized for both CdL_2 and CdL_2^1 and that replacement of L by L^1 does not produce a significant effect on the Cd-S and Cd-N distances.

We tried to verify indications of NMR data (Mazalov *et al.*, 1997) that benzene solutions contain $[CdL_2]_2$ dimers which are a basis for packing in the solid state. The first model included four S atoms at equal distances from the Cd and one S atom of the bridging bidentate diethyldithiocarbamate, which is coordinated to the neighboring Cd atom in the dimer (Table 1). The three-shell model 2S+2S+S with two pairs of S atoms lying at close distances and S atom coordinated to the neighboring Cd atom gave interatomic Cd-S distances of 2.60 Å, 2.55 Å, and 2.75 Å that are close to those for solid CdL_2 : 2.60 Å, 2.63 Å; 2.52 Å; 2.52 Å, 2.77 Å (XRD data Shugam & Agre, 1968). Variation of the number of sulfur atoms in the surroundings of the cadmium atoms in this model gave 2.0, 2.13, and 1.18 for this distances, respectively. The resulting interatomic distances and coordination numbers support the existence of dimers in benzene solutions. If the Cd-Cd atomic pair were identified at a distance about 3.58 Å which is equal to those for solid complex (Shugam & Agre, 1968), this would be an unambiguous support of the existence of dimers in solution. However, the dimer is relatively free to make vibration with all degrees of freedom in solution and due to high dynamic components of the Debye-Waller factors this fact may not be unambiguously established from EXAFS data. A model including the CdL_2 monomer in which the benzene molecule is coordinated by the cadmium atom was also tested. This model gave only slightly improved fitting index. Analysis of EXAFS

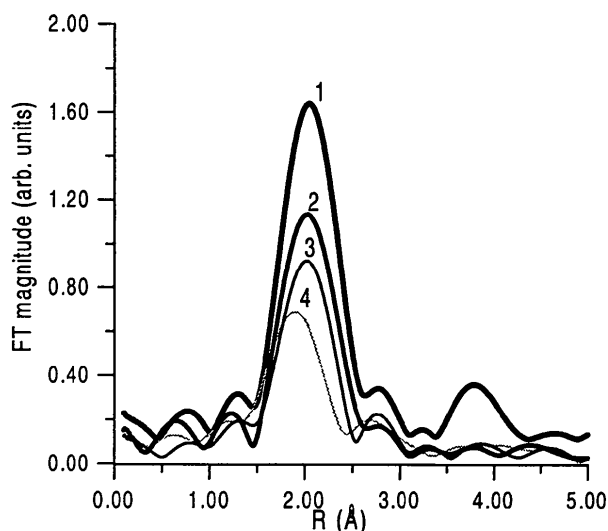


Figure 3
Fourier transform magnitude Zn K EXAFS spectra of ZnL_2 in benzene - 1, solid state - 2, tributylphosphine - 3, pyridine - 4.

data with the assumption that the solution contains simultaneously monomers and dimers coordinating solvent molecules is not possible because of many parameters in the fitting procedure.

The amplitude of the main maximum of Fourier transform modulus of $k^2\chi(k)$ for tributylphosphine (TBP) solution of CdL_2^1 increases by ~20% in comparison with other solutions. The increase can be caused by the metal atoms coordination of TBP molecules which was established using NMR data (Mazalov *et al.*, 1997). However, the introduction into the model of one or two phosphorus atoms in addition to the four sulfur atoms decreases the fitting index R_{EXAFS} by only 20%. The discrepancy between the model and the experimental data may be caused by the fact that the available version of the EXCURV-92 package uses the harmonic approximation to describe the root-mean displacement of atoms. Assumptions of high anharmonicity is supported by the fact that the determined Cd-P distance of 2.73 Å is longer than the characteristic distance of 2.57 Å for chemical bonding in the solid $(Et_2NCS_2)_2Cd(PEt_3)$ complex with 4S+P cadmium atoms surrounding (Zeng *et al.*, 1994).

3.2. Zn and Cu dialkyldithiocarbamate molecules in solutions

ZnK and CuK EXAFS and XANES spectra were measured for solid of complexes ZnL_2 , $ZnL_2(1,10\text{-phenanthroline})$ and CuL_2 and their solutions in TBP, benzene, Py which are characterized by different donor numbers.

ZnK XANES spectra measured on solid ZnL_2^1 complex and its solutions are presented in the Fig. 2. In all the solutions the spectra exhibit valuable changes in comparison with the spectrum of the solid complex. Features A, B and C shows clearly visible changes of their sharpness, shape, position and intensity indicating variations of Zn atoms surrounding geometry and symmetry in solutions. Possibility of Py and TBP molecules coordination by Zn atoms in solutions is supported by the existence of solid compounds with 4S+2N and 4S+P Zn atoms surroundings such as $ZnL_2(1,10\text{-phenanthroline})$ (Bell *et al.*, 1989) and $ZnL_2P(Alkyl)_3$ (Zeng *et al.*, 1994) complexes. ZnK XANES spectra measured on solid $ZnL_2(1,10\text{-phenanthroline})$ complex and its solutions are not presented in the paper because all of them are identical. In comparison with ZnL_2 complex in this case Zn atoms are surrounded by 4S+2N atoms and there are not vacant places around them to attach solvent molecules.

Fourier transform magnitudes of the $k^2\chi(k)$ values calculated in the k range from 3 \AA^{-1} to 12 \AA^{-1} for ZnL_2 and its solutions are presented in the Fig. 3. In comparison with solid complex on the radial distribution curve of its solution in benzene valuable increase of the main maximum and appearing of the intensive maximum in the region of $\sim 4 \text{ \AA}$ which can be attributed to Zn-Zn distance in dimers are observed. Fitting based on the dimeric model including $4\text{S}+\text{S}+\text{Zn}$ surrounding of Zn atoms in this case gave the following results: $R_{\text{EXAFS}}=14.5\%$, $R(\text{Zn}-4\text{S})=2.35 \text{ \AA}$, $R(\text{Zn}-\text{S})=2.43 \text{ \AA}$, $R(\text{Zn}-\text{Zn})=3.78 \text{ \AA}$, $\sigma^2(\text{Zn}-4\text{S})=0.006 \text{ \AA}^2$, $\sigma^2(\text{Zn}-\text{S})=0.07 \text{ \AA}^2$, $\sigma^2(\text{Zn}-\text{Zn})=0.075 \text{ \AA}^2$. In comparison with XRD data for the solid dialkyldithiocarbamate compounds (Motevally *et al.*, 1996) ZnL_2 in the benzene solution while Zn-4S distance within the error bar is coincides with the average value for first 4 shells for the solid compounds but the longer distance is shortened valuably. These shortening makes bonding between molecules within dimeric units harder and makes it possible to detect Zn-Zn distance in benzene solution while in the solid complex respective maximum almost are not visible. The discrepancy can be explained by a valuable Zn-Zn structural or dynamic disordering in the solid complex caused by the Zn-S-Zn bond bending. It seems such bending can be easy provoked because in solid bis(dialkyldithiocarbamates) of zinc which have the similar dimeric structure replacement of the alkyl group leads to Zn-Zn distance variations from 3.55 \AA to 3.97 \AA (Motevally *et al.*, 1996).

The Fourier transform magnitude for ZnL_2 solutions in Py and TBP presented in the Fig. 3 show valuable decrease of the main maximum in comparison with the solid complex indicating changes of Zn atoms local surrounding geometry confirming our previous supposition about coordination of Py and TBP molecules by Zn. Unfortunately, all the attempts to construct appropriate structural models giving good results in the fitting procedure failed in these cases possible because of oscillation of atoms anharmonicity. Calculations of the ZnK XANES were not done for all the samples because a wide variety of structural models including angular parameters can be supposed and appropriate limited number of them have not been selected up to now.

CuK XANES spectra measured on solid CuL_2 complex and its solution in Py and TBP are presented in the Fig. 4. Valuable changes in the pre-edge and above the edge regions appear in the both solutions in comparison with the solid complex. Pre-edge structure can be analyzed taking into account 1s-hole screening by additional Cu3d electron density appearing as a result of charge transfer processes from ligands to absorbing atom initiated by 1s level ionization. Such screening leads to a lowering of 1s-4p transition energy and to appearing of so called «shake-down» satellites on the pre-edge XANES region with energy shifts $\sim 5\text{eV}$ respecting to main maximum in accordance with theoretical (Bair & Goddard, 1980) and experimental (Kozugi *et al.*, 1984) results. Polarization dependencies of CuK XANES measured on compounds with square-planar surrounding of Cu atoms reveals 1s-4p_{xy} transitions to the vacant states localized in plane as well as a transition to 4p_z vacant states localized perpendicular to the plane when the last one is shifted to lower energy on the value of $\sim 5\text{eV}$ (Kozugi *et al.*, 1984). Both transitions are accompanied by respective shake-down satellite shifted to lower energy on the value of $\sim 5\text{eV}$.

The main maximum on the CuK XANES spectrum of solid CuL_2 complex can be attributed to 1s-4p_{xy} transition while pre-edge features to a mixture of the 1s-4p_z transition and all the «shake-down» satellites. The spectra in solutions exhibit main maximum and one pre-edge feature only. This fact could be explained by additional coordination of the liquids molecules by the

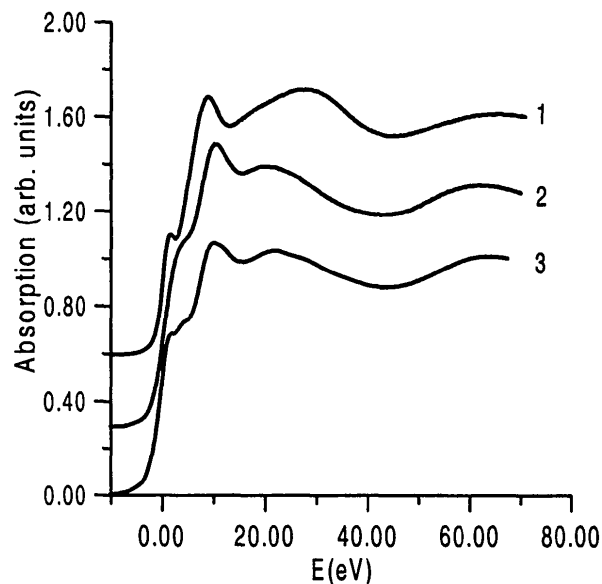


Figure 4
CuK XANES spectra of CuL_2 in tributylphosphine -1, pyridine -2, solid state -3.

Zn atoms when a bonding with P or N atoms causes changes of the 4p_z orbitals energy and occupancy. Energy shifts of the main maximums and satellites in the spectra of solutions may be caused by changes of energy localization of the whole set of the 4p-type levels which is depend on chemical specificity of the coordinated atom. Unfortunately, we could not synthesized model compound where Cu atoms have $4\text{S}+2\text{N}$ or $4\text{S}+2\text{P}$ surroundings to compare their XANES shapes and approve our interpretation.

The amplitude of the main maximum on the Cu radial distribution function for the TBP solutions differs from that of the Py solution and of the solid complex which confirm our supposition about coordination of TBP molecules by Cu.

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