A study of the coordination environment in aqueous cadmium-thiol complexes by EXAFS spectroscopy: experimental vs. theoretical standards

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Using EXAFS, we investigated the changes in the local structure of Cd(II) complexes formed with a series of low-molecular-weight thiols at different thiol/cadmium stoichiometries. For dilute solutions, a comparison of theoretical and experimental standards proved the latter approach superior. The number of bound oxygen atoms decreased while the number of sulfur atoms increased as the thiol/cadmium ratios increased, indicating that up to four thiol compounds can bind to cadmium in aqueous solutions. The computer code FEFFIT was modified to employ experimental and theoretical standards with equal facility.

Keywords: dilute solutions, thiols, cadmium complexation

1. Introduction.

Multiple scattering effects contribute significantly to the EXAFS of metals ions in concentrated samples. Most current *ab initio* EXAFS theories (e.g. FEFF) account for such effects, and thus can be used to analyze the coordination environment beyond the innermost coordination shells. However, using theoretical rather than experimental standards may not be the ideal approach to analysing dilute solutions in which multiple scattering effects are not significant and constructing reliable theoretical standards is complicated.

We investigated the changes in the local structure of Cd(II) complexes formed with a series of low-molecular-weight thiols of biochemical and environmental significance at different thiol/cadmium stoichiometries. For the EXAFS analysis, we used computer code FEFFIT (Stern, 1995). We modelled the spectra using both Cd-O and Cd-S contributions extracted from the experimental EXAFS data of CdSO$_4$ (aqueous solution) and CdS, respectively. Due to the low cadmium concentration and, therefore, the short *k*-range in EXAFS data at each stoichiometry, we performed simultaneous multiple-data-set analyses.

2. EXAFS experiment.

The Cd K-edge X-ray absorption coefficients were measured in fluorescence mode using the 13 element Ge detector at the X18-B Beamline of the NSLS (Brookhaven National Laboratory) for the samples of 2-mercaptoethylamine (MPEA), 2-mercaptoethyl-sulfonate (MPES) and 3-mercaptopropionic acid (MPA) and for the reference compounds (aqueous solutions of CdSO$_4$ and solid CdS). These thiols represent simple hydrophilic compounds with contrasting polar terminal groups (-NH$_2$ in MPEA; -SO$_3^-$ in MPES; -COOH in MPA) which are typical of molecules present in biological and environmental systems. The X-ray energy range was varied from 200 eV below to 1000 eV above the Cd K-edge energy (26710 eV) using Si (111) monochromator. Several measurements of each sample were made to improve the signal-to-noise ratio. The individual scans for each sample were aligned in the X-ray energy, interpolated to the same energy grid and averaged.

3. EXAFS analysis using experimental standards.

In the single-electron, single-scattering approximation, the EXAFS signal $\chi(k)$, generated by the N_1 number of oxygen atoms at the first-neighbor distance R_1 and by the N_2 sulfur atoms at distance R_2 from the central Cd atom, could be written:

$$
\chi(k) = \sum_{i=1}^{2} \chi_i(k)
$$
$$
= \sum_{i=1}^{2} \frac{N_i S_0^2}{k R_i^2} f_i(k) \exp(-2k^2\sigma_i^2) \sin(2kR_i + \delta_i(k)), \qquad (1)
$$

where $\chi_i(k)$ is a partial contribution by O atoms ($i = 1$) and S atoms ($i = 2$), σ_i^2 is the mean square deviation of the bond length, S_0^2 is the passive electrons reduction factor while $f_i(k)$ and $\delta_i(k)$ are the photoelectron backscattering amplitude and the respective total phase shifts at either oxygen ($i = 1$) or sulfur ($i = 2$). These two functions can be calculated theoretically, using a model with the structure similar to that in the unknown sample, or experimentally (Stern, 1983).

For the purpose of accurately evaluating the numbers of O (N_1) and S (N_2) neighbors around Cd at different Thiols/Cd ratios, the prerequisite is an unambiguous set of $f(k)$ and $\delta(k)$ functions for the Cd-O and Cd-S pair interactions. At first, we attempted to generate the $f(k)$ and $\delta(k)$ functions for the Cd-O interactions using the *ab initio* FEFF7 code (Zabinsky, 1995). Since hydration of Cd^{2+} ions is possible at low Thiols/Cd ratios, the FEFF7 calculations of Cd-O model interactions were performed for three models: the Cd[H$_2$O]$_6$ octahedron with and without H atoms (models A and *B*) and the bulk CdO (model *C*). Due to the transferability of EXAFS scattering amplitude and phase, $f(k)$ and $\delta(k)$, generated by the same pair of absorbing (Cd) and backscattering (O) atoms in model *A*, are expected to be similar to their respective scattering functions calculated for models *B* and *C*. However, even though the difference between $f(k)$ functions calculated with models *B* and *C* (where no H atoms were included) was less than 10%, the results for $f(k)$ obtained for the model *A* were drastically removed (more than 40%) from those calculated with the two other models. The difficulty of FEFF7 code in accounting for H atoms is expected in our case as the Cd-O distance is much longer than the O-H distance and,

therefore, constructing the muffin tin radii in FEFF7 calculation is complicated[‡].

Because of the difficulties in constructing an adequate theoretical model for Cd-O interaction, we used experimental standards to obtain the scattering amplitudes and phases of both Cd-O and Cd-S interactions. This procedure is justified for the isolated shell analysis provided that the contributions of the nearest and most distant neighbors, including multiple scattering, do not overlap, as in the present case. Our procedure of extracting the scattering functions from the experimental standards follows closely that described in Stern and Heald (1983).

Aqueous solution of $CdSO_4$ and CdS powder were the experimental standards for Cd-O and Cd-S interactions, respectively. By back-Fourier transforming their Cd K-edge EXAFS signals $\chi_{(S)i}(k) = A_i(k)\sin P_i(k)$, where subscript (S) indicates "standard", we obtained their amplitudes $A_i(k)$ and phases $P_i(k)$ which are related to the unknown scattering functions $f_i(k)$ and $\delta_i(k)$ as follows:

$$A_i(k) = \frac{N_{(S)i}S_0^2}{kR_{(S)i}^2}f_i(k)\exp(-2k^2\sigma_{(S)i}^2),$$
$$P_i(k) = 2kR_{(S)i} + \delta_i(k). \qquad (2)$$

Due to the transferability of amplitudes and phases for the same atomic pairs, $f_{(S)i}(k) = f_i(k)$, and $\delta_{(S)i}(k) = \delta_i(k)$ in Eq. (2). In accordance with the previously published results, the reference Cd-O and Cd-S distances $R_{(S)i}$ were set to 2.28 Å and 2.52 Å, respectively. The coordination numbers of O and S in the standard compounds were set to $N_{(S)1} = 6$ and $N_{(S)2} = 4$. Using new variables $\Delta R_i = R_i - R_{(S)i}$ and $\Delta\sigma_i^2 = \sigma_i^2 - \sigma_{(S)i}^2$ defined as corrections to the Cd-O and Cd-S distances and disorders in the unknown samples relative to those in the standard compounds, we combined Eqs. (1) and (2) in order to express the EXAFS signal in the unknown sample through the measured quantities ($A_i(k)$ and $P_i(k)$) and fitting variables (N_i, ΔR_i and $\Delta\sigma_i^2$):

$$\chi(k) = \sum_{i=1}^{2}\frac{N_i}{N_{(S)i}}\frac{R_{(S)i}^2}{(R_{(S)i} + \Delta R_i)^2}A_i(k)$$
$$\times\exp(-2k^2\Delta\sigma_i^2)\sin(2k\Delta R_i + P_i(k)) \qquad (3)$$

These structural parameters (i.e., Cd-O and Cd-S coordination numbers, corrections to the reference Cd-O and Cd-S bond lengths and their disorders, as well as the corrections to the photoelectron energy origin, ΔE_i) were obtained by fitting the Eq. (3) to the experimental data using the computer code FEFFIT (Stern, 1995). FEFFIT fits the data using non-linear least square method, and evaluates uncertainties in the results. We tested the quality of the experimental amplitude and phase functions, $A_i(k)$ and $P_i(k)$, by fitting Eq. (3) to the data of $CdSO_4$ and the CdS, i.e., the same compounds from which the experimental Cd-O and Cd-S interactions were extracted. The fit results are shown in Fig. 1. The reliability of our procedure is illustrated by the excellent agreement of the obtained coordination numbers for the Cd-O (6.1 ± 0.3) and Cd-S pairs (4.0 ± 0.1) with those known for these

reference compounds (6 and 4, respectively), and by negligibly small values obtained for ΔR_i and $\Delta\sigma_i^2$.
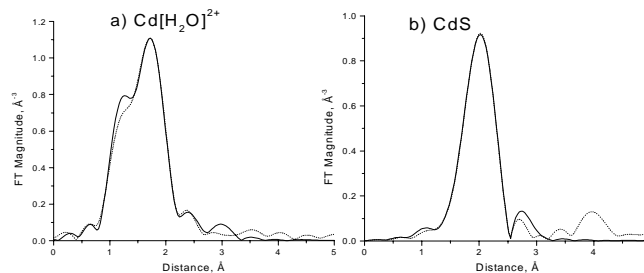
Figure 1
Fourier transform magnitudes of the fit (solid) and EXAFS data (dots) of Cd in (a) aqueous solution of $CdSO_4$ and (b) CdS. Fits were performed using experimental standards extracted from the same data.

The FEFFIT program, designed to use FEFF-calculated amplitudes and phases in the theoretical EXAFS equation (1), turned out to work remarkably well in the present case where the amplitudes and phases were extracted from experimental standards. Indeed, the modified EXAFS equation (3) has the same functional form as in (1) and the same capabilities of FEFFIT can be applied to treat the "experimental" and "theoretical" standards with equal facility, or even use the combination of "experimental" (for one group of interactions) and "theoretical" (for another group) standards to refine EXAFS data. Additionally, the possibility to fit concurrently several data sets of the otherwise similar systems, with monotonic variation of external conditions (e.g., concentration of thiols, as in the present work) is a powerful tool to analyze EXAFS data of dilute solutions. In that case, the information content in the individual data set is limited by the short k-range, as demonstrated below.

4. Data analysis of Cd-thiols complexes.

EXAFS data were processed and analysed using the UWXAFS data analysis package (Stern, 1995). To obtain structural information from the fit, it was crucial to circumvent one of the major obstacles in analysing EXAFS data in disordered samples with a complex chemical and structural environment around the absorbing atom. This obstacle appears when adjustable parameters equal or exceed the independent data points in number. The total number of fitting parameters, if no constraints are applied, is 6. For all the samples, both the Δk (2 - 9 Å^{-1}) and Δr (1.5 - 2.4 Å) data ranges (over which the fit is being made) were rather narrow and the corresponding number of independent data points, $N_{idp} = 2\Delta k\Delta r/\pi + 2$, was equal to ~ 6 points, i.e., equal to the number of fitting parameters. Therefore, the number of degrees of freedom in the fit was zero.

To reduce the number of the fit variables, the background-subtracted, edge-step normalized EXAFS data for all the samples (MPEA, MPES and MPA) with all Thiols/Cd ratios were processed concurrently, using the constraints below for all data. The corrections ΔE_{Cd-O} for the photoelectron energy origin and E_0, for the model Cd-O contribution were equalised for all data. This is a reasonable approximation since the raw data were aligned in energy prior to the EXAFS analysis. Likewise, the corrections ΔE_{Cd-S} for the model Cd-S contributions were also constrained to be the same in all the samples. The two fitting parameters, ΔE_{Cd-O} and ΔE_{Cd-S}, were varied independently in the

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[‡] The next version of this program, FEFF8, has implemented a new algorithm, recently tested (Frenkel, 2000), which allows to treat hydrogen atoms more reliably in constructing muffin-tin potentials.

fits because the ionization potentials in the experimental standards, the aqueous solution of Cd sulfate and solid Cd sulfide may be different. Another approximation was made assuming the interatomic Cd-S and Cd-O pair interaction potentials unaffected by the changes in the thiol concentrations. Therefore, the corresponding bond length disorders, σ^2, of all the Cd-O bonds and all the Cd-S bonds in all the samples were not varied independently. Rather, we varied only two variables, σ^2_{Cd-O} and

σ^2_{Cd-S} for all the samples. The other variables were the coordination numbers (N_{Cd-O} and N_{Cd-S}) and corrections to the model Cd-O and Cd-S distances (ΔR_{Cd-O} and ΔR_{Cd-S}), which were varied independently for all the samples. The variables numbered 60, far below the 75 relevant independent data points. The data (at highest and lowest Thiols/Cd ratios) and fits are shown in Fig. 2.
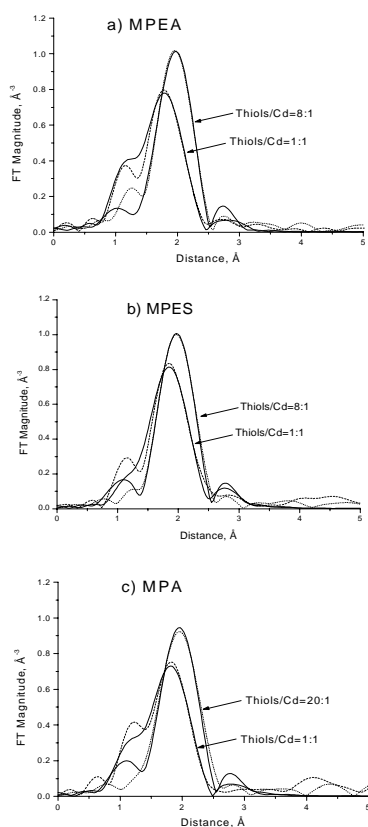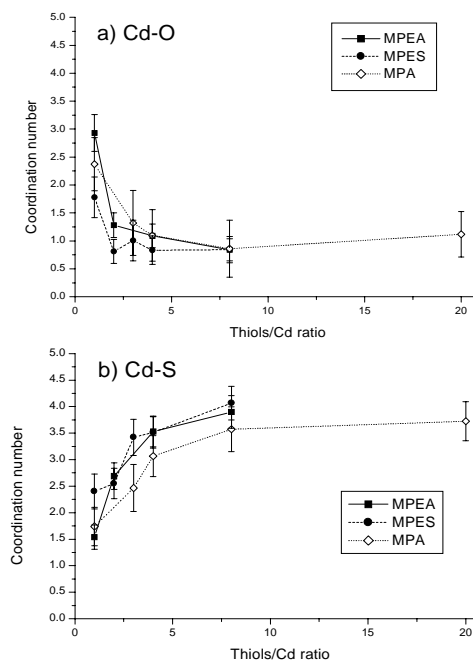

Figure 2
Fourier transform magnitudes of the fit (solid) and data (dots) for the MPEA (a), MPES (b) and MPA (c) samples for the lowest and highest Thiols/Cd ratios in each sample.

Figure 3 demonstrates that the number of bound oxygen atoms decreased while the number of sulfur atoms increased as the Thiol/Cd ratios increased. The total number of sulfur atoms coordinated to cadmium approached four with all of the thiols examined. The decrease of Cd-O coordination is expected because more sulfur atoms replace oxygens when the thiol concentration increases. The saturation of Cd-S coordination number at the level of four sulfurs per Cd atom agrees with that in CdS, suggesting that a maximum of four thiol compounds can bind to cadmium in aqueous solution. Although the coordination number for Cd(II) can be as high as six with smaller ligands such

as oxygen and nitrogen, the maximum of four for sulfur may suggest that a steric limitation probably occurs with sulfur ligands because of their larger size.

Figure 3
Coordination numbers of Cd-O (a) and Cd-S (b) bonds.

5. Summary and conclusions.

For the EXAFS analysis of aqueous solutions of cadmium-thiol complexes with different Thiol/Cd stoichiometries, we used computer code FEFFIT, which was modified to employ experimental and theoretical standards with equal facility. We modelled the spectra using both Cd-O and Cd-S contributions, extracted from the experimental EXAFS data of $CdSO_4$ (aqueous solution) and CdS (powder), respectively. Local structure and error analyses were performed by multiple data set refinement. The results demonstrated that the Cd-O coordination number gradually decreased while the Cd-S number increased, saturating at four, with the increase of Thiols/Cd ratio, suggesting that up to four thiol compounds can bind to cadmium in aqueous solution. Our results suggest that using experimental standards in EXAFS analysis is advantageous for diluted systems.

References

Frenkel, A.I., Korshin, G.V., & Ankoudinov, A. (2000). Environ. Sci. Technol., **34**, 2138-2142.
Stern, E.A. & Heald, S.M. (1983). Handbook on Synchrotron Radiation, Vol. 1, Ch.10, ed. by Koch, E.E., North-Holland, 1983.
Stern, E.A., Newville, M., Ravel, B., Yacoby, Y., & Haskel, D. (1995). Physica B, **208&209**, 117-120.
Zabinsky, S. I., Rehr, J. J., Ankudinov, A., Albers, R. C. & Eller, M. J. (1995). Phys. Rev. B, **52**, 2995-3009.