Soft x-ray absorption study of Co-Au multinuclear complexes with D-penicillaminates

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Abstract

We have examined local 3d electronic structures of Co-Au multinuclear complexes with molecules D-penicillaminate (D-pen) $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ medicinal and $[Co_3 {Au_3(tdme)(d-pen)_3}_2]$ by means of Co L-edge soft X-ray absorption (XAS) spectroscopy, where PPh₃ denotes triphenylphosphine and tdme stands for 1,1,1-tris[(diphenylphosphino)methyl]ethane. We have successfully obtained the radiation damage-free XAS spectra of these compounds reflecting their intrinsic electronic states. The Co L-edge XAS spectra indicate the localized ionic 3d electronic states in both materials. The experimental spectra are well explained by spectral simulation for a localized Co ion under crystalline electric fields (CEF) with the full multiplet theory. The CEF value has been estimated to be larger than that the high spin (HS)-low spin (LS) crossover for $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ while the value for $[Co_3{Au_3(tdme)(d-pen)}_3]_2]$ is smaller than the HS-LS crossover, which verifies that the ions are in the LS Co³⁺ state in the former compound and in the HS Co^{2+} state in the latter.

1. Introduction

The electronic structure of a transition metal ion in materials is important for their functions not only in various inorganic crystalline solids but also in complex with organic molecules as seen in hemoglobin. Actually, many transition metal complexes with intriguing natures¹⁻⁴ have been synthesized. Meanwhile, D-penicillaminate (D-pen) is employed as a heavy metal antagonist⁵⁻⁷ since it has a nature of building metal coordination systems. Such a aminothiolate would also be a candidate of raw materials for newly functional metal multinuclear coordination systems. So far, many metal complexes with D-pen have been thus developed^{4,8,9}. Among them, it has been reported that the Co²⁺ ions in single-crystalline $[Co_3{Au_3(tdme)(D-pen)_3}_2]$ (tdme denotes 1,1,1-tris[(diphenylphosphino)methyl]ethane) are unusually stabilized in an octahedral coordination environment surrounded by two aliphatic thiolato, two amine, and two carboxylate donors¹⁰, as shown in Fig. 1. On the other hand, the Co ions in another Co-Au trinuclear complex $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ (PPh₃ stands for triphenylphosphine) have been reported as in the Co^{3+} state although the local coordination environment is similar to that in $[Co_3{Au_3(tdme)(d-pen)_3}_2]$ except for their bond length¹¹. The valence and spin states of the Co ions in these crystals have been estimated from their crystal color, magnetic susceptibility, and light absorption in visible and UV region^{10,11}. However, direct verifications by using an element-selective probe are still lacking.

In the high-energy electron spectroscopic field, K-edge X-ray absorption fine structure (XAFS) has been applied to transition metal complexes 12-14, where possible deterioration of measured samples caused by irradiation have not been so serious. However, it is difficult to obtain the local 3d electronic structure by XAFS as well as K-edge X-ray absorption near-eadge structure (XANES) due to the s-to-p excitation process. On the other hand, L_{2.3}-edge soft X-ray absorption (XAS) spectroscopy in the soft X-ray region is powerful for directly probing the local element-specific electronic structure^{15–21}. However, the application of L_{2,3}-edge XAS to transition metal complexes is still new frontier because sample degradations caused by soft X-ray irradiations have often prevented us from acquisitions of reliable spectra^{22,23}. This technical difficulty has been solved by optimizing photon density and properly changing sample position. Here we present the local 3d electronic structures of the Co-Au multinuclear complexes $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and $[Co_3 {Au_3(tdme)(D-pen)_3}_2]$ investigated by the Co L_{2,3}-edge soft X-ray XAS. It has been verified that the Co ions are in the low-spin (LS) Co³⁺ state for the former compound whereas they are in the high-spin (HS) Co^{2+} state for the latter system on the basis of the comparisons of the experimental spectra with spectral simulations for a localized ion under the crystalline electronic fields (CEF) with taking the full multiplet theory into account.



Figure 1. Molecular structure of (a) $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$, (b) $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$. Ph and Me denote the phenyl and methyl groups. (a-2) and (b-2) show the local structure around the Co ions and the bond lengths Co-O, Co-N, and Co-S estimated from the X-ray diffraction. These complexes have the ligand environment in octahedral symmetry, displayed as gray marks^{10,11}.

2. Experimental

The XAS measurements were carried out at BL-11 of Synchrotron Radiation Center in Ritsumeikan University, Japan. In this beamline, so-called varied-line-spacing plane gratings were employed, supplying monochromatic photons with hv = 40-1000 eV. The Co L_{2,3}-edge XAS spectra (hv = 760-810 eV) were taken simultaneously in the total electron yield (TEY), partial fluorescence yield (PFY) and partial electron yield (PEY) modes with a photon energy

resolution of ~300 meV. The experimental geometry is shown in the Fig. 2(a). In the PFY mode, a large-area silicon drift detector capturing photon energy-dependent luminescence was set to 45° with respect to the photon propagation in the xy plane. For the Co $L_{2,3}$ -edge XAS measurements, the luminescence with hv = 700–950 eV including the Co L lines was detected as a signal. On the other hand, in the PEY mode, the micro channel plate (MCP) detecting the Auger and secondary electrons was set in the 45°-depression to the photon propagation. In the front of MCP, a gold mesh was installed to be able to apply a voltage. We applied the voltage of -550 V to the mesh for the Co L-edge measurements in order to suppress a strong background caused by the C, N and O K-edge absorptions in the spectra.

 $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and $[Co_3{Au_3(tdme)(D-pen)_3}_2]$ were synthesized by using the precursors and $Co(CH_3COO)_2 \cdot 4H_2O$ in the water. The details of the synthesis have been reported in Refs. 10, 11. These powder-like single crystalline samples were thinly expanded on the conductive carbon tape attached on the sample holder in air before transferring them into the vacuum chamber. Since the single-crystal sizes of every piece were smaller than ~100 µm, neither cleaving (fracturing) nor scraping of the samples in situ for obtaining the clean surfaces was feasible for the XAS measurements. However, we believe that the intrinsic XAS spectra of these samples have been obtained as discussed later probably due to the stability of the ionized Co states in the compounds, in which the Co ions have already been "oxidized" in a chemical sense. We repeatedly measured the spectra on the same and different sample positions, confirming the data reproducibility with neither serious radiation damage nor sample-position dependence of the Co L_{2,3}-edge XAS spectra. The measurements were performed at room temperature.

3. Results

The raw Co L_{2,3}-edge XAS spectra of $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ in the TEY, PFY, and PEY modes are shown in Fig. 2(b). There is a double-peak structure of the L₃- (hv \approx 780 eV) and L₃- (hv \approx 794 eV) edges due to the Co 2p core-hole spin-orbit coupling in all spectra. The overall spectral features are mutually consistent among these three spectra without showing a serious peak shift, indicating that we have successfully obtained the intrinsic XAS spectra. On the other hand, there are some detailed discrepancies among the spectra. A shoulder structure at hv = 779 eV in the spectra in the TEY and PEY modes is markedly suppressed in the PFY spectrum. On the basis of the probing depth of each mode¹⁶, we can judge that this shoulder would be due to a surface contribution deviated from the bulk ones. Between the two main L_{2,3}-edge peaks, another shoulder is seen at hv = 782 eV in both TEY and PEY spectra, being overlapped with an asymmetric tail in the PFY spectrum. Such an asymmetric tail is also seen



Figure 2. (a) Experimental geometry in the total electron yield (TEY), partial fluorescence yield (PFY) and partial electron yield (PEY) modes. (b) Co $L_{2,3}$ -edge XAS raw spectra of $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ in the TEY (red solid line), PFY (green solid line) and PEY (blue solid line) modes. Linear background of the spectra in the PEY mode is displayed by a dashed line. The linear background for the spectrum in the PEY mode has been determined from the raw spectral weight in the region of hv = 765-772 eV.

on the high-hv side of the L₂ edge in the PFY spectrum. These tails would originate from so-called self-absorption effects^{16,24,25}, by which the spectral shape can be deviated from the intrinsic one. In addition, a background of the spectrum in the TEY mode depends on hv, where it is stronger for low-hv side than those for high-hv side. This fact suggests that the intrinsic Co L_{2,3}-edge XAS spectral weight is remarkably weaker than the background yielded by high-energy tails of the C, N, O K-edge absorptions caused by a tiny Co element ratio as

C : N : O : Co = 46 : 2 : 8 : 1 for $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$. In the PEY mode, on the other hand, the background is relatively weaker than the Co L2;3-edge XAS spectral weight owing to the suppression of the contribution of electrons with their kinetic energy less than 550 eV to the spectral intensity. This background increases slightly and linearly with hv, as shown in Fig. 2(b). Therefore, we have concluded that the spectrum in the PEY mode is the most reliable for the quantitative discussions shown below although it is relatively surface-sensitive.

The background-subtracted Co $L_{2,3}$ -edge XAS spectra of $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and $[Co_3 {Au_3(tdme)(D-pen)_3}_2]$ in the PEY mode are shown in Fig. 3. The characteristic spectral structures from the bulk nature are labeled as A-D and a-f in spectra, respectively. A metal-like asymmetric tail of the L₃ main peak^{16,26} is not seen at all. A possible satellite structure in the photon energy of 5-6 eV higher than the main peaks called as a charge-transfer satellite is negligible. Such a satellite originates from hybridizations between the Co 3d and ligand p orbitals described by configuration interactions on the basis of the cluster model^{27,28} or Anderson impurity model²⁹. Therefore, the absence of the satellite suggests that these spectra can be well explained by local ion models without explicitly considering the hybridization effects. Let us compare our spectra with those reported for inorganic Co compounds EuCoO₃ (pure LS-Co³⁺), Sr₂CoO₃Cl (pure HS-Co³⁺), and CoO (pure HS- Co^{2+}) (Refs. 30–32) indicated in Fig. 3, where the characteristic spectral structures are also labeled as A'-D', a'-f', and α , respectively. The spectral features of $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ are inconsistent with those of Sr₂CoO₃Cl near the L₂ edge, while the structures A-D seem to correspond well with those A'-D' for EuCoO₃. Therefore, it is concluded that the Co ions of $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ are in the LS-Co³⁺ state. On the other hand, the structures a-d in the spectrum of $[Co_3{Au_3(tdme)(D-pen)_3}_2]$ are similar to those a'-d' in the spectrum of CoO at the L₃ edge although they are somehow smeared. The spectral shape of $[Co_3 {Au_3(tdme)(D-pen)_3}_2]$ at the L₂ edge seems to be rather different from that of CoO, but the L_3 - L_2 splitting energy is mutually consistent. We can thus judge that the Co ions in $[Co_3{Au_3(tdme)(D-pen)_3}_2]$ are in the HS-Co²⁺ state. We consider that a shoulder structure at hv = 779 eV in the spectrum of $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ is caused by the surface Co^{2+} contribution corresponding to the peak b for $[\text{Co}_3{\text{Au}_3(\text{tdme})(\text{D-pen})_3}_2]$, where the Co^{2+} state is favored in the surface due to its larger ionic radius than that for the Co^{3+} state.



Figure 3. Co $L_{2,3}$ -edge XAS spectra in the PEY mode for $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$ (black solid lines) compared with those reported for CoO (HS-Co²⁺ :blue solid line), Sr₂CoO₃Cl (HS-Co³⁺ :green solid line), and EuCoO₃ (LS-Co³⁺ :red solid line) cited from Refs. 30–32. The characteristic spectral structures are labelled as A-D, a-f in our experimental spectra and as A'-D', a'-d', α in the reference spectra respectively.

4. Discussions

As mentioned before, $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$ have the octahedral coordination environment. In addition, the average of the bond lengths of $[Co{Au(PPh_3)(D-pen)}_2]ClO_4 (2.03 \text{ Å}) and [Co_3{Au_3(tdme)(D-pen)}_3]_2] (2.25 \text{ Å}) estimated by$ X-ray diffraction are longer than those of EuCoO₃ (1.93 Å) and CoO (2.10 Å) (Refs. 33 and 34), which might allow to discuss the Co L_{2,3}-edge XAS spectral shape in view of the localized Co ions under CEF. We have performed spectral simulations for the Co ion^{35,36} in cubic O_h symmetry using the XTLS 9.0 program³⁷. All atomic parameters such as the 3d-3d and 2p-3d Coulomb and exchange interactions (Slater integrals), and the 2p and 3d spin-orbit couplings have been obtained using Cowan's code³⁸ based on the Hartree-Fock method. The Slater integrals were reduced to 80% (Refs. 20 and 39) to reproduce the Co L_{2,3}-edge XAS spectra, as shown in Table I. The actual local symmetry of the Co ions is lower than the cubic ones for both materials. However, the CEF splitting 10Dq between the t_{2g} and e_g states in the O_h symmetry is crucial for determining the local spin state (HS or LS) of the Co ions. Therefore, the simulations in the O_h symmetry would give the meaningful information of the 3d electronic states. The simulation results for Co^{3+} and Co^{2+} as a function of 10Dq in the O_h symmetry is shown in Fig. 4, being consistent with previous calculation results³⁶. The feature A"-D" and a"-f" denote the characteristic structures for the Co ions, respectively. For the spectra of Co^{3+} , the shoulder structure B" (D") is reduced and shifted to the higher photon energy with increasing 10Dq. As well as the feature of B" and D", the structure c" (f") is shifted to the higher photon energy in the spectra of Co^{2+} . On the contrary, the structure a" is shifted to the low-hv side with increasing 10Dq.

	$2p^63d^6$	$2p^53d^7$	$2p^63d^7$	$2p^53d^8$
$F^2(3d3d)$	10.138	10.743	9.295	9.925
$F^4(3d3d)$	6.339	6.720	5.775	6.172
$F^2(2p3d)$	_	6.321	_	5.810
$G^{1}(2p3d)$	_	4.760	_	4.317
$G^{3}(2p3d)$	_	2.709	_	2.455
ζ_{3d}	0.074	0.092	0.066	0.083
ζ_{2p}	_	9.742	_	9.744

Table I. Values of the Slater integrals, the spin-orbit couplings (ζ) in units of eV for the various Co configurations for the theoretical calculations.



Figure 4. Simulated Co $L_{2,3}$ -edge XAS spectra with the full-multiplet theory for Co³⁺ and Co²⁺ ions as a function of the crystalline electric field splitting 10Dq in the O_h symmetry. Gaussian and Lorentzian broadnings were set to ~300 and ~400 meV to reproduce the XAS spectra. The characteristic structures are labelled as A"-D" and a"-f" in the spectra of Co³⁺ and Co²⁺, respectively.

Our results show that the energy difference between A (b) and B (c) of $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ ($[Co_3{Au_3(tdme)(D-pen)}_3]_2]$) is 2.28 eV (1.22 eV). Figure 5 shows the comparison of the experimental spectra with the best simulated ones by optimizing 10Dq so as to reproduce the energy difference. From these analyses, we have determined the 10Dq value of 3.0 ± 0.2 eV for $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and 1.0 ± 0.2 eV for $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$. These 10Dq values lead to the low-spin (high-spin) state for the former (latter) compound, being consistent with the magnetic susceptibility and the optical absorption results. Detailed quantitative inconsistency of the line shape at the L₃ edge between $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$ and the HS-Co²⁺ state might be caused by the difference in symmetry.



Figure 5. Comparison of experimental (black solid lines) and theoretically reproduced (red solid lines) spectra for $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$ with 10Dq = 3.0 and 1.0 eV, respectively. The XAS final-state multiplet structures (green solid line) are also shown.

Note that our optimized 10Dq value of 3.0 eV for the LS-Co³⁺ states is much (more than 3 times) larger than that for EuCoO₃ (Ref. 31) since our value corresponds to a renormalized 10Dq in which the hybridization effects (anisotropy in the hybridization in a rigorous sense)

are implicitly included. This is higher than the value of the LS-HS crossover ≈ 2.2 eV (Ref. 39). The estimated 10*Dq* of 1.0 eV for the HS-Co²⁺ state is expected to be much smaller than that of the LS-HS crossover for Co²⁺ (~2.0-2.5 eV). Such a small 10Dq value might unusually stabilize the Co²⁺ state in [Co₃{Au₃(tdme)(D-pen)₃}₂]. When we consider the fact that the Co³⁺ ions have the smaller ionic radius than that for the Co²⁺ ions in these compounds, the larger 10*Dq* in [Co{Au(PPh₃)(D-pen)}₂]ClO₄ is understood as a consequence of the strong hybridization caused by the shorter distance between the Co and neighboring ions.

4. Conclusions

We have studied the 3d electronic structure of the Co-Au multinuclear complex with medicinal molecules D-penicillaminate $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$ probed by Co L2;3-edge XAS. There are no observation of the satellite structure in $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$, indicating that the Co ions are strongly localized. From the spectral calculations for the ions under CEF in the O_h symmetry, we have verified that the Co ions are in the LS-Co³⁺ state for $[Co{Au(PPh_3)(D-pen)}_2]ClO_4$ and in the HS-Co²⁺ state for $[Co_3{Au_3(tdme)(D-pen)}_3]_2]$ with much smaller 10Dq, which are consistent with the magnetic susceptibility and the optical absorption results.

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