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Polarized XANES of $Co(III)(NH_3)_6$ Molecular Crystals

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Polarized single crystal x-ray absorption spectra have been measured for $Co(NH_3)_6(ClO_4)_2Cl$:KCl. These spectra show pronounced orientation dependence for several features on the high energy side of the Co K absorption edge. The Co in this salt has a trigonally distorted octahedral structure with N-Co-N angles of 89.5^0 and 90.5^0, hence first shell scatterers cannot account for the observed orientation dependence. As we show below, the orientation dependent features can be interpreted in terms of a single-scattering EXAFS model involving scattering from a perchlorate which is hydrogen-bonded to the $Co(NH_3)_6^{3+}$ ion.

$Co(NH_3)_6(ClO_4)_2Cl$:KCl was prepared by the method of Wilson and Solomon [1] and single crystals were oriented by standard diffraction methods. In initial experiments, the $Co(NH_3)_6^{3+}$ molecules were oriented so that both the propagation ($\boldsymbol{k}$) and polarization ($\boldsymbol{e}$) vectors were contained in one of the CoN4 planes. The crystal was rotated about $\boldsymbol{e} \cdot \boldsymbol{k}$ and XANES spectra were measured every 15 degrees for a total of thirteen different orientations of $\boldsymbol{e}$. In a second experiment, the polarization vector was oriented either parallel or perpendicular to the crystallographic 3-fold axis.

In order to compare different orientations it was necessary to develop a procedure for the precise, reproducible normalization of experimental XANES spectra. In brief, this method [2] involves subtraction of a low order polynomial from the data followed by multiplication by a scale factor. The polynomial and scale factor are adjusted to maximize the agreement, both below and above the edge, with tabulated x-ray absorption cross section.

The packing in $Co(NH_3)_6(ClO_4)_2Cl$:KCl consists of infinite chains of $Co(NH_3)_6^{3+}$ - ClO_4^- - Cl^- - K^+ - Cl^- - ClO_4^- -... parallel to **c**. Each unit cell contains three such chains with a displacement of 1/3 **c**. In the **c** direction there are two adjacent ClO_4^- groups with Co-O and Co-Cl distances of 3.67 and 5.12 Å, respectively. The six Cl^- ions from adjacent chains lie closer to the $\boldsymbol{ab}$ plane with a Co-Cl distance of 4.21 Å. These ClO_4^- and Cl^- ions will give rise to spectroscopic features polarized parallel and perpendicular, respectively, to **c**. Other near neighbors include the six ClO_4^- groups (Co-Cl = 5.6 Å) and six K^+ ions (6.08Å) on adjacent chains. These groups will have nearly isotropic spectral features. The spectra measured for 13 different orientations of $\boldsymbol{e}$ within the CoN_4 plane are shown in Fig. 1. The features labeled A, B, C, and D clearly show a systematic dependence on orientation, with the two-fold periodicity characteristic of a dipole allowed transition. Because of the nearly octahedral symmetry within the $Co(NH_3)_6^{3+}$ ion, these orientation dependent features must be due to the scattering contributions from distant groups. The experimental spectra, χ, can be described in terms of the components χ_a, χ_b, and χ_c, where **b*** is defined to be perpendicular to **a** and **c**.

$$\chi = \chi_a\cos^2\alpha + \chi_b{}^*\cos^2\beta + \chi_c\cos^2\gamma \qquad (1)$$

In Eq. 1, α, β and γ represent the angles between $\boldsymbol{e}$ and **a**, **b*** and **c** axes respectively. Since a, b* and c are mutually perpendicular and since χ_a and

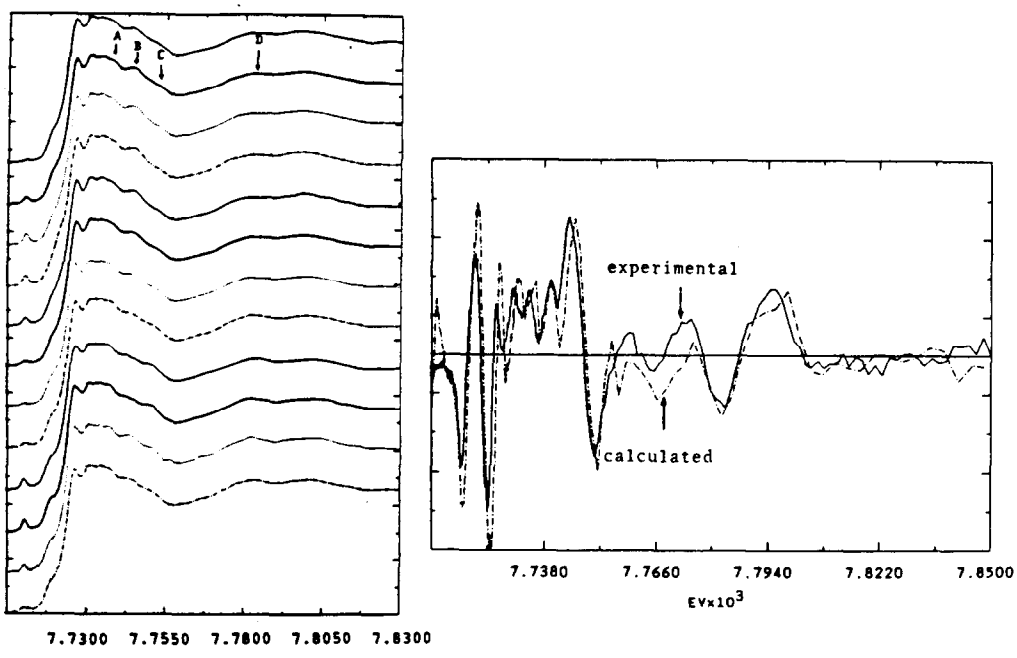

Figure 1 (left). Orientation dependent XANES for $Co(NH_3)_6^{3+}$.
Figure 2 (right). Calculated x_a-x_c for $Co(NH_3)_6^{3+}$.

x_b* are required by symmetry to be identical, equation (1) can be rewritten:

$$\chi = \chi_a + (\chi_c - \chi_a)\cos^2\gamma \qquad (2)$$

This linear system of equations can then be solved for χ_a and $(\chi_c-\chi_a)$. The second experiment (spectra measured with *e* parallel and perpendicular to c) gives $\chi_c-\chi_a$ directly. These two different approaches give very similar results, as shown in Fig. 2.

In the limit of the octahedral Co site symmetry, $\chi_a-\chi_c$ should be zero. Although not strictly octahedral, the deviation of the nearest neighbors from O_h symmetry is too small to account for the observed orientation dependence. The spectra in Fig. 2 are qualitatively similar to EXAFS oscillations, although they are strongly damped, and not observable for k > 6 $Å^{-1}$. A Fourier analysis of these data shows that the frequencies of the oscillations are consistent scatterers at ca. 3.4 and 4.9 Å and they can be simulated using empirical EXAFS amplitude and phase functions. The Cl^- ion which is closer to the Co does not make a detectable contribution to the observed orientational anisotropy. A possible explanation is that the axial ClO_4^- is hydrogen bonded to the NH_3 ligands.

Several conclusions can be drawn from this study: The orientation dependent features of $Co(NH_3)_6^{3+}$ single crystal XANES spectra can be understood using a simple, single scattering model. Apparently, hydrogen H bonding makes possible the unique room temperature observation of EXAFS-like oscillations from distant (> 5Å), non-covalently bonded groups. Because these are strongly damped are only observable for $k < 6Å^{-1}$, and are thus most readily detectable in polarized measurements. Recent variable temperature isotropic measurements demonstrate that these oscillations show the expected enhancement at low temperature.

1. R. B. Wilson and E. I. Solomon, *J. Amer. Chem. Soc.*, *102*, (1980) 4085.
2. G. S. Waldo and J. E. Penner-Hahn, these proceedings.