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X-Ray absorption spectroscopic studies of the Cr(IV) 2-ethyl-2-hydroxybutanoato(1−) complex†

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The first X-ray absorption spectrum of the rare Cr(IV) oxidation state has been obtained for the complex with the ehbaH ligand [ehbaH = 2-ethyl-2-hydroxybutanoate(1−)] in frozen aqueous solution (14 K), showing that at pH = 3.5 and in a large excess of the ligand, the predominant form of Cr(IV) is the five-coordinate oxo complex, [$Cr^{IV}O(ehbaH)_2]^0$.

Considerable interest[1,2] has been generated in the aqueous chemistry of Cr(IV) owing to its potential role as an active intermediate in Cr(VI)-induced genotoxicities.[3,4] The structure of a relatively stable Cr(IV)–ehba complex,[5] which has been studied in detail with respect to its reactivity with biomolecules,[6] has been the subject of considerable debate.[7–9] Alternative structures proposed contain either one multiple and four single Cr–O bonds (as in the crystallographically characterised Na[$Cr^VO(ehba)_2$]),[10] or six single Cr–O bonds [as in Cr(III)-ehba complexes].[8,9] To differentiate between these possibilities, XAS[5] of the Cr(V/IV/III)–ehba complexes in frozen solutions (14 K) were obtained. To our knowledge, this is the first XAS study of a Cr(IV) complex.

The K-edge XAS was recorded using the Australian National Beamline Facility at the Photon Factory, Tsukuba, Japan.[11] The Cr(IV) solutions were prepared by the addition of 10 mM Cr(VI) to 1.0 M ehba buffer containing 0.10 M As(III) (pH 3.5, 20 °C)[2] and were frozen in liquid N_2 at 50 ± 5 s after mixing, which corresponded to 88 ± 2% of total Cr existing in the Cr(IV) form (measured by UV–VIS spectroscopy).[2,11] The solution of Cr(V) was prepared by dissolving 10 mM of Na[$Cr^VO(ehba)_2$][12] in ehba buffer (1.0 M, pH 3.5, 20 °C). The reaction of 10 mM Na[$Cr^VO(ehba)_2$] with 50 mM of $FeSO_4$ (1.0 M ehba buffer, pH 3.5, *ca.* 1 min at 20 °C) resulted in quantitative formation of a Cr(III)–ehba complex.[13] The solutions of Cr(V) and Cr(III) were stable for at least 15 min at 20 °C (UV–visible spectroscopy) and were frozen in liquid N_2 at *ca.* 2 min after preparation. Photodamage of the samples during the exposure to X-rays was minimized by: (i) using cryogenic conditions (14 K);[14] (ii) moving the beam to a fresh spot on the sample after each set of five scans; and (iii) changing to a fresh sample after 12 h of exposure. The absence of significant photodamage was evident from (i) the absence of observable colour changes in the samples after 12 h of exposure;[15] and (ii) the absence of significant changes in the pre-edge and edge features of the XAS.[11] Averaging, background subtraction and the calculation of theoretical XAFS spectra were performed using the XFIT software package,[16] as described previously,[17] and appropriate constraints and restraints.[11,18] Most of the errors in the determined XAFS bond lengths estimated from the Monte Carlo analysis of the noise in the data[16] did not exceed the conservative systematic error of 0.02 Å.[17] HyperChem software[19] was applied for building the molecular models used to initialise the MS XAFS calculations.

The XANES[5] spectrum of the Cr(IV) complex is compared with those of the Cr(V) and Cr(III) complexes in Fig. 1. In agreement with literature data,[20] the edge energy increases along the series Cr(III) < Cr(IV) < Cr(V). The pre-edge region of the Cr(III)–ehba complex features two weak absorption maxima (symmetry-forbidden 1s → 3d transitions), characteristic for octahedral Cr(III) complexes.[21] By contrast, a more intense pre-edge peak was observed in the XANES of the Cr(IV)–ehba complex, when the edge jump was normalised. This feature gains intensity from a decrease in symmetry from an octahedral geometry and/or an increase in π bonding compared to Cr(III).[21] The pre-edge absorbance for the Cr(IV)–ehba complex is *ca.* three times less intense than that for the Cr(V)–ehba complex (Fig. 1).

The SS fits of the XAFS spectra were used to compare the coordination numbers and the Cr–O bond distances in the first coordination shells of the Cr(V/IV/III)–ehba complexes.[11] Acceptable models are those possessing both low goodness-of-fit values (R < 8%) and physically reasonable values of the threshold energy E_0, the scale factor S_0^2 and the Debye–Waller factors σ_i^2.[11] As expected, the first coordination shell of the Cr(III)–ehba complex was best fitted by the model containing six single Cr–O bonds,[22] and that of the Cr(V)–ehba complex is best fitted by the model containing four single (1.85 Å) and one multiple (1.55 Å) Cr–O bond.[23] Notably, additions of extra [*i.e.* seventh for Cr(III) and sixth for Cr(V)] long (2.2 Å) Cr–X distances to the models significantly improved the R values, but led to unreasonably high σ^2 values.[11] This feature probably reflects the influence of more distant coordination shells.

The best fit for the first coordination shell of the Cr(IV)–ehba complex includes: (i) two Cr–O bonds with lengths (1.89 Å) corresponding to those of the Cr–O(carboxylato) bonds in Na[$Cr^VO(ehba)_2$];[10] (ii) two longer (2.07 and 2.26 Å) Cr–O bonds, assigned to the protonated alkoxo groups of the ligand;[24] and (iii) one short (1.55 Å) Cr–O bond, corresponding to the oxo ligand.[10] As for Cr(V)–ehba, addition of a sixth long (⩾2.0 Å) Cr–O bond to the model, though improving the R value slightly, led to unreasonably high σ^2 values.[11] Any models including only single Cr–O bonds (⩾1.7 Å), similar to the alternative structure proposed,[8] gave very poor fits.[11] The best model for

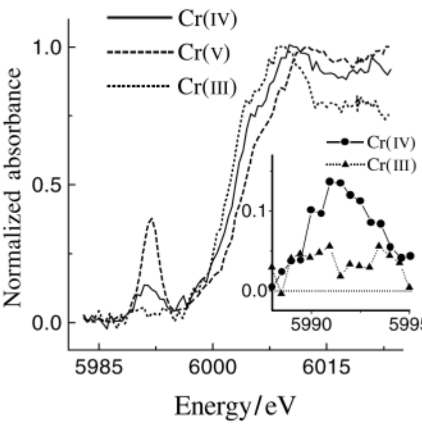
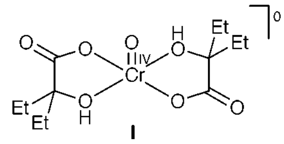


Fig. 1 XANES spectra of frozen (14 K) 10 mM solutions of Cr(V/IV/III)–ehba complexes in 1.0 M ehba buffers, pH 3.5 (average of 20 scans).

† Electronic supplementary information (ESI) available: refer to ref. 11. See http://www.rsc.org/suppdata/cc/1999/2339/

Cr(V)–ehba (*i.e*. with deprotonated alkoxo groups of the ligands) was unsuitable for Cr(IV)–ehba.[11] Thus, comparisons amongst the SS XAFS fits of the first coordination shells for the Cr(V/IV/III)–ehba complexes are consistent with a five-coordinate oxo complex structure **I** for the Cr(IV) complex.



I

When the XAFS of **I** was fitted using MS that included all non-hydrogen atoms[11] a good fit resulted (Fig. 2, R = 18.5%), including significant contributions (⩾10%) of 34 MS paths.[11] In the MS XAFS calculations, bond lengths and angles within the ligands were restrained to be consistent with those within the ehbaH ligand of the crystallographically characterised NH_4-[V^{IV}O(ehba)(ehbaH)] complex,[3] but the angles involving the O donors of **I** were allowed to change freely. The refined structure of **I** was of a distorted trigonal-bipyramidal geometry,[11] similar to those of the Cr(V) and V(IV) ehba complexes.[3,10] However, further studies are required to establish the reliability of the bond angles in **I** determined from the MS XAFS calculations. The Cr–O bond lengths determined from the MS analysis (1.56, 1.89, 1.90, 2.06 and 2.24 Å), were the same, within the experimental error, as those determined by SS calculations.

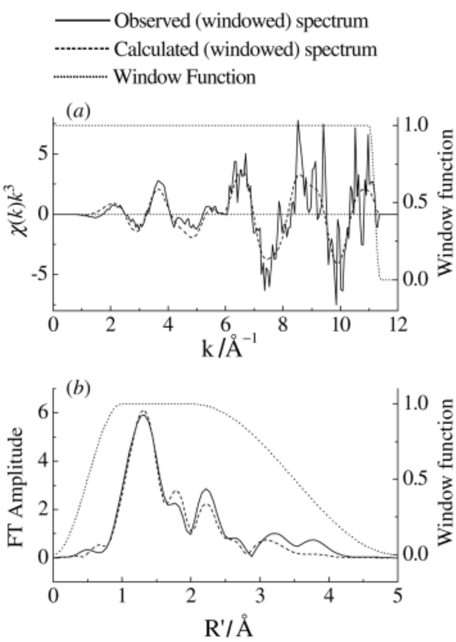


Fig. 2 (a) XAFS spectrum and (b) its Fourier transform for 10 mM **I** (1.0 M ehba buffer, pH 3.5, 14 K, average of 60 scans).

Thus, the SS and MS fitting of the XAFS data, together with the XANES and previous UV–VIS spectroscopic and kinetic studies,[1,2,6] point to **I** as the structure for the Cr(IV) complex under the reaction conditions, while an alternative structure ([$Cr^{IV}(OH)_2$$(ehbaH)_2$])[1,8] is eliminated by the XAFS data.

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5 Abbreviations: ehba = 2-ethyl-2-hydroxybutanoate(2−); XAS = X-ray absorption spectra; XANES = X-ray absorption near-edge structure; XAFS = X-ray absorption fine structure; SS = single scattering; and MS = multiple scattering.
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24 The V–O(alcohol) bond length in NH_4[V^{IV}(ehba)(ehbaH)] is 1.95 Å.[3] The presence of unusually long (> 2 Å) Cr–O bonds in **I** is consistent with the ease of loss of one ehbaH ligand in solution.[1,2]

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