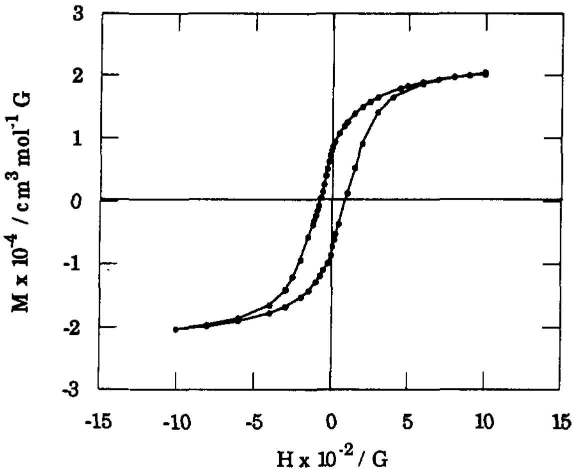

Figure 3. Hysteresis loop $M = f(H)$ at 3 K.

pounds. The magnetization vs field curve of our sample at 3 K shows a hysteresis loop with a coercitive field H_C = 71 G and a remnant magnetization M_R of 7.6 × 10^3 cm^3 mol^{-1} G (Figure 3).[11] The magnetization at high field (H = 4000 G) corresponds to the expected value for parallel spins $S_{Ni} = 1$ and $S_{Cr} = {}^3/_2$.

All these features are consistent with the behavior of a ferromagnet synthesized from molecules (i.e., molecular-based). The value of T_c is sensitive to the stoichiometry, correlated to the water content.[12] Neutron diffraction, X-ray absorption experiments, and chemical conditioning of the compound, with fewer or no water molecules, are in progress to elucidate the effect of water molecules upon T_c.

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(11) The H_C and M_R values are not an intrinsic property of the material, since they depend upon (i) the value when the applied field is reversed (here, H = 1000 G) and (ii) the grain size of the sample. Increasing the grain size is underway.

(12) From our own experience and from a private communication from Prof. D. Babel.

Valence Contrast by Synchrotron Resonance Scattering: Application to a Mixed-Valence Manganese Compound

Y. Gao, A. Frost-Jensen,[†] M. R. Pressprich, and P. Coppens*

Chemistry Department
State University of New York at Buffalo
Buffalo, New York 14214

A. Marquez and M. Dupuis

IBM Corporation, Data Systems Division
Department 48B/MS 428, Kingston, New York 12401

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The tunability of synchrotron radiation makes it possible to vary the scattering power of atoms of specific elements in the vicinity of the atomic absorption edges. The effect is due to the contribution of low-lying electronically excited states to the X-ray scattering process, which is accounted for in the second Born approximation of X-ray scattering theory. The variation of the anomalous components of the atomic scattering, f' and f'', may be used to create a contrast between multiwavelength results that can be applied in the determination of atomic site occupancy.[1] In addition, the variation shows a chemical shift which is about 2.5 eV for each increase in unit of formal valency of vanadium,[2] and about 5 eV for Fe in $Fe^{II}(NH_4)_2(SO_4)_2\cdot 6H_2O$ relative to $Fe^{III}(NO_3)_3$.[3] This difference can be used to obtain direct information on the electronic environment of specific atoms, as shown in powder diffraction studies of mixed-valence solids by Attfield[4] (Eu_3O_4), by Wilkinson, Cheetham, and Cox[5] ($GaCl_2$), and in our work on $NbSe_3$.[6] We report here on a first application to a mixed-valence molecular crystal, in which f' is determined from the refinement of a set of selected reflection data collected at eight wavelengths on both sides of the absorption edge.

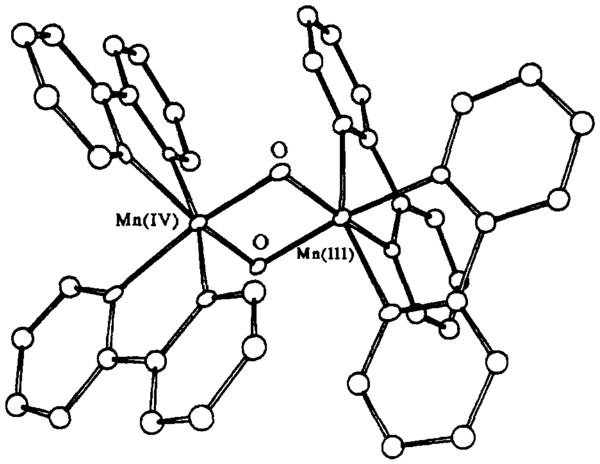

Figure 1. Diagram of the cation.

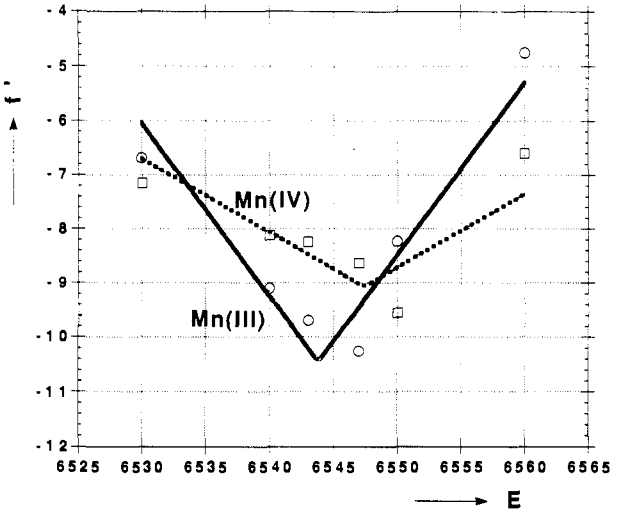

Figure 2. Triangle fit to f' values: solid line, Mn(III); broken line, Mn(IV).

The enzyme-photosystem model compound (μ-dioxo)Mn(2,2′-bipyridyl)$_2$)$_2$ $(BF_4)_3\cdot 3H_2O$ (Figure 1) was synthesized as described elsewhere.[7] It is centrosymmetric and isomorphous to the previously reported perchlorate salt.[8] A nearly cube-shaped crystal of volume 0.0135 mm^3 was used for data collection at the SUNY X3 beamline at Brookhaven National Laboratory.

The intensities of a selected set of 24 reflections were collected at eight different energies around the Mn K edge at 6540 eV, using a Si(111) double-crystal monochromator. Structure factors obtained after absorption correction were refined in terms of the

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* Author to whom correspondence should be addressed.

[†] Current address: Aarhus University, DK8000 Aarhus, C, Denmark.

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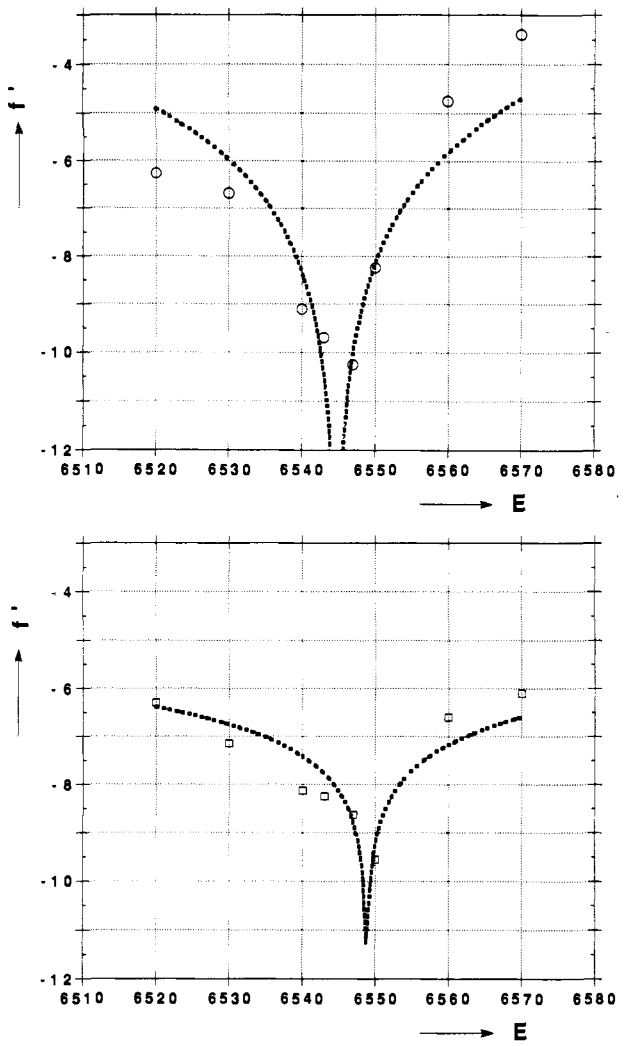

Figure 3. Curve fit to f' values of Mn(III) (top) and Mn(IV) (bottom).

Table I. E_0 Values from Fitting Procedure

	E_0 (eV)	
	triangle fit	curve fit
Mn(III)	6543.8 (10)	6544.8 (10)
Mn(IV)	6547.5 (26)	6548.8 (24)
$E_0\{Mn(IV)\} - E_0\{Mn(III)\}$	3.7	4.0

Table II. 1s Binding Energies from an All-Electron Calculation of the $(\mu\text{-}O_2)(Mn(NH_3)_4)_2$ Ion

Mn(III)	−240.9647 au
Mn(IV)	−241.0814 au
$E_0\{Mn(IV)\} - E_0\{Mn(III)\}$	0.1167 au = 3.17 eV

real part (f') of the anomalous scattering factors of the two resonating atoms, other structural parameters being kept fixed at the full data set values. Results are shown in Figure 2. The smooth variation of f' indicates that its change with energy is quite well determined. This is confirmed by the reproducibility of f' values in two different experimental runs. Examination shows the Mn(IV) minimum to be at several electronvolts above that for Mn(III). Two curve-fitting methods have been tested to obtain quantitative results. In the first, the *triangle method*, a downward pointing V described by

$$f' = f'_0 + |E - E_0|\delta \qquad (1)$$

is fitted to the central six points of each curve, where the variable parameters f'_0 and E_0 are respectively the f' value and the energy at the minimum, and δ is the slope.

In the second method, the expression

$$f' = \frac{g_k}{x^2}\ln|x^2 - 1| + \Delta \qquad (2)$$

based on an empirical equation given by James,[9] is fitted to all eight points. Here the parameter g_k is the oscillator strength, and $x = E/E_0$. Δ is a parameter added to the James equation to allow a vertical shift of f'. Though neither fit reproduces the data points exceedingly well due to the empirical nature of the curves and neglect of fine structure (Figures 2 and 3 and Table I), the methods agree quite well on the magnitude of the shift of about 4 eV. This result is in agreement with the 3.2-eV difference in binding energies obtained in our all-electron large basis set ab-initio calculation of the $(\mu\text{-}O_2)(Mn(NH_3)_4)_2$ analogue (Table II). This calculation also yielded a near IR electronic transition of 10 020 cm^{-1} compared with the value of ≈830 nm (=12 048 cm^{-1}) reported for the parent complex.[7]

Clearly Mn atoms of different valency can be distinguished in a careful experiment. This study shows that direct, site-specific information on the valence of atoms in molecular complexes can be obtained by resonance diffraction.

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Supplementary Material Available: f' values as a function of the photon energy (1 page). Ordering information is given on any current masthead page.

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Diastereoselectivity in the Amine-Directed Hydrocarboxylation

Marie E. Krafft,*[,1] Xiang Y. Yu, Stephen E. Milczanowski, and Karen D. Donnelly

Department of Chemistry
The Florida State University
Tallahassee, Florida 32306-3006

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We have previously described a regioselective directed hydrometalation/carbonylation[2] of bidentate olefinic amine Rh(I) complexes (eq 1: R′, R″ = H; R = H, alkyl).[3-5] Our continued studies probed the diastereofacial selectivity of the process as influenced by the existence of stereogenic centers on the tether connecting the alkene and amine (eq 1: R = R′ = R″ = alkyl, H). We now report that the amine-directed hydrocarboxylation

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