X-Ray Absorption Spectroscopic Studies of Ruthenium–Octaethylporphyrin Dimers

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A series of metal–metal bonded dimeric ruthenium porphyrin complexes have been characterized by means of *X*-ray absorption spectroscopy, Ru–Ru bond lengths for $Ru^{2.5+}$ and Ru^{3+} complexes having been determined by EXAFS to be 2.29 and 2.22 Å, respectively; electronic configurations also have been confirmed by *X*-ray absorption near edge spectroscopy.

As part of a continuing study of porphyrin complexes with multiple metal–metal bonds, we have measured the K-edge EXAFS and L-edge *X*-ray absorption edge spectra of octaethylporphyrin dimers of $Ru^{2.0+}$, $Ru^{2.5+}$, and $Ru^{3.0+}$ $\{[Ru(oep)]_2{}^{n+}, n = 0, 1, 2\}$. These complexes contain Ru–Ru bonds of order 2, 2.5, and 3, respectively,[1] and may serve as model compounds for other porphyrin complexes of Ru in the same formal oxidation states, but with unknown bonding properties. Present efforts towards the synthesis of ruthenium-containing porphyrinic molecular metals and molecular ferromagnets can benefit from such model studies.

Other workers have reported structural information about metal–metal bonded complexes of $Ru^{2.0+}$, $Ru^{2.5+}$, and $Ru^{3.0+}$.[2] Of the few structurally characterized compounds with multiple Ru–Ru bonds, most have bridging ligands between the metal centres, and most contain $Ru^{2.5+}$.[3] One notable exception is a study by Warren and Goedken which involved a systematic variation of the ruthenium oxidation state in dimeric annulene macrocycline complex ($[Ru_2L_2]^{n+}$, $n = 0, 1, 2$; $L = C_{22}H_{22}N_4{}^{2-}$). However, structural information was reported only for the first two compounds in this series.[4]

We have recently reported the synthesis, electrochemical, and spectral properties for the series $[Ru(oep)]_2{}^{n+}$, $n = 0, 1$ and 2.[1] Electronic configurations of these complexes were assigned as $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*(2-n)}$ which agrees with the assignment by Warren and Goedken for $[Ru_2L_2]$ being in a similar ligand field environment.[4] From the *X*-ray crystal structure of $[Ru(oep)]_2$, an Ru–Ru bond length of 2.408 Å has been determined[5] which is comparable with the 2.379 Å length in $[Ru_2L_2]$.[2b] However, single crystals suitable for X-ray analysis have not been obtained for the oxidized Ru(oep) dimers. Because the Ru–Ru bond lengths and electronic configurations are of primary interest, we have undertaken *X*-ray absorption spectroscopic (XAS) studies of the $[Ru(oep)]_2{}^{n+}$ dimers. EXAFS studies can provide bond lengths for samples which do not possess long-range order as required for *X*-ray crystallographic analysis, and edge spectra are generally sensitive to the electronic configuration of the absorbing atom.[6] Ru K-edge EXAFS and L-edge *X*-ray absorption edge spectra were measured at Stanford Synchrotron Radiation Laboratory (SSRL).† The data so obtained were analysed using the parameterized method that we have described in detail.‡ A comparison between the data and the fits is shown in Figure 1 and the numerical results are summarized in Table 1. EXAFS data were taken at both room temperature and 5 K; no significant differences in results were found between the two data sets.

As a reference compound, [Ru(oep)]$_2$ was used in order to check the reliability of our results. The Ru–N and Ru–Ru bond lengths determined by EXAFS agree very well with those determined by *X*-ray crystallographic analysis. A comparison of the Ru–Ru bond lengths among the dimer series reveals a decrease in the Ru–Ru bond length with increasing oxidation, which is consistent with the proposed increase in bond order between the metal atoms. The 2.23 Å length found for the Ru–Ru bond in [Ru(oep)]$_2^{2+}$ compares with the shortest Ru–Ru bond ever reported {2.238 Å in [Ru$_2$(mph)$_4$]·CH$_2$Cl$_2$; mph = 6-methylpyridin-2-olate},[2b] and is somewhat shorter than the 2.311 Å Ru–Ru bond length in [Ru(CH$_2$CMe$_3$)$_3$]$_2$.[2d] The shortening of the Ru–N bond lengths with increasing oxidation is consistent with the expected decreasing ionic radius of Ru. There are no changes in the Ru–C bond lengths greater than the experimental error. These results are qualitatively consistent with those estimated from a Raman study.[7]

The reported values[3] for the Ru–Ru bond lengths in the Ru$^{2.5+}$ dimers vary between 2.248 to 2.292 Å, with only one value less than 2.267 Å. Our value (2.29 Å) lies within this range, as well. There is no apparent difference between [Ru$_2$(O$_2$CR)$_4$]$^+$ and [Ru$_2$L$_2$]$^+$ systems, and thus the existence of bridging ligands and the ligation by oxygen rather than nitrogen do not appear to affect the Ru–Ru bond length in these materials. However, the orbital ordering and electronic configuration[8] of $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$ that has been assigned to Ru$^{2.5+}$ in [Ru$_2$(O$_2$CR)$_4$]$^+$ differs from $\sigma^2\pi^4\delta^2\delta^{*2}\pi^*$ that has been assigned to Ru$^{2.5+}$ in the macrocycline systems. In order to gain some insight into the orbital occupancy and ordering in the Ru(oep) dimer series, both L$_2$ and L$_3$ *X*-ray absorption edge spectra were measured. For these compounds, these two

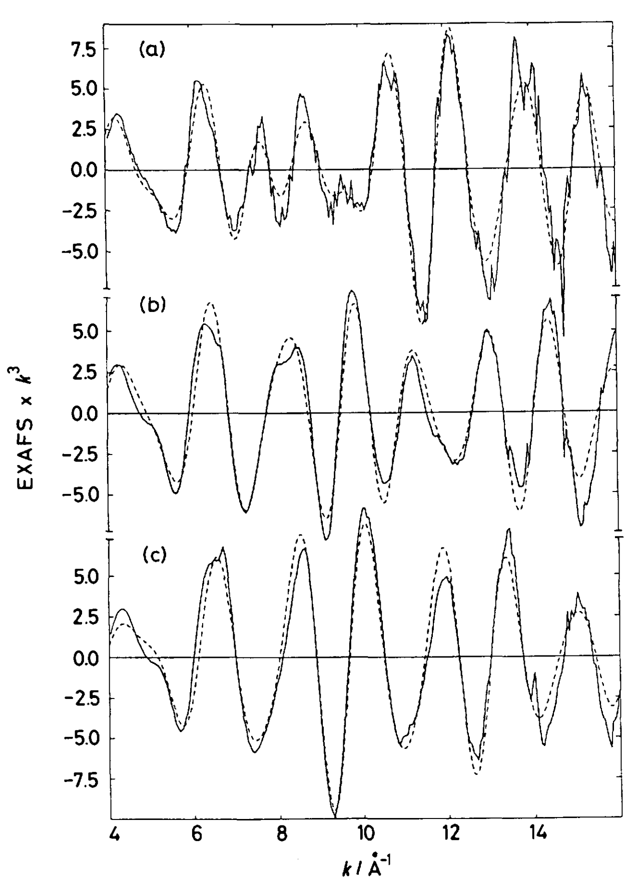

Figure 1. EXAFS data (solid line) and least squares fitting of three-shell model (dashed line) for (a) [Ru(oep)]$_2$, (b) [Ru(oep)]$_2^+$, and (c) [Ru(oep)]$_2^{2+}$.

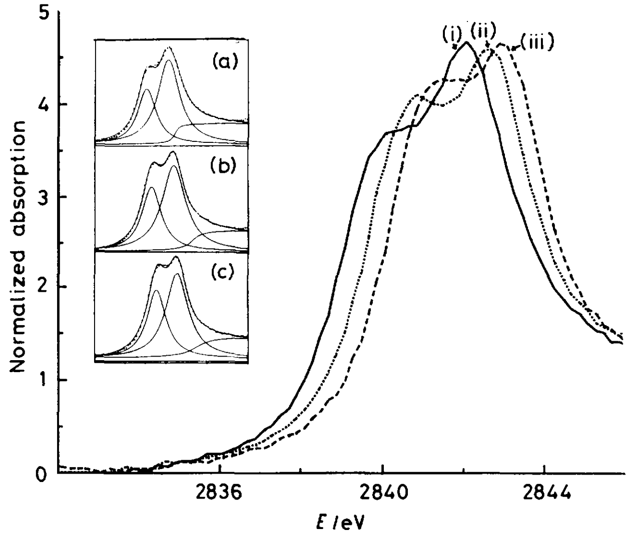

Figure 2. The *X*-ray absorption L$_3$ edge spectra for (i) [Ru(oep)]$_2$, (ii) [Ru(oep)]$_2^+$, and (iii) [Ru(oep)]$_2^{2+}$. Inset shows the fit and individual transitions from non-linear least-squares deconvolutions for (a) [Ru(oep)]$_2$, (b) [Ru(oep)]$_2^+$, and (c) [Ru(oep)]$_2^{2+}$.

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† Samples were prepared and maintained under an inert atmosphere. For Ru EXAFS, the powdered compounds were mixed with a small amount of boron nitride and placed in a 1 mm thick aluminium spacer with Mylar film windows. The EXAFS data were measured in transmission mode using Ar-filled ionization chambers with radiation from a Si(220) monochromator on beam line 7–3 at the SSRL. An Oxford Instruments continuous flow liquid helium cryostat was used for the 5 K measurements. For Ru L-edge *X*-ray absorption spectra, the powdered samples were spread out on Mylar film which was fastened to an aluminium spacer. A 0.25 mil polypropylene film was used as a window. XAS measurements were taken in fluorescence mode with a fluorescence detector of the Stern/Heald design (E. A. Stern and S. M. Heald, *Rev. Sci. Instr.*, 1979, **50**, 1579) using a Si(111) monochromator on beam line 2–3 at SSRL. The entire beam path, including the I_0 ionization chamber detector was filled with He.

‡ EXAFS data reduction and analyses were performed as previously reported in S. P. Cramer and K. O. Hodgson, *Prog. Inorg. Chem.*, 1979, **25**, 1; R. A. Scott, *Methods Enzymol.*, 1985, **117**, 414. Energy calibration was done with the internal standard method (R. A. Scott, J. E. Hahn, S. Doniach, H. C. Freeman, and K. O. Hodgson, *J. Am. Chem. Soc.*, 1982, **104**, 5364), assigning the first inflection point of Ru metal as 22119.3 eV. The normalized background-subtracted spectra were converted to *k*-space by assigning a threshold energy, E_0, of 22135 eV. The photoelectron wave vector k is defined as $k = \sqrt{\{[2m_e(E - E_0)]/\hbar^2\}}$, where m_e is the electron mass. Curve fitting techniques were applied using empirical phase and amplitude parameters for various Ru–X scattering pairs obtained from the following models at 5 K and at room temperature: Ru–Ru, Ru metal (E. O. Hall and J. Crangle, *Acta. Crystallogr.*, 1957, **10**, 290); Ru–N, Ru(2,2′-bipyridyl)$_3$Cl$_2$·6H$_2$O (D. P. Rillema and D. S. James, *J. Chem. Soc., Chem. Comm.*, 1979, 849); Ru–C, [Ru(oep)]$_2$.[5]

Table 1. EXAFS results for $[Ru(oep)]_2^{n+}$, $n = 0, 1, 2$.

			Ru–N		Ru–Ru		Ru–C	
$[Ru(oep)]_2$	Room temp.	1.0	4.2	2.05	1.9	2.40	8.0	3.08
	5 K	1.3	4.4	2.05	1.5	2.40	8.2	3.08
	Cryst.[d]		4.0	2.050(5)	1.0	2.408(1)	8.0	3.080
$[Ru(oep)]_2^+$	Room temp.	1.2	3.8	2.03	2.1	2.29	6.6	3.07
	5 K	1.2	4.2	2.03	2.1	2.29	6.0	3.06
$[Ru(oep)]_2^{2+}$	Room temp.	1.5	3.1	2.01	2.6	2.24	6.5	3.07
	5 K	1.5	3.3	2.00	1.9	2.22	5.5	3.06

[a] The quality of these fits is indicated by the minimization function value:

$$F = \{[\Sigma k^6(\text{data} - \text{fit})^2]/[\text{no. of points}]\}^{1/2}.$$

[b] The error in the co-ordination number (CN) is of the order of ±30%. Because the empirical Ru–Ru parameters were taken from Ru metal in which the Ru–Ru bond is relatively weak, the Ru–Ru co-ordination numbers for multiple bonds were overestimated such that the stronger the bond, the larger is the apparent co-ordination number between the bonded atoms. [c] Estimated experimental error in these bond lengths as determined by EXAFS is ±0.02 Å. [d] Crystallographic data.[5]

Table 2. Results of deconvolution[a] of L_3 *X*-ray absorption edge spectra for $[Ru(oep)]_2^{n+}$, $n = 0, 1, 2$.

	Lower energy		Higher energy	
	Peak position/eV	Peak height[b]	Peak position/eV	Peak height[b]
$[Ru(oep)]_2$	2840.09	2.64	2842.23	4.01
$[Ru(oep)]_2^+$	2840.56	2.97	2842.74	3.95
$[Ru(oep)]_2^{2+}$	2841.07	3.09	2843.09	3.86

[a] The data were deconvoluted by non-linear least-squares fitting to the following equation:

$$f(x) = b + \sum_{i=1}^{2}\{\omega_{p,i}\,\Gamma_i^2/[(x - \omega_{0,i})^2 + \Gamma_i^2]\} + 0.5 + \arctan\,[(x - \omega_{\text{continuum}})/\Gamma_{\text{continuum}}]/\pi.$$

This represents a constant term to account for the non-zero intercept, two Lorentzian absorption peaks, and an arctangent absorption into the continuum. All r^2 (squared correlation coefficient) values $\geqslant 0.99$. [b] Normalized absorption.

spectra exhibited basically the same features; we report here only the L_3 edge spectra (see Figure 2). After normalization, the spectra were deconvoluted to separate overlapping absorption transitions. The results (see Figure 2 inset and Table 2) show that all three oxidation states have two similar transitions. This implies that all three oep dimers have the same two partially occupied and/or unoccupied energy levels. As noted in the literature, the predominant cause of splitting in these $L_{2,3}$ edges derives from ligand field effects,[6b,6c,9] not from the effects of spin–orbit coupling which for Ru are typically an order of magnitude smaller.[6b] Thus, it is reasonable to assign the splitting in these edges to the ligand field effects. In contrast to the case of $Ru(NH_3)_6^{3+}$ where the L_2 and L_3 edges differ because of the absence of an allowed $2p_{1/2} \rightarrow t_2$ transition,[6b] these Ru porphyrin edges show clearly the same two distinct transitions at both the L_2 and L_3 edges with splittings of more than 2 eV, consistent with assignment to the same partially occupied and/or unoccupied energy levels. In view of the proposed MO diagrams for the complexes,[1,4] these two levels may be assigned as π^* and σ^*. The higher energy absorption is relatively unaffected by oxidation of the Ru which suggests that it involves an excitation into an unoccupied level. This, along with the increase in the intensity of the lower energy absorption, is consistent with a molecular orbital ordering scheme of $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*(2-n)}$. The decrease in occupancy of the π^* level upon oxidation represents an increase in the available density of states and thus an increase in the transition probabilities. We can reject the alternative ordering because n.m.r. data indicate that the doubly oxidized dimer is diamagnetic; a scheme and orbital occupancy of $\sigma^2\pi^4\delta^2\pi^{*2}$ would be paramagnetic with two unpaired electrons.

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References

1 J. P. Collman, J. W. Prodelliet, and C. R. Leidner, *J. Am. Chem. Soc.*, 1986, **108**, 2916.

2 (a) W. Clegg, *Acta Crystallogr., Sect. B*, 1980, **36**, 3114; (b) F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms,' Wiley Interscience, New York, 1982; (c) F. A. Cotton and R. A. Walton, *Struct. Bonding (Berlin)*, 1985, **60**, 1; (d) R. P. Touze, M. Motevalli, M. B. Hursthouse, and G. B. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1984, 799.

3 A. Bino, F. A. Cotton, and T. R. Felthouse, *Inorg. Chem.*, 1979, **18**, 2599.

4 L. F. Warren and V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 1978, 909.

5 J. P. Collman, C. E. Barnes, P. E. Swepston, and J. A. Ibers, *J. Am. Chem. Soc.*, 1984, **106**, 3500.

6 (a) A. Bianconi, in 'X-ray Absorption,' eds. D. C. Konnigsberger and R. Prins, Wiley Interscience, New York, 1988; (b) T. K. Sham, *J. Am. Chem. Soc.*, 1983, **105**, 2269; (c) T. K. Sham, *J. Chem. Phys.*, 1985, **83**, 3222.

7 C. O. Tait, J. M. Garner, J. P. Collman, A. P. Sattleberger, and W. H. Woodruff, *J. Am. Chem. Soc.*, in the press.

8 J. G. Norman, Jr., G. E. Renzoni, and D. A. Case, *J. Am. Chem. Soc.*, 1979, **101**, 5256.

9 B. Hedman, J. E. Penner-Hahn, and K. O. Hodgson, in 'EXAFS and Near Edge Structure III,' Springer-Verlag, Berlin, 1984, p. 64.