

Combination of EXAFS and Electronic Spectroscopy to determine the Structure of Nickel(IV) Complexes

Andrew T. Steel,^{a,b} Martinus C. Feiters,^{a,b} C. David Garner,^{*a} S. Samar Hasnain,^b William Levason,^{*c} and Simon J. Higgins^c

^a The Chemistry Department, Manchester University, Manchester M13 9PL, U.K.

^b The Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.

^c The Chemistry Department, Southampton University, Southampton SO9 5NH, U.K.

The structure of a transition metal complex may, in favourable cases, be determined by combining the information obtained from *d-d* spectroscopy, which indicates the nature of the ligand field, and metal (*K*)-edge EXAFS, from which the metal-ligand distances may be obtained; the approach is illustrated for tetragonally distorted, pseudo-octahedral Ni^{IV} complexes: [NiCl₂{*o*-C₆H₄(PMe₂)₂}]₂²⁺ (Ni-Cl = 2.26, Ni-P = 2.22 Å), [NiCl₂{*o*-C₆H₄(AsMe₂)₂}]₂²⁺ (Ni-Cl = 2.27, Ni-As = 2.36 Å).

During the last decade, owing to the availability of synchrotron radiation, *X*-ray absorption spectroscopy in general, and the extended *X*-ray absorption fine structure (EXAFS) associated with absorption edges in particular, has developed into a powerful technique for the characterisation of local structure about specific atoms.¹⁻³ A major advantage of this technique is that it can be applied to non-crystalline samples. Furthermore, the local environment about virtually all atoms with atomic number ≥ 20 may be investigated at concentrations ≥ 10 p.p.m. Significant advances have been achieved by the measurement of the EXAFS of metal centres in a wide variety of biological systems and in heterogeneous catalysts of industrial relevance; also, valuable information has been obtained for inorganic glasses and other amorphous phases. However, the direct impact of EXAFS on chemistry has been relatively slight, despite the general need to obtain accurate structural information for non-crystalline chemical systems.

EXAFS contains information concerning the nature, number, distance, and disorder of the atoms surrounding the primary absorber. Distance information up to *ca.* 3.5 Å is usually clearly manifest in the frequency of the EXAFS oscillations and an accuracy of *ca.* ± 0.02 Å in interatomic distances is typically obtained. However, it can be difficult to distinguish between back-scattering atoms of a similar atomic number and the occupation number (*N*) of a shell is strongly correlated with the disorder (Debye-Waller) parameter within the EXAFS amplitude envelope, and often, uncertainties of ± 1 in *N* can occur. These weaknesses, plus a lack of angular information, perhaps makes EXAFS unattractive to chemists who are accustomed to the precision and three-dimensional perspective provided by *X*-ray crystallography.

We have been interested in combining EXAFS information with other spectroscopic data to demonstrate that, thereby, it is possible to obtain a comprehensive structural characterisation of a local environment within a non-crystalline chemical sample. The complexes [NiCl₂{*o*-C₆H₄(PMe₂)₂}]₂²⁺ and [NiCl₂{*o*-C₆H₄(AsMe₂)₂}]₂²⁺ were chosen for investigation because of the intrinsic chemical interest in obtaining structural data for this metal in its rare (+IV) oxidation state and, also, because the instability of these complexes in solution has prevented the production of single crystals for *X*-ray crystallographic study.

X-Ray absorption spectra at the nickel *K*-edge were recorded for [NiCl₂{*o*-C₆H₄(PMe₂)₂}]₂[ClO₄]_{*n*} (*n* = 1, 2) and [NiCl₂{*o*-C₆H₄(AsMe₂)₂}]₂[ClO₄]₂ at the Daresbury Synchrotron Radiation Source operating at 1.8 GeV with a current of 200–300 mA, using a Si 220 channel-cut crystal monochromator. The extraction and interpretation of the EXAFS was accomplished in the manner described previously.⁵ The accuracy of the structural interpretations was verified by corresponding studies of [Ph₃MeP]₂[NiCl₄] and

[Ni{*o*-C₆H₄(ZMe₂)₂}[ClO₄]₂ (Z = P or As), since *X*-ray crystallographic data are available for these nickel complexes (Table 1).⁶⁻⁸

The electronic spectra of [NiCl₂{*o*-C₆H₄(ZMe₂)₂}]₂²⁺ (Z = P or As) are similar in profile to those of the corresponding isolectronic (*d*⁶) *trans*-[CoCl₂{*o*-C₆H₄(ZMe₂)₂}]₂⁺ complex, with the lowest energy transition (¹A₁ → ¹E) shifted by *ca.* 500 cm⁻¹ to higher energy for the Ni^{IV} complexes.⁹ Moreover, the far i.r. spectra of these complexes show a single M-Cl stretching mode.^{9,10} Hence, there is convincing spectroscopic evidence that nickel is in a tetragonally distorted octahedral ligand field (Z₄Cl₂). Also, the *d-d* and i.r. spectroscopic properties of [NiCl₂{*o*-C₆H₄(PMe₂)₂}]₂[ClO₄]₂ are consistent with this Ni^{III} complex being isostructural with its arsenic analogue, the structure of which has been established in *trans*-[NiCl₂{*o*-C₆H₄(AsMe₂)₂}]₂Cl.¹¹

The above information, together with the confidence obtained from the successful interpretation of the nickel *K*-edge EXAFS for related complexes of a known structure, provided the basis for the analysis of the EXAFS data for the Ni^{III} and two Ni^{IV} complexes. The results are summarised in Table 1. The Ni-Cl and Ni-P bond lengths for [NiCl₂{*o*-C₆H₄(PMe₂)₂}]₂[ClO₄]₂ are as expected, given the structural data for the analogous arsenic complex and the difference in the Ni-Z distances manifest by the [Ni{*o*-C₆H₄(ZMe₂)₂}]₂²⁺ complexes. Comparisons of the Ni-Z and Ni-Cl bond lengths in [NiCl₂{*o*-C₆H₄(ZMe₂)₂}]₂ⁿ⁺, for *n* = 1 or 2, reveal small variations in Ni-Z between corresponding Ni^{III} and Ni^{IV} complexes but a significant reduction in Ni-Cl.

Table 1. Bond lengths (Å) obtained for some nickel complexes.

Complex	Bond	Length	
		<i>X</i> -Ray	EXAFS ^a
[NiCl ₄] ²⁻	Ni-Cl	2.27(1) ^b	2.25 ^c
[Ni{ <i>o</i> -C ₆ H ₄ (PMe ₂) ₂ }] ₂ ²⁺	Ni-P	2.205(5) ^d	2.19 ^e
[Ni{ <i>o</i> -C ₆ H ₄ (AsMe ₂) ₂ }] ₂ ²⁺	Ni-As	2.29(1) ^f	2.29 ^e
[NiCl ₂ { <i>o</i> -C ₆ H ₄ (PMe ₂) ₂ }] ₂ ⁺	Ni-Cl		2.41 ^g
	Ni-P		2.25 ^g
[NiCl ₂ { <i>o</i> -C ₆ H ₄ (AsMe ₂) ₂ }] ₂ ⁺	Ni-Cl	2.425(3) ^h	2.41 ^g
	Ni-As	2.342(2) ^h	2.33 ^g
[NiCl ₂ { <i>o</i> -C ₆ H ₄ (PMe ₂) ₂ }] ₂ ²⁺	Ni-Cl		2.26 ^e
	Ni-P		2.22 ^e
	Ni-Cl		2.27 ^e
[NiCl ₂ { <i>o</i> -C ₆ H ₄ (AsMe ₂) ₂ }] ₂ ²⁺	Ni-Cl		2.27 ^e
	Ni-As		2.36 ^e

^a The estimated uncertainty in these bond lengths is 0.01–0.02 Å.

^b [Ph₃MeAs]⁺ salt, ref. 6. ^c [Ph₃MeP]⁺ salt. ^d 2[I₃]⁻, 2I₂ salt; ref. 7.

^e 2[ClO₄]⁻ salt. ^f 2I⁻ salt, ref. 8. ^g [ClO₄]⁻ salt. ^h Cl⁻ salt, ref. 11.

This is consistent with the removal of the metal–ligand σ -antibonding electron, known to be principally in $3d_{z^2}$,¹² upon oxidation and clearly demonstrates that this process is metal centred (*i.e.* $\text{Ni}^{\text{III}} t_{2g}^6 e_g^1 \rightarrow \text{Ni}^{\text{IV}} t_{2g}^6 e_g^0$). The changes in the Ni–Cl bond lengths observed upon oxidation are inconsistent with the $[\text{NiCl}_2\{o\text{-C}_6\text{H}_4(\text{ZMe}_2)_2\}]^{2+}$ complexes containing dithiolene-like, cation radical ligands. Hence, these species are satisfactorily described as Ni^{IV} and, as such, are the only known examples containing neutral ligands.

Thus, we have shown that the interpretation of EXAFS can be greatly enhanced by the availability of suitable spectroscopic data, especially when this details the nature, number, and angular distribution of the atoms surrounding the primary absorber. *d–d* Spectroscopy, which provided the vital complementary information used here, is especially useful for the study of d-transition metal complexes; in other situations, *f–f* transitions, vibrational and/or magnetic resonance data could provide similar information. Therefore, we hope that this study will enhance the application of EXAFS, in combination with other spectroscopic techniques, to define accurately the local environment about specific atoms in various phases of chemical interest.

Added in proof: The crystal structure of $[\text{NiCl}_2\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2][\text{PF}_6] \cdot 2\text{H}_2\text{O}$ has been reported since the submission of this communication, C. Mahadevan, M. Seshasayee, B. L. Ramakrishna, and P. T. Manoharan, *Acta Crystallogr., Sect. C*, 1985, **41**, 38. The Ni–Cl and Ni–P distances of 2.424(4) and 2.255(3) Å, respectively, are in good agreement with the corresponding EXAFS values of Table 1.

We are grateful to the S.E.R.C. for support (W. L.), a postgraduate studentship (S. J. H.), and provision of funds to establish the EXAFS Service; the Director of The Daresbury Laboratory is thanked for the provision of facilities.

Received, 31st December 1984; Com. 1792

References

- 1 'EXAFS Spectroscopy: Techniques and Applications,' eds. B. K. Teo and D. C. Joy, Plenum Press, New York, 1981.
- 2 S. P. Cramer and K. O. Hodgson, *Prog. Inorg. Chem.*, 1979, **25**, 1.
- 3 P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, *Rev. Mod. Phys.*, 1981, **53**, 769.
- 4 L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3126 and references therein.
- 5 N. J. Blackburn, S. S. Hasnain, G. P. Diakun, P. F. Knowles, N. Binsted, and C. D. Garner, *Biochem. J.*, 1983, **213**, 765.
- 6 P. Pauling, *Inorg. Chem.*, 1966, **5**, 1498.
- 7 L. R. Gray, S. J. Higgins, W. Levason, and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1984, 1433.
- 8 N. C. Stephenson, *Acta Crystallogr.*, 1964, **17**, 592.
- 9 S. J. Higgins, Ph.D. Thesis, Southampton University, 1984.
- 10 K. Konya and K. Nakamoto, *Spectrochim. Acta, Part A*, 1973, **29**, 1965.
- 11 P. K. Bernstein, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 3040.
- 12 C. N. Sethulakshmi, S. Subramanian, M. A. Bennett, and P. T. Manoharan, *Inorg. Chem.*, 1979, **18**, 2520.