

## Nickel *K*-Edge Extended *X*-Ray Absorption Fine Structure Studies of Tris(Diamine) Complexes of Nickel(II) and their Halogen Oxidation Products\*

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Nickel *K*-edge extended *X*-ray absorption fine structure data are reported for the tris(diamine) complexes  $[\text{Ni}(\text{L-L})_3]\text{X}_2$  [ $\text{L-L} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (en),  $\text{H}_2\text{NCHMeCH}_2\text{NH}_2$  (pn),  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHMe}$ ,  $\text{H}_2\text{NCH}_2\text{CMe}_2\text{NH}_2$ , and  $\text{H}_2\text{NCH}(\text{CH}_2)_4\text{CHNH}_2$ ;  $\text{X} = \text{Cl}$ , Br, sometimes F or  $\text{BF}_4$ ]. In all cases the data show two clearly defined shells of six nitrogen and six carbon atoms respectively, and for the cyclohexanediamine complexes a third shell of six carbons is well defined. However for the pn,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHMe}$ , and  $\text{H}_2\text{NCH}_2\text{CMe}_2\text{NH}_2$  complexes the  $\text{Ni} \cdots \text{C}(\text{Me})$  distances are not clearly defined, and the data could not distinguish between  $\text{Ni} \cdots \text{N}(\text{Me})$  and  $\text{Ni} \cdots \text{NC}_{\text{backbone}}$  distances. The initial chlorine oxidation products of the nickel(II) complexes suspended in dry  $\text{CCl}_4$ , have been shown to be  $[\text{Ni}(\text{diamine})_3]\text{Cl}_3$ , which decompose to known  $[\text{Ni}(\text{diamine})_2\text{X}_2]\text{X}$  or mixed-valence materials in solution.

Nickel(II) complexes of chelating diamines have been much studied over the last thirty years, and a large body of spectroscopic and structural data is available.<sup>1,2</sup> More recently it has been reported<sup>3,4</sup> that halogen oxidation of these complexes results in the formation of either nickel(III) or mixed-valence nickel(II)nickel(IV) materials. The latter, which belong to Class II in the Robin and Day scheme, have anisotropic semiconductor properties. The mixed-valence complexes are insoluble in or decomposed by solvents, and thus crystals for *X*-ray studies have proved unobtainable. However we<sup>5</sup> and others<sup>6</sup> have shown that structural data on these materials are obtainable by the extended *X*-ray absorption fine structure (EXAFS) technique. In other studies we have shown<sup>7</sup> that the combination of nickel and ligand-donor (P, Cl, or Br) *K*-edge EXAFS data can in favourable cases provide stereochemical information. Nickel-ligand bond length data have also been obtained for several series of complexes of  $\text{Ni}^{\text{III}}$  and  $\text{Ni}^{\text{IV}}$ .<sup>8</sup>

The present paper describes the results of nickel *K*-edge EXAFS studies on a variety of tris(diamine) complexes of nickel(II). A major aim was to establish whether the EXAFS technique can provide reliable structural information beyond the first co-ordination sphere of the metal, which would be of value in the more complex systems. Also described are attempts to characterise the initial halogen oxidation products of these complexes. In solution halogen oxidation removes one diamine (above), but we hoped that in the solid state  $[\text{Ni}(\text{diamine})_3]\text{X}_3$  might be obtainable, analogous to the known<sup>9,10</sup> tris(2,2'-bipyridyl)- and bis(1,4,7-triazacyclononane)-nickel(III) complexes.

### Experimental

Hydrated nickel(II) salts and the diamine ligands (B.D.H., Aldrich, or ALFA) were used as received. I.r. spectra were recorded from Nujol mulls of the complexes on Perkin-Elmer PE 580B and 983G spectrometers, and diffuse-reflectance spectra using the appropriate attachment on a Perkin-Elmer PE 554 using  $\text{BaSO}_4$  as diluent and reference. E.s.r. spectra were recorded for powdered samples in sealed quartz tubes on a Varian E3 *X*-band spectrometer, referenced against diphenylpicrylhydrazyl (dpph). The tris(diamine) complexes  $[\text{Ni}(\text{L-L})_3]\text{X}_2$  [ $\text{L-L} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (en),  $\text{H}_2\text{NCHMeCH}_2\text{NH}_2$  (pn),  $\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$  (tn),  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHMe}$ ,  $\text{H}_2\text{NCH}_2\text{CMe}_2\text{NH}_2$ , and  $\text{H}_2\text{NCH}(\text{CH}_2)_4\text{CHNH}_2$ ;  $\text{X} = \text{Cl}$ , Br, some-

times F or  $\text{BF}_4$ ] were made by literature routes,<sup>11,12</sup> from the appropriate nickel(II) salt and the diamine in a 1:3.5 mol ratio in ethanol, with 2,2-dimethoxypropane added as a dehydrating agent. The complex  $[\text{Ni}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3][\text{BF}_4]_2$  was made similarly, but tris(diamine) complexes of this ligand do not form in the presence of halide ions.<sup>13</sup> All had satisfactory analyses. Samples were stored in sealed containers, and were checked for the absence of water by i.r. spectroscopy before data collection.

**Nickel(III) Complexes.**—Halogen oxidation of these complexes was carried out with rigorous exclusion of moisture, using standard Schlenk-tube and dry-box techniques. The thoroughly pre-dried, finely powdered  $[\text{Ni}(\text{L-L})_3]\text{X}_2$  ( $\text{X} = \text{Cl}$  or Br) (*ca.* 0.2 g) was placed in a round-bottomed flask, and dry  $\text{CCl}_4$  (10  $\text{cm}^3$ , from  $\text{CaH}_2$ ) distilled in under vacuum. The resulting suspension was stirred whilst a slow stream of dry chlorine or bromine diluted with nitrogen was bubbled in. After 2 h the solid was filtered off and dried *in vacuo*, and the orange-yellow powder removed in a glove-box. The complex  $[\text{Ni}(\text{tn})_3]\text{Cl}_3$  reverted to the nickel(II) complex on standing. The other complexes appeared stable for some weeks in a glove-box, but decomposed very rapidly in moist air {Found: C, 21.0; H, 7.1; N, 24.3.  $[\text{Ni}(\text{en})_3]\text{Cl}_3$ ,  $\text{C}_6\text{H}_{24}\text{Cl}_3\text{N}_6\text{Ni}$  requires C, 20.8; H, 6.9; N, 24.3. Found: C, 27.6; H, 7.8; N, 21.4.  $[\text{Ni}(\text{tn})_3]\text{Cl}_3$ ,  $\text{C}_9\text{H}_{30}\text{Cl}_3\text{N}_6\text{Ni}$  requires C, 27.9; H, 7.7; N, 21.4. Found: C, 42.8; H, 8.6; N, 16.3.  $[\text{Ni}\{\text{H}_2\text{NCH}(\text{CH}_2)_4\text{CHNH}_2\}_3]\text{Cl}_3$ ,  $\text{C}_{18}\text{H}_{42}\text{N}_6\text{Ni}$  requires C, 42.5; H, 8.3; N, 16.5. Found: C, 33.3; H, 8.3; N, 19.5.  $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CMe}_2\text{NH}_2)_3]\text{Cl}_3$ ,  $\text{C}_{12}\text{H}_{36}\text{Cl}_3\text{N}_6\text{Ni}$  requires C, 33.5; H, 8.4; N, 19.6. Found: C, 27.9; H, 7.9; N, 21.4.  $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHMe})_3]\text{Cl}_3$ ,  $\text{C}_9\text{H}_{30}\text{Cl}_3\text{N}_6\text{Ni}$  requires C, 27.9; H, 7.7; N, 21.4. Found: C, 27.5; H, 8.2; N, 21.3.  $[\text{Ni}(\text{pn})_3]\text{Cl}_3$ ,  $\text{C}_9\text{H}_{30}\text{Cl}_3\text{N}_6\text{Ni}$  requires C, 27.9; H, 7.7; N, 21.4%}.

Nickel *K*-edge EXAFS data were recorded in transmission mode on station 7.1 at the Daresbury Synchrotron Radiation Source, with an operating energy of 2.0 GeV and average currents of 160 mA, and using a silicon (111) order-sorting monochromator, with harmonic rejection achieved by stepping off the peak of the rocking curve by 50% of full height level. Samples were diluted with boron nitride (*ca.* 10% w/w Ni)

\* Non-S.I. unit employed:  $\text{eV} \approx 1.60 \times 10^{-19}$  J.

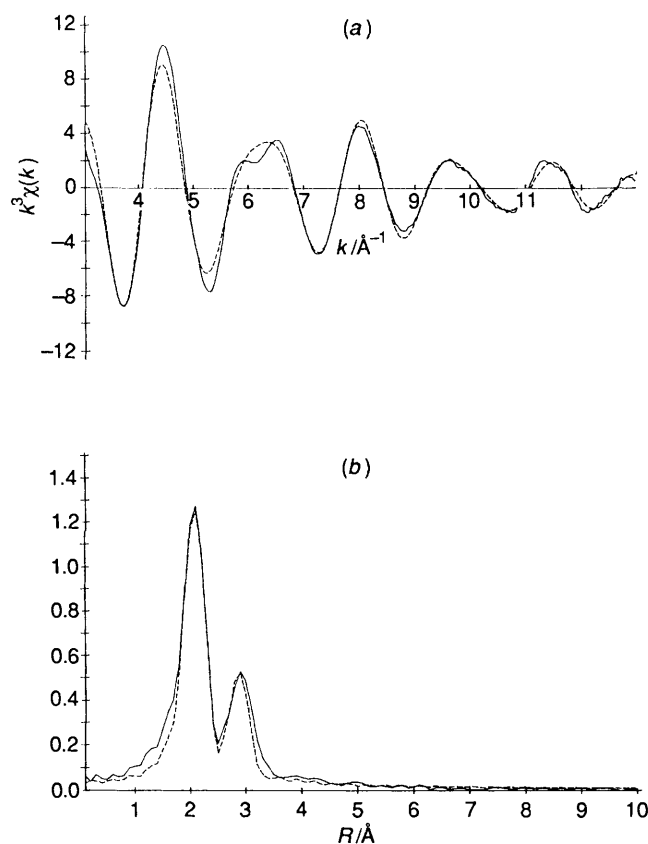


Figure 1. (a) The background-subtracted EXAFS data and (b) the corresponding Fourier transform for  $[\text{Ni}(\text{pn})_3]\text{Cl}_2$ . (—), Experimental; (---), calculated data

and run in aluminium holders between Sellotape strips (*ca.* 1 mm thick samples). Data treatment utilised the programs PAXAS<sup>14</sup> and EXCURVE<sup>15</sup> on single scans for each complex. Phase shifts were derived from *ab initio* calculations,<sup>15</sup> the muffin-tin radii being adjusted to ensure consistent  $V_0$  values. The initial fits were developed using Fourier-filtered data over the range 1–3 Å. The parameter sets obtained were then iterated against raw data, further shells being added as appropriate, and statistical tests of their significance made. The values of AFAC and VPI\* were mapped, altered, and the set iterated until a consistent minimum for their values was obtained for each complex. A natural grouping with the counter anion present was noted, and final fits were generated using average values of AFAC and VPI for each series of complexes with a constant counter anion.

## Results and Discussion

The  $[\text{Ni}(\text{L-L})_3]\text{X}_2$  complexes used in this study are listed in Table 1. Their spectroscopic properties were unexceptional, in particular the presence of  $\text{NiN}_6$  chromophores was confirmed by the diffuse-reflectance spectra of the solids, which contained the three spin-allowed  $d-d$  transitions  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  $\rightarrow {}^3T_{1g}$ , and  $\rightarrow {}^3T_{1g}(P)$  typical of pseudo-octahedral  $\text{Ni}^{II}$ .<sup>16</sup> Weaker features corresponding to spin-forbidden bands were often evident. The energies of the major bands were little influenced

by changes in counter ion, but N-methylation of the diamines leads to weaker ligand fields.<sup>16</sup>

**EXAFS.**—Generally the transmission EXAFS data at the nickel  $K$ -edge were recorded out to  $k = 16 \text{ \AA}^{-1}$  beyond the absorption edge, although the quality of data at high  $k$  values varied considerably. Data sets used in the analysis were  $\geq 11 \text{ \AA}^{-1}$  in length.

There are very little  $X$ -ray crystallographic data on nickel(II) tris(diamine) complexes, but those available on tris- and bis(diamine) complexes are listed in Table 1 for comparison purposes. EXAFS data are limited to a brief study of  $[\text{Ni}(\text{en})_3][\text{NO}_3]_2$ ,<sup>17</sup> which however did not assign all the features in the spectrum. The Ni–N bond lengths and the Ni...C non-bonded distances obtained from the EXAFS data are given in Table 1 and Figure 1 shows a typical example. The data are in excellent agreement with those determined by  $X$ -ray crystallography. As expected these first- and second-shell distances within the cations are independent of the counter anion present, within the limits of experimental uncertainty in the data ( $\pm ca.$  0.02 Å in the first shell and  $\pm ca.$  0.04 Å in the second), and this consistency supports the data quality and interpretation. The basic model emerging from these calculations is of two shells, the first of six nitrogens and the second of the six carbons from the ligand backbones which are bonded to the nitrogens. These are clearly well defined in the data for all the complexes studied. From these data it is possible to calculate average Ni–N–C bond angles which lie in the range 107–109°.

For N-methyl-substituted ligands, calculations suggest that the Ni...Me distance should be *ca.* 3 Å irrespective of the orientation of the substituent, which is similar to the distance Ni...C<sub>backbone</sub>. EXAFS cannot distinguish the two types of carbon, in that attempts to split the shell into two gave chemically anomalous distances. However there is some evidence in the larger Debye–Waller factors observed for the second shell in the complexes of the N-methyl ligand for the static disorder resulting from the slightly different distances. Carbon backbone substituents can be either equatorial or axially disposed, and calculations suggest distances of *ca.* 4.4 or *ca.* 3.8 Å respectively. The ligand 1,2-diaminocyclohexane is known<sup>18</sup> to co-ordinate as the *trans* isomer to octahedral metal centres, and thus the methylene carbons in the 3,6 positions will be forced equatorial. There is a peak in the Fourier transform in the data from each of these complexes corresponding to a 6C shell at *ca.* 4.48 Å. The addition of this shell to the model produces an 18% decrease in the  $R$  factor, and it passes both the statistical significance<sup>19</sup> and the Joyner tests.<sup>20</sup> The case of 1,2-diaminopropane complexes is less clear, in that only three carbons would be involved in the third shell, and moreover there is no strong requirement as to which conformation is adopted. The EXAFS data nonetheless contain a shell at *ca.* 4.46 Å, and if this is added into the calculations it passes the Joyner test, but fails the statistical significance test (the integral of the peak < 10% of the integral of the experiment, and the  $R$  factor is reduced by only 9%). It would seem that although the shell is present in the EXAFS data it is not well enough defined to have a significant effect on the goodness of fit, and the pn systems thus seem better fitted to the two-shell model only. Similarly for complexes of  $\text{H}_2\text{NCH}_2\text{CMe}_2\text{NH}_2$  the methyl substituents are not clearly seen and a two-shell model is appropriate.

**Halogen Oxidation.**—All attempts to oxidise  $[\text{Ni}(\text{diamine})_3]\text{X}_2$  with halogens in solution result in removal of one diamine, and the formation of either  $[\text{Ni}(\text{diamine})_2\text{X}_2]\text{X}$  or nickel(IV)nickel(IV) species depending upon the particular diamine present.<sup>3,4</sup> Cyclic voltammetry of various  $[\text{Ni}(\text{diamine})_3][\text{BF}_4]_2$  in MeCN solution revealed only completely

\* AFAC = the energy-independent amplitude factor intended to allow for reduction in the amplitude due to multiple excitation; VPI = the constant imaginary potential used to describe the lifetime of the photoelectron.

**Table 1.** Structural data for the nickel(II) diamine complexes

Complex	Shell	$R/\text{\AA}$	$A^a/\text{\AA}^2$	$R^b$
[Ni(en) <sub>3</sub> ]F <sub>2</sub>	1 6N	2.11	0.013	21.5
	2 6C	2.89	0.017	
[Ni(en) <sub>3</sub> ]Cl <sub>2</sub>	1 6N	2.10	0.010	22.9
	2 6C	2.89	0.013	
[Ni(en) <sub>3</sub> ]Br <sub>2</sub>	1 6N	2.11	0.013	24.9
	2 6C	2.92	0.006	
[Ni(en) <sub>3</sub> ][BF <sub>4</sub> ] <sub>2</sub>	1 6N	2.11	0.012	16.2
	2 6C	2.91	0.015	
[Ni(pn) <sub>3</sub> ]F <sub>2</sub>	1 6N	2.10	0.010	22.4
	2 6C	2.89	0.017	
[Ni(pn) <sub>3</sub> ]Cl <sub>2</sub>	1 6N	2.11	0.012	19.0
	2 6C	2.92	0.013	
[Ni(pn) <sub>3</sub> ]Br <sub>2</sub>	1 6N	2.11	0.012	18.0
	2 6C	2.91	0.013	
[Ni(pn) <sub>3</sub> ][BF <sub>4</sub> ] <sub>2</sub>	1 6N	2.10	0.011	17.6
	2 6C	2.91	0.014	
[Ni(pn) <sub>3</sub> ][BF <sub>4</sub> ] <sub>2</sub>	1 6N	2.10	0.011	15.9
	2 6C	2.91	0.014	
	3 3C	4.46	0.010	
[Ni{H <sub>2</sub> NCH(CH <sub>2</sub> ) <sub>4</sub> CHNH <sub>2</sub> } <sub>3</sub> ]Cl <sub>2</sub>	1 6N	2.10	0.010	21.0
	2 6C	2.92	0.013	
	3 6C	4.46	0.018	
[Ni{H <sub>2</sub> NCH(CH <sub>2</sub> ) <sub>4</sub> CHNH <sub>2</sub> } <sub>3</sub> ]Br <sub>2</sub>	1 6N	2.11	0.011	18.6
	2 6C	2.93	0.014	
	3 6C	4.48	0.020	
[Ni{H <sub>2</sub> NCH(CH <sub>2</sub> ) <sub>4</sub> CHNH <sub>2</sub> } <sub>3</sub> ][BF <sub>4</sub> ] <sub>2</sub>	1 6N	2.10	0.011	18.8
	2 6C	2.92	0.015	
[Ni{H <sub>2</sub> NCH(CH <sub>2</sub> ) <sub>4</sub> CHNH <sub>2</sub> } <sub>3</sub> ][BF <sub>4</sub> ] <sub>2</sub>	1 6N	2.10	0.011	15.4
	2 6C	2.92	0.015	
	3 6C	4.48	0.021	
[Ni(H <sub>2</sub> NCH <sub>2</sub> CMe <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> ]Cl <sub>2</sub>	1 6N	2.11	0.010	21.8
	2 6C	2.95	0.016	
[Ni(H <sub>2</sub> NCH <sub>2</sub> CMe <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> ]Br <sub>2</sub>	1 6N	2.12	0.013	20.0
	2 6C	2.96	0.019	
[Ni(H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NHMe) <sub>3</sub> ]Cl <sub>2</sub>	1 6N	2.12	0.013	20.0
	2 9C	2.91	0.025	
[Ni(H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NHMe) <sub>3</sub> ]Br <sub>2</sub>	1 6N	2.11	0.017	17.2
	2 9C	2.90	0.031	
[Ni(Me <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> ][BF <sub>4</sub> ] <sub>2</sub>	1 6N	2.08	0.013	21.3
	2 12C	2.91	0.040	
[Ni(en) <sub>3</sub> ][MeCO <sub>2</sub> ] <sub>2</sub> <sup>c</sup>	Ni-N 2.13 (av.), Ni...C 2.92 (av.)			
[Ni <sub>2</sub> (en) <sub>4</sub> Cl <sub>2</sub> ] <sub>2</sub> <sup>d</sup>	Ni-N 2.10 (av.), Ni...C 2.92 (av.)			
[Ni(Me <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)(NO <sub>2</sub> )]ClO <sub>4</sub> <sup>e</sup>	Ni-N 2.14 (av.), Ni...C 2.93 (av.), Ni...C <sub>ax</sub> 3.04 (av.), Ni...C <sub>eq</sub> 3.06 (av.)			
[Ni{H <sub>2</sub> NCH(CH <sub>2</sub> ) <sub>4</sub> CHNH <sub>2</sub> } <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> <sup>f</sup>	Ni-N 2.10 (av.), Ni...C 2.95 (av.), Ni...C <sub>ca</sub> 4.4			
[Ni(H <sub>2</sub> NCH <sub>2</sub> CMe <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> (CCl <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> ] <sup>g</sup>	Ni-N 2.07 (av.), Ni...C 2.94 (av.), Ni...C <sub>eq</sub> ca. 4.3, Ni...C <sub>ax</sub> ca. 3.8			

<sup>a</sup> Debye-Waller factor  $A = 2\sigma^2$ , where  $\sigma$  = root-mean-square deviation in internuclear distance.  $E_0$  lay in the range 21.5–24.9 eV. AFAC values were 0.70 (F), 0.75 (Cl), 0.73 (Br), and 0.69 (BF<sub>4</sub> salt), and VPI values –1.55 (F), –2.51 (Cl), –1.79 (Br), and –1.11 (BF<sub>4</sub>). <sup>b</sup> Defined in ref. 19. <sup>c</sup> R. E. Cramer, W. Van Doorne, and J. T. Huneke, *Inorg. Chem.*, 1976, **15**, 529. <sup>d</sup> K. O. Joung, C. J. O'Connor, E. Sinn, and R. L. Carlin, *Inorg. Chem.*, 1979, **18**, 804. <sup>e</sup> A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom, and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2085. <sup>f</sup> A. V. Capilla, R. A. Aranda, and F. Gomez-Beltran, *Cryst. Struct. Commun.*, 1980, **9**, 147. <sup>g</sup> S. Garcia-Granda and F. Gomez-Beltran, *Acta Crystallogr., Sect. C*, 1984, **40**, 949.

irreversible oxidation waves at highly positive potentials. In attempts to form [Ni(diamine)<sub>3</sub>]X<sub>3</sub> we therefore examined reactions of various tris(diamine) complexes with chlorine or bromine vapour either on the powdered solid or upon a suspension of the solid in CCl<sub>4</sub>. The former method did not yield reproducible products, but the latter gave orange-yellow powders when chlorine was the oxidant used. These complexes have satisfactory analyses for [Ni(diamine)<sub>3</sub>]X<sub>3</sub>. All are extremely moisture sensitive, decomposing very rapidly upon exposure to moist air or on dissolution in common organic solvents. The decomposition products include [Ni(diamine)<sub>2</sub>-X<sub>2</sub>]X and in some cases mixed-valence materials. The i.r. spectra show no evidence for Ni–Cl vibrations,<sup>4</sup> whilst the u.v.–

visible and e.s.r. spectra (Table 2) are quite different from those<sup>3,4</sup> of [Ni(diamine)<sub>2</sub>X<sub>2</sub>]X, which suggest that NiN<sub>6</sub> species are present. The extreme moisture sensitivity has prevented reproducible bulk susceptibility measurements. However the powdered solids exhibit broad, usually featureless e.s.r. spectra with  $g_{av}$ . ca. 2.1 (Table 2) consistent with a low-spin  $d^7$  ion,<sup>21</sup> although their solution instability prevents better resolved spectra from being obtained. The diffuse-reflectance u.v.–visible spectra contain several features in the range ca. 19 000–27 000 cm<sup>-1</sup> which can be tentatively assigned as  $d-d$  transitions, and broad features > 33 000 cm<sup>-1</sup> which are N→Ni charge-transfer bands. Attempts to obtain bromide complexes have been generally unsuccessful; the products of [Ni(diamine)<sub>3</sub>]-

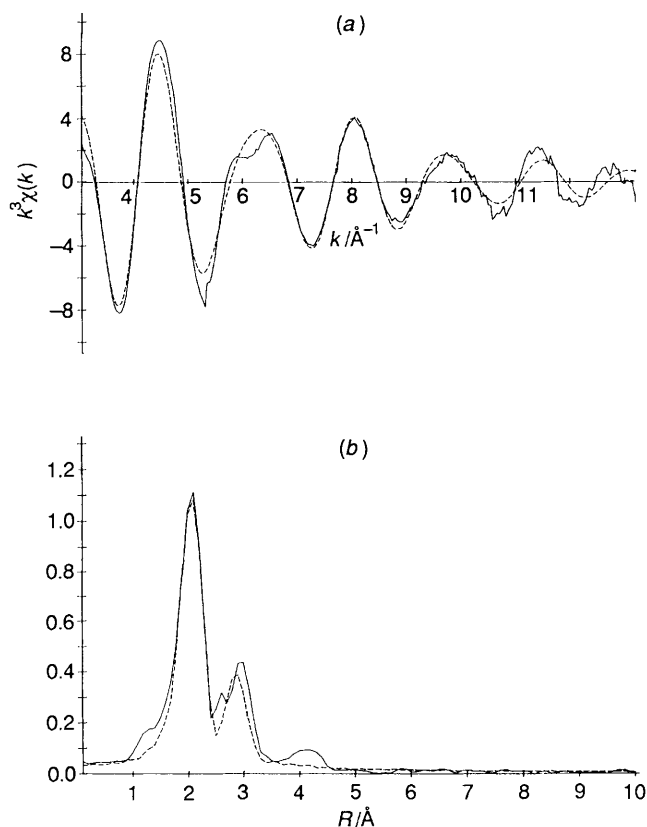
**Table 2.** Spectroscopic data for the nickel(III) complexes

Complex	E.s.r. $g_{av.}$	$E_{max.}/cm^{-1}$ (diffuse reflectance)
[Ni(en) <sub>3</sub> ]Cl <sub>3</sub>	2.14	22 500 (sh), 24 000 (sh), 30 000
[Ni(tn) <sub>3</sub> ]Cl <sub>3</sub>	2.14	21 500 (sh), 25 000 (sh), 29 900
[Ni(pn) <sub>3</sub> ]Cl <sub>3</sub>	2.11	22 000 (sh), 24 000 (sh), 30 700
[Ni(H <sub>2</sub> NCH <sub>2</sub> CMe <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> ]Cl <sub>3</sub>	2.13	21 500 (sh), 25 000 (sh), 28 000
[Ni(H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NHMe) <sub>3</sub> ]Cl <sub>3</sub>	2.13	18 900 (sh), 22 500 (sh), 26 600
[Ni{H <sub>2</sub> NCH(CH <sub>2</sub> ) <sub>4</sub> CHNH <sub>2</sub> } <sub>3</sub> ]Cl <sub>3</sub>	2.11	21 500 (sh), 24 000 (sh), 27 000

**Table 3.** Structural data for the nickel(III) complexes

Complex	Shell	$R/\text{Å}$	$A^a/\text{Å}^2$	$R^b$
[Ni(en) <sub>3</sub> ]Cl <sub>3</sub>	1 6N	2.09	0.018	21.4
	2 6C	2.85	0.024	
[Ni(pn) <sub>3</sub> ]Cl <sub>3</sub>	1 6N	2.10	0.014	22.4
	2 6C	2.90	0.021	
[Ni(H <sub>2</sub> NCH <sub>2</sub> CMe <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> ]Cl <sub>3</sub>	1 6N	2.08	0.020	26.2
	2 6C	2.84	0.024	
[Ni{H <sub>2</sub> NCH(CH <sub>2</sub> ) <sub>3</sub> CHNH <sub>2</sub> } <sub>3</sub> ]Cl <sub>3</sub>	1 6N	2.10	0.016	23.4
	2 6C	2.90	0.022	
	3 6C	4.49	0.021	
[Ni(bipy) <sub>3</sub> ][ClO <sub>4</sub> ] <sub>3</sub>	Ni-N 2.022(6) (× 2), 2.000(5) (× 2), 1.924(6) (× 2) <sup>c</sup>			
[Ni(bipy) <sub>3</sub> ]SO <sub>4</sub> ·7.5H <sub>2</sub> O	Ni-N 2.080(6), 2.087(5), 2.089(4), 2.090(6) (× 2), 2.098(4) Å <sup>d</sup>			
[NiL <sub>2</sub> ] <sub>2</sub> [S <sub>2</sub> O <sub>6</sub> ] <sub>3</sub> <sup>e</sup>	Ni-N 2.107, 2.111, 1.964, 1.985, 1.970, 1.965(5) <sup>f</sup>			
[NiL <sub>2</sub> ](NO <sub>3</sub> )Cl <sup>e</sup>	Ni-N 2.093, 2.098, 2.202, 2.111 (× 2), 2.116(4) <sup>g</sup>			

<sup>a,b</sup> As in Table 1. <sup>c</sup> Ref. 9. <sup>d</sup> A. J. Finney, M. A. Hitchman, D. L. Kepert, C. L. Raston, G. L. Rowbottom, and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2177. <sup>e</sup> L<sub>2</sub> = 1,4,7-triazacyclononane. <sup>f</sup> Ref. 10. <sup>g</sup> L. J. Zompa and T. N. Margulis, *Inorg. Chim. Acta*, 1978, **28**, L157.

**Figure 2.** (a) The background-subtracted EXAFS data and (b) the corresponding Fourier transform for [Ni(pn)<sub>3</sub>]Cl<sub>3</sub>. Key as in Figure 1

Br<sub>2</sub> + Br<sub>2</sub> reactions were orange-brown, e.s.r.-silent materials of variable composition.

Structural data for the [Ni(diamine)<sub>3</sub>]Cl<sub>3</sub> complexes were obtained by the EXAFS technique. As a result of their moisture sensitivity, all samples were prepared in pre-dried BN, in a glove-box, and run in sealed cells. The results are listed in Table 3 and an example is shown in Figure 2. Literature data show that Ni<sup>II</sup>-N and Ni<sup>III</sup>-N bond lengths usually lie in the ranges 2.1–2.2 and 1.9–2.0 Å respectively<sup>21</sup> although values are only available on two pairs of NiN<sub>6</sub> species, tris(2,2'-bipyridyl)- and bis(1,4,7-triazacyclononane)-nickel-(II) and -(III).<sup>9,10</sup> The nickel(III) complexes are appreciably distorted as a result of the Jahn-Teller effect, but if we compare the average bond lengths for Ni<sup>II</sup> and Ni<sup>III</sup> (Table 3) there appears to be a shortening of ≤0.1 Å on oxidation. The EXAFS data for the diamine complexes show that the Ni-N and Ni...C distances are slightly shorter on average than in the nickel(II) precursors, but the Debye-Waller factors are larger which may reflect the disorder produced by the Jahn-Teller distortion. The data clearly demonstrate that the nickel is surrounded by six nitrogens and that no halogen co-ordination is present (*cf.* ref. 5). The fact that the Ni-N bond lengths are not more shortened upon oxidation is slightly surprising, but the results from several samples and with different diamines are consistent. We discount the possibility that the materials studied contained mainly nickel(II) either due to only surface oxidation or to decomposition on the following grounds: (a) after regrinding in a glove-box there was no spectroscopic evidence for the presence of Ni<sup>II</sup> {in the partially decomposed [Ni(tn)<sub>3</sub>]Cl<sub>3</sub> (see Experimental section) the Ni<sup>II</sup> is clearly evident in the u.v.-visible spectrum}; and (b) decomposition in most cases leads to Ni<sup>III</sup> or mixed-valence materials not to Ni<sup>II</sup>.

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