

# Experimental determination of the electron configuration of the nickel ion in a complexed macrocycle by X-ray diffraction

Garry T. Smith,<sup>a</sup> Paul R. Mallinson,<sup>\*b</sup> Robert D. Peacock,<sup>b</sup> Louis J. Farrugia,<sup>b</sup> Ian A. Fallis,<sup>b</sup> Christopher S. Frampton<sup>b</sup> and Judith A. K. Howard<sup>a</sup>

<sup>a</sup> Chemistry Department, University of Durham, South Road, Durham, UK DH1 3LE

<sup>b</sup> Chemistry Department, University of Glasgow, Glasgow, UK G12 8QQ

The results of a multipole analysis with high-resolution X-ray diffraction data for  $[\text{Ni}(\text{H}_3\text{L})][\text{NO}_3][\text{PF}_6]$  [ $\text{H}_3\text{L} = N,N',N''\text{-tris}(2\text{-hydroxy-3-methylbutyl})\text{-1,4,7-triazacyclononane}$ ], to determine the electron configuration in the  $C_3$  symmetry-adapted orbitals of the Ni ion, are consistent with higher occupancy of the crystal-field stabilised  $e(t_2g)$  orbitals relative to the destabilised  $e(e_g)$  pair, suggesting a predominantly ionic metal–ligand interaction.

Recently a number of transition-metal complexes of chiral pendant-arm triazamacrocyclic ligands such as  $N,N',N''\text{-tris}(2\text{-hydroxy-3-methylbutyl})\text{-1,4,7-triazacyclononane}$  ( $\text{H}_3\text{L}$ ) have been synthesised.<sup>1–3</sup> When the metal ion is divalent, the ligand remains protonated and monomers such as  $[\text{Ni}(\text{H}_3\text{L})]^{2+}$  are formed. If the oxidation state of the metal ion is greater than 2, however, every second ligand deprotonates to give dimers, such as  $[\text{Co}^{\text{III}}(\text{LH}_3\text{LCo})^{\text{III}}]^{3+}$ ,  $[\text{Mn}^{\text{II}}(\text{LH}_3\text{L})\text{Mn}^{\text{IV}}]^{3+}$  and  $[\text{Zn}^{\text{II}}(\text{LH}_3\text{L})\text{V}^{\text{III}}]^{3+}$ ; the halves of the dimer being connected by strong hydrogen bonds. This work was undertaken to determine experimentally the electron density distribution in a complexed macrocycle, to examine the metal-centred orbitals, and to attempt to characterize the metal–ligand interaction, in a system too large to be treated by high quality theoretical calculations. The results are topical because of recent interest<sup>4</sup> in metal complexation by macrocyclic ligands, for biological and industrial applications.

The symmetry of the nickel complex (Fig. 1), having crystallographically imposed point group  $C_3$ , is not the most

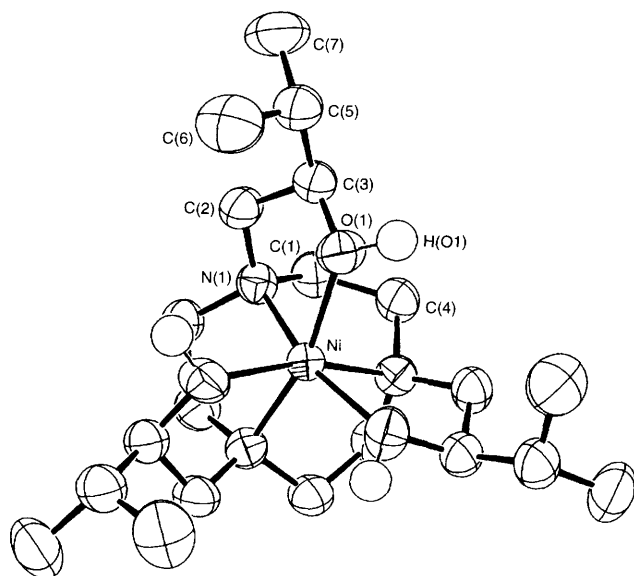


Fig. 1 The complex cation viewed along the  $C_3$  axis, showing the labelling of the atoms and anisotropic displacement ellipsoids drawn at the 90% level

common in transition-metal chemistry. In a recent study of a cobalt(II) complex<sup>5</sup> a significant trigonal distortion (to point group  $C_{3i}$ ) of the charge distribution expected for a near-octahedral ligand field was found. In this case the symmetry of the ligand field itself is  $C_3$ . A multipole model of the crystalline charge density distribution has been fitted to high-resolution X-ray diffraction data (Table 1), from which we calculate here the  $C_3$  symmetry-adapted d-orbital populations to establish the electron configuration of the  $\text{Ni}^{2+}$  ion.

The Ni–N [2.063(1) Å] and Ni–O [2.094(1) Å] distances found in this experiment<sup>†</sup> do not differ significantly from those determined in the crystal structure reported previously.<sup>3</sup> The charge of +1.83(2) electrons obtained from the valence monopole population coefficient for the nickel atom suggests oxidation to give a configuration  $3d^84s^0$ . A formal charge of +2 on the metal ion is expected to increase the  $3d\text{--}4s$  separation,<sup>10</sup>

Table 1 Experimental data for  $[\text{Ni}^{\text{II}}(\text{H}_3\text{L})][\text{NO}_3][\text{PF}_6]$  [ $\text{H}_3\text{L} = N,N',N''\text{-tris}(2\text{-hydroxy-3-methylbutyl})\text{-1,4,7-triazacyclononane}$ ]

Formula	$\text{C}_{21}\text{H}_{45}\text{F}_6\text{N}_4\text{NiO}_6\text{P}$
<i>M</i>	653.28
Crystal system	Cubic
Space group	$P2_13$
<i>T</i> /K	123(1)
<i>a</i> /Å	14.008(2)
<i>U</i> /Å <sup>3</sup>	2748.7(7)
<i>Z</i>	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.578
Crystal dimensions/mm	$0.4 \times 0.4 \times 0.6$
$\mu/\text{cm}^{-1}$	8.47
Capillary	none
Range of corrections for absorption	0.774–0.804
Isotropic extinction	Gaussian mosaic spread 15 s domain size $3 \times 10^{-5}$ cm
Radiation ( $\lambda/\text{Å}$ )	Mo–K $\alpha$ (0.7107)
Scan type	$\theta\text{--}2\theta$
$(\sin \theta/\lambda)_{\text{min}}\text{--}(\sin \theta/\lambda)_{\text{max}}/\text{Å}^{-1}$	0.05–1.08
Range <i>hkl</i>	–1–30, 0–30, –17 to 10
<i>t</i> / <i>h</i>	642
No. standard reflections	5 (8 8 $\bar{8}$ , 0 4 9, 0 4 $\bar{9}$ , 0 26 0, 4 0 4)
No. reflections measured	20445
No. symmetry-independent reflections	6017
No. of $I > 2\sigma(I)$ reflections	5095
No. symmetry-related and repeated reflections	5971
Agreement factor $R = \sum  I - \bar{I}  / \sum I$	0.017
Refined on	<i>F</i>
<i>R</i>	0.0221
<i>R</i> <sub>w</sub>	0.0156
<i>S</i>	1.08
No. variables	413
Weighting scheme, <i>w</i>	$1/\sigma^2(F) = 4F^2/\sigma^2(F)^2$ , $\sigma^2(F^2) = \sigma_{\text{counting}}^2(F^2) + P^2F^4$
Highest residual density $e \text{ Å}^{-3}$ (at the nuclear position of P)	0.4

so that the 4s orbital should be unoccupied and should differ in energy sufficiently for 3d–4s mixing, where symmetry allowed, to be negligible. Likewise we assume that 4p participation may be ignored, and attribute all density in the valence expansion to the metal d-orbital occupation.

The environment of the Ni atom has point symmetry  $C_3$ . Considering the splitting of the d orbitals in this relatively low-symmetry field (compared with an octahedral environment), we take the d-orbital set usually associated with an  $O_h$  complex and then cant the coordinate frame such that the principal axis, z, now lies along a threefold axis. The transformed orbital set becomes:

$$\begin{aligned}
 & d_{x^2} \\
 t_{2g}: & \sqrt{\frac{2}{3}} d_{x^2-y^2} - \sqrt{\frac{1}{3}} d_{xz} \\
 & \sqrt{\frac{2}{3}} d_{xy} + \sqrt{\frac{1}{3}} d_{yz} \\
 e_g: & \sqrt{\frac{1}{3}} d_{x^2-y^2} + \sqrt{\frac{2}{3}} d_{xz} \\
 & \sqrt{\frac{1}{3}} d_{xy} - \sqrt{\frac{2}{3}} d_{yz}
 \end{aligned}$$

Further, if a trigonal distortion is introduced by rotation of one trio of ligands relative to the other (in our case the three N atoms relative to the three O atoms), the  $t_{2g}$  set splits into an  $a_1$  orbital deriving from the  $d_{z^2}$ , and a degenerate e pair, which we denote  $e(t_{2g})$  to indicate its parentage. The  $e_g$  pair becomes  $e(e_g)$ .

The equivalence of a multipole expansion of order 0, 2 and 4 to a complete set of 3d3d orbital products assuming equivalent radial functions has been presented previously in the literature.<sup>11,12</sup> For the Ni atom in this instance we have used Clementi's Hartree–Fock wavefunctions<sup>13</sup> for the radial functions of order 0, 2, and 4. Applying the transformation matrix appropriate for symmetry-adapted orbitals in trigonal complexes<sup>11</sup> leads to the d-orbital populations shown in Table 2; the last entry corresponds to a term describing the symmetry-allowed mixing of the  $e(t_{2g})$  and  $e(e_g)$  orbitals.

The results of the d-orbital population analysis may be interpreted within the independent particle model of atomic and molecular structure. Within this approximation, we describe the molecular structure in terms of orbitals with integral occupation numbers between 0 and 2 inclusive. We are therefore assuming that the effects of electron correlation, or equivalently, configuration interaction (CI) are absent.<sup>14</sup> This is equivalent to a description of the density by an idempotent first-order density matrix of d–d orbital products.<sup>15</sup> In theory, any observed deviation from integral occupation numbers may be attributed either to CI or to the effect of covalency between the metal and ligating atoms.

Given the fact that no constraint at all is imposed upon the d-orbital populations *via* the multipole parameters (other than those required by symmetry), and assuming a  $d^8$  configuration, the results are consistent with population of the orbitals in

**Table 2** Symmetry-adapted d-orbital populations

Orbital	Population (experiment)	Population (crystal field theory)
$a_1(d_{z^2})$	1.72(6)	2.00
$e(t_{2g})$	4.23(7)	4.00
$e(e_g)$	2.22(7)	2.00
$e(t_{2g})e(e_g)$	−0.33(13)	—

increasing energy order, the stabilised  $a_1(d_{z^2})$  and  $e(t_{2g})$  orbitals being expected to be fully occupied. With the exception of  $a_1$ , the experimental populations in Table 2 are scarcely significantly different from the set of crystal-field theoretical populations, the destabilised  $e(e_g)$  orbitals having an occupancy of approximately one electron each. The depletion of the  $a_1$  population by 0.28(6) electrons is possibly a CI effect.

The charge of +1.83(2) electrons on the  $Ni^{2+}$  ion in the  $H_3L$  complex found from multipole refinement is close to its formal value of +2. On the basis that the asphericity of this ion is essentially due to different occupancies of d orbitals, analysis of the multipole populations in terms of symmetry-adapted orbital occupancies leads to an experimentally derived electron configuration in accord with expectation from crystal-field theory. This in turn suggests that the metal and ligand have a predominantly ionic interaction. The nature of the ligand–metal bonding is presently being characterized further by means of topological analysis of the electron density distribution in the metal coordination sphere.

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### Footnote

† Single-crystal, high-resolution, low-temperature X-ray diffraction data from dark blue octahedral crystals of  $[Ni^{II}(H_3L)](NO_3)[PF_6]$  were collected using the same equipment and procedure as described in an earlier paper.<sup>6</sup> Data reduction was carried out with the DREAM suite of programs,<sup>7</sup> including an analytical absorption correction computed with ABSORB.<sup>8</sup> The intensities of standard reflections were fitted to cubic polynomials, which were used for scaling the data. Corrections were made for absorption by the crystal and capillary, but not for thermal diffuse scattering. The range of absorption factors, agreement factor for the averaging of equivalent reflections, crystal data and other experimental details are summarized in Table 1. Multipole analysis was carried out using the package XD.<sup>9</sup>

*Supplementary material available:* Residual density distribution in the planes defined respectively by the Ni and ligating O and N atoms, the P and two F atoms, and the nitrate group. Coordinates and anisotropic displacement parameters. Bond lengths and angles. Monopole charges,  $\kappa'$  and  $\kappa''$  values obtained from the refinement. Multipole population coefficients. Definitions of local axes. Observed and calculated structure factors.

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