A Comparison of the Angular-overlap and Crystal-field Models in interpreting the Magnetic Properties of Hexakis(pyridine *N*-oxide)nickel(II) Tetrafluoroborate

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The angular-overlap model (a.o.m.) has been applied to the title complex where the local metal symmetry is S_6. A.o.m. parameters have been obtained which fit the magnetic anisotropy and average magnetic susceptibility and the results are compared with those from a crystal-field model. General expressions are presented which relate the a.o.m. parameters to an 'effective crystal field' expressed in terms of coefficents of spherical harmonics. The NiO_6 core has almost exact octahedral symmetry and in this case the a.o.m. increases the effective symmetry from S_6 to D_3. From the *X*-ray crystal structure, the Ni–O–N angle is 119° and, if one assumes that the oxygen atom is sp^2 hybridized, it is possible to obtain values for all the three a.o.m. parameters. These are found to be $e_\sigma = 4\,393$, $e_{\pi x} = 830$, and $e_{\pi y} = 1\,660$ cm^{-1}.

SINCE the *ab initio* calculation of energy levels for the majority of transition-metal complexes presents a problem of enormous complexity, it is not surprising that semiempirical methods are often employed. The angular-overlap model (a.o.m.) is such a method [1-3] and is applicable to systems where the energies of the various ligand orbitals differ greatly from those of the metal *d* manifold. The a.o.m. assumes that metal *d*-orbital splittings arise through covalent interaction with those ligand orbitals which have the correct symmetry for overlap. Interaction with the occupied ligand orbitals, at low energy, will tend to raise the energies of the *d* orbitals whilst the higher-energy unoccupied ligand orbitals will exert an opposite effect. As a major simplifying assumption, the a.o.m. neglects that small degree of mixing between the metal *d* and ligand orbitals which arises from this covalent interaction. Moreover, ligand–ligand interactions are usually considered negligible and the effect of individual ligands assumed additive.

Procedures are well established for performing such summations and obtaining all the one-electron matrix elements between metal *d* orbitals. Here we have a point of contact with other ligand-field models since one can create a fictitious operator which would generate the same matrix elements when acting on our chosen basis set.[4] It is most convenient to express this operator as a series of spherical harmonics centred on the metal ion. The many-electron system can then be dealt with using standard tensor-operator techniques. In theory, the series of spherical harmonics is infinite but, in practice, it is limited to terms having *L* values of 2 and 4 for *d* electrons while the allowed values of *M* are determined by symmetry. The total Hamiltonian for the system must transform as the totally symmetric representation of the appropriate symmetry group, and the number of crystal-field parameters required by symmetry is equal to the number of times the totally symmetric representation (Γ_1) occurs in the decomposition of the full spherical group. These are listed in the full rotation-group compatibility tables given by Koster *et al.*[5]

In the present paper we interpret the magnetic properties of $[Ni(pyo)_6][BF_4]_2$ (pyo = pyridine *N*-oxide) using the angular-overlap model and compare the results with those published earlier using the point-charge approximation to the crystal field.[6] This complex was chosen because: (*a*) it is easy to diagonalize the complete 45 × 45 matrix of the d^8 configuration; (*b*) the magnetism of distorted octahedral nickel complexes is fairly simple to interpret since it is dominated by the $^3A_{2g}(O_h)$ ground state; (*c*) the site symmetry [7] of the nickel ion is sufficiently high (S_6) that the number of parameters required is not too large; and (*d*) the crystal and molecular magnetic susceptibilities are identical by symmetry.

RESULTS AND DISCUSSION

It is not the brief of this paper to discuss in detail the principles underlying the crystal-field and angular-overlap models as these have been the subject of extensive articles.[8,9] Inspection of the compatability tables of Koster *et al.*[5] shows there should be four independent parameters to express the ligand field for a *d* configuration in S_6 symmetry. One might choose the coefficients of Y_2^0, Y_4^0, and Y_4^3. This gives four parameters since the coefficients of Y_4^3 may in general be complex. Here we have taken the molecular *z* axis to be along the three-fold axis. By choosing the correct direction for the *y* axis it would, of course, be possible to generate a totally real potential but symmetry in no way fixes this direction. If the symmetry is increased to D_3 or D_{3d} a real potential will result if the *y* axis lies along one of the

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[1] C. E. Schäffer, *Structure and Bonding*, 1968, **5**, 68.

[2] C. E. Schäffer, *Pure Appl. Chem.*, 1970, **24**, 361.

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[8] M. Gerloch and R. C. Slade, 'Ligand Field Parameters,' Cambridge University Press, 1973.

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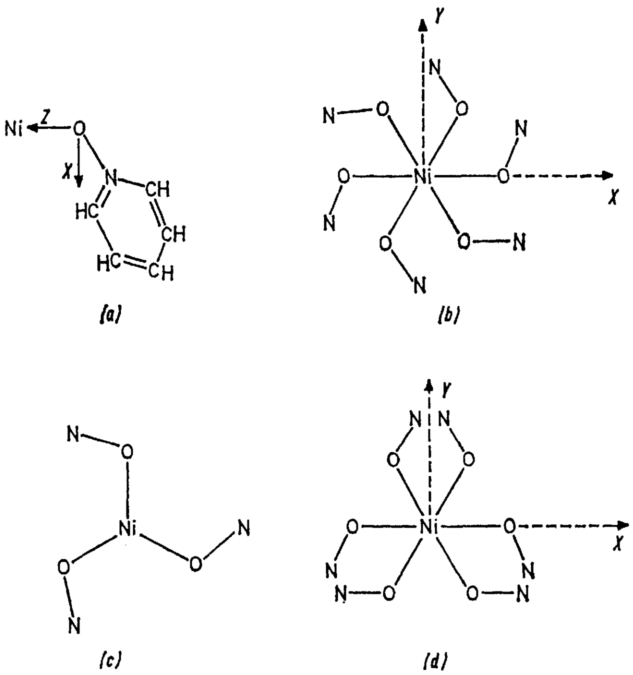
symmetry-defined two-fold axes. In this case the direction chosen for the y axis is fixed and the number of parameters reduced to three. In this paper we are primarily concerned with magnetic-susceptibility measurements. Magnetic susceptibility, being a second-rank tensorial property, in a system of three-fold symmetry will be axial, and the choice of y direction is arbitrary. That is, the calculated properties will be independent of the phase of the c_{43} coefficient. Moreover, there are peculiarities of S_6 symmetry for the $[M(pyo)_6]^{2+}$ system which can cause both models to increase the effective symmetry so that almost exactly real potentials will be calculated. In the point-charge model it is assumed that the crystal field is dominated by the atoms directly co-ordinated to the metal ion and in $[Ni(pyo)_6]^{2+}$ the NiO_6 core has exact D_{3d} symmetry and requires only three parameters. In this model the trigonal component of the crystal field arises from a distortion along the three-fold molecular axis and is a function of the angle (θ) subtended by any nickel–ligand bond and the three-fold axis. In a previous paper[6] it was shown that θ cannot be uniquely determined from the magnetic susceptibility but corresponds to a small trigonal elongation of the octahedron.



(a) The local co-ordinate frame used in defining the a.o.m. parameters. (b) The global co-ordinate frame with the Z axis collinear with the crystal c axis. (c) Molecular sub-unit having C_3 symmetry. (d) Hypothetical molecule having D_3 symmetry. If the NiO_6 group has exact O_h symmetry, the a.o.m. cannot distinguish between (b) and (d). All the axes form a right-handed set

In the a.o.m. the contributions from each ligand are assumed to be additive and since all the ligand molecules are equivalent by symmetry we can restrict our attention to the nickel ion and a single pyridine N-oxide molecule. The bonding between the nickel ion and the oxygen atom is characterized by a π contribution in the Ni–O–N plane ($e_{\pi x}$), a π contribution normal to this plane ($e_{\pi y}$), and a symmetric σ-bonding contribution (e_σ). The local co-ordinate frame is shown in Figure (a). The atom co-ordinates obtained from the X-ray crystal structure[7] are used to define these directions. Although the NiO_6 core has rigorous D_{3d} symmetry, the oxygen atoms are at almost exactly octahedral positions. This means that the trigonal field in the a.o.m. is dominated by the anisotropy in the π bonding ($E_3 = e_{\pi x} - e_{\pi y}$). As demonstrated in the Appendix, the imaginary terms in the potential exactly disappear when $\theta = \cos^{-1}(1/3^{\frac{1}{2}})$ (that is the octahedral angle). Moreover, the imaginary component of c_{43} will be negligible compared with the real, even for substantial distortions away from the octahedral angle for realistic values of a.o.m. parameters.

It is not possible to obtain $e_{\pi x}$ and $e_{\pi y}$ separately unless some additional relation is assumed and the situation is analogous to the point-charge model where the trigonal field was essentially defined by $A_2^0\langle r^2\rangle = \frac{3}{2}\rho_2(3\cos^2\theta - 1)$ and it was not possible to obtain separate values for ρ_2 and θ.

Since we are only interested in comparing ligand-field effects, the values of all the other parameters were the same as used in the point-charge calculation (F_2 1 306 cm^{-1}, F_4 93 cm^{-1}, ζ 550 cm^{-1}, and k 1.0). If the ligating atoms are at exactly octahedral positions, the angular-overlap parameters are related to the crystal-field splitting parameter $10Dq$ by equation (1). In the

$$10Dq = 3e_\sigma - 2(e_{\pi x} + e_{\pi y}) \qquad (1)$$

initial calculations the octahedral part of the potential was kept constant at the spectroscopically determined value[10] by using the relations (2) and (3). It was found

$$10Dq = 3e_\sigma = 8\,200\ \text{cm}^{-1} \qquad (2)$$

$$e_{\pi x} = -e_{\pi y} \qquad (3)$$

that the sign of the magnetic anisotropy and the zero-field splitting (D) of the ground state were completely determined by the sign of E_3, and, for $E_3 = -830$ cm^{-1}, $\Delta\chi$ and D were virtually identical with the values calculated from the point-charge model (Table 1). It is highly unlikely that $e_{\pi x}$ and $e_{\pi y}$ would have opposite signs and a much more realistic set of parameters can be obtained if we assume that the oxygen atom is sp^2 hybridized since it is then easy to show that $e_{\pi x} = \frac{1}{2}e_{\pi y}$. This assumption seems reasonable since the Ni–O–N angle is 119.0 ± 0.1°. After substitution into equation (1) and using $E_3 = -830$ cm^{-1} we obtain $e_\sigma = 4\,393$, $e_{\pi x} = 830$, and $e_{\pi y} = 1\,660$ cm^{-1}. The values of $\Delta\chi$ and D calculated from these parameters are also shown in Table 1. The slight discrepancy in the values obtained from the two a.o.m. calculations is due to the fact that the oxygen atoms are not at exactly octahedral positions

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[10] J. Reedijk, *Rec. Trav. chim.*, 1969, **88**, 499.

and hence equation (1) is not strictly valid. The average magnetic moment is essentially independent of the trigonal field and the three sets of parameters in Table 1 give the same values of $\bar{\mu}$ to within 0.005 B.M.* for $2 \leqslant T \leqslant 300$ K. Below 30 K the effects of magnetic exchange become important and the experimental values of $\bar{\mu}$ and $\Delta\chi$ are both decreased.[11,12]

The positive signs of $e_{\pi x}$ and $e_{\pi y}$ mean that electron donation in the π bonding is from ligand to metal as expected. For a distorted octahedral nickel complex such an effect occurs in second order since the $^3A_{2g}(O_h)$ state is split by the admixture of excited energy levels whose orbital degeneracy has been lowered by the trigonal field. These excited states do not have a filled $t_{2g}{}^6$ electron configuration and are split in a manner which is indicative of ligand-to-metal π donation. Whether these are reasonable values is undetermined at present since there are not many literature values with which they can be compared. The calculations were made on the assumption that the orbital-reduction factor was unity and any decrease in the value of k would need a corresponding increase in the π-bonding anisotropy and hence in the individual values of $e_{\pi x}$ and $e_{\pi y}$. The values given in Table 1 are therefore lower limits to these parameters and it is apparent that the a.o.m. implies significant π bonding between the nickel ion and the oxygen atom. Consequently there can be little π bonding between the oxygen and nitrogen atoms, particularly as the Ni–O–N plane is inclined at 72° to the pyridine ring. In an earlier paper[13] on the donor properties of 4-substituted pyridine N-oxides it was suggested that there was a relation between the electron-donor or -acceptor properties of the 4-substituent and the degree of π bonding in the N–O bond which was manifested in both the visible and i.r. spectra. The X-ray structure and present work suggest that any such correlation is fortuitous.

TABLE 1

Experimental and calculated values of $(\chi_\perp - \chi_\parallel)$ in $[Ni(pyo)_6][BF_4]_2$. Units are 10^{-9} m^3 mol^{-1}

	$\chi_\perp - \chi_\parallel$			
		Angular-overlap model[a]		
T/K	Point-charge[a,b] model	Set 1[c]	Set 2[d]	Experimental values
300	2.38	2.07	2.14	
200	3.71	3.32	3.39	2.94
150	5.28	4.78	4.86	4.75
100	9.10	8.38	8.48	9.14
50	26.0	24.7	24.6	28.5
20	125.9	122.9	120.1	121.5
10	448	444	431	351
6.5	991	984	955	769
Zero-field splitting/cm^{-1}	3.62	3.63	3.47	

[a] $F_2 = 1\,306$ cm^{-1}, $F_4 = 93$ cm^{-1}, $\zeta = 550$ cm^{-1}, and $k = 1.0$. [b] $\rho_4 = 4\,920$ cm^{-1} and $A_0{}^2\langle r^2\rangle = 925$ cm^{-1}. [c] $e_\sigma = 2\,733$ cm^{-1} and $e_{\pi x} = -e_{\pi y} = -415$ cm^{-1}. [d] $e_\sigma = 4\,393$ cm^{-1}, $e_{\pi x} = 830$ cm^{-1}, and $e_{\pi y} = 1\,660$ cm^{-1}.

Conclusions.—Although S_6 symmetry requires four crystal-field parameters, the effective number of parameters is reduced to two for both the a.o.m. and point-charge models of $[Ni(pyo)_6][BF_4]_2$. In the a.o.m. the magnetic anisotropy is attributed to asymmetric π bonding between the nickel ion and the oxygen atoms which are at essentially octahedral positions, while in the point-charge model the anisotropy arises from a crystallographically undetected elongation of the NiO_6 polyhedron. This is in agreement with the predictions of Bergendahl and Wood[14] who suggested that the magnetic and spectroscopic properties of the isomorphous $[Co(pyo)_6][ClO_4]_2$ would be indicative of an octahedron extended along the three-fold axis. Crystal structures of $[M(pyo)_6][X]_2$ have been determined for $X = ClO_4$ and M = Hg,[15] Co,[13] Cu, or Fe[16] and $X = BF_4$ and M = Ni,[7] and in each case the oxygen atoms are in essentially octahedral positions with the pyridine rings inclined at *ca.* 75° to the M–O–N plane. The M–O–N angle is 114° in the mercury complex and *ca.* 119° in the others, and the great similarity in coordination implies that the point-charge and angular-overlap calculations in these other systems should arrive at similar conclusions. The copper complex is Jahn–Teller active and undergoes a number of phase transitions on cooling, but magnetic measurements on both the iron and cobalt complexes have been made in order to test this hypothesis. The good agreement between the magnetic anisotropy calculated from both models lends credence to the earlier suggestion that the zero-field splitting is temperature dependent,[6,12] but direct confirmation of this by e.s.r. is not possible unless very high magnetic-field strengths are used.

In nickel systems of S_6 or D_3 symmetry it seems to be a general rule that oxygen-bonded ligands show much greater zero-field splittings than do the nitrogen-bonded ones,[17] and this most probably reflects their greater π-bonding anisotropy.

APPENDIX

Analytical expressions in terms of a.o.m. parameters for the potential expanded in spherical harmonics centred on the metal may be derived following method B of ref. 4. The method essentially involves calculation of a potential for each ligand in its local axis frame and their addition after transformation into a common global frame. It should be noted at this stage that there is a misprint in

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

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[16] D. Taylor, personal communication.

[17] J. Reedijk and B. Nieuwenhuijse, *Rec. Trav. chim.*, 1972, **91**, 533.

TABLE 2

Coefficients of the spherical harmonics for a ligand field of S_6 or D_3 symmetry in terms of a.o.m. parameters and Euler angles

Real parts of C_{kq} (for S_6 and D_3 symmetries)

$$c_{20} = \frac{3}{2}\left(\frac{\pi}{5}\right)^{\frac{1}{2}} [E_1(3\cos2\beta + 1) + 3E_3(1 - \cos2\beta)\cos2\alpha]$$

$$c_{40} = \frac{3}{80}\pi^{\frac{1}{2}} [E_2(35\cos4\beta + 20\cos2\beta + 9) - 10E_3(7\cos4\beta - 4\cos2\beta - 3)\cos2\alpha]$$

$$c_{43} = \frac{3}{4}\left(\frac{7\pi}{5}\right)^{\frac{1}{2}} [2E_3\sin2\beta(\cos2\beta + 1)\cos2\alpha - E_2\sin2\beta(\cos2\beta - 1)]$$

Imaginary part of c_{43} (for S_6 symmetry only)

$$c_{43} = -\frac{3}{4}\left(\frac{7\pi}{5}\right)^{\frac{1}{2}} E_3\sin\beta(3\cos2\beta + 1)\sin2\alpha$$

Where $B = \theta =$ the octahedral angle $[\cos^{-1}(1/3^{\frac{1}{2}})]$

$$c_{20} = 6\left(\frac{\pi}{5}\right)^{\frac{1}{2}} E_3\cos2\alpha$$

$$c_{40} = \frac{2}{15}\pi^{\frac{1}{2}} [20E_3\cos2\alpha - 7E_2]$$

$$c_{43} = \frac{2}{3}\left(\frac{14\pi}{5}\right)^{\frac{1}{2}} [E_3\cos2\alpha + E_2]$$

The following definitions are used in the above equations:

$E_1 = 2e_\sigma + e_{\pi x} + e_{\pi y}$
$E_2 = 3e_\sigma - 2e_{\pi x} - 2e_{\pi y}$
$E_3 = e_{\pi x} - e_{\pi y}$

Table 3 of this reference and the expression for c_{40} in the ligand frame is incorrect. The correct expression is (A1).

$$c_{40} = (\pi^{\frac{1}{2}}/5)(6e_\sigma - 4e_{\pi x} - 4e_{\pi y}) \qquad \text{(A1)}$$

The relation between the local frames and the global frame is expressed in terms of rotation through Euler angles (α, β, γ). We use the global axis frame illustrated in Figure (*b*) which is the same as that adopted by Gerloch *et al.*[18] This means that β corresponds to the usual trigonal angle θ, γ is fixed by the choice of axis frame for each ligand, and α depends on the orientation of the principal π directions on the ligands.[19] We only perform our addition over the top three ligands of the system (a sub-unit with C_3 symmetry). True values for coefficients for the complete system will simply be doubled in S_6 symmetry. The same will be true in D_3 symmetry except that imaginary terms will exactly cancel. The derived equations are listed in Table 2 in the general case and also for the special case where $\beta = \theta =$ the octahedral angle $[\cos^{-1}(1/3^{\frac{1}{2}})]$. Here it should be noted that the imaginary term disappears and S_6 and D_3 symmetry are equivalent. For $[\mathrm{Ni(pyo)_6}]^{2+}$, $\alpha = 69.86$, $\beta = 54.95$, and $\beta_{\mathrm{oct.}} = 54.74°$.

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