Metal–Ligand Bonding Parameters and Magnetic Properties of Some Previously Reported Tetragonal Nickel(II) Complexes†

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The variation of the magnetic moments of the complexes [Ni(py)$_4$X$_2$] (py = pyridine), [Ni(Hpz)$_4$X$_2$] (Hpz = pyrazole), [Ni(mim)$_4$X]X (mim = 2-methylimidazole, X = Cl or Br), and [Ni(en)$_2$(NO$_2$)$_2$] (en = 1,2-diaminoethane) over the temperature range 300—4.3 K is reported. The magnetic behaviour, which is strongly influenced by the zero-field splitting of the ground state of each complex, has been interpreted in conjunction with the previously reported *d*—*d* transition energies in terms of angular overlap and metal–ligand σ- and π-bonding parameters. Though some anomalies are observed, notably the low values of the halide interactions in the pyrazole complexes and the zero-field splittings of the bromo complexes, the parameters which best reproduce the experimental data generally compare favourably with those derived in other studies on similar systems, and with the expectations of simple theory.

Considerable progress has recently been made in understanding the magnetic interactions occurring between transition-metal ions linked by bridging ligands.[1] The metal ion with an orbitally non-degenerate ground state which has been studied most widely by magnetochemical techniques is nickel(II). This forms a variety of polymeric complexes, some of which are ferromagnetic and others antiferromagnetic, and much emphasis has been laid on attempting to understand these differences in terms of superexchange pathways.[1–5] While it has been recognized that the magnetic behaviour may be complicated by a zero-field splitting of the ground state of each metal ion, this has usually been taken into account simply by adding a splitting parameter chosen to optimize the magnetic results, without recourse to the implications this has on the excited-state energy levels. It would clearly be useful if the optical spectrum and/or the metal–ligand bonding parameters could be utilized to provide an estimate of the likely value of the zero-field splitting.

The optical spectra of the *trans*-distorted tetragonal complexes [Ni(py)$_4$X$_2$] (py = pyridine), [Ni(Hpz)$_4$X$_2$] (Hpz = pyrazole), [Ni(mim)$_4$X]X (mim = 2-methylimidazole, X = Cl or Br), and [Ni(en)$_2$(NO$_2$)$_2$] (en = 1,2-diaminoethane) have recently been interpreted in terms of metal–ligand bonding parameters,[6,7] and the purpose of the present study is to extend this analysis to include magnetic properties. We have therefore measured the magnetic susceptibilities of the compounds over the temperature range 300—4.3 K. This should not only allow a more reliable estimate of the bonding parameters than was possible on the basis of the electronic spectral data alone, but also provide information on the extent to which the magnetic properties of low-symmetry nickel(II) complexes may be predicted using ligand-field calculations. It was hoped that this would be helpful in interpreting the superexchange interactions in a number of novel polymeric nickel(II) nitrite complexes which we prepared recently.[8] The computer program CAMMAG, recently developed by Gerloch and co-workers,[9] which calculates the energy levels and magnetic properties of a metal complex within the framework of the angular overlap model (a.o.m.) of bonding,[10] was used for the analysis. This has been applied successfully in similar studies of the complexes of other metal ions[11] and has the advantage that the physical properties of the compounds, and in particular the zero-field splitting, may be related to metal–ligand σ- and π-bonding parameters which are of direct chemical significance.[12,13]

Experimental

The preparation, characterization, and electronic spectral properties of each of the complexes have already been reported.[7,14] Magnetic susceptibility measurements were carried out using an Oxford Instruments Faraday balance operating at a field strength of 5—50 kG and a field gradient of 1 000 G cm^{-2}. Calculation details are given elsewhere.[15]

Results and Discussion

Assuming that δ interactions are insignificant, the a.o.m. describes each metal–ligand interaction in a complex in terms of the bonding parameters e_σ, $e_{\pi s}$, and $e_{\pi c}$.[10,12,13] The energy states of the complex are then obtained by summing the effects of all the ligands using the angular overlap matrix defined by the geometry of the complex, with the effects of interelectron repulsion and spin–orbit coupling being introduced by means of the appropriate coupling constants. The ground-state wavefunction, as specified by the eigenvectors of the above procedure, can then be used to calculate the molecular *g* values and magnetic properties of the complex. In the present study, the computer program CAMMAG, written by Gerloch and co-workers,[9] was used to perform the above calculations, the angular overlap matrix being calculated within the program using the metal and ligand positions obtained from the crystal-structure data available for each of the complexes.

In general, it is impossible to determine unambiguously all three of the above a.o.m. parameters for each ligand in a mixed-ligand complex, and various constraints have been proposed to make the probem manageable.[7,12,16] In a previous interpretation of the optical spectra of the halide complexes of the present pyridine, pyrazole, and 2-methylimidazole nickel(II) complexes using the a.o.m., it was assumed that the π bonding due to the amine ligands is isotropic about the metal–ligand bond axis (*i.e.* $e_{\pi s} \approx e_{\pi c}$), and that the ratio of the halide σ- and π-bonding interactions is proportional to the ratio of the squares of the metal–ligand diatomic overlap integrals.[7] Both assumptions are undesirable. The π interaction with the orbitals lying in the

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† *Non-S.I. units employed*: B.M. = 9.27×10^{-24} A m^2, G = 10^{-4} T.

Table 1. Observed and calculated electronic transition energies of the complexes (calculated values in parentheses)

Complex	Excited-state energy/cm^{-1}		
	$^3T_{2g}$	$^3T_{1g}(F)$	$^3T_{1g}(P)$
$[Ni(py)_4Cl_2]$[a]	9 040, 11 730	14 930, 16 820	26 750
	(7 840, 8 950, 11 810)	(14 790, 14 940, 16 620)	(24 250, 26 060, 26 302)
$[Ni(py)_4Br_2]$[a]	7 750, 8 430, 11 490	14 080, 16 390	26 300
	(7 890, 8 390, 11 425)	(13 735, 16 270, 17 000)	(25 730, 26 800, 27 710)
$[Ni(Hpz)_4Cl_2]$[b]	8 000, 10 950	13 100, 16 400	26 500
	(8 040, 10 410, 10 910)	(13 085, 16 360, 17 010)	(26 480, 27 080, 27 900)
$[Ni(Hpz)_4Br_2]$[b]	7 240, 10 900	12 000, 15 900	25 800
	(7 270, 10 290, 10 600)	(11 910, 15 860, 16 190)	(25 980, 26 290, 27 450)
$[Ni(mim)_4Cl]Cl$[a]	5 500, 6 050, 10 500	11 500, 15 150	23 000, 26 000
	(5 610, 5 940, 11 170)	(11 700, 14 350, 14 520)	(23 180, 25 560, 25 780)
$[Ni(mim)_4Br]Br$[a]	5 150, 10 300	11 600, 15 300	22 800, 24 800
	(5 220, 5 600, 11 060)	(11 650, 14 630, 15 010)	(22 720, 25 460, 25 690)
$[Ni(en)_2(NO_2)_2]$[c]	11 400, 12 200, 12 400		
	(11 290, 12 150, 12 460)	(18 050, 19 125, 20 000)	(29 620, 30 550, 30 955)

[a] Experimental data from ref. 7. [b] Experimental data from ref. 31. [c] Experimental data from ref. 8.

Table 2. Angular overlap and zero-field splitting parameters

Complex	Ni–X/pm	ξ/cm^{-1}	k	In-plane ligand		Axial ligand		D/cm^{-1}[c]	D_p/cm^{-1}[d]
				e_σ	e_π[a]	e_σ	e_π[b]		
$[Ni(py)_4Cl_2]$	244[e]	480	0.74	4 400	1 020	3 000	560	4.8	5.1
$[Ni(py)_4Br_2]$	258[f]	475	0.90	4 500	800	1 900	200	6.9	5.9
$[Ni(Hpz)_4Cl_2]$	251[g]	540	0.95	4 500	600	1 550	250	7.7	6.8
$[Ni(Hpz)_4Br_2]$	268[g]	420	0.90	4 450	600	1 000	160	6.0	7.4
$[Ni(mim)_4Cl]Cl$	[h]	400	0.90	4 600	1 500	3 000	1 000	11.0	15.8
$[Ni(mim)_4Br]Br$	253[h]	380	0.85	4 800	1 600	1 800	350	8.2	15.5
	357[h]					80	0		
$[Ni(en)_2(NO_2)_2]$	209[i]	550	0.90	3 900	0	4 200	−200	−1.6	−1.3

[a] π-Bonding parameter orthogonal to the plane of the ligand; in-plane π-bonding parameter assumed to be negligible. [b] π Bonding assumed to be symmetrical about the metal–ligand bond axis except for NO_2^-, where the π bonding in the plane of the nitrite was assumed to be negligible. [c] Calculated using a.o.m. [d] Calculated using simple perturbation expression; see text. [e] G. J. Long and P. J. Clarke, *Inorg. Chem.*, 1978, **17**, 1394. [f] A. S. Antsishk and M. A. Porai-Koshits, *Kristallografiya*, 1958, **3**, 676. [g] Ref. 36. [h] Ref. 33. [i] Ref. 22.

plane of the aromatic ligands is expected to be much less important than that with the orbitals normal to the ligand plane. Also, it is questionable how well the σ- and π-bonding interactions of the halide ions will be represented by the calculated overlap integrals. In the present study, as in other similar ones,[11,17,18] the π interactions in the plane of each aromatic amine ($e_{\pi s}$), and in the plane of the nitrite ligands, were set equal to zero. However, no restriction was placed on the values of the σ- and π-bonding parameters of each halide, except that of axial symmetry about the metal–halide bond ($e_{\pi s} = e_{\pi c} = e_\pi$). The π-bonding parameter of 1,2-diaminoethane was assumed to be zero; studies on other systems have shown that π interactions with this type of ligand are indeed small.[19,20]

In optimizing agreement with the experimental measurements, the a.o.m. parameters were first varied to produce calculated excited-state energies in good agreement with those observed experimentally. The effective spin–orbit coupling constant, ξ, and orbital reduction parameter, k, were then varied until the best fit between the calculated and experimental magnetic susceptibility data was obtained.

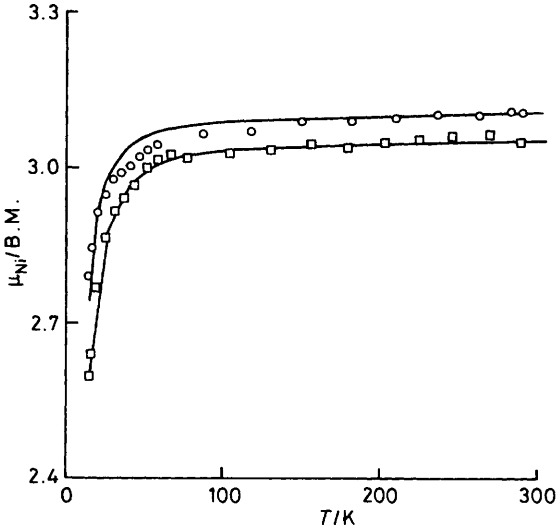

Figure 1. Magnetic moments (per Ni) as a function of temperature for $[Ni(py)_4Cl_2]$ (□) and $[Ni(py)_4Br_2]$ (○). The solid lines represent the best-fit variations calculated using the parameters listed in Table 2

The observed and calculated spin-allowed electronic transition energies of the complexes are listed in Table 1. Agreement between the two sets of data is generally satisfactory (within *ca.* 500 cm^{-1}), although it should be noted that, in one or two cases, predicted components of bands are not resolved experimentally. The angular overlap parameters used in the calculations are listed in Table 2, together with the values of ξ, k, and the zero-field splitting parameter D. The temperature dependence of the magnetic moments, μ, of $[Ni(py)_4X_2]$ (X = Cl or Br) is shown in Figure 1. It is apparent that in each case little change occurs above *ca.* 20 K but that below this temperature the magnetic moment drops sharply. This

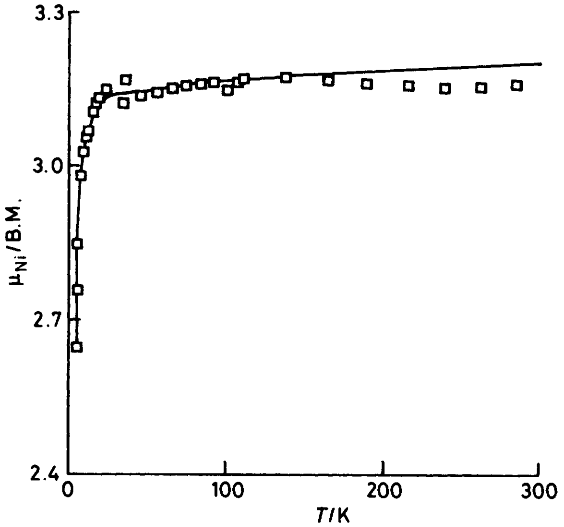

Figure 2. Magnetic moment (per Ni) as a function of temperature for $[Ni(Hpz)_4Cl_2]$ (□). The solid line represents the best-fit variations calculated using the parameters in Table 2 {Note: the data for $[Ni(Hpz)_4Br_2]$ are very similar and show better agreement with calculated values in the high-temperature region}

behaviour is characteristic of an isolated metal complex with tetragonal symmetry and a relatively small zero-field splitting of the ground state, and it can be seen that the variation of the magnetic moment calculated on this basis is in reasonable agreement with experiment. The behaviour of the magnetic moments of $[Ni(Hpz)_4X_2]$ (X = Cl or Br) is basically similar to that of the pyridine complexes, and agreement between the calculated and experimental values is very good in the low-temperature region, with some divergence at higher temperature, especially in the case of X = Cl (Figure 2).

Both complexes $[Ni(mim)_4X]X$ (X = Cl or Br) have magnetic moments which fall gradually as the temperature is lowered from *ca.* 180 to *ca.* 60 K, and then drop sharply as the temperature falls below this value (Figure 3). The gradual decrease in μ_{Ni} at higher temperatures implies that weak antiferromagnetic coupling occurs between the metal ions in both complexes, and this is confirmed by the plot of magnetic susceptibility against temperature, which shows a maximum at *ca.* 6 K in each case. The broad nature of the curve maximum suggests that the exchange involves chains rather than dimeric units, in agreement with the crystal structures of the complexes (see subsequent discussion).[7] Satisfactory agreement with experiment was obtained for the temperature variation of both the magnetic moment and susceptibility of each complex by adding a small contribution due to magnetic exchange, formulated in the Heisenberg linear coupling model,[21] to the values calculated using the angular overlap model (Figure 3). The magnetic-exchange parameters were estimated to be $J = -1.1 \pm 0.1$ and $J = -1.3 \pm 0.1$ cm^{-1} for the chloro and bromo complexes, respectively.

The variation of the magnetic moment of $[Ni(en)_2(NO_2)_2]$ also shows a gradual decrease as the temperature is lowered (Figure 4). Such behaviour appears typical of a large zero-field splitting of *ca.* 10 cm^{-1}, which is not in agreement with the value of $D = -1.6$ cm^{-1} deduced from the spectral analysis. Field-dependent magnetization measurements at 4.3 K could not be fitted to a single value of D, thus suggesting the presence of weak antiferromagnetic exchange in this system also. The data could be fitted satisfactorily assuming a dimeric spin Hamiltonian (two molecules occupy the unit cell of the complex),[22] and adding a contribution defined by $J = -0.45 \pm 0.02$ cm^{-1} to the magnetic moments estimated using the a.o.m. (Figure 4). It should be noted that the complex $[Ni(NH_3)_4(NO_2)_2]$ shows very similar magnetic behaviour to that reported here for $[Ni(en)_2(NO_2)_2]$. Initially, the data for the ammonia complex were interpreted in terms of a large zero-field splitting ($D = \pm 10.4$ cm^{-1})[23] but subsequent, more detailed studies also indicated the presence of weak magnetic exchange,[24] and a zero-field splitting of $D < 2$ cm^{-1}, compatible with that estimated for $[Ni(en)_2(NO_2)_2]$ in the present work.

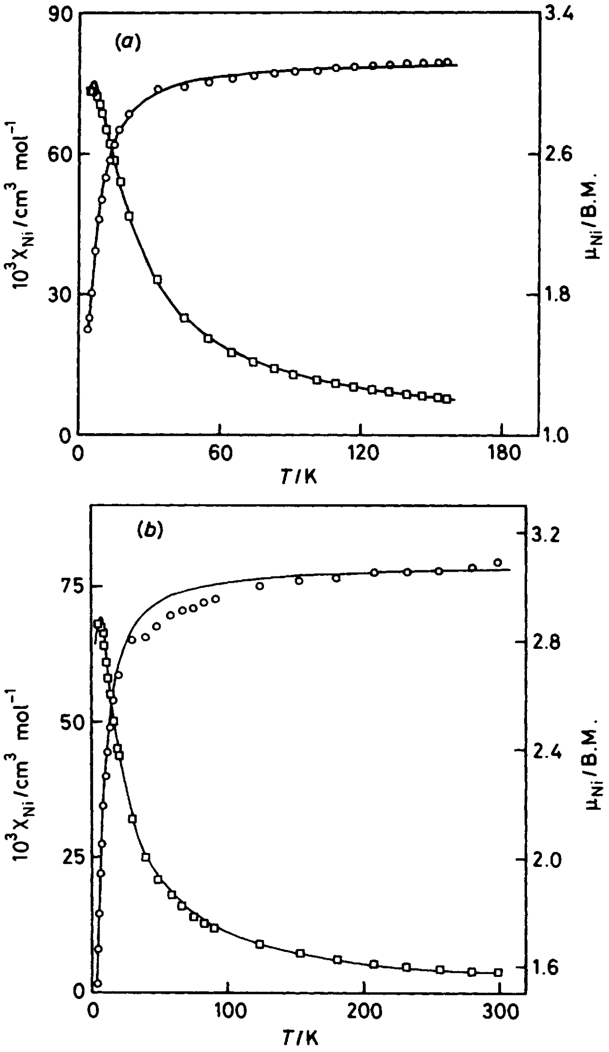

Figure 3. Magnetic moments (per Ni) (○) and magnetic susceptibilities (□) as a function of temperature for (*a*) $[Ni(mim)_4Cl]Cl$ and (*b*) $[Ni(mim)_4Br]Br$. The solid lines represent the best-fit variations using the parameters listed in Table 2 and exchange parameters $J = -1.1$ (*a*) and -1.3 cm^{-1} (*b*)

Metal–Ligand Bonding Parameters.—Recently, considerable interest has been shown in interpreting angular overlap parameters in terms of metal–ligand bonding interactions.[11–13,16–20] For instance, the negative values of e_π deduced for several nickel(II) phosphine and quinoline complexes have been taken to indicate π-acceptor character for these ligands.[25] The extent to which bonding parameters may be transferred from one complex to another has also aroused considerable interest.[12,13] While insufficient reliable data are yet available to be certain on the point, it does appear that, among complexes involving similar metal ions and ligands, the

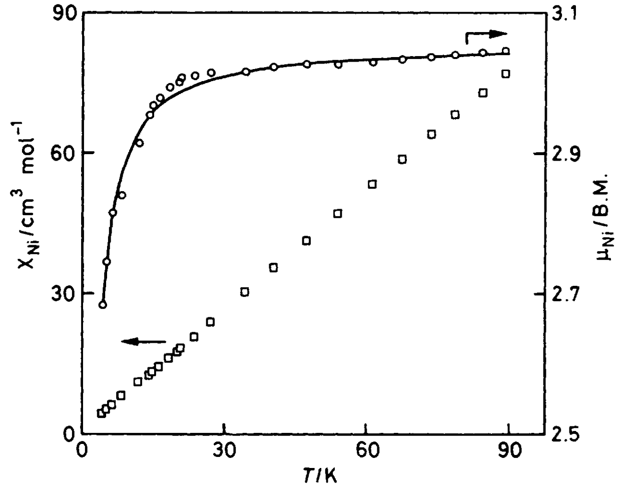

Figure 4. Magnetic moments (○) and reciprocal susceptibilities (□) of $[Ni(en)_2(NO_2)_2]$ as a function of temperature. The solid line represents the best-fit variations calculated using the parameters in Table 2 and a dimeric exchange parameter $J = -0.45$ cm^{-1}

bonding parameters of a particular ligand are broadly constant.[11,13,26] Also, variations in the bonding parameters appear to obey chemical 'commonsense'. Thus, if a series of complexes is compared involving different bond lengths, the bonding parameters tend to decrease as bond length increases. However, when comparing complexes in which a feature such as the oxidation state of the metal or its co-ordination number changes, then quite large differences in the bonding parameters of a ligand can be observed.[13,26] The out-of-plane π-bonding parameter of pyridine is of interest in this context. Several studies of complexes of this ligand with bivalent metal ions have implied a small positive value of e_π.[7,27,28] The optical spectra of a range of chromium(III) complexes, on the other hand, have been analyzed in terms of a small negative value of e_π, suggesting that here the pyridine functions as a weak π acceptor,[29] though this interpretation has been queried.[30]

The present analysis yields values of $e_\sigma \approx 4\,500$ and $e_{\pi c} \approx 900$ cm^{-1} for pyridine in $[Ni(py)_4X_2]$ (X = Cl or Br) (Table 2). These values are similar to those derived previously[7] from an analysis of the electronic spectra of the complexes, and are marginally larger than those reported[27] for a range of similar iron(II) and cobalt(II) pyridine complexes ($e_\sigma \approx 4\,000$, $e_{\pi c} \approx 100$ cm^{-1}). Very similar parameters ($e_\sigma \approx 4\,500$, $e_{\pi c} \approx 600$ cm^{-1}) were obtained in the present study for the amine ligands in the analogous pyrazole complexes (Table 2). These values are significantly smaller than those derived from a previous analysis of the electronic spectra ($e_\sigma \approx 5\,400$, $e_\pi \approx 1\,350$ cm^{-1}),[7] but are similar to those deduced for $[Co(Hpz)_4Cl_2]$ ($e_\sigma \leqslant 4\,300$, $e_\pi \leqslant 250$ cm^{-1}).[28] The values obtained in the present study for the 2-methylimidazole ligands are again independent of the halide, being rather larger than those of the other aromatic amines mentioned above. Here, the value of e_σ is smaller than that deduced previously from the electronic spectral data alone ($e_\sigma \approx 5\,900$, $e_{\pi c} \approx 1\,400$ cm^{-1})[7] though the e_π parameters are comparable. In comparing the present results with those from other studies, it must be stressed that the values depend upon the constraints placed upon the parameters, which, as outlined in the preceding section, are not always the same.

In agreement with the position of these ligands in the spectrochemical series, the present study suggests that the halide ions produce significantly weaker σ and π interactions than the amine ligands (Table 2). As expected, the π interaction is much smaller than the σ interaction, the ratio e_π/e_σ being *ca.* 0.2 and *ca.* 0.15 for chloride and bromide, respectively. This ratio is quite similar to that deduced in other systems, and is, in fact, approximately that expected from simple overlap considerations.[7] For the pair of complexes formed by any particular amine the chloride σ- and π-bonding parameters are greater than those of bromide, as would be expected from the relative positions of these ligands in the spectrochemical series. However, when the complexes of different amines are compared it is found that, while the halide parameters of the 2-methylimidazole and pyridine complexes are quite similar, much smaller values are deduced for both halides for the pyrazole complexes. The very weak axial ligand field in the pyrazole complexes has been noted in several previous studies.[31,32] The fact that both Cl and Br produce a similar effect in $[Ni(mim)_4X]X$ and $[Ni(py)_4X_2]$ is in good agreement with the predictions of the a.o.m. in its simplest form, in which the influence of the stereochemistry of a complex on the magnitude of the bonding parameters is ignored.[10] While in the pyridine complexes the metal is six-co-ordinate, in $[Ni(mim)_4Br]Br$ the nickel(II) is effectively five-co-ordinate (the *trans* Ni–Br bond lengths are 253 and 357 pm)[33] and the more distant halide may be assumed to have an insignificant effect on the *d* orbitals (values of $e_\sigma = 80$ and $e_\pi = 0.0$ cm^{-1}, based on overlap considerations,[7] were used in the calculations). The analogous chloro complex is isostructural with the bromo complex.[7] However, the bond lengths are unknown and the quoted bonding parameters represent the effects of both chlorides.

The e_σ and e_π values obtained in the present study for the above four complexes are quite similar to those reported for similar six-co-ordinate complexes of bivalent metal ions;[11,13,26] significantly higher values ($e_\sigma \approx 4\,000$, $e_\pi \approx 1\,500$ cm^{-1}) have been reported for a number of mixed-ligand pseudo-tetrahedral nickel(II) halide complexes.[25,34,35] The markedly lower values deduced in the present study for the e_σ and e_π parameters of the halide ions in the pyrazole complexes may reflect the unusually long metal–halide bond lengths in these complexes (Table 2).[36] However, the decrease in e_σ of almost 50% seems more than would be expected on this basis alone. Simple theory suggests that the perturbation of the *d* orbitals by the ligands should be inversely proportional to the fifth or sixth power of the bond length,[37] and this is borne out by experiment.[38] On this basis the observed bond lengths would suggest a decrease of only *ca.* 15% for e_σ (Cl$^-$), on going from $[Ni(py)_4Cl_2]$ to $[Ni(Hpz)_4Cl_2]$, and 20—30% for e_σ (Br$^-$), on going from $[Ni(py)_4Br_2]$ and $[Ni(mim)_4Br]Br$ to $[Ni(Hpz)_4Br_2]$. In the two pyrazole complexes the halide ions are hydrogen bonded to the amine ligands[34] and it has been suggested that this may reduce their power to bond to the metal ion.[31]

Another possibility is that the d_{z^2} orbital is depressed in energy because of the relatively large tetragonal component of the ligand field. It is now well established that in square-planar complexes the d_{z^2} orbital is depressed by 5 000—10 000 cm^{-1} from the energy expected from simple ligand-field arguments.[39] This depression has often been ascribed to configuration interaction between the metal $a_{1g}(d_{z^2})$ and $a_{1g}(s)$ orbitals,[40] though recently an alternative explanation within the framework of ligand-field theory has been proposed[41] involving the concept of ligand-field 'voids'. Whatever the cause of the depression, the effect should make the e_σ values of the axial ligands smaller than might otherwise be expected, as is indeed observed for the pyrazole complexes. However, it should be noted that the e_σ parameters of the five-co-ordinate 2-methylimidazole complexes are quite 'normal' despite the fact that these also have large tetragonal components to the ligand field. No firm conclusions can yet be drawn concerning the extent of an 'anomalous' depression of the d_{z^2} orbital in these nickel(II) complexes.

The value of $e_\sigma = 3\,900$ cm^{-1} for the amine groups in

$[Ni(en)_2(NO_2)_2]$ is quite similar to that reported for other complexes of this kind.[11,26] The parameters deduced for the nitro groups in this complex, $e_\sigma = 4\,200$, $e_\pi = -200$ cm^{-1}, are in agreement with the high position in the spectrochemical series of the nitrite ion bound in this way,[42] and imply that it is a stronger σ donor than 1,2-diaminoethane and functions as a very weak π acceptor. These results are in agreement with qualitative arguments concerning the way in which the metal–ligand interaction depends upon the type of nitrite co-ordination.[43]

Zero-field Splitting Parameters.—The zero-field splitting of the ground state of a complex with tetragonal symmetry is defined by: $D = E(1,-1) - E(0)$, where $E(1,0,-1)$ represents the energy of the state having spin quantum number $m_S = 1,0,-1$.[44] The effect is caused by the fact that the split components of the excited $^3T_{2g}$ and $^3T_{1g}$ states are connected *via* spin–orbit coupling to different spin components of the ground state. In general terms it is therefore expected that a large difference between the axial and in-plane ligand field will cause a significant splitting of the excited states, and a correspondingly large zero-field splitting. It is also noteworthy that the (± 1) spin doublet of the ground state is coupled to the ^3E_g orbital doublet of the first excited state, while the (0) spin singlet is connected to the non-degenerate $^3B_{2g}$ state. If the axial ligand is weaker than the in-plane ligand, the ^3E_g level should be lower in energy than the $^3B_{2g}$ level, resulting in a positive sign for D.[42] In some of the complexes a small rhombic component to the ligand field is also present, giving rise to a slight splitting of the (± 1) spin components; the quoted values of D (Table 2) represent the energy difference between the mean of these and the (0) spin state.

In the present halide complexes the axial ligand field is always less than the in-plane field, but increases sequentially along the series $[Ni(mim)_4X]X < [Ni(Hpz)_4X_2] < [Ni(py)_4X_2]$. It is therefore expected that D should be positive in sign, and progressively decrease along this series. For the chloride complexes this is indeed found to be the case (Table 2). However, for the bromide complexes, rather similar values for D are observed for all three complexes. As the tetragonal component to the ligand field increases, on replacing chloride by bromide, it is expected that D should increase when the two complexes of any one amine are compared. This is the case for the pyridine complex, but not for those of the other two amines, where slight decreases in D are observed. This apparent anomaly is due to the low value of the effective spin–orbit coupling constant in the bromide complexes of 2-methylimidazole and pyrazole. A greater degree of covalency is expected for this ligand compared with chloride, though it is not clear why a similar effect is not observed for the pyridine complexes. In the case of $[Ni(en)_2(NO_2)_2]$ the axial ligand is slightly stronger than the in-plane ligand, so that D should take a small negative value, and the data support this conclusion (Table 2). Reedijk and co-workers,[45] in an independent study of $[Ni(Hpz)_4X_2]$ (X = Cl or Br), obtained similar D values to those reported here. In this earlier work, which involved specific heat, magnetic saturation, and susceptibility measurements down to 2 K, spin-Hamiltonian methods were used to deduce the D values.

When the departure of the ligand field from octahedral symmetry is small, perturbation theory may be used to obtain an approximate estimate of the zero-field splitting:[44,45,*] $D_p \approx \xi^2[E(^3E_g) - E(^3B_{2g})]$. Substitution of the appropriate values of the excited-state energies (Table 1) into this equation, together with an effective one-electron spin–orbit coupling constant, $\xi \approx 450$ cm^{-1} for the chloro and nitro complexes, and $\xi \approx 400$ cm^{-1} for the bromo complexes, yields the estimates of D_p shown in Table 2.

Agreement with the values obtained using the complete a.o.m. treatment is reasonable (within *ca.* 20%) in every case except the highly distorted $[Ni(mim)_4X]X$ complexes. This means that it should be possible to use the simple perturbation approach to obtain an indication of the sign and order of magnitude of D in tetragonally distorted nickel(II) complexes in which the magnetic properties are dominated by exchange interactions.

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