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The *d*-Orbital Energies in a Planar Nickel(II) Amine Complex. Evidence for 4*s*–3*d* Orbital Mixing

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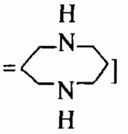
The relative energies of the *d*-orbitals in planar metal complexes have been the subject of considerable interest and controversy [1], particularly as they provide a useful way of testing the application of simple bonding models to transition metal compounds [2]. Perhaps the best method of establishing *d*-orbital energies is using single crystal polarized electronic spectroscopy and in this way the energy sequence $d_{x^2-y^2} \gg d_{xy} > d_{xz,yz} > d_{z^2}$ was determined for the planar ions MCl_4^{2-} (M = Pd[3], Pt[4] and Cu[5]). The energy levels in these ions were found to be in agreement with simple theory except that the d_{z^2} orbital was unexpectedly low in energy, and it has recently been proposed that this may be the result of configuration interaction with the higher energy metal *s* orbital [6, 7]. Nickel(II) readily forms planar complexes with saturated amines which sterically hinder axial ligation, and the knowledge of the *d*-orbital energies in such a compound would be especially interesting as simple theory suggests that covalent π-bonding should be absent. Recently, bis-(1,5-diazacyclooctane)nickel(II) perchlorate dihydrate

[$Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$, DACO = ]

was reported to contain planar $Ni(DACO)_2^{2+}$ units having effective D_{4h} symmetry and with no ligands coordinated along the z axis [8]. The room-temperature polarized crystal spectrum of this compound consisted of a single asymmetric peak, which could be resolved into the expected three components by gaussian analysis. The polarization properties of the bands suggested the energy sequence $d_{x^2-y^2} \gg d_{xy} > d_{xz,yz} > d_{z^2}$ but the precise energies of the *d*-orbitals were not derived [8]. In order to obtain these as accurately as possible the polarized spectrum of $Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$ has been remeasured at low temperature and the resulting energy levels have been interpreted in terms of current bonding models.

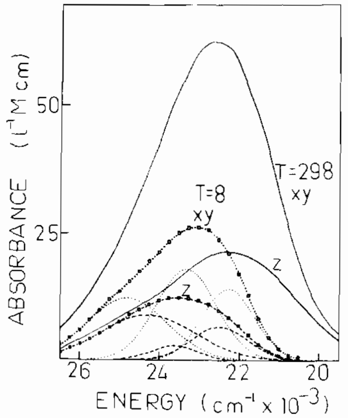


Figure 1. The polarized spectra of the (100) crystal face of $Ni(DACO)_2^{2+}$ with the electric vector approximately parallel to the *z* molecular axis and in the *xy* plane, measured at 298K and 8K. For the low temperature spectra the experimental results are shown as squares and the "best fit" gaussian curves and their resultant sums are indicated by dotted and dashed lines for the *xy* and *z* spectra, respectively. Quantitative absorbances (litres mol^{-1} cm) were obtained by measuring the crystal thickness using a microscope; these are probably accurate to ±15%.

Experimental

$Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$ was prepared as described previously [17] (analysis: calculated C = 27.61, H = 6.18; found C = 27.20, H = 6.33). The compound crystallized as plates with the (100) face well developed. The electronic spectrum of a masked crystal was measured using a Cary 17 spectrophotometer at room temperature and 8K with the electric vector of polarized light parallel and perpendicular to the *c* crystal axis (Figure). For the former spectrum the electric vector lies in the *xy* molecular plane, while for the latter it is almost exactly along the *z* axis [8]. The sample was cooled using an Oxford Instruments CF200 cryostat. The room temperature spectra are similar to those reported by Royer *et al.* [8]. In agreement with a vibronic intensity mechanism the spectra show a significant decrease in intensity on cooling, suggesting that low energy vibrations are responsible for much of the intensity. Unfortunately, however the resolution of the asymmetric bonds into their components is not markedly improved in the low temperature spectra. Three peaks are expected in this region for a low-spin nickel(II) complex of D_{4h} symmetry, due to the transitions ${}^1A_{1g} \rightarrow {}^1A_{2g}$ (d_{xy}), ${}^1A_{1g} \rightarrow {}^1B_{1g}$ (d_{z^2}) and ${}^1A_{1g} \rightarrow {}^1E_g$ ($d_{xz,yz}$), the *d*-orbital from which an electron is excited being shown in parenthesis. Each low-temperature spectrum was resolved into the "best" set of three gaussian components by a non-linear least squares procedure. Although gaussian analyses of this kind are often

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unreliable, the present results are supported by the close similarity in position and half-width of the components in the two polarizations (see Figure). Also, except for a shift of ~800 cm^{-1} to higher energy in each band maximum, the present analysis agrees well with that performed previously on the room temperature spectra [8].

Discussion

Derivation of the d*-Orbital Energies*

For a low-spin nickel(II) complex of D_{4h} symmetry the only transition forbidden by the vibronic selection rules is $^1A_{1g} \rightarrow {}^1A_{2g}$ in *z* polarization [8], and as the main difference between the (*z*) and (*xy*) spectra of $Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$ is the dramatic decrease of the central peak in (*z*) polarization, this may be assigned to the above transition. The selection rules do not allow the assignment of the other two peaks. In a nickel complex of this kind the *relative d*-orbital energies may be calculated exactly from the three low-energy spin-allowed transitions, assuming a fixed value of *B*; this was done for $Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$ using the matrix elements and fitting procedure given elsewhere [9]. Taking the values B = 800 cm^{-1}, C = 3,360 cm^{-1} (*cf.* free ion values B = 1084 cm^{-1}, C = 4831 cm^{-1} [10]) the spectral assignment I ($^1A_{1g} \rightarrow {}^1B_{1g}$ = 22,370, $^1A_{1g} \rightarrow {}^1A_{2g}$ = 23,480 cm^{-1}, $^1A_{1g} \rightarrow {}^1E_g$ = 24,540 cm^{-1}) yields the energies $E(d_{x^2-y^2})$ = 28,852 cm^{-1}, $E(d_{xy})$ = 3,765 cm^{-1}, $E(d_{z^2})$ = 1,430 cm^{-1}, relative to $E(d_{xz,yz})$ arbitrarily set to zero, while assignment II, in which the energies of the $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions are reversed, gives the values $E(d_{x^2-y^2})$ = 26,698 cm^{-1}, $E(d_{z^2})$ = –2,980 cm^{-1} and $E(d_{xy})$ = 1.590 cm^{-1}. The only other transitions calculated to lie below 30,000 cm^{-1} are $^1A_{1g} \rightarrow {}^3E_g$ at ~12,800 cm^{-1} and $^1A_{1g} \rightarrow {}^3A_{2g}$ at ~15,800 cm^{-1}, but these spin-forbidden transitions were not observed experimentally. Changing *B* and *C* by 10% produced shifts of less than 500 cm^{-1} in the calculated d-orbital energies.

Interpretation of the d*-Orbital Energies*

Perhaps the best simple bonding scheme currently available to rationalize the energy levels in metal complexes is the angular overlap model (*aom*) of Jϕrgensen and Schäffer [11]. This proposes that the energy *e* by which a *d*-orbital is raised upon interaction with one ligand orbital is proportional to the diatomic overlap integral *S*:

$$e_i = S_i^2 K_i \tag{1}$$

where *i* denotes that the interaction may be either σ or π in nature. For a ligand which is effectively isotropic to rotation about the metal–ligand bond axis the "strength" of the interaction may therefore be expressed in terms of two constants, K_σ and K_π. The total energy *E* of each orbital is obtained by summing over all the ligands, and for a planar complex these are given by:

$$E(d_{x^2-y^2}) = 3e_\sigma \tag{2a}$$

$$E(d_{z^2}) = e_\sigma \tag{2b}$$

$$E(d_{xy}) = 4e_\pi \tag{2c}$$

$$E(d_{xz,yz}) = 2e_\pi \tag{2d}$$

In the present case the problem is overdetermined, as the three experimentally observed energy differences are given in terms of just two parameters, e_σ and e_π. Equations 2c and 2d give e_π, and also the free ion *d*-energy ($-2e_\pi$, relative to $E(d_{xz,yz})$ in the complex), while $E(d_{x^2-y^2})$ then gives e_σ. The transition energies of assignment I then yield the values e_σ = 10,870 cm^{-1}, e_π = 1,885 cm^{-1} while those of assignment II give e_σ = 9,430 cm^{-1}, e_π = 795 cm^{-1}. Substitution of the diatomic overlap integrals S_σ = 0.1048, S_π = 0.0684 [12] appropriate to the Ni–N bond length of 1.945 Å in the $Ni(DACO)_2^{2+}$ ion [8] give the values K_σ = 0.990 × 10^6 cm^{-1}, K_π = 0.403 × 10^6 cm^{-1} and K_σ = 0.859 × 10^6 cm^{-1}, K_π = 0.170 × 10^6 cm^{-1} for assignments I and II respectively. As expected, the π-interaction is much weaker than the σ-interaction. In its simple form the *aom* predicts $e_\pi = K_\pi$ = 0 for a non π-bonding ligand. The observed splitting of the d_{xy} and d_{xz}, d_{yz} orbitals could be caused by a small electrostatic contribution to the bonding [2], or by interelectron repulsion effects associated with the different ligand interaction with the $d_{x^2-y^2}$ and d_{z^2} orbitals [13]. The electronic spectrum of the analogous complex $Cu(DACO)_2(ClO_4)_2 \cdot 2H_2O$ has peaks at 18,200, 20,800 and 23,100 cm^{-1}, and these have been assigned fairly unambiguously as $^2B_{1g} \rightarrow {}^2B_{2g}(d_{xy})$, $^2B_{1g} \rightarrow {}^2E_g(d_{xz,yz})$ and $^2B_{1g} \rightarrow {}^2A_{1g}(d_{z^2})$, respectively [8]. The crystal structure of the copper complex is unknown, but if, as seems probable, the molecular geometry is similar to that of the nickel compound, equations 2 a, c and d yield the parameters e_σ = 7,800 cm^{-1}, e_π = 1,300 cm^{-1}. The ratio e_σ:e_π is almost identical to that obtained from assignment I of the spectrum of $Ni(DCAO)_2^{2+}$, suggesting that this assignment is more likely to be correct. The lower magnitudes of the copper parameters are consistent with the longer metal–ligand bond length expected in this complex [14].

The main discrepancy between the *aom* and the observed spectrum of $Ni(DACO)_2^{2+}$ occurs in the energy of the d_{z^2} orbital. This is a σ-antibonding orbital, and in a planar complex it should be raised to 1/3 the energy of the $d_{x^2-y^2}$ orbital (a fact which has often been ignored in qualitative discussions of the bonding in planar complexes). Thus, in a planar complex where π-bonding is negligible the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ should occur at ~2/3 the energy of $d_{xy,xz,yz} \rightarrow d_{x^2-y^2}$, instead of being clustered together with these transitions, as is the case with Ni(DACO)$_2^{2+}$. It therefore seems that in Ni(DACO)$^{2+}$ the d_{z^2} orbital is depressed in energy compared with the predictions of the simple bonding model. A similar depression has been noted in planar CuCl$_4^{2-}$, and rationalized in terms of configuration interaction with the 4*s* orbital [6, 7]; in the D_{4h} point group these orbitals are connected by a matrix element proportional to the difference in ligand interaction along *x* and *z* [7]. In Ni(DACO)$_2^{2+}$ assignment I suggests a depression of 5,700 cm^{-1} (eqn. 2b) in good agreement with the value of ~5,000 cm^{-1} estimated for CuCl$_4^{2-}$ [6] (assignment II would require a depression of almost twice this value). Assuming a value of ~150,000 cm^{-1} for the energy of the nickel 4s orbital [15], perturbation theory indicates a mixing coefficient of ~0.2 for the 4*s* orbital in the lower energy wavefunction. While this cannot be confirmed directly in Ni(DACO)$^{2+}$, EPR studies of the isotropic hyperfine coupling constants of low-spin planar cobalt(II) complexes with $^2A_{1g}(d_{z^2})$ groundstates suggest that the unpaired electron spends 3–6% of its time in the metal 4*s* orbital [15]. This implies a mixing coefficient of ~0.2 in these compounds also, in good agreement with the present optical studies.

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