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Electronic Spectra of Planar Chelate Nickel(II) Complexes

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The electronic spectra of Ni(L–L)$_2$ complexes, where L–L is a bidentate ligand: DPM, dipivaloylmethene; Et$_2$dtc, N,N-diethyldithiocarbamate; Et$_2$-dtp, diethyldithiophosphate; EMG, ethylmethylglyoximate, have been interpreted by Crystal Field (CF) and Angular Overlap Methods (AOM). The real geometries of the complexes were used in these interpretations. The effect of the chelate angle (α) on the s–d mixing as well as that of the configurational and spin–orbital interaction on the transition energies have been traced. The parameters derived from the d–d spectral analysis have been used to interpret the charge transfer spectra (by the empirical Jǿrgensen's method) and the d-photoionization energies, calculating the deviations from the d-multiplet baricentre.

Introduction

Planar chelate nickel(II) complexes have thus far been extensively studied both experimentally [1–10] and theoretically [11–13]. The geometry of these complexes was found [6–9] to differ from the square planar one and the chelate angle (α) which quantitizes this deviation differs from 90°. Though the molecular structure of the Ni(bidentate)$_2$ complexes were known prior to the studies on their electronic spectra, these spectra were treated in D_{4h} symmetry [14] or the correct D_{2h} symmetry but using $\alpha = 90$ [13, 15]. Low-temperature spectral measurements have revealed [1, 3] the presence of 4 bands assignable to d–d transitions. This finding would be ignored in the D_{4h} treatments [16] and obscured by the $\alpha = 90$ assumption (two degenerate orbitals) in the D_{2h} treatment.

Table 1 shows the low-energy electronic spectra (10–35 kK) as well as relevant structural data for the studied Ni(II) complexes.

Similar results for the bis-chelate copper(II) complexes [17–20] have shown that the retention of the bite angle α as a variable in the matrix elements of the crystal field (CF) and angular overlap method (AOM) improves substantially the interpretation of the electronic and photoelectronic spectra of these compounds [21–23].

The planar geometry of the complexes under consideration makes possible the distinction between the in-plane and out-of-plane bonds. AOM [23] but not the conventional CF theory [22] can account for this difference, probably because of the greater number of AOM parameters and the resulting greater flexibility.

s–d Interaction was revealed recently [15, 24] to have a profound effect on the orbital energies and electronic spectra of planar D_{4h} complexes.

TABLE I. Structural Data and Crystal Spectra (in kK) of Planar Chelate Nickel(II) Complexes.

Complex^a	Ni(DPM)$_2$	Ni(Et$_2$dtc)$_2$	Ni(Et$_2$dtp)$_2$	Ni(EMG)$_2$	Ni(DMG)$_2$
R(Ni–L) (A)	1.836^b	2.201(2)^c	2.233^d	1.85(1)^e	1.85(1)^f
α	94.6^b	79.2^c	88.0^d	82.0^e	80.0^f
	16.0 y/z^j	15.9 x^g	14.9 $x > y^i$	20.2^h	18.6^h
	18.5 x^j	17.0 y^g	17.2 z^i	24.7^h	24.4^h
	20.0 x^j	19.0 z^g		26.0^h	25.3^h
		21.0 x^g	19.2 $x > y^i$	31.0^h	29.7^h

^{a}DMP, dipivaloylmethene; Et$_2$dtc, diethyldithiocarbamate; Et$_2$dtp, diethyldithiophosphate; EMG, ethylmethylglyoximate; DMG, dimethylglyoximate. ^{b}[7]. ^{c}[6]. ^{d}[10]. ^{e}[8]. ^{f}[9]. ^{g}[1, 3]. ^{h}[2]. ^{i}[1, 4]. ^{j}[5].

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TABLE II. State Energies of d^8 in D_{2h}, ${}^1A_g$ (hole formalism).

$(\overset{-}{a}_g)^2$	$(b_{2g})^2$	$(b_{3g})^2$	$(\overset{+}{a}_g)^2$	$(b_{1g})^2$	$(\overset{+}{a}_g, \overset{-}{a}_g)$
$4F_2 + 85F_4$ $-2E(x^2 - y^2)$	$3F_2 + 20F_4$	$3F_2 + 20F_4$	$4F_2 + 15F_4$	$35F_4$	$-\sqrt{2}A^{\pm}$
	$4F_2 + 85F_4$ $-2E(xz)$	$3F_2 + 20F_4$	$F_2 + 30F_4$	$3F_2 + 20F_4$	$\sqrt{6}(F_2 - 5F_4)$
		$4F_2 + 85F_4$ $-2E(yz)$	$F_2 + 30F_4$	$3F_2 + 20F_4$	$-\sqrt{6}(F_2 - 5F_4)$
			$4F_2 + 85F_4$ $-2E(z^2)$	$4F_2 + 15F_4$	$-\sqrt{2}A^{\pm}$
				$4F_2 + 85F_4$ $-2E(xy)$	0
					$70F_4 - E(z^2)$ $-E(x^2 - y^2)$

It is the purpose of the present work to interpret the spectra given in Table I by the AOM, taking explicitly into account the effect of the chelate angle and that of the s–d interaction in D_{2h} symmetry on the orbital energy and the d–d transition energies.

Theory

The expressions for the AOM orbital energies in D_{2h} symmetry have been obtained previously [21–22]. The a_g d–AO in D_{2h} are d_{z^2} and $d_{x^2-y^2}$ of Ni and these orbitals may mix with the s-AO of M. The lowering in energy of these d-AO's under the effect of mixing with the higher energy s-AO is given by the second order perturbation theory [24]:

$$\Delta E_{sd}(z^2) = -\frac{(s|A(D_{2h})|z^2)}{E(s) - E(z^2)} \tag{1}$$

$$\Delta E_{sd}(x^2 - y^2) = -\frac{(s|A(D_{2h})|x^2 - y^2)}{E(s) - E(x^2 - y^2)} \tag{2}$$

The numerators are the matrix elements of the AOM operator, $A(D_{2h})$. Using standard procedure [25], we obtained:

$$(s|A(D_{2h})|z^2) = -2e'_\sigma \tag{3}$$

$$(s|A(D_{2h})|x^2 - y^2) = -2\sqrt{3}\cos\alpha\, e'_\sigma \tag{4}$$

In these expressions $e'_\sigma = (s|A_z|d)$, where A_z is the ligand field operator of a donor atom located on the z-axis. Equation (4) vanishes at $\alpha = 90°$, as might be expected for D_{4h} symmetry. Substituting (3) and (4) into (1) and (2), respectively, we obtain

$$\Delta E_{sd}(z^2) = -\frac{4e'^2_\sigma}{E(s) - E(z^2)} \tag{5}$$

$$\Delta E_{sd}(x^2 - y^2) = -\frac{12e'^2_\sigma \cos^2\alpha}{E(s) - E(x^2 - y^2)} \tag{6}$$

We use further the notation for $\Delta E_{sd}(z^2)$ introduced elsewhere [24]:

$$\Delta E(z^2) = -\sigma_{sd} \tag{7}$$

The denominator in eqn. (6) may be transformed as follows:

$$E(s) - E(x^2 - y^2) = [E(s) - E(z^2)] \times \\ \times \left[1 + \frac{E(z^2) - E(x^2 - y^2)}{E(s) - E(z^2)}\right] \tag{8}$$

It has been found [15] for planar N-containing Ni(II) complexes that the following inequality holds

$$E(z^2) - E(x^2 - y^2) \ll E(s) - E(z^2) \tag{9}$$

TABLE III. State Energies of d^8 in D_{2h}, $^1B_{1g}$ (hole formalism).

(a_g^-, b_{1g})	(b_{2g}, b_{3g})	(a_g^+, b_{1g})
$4F_2 + 50F_4 - E(x^2 - y^2) - E(xy)$	0	$-A^{\pm}$
	$F_2 + 65F_4 - E(xz) - E(yz)$	$\sqrt{3}(2F_2 - 10F_4)$
		$70F_4 - E(z^2) - E(xy)$

TABLE IV. State Energies of d^8 in D_{2h}, $^1B_{2g}$ (hole formalism).

(b_{2g}, a_g^-)	(a_g^+, b_{2g})	(b_{3g}, b_{1g})
$F_2 + 65F_4 - E(xz) - E(x^2 - y^2)$	$-\sqrt{3}(F_2 - 5F_4) - A^{\pm}$	$-3F_2 + 15F_4$
	$3F_2 + 55F_4 - E(z^2) - E(xz)$	$-\sqrt{3}(F_2 - 5F_4)$
		$F_2 + 65F_4 - E(yz) - E(xy)$

TABLE V. State Energies of d^8 in D_{2h}, $^1B_{3g}$ (hole formalism).

(b_{3g}, a_g^-)	(b_{2g}, b_{1g})	(a_g^+, b_{3g})
$F_2 + 65F_4 - E(yz) - E(x^2 - y^2)$	$3F_2 - 15F_4$	$\sqrt{3}(F_2 - 5F_4) - A^{\pm}$
	$F_2 + 65F_4 - E(xz) - E(xy)$	$-\sqrt{3}(F_2 - 5F_4)$
		$3F_2 + 55F_4 - E(z^2) - E(yz)$

TABLE VI. State Energies of d^8 in D_{2h}, $^3B_{1g}$ (hole formalism).

(a_g^-, b_{1g})	(b_{2g}, b_{3g})	(a_g^+, b_{1g})
$4F_2 - 20F_4 - E(x^2 - y^2) - E(xy)$	$6F_2 - 30F_4$	$-A^{\pm}$
	$-5F_2 + 25F_4 - E(xz) - E(yz)$	0
		$-8F_2 + 40F_4 - E(z^2) - E(xy)$

Hence the second term in (8) may be neglected and after substituting in (6) with (7) and (8) we obtain for $E(x^2 - y^2)$:

$$\Delta E_{sd}(x^2 - y^2) = -3\cos^2\alpha\ \sigma_{sd} \tag{10}$$

We shall introduce further the s–d corrections obtained above to the orbital energies published elsewhere [21]:

$$E(z^2) = e_\sigma - \sigma_{sd}$$

TABLE VII. State Energies of d^8 in D_{2h}, $^3B_{2g}$ (hole formalism).

(b_{2g}, a_g^-)	(a_g^+, b_{2g})	(b_{3g}, b_{1g})
$-5F_2 + 25F_4 - E(x^2 - y^2) - E(xz)$	$3\sqrt{3}(F_2 - 5F_4) + A^{\pm}$	$-3F_2 + 15F_4$
	$F_2 - 5F_4 - E(xz) - E(z^2)$	$3\sqrt{3}(F_2 - 5F_4)$
		$-5F_2 + 25F_4 - E(yz) - E(xy)$

TABLE VIII. State Energies of d^8 in D_{2h}, $^3B_{3g}$ (hole formalism).

(b_{3g}, a_g^-)	(b_{2g}, b_{1g})	(a_g^+, b_{3g})
$-5F_2 + 25F_4 - E(x^2 - y^2) - E(yz)$	$3F_2 - 15F_4$	$-3\sqrt{3}(F_2 - 5F_4) + A^{\pm}$
	$-5F_2 + 25F_4 - E(xz) - E(xy)$	$3\sqrt{3}(F_2 - 5F_4)$
		$F_2 - 5F_4 - E(yz) - E(z^2)$

$$\begin{aligned}
E(x^2 - y^2) &= 3(e_\sigma - \sigma_{sd})\cos^2\alpha + 4e_{\pi s}\sin^2\alpha \\
E(xz) &= 2(e_{\pi c} + e_{\delta s}) - 2\cos\alpha(e_{\pi c} - e_{\delta s}) \\
E(yz) &= 2(e_{\pi c} + e_{\delta s}) + 2\cos\alpha(e_{\pi c} - e_{\delta s}) \\
E(xy) &= 3e_\sigma\sin^2\alpha + 4e_{\pi s}\cos^2\alpha \\
A^{\pm} &= (z^2 | A(D_{2h}) | x^2 - y^2) = \sqrt{3}\, e_\sigma\cos\alpha
\end{aligned} \tag{11}$$

These expressions transform into those for D_{4h} symmetry at $\alpha = 90°$ [25].

We have written the symmetry-adapted determinant functions for d^8 in D_{2h}. Using the matrix elements (11) and cauclating the matrix elements of the interelectron repulsion operator, we obtained the results collected in Tables II–VIII. In these tables F_o, F_2 and F_4 are the Slater-Condon electron repulsion parameters, E's are given by (11). We have preferred F_i instead of Racah's parameters A, B, D since the variations of F_i are directly related to changes in the M charge other than B and C [26].

When writing the determinant wave functions we have used the order of orbitals $a_g^+(d_{z^2})$, $b_{2g}(d_{xz})$, $b_{3g}(d_{yz})$, $a_g^-(d_{x^2-y^2})$, $b_{1g}(d_{xy})$.

A single ^3A_g state arises from the configuration (a_g^+, a_g^-) and its energy is:

$$^3A_g(a_g^+, a_g^-) = -8F_2 + 40F_4 - E(z^2) - E(x^2 - y^2)$$

Note that the signs in front of the orbital energies are negative, so that the above results hold for d^8. The same results may be used also for d^2 after changing the signs in front of the orbital energies.

It should also be noted that $A = F_o - 49F_4$ has been dropped out of the diagonal elements in Tables II–VIII for the d^8 configuration. For d^8, besides changing the signs in front of the orbital energies, $28A - 42B + 21C = 28F_o - 42F_2 - 427F_4$ should be added to all diagonal elements.

Results and Discussion

Interpretation of the Ligand Field Spectra

Table IX shows the calculated d–d transition energies as well as the AOM parameters inferred from the spectral analysis. To check the assignment we have calculated the M–L overlap integrals with experimental M–L bond lengths. In these calculations sp^2 hybrids for N and O of the ligands and pure p for S were used. The calculated parameter ratios $e_{\pi c}/e_\sigma$ and $e_{\pi s}/e_{\pi c}$ are close to those obtained from the spectral analysis. Thus, for example $e_{\pi c}/e_\sigma$ = 0.18 and $e_{\pi s}/e_{\pi c}$ = 0.09 were obtained from the spectra and 0.12 and zero, respectively, from the overlap integrals. The zero value for $e_{\pi s}/e_{\pi c}$ is easily explained by considering that the nitrogen atoms in $Ni(EMG)_2$ have no free in-plane pi-electron pairs.

Since for $Ni(DMG)_2$ there are metal–metal intermolecular contacts [9], we prefer to interpret the $Ni(EMG)_2$ for which such contacts are found lacking [8]. We shall, however, subsequently compare

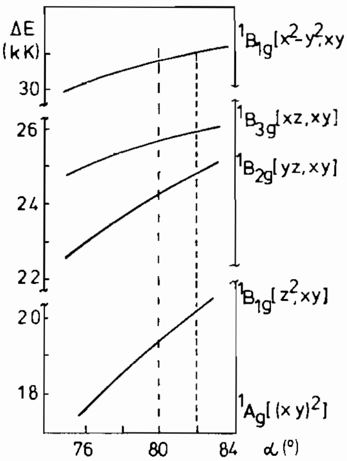

Fig. 1. Variation of the transition energies ΔE (in kK) as a function of the bite angle, α. The parameters used to calculate ΔE are those of $Ni(EMG)_2$ (see Table IX).

the electronic spectra and the molecular structure of these two complexes.

The number of observed singlet–singlet transitions depends on the energy difference for the states $^1B_{2g}(b_{3g}, b_{1g})$ and $^1B_{3g}(b_{2g}, b_{1g})$ (*vide infra*). It is seen from Tables IV and V (CI neglected) that this difference is

$$\Delta E = E(^1B_{2g}) - E(^1B_{3g}) = 4\cos\alpha(e_{\pi c} - e_{\delta s}) \tag{12}$$

For the complexes under consideration $e_{\pi c} - e_{\delta s} \approx 0.8 - 2.6$ kK so that α is of major importance. For the complexes $Ni(Et_2dtc)_2$ ($\alpha = 79.2°$) and $Ni(EMG)_2$ ($\alpha = 82°$) the difference ΔE is about 2 kK and the two transitions appear as separate bands.

For $Ni(DPM)_2$ ($\alpha = 95°$) and $Ni(Et_2dtp)_2$ ($\alpha = 88°$) this difference does not exceed 0.4 kK; the two bands coalesce so that only 3 bands are observed in the electronic spectrum.

Figure 1 presents the variation of the d–d transition energies with the chelate angle using the parameters of the $Ni(EMG)_2$ complex. The effect of α is more strongly expressed for the two low energy d–d transitions. Assuming that the AOM parameters would be the same for the two complexes $Ni(EMG)_2$ and $Ni(DMG)_2$ it is seen from the two α values (82 and 80°, respectively) that the spectra of the two complexes may be explained in terms of the α-variation. In fact the $Ni(DMG)_2$ bands are found at lower energies whereas those of $Ni(EMG)_2$ appear at higher energies: 19.5, 24.3, 25.7 and 30.8 kK at $\alpha = 80°$ (compare with Table I).

The s–d mixing affects the z^2 and $x^2 - y^2$ and consequently the transition energies $^1A_g \rightarrow {}^1B_{1g}$ (z^2, xy) and $^1A_g \rightarrow {}^1B_{1g}(x^2 - y^2, xy)$.

It follows from (10) that the decrease in $d_{x^2-y^2}$ energy depends heavily on the bite angle, and that it is negligible at α values close to 80°. In fact $\Delta E(x^2 - y^2)$ amounts to 0.54 at 80° and $\sigma_{sd} \sim 6$kK, whereas $\Delta E(z^2)$ is 6 kK for the same parameter values. Evidently, this difference in the behaviour of the two a_g-orbitals is due to their different angular properties and the effect of the ligand location, taken into account by α. Hence the $^1A_g \rightarrow {}^1B_{1g}(x^2 - y^2, xy)$ would depress its energy under the effect of σ_{sd} mainly via mixing of the two states $^1B_{1g}(x^2 - y^2, xy)$ and $^1B_{1g}(z^2, xy)$ effected by the off-diagonal elements (Table III).

The d-orbital order, derived from the spectral analysis is:

$$xy \gg z^2 > yz > xz > x^2 - y^2 \tag{13}$$

for the complexes $Ni(Et_2dtc)_2$, $Ni(et_2dtp)_2$ and $Ni(EMG)_2$ and

$$xy \gg z^2 > x^2 - y^2 \gtrsim xz > yz \tag{13a}$$

for $Ni(DPM)_2$, which is the well known Belford-Hitchmann order [18a] for the acetylacetonates. Sequence (13) coincides with the Dingle order [3] for $Ni(Et_2dtc)_2$ and that for $Cu(Et_2dtc)_2$ [23], but differs as to the positions of $x^2 - y^2$ and z^2, which is immaterial when there is large mixing between the a_g-orbitals (eqn. 11).

The two alternative ground states are $^1A_g(xy, xy)$ and $^3B_{1g}(z^2, xy)$. For ^1A_g to be the ground state the following inequality must hold (CI neglected).

$$12F_2 + 45F_4 < e_\sigma(3\sin^2\alpha - 1) + \sigma_{sd} + 4e_{\pi s}\cos^2\alpha \tag{14}$$

For values close to 90° we obtain

$$12F_2 + 45F_4 < 2e_\sigma + \sigma_{sd} \tag{15}$$

It is seen from this inequality that σ_{sd} further to e_σ contributes for a singlet ground state. The e_π and e_δ AOM parameters are absent from (14), hence π and δ bonds in the planar Ni(II) complexes to a first order approximation are not important in determining the ground state spin multiplicity.

In the D_{2h} symmetry, the first order spin orbit coupling is zero. The second order spin orbit interaction* splits the triplets by less than 1 kK and the singlets are shifted by less than 0.3 kK. The squared mixing coefficients between the singlet and triplet state functions do not exceed 0.04. Hence the spin–orbit interaction is obviously not a major factor for the spectral behaviour of the Ni(II) complexes.

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*The full state energy matrices of the d^2 and d^8 configurations in the double D_{2h}' group may be obtained from the authors on request.

TABLE IX. Calculated and Experimental d–d Transitions Energies and AOM and Electron Repulsion Parameters, Derived from d–d Spectral Analysis (in kK).

Transitions	Calculated Transition Energies[a]			
	$Ni(DPM)_2$ NiO_4	$Ni(Et_2dtc)_2$ NiS_4	$Ni(EMG)_2$ NiN_4	$Ni(Et_2dtp)_2$ NiS_4
$^1A_g \rightarrow {}^1B_{1g}$	15.87(16.0)	15.62(15.9)	20.20(20.2)	14.89(14.9)
$\rightarrow {}^1B_{2g}$	19.83 (20.0)	17.10(17.0)	24.70(24.7)	17.42 (17.2)
$\rightarrow {}^1B_{3g}$	19.56	19.10(19.0)	26.00(26.0)	17.82
$\rightarrow {}^1B_{1g}$	18.79(18.5)	21.03(21.0)	31.00(31.0)	19.23(19.2)
Calculated AOM and interelectron repulsion parameters[b]				
e_σ	8.02	8.22	11.0	7.65
$e_{\pi s}$	0.51	0	0.18	0.33
$e_{\pi c}$	0.84	1.86	2.00	1.61
e_δ	–	–0.81	–	–1.00
σ_{sd}	2.67	5.84	3.21	4.21
F_2	0.20	0.60	0.90	1.20
F_4	0.13	0.20	0.05	0.14

[a] For comparison the experimental values are given in parenthesis (see Table I). [b] These parameter values fit both the d–d, CT and PES transitions (*vide infra*).

Discussion of the spectral Parameters

It is seen from Table IX that the σ_{sd} values obtained are lower than those expected from the equation $\sigma_{sd} = e_\sigma$, put forward recently [24]. On the other hand they are close to σ_{sd} for other planar complexes [15, 27]. In general the σ_{sd} variations follow Pearson's soft and hard base concepts [27b]. Thus for example, σ_{sd} for the soft-base dithiocarbamate is twice as large as for the other two complexes with nitrogen and oxygen as donor atoms. It is seen from Tables II and III that the energy of the $^1B_{1g}(z^2, xy) \rightarrow {}^1A_g(xy, xy)$ transition (CI neglected) is

$$-4F_2 - 15F_4 + e_\sigma(3\sin^2\alpha - 1) - \sigma_{sd} =$$

$$= -4F_2 - 15F_4 + e'_\sigma(3\sin^2\alpha - 1) \qquad (16)$$

where e'_σ was introduced to compensate for the neglect of σ_{sd} in the right hand side of (16). Hence

$$e'_\sigma = e_\sigma + \frac{\sigma_{sd}}{3\sin^2\alpha - 1} \qquad (17)$$

The second term in this equality is a positive quantity when $\sigma_{sd} > 0$ and $3\sin^2\alpha - 1 > 0$, or $\alpha > 35°$. These conditions obviously hold for all chelate complexes (see for example [6–9]), hence e'_σ derived from electronic spectra with the neglect of σ_{sd} would have larger values than when s–d mixing is accounted for.

The $e_{\pi c}$ and $e_{\pi s}$ parameters span the following order:

$e_{\pi c}$: N ~ S > O

and

$e_{\pi s}$: O > N ~ S ≈ zero

The $e_{\pi c}$ values are higher than those of $e_{\pi s}$. This may be explained when taking into account that the ligands are conjugated systems with out-of-plane pi-orbitals. The zero value of the $e_{\pi s}$ parameter for $Ni(Et_2dtc)_2$ may be attributed to ∡CSM ~90° so that the sulphur orbitals should be pure p-AO and there are no $p_\pi(S)$ in the molecular plane. For $Ni(EMG)_2$ the donor nitrogen atoms have no available in-plane pi-orbital hence $e_{\pi s} \sim 0$ is to be expected. The low $e_{\pi s}$ value for this complex, as well as for $Ni(Et_2dtp)_2$ is due to the electrostatic contribution to the AOM parameters [28, 15].

The negative e_δ value for $Ni(Et_2dtc)_2$ and $Ni(Et_2dtp)_2$ is compatible with sulphur d-orbitals being located higher than the d_δ AO of Ni. The absolute value of this parameter shows that it cannot be neglected for complexes with sulphur donor atoms.

Charge Transfer Transitions

We have calculated the CT transition energies by a modification of the Jørgensen method [29], in

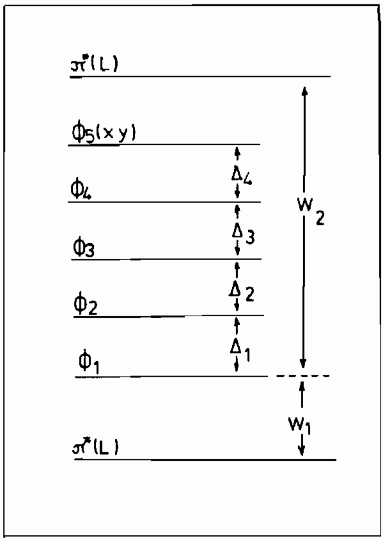

Fig. 2. Illustration of the energy differences and notation of quantities used in the empirical Jørgensen's method for calculating the CT-transition energies.

TABLE X. Calculated and Experimental [1, 3] Transition Energies, Polarizations and Assignment of the CT Transitions of $Ni(Et_2dtc)_2$ (kK).

Transition energies			Assignment
Calc.	Experimental		
	Crystal [3]	Soln [3]	
23.59	23.0 (x, y, z)	23.0	xy
		25.6	solv?
30.30		31.0	z^2, x^2-y^2
31.65			yz

which we use the spectral parameters obtained from the d–d spectral analysis [30]. Among the complexes under consideration only $Ni(Et_2dtc)_2$ and $Ni(EMG)_2$ display two or more CT bands in the UV spectrum.

The expressions for the CT transitions of d^8 M in D_{2h} ligand field can be written as [29, 30]:

$$\pi \rightarrow xy = W_1 + \Delta_1 + \Delta_2 + \Delta_3 + \Delta_4 - 8(E-A) + 4/3\ D$$

$$\phi_1 \rightarrow \pi^* = W_2 + 7(E-A) - 1/3\ D$$

$$\phi_2 \rightarrow \pi^* = W_2 - \Delta_1 + 7(E-A) - 1/3\ D \qquad (18)$$

$$\phi_3 \rightarrow \pi^* = W_2 - \Delta_1 - \Delta_2 + 7(E-A) - 1/3\ D$$

$$\phi_4 \rightarrow \pi^* = W_2 - \Delta_1 - \Delta_2 - \Delta_3 + 7(E-A) - 1/3\ D$$

where $\Delta_1 = E(xy) - E(z^2)$, $\Delta_2 = E(z^2) - E(yz)$, $\Delta_3 = E(yz) - E(xz)$ and $\Delta_4 = E(xz) - E(x^2-y^2)$, together with W_1 and W_2 are denoted in Fig. 2. E – A is a one-electron parameter, D is the spin-pairing parameter [29]. We have used W_1 = 29.3 kK, W_2 = 19.6 kK, found for a large number of tris-dtc complexes, and E – A = 2.7 kK found for the first transition series [30] to interpret the CT transitions of $Ni(Et_2dtc)_2$ (Table X).

The energy of the first parity allowed CT transition (L → M) we have calculated by another procedure [31] based on linear relationships between the ligand field parameters and the atomic characteristics (electronegativity, charge, number of valence electrons). The value obtained is 23.51 kK, rather close to the one given in Table X.

The CT transitions of $Ni(DMG)_2$ have been considered previously [2]. The high-intensity maxima at 23, 26.2 and 27.4 kK (not listed in Table I) have been assigned to $z^2 \rightarrow p_z\pi$, $yz \rightarrow p_z\pi$ and $xz \rightarrow p_z\pi$ transitions, respectively. The d–AO order obtained from the d–d spectral analysis is consistent with this interpretation of the CT transitions. It is seen that the d–d transitions are shifted by about 2 kK from the corresponding CT M → L transition. In the Jørgensen method this implies that the spacing between the vacant xy orbital and the antibonding MO is also about 2 kK.

Photoelectronic Spectra

We have used the parameters listed in Table IX to interpret the photoelectronic spectra of $Ni(Et_2dtc)_2$ and $Ni(DPM)_2$. Regardless of the expected deviations from the Koopmans theorem for d-orbital ionizations [32], we assume that these deviations are equal for the slightly antibonding d–AO of Ni. A detailed description of the computational procedure was given elsewhere [23]. The expressions for d-photoionization from the respective d-orbitals are:

$$\begin{aligned} IE(b_{3g}) &= IE_o + 5B - E(b_{3g}) \\ IE(b_{2g}) &= IE_o + 5B - E(b_{2g}) \\ IE(a'_g) &= IE_o + 20(1-c^2)B - E(a'_g) \qquad (19) \\ IE(a''_g) &= IE_o + 20c^2B - E(a''_g) \\ (a'_g|H|a''_g) &= +20c\sqrt{1-c^2}B \end{aligned}$$

where IE_o is the d-ionization energy of the unperturbed free atom or ion, $B = F_2 - 5F_4$ is the Racah

TABLE XI. d-Photoelectron Spectra of Three Planar Chelate Complexes of Nickel(II) (in eV).

Ionization from orbital	$Ni(Et_2dtc)_2$		Ionization from orbital	$Ni(DPM)_2$		Ionization from orbital	$Ni(Et_2dtp)_2$	
	Calc.	Exp [35]		Calc.	Exp. [36]		Calc.	Exp [37]
z^2	6.98	6.95 7.13	$x^2 - y^2$	7.32	7.40	z^2	8.11	8.37
yz	7.76	7.84	z^2	7.86	7.85	yz	8.42	
xz	8.01	8.10	yz	8.05	8.00	xz	8.45	
$x^2 - y^2$	8.45	8.66	xz	8.08		$x^2 - y^2$	9.46	9.20

parameter, calculated with F_2 and F_4 taken from the d–d and CT spectral analyses, and $E(x_i)$ are the orbital energies, calculated with the AOM parameters listed in Table IX, relative to the assumed zero of the multiplet (IE_o). a_g' and a_g'' have been used to denote the symmetric and antisymmetric combination of the z^2 and $x^2 - y^2$ orbital mixed under the effect of the ligand field operator. The mixing coefficient c is the multiplier of z^2 in the symmetric combination.

As seen from (19), the off-diagonal element appearing between states resulting from a_g ionizations has been accounted for. The only unknown quantity in (19) is IE_o and following the electroneutrality principle [33] which predicts a charge of Ni close to zero we have used $IE_o = 7.63$ eV = 61.54 kK [34], which is the first ionization energy of Ni. The results of these calculations are listed in Table XI.

A survey of eqns. (19) and Table XI shows the following peculiar feature. Since the energies of the filled d–AO's, referred to the baricentre have negative values, and they feature with a negative sign in (19), it follows that $IE < IE_o$ or $IE > IE_o$ depending on the value of B. When $B < 0$, a single or several d-ionization energies may be observed at values lower than IE_o and this is the case with $Ni(Et_2dtc)_2$ and $Ni(DPM)_2$. The opposite case ($B = 0.500$ kK > 0) has been observed for $Ni(Et_2dtp)_2$. This is in good agreement with the higher M–L bond ionicity for this complex [10a].

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