Inorganica Chimica Acta, 61 (1982) 199–206

d–s-Mixing as a Rationale for Structural Similarities between hexacoordinated Ni(II)- and Cu(II)-Complexes

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Received December 18, 1981

The role of d–s-mixing has been investigated in hexacoordinated complexes of Cu(II) and Ni(II). It is concluded that the structural, spectral, thermodynamic and kinetic similarities between both sets of complexes might be related to the interaction between 3d$_{z^2}$ and 4s under the influence of axial elongation.

Introduction

The Ligand Field (LF) theory of transition metal ions is essentially a d-orbital model. This model is at the basis of most discussions on the electronic structure of coordination compounds; it has scored remarkable successes in rationalizing spectra [1], magnetic [2] and structural [3] data, and thermal [4] or photochemical [5] reactivity trends for a host of complexes, including almost every element of the transition series.

Occasionally it was realized that, under certain symmetry conditions, other metal orbitals (notably the vacant (n + 1)s- and (n + 1)p-orbitals) could mix in with the nd-orbitals, resulting in hybrids with altered bonding capabilities [6]. Although this mixing interferes with the basic assumptions of ligand field theory, in practice it was considered to be of only secondary importance [7].

However in recent years, rapidly accumulating spectroscopical evidence on square planar complexes has shown that—contrary to previous belief—(n + 1)s–nd$_{z^2}$-mixing leads to effects of the same order of magnitude as the first order LF-energies [8–10]. Corrections of this magnitude should also be expected to have predictable consequences for the structural, thermodynamic and kinetic properties of metal complexes. As a matter of fact, they can offer a rationale for certain apparent anomalies, which remain puzzling in a d-only treatment.

Recently, Yamatera, one of the initiators of the angular overlap model (AOM) [11], recognized the important role of d–s-mixing in the structural chemistry of Cu(II)-complexes [12]. The very same conclusions were reached independently by Gerloch [13] and Burdett [14]. It is our purpose to extend these ideas to the more intricate question of the structural similarities between hexacoordinated d^8- and d^9-complexes.

Structural Features of Six-Coordinated Ni(II)- and Cu(II)-Complexes

It is well known [15] that the vast majority of six-coordinated Cu(II)-complexes contains four normal (short) equatorial bonds and two long axial bonds, reflecting the Jahn–Teller elongation of the degenerate ^2E_g octahedral ground-state ($t_{2g}^6e_g^3$). Another manifestation of essentially the same distortional preference is the formation of $Cu(NH_3)_4(H_2O)_2^{2+}$ in aqueous ammonia, where the weak H_2O-ligands occupy the axial sites [16]. As mentioned in the Introduction, this preference for axial elongation has been attributed by several authors to d–s-mixing [12–14]. The argument of these authors goes as follows: the elongated octahedron (EO) is more stabilized than the compressed octahedron (CO), because in EO the ground state corresponds to $(z^2)^2(x^2 - y^2)^1$, while in CO the ground state corresponds to $(z^2)^1(x^2 - y^2)^2$. In the D_{4h}-symmetry (common to EO and CO), d$_{z^2}$ and s span a_{1g}-representations, while d$_{x^2-y^2}$ is a basis for b_{1g}. Therefore, only d$_{z^2}$ is stabilized by the d–s-mixing, and the maximal occupation of this orbital leads to the most stable structure.

Octahedral Ni(II)-complexes on the other hand have their metal e_g-orbitals occupied by only two electrons, corresponding to a ground state configuration $(z^2)^1(x^2 - y^2)^1$. Yet, for no obvious reason, they exhibit a remarkable structural resemblance to the copper case [7, 17]. This can be concluded from a spectral analysis (A) and from kinetic indications (B).

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A. Spectra of trans-NiN_4X_2*-Complexes*

The tendency for axial elongation is observed in several *trans*-NiN_4X_2-complexes, where N_4 stands for an equatorial coordination consisting of four nitrogen donors: X is an axial π-donor ligand, with moderate σ-strength. Table I shows some pertinent examples, taken from low temperature spectral studies on various tetragonal complexes [18]. It is seen from the Table that the axial ligand field strength (10 Dq_X) is smaller than the value obtained for an octahedral NiX_6-complex, a fact which is consistent with axial elongation. This elongation appears to be more pronounced when the equatorial σ-strength (σ_{eq}) is increased. For the largest σ-donor of the series in Table I, there is a definite tendency towards asymmetrization of the tetragonal axis, and the metal is somewhat lifted out of the equatorial plane.

TABLE I. 10 Dq_X-value (in cm^{-1}) for a Series of *trans*-NiN_4X_2-complexes [18] (X = Cl, Br) as a Function of the Equatorial σ-Parameters. R_{Ni-X} is the Metal–X-Distance in pm. Octahedral NiX_6^{4-}-Complexes are Included for Comparison.

	σ_{eq}	10 Dq_X	R_{Ni-X}	Ref.
$NiCl_6^{4-}$		7200		19[a]
$Ni(py)_4Cl_2$	4670	6780	244	20, 21, 26
$Ni(pyr)_4Cl_2$	5480	6100	251	21
$[Ni(im)_4Cl]Cl$	6020	6510		21[b]
		270		
$Ni(s\text{-}Et_2en)_2Cl_2$	3972	6240		22
$NiBr_6^{4-}$		6800		19[a]
$Ni(py)_4Br_2$	4500	5990	258	21
$Ni(pyr)_4Br_2$	5440	4980	268	21
$[Ni(im)_4Br]Br$	5820	6410	253	21[b]
		240	357	
$Ni(s\text{-}Et_2en)_2Br_2$	3923	6110		22

[a] NiX_2 crystal spectra. [b] Square pyramidal complexes, with one additional loose Ni–X bond.

It is important to stress here that the ligand field parameters proposed in the literature are not entirely satisfactory. In Table I we had to make a selection of non-conflicting values. For certain complexes, such as $Ni(en)_2(NCS)_2$ or $Ni(s\text{-}Et_2en)_2(H_2O)_2^{2+}$, the published [22, 23] σ_X values are extremely small, and $\pi_X < 0$, while for apparently very similar complexes [23, 24], such as *trans*-$Ni(NH_3)_4(NCS)_2$ or $Ni(as\text{-}Me_2en)_2$(trichloro-acetate)$_2$, normal σ_X-values and positive π_X-parameters are proposed [25]. The main source of this inconsistency seems to be the controversial assignment of certain spectral bands.

B. Kinetic Indications

An extreme tetragonal elongation carries the octahedron over into a square plane. The equilibrium of both structures is indeed observed for several Ni(II)-complexes. The typical behavior of Lifschitz salts (diamagnetic square planar Ni(II)N_4) is a well documented example [17]. In a solvent with moderate σ-donor characteristics, a paramagnetic six-coordinated complex is formed, but in some cases, the low spin species can be restored in a reversible process and an equilibrium between both forms is established. Interestingly, *only* the hexacoordinated *trans*-isomer can undergo a spin flip reaction to a square plane [27, 28]:

$$
\begin{aligned}
&cis\text{-Ni}[2,3,2\,\text{tet}](H_2O)_2^{2+} \xrightleftharpoons{\text{slow}} \\
&\qquad trans\text{-Ni}[2,3,2\,\text{tet}](H_2O)_2^{2+} \xrightleftharpoons{\text{fast}} \\
&\qquad\qquad \text{Ni}[2,3,2\,\text{tet}]^{2+} + 2H_2O
\end{aligned}
\tag{1}
$$

where 2, 3, 2 tet stands for 1, 4, 8, 11-tetraazaundecane.

The great majority of NiN_4X_2-complexes have *trans*-configurations, although it is true that a *cis*-geometry can be stabilized in certain solvents (or because of steric effects, such as a more favorable folding of the chain that encloses the N-donor atoms [27, 29]).

The few examples given above illustrate a claim [7, 17]—which is often renewed—that Ni(II)- and Cu(II)-complexes in a certain sense belong to the same family. This observation presents a curious problem for the d-only model [7]. Indeed, the Jahn–Teller effect cannot be operational in the orbitally non-degenerate ground state of Ni(II)-complexes. Even the d–s-mixing model, as far as it is based on the occupation of d_{z^2}, cannot be invoked here since both e_g-orbitals are equally occupied in the $^3A_{2g}$-ground state of d^8-systems. It is the purpose of this note to show that d–s-mixing might nevertheless play a role in the structural chemistry of Ni(II)-compounds, which is to some extent related to the role it plays in Cu(II)-complexes.

Description of the Model

For one ligand on the z-axis, ligand field theory—in its AOM-version [8, 30, 31]—introduces two parameters (to the neglect of δ-interactions):

$$
\begin{aligned}
&(z^2|V^z|z^2) = \sigma \\
&(xz|V^z|xz) = (yz|V^z|yz) = \pi
\end{aligned}
\tag{2}
$$

For one ligand on an arbitrary p-axis, specified by angular coordinates (θ, φ), one introduces the rotation matrix $\mathbb{D}(\theta, \varphi)$ transforming the standard basis set

$$\mathbb{d} = (z^2, yz, xz, xy, x^2 - y^2)$$

into a set of rotated d-functions, $\mathbb{d}'$, where $(z^2)'$ has rotational symmetry about the p-axis

$$\mathbb{d}' = \mathbb{d}\mathbb{D} \tag{3}$$

From this transformation, any matrix-element $(d_i|V^p|d_j)$ can be expressed in terms of σ and π. If more than one ligand is present, the total Hamiltonian is taken to be additive in the ligand contribution.

In order to describe the d–s-interaction in the case of one ligand, one additional parameter is needed. If the ligand is situated on the z-axis, we introduce $(z^2|V^z|s) = h$ while the other four matrix elements between s- and d-orbitals are zero by symmetry. Therefore

$$(d_i|V^z|s) = \delta_{i1}h \tag{4}$$

For an arbitrary ligand position on the p-axis, the transformation matrix of eqn. 3 can be used to yield

$$(d_i|V^p|s) = D_{i1}h \tag{5}$$

The angular part of the interaction element is thus contained in the first column of the $\mathbb{D}$-matrix; its elements are shown in Table II.

TABLE II. The Angular Coefficients of the d–s-interaction Elements, for an Arbitrary Direction (θ, φ).

i	$D_{i1}(\theta, \varphi)$
z^2	$1/2(3\cos^2\theta - 1)$
yz	$\sqrt{3}\cos\theta\sin\theta\sin\varphi$
xz	$\sqrt{3}\cos\theta\sin\theta\cos\varphi$
xy	$(\sqrt{3}/2)\sin^2\theta\sin 2\varphi$
$x^2 - y^2$	$(\sqrt{3}/2)\sin^2\theta\cos 2\varphi$

If several ligands are present, one assumes $V = \sum_L V^L$ and

$$(d_i|V|s) = \sum_L D_{i1}^L h^L \tag{6}$$

If the d_i-orbitals diagonalize the matrix of V—a condition which is satisfied for the D_{4h}-complexes under consideration—the orbital energy can be written as

$$E_i = E^0 + E_i' + E_i'' + \ldots \tag{7}$$

where the first term in the sum is the zero$^{\text{th}}$ order energy of the nd-orbitals, the second term is the first order ligand field expression:

$$E_i' = \sum_L (d_i|V^L|d_i) \tag{8}$$

and the last term is the second order energy describing the d–s-interaction introduced by eqn. 6:

$$E_i'' = -\frac{(d_i|V|s)^2}{E^0_{(n+1)s} - E^0_{nd}} = -\frac{(d_i|V|s)^2}{\Delta E} \tag{9}$$

It is possible to combine the metal-dependent proportionality constant ΔE and the d–s-mixing parameters h^L into one single semi-empirical parameter per M–L-interaction. Following Smith [8], we define

$$e^L = (h^L)^2 \cdot (\Delta E)^{-1} \tag{10}$$

and, combining eqns. 6, 9 and 10, one obtains

$$E_i'' = -\sum_L \sum_{L'} D_{i1}^L D_{i1}^{L'} (e^L)^{1/2} (e^{L'})^{1/2} \tag{11}$$

For instance, for a square planar complex with four equal ligands (all $e^L = e$), one obtains

$$E_1'' = E''(z^2) = -4e \tag{12}$$

In the notation of our previous work [10], the second order energy correction of the d_{z^2}-orbital ($-4e$), was represented by ($-\sigma_{sd}$). For a hexacoordinated *trans*-disubstituted complex with two equal axial ligands (e^{ax}) and four equatorial ligands (e^{eq}), one obtains

$$E_1'' = E''(z^2) = -4e^{ax} - 4e^{eq} + 8(e^{ax}e^{eq})^{1/2} \tag{13}$$

Clearly, if $e^{ax} = e^{eq}$, $E_1'' = 0$, and indeed, in O_h-symmetry, no d–s-mixing is allowed. On the other hand, d–s-mixing is maximal if e^{ax} and e^{eq} are maximally different (that is, in the square plane (eqn. 12)). Recent spectral studies of square planar complexes suggest an empirical relation that allows an estimate of the required parameter e. Indeed, whereas the conventional d-only model predicts d_{z^2} to be the highest doubly occupied orbital in d^8- and d^9-square planar complexes, the empirical evidence strongly suggests that d_{z^2} be the lowest d-orbital, as shown in Fig. 1.

From a detailed analysis of the crystal spectra of planar ML_4-complexes [M = Pt(II), Pd(II); L = Cl^-, Br^-], it was suggested that the z^2-stabilization is approximately equal to the first order σ-parameter:

$$4e \approx \sigma \tag{14}$$

As a consequence, the modified z^2-orbital is almost non-bonding, a result consistent with more elaborate MO-calculations [33, 34]. Similar conclusions were reached by others for Cu(II)- and Ni(II)-complexes. The most clear-cut examples are the square planar compounds of divalent copper, because of the unambiguous assignment of its excited states. Parameters and orbital energies for two cases are listed in Table III. Similar observations are also available for Ni(II)-complexes [9, 37], where transitions from the four occupied d-orbitals are found to be clustered together, contrary to the predictions of the d-only model. A detailed analysis of Co(II)-square planar complexes has been carried out along similar lines, and will be presented separately.

Therefore, the validity of eqn. 14 seems to be rather general. In what follows, we will assume that

TABLE III. Assignment of the Orbital Transitions to the Observed Bands in Square Planar Cu(II)-Complexes (all Energies in cm^{-1}); Dacoda Stands for 1,5-Diazacyclooctane.

	$xy \rightarrow x^2 - y^2$	$(xz, yz) \rightarrow x^2 - y^2$	$z^2 \rightarrow x^2 - y^2$	σ	π	e	Ref.
$CuCl_4^{2-}$	12500	14250	17000	5333	875	1580	35. 36
$Cu(dacoda)_2^{2+}$	18200	20800	23100	7800	1300	1875	37

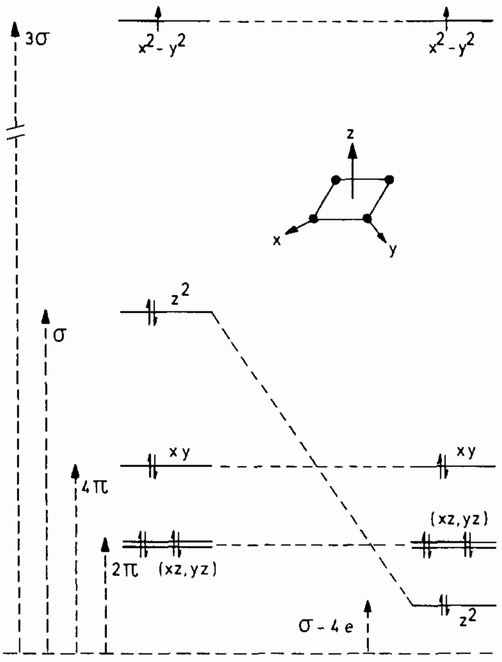


Fig. 1. Orbital energy diagram for a d^8 (or d^9) square planar ML$_4$-complex. Parametrization according to the conventional d-only model (left hand side), and with d–s-mixing (right hand side). See also ref. 32.

eqn. 14 remains also valid in mixed ligand complexes; that is, we will assume that a strong σ-donor contributes more to d–s-mixing than its weak field neighbors. Under this assumption, it becomes possible to treat the structural consequences of d–s-mixing in a very simple way.

Application of the Model to Tetragonal Distortions

A. Octahedral Complexes

Within the framework of ligand field theory, a meaningful comparison of octahedral and tetragonal structures can only be carried out if the d-orbital barycenter is maintained at constant energy. If the octahedral ligand field is designated as V_o and the distortions as ΔV, the resulting tetragonal field is given by

$$V = V_o + \Delta V \qquad (15)$$

Conservation of the barycenter energy implies that ΔV should not contain any components, spanning the a_{1g}-representation of the octahedral group [44]. This requirement can most easily be expressed by writing explicitly the individual ligand contributions to the crystal field potentials. Let $V^{\pm x}$ be the Hamiltonian corresponding to the field of one ligand on the ±x-axis, and $2V^x = V^{+x} + V^{-x}$ the total field on the x-axis; then

$$V_o = 2(V_o^x + V_o^y + V_o^z) \qquad (16)$$

$$V = 2(V^x + V^y + V'^z)$$

In eqns. 16, the octahedral components V_o^x, V_o^y and V_o^z can be transformed into each other by the proper rotation operators. For the tetragonal field, V^x and V^y are symmetry-connected; they correspond to equal field strengths on the x- and y-axes. V'^z represents a field of different magnitude, designated by a primed operator. If P is the projection operator for the octahedral a_{1g}-representation, the condition $P(\Delta V) = 0$ implies that V must be chosen in such a way that $PV = V_o$. Now

$$PV = 2(\overline{V^x} + \overline{V^y} + \overline{V^z})$$

where for instance

$$\overline{V^x} = \frac{1}{3}(2V^x + V'^x)$$

The same expression holds for y and z. The condition $PV = V_o$ entails $\overline{V^x} = V_o^x$, *etc.* Hence,

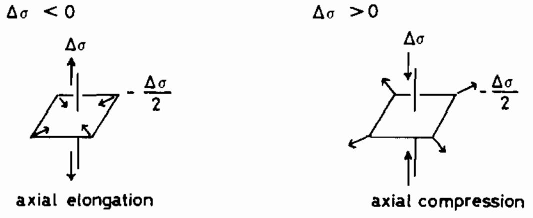
$$\Delta V = 2\Delta V^z - \Delta V^x - \Delta V^y \qquad (17)$$

where

$$\Delta V^x = V'^x - V_o^x,$$

and identically for ΔV^y and ΔV^z. Therefore, the distortional coordinate modifies the field along the z-axis twice as much (and in the opposite direction) as the field along the x- and y-axes.

This leads to the following scheme, where the axial parameters are modified by a parameter increment $\Delta\sigma$, and the equatorial parameters at the same time



Scheme I

by $-\Delta\sigma/2$. We adopt the convention that $\Delta\sigma < 0$ for an axial elongation, $\Delta\sigma > 0$ for an axial compression.

The first-order energies, as a function of $\Delta\sigma$, are given by

$$\begin{aligned} E'(z^2) &= (z^2|V_o + \Delta V|z^2) = 3\sigma + \tfrac{3}{2}\Delta\sigma \\ E'(x^2-y^2) &= (x^2-y^2|V_o + \Delta V|x^2-y^2) = 3\sigma - \tfrac{3}{2}\Delta\sigma \end{aligned} \qquad (18)$$

The occupation of both orbitals by one electron (d^8; $^3A_{2g}$ in O_h; $^3B_{1g}$ in D_{4h}) does not lead to a $\Delta\sigma$-dependence of the ground state energy of the Ni(II)-complexes. Applying eqn. 14 to the present case, one finds

$$\begin{aligned} e^{ax} &= \tfrac{1}{4}(\sigma + \Delta\sigma) \\ e^{eq} &= \tfrac{1}{4}(\sigma - \tfrac{1}{2}\Delta\sigma) \end{aligned} \qquad (19)$$

Substitution of eqn. 19 into eqn. 13 yields:

$$\begin{aligned} E''(z^2) &= -2\sigma - \frac{\Delta\sigma}{2} + 2[(\sigma + \Delta\sigma)(\sigma - \tfrac{1}{2}\Delta\sigma)]^{1/2} \\ &\approx -\frac{9}{16}\frac{(\Delta\sigma)^2}{\sigma} + \frac{9}{64}\frac{(\Delta\sigma)^3}{\sigma^2} - \ldots \end{aligned} \qquad (20)$$

and

$$E(^3B_{1g}) = E(^3A_{2g}; O_h) + E''(z^2)$$

Apparently, $E''(z^2)$ does not contain a linear term in $\Delta\sigma$. This was to be expected, since, in the limit of infinitesimally small $\Delta\sigma$, the linear term should be proportional to the first order Jahn–Teller matrix element; for a tetragonal distortion of the non-degenerate octatehedral ground state, this matrix element has to vanish [38]. Yet, $E''(z^2)$, and therefore the ground state energy of octahedral Ni(II)-complexes does contain a small anharmonicity term $\Delta\sigma^3/\sigma^2$, favoring slightly axial elongation. Figure 2A compares $E''(z^2)$ for both axial elongation and axial compression, assuming a standard value of $\sigma = 4000$ cm^{-1}. The energetic effect of d–s-mixing can be seen to be very small. Octahedral Ni(II)L_6-complexes are expected to resist deviations from their highly symmetric geometry; this expectation is confirmed by crystallographic data [45].

As a contrast to the Ni(II)-case, Fig. 2B shows the corresponding diagram for the d^9-systems. The octahedral ^2E_g-state is split into a $^2A_{1g}(z^2)^1$ and $^2B_{1g}(x^2-y^2)^1$-state. For an elongated octahedron ($\Delta\sigma < 0$), the ground state is $^2B_{1g}$, for a compressed octahedron ($\Delta\sigma > 0$), the ground state is $^2A_{1g}$. The energy of these states is given by

$$\begin{aligned} &\Delta\sigma < 0: \\ &E(^2B_{1g}) = E(^2E_g) + \tfrac{3}{2}\Delta\sigma + 2\,E''(z^2; \Delta\sigma < 0) \\ &\Delta\sigma > 0: \\ &E(^2A_{1g}) = E(^2E_g) - \tfrac{3}{2}\Delta\sigma + E''(z^2; \Delta\sigma > 0) \end{aligned} \qquad (21)$$

The first order terms in eqn. 21 illustrate the well-known fact that d^9-systems are characterized by a large, though non-preferential Jahn–Teller effect. The second-order interactions $E''(z^2)$ determine the *sense* of the distortion. The presence of the factor 2

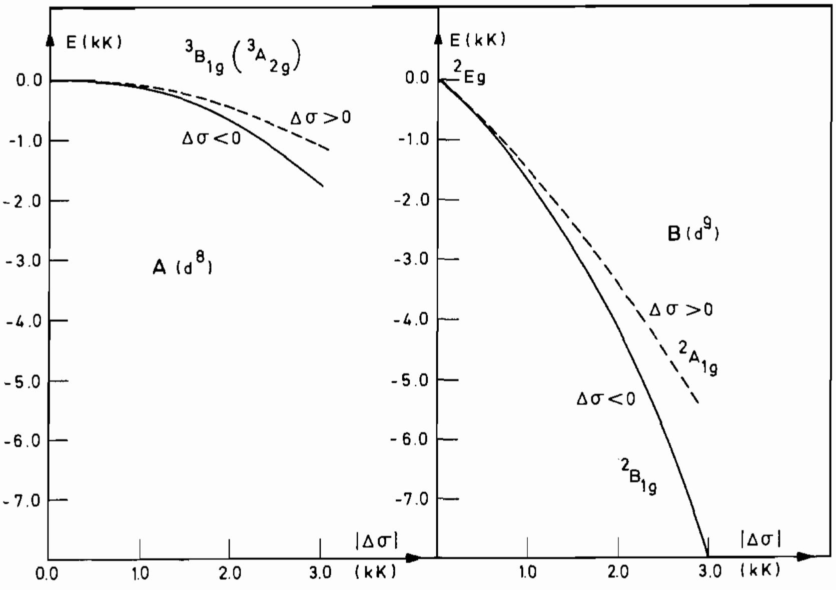


Fig. 2. Comparison of axial (full line) *versus* equatorial (dashed line) elongation in octahedral d^8 (A) or octahedral d^9 (B)-complexes. The ordinate axis shows the energy contribution of the metal σ-orbitals as a function of the absolute value of the distortion parameter Δσ. All energies (in kK) are shown relative to the O_h-ground state (zero level). In Fig. 2A, both curves refer to the $^3B_{1g}$-state; in Fig. 2B, Δσ < 0 refers to $^2B_{1g}$, and Δσ > 0 to $^2A_{2g}$ (the parent octahedral state is ^2E_g).

in $^2B_{1g}$, and not in $^2A_{1g}$, has been stressed by several authors [12–14]. The difference between elongation and compression is even more pronounced when one accounts for the fact that $E''(z^2; \Delta\sigma < 0) < E''(z^2; \Delta\sigma > 0)$, because of the term in $(\Delta\sigma)^3/\sigma^2$.

B. Trans-*NiN₄X₂-Complexes*

In general, the X-ligands will be the weaker σ-donors: $\sigma_X < \sigma_N$. With

$$e^{ax} = \tfrac{1}{4}(\sigma_X + \Delta\sigma)$$

$$e^{eq} = \tfrac{1}{4}\left(\sigma_N - \frac{\Delta\sigma}{2}\right)$$

one finds from eqn. 13:

$$\begin{aligned}E''(z^2) &= -\sigma_X - \sigma_N - \tfrac{1}{2}\Delta\sigma + \\ &\quad + 2[(\sigma_X + \Delta\sigma)(\sigma_N - \tfrac{1}{2}\Delta\sigma)]^{1/2} \\ &\approx -\sigma_X - \sigma_N + 2(\sigma_X\sigma_N)^{1/2} \\ &\quad + \frac{\Delta\sigma}{2(\sigma_X\sigma_N)^{1/2}}[2\sigma_N - \sigma_X - (\sigma_X\sigma_N)^{1/2}] \\ &\quad - \frac{(\Delta\sigma)^2}{16(\sigma_X\sigma_N)^{3/2}}(2\sigma_N + \sigma_X)^2 \\ &\quad + \frac{(\Delta\sigma)^3}{64(\sigma_X\sigma_N)^{5/2}}(2\sigma_N + \sigma_X)^2(2\sigma_N - \sigma_X) \\ &\quad - \ldots\end{aligned} \tag{22}$$

A graphical representation of these results is shown in Fig. 3A, assuming [39] $\sigma_N = 4000\ \text{cm}^{-1}$, $\sigma_X = 3200\ \text{cm}^{-1}$. The most striking difference between eqns. 22 and 20 is the appearance of a linear term in $\Delta\sigma$. Clearly, in the presence of a tetragonal field, the distortion mode considered is totally symmetric, so that the O_h-symmetry restriction no longer holds. As a result, the tetragonal field strongly reinforces the tendency towards axial elongation (compare Figs. 2A and 3A): rather small tetragonal perturbations induce large structural instabilities. We suggest that this effect is responsible for the resemblance between hexacoordinated d^9- and d^8-systems, although the former ones are Jahn–Teller-unstable, while the latter ones are not. It is true that the effect is more important in Cu(II)-complexes, where the distortion almost expels the axial ligands [8]. In Ni(II)-compounds, the effect is definitely less pronounced, but it can be increased by increasing the difference between σ_N and σ_X, in much the same way as exemplified in Table I. As a final remark, Fig. 3A demonstrates the large stabilization of d_{z^2} for extreme distortions. In a certain sense, the d–s-mixing can be said to have a catalyzing effect on the spin cross-over from octahedron to square plane, as suggested by the kinetic data.

C. Cis-*NiN₄X₂-Complexes*

Although only very few *cis*-complexes have been studied so far [40], it is interesting to carry out a comparative d–s-mixing analysis. Since one has to consider two different equatorial ligands, one writes in this case:

$$e^{ax} = \tfrac{1}{4}(\sigma_N + \Delta\sigma) \qquad e^{eqN} = \tfrac{1}{4}(\sigma_N - \tfrac{1}{2}\Delta\sigma) \qquad e^{eqX} = \tfrac{1}{4}(\sigma_X - \tfrac{1}{2}\Delta\sigma) \tag{23}$$

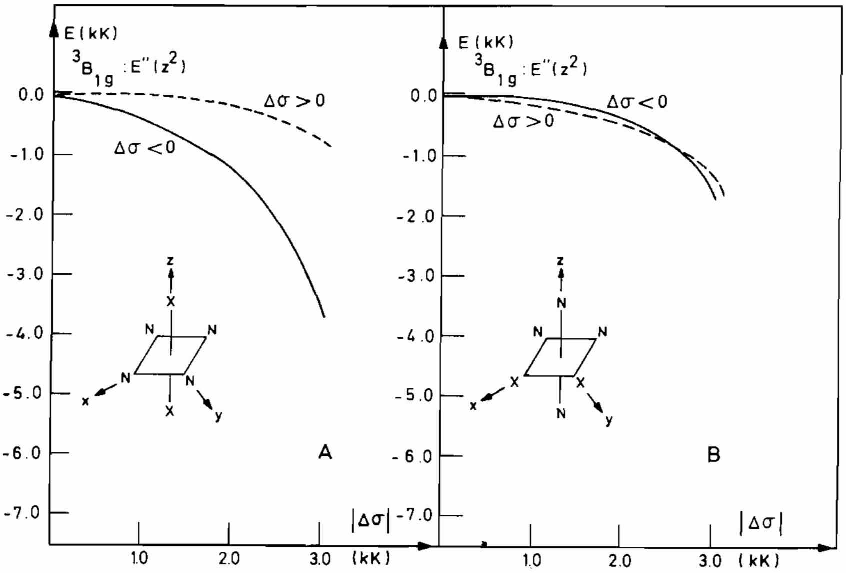


Fig. 3. Second order corrections to the ground state energy in disubstituted d^8complexes, as a result of axial (full line) *versus* equatorial (dashed line) elongation. (A) refers to a *trans*-complex, (B) to a *cis*-complex. All energies are in kK.

and

$$E''(z^2) = -4e^{ax} - e^{eqN} - e^{eqX} + 4(e^{ax}e^{eqN})^{1/2} + 4(e^{ax}e^{eqX})^{1/2} - 2(e^{eqN}e^{eqX})^{1/2} \qquad (24)$$

The results are illustrated in Fig. 3B, for the same numerical values of σ_N and σ_X as for the *trans*-complexes. In Fig. 3B the preference for either axial or equatorial elongation is much less pronounced than for *trans*-complexes. The two curves remain very close together at all points of Fig. 3B, and there is a cross-over region for large $\Delta\sigma$-values. For weak σ_X-donors a comparison of Figs. 3A and 3B offers an orbital rationale for the thermodynamic predominance of *trans*-ligation, and for the kinetic differences between *cis*- and *trans*-complexes.

Concluding Remarks

i) The introduction of d–s-mixing is seen to have qualitative structural consequences which are in apparent agreement with the experimental observations. Even in the absence of a Jahn–Teller effect, the high spin Ni(II)-ground states are expected to be axially elongated in the presence of a preexisting tetragonal perturbation.

ii) One problematic point of the present approach is the large numerical value of the e-parameter, which seems difficult to reconcile with its proposed second order nature. Combining eqns. 10 and 14, one obtains

$$e = \frac{h^2}{\Delta E} \approx \frac{\sigma}{4}$$

Since ΔE can be estimated [41] at 4–6 μm^{-1}, the fundamental mixing parameter $h = (z^2|V^z|s)$ must be of the same order of magnitude as $\sigma = (z^2|V^z|z^2)$.

iii) It is interesting to observe that the holohedron concept cannot be applied to d–s-mixing in the same way as in the d-only model [42]. Compare for instance the two structures in Scheme II.

Scheme II

C_{4v} D_{4h}

The ligand field matrix $(d_i|V|d_j)$ is identical in both cases, but the matrix $(d_i|V|s)$ is not. More specifically, $E''(z^2)$ $(-0.250)\sigma$ for the C_{4v}-complex, but only $(-0.086)\sigma$ in the D_{4h}-complex. This result suggests that the most stabilizing distortion can be produced by an asymmetric axial elongation, which weakens one axial site more than its antipode. In fact, the $[Ni(im)_4X]$ X-complexes of Table I, where the tetragonal perturbation is very large, are characterized by just such an asymmetrical ligation.

iv) It is remarkable that a recent *ab initio* Hartree-Fock-calculation [43] (with a rather small basis set) was unable to predict any significant preference for axial elongation in the $Cu(H_2O)_6^{++}$-complex.

Acknowledgements

The authors are indebted to the Belgian Government (Programmatie van het Wetenschapsbeleid). One of us (A. C.) thanks the Belgian Science Foundation (N.F.W.O.) for a postdoctoral fellowship.

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