249. The Electronic Fine Structure of Co(II)-Complexes with *Schiff*-Base Ligands

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Summary

Multiple-scattering-Xα MO-calculations are reported for Co(acacen). The results are essentially in agreement with extended *Hückel* calculations and EPR. data. Particular emphasis has been placed on the calculation of the electronic structure and one-electron properties, *i.e.* state energies diagram, spin-orbit coupling and hyperfine coupling based on a ligand field interpretation of the Xα-results, which allow to rationalize the main features of the EPR. spectra.

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1. Introduction. – Co(II) forms low-spin d^7-complexes with tetradentate *Schiff* bases [1] which impose an approximately planar ligand field with nearly C_{2v}-symmetry (*Fig. 1*). Although such complexes have been known for a long time [2], their detailed electronic structure has been investigated intensively only during the past 20 years [3]. The O-binding properties of some of these compounds [4], and

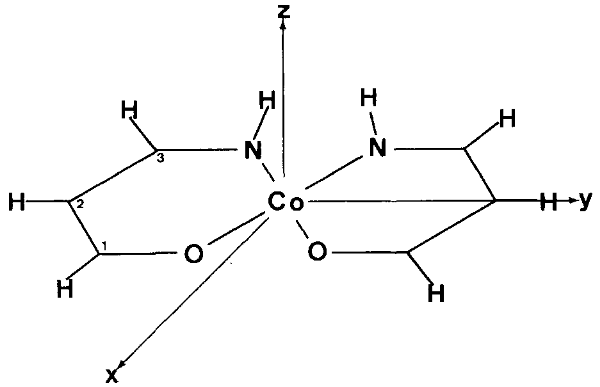

Fig. 1. *Cartesian coordinate system of Co(acacen)*

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moreover the very peculiar electronic structure of these complexes [1] were a particular stimulus to this kind of work.

Owing to the planar coordination, the set of five degenerate 3d-orbitals of the free metal ion is split into a group of four MO's which lie close together and one which is distinctly higher in energy. If we choose the Cartesian coordinate system in the usual way *(Fig. 1)* the electronic energy levels may be labelled according to the irreducible representations of $C_{2v}(x)$ [1] and the qualitative ligand field splitting given in *Figure 2* results. This arrangement which is also undoubtedly characteristic of complexes of other metal ions with similar ligands, gives rise to quite 'normal' electronic states, *e.g.* d^9 or d^8 transition-metal ions where in the ground state the closely spaced group of four orbitals is completely filled. In the case of Co(II) d^7, this group accomodates only seven electrons, leaving a 'one-hole' configuration of the set. Due to the proximity of these orbitals, four spin-doublets of similar energies are expected. One of these, *i.e.* the $|(dxy)^2 dx^2-y^2\ {}^2A_1\rangle$ hole configuration, is shifted to significantly higher energies by electron repulsion as predicted by qualitative ligand field theory, leaving three doublets, namely $|(dxy)^2 dyz\ {}^2A_2\rangle$, $|(dxy)^2 dz^2\ {}^2A_1\rangle$ and $|(dxy)^2 dxz\ {}^2B_1\rangle$ close together. All these three states interact strongly by spin-orbit coupling since their energy separation is comparable to the spin-orbit coupling constant of the Co-atom [1]. This has strong effects on the EPR. spectra which show g-values very far from $g_e = 2.0023$ [4].

Not only are doublets very close to the ground state but also several quartets arising by promotion of one electron from the set of four orbitals to the higher-lying level have similar energies because the spin-pairing energy almost compensates the promotional energy [1]. Therefore the unusual feature of these complexes is the fact that, within a range of about $5 \cdot 10^3$ cm^{-1} above the ground state a great number of doublet and quartet states are located.

This paper gives a theoretical description of these states. This description will be done in two steps: *i)* a multiple-scattering (MS) Xα-calculation of *N,N'*-ethylenebis(acetylacetoneiminato)cobalt(II) (Co(acacen)); will be carried out; *ii)* the results of this calculation will be used to evaluate the parameters required for a ligand field calculation of the low-lying states of Co(II)-complexes with *Schiff* bases and of the Co-EPR. parameters using the same model we have developed in an earlier work [1].

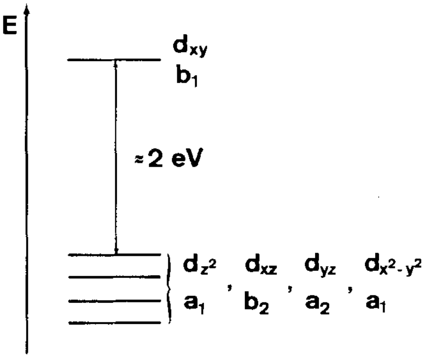

Fig. 2. *d-Orbital energy scheme for planar complexes*

Further calculations of the g- and A-tensors of the ligand atoms of Co(acacen) and of the quadrupole tensor of the Co-atom [5] will be reported in a subsequent publication [6].

2. MS-Xα-Calculation of Co(acacen). – The geometry of the complex was derived from X-ray crystallographic data [7]. Since the deviation from C_{2v}-symmetry is not significant we have chosen to impose this symmetry in our calculation. The internal coordinates of the first coordination sphere are then: Co–O 1.85Å, Co–N 1.85Å, O–Co–N 95°, N–Co–N 88°.

The standard MS-Xα-method [8] in both versions, spin-restricted and spin-unrestricted, is used. Electronic excitation energies are calculated using the transition state procedure [9]. The values of the MS-Xα-parameters are summarized in *Table 1*. The values of the atomic exchange parameters α are those optimized by *Schwarz* [10], except for the H-atom where we have chosen the spin-unrestricted value [11]. A weighted average of these atomic values is used for the α-value in the interatomic (intersphere) and extramolecular (outer-sphere) regions. For such a large system as Co(acacen), the overlapping-spheres procedure must be used to circumvent the limitation of the muffin-tin approximation. Overlapping atomic sphere radii were taken to be 88% of the atomic charge densities, a value that generally leads to very similar spheres radii as those obtained using the procedure suggested by *Norman* [12]. The only exception is the radius of the Co-sphere, which has been arbitrarily enlarged so as to exhibit a 25%-overlapping with the O- and N-ligands, this value having been shown to be adequate for numerous transition metal complexes [13–15]. The maximum l-value used in the partial wave expansions is l=2 for the outer sphere and for Co, l=1 for C, N, O, and l=0 for H.

The results of the spin-restricted MS-Xα-calculation are presented in *Table 2*. The energy levels are in agreement with the predicted splitting in *Figure 2* and also with the extended *Hückel* results we reported earlier (*cf.* [1] and *Sect. 4*), except for the second a_1-level which is inverted with b_1 in the EHMO-calculation. Four of the five d-orbitals interact weakly with the ligand system and remain relatively close in energy:

Table 1. *MS-Xα-Parameters*

Region	Atomic exchange parameter α	Sphere radius [a.u.]
Co	0.71018	2.75294
O	0.74447	1.61680
C_1	0.75928	1.56342
C_2	0.75928	1.63341
C_3	0.75928	1.59543
N	0.75197	1.60723
$H(C_1)$	0.777725	1.22235
$H(C_2)$	0.777725	1.22066
$H(C_3)$	0.77725	1.22147
H(N)	0.77725	1.12165
Outer-sphere	0.76185	9.30686
Intersphere	0.76185	–

Table 2. *Upper valence energy levels*[a]) *and charge distribution of Co(acacen)*

Orbital	Occ.	Energy [eV]	Charge distribution [%]							
			Co(3d)	Co(4s)	O	C_1	C_2	C_3	N	Inter
$2b_2$	0	−1.646	78	0	10	0	0	1	9	2
$4a_2$	1	−4.147	59	0	10	1	9	1	8	12
$13a_1$	2	−4.661	92[b])	0	4	1	0	0	0	3
$4b_1$	2	−4.842	78	0	1	5	0	6	1	9
$12a_1$	2	−5.113	79[c])	8	0	0	0	0	0	13

[a]) Only levels with preponderant metal 3d-character are displayed. [b]) Almost pure dx^2-y^2 partial wave contribution. [c]) Almost pure dz^2 partial wave contribution.

i) dxz interacts very weakly with a b_1-π-orbital of the ligand:

$$|4b_1\rangle^{1)} = 0.90dxz + 0.20(pz(C_1) + pz(C_1')) - 0.22(pz(C_3) + pz(C_3'))$$

ii) dyz is the most delocalized of the five d-orbitals due to its interaction with an a_2-π-orbital of the ligand with matching energy. It is this difference of interaction which explains the orthorhombic splitting observed in the magnetic tensors [1].

$$\begin{aligned}|4a_2\rangle^{1)} = {} & 0.80dyz - 0.26(pz(O) - pz(O')) \\ & + 0.07(pz(C_1) - pz(C_1')) + 0.28(pz(C_2) - pz(C_2')) \\ & - 0.11(pz(C_3) - pz(C_3')) - 0.22(pz(N) - pz(N'))\end{aligned}$$

iii) dx^2-y^2 makes essentially a π-type interaction with the in-plane p-orbitals of the O-atom:

$$|13a_1\rangle^{1)} = 0.12dz^2 + 0.97dx^2 - y^2 + 0.16(px(O) - px(O'))$$

iv) dz^2 requires special consideration. In absence of axial perturbation, as it is the case in our present calculation, the MO

$$|12a_1\rangle^{1)} = 0.92dz^2 - 0.13dx^2 - y^2 + 0.38\,4s\rangle$$

is almost purely metallic. When an axial perturbation is present however, the dz^2-orbital is strongly destabilized by an axial σ-interaction and it is this latter interaction which is responsible for the change of the ground state upon coordination of an axial base (*cf.* [1] and *Sect. 4*).

v) Finally the dxy-orbital which makes a strong σ-antibonding interaction with the coordinating O- and N-atoms, lies about 2.5 eV above the set of the other four d-orbitals. Despite this large separation the dxy-orbital plays an important role when state energies are considered. Promotion of one electron from a lower-lying doubly occupied orbital creates a quartet state for which the spin-pairing energy nearly balances the promotional energy. This is shown in *Table 3* and will be discussed in more detail in the next section.

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[1]) The LCAO-MO's are obtained by projection of the MS-Xα numerical wave function on a double-zeta STO-basis [16]. Only coefficients larger than 0.1 are given. C_1', C_2', C_3' and N' refer to the atoms located on the second ligand moiety.

3. State energies. – *Table 3* presents the state energies of several excited configurations as calculated using the transition state procedure of the MS-Xα-model. It is seen that three doublets are found at lower energies than the first member of a series of three quartets. This energy scheme is in qualitative agreement with previous ligand field results [1] [19], except for the position of the two $^2A_1$-doublets: the stability of the lowest $^2A_1$ arising from the $13a_1\downarrow \rightarrow 4a_2\downarrow$ transition is significantly overestimated and conversely the stability of the second $^2A_1$ resulting from the $12a_1\downarrow \rightarrow 4a_2\downarrow$ transition is underestimated. However, being a one-electron model, the MS-Xα-method is not suitable for a quantitative description of the multiplet structure of Co(acacen).

To evaluate the state energies of Co(acacen), we refined our description by using a conventional ligand field model [17], for which two sets of parameters are needed: *i*) the ligand-field splitting energies, (ii) the *Racah* parameters B and C. We chose the former ones as equal to the MS-Xα-energies of *Table 2*. This is justified because in the MS-Xα-method the two-electron interactions are statistically averaged over the calculated configuration and because the total electronic distribution of the complex does not vary much if changing ligand field configurations in non-spin-polarized calculations. Thus, it results that the interelectronic repulsion contribution to the energies of the ligand field levels (*i.e.* the five levels with predominant metal d-character) is almost independent upon variation of the ligand field configurations and the energy separation between the corresponding levels is a good estimale of the ligand field splittings. It is in fact this very reason which is responsible for the inadequacy of the MS-Xα-method to describe quantitatively the multiplet structure of Co(acacen) we have reported above (for more details *cf.* [26] [27]). The latter ones are more subtle to estimate. We have previously observed [13] that the radial part of the MS-Xα-3d wave function fits nicely with the HF-function given by *Watson* [18] for a metal ion with similar charge. Using the radial part of the 3d-Co(II) function given by *Watson* we calculate $B = 1167\ cm^{-1}$ and $C = 4900\ cm^{-1}$. To account for the delocalization of the 3d-electrons over the ligand and for electron correlation effects, these free-ion values have to be reduced. The dependence of the singly excited-state energies of Co(acacen) as a function of B (keeping the ratio C/B at its free-ion value 4.2) is given in *Figure 3*. It is seen from this figure that the nature of the ground state critically depends upon the reduction of the *Racah* parameters. An obvious way to calculate the reduction factor is to take the weighted mean of the metal 3d-populations of the occupied MO's with predominant metal character to account for the delocalization of the electron

Table 3. *State energies of Co(acacen) calculated using the transition state procedure*

Transition	State	$\Delta\varepsilon$ [eV]
	Ground state $^2A_2$	0.00
$13a_1\downarrow \rightarrow 4a_2\downarrow$	$^2A_1$	0.51
$4b_1\downarrow \rightarrow 4a_2\downarrow$	$^2B_1$	0.69
$12a_1\downarrow \rightarrow 4a_2\downarrow$	$^2A_1$	0.98
$13a_1\downarrow \rightarrow 12b_2\uparrow$	$^4B_1$	1.18
$4b_1\downarrow \rightarrow 12b_2\uparrow$	$^4A_1$	1.54
$12a_1\downarrow \rightarrow 12b_2\uparrow$	$^4B_1$	1.85

over the ligand and to add 20% to account for electron correlation effects [26]. Thus we obtain a reduction factor of 60% which corresponds to the dashed line in *Figure 3* ($B = 700$ cm^{-1} and $B = 2940$ cm^{-1}). As *Hitchman* used values of $B = 750$ cm^{-1} and $C = 3150$ cm^{-1} in his calculation on Co(salen) [19] it is seen that there is a very good agreement between the two procedures.

A comparison of the calculated state energies with the optical absorption spectrum of Co(acacen) is not feasible due to lack of reliable analysis of the ligand field bands in a single-crystal study [1].

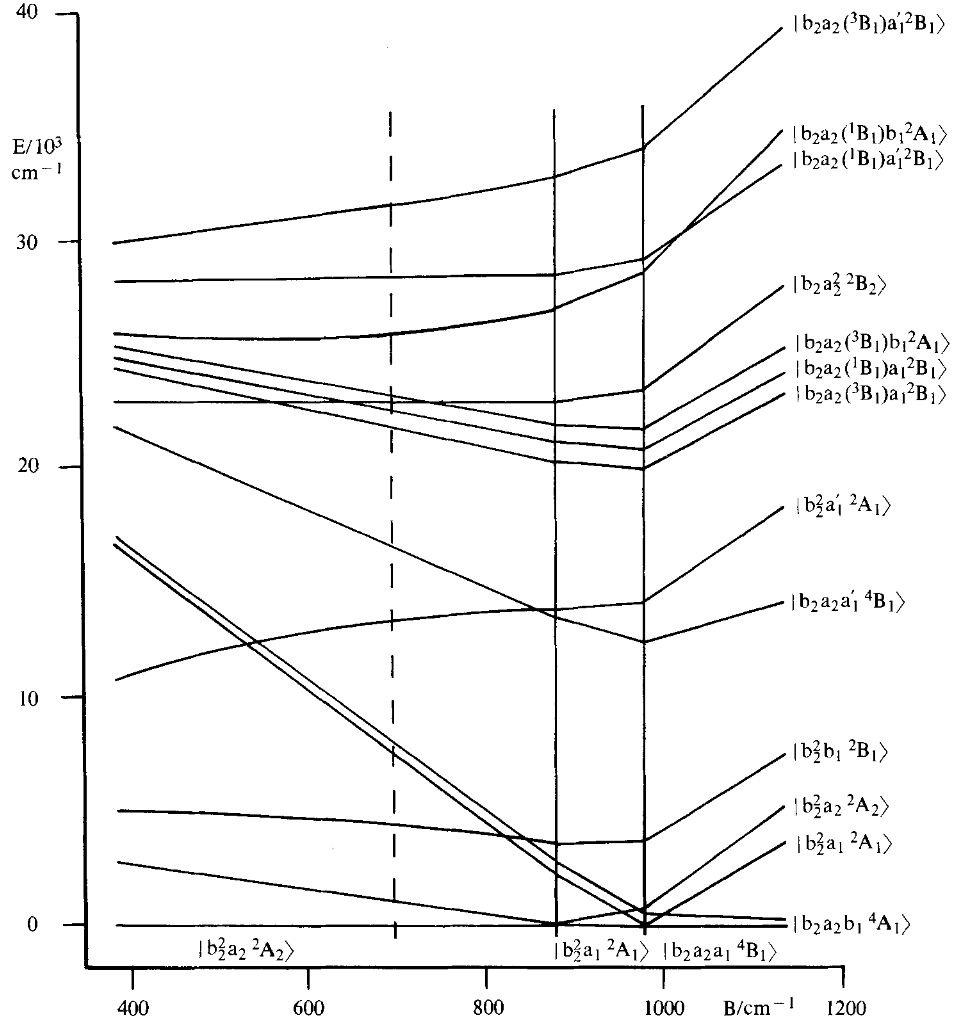

Fig. 3. *Energy diagram of singly excited states of Co(acacen)* ($C = 4.2 \cdot B$, the hole formalism is used to label the configurations, *e.g.* the ground state configuration is $b_2{}^2a_2$. In order to differentiate between $12a_1$ and $13a_1$ we define $a_1 := 12a_1$ and $a_1' := 13a_1$)

The ultimate goal of this work is to calculate the EPR. parameters of Co(II)-complexes with *Schiff* bases. Thus we shall next construct a *Kramers* doublet of the ground state by mixing the low-lying excited states into the $^2A_2$-state under spin-orbit coupling and then use it to calculate the g- and A-tensors.

4. *Zeeman* splitting and hyperfine coupling. – From the whole bunch of states given in *Figure 3* we select the five lowest ones in energy ($< 10^4$ cm^{-1}) and use them to set up the ground state doublet by including spin-orbit coupling. Excited states with energies greater than thirty times the spin-orbit coupling constant ($= 360$ cm^{-1}) do not perturb the ground state significantly. This value of the spin-orbit coupling constant has been obtained as before by multiplying the free-ion value [20] by the metal 3d-population of $4a_2$. Since the double group C_{2v}^* possesses one single irreducible representation $E_{1/2}$, all states are allowed to mix and a set of fourteen symmetry-adapted determinantal basis functions is obtained: $|^2A_2+1/2\rangle$, $|^2A_2-1/2\rangle$, $|^2A_1+1/2\rangle$, $|^2A_1-1/2\rangle$, $|^2B_1+1/2\rangle$, $|^2B_1-1/2\rangle$, $|^4B_1+3/2\rangle$, $|^4B_1+1/2\rangle$, $|^4B_1-1/2\rangle$, $|^4B_1-3/2\rangle$, $|^4A_1+3/2\rangle$, $|^4A_1+1/2\rangle$, $|^4A_1-1/2\rangle$, $|^4A_1-3/2\rangle$.

Diagonalization of the corresponding spin-orbit matrix yields a set of seven pairwise degenerate *Kramers* doublets and only the lowest one in energy is needed for the calculation of the *Zeeman* splitting and of the hyperfine coupling. The two components of this doublet can be represented as

$$\psi\pm\rangle = \sum_{\mu} c_{\mu}^{\pm}\, \Phi_{\mu} \tag{1}$$

where Φ_μ are the determinantals listed above and c_μ^+ and c_μ^- are the two eigenvectors corresponding to the lowest eigenvalue.

The *Zeeman* splitting is obtained by calculation of the matrix elements of the *Zeeman* operator, $V_{Ze} = \beta_e \vec{H}(\vec{L} + g_e\vec{S})$, with the *Kramers* doublet $\psi\pm\rangle$, *i.e.*

$$\langle\psi\pm|V_{Ze}|\psi\pm\rangle = \sum_{\mu,\nu} (c_\mu^{\pm})^* c_\nu^{\pm} \langle\Phi_\mu|V_{Ze}|\Phi_\nu\rangle \tag{2}$$

This matrix is equal to the *Zeeman* matrix of the spin hamiltonian: $\langle\pm|\beta_e\vec{H}g\vec{S}\vec{I}\pm\rangle$ evaluated over components of the effective spin and one yields for the g-tensor expressed in the coordinate system of *Figure 1:*

$$\begin{pmatrix} g_{iz} & g_{ix} - ig_{iy} \\ g_{ix} + ig_{iy} & -g_{iz} \end{pmatrix} = 2\begin{pmatrix} \langle\psi+|L_i + g_e S_i|\psi+\rangle & \langle\psi+|L_i + 2\,S_i|\psi-\rangle \\ \langle\psi-|L_i + g_e S_i|\psi+\rangle & \langle\psi-|L_i + 2\,S_i|\psi-\rangle \end{pmatrix} \tag{3}$$

$i = x, y, z$

where β_e = *Bohr*'s magneton of the electron, $\vec{H}$ = external magnetic field, $\vec{L}$ = angular momentum operator, $g_e = 2.0023$, and $\vec{S}$ = spin operator. Since our coordinate system is coincident with the main axis system of the g-tensor [1], we obtain the latter one directly in diagonal form.

For the calculation of the hyperfine coupling, three contributions have to be considered: *i*) the *Fermi* contact term $H_{hf}^{F} = \frac{1}{3}\pi g_e \beta_e g_{Co} \beta_N \delta(\vec{r}) \vec{S} \cdot \vec{I}$; *ii*) the (electron spin)-(nuclear spin) dipole coupling $H_{hf}^{DD} = g_e \beta_e g_{Co} \beta_N 3(\vec{S} \cdot \vec{r})(\vec{I} \cdot \vec{r}) - r^2(\vec{S} \cdot \vec{I})/r^5$; *iii*) the (nuclar spin)-(orbital momentum) coupling $H_{hf} = 2 g_e \beta_e \beta_N (I \cdot \vec{\nabla}(r^{-1}) x \vec{p})$, where g_{Co} = gyromagnetic value of the Co-nucleus, β_N = nuclear magneton, $\delta(\vec{r})$ = *Dirac*'s delta, $\vec{r}$ = coordinate of the electron, $\vec{I}$ = nuclear spin operator, $\vec{p}$ = linear momentum of the electron. The calculation of the matrix elements of this operator is more conveniently performed using the method of the operator equivalents [21]:

$$H_{hf}^{tot} = \vec{V} \cdot \vec{I} =$$

$$P\left[\vec{L} + \left\{\frac{2l(l+1)}{(2l-1)(2l+3)} - \varkappa\right\}\vec{S} - \frac{3}{(2l-1)(2l+3)}\left\{(\vec{L} \cdot \vec{S})\vec{L} + \vec{L}(\vec{L} \cdot \vec{S})\right\}\right] \cdot \vec{I} \qquad (4)$$

where $P = 2 g_{Co} \beta_e \beta_N \langle r^{-3} \rangle$ (here we approximate $g_e = 2$), and where the term $-P\varkappa\vec{S} \cdot \vec{I}$ describes the *Fermi* contact interaction. The MS-Xα-method has been used to determine the values of the P- and $\varkappa$-parameters in the following way: *i*) as spin-polarization effects have negligible effects on the P-parameter in a similar case [22], the results of non-spin-polarized calculation have been used to estimate the $\langle r^{-3} \rangle$ expectation value over an LCAO-projection of the metal 3d-radial part of the $4a_2$-MO [22]. This yields a value $\langle r^{-3} \rangle = 6.45$ a.u. Multiplying then this value by the metal 3d-population of $4a_2$ and converting into conventional units of $10^{-4} \cdot cm^{-1}$, we obtain $P = 161 \cdot 10^{-4}\ cm^{-1}$; *ii*) $\varkappa$ is obtained from the relation:

$$a_F = \frac{8}{3}\pi g_e \beta_e g_{Co} \beta_N [\rho\uparrow(O) - \rho\downarrow(O)] = -P \cdot \varkappa \qquad (5)$$

where $\rho\uparrow(O)$ and $\rho\downarrow(O)$ are spin-up and spin-down electronic densities, respectively, as obtained from spin-polarized MS-Xα-calculations:

$$\rho^{\downarrow\uparrow}(O) = \sum_{s} \rho_s^{\downarrow\uparrow}(O) = \sum_{s} n_s^{\downarrow\uparrow} |u_s^{\downarrow\uparrow}(O)|^2 \qquad (6)$$

The summation extends to all valence and core MO's $u_s^{\downarrow\uparrow}(r)$ having an s-component in the metal sphere, $n_s^{\downarrow\uparrow}$ being the occupation number of each MO [22].

The contributions of the various ns-shells to a_F are presented in *Table 4*. It is seen that the substantial negative *Fermi* contact term arises from the balance of 2s and 3s spin densities, which have opposite signs because of the opposite spin-polarization effects induced by the 3d open-shell.

The calculation of the hyperfine tensor elements A_{ij} is performed in the same way as the g_{ij}-elements, *i.e.*

$$A_{ix} = 2\,\mathrm{Re}\langle \psi + | V_i | \psi - \rangle \qquad (7a)$$

$$A_{iy} = 2\,\mathrm{Im}\langle \psi + | V_i | \psi - \rangle \qquad (7b)$$

$$A_{iz} = 2\langle \psi + | V_i | \psi + \rangle \qquad (7c)$$

$$i = x, y, z$$

Table 4. *Contributions from the different s-shells to the* Fermi *contact interaction of the metal hyperfine tensor of Co(acacen)*

Shell	$\rho\uparrow(O)-\rho\downarrow(O)$ [a.u.]
1s	– 0.0176
2s	– 0.4226
3s	0.2438
4s	– 0.0188
Total	– 0.2152
$a_F[10^{-4}\,cm^{-1}]$	– 76.0

Since the main axes of the A- and g-tensors are identical, the A-tensor is also obtained in diagonal from. The calculation of all these matrix elements within the basis set of the symmetry-adapted determinantal wave functions listed earlier is carried out easily using the computer program LSZH [23].

It has been demonstrated in the past that the EPR. parameters are extremely sensitive on the position of the dz^2-energy level [1]. Even axial perturbations as small as packing effects observed for Co(acacen) diluted in different host lattices have strong effects on both the g- and the A-tensor. This extreme sensitivity of the dz^2-orbital upon axial perturbation is displayed in *Figure 4* where the energies of EHMO's of Co(acacen) with dominant metal character are shown as a function of the separation between the central Co-atom and NH_3 along the z-axis. It is therefore reasonable to treat the dz^2-energy as a variable parameter and to calculate the EPR. parameters as a function of it.

At this point of the calculation, let us summarize the method used to determine the parameters needed: *i*) *Racah*'s parameters B and C and the spin-orbit coupling constant ξ have been derived from the free-ion values reduced by the MS-Xα-covalency; *ii*) ligand-field splitting energies are those directly obtained from the MS-Xα-eigenvalues of the MO's with predominant metal character, except for dz^2 which is treated as a variable; *iii*) P and $\varkappa$ hyperfine-coupling parameters have been calculated from the MS-Xα wave functions using the method described in [22].

The results of this calculation is shown in *Figure 5.* It is necessary to take $\varkappa$ dependent upon the contribution of dz^2 to the ground-state *Kramers* doublet. Indeed, inspection of *Table 2* shows that the $12a_1$-orbital with preponderant dz^2-character contains 8% Co(4s) as well. This implies an augmentation of the spin density at the origin when the $^2A_1$-contribution to the ground state increases. It is therefore sensible to scale $\varkappa$ with the square of the mixing coefficient c of $^2A_1$ in *Equation 1.* Thus, we define the *Fermi* contact term as $a_F = a_O + sc^2(^2A_1)$. The scaling factor s can be estimated by supposing $c^2(^2A_1) = 1$, *i.e.* pure $^2A_1$ ground state. The second term of our equation is the population of Co(4s) multiplied by the isotropic hyperfine-coupling constant of the ^{59}Co-nucleus, *i.e.* $s = 0.08 \cdot 1223 \cdot 10^{-4} cm^{-1}$ [25]. The first term a_O can be estimated from our MS-Xα-value of $a_F = -76.0 \cdot 10^{-4} cm^{-1}$ and from the mixing coefficient $c(^2A_1)$ obtained for Δ *(Fig. 5)* equal to the calculated MS-Xα-value of Co(acacen), *i.e.* $c(^2A_1) = 0.2684$. Thus, $a_F = a_O + 98 \cdot 10^{-4} c^2(^2A_1) = -76 \cdot 10^{-4} = a_O + 98 \cdot 10^{-4} \cdot 0.2684^2$ and we get $a_O = -83 \cdot 10^{-4} cm^{-1}$. Thus, $a_F/10^{-4} cm^{-1} = -83 + 98\, c^2(^2A_1)$ or $\varkappa = 0.5 - 0.6\, c^2(^2A_1)$.

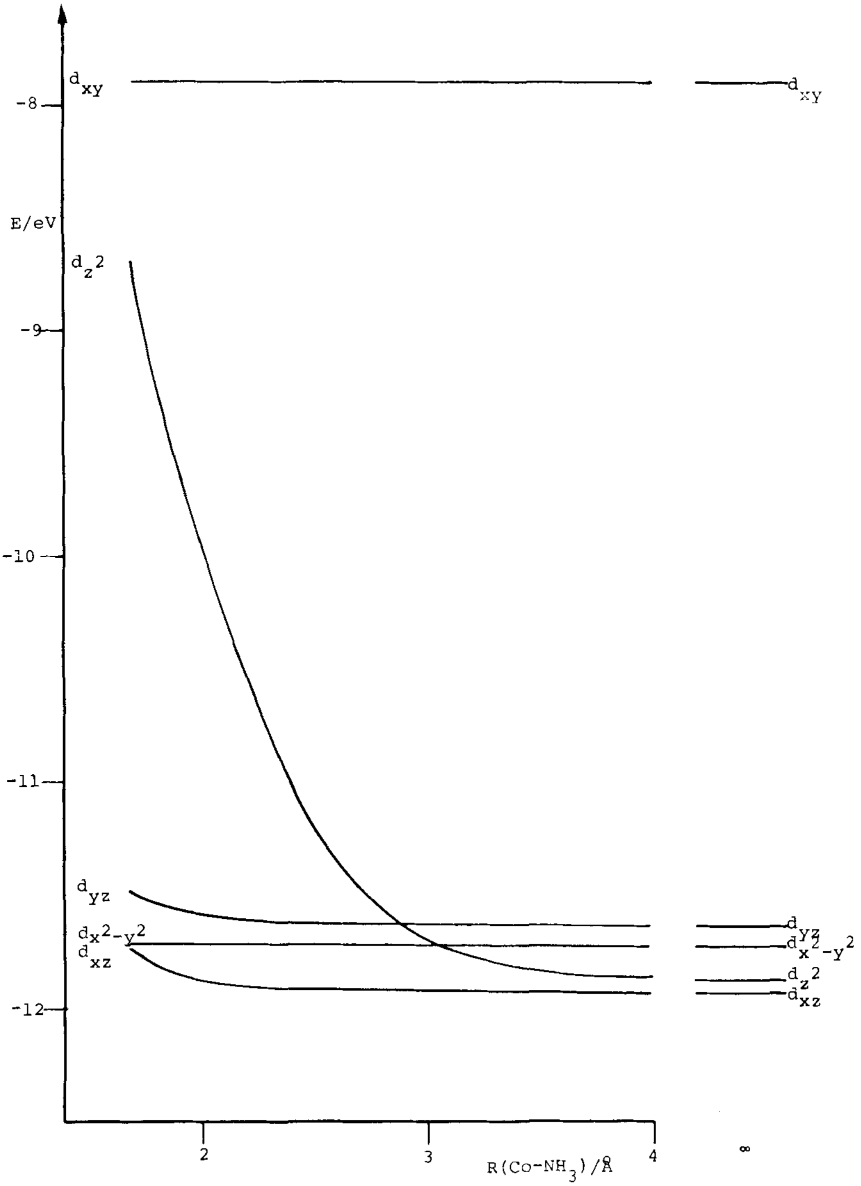

Fig. 4. *EHMO-energies of the ligand field levels of Co(acacen) as functions of an axial perturbation* (The axial perturbation is simulated by the steady approach of an NH$_3$-molecule (N–H: 1.008Å, H–N–H: 107.3°) along the z-axis. Standard valence-orbital ionization potentials have been used for all atoms [24] except for Co where we used the end VOIP's obtained from an EHMO-calculation with quadratic charge iteration on the central ion ($H_{ss} = -9.75$ eV, $H_{pp} = -5.394$ eV, $H_{dd} = -12.26$ eV). Single-zeta STO were used for all basis functions except for Co(3d) in which case double-zeta function are used [16])

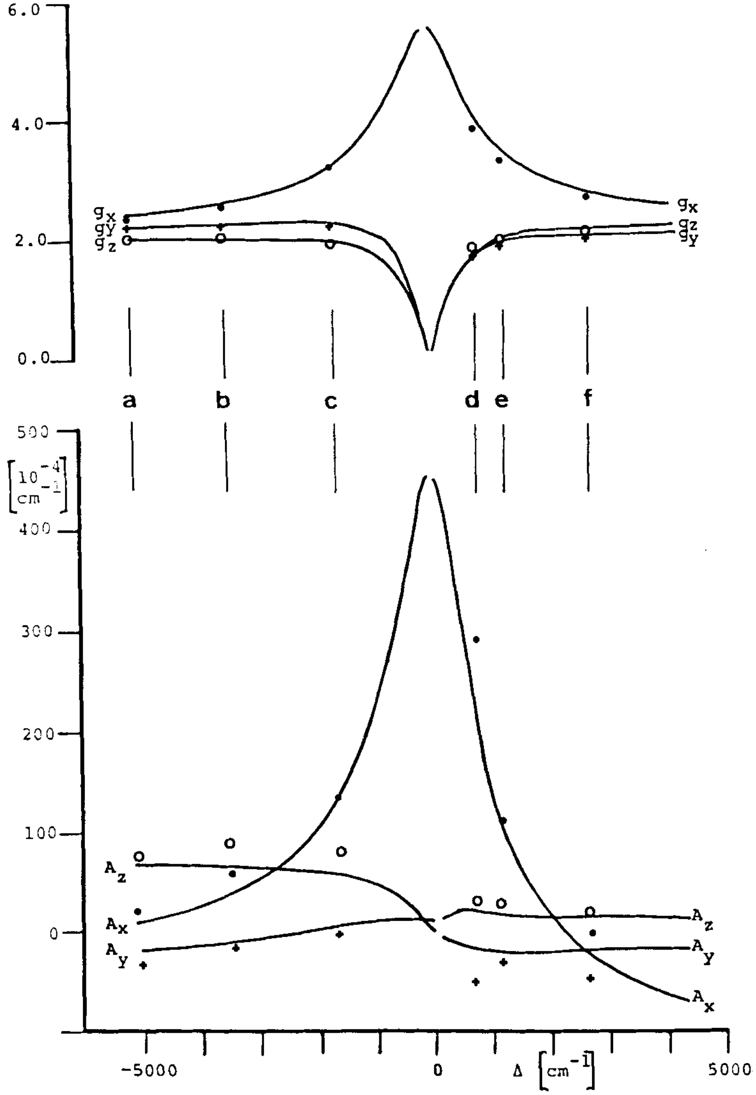

Fig. 5. *g- and A-tensor elements as a function of* $\Delta := E(^2A_1) - E(^2A_2) = \varepsilon(dz^2) + const.$ (const. depends upon factors which are insensitive towards axial perturbations; $B = 700\ cm^{-1}$, $C = 2940\ cm^{-1}$, $\xi_{SO} = -360\ cm^{-1}$, $\varkappa = 0.5 - 0.6c^2(^2A_1)$, $P = 160 \cdot 10^{-4}\ cm^{-1}$, a: Co(saphen)$py_2$, b: Co(bzacacen)py, c: $Co(salen)_2$, d: Co(salen), e: Co(acacen), f: Co(amben); all experimental data are from [1]. Note the discontinuity in the y- and z-components of both tensors at $\Delta = 0$. This is due to the fact that the spin-orbit operator mixes $|^2A_2+\rangle$ with $|^2A_1-\rangle$ and $|^2A_2-\rangle$, with $|^2A_1+\rangle$, respectively. Thus, the correspondence between the two components of the *Kramers* doublet with those of the effective spin changes at $\Delta = 0$)

In addition to the predicted curves of the g- and A-tensors, *Figure 5* displays also the corresponding experimental values of some low-spin Co(II)-complexes with *Schiff* bases as ligand chosen such as to spread over the whole range of Δ. Bearing in mind that these curves have been obtained *'ab initio'*, it is seen that the agreement between theory and experiment is very satisfactory. This suggests that the proposed model allows to predict the EPR. data of all low-spin Co(II)-complexes with *Schiff* bases and related ligands.

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