

The Energy Levels of Some 5-Coordinate Adducts of Cobalt(II) Schiff's Base Complexes

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The state energies of a series of low-spin 5-coordinate adducts of N,N' -ethylenebis(salicylaldiminato)cobalt(II), $Co(salen)$, and the high-spin complex $Aquo-N,N'$ -ethylenebis(3-methoxysalicylideneiminato)cobalt(II), $Co(3MeOsalen) \cdot H_2O$, have been calculated using ligand bonding parameters derived from analogous copper(II) complexes by means of the angular overlap simple molecular orbital model. The results are in reasonable agreement with the electronic and EPR spectra, and magnetic properties of the complexes and suggest that the ground state of 4-coordinate $Co(salen)$ is $^2A_2(d_{yz})$, with this changing to $^2A_1(d_z^2)$ in the low-spin adducts of this complex, and to $^4B_1(d_{yz}, d_z^2, d_{x^2-y^2})$ in $Co(3-MeOsalen) \cdot H_2O$, the unpaired electrons occupying the orbitals in parentheses. The calculations suggest that the lowest spin quartet and doublet states are quite close in energy in the 5-coordinate complexes. The relative importance of the structural changes accompanying axial ligand coordination on the state energies was investigated and it was found that the axial ligand perturbation has little direct effect on the energy difference between the low-lying spin doublet and quartet states. The relative lowering in energy of the quartet states on adduct formation was found instead to be correlated with the increase in the in-plane bond lengths and, to a lesser extent, the raising of the cobalt(II) ion out of the plane of the Schiff's base ligand.

Introduction

The tendency of planar 4-coordinate complexes to form base adducts is well established for many first row transition metal ions. This process is of considerable theoretical interest because of the changes in the nature of the ground state which often accompany adduct formation. The d^7 electron configuration of cobalt(II) is especially interesting in this respect, first because of the controversy over the ground state of planar complexes of this ion and second because of the ability of many of the adducts of cobalt(II) complexes to reversibly absorb molecu-

lar oxygen [1]. In particular, there have been numerous studies of the EPR spectra of low-spin cobalt(II) complexes, and the way in which these change on the formation of adducts with bases of varying strength [2–10]. The energy levels of an idealized square pyramidal cobalt(II) complex have been treated theoretically using the crystal field approach [11, 12]. A potentially useful alternative method of parametrizing the d-orbital energies in a series of metal complexes of this kind is the angular overlap simple molecular orbital model (*aom*) developed by Schäffer and Jørgensen [13]. This model relates the energy by which a metal d-orbital is raised upon interaction with one ligand orbital to the square of the overlap integral. The total energy of each d-orbital is obtained by summing over all the ligand orbitals using the angular overlap matrix appropriate to the geometry of the complex in question. The *aom* is thus particularly well suited to the treatment of a series of complexes of similar ligands in which the geometry varies in a known manner and it has been used with some success to rationalize the d-orbital energy changes which accompany the formation of 5-coordinate adducts by planar copper(II) β -ketoenolate complexes [14] as well as discussing the energy levels of several complexes of general type $Ni(\text{ligand})_4X_2$ [15] and $[Cr(\text{ligand})_4X_2]^+$ [16]. Recently, the *aom* was used [17] to estimate d-orbital and state energies of planar, 4-coordinate N,N' -Ethylenebis(salicylaldiminato)cobalt(II), $Co(salen)$, using ligand bonding parameters derived with appropriate corrections from analogous copper(II) Schiff's base complexes. The results, which were in good agreement with the observed EPR and electronic spectra of the complex, suggested that the unpaired electron occupies the d_{yz} orbital in $Co(salen)$. The model was also used to deduce the energy levels in the dimeric form of the complex, $Co(salen)$ dimer, in which the fifth bond is to an oxygen atom of a neighbouring molecule, and its pyridine adduct, $Co(salen) \cdot py$, though neglecting the fact that the metal ion is raised out of the plane of the salen ligand in these latter complexes. It correctly predicted a d_z^2 ground state for these 5-coordinate complexes and also

provided good agreement with their EPR and electronic spectra. It is known that some adducts of Co(salen) and complexes with closely related ligands are high-spin [18–20], and the square-pyramidal geometry of one of these, Aquo- NN' -ethylenbis(3-methoxysalicylideneiminato)cobalt(II), $\text{Co}(\text{3MeO-salen})\cdot\text{H}_2\text{O}$, has been established by X-ray crystallography [21]. The purpose of the present study is to extend the previous model to include $\text{Co}(\text{3MeO-salen})\cdot\text{H}_2\text{O}$ and to investigate in detail the way in which the various geometrical changes which accompany adduct formation affect the electronic structure of the cobalt(II) ion.

Experimental

$\text{Co}(\text{3MeOsalen})\cdot\text{H}_2\text{O}$ was prepared by mixing equimolar proportions of cobaltous acetate and the ligand each dissolved in dimethylformamide and filtering the resulting crop of red crystals. The reaction and crystallization were carried out using degassed solutions in a nitrogen atmosphere.

Analytical Results

Found, C = 52.87, H = 5.25, calculated for $\text{CoC}_{18}\text{H}_{20}\text{N}_2\text{O}$, C = 53.60, H = 5.00.

The electronic spectrum of the complex was measured as a mull in kel-F vacuum grease at room temperature and 77K using a Cary 17 spectrophotometer.

Discussion

Calculation of the Energy Levels in the Complexes

Within the framework of ligand field theory, if spin-orbit coupling is neglected the state energies of a cobalt(II) complex may readily be calculated from the effects of interelectron repulsion and the metal-ligand interaction. The main problem about predicting the state energies in a complex such as Co(salen) lies in the choice of reasonable ligand bonding parameters. Recently, this problem was tackled by using *aom* metal-ligand bonding parameters derived from an analysis of the electronic spectrum of analogous copper(II) complexes, which are comparatively simple to interpret as interelectron repulsion effects are absent [17].

The *aom* relates the energy e by which a d-orbital is raised upon interaction with a ligand orbital to the square of the diatomic overlap integral S via the equation [13]:

$$e = S^2 K, \text{ where } K = H_L^2 / (H_M - H_L) \quad (1)$$

Here H_L and H_M are the diagonal matrix elements of the ligand and metal orbitals, respectively. The total energy of each d-orbital is then obtained by summing

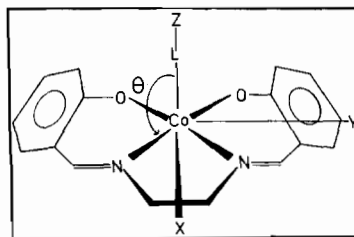


Figure 1. Schematic diagram showing the molecular structure and coordinate system of an adduct of a cobalt(II) Schiff's base complex.

over all the ligands, including both σ and π -effects, by means of the angular overlap matrix appropriate to the geometry of the complex. The field "strength" of a single donor atom of a ligand such as salen can then be represented by the three parameters e_σ , $e_{\pi_{\parallel}}$ and $e_{\pi_{\perp}}$, where e_σ represents the σ -interaction, $e_{\pi_{\parallel}}$ the π -interaction at right angles to the plane of the ligand, and $e_{\pi_{\perp}}$ the π -interaction in the plane of the ligand. Note that in keeping with the concept of "holahedrized symmetry" [13] these parameters represent the average effect of each *trans* pair of oxygen and nitrogen atoms of a ligand such as salen. The general structure of an adduct of Co(salen) is illustrated in Figure 1 together with the coordinate system which by convention has always been used to describe complexes of this kind. If, as a first approximation, the difference in ligand interaction along the x and y axes is neglected, the equations for the energy of each d-orbital are [14]:

$$E(xy) = 0.75 (1 - \cos 2\theta)^2 e_\sigma(xy) + \sin^2 2\theta e_{\pi_{\parallel}}(xy) \quad (2a)$$

$$E(z^2) = e_\sigma(z) + 4 \{ (0.25 + 0.75 \cos 2\theta)^2 e_\sigma(xy) + 0.75 \sin^2 2\theta e_{\pi_{\parallel}}(xy) \} \quad (2b)$$

$$E(x^2 - y^2) = 4 \sin^2 \theta e_{\pi_{\perp}}(xy) \quad (2c)$$

$$E(xz) = E(yz) = e_\pi(z) + 2 \{ (\cos^2 \theta + \cos^2 2\theta) e_{\pi_{\parallel}}(xy) + 0.75 \sin^2 2\theta e_\sigma(xy) \} \quad (2d)$$

Here the symbol z in parenthesis indicates the axial ligand, while xy refers to the in-plane salen ligand. The π -interaction of the axial ligand, which is a relatively small perturbation, is assumed to be isotropic about the bond axis. Note that when the angle $\theta = 90^\circ$ the equations reduce to those used previously [17] for a planar complex having an axial ligand perturbation.

The relevant bond lengths and angles in $\text{N,N}'$ -ethylenbis(acetylacetonimine)copper(II), Cu(acacen), and the cobalt(II) Schiff's base complexes are given in Table I together with the ligand bonding parameters derived for each complex. (Cu(acacen) has been considered, rather than Cu(salen) itself, as the latter complex exists as loosely bound dimers in

TABLE I. Structural Details, Diatomic Overlap Integrals and Ligand Bonding Parameters of Various Schiff's Base complexes.

Complex	Bond Lengths (pm)			Angle θ	Ref.	$S^2 \times 10^3$ ^a		Ligand Bonding Parameters ($\text{cm}^{-1} \times 10^{-3}$) ^b				
	Donor Atom	in-plane	axial			σ	π	$e_{\sigma}(xy)$	$e_{\pi_{\perp}}(xy)$	$e_{\pi_{\parallel}}(xy)$	$e_{\sigma}(z)$	$e_{\pi}(z)$
Cu(acacen)	O	192	—	90°	27	8.501	2.632	9.2	2.8	4.6	—	—
	N	192	—			9.526	3.636					
Co(salen)	O	185.2	—	90°	28	9.860	3.481	11.666	4.036	6.631	—	—
	N	184.6	—			10.920	4.733					
Co(salen) dimer	O	192	—	94.5°	29	8.501	2.632	10.431	3.293	5.410	3.008	0.437
	N	189	—			10.080	4.070					
	O	—	226			3.422	0.581					
Co(salen)•py ⁱ	O	190	—	96°	30	8.892	2.862	10.550	3.338	5.484	6.997	0.976
	N	190	—			9.900	3.931					
	N	—	210			7.396	1.756					
Co(3MeOsalen)•H ₂ O	O	195	—	102°	21	7.930	2.323	8.546	2.204	3.621	4.863	1.247
	N	205	—			7.293	2.162					
	O	—	212			5.141	1.040					

^aSquare of the diatomic overlap integral between Cu¹⁺ 3d and ligand 2p orbitals at the bond distance indicated. Data from reference 26. ^bSee text for method of calculation.

the solid state; the EPR and solution electronic spectra of the two complexes are virtually identical [22]. The bonding parameters of Cu(acacen) were derived directly from the single crystal electronic spectrum of this complex [23] using equations 2(a)–(d). The electronic spectrum of Cu(acacen) consists of two peaks at 16,400 and 18,400 cm⁻¹ which may be assigned to the transitions $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{z^2} \rightarrow d_{xy}$, respectively; the transitions $d_{xz} \rightarrow d_{xy}$ and $d_{yz} \rightarrow d_{xy}$ are probably obscured under the higher energy peak [22]. In using the bonding parameters derived for the copper complex to calculate those for the various cobalt(II) complexes a correction must be made both for the change in metal ion and for the differences in bond lengths. On going from a copper(II) complex to a cobalt(II) complex with an identical structure the metal–ligand overlap integrals are expected to increase because of the expansion of the d-orbitals, but the constant K of equation 1 is expected to decrease because of the greater energy separation of the metal and ligand orbitals. Available evidence suggests that these two effects approximately balance [22, 24], and that an increase of ~10% in the ligand bonding parameters is to be expected on going from a copper(II) complex to a cobalt(II) compound with an identical structure. The ligand bonding parameters of the cobalt(II) complexes were therefore calculated using equation 1 by estimating those for an analogous copper(II) complex with an identical structure, and increasing these by 10%, and the results are given in Table I. The parameters for

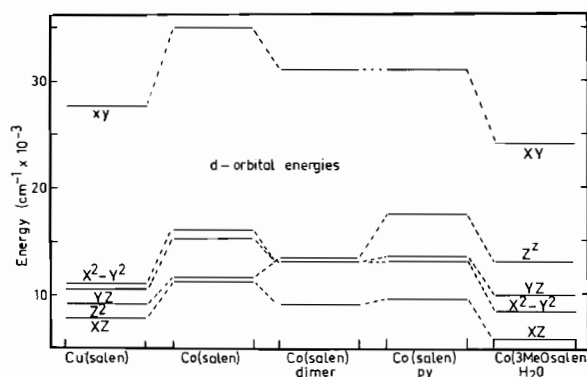


Figure 2. d-Orbital energies estimated for Cu(salen) and the cobalt(II) Schiff's base complexes.

the axial ligands in Co(salen) dimer, Co(salen)•py, and Co(3MeOsalen)•H₂O were calculated using the constants $K_{\sigma} = 8.79 \times 10^5 \text{ cm}^{-1}$, $K_{\pi} = 7.52 \times 10^5 \text{ cm}^{-1}$ reported for the acetylacetonate anion [15], $K_{\sigma} = 9.46 \times 10^5 \text{ cm}^{-1}$, $K_{\pi} = 5.56 \times 10^5 \text{ cm}^{-1}$ for quinoline [15], and $K_{\sigma} = 8.6 \times 10^5 \text{ cm}^{-1}$, $K_{\pi} = 10.9 \times 10^5 \text{ cm}^{-1}$ for water [25] bonded to copper(II), respectively. Diatomic overlap integrals reported by Smith [26] were used in the calculations. The bonding parameters were used to calculate the d-orbital energies in each complex using equations 2(a)–(d) and these are shown diagrammatically in Figure 2. Here, the small rhombic contribution to the

TABLE II. Calculated and Observed State Energies of the Cobalt(II) Schiff's Base Complexes.

State Symmetry ^a	State Energies (cm ⁻¹ × 10 ⁻³)							
	Co(salen)		Co(salen) dimer		Co(salen)•py ⁺		Co(3MeOsalen)•H ₂ O	
	calc.	obs. ^b	calc.	obs. ^b	calc.	obs. ^b	calc.	obs.
⁴ A ₂	11.16		12.03		14.85		13.00	14.30
⁴ B ₁	11.16		9.86		11.62		9.61	10.90
⁴ A ₁	4.40		5.31		8.47		6.18	7.20
⁴ B ₂	4.07		2.51		2.54		1.72	
⁴ A ₂	3.54		3.65		4.64		3.05	
⁴ B ₁	3.31		1.71		1.66		0.00	
² B ₂	19.99		15.53		12.57	13.50	11.49	
² A ₁	19.46		19.66		20.24		18.74	
² B ₁	19.00		18.34		19.48		17.76	
² A ₂	18.63		17.70		18.91		17.33	
² B ₂	16.99		16.25		15.87		15.26	
² B ₁	16.38		15.84		15.71		14.15	15.75
² A ₁	8.39	8.30(16)	11.48	11.50	14.88	~16.00	14.94	
² B ₁	3.88	3.90(65)	6.56	6.10	9.81	9.00	10.44	
² A ₂	0.00		2.68	3.00 ^c	5.91	6.00	6.55	
² A ₁	0.97	1.10 ^c	0.00		0.00		1.51	

^aDefined according to the C_{2v}(x) point group of Co(salen). ^bExperimental data from reference 17; the spectrum of Co(salen) refers to a chloroform solution with the numbers in parentheses indicating molar extinction coefficients, while the transition energies of the other complexes were obtained from reflectance spectra at 77K. ^cEnergies deduced from the EPR parameters.

ligand field, estimated at $E(yz) - E(xz) \approx 2,500$ cm⁻¹ in Cu(salen) [22] has been included; because of the stronger metal-ligand interaction this splitting is expected to increase on going to the cobalt(II) complexes, and has been set at 4000 cm⁻¹ in each case. The state energies of each cobalt(II) complex were calculated using the matrix elements for the d³ electron configuration in a ligand field of D_{4h} symmetry reported by Perumareddi [31], these being directly applicable to the d⁷ configuration provided that the signs of all the ligand field interactions are reversed. Since Perumareddi's matrix elements are expressed in terms of crystal field parameters, the following conversion factors were used:

$$\begin{aligned}
 10Dq &= E(xy) - E(x^2 - y^2) \\
 Ds &= (E(z^2) - E(xy) + E(xz) - E(x^2 - y^2))/7 \\
 Dt &= \{3(E(z^2) - E(xy)) - 4(E(xz) - \\
 &\quad E(x^2 - y^2))\}/35
 \end{aligned}$$

In addition, the effect of the rhombic component to the ligand field was included by adding the terms:

$$\begin{aligned}
 \langle d_{yz} | V_{\text{ligand field}} | d_{yz} \rangle &= 2000 \text{ cm}^{-1} \\
 \langle d_{xz} | V_{\text{ligand field}} | d_{xz} \rangle &= -2000 \text{ cm}^{-1}
 \end{aligned}$$

wherever appropriate. The effects of interelectron repulsion were included by means of the Racah parameters B and C. These will be reduced from the free ion values of B = 1115 cm⁻¹ and C = 4366 cm⁻¹ both by the decrease in effective nuclear charge on the metal (the values for Co¹⁺ are B = 878 cm⁻¹ and C = 3828 cm⁻¹) [32], and by covalency in the bonding. Values of B = 750 cm⁻¹ and C = 3250 cm⁻¹ were used in the calculations, these being consistent with the reduction in the spin-orbit coupling constant suggested by the EPR parameters of the complexes (see later). The calculated state energies below ~20,000 cm⁻¹ are listed in Table II and shown diagrammatically for each complex in Figure 3. The states are designated by symmetry labels appropriate to the C_{2v}(x) point group of Co(salen). It should be noted that the fact that x is the symmetry axis, rather than the more conventional z, means that a non-standard character table must be used to derive the symmetry labels [23]; this has sometimes led to the use of incorrect symmetry labels in the past [7, 33]. The predominant electron configuration corresponding to each state is also shown in Figure 3 for the states of low energy. In general, the states were found to correspond quite closely to the configurations shown, particularly for the low energy spin doublet states, and the low energy spin quartet states in the

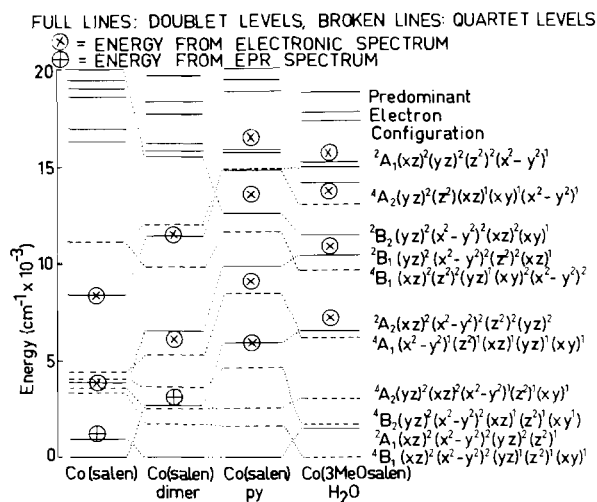


Figure 3. State energies in the cobalt(II) Schiff's base complexes.

five coordinate complexes. That is to say, interelectron repulsion does not significantly mix the states derived from a strong field approach in complexes of this kind, so that it is a much better approximation to use these wavefunctions in interpreting the EPR and magnetic properties of the complexes rather than the components of the wavefunctions appropriate to an octahedral complex, as has recently been suggested [34, 35]. A comparison of the d-orbital and state energies, however, shows that interelectron repulsion does have a significant effect on the energy levels of the complexes. In particular, as has been pointed out by Griffith [36], the ${}^2A_1(d_{x^2-y^2})$ state (the d-orbital containing the unpaired electron being shown in parentheses) is some 20B higher in energy than a simple comparison of d-orbital energies would indicate, making it most unlikely that this could ever be the groundstate in a cobalt(II) complex, as has sometimes been suggested in the past [37]. This effect also makes it improbable that the rhombic component to the ligand field will cause any significant contamination of the ${}^2A_1(d_{z^2})$ state by ${}^2A_1(d_{x^2-y^2})$, since the latter state will be too high in energy. It has been suggested by McGarvey and coworkers [7, 33] than an admixture of this kind might be of considerable importance in the interpretation of the EPR parameters of low-spin cobalt(II) complexes.

Comparison with Experiment

4-coordinate Co(salen)

The ground state of Co(salen) and related complexes has long been the subject of controversy. On the basis of single crystal EPR measurements Zelewsky proposed a ${}^2A_2(d_{yz})$ ground state [38], while also on the basis of EPR measurements Ugo *et al.* [3] have

suggested that the groundstate is ${}^2A_1(d_{z^2})$. Both propositions have received support from various other workers [39], and each has been supported by sophisticated molecular orbital calculations [40, 41] and contact shift nmr studies [42, 43]. The present calculations predict a ${}^2A_2(d_{yz})$ ground state for Co(salen), but with the ${}^2A_1(d_{z^2})$ state only ~ 1000 cm^{-1} higher in energy. The accuracy of the calculation is certainly not sufficient to allow the two possible groundstates to be distinguished unambiguously by this means alone. However, the electronic spectrum of Co(salen) provides confirmatory evidence that the ground state probably is ${}^2A_2(d_{yz})$. The spectrum of Co(salen) shows two peaks at 3900 cm^{-1} and 8300 cm^{-1} (Figure 3) and, in good agreement with the calculation (Table II), these may be assigned to transitions to the ${}^2B_1(d_{xz})$ and ${}^2A_1(d_{x^2-y^2})$ states, respectively. The intense absorption commencing at $\sim 17,000$ cm^{-1} is assigned to a variety of spin-allowed transitions, probably combined with one or more metal \rightarrow ligand charge transfer transitions. The relative intensities of the peaks at 3900 cm^{-1} ($\epsilon = 65$) and 8,300 cm^{-1} ($\epsilon = 16$) in Co(salen) and related complexes [44, 45] argue in favour a ${}^2A_2(d_{yz})$ ground state. The intensity of the latter peak is rather low for a non-centrosymmetric complex, leading in fact to its original assignment as a spin-forbidden transition [45]. However, in the non-centrosymmetric pointgroup $C_{2v}(x)$, transitions to both the ${}^2B_1(d_{xz})$ and ${}^2A_1(d_{x^2-y^2})$ are orbitally allowed if the ground state is ${}^2A_1(d_{z^2})$, while only that to the ${}^2B_1(d_{xz})$ state is formally allowed by an electric dipole mechanism if the groundstate is ${}^2A_2(d_{yz})$ [17, 23]. The low intensity of the peak at 8,300 cm^{-1} is thus easily rationalized if the groundstate is ${}^2A_2(d_{yz})$, but not if it is ${}^2A_1(d_{z^2})$. These arguments are supported by the fact that a peak at ~ 8500 cm^{-1} is observed with an intensity very similar to that in Co(salen) in analogous centrosymmetric complexes such as bis(salicylaldiminato)cobalt(II) [45] in which the intensity *must* be derived solely from a vibronic mechanism. The state energies of the present calculations also provide reasonable agreement with the EPR parameters of Co(salen) if the ground state is ${}^2A_2(d_{yz})$, but not if it is ${}^2A_1(d_{z^2})$. Using parameters derived from the calculated state energies, with the energy of the ${}^2A_1(d_{z^2})$ state set at 1100 cm^{-1} , in the comprehensive equations derived by McGarvey [7] (which use perturbation theory carried out to second order and include all relevant spin doublet and quartet states) produces the values $g_x = 3.894$, $g_y = 1.662$, $g_z = 1.792$, $A_x = 298$, $A_y = -43$, $A_z = 24 \times 10^{-4}$ cm^{-1} which may be compared with the experimental values [38] $g_x = 3.805$, $g_y = 1.660$, $g_z = 1.740$, $A_x = \pm 291$, $A_y = \pm 52$, $A_z = \pm 30 \times 10^{-4}$ cm^{-1} . In these calculations a value of the spin-orbit coupling constant $\lambda = 350$ cm^{-1} was used, this representing a reduction of $\sim 75\%$ when

compared with the value of 456 cm^{-1} estimated for Co^{1+} [46]. The EPR parameters were also calculated assuming a ${}^2A_1(d_{z^2})$ ground state and allowing the energy of the ${}^2A_2(d_{yz})$ to vary, but even allowing for a large admixture of the ${}^2A_1(d_{x^2-y^2})$ state into the ground state (which, as has already been discussed, seems unlikely) agreement with experiment was invariably very poor with g_z and g_y always being reversed in magnitude when compared with the experimental values. Finally, it should be mentioned that McGarvey has shown [33] that the EPR line-widths observed for complexes of this kind suggest a negligible ligand superhyperfine structure, and that this is incompatible with a ${}^2A_1(d_{z^2})$ ground state, as the d_{z^2} orbital can form σ -bonds with the salen ligand. A broadening of the lines due to such an interaction has been reported [6] for adducts which are known to have ${}^2A_1(d_{z^2})$ ground states. All in all, although the matter cannot be considered completely settled, the weight of current evidence certainly seems to favour a ${}^2A_2(d_{yz})$ ground state in 4-coordinate $\text{Co}(\text{salen})$ and similar complexes.

5-coordinate complexes

The calculations predict that on going from $\text{Co}(\text{salen})$ to $\text{Co}(\text{salen})$ dimer to $\text{Co}(\text{salen})\cdot\text{py}$ the ground state becomes ${}^2A_1(d_{z^2})$ with the electronic transitions to the ${}^2A_2(d_{yz})$, ${}^2B_1(d_{xz})$ and ${}^2A_1(d_{x^2-y^2})$ states moving progressively to higher energies as the axial ligand perturbation and energy of the d_{z^2} orbital increase (Figure 2). The calculated state energies are in good agreement with the observed electronic spectra of the complexes (Table II, Figure 3). Moreover, substitution of the state energies in McGarvey's equations produce EPR parameters in good agreement with experiment. Calculated values are $g_x = 2.71$, $g_y = 2.33$, $g_z = 2.02$, $A_x = 134$, $A_y = 52$, $A_z = 101 \times 10^{-4}\text{ cm}^{-1}$ for $\text{Co}(\text{salen})$ dimer and $g_x = 2.38$, $g_y = 2.26$, $g_z = 2.03$, $A_x = 42$, $A_y = 16$, $A_z = 93 \times 10^{-4}\text{ cm}^{-1}$ for $\text{Co}(\text{salen})\cdot\text{py}$, compared with experimental values [47] of $g_x = 2.69$, $g_y = 2.31$, $g_z = 2.00$, $A_x = \pm 126$, $A_y = \pm 58$, $A_z = \pm 110 \times 10^{-4}\text{ cm}^{-1}$ and $g_x = 2.41$, $g_y = 2.24$, $g_z = 2.01$, $A_x = \pm 41$, $A_y = \pm 24$ and $A_z = \pm 91 \times 10^{-4}\text{ cm}^{-1}$ for the two complexes, respectively. The calculations also suggest that on going from 4-coordinate $\text{Co}(\text{salen})$ to the 5-coordinate complexes some of the spin-quartet states move to lower energy, and are quite close to the ground state. This is consistent with the fact that the magnetic moments of both $\text{Co}(\text{salen})$ dimer and $\text{Co}(\text{salen})\cdot\text{py}$ are known to vary significantly with temperature [3, 19, 35] with the pyridine complex showing the greater variation. This was taken to indicate the presence of spin quartet states at only ~ 500 to 1000 cm^{-1} from the ground state in these compounds [3, 35]. While detailed measurements have not yet been made on 4-coordinate $\text{Co}(\text{salen})$, the magnetic moment of this complex apparently changes little

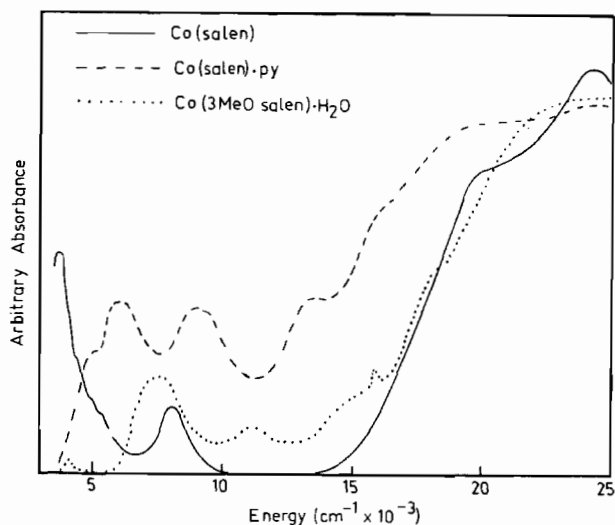


Figure 4. Electronic absorption spectra of some cobalt(II) Schiff's base complexes. Those of $\text{Co}(\text{salen})\cdot\text{py}$ and $\text{Co}(\text{3MeO salen})\cdot\text{H}_2\text{O}$ are by reflectance at $\sim 77\text{K}$, while that of $\text{Co}(\text{salen})$ is in chloroform solution. In each case absorbance is arbitrary and not proportional to extinction coefficient.

between 77K and 298K [3, 19]. When it is remembered that the doublet-quartet energy separation depends critically upon the value of the Racah parameter C used in the calculations, the calculated separations of 3300 cm^{-1} for $\text{Co}(\text{salen})$, 1710 cm^{-1} for $\text{Co}(\text{salen})$ dimer and 1655 cm^{-1} for $\text{Co}(\text{salen})\cdot\text{py}$ are in good agreement with the experimental results.

The calculations suggest that the compound $\text{Co}(\text{3MeOsalen})\cdot\text{H}_2\text{O}$ should be high spin, in agreement with experiment [19], but suggests that the ${}^2A_1(d_{z^2})$ state is only $\sim 1500\text{ cm}^{-1}$ above the ${}^4B_1(d_{z^2}, d_{xy}, d_{yz})$ ground state level. It seems clear that in compounds of this kind the lowest energy spin-doublet and quartet states are always very close in energy, and the nature of the ground state in any particular molecule may well be decided by factors such as ligand-ligand interactions. Thus, $\text{Co}(\text{3EtOsalen})\cdot\text{H}_2\text{O}$ is low-spin [19], while a number of adducts of $\text{Co}(\text{salen})$ and related molecules with nitrogenous bases are thought to show equilibria between high and low-spin forms [48]. The low temperature electronic spectrum of $\text{Co}(\text{3MeOsalen})\cdot\text{H}_2\text{O}$ is shown in Figure 4, together with those of $\text{Co}(\text{salen})$ and $\text{Co}(\text{salen})\cdot\text{py}$ for comparison. The spectrum differs somewhat from that of low-spin $\text{Co}(\text{salen})\cdot\text{py}$, though probably not enough to allow the spin-state of an adduct to be deduced solely from its electronic spectrum. The calculated and observed transition energies of $\text{Co}(\text{3MeOsalen})\cdot\text{H}_2\text{O}$ are given in Table II and illustrated schematically in Figure 3. The agreement is reasonable, with the calculated quartet state being in each case $\sim 1000\text{ cm}^{-1}$ lower in energy than the observed transition. It should be noted that several

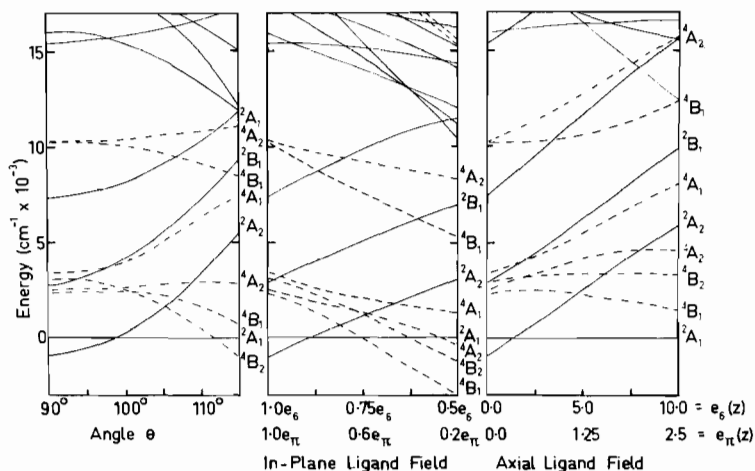


Figure 5. Variation of the state energies of Co(salen) as a function of the depression angle θ , the in-plane ligand field strength (e_σ and e_π represent the ligand bonding parameters of the salen ligand), and the axial ligand field strength ($e_\sigma(z)$ and $e_\pi(z)$ being the axial ligand σ and π -bonding parameters in $\text{cm}^{-1} \times 10^{-3}$).

spin-doublet states lie very close to each quartet state (Table II), which may contribute to the broad nature of the peaks. The weak, sharp peak at $\sim 16,000 \text{ cm}^{-1}$ is assigned as a spin-forbidden transition. Several such transitions are predicted to occur in this region (Table II), and a likely candidate is that to the ${}^2B_1(d_{xy}, d_z^2, d_{yz})$ state. As this is due essentially to a "spin-flip", it is relatively insensitive to the ligand field, and hence should give rise to a peak with a small band width.

Factors Affecting the Electronic Structure of 5-Coordinate Adducts of Planar Cobalt(II) Complexes

The overall structural changes which accompany the addition of an axial ligand to an initially planar cobalt(II) complex are well established [11, 21]. As the axial bond length decreases, so the in-plane bond lengths and the angle θ tend to increase. These changes are well illustrated by a comparison of the structural details listed in Table I. It is also well established that these changes tend to stabilize the ${}^2A_1(d_z^2)$ state compared with other low energy spin doublet states, and spin quartet states compared with spin doublet states in general, and these conclusions are borne out by the present calculations. Through the series Co(salen), Co(salen) dimer, Co(salen)·py to Co(3MeOsalen)·H₂O the energy separation $d_{xy} - d_z^2$ progressively decreases, as does the overall d-orbital splitting (Figure 2). This is due to the increasing interaction between the axial ligand and the d_z^2 orbital, and the decreasing metal-ligand interaction with the in-plane ligands. A lesser effect is the relative destabilization of the d_{xz} and d_{yz} orbitals due first to the increasing interaction with the π -orbitals of the axial ligand and second to the σ -interaction with the salen ligand which accompanies the angular distortion (equation 2d). The changes in the state

energies which accompany these d-orbital variations mean that the groundstate alters from ${}^2A_2(d_{yz})$ in 4 coordinate Co(salen) to ${}^2A_1(d_z^2)$ in Co(salen) dimer and Co(salen)·py and to ${}^4B_1(d_{yz}, d_z^2, d_{xy})$ in Co(3MeOsalen)·H₂O.

There has been considerable interest in the relative importance of the factors influencing the energy separation between the low energy spin doublet and quartet states in complexes of this kind, first because some adducts apparently exhibit spin equilibria [48] and second because various workers have attempted to correlate the EPR spectra of adducts of low spin cobalt(II) complexes with the nature of the axial ligands [2, 5, 7] and the EPR parameters, particularly the hyperfine constants, are rather sensitive to the energies of the excited quartet states [7]. The relative energies of the spin quartet and spin doublet states depend upon the Racah parameter C, and as this is reduced by electron delocalization onto the ligands, greater covalency is expected to favour a low-spin ground state. Since complexes with ligands bonding via nitrogen tend to be more covalent than those coordinated via oxygen, other things being equal there will be a greater tendency for adducts with nitrogen bases, such as Co(salen)·py, to be low spin than those such as Co(3MeOsalen)·H₂O where the axial ligand bonds via oxygen. The structural factors which have been identified as important in lowering the energies of the spin quartet states relative to the spin doublet states are the strength of the axial ligand field [7], the decreasing in-plane ligand field [17] and the raising of the cobalt(II) ion out of the xy plane [12, 35]. The relative importance of these three factors was therefore investigated by considering each effect in turn on the state energies of Co(salen) and the results are shown in Figure 5, the energies being shown relative to the ${}^2A_1(d_z^2)$ state.

The midpoint of each perturbation was taken to be the value of that parameter observed for $\text{Co}(\text{3MeOsalen})\cdot\text{H}_2\text{O}$. The calculations clearly show that the perturbation of the axial field itself causes almost no lowering in energy of the spin-quartet states. For depression angles less than $\sim 102^\circ$ this perturbation also causes little lowering of the quartet states; in practice, observed angular distortions are usually less than this [11]. However, the spin quartet states do decrease significantly in energy when the in-plane ligand perturbation is decreased, and it would seem that as far as structural changes are concerned, it is this factor which dominates the separation in the spin states in complexes of this kind. The relative unimportance of the axial ligand as a *direct* influence in this matter is well illustrated by the fact that the axial perturbation in $\text{Co}(\text{3MeOsalen})\cdot\text{H}_2\text{O}$ is actually *less* than that in $\text{Co}(\text{salen})\cdot\text{py}$ (Table I). It is thus clearly the longer in-plane Co–O and Co–N bond lengths, and to a lesser extent the greater angular distortion, in the former complex which are to be correlated with its high spin groundstate. It may be noted in this context that the transfer of an electron from the d_{yz} to the d_{xy} orbital which occurs when the groundstate changes from ${}^2A_1(d_z^2)$ to ${}^4B_1(d_{yz}d_z^2d_{xy})$ is expected to increase the metal–ligand repulsion in the xy plane and to decrease the resistance to the angular distortion provided by the d-electrons, while producing little change to the metal–ligand interaction along the z axis; this is, of course, in line with the observed structural changes. The energy separation of the ${}^2A_1(d_z^2)$ and ${}^2A_2(d_{yz})$ states is extremely sensitive to both the axial and in-plane ligand fields and it is probably this fact which gives rise to the observation of the EPR signals due to several different species in frozen chloroform solutions of $\text{Co}(\text{salen})$ [3]. The EPR spectra themselves are very sensitive to small changes in the energy separation of these states in $\text{Co}(\text{salen})$ [17], so that the existence of species having only minor variations in solvation or ligand conformation may well be distinguished.

Conclusions

A method of deriving the state energies of a series of cobalt(II) Schiff's base complexes from the d-orbital energies observed directly for an analogous copper(II) complex has been described. The calculated d-orbital energies of the cobalt(II) complexes are self-consistent and chemically reasonable, and the state energies are in agreement with the magnetic properties and EPR and electronic spectra of the complexes. It would therefore seem that the method might usefully be applied to other systems where the nature of the ground state is in doubt, such as the adducts of some iron porphyrin complexes. The

effects of the structural changes which accompany the formation of an adduct by a planar cobalt(II) complex have been investigated and it was found that the decrease in the in-plane ligand field strength plays the dominant role in stabilizing the high spin state in adducts of this kind.

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References

- 1 See, for example, P. Fantucci and V. Valenti, *J. Am. Chem. Soc.*, **98**, 3832 (1976) and references therein.
- 2 F. Ann Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).
- 3 C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo and Venazio Valenti, *J. Chem. Soc. Dalton Trans.*, 754 (1973).
- 4 C. Floriani, G. Fachinetti and F. Calderazzo, *J. Chem. Soc. Dalton Trans.*, 765 (1973).
- 5 B. B. Wayland, M. E. Abd-elmageed and L. F. Mehne, *Inorg. Chem.*, **14**, 1456 (1975).
- 6 A. Rockenbauer, E. Budo-Zahonyi and L. I. Simardi, *J. Chem. Soc. Dalton Trans.*, 1729 (1975).
- 7 B. R. McGarvey, *Canad. J. Chemistry*, **54**, 2498 (1975).
- 8 P. W. Lau and W. C. Lin, *J. Inorg. Nucl. Chem.*, **37**, 2389 (1975).
- 9 W. C. Lin and P. W. Lau, *J. Am. Chem. Soc.*, **98**, 1447 (1976).
- 10 W. C. Lin, *Inorg. Chem.*, **15**, 1114 (1976).
- 11 L. Sacconi, *Coord. Chem. Rev.*, **8**, 351 (1972).
- 12 J. A. Varga and C. A. L. Becker, *Canad. J. Chem.*, **52**, 579 (1973).
- 13 C. E. Schäffer, *Structure and Bonding*, (Springer, Berlin), **5**, 68, 14, 69 (1973); C. K. Jørgensen, "Modern Aspects of Ligand Field Theory", North Holland, Amsterdam (1970).
- 14 M. A. Hitchman, *Inorg. Chem.*, **13**, 2218 (1974).
- 15 M. A. Hitchman, *Inorg. Chem.*, **11**, 2387 (1972).
- 16 E. Pedersen and H. Toftlund, *Inorg. Chem.*, **13**, 1603 (1974).
- 17 M. A. Hitchman, *Inorg. Chem.*, **16**, 1985 (1977).
- 18 M. Calvin and C. H. Barkelew, *J. Am. Chem. Soc.*, **68**, 2267 (1946).
- 19 A. Earnshaw, P. C. Hewlett, E. A. King and L. F. Larkworthy, *J. Chem. Soc. A*, 241 (1968).
- 20 L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, **10**, 1498 (1971).
- 21 M. Calligaris, G. Nardin and L. Randaccio, *J. Chem. Soc. Dalton Trans.*, 1903 (1974).
- 22 See reference 17 for a detailed discussion of the derivation of the energy levels in $\text{Cu}(\text{acacen})$, and by analogy $\text{Cu}(\text{salen})$, and the estimation of the bonding parameters of the cobalt(II) complexes.
- 23 C. D. Olson, G. Basu and R. Linn Belford, *J. Coord. Chem.*, **1**, 176 (1971).

- 24 M. A. Hitchman, *J. Chem. Soc. Faraday Trans. II*, **68**, 846 (1972).
- 25 M. A. Hitchman and T. D. Waite, *Inorg. Chem.*, **15**, 2150 (1976).
- 26 D. W. Smith, *J. Chem. Soc. A*, 1498 (1970).
- 27 G. R. Clark, D. Hall and T. N. Waters, *J. Chem. Soc. A*, 823 (1969).
- 28 W. P. Schaeffer and R. E. Marsh, *Acta Cryst.*, **B25**, 1675 (1969).
- 29 R. Delasi, S. L. Holt and B. Port, *Inorg. Chem.*, **10**, 1498 (1971).
- 30 M. Calligaris, D. Minichelli, G. Nardin and L. Randaccio, *J. Chem. Soc. A*, 2411 (1970).
- 31 J. R. Perumareddi, *Coord. Chem. Rev.*, **4**, 73 (1969).
- 32 J. S. Griffith, "Theory of Transition Metal Ions", Cambridge, 1964, p. 437.
- 33 V. Malatesta and B. R. McGarvey, *Canad. J. Chem.*, **53**, 3791 (1975).
- 34 K. S. Murray and R. M. Sheahan, *Chem. Comm.*, 475 (1975).
- 35 K. S. Murray and R. M. Sheahan, *J. Chem. Soc. Dalton Trans.*, 999 (1976).
- 36 Ref. 32, page 372.
- 37 L. M. Engelhardt, J. D. Duncan and M. Green, *Inorg. Nucl. Chem. Lett.*, **8**, 725 (1972); E. I. Ochiai, *Chem. Comm.*, 489 (1972).
- 38 A. von Zelewsky and H. Fierz, *Helv. Chim. Acta*, **56**, 977 (1973).
- 39 For a detailed list of the proponents of each point of view, see references 17 and 33.
- 40 P. Fantucci and V. Valenti, *J. Am. Chem. Soc.*, **98**, 3832 (1976).
- 41 A. Dedieu, M. Rohmer and A. Veillard, *J. Am. Chem. Soc.*, **99**, 5789 (1976).
- 42 K. Migiya, M. Iwaizuru and T. Isobe, *J. Am. Chem. Soc.*, **97**, 4228 (1975).
- 43 C. Srivanavit and D. G. Brown, *J. Am. Chem. Soc.*, **99**, 4447 (1976).
- 44 F. L. Urbach, R. D. Bereman, J. A. Topich, M. Hariharan and B. J. Kalbacher, *J. Am. Chem. Soc.*, **96**, 5063 (1974).
- 45 H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jap.*, **37**, 8 (1964).
- 46 See reference 32. Note that this reduction is assumed to be due to electron delocalization onto the ligands, and since it occurs both in the mixing of each excited state into the groundstate by spin-orbit coupling and in the derivation of the g values by considering the interaction of the operator $\beta H(2s+1)$ with the ground state wavefunctions it represents in effect the unpaired electron density population of the d orbitals raised to the fourth power. This reduction is thus quite compatible with the ~85% reduction due to covalency assumed for the Racah parameters, where the d-orbital population occurs to the second power. Note also that the reduction in effective nuclear charge of the cobalt ion is assumed to lower the spin-orbit coupling constant from the free ion value for Co^{2+} of 533 cm^{-1} . See reference 17 for a more detailed discussion of the method of derivation of the EPR parameters.
- 47 C. Busetto, F. Cariati, P. Fantucci, D. Galizzioli and F. Morazzoni, *J. Chem. Soc. Dalton Trans.*, 1713 (1973).
- 48 L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, **11**, 457 (1972).