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Electronic Structure of Low-Spin Cobalt(II) Schiff Base Complexes

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The state energies of four-coordinate *N,N'*-ethylenebis(salicylaldiminato)cobalt(II), Co(salen), the dimeric form of this complex, Co(salen) dimer, and its pyridine adduct, Co(salen)·py, have been estimated using ligand bonding parameters derived from analogous copper(II) complexes using the angular overlap simple molecular orbital model. The measured electronic spectra of the complexes are in good agreement with the calculations, and the relative intensities of the "d–d" transitions of Co(salen) suggest a $^2A_2(d_{yz})$ ground state for this compound. It is shown that interelectron repulsion contributes significantly to the state energies in these complexes; in particular the $^2A_1(d_{x^2-y^2})$ state is at rather high energy, making any significant admixture of this with the $^2A_1(d_{z^2})$ state in these compounds unlikely. The excited-state energies have been used to estimate the EPR parameters of the complexes, and these agree with experiment, with four-coordinate Co(salen) having a $^2A_2(d_{yz})$ ground state but with the $^2A_1(d_{z^2})$ state only ~1100 cm^{-1} higher in energy and Co(salen) dimer and Co(salen)·py each having $^2A_1(d_{z^2})$ ground states. It is shown that the EPR parameters of a wide range of cobalt(II) Schiff base complexes and their adducts can be rationalized using a bonding scheme analogous to that of four-coordinate Co(salen) but with the relative energy of the $^2A_1(d_{z^2})$ state varying from one compound to another.

Introduction

The electronic structures of the planar, low-spin Schiff base complexes of cobalt(II) have long been the subject of interest,[1–4] largely because of their ability to reversibly absorb molecular oxygen under certain conditions.[1b,e] The best known of this series of complexes, (*N,N'*-ethylenebis(salicylaldiminato))cobalt(II), Co(salen), exists in two crystal modifications, one of which contains a molecule of chloroform of crystallization, and in which the complex is effectively planar,[5] while the second, Co(salen) dimer, contains loosely bound dimers, with each approximately planar molecule containing a fifth bond to an oxygen atom of a neighboring complex.[6] The cobalt(II) Schiff base complexes also generally easily form base adducts, and that of Co(salen) with pyridine, Co(salen)·py, has a square-based pyramidal geometry with a comparatively short axial bond to the pyridine nitrogen atom.[7] While it is well established that the base adducts have ground-state electron configurations in which the single unpaired electron occupies the d_{z^2} orbital,[1f,g,n,r] the ground state wave functions of the planar complexes without axial ligation have remained controversial. On the basis of EPR studies of several four-coordinate planar complexes, Green et al.[11] and Ochiai[1m] proposed that the single unpaired electron occupies the $d_{x^2-y^2}$ orbital, and the electronic spectra of several complexes were interpreted on this basis.[1i] However, the orientation of the **g** and hyperfine tensors of Co(salen) diluted into the analogous nickel complex, reported by Zelewsky and Fierz,[1s] renders this assignment untenable. Instead, Zelewsky proposed that the unpaired electron resides in the d_{yz} orbital, and supporting evidence for this assignment has recently been provided by NMR[1x] and photoelectron spectroscopy.[1w] However, also on the basis of EPR studies, Busetto et al.[1o–q,4] and other workers[1r,u,y] have suggested that in these complexes the unpaired electron occupies the d_{z^2} orbital. Recently, McGarvey has published[2] detailed equations for the interpretation of the EPR parameters of a low-spin cobalt(II) complex having either a d_{yz} or d_{z^2} ground state, taking into account the fact that the d_{z^2} and $d_{x^2-y^2}$ orbitals might be mixed by low-symmetry elements of the ligand field. Malatesta and McGarvey[3] found that while there was some evidence for a d_{yz} ground state in the complexes they studied, it was impossible to differentiate unambiguously between this and a ground state involving an orbital produced by a significant admixture of $d_{x^2-y^2}$ into d_{z^2}.

This ambiguity might perhaps be resolved theoretically by considering the effects of the ligand field, interelectron repulsion, and spin–orbit coupling upon the free d-electron wave functions. This approach has recently been successfully applied to the interpretation of the magnetic properties of a large variety of low-symmetry metal complexes,[8] including the NiF_6^{3-} ion[9] which, like the complexes considered here, has a low-spin d^7 electron configuration. The main problem in applying a model of this kind to the cobalt(II) Schiff base complexes arises from the uncertainty in the choice of the ligand field parameters. The method presented here utilizes ligand bonding parameters derived from the electronic and EPR spectra of analogous copper(II) complexes, which are more easily interpreted than those in the cobalt(II) complexes, as interelectron repulsion is effectively absent. These have been used, with appropriate corrections and the addition of interelectron repulsion, to estimate the energies and composition of the electronic states of Co(salen), Co(salen) dimer, and Co(salen)·py. The calculations were carried out within the framework of the angular overlap simple molecular orbital model developed by Schäffer[10] and Jørgensen,[11] which has proved an effective way of correlating ligand bonding parameters for a series of structurally related complexes.[8,12] It is found that the electronic structures derived in this manner are self-consistent and satisfactorily account for the electronic and EPR spectra of Co(salen), Co(salen) dimer, Co(salen)·py and also for the EPR parameters of most related complexes.

Experimental Section

Co(salen) dimer and Co(salen)·py were prepared by the method of Calvin.[1b] Zn(salen)·H$_2$O was prepared by boiling an equimolar mixture of zinc acetate and the ligand in aqueous ethanol. Upon filtering and allowing the resulting solution to stand overnight, a pale yellow microcrystalline precipitate of the desired product formed which was collected, washed with acetone, and dried briefly in vacuo. Anal. Calcd for Co(salen) dimer: C, 59.9; H, 4.3; N, 8.6. Found: C, 59.3; H, 4.1; N, 8.6. Calcd for Co(salen)·py: C, 62.4; H, 4.7; N, 10.4. Found: C, 62.1; H, 4.4; N, 10.0. Calcd for Zn(salen)·H$_2$O: C, 55.4; H, 4.6; N, 7.9. Found: C, 55.1; H, 4.4; N, 7.7.

Electronic spectra were measured using a Zeiss PMQII spectrophotometer. Solution spectra were also measured on a Cary 17 spectrophotometer, and in the region 3700–4000 cm^{-1} on a Perkin-Elmer 477 machine.

Discussion

Symmetry of Co(salen). The molecular structure of Co(salen) is shown schematically in Figure 1, together with the coordinate system which, by convention, has always been used to discuss this series of complexes. The molecule belongs to the point group $C_{2v}(x)$. It is to be noted that with this choice of coordinate system the unique symmetry axis is *x* rather than the more conventional *z*. This fact, which has sometimes been overlooked,[13] means that a nonstandard character table must be used to derive the symmetry labels applicable to the wave functions of the complexes; the transformation properties of

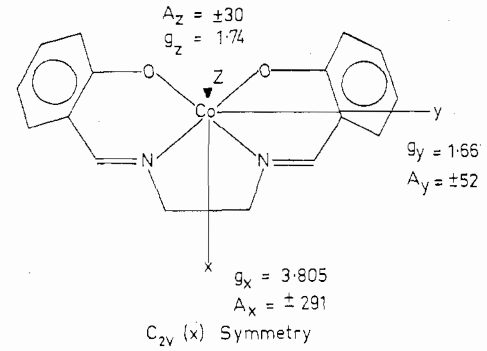

Figure 1. Molecular structure, coordinate system, and EPR parameters of Co(salen). A values are in $\mathrm{cm}^{-1} \times 10^4$.

the d orbitals in the $C_{2v}(x)$ point group are as follows: d_{z^2} and $d_{x^2-y^2}$, A_1; d_{xy}, B_2; d_{xz}, B_1; d_{yz}, A_2. The **g** and metal hyperfine values reported[1s] for Co(salen), diluted into the analogous nickel complex, are also shown in Figure 1. It is of interest to note that these tensors have approximate axial symmetry, but with the symmetry axes lying in the plane of the molecule (coinciding, in fact, with the symmetry axis of the point group). This seems to be a quite general feature of the EPR parameters of planar four-coordinate cobalt(II) complexes.[2] Rather similar EPR spectra have been reported for some analogous Schiff base complexes derived from the acetylacetonate anion: *N*,*N'*-bis(2-penten-4-one)-(*R*)-(−)-propane-1,2-diaminocobalt(II), Co(acac)(−)pn, in ordered nematic phases;[1u] *N*,*N'*-ethylenebis(benzoylacetone iminato)cobalt(II), Co(benacacen), diluted into the corresponding nickel complex.[3] Similar EPR spectra have also been reported for analogous complexes in which the oxygen atoms have been replaced by NH groups: *N*,*N'*-ethylenebis(*o*-aminobenzylideniminato)cobalt(II), Co(amben), diluted into the corresponding nickel complex;[3,14] *N*,*N'*-bis(*o*-aminobenzylidene)-(*R*,*R*)-(−)-cyclohexane-1,2-diaminocobalt(II), Co(amben)(−)chxn, in ordered nematic phases.[1u]

d-Orbital Sequence in Analogous Copper(II) Complexes. Although Cu(salen) itself crystallizes in a structure in which the metal ion experiences weak axial ligand interactions,[15] the closely related complex *N*,*N'*-ethylenebis(acetylacetone iminato)copper(II), Cu(acacen), crystallizes in a modification which is strictly planar and four-coordinate.[16] The two complexes have virtually identical spectra on solution in inert solvents.[17] The electronic spectrum of single crystals of Cu(acacen) has been studied in detail by Olson et al.[18] down to 4 K. The observed "d–d" spectrum consists of two peaks, at 16 400 and 18 400 cm^{-1} which may be unambiguously assigned from their polarization properties to the transitions $^2A_1(d_{z^2}) \rightarrow {}^2B_2(d_{xy})$ and $^2A_1(d_{x^2-y^2}) \rightarrow {}^2B_2(d_{xy})$, though which transition corresponds to which peak could not be deduced. Unfortunately, the peaks due to the transitions $^2B_1(d_{xz})$ and $^2A_2(d_{yz}) \rightarrow {}^2B_2(d_{xy})$ could not be resolved, and it seems likely that these are obscured, either under the peaks in the visible region or beneath the intense charge-transfer absorption commencing at ~22 500 cm^{-1}.

The EPR parameters of Cu(salen) diluted into single crystals of the analogous nickel complex have been measured by Scullane and Allen,[19] who observed g values of $g_x = 2.049$ (4), $g_y = 2.046$ (4), and $g_z = 2.192$ (4) where the figure in parentheses represents the possible error. The g values are related to the excited-state energies via the orbital reduction parameters k_x, k_y, and k_z by the equations

$$g_x = 2.0023 - 2\lambda k_x^2/E(d_{xz}) \quad (1a)$$

$$g_y = 2.0023 - 2\lambda k_y^2/E(d_{yz}) \quad (1b)$$

$$g_z = 2.0023 - 8\lambda k_z^2/E(d_{x^2-y^2}) \quad (1c)$$

where λ is the spin–orbit coupling constant (−828 cm^{-1}) and E is the energy of the excited state in which the electron occupies the d orbital in parentheses. By use of the approximations $g_\perp = (g_x + g_y)/2$ and $k_\perp = (k_x + k_y)/2$ eq 1a–c yield a value of $k_\perp^2 > 0.61$ if the energies of the $^2B_1(d_{xz})$ and $^2A_2(d_{yz}) \rightarrow {}^2B_2(d_{xy})$ transitions lie above 22 500 cm^{-1} or a value of $k_\perp^2 \approx 0.50$ if they are obscured under the peak at 18 400 cm^{-1}. The latter assignment seems more likely, when compared with the values observed for other planar copper complexes having unambiguously assigned electronic spectra and accurately known g values. For instance, data obtained for eight planar copper(II) complexes, each involving either a saturated or unsaturated ligand bonding via nitrogen atoms, yield an average of $k_\perp^2 = 0.49 \pm 0.05$,[20] while for three bis(acetylacetonato)copper(II) complexes a value of $k_\perp^2 = 0.55 \pm 0.05$ is obtained.[21] There are good theoretical reasons for expecting the $d_{x^2-y^2}$ orbital to be higher in energy than d_{xz} and d_{yz} in a planar complex, so that the transition $^2A_1(d_{x^2-y^2}) \rightarrow {}^2B_2(d_{xy})$ can probably be assigned to the transition at 16 400 cm^{-1} in the spectrum of Cu(acacen), with $^2A_1(d_{z^2}) \rightarrow {}^2B_2(d_{xy})$ being at 18 400 cm^{-1}.

The in-plane g anisotropy in Cu(salen) is directly related to the difference in ligand interaction with the d_{xz} and d_{yz} orbitals. For this complex the anisotropy is small, less, in fact, than experimental error, and this would seem to be a general feature of compounds of this kind.[22] This suggests that the splitting between the d_{xz} and d_{yz} orbitals is also small, probably less than ~3000 cm^{-1}. In the analogous bis(acetylacetonate)copper(II) complexes the energy separation between d_{xz} and d_{yz} can be detected directly in the electronic spectra,[12c] with the d_{yz} orbital between ~500 and ~2500 cm^{-1} higher in energy than d_{xz}. A similar splitting of these levels in the copper(II) Schiff base complexes seems reasonable.

Summarizing the above inferences, the most likely energy sequence of the d orbitals in Cu(salen) is $d_{xy} >> d_{x^2-y^2} > d_{z^2} \approx (d_{yz} > d_{xz})$. This energy pattern is illustrated in Figure 2. As the above sequence can only be considered tentative, the subsequent calculations were also performed with the $^2A_2(d_{yz})$ and $^2B_1(d_{xz}) \rightarrow {}^2B_2(d_{xy})$ transitions set at ~22 500 cm^{-1} and with the assignments of the $^2A_1(d_{z^2})$ and $^2A_1(d_{x^2-y^2}) \rightarrow {}^2B_2(d_{xy})$ transitions both as above and reversed. However, each of these latter alternatives predicted state energies for the Co(salen) complexes quite incompatible with the observed electronic and EPR spectra.

Ligand Bonding Parameters in the Complexes. In order to use the d-orbital energies estimated for Cu(salen) to deduce those in the analogous cobalt(II) compounds, it is desirable to parametrize the ligand field bonding parameters of the Schiff base ligand, and this was done using the angular overlap model (AOM).[10,11] This gives the energy e by which a metal d orbital is raised upon interaction with a ligand orbital as

$$e = S^2C \quad (2a)$$

$$C = H_L^2/(H_M - H_L) \quad (2b)$$

Here S is the diatomic overlap integral and C is a constant related to the diagonal matrix elements of the ligand (H_L) and metal (H_M) orbitals. The total energy of each d orbital is then obtained by summing over the σ and π orbitals of all of the ligand donor atoms using the angular overlap matrix appropriate to the geometry of the complex. The AOM has the big advantage that the ligand bonding parameters derived for one complex can readily be used to predict the d-orbital energies in other related complexes with different structures, and in this way the model has recently been used to rationalize the EPR and optical spectra of several series of structurally related compounds.[8,12,23]

As the EPR spectra of the copper(II) Schiff base complexes strongly suggest that the departure of the ligand field from

Table I. Structural Details, Diatomic Overlap Integrals, and Ligand Bonding Parameters of Various Schiff Base Complexes

	Bond lengths, pm				$S^2 \times 10^3$ [a]		Ligand bonding parameters, $\text{cm}^{-1} \times 10^{-3}$ [b]				
Complex	Donor atom	In plane	Axial	Ref	σ	π	$e_\sigma(xy)$	$e_{\pi\perp}(xy)$	$e_{\pi\parallel}(xy)$	$e_\sigma(z)$	$e_\pi(z)$
Cu(acacen)	O	192			8.501	2.632					
	N	192		16	9.526	3.636	9.2	2.8	4.6		
Co(salen)	O	185.2			9.860	3.481					
	N	184.6		5	10.920	4.733	11.666	4.036	6.631		
Co(salen) dimer	O	192			8.501	2.632					
	N	189		6	10.080	4.070	10.431	3.293	5.410	3.008	0.437
	O		226		3.422	0.581					
Co(salen)·py	O	190			8.892	2.862					
	N	190		7	9.900	3.931	10.550	3.338	5.484	6.997	0.976
	N		210		7.396	1.756					

[a] Square of the diatomic overlap integral between Cu^+ 3d and ligand 2p orbitals at the bond distance indicated. Data are from ref 25.
[b] See text for method of calculation.

axial symmetry is relatively small, the bonding parameters have been derived assuming axial symmetry, with the rhombic component being added subsequently as a perturbation. The total energy E by which each d orbital is raised upon complex formation in a planar complex with one ligand occupying an axial position is given by [10,12c]

$$E(\mathrm{d}_{xy}) = 3e_\sigma(xy) \tag{3a}$$

$$E(\mathrm{d}_{z^2}) = e_\sigma(xy) + e_\sigma(z) \tag{3b}$$

$$E(\mathrm{d}_{x^2-y^2}) = 4e_{\pi\perp}(xy) \tag{3c}$$

$$E(\mathrm{d}_{xz}, \mathrm{d}_{yz}) = 2e_{\pi\parallel}(xy) + e_\pi(z) \tag{3d}$$

Here $e_\sigma(xy)$ represents the energy by which the d orbital is raised upon interaction with one ligand donor atom in the xy plane, while $e_\sigma(z)$ represents the σ interaction of the axial ligand (this being zero when a four-coordinate complex is considered). The π interaction with the Schiff base is separated into two components, $e_{\pi\perp}(xy)$ and $e\pi_{\parallel}(xy)$, representing the interaction in and out of the plane of the ligand, respectively; the comparatively weak π interaction with the axial ligands $e_\pi(z)$ is assumed to be symmetrical about the bond axis. It is to be noted that in these expressions the parameters represent the arithmetic mean of the perturbations due to the oxygen and nitrogen atoms of the Schiff base, following the concept of "holehedrized symmetry" incorporated in the AOM.[10,11] Also, the fact that in the five-coordinate complexes the cobalt ion is raised slightly out of the plane of the Schiff base ligand has been ignored; however the distortions involved would have an insignificant effect on the d-orbital energies.[12a]

Insertion of the relevant energy differences $E(\mathrm{d}_{xy}) - E(\mathrm{d}_{z^2})$ etc. in eq 3a–3d readily allows the estimation of the three ligand bonding parameters $e_\sigma(xy)$, $e_{\pi\perp}(xy)$, and $e\pi_{\parallel}(xy)$ characteristic of the Schiff base in Cu(acacen). Since the electronic spectra of Cu(salen) and Cu(acacen) in inert solvents are virtually identical,[17] as are the EPR parameters of these complexes diluted into the analogous nickel compounds,[19,24] it seems reasonable to assume that the same bonding parameters also apply to the ligand in Cu(salen). In order to deduce the d-orbital energies in the Co(salen) complexes, the bonding parameters must be corrected for the changes in bond length and metal ion. Also, for the five-coordinate compounds the effects of the axial ligands must be included. From eq 2a it is seen that a change in bond length produces an alteration in ligand interaction proportional to the change in the square of the overlap integral. The variation in metal–ligand interaction on going from a copper(II) to a cobalt(II) complex with an identical structure will be affected first by an increase in the overlap integral, due to the expansion of the d orbitals accompanying the lower effective nuclear charge on the metal, and second by a decrease in the constant C, because of the greater energy separation of the metal and ligand orbitals as represented by the term $(H_\mathrm{M} - H_\mathrm{L})$ in eq 2b. Theoretically, it is expected that these effects will approximately balance, and available evidence suggests that a slight increase (~5%) is to be expected on going from a copper complex to a nickel compound with an identical structure.[12b] Thus, on going from a copper(II) to a cobalt(II) complex with an identical structure, an increase of ~10% in the metal–ligand interaction seems reasonable. The ligand bonding parameters in the cobalt(II) Schiff base complexes were therefore estimated by calculating those expected in an analogous copper(II) complex with an identical structure and increasing these values by 10%. The procedure was also followed assuming a 5% and a 15% increase, but this produced only minor shifts (from 500 to 2000 cm^{-1}) in the calculated state energies of the cobalt complexes. The low-energy spin-doublet states of importance in determining the EPR parameters were particularly insensitive to these changes. That this procedure may reasonably be expected to correctly predict the approximate d-orbital energies in the cobalt complexes can be tested by using the ligand bonding parameters $C_\sigma = 8.6 \times 10^5\ \text{cm}^{-1}$ and $C_\pi = 10.9 \times 10^5\ \text{cm}^{-1}$ recently estimated[12d] for the water molecule toward Cu^{2+} in a range of complexes containing the $Cu(H_2O)_6^{2+}$ ion to predict the ligand field splitting parameter Δ for the hexaaquocobaltate(II) ion. The Co–O bond length in $Co(H_2O)_6^{2+}$ is 209 pm,[26] and the Cu(3d)–O(2p) diatomic σ and π overlaps at this distance are 7.465×10^{-2} and 3.445×10^{-2}, respectively.[25] Substitution of these values into eq 2a followed by a 10% increase in e_σ and e_π allows a value of $\Delta = 10\,100\ \text{cm}^{-1}$ to be estimated from the equation[10]

$$\Delta = 3e_\sigma - 4e_\pi$$

This is in good agreement with the value of $10\,000\ \text{cm}^{-1}$ observed experimentally.[27] The effects of the axial ligation in Co(salen) dimer and Co(salen)·py were incorporated, via eq 2a, by use of the bonding parameters $C_\sigma = 8.79 \times 10^5\ \text{cm}^{-1}$ and $C_\pi = 7.52 \times 10^5\ \text{cm}^{-1}$, estimated for the acetylacetonate anion, and $C_\sigma = 9.46 \times 10^5\ \text{cm}^{-1}$ and $C_\pi = 5.56 \times 10^5\ \text{cm}^{-1}$, calculated for quinoline, toward copper(II),[12c] respectively. The ligand bonding parameters calculated for the various complexes, together with the information used to derive them, are listed in Table I.

Estimation of the d-Orbital and State Energies in the Complexes. Substitution of the ligand bonding parameters listed in Table I into eq 3a–3d yields the d-orbital energies expected for the cobalt(II) Schiff base complexes, and these are shown in Figure 2, with the additional feature that the energy separation expected between d_{xz} and d_{yz} is included (this being estimated as $3000\ \text{cm}^{-1}$ by comparison with the analogous copper complex). It is apparent that the major change on going to four-coordinate Co(salen) is a pronounced increase in all of the d-orbital energies, this being due largely to the shorter bond lengths in the cobalt complex (Table I). As expected, the main effect on going from Co(salen) to Co(salen)

Table II. Calculated and Observed State Energies below 25 000 cm^{-1} for the Cobalt(II) Schiff Base Complexes

State symmetry^a	Energy, cm^{-1} × 10^{-3}					
	Co(salen)		Co(salen) dimer		Co(salen)·py	
	Calcd	Obsd^b	Calcd	Obsd^c	Calcd	Obsd^c
$^4A_1$	22.516		23.427		26.693	
$^4A_2$	10.577		10.100		12.138	
$^4B_1$	10.539		11.760		14.565	
$^4B_2$	3.995		2.771		2.928	
$^4A_1$	3.663		5.307		8.396	
$^4A_2$	3.336		3.733		4.561	
$^4B_1$	3.159		2.241		2.315	
$^2A_2$	23.246		24.574		27.317	
$^2B_2$	23.126		22.890		25.129	
$^2A_2$	22.978		23.022		25.394	
$^2B_2$	22.561		24.680		27.903	
$^2A_1$	21.268		23.217		26.337	
$^2B_2$	20.427		16.088		13.024	13.500
$^2B_1$	19.696		19.454		20.313	
$^2A_1$	19.509		19.771		20.620	
$^2B_2$	18.981		20.444		23.364	
$^2B_1$	18.843		18.556		19.353	
$^2A_2$	18.096		16.814		16.528	
$^2B_2$	16.513		15.693		16.010	
$^2B_1$	16.297		17.996		19.276	
$^2A_1$	7.900	8.300 (16)	11.408	11.500	14.780	~16.000
$^2B_1$	2.909	3.900 (65)	5.925	6.100	9.054	9.000
$^2A_2$	0.000		3.010		6.128	6.000
$^2A_1$	0.480		0.000		0.000	

^{a} Defined according to the point group $C_{2v}(x)$. ^{b} Measured in chloroform solution; figures in parentheses represent the extinction coefficient in mol^{-1} L cm^{-1}. ^{c} Measured by reflectance technique at ~77 K.

dimer to Co(salen)·py is a significant and progressive increase in the energy of the d_{z^2} orbital.

Having established the ligand bonding parameters, we find the calculation of the state energies of the cobalt complexes is straightforward, and this was done using the matrix elements published for the d^3 electron configuration by Perumareddi[29] (these being directly applicable to the d^7 system provided that the sign of all the ligand field parameters is reversed). Since Perumarreddi's matrix elements are expressed in terms of the crystal field parameters *Dq*, *Ds*, and *Dt*, the following conversion factors were used[8]

$$Dq = [3e_\sigma(xy) - 4e_{\pi\perp}(xy)]/10$$

$$Ds = [e_\sigma(z) - 2e_\sigma(xy) + e_\pi(z) + 2e_{\pi\parallel}(xy) - 4e_{\pi\perp}(xy)]/7$$

$$Dt = [3(e_\sigma(z) - 2e_\sigma(xy)) - 4(e_\pi(z) + 2e_{\pi\parallel}(xy) - 4e_{\pi\perp}(xy))]/35$$

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

$$\langle d_{yz}|V_{\text{ligand field}}|d_{yz}\rangle = 1500\ \text{cm}^{-1}$$

$$\langle d_{xz}|V_{\text{ligand field}}|d_{xz}\rangle = -1500\ \text{cm}^{-1}$$

where appropriate. The effects of interelectron repulsion were included by means of the Racah parameters *B* and *C*. These are expected to 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 Co$^+$ are B = 878 cm^{-1} and C = 3828 cm^{-1} [30]) and by electron delocalization onto the ligand orbitals. Values of B = 750 cm^{-1} and C = 3150 cm^{-1} were used in the calculations.

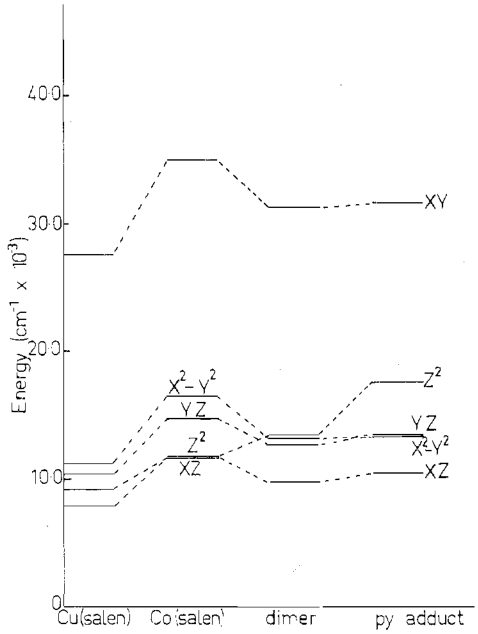

Figure 2. d-Orbital energies estimated for Cu(salen), four-coordinate salen, Co(salen) dimer, and Co(salen)·py.

The state energies, defined by symmetry labels appropriate to the $C_{2v}(x)$ point group (Figure 1) are listed in Table II and shown schematically in Figure 3, up to a maximum energy of 25 000 cm^{-1}. The electron configurations of the states important in the interpretation of the EPR and electronic spectra are also shown in Figure 3. In the subsequent discussions, symmetry labels appropriate to the $C_{2v}(x)$ point group will be used throughout, although strictly speaking Co(salen) dimer and Co(salen)·py are of lower symmetry than this, belonging to the C_{1h} point group. This does not affect the interpretation of the EPR spectra, or "d–d" transition energies.[31] For four-coordinate Co(salen) the calculations suggest a $^2A_2(d_{yz})$ ground state (the d orbital in parentheses indicating that containing the unpaired electron) but place the $^2A_1(d_{z^2})$ state only ~500 cm^{-1} higher in energy. The only other spin-doublet states below ~16 000 cm^{-1} are $^2B_1(d_{xz})$ at ~3000 cm^{-1} and $^2A_1(d_{x^2-z^2})$ at ~8000 cm^{-1}. The principal effect on going to Co(salen) dimer and Co(salen)·py is the progressive lowering in energy of the $^2A_1(d_{z^2})$ and $^2B_2(d_{xy})$ states relative to the other spin-doublet states (Figure 3). This is directly related to the increasing energy of the d_{z^2} orbital and con-

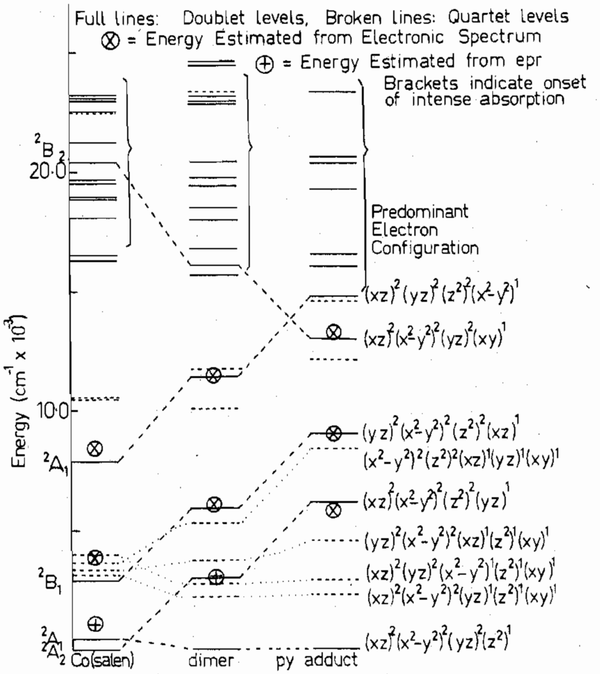

Figure 3. State energies in four-coordinate Co(salen), Co(salen) dimer, and Co(salen)·py.

sequent decrease in energy separation between d_{z^2} and d_{xy}, which accompany axial ligation (Figure 2). The calculations suggest that in four-coordinate Co(salen) a variety of spin-quartet states lie some 3000–4000 cm^{-1} above the ground state and that some of these move to even lower energy in the axially ligated complexes. This is in agreement with the magnetic susceptibility measurements, which suggest the presence of low-lying quartet states in Co(salen) dimer and Co(salen)·py.[1d,i] It is noteworthy that this lowering in energy of the quartet states is not a *direct* result of the axial ligand perturbation, as has sometimes been implied,[2] but is in fact due more to the slight increase in in-plane bond lengths which accompany the change from four- to five-coordination (Table I). It is in fact the balance between the $d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{xy}$ promotion energies and the spin-pairing energy which dominates the energy separation between the lowest energy spin-doublet and -quartet states (see wave functions in Figure 3).

A comparison between Figures 2 and 3 shows very clearly that the energy levels of cobalt(II) complexes cannot be derived solely from considerations of the d-orbital energies. In particular, the $^2A_1(d_{x^2-y^2})$ state is much higher in energy than such arguments would suggest. This results from the effects of interelectron repulsion, which make the $^2A_1(d_{x^2-y^2})$ state ~20*B* higher in energy than $^2A_1(d_{z^2})$ and ~15*B* higher than $^2A_2(d_{yz})$ and $^2B_1(d_{xz})$. It therefore seems unlikely that the rhombic component of the ligand field will cause drastic mixing of the $^2A_1(d_{z^2})$ and $^2A_1(d_{x^2-y^2})$ wave functions. The matrix element connecting these states is proportional to the difference in ligand perturbation along the *x* and *y* axes, and as these bisect the bond directions (Figure 1), it seems probable that this will be fairly small.[12d] The suggestion by McGarvey[2,3] that the *g* values of planar cobalt(II) complexes having C_{2v} or D_{2h} symmetry may be drastically affected by the mixing of the $d_{x^2-y^2}$ and d_{z^2} orbitals if the ground state is $^2A_1$ therefore seems unlikely to be followed in practice except in unusual circumstances. In agreement with this, the EPR parameters of Co(salen) dimer and Co(salen)·py imply a negligible mixing of the above states in these complexes (see following section).

Finally, it should be said that the eigenvectors of the calculations show that the wave functions describing the states in these compounds correspond to a good approximation to the strong-field functions of a complex of C_{2v} symmetry. This means it is quite valid, for instance, to equate the lowest energy states of $^2A_2$ and $^2A_1$ symmetry with the electron configurations $(d_{xz})^2(d_{x^2-y^2})^2(d_{z^2})^2(d_{yz})^1$ and $(d_{xz})^2(d_{x^2-y^2})^2(d_{yz})^2(d_{z^2})^1$ [in fact, the $^2A_1$ state is extremely "pure"; the $^2A_2$ state contains small amounts of the configurations $(d_{x^2-y^2})^2(d_{yz})^2(d_{xz})^1(d_{z^2})^1(d_{xy})^1$ and $(d_{x^2-y^2})^2(d_{xz})^2(d_{xy})^2(d_{yz})^1$, but calculations show[32] that the presence of these would not significantly affect the EPR parameters of the complexes]. It is therefore a far better approximation to use these strong-field functions, as has generally been done in the interpretation of the electronic structure of low-spin cobalt(II) complexes, than to use the components of the octahedral wave functions of cobalt(II) as has recently been suggested.[1y,33]

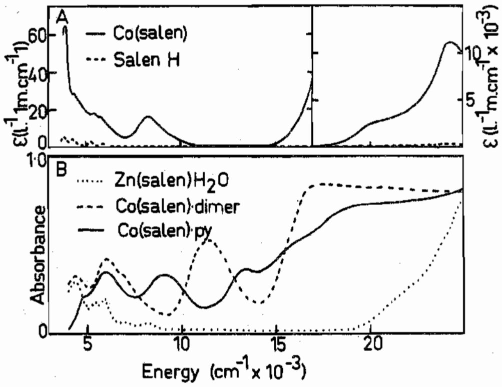

Figure 4. Electronic spectra: (A) Co(salen) and protonated salen, salenH, in chloroform solution; (B) Co(salen) dimer, Co(salen)·py, and Zn(salen)·H$_2$O measured by reflectance at ~77 K.

Electronic Spectra of the Cobalt Complexes. The solution spectra of a variety of low-spin cobalt(II) Schiff base complexes have been reported by Nishikawa and Yamada,[1c] who found that the spectra all showed a weak, sharp peak at ~8500 cm^{-1} (ϵ ~15 mol^{-1} L cm^{-1}) and much more intense absorption above ~18 000 cm^{-1}. It was suggested[1c] that the peak at ~8500 cm^{-1}, which was tentatively assigned as a spin-forbidden transition, is characteristic of the presence of planar, low-spin cobalt(II). More recently, Busetto et al.[1p,q] have reported the reflectance spectra of Co(salen) dimer and Co(salen)·py, while Hipp and Baker[1i] and Urbach et al.[1u] have reported the spectra of solutions of various complexes with substituted Schiff base ligands.

In the present study, the reflectance spectra of Co(salen) dimer and Co(salen)·py were recorded over the range 4000–25 000 cm^{-1} at temperatures down to 77 K, and the low-temperature spectra are shown in Figure 4B, together with those of Zn(salen)·H$_2$O for comparison. The energies of the band maxima attributable to "d–d" transitions, together with their assignments, are listed in Table II; the positions of the peak maxima agree well with those reported previously[1p,q] except for the observation of an extra weak band at ~16 000 cm^{-1} in the spectrum of Co(salen)·py and the fact that the peak at 4000 cm^{-1} in the spectrum of Co(salen) dimer is assigned as an infrared overtone in the present work.[34] The spectrum of a chloroform solution of Co(salen) was also recorded (Figure 4A, Table II). The observed spectrum is similar to that reported for this complex by Yamada,[1c] except for the additional peak at 3900 cm^{-1}, and is very similar to the spectrum of Co(acac)(−)pn described by Urbach et al.[1u] The present assignments ascribe the other weak peaks observed below ~6500 cm^{-1} in these and other related complexes to infrared overtones of ligand vibrations and/or spin-forbidden transitions.

The good agreement between the calculated state energies and observed band maxima (Table II, Figure 3) provides some

Table III. Calculated and Observed EPR Parameters for the Cobalt(II) Schiff Base Complexes

	Co(salen)		Co(salen) dimer				Co(salen)·py			
	Calcd	Obsd[a]	Calcd	Calcd	Calcd	Obsd[b]	Calcd	Calcd	Calcd	Obsd[b]
b			−0.1	0.0	0.1		−0.1	0.0	0.1	
$10^4 K$, cm^{-1}	−60.0		30.0	25.0	20.0		−5.0	10.0	10.0	
EPR parameters										
g_x	3.876	3.805	2.61	2.70	2.79	2.69	2.33	2.39	2.43	2.41
g_y	1.667	1.660	2.36	2.32	2.27	2.31	2.28	2.25	2.21	2.24
g_z	1.799	1.740	2.00	2.00	2.00	2.00	2.01	2.01	2.01	2.01
A_x	294.0	±291.0	141.0	134.0	127.0	±126.0	42.0	45.0	33.0	±41.0
A_y	−43.0	±52.0	50.0	57.0	66.0	±58.0	−16.0	15.0	32.0	±24.0
A_z	24.0	±30.0	107.0	105.0	98.0	±110.0	79.0	97.0	95.0	±91.0

[a] Data from ref 20. [b] Data from ref 18; note the orientation of the g and A tensors is unknown except for g_z and A_z in Co(salen)·py and has been assumed to be that giving the best agreement with the calculations.

confirmation that the model used to estimate the excited states is meaningful. The energies of the electronic transitions of four-coordinate Co(salen) cannot be used to distinguish between the two possible ground states of this complex. However, in the noncentrosymmetric $C_{2v}(x)$ point group certain electronic transitions will be formally allowed by an electric dipole mechanism. Considering the transitions to the $^2B_1(d_{xz})$ and $^2A_1(d_{x^2-y^2})$ states, if the ground state is $^2A_1(d_{z^2})$, both transitions are allowed, while if the ground state is $^2A_2(d_{yz})$, only that to the $^2B_1(d_{xz})$ state is allowed by a static mechanism.[18] The fact that the transition to the $^2B_1(d_{xz})$ state is about 4 times as intense as that to the $^2A_1(d_{x^2-y^2})$ level therefore tends to suggest a $^2A_2(d_{yz})$ ground state for this complex. This assignment is supported by the fact that a peak at ~8500 cm^{-1} is observed with an intensity similar to that in Co(salen) in analogous centrosymmetric complexes, such as bis(salicylaldiminato)cobalt(II), in which the two nitrogen ligand atoms are trans rather than cis and in which the intensity must be derived solely from a vibronic mechanism.[1c]

The calculations suggest that a large number of spin-allowed transitions are expected above ~16 000 cm^{-1} in each of Co(salen), Co(salen) dimer, and Co(salen)·py, with the onset of these moving to lower energy in this sequence, as is observed experimentally. However, the high intensity of the absorption in this region argues that one or more charge-transfer transitions also contribute to this part of the spectrum. The low third ionization energy of cobalt, combined with the likely presence of low-energy ligand π^* orbitals, makes it probable that these are metal → ligand in nature.

EPR Parameters of the Cobalt Complexes. McGarvey has derived expressions for the EPR parameters of a low-spin cobalt(II) complex both having a $^2A_1(d_{z^2})$ and $^2A_2(d_{yz})$ ground state using second-order perturbation theory and including all possible spin-doublet and -quartet states.[2,3] These equations together with the definitions of the perturbation coefficients are given as supplementary material. They differ from those reported by McGarvey only in the symmetry labels of the wave functions[13] and the representation of the parameter P in the expressions for the dipolar contribution to the metal hyperfine constants. The dipolar hyperfine contribution, as opposed to the isotropic component given by the constant K, represents the interaction between the unpaired electron density in the d orbitals and the nuclear magnetic moment. The constant P, defined as $P = 2.0023 g_N \beta_e \beta_N \langle r^{-3} \rangle_{av}$, is related to the effective radius of the d orbitals. In a complex, P will be reduced from the free-ion value[35] of 254×10^{-4} cm^{-1} for Co^{2+}, first by the decreased effective nuclear charge and second by the delocalization of the metal electrons onto the ligands. In the equations for the hyperfine parameters, the effects of electron delocalization have already been included for the minor components of the ground-state wave function in the reduced value of the spin–orbit coupling constant used in the perturbation coefficients but have not been included for the contributions from the major components d_{yz} for $^2A_2$ or the d_{z^2}, $d_{x^2-y^2}$ mixture for $^2A_1$. To account for this, a value of $P = 228 \times 10^{-4}$ cm^{-1}, as estimated for Co^+,[35] was used in the calculations, and an orbital reduction factor k was introduced to modify the contributions from the major ground-state component. The constant k can be related to the square of the molecular orbital coefficient of the major d component of the ground state and was set equal to 0.85 in the calculations.

The EPR parameters of four-coordinate Co(salen), Co(salen) dimer, and Co(salen)·py were estimated with coefficients derived from the calculated excited-state energies (Table II), except when experimental data from the electronic spectra were available, when these were used preferentially. A value of the spin–orbit coupling coefficient of 350 cm^{-1} was used in the calculations (this represents a reduction of ~75% compared with the value of 456 cm^{-1} estimated for Co^+ or ~65% compared with that of 533 cm^{-1} for Co^{2+} [30]). The actual coefficients used in the calculations are given in the supplementary material, and the calculated EPR parameters, together with those observed experimentally, are listed in Table III. The parameters estimated for four-coordinate Co(salen) were found to be extremely sensitive to the energy of the $^2A_1(d_{z^2})$ state and those shown are for the energy of this state giving the best agreement with experiment, namely, 1100 cm^{-1}. The effect of varying the energies of the low-lying quartet states was also tested, but the g and A values were found to be rather insensitive to changes of up to ~1000 cm^{-1} in these. The agreement between the calculated and observed EPR parameters is excellent for Co(salen) dimer and Co(salen)·py and reasonable for four-coordinate Co(salen), when it is remembered that the model includes only a very superficial treatment of the effects of covalency. For Co(salen)·py and Co(salen) dimer the effect of an admixture of a small amount of the $d_{x^2-y^2}$ into the $^2A_1(d_{z^2})$ ground state, to give a new wave function of the form $a d_{z^2} + b d_{x^2-y^2}$, was investigated. However, it can be seen (Table III) that such an admixture produces a poorer agreement with experiment, confirming the suggestion that interelectron repulsion is likely to keep any mixing of this kind at a small level in low-spin cobalt(II) complexes. For four-coordinate Co(salen) EPR parameters were also calculated assuming the ground state to be $^2A_1(d_{z^2})$ and allowing the relative energy of this state and the extent of the admixture of $^2A_1(d_{x^2-y^2})$ to vary, but agreement with experiment was invariably very poor, with g_z and g_y being always reversed in magnitude from those observed experimentally. This confirms the evidence from the electronic spectrum that this complex has a $^2A_2(d_{yz})$ ground state.

As the main factor which changes over the series of cobalt complexes is the relative energy of the $^2A_1(d_{z^2})$ state, it is of interest to consider how the EPR parameters alter as a function of this variable, and this is shown in Figure 5. The calculations were performed with perturbation coefficients estimated by setting the absolute values of all state energies other than $^2A_1(d_{z^2})$ equal to those deduced (or, where possible, observed) for four-coordinate Co(salen) (Table II). The experimentally

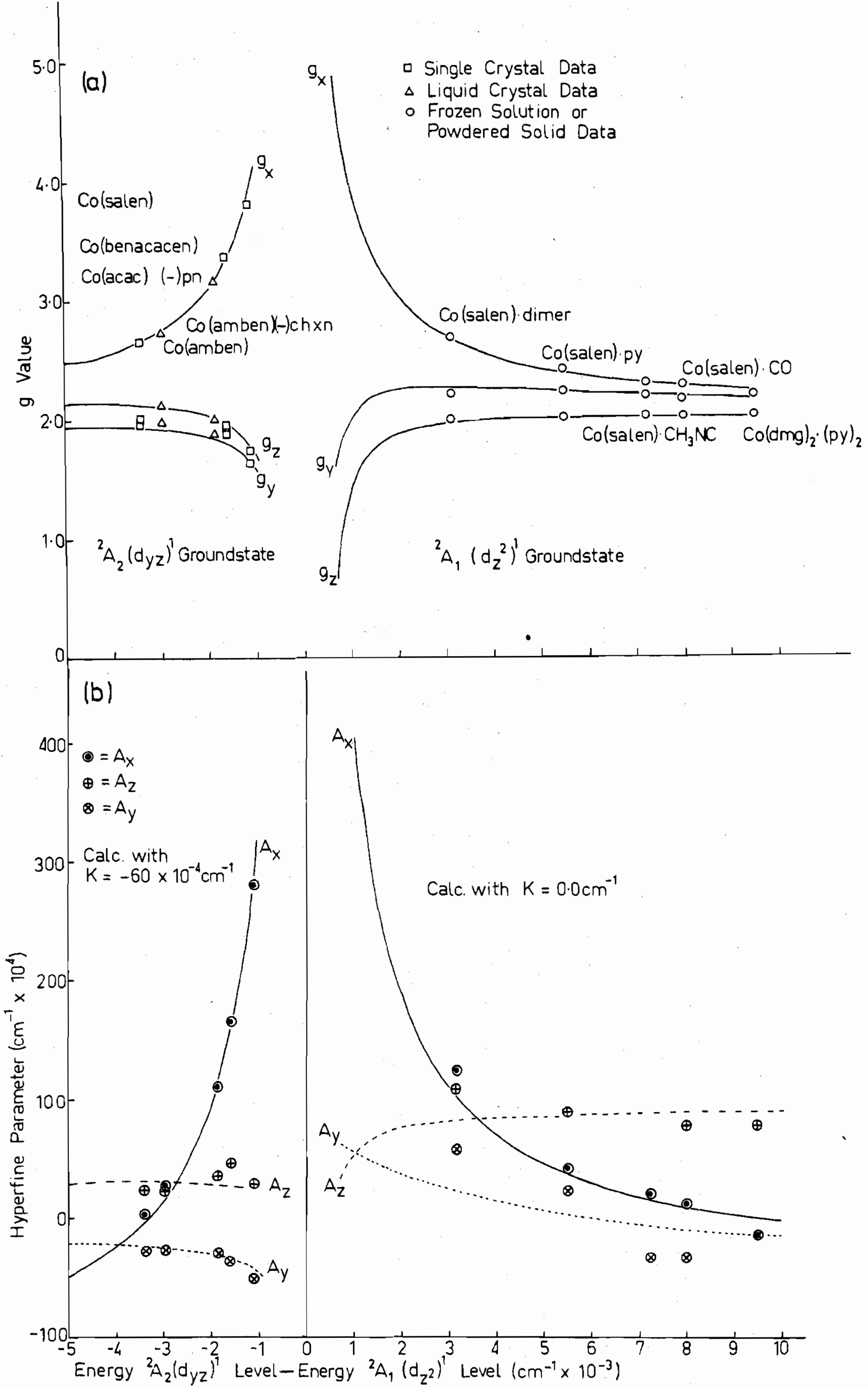

Figure 5. Plots of the metal hyperfine constants (b) and *g* values (a) of the cobalt(II) Schiff base complexes calculated as a function of the energy separation of the $^2A_2(d_{yz})$ and $^2A_1(d_{z^2})$ states; the values observed experimentally for Co(salen) and related complexes are included on the diagram.

observed EPR parameters reported for various cobalt(II) Schiff base complexes and their adducts are shown on the diagrams, with energy separations between $^2A_1(d_{z^2})$ and $^2A_2(d_{yz})$ states chosen to give optimal agreement with the calculated curves. It can be seen that when the $^2A_2(d_{yz})$ state lies significantly below the $^2A_1(d_{z^2})$ state in energy, a g-value sequence $g_x \gg g_z > g_y$ is observed. As the $^2A_1(d_{z^2})$ state decreases in energy, approaching $^2A_2(d_{yz})$, g_x rises sharply, while g_z and g_y fall below 2. When $^2A_1(d_{z^2})$ falls below $^2A_2(d_{yz})$ in energy, g_x still has a very high value, but g_y now lies above g_z. This reversal of g_y and g_z results very largely from the first-order contribution of the $^2B_1(d_{xz})$ excited state to the g values; when the ground state is $^2A_1(d_{z^2})$, this is to g_y, while when $^2A_2(d_{yz})$ is the ground state, it is to g_z (see ref 2 and supplementary material). Thus, as has been pointed out by McGarvey,[2,3] the relative values of g_y and g_z in compounds of this kind probably give the best single indication of the likely nature of the ground state. As the $^2A_1(d_{z^2})$ state becomes increasingly stabilized, g_x decreases, while g_y and g_z increase until, when the energy separation between $^2A_2(d_{yz})$ and $^2A_1(d_{z^2})$ is large compared with the splitting between $^2A_2(d_{yz})$ and $^2B_1(d_{xz})$, the g and A tensors approach axial symmetry but with z now the symmetry axis. The EPR parameters of the dipyridine adduct of bis(dimethylglyoxime)cobalt(II)[36] conform well to this limiting situation (Figure 5).

The EPR parameters of the four-coordinate complexes Co(salen), Co(acacen)(−)pn, and Co(benacacen) all lie close to the curves calculated for a $^2A_2(d_{yz})$ ground state, with the $^2A_1(d_{z^2})$ state some 1000–2000 cm^{-1} higher in energy. The electronic structures of these complexes are expected to be quite similar, as they all involve coordination of two oxygen and two nitrogen ligand donor atoms. The parameters g_x and A_x are extremely sensitive to the energy separation between these two states in this region, so that small changes in coordination geometry are expected to produce significant variations in the EPR spectra of the complexes. This may explain why these complexes often show spectra characteristic of more than one species in frozen solutions.[1p,v] For instance, Co(salen) exhibits the spectra of three different species in frozen dichloromethane,[1v] with g_x = 3.34, 3.28, and 3.23 and A_x = ±153, ±141, and ±125 × 10^{-4} cm^{-1}. From Figure 5 these represent species, possibly with different ligand conformations or solvent interactions, differing from one another by only ~75 cm^{-1} in the energy separation $^2A_2(d_{yz}) - {}^2A_1(d_{z^2})$. The figure also suggests that in the presence of very weak axial ligation, the $^2A_2(d_{yz})$ and $^2A_1(d_{z^2})$ states should be virtually degenerate. A study of the EPR spectra of Co(salen) or a related complex in a series of very weakly coordinating solvents would therefore be of some interest.

Recently, Cariati et al. have reported[4] the EPR spectrum of Co(acacen) diluted into the analogous nickel complex and observed the values $g_x = 3.26$, $g_y = 1.88$, $g_z = 2.00$, $A_x = \pm 115.8 \times 10^{-4}$ cm^{-1}, $A_y = \pm 37.5 \times 10^{-4}$ cm^{-1}, $A_z = \pm 34.5 \times 10^{-4}$ cm^{-1}. These values have not been included on Figure 5 as the in-plane principal axes of the g and A tensors were found not to coincide with those shown in Figure 1 but to lie much closer to the bond directions. This means that the effective symmetry of the cobalt complex cannot be higher than C_{1h}, which contrasts markedly with all the other complexes of this kind which have been studied and is particularly surprising as the bond lengths in the nickel host complex were found to be equivalent along the directions of the in-plane EPR axes.[4] The low effective symmetry of the complex precludes any detailed discussion of the EPR parameters.[37] However, it can be noted that if the d orbitals are all quantized along the directions of the EPR axes, i.e., approximately along the bonds, then McGarvey's equations may be used to interpret the EPR parameters with the proviso that the d_{xy} and $d_{x^2-y^2}$ orbitals are interchanged in all of the expressions. Since excited states involving these orbitals make only minor contributions to the EPR parameters, this may well explain why, except for the rotation of the in-plane EPR axes, the g and A values observed for Co(acacen) are very similar to those of the closely analogous complexes Co(benacacen) and Co(acacen)(−)pn and provide a good fit to the calculated curves if Co(acacen) has a $^2A_2(d_{yz})$ ground state with the $^2A_1(d_{z^2})$ state ~1700 cm^{-1} higher in energy (Figure 5). This assignment agrees with a recent molecular orbital calculation[38] on this complex.

The compounds Co(amben) and Co(amben)(−)chxn, both of which involve coordination of four nitrogen atoms, have EPR parameters suggesting $^2A_2(d_{yz})$ ground states but with a greater energy separation of the $^2A_1(d_{z^2})$ excited state (3000–3500 cm^{-1}) than those observed for the complexes with two oxygen and two nitrogen ligand donor atoms. However, while the parameters observed for Co(amben)(−)chxn agree quite well with the calculated curves, the value of g_z observed for Co(amben), which has been measured accurately by two groups of workers independently,[3,14] is significantly lower than the theoretical curve predicts. This might be due to the greater covalency expected in these complexes or, as has been suggested by Malatesta and McGarvey,[3] to a large separation of the $^2A_2(d_{yz})$ and $^2B_1(d_{xz})$ states in this complex, or a combination of these factors. It is noteworthy that the electronic spectra of these compounds differ somewhat from those of Co(salen) and its analogues, having a weak peak at ~6000 cm^{-1} (ϵ ~20 mol^{-1} L cm^{-1}) and a much more intense one at ~11 000 cm^{-1} (ϵ ~75 mol^{-1} L cm^{-1}),[1u] before the onset of the intense charge-transfer absorption at ~15 500 cm^{-1}. If, by analogy with Co(salen), the peak at 11 000 cm^{-1} is assigned to the transition $^2A_2(d_{yz}) \rightarrow {}^2B_1(d_{xz})$, it implies an extremely large separation between these states in Co(amben). This is particularly anomalous, as the EPR parameters suggest a virtual degeneracy of the states in the corresponding copper complex.[3,14] The present work suggests that these states are also separated by a fairly large amount (~4000 cm^{-1}) in Co(salen) and related complexes. A possible reason for this general feature could be the low energy of the metal → ligand charge-transfer state in these cobalt complexes. If this charge-transfer state has $^2A_2$ symmetry, configuration interaction could lower the energy of the $^2A_2(d_{yz})$ state relative to $^2B_1(d_{xz})$ and the other "d" states in these compounds, and molecular orbital calculations by Zelewsky and co-workers[39] suggest the presence of just such an effect. However, it seems clear that further work is required before the electronic structures of Co(amben) and its analogues can be satisfactorily explained. A firm assignment of the "d–d" spectra of one of these compounds, perhaps provided by a single-crystal study, would seem especially desirable.

The EPR parameters of the axially ligated complexes Co(salen) dimer and Co(salen)·py agree well with the curves calculated for a $^2A_1(d_{z^2})$ ground state, as do those reported[1z] for the adducts Co(salen)·CH$_3$NC and Co(salen)·CO with, as expected, the latter complexes exhibiting an even greater axial ligand perturbation (Figure 5). It should be noted however, that the experimental work on the last four compounds provides no data on the orientation of the g and A tensors (except for g_z and A_z of Co(salen)·py) and these have been assumed to agree with the calculations. A single-crystal EPR analysis of one of these complexes to confirm this would be desirable.

In computing the hyperfine parameters, good agreement with the experimental values is obtained for the complexes having $^2A_2(d_{yz})$ ground states using a value of the isotropic coupling constant $K = -60 \times 10^{-4}$ cm^{-1} (Figure 5b). When electron delocalization is taken into account, this agrees well with the theoretical value of $K = -85 \times 10^{-4}$ cm^{-1} estimated for an unpaired electron in a cobalt(II) d orbital.[35] For the complexes with a $^2A_1(d_{z^2})$ ground state, however, a considerably higher value of K is necessary to produce optimum agreement with experiment ($+25 \times 10^{-4}$ cm^{-1} for Co(salen) dimer; $+10 \times 10^{-4}$ cm^{-1} for the adducts of Co(salen)). This may be explained in terms of a direct admixture of a small amount of metal 4s electron density into the ground-state wave function, as theory suggests[35] that this should produce a positive contribution to K. Such an admixture has been invoked to explain the hyperfine parameters in various phthalocyanine[2] and dimethylglyoxime[36] complexes of cobalt(II). As the 4s orbital belongs to the A_1 representation in the $C_{2v}(x)$ point group, it is allowed by symmetry to admix with a ground state of $^2A_1$ but not $^2A_2$ symmetry, so that the different values of K observed for the two kinds of complex provide further confirmation of the correctness of the ground-state assignments.

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Registry No. Cu(acacen), 14263-53-7; Co(salen), 14167-18-1; Co(salen) dimer, 25237-52-9; Co(salen)·py, 18309-20-1; salenH, 62521-28-2; Zn(salen), 14167-22-7; Co(benacacen), 36802-28-5; Co(acac)(−)pn, 53217-38-2; Co(amben)(−)chxn, 53317-70-7; Co(amben), 21177-97-9; Co(salen)·CO, 54985-91-0; Co(salen)·CH_3NC, 54985-92-1; $Co(dmg)_2$·2 py, 26160-03-2.

Supplementary Material Available: The equations used to derive the molecular g and hyperfine values for a $^2A_2(d_{yz})$ and $^2A_1(d_{z^2})$ ground state, the latter allowing for the possibility of configuration interaction with the $^2A_1(d_{x^2-y^2})$ state and the actual values of the coefficients used in the calculations also being given (5 pages). Ordering information is given on any current masthead page.

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