Nuclear Magnetic Resonance Studies of Low-spin Complexes of Cobalt(II) with Schiff Bases. *NN'*-1,1-Dimethylethylenebis(salicylideneiminato)-cobalt(II) in Pyridine

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Isotropic paramagnetic proton n.m.r. shifts have been measured for the low-spin title complex in [$^2H_5$]pyridine. The temperature dependence of the shifts shows large deviations from the Curie law. The deviation is interpreted in term of the effects of temperature-dependent ligand field on mixing of excited electronic configurations with the ground state. The contact shifts evaluated from the isotropic shifts are shown to arise from spin delocalization through both σ and π orbitals, the latter having a smaller contribution than the former. The pattern of the contact shift is explained by the ground-state configuration of Co^{II} where the unpaired electron is primarily in the d_{z^2} orbital, and by the non-planar structure of the complex.

LOW-SPIN Schiff-base complexes of cobalt(II) are regarded as a model for vitamin B_{12r} because of their ability to reversibly bind molecular oxygen in the presence of bases.[1-8] It is known that when these low-spin cobalt(II) complexes are present in non-co-ordinating solvents they are planar and four-co-ordinated,[7b,8,9] whereas in co-ordinating solvents they form solvent adducts having a non-planar structure.[7b,8] A few interesting n.m.r. investigations have been reported for planar low-spin cobalt(II) complexes.[10-13] La Mar and Walker[11] and Hill *et al.*[12] reported that the n.m.r. spectra of the planar cobalt(II) porphyrins in chloroform, which have a ground state with an unpaired electron in the d_{z^2} orbital, show rather small contact contributions due to σ-spin delocalization. On the other hand, we have shown previously[13] that the isotropic shifts of the low-spin salicylaldehyde Schiff-base complexes of Co^{II} in chloroform have appreciable contact contributions due to π-spin delocalization. We concluded from the observed isotropic shifts that *NN'*-ethylenebis(salicylideneiminato)cobalt(II), [Co(salen)], in $CDCl_3$ has an electronic ground state with the unpaired electron primarily in the d_{yz} orbital.

Few n.m.r. studies have been reported for low-spin non-planar cobalt(II) complexes in co-ordinating solvents, although the complexes are known to have ground states in which the unpaired electron is in the d_{z^2} orbital.[5,7b,8] In view of the fact that oxygenation of low-spin Schiff-base complexes of Co^{II} is facilitated by the presence of bases,[1-8] and that the n.m.r. technique sometimes provides valuable information about the nature of the metal–ligand bonding,[14] it seems interesting to examine base monoadducts of the cobalt(II) complexes by n.m.r. spectroscopy. In the present work, we have examined the n.m.r. spectrum of *NN'*-1,1-dimethylethylenebis(salicyclideneiminato)cobalt(II), [Co(saldmen)], in [$^2H_5$]pyridine. This complex was chosen because it was considered to exist mostly as a pyridine monoadduct in pyridine solution from e.s.r. and magnetic-susceptibility investigations, although other cobalt(II) Schiff-base complexes such as [Co(salen)] and its methyl derivatives have been found to be in equilibrium between pyridine mono- and di-adducts in pyridine solution.[15]

Recently, Srivanavit and Brown[16] reported that n.m.r. isotropic shifts of *NN'*-ethylenebis(acetylacetoniminato)cobalt(II), [Co(acacen)], and *NN'*-ethylenebis(trifluoroacetylacetoniminato)cobalt(II), [Co(tfacacen)], in $CDCl_3$ and [$^2H_6$]dimethyl sulphoxide have significant contact contributions, which are due to delocalization of the unpaired spin through a π orbital. They explained this delocalization as arising from non-zero overlap between the cobalt $3d_{z^2}$ orbital and the ligand π orbital by distortion from the planar structure of the molecule, assuming that the unpaired electron occupies the $3d_{z^2}$ orbital. The pattern of n.m.r. isotropic shifts in their system is quite similar to that observed for [Co(salen)] in $CDCl_3$, but their conclusion is in contrast with ours for the same system. The situation considered is rather similar to that in the present work. In this paper we also comment on Srivanavit and Brown's conclusion.

EXPERIMENTAL

The complex [Co(saldmen)] (Figure 1) was prepared as described in the literature.[9] Sample solutions for n.m.r. measurements were prepared by dissolving the complex (*ca.* 3 mg) in degassed [$^2H_5$]pyridine (0.3 cm^3) on a vacuum line. Hydrogen-1 n.m.r. spectra were recorded on a JEOL-JNM-PS-100 spectrometer operated at 100 MHz and equipped with a variable-temperature probe and a temperature controller. Tetramethylsilane was used as an internal

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[1] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946.

[2] G. Amiconi, M. Brunori, E. Antonini, G. Tauzher, and G. Costa, *Nature*, 1970, **228**, 549.

[3] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55.

[4] D. L. Diemente, B. M. Hoffman, and F. Basolo, *Chem. Comm.*, 1970, 467.

[5] B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.

[6] C. Busetto, C. Neri, N. Palladino, and E. Perroti, *Inorg. Chim. Acta*, 1971, **5**, 129.

[7] (*a*) E. Ochiai, *J.C.S. Chem. Comm.*, 1972, 489; (*b*) *J. Inorg. Nuclear Chem.*, 1973, **35**, 1727.

[8] C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, and R. Ugo, *J.C.S. Dalton*, 1973, 754.

[9] H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Japan*, 1964, **37**, 8.

[10] R. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, 1969, **8**, 2265; 1971, **10**, 1324.

[11] G. N. La Mar and F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **95**, 1790.

[12] H. A. O. Hill, P. J. Sadler, and R. J. P. Williams, *J.C.S. Dalton*, 1973, 1663.

[13] K. Migita, M. Iwaizumi, and T. Isobe, *J. Amer. Chem. Soc.*, 1975, **97**, 4228.

[14] G. N. La Mar, W. DeW. Horrocks, jun., D. R. Eaton, and M. F. Rettig in 'NMR of Paramagnetic Molecules,' eds. G. N. La Mar, W. DeW. Horrocks, jun., and R. H. Holm, Academic Press, New York, 1973, chs. 3—6.

[15] M. Chikira, K. Migita, T. Kawakita, M. Iwaizumi, and T. Isobe, *J.C.S. Chem. Comm.*, 1976, 316.

[16] C. Srivanavit and D. G. Brown, *Inorg. Chem.*, 1975, **14**, 2950.

reference. Isotropic shifts are referenced against the corresponding free ligand and expressed in p.p.m.

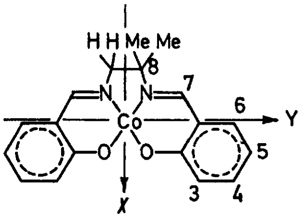

FIGURE 1 Schematic illustration of [Co(saldmen)] and definition of the co-ordinate system. The z axis is normal to the xy plane

The e.s.r. spectrum of [Co(saldmen)] was recorded at 77 K and the g values obtained were used in the calculation of the dipolar contribution to the n.m.r. isotropic shifts. Tetrahydrofuran–pyridine (10 : 1) was used as solvent to avoid crystallization of the solvent. Sample solutions for the e.s.r. measurements were prepared similarly to those for the n.m.r. measurements. The e.s.r. measurements were carried out with a Hitachi model 771 X-band spectrometer with 100-kHz field modulation. Diphenylpicrylhydrazyl (dpph) powder was used as a reference for the determination of g values.

RESULTS AND DISCUSSION

Hydrogen-1 *N.M.R. Spectra and Temperature Dependence of the Isotropic Shifts.*—The ^1H n.m.r. spectrum of [Co(saldmen)] in [$^2H_5$]pyridine at 307 K is illustrated in Figure 2. Signal assignments were made by comparison with the spectra of [Co(salen)] and its methyl derivatives in the same solvent.[17] Each of the signals due to the protons at the 4, 5, 6, and 7 positions split into two peaks at >253 K, although at lower temperatures the splittings were not detected by the increase of linewidths. Such splittings are due to differences between the chemical shifts of the protons at the corresponding two positions in the ligand, arising from asymmetry in the ethylene bridge. The absorption due to the protons at the 3 position was a single line at −12.97 p.p.m. from $SiMe_4$ (see Figure 2), but its integrated intensity corresponds to nearly one half of the other proton lines. From the line shape of the pyridine α proton, the other line due to the protons at the 3-position is estimated to be overlapped by the absorption of the α-proton of undeuteriated pyridine.*

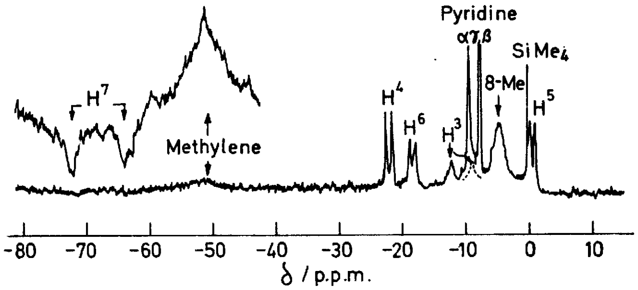

FIGURE 2 Hydrogen-1 n.m.r. spectrum at 100 MHz of [Co(saldmen)] in [$^2H_5$]pyridine at 307 K. The signal due to the protons at the 7 position was observed as an out-of-phase signal, located at 8 kHz to the high-field side of the normal n.m.r. signal for these protons

The temperature dependence of the isotropic shifts for [Co(saldmen)] in pyridine is somewhat anomalous (see Figure 3). The isotropic shifts did not obey the Curie law, although in the low-temperature range the isotropic shifts for the 3, 4, 6, and methyl protons linearly decreased as $1/T$ decreased and were extrapolated to *ca.* +5 p.p.m. at $1/T = 0$. In the high temperature range the temperature dependence of the isotropic shifts of these protons extensively deviated from the linear variation with $1/T$.

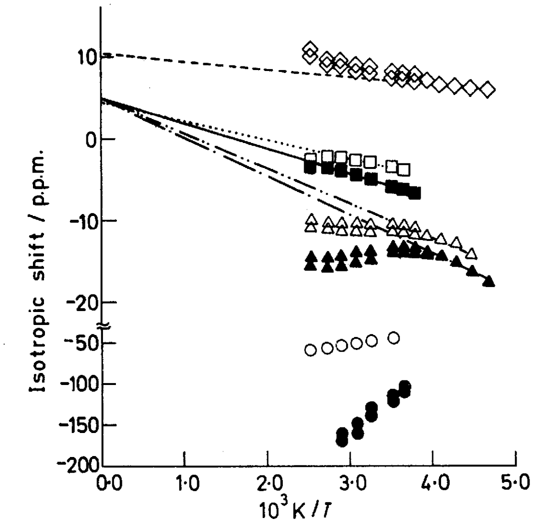

FIGURE 3 Plot of isotropic shifts against $1/T$ for [Co(saldmen)] in [$^2H_5$]pyridine: (◇) H^5; (□) 8-Me; (■) H^3; (△) H^6; (▲) H^4; (○) CH_2; (●) H^7

For the 5, 7, and methylene protons, the deviation from the Curie law was even more remarkable over the entire temperature range; the isotropic shifts diverged increasingly from zero as $1/T$ decreased. In general, the deviation from the Curie law became more marked at higher temperatures.

It has been reported that some five- and six-co-ordinate low-spin cobalt(II) complexes show anomalous magnetic behaviour.[18,19] These anomalies have been explained by assuming temperature-dependent ligand fields; it was considered that the ligand fields decrease with increasing temperature and as a result high-spin electronic configurations contribute to the ground state at high temperatures.[19] The anomaly observed in the present work also seems to be due to the effects of temperature-dependent ligand fields. As in the previous cases,[19] the ligand field of the in-plane ligand as well as the axial one may decrease with increasing temperature.

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* The splittings of the proton lines were observed to vary with the bases used as solvents. Further investigation of these splittings is in progress, and details of the results will be discussed elsewhere.

[17] K. Migita, M. Iwaizumi, M. Chikira, and T. Isobe, unpublished work.

[18] L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, 1972, **11**, 457.

[19] D. L. Williams, D. W. Smith, and R. C. Stoufer, *Inorg. Chem.*, 1967, **6**, 590.

Such a decrease in ligand field will lead to mixing of the high-spin excited states with the ground state, and hence it will affect the contact and dipolar shifts through changes in unpaired-spin delocalization and g values. As the protons with large contact contributions have a tendency to show large deviations from the Curie law (see Table 1, Figure 3, and the following discussion), the changes in the contact shifts seem to be the major effect in the anomaly. If the ground state is assumed to be $^2A_1$, which has an unpaired electron in the d_{z^2} orbital, the preferred excited high-spin state for mixing with the ground state is $^4B_1$ having unpaired electrons in the d_{yz}, d_{z^2}, and d_{xy} orbitals,[20,*] and the mixing can facilitate spin delocalization through both the σ and π systems. It may be worthwhile to note here that a decrease in only the axial ligand field due to pyridine will not necessarily lead to greater mixing of the high-spin electronic configuration, since changes from octahedral to tetragonal symmetry of ligand fields tend to raise the energy of high-spin excited states.[20] The observed anomaly in the temperature dependence of the isotropic shifts suggests concurrent decreases in the ligand field of the in-plane as well as the axial ligand at high temperatures.

TABLE 1

Dipolar and contact contributions to the isotropic shifts and hyperfine coupling constants of [Co(saldmen)]

Solvent (T/K)	Position	Shift/p.p.m. Isotropic	Shift/p.p.m. Dipolar [a]	Shift/p.p.m. Contact	a_N/G
[$^2H_5$]Pyridine (243)	3	−7.80 [b]	−4.31	−3.49	0.034
	4	−14.57	−0.60	−13.97	0.136
	5	6.52	0.12	6.40	−0.062
	6	−12.44	0.22	−12.66	0.124
	7	−68.0 [b]	−3.19	−64.8	0.633
	8-Me	−5.00	−4.95 [c]	−0.05	0.001
	CH_2	−36.0 [b]	−12.34 [c]	−23.7	0.231
$CDCl_3$ [d] (312)	3	[e]	−12.78		
	4	−6.85	1.82	−8.67	0.099
	5	34.27	5.92	28.35	−0.325
	6	−1.51	11.72	−13.23	0.152
	8-Me	−22.60	−23.37 [c]	−0.77	−0.009

[a] The g values used in the calculation for the pyridine monoadduct are $g_{xx} = 2.49$, $g_{yy} = 2.25$, and $g_{zz} = 2.01$, and those for the pyridine-free complex are $g_{xx} = 3.64$, $g_{yy} = 1.85$, and $g_{zz} = 1.89$, which were obtained in CH_2Cl_2 solution (M. Chikira, T. Kawakita, and T. Isobe, *Bull. Chem. Soc. Japan*, 1974, **47**, 1283). [b] Extrapolated values at 243 K. [c] Averaged values for the two methylene protons or two methyl groups. [d] Experimental data were taken from ref. 13. [e] Not observed.

Separation of the Contact and the Dipolar Contributions to the Observed Isotropic Shifts.—One of the most interesting problems in the present work is to determine the origins of the isotropic shifts in the base monoadducts of the low-spin Schiff-base cobalt(II) complexes or how the metal–ligand interactions are affected by formation of base adducts. Separation of the observed isotropic shifts into contact and dipolar shifts has been attempted by use of equations (1)—(3),[21] where a_N is the hyperfine

$$(\Delta H/H)^{\text{iso.}} = (\Delta H/H)^{\text{con.}} + (\Delta H/H)^{\text{dip.}} \quad (1)$$

$$(\Delta H/H)^{\text{con.}} = -\frac{a_N\beta S'(S'+1)(g_{xx}+g_{yy}+g_{zz})}{9h\gamma_N kT} \quad (2)$$

$$(\Delta H/H)^{\text{dip.}} = \frac{\beta^2 S'(S'+1)}{18kTR^3}\,[(2g_{zz}^2 - g_{xx}^2 - g_{yy}^2)\text{-}(1-3\cos^2\theta) + 3(g_{yy}^2 - g_{zz}^2)\sin^2\theta\cos 2\Omega] \quad (3)$$

coupling constant, R is the distance from the metal ion to the ligand nucleus, and θ is the angle between the z axis and the vector, σ, joining the metal and the ligand nucleus, and Ω is the angle between the x axis and the projection of σ in the xy plane. The g values in the equations were obtained from the e.s.r. spectrum at 77 K (see Figure 4). The isotropic shifts were analyzed at the lowest temperature available in the experiment (243 K) to avoid complications arising from the fact that at high temperatures the g values may deviate appreciably from those evaluated from e.s.r. at 77 K, and also that the mixing of the high-spin states may become more extensive. In the calculation of the dipolar terms, the principal axes of the g tensor were taken as shown in Figure 1. Although the real principal axes may not coincide strictly with these axes, as is seen from the splittings in the n.m.r. signals of the 4, 5, 6, and 7 positions, the error in the g factors will not significantly affect the conclusions discussed below because the contribution of the dipolar terms is not very large in the present case (see Table 1). The geometric factors were determined from X-ray structural data for the pyridine monoadduct of [Co-

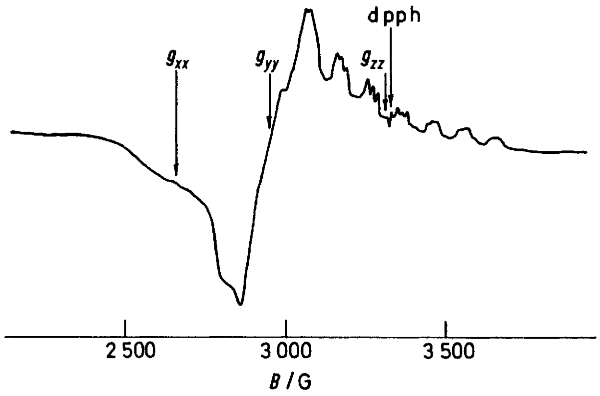

FIGURE 4 X-Band e.s.r. spectrum of [Co(saldmen)] in tetrahydrofuran–pyridine (10 : 1)

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[*] C_{2v} symmetry is assumed, taking the z axis as the C_2 axis.

[20] B. R. McGarvey, *Canad. J. Chem.*, 1975, **53**, 2498.

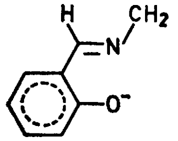
[21] Ch. 1 of ref. 14.

(salen)].[22] The contact terms were obtained by subtracting the dipolar terms from the observed isotropic shifts. Table 1 gives the results for the analysis of the isotropic shifts. The data for the pyridine-free complexes are also given in the Table for the purposes of comparison.

Spin Delocalization on to the Ligand.—We have reported previously that the contact interaction in [Co(salen)] and [Co(saldmen)] in $CDCl_3$ can be explained by the α-spin delocalization involving $M \leftarrow L$ charge transfer from the highest-filled π molecular orbital (m.o.) of the ligands.[13] In these cases, the protons at the 5 position show the largest high-field contact shift, while the protons at the 4 and 6 positions show low-field contact shifts of relatively small magnitude. This pattern of spin delocalization *via* the π orbital is well documented from valence-bond (v.b.) [23] and m.o. calculations (see below).

On the other hand, it has sometimes been observed that, in systems of σ delocalization, spin densities are attenuated markedly by the number of intervening bonds and show relatively small hyperfine coupling constants except for the positions which are on a zig-zag route from the metal.[24] A typical example of such σ-spin delocalization is bis(salicylaldehydato)nickel(II) in pyridine, where the unpaired electrons mainly occupy $3d_{z^2}$ and $3d_{xy}$ orbitals of nickel; the protons at the 4 position which are on the zig-zag route from the metal to the salicylaldehydate ligand show a large low-field shift (−18.88 p.p.m.), although the other protons show small isotropic shifts (−1.19 to 6.45 p.p.m.) at ambient temperatures.[25]

The INDO method was applied to calculate the effects of placing the unpaired electron in the σ and π orbitals of the saldmen ligand respectively. As an approximation, the calculation was made for the following half of the



ligand. For the calculation of spin delocalization *via* σ orbitals a hydrogen atom was placed as a spin probe at a distance of 2 Å from the oxygen and nitrogen atoms in the plane of the ligand. The calculated proton hyperfine coupling constants are given in Table 2. The values were normalized so that the ligand contained one unpaired electron. The feature mentioned above is well illustrated in the calculated hyperfine coupling constants. The 4 and 7 positions, which show the large hyperfine coupling constants due to the σ-spin delocalization, are situated on the zig-zag route from the metal.

In view of the above facts, the relatively large low-field contact shifts observed for the 4, 7, and methylene positions may be attributed to the σ delocalization of the unpaired α spin. It has been pointed out in the e.s.r. investigation that [Co(salen)] and [Co(saldmen)] in basic solvents will have a ground-state configuration with the unpaired electron in the d_{z^2} orbital.[7b,8] The obervation of the spin delocalization through the σ system is consistent with expectation for this ground-state configuration of the cobalt(II) ion.

TABLE 2

Calculated hyperfine coupling constants for σ and π delocalization of the unpaired electron *

	Hyperfine coupling constant(G)		
		π delocalization	
Position	σ delocalization	HOMO	LUMO
3	0.210	−1.709	−0.674
4	0.676	1.029	−1.589
5	0.034	−2.518	0.978
6	0.126	0.621	−2.420
7	8.455	0.846	−1.593
CH_2	2.044	2.191	4.259

* The hyperfine coupling constants were normalized so that the ligand contained one unpaired electron.

On the other hand, the observed high-field contact shift for the protons at the 5 position seems to suggest α-spin delocalization into the highest-occupied π orbital as in the case of [Co(salen)] and [Co(saldmen)] in $CDCl_3$,[13] although the contribution of π delocalization in the pyridine monoadduct is considered to be much smaller than in the base-free complexes. Such α-spin delocalization into the π orbital of the ligand may be attributed to the non-zero overlap between the d_{z^2} orbital of the cobalt and the ligand π orbitals caused by the distortion from a planar to a pyramidal structure on formation of the pyridine monoadduct.[26] From a comparison with the theoretical hyperfine coupling constants, the delocalization of the unpaired electron into the σ and highest-occupied π orbitals is estimated to be 6—10 and 2—7%, respectively. For the pyridine-free complex of [Co(saldmen)], the delocalized unpaired spin in the ligand π orbital is estimated to be *ca.* 8—18%, based on the INDO calculation in Table 2.* Apparently, the π delocalization of the unpaired electron decreases on formation of the pyridine monoadduct, reflecting well the change in the ground-state configuration of cobalt(II) ion from $(d_{xy})^2(d_{yz})^1$ to $(d_{xy})^2(d_{z^2})^1$ in the hole representation.

Previously, Maki and McGarvey [27] showed, in an e.s.r. study of bis(salicylideneiminato)copper(II), that 25% of the unpaired electron is delocalized on to the ligand of the copper(II) complex. In view of the fact that in this complex the unpaired electron in the d_{xy} orbital points

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* In a previous paper [13] we estimated the delocalized unpaired spin as *ca.* 4—9% based on a v.b. calculation.[23] The difference in the present estimated spin densities and those based on the v.b. calculation may arise from the difference in spin-correlation effects between the two methods.

[22] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

[23] R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, 1964, **86**, 379.

[24] I. Morishima, K. Okada, and T. Yonezawa, *J. Amer. Chem. Soc.*, 1972, **94**, 1425.

[25] K. E. Schwarzhans, *Angew. Chem. Internat. Edn.*, 1970, **9**, 946.

[26] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

[27] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 35.

towards the co-ordinated atoms and that the unpaired electron of [Co(saldmen)] in pyridine occupies the d_{z^2} orbital which is expected to have available one third of the d_{xy} orbital for overlap with the ligand σ orbitals,[20] the spin densities delocalized into the σ orbitals of the ligand observed in the present case seem quite reasonable.

Relation between Ground-state Configurations and Mechanisms of Spin Delocalization in Low-spin Cobalt(II) *Complexes*.—There are close relations between metal orbitals possessing unpaired electrons and mechanisms of spin delocalization. Certain low-spin planar complexes of Co^{II}, such as cobalt(II) porphyrins [11,12] and bis(dithioacetylacetonato)cobalt(II),[10] have an unpaired electron in the d_{z^2} orbital and show relatively small contact shifts due to the σ-spin delocalization. Although an unpaired electron of [Co(saldmen)] in pyridine occupies the d_{z^2} orbital, as in cobalt(II) porphyrins, the contact shifts can be attributed to spin delocalization through both σ and π orbitals. The π delocalization is considered to arise from non-zero overlap between the cobalt d_{z^2} orbital and the ligand π orbital by pyramidal distortion of the molecule. On the other hand, [Co(salen)] and [Co(saldmen)] in $CDCl_3$ have a planar structure and their unpaired electron occupies the d_{yz} orbital. Reflecting such an electronic configuration, these complexes show spin delocalization on to the ligands through the π orbital. The π-spin delocalization occurs by transfer of α spin from the highest-occupied ligand π orbital to the cobalt d orbitals, although the π delocalization in [Co(saldmen)] in pyridine is much smaller than that in [Co(salen)] or [Co(saldmen)] in non-co-ordinating solvents, reflecting the electronic configurations of the metal.

Recently, Srivanavit and Brown [16] found that the ligand protons of [Co(acacen)] and [Co(tfacacen)] in $CDCl_3$ and $[^2H_6]$dimethyl sulphoxide show n.m.r. contact shifts due to spin delocalization into the highest-occupied π orbital of the ligand. They attributed the observation to non-zero overlap between the ligand π orbital and the unpaired electron in the d_{z^2} orbital in the ground state. This model is the same as that employed in the present work. However, in their case σ-spin delocalization was not observed in spite of the fact that the $(d_{xy})^2(d_{z^2})^1$ configuration was assumed. The pattern of the isotropic shifts was rather similar to that for [Co(salen)] and [Co(saldmen)] in $CDCl_3$. Furthermore the spin densities delocalized into the ligand π orbital in [Co(acacen)] and [Co(tfacacen)] are estimated to be 6—15%,[*] which are of approximately the same magnitude as those for [Co(salen)] and [Co(saldmen)] in $CDCl_3$. From these facts, we estimate that [Co(acacen)] and [Co(tfacacen)] may have a ground state with the unpaired electron in the d_{yz} orbital as in the case of [Co(salen)] and [Co(saldmen)] in $CDCl_3$. In the course of our study of [Co(saldmen)], we observed that the main species in dimethyl sulphoxide at ambient temperatures may be the base-free complex which has an electronic state having its unpaired electron in the d_{yz} orbital.[†]

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[*] Evaluated from Table III of ref. 16.

[†] The n.m.r. spectrum of [Co(saldmen)] in $[^2H_6]$dimethyl sulphoxide at ambient temperature showed quite similar isotropic shifts to those observed in $CDCl_3$ rather than the shifts in pyridine, although the e.s.r. spectrum of dimethyl sulphoxide at 77 K showed a 'basic pattern' which is common to base monoadducts.[7b,28]

[28] T. Kawakita, M. Chikira, and T. Isobe, unpublished work.