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Spin-State Differences and Spin Crossover in Five-Coordinate Lewis Base Adducts of Cobalt(II) Schiff Base Complexes. Structure of the High-Spin (*N*,*N'*-*o*-Phenylenebis(salicylaldiminato))cobalt(II)-2-Methylimidazole Adduct

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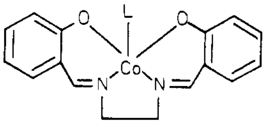
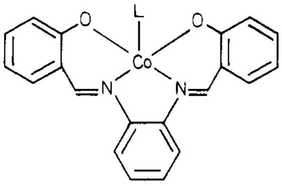
The preparations and spectral and magnetic properties of a range of five-coordinate Co(II) Schiff base adducts of the types [Co(salen)L] and [Co(saloph)L] are reported, where salen^{2-} and saloph^{2-} are the dianions of the tetradentate ligands *N*,*N'*-ethylenebis(salicylaldimine) and *N*,*N'*-phenylenebis(salicylaldimine). A variety of imidazole and benzimidazole Lewis bases (L) have been used and shown to influence the electronic states of the Co(II) atom in a sensitive manner. Many of the complexes show spin crossover between the high-spin (quartet) and low-spin (doublet) states of this d^7 system. The χ_{Co}^{-1} vs. *T* plots show "minimax" behavior in some cases. The influences of the L group and the in-plane ligand on the spin state of the central metal ion are discussed in terms of σ- and π-bonding capabilities. Structural features also influence the spin states of the Co(II) ion. A crystal structure determination of [Co(saloph)(2-MeImd)] (monoclinic, $P2_1/n$; a = 14.380 Å, b = 14.355 (8) Å, c = 9.971 (5) Å, β = 98.33 (5)°) reveals a distorted square-pyramidal environment in which one of the "in-plane" Co–N bonds is longer than the Co–N(2-MeImd) distance and in which the Co atom is raised 0.45 Å out of the saloph best plane. The geometry of this high-spin molecule is compared to that of some related low-spin four- and five-coordinate complexes, and the differences are discussed in terms of d-orbital occupancies. Finally, a short résumé of recent theories on the mechanisms for spin crossovers in solid complexes of Fe(II) and Fe(III) is given and related to the crossover phenomenon in Co(II) complexes of the present type.

Introduction

In this paper we describe a detailed study of the magnetic behavior of a range of five-coordinate cobalt(II) Schiff base chelates of the types [Co(salen)L] and [Co(saloph)L], which contain a Lewis base, L, coordinated to the Co atom. We were particularly interested in following up early preliminary reports of spin-crossover behavior in such compounds based mainly on solution studies.[1,2] Though spin crossovers in iron(III) and iron(II) systems have been widely studied, examples in cobalt(II) complexes are still relatively rare.[3,4] This is particularly true for tetradentate chelated species of the present types. Complexes of the kind Co(salen)py have been shown to be essentially low-spin d^7 species, in which the $d_{z^2}{}^1$ configuration and electronic energy levels have been thoroughly probed by means of magnetic, optical, ESR, and NMR measurements.[5] Our own studies[6] and those of others[7-9] have shown that quartet states lie very close in energy to the doublet ground states for these adducts. Until the present work, few authentic examples in which a quartet state became the ground state have been observed, the best studied being the high-spin aquo adduct Co(3-MeOsalen)·H$_2$O.[9,10a,11] The possibility of finding a combination of axial base and "in-plane" Schiff base ligand that could give rise to quartet ⇄ doublet spin-crossover behavior was therefore high. Our approach has been to carefully vary the Lewis base L among a group of imidazole derivatives and to monitor the spin state of the Co(II) center by means of variable-temperature magnetic measurements. Correlations are made with basicities andd bonding properties of L and with the structural features of the present and related complexes. The crystal structure of one example in the series, viz. Co(saloph)(2-MeImd), is described. This complex shows high-spin behavior. We have unfortunately not been able to obtain crystals suitable for a structural determination on one of the spin-crossover compounds for comparison.



[Co(salen)L]



[Co(saloph)L]

Studies of the present kind may help in understanding the factors that determine spin-state changes in axially ligated heme systems found in a number of important iron proteins.

Experimental Section

Materials. The Schiff base ligands *N*,*N'*-ethylenebis(salicylaldimine) (salenH$_2$) and *N*,*N'*-*o*-phenylenebis(salicylaldimine) (salophH$_2$) were prepared by the condensation of 1 mol of diamine and 2 mol of salicylaldehyde in absolute ethanol. The resulting yellow solids were then crystallized from absolute ethanol. Solid imidazoles were recrystallized once from benzene and once from ethanol before use; liquid imidazoles were distilled under reduced pressure (twice) before use. [Co(salen)]$_2$ and Co(saloph) were prepared by the method of West[12] but with dimethylformamide as solvent. Co(salen)py was prepared by the literature method.[6]

All preparations of cobalt complexes were carried out with use of Schlenk apparatus under an atmosphere of purified nitrogen. Solvents were deoxygenated before use by the usual pump–flush method on a double-line vacuum system.

Abbreviations used for bases: pyridine, py; imidazole, Imd; *N*-methylimidazole, *N*-MeImd; 2-methylimidazole, 2-MeImd; 1,2-di-

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methylimidazole, 1,2-diMeImd; benzimidazole, benzimd; 5,6-dimethylbenzimidazole, 5,6-diMebenzimd; 2-methylbenzimidazole, 2-Mebenzimd; 4-phenylimidazole, 4-PhImd; 5-chloro-*N*-methylimidazole, 5Cl-*N*-MeImd.

Synthesis of Cobalt Complexes. The complexes were obtained by methods A–D, and representative examples are described in detail. Analytical data were satisfactory for the complexes.

Method A. [Co(salen)(2-MeImd)] was prepared by a method similar to that described by Marzilli and Marzilli.[1] A 0.65-g amount of $[Co(salen)]_2$ (2.00 mmol) was dissolved in 250 mL of methylene chloride and then added to a solution of 1.64 g of 2-methylimidazole (20.0 mmol) in 80 mL of the same solvent. The mixture was allowed to stand for 2 h, and the resulting orange precipitate was filtered, washed with methylene chloride, and finally dried in vacuo at 80 °C for 9 h.

[Co(salen)(Imd)] and **[Co(salen)(benzimd)]** were prepared likewise, and each contained $^1/_8$ CH_2Cl_2 of solvation as judged by microanalytical and weight loss data.

Method B. [Co(salen)(5,6-diMebenzimd)]. A 0.35-g amount (1.41 mmol) of cobalt(II) acetate tetrahydrate, 0.44 g (1.41 mmol) of salenH_2, and 0.50 g (3.4 mmol) of 5,6-dimethylbenzimidazole were refluxed in a mixture of 5 mL of DMF and 15 mL of absolute ethanol for 30 min. The mixture was then slowly cooled, and the fine orange precipitate was filtered and dried under a stream of nitrogen and then in a vacuum desiccator for 15 h.

[Co(salen)(1,2-diMeImd)] and **[Co(saloph)(5,6-diMebenzimd)]** were prepared likewise.

Method C. [Co(saloph)(2-MeImd)] was prepared by refluxing 0.80 g (2.53 mmol) of salophH_2 and 0.63 g (2.53 mmol) of cobalt(II) acetate tetrahydrate with ca. 1 g (20 mmol) of 2-methylimidazole in 50 mL of DMF for 30 min. The resulting deep red crystals were washed with ethanol and then dried in vacuo at 80 °C for 30 min. Those used for the X-ray crystal structure determination were dried in a stream of dry nitrogen.

[Co(saloph)(benzimd)] and **[Co(saloph)(Imd)]** were prepared in the same manner. Repeated attempts to prepare [Co(saloph)(Imd)] by the literature method[1] were unsuccessful.

Method D. [Co(saloph)(*N*-MeImd)]. A 0.60-g amount (1.80 mmol) of salophH_2 and 0.47 g (1.89 mmol) of cobalt(II) acetate tetrahydrate were refluxed in a mixture of 20 mL of DMF and 5 mL of freshly distilled *N*-methylimidazole for 30 min. After cooling no precipitate formed and so approximately 10 mL of solvent was removed and 15 mL of absolute ethanol added. The solution was then allowed to stand for 4 h, and the resulting deep red crystals were filtered, washed with ethanol, and dried in vacuo at 60 °C for 4 h.

Physical Measurements. Analyses were carried out by the Australian Microanalytical Service, Melbourne, Australia. ESR spectra were recorded on a Varian E12 spectrometer fitted with an Oxford Instruments flow system, at a microwave frequency of 9.151 GHz. Samples were run as powders or as frozen methylene chloride glasses.

Room-temperature magnetic susceptibilities were measured by the Faraday method at four different field strengths between 5 and 6.5 kG, and all susceptibilities were found to be independent of the strength of the applied field. Each complex was prepared at least twice, and the moments agreed to within 0.05 μ_B.

Variable-temperature magnetic susceptibilities were measured over the temperature range 4.2–300 K on an extensively modified Oxford Instruments Faraday magnetometer, with main field strengths of 10 and/or 40 kG, and a gradient field of 1000 G/cm as calibrated against pure nickel.[13] Samples of between 10 and 20 mg were placed in a gold bucket and suspended from a Sartorius electronic microbalance by a fine quartz fiber. Measurements at temperatures between 4.2 and 20 K were made manually while automatic data logging equipment was used at higher temperatures. The temperature resolution was ca. 0.05 K below 20 K and ca. 0.1 K above 20 K. The moments were reproducible to 0.01 μ_B between independent runs.

Description of the X-ray Diffraction Study and Solution of the Structure. The deep red acicular crystal of [Co(saloph)(2-MeImd)] finally selected for the structural analysis was of approximate dimensions 0.30 × 0.25 × 0.10 mm. The unit cell parameters were obtained by a least-squares refinement of the angular settings of 25 medium-high-angle reflections (Table I). Intensity data were corrected for Lorentz and polarization effects. A numerical absorption correction was also applied.[14]

Table I. Summary of Crystal Data and Intensity Data Collection for [Co(saloph)(2-MeImd)]

A. Crystal Parameters

$a = 14.380\ (8)$ Å	$D_{\mathrm{measd}} = 1.47\ (2)$ g cm^{-3} (by flotation)
$b = 14.355\ (8)$ Å	$D_{\mathrm{calcd}} = 1.485$ g cm^{-3}
$c = 9.971\ (5)$ Å	$Z = 4$
$\beta = 98.33\ (5)$°	cryst syst: monoclinic
$V = 2036.6$ Å^3	space group: $P2_1/n$ (C_{2n}^{5}, No. 14)
mol formula: $C_{24}H_{20}CoN_4O_2$	mol wt: 455.4

B. Measurement of Intensity Data

diffractometer: Philips PW1100
radiation: graphite-monochromated Mo Kα (0.71069 Å)
data collection: ω mode (θ range 3–30°)
refractions measd: $+h,+k,+l$
scan rate: 0.04° s^{-1}
scan width: $(1.34 + 0.3 \tan \theta)$° in 2θ
bkgd estimation: stationary cryst, stationary counter at the extremities of each scan, each for half the time taken for the scan
std reflcns: 3 every 2 h, no decay obsd
reflcns collected: 5925; 2960 ($I > 3\sigma(I)$)
abs coeff: $\mu = 8.1$ cm^{-1}
transmission factors: 0.9012, 0.8224

Table II. Final Positional and Thermal Parameters for [Co(saloph)(2-MeImd)][a]

atom	*x*	*y*	*z*	*U*, Å^2
Co	0.22063 (4)	0.16385 (5)	0.08391 (6)	*b*
O(1)	0.1210 (2)	0.1350 (2)	0.1944 (4)	0.0357 (9)
O(2)	0.3168 (2)	0.1046 (2)	0.2189 (3)	0.0339 (8)
N(1)	0.1306 (3)	0.1511 (3)	−0.0920 (4)	0.0315 (10)
N(2)	0.3150 (3)	0.1440 (3)	−0.0594 (4)	0.0303 (9)
N(3)	0.2535 (3)	0.3042 (3)	0.1054 (4)	0.0301 (9)
N(4)	0.2528 (3)	0.4538 (3)	0.1600 (4)	0.0360 (10)
C(1)	0.0317 (3)	0.1202 (4)	0.1522 (5)	0.0311 (11)
C(2)	−0.0289 (4)	0.0995 (4)	0.2481 (6)	0.0410 (13)
C(3)	−0.1224 (4)	0.0826 (4)	0.2102 (6)	0.0457 (14)
C(4)	−0.1631 (4)	0.0842 (4)	0.0763 (6)	0.0508 (15)
C(5)	−0.1077 (4)	0.1044 (4)	−0.0207 (6)	0.0482 (15)
C(6)	−0.0093 (4)	0.1229 (4)	0.0132 (5)	0.0353 (12)
C(7)	0.0410 (4)	0.1357 (4)	−0.0983 (6)	0.0386 (13)
C(8)	0.1724 (3)	0.1580 (4)	−0.2123 (5)	0.0334 (11)
C(9)	0.1220 (4)	0.1689 (4)	−0.3426 (6)	0.0461 (13)
C(10)	0.1701 (4)	0.1756 (4)	−0.4536 (6)	0.0514 (15)
C(11)	0.2666 (4)	0.1725 (5)	−0.4369 (6)	0.0541 (15)
C(12)	0.3173 (4)	0.1631 (4)	−0.3081 (6)	0.0455 (13)
C(13)	0.2699 (3)	0.1544 (4)	−0.1964 (5)	0.0327 (11)
C(14)	0.4091 (3)	0.1032 (4)	0.2220 (5)	0.0309 (11)
C(15)	0.4662 (4)	0.0902 (4)	0.3446 (6)	0.0432 (14)
C(16)	0.5634 (4)	0.0832 (4)	0.3532 (6)	0.0486 (15)
C(17)	0.6061 (4)	0.0892 (4)	0.2400 (6)	0.0529 (16)
C(18)	0.5514 (4)	0.1030 (4)	0.1150 (6)	0.0479 (15)
C(19)	0.4531 (3)	0.1110 (4)	0.1034 (5)	0.0327 (12)
C(20)	0.4021 (4)	0.1229 (4)	−0.0324 (5)	0.0361 (12)
C(21)	0.2118 (3)	0.3701 (4)	0.1703 (5)	0.0309 (11)
C(22)	0.3246 (4)	0.4412 (4)	0.0857 (6)	0.0465 (14)
C(23)	0.3253 (4)	0.3496 (4)	0.0525 (6)	0.0439 (13)
C(24)	0.1307 (5)	0.3566 (5)	0.2432 (7)	0.0618 (18)

[a] Estimated standard deviations in the final digits are given in parentheses. [b] The form of the thermal ellipsoid of cobalt is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$ with $U_{11} = 0.0261\ (3)$, $U_{22} = 0.0318\ (3)$, $U_{33} = 0.0226\ (3)$, $U_{23} = 0.0020\ (4)$, $U_{13} = 0.0023\ (2)$, and $U_{12} = -0.0009\ (3)$.

The structure was solved via a three-dimensional Patterson synthesis, which readily yielded the position of the cobalt atom. A difference Fourier synthesis revealed unambiguously the positions of all remaining non-hydrogen atoms. Several cycles of full-matrix least-squares refinement—using the SHELX program[14]—reduced $R = \sum||F_o| - |F_c||/\sum|F_o|$ to 0.072, with the cobalt atoms being refined anisotropically. Addition of hydrogen atoms in their geometrically calculated positions

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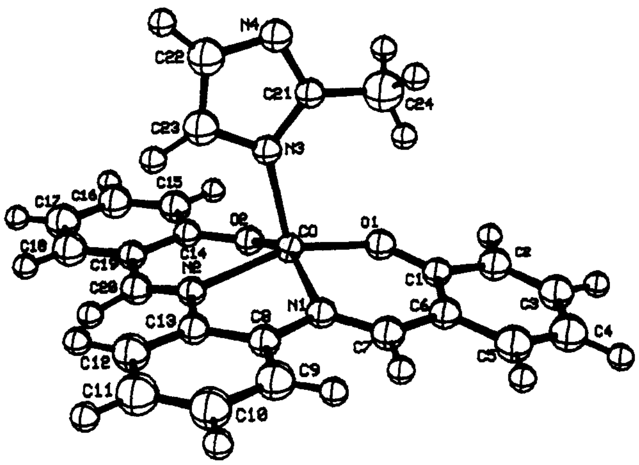

Figure 1. ORTEP diagram of [Co(saloph)(2-MeImd)].

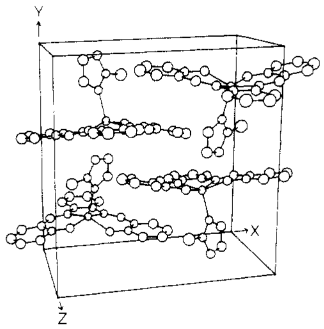

Figure 2. Molecular packing of [Co(saloph)(2-MeImd)].

(except that on N(4), which could not be uniquely defined) reduced R to 0.067. At convergence $R = 0.064$ and $R_w = (\sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o| = 0.062$, $w = 1/\sigma^2(F)$.

The atomic scattering factors for neutral Co, O, N, C, and H were taken from ref 15. Anomalous dispersion corrections were applied. The final atomic parameters are given in Table II. A list of observed and calculated structure factors is available as supplementary material.

Results and Discussion

Synthesis of Complexes. The literature methods for preparing crystalline Lewis base adducts of Co(salen) and Co(saloph) look deceptively simple.[1,16] However, care is needed to ensure coordination of the axial ligand, L, and to avoid contamination with oxygenated or oxidized species (see Appendix). Only in the cases of the 2-methylimidazole, benzimidazole, and imidazole adducts of Co(salen) were we able to use dichloromethane as the reaction medium to obtain pure compounds (see method A, Experimental Section). In all other derivatives we developed alternative methods, B–D, which were based on the "in situ", reactions of Co(II) acetate, Schiff-base ligand, and excess axial ligand, L, in various solvent mixtures containing dimethylformamide and ethanol, the latter generally serving as a precipitant. The axial base is clearly able to displace any DMF that may be coordinated to the Co atom. For reasons not immediately obvious we have generally had difficulty in obtaining analytically pure compounds when starting with liquid heterocyclic bases such as *N*-MeImd, 5Cl-*N*-MeImd, 1,2-diMeImd, and pyridine, although in some cases the analytical values were close to being acceptable.

Description and Discussion of the Structure of [Co(saloph)(2-MeImd)]. The structure is composed of discrete molecules of [Co(saloph)(2-MeImd)] (Figure 1), which, if the molecule is considered as a pyramid, are stacked point to base, approximately parallel to the *b* axis (Figure 2).

Table III

Bond Lengths (Å) with Standard Deviations

Co-O(1)	1.973 (3)	C(2)-C(3)	1.365 (7)
Co-O(2)	1.977 (3)	C(3)-C(4)	1.378 (8)
Co-N(1)	2.032 (4)	C(4)-C(5)	1.369 (8)
Co-N(2)	2.127 (4)	C(5)-C(6)	1.431 (7)
Co-N(3)	2.073 (4)	C(1)-C(6)	1.425 (7)
C(1)-O(1)	1.310 (6)	C(6)-C(7)	1.424 (7)
C(1)-C(2)	1.415 (7)	N(1)-C(7)	1.300 (6)
N(3)-C(21)	1.337 (6)	C(21)-C(24)	1.473 (8)
N(3)-C(23)	1.389 (7)	N(4)-C(22)	1.367 (7)
C(21)-N(4)	1.349 (6)	C(22)-C(23)	1.356 (8)
C(14)-O(2)	1.324 (5)	N(1)-C(8)	1.421 (6)
C(14)-C(15)	1.384 (7)	N(2)-C(13)	1.432 (6)
C(15)-C(16)	1.391 (8)	C(8)-C(9)	1.402 (7)
C(16)-C(17)	1.364 (8)	C(9)-C(10)	1.391 (8)
C(17)-C(18)	1.388 (8)	C(10)-C(11)	1.375 (8)
C(18)-C(19)	1.406 (7)	C(11)-C(12)	1.388 (8)
C(14)-C(19)	1.424 (7)	C(12)-C(13)	1.394 (7)
C(19)-C(20)	1.453 (7)	C(8)-C(13)	1.389 (7)
N(2)-C(20)	1.279 (6)		

Bond Angles (deg) around Cobalt[a] with Standard Deviations

O(1)-Co-O(2)	91.3 (1)	O(2)-Co-N(1)	147.6 (2)
O(1)-Co-N(1)	92.3 (1)	O(1)-Co-N(3)	108.6 (2)
O(2)-Co-N(2)	87.0 (1)	O(2)-Co-N(3)	102.8 (1)
N(1)-Co-N(2)	78.3 (2)	N(1)-Co-N(3)	106.5 (2)
O(1)-Co-N(2)	158.8 (1)	N(2)-Co-N(3)	92.4 (2)

[a] All other bond angles are omitted for the sake of brevity.

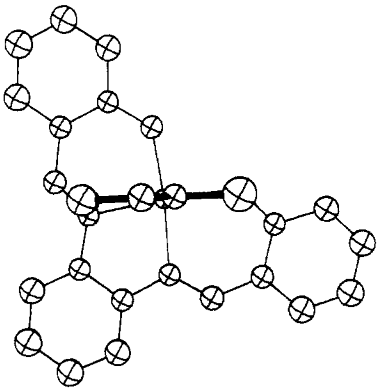

Figure 3. ORTEP diagram showing disposition of the 2-methylimidazole ring relative to the Co(saloph) moiety.

Bond lengths within the saloph ligand (Table III) are similar to those reported for Co(saloph),[17] and the ligand adopts an approximate umbrella shape, one salicylaldimine moiety being slightly twisted about the C(20)–O(2) direction. The result of this is that the O(2) atom is significantly shifted (0.336 (3) Å) out of the plane O(1)N(1)N(2). The bond angles O(1)–Co–N(2) = 158.8 (1)° and O(2)–Co–N(1) = 147.6 (2)° also reflect this.

The Co atom is 0.452 (1) Å out of the plane O(1)O(2)N(1)N(2) and is displayed toward the 2-methylimidazole moiety. The 2-methylimidazole group lies almost parallel to the O(1)CoN(2) plane, the torsion angle C(21)–N(3)–Co–O(1) being −6.0 (5)° (C(23)–N(3)–Co–N(2) = −8.9 (4)°) (Figure 3). Bond angles around the Co atom are listed in Table III and show (as can be seen from Figure 1 or 3) that the 2-MeImd moiety is not perpendicular to the Co(saloph) moiety but is pushed back because of steric interaction between the methyl group (C(24)) and the oxygen atom O(1) (distances O(1)–H(C24) = 2.28 Å and N(2)–H(C23) = 2.66 Å) such that the N(3)–Co–N(2) angle is 92.4 (2)° and N(3)–Co–O(1) = 108.6 (2)°.

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Table IV. Crystallographic Data and Magnetic Moments for Some Four- and Five-Coordinate Co^{II} Schiff Base Compounds

	$Co(salen)CHCl_3$[18]	Co(saloph)[17]	$[Co(salen)]_2$[19]	Co(salen)py[20]	Co(saloph)-(2-MeImd)[a]	$Co(3\text{-}MeOsalen)H_2O$[11]
μ_{eff}^{295K}/μ_B	2.38	2.74	2.25	2.30	4.19	4.39
Co-O/Å	1.87 1.84	1.84	1.90	1.96	1.97	1.95
Co-N/Å	1.86 1.83	1.87	1.81	1.80	2.03 2.13	2.05
$Co\text{-}O_A$/Å[b]			2.25			2.12
$Co\text{-}N_A$/Å[b]				2.10	2.07	
N-Co-N/deg	86.9	86.5	84.6	85.3	78.3	78.6
O-Co-O/deg	85.5	84.2	88.0	86.7	91.3	92.3
d/Å[c]	0.00	0.01	0.15	0.20	0.45	0.43

[a] This work. [b] A refers to axial atoms. [c] d is distance of Co from ligand plane.

The structural properties of the coordinated atoms in [Co(saloph)(2-MeImd)] are compared in Table IV with those of some closely related cobalt(II) Schiff base compounds.[11,17-20] It becomes apparent on examination of this table that the structural parameters of the two high-spin species [Co(saloph)(2-MeImd)] and $[Co(3\text{-}MeOsalen)\cdot H_2O]$ are similar, yet they are markedly different from the two low-spin four-coordinate complexes. The two five-coordinate species $[Co(salen)]_2$ and [Co(salen)py] have coordination parameters intermediate between these two extremes. The last two complexes are essentially low spin but do show the influence of high-spin states at high temperatures as evidenced by susceptibility measurements.[6]

The dependence of metal–ligand distance on spin state can be correlated with the nature of the occupied d orbitals in a manner similar to that recently described by Hitchman for compounds of Co(II) and Fe(II).[21] The low-spin four- and five-coordinate complexes have the single d electron in an out-of-plane d_{yz} or d_{z^2} orbital[5-7] while the high-spin complexes have electrons occupying the in-plane d_{xy} orbital, which points toward the O and N donor atoms. The increase in Co–O and Co–N distances in going from low- to high-spin states therefore follows since the d_{xy} orbital is unoccupied in the low-spin species. Associated with this increase in the Co–O and Co–N bond distances is a decrease in the N–Co–N bond angle from ca. 86° in the four-coordinate low-spin compounds to ca. 78° in the high-spin compounds and a subsequent increase in the O–Co–O bond angle from ca. 85 to 92°. These bond angle changes have been previously noted by Calligaris et al.[11] and are probably due to the necessity of maintaining a constant N–N bite of ca. 2.6 Å in order to obtain five-member ring enclosure. The less rigid O–O bite then increases to maintain the square-planar geometry.

A second point of note is the increase in the out-of-plane displacement of the Co center from a minimum of 0.00 Å in $Co(salen)\cdot CHCl_3$ to a maximum value of 0.45 Å in $[Co(3\text{-}MeOsalen)\cdot H_2O]$. Again it is observed that the two high-spin compounds display a similar out-of-plane displacement, as do the low-spin four-coordinate species, with the two low-spin five-coordinate species having a displacement intermediate between these two extremes. The latter observation adds support to the presence of high-spin contribution in $[Co(salen)]_2$ and [Co(salen)py]. This relationship between the spin state of the metal and its degree of out-of-plane displacement has been previously noted for some iron porphyrins, and it is probable that the displacement of the metal out of the plane is due to the increased occupation of the in-plane d orbital in the high-spin species.[22]

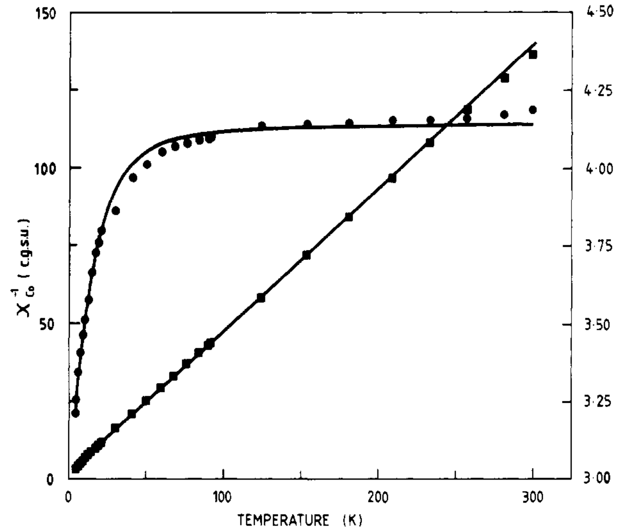

Figure 4. Magnetic moments and reciprocal susceptibilities (per Co) vs. temperature for [Co(saloph)(2-MeImd)]. Solid lines are calculated with use of the spin Hamiltonian analysis described in the text.

In the absence of a confirmatory structure on one of the present spin-crossover complexes we would predict that the structural features of the high-spin would be observed at high temperatures (ca. 300 K) while that of the low-spin type would exist at low temperatures as has been observed recently[23] in the case of the iron(III) porphyrin $[Fe(OEP)(3\text{-}Cl\text{-}py)_2]ClO_4$.

Magnetic Properties. The magnetic susceptibilities of powdered samples were determined over the temperature range 4.2–300 K with a Faraday balance. Tables of χ_{Co} vs. T for all the complexes studied are provided as supplementary data. Representative plots of χ_{Co}^{-1} and μ_{Co} as a function of temperature are shown in Figures 4–9.

Two of the complexes studied show Curie–Weiss behavior over the temperature range studied and obey the relation $\chi_{Co} = C/(T + \Theta)$. The slopes of the reciprocal susceptibility plots yield Curie constants, C, for low-spin Co(saloph) of 1.5 and for high-spin [Co(saloph)(2-MeImd)] of 0.5. The magnetic moment of Co(saloph) remains independent of temperature between 240 and 20 K and then decreases a little from 2.20 to 2.05 μ_B at 4.2 K. This decrease may be due to weak intermolecular exchange coupling between neighboring cobalt atoms, although the crystal structure of Co(saloph) does not reveal any close Co···Co interactions.[17]

The magnetic moment of [Co(saloph)(2-MeImd)] is virtually independent of temperature at higher temperatures, dropping from 4.19 μ_B at 296 K to 4.10 μ_B at 50 K (Figure 4). Below 50 K it drops more rapidly, reaching 3.2 μ_B at 4.2

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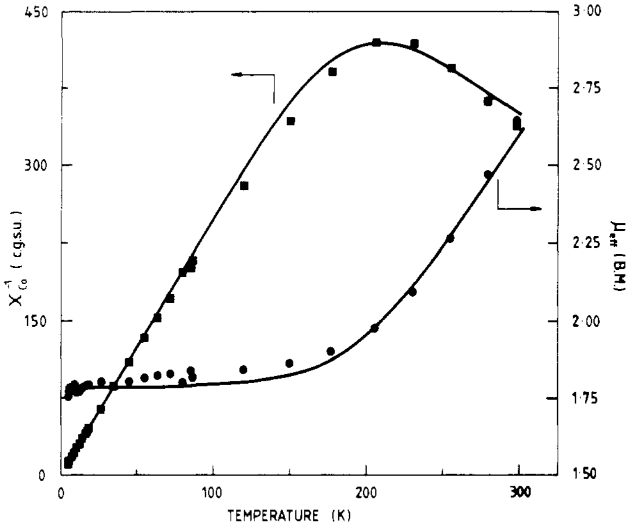

Figure 5. Magnetic moments and reciprocal susceptibilities (per Co) vs. temperature for [Co(salen)(5,6-diMebenzimd)]. Solid lines are calculated with use of the parameters given in Table VI.

K. We interpret this behavior in terms of zero-field splitting of a $^4B_1$ ground state with no contribution from a doublet state even at low temperatures. The magnetic data for [Co(saloph)(2MeImd)] could be fitted very well to the appropriate axial spin Hamiltonian

$$\mathcal{H} = g\beta H\cdot S + D[S_z^2 - \tfrac{1}{3}S(S + 1)]$$

where $S = {}^3/_2$. The susceptibility was then calculated after diagonalization of the resultant 4 × 4 matrix. The best fit parameters are $g = 2.14$ and $|D| = 22.6$ cm^{-1}. The plot of the best fit is shown in Figure 4. Small deviations below 100 K probably reflect the need to include a small rhombic (E) zero-field splitting term into the Hamiltonian. Although the sign of D cannot be deduced directly from the powder susceptibility data, the ESR spectrum of a powdered sample of [Co(saloph)(2-MeImd)] at 4.2 K shows lines with effective g values at 7.6, 2.2 (strong), and 1.51, which is generally compatible with the presence of rhombically distorted high-spin Co(II). The large anisotropy results from a combination of low-symmetry and bonding effects. Comparison of these g values with the recent calculations of Pilbrow[24] and Gatteschi[25,26] suggests that the $M_s = \pm{}^3/_2$ doublet lies lower than the $M_s = \pm{}^1/_2$ doublet. However, preliminary results of a magnetization study[27] using fields between 5 and 50 kG strongly suggest that D is positive and equal to 23.5 cm^{-1}.

Apart from Co(saloph) and [Co(saloph)(2-MeImd)] all the other complexes studied showed deviations from Curie behavior, especially at high temperatures. In some, a maximum in χ_{Co}^{-1} was observed at high temperatures while in others the "minimax" behavior, characteristic of a spin-equilibrium situation, was observed. Since the minimum is always at higher temperature than the maximum, it is probable that those compounds showing just a maximum would also display a minimum at $T > 300$ K. The room-temperature magnetic moments of the compounds vary in magnitude from those that are essentially low spin (e.g. [Co(salen)(Imd)], 1.9 μ_B) to those that are close to being high spin (e.g. [Co(saloph)(benzimd)], 4.16 μ_B).

[Co(salen)(5,6-diMebenzimd)] is an example of a compound showing a maximum in χ_{Co}^{-1} at about 200 K (Figure 5). Below the maximum the susceptibilities follow a Curie–Weiss temperature dependence with a magnetic moment at 4.2 K equal to 1.8 μ_B indicative of a low-spin doublet ground state. μ_{Co} increases quite rapidly from 1.8 to 2.64 μ_B between 180 and 300 K on account of increased occupation of thermally accessible quartet states. [Co(salen)py] also exhibits a similar χ_{Co}^{-1}/T plot with a maximum at ca. 270 K and a corresponding increase in μ_{Co} from 2.1 to 2.3 μ_B in this region. We had previously observed this behavior in single-crystal magnetic anisotropy studies on [Co(salen)py] and associated it with the influence of low-lying quartet states.[6] The moment levels off to a value of 1.95 μ_B in the low-temperature region but, as can be seen in Figure 6, a small increase to 1.99 μ_B occurs between 9 and 4.2 K, which possibly arises through the presence of a trace impurity but could be due to intrinsic weak ferromagnetic interactions as observed recently in "active" Co(salen) samples.[28] [Co(saloph)(5,6-diMebenzimd)] is a good example of the compounds that display the spin-crossover "minimax" susceptibility behavior. The temperature dependencies of χ_{Co}^{-1} and μ_{Co} are shown in Figure 7. The moment changes grad-

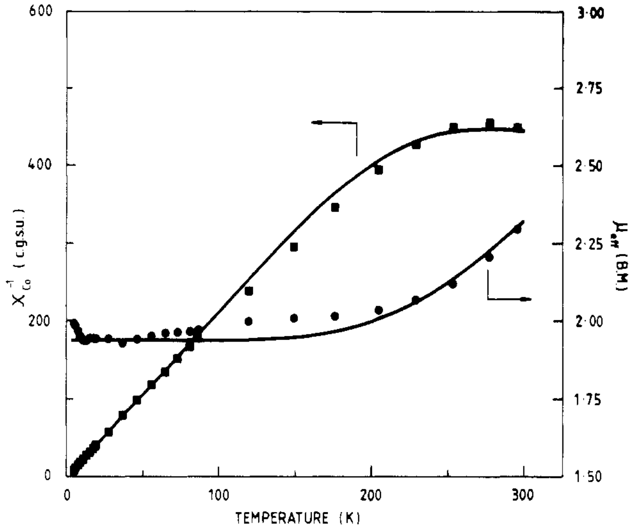

Figure 6. Magnetic moments and reciprocal susceptibilities (per Co) vs. temperature for [Co(salen)py]. Solid lines are calculated with use of the parameters given in Table VI.

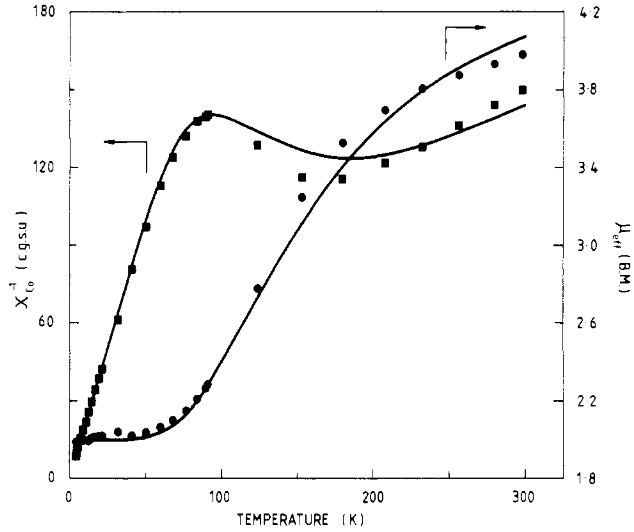

Figure 7. Magnetic moments and reciprocal susceptibilities (per Co) vs. temperature for [Co(saloph)(5,6-diMebenzimd)]. Solid lines are calculated with use of the parameters given in Table VI.

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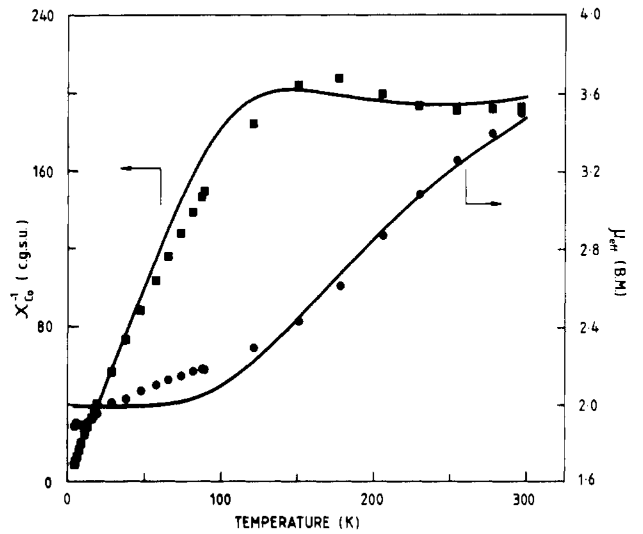

Figure 8. Magnetic moments and reciprocal susceptibilities (per Co) vs. temperature for [Co(salen)(2-MeImd)]. Solid lines are calculated with use of the parameters given in Table VI.

Table V. Comparison of Magnetic Moments (at 295 K) and Temperatures of Maxima and Minima in χ_{Co}^{-1} Plots for Co(II) Schiff Base Complexes

L	$T(\chi_{max}^{-1})$, K	$T(\chi_{min}^{-1})$, K	μ_{Co}(295 K), μ_B
	Co(salen)L		
py	270	N/O[a]	2.30
5,6-diMebenzimd	200	N/O	2.64
2-MeImd	186	260	3.50
1,2-diMeImd	120	300	3.34
	Co(saloph)L		
Imd	230	N/O	2.74[b]
N-MeImd	140	240	3.54
5,6-diMebenzimd	90	180	3.99

[a] N/O = not observed below 300 K. [b] At 230 K.

ually from a low-spin value, 1.98 μ_B at 4.3 K, to one close to the high-spin value, 3.99 μ_B at 300 K. Temperatures greater than 300 K would be required to fully populate the high-spin state and achieve a constant μ_{Co} value. The shapes of the plots in Figure 7 are similar to those displayed[3,4] by other spin-crossover compounds of Fe^{II}, Fe^{III}, and Co^{II}. In contrast to the case for the high-spin saloph analogue, the complex [Co(salen)(2-MeImd)] also shows minimax behavior with the temperature at which the maximum in χ_{Co}^{-1} occurs being higher than that in [Co(saloph)(5,6-diMebenzimd)]. The susceptibility and moment plots for [Co(salen)(2-MeImd)] are shown in Figure 8; μ_{Co} increases from 1.91 μ_B at 4.3 K to 3.50 μ_B at 297 K.

The temperatures at the maxima and minima in χ_{Co}^{-1} for the various complexes are given in Table V together with the room-temperature magnetic moments. Since $T(\chi_{max}^{-1})$ represents the onset of the increase in μ_{Co} from the $S = {}^1/_2$ value to the $S = {}^3/_2$ value, which is a consequence of a crossover between these two spin states, the magnitude of $T(\chi_{max}^{-1})$ gives an indication of the energy difference between the low- and high-spin states.

To see if this bears out in a more quantitative fashion, we have used the theoretical approach of Martin et al.,[29] which was initially developed to explain similar magnetic behavior in various $[Co^{II}(terpy)_2]^{2+}$ complexes. The model assumes octahedral symmetry and considers one doublet state, ^2E, and one quartet state, $^4T_1$, separated by energy E. The degeneracy of these states is removed by a combination of spin–orbit coupling and first- and second-order Zeeman effects to yield 14 energy levels. A Boltzmann distribution over these levels yields the following expression for the expected magnetic moment μ_{eff}:

Table VI. Values of E, C and μ_E for the Calculated Curves[a] in Figures 5–8

L	E, cm^{-1}	C	μ_E, μ_B	$T(\chi_{max}^{-1})$, K
	Co(salen)L			
py	1325	0.30	1.90	270
5,6-diMebenzimd	1285	0.15	1.75	200
2-MeImd	895	0.29	1.95	186
1,2-diMeImd	850	0.40	1.68	120
	Co(saloph)L			
Imd[b]	950	0.39	2.01	~230
N-MeImd	875	0.275	1.85	140
5,6-diMebenzimd	845	0.13	1.96	90

[a] See text for meaning of parameters: $\zeta = 475$ cm^{-1}; $\gamma = 1.5$. [b] χ_{Co} in 4.2–50 K region gave good fit to $S = {}^1/_2$ dimer theory: $J = -1.3$ cm^{-1}, $g = 2.19$.

$$\begin{aligned}\mu_{eff}{}^2 = {} & [150\gamma x C\mu_E{}^2 + 25(\gamma x(5-\gamma)^2 - 20(2-\gamma)^2) \times \\ & \exp(-(E/\zeta + 5\gamma/6)x) + 2(5\gamma x(11+2\gamma)^2 + 88(2 - \\ & \gamma)^2)\exp(-(E/\zeta + \gamma/3)x) + \\ & 9(35\gamma x(3+\gamma)^2 + 36(2-\gamma)^2)\exp(-(E/\zeta - \\ & \gamma/2)x)]\langle 72\gamma x[2C + \exp(-(E/\zeta + 5\gamma/6)x) + \\ & 2\exp(-(E/\zeta + \gamma/3)x) + 3\exp(-(E/\zeta - \gamma/2)x]\rangle^{-1} \qquad (1)\end{aligned}$$

where μ_E is the magnetic moment for the ^2E state, which is expected to be on the order of 1.8 μ_B and nearly independent of temperature, x is ζ/kT, ζ is the one-electron spin–orbit coupling constant, E is the separation of the zero-point energies of the $^4T_1$ and ^2E states, and $C \approx Q_E/Q_T$, the ratio of the vibrational partition functions in the high- and low-spin states. γ derives from the strength of the ligand field in the $^4T_1$ state and lies between −1.5 for weak-field $|d^7\,F^4\,{}^4T_1\rangle$ and −1.0 for strong-field $|t_2{}^5e^2\,{}^4T_1\rangle$ (Figgis and others[30] use the letter A instead of γ).

Application of this model to the present compounds involves a number of approximations. The symmetry of the ligand field is C_{2v} at best, and therefore, splittings of the ^2E and $^4T_1$ states will occur. It is known that a large number of quartet and doublet states having no orbital degeneracy lie within 0 and 15 000 cm^{-1} of the ground doublet state in compounds such as Co(salen)py and $[Co(salen)]_2$.[6,7] The present model therefore considers only a limited number of low-lying ligand field states, although the spin–orbit sublevels makeup for this deficiency to some extent. We point out further limitations of this simplistic model later in relation to current theories of spin crossover.

Despite these limitations we have been able to obtain good fits of the observed data to eq 1. The calculated plots are shown in Figures 5–8, and the corresponding best fit parameters are given in Table VI. ζ was kept constant at 475 cm^{-1} and γ held at −1.5. As in the previous work of Martin et al.[29] it was found that μ/T data were not sensitive enough to allow unique determination of ζ and γ.

Perusal of Table VI shows that the energy differences, E, does indeed correlate with the value of $T(\chi_{max}^{-1})$. In all the complexes listed, the high-spin state lies within a range 800–1400 cm^{-1} above the low-spin state. The compares with E = 1110–1700 cm^{-1} for various $[Co(terpy)_2]^{2+}$ complexes.[29] The C values for the present compounds are in the range

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(30) See e.g.: Mabbs, F. E.; Machin, D. J. "Magnetism and Transition Metal Complexes"; Chapman and Hall: London, 1973; Chapter 4.

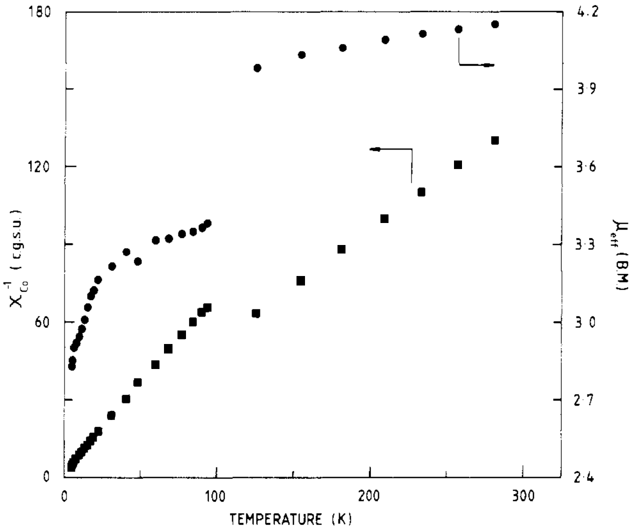

Figure 9. Magnetic moments and reciprocal susceptibilities (per Co) vs. temperature for [Co(saloph)(benzimd)] showing sharp transition at ca. 110 K.

0.15–0.40, which is generally higher than that deduced for the terpy systems. The C values for the pair of adducts [Co(salen)(5,6-diMebenzimd)] and [Co(saloph)(5,6-diMebenzimd)] are very similar, but without structural data and independent evaluation of the parameters, this result may be fortuitous. The μ_E values can be seen in Figures 5–8 to be reasonably constant at low temperatures and in the expected range, except in the case of [Co(salen)(1,2-diMeImd)] in which it is just below the spin-only value. In one case, [Co(saloph)(Imd)], the moment continues to decrease at very low temperatures and we believe that this is due to the occurrence of weak antiferromagnetic coupling. Application of a $S = {}^1/_2$ dimer equation to μ_{Co} in the 4.2–50 K region gave a best fit J value of -1.3 cm^{-1} and a g value of 2.19.

The magnetic properties of one complex, [Co(saloph)(benzimd)], show a sharp transition in μ_{Co} at 110 K (Figure 9). Above and below this temperature the susceptibilities follow Curie–Weiss behavior but with different slopes. The moment does not level off to a low-spin value even at 4.2 K, which suggests that the sharp transition may be a structural phase transition, an incomplete spin-state change, or a combination of both.[4,31] The continuing decrease in μ_{Co} at very low temperatures could be due to zero-field splitting and/or thermal depopulation of the quartet state or to weak antiferromagnetic coupling effects. A poorly resolved ESR spectrum measured on a neat polycrystalline sample at 4.2 K showed evidence for high-spin lines as well as lines at $g \approx 2$. It is not clear, therefore, whether this compound does undergo a spin-state change or is essentially of the high-spin type as exemplified by [Co(saloph)(2-MeImd)]. The balance of evidence would favor a spin-state change. We are aware of only one other example of an abrupt transition in a Co^{II} compound, that is a six-coordinate Schiff base adduct, Co(H$_2$fsaen)(py)$_2$, studied by Kahn etal.[32] A sharp $S = {}^3/_2 \leftrightarrow S = {}^1/_2$ crossover has also been observed in the five-coordinate Fe(II) nitrosyl Fe(salen)(NO).[33]

Electronic Spectra. Spectra were obtained at room temperature and at 8 K on a number of the complexes prepared in the form of Kel-F mulls (kindly measured by Dr. M. A. Hitchman, University of Tasmania). In most cases the spectra are broad and not very well resolved. Between 500 and 10000 cm^{-1} there is in all cases, except for [Co(saloph)(2-MeImd)] and [Co(saloph)(Imd)], a gradual increase in intensity with some shoulders just discernible. Peaks are better resolved in the region 10000–26000 cm^{-1}. The 2-methylimidazole and imidazole adducts of Co(saloph) generally display better resolved bands than the other derivatives. The spectrum of the high-spin 2-MeImd adduct shows some similarities to those of the pentadentate N$_3$O$_2$ derivatives of the type Co(salDPT).[34–36] Band positions for the complexes studied are given in Table VII.

Table VII. Visible Spectra of Co(II) Schiff Base Adducts (Kel-F mulls, 295 K, cm^{-1})

L	positions of band maxima or shoulders (sh)[e]
	[Co(salen)L]
py[7]	6000, 9000, 13 500, ca. 16 000
2-MeImd[a]	5000 sh, ca. 10 000, 13 986 sh, 22 730 br, 26 315
5,6-diMebenzimd[b]	5000 sh, 9091, 13 986 sh, 22 730 vs
	[Co(saloph)L]
Imd[b]	5000 sh, 7143 sh, 9524, 13 900 sh, 21 740 vs, 26 315
2-MeImd[c]	4762 sh, 5882,[d] 7071 sp, 8696–10 000, 13 513, 23 800, 26 315 sh
N-MeImd[d]	4762 sh, 5263 sh, 9090 sh, 14 084, 21 740 sh, 25 000 vs
5,6-diMebenzimd[d]	4762 sh, 5050 sh, 8000 sh, 9524 sh, 13 160, 22 220, 26 315

[a] Between 295 and 8 K intensities decrease, some bands shift. [b] Between 295 and 8 K intensities change, some band shift. [c] Between 295 and 8 K intensities change for bands above 13 500 cm^{-1}. [d] Between 295 and 8 K intensities decrease. [e] Abbreviations: br, broad; sp, sharp; vs, very strong.

The most notable features of the spectral results are the changes observed in some of the band positions and their intensities for [Co(saloph)(Imd)], [Co(saloph)(N-MeImd)], [Co(salen)(5,6-diMebenzimd)], and [Co(salen)(2-MeImd)] as the temperature is lowered from 295 to 8 K. The bands that occur between 13000 and 26000 cm^{-1} generally decrease markedly in intensity on lowering the temperature to 8 K. The spectral changes are generally compatible with the occurrence of a spin-state change. Unfortunately, it is not easy to readily distinguish the spin state of compounds of the spectra are often quite similar.[7,10a,27] However, changes such as those described above do show that the electronic structures of the molecules are different at 295 K than they are at 8 K. Related changes of this kind were first noted by Sacconi etal.[37] for a five-coordinate complex, Co(NNP)(NCS)$_2$. Recently Reinen et al.[38] observed only very small changes in the band positions of the spin-crossover Co(terpy)$_2$$^{2+}$ complexes, the room-temperature spectra of which had previously been reported by Martin et al.[29]

Factors That Affect the Doublet–Quartet Energy Separation. In this section we see if it is possible to identify any electronic or structural effects that determine, or at least contribute to, the nature of the spin crossover in these five-coordinate Co(II) compounds. It has been 10 years since Morassi, Bertini, and Sacconi noted that the factors which influenced the energies of the spin states in the present class of compounds were not immediately obvious.[39]

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Table VIII. Room-Temperature Magnetic Moments vs. Proton Basicities of Axial Ligands

base	pK_a	μ_{eff}, μ_B	
		Co(salen)	Co(saloph)
Imd	6.95	1.90	3.34
N-MeImd	7.27	$3.4^{a,b}$	3.54
1,2-diMeImd	7.84	3.34	*a*
2-MeImd	7.86	3.50	4.19
benzimd	4.98	2.61	4.16
5,6-diMebenzimd	5.48	2.64	3.99
py	5.17	2.30	$2.9^{a,b}$
water		*a*	3.47

[a] These adducts could not be isolated pure in crystalline state.
[b] From ref 1; refers to methylene chloride solutions.

Considering first the electronic and bonding effects, we begin by comparing the room-temperature moments with the proton basicities (pK_a) of the axial bases. Providing[40] that the axial bases are grouped into structurally and chemically related classes, i.e. imidazoles, benzimidazoles, and non-imidazoles, then it can be seen in Table VIII that in both the Co(salen) and Co(saloph) series an increase in pK_a correlates with an increase in μ_{eff} at room temperature. Thus, an increase in pK_a corresponds to a decrease in the quartet–doublet energy separation. Since pK_a values are a rough measure of the σ-donor ability of the base, it would appear that a stronger σ donor gives rise to a lowering of the quartet energy levels and hence to stabilization of the high-spin state. Hitchman[7] has recently reported angular-overlap calculations of both the d-orbital energies and the state energies of compounds of the [Co(salen)L] type. As expected, the axial base σ-bonding parameter only affects the energy of the d_{z^2} cobalt orbital directly but has a small effect on the energy of the lowest quartet state ($^4B_1$). Nevertheless the effect on the $^4B_1$ level is on the same order as that observed here; viz., a larger e_σ leads to a gradual lowering of the $^4B_1$ level relative to the ground $^2A_1$ state. Small effects of this kind may be enough to influence the magnetic properties at the crossover region. Certainly the present results show that Hitchman's general prediction[7] that N-donor ligands would be more likely to lead to low-spin (more covalent) behavior than O-donor ligands needs to be modified somewhat. We have found,[41] for instance, that the 2-MeImd and 5,6-diMebenzimd adducts of Co(3-MeOsalen) have room-temperature moments similar to that of the high-spin H_2O adduct, the spectrum and bonding of which were studied in detail by Hitchman.[10b]

All of the present N-donor ligands are, of course, capable of forming π bonds involving suitably oriented orbitals on Co such as the d_{yz} and d_{xz} orbitals. In the AOM context the e_π parameter for an axial ligand is expected to be less than a fourth of that of e_σ and, like the latter, does not influence the energy of the lowest quartet state very much.[7,10a] It is difficult to quantify the π-bonding capacities of the present imidazole and benzimidazole ligands relative to each other to see if there is any trend with respect to the energy of the quartet state. Separate studies on NiL_4X_2 complexes show that 2-MeImd is a stronger π donor than pyridine.[42] If this translates to the present systems, it appears that a stronger π donor gives a lowering of the quartet state. We note, as others have, that the energy separation of the $^2A_1(d_{z^2})$ and $^2A_2(d_{yz})$ states is very sensitive to both axial and in-plane ligand fields, and it is this that leads to anisotropy differences in *g* values and principal susceptibilities in low-spin molecules.[5-7]

In contrast to the insensitivity of the quartet energy toward axial ligand effects, Hitchman's calculations[10a] showed that decreasing the in-plane field strength led to a rapid lowering of the quartet-state energy. This correlates with the increased Co–N and Co–O (Schiff base) bond lengths described earlier. In the present series of five-coordinate compounds the general order of μ_{Co} for a particular axial base is saloph > salen, which implies that the doublet–quartet state separation is higher in [Co(salen)L] than in [Co(saloph)L]. There are, unfortunately, few (if any) independent estimates of the relative ligand field strengths or σ- and π-bonding capacities of these tetradentate chelating groups to test out this trend.

As well as the bonding effects described above, Hitchman showed[10a] that increasing distortions from square-pyramidal geometry expressed as the depression angle, θ, equal to N(axial)–Co–N(in plane) could lead to a rapid decrease in the quartet-state energy, especially when θ was greater than ca. 102°. This distortion results in the raising of the Co(II) atom out of the N_2O_2 plane. It seems clear that this kind of distortion is having an important effect on the spin state of the present molecules. We see from Table III that in Co(saloph)(2-MeImd) the angle $N(1)–Co–N(3)_{axial}$ is 106.5°, which should result in a marked lowering of the quartet level, as observed. A related kind of distortion should be present in the benzimidazole adducts, leading to a lower doublet–quartet separation in the Co(saloph) and Co(salen) compounds when compared to that in the imidazole analogues. This appears to be so.

In summary, there is a delicate balance between geometrical and bonding effects which give rise to variations in the small doublet–quartet energy separation found in the present five-coordinate compounds. It is difficult to distinguish geometrical from bonding–electronic effects since one affects the other. Furthermore, it is possible that axial ligand–in-plane ligand interactions of the kind observed in the structure of [Co(saloph)(2-MeImd)] not only affect the geometric dependence of the state energies but may also modify the important in-plane σ- and π-bonding contributions to the state energies in an indirect manner.

Comments on the Nature of the Spin Crossover in Co(II) Compounds. In the previous two sections the theoretical model used to fit the susceptibilities and the subsequent interpretations of the energy levels have implicitly assumed the presence of *one* kind of molecule with a particular set of energy levels. The non-Boltzmann dependence in χ_{Co} at the "minimax" region was achieved theoretically by including the ratio of vibrational partition functions for the high- and low-spin states. More rigorous quantum chemically spin-mixed models, recently applied to Fe^{III} and Co^{II} systems, have required the ligand field levels to vary in energy as a function of temperature in order to describe the unusual temperature dependence of susceptibility.[6,43] In cases displaying abrupt spin changes, such as various Fe(II) diimine systems, the non-Boltzmann behavior cannot easily be achieved by either of these devices.

Gütlich[4] has recently summarized the various theories that have been put forward to account for spin transitions in Fe(II) complexes of both the abrupt type (e.g., $Fe(phen)_2(NCS)_2$) and of the gradual type (e.g. $[Fe(picolylamine)_3]Cl_2$). Within a thermodynamic framework he contrasted the Ising-type theory of König[44] with the "cluster" (domain) theory of Sorai and Seki,[45] which he himself later extended. There are a number of common themes to both these approaches. They both assume the presence of *two* kinds of molecules at the crossover region, the high-spin and the low-spin molecules.

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(41) Kennedy, B. J.; Murray, K. S., unpublished work.
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(44) König, E.; Ritter, G.; Irler, W.; Nelson, S. M. *Inorg. Chim. Acta* **1979**, *37*, 169 and references therein.
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Some kind of cooperative phenomenon occurs via coupling between the electronic structure of the metal ion and the phonon system of the lattice. The domain model assumes that molecules within a domain all have the same spin, and these interact cooperatively with a neighboring domain of different spin. Recent NMR and ESR studies by McGarvey on Fe(phen)$_2$(NCS)$_2$ tend to favor the Ising-type theory rather than the domain theory at temperatures below the transition temperature.[46,47]

From the experimental point of view Gütlich[4] and Hendrickson[31] have shown that the detailed nature of the spin change in Fe(II) and Fe(III) complexes can be influenced by such factors as the method of preparation, the grinding of the sample crystallites, the doping of the sample with other metal ions, the presence of crystal defects, etc. In some six-coordinate Fe(III) Schiff base complexes, for instance, Hendrickson et al.[31] found that such factors can give rise to incomplete transitions to the low-spin state. This leaves a "plateau" in the μ_{eff} curve at low temperature. The results were interpreted in terms of a nucleation and growth mechanism for the spin-crossover phase transition in the solid samples.

All of this survey leads us to ask the question as to the nature of the spin transition on Co(II) d^7 complexes of the present (and other) types. The structural and spectral data reported here strongly suggest the presence of high-spin *and* low-spin molecules, whose concentration ratio varies with temperature. As far as we can ascertain, the μ_{eff}/T plots are reversible, with no hysteresis on sample grinding effects, and with one exception, no "plateau" in μ_{Co} typical of an incomplete transition to the low-spin values. It seems reasonable, therefore, to conclude that the kinds of cooperative mechanisms described above for iron systems will also apply to the present cobalt(II) compounds although there will probably be differences in the fine details. More extensive experimental measurements (e.g. variable-temperature ESR studies of neat and doped samples) on these and other cobalt(II) crossover systems are required to test out this proposal.

Ammeter[48] has recently described spin-crossover systems in terms of two potential energy surfaces for the high- and low-spin molecules, respectively, with very small zero-point energy differences between the two. The active coordinate in the crossover situation is totally symmetric and is usually a metal–ligand vibration. Implicit in the calculations of Ammeter is the rare occurrence (if ever) of a one-molecule electronic model, e.g. of the quantum-mixed spin type referred to above.[43] In simple terms this means that the differences in geometries, d-orbital occupancies, electronic spectra, etc. of high- and low-spin states is symptomatic of two different molecules being present rather than one. The mixed-spin models and the simple model used here to calculate μ_{Co} do, nevertheless, give reasonable estimates of the energy separations involved. In a paper just received we note that Kremer, Henke, and Reinen have considered many of the points raised here in relation to spectral and magnetic studies on [Co(terpy)$_2$]X$_2$ complexes (X = Cl, Br, I, NO$_3$, ClO$_4$).[38] While the results do not clearly distinguish between the two mechanisms for spin crossover, it was concluded that the cooperative–two-molecule model was probably more appropriate than a thermal spin-equilibrium model. Interestingly, these authors have combined the potential energy approach used by Ammeter[48] with the cooperative model for spin transitions.[4,31,44,45]

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Appendix

A study of the oxygen-binding capabilities of the present Lewis base adducts would be well worthwhile, particularly from the point of view of comparing the oxygenation of high-spin and spin-crossover species to that of the well-studied low-spin derivative [Co(salen)py]. In the polycrystalline state the present compounds are stable toward oxygenation. However, they do react with O$_2$ in solution. Since the magnetic moments in solution of the Co(II) compounds appear to be similar to those in the solid state,[1] a study of moments, ESR spectra, and formation constants of oxygenated species in solution could prove illuminating. (We thank a reviewer for highlighting this facet of the chemistry of these compounds.)

Registry No. Co(salen)(Imd), 36444-92-5; Co(salen)(1,2-diMeImd), 88303-29-1; Co(salen)(2-MeImd), 36444-93-6; Co(salen)(benzimd), 36527-64-7; Co(salen)(5,6-diMebenzimd), 36444-94-7; Co(salen)(py), 30227-50-0; Co(saloph)(Imd), 52564-73-5; Co(saloph)(*N*-MeImd), 52646-10-3; Co(saloph)(2-MeImd), 88303-30-4; Co(saloph)(benzimd), 88303-31-5; Co(saloph)(5,6-diMebenzimd), 88303-32-6; Co(saloph)(water), 32269-79-7; [Co(salen)]$_2$, 25237-52-9.

Supplementary Material Available: Listings of observed and calculated structure factors and of experimental magnetic susceptibilities (27 pages). Ordering information is given on any current masthead page.

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