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Magnetic Properties of High-spin and Spin-crossover Five-coordinate Cobalt(II) Schiff Base Compounds

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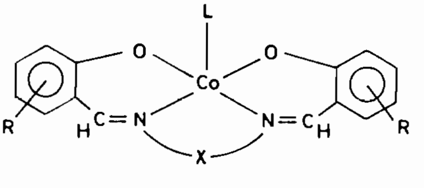
Abstract

The preparations and magnetic properties of a range of five-coordinate Co(II) Schiff base adducts of the type [Co(3-MeO-salen)L] and [Co(5-Cl-salen)L] are reported, where 3-MeO-salen^{2-} and 5-Cl-salen^{2-} are the dianions of the tetradentate ligands *N,N'*-ethylenebis(3-methoxysalicylaldimine) and *N,N'*-ethylenebis(5-chlorosalicylaldimine). 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. In some cases this results in a spin-crossover between the high-spin (quartet) and low-spin (doublet) states of this d^7 system, while others have a quartet ground state. Spin Hamiltonian theory has been used to deduce the values of the zero-field splitting parameters, *D* and *E*, and, where appropriate, the exchange coupling parameter, *J* in the high-spin complexes. Finally, a short discussion of the low temperature magnetization properties of the commonly employed calibrant Hg[Co(NCS)$_4$] is given.

Introduction

For a number of years we [1, 2] and others [3–6] have been interested in the electronic properties of five-coordinate cobalt(II) Schiff base complexes of the type Co(salen)L, where salen^{2-} = *N,N'*-ethylenebis(salicylaldiminato) dianion and L is a Lewis base coordinated to the cobalt atom (shown below). The original stimulus for much of this work was the observation by Tsumaki [7] that Co(salen) was capable of reversibly binding dioxygen, and numerous attempts have been made to relate the structural and electronic properties of these types of molecules with their ability to bind dioxygen. By comparison with the large amount of work available for the low-spin d^7 complexes there are few well authenticated examples which have a quartet ground state, the best studied being the high-spin aquo complex [Co(3-MeO-salen)·H$_2$O] [8, 9].

As we described in a recent paper [2], spin-crossover behaviour is observed in some imidazole type Lewis base adducts of Co(salen) and Co(saloph), and in that work it was noted that sterically hindered bases, such as 2-methylimidazole, tended to lower the doublet/quartet separation, especially if they were good σ donors. In the case of [Co(saloph)(2-Me-Imd)] it was found that a quartet ground state was stabilized. Previous to this work Angular Overlap calculations by Hitchman [6, 9] of the d-orbital and state energies had indicated that the energies of the various quartet states were most influenced by the in-plane ligand field. Hitchman contended that it was the reduction of the ligand field strength, amongst other structural factors, that resulted in the quartet state being lowest in [Co(3-MeO-salen)·H$_2$O)].



salen R = H, X = C_2H_4
3-MeO-salen R = 3-MeO, X = C_2H_4
5-Cl-salen R = 5Cl, X = C_2H_4
saloph R = H, X = *o*-C_6H_4

In the present work we have utilized both of the above observations to prepare a number of high-spin and spin-crossover complexes of the type Co(3-MeO-salen)L and Co(5-Cl-salen)L. The average magnetic susceptibilities of three of these *viz.* Co(3-MeO-salen)L; L = H$_2$O, 2-Me-Imd and 5,6-diMebenzimd measured between 4.3 and 300 K appear typical of mononuclear high-spin *S* = 3/2 complexes with a large zero-field splitting (ZFS). Average magnetization of these, as well as of the structurally characterized high-spin complex [Co(saloph)(2-Me-Imd)] [2], were measured between 4–40 K at fields of between 5–50 kGauss in order to uniquely determine the nature of the ZFS. Obtaining ZFS parameters by this technique is important, not only from the general point of view of understanding the electronic structures of high-spin Co(II) complexes [10], but also from the bioinorganic point of view since Makinen *et al.* have recently related ZFS of the quartet ground state to

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the coordinate geometry around Co in Co^{II} carboxypeptidase and in model systems [11, 12].

The magnetic susceptibilities of the other Co(5-Cl-salen)L and Co(3-MeO-salen)L complexes appear typical of spin-crossover behaviour [13].

Experimental

All preparations of cobalt complexes were carried out with the 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. Schiff base ligands and imidazoles were purified as in the previous study [2]. [Co(3-MeO-salen)·H_2O] was prepared by the method of West [14] but with dimethylformamide as solvent. [Co(saloph)(2-Me-Imd)] was prepared as described previously [2].

[Co(3-MeO-salen)(2-Me-Imd)]

0.35 g (1.41 mmol) of cobalt(II) acetate tetrahydrate, 0.46 g (1.41 mmol) of 3-MeO-salenH_2 and 0.5 g (6 mmol) of 2-methylimidazole 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 resulting yellow–brown powder collected by filtration, and dried under a steam of nitrogen and finally in a vacuum dessicator for 15 h. All other adducts of Co(3-MeO-salen) and of Co(5-Cl-salen) were prepared in an analogous manner. Satisfactory analytical data (C, H, N) were obtained for all compounds.

Average magnetic susceptibilities were measured between 4.2 and 300 K on an Oxford Instruments Superconducting Faraday balance operating with a main field of 10 kG and a field gradient of 1000 G/cm [15, 16]. Magnetization measurements between 4 and 40 K were performed on samples dispersed in a vaseline paste. Measurements at 4.2 K were performed with increasing and decreasing field strengths up to a maximum of 50 kG and no field dependent hysteresis was observed. Ligand corrections were taken from Pascals constants [17]. Corrections were also made for the diamagnetic vaseline paste and the gold sample holder.

Results and Discussion

High-spin Complexes

The temperature dependence of μ_{Co} for the four compounds [Co(saloph)(2-Me-Imd)] and Co(3-MeO-salen)L, L = 2-Me-Imd, H_2O and 5,6-diMebenzimd are all very similar and a representative plot is shown in Fig. 1, where it is seen that μ_{Co} for [Co(saloph)(2-Me-Imd)] decreases only very slowly from 4.19 BM at 295 K to 4.10 BM at 50 K and then much more rapidly below this presumably as a consequence of ZFS of the quartet ground state, eventually reaching 3.2 BM at 4.2 K. For a monomeric $S = 3/2$ complex the effective spin Hamiltonian can be written as:

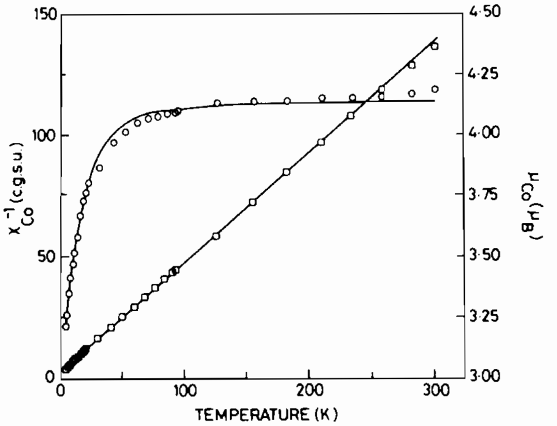

Fig. 1. Magnetic moments (○) and reciprocal susceptibilities (□) (per Co) *vs.* temperature for [Co(saloph)(2-Me-Imd)]. The solid lines represent the best fit to the parameters given in the text.

$$\mathcal{H} = g\beta HS + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \qquad (1)$$

The magnetization, M, at a given field is calculated by computer diagonalization of the resultant matrix using the exact thermodynamic expression [18]. Average susceptibilities were obtained through the use of a spatial averaging technique [19, 20]. Initially the data were interpreted using a simple axial spin Hamiltonian, *i.e.* $E = 0$ and best fit parameters of $|D| = 22.6 \pm 0.5$ cm^{-1} and $g = 2.14 \pm 0.02$ were obtained. Almost identical behaviour was observed for [Co(3-MeO-salen)(2-Me-Imd)] and the best fit parameters were $|D| = 24 \pm 1$ cm^{-1} and $g = 2.11 \pm 0.02$. As has been noted in various other studies, powder susceptibilities are typically insensitive to the sign of D [21–23] and for all four complexes similar quality fits to the data could be obtained with either positive or negative values of D. Similarly, although the addition of a small rhombic term led to a slight improvement in the quality of the fits, the data were reasonably insensitive to the magnitude of E, and hence an accurate determination of the size of E was not possible [16, 21].

Magnetization measurements over a wide range of magnetic fields at low temperatures often enable the sign of D to be determined as well as providing an estimate of the size of any rhombic splitting. In addition to providing a much more sensitive probe to ZFS in monomeric complexes, such magnetization measurements are very sensitive to any weak exchange effects that may be present. Initial calculations with $E = 0$ showed D to be positive for both [Co(saloph)-

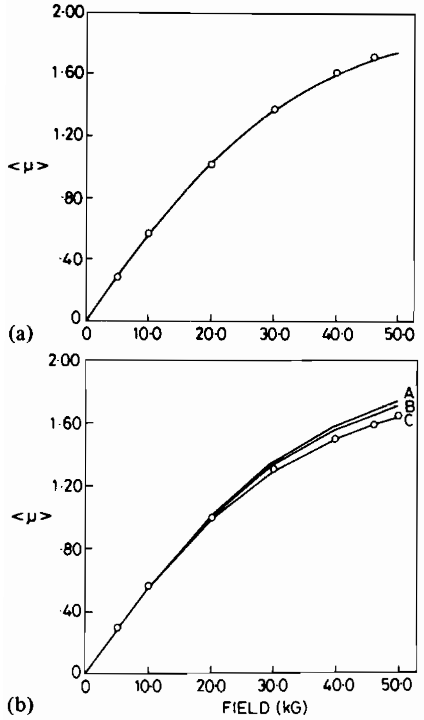

Fig. 2. Reduced moments *vs.* field at 4.2 K for (a) [Co(saloph)(2-Me-Imd)], the solid line is calculated with $D = 22.0$ cm^{-1} and $E = 3.0$ cm^{-1} and (b) [Co(3-MeO-salen)(2-Me-Imd)]. The solid lines are: A, $D = 22.0$ cm^{-1}, $E = 0$ cm^{-1}; B, $D = 22.0$ cm^{-1}, $E = 3.0$ cm^{-1}; C, $D = 22.0$ cm^{-1}, $E = 6.0$ cm^{-1}.

(2-Me-Imd)] and [Co(3-MeO-salen)(2-Me-Imd)], although at higher fields, $H > 30$ kG, the agreement between the observed and calculated susceptibilities becomes progressively worse, with the calculated values being too high. As can be seen from Fig. 2b the addition of a small rhombic term has a marked effect at higher fields and for [Co(3-MeO-salen)(2-Me-Imd)] it is apparent that an acceptable fit is obtained with $E/D \simeq 1/3$. The final parameters are $D = 22.0 \pm 0.5$ cm^{-1}, $E = 6.0 \pm 0.5$ cm^{-1} and $g = 2.11 \pm 0.02$. For [Co(saloph)(2-Me-Imd)] a slightly smaller rhombic term is appropriate and best fit parameters of $D = 22.0 \pm 0.5$ cm^{-1}, $E = 3.0 \pm 2$ cm^{-1} and $g = 2.14 \pm 0.02$ were obtained. The larger uncertainty in E for this compound reflects the smaller observed size of this splitting. It is interesting to note that these two complexes, which can be viewed as having essentially the same axial ligand field, have the same value of D. Furthermore the D values are in the range given by Makinen *et al.* [11] for five-coordinate geometries in 'simple' high-spin species and in a proposed five-coordinate Co-carboxypeptidase adduct [12].

The magnetic properties of [Co(3-MeO-salen)·H_2O] have been studied between 80 and 300 K by several groups [4, 24], and μ_{Co} was found to be virtually temperature independent in this temperature range. At lower temperatures we have found that samples tend to display an irreversible saturation/alignment effect in the presence of large applied fields. To avoid such effects the variable temperature susceptibilities of a neat powder sample were obtained using a 5 kG applied field. Fitting these data gave $|D| = 16.0$ cm^{-1} and $g = 2.27$, however as can be seen from Fig. 3 such a value of D, either positive or negative, does not reproduce the observed magnetization data at 4.2 K. In this case, now χ_{calc} is always less than χ_{obs}, which suggested the need for a smaller ZFS. The addition of a rhombic term failed to improve the quality of the fit. Studies on some related Mn(III) [22] and Fe(III) [25] Schiff base complexes suggested that this may be a consequence of weak magnetic exchange. Examination of the published [8] X-ray structural data of [Co(3-MeO-salen)·H_2O] shows the complex to exist as associated H-bonded dimers with a closest O...O distance of only 2.85 Å. Although the symmetry of the cobalt ion is probably less than axial, it is nevertheless possible to obtain an acceptable fit to the data with a dimeric spin Hamiltonian of the type:

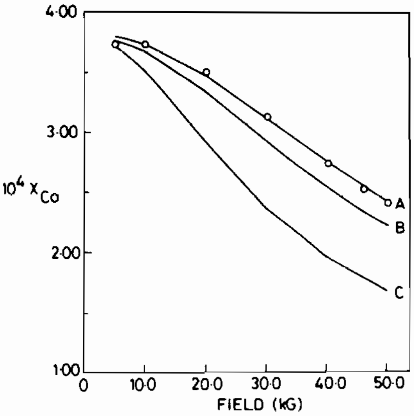

Fig. 3. Susceptibilities *vs.* field for [Co(3-MeO-salen)·H_2O] at 4.2 K. The solid lines are: A, $D = 7.0$ cm^{-1}, $J = -0.14$ cm^{-1}; B, $D = +16.0$ cm^{-1}, $J = 0$ cm^{-1}; C, $D = -16$ cm^{-1}, $J = 0$ cm^{-1}.

$$\mathcal{H} = g\beta HS + D[S_{z^2} - \tfrac{1}{3}S(S+1)] - 2JS_1S_2 \qquad (2)$$

Best fit parameters of $D = 7.0 \pm 0.5$ cm^{-1}, $J = -0.14 \pm 0.02$ cm^{-1} and $g = 2.27 \pm 0.01$ were obtained (Fig. 3). A similar dimeric packing has recently been observed in the high-spin Fe(III) complex [Fe(3-MeO-salen)(5-Ph-Imd)(H_2O)]BPh_4 which also shows weak antiferromagnetic coupling at low temperatures [25].

The fourth high-spin complex studied, [Co(3-MeO-salen)(5,6-diMebenzimd)], has a room temperature magnetic moment of 4.45 BM which decreases very rapidly below 50 K, reaching 3.8 BM at 4.2 K. The variable temperature susceptibilities were fitted to eqn. (1) with $|D| = 22.0$ cm^{-1} and $g = 2.30$. Attempts to fit the magnetization data to either eqn. (1) or (2) were unsuccessful, the calculated value of D being highly field dependent. Although it is difficult to prove that no magnetic impurities, such as Co(II) oxides, are present in the sample, the good analytical data and the observed field independence of the susceptibilities at *ca.* 40 and 300 K argues against the presence of any magnetic impurity. As indicated in 'Introduction', and described in more detail below, it is known that the doublet/quartet separation in these types of five-coordinate complexes is small, often leading to spin-crossover behaviour. It is tempting, therefore to ascribe the observed behaviour to the presence of a small number of low-spin Co(II) sites in the material. Recently a number of Fe(II) [26] and Fe(III) [27, 28] complexes which display variable temperature susceptibilities which appear typical of a high-spin complex with large zero-field splitting, have been shown by Mössbauer spectroscopy to possess a small number of low-spin sites. Attempts to detect the presence of low-spin molecules in the present complex by ESR spectroscopy were unsuccessful. These complexes gave only very poorly resolved powder spectra, even at liquid helium temperatures.

Spin-crossover Complexes

The four adducts of [Co(salen)L], with L = Imd, 2-Me-Imd, Benzimd and 5,6-diMebenzimd, showed non-Curie susceptibility behaviour at high temperatures with a maximum in χ_{Co}^{-1} *versus* T very similar to that previously observed [2] in [Co(salen)(5,6-diMebenzimd)] and typical of spin-crossover behaviour. The corresponding magnetic moments decreased rapidly between 300 and 200 K from the room temperature value of *ca.* 3 μ_B to the low-spin plateau value of *ca.* 1.9 μ_B, Fig. 4. The data could be fitted reasonably well by the simple model used previously [2] and the best-fit results are given in Table I. In this model E is the energy separation between ^{2}E and ^{4}T$_1$ states; μ_E is the magnetic moment of the ^{2}E state and $C \simeq Q_E/Q_T$, the ratio of the vibrational partition functions in the high- and low-spin states. A parameter representing the strength of the ligand field in the high-spin ^{4}T$_1$ state, γ, was held at the value 1.5, while the spin-orbit coupling constant, was held at the value 475 cm^{-1}. The energy separation, E, is reasonably independent of the axial ligand, L, and not as sensitive to changes in L as was the case for the [Co(salen)L] and [Co(saloph)L] adducts. The magnitude of E is generally larger than in the salen and saloph systems. The present values of C are smaller than found in the other compounds.

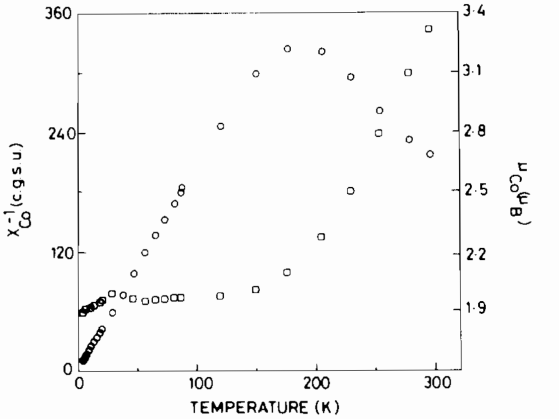

Fig. 4. Magnetic moments (□) and reciprocal susceptibilities (○) (per Co) *vs.* temperature for [Co(5-Cl-salen)(5,6-diMebenzimd)].

The remaining two complexes studied showed considerable deviations from Curie behaviour, especially at high temperatures. As seen from Fig. 5 μ_{Co} for [Co(3-MeO-salen)(Imd)] decreases from 3.23 BM at 295 K to 2.5 BM at 50 K and then much more rapidly below this, reaching 2.1 BM at 4.2 K. Below *ca.* 100 K the susceptibilities are essentially Curie like, as seen from the linear plot of χ_{Co}^{-1} *versus* T, while above 100 K a distinct variation away from Curie behaviour is noted. Unlike the spin-crossover

TABLE I. Magnetic Moments, $T(\chi^{-1}{}_{max})$ and Best-fit[a] Parameters for Spin-crossover Complexes

Complex	$\mu_{Co}{}^{295K}$ (μ_B)	$T(\chi^{-1}{}_{max})$ (K)	E (cm^{-1})	C	μ_E (μ_B)
[Co(5-Cl-salen)L]					
L = Imd	2.86	215	1420	0.05	1.91
2MeImd	2.93	205	1320	0.07	1.90
Benzimd	3.21	200	1330	0.05	1.87
5,6-diMeBenzimd	3.31	175	1280	0.06	1.90
[Co(3-MeO-salen)L]					
L = Imd	3.23	b			
Benzimd	3.63	b			

[a] See text for definition of parameters E, C and μ_E. [b] Maximum not observed (see text). Fits not attempted.

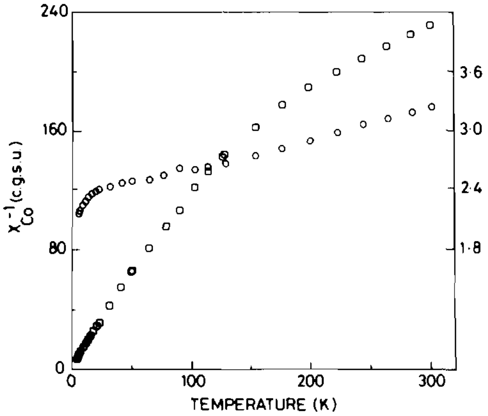

Fig. 5. Magnetic moments (○) and reciprocal susceptibilities (□) (per Co) *vs.* temperature for [Co(3-MeO-salen)(Imd)].

compounds [Co(5-Cl-salen)L], which show a pronounced maximum in the χ_{Co}^{-1} *versus T* plot at *ca.* 230 K, no maximum is observed in the present case below 300 K. In addition, we note the plateau value of $\mu_{Co} \simeq 2.5$ BM is much higher than expected for a pure low-spin Co(II) complex ($\mu_{Co} \simeq 1.8$–2.0 BM). These results indicate that [Co(3-MeO-salen)(Imd)] shows a gradual incomplete spin-crossover with a large residual high-spin fraction even at very low temperatures. The rapid decrease in μ_{Co} below $\simeq 30$ K is probably a consequence of ZFS of the residual high-spin molecules, although very weak exchange interactions cannot be discounted. [Co(3-MeO-salen)-(Benzimd)] shows almost identical behaviour with μ_{Co}^{295} equal to 3.63 BM.

It is interesting to speculate on the reason why these two adducts should fail to show maxima or minima in χ_{Co}^{-1}. It is possible that the poor solubility of the 3-MeO-salen adducts in the DMF/ethanol preparative mixture, compared to the salen, 5-Cl-salen or saloph adducts, results in poorly crystalline material, with a large number of defects. Hendrickson and co-workers [28, 29] have shown that small lattice defects caused by, for example, prolonged mechanical grinding, are capable of influencing the nature of a spin-crossover and altering the ratio of high- and low-spin molecules and hence the temperature dependence of μ; it is possible this is occurring here. It may be that the use of alternative solvent mixtures may result in more crystalline samples which display more complete spin-crossover behaviour.

Finally comparison of the present results with those given previously for the salen and saloph adducts [2] allows a comparison to be made of the doublet-quartet separation as a function of the in-plane chelating ligand. Thus, for a particular L, the separation is generally in the order 3-MeO-salen < saloph < salen < 5-Cl-salen.

Comments on the Low Temperature Magnetization of Hg[Co(NCS)$_4$]

In recent years there has been some controversy about the exact low temperature magnetic properties of the commonly employed calibrant Hg[Co(NCS)$_4$] [30–32]. In part the differences found in different laboratories are a result of the magnetic field chosen for the study and can be accounted for by considering the effect of the applied field on susceptibility at low temperatures. Our own work indicates that at low temperatures samples of Hg[Co(NCS)$_4$] tend to align in high magnetic fields, and we believe this is why Räde [30] found a positive θ value indicative of ferromagnetic exchange. Magnetization measurements by Hatfield *et al.* [32] on Hg[Co(NCS)$_4$] are similar to those reported here for [Co(3-MeO-salen)·H_2O] and it appears likely that the inability of these workers to explain their data in terms of a simple axial Hamiltonian is due to weak antiferromagnetic exchange. The presence of both a large ZFS and weak magnetic exchange in Hg[Co(NCS)$_4$] makes this calibrant unsuitable for use as a calibrant below *ca.* 50 K.

Acknowledgements

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