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Magnetic interactions in dinuclear complexes of Cr(salen)$^+$

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Abstract

The reaction of *N,N'*-ethylenebis(salicylideneiminato)diaquochromium(III) chloride, $[Cr(salen)(H_2O)_2]Cl$, with bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)diaquametal(II), $M(hfa)_2(H_2O)_2$ (M = Cu, Ni or Co), in aqueous ethanol results in the isolation of dinuclear complexes, $[Cr(salen)(solvent)_2M(hfa)_2]Cl$. The compounds are characterized by IR and UV–Vis spectroscopy and variable temperature magnetic susceptibility. The Cr(III)–Cu(II) complex is ferromagnetically coupled with $J = 9.7$ cm^{-1} and the Cr(III)–Ni(II) and Cr(III)–Co(II) complexes are antiferromagnetically coupled with $J = -11.3$ and -6.7 cm^{-1}, respectively. The analogous reactions with $Fe(hfa)_2$ and $Mn(hfa)_2(H_2O)_2$ do not yield dinuclear complexes. The former gives electron transfer products and the latter, the anion exchange product, Cr(salen)(hfa). The analogous reactions of Fe(salen)Cl with $M(hfa)_2$ (M = Cu, Ni, Co, or Mn) result in the formation of Fe(salen)(hfa) (M = Co, Ni or Mn) and Cu(salen) (M = Cu).

Introduction

Dinuclear complexes are used to mimic the magnetic properties of spin coupled enzymes [1], test theories regarding the orbital basis of magnetic interactions [2] and provide examples of complexes with unusually high spin states [3]. One of the earliest and most important methods for the preparation of dinuclear compounds containing dissimilar metal ions utilizes one metal complex with appropriate donor atoms as a ligand to a second, acidic metal complex. This method is typified by the reaction of metal complexes of tetradendate Schiff bases (TSB) such as bis(salicylidene)ethylenediamine (H_2salen) and H_2prpen** with metal halides, nitrates, perchlorates or β-diketonates [4].

$$\mathrm{MTSB} + \mathrm{M'X_2} \longrightarrow \mathrm{MTSBM'X_2}$$

If both M and M' are paramagnetic, it is possible to investigate the sign and magnitude of the magnetic exchange interaction, which will depend on both structural and electronic factors. The two metal ions, M and M', are bridged via the two phenolate oxygen atoms of the Schiff base as shown in Fig. 1 for the adduct of Cr(salen)$^+$ with bis(1,1,1,5,5,5-hexafluoropenta-2,4-dionato)metal(II) ($M(hfa)_2$) complexes that were prepared in the present study. In previous work, dinuclear complexes formed in the reaction of Cu(salen) and Cu(prpen) [5] with $M(hfa)_2$ (M = Cu, Ni, Co, Fe and Mn), which have similar structures to those in the present study, are all antiferromagnetically coupled due to the overlap of the $d_{x^2-y^2}$ orbital of copper with the magnetic orbital, e_g, of the second metal ion.

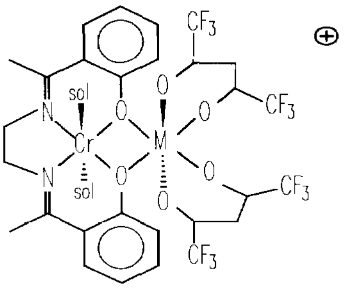

Fig. 1. Structure of dinuclear complexes prepared in this study. Sol = H_2O, M = Cu(II). Sol = C_2H_5OH, M = Ni(II), Co(II).

This work reports the magnetic characterization of dinuclear complexes prepared by the reaction of $[Cr(salen)(H_2O)_2]Cl$ and $M(hfa)_2(H_2O)_2$ (M = Cu, Ni and Co). Dinuclear complexes containing Cr(III) can exhibit both ferromagnetic [6] and antiferromagnetic [7] coupling depending on the identity of the second metal and the geometry of the complex. This is of particular interest because of the relatively few examples of heterodinuclear systems that are ferromagnetically coupled [8]. Despite this, few heterodinuclear complexes containing Cr(III) have been synthesized. The Cr(III)–Cu(II) complex reported here is predicted to be ferromagnetic due to the orthogonality of the magnetic orbitals of chromium, t_{2g}, with the $d_{x^2-y^2}$ orbital of copper. The Cr(III)–Ni(II) and Cr(III)–Co(II) com-

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**H_2prpen is an analogous Schiff base in which salicylaldehyde is replaced by 2-hydroxypropiophenone.

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plexes prepared here, in which both metal ions are octahedral, appear to be the first examples of magnetic coupling in these pairs of metal ions. For the Cr(III)–Ni(II) case, two geometry dependent possibilities were predicted by Ginsberg [9]. A Cr(III)–Ni(II) dinuclear complex consisting of two octahedral metal atoms sharing a vertex (180° bridge) was predicted to be ferromagnetic while one consisting of two octahedral metal atoms sharing an edge (90° bridge) was predicted to be antiferromagnetic. No examples of the first case are presently available, the only ferromagnetically coupled Cr(III)–Ni(II) system being a tetranuclear complex [10]. The Cr(III)–Ni(II) dinuclear complex prepared in this work provides the first example of the edge sharing case, in which antiferromagnetic coupling is predicted. The Cr(III)–Co(II) complex is also predicted to be antiferromagnetically coupled due to the overlap of magnetic orbitals on the two metal ions.

The reaction of Fe(salen)Cl with $M(hfa)_2(H_2O)_2$ was also investigated because of the possibility of producing novel high spin complexes containing a d^5 Fe(III) ion coupled to another metal ion. However, this synthetic strategy produced only the exchange products, M(salen) and Fe(salen)(hfa).

Experimental

Equipment

UV–Vis spectra of the complexes in ethanol solution were obtained on a computer controlled Perkin-Elmer Lamda 4 UV–Vis spectrometer using software obtained from Softways. IR spectra were obtained from samples in KBr on a Perkin-Elmer model 1750 FT IR instrument. The magnetic susceptibilities were measured for solid samples between 80 and 300 K on a computer controlled Faraday system which consists of a Cahn 2000 microbalance, Applied Magnetics electromagnet, Lake Shore Cryotronics temperature controller, platinum resistance thermometer and Abbess instrument cryostat. A Data Translation A/D board and AT computer were used to monitor the microbalance output and temperature readings. The instrument was calibrated with $HgCo(NCS)_4$ [11]. The raw data were corrected for the susceptibility of the holder and the diamagnetism of the ligand atoms by Pascal's constants [12] and converted to molar susceptibilities from which the magnetic moments were calculated as $\mu = 2.828\ (\chi_M T)^{0.5}$. The molar susceptibilities were fitted to the appropriate theoretical equation to determine the values of g and J, the coupling constant, by means of a non-linear regression analysis program, Grafit (SIGMA Chemical).

Starting materials

The starting compounds, $[Cr(salen)(H_2O)_2]Cl$ [13], Fe(salen)Cl [14] and $M(hfa)_2(H_2O)_2$ [15] were prepared as described previously.

Synthesis of $[Cr(salen)(solvent)_2M(hfa)_2]Cl$ (M = Cu, Ni and Co)

The dinuclear complexes were prepared as described below for $[Cr(salen)(H_2O)_2Cu(hfa)_2]Cl$. $[Cr(salen)(H_2O)_2]Cl$ (0.1253 g) was dissolved in 20 ml water with gentle warming. $Cu(hfa)_2(H_2O)_2$ (0.1653 g) was dissolved in 15–20 ml 95% ethanol and added all at once to the still warm solution of $[Cr(salen)(H_2O)_2]Cl$. The mixture was heated to the boiling point, filtered hot, and cooled. The reaction mixture was filtered on cooling to give 0.052 g $[Cr(salen)(H_2O)_2Cu(hfa)_2]Cl$ (19%). *Anal.* Found: C, 36.01; H, 2.16; N, 3.22. Calc. for $C_{26}H_{20}CrCuClF_{12}N_2O_8$: C, 36.0; H, 2.33; N, 3.23%.

The analysis data for the complexes prepared from the reaction of $[Cr(salen)(H_2O)_2]Cl$ with $Co(hfa)_2(H_2O)_2$ and $Ni(hfa)_2(H_2O)_2$ indicate coordination of two ethanol ligands rather than water. Yield for $[Cr(salen)(C_2H_5OH)_2Ni(hfa)_2]Cl$: 16%, dark brown crystals. Yield for $[Cr(salen)(C_2H_5OH)_2Co(hfa)_2]Cl$: 22%, orange–brown crystals.

Synthesis of Cr(salen)(hfa)

Reaction of $[Cr(salen)(H_2O)_2]Cl$ with $Mn(hfa)_2(H_2O)_2$ as described above produced brown crystals which were characterized as the mononuclear species, Cr(salen)(hfa) (42%). *Anal.* Found: C, 48.13; H, 3.08; N, 5.49. Calc. for $C_{21}H_{15}CrF_6N_2O_4$; C, 48.0; H, 2.88, N, 5.33%.

Reaction of $[Cr(salen)(H_2O)_2]Cl$ with $Fe(hfa)_2$

This reaction was carried out under inert atmosphere because of the oxygen sensitivity of $Fe(hfa)_2$, but otherwise in accordance with the preparation of $[Cr(salen)(H_2O)_2Cu(hfa)_2]Cl$ as described above. A purple–red powder precipitated immediately upon mixing the solutions of $Fe(hfa)_2$ and $[Cr(salen)(H_2O)_2]Cl$. The product contained the salen ligand as shown by IR and UV–Vis spectra and has tentatively been identified as Cr(salen).

Reactions of Fe(salen)Cl with $M(hfa)_2(H_2O)_2$ (M = Cu, Ni, Co and Mn)

Reactions of Fe(salen)Cl with $Ni(hfa)_2(H_2O)_2$, $Cu(hfa)_2(H_2O)_2$, $Co(hfa)_2(H_2O)_2$ and $Mn(hfa)_2(H_2O)_2$ were carried out as described below. Fe(salen)Cl was dissolved in a minimum amount of 95% ethanol. One equivalent of the metal hexafluoroacetylacetonate was added as a solid. The solution was heated to reflux, filtered hot, and the precipitate which formed on cooling was collected by filtration. The product formed from reaction of the chromium complex with $Cu(hfa)_2(H_2O)_2$ was identified as Cu(salen) on the basis of IR and UV–Vis spectra. The reactions with Ni(II), Co(II) and Mn(II) hexafluoroacetylacetonates produced $Fe(salen)(hfa)\cdot(H_2O)_x$ as evidenced by elemental analysis and IR and UV–Visible spectra. Anal. Found: C, 47.69; H, 2.37; N, 5.14. Calc. for $C_{21}H_{15}FeF_6N_2O_4$: C, 47.6; H, 2.84; N, 5.29%.

Results and discussion

Synthesis

The copper(II), nickel(II) and cobalt(II) hexafluoroacetylacetonates and $[Cr(salen)(H_2O)_2]Cl$ reacted in aqueous ethanol according to the following equation

$$[Cr(salen)(H_2O)_2]Cl + M(hfa)_2(H_2O)_2 \longrightarrow Cr(salen)(solvent)_2M(hfa)_2]Cl$$

The general procedure followed for the reaction of $[Cr(salen)(H_2O)_2]Cl$ with the various $M(hfa)_2(H_2O)_2$ complexes consisted of mixing equimolar solutions of the chromium complex in water and the metal hexafluoroacetylacetonate in 95% ethanol, heating to the point of reflux, and collecting the precipitate which formed on cooling. Except for the adduct of $[Cr(salen)(H_2O)_2]Cl$ and $Cu(hfa)_2(H_2O)_2$, which formed immediately, the products precipitated over a period of several hours to several days. The longer isolation time for the Cr(III)–Ni(II) and Cr(III)–Co(II) complexes could account for the exchange of coordinated water for ethanol, which was observed for these complexes but not for the Cr(III)–Cu(II) adduct.

Besides the dinuclear adduct formed by association of the acidic metal hexafluoroacetylacetonate with the phenolic oxygens of the chromium(III) salen complex, exchange products, M(salen) (metal exchange) or Cr(salen)(hfa) (anion exchange), are other possible outcomes of this reaction. The exchange of the salen ligand is unlikely for the kinetically inert chromium complex and was not observed under these reaction conditions. That metal exchange did not occur within the dinuclear complexes was demonstrated by chromatography of the products on alumina with methanol and spectral verification of thc presence of $Cr(salen)(sol)_2{}^+$. The $M(hfa)_2$ complexes were removed from the $Cr(salen)(sol)_2{}^+$ ion under these conditions and were observed as brightly colored bands at the top of the columns. Anion exchange was observed in the reaction of $[Cr(salen)(H_2O)_2]Cl$ with $Mn(hfa)_2(H_2O)_2$ to give Cr(salen)(hfa).

$$[Cr(salen)(H_2O)_2]Cl + Mn(hfa)_2(H_2O)_2 \longrightarrow Cr(salen)(hfa)$$

TABLE 1. IR and UV–Vis absorptions and room temperature magnetic moments of complexes prepared in this study

$[Cr(salen)(H_2O)_2Cu(hfa)_2]Cl$	$[Cr(salen)(C_2H_5OH)_2Ni(hfa)_2]Cl$	$[Cr(salen)(C_2H_5OH)_2Co(hfa)_2]Cl$	Cr(salen)(hfa)
IR absorptions (cm^{-1})			
1645(s)	1645(s)	1644(s)	1666
1631	1631(s)	1631(s)	1631(s)
1603	1606	1604	1602
1548	1550	1550	1542
1529	1525	1526	1448
1510	1510	1509	1340
1471	1470	1470	1297
1451	1450	1449	
			1248
1257(s)	1260(s)	1260(s)	1194
1201(s)	1200(s)	1198(s)	1148
1148(s)	1150(s)	1148(s)	1127
796	793	796	790
754	749	749	752
674	674	670	623
UV–Vis absorptions (nm)			
222.7	221	221.6	221.6
285.2(sh)	281.9	285.8(sh)	278.0
300.2	304.3	299.1	307.9
393.7	388.2	387.6	387.6
Room temperature magnetic moments			
4.04	4.84	5.89	3.81

The manganese complex was the only hfa complex observed to lose hfa in the reaction with [Cr(salen)(H_2O)$_2$]Cl. Facile ligand exchange for Mn(hfa)$_2$(H_2O)$_2$ is consistent with the zero crystal field stabilization energy predicted for a high spin d^5 ion. It is likely that the salen ligand adopts a bent coordination geometry to accommodate the *cis* hfa group as has been observed previously with iron complexes of salen [16].

The reaction of Fe(salen)Cl with M(hfa)$_2$(H_2O)$_2$ did not produce the desired dinuclear complexes. With Cu(hfa)$_2$(H_2O)$_2$, Fe(salen) underwent metal exchange, resulting in the precipitation of Cu(salen). The product was identified by comparison of IR and UV–Vis spectra with spectra of an authentic sample of Cu(salen). The reaction of Fe(salen)Cl with either Ni(II), Co(II) or Mn(II) hexafluoroacetylacetonate produced a reddish brown crystalline product which was identified as Fe(salen)(hfa) by elemental analysis and IR and UV–Vis spectra.

Spectra

The IR spectra (see Table 1) of the three dinuclear complexes are almost superimposable and contain absorptions found in the IR spectra of both [Cr(salen)(H_2O)$_2$]Cl and M(hfa)$_2$(H_2O)$_2$. Two almost overlapping bands centered at 1645 and 1631 cm^{-1} in all three complexes are assigned to the chelated carbonyl stretch of hfa and the imine stretch of salen, respectively. These two bands are unchanged from their positions in the original complexes. The most prominent bands in the spectra are three very strong absorptions of the hfa ligands between 1260 and 1145 cm^{-1}. The positions of these bands are also very little changed from their positions in the M(hfa)$_2$(H_2O)$_2$ complexes. The region between 1610 and 1300 cm^{-1} contains a large number of medium to weak intensity absorptions attributable to both the salen and hfa ligands. Cr(salen)(hfa) exhibits a similar IR spectrum to the dinuclear complexes but with some notable differences. The absorptions due to the salen ligand are present at nearly the same positions as in [Cr(salen)(H_2O)$_2$]Cl. Of these, the imine absorption at 1631 cm^{-1} is the most prominent in the spectrum. In addition, four medium to strong intensity absorptions appear in the region of 1248–1127 cm^{-1}, attributable to hfa. The band located at about 1645 cm^{-1} in the IR spectra of the M(hfa)$_2$(H_2O)$_2$ complexes and the dinuclears derived from them is absent in Cr(salen)(hfa). An absorption of medium intensity appears at 1666 cm^{-1}, which may be due to the chelated hfa carbonyl. The shift toward the normal carbonyl frequency may indicate that hfa is less tightly bound in this complex than in M(hfa)$_2$(H_2O)$_2$.

The UV–Vis spectral maxima in ethanol are also given in Table 1. The maximum at 277.5 nm of [Cr(salen)(H_2O)$_2$]Cl is red shifted 4.5 to 8 nm in the dinuclear adducts while the major absorption of the hfa ligand, found between 305 and 311 nm in M(hfa)$_2$(H_2O)$_2$, is blue shifted 6 to 7.5 nm in the dinuclear adducts. The UV–Vis spectrum of Cr(salen)(hfa) in ethanol contains absorptions due to both the salen and hfa ligands but does not exhibit the shifts observed in the dinuclear cases.

Magnetism

The variable temperature magnetic susceptibility data for the three dinuclear complexes, [Cr(salen)-(solvent)$_2$M(hfa)$_2$]Cl (M = Cu, Ni, and Co), were analyzed by the theoretical equations derived from the Heisenberg spin exchange Hamiltonian

$$\mathscr{H} = -2JS_1S_2$$

where J is the coupling constant and S_1 and S_2 are the spin states of the two metal ions [17]. These equations are given below. [Cr(salen)(H_2O)$_2$-Cu(hfa)$_2$]Cl, $S_1 = 3/2$, $S_2 = 1/2$

$$\chi = \frac{Ng^2\beta^2}{kT}\,\frac{(2+10\exp(4J/kT)}{(3+5\exp(4J/kT)} + N\alpha$$

[Cr(salen)(ethanol)$_2$Ni(hfa)$_2$]Cl, $S_1 = 3/2$, $S_2 = 1$

$$\chi = \frac{Ng^2\beta^2}{4kT}\,\frac{(1+10\exp(3J/kT)+35\exp(8J/kT))}{(1+2\exp(3J/kT)+3\exp(8J/kT))}\,N\alpha$$

[Cr(salen)(ethanol)$_2$Co(hfa)$_2$]Cl, $S_1 = 3/2$, $S_2 = 3/2$

$$\chi = \frac{Ng^2\beta^2}{kT}$$

$$\frac{(2\exp(2J/kT)+10\exp(6J/kT)\ +28\exp(12J/kT))}{(1+3\exp(2J/kT)+5\exp(6J/kT)+7\exp(12J/kT))} + N\alpha$$

In the above equations N is Avogadro's number, g is the gyromagnetic ratio, β is the Bohr Magneton, k is Boltzman's constant, and $N\alpha$ is the temperature independent paramagnetism, which is estimated from literature values. Values of g and J determined by nonlinear regression analysis are given in Table 2, and the fits of the experimental data to the theoretical equations are shown in Fig. 2.

The Cr(III)–Cu(II) complex is ferromagnetic as predicted on the basis of the orthogonality of the t_{2g} orbitals of chromium(III) with the $d_{x^2-y^2}$ orbital of copper(II). It was necessary to include a small interdimer coupling term for this complex as described previously [18]. Ferromagnetism has also been observed for the Cr(III)–Cu(II) complexes, Cu(fsa$_2$en)Cr(H_2O)$_2^+$ and Cr(tpp)(CuIm)Cl [6]. The magnitude of J in the present complex is considerably smaller than that observed for Cu(fsa$_2$en)Cr(H_2O)$_2^+$, despite a similar bridging geometry, which may reflect distortions from planarity. The Cr(III)–Ni(II) complex is antiferromagnetic, in

TABLE 2. Magnetic parameters for exchange coupled complexes

Compound	g	J (cm^{-1})	$N\alpha$	$\chi_v^{2\,a}$
[Cr(salen)$(H_2O)_2$Cu$(hfa)_2$]Cl	1.91	9.67	0.000150	2.70×10^{-7}
[Cr(salen)$(C_2H_5OH)_2$Ni$(hfa)_2$]Cl	2.099	−11.3	0.000200	1.89×10^{-7}
[Cr(salen)$(C_2H_5OH)_2$Co$(hfa)_2$]Cl	2.202	−6.77	0.000500	3.71×10^{-8}

$^a\chi_v^2$ = reduced chi squared.

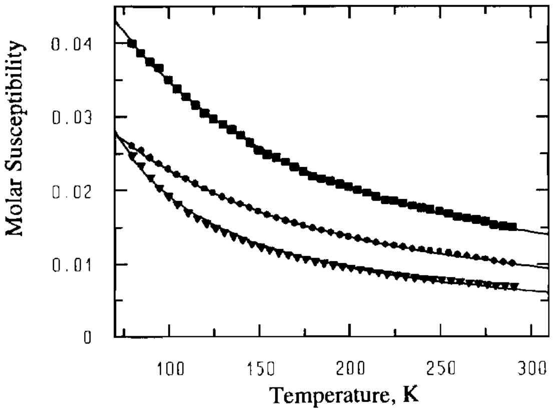

Fig. 2. Fits of experimental susceptibility for Cr–Cu (▼), Cr–Ni (●) and Cr–Co (■) dinuclear complexes.

agreement with Ginsberg's prediction for the two octahedral metal ions sharing an edge [9]. The Cr(III)–Co(II) complex contains the same exchange pathway as the Cr(III)–Ni(II) case, e_g–$p_z - d_{yz}$, and is also antiferromagnetic as predicted. The distortions from pure octahedral geometry are great enough that the Cr(III)–Co(II) complex gives a satisfactory fit without inclusion of spin–orbit coupling.

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