

INVESTIGATION ON CROSS-OVER COMPLEXES. MAGNETIC PROPERTIES OF IRON(III)
COMPLEXES WITH SEVERAL SCHIFF BASES

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Iron(III) complexes with several tetradentate Schiff Bases $[\text{FeLXY}]^{n+}$ and $[\text{Fe salen CN}]$ were synthesized, where L is a tetradentate Schiff Base including salen = NN'-ethylenebis(salicylideneiminate), X and Y represent imidazole and cyanide ion. Magnetic susceptibilities and ESR spectra were measured for these complexes from liquid nitrogen to room temperatures. The results have revealed that those complexes consist of four types in view of the spin states, that is high-spin ($S = 5/2$), low-spin ($S = 1/2$), intermediate ($S = 3/2$) and spin-equilibrium ($S = 1/2 \rightleftharpoons S = 5/2$) states.

The energy levels for a d^5 ion in an octahedral field were calculated by Tanabe and Sugano.¹⁾ According to the Tanabe-Sugano diagram the ground state changes from 6A_1 to 2T_2 at a certain ligand field strength, when the ligand field strength is increased. The so called "cross-over complexes", which locate very close to the cross-over point of the ground state energy levels in the energy diagram, have attracted much interests for their magnetic properties in recent years. Hemoglobin derivatives and some S-coordinated Fe(III) complexes have been known as examples of the cross-over complexes.^{2), 3), 4)} Recently, the existence of the spin-equilibrium has been confirmed on the basis of the XPS, ESR and Mössbauer studies for some tris(dialkyldithiocarbamato)iron(III) and tris(monothio- β -diketonato)iron(III) complexes.^{5), 6), 7)}

Being interested in cross-over complexes, we have attempted in this study to synthesize new cross-over complexes with some planar tetradentate Schiff Bases, varying axial ligands.

The synthetic procedures for the new complexes will be reported in a separate paper. The analytical data of the complexes obtained are shown in Table I with the magnetic moment, μ_{eff} , at room temperature. As can be seen in the table, μ_{eff} varies remarkably with a change of axial ligands as well as of equatorial ligands. The magnetic susceptibilities were shown as a function of temperature in Fig. 1. As seen in the diagram, $[\text{Fe salen Im}_2]\text{Bph}_4$, $[\text{Fe salen CN}]\text{CH}_3\text{OH}$ and $[\text{Fe acacen Im}_2]\text{Bph}_4$ display nearly constant magnetic moments over the temperature range, giving the values at room temperature 5.89, 3.92 and 2.17 BM, respectively. This fact clearly indicates that they are of the high-spin ($S = 5/2$), the intermediate-spin ($S = 3/2$) and the low-spin ($S = 1/2$) types, respectively. On the other hand, magnetic moments of $[\text{Fe bzacen Im}_2]\text{Bph}_4$, $[\text{Fe 3-meOsalen Im}_2]\text{Bph}_4$, remarkably decrease with lowering of temperature as seen in Fig. 1. These results are strongly suggesting that those

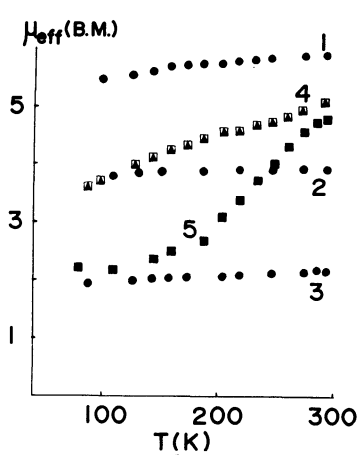
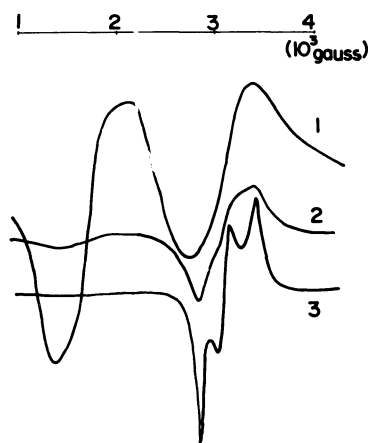


Fig. 1. Temperature dependence of μ_{eff} .

1. [FesalenIm₂]Bph₄
2. [FesalenCN]
3. [FeacacenIm₂]Bph₄
4. [Fe3-MeOsalenIm₂]Bph₄
5. [FebzacenIm₂]Bph₄

Fig. 2. ESR spectra of [FebzacenIm₂]Bph₄

1. 295 K
2. 245 K
3. 209 K



complexes belong to cross-over complexes.

In order to confirm this, ESR spectra were measured for those complexes at various temperatures. The results for [FebzacenIm₂]Bph₄ were shown in Fig. 2 as a typical example. On the basis of previous ESR studies on iron(III) complexes⁸⁾ and of the present results for [FesalenIm₂]Bph₄, [FeacacenIm₂]Bph₄, the band around 1600 G should be attributed to the absorption due to a high-spin complex, and the band around 3000 G to the one due to a low-spin complex. As seen in Fig. 2, the intensity of the band around 1600 G extremely decreases relative to that of the band around 3000 G with lowering of temperature, and the position of the 3000 G band, (i.e., the g-value) does not depend on temperature. From the above facts, we may conclude that those two complexes are of a doublet (S = 1/2) ground state with a thermally accessible sextet (S = 5/2) state, and the two spin-states are in equilibrium for the temperature range.

Table I

	C		H		N		μ_{eff} (B.M.) (295 K)
	found	calcd.	found	calcd.	found	calcd.	
[FesalenIm ₂]Bph ₄	71.06	71.06	5.50	5.44	10.84	10.81	5.89
[FesalenCN]·CH ₃ OH	56.03	56.86	4.32	4.77	10.82	11.05	3.92
[FeacacenIm ₂]Bph ₄	68.35	68.77	6.36	6.32	11.46	11.46	2.17
[FebzacenIm ₂]Bph ₄	72.31	72.82	5.88	5.88	9.87	9.80	4.79
[Fe3-MeOsalenIm ₂]Bph ₄	68.65	68.83	5.61	5.54	10.03	10.03	5.03

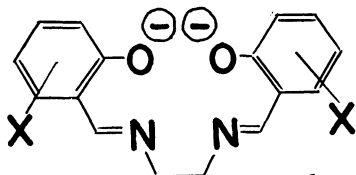
Abbreviation of the ligands

salen:

X = H

3-MeOsalen:

X = 3-CH₃O

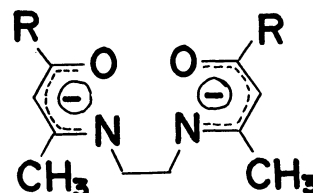


acacen:

R = CH₃

bzacen:

R = C₆H₆



References

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