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Complex Compounds of Iron(II, III) with 2-(2'-Pyridyl)Benzimidazole

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Complex compounds of iron(II,III) with 2-(2′-pyridyl)-benzimidazole (PBZ) of the types: (a) $[Fe(PBZ)_3]X_2 . nH_2O$ *(where X =* Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, *and* $\frac{1}{2}SO_4^{2-}$*); (b)* $[Fe(PBZ)_2X_2] . 2H_2O$ *(X =* NCS^- *or* CN^-*); and (c)* $[Fe(PBZ)_2(H_2O)_2]X$, *(where X =* SO_4^{2-}, $C_2O_4^{2-}$, *and* $S_2O_3^{2-}$*) are reported. The compound* $[Fe(PBZ)_2(NCS)_2]$ *has been obtained in* cis *and* trans *form. The complexes show room temperature magnetic moments in the range, 4.96-5.46 B.M., corresponding to* $^5T_{2g}$ *state. From the electronic reflectance spectra the crystal field parameters10Dq, B and β have been obtained. One binuclear complex,* $[(PBZ)_2(SO_4)Fe\text{-}O\text{-}Fe(SO_4)(PBZ)_2]$ *17H₂ and a tris-chelate* $[Fe(PBZ)_3]Cl_3$ *of iron(III) with* $^2T_{2g}$ *ground state were also obtained.*

Introduction

Complexes of transition elements with 2-(2′-pyridyl)benzimidazole (PBZ) have been reported by us.[1] A detailed study of the complexes of 2-(2′-pyridyl)-benzimidazole with iron was thought to be worthwhile because of the pharmacological activities of benzimidazoles and their metal complexes. From the formation constants and i.r. spectra of some of its metal complexes it has been shown[2-4] that PBZ coordinates through the pyridine nitrogen and the tertiary nitrogen of the imidazole ring.

In the present investigation iron(II,III) complexes of PBZ have been prepared and their structure have been investigated by magnetic, spectral and electrical conductance studies.

Iron(II) Complexes. Iron(II) forms three types of complexes:

(i) $[Fe(PBZ)_3]X_2 . nH_2O$, where $X = Cl^-$, Br^-, I^-, NO_3^-, ClO_4^- and $\frac{1}{2}SO_4^{2-}$; n = 2 or 3.

(ii) $[Fe(PBZ)_2X_2] . nH_2O$, where X = NCS^- or NC^- and n = 0 or 2, and

(iii) $[Fe(PBZ)_2](H_2O)_2]X$, where X = SO_4^{2-}, $S_2O_3^{2-}$ or $C_2O_4^{2-}$.

The tris-chelated complex salts of the type (i) are obtained from an aqueous-alcoholic solution of iron (II) salts and the ligand, followed by concentration or by addition of the respective anions as sodium or potassium salt in large excess. The complex salts are soluble in ethanol and DMF but insoluble in cold water. In DMF solution the electrical conductance values are in the range expected for bi-univalent electrolytes,[5] Table I. The complexes slowly lose water on heating and become anhydrous at about 130°C. The hydrated complex chloride and nitrate, which are red-violet in colour, become dull red on dehydration but the orange-red perchlorate complex remains unchanged. The complexes have magnetic moments in the range 4.96-5.19 B.M. at room temperature (301° K). The electronic absorption spectra of the complexes in ethanol or DMF show an intense charge transfer band near 490 nm but no *d-d* transition could be observed. The reflectance spectra of the complexes, however, show a broad but weak band near 850 nm (Table I), in addition to the charge transfer band.

The dithiocyanato complex $[Fe(PBZ)_2(NCS)_2] .2H_2O$, has been obtained in two colour modifications: carmine-red and violet-red. The former is obtained when the compound is precipitated in the cold, and is then transformed into the latter by digestion on a steam bath for a few minutes in presence of sodium acetate. The two forms differ appreciably in their i.r. and reflectance spectra as well as in their magnetic moments at room temperature (violet-red, 5.46 B. M. and carmine-red, 5.29 B.M.). Both forms show an appreciable electrical conductance in DMF (Table I), which is attributed to solvation.

The reflectance spectra of the two varieties differ appreciably in intensity and band position; the charge transfer band of the carmine-red form occurs at 515 nm while that of the violet-red form occurs at 530 nm. In the infrared region, the carmine-red form displays a distinct and broad band near 850 nm, while the violet-red form does not exhibit such distinct band; only a broad shoulder was detected near 860-900 nm. The electronic absorption spectra of both forms in DMF or in ethanol are, however, similar and show only an intense charge transfer band at 495 nm, indicating that in solution the two forms lose identity and the same species exist.

In the i.r. spectrum of the carmine-red form the CN stretching absorption is split into two components at 2080 and 2005 cm^{-1}. The i.r. spectrum of violet-red form, however, gives only one CN stretching

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Table I. Analytical results, conductivity (in DMF at 28-30°C), Magnetic moment values (at 301-305°K), and spectral bands of iron(II, III) complexes with PBZ (L).

Compounds	% Metal		% Nitrogen		% Anions		% Water		μ_{eff}	λ_m	Spectal bands	
	Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	(B.M.)	ohm^{-1}	C—T	$^5T_{2g}\rightarrow{}^5E_g$
$[FeL_3]Cl_2 . 3H_2O$	7.39	7.29	16.31	16.46	9.88	9.26	7.21	7.05	4.96	168	510a,490d	850
$[FeL_3]Br_2 . 3H_2O$	6.69	6.53	14.63	14.73	18.81	18.86	6.56	6.32	5.16	152	490d	—
$[FeL_3]I_2 . 2H_2O$	6.18	6.00	13.58	13.53	27.38	27.25	—	—	5.19	—	515a,490d	850
$[FeL_3](Cl_4)_2 . 3H_2O$	6.37	6.24	13.89	13.99	22.01	22.24	6.16	6.04	4.96	—	(ε_{max}-1382)	
											520a,490d	850
$[FeL_3](NO_3)_2 . 3H_2O$	6.93	6.81	18.61	18.80	—	—	6.69	6.59	5.11	173	(ε_{max}-1390)	
$[FeL_3]SO_4 . 2H_2O$	7.31	7.22	16.11	16.29	12.51	12.42	4.91	4.66	5.19	—	—	—
$[FeL_2(H_2O)_2]SO_4$	9.78	9.66	14.49	14.53	16.38	16.61	—	—	5.36	—	—	—
$[FeL_2(H_2O)_2]C_2O_4$	9.84	9.81	14.48	14.74	15.71	15.44	—	—	5.38	—	500a	880
$[FeL_2(H_2O)_2]S_2O_3$	9.42	9.38	14.02	14.14	18.56	18.86	—	—	5.41	130	510a,490d	840
cis-$[FeL_2(NCS)_2]$	9.91	9.95	19.82	19.96	—	—	—	—	5.28	28	—	—
											—	—
trans-$[FeL_2(NCS)_2] . 2H_2O$	9.37	9.33	18.61	18.72	19.71	19.41	6.13	6.02	5.46	40	515a,495d	850
											(ε_{max}-1380)	
$[FeL_2(NC)_2] . 2H_2O$	10.71	10.47	20.71	20.97	—	—	6.61	6.74	5.28	30	530a,495d	900
$[Fe_2(O)L_4(SO_4)_2] . 17H_2O$ **	8.05	7.94	11.98	12.01	13.58	13.56	10.30	10.88*	2.11	—	—	—

** Found: C, 40.1; H, 5.01% required C,40.96; H,4.98%, * for $8H_2O$ only, C-T = charge transfer band, a = reflectance band, d = bands in DMF and bands are in nm

band at 2080 cm^{-1}. The CS stretching of thiocyanate group, which usually occurs in the range 680-860 cm^{-1}, could not be located due to ligand vibrations in this region. The splitting of the CN stretching band is usually indicative[6] of *cis* coordination of thiocyanate group. König and Madeja[7] have attributed the splitting observed in i.r. spectra of $[Fe(phen)_2(NCS)_2]$, $[Fe(bipy)_2(NCS)_2]$ and $[Fe(2,9\text{-dimethyl-phen})_2(NCS)_2]$ to be indicative of a *cis* configuration. Thus from the splitting of the CN stretching band it may be inferred that the carmine-red form has a *cis* configuration whereas the violet-red form has a *trans* configuration. Howevery, the existance of a mixture cannot be completely ruled out. It is somewhat difficult to suggest whether the thiocyanate groups are N or S bonded. If the broad and strong i.r. band observed in the complexes near 818 cm^{-1} (814 cm^{-1} in ligand) is regarded as arising from the CS stretching mode then the thiocyanate is coordinated through the nitrogen atom. This mode of coordination appears to be more probable due to the class "a" character of Fe^{II} ion.

The dicyano bis-chelated complex, $[Fe(PBZ)_2(CN)_2]$ is obtained as a deep violet-red precipitate when an aqueous-ethanolic solution of the ligand and ferrous ammonium sulphate (1:2 molar ratio) is treated with an acetic and sodium acetate buffered solution of KCN. The complex dissolves in DMF producing a violet-red solution which is unstable. The absorption spectrum of a freshly prepared solution in DMF shows only an intense charge transfer band at 490 nm, similar to the tris-chelated complexes. In contrast the reflectance spectrum of the complex shows the charge transfer band at 510 nm as well as a broad and weak band near 840 nm. In DMF, the complex shows appreciable conductance probably due to solvation. The complex is paramagnetic (5.28 B.M.) at room temperature. The i.r. spectrum of the complex shows a strong CN stretch at 2080 cm^{-1}, indicative of a coordinated cyanide group.[8]

The diacido complexes lose all the water molecules below 120°C from which the water molecules are presumed to be uncoordinated and is supported by the absence of i.r. absorption frequencies of coordinated water (835 and 1600 cm^{-1}).[9]

Diaquobis-chaletd complex salts: $[Fe(PBZ)_2(H_2O)_2]X$, ($X = SO_4^{2-}$, $C_2O_4^{2-}$ or $S_2O_3^{2-}$). The diaquo-complex sulphate $[Fe(PBZ)_2(H_2O)_2]SO_4$, is obtained as a vermillion-red precipitate, when an ethanolic solution of the ligand is treated with a saturated aqueous solution of ferrous ammonium sulphate containing a few drops of dil. H_2SO_4. The complex sulphate could not be isolated if the proportion of ethanol in solution is less than 90%. The from aqueous-ethanolic solution of ferrous chloride and ligand containing a large amount of sodium oxalate or thiosulphate. The diaquo-complex halide or nitrate could not be isolated even in absolute ethanol, perhaps due to their extreme solubility or formation of the tris-chelated species.

The complexes are paramagnetic and the moments are in the range of 5.36-5.41 B.M. at room temperature. The complex sulphate and thiosulphate show a broad charge transfer band at 500 nm and a broad shoulder near 880 nm. The i.r. spectra of complexes show the characteristics of uncoordinated oxalate (C=O) stretch at 1680 cm^{-1}) and sulphate group (broad and strong SO band at 1105-1140 cm^{-1}).[8] The complexes do not lose water, when heated up to 200° C, indicating that the water molecules are coordinated. The appearance of a new medium and broad band at 835 cm^{-1} in the i.r. spectrum of complex sulphate, and 830 cm^{-1} in the complex oxalate also supports the coordination of water molecules in diaquobischelated complexes.[9]

Discussion

Six-coordinated iron(II) complexes with ground

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(8) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », John Wiley, New York, 1967, p. 173.

(9) Ref. 8, page 167.

state ${}^5T_{2g}$, ${}^3T_{2g}$ and ${}^1A_{1g}$ are known,[10-12] and show temperature independent magnetic moments of 5.5, 3.9, and 2.80 B.M. respectively. Iron(II) complexes with 2-(2'-pyridyl)imidazole[13] and 2-(2'-pyridylamine)-4-(2-pyridyl)thiazole[14] show anomalous magnetic moment (2.3-4.67 B.M.) which have been attributed to a ${}^5T_{2g} \rightarrow {}^1A_{1g}$ equilibrium.

In the present case iron(II) complexes show μ_{eff} 4.96-5.46 B.M. at room temperature and no anomally could be detected, although the ligands PBZ is apparently similar to 2-(2'-pyridyl)imidazole. This can be attributed to steric volume of the bulky ligand causing an increase in metal-ligand distance and thereby decreasing Δ sufficiently enough to alter the ground state to the high-spin ${}^5T_{2g}$.

Spectral Behaviour. For high-spin octahedral iron (II) complexes absorption arising from ${}^5T_{2g} \rightarrow r^5E_g$, ${}^3T_{1g}$, ${}^3T_{2g}$ ..... transitions are expected.[15] The spectra of high-spin octahedral complexes, however, exhibits only the ${}^5T_{2g} \rightarrow {}^5E_g$ transition and the other transitions are not identified. In the present study the complexes show a srong charge transfer band at 490-530 nm and a broad *d-d* band near 850 nm, which is assigned to the ${}^5T_{2g} \rightarrow {}^5E_g$ transition (Table I).

It has been shown from the analysis of magnetic data of high-spin octahedral iron(II) complexes that Δ (${}^5T_{2g}$) should be equal to the spin-pairing energy, $5/2\ B+4C \approx 18.5\ B$ (assuming the usual relationship $C \approx 4B$). Thus a qualitative idea about the Racah interelectronic repulsion parameter B and nephelauxetic coefficient β have been obtained from the 10 Dq value sand are given in the Table below:

Complex	10 Dq(cm^{-1})	B (cm^{-1})	β
[Fe(PBZ)$_3$](ClO$_4$)$_2$	11,770	636	0.61
Cis[Fe(PBZ)$_2$(NCS)$_2$]	11,770	636	0.61
[Fe(PBZ)$_2$(NC)$_2$]	11,900	643	0.61

(B free ion value 1024 cm^{-1})[7]

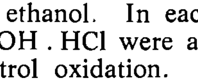
Thus the degree yof covalency in these complexes appears to be of the same order as for [Fe(phen)$_2$(NCS)$_2$] (B = 640 cm^{-1} and β = 0.61), which has ${}^5T_{2g}$ ground state.[7]

Iron(III) Complexes. Chiswell *et al.*[4] have reported the preparation of the trischelated complex, Fe(PBZ)$_3$Cl$_3$. We have also prepared the same compound and found it to be a spin-paired complex with magnetic moment of 2.52 B.M. at room temperature. Besides, another yellows-brown iron(III) complex was obtained having the analytical result corresponding to the formula, Fe$_2$(PBZ)$_4$(O)(SO$_4$)$_2$. 17H$_2$O. The compound is insoluble in water and common organic solvents. The complex gradually loses 8 water molecules when heated up to 120°C. The remaining water molecules are not lost, even on heating upto 150°C, probably these water molecules are held strongly in the crystal lattice. Similar behaviour of lattice water has been reported in case of some iron(III) compounds with phenonthroline.[16]

The tris-chelated complex chloride, [Fe(PBZ)$_3$]Cl$_3$ is highly soluble in DMF or ethanol. In aqueous solution th ecomplex decomposes and a brownish-red product of indefinite composition is formed. In the reflectance spectrum of the complex no *d-d* transition could be detected in the region 400-1,000 nm. It shows a magnetic moment of 2.52 B.M. at room temperature (305°K), which is indicative of octahedral iron(III) in ${}^2T_{2g}$ state (cf. 2.47 B.M. for [Fe(en)$_3$Cl]$_3$[17] at 285°K).

Structure of the binuclear comple: Fe$_2$(PBZ)$_4$O · (SO$_4$)$_2$. 17H$_2$O. Gains, Hammelt and Walden[18] reported the formation of a dihydroxo-bridged binuclear complex of iron(III), [(Phen)$_2$Fe(OH)$_2$Fe(phen)$_2$]Cl$_4$. 5H$_2$O. From a detailed study of magnetic behaviour, X-ray data and far infrared spectra, Lewis *et al.*[16] finally proposed oxygen-bridged structure: [(phen)$_2$(Cl)Fe-O-Fe(Cl)(phen)$_2$]Cl$_2$. 6H$_2$O in preference to the hydroxo-bridged structure as suggested by Walden and others.[18,19]

In the present case the i.r. spectrum of the complex exhibits the vibration of coordinated unidentate (C_{3v}) sulphate group[8] and bands are located at 1140, 1045 (ν_3) and 950 cm^{-1} (ν_1). The strong and slightly broad band at 825 cm^{-1} in the i.wr. spectrum of the complex appears to be indicative of Fe-O-Fe vibration[16] as observed for [Fe$_2$O(Salen)$_2$] (where Salen = bis-salicylaldehyde-ethylenediamine) and Fe$_2$O.(phen)$_4$X$_4$. nH$_2$O (where X = Cl$^-$, Br$^-$, NO$_3^-$, ClO$_4^-$, and ½ SO$_4^{2-}$) (in th erange 820-840 cm^{-1}). The presence of hdroxo-bridging was ruled out due to absence of the expected (OH) bending mode in the range 950-1100 cm^{-1}, as suggested by Ferraro and Walker.[20] The complex shows magnetic moments of 2.11 B.M. at room temperature, which is indicative of octahedral iron(III) in ${}^2T_{2g}$ state (cf. 1.97 B.M. for [Fe$_2$O(phen)$_4$Cl$_4$] . H$_2$O at 285°K).[16] Thus on the basis of the foregoing discussion an oxo-bridged structure (I) is assigned to the dinuclear complex Fe$_2$(PBZ)$_4$O · (SO$_4$)$_2$.



$$\begin{array}{ccc}(PBZ)_2Fe & - O - & Fe(PBZ)_2 \\ | & & | \\ SO_4 & & SO_4\end{array}$$

I

Experimental Section

All preparations of iron(II) complexes were carried out under purified nitrogen atmosphere using air-free water and ethanol. In each preparation a few crystals of NH$_2$OH . HCl were added to ferrous salts solution to control oxidation. The complexes were dried in vacuum over CaCl$_2$. The ligand was prepar-

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ed by the method of Leko and Vlajinats.[21]

Tris}2-(2-pyridyl)benzimidazole}iron(II) sulphate. An aqueous solution of ferrous sulphate (0.56 g in 10 ml water and 2-3 drops of dil. H_2SO_4) was treated with an ethanolic solution of the ligand (1.2 g in 40 ml) and the resulting deep red solution was concentrated in vacuum to about one fourth of its bulk. On cooling, deep red crystals of the complex sulphate separated, which was filtered, washed with cold water and dried.

The chloride, bromide and nitrate of the above complex were prepared similarly to the complex sulphate, using an aqueous solution of freshly prepared iron (II) chloride, bromide and nitrate respectively.

Tris}2-(2-pyridyl)benzimidazole}iron(II) perchlorate and iodide. The resulting deep red solution was treated with an aqueous solution of $NaClO_4$, when an orange-red crystalline precipitate of the complex separated. The complex was filtered, washed with aqueous ethanol and dried.

The complex iodide was prepared similarly to the complex perchlorate using KI instead of $NaClO_4$.

Diaquobis}2-(2-pyridyl)benzimidazole}iron(II) sulphate. A solution of ferrous ammonium sulphate (1.5 g in 5-7 ml water and 3-4 drops dil. H_2SO_4) was treated with hot ethanolic solution of the ligand (1.5 g in 60 ml) with stirring. From the resulting red solution, a vermillion-red precipitate separated. The precipitate was filtered, washed with aqueous-ethanol, and dried.

The diaquo bis-chelated complex oxalate/thiosulphate was obtained as a brick-red precipitate when an aqueous ferrous chloride solution containing excess of $Na_2C_2O_4/Na_2S_2O_3$ was treated with ethanolic solution of the ligand.

Cis-Diisothiocyanatobis}2-(2-pyridyl)benzimidazole}iron(II). The aqueous solution of ferrous ammonium sulphate (0.72 g in 20 ml) was treated with an ethanolic solution of the ligand (0.72 g in 40 ml). The resulting deep red solution was treated with an ice-cold solution of KCNS (2 g in 5 ml). On cooling carmine-red crystals of *cis*-form separated. The compound was filtered, washed and dried.

Trans-Diisothiocyanatobis}2-(2-pyridyl)benzimidazole}iron(II) dihydrate. The deep-red solution of *cis*-diisothiocyanato complex was treated with CH_3COONa (3 g in 5 ml) and digested on a steam bath for a few minutes when a violet-red compound separated.

Dicyanobis}2-(2-pyridyl)benzimidazole}iron(II) dihydrate. The deep-red solution obtained on mixing an aqueous solution of ferrous ammonium sulphate and the ethanolic solution of the ligand was treated with a cold aqueous solution of KCN buffered with sodium acetate and acetic acid. A violet-red precipitate separated immediately, which was filtered quickly, washed with cold water, and dried.

Disulphato-μ-oxo-tetrakis}2-(2-pyridyl)benzimidazole}diferrate. A hot aqueous solution of ferric ammonium sulphate (2 g in 10 ml) was added to a hot ethanolic solution of the ligand (2 g in 60 ml) with stirring. A yellowish-brown precipitate separated immediately, which was filtered and washed thoroughly with aqueous ethanol and dried.

The compound was found to contain: C, 40.82; H, 5.01; N, 11.98 and Fe, 8.05% and required for $Fe_2(PBZ)_4O(SO_4)_2 . 17H_2O$: C, 40.96; H, 4.98; N, 12.01 and Fe, 7.94%.

The magnetic susceptibilities of the complexes were determined on Gouy balance at room temperature. μ_{eff} was calculated making diamagnetic corrections Pascals's constant.[22]

Reflectance and absorption spectra. The electronic absorption spectra of the solutions were measured on a Hilger and Watts Uvispek Spectrophotometer model No. H700 with silica prism. A Hilger-Uvispek standard reflectance attachment was used to measure the reflectance spectra, with $MgCO_3$ as the standard.

Conductivity measurements. The electric conductivities of the solutions were measured at room temperature in DMF.

Iron(II) and iron(III) salts, solvents and chemicals used were E. Merk's extra pure or B.D.H. A.R. quality.

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