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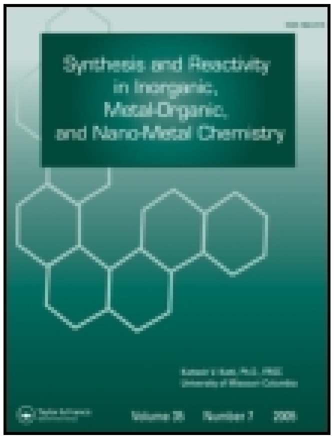

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Complexes of Iron(III) with N,N′-bis(4-Antipyrylmethylidene)ethylenediamine

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Complexes of Iron(III) with N,N′-*bis*(4-Antipyrylmethylidene)ethylenediamine

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ABSTRACT

Iron(III) complexes of the Schiff base N,N′-bis(4-antipyrylmethylidene)-ethylenediamine (BAME) having the general formulae $[Fe(BAME)_2X]X_2$ ($X = ClO_4$ or NO_3) and $[Fe(BAME)_2X_2]X$ ($X = SCN$, Cl or Br) have been s+ynthesized and characterized by elemental analyses, electrical conductance in non-aqueous solvents, infrared and electronic spectra, and magnetic susceptibility measurements. In these complexes, BAME acts as a neutral bidentate ligand coordinating through both azomethine nitrogen atoms. In the perchlorate and nitrate complexes, one of the anions is bidentate while in the thiocyanate complex, two of the anions are bound in a monodentate fashion to the metal ion. In the chloride and bromide complexes, two of the halide ions are coordinated. A high-spin octahedral geometry is assigned around Fe(III) in all of these complexes.

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INTRODUCTION

The biological activities of antipyrine based ligands and their metal complexes are well known.[1,2] Iron complexes were the earliest metal complexes used in the treatment of hypochromic anaemia.[3] In view of this and as a continuation of our earlier investigation on Schiff base metal complexes,[4–10] we report here the synthesis and characterisation of the Fe(III) complexes of a Schiff base ligand, *viz.*, N,N′-bis(4-antipyrylmethylidene)ethylenediamine, which is an antipyrine derivative (Figure 1).

RESULTS AND DISCUSSION

The formation of the complexes may be represented by the general equation shown below.

$$FeX_3 + 2BAME \rightarrow Fe(BAME)_2X_3 (X = ClO_4, NO_3, SCN, Cl \text{ or } Br)$$

The complexes are dark brown solids. They are soluble in acetonitrile, DMF, ethanol, and nitrobenzene but insoluble in benzene, ethyl acetate, and toluene. The analytical data (Table 1) show that the complexes can be represented as: $Fe(BAME)_2X_3$ ($X = ClO_4$, NO_3, SCN, Cl or Br).

Electrical Conductance

The molar conductance values of the complexes (Table 2) in acetonitrile, DMF and nitrobenzene fall in the range suggested for 1:2 electrolytes for the perchlorate and nitrate complexes.[11] The thiocyanate, chloride, and bromide complexes behave as 1:1 electrolytes. Thus, the complexes may be formulated as $[Fe(BAME)_2X]X_2$ [$X = ClO_4$ or NO_3) and $[Fe(BAME)_2X_2]X$ ($X = SCN$, Cl or Br).

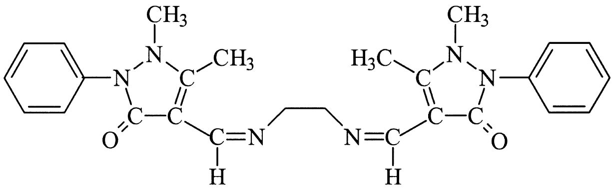


Figure 1. N,N′-Bis(4-antipyrylmethylidene)ethylenediamine.

Table 1. Analytical data[a] of the iron(III) complexes of BAME.

Compound	Molecular formula	Formula weight	Metal (%)	Anion (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Yield (%)	M.p. (°C)
BAME	$C_{26}H_{28}N_6O_2$	456.55	–	–	68.32 (68.40)	6.24 (6.18)	18.34 (18.41)	80	185
$[Fe(BAME)_2(ClO_4)](ClO_4)_2$	$C_{52}H_{56}Cl_3FeN_{12}O_{16}$	1267.30	4.38 (4.41)	23.59 (23.54)	49.20 (49.28)	4.10 (4.14)	13.22 (13.26)	92	178
$[Fe(BAME)_2(NO_3)](NO_3)_2$	$C_{52}H_{56}FeN_{15}O_{13}$	1154.97	4.80 (4.84)	–	54.12 (54.07)	4.48 (4.54)	18.12 (18.19)	90	174
$[Fe(BAME)_2(SCN)_2](SCN)$	$C_{55}H_{56}FeN_{15}O_4S_3$	1143.19	4.82 (4.89)	–	57.72 (57.78)	4.78 (4.85)	18.42 (18.38)	93	219
$[Fe(BAME)_2Cl_2]Cl$	$C_{52}H_{56}Cl_3FeN_{12}O_4$	1075.31	5.10 (5.19)	9.82 (9.89)	58.12 (58.08)	4.81 (4.87)	15.68 (15.63)	89	170
$[Fe(BAME)_2Br_2]Br$	$C_{52}H_{56}Br_3FeN_{12}O_4$	1208.68	4.60 (4.62)	19.78 (19.83)	51.72 (51.67)	4.40 (4.34)	13.88 (13.91)	88	194

[a] Calculated values in parentheses.

Table 2. Molar conductance[a] data of the iron(III) complexes[b] of BAME.

Complex	CH_3CN	DMF	$C_6H_5NO_2$
$[Fe(BAME)_2(ClO_4)](ClO_4)_2$	307.44	170.19	61.49
$[Fe(BAME)_2(NO_3)](NO_3)_2$	296.46	153.72	57.09
$[Fe(BAME)_2(SCN)_2](SCN)$	120.78	74.66	19.76
$[Fe(BAME)_2Cl_2]Cl$	126.27	77.96	21.41
$[Fe(BAME)_2Br_2]Br$	153.72	88.9	25.25

[a] $Ohm^{-1}\ cm^2\ mol^{-1}$.

[b] 10^{-3} M solution.

Infrared Spectra

The important infrared spectral bands of BAME and its complexes are given in Table 3. The bands at 1650 and 1594 cm^{-1} are attributable to the stretching vibrations of the carbonyl and azomethine groups, respectively.[6] In the complexes the band at 1594 cm^{-1} is blue-shifted to the 1,607–1,612 region indicating the coordination of both azomethine nitrogens. But the band at 1650 cm^{-1} remains practically unaltered, suggesting non-coordination of both carbonyl oxygens in these complexes.[6]

In the perchlorate complex, the triply-split band maxima at 1142, 1110 and 1024 cm^{-1} are due to the ν_8, ν_6 and ν_1 vibrations, respectively, of the perchlorate group of C_{2v} symmetry. This indicates that at least one of the perchlorate groups must be coordinated in a bidentate fashion. The band at 1089 cm^{-1} is assigned to ν_3 vibration of the ionic perchlorate of T_d symmetry. The vibrational frequencies observed at 942 and 636 cm^{-1} corresponding to ν_2 and ν_3 vibrations of the perchlorate group of C_{2v} symmetry and the band at 627 cm^{-1} due to the ν_4 vibration of the ionic perchlorate, which are not present in the spectrum of the free ligand, support the coexistence of both ionic and coordinated perchlorate groups in this complex.[6]

In the nitrate complex, two strong bands at 1475 and 1280 cm^{-1} are attributable to ν_4 and ν_1 stretching vibrations, respectively, of the coordinated ion of C_{2v} symmetry. Since $\nu_4 - \nu_1$ is 195 cm^{-1}, the nitrate ion is bidentate.[12] A very strong band at 1380 cm^{-1} and a medium intensity band at 824 cm^{-1} are due to ν_3 and ν_2 vibrations, respectively, of uncoordinated nitrate ion of D_{3h} symmetry.

In the thiocyanate complex, a sharp band at 2053 cm^{-1} is attributable to N-coordinated thiocyanate ion.[8] This is supported by the presence of a medium intensity band at 478 cm^{-1} and a weak band at 852 cm^{-1}.

Table 3. Important IR spectral bands (cm^{-1}) of BAME and its iron(III) complexes.[a]

BAME	$[Fe(BAME)_2(ClO_4)]$-$(ClO_4)_2$	$[Fe(BAME)_2(NO_3)]$-$(NO_3)_2$	$[Fe(BAME)_2(SCN)_2]$-(SCN)	$[Fe(BAME)_2Cl_2]Cl$	$[Fe(BAME)_2Br_2]Br$	Assignment
1650 s	1648 s	1647 s	1648 s	1648 s	1648 s	ν(C = O)
1594 s	1610 s	1608 s	1607 s	1612 s	1610 s	ν(C = N)
–	1142 m	–	–	–	–	ν_8-coordinated ClO_4
–	1110 s	–	–	–	–	ν_6-coordinated ClO_4
–	1024 m	–	–	–	–	ν_1-coordinated ClO_4
–	942 w	–	–	–	–	ν_2-coordinated ClO_4
–	636 m	–	–	–	–	ν_3-coordinated ClO_4
–	1089 s	–	–	–	–	ν_3-ionic ClO_4
–	627 m	–	–	–	–	ν_4-ionic ClO_4
–	–	1475 s	–	–	–	ν_4-coordinated NO_3
–	–	1280 m	–	–	–	ν_1-coordinated NO_3
–	–	1380 s	–	–	–	ν_3-ionic NO_3
–	–	824 m	–	–	–	ν_2-ionic NO_3
–	–	–	2053 s	–	–	ν(C – N)
–	–	–	852 w	–	–	ν(C – S)
–	–	–	478 m	–	–	δ(NCS)
–	–	–	–	310 m	–	ν(Fe – Cl)
–	–	–	–		289	ν(Fe – Br)
–	452 w	455 w	454 w	450 w	455 w	ν(Fe – N)

[a] s = strong, m = medium, w = weak.

In the spectra of halide complexes, Fe–Cl and Fe–Br stretching vibrations are observed at 310 and 289 cm^{-1} which are absent in the ligand spectrum.[8]

The above spectral observations along with the conductance data indicate that one of the perchlorate and nitrate ions, two of the thiocyanates, and both chloride and bromide ions are coordinated in these complexes. Furthermore, Fe–N stretching vibrations are observed at about 450 cm^{-1} in all these complexes.[8]

Electronic Spectra

The electronic spectral data of the ligand and complexes with their tentative assignments are given in Table 4. BAME shows two absorption maxima at 25,000 and 40,322 cm^{-1}, corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$

Table 4. Electronic spectral data and magnetic moments of the iron(III) complexes of BAME.

Compound	Abs. max. (cm^{-1})	Tentative assignment	μ_{eff} (B.M.)
BAME	25,000	$n \rightarrow \pi^*$	–
	40,322	$\pi \rightarrow \pi^*$	
$[Fe(BAME)_2(ClO_4)](ClO_4)_2$	24,390	$n \rightarrow \pi^*$	5.84
	40.485	$\pi \rightarrow \pi^*$	
	33, 222	Charge transfer	
	21,598	$^6A_{1g} \rightarrow {}^4T_{1g}$	
$[Fe(BAME)_2(NO_3)](NO_3)_2$	24,691	$n \rightarrow \pi^*$	5.96
	40,983	$\pi \rightarrow \pi^*$	
	33,333	Charge transfer	
	20,533	$^6A_{1g} \rightarrow {}^4T_{1g}$	
$[Fe(BAME)_2\ (SCN)_2](SCN)$	24813	$n \rightarrow \pi^*$	5.88
	40,485	$\pi \rightarrow \pi^*$	
	33,898	Charge transfer	
	21,645	$^6A_{1g} \rightarrow {}^4T_{1g}$	
$[Fe(BAME)_2Cl_2]Cl$	24,630	$n \rightarrow \pi^*$	5.71
	40,650	$\pi \rightarrow \pi^*$	
	33,333	Charge transfer	
	21,978	$^6A_{1g} \rightarrow {}^4T_{1g}$	
$[Fe(BAME)_2Br_2]Br$	24875	$n \rightarrow \pi^*$	5.74
	40,816	$\pi \rightarrow \pi^*$	
	33,333	Charge transfer	
	20,746	$^6A_{1g} \rightarrow {}^4T_{1g}$	

transitions, respectively. In the complexes, n → π* transitions are red-shifted to the regions 24,390–24,875 cm^{-1}, while π → π* transitions are blue-shifted to the regions 40,485–40,983 cm^{-1}. The band in the region 20,533–21,978 cm^{-1} of the complexes is attributed to the $^6A_{1g} \rightarrow {}^4T_{1g}$ transition, which is consistent with octahedral geometry around Fe(III) ion.[13,14] An intense absorption band in the 33,222–33,898 cm^{-1} region may be due to a charge transfer process.

Magnetic Moment Data

The molar magnetic moments of the complexes are given in Table 4. The values vary in the range 5.71–5.96 B.M., suggesting high-spin octahedral configuration around the Fe(III) ion.[15,16]

Based on the above observations the following tentative structures may be assigned to the complexes (Figure 2).

EXPERIMENTAL

Materials

The metal salts were prepared from Analar ferric carbonate and the respective 50% acids and crystallizing out the salts by evaporating the solution on a steam bath. Ferric thiocyanate was prepared by the method reported earlier.[17]

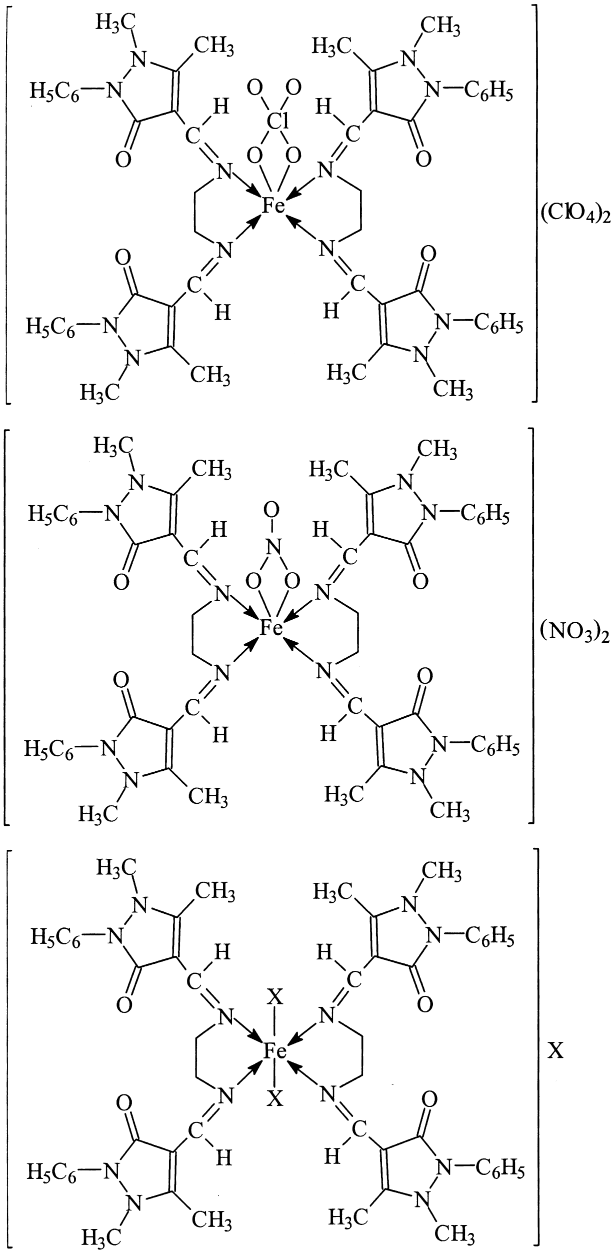
Preparation of the Ligand

The ligand N,N′-bis(4-antipyrylmethylidene)ethylenediamine was prepared and characterized as described earlier.[6]

Preparation of BAME Complexes

Perchlorate, Nitrate, Thiocyanate and Bromide Complexes

A quantity of one mmol of $Fe(ClO_4)\cdot 6H_2O$ (0.4623 g), $Fe(SCN)_3\cdot 6H_2O$ (0.3381 g) or $FeBr_3\cdot 6H_2O$ (0.4037 g) in ethyl acetate (10 mL) or $Fe(NO_3)_3\cdot 6H_2O$ (0.3499 g) in methanol (10 mL) was added to a boiling suspension of 2.2 mmol (1.0044 g) of BAME in ethyl acetate (100 mL). The mixture was



where X = SCN, Cl or Br

Figure 2. Tentative structures of Fe(III) complexes of BAME.

refluxed for about 3 h on a steam bath. The resulting solution was concentrated to half of its original volume and cooled. The complexes precipitated on cooling were filtered and washed several times with hot benzene to remove the excess ligand. The complexes were dried under vacuum over phosphorus(V) oxide.

Chloride Complex

A quantity of one mmol of $FeCl_3 \cdot 6H_2O$ (0.2703 g) in acetone (10 mL) was added to a boiling suspension of 2.2 mmol (1.0044 g) of BAME in acetone (100 mL). The complexes were separated by the same procedure as described above.

Analyses and Physical Methods

All the complexes were analyzed for metal contents by the standard method[18] and for perchlorate by the Kurz method.[19] The electrical conductance of the complexes in acetonitrile, DMF and nitrobenzene (10^{-3} M solutions) were measured at room temperature using a Toshniwal conductivity bridge with a dip-type conductance cell (cell constant = 1.098). The infrared spectra of the ligand and complexes were recorded in the range 4,000–400 cm^{-1} on a Shimadzu IR 470 spectrophotometer in KBr disc and in the range 400–200 cm^{-1} on a Perkin Elmer 983 IR spectrophotometer in polyethylene powder. Electronic spectra of the ligand and the complexes in the solid state (using a paste with Nujol) were measured in the range 200–1,100 nm on a Shimadzu UV 160A spectrophotometer. The elemental analyses (C, H and N) were carried out on a Heraeus CHNO rapid analyser. The magnetic moments were measured at room temperature by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant.

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