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IRON(III) COMPLEXES OF 1,2-DI(IMINO-4′-ANTIPYRINYL)ETHANE

N. T. Madhu [a] & P. K. Radhakrishnan [b]

[a] School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills PO, Kottayam, Kerala, 686 560, India

[b] School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills PO, Kottayam, Kerala, 686 560, India

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IRON(III) COMPLEXES OF 1,2-DI(IMINO-4′-ANTIPYRINYL)ETHANE

N. T. Madhu and P. K. Radhakrishnan*

School of Chemical Sciences, Mahatma Gandhi
University, Priyadarshini Hills PO, Kottayam-686 560,
Kerala, India

ABSTRACT

Iron(III) complexes of the Schiff base 1,2-di(imino-4′-antipyrinyl)ethane (L) have been prepared and characterized by elemental analyses, electrical conductance in non-aqueous solvents, infrared and electronic spectra as well as magnetic susceptibility measurements. The complexes have the general formula $[Fe(L)(ClO_4)](ClO_4)_2$ and $[Fe(L)X_2]X$ ($X{=}NO_3$, SCN, Cl or Br). L acts as a neutral tetradentate ligand coordinating through both carbonyl oxygens and both azomethine nitrogens. In the perchlorate complex, one of the perchlorate ions is coordinated bidentately while in the nitrate and thiocyanate complexes two of the anions are coordinated monodentately 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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*Corresponding author. E-mail: mgu@md2.vsnl.net.in

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INTRODUCTION

Because of their different coordination possibilities and, consequently, their flexible complexing behaviour, the synthesis and structural investigations on pyrazolone-based ligands and their metal complexes have attracted the attention of many investigators[1,2]. Iron complexes were the earliest metal compounds studied in medicinal chemistry. They were and are used to treat hypochromic anemia caused by iron deficiency[3]. In view of this and as part of our earlier investigations[4–8] on metal complexes of pyrazolone derivatives, we report here the synthesis and characterization of iron(III) complexes of a Schiff base ligand which is a pyrazolone derivative (Fig. 1).

RESULTS AND DISCUSSION

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

$$FeX_3 + L \rightarrow Fe(L)X_3 \ (X = ClO_4,\ NO_3,\ SCN,\ Cl \text{ or } Br).$$

The complexes are dark brown solids, except the thiocyanate complex, which is olive green. All of them except the thiocyanate complex are soluble in acetonitrile, DMF, DMSO, ethanol, methanol and nitrobenzene, but insoluble in benzene, chloroform, ethyl acetate and toluene. The thiocyanate complex is soluble in DMF, DMSO and methanol, but insoluble in acetone, acetonitrile, benzene, chloroform, ethyl acetate and nitrobenzene.

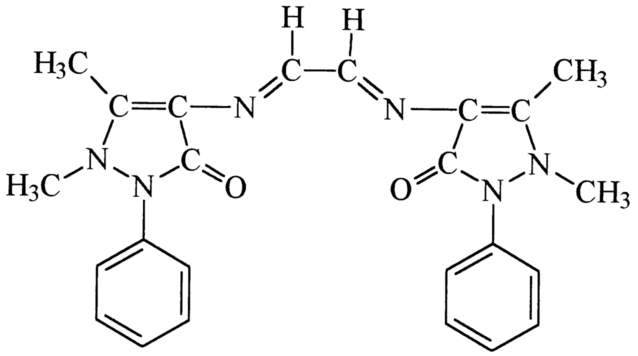

Figure 1. 1,2-Di(imino-4′-antipyrinyl)ethane.

The elemental analysis data (Table I) suggest that the present complexes may be formulated as: $Fe(L)X_3$ ($X = ClO_4$, NO_3, SCN, Cl or Br).

Electrical Conductance

The molar conductance values of the complexes (Table II) in acetonitrile, DMF, methanol and nitrobenzene are in the range expected for 1:2 electrolytes for the perchlorate complex[9]. The nitrate, thiocyanate, chloride and bromide complexes behave as 1:1 electrolytes[9]. Thus, the complexes may be formulated as $[Fe(L)(ClO_4)](ClO_4)_2$ and $[Fe(L)X_2]X$ ($X = NO_3$, SCN, Cl or Br).

Infrared Spectra

The important infrared spectral data of L and its complexes are presented in Table III. The band at $1650\,cm^{-1}$, characteristic of $\nu(C{=}O)$ of L, is shifted to the region 1597–$1630\,cm^{-1}$ in the complexes indicating the coordination of both carbonyl oxygens[6,7]. Another intense band at $1576\,cm^{-1}$, attributable to C=N stretching in L, is shifted to the region 1560–$1538\,cm^{-1}$ in the complexes indicating the coordination of both azomethine nitrogens[7].

In the perchlorate complex, the triply-split band maxima at 1140, 1105 and $1020\,cm^{-1}$ are due to the ν_8, ν_6 and ν_1 vibrations, respectively, of the perchlorate ion of $C_{2\nu}$ symmetry, indicating the coordination of the perchlorate ion in a bidentate fashion[7]. But the band at $1085\,cm^{-1}$ is assigned to the ν_3 vibration of uncoordinated perchlorate of T_d symmetry[7]. The vibrational frequencies at 935 and $640\,cm^{-1}$ corresponding to the ν_2 and ν_3 vibrations, respectively, of the perchlorate ($C_{2\nu}$) ion and the band at $625\,cm^{-1}$ due to the ν_4 vibration of perchlorate (T_d) ion, also support the coexistence of both uncoordinated and bidentately coordinated perchlorate ions in this complex[7].

In the nitrate complex, two medium bands at 1430 and $1315\,cm^{-1}$ are attributable to the ν_4 and ν_1 stretching vibrations, respectively, of the nitrate ion of $C_{2\nu}$ symmetry[10]. Since ν_4–ν_1 is $115\,cm^{-1}$, the nitrate ion is monodentately coordinated[10]. A very strong band at $1380\,cm^{-1}$ and a medium-intensity band at $820\,cm^{-1}$ are due to the ν_3 and ν_2 vibrations, respectively, of uncoordinated nitrate ion (D_{3h})[6,7].

In the thiocyanate complex, a sharp band at $2050\,cm^{-1}$ is in accordance with the N-coordinated thiocyanate ion[7]. Further, the bands at $480\,cm^{-1}$ and $855\,cm^{-1}$ stand as additional evidence for N-coordinated thiocyanate ion[7].

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Table I. Analytical Data[a] of the Iron(III) Complexes of L

Complex	Empirical Formula	Formula Weight	Fe (%)	X[b] (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Yield (%)	M.p. (°C)
$[Fe(L)(ClO_4)](ClO_4)_2$	$C_{24}H_{24}N_6O_{14}Cl_3Fe$	782.51	7.08 (7.13)	37.97 (38.12)	36.81 (36.83)	3.10 (3.09)	10.75 (10.73)	88	151
$[Fe(L)(NO_3)_2]NO_3$	$C_{24}H_{24}N_9O_{11}Fe$	670.19	8.31 (8.33)	–	42.97 (43.00)	3.52 (3.60)	18.81 (18.80)	87	147
$[Fe(L)(SCN)_2]SCN$	$C_{27}H_{24}N_9O_2S_3Fe$	658.30	8.42 (8.48)	–	49.13 (49.24)	3.60 (3.67)	19.08 (19.14)	90	191
$[Fe(L)Cl_2]Cl$	$C_{24}H_{24}N_6O_2Cl_3Fe$	590.62	9.50 (9.45)	17.91 (18.00)	48.78 (48.80)	4.07 (4.09)	14.21 (14.22)	93	212
$[Fe(L)Br_2]Br$	$C_{24}H_{24}N_6O_2Br_3Fe$	723.99	7.79 (7.71)	33.08 (33.11)	39.82 (39.81)	3.30 (3.34)	11.59 (11.60)	89	241

[a] Calculated values in parentheses.

[b] $X = ClO_4$, Cl or Br.

Table II. Molar Conductance Data of the Iron(III) Complexes of L (in ohm^{-1}cm^{2} mol^{-1})

	Molar Conductance[a]			
Complex	$C_6H_5NO_2$	CH_3CN	DMF	CH_3OH
$[Fe(L)(ClO_4)](ClO_4)_2$	49.09	288.08	144.04	180.68
$[Fe(L)(NO_3)_2]NO_3$	22.16	161.20	77.56	90.14
$[Fe(L)(SCN)_2]SCN$	–	–	88.64	99.72
$[Fe(L)Cl_2]Cl$	21.05	121.11	66.48	104.81
$[Fe(L)Br_2]Br$	22.64	159.08	91.08	106.10

[a] 10^{-3} M solutions.

In the far-infrared spectra of the halide complexes, the Fe-Cl and Fe-Br stretching vibrations are at 313 and 285 cm^{-1}, respectively[7], which are absent in the ligand spectrum.

The above spectral observations along with the conductance data indicate that one of the perchlorates, two of the nitrates, thiocyanates, chlorides and bromides are coordinated in these complexes. Further, the ν(Fe-O) and ν(Fe-N) stretching vibrations are observed at about 555 and 460 cm^{-1}, respectively, in all of the complexes[7,8].

Electronic Spectra

The electronic spectral data of L and its complexes with the tentative assignments are presented in Table IV. L shows two band maxima at 26,180 cm^{-1} and 39,220 cm^{-1} corresponding to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively[7]. In the complexes, the $n \rightarrow \pi^*$ bands are red-shifted to the 25,309–25,614 cm^{-1} region and the $\pi \rightarrow \pi^*$ bands are blue-shifted to the 39,682–40,322 cm^{-1} region compared to that of L. All of the complexes exhibit a band in the 22,026–23,509 cm^{-1} region corresponding to the $^6A_{1g} \rightarrow {}^4E_g(G)$ transition, consistent with octahedral Fe(III)[11,12]. Further, all of the complexes exhibit an intense absorption band in the region 33,222–33,333 cm^{-1}, which might be due to a charge transfer transition.

Magnetic Moment Data

The molar magnetic moments of the complexes are presented in Table IV. The values are in the range 5.84–5.97 BM and suggest a high-spin octahedral geometry around Fe(III) in these complexes[13,14].

Table III. Important Infrared Spectral Bands (cm^{-1}) of L and Its Iron(III) Complexes

L	$[Fe(L)(ClO_4)](ClO_4)_2$	$[Fe(L)(NO_3)_2]NO_3$	$[Fe(L)(SCN)_2]SCN$	$[Fe(L)Cl_2]Cl$	$[Fe(L)Br_2]Br$	Assignment
1650 s	1598 s	1630 s	1597 s	1602 s	1624 s	ν(C=O)
1576 s	1554 s	1560 s	1538 s	1546 s	1557 s	ν(C=N)
–	1140 m	–	–	–	–	ν_8-coordinated ClO_4
–	1105 s	–	–	–	–	ν_6-coordinated ClO_4
–	1020 m	–	–	–	–	ν_1-coordinated ClO_4
–	935 w	–	–	–	–	ν_2-coordinated ClO_4
–	640 w	–	–	–	–	ν_3-coordinated ClO_4
–	1085 s	–	–	–	–	ν_3-ionic ClO_4
–	625 m	–	–	–	–	ν_4-ionic ClO_4
–	–	1430 m	–	–	–	ν_4-coordinated NO_3
–	–	1315 m	–	–	–	ν_1-coordinated NO_3
–	–	1380 s	–	–	–	ν_3-ionic NO_3
–	–	820 m	–	–	–	ν_2-ionic NO_3
–	–	–	2050 s	–	–	ν(C-N)
–	–	–	855 w	–	–	ν(C-S)
–	–	–	480 m	–	–	δ(NCS)
–	–	–	–	313 m	–	ν(Fe-Cl)
–	–	–	–	–	285 m	ν(Fe-Br)
–	555 w	555 w	555 w	550 w	550 w	ν(Fe-O)
–	460 w	465 w	460 w	460 w	460 w	ν(Fe-N)

s = strong; m = medium; w = weak.

Table IV. Electronic Spectral Data and Magnetic Moments of Iron(III) Complexes of L

Compound	Abs. Max. (cm^{-1})	Tentative Assignments	μ_{eff} (BM)
L	26,180	$n \rightarrow \pi^*$	–
	39,220	$\pi \rightarrow \pi^*$	
$[Fe(L)(ClO_4)](ClO_4)_2$	25,316	$n \rightarrow \pi^*$	5.85
	39,840	$\pi \rightarrow \pi^*$	
	33,222	Charge transfer	
	23,213	$^6A_{1g} \rightarrow {}^4E_g(G)$	
$[Fe(L)(NO_3)_2]NO_3$	25,614	$n \rightarrow \pi^*$	5.90
	39,682	$\pi \rightarrow \pi^*$	
	33,222	Charge transfer	
	23,509	$^6A_{1g} \rightarrow {}^4E_g(G)$	
$[Fe(L)(SCN)_2]SCN$	25,390	$n \rightarrow \pi^*$	5.87
	40,322	$\pi \rightarrow \pi^*$	
	33,333	Charge transfer	
	22,026	$^6A_{1g} \rightarrow {}^4E_g(G)$	
$[Fe(L)Cl_2]Cl$	25,390	$n \rightarrow \pi^*$	5.97
	40,003	$\pi \rightarrow \pi^*$	
	33,222	Charge transfer	
	23,154	$^6A_{1g} \rightarrow {}^4E_g(G)$	
$[Fe(L)Br_2]Br$	25,390	$n \rightarrow \pi^*$	5.84
	40,001	$\pi \rightarrow \pi^*$	
	33,222	Charge transfer	
	23,213	$^6A_{1g} \rightarrow {}^4E_g(G)$	

Based on the results of the present study, the structures shown in Fig. 2 may be assigned to the complexes.

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[15].

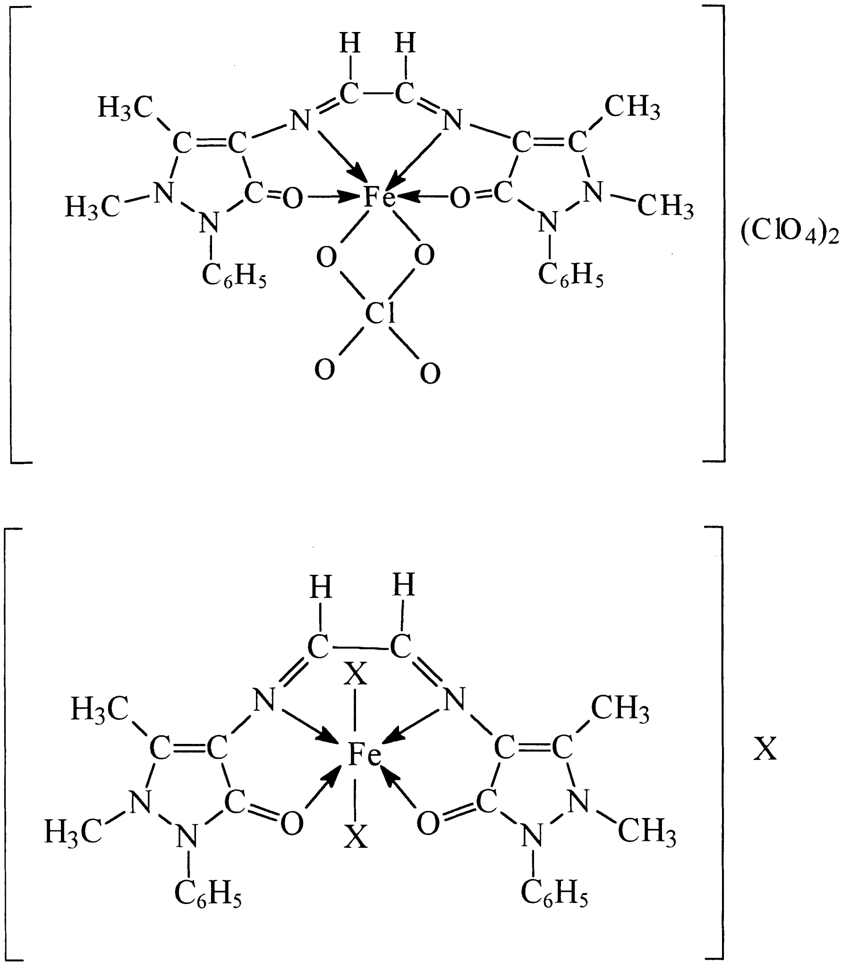

Figure 2. Tentative structures of Fe(III) complexes of L.

Preparation of the Ligand

The ligand, 1,2-di(imino-4′-antipyrinyl)ethane (L) was prepared and characterized as described previously[6].

Preparation of Complexes

Perchlorate, Chloride, and Bromide Complexes

One mmol of $Fe(ClO_4)_3{\cdot}6H_2O$ (0.3628 g), $FeCl_3{\cdot}6H_2O$ (0.2703 g) or $FeBr_3{\cdot}6H_2O$ (0.4036 g) in methanol (10 mL) was added to a boiling suspension of 1.2 mmol of L (0.4294 g) in methanol (100 mL). This mixture was refluxed for about 2 h on a boiling water bath. The dark brown solution obtained on reflux was cooled and filtered. On evaporating the solvent to half of its volume and subsequent cooling to room temperature, the complex separated, was filtered and repeatedly washed with hot ethyl acetate to obtain dark brown solids of the pure complexes. Finally, the complexes were recrystallised from methanol then dried under vacuum over phosphorus(V) oxide.

Nitrate and Thiocyanate Complexes

One mmol of $Fe(NO_3)_3{\cdot}6H_2O$ (0.3498 g) or $Fe(SCN)_3{\cdot}6H_2O$ (0.3498 g) in methanol (10 mL) was added to a boiling suspension of 1.2 mmol of L (0.4294 g) in ethyl acetate (100 mL). This mixture was refluxed for about 2 h on a water bath. The precipitated complex was filtered and washed several times with hot ethyl acetate to remove the excess ligand. Finally the complexes were recrystallised from methanol and dried under vacuum over phosphorus(V) oxide.

Physical Methods of Analysis

All the complexes were analyzed for metal and halide content by the standard methods[16]. All other physical methods were the same as described earlier[7].

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REFERENCES

1. Costisor, O.; Linert, W.; Deusch, S.; Stanescu, C. Novel Complexes of Antipyrine Ligands: Dinuclear Copper(II), Cobalt(II) and Nickel(II) Complexes of N,N′-Tetra(4-antipyrylmethyl)-1,2-diaminoethane. J. Coord. Chem. **1994**, *33*, 229–234.
2. Costisor, O.; Mracec, M.; Jóri, Z.; Labádi, I.; Linert, W. Mixed-Ligand Complexes of Co(II) and Cu(II) with Pyrazoloinc Mannich Bases and 2-Aminobenzothiazole. Synth. React. Inorg. Met.-Org. Chem. **2000**, *30* (8), 1489–1504.
3. Schwietert, C.W.; McCue, J.P. Coordination Compounds in Medicinal Chemistry. Coord. Chem. Rev. **1999**, *184*, 67–89.
4. Radhakrishnan, P.K.; Indrasenan, P.; Nair, C.G.R. Complexes of Lanthanide Nitrates with 4-N-(2′-Hydroxybenzylidene)aminoantipyrine. Polyhedron **1984**, *3* (1), 67–70.
5. Joseph, S.; Radhakrishnan, P.K. Yttrium and Lanthanide Iodide Complexes of N,N′-bis(4-antipyrylmethylidene)ethylenediamine. Polyhedron **1999**, *18*, 1884.
6. Madhu, N.T.; Radhakrishnan, P.K. Complexes of Nickel(II) with 1,2-Di(imino-4′-antipyrinyl)ethane and 4-N-(4′-Antipyrylmethylidene)-amino antipyrine. Synth. React. Inorg. Met.-Org. Chem. **2000**, *30* (8), 1561–1579.
7. Madhu, N.T.; Radhakrishnan, P.K. Cobalt(II) Complexes of 1,2-Di(imino-4′-antipyrinyl)ethane and 4-N-(4′-Antipyrylmethylidene)-aminoantipyrine. Trans. Met. Chem. **2000**, *25*, 287–292.
8. Madhu, N.T.; Radhakrishnan, P.K. Copper(II) Complexes of 1,2-Di(imino-4′-antipyrinyl)ethane and 4-N-(4′-Antipyrylmethylidene)-aminoantipyrine. Synth. React. Inorg. Met.-Org. Chem. **2001**, *31* (2), 315–330.
9. Geary, W.J. The Use of Conductivity Measurements in Organic Solvents for the Characterisation of Coordination Compounds. Coord. Chem. Rev. **1971**, *7*, 81–22.
10. Nakamoto, K. Coordination Compounds. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 4th Edn.; John Wiley and Sons, Inc.: New York, 1986; 253, 254.
11. Lever, A.B.P. Electronic Spectra of d^n Ions. In *Inorganic Electronic Spectroscopy*; 2nd Edn.; Elsevier: Amsterdam, 1984; 453.

12. Islam, M.S.; Uddin, M.M. Mixed-Ligand Complexes of Cr(III), Fe(III) and Ru(III) Diphenates with Hetrocyclic Bases. Synth. React. Inorg. Met.-Org. Chem. **1991**, *21* (6&7), 1093–1105.
13. Cotton, F.A.; Wilkinson, G. The Elements of First Transition Series. In *Advanced Inorganic Chemistry*; 3rd Ed.; Wiley Eastern Ltd.: New Delhi, 1992; 867.
14. Narang, K.K.; Singh, V.P. Synthesis, Characterisation, Thermal Studies and Biological Activity of Iron(III) Complexes with Some Acylhydrazines. Synth. React. Inorg. Met.-Org. Chem. **1993**, *23* (6), 971–989.
15. Ram, A.N.S.; Sarasukutty, S.; Prabhakaran, C.P. Iron(III) Thiocyanate Complexes with Some Schiff Bases. Curr. Sci. (India). **1976**, *45*, 514.
16. Bassett, J.; Denney, R.C.; Jeffery, G.H.; Mendham, J. Titrimetric Analysis. In *Vogel's Text Book of Quantitative Inorganic Analysis*; 5th Ed.; ELBS: London, 1961; 330.

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