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MANGANESE(II) COMPLEXES OF 1,2-DI(IMINO-4'-ANTIPYRINYL)ETHANE

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MANGANESE(II) COMPLEXES OF 1,2-DI(IMINO-4'-ANTIPYRINYL)ETHANE

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ABSTRACT

Manganese(II) complexes of the Schiff base 1,2-di(imino-4'antipyrinyl)-ethane (GA) have been synthesized 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 formulae [Mn(GA)X₂] (X = ClO₄, NO₃, Cl, Br or I). GA acts as a neutral tetradentate ligand coordinating through both carbonyl oxygens and both azomethine nitrogens. Both anions are coordinated to the metal ion and the perchlorate as well as nitrate ions are monodentate. A highspin octahedral geometry is assigned around Mn(II) in all of these complexes.

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INTRODUCTION

Antipyrine and its derivatives possess antibacterial¹ and anti-inflammatory² properties. Recently, it has been reported that a manganese complex with terpyridine effects the four-electron oxidation of water to oxygen, mimicking the production of oxygen from water during photosynthesis³. In view of this, and as part of our earlier investigations on Schiff base-metal complexes^{4–8} of antipyrine derivatives, we report here the synthesis and characterization of a new series of Mn(II) complexes of the Schiff base 1,2di(imino-4'-antipyrinyl)ethane (GA) which is an antipyrine derivative (Fig. 1).

RESULTS AND DISCUSSION

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

 $MnX_2 + GA \rightarrow Mn(GA)X_2$ (X = ClO₄, NO₃, Cl, Br or I)

The elemental analyses data (Table I) of the complexes suggest that the present complexes may be formulated as $Mn(GA)X_2$ (X = ClO₄, NO₃, Cl, Br or I).

The molar conductance values of the complexes (Table II) in acetonitrile, DMF and nitrobenzene $(10^{-3} \text{ M solutions})$ suggest non-electrolytic behaviour⁹. The slightly higher values observed in acetonitrile and DMF⁹ may be due to the partial displacement of coordinated anions by the solvent molecules. Thus, the complexes may be formulated as [Mn(GA)X₂] (X = ClO₄, NO₃, Cl, Br or I).



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

	Empirical	Formula	Mn	Anion	Carbon	Hydrogen	Nitrogen	Yield	M.p.
Complex	Formula	Weight	(%)	(%)	(%)	(%)	(%)	(%)	(°C)
$[Mn(GA)(ClO_4)_2]$	$C_{24}H_{24}N_6O_{10}Cl_2Mn$	682.18	8.03	29.15	42.24	3.50	12.32	91	140
			(8.05)	(29.14)	(42.25)	(3.54)	(12.31)		
$[Mn(GA)(NO_3)_2]$	$\mathrm{C}_{24}\mathrm{H}_{24}\mathrm{N}_8\mathrm{O}_8\mathrm{Mn}$	607.31	9.01	I	47.42	3.95	18.45	90	152
			(9.04)		(47.46)	(3.97)	(18.44)		
$[Mn(GA)Cl_2]$	$\mathrm{C}_{24}\mathrm{H}_{24}\mathrm{N}_{6}\mathrm{O}_{2}\mathrm{Cl}_{2}\mathrm{Mn}$	554.25	9.90	12.80	51.97	4.30	15.15	90	141
			(9.91)	(12.79)	(52.00)	(4.36)	(15.16)		
$[Mn(GA)Br_2]$	$\mathrm{C}_{24}\mathrm{H}_{24}\mathrm{N}_{6}\mathrm{O}_{2}\mathrm{Br}_{2}\mathrm{Mn}$	643.18	8.50	24.85	44.81	3.77	13.01	88	174
			(8.54)	(24.84)	(44.81)	(3.75)	(13.06)		
$[Mn(GA)I_2]$	$\mathrm{C}_{24}\mathrm{H}_{24}\mathrm{N}_{6}\mathrm{O}_{2}\mathrm{I}_{2}\mathrm{Mn}$	737.16	7.45	34.40	39.13	3.26	11.40	90	180
			(7.45)	(34.42)	(39.10)	(3.27)	(11.39)		

Table I. Analytical Data^a of the Manganese(II) Complexes of GA

Table II. Molar Conductance Values of the Manganese(II) Complexes of GA (in $Ohm^{-1} cm^2 mol^{-1}$)

Complex	C ₆ H ₅ NO ₂	CH ₃ CN	DMF
$[Mn(GA)(ClO_4)_2]$	7.30	90.05	31.76
$[Mn(GA)(NO_3)_2]$	4.26	87.63	36.32
[Mn(GA)Cl ₂]	3.35	48.68	38.00
$[Mn(GA)Br_2]$	4.86	48.68	49.01
$[Mn(GA)I_2]$	4.80	81.84	30.31

Infrared Spectra

The IR assignments for the relevant bands of GA and its complexes are presented in Table III. The strong band at 1650 cm^{-1} due to the C=O stretching vibration of GA is shifted to the region $1604-1620 \text{ cm}^{-1}$ in the complexes, indicating the coordination of both carbonyl oxygens⁷. The strong band at 1576 cm^{-1} attributable to the C=N stretching vibration of GA is shifted to the region $1590-1592 \text{ cm}^{-1}$ in the complexes indicating the coordination of both azomethine nitrogens¹⁰.

The perchlorate complex shows doubly split strong band maxima at 1158 and 1080 cm^{-1} and another medium intensity band at 920 cm^{-1} . These are assigned to the v_4 and v_3 vibrations, respectively, suggesting unidentate coordination of both perchlorate ions¹¹.

The nitrate complex shows two strong bands occurring at 1420 and 1315 cm^{-1} which are attributed to the v_4 and v_1 stretching frequencies of the coordinated nitrate ions. Since $v_4 - v_1 = 105 \text{ cm}^{-1}$, both nitrate ions are unidentately coordinated.¹¹

In the far-infrared spectra of halide complexes the Mn-Cl, Mn-Br and Mn-I stretching vibrations⁷ occur at 312, 282 and 150 cm^{-1} , respectively, which are absent in the spectrum of the free ligand. Further, the *v*(Mn-O) and *v*(Mn-N) stretching vibrations are observed at about 540 and 460 cm⁻¹, respectively, in all of the complexes⁷.

The above results along with the conductance data indicate that both anions are coordinated to the metal ion in these complexes.

Electronic Spectra

The electronic spectral bands of GA and its complexes with their tentative assignments are presented in Table IV. In the complexes, both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are found as blue-shifted to the region 27,037–28,481 cm⁻¹ and 41,493–45,871 cm⁻¹, respectively, compared to that of GA.

Complexes
Manganese(II)
Its]
and
GA
of
(cm^{-1})
Absorption
IR
Important

	Table III.	Important I	R Absorption	(cm^{-1}) of C	JA and Its M	langanese(II)) Complexes		
Compound	$\nu(C=O)$	$\nu(C=N)$	$v_4(\text{ClO}_4)$	$v_3(ClO_4)$	$\nu(M-X^b)$	$v_1(NO_3)$	$v_4(NO_3)$	v(M-O)	ν(M-N)
GA	1650 s	1576 s	I			I	I	Ι	I
[Mn(GA)(ClO ₄) ₂]	1616s	1582 s	1158 s 1080 s	920 w	I	I	I	540 w	460 w
$[Mn(GA)(NO_3)_2]$	$1604\mathrm{s}$	1582 s		Ι	Ι	1315s	1420 s	545 w	460 w
$[Mn(GA)Cl_2]$	1616 s	1582 s	Ι	I	312 w	Ι	Ι	543 w	465 w
$[Mn(GA)Br_2]$	$1620\mathrm{s}$	1582 s	Ι	Ι	282 w	Ι	Ι	545 w	460 w
$[Mn(GA)I_2]$	1616 s	1582 s	Ι	Ι	150 w	I	I	540 w	465 w

 $^{\rm a}s\!=\!{\rm strong};\;w\!=\!{\rm weak};\;^{\rm b}X\!=\!{\rm Cl},\;{\rm Br}$ or I.

Table IV. Electronic Spectral Data and Magnetic Moments of Manganese(II) Complexes of GA

Compound	Abs. Max. (cm^{-1})	Tentative Assignments	$\mu_{\text{eff}}(BM)$
GA	38,197 25,497	$\pi \to \pi^*$ $n \to \pi^*$	_
[Mn(GA)(ClO ₄) ₂]	41,841 28,481 22,140	$\pi ightarrow \pi^*$ $n ightarrow \pi^*$ ${}^6\mathrm{A}_{1\mathrm{g}} ightarrow {}^4\mathrm{T}_{2\mathrm{g}}$	5.82
[Mn(GA)(NO ₃) ₂]	45,871 28,115 22,142	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^6A_{1g} \rightarrow {}^4T_{2g}$	5.91
[Mn(GA)Cl ₂]	41,493 28,037 22,511	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^6A_{1g} \rightarrow {}^4T_{2g}$	6.00
[Mn(GA)Br ₂]	45,045 27,442 22,525	$\pi \to \pi^*$ $n \to \pi^*$ $^6A_{1g} \to {}^4T_{2g}$	5.83
[Mn(GA)I ₂]	45,045 27,037 22,405	$\begin{array}{c} \pi \rightarrow \pi^{*} \\ \mathbf{n} \rightarrow \pi^{*} \\ ^{6}\mathbf{A}_{1\mathrm{g}} \rightarrow {}^{4}\mathbf{T}_{2\mathrm{g}} \end{array}$	5.85

All the complexes show low intensity peaks around 22,000 cm⁻¹ corresponding to the ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$, spin forbidden transition, consistent with an octahedral geometry¹².

Magnetic Moment Data

The molar magnetic moments of the complexes are presented in Table IV. The values lie in the 5.82-6.00 BM range, very close to those expected for high-spin octahedral geometry¹³.

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

EXPERIMENTAL

Materials

The metal salts, $Mn(ClO_4)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $MnBr_2 \cdot 4H_2O$ and $MnI_2 \cdot 4H_2O$, were prepared from Analar BDH



 $(X = ClO_4, NO_3, Cl, Br or I)$



manganese carbonate and the respective 50% acids and crystallizing out the salts by evaporating the solution on a steam bath.

Preparation of the Ligand

The ligand 1,2-di(imino-4'-antipyrinyl)ethane (GA) was prepared and characterized as reported earlier⁶.

Preparation of Complexes

One mmol of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.3617 g), $Mn(NO_3)_2 \cdot 6H_2O$ (0.2869 g), $MnCl_2 \cdot 4H_2O$ (0.1978 g), $MnBr_2 \cdot 4H_2O$ (0.2867 g) or $MnI_2 \cdot 4H_2O$ (0.3807 g) in acetone (10 mL) was added to a boiling suspension of 1.2 mmol of GA (0.4294 g) in acetone (100 mL). The mixture was refluxed for about 3 h on a boiling water bath. The precipitated complex was filtered and washed repeatedly with hot ethyl acetate to remove the excess ligand. It was then recrystallised from acetonitrile and dried in vacuum over phosphorus(V) oxide. (*Warning! Perchlorate salts with organic compounds are potentially explosive. They should be handled in small quantities and with caution.*)

Physical Methods of Analysis

All the complexes were analyzed for metal and halide contents by standard methods¹⁴ and the perchlorate content by the Kurz method¹⁵. The electrical conductance of the complexes in nitrobenzene, DMF and acetonitrile $(10^{-3} \text{ M solutions})$ were measured at room temperature using a Toshniwal conductivity bridge with a dip-type conductance cell (cell constant 0.9737). The infrared spectra of the ligands and the complexes were recorded in the range 4000–400 cm⁻¹ on a Shimadzu IR 470 spectrophotometer in KBr disc and in the range $400-200 \text{ cm}^{-1}$ on a Perkin Elmer 983 IR spectrophotometer in polyethylene powder. The electronic spectra of the ligands and the complexes in the solid state (paste with Nujol) were measured in the range 200–1100 nm on a Shimadzu UV 160 A spectrophotometer. The elemental analyses (C, H and N) were carried out on a Heraeus CHNO rapid analyzer. The magnetic moments were measured at room temperature by the Gouy method using mercury(II)tetrathiocyanatocobaltate(II) as the calibrant.

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REFERENCES

- Alaudeen, M.; Abraham, A.; Radhakrishnan, P.K. Synthesis and Antibacterial Activity of Rare Earth Perchlorate Complexes of 4-(2'-Hydroxynaphthylazo)antipyrine. Proc. Indian Acad. Sci. (Chem. Sci.) 1995, 107 (2), 123–126.
- Singh, L.; Mohan, G.; Parashar, R.K.; Tripathi, S.P.; Sharma, R.C. Studies on Anti-inflammatory Activity of Some Lanthanone Complexes of Bioactive Organic Molecules. Curr. Sci. 1986, 55, 846–848.
- Limurg, J.; Vrettos, J.S.; LiableSands, L.M.; Rheingold, A.L.; Crabtree, R.H.; Brudvig, G.W. A Functional Model for O-O Bond Formation by the O-2-evolving Complex in Photosystem II. Science 1999, 283 (5407), 1524–1527.
- Radhakrishnan, P.K.; Indrasenan, P.; Nair, C.G.R. Complexes of Lanthanide Nitrates with 4-N-(2'-Hydroxybenzylidene)-Amionoantipyrine. Polyhedron 1984, 3 (1), 67–70.

MANGANESE(II) COMPLEXES

- Joseph, S.; Radhakrishnan, P.K. Yttrium and Lanthanide Iodide Complexes of N,N'-Bis(4-antipyrylmethylidene)ethylenediamine. Polyhedron 1999, 18, 1884.
- Madhu, N.T.; Radhakrishnan, P.K. Complexes of Nickel(II) with 1,2-Di(imino-4'-antipyrinyl)ethane and 4-N-(4'-Antipyrylmethylidene)aminoantipyrine. Synth. React. Inorg. Met.-Org. Chem. 2000, 30 (8), 1561–1579.
- Madhu, N.T.; Radhakrishnan, P.K. Cobalt(II) Complexes of 1,2-(Diimino-4'-antipyrinyl)ethane and 4-N-(4'-Antipyrylmethylidene)aminoantipyrine. Trans. Met. Chem. 2000, 25, 287–292.
- 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), ■.
- 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. Liu Guofa; Na Chongwu; Li Bin; Mao Kunyuan. Complexes of Lanthanide Nitrates with a Schiff Base Derived from *o*-Vanillin and *p*-Toluidine. Polyhedron **1990**, *9*, 2019–2022.
- Nakamoto, K. Coordination Compounds. In *Infrared and Raman* Spectra of Inorganic and Coordination Compounds, 4th Ed.; John Wiley and Sons, Inc.: New York, 1986; 253, 254.
- 12. Lever, A.B.P. Electronic Spectra of dⁿ Ions. In *Inorganic Electronic Spectroscopy*, 2nd Ed.; Elsevier: Amsterdam, 1984; 449.
- Valavi, S.G.; Yusuff, K.K.M. Synthesis and Characterisation of Some Transition Metal Complexes of 2,3-Bis-hydrazinoquinoxaline. Synth. React. Inorg. Met.-Org. Chem. 1995, 24 (8), 1309–1318.
- 14. 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, 379.
- 15. Kurz, E.; Kober, G.; Berl, M. Determination of Perchlorates by Fusion with Nitrite. Anal. Chem. **1958**, *30* (12), 1983–1986.

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