

Mössbauer & Other Spectral Studies on Iron(III) Complexes with Ligands Containing Amide Group

V RAVINDAR & P LINGAIAH*

Department of Chemistry, Kakatiya University, Warangal 506 009

and

M VITHAL & R JAGANNATHAN

School of Chemistry, University of Hyderabad, Hyderabad 500 134

Received 21 May, 1984; revised and accepted 21 January 1985

Complexes of iron(III) with 2-(acetyl amino)benzoic acid, 2-(benzoyl amino)benzoic acid, maleanilic acid, malea-1-naphthanilic acid, 2-(aminocarbonyl)benzoic acid, 2-[(phenyl amino) carbonyl]benzoic acid, 2-[(1-naphthalenyl amino)carbonyl]benzoic acid, 2-[(2-aminophenyl amino)carbonyl]benzoic acid, 2-aminobenzanilide and 2-(aminobenzoyl)benzoic acid have been prepared. These have been characterized on the basis of chemical analyses, magnetic susceptibility and IR, NMR, electronic and Mössbauer spectral data.

Metal ion interaction with ligands containing amide group plays a vital role in a vast number of widely differing biological processes^{1,2}. In addition, amide group containing compounds such as aminopterin, phenylalanine mustard, D-pencillamine, 6-mercaptopurine and 5-fluorouracil, which are used as therapeutic agents in the treatment of cancer, are found to have increased anticancer activities when administered as metal complexes³. Complexes of many amide containing ligands such as pyrazine-2-amide⁴, N-(picolinamide)salicylaldimine⁵, N-benzyl-N-pyridiniumthiocarbamide^{6,7} and salicylamide^{8,9} have been prepared and characterized. In view of the biological significance and diverse coordinating behaviour of ligands containing amide group, it was considered worthwhile to study the interaction of some of these compounds with iron(III). In the present investigation, complexes of iron(III) with 2-(acetyl amino)benzoic acid (AABAH), 2-(benzoyl amino)benzoic acid (BABAH), maleanilic acid (MAH), malea-1-naphthanilic acid (MNAH), 2-(aminocarbonyl)benzoic acid (ACBAH), 2-[(phenyl amino)carbonyl] benzoic acid (PACBAH), 2-[(1-naphthalenyl amino)carbonyl] benzoic acid (NACBAH), 2-[(2-aminophenyl amino)carbonyl] benzoic acid (APACBAH), 2-aminobenzanilide (ABn), and 2-(aminobenzoyl)benzoic acid (ABBAH) are discussed.

Materials and Methods

All the chemicals used were of AR grade. ABBAH was obtained from Aldrich Chemical Company (USA). All the other ligands were prepared by the literature methods^{10,11}.

To a warm absolute ethanolic solution of the metal salt (1 mmol), dehydrated with a few ml of 2,2-dimethoxypropane, a warm ethanolic solution of the ligand (3 mmol) was added dropwise with stirring. The mixture was refluxed on a water bath for 1 hr; on cooling, a brick red solid separated out which was washed with ethanol, and ether and dried *in vacuo*.

The complexes were analysed for metal content by standard method. The carbon, hydrogen and nitrogen analyses were obtained from the Microanalytical Laboratory, Calcutta University, Calcutta.

The low frequency IR spectra were measured in the range 600-200 cm^{-1} on a Perkin-Elmer 577 spectrophotometer available at I.I.Sc., Bangalore. Mössbauer spectra were recorded using an Elsint spectrometer working in constant acceleration mode in conjunction with a multi-channel analyser (promeda) using 512 channels. Each spectrum was recorded in 256 channels with its mirror image in equal number of channels. The details of the other measurements are the same as given earlier¹⁰.

Results and Discussion

All the complexes are stable at room temperature and are nonhygroscopic. The complexes are slightly soluble in MeOH, EtOH, and freely soluble in DMF and DMSO. Some of the complexes are soluble in water also.

Analytical data (Table 1) indicate that the metal chelates of AABAH, BABAH, MAH, MNAH, ACBAH, PACBAH, NACBAH and ABn have 1:3 (metal:ligand) stoichiometry whereas those of APACBAH and ABBAH have 1:2 stoichiometry. The molar conductance values of AABAH, BABAH,

Table 1—Analytical and Physical Data of Iron(III) Complexes

Complex	Colour	Decom. temp. (°C)	Found (Calc.), %				Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)	μ_{eff} (B.M.)
			M	C	H	N		
[Fe(AABA) ₃]	Brick red	230	9.32 (9.40)	54.45 (54.92)	4.13 (4.02)	7.04 (7.10)	16	5.91
[Fe(BABA) ₃]	Light brown	260	7.36 (7.22)	64.27 (64.90)	3.70 (3.81)	5.51 (5.42)	20	6.02
[Fe(MA) ₃]	Reddish brown	220	9.06 (8.92)	57.71 (57.52)	3.64 (3.83)	6.82 (6.71)	22	5.94
[Fe(MNA) ₃]	Light snuff	210	7.03 (7.19)	65.08 (64.96)	3.65 (3.86)	5.35 (5.41)	20	5.96
[Fe(ACBA) ₃]	Light brown	225	9.97 (10.19)	52.41 (52.56)	3.17 (3.28)	7.58 (7.66)	24	5.90
[Fe(PACBA) ₃]2H ₂ O	Snuff	250	6.64 (6.87)	61.93 (62.08)	4.04 (4.18)	5.02 (5.17)	16	5.73
[Fe(NACBA) ₃]	Brown	260	6.21 (6.03)	69.25 (69.98)	3.72 (3.88)	4.62 (4.53)	18	5.61
[Fe(APACBA) ₂]NO ₃	Dark red	290	9.02 (8.89)	53.37 (53.51)	3.39 (3.50)	11.27 (11.15)	65	6.01
[Fe(ABn) ₃](NO ₃) ₃	Dirty yellow	255	6.20 (6.36)	53.45 (53.31)	4.02 (4.10)	14.18 (14.35)	185	5.97
[Fe(ABBA) ₂]NO ₃	Yellow	280	9.45 (9.34)	56.11 (56.20)	3.18 (3.34)	7.21 (7.02)	70	6.05

MAH, MNAH, ACBAH, PACBAH and NACBAH complexes in DMF at 10⁻³M concentration are low (Table 1) suggesting that they are non-electrolytes. The complexes of APACBAH and ABBAH, however, exhibit molar conductance values in the range 60-70 ohm⁻¹cm²mol⁻¹ indicating that they are 1:1 electrolytes. The complex of ABn ($\Lambda_M = 185$ ohm⁻¹cm²mol⁻¹) is a 1:3 electrolyte.

The thermogram of Fe(III)-PACBA complex exhibits two clear-cut stages: one corresponding to dehydration and the other to decomposition with the loss of organic moiety. The dehydration curve corresponds to the loss of two water molecules in the temperature range 80-120°C (calc. = 4.43%; found. = 4.32%). Also, the DTA of this complex shows an endothermic peak in the above range further giving evidence for the presence of water molecules. The loss of water molecules in this low temperature range indicates that they are lattice-held¹². On the other hand, the thermogram of Fe(III) NACBA complex shows only a single decomposition curve commencing at 260°C which corresponds to the loss of organic moiety. The final products of decomposition in both the complexes above 520°C correspond to the metallic oxide (PACBA complex: calc. = 80-32%; found. = 79.86%; NACBA complex: calc. = 82.75%; found. = 81.95%).

Infrared spectra

The ligands containing carboxylic acid group show strong IR bands around 1700 and 1330 cm⁻¹ due to C

= O and C - OH stretching modes¹³ of the carboxylic group, respectively. These bands disappear in the complexes and are replaced by two bands at ~1550 and ~1380 cm⁻¹ assigned to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$, respectively¹⁴.

The $\nu(\text{N} - \text{H})$ frequency in AABAH and BABAH shifts to lower frequency side by 100-120 cm⁻¹ in complexes indicating that the nitrogen of the amide group is coordinated¹⁵. A band at 1650 cm⁻¹ in these ligands, assignable to $\nu(\text{C} = \text{O})$ of the amide group, shows practically no shift in the complexes, thus ruling out coordination through amide oxygen. In the MAH, MNAH, ACBAH, PACBAH, NACBAH and APACBAH complexes, $\nu(\text{N} - \text{H})$ shifts towards higher frequency compared with the position in ligand spectra, indicating non-participation of nitrogen atom in coordination¹⁶. This may be due to the formation of metal to oxygen bond which increases the electron demand by the donor oxygen atom and blocks the resonance between this oxygen and the nitrogen resulting in an increase in the N - H stretching frequency. In agreement with the above view, $\nu(\text{C} = \text{O})$ (or the amide-I frequency) in the above set of ligands undergoes a negative shift (40 cm⁻¹) in the complexes, indicating coordination of this group through oxygen¹⁶. The coordination through oxygen is also inferred by the positive shift (20 cm⁻¹) of C - N stretching frequency¹⁷ in the complexes.

The amine (N - H) frequency in APACBAH, ABBA and ABn complexes undergoes a lower shift showing that nitrogen of this group is coordinating.

The Fe(III)-PACBA complex shows a broad band in the region $3500\text{--}3200\text{ cm}^{-1}$ which indicates the presence of water molecules. However, it does not show a band in the region $900\text{--}830\text{ cm}^{-1}$ which suggests that water molecules are uncoordinated¹⁸.

Further, the far infrared spectra of the respective complexes show non-ligand bands corresponding to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations¹⁹.

NMR spectra

The NMR spectrum of ligand BABAH shows (values in δ scale) a resonance signal due to NH proton at 6.70 ppm which is not observed in its complex in the range studied (0-15 ppm), implying a large down field shift of this proton, and suggesting that the amide group nitrogen participates in coordination. In addition, a signal at 12.18 ppm in the ligand spectrum, assignable to carboxylic proton, disappears in the spectrum of the complex indicating deprotonation of carboxylic group and the involvement of oxygen of carboxylate ion in chelation.

A similar comparison of the NMR spectrum of ligand MAH with that of its Fe(III) complex shows that the proton of amido group undergoes only a small down field shift (from 3.30 to 3.42 ppm) indicating the

non-involvement of NH group in coordination. The signal at 10.35 ppm in the ligand, assignable to carboxylic proton, disappears in the complex confirming the participation of this group in bonding.

Electronic spectra and magnetic moments

The high-spin iron(III) complexes contain five unpaired electrons; all $d-d$ transitions are spin forbidden and hence should be weak. A pattern of four bands is usually expected for octahedral geometry corresponding to the transitions²⁰:

$${}^4T_{1g} \leftarrow {}^6A_{1g}, {}^4T_{2g} \leftarrow {}^6A_{1g}$$

$${}^4E_g \leftarrow {}^6A_{1g} \text{ and } {}^4T_{1g}(\text{D}) \leftarrow {}^6A_{1g}$$

But all the four transitions are not observed in most of the complexes. The Fe(III) complexes reported here reveal two or three bands assignable to one or the other transitions given above. Though $d-d$ transitions are forbidden in high-spin Fe(III) complexes, the high intensity of the band at $\sim 23000\text{ cm}^{-1}$ may be ascribed to borrowing of intensity from a low lying charge transfer band of the ligand²⁰. Thus, the band at 23000 cm^{-1} is due to the transition ${}^4T_{2g} \leftarrow {}^6A_{1g}$ in an octahedral field and is intensified due to the presence of a nearby charge-transfer band of the ligand. The

Table 2—Mössbauer and Electronic Spectral Data of Iron(III) Complexes

Complex	Mössbauer parameters*		Electronic spectral bands (cm^{-1})	Tentative assignment
	δ (mm/sec)	ΔE_q		
[Fe(AABA) ₃]	0.43	0.71	16782 23040 27605	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$ ${}^4E_g \leftarrow {}^6A_{1g}$
[Fe(BABA) ₃]	0.42	0.78	15625 22976 28105	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$ ${}^4E_g \leftarrow {}^6A_{1g}$
[Fe(MA) ₃]	0.41	0.81	15873 21276	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$
[Fe(MNA) ₃]	0.39	0.75	16050 21505	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$
[Fe(ACBA) ₃]	0.41	0.72	17857 22624	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{1g} \leftarrow {}^6A_{1g}$
[Fe(PACBA) ₃] $\cdot 2\text{H}_2\text{O}$	0.35	0.77	15625 23041 27027	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$ ${}^4E_g \leftarrow {}^6A_{1g}$
[Fe(NACBA) ₃]	0.32	0.78	18867 22371 26178	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$ ${}^4E_g \leftarrow {}^6A_{1g}$
[Fe(APACBA) ₂] NO_3	0.42	0.68	15384 22675 27027	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$ ${}^4E_g \leftarrow {}^6A_{1g}$
[Fe(ABn) ₃] $(\text{NO}_3)_3$	0.36	0.69	16660 22522	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$
[Fe(ABBA) ₂] NO_3	0.38	0.70	16949 21739	${}^4T_{1g} \leftarrow {}^6A_{1g}$ ${}^4T_{2g} \leftarrow {}^6A_{1g}$

* δ is isomer shift relative to iron foil and E_q is quadrupole splitting.

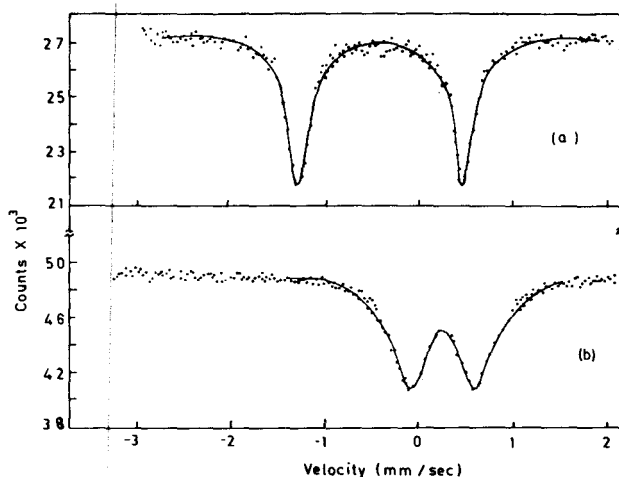


Fig. 1—Mössbauer spectra of (a) sodium nitroprusside and (b) Fe(III)-ABn complex.

magnetic moment data of the complexes are given in Table 1. The moments obtained for the present iron (III) complexes of all the ligands indicate that they are of spin-free octahedral type. However, somewhat low moments associated with Fe(III)-PACBA and Fe(III)-NACBA complexes might be attributed to distortion from octahedral structure with considerable π -bonding²².

Mössbauer spectra

Mössbauer spectrum of a representative complex, Fe(III)-ABn complex, is shown in Fig. 1. Isomer shift and quadrupole splitting values are collected in Table 2. All the quadrupole-split spectra exhibited full-width at half maximum (fwhm) for the individual components between 0.24 and 0.4 mm/sec.

The isomer shifts for the iron(III) complexes of all the ligands reveal that they are of high-spin type, for which the values lie in the range 0.3 to 0.5 mm/sec confirming the octahedral geometry around iron(III)^{23,24}. The quadrupole splitting data also seem to underline this point. The isomer shift range is very small for all the complexes, inspite of the different sizes of the various ligands. This is due to the presence of a similar configuration around the metal ion and similar geometry of all the complexes.

The line width represents the nature of iron site in the crystal lattice. If it is more than natural line width, there may be more than one iron sites present in the crystal. The line width (0.2 to 0.4 mm/sec) of iron(III) complexes with all the ligands indicate the presence of a single iron site in the crystal.

Acknowledgements

One of the authors (VR) is grateful to the CSIR, New Delhi, for the award of a Senior Research Fellowship.

References

- 1 Raymond K N & Carrano C J, *Acc chem Res*, **12** (1979) 183.
- 2 Molendin C & Martell A E, *Coord Chem Rev.*, **19** (1976) 1.
- 3 Williams D R, *Chem Rev.*, **72** (1972) 203.
- 4 Sanyal G S, Modak A B & Mudi A K, *Indian J Chem*, **20A** (1980) 510.
- 5 Agarwal R C, Singh N K & Singh R P, *Inorg Chem*, **20** (1981) 2794.
- 6 Sen D, Banerjee B D, Kumar P A & Sen S S, *Indian J Chem*, **21A** (1982) 1096.
- 7 Deshpande S V & Srivastava T S, *Polyhedron*, **2** (1983) 761.
- 8 Wiersema A K & Windle J J, *J phys Chem*, **68** (1964) 2316.
- 9 Pannu B S S, Chopra S L & Parmer S S, *Indian J Chem*, **9** (1971) 1396.
- 10 Ravindar V, Swamy S J, SriHari S & Lingaiah P, *Transition Met Chem*, **9** (1984) 103.
- 11 Clark R H & Wagner E C, *J org Chem*, **9** (1944) 55.
- 12 Nikolaev A V, Logvinenko V A & Myachina L I, *Thermal analysis*, Vol 2 (Academic press, New York), 1969, 779.
- 13 Hadzi D & Pintar M, *Spectrochim Acta*, **8** (1959) 249.
- 14 Agarwal R C & Chandrashekhar V, *J inorg nucl Chem*, **41** (1979) 1057.
- 15 Sandhu S S, Manhas B S, Mittal M R & Parmer S S, *Indian J Chem*, **7** (1969) 286.
- 16 Pannu B S & Chopra S L, *J Indian chem Soc*, **51** (1974) 387.
- 17 Saha N, Krishna M D & Ashok K A, *Indian J Chem*, **20A** (1980) 744.
- 18 Lucchesi P J & Glasson W A, *J Am chem Soc*, **78** (1956) 1347.
- 19 Nakamoto K, *Infrared spectra of inorganic and coordination compounds* (John Wiley, New York), 1970.
- 20 Bertrand J A & Eller P G, *Inorg Chem*, **13** (1974) 927.
- 21 Figgis B N, *Introduction to ligand fields* (Interscience, New York), 1966.
- 22 Burman S & Satyanarayana D N, *J coord Chem*, **11** (1982) 219.
- 23 Greenwood N N & Gibb T C, *Mössbauer spectroscopy* (Chapman and Hall, London), 1971.
- 24 Dockum B W & Reiff W M, *Inorg chim Acta*, **35** (1979) 285.
- 25 Galeazzi G U R, Valle G & Calogero S, *Transition Met Chem*, **6** (1981) 325.