Spectroscopic and X-Ray Diffraction Studies of Chelates of 2-Hydroxy-4-Aminobenzoic Acid with Group IB and IIB Metals

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Summary: The present study is based on the formation of chelates of 2-hydroxy-4-aminobenzoic acid (sod. salt) with group IB and IIB metals. The synthesised compounds were characterised using techniques such as atomic absorption, infrared spectroscopy, elemental analysis and X-ray diffraction.

Introduction

The number of elements that are known to be biologically important, occur in body tissues and body fluids in small amounts. Essential physiological, biological, non-biological functions have been established for copper, cobalt, zinc, iodine, manganese, molybdenum etc. Their functions are catalytic in nature. They activate certain enzymes and are essential components of vitamins and harmones. Recently the combining capacity of transition metals like, copper, silver, zinc, cadmium, mercury and nickel has indicated considerable importance with various ligands. A brief account of medicinal importance of copper, zinc, cadmium, mercury, nickel, etc. has already been reported [1]. Different transition metal chelates play an important role in biological and non-biological systems in various ways. In this connection it has been observed that complexes with appropriate ligands are chemically more significant and specific than the metal cations on their own as evident from the activity of metal-containing enzymes. Moreover, by modifying electronic or steric factors in a chelating molecules, a change in biological activity suggests that metal chelation *in vivo* cannot be ignored. Thus, biological activity of some drugs like salicylates has been attributed to metal chelation, whereas six isomers of oxine which are incapable of chelation lack antibacterial activity as pointed out by Albert [2]. Weinberg has discussed the effects of metal ion in the bacterial growth inhibition caused by tetracycline antibiotic on the basis of metal chelation [3]. Efficacy of metal chelation has also been demonstrated in the protection of breastfed infants against certain infectious diseases, since lactoferrin found in mother milk appears to be the most potent antibacterial transferrin [4].

In view of the pronounced effects of chelation *in vivo* and their importance in analysis of various species in variety of substances, a systematic work on the chelation of various salicylates and their related molecules with group IB and IIB metals and uranyl nitrate has been undertaken. This paper describes the synthesis of chelates of these metals with 2-hydroxy-4-aminobenzic acid (sod. salt) and their characterisation by techniques like combustion analysis, atomic absorption, infrared spectroscopy and x-ray diffraction.

Results and Discussion

The present investigations were under taken firstly to synthesise metal derivatives of 2-hydroxy-4-aminobenzoic acid (sod. salt). In this connection the said ligand was treated with group IB and IIB metals e.g. Cu^{++}, Ag^{+}, Zn^{++}, Cd^{++}, Hg^{++}, Ni^{++} and UO_2^{++}. The structures of the salicylates thus synthesised were determined on the basis of their elemental analysis and further analysed by infrared spectra. The infrared spectra of synthetic compounds recorded in KBr (disc) and nujol, exhibited shift in position and intensity of various peaks due to chelation with different cations. Moreover, certain new bands also appeared in their spectra, while some absorptions disappeared. The presence of water was confirmed from a broad absorption in the range of 3600-3200 cm^{-1}. and a weak band between 1640-1610 cm^{-1} and around 910 ± 10 cm^{-1}. The metal-ligand vibrations (M-O

stretching bands) usually appeared below 650 cm^{-1} [5].

The XRD pattern showing the chelation of 2-hydroxy-4-amino-benzoic acid with copper (II) chloride is shown in Fig. I, which does not show the peaks belonging to the starting materials and thus indicates the formation of a new compound. The diffractograph showed small number of reflection peaks, which clearly indicate that this compound is of high symmetry. The XRD pattern for the chelate of 2-hydroxy-4-amino benzoic acid with cadmium (II) chloride is also shown in Fig. 1. The formation of the new compound was inferred from its XRD pattern which lacked peaks of the original materials. Moreover, the diffractograph showed that the unit cell of this compound is again of high symmetry, because small number of reflection peaks are present even in this system.

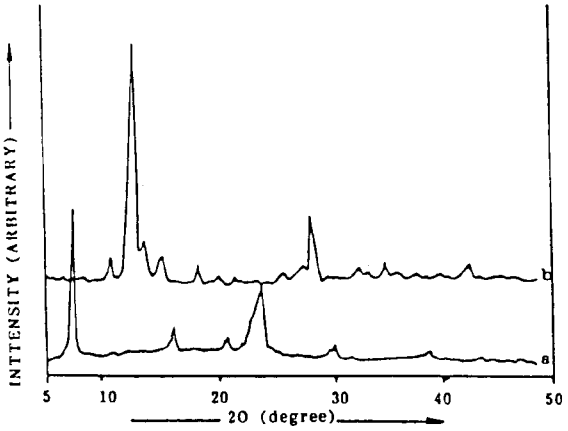

Fig.1: XRD Patterns of chelates of 2-hydroxy-4-aminobenzoic acid with (a) copper (II) chloride and (b) cadmium (II) chloride.

The XRD patterns of chelates of this hydroxy acid with nickel(II) chloride, silver (I) nitrate and uranyl (II) nitrate have been depicted in Fig. 2, while those of mercury (II) acetate and zinc (II) chloride in Fig. 3 respectively. When compared with the original compounds, their reflection patterns also indicated the formation of chelates in all the cases. The unit cells for these new compounds are of low symmetry, because a large number of well defined peaks are present in their diffractographs.

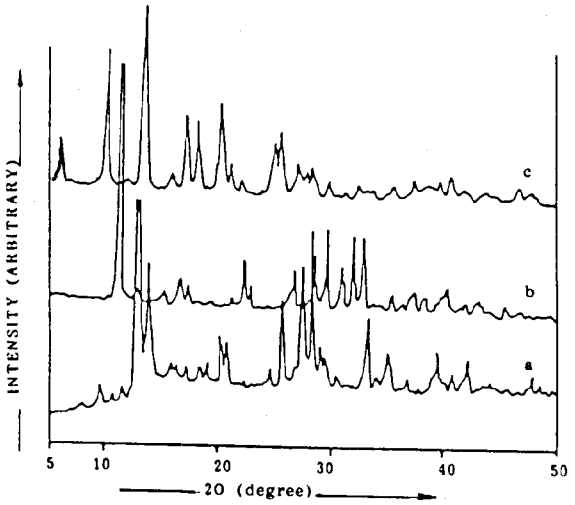

Fig.2: XRD patterns of chelates of 2-hydroxy-4-aminobenzoic acid with (a) nickel (II) acetate (b), silver (I) nitrate and (c) uranyl (II) nitrate.

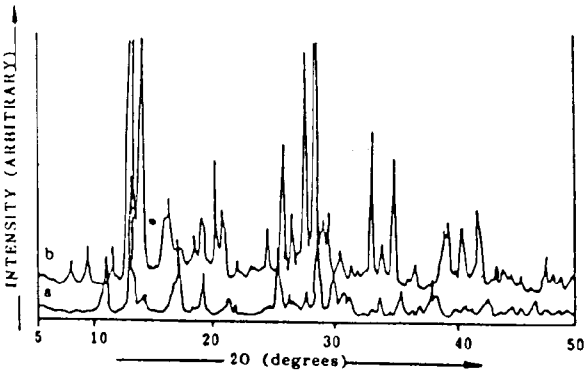

Fig. 3: XRD patterns of chelates of 2-hydroxy-4-aminobenzoic acid with (a) mercury (II) acetate and (b) zinc (II) chloride.

Experimental

The analytical grade chemicals used were 2-hydroxy-4-aminobenzoic acid (sod. salt), copper (II) chloride, zinc (II) chloride silver (I) nitrate, cadmium(II) chloride, nickel (II) acetate, mercury (II) acetate, uranyl nitrate, potassium bicarbonate etc. The solvents used consisted of acetone, methanol, chloroform, carbon tetrachloride, dimethylsulphoxide, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, tetrahydrofuran, dioxan, petroleum

ether (40-60°), etc. which were distilled before used wherever deemed essential.

The following instruments were used for the characterisation of the synthesised compounds:

I) Atomic absorption spectrophotometer (Hitachi 270-30).
ii) Atomic absorption spectrophotometer (Hitachi Polarised Zeeman).
iii) X-Ray diffractometer (Figaku D-Max/11A).

X-Ray diffraction

The X-ray diffraction data (2θ values and integrated intensities of reflection in the X-ray diffraction patterns) of the samples, starting materials and prepared salicylates in the present study were obtained by conducting the diffraction experiment under following conditions:

Target	CuK (Ni filtered)
Tube voltage and current	40 KV and 25 m A
Goniometer scanning speed	I°/min
Ratemeter time constant	I second
Divergence and anti scatter	I°
Receiving slit	0.15 mm
Detector	Scintillation counter
Angle range	5°-50° (2θ)

Reaction of 2-hydroxy-4-aminobenzoic acid (sod. salt) with copper (II) chloride

2-Hydroxy-4-aminobenzoic acid (sod. salt) (2.11 g; 0.01 mole) was slowly mixed with copper (II) chloride (1.70 g; 0.01 mole) solution in water (25 mL) with constant stirring. The dark green crystals thus obtained were filtered off, washed several times with hot water and finally with hot alcohol. The product was dried in air and kept under vacuum for 48 hours to obtain a green complex (I) (2.88 g; 85%) (m.p. 240°C), soluble in dimethysulphoxide and dimethylformamide.

Reaction of 2-hydroxy-4-aminobenzoic acid (sod. salt) with silver (I) nitrate

2-hydroxy-4-aminobenzoic acid (sod. salt) (2.11 g; 0.01 mole) dissolved in water (25 mL) was slowly added to silver (I) nitrate (1.70 g; 0.01 mole) solution in water (25 mL) with constant stirring. The white crystals thus obtained were filtered off and washed several times with hot water. The product was dried in air and kept under vacuum for 48 hours to obtain white complex (II) (2.25 g; 77 %) (m.p. 170°C), soluble in ethanol, methanol, dimethylsuphoxide and dimethylformamide.

Reaction of 2-hydroxy-4-aminobenzoic acid (sod. salt) with zinc (II) chloride

2-hydroxy-4-aminobenzoic acid (sod. salt) (2.11 g; 0.01, mole) dissolved in water (25 mL) was slowly added to zinc (II) chloride (1.36 g; 0.01 mole) solution in water (25 mL) with constant stirring. The white crystals thus obtained were filtered off and washed many times with hot water. The product was dried in air and kept in vacuum for 48 hours to obtain white complex (III) (3.33 g; 89%) (m.p. 250°C), soluble in methanol and dimethylsulphoxide.

Reaction of 2-hydroxy-4-aminobenzoic acid (sod. salt) with cadmium (II) chloride

2-hydroxy-4-aminobenzoic acid (sod. salt) (2.11 g; 0.01 mole) dissolved in water (25 mL) was added to cadmium (II) chloride (2.28 g; 0.01 mole) solution in water (25 mL). The white crystals thus obtained were filtered off, washed with hot water and finally with hot alcohol. The product was dried in air and kept under vacuum for 48 hours to obtain white complex (IV) (1.98 g; 40 %) (m.p. 260°C).

Reaction of 2-hydroxy-4-aminobenzoic acid (sod. salt) with mercury (II) acetate

2-hydroxy-4-aminobenzoic acid (sod. salt) (2.11 g; 0.01 mole) dissolved in water (25 mL) was added to mercury (II) acetate (3.10 g; 0.01 mole) solution in water (25 mL), slowly but with constant stirring. The white crystals thus obtained were filtered off, washed many times with hot water. The product was dried in air and kept under vacuum for 48 hours to obtain complex (V) (92.185 g; 39 %) (m.p. 185°C), soluble in dimethylsulphoxide and dimethylformamide.

Reaction of 2-hydroxy-4-aminobenzoic acid (sod. salt) with nickel (II) acetate

2-hydroxy-4-aminobenzoic acid (sod. salt) (2.11 g; 0.01 mole) dissolved in water (25 mL) was

slowly added to nickel (II) acetate (2.48 g; 0.01 mole) solution in water (25 mL) with constant stirring. The reaction mixture was refluxed for one hour. The light green crystals thus obtained were filtered off, washed several times with hot water. The product was dried in air and kept under vacuum for 48 hours to obtain complex (VI) (1.29 g; 32 %) (m.p. 190°C), soluble in dimethyl-sulphoxide and dimethylformamide.

Reaction of 2-hydroxy-4-aminobenzoic acid (sod. salt) with uranyl nitrate

2-hydroxy-4-aminobenzoic acid (sod. salt) (2.11 g; 0.01 moles) dissolved in water (25 mL) was slowly added to uranyl nitrate (5.02 g; 0.01 mole) solution in water (25 mL) with constant stirring. The yellow brown crystals thus obtained were filtered off and washed many times with hot water. The product was dried in air and kept under vacuum to obtain yellow complex (VII) (2.34 g; 43%) (m.p. 170°C), which was soluble in acetone, dimethylsulphoxide and dimethylformamide.

Table-1: Analytical data of complexes

S.No.	Molecular formula		Analysis % Calcd	Found
1.	$(C_7H_6N_3)_2Cu(H_2O)$	C	39.60	39.59
		H	04.72	04.69
		N	06.60	06.54
		Cu	14.99	13.00
II.	$(C_7H_6O_3N)\ Ag(H_2O)$	C	28.60	28.58
		H	03.07	03.11
		N	09.55	09.59
		Ag	36.80	36.75
III.	$(C_7H_6O_3N)_2Zn(H_2O)_4$	C	44.90	44.98
		H	04.28	04.30
		N	07.50	07.45
		Zn	17.78	17.80
IV.	$(C_7H_6O_3)_2Cd\ (H_2O)_4$	C	34.20	34.28
		H	04.48	04.50
		N	05.71	05.69
		Cd	22.80	22.91
V.	$(C_7H_6O_3N)_2\ Ni(H_2O)_2$	C	42.20	42.28
		H	04.02	04.10
		N	07.03	07.08
		Ni	14.70	14.81
VI.	$(C_7H_6O_3N)_2\ Hg(H_2O)_3$	C	30.10	30.15
		H	03.22	03.29
		N	05.01	04.98
		Hg	35.85	35.87
VII	$(C_7H_6O_3N)_2\ UO_2(H_2O)_2$	C	30.88	30.80
		H	02.53	02.57
		N	05.10	04.96
		U	43.65	43.75

Table-2: Infrared spectra

S.No.	Compounds	Band (cm^{-1}) and intensity				
	2-Hydroxy-4-aminobenzoic acid (sod. salt)	3450s, 1650m, 1318m, 1050m, 640m,	2960s, 1600s, 1240w, 980s,	2829s, 1610s, 1200m, 900s,	2880w, 1470m, 1180m, 820s,	1760w, 1390m, 1110w, 720m,
I	$(C_7H_6O_3N)_2\ Cu(H_2O)$	3380, 1620m, 1340sh, 1100m, 699m,	3200s, 1590s, 1290m, 970m, 620s,	3160, 1460s, 1160m, 840m,785m	2940s, 1400m, 1122m, 720s,	2860s,
II	$(C_7H_6O_3N)\ Ag(H_2O)$	3600s, 1560s, 1200w, 710 w,	2900s, 1518s, 980w, 640sh,	2880s, 1470m, 850b, ,	1630s, 1390s, 790w,	1600s, 1310m, 730w,
III	$(C_7H_6O_3N)_2\ Zn(H_2O)_4$	3540bw, 1550w, 1360m, 800w,	3208s, 1570m, 1310m, 740w,	2960s, 1530s, 1070b, 710w	2900s, 1480s, 980m, 640sh,	1620s, 1400m, 860w
IV	$(C_7H_6O_3N)_2\ Cd(H_2O)_4$	3350, 1530s, 1070b, 710w,	2960s, 1480s, 980m, 640sh,	1620s, 1400m, 860m,	1650s, 1360m, 800w,	1570m, 1310m, 740w,
V	$(C_7H_6O_3N)_2\ Ni(H_2O)_2$	3400, 1650w, 1365sh, 730s,	3200w, 1630w, 1070bs, 640sh,	2960s, 1480s, 785s,	2900sh, 1400s, 860s,	2390w, 700s,
VI	$(C_7H_6O_3N)_2\ Hg(H_2O)_3$	3350s, 1390m, 790w,	2950s, 1170s, 730m,	2870s, 1040s, 650w,	1610s, 970s, 610m,	1470s, 840s
VII	$(C_7H_6O_3N)_2\ UO_2(H_2O)_2$	3450s, 1600w, 1030w, 620m,	2960s, 1510w, 1170m	2850s, 1470w, 900m,	1650s, 1380s, 850m	1630m, 1300w, 640m,

The analytical data and infrared spectral absorptions of all the compounds mentioned above are given in Table-1 and 2 respectively.

References

1. Bushra Khan, C.M. Ashraf and M.Z. Iqbal, *Hamdard Medicus*, **37**(2), 89 (1994)
2. A. Albert and S.D. Rubbo, *Brit. J. Exptl. Pathol.* **28**, 69 (1947).
3. E.D. Weinberg, *Bacterial Rev.*, **21**, 45 (1957).
4. A. Bezkoroviny, Biochemistry of Non-heme Iron, Plenum Press, New York, p. 336 (1980).
5. M. Mikami, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).