MÖSSBAUER STUDIES ON THE COMPLEXES OF TIN(IV) WITH SOME MONOHYDROXAMIC ACIDS

HYDROXAMIC acids are known to be excellent analytical reagents[1] and have important biological activities[2]. We have been interested both in the analytical chemistry[3,4] and complex chemistry[5,6] of the hydroxamic acids. N-Phenylbenzohydroxamic acid was reported to react with tin(II) and tin(IV) in dilute hydrochloric acid solution to give a common product of the composition $Sn(C_{13}H_{11}O_2N)_2Cl_2$ or $Sn(C_{13}H_{10}O_2N)_2Cl_2$ having tin in tin(II) or tin(IV) oxidation states[7]. However, later work[8,9] suggested that tin was in tin(IV) state in this complex. Consequently, in order to resolve this apparent anomaly, we showed[5] that the complexes obtained in dilute hydrochloric acid medium were in fact R_2SnCl_2 (where RH=hydroxamic acid) having tin in tin(IV) oxidation state based on molar ratio determination for complete precipitation and by thermogravimetric analysis of the complexes obtained by utilizing N-phenylbenzohydroxamic acid (PBHAH) and its three analogues, namely, N–2–methylphenylbenzohydroxamic acid (2-MePBHAH), N-3-methylphenylbenzohydroxamic acid (3-MePBHAH) and N-4-methylphenylbenzohydroxamic acid (4-MePBHAH). We have now utilized Mössbauer spectroscopic technique to determine unambiguously the valence state of tin in the complexes thus obtained, as this technique has been extensively used for the same purpose[10]. The isomer shift (δ) of tin(II) compounds with respect to $^{119m}BaSnO_3$ as source is greater than that of white tin or β-tin ($2{\cdot}56 \pm 0{\cdot}02$ mm/sec) whereas the δ value of tin(IV) is less than this value[10].

The compounds were prepared by adding 2·5–3 mole proportion of the required hydroxamic acid to an acidic solution (4 — 6N HCl) of $SnCl_2$ or $SnCl_4$[5,6], and were recrystallized from aqueous-acetone. Mössbauer spectra were recorded in a cam-drive, constant acceleration spectrometer[11] using $^{119m}BaSnO_3$ source as the zero of the isomer shift.

All the compounds have δ values distinctly below that of β-tin (Table I) whether they have been obtained from tin(II) or tin(IV) chloride, suggesting that tin is in tin(IV) oxidation state in all the compounds. The isomer shift of the complexes lies between 0·27 and 0·44 mm/sec, which is characteristic of tin(IV) compounds with coordination number six[12]; the results are also in close agreement with many six-coordinate complexes[12]. The compounds studied here did not have any resolvable quadrupole splitting (Q.S). It is, however, known that the Q.S. value of many six-coordinate tin complexes is zero[12] especially when tin is bonded to atoms having non-bonding p_π-electrons even when they all are not the same[10,12]. According to point charge calculations[13,14], in octahedral complexes of the type A_2SnB_4, the *trans*-isomer should have a splitting that is double that of the *cis*-isomer, and this is borne out by the fact that many *cis*-compounds have zero Q.S.[15]. The tin(IV) hydroxamato complexes studied here are of the type A_2SnB_4 (A = Cl, B = O of the ligands) where the hydroxamato ions behave as bidentate ligands. In the absence of any resolvable Q.S. in these complexes, they may be regarded as *cis*-octahedral (C_{2v}) according to the point charge arguments[13,14]. This is also substantiated by the appearance of two bands due to ν(Sn–Cl) mode for each complex (Table I) in the region 325–347 cm^{-1} in the infrared spectra of the complexes, and X-ray crystal structure of dichlorobis (N-phenylbenzohydroxamato) tin(IV)[16].

TABLE I

^{119m}Sn Mossbauer and IR data

Compound[a]	Isomer shift, δ ($\pm 0{\cdot}06$) (mm/sec)	Line width, Γ ($\pm 0{\cdot}06$) (mm/sec)	ν(Sn–Cl) cm^{-1}
$(PBHA)_2SnCl_2$	0·41	1·62	332s, 325s
$(PBHA)_2SnCl_2$*	0·43	1·57	
$(2\text{-MePBHA})_2SnCl_2$	0·40	1·38	344s, 332s
$(2\text{-MePBHA})_2SnCl_2$*	0·43	1·29	
$(3\text{-MePBHA})_2SnCl_2$	0·27	1·42	347s, 330s
$(3\text{-MePBHA})_2SnCl_2$*	0·32	1·38	
$(4\text{-MePBHA})_2SnCl_2$	0·44	1·65	332s, 325sh
$(4\text{-MePBHA})_2SnCl_2$*	0·41	1·26	

[a] Complexes marked with asterisk were obtained from $SnCl_2$ and without asterisk from $SnCl_4$.

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GADOLINIUM(III) MYOGLOBIN: INTERACTION OF Gd(III) MESOPORPHYRIN IX WITH APOMYOGLOBIN

CERTAIN lanthanide cations are excellent spectroscopic probes of their immediate environment in enzymes and proteins[1]. Recently, the formation of ytterbium(III) myoglobin was detected by the interaction of ytterbium(III) mesoporphyrin IX with apomyoglobin using spectroscopic techniques[2,3]. In this paper, we describe the first report on the detection, synthesis and spectral properties of gadolinium(III) myoglobin. Its comparative studies with europium(III) myoglobin have also been briefly described.

The hydroxy derivative of gadolinium(III) mesoporphyrin IX [Gd(III)–MP–IX)] was prepared by heating anhydous gadolinum trichloride (250 mg) and mesoporphyrin IX dimethyl ester (50 mg) in 2 g of imidazole melt at 210°–215° C for 2½ hours[4]. The imidazole was sublimed under reduced pressure to get a residue of gadolinium trichloride and dimethyl ester of Gd(III)–MP–IX. The Gd(III)–MP–IX was prepared from its dimethyl ester by hydrolyzing the ester with 30% potassium hydroxide in methanol. The Gd(III)–MP–IX was furtl er purified on silica gel (grade V) column equilibrated with methanol. The Gd(III)–MP–IX was eluted from the column using methanol as eluting solvent. The concentrated methanol solution of Gd(III)–MP–IX was stored at 5° C.

The preparation of gadolinium(III) myoglobin [Gd(III)–Mb] is as follows: The Gd(III)–MP–IX (1·5 moles) in a small quantity of pyridine was mixed with apomyoglobin[5] (1 mole) in 0·1 M Tris-HCl buffer of pH 8. The mixture was immediately passed through a long column of Sephadex G–25 equilibrated with 10 mM potassium phosphate buffer of pH 7·2. The column was eluted with the same buffer. The middle fraction was collected and further concentrated in collodian bag (Schleicher and Schuell, UH 100/10). The Gd(III)–Mb was stored at 5° C.

The hydroxy derivative of europium(III) mesoporphyrin IX [Eu(III)–MP–IX] and europium(III) myoglobin [Eu(III)–Mb] were prepared in a manner similar to the preparations of Gd(III)–MP–IX and Gd(III)–Mb respectively. The 1:1 complex formation between gadolinium(III) mesoporphyrin IX and apomyoglobin was established by difference spectroscopy in the visible region. The difference spectrum of Gd(III)–MP–IX and apomyoglobin in molar ratio of 1:1 against the same concentration of Gd(III)–MP–IX shows a negative peak at 398·5 nm and a positive peak at 406·5 nm. This 1:1 complex formation between Gd(III)–MP–IX and apomyoglobin was further established by passing a mixture of Gd(III)–MP–IX–pyridine complex and apomyoglobin in molar ratio of 1·2:1 through a long Sephadex G–25 column. The various Gd(III)–MP–IX–protien complex fractions obtained from the column show only a characteristic Soret, α and β bands and thus point to the existence of only 1:1 complex of Gd-(III)–MP–IX and apomyoglobin.

The absorption spectra of Gd(III)–Mb and Eu(III)–Mb are given in Table I. The spectra of Gd(III)–MP–IX and Eu(III)–MP–IX in various solvents are also given in the table for comparison. The Soret, α, and β bands of metal porphyrins in various solvents are red shifted in the order: pyridine > methanol > Tris-HCl buffer. The Soret bands of the metal(III)–Mb are about 4 nm red shifted as compared to the corresponding values of metal porphyrins in Tris-HCl buffer of pH 8. These results show that the Gd(III)–Mb and Eu(III)–Mb have very similar environment at the metal site.

In order to establish the site of binding of Gd(III)–MP–IX in Gd(III) Mb, the Gd(III)–MP–IX was displaced from Gd(III)-Mb by Fe(III)-protoporhyrin IX–chloride (hemin) using difference spectroscopy. The spectrum shows two positive peaks at 399·5 and 413·5 nm and a trough at 406 nm. This result shows that the Fe(III) Mb is formed by displacing Gd(III)-MP IX from Gd(III)-Mb by hemin in the sample