

## Preparation and Characterization of 2-Mercaptobenzoic Acid Complexes of Mercury – Lead and Mercury – Cadmium

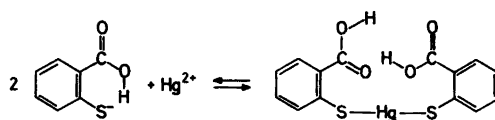
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Using bis(2-mercaptobenzoato)-*S*-mercury(II) as a starting ligand, the preparation of complexes of empirical formulae  $\text{Hg}(\text{C}_{14}\text{H}_8\text{O}_4\text{S}_2)\text{Pb}\cdot 2\text{H}_2\text{O}$  and  $\text{Hg}(\text{C}_{14}\text{H}_8\text{O}_4\text{S}_2)\text{Cd}\cdot 2\text{H}_2\text{O}$  is described. The infrared spectra, in the region  $4000-200\text{ cm}^{-1}$ , and  $^{199}\text{Hg}$  and  $^1\text{H}$  NMR spectra of these complexes are discussed. It has been concluded that the coordination of lead(II) and cadmium(II) occurs through oxygen while the sulfur mercury bonds are not altered appreciably.

The analytical applications of 2-mercaptobenzoic acid (TSA) are widely known.<sup>1</sup> Recently, it has been used as an extracting agent for chromium(III)<sup>2</sup> and as a quantitative precipitant for mercury between pH 2.5 and 5.5.<sup>3</sup> Its importance in pharmaceutical and biological applications stems from its uses (in the form of mono-complex of methylmercury) as a diuretic<sup>4</sup> and preservative in eye drops.<sup>5</sup> Also, it has been found to inhibit the activity of metal-dependant enzymes.<sup>6</sup> The inhibition of the activity of metalloenzymes is a result of its ability to bind a variety of metal ions, thus competing with the enzyme.

In a previous paper,<sup>7</sup> we have reported the binding ability of TSA with divalent zinc, cadmium, lead and mercury. It has been shown that the coordination of TSA in the complexes of Zn(II), Cd(II) and Pb(II) occurs through both sulfur and oxygen atoms, while in the case of mercury it coordinates through sulfur only. Two complexes were described; the mono-complex, which contains a free carboxyl group and the bis-complex which contains two carboxyl groups. A molecular model of the bis(2-mercaptobenzoato)-*S*-mercury(II) (BTM) shows that the two carboxyl groups, in the *cis*-form, are near one another, hence the two groups may



interact through hydrogen bonding. The binding constant ( $\beta_2$ ), in 75 % dioxane-water mixture, for the reaction is of the order of  $10^{27}$ .<sup>7</sup> Thus, in principle, the two carboxylate groups are available to form two coordinate bonds with metal ions of weak class b properties, without altering the Hg – S bonds appreciably. Metal ions which are candidates for such reaction include Pb(II), Cd(II), lanthanoids(III), *etc.* In this paper we shall attempt to prepare such mixed semplexes. The complexes include those of lead(II) and cadmium(II) ions.

### EXPERIMENTAL

BTM was prepared as described earlier.<sup>7</sup> It has been found that its disodium salt tends to produce grey granules consisting of metallic mercury. The ammonium salt, yellow with absorption maximum at 290 nm, is stable. The 1:1 BTM:Pb (BTMPb) was prepared by dissolving 0.5 g of BTM (1 mmol) in 6 ml of 10 %  $\text{NH}_3$  (7 mmol). The solution was added, while stirring, to 1 mmol of  $\text{Pb}(\text{NO}_3)_2$  dissolved in 25 ml of water. The pH was adjusted to 6.0 with dilute hydrochloric acid. The precipitate, pale yellow, was filtered off, washed with water, hot ethanol and then dried under vacuum. Found: Pb 27.27; Hg 26.34; S 8.60; H 1.18 and C 23.60. Calc. for  $\text{Hg}(\text{C}_{14}\text{H}_8\text{O}_4\text{S}_2)\text{Pb}\cdot 2\text{H}_2\text{O}$ : Pb 27.79; Hg 26.90; S 8.58; H 1.61 and C 22.53.

The same above procedure is used to prepare the cadmium complex (BTMCd), pale green. Found: Cd 17.22; Hg 30.04; S 9.84; H 1.66 and C 26.94.

Calc. for  $\text{Hg}(\text{C}_{14}\text{H}_8\text{O}_4\text{S}_2)\text{Cd}\cdot 2\text{H}_2\text{O}$ : Cd 17.27; Hg 30.82; S 9.83; H 1.84 and C 25.80.

All the above analyses were made by Alfred Berhardt Mikroanalytisches Laboratorium, West Germany.

Deuterated BTM was prepared by dissolution of BTM in warm dioxane – deuterium oxide mixture and evaporation at room temperature *in vacuo*.

## RESULTS AND DISCUSSION

Mixed metal complexes of 2-mercaptobenzoic acid containing two metal ions per complex are prepared. The two complexes are bis(2-mercaptobenzoato)-*O*-lead(II)-*S*-mercury(II) (BTMPb) and bis(2-mercaptobenzoato)-*O*-cadmium(II)-*S*-mercury(II) (BTMcd). The complexes were characterized through elemental analysis, TGA, IR and  $^{199}\text{Hg}$  and  $^1\text{H}$  NMR spectroscopy. The complexes in dimethylsulfoxide and in the solid state are currently under investigation by X-ray diffraction.

TGA showed that the complexes are stable up to 230 °C but decompose readily around 250 °C. This analysis was carried out with the aim of investigating the nature of the two water molecules in these complexes, but unfortunately no distinct change in the thermal gravimetric curve corresponding to water molecules was detectable.

Infrared spectra of the complexes were recorded using a Perkin-Elmer 180-spectrometer, equipped

with air-drier, in nujol mulls between CsI discs (in the range 500–200  $\text{cm}^{-1}$ ) and in KBr discs (in the range 4000–500  $\text{cm}^{-1}$ ). No change in the positions of different bands are detected on changing the medium. Detailed assignments of the bands cannot be made unambiguously, but nevertheless certain conclusions can be reached.

The spectrum of BTM in the region 3200–2500  $\text{cm}^{-1}$  showed a broad absorption band with many submaxima. Such absorption is characteristic of OH-stretching vibration of dimeric carboxyl groups.<sup>8</sup> The investigation of the IR-spectra of a number of carboxylic acids has shown that the OH-stretching vibration frequency of a monomer carboxylic acid lies near 2550  $\text{cm}^{-1}$  while that of dimeric species gives rise to a broad absorption region with many submaxima between 3000–2500  $\text{cm}^{-1}$  (see Ref. 8 and references therein). In general, therefore, the broad band absorption in the BTM, and especially the absorption near 2700  $\text{cm}^{-1}$ , is a strong indication of the presence of a hydrogen-bonded OH-group. This interpretation is supported by the fact that the spectrum of the deuterated BTM shows that part of the broad absorption band, centered at 2550  $\text{cm}^{-1}$ , has shifted 270  $\text{cm}^{-1}$  to lower frequency, *i.e.* appeared at 2280  $\text{cm}^{-1}$ . Another medium broad band, centered at 925  $\text{cm}^{-1}$  also shifted to lower frequency and appeared as a sharp strong band at 855  $\text{cm}^{-1}$ . This band could be

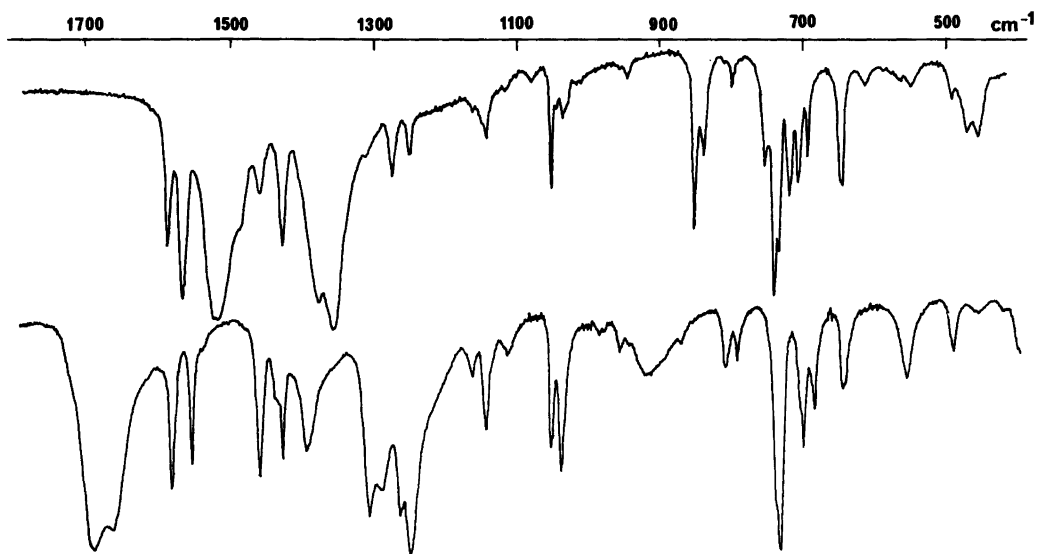


Fig. 1. Infrared spectra of BTM (lower) and BTMPb (upper) complexes in KBr discs.

assigned to the OH-out-of-plane deformation.<sup>8</sup> The isotopic ratio for the two bands is  $1.10 \pm 0.02$ . No other significant change was observed in the spectrum of BTM on deuterium substitution.

The spectrum of the BTMPb shows the complete disappearance of the broad OH-stretching frequency in the region  $3200-2500 \text{ cm}^{-1}$  leaving a weak broad band in the region  $3550-3350 \text{ cm}^{-1}$ . This band could be due to lattice water.<sup>9</sup> The spectrum also showed the disappearance of the band at  $925 \text{ cm}^{-1}$ , which was assigned to OH-out-of-plane deformation, Fig. 1. The three doublet bands of the carbonyl stretching frequencies at 1682, 1305 and  $1269 \text{ cm}^{-1}$  (average) in the BTM, have also disappeared, Fig. 1. The three bands did not show any appreciable shift on deuteration. The disappearance of the carbonyl stretching frequencies in the spectrum of BTMPb-complex is accompanied by the appearance of two doublet bands at 1522 and  $1370 \text{ cm}^{-1}$  arising from the carbonyl asymmetric and symmetric stretching frequencies, respectively. The above changes in the spectrum of BTM complex confirm the replacement of the protons of the hydrogen-bonded carboxyl groups by lead(II).

Metal-sulfur stretching vibration lies in the range  $480-210 \text{ cm}^{-1}$ ,<sup>10</sup> and the Hg-S stretching band, in the BTM-complex, was assigned near  $298 \text{ cm}^{-1}$ .<sup>7</sup> The general feature of the spectrum of BTMPb in this region is very much the same as that of the BTM-complex. A shift of a few  $\text{cm}^{-1}$  in all the bands is observed. The similarity between the spectra of BTM and BTMPb complexes in this region indicates that the Hg-S bonds are not altered appreciably.

The general feature of the IR-spectrum of BTMCd-complex is very much the same as that of BTMPb-complex, but the bands are slightly broader.

It should be emphasized, that although detailed assignment of the IR-bands has not been possible, the IR-spectral data of these complexes indicate that the coordination of the Pb(II) and Cd(II) ions occurs through oxygen while the Hg-S bonds are not altered appreciably.

<sup>199</sup>Hg nuclear magnetic spectra were obtained in natural abundance in a 10 mm tube at 16.1 MHz, using a Bruker cpx-90 spectrometer, at 20°C. The field was locked to the <sup>2</sup>H signal of an external capillary of D<sub>2</sub>O. Saturated Hg(NO<sub>3</sub>)<sub>2</sub> solution was used as external reference. Concentrations ranging from 0.2–0.5 M of these complexes were used to observe mercury signals. The <sup>1</sup>H NMR spectra were obtained on a Bruker wp-200 spectrom-

Table 1. <sup>199</sup>Hg and <sup>1</sup>H chemical shifts of 2-mercaptobenzoic acid complexes of mercury-lead and mercury-cadmium.

Compound	Hg <sup>a</sup> (ppm)	H3 <sup>b</sup> (Hz)	H4 (Hz)	H5 (Hz)	H6 (Hz)
TSA	—	1511.1	1485.3	1447.0	1591.9
BTM	1235.0	1523.5	1458.4	1436.4	1525.1
BTMPb	1187.0	1497.4	1437.7	1432.0	1475.8
BTMCd	1328.5	1491.6	1428.7	1421.7	1454.0

<sup>a</sup>Shifts to low-field relative to saturated Hg(NO<sub>3</sub>)<sub>2</sub> solution; mercury signal of saturated Hg(NO<sub>3</sub>)<sub>2</sub> is at  $-2460 \text{ ppm}$  from Me<sub>2</sub>Hg. <sup>b</sup>Shifts to low-field relative to internal TMS.

eter, at 25°C. Tetramethylsilane was used as an internal standard. The spectra of the complexes were resolved by simulating the theoretical spectra with the aid of an iterative program, PANIC, supplied by Bruker. Table 1 represents a summary of the chemical shifts of these complexes.

It is to be noticed from Table 1 that for each complex studied only one mercury signal is observed. This indicates that only one conformation exists, in DMSO, for each of the complexes studied. Table 1 also shows that the mercury signal of BTM is shifted to a lower-field on complexing cadmium and to a higher-field on complexing lead. This could be explained by considering two factors influencing the chemical shift of mercury in these complexes. Firstly, the weakening of Hg-S bonds as a result of the presence of another cation, in this case a shift to low-field in the mercury signals should be observed,<sup>11</sup> secondly, the presence of another cation with its solvation sphere nearby. This will influence the dispositions of DMSO molecules around the mercury ion and consequently the coordination of mercury. The larger the cation the greater the effect. The chemical shift of mercury in various compounds is known to be sensitive to the coordination sphere.<sup>11,12</sup> Table 1 shows that the signals of various aromatic protons, except H3, of 2-mercaptobenzoic acid are shifted to a high-field upon complexing mercury. This is inconsistent with the breaking-down of the hydrogen bonding between 2-mercaptobenzoic acid and solvent molecules.<sup>13,14</sup> Further up-field shifts in all the signals are observed on further complexation of lead(II). On substituting a stronger binding ion, Cd(II), instead of Pb(II) ion,<sup>7</sup> the positions of the signals continue to move up-field. This is reflected clearly

in the chemical shifts of H6, which is the nearest proton to the carbonyl group, *i.e.* it is also influenced by the variation in the effect of the chemical shift anisotropy of the carbonyl group resulting from various orientations relative to the aromatic protons.<sup>15,16</sup> Table 1 shows that only one set of signals appeared for both aromatic rings. This clearly indicates that the two rings are experiencing the same chemical environments, *i.e.* symmetrically disposed around the two metal ions.

The coupling constants between these protons, in the free and bound TSA, are nearly the same irrespective of the type of interactions involved with the sulfhydryl and the carboxyl groups. The values of the coupling constants are,  $J_{34} = 7.95 \pm 0.05$ ,  $J_{35} = 1.10 \pm 0.04$ ,  $J_{36} = 0.40 \pm 0.03$ ,  $J_{45} = 7.43 \pm 0.03$ ,  $J_{46} = 1.64 \pm 0.04$  and  $J_{56} = 7.70 \pm 0.05$ . The results indicate that the above interactions cause weak or no perturbation in the ring moiety.

*Acknowledgements.* The author is on a 10-month visit to the Inorganic Chemistry Department, Royal Institute of Technology, Stockholm, supported by the International Seminar in Chemistry and Physics, University of Uppsala, Uppsala, Sweden; he wishes to thank Dr. H. Stymne for putting the IR-equipment at his disposal and Professors I. Grenthe and U. Henriksson for useful discussions.

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Received June 12, 1981.