

## An Example of Hg-NCS Bonding

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Thiocyanates of Group II B metals offer interesting examples of the mode of metal-thiocyanate bonding. Whereas zinc(II) and mercury(II) form M-NCS and M-SCN complexes respectively, cadmium(II) is intermediate in character in that both Cd-NCS and Cd-SCN species have been observed [1]. The mode of metal-thiocyanate bonding can be distinguished from the frequency ranges in the infrared spectrum for the three fundamental vibrational modes of the thiocyanate group [2], viz.,  $\nu$ CN,  $\nu$ CS and the doubly-degenerate  $\delta$ NCS. Moreover, the internal standard ratio for the integrated absorption intensity of the CN stretching band in thiocyanato complexes offers the most definitive criterion in distinguishing the mode of metal-thiocyanate bonding [3, 4]. The use of salicylic acid [3] and 1,4-dicyanobenzene [4] facilitates the determination of the relative  $\nu$ CN integrated intensity ratio, otherwise known as internal standard ratio (ISR) in the solid state. Several monomeric complexes of mercury(II) thiocyanate with nitrogen, oxygen, phosphorus, arsenic and sulphur donor ligands are known with terminal Hg-SCN bondings [5-10]. Some thiocyanate-bridged dimeric complexes of mercury(II) are also known [6, 7]. We now report the isolation of a mercury(II) thiocyanate complex with hexamethylenetetramine, a potentially tetradentate ligand. The compound isolated has a 4:1 stoichiometry (metal:ligand) and has been characterized by analytical data, molecular conductance, molecular weight and infrared spectral measurements down to  $200\text{ cm}^{-1}$  in the solid state. It is shown that (i) hexamethylenetetramine acts as a tetradentate ligand bonding to four different mercury(II) ions, (ii) NCS groups are exclusively N-bonded to mercury(II) (*i.e.*, Hg-NCS), and (iii) the complex has a monomeric tetranuclear structure in the solid state. The relative internal standard ratio of the integrated absorption intensity of the CN stretching band, as determined in salicylic acid, also confirms the Hg-NCS bonding.

Hexamethylenetetramine was obtained from Dr. Theodor Schuchardt GmbH & Co., Munich, and used as such. The mercury(II) thiocyanate complex was prepared by boiling an ethanolic solution of  $\text{K}_2\text{Hg}(\text{SCN})_4$  and the ligand in excess. The mixture was filtered hot and the complex which crystallized out

on cooling was suction-filtered, washed with ethanol and anhydrous ether and dried under vacuum. Stoichiometry of the complex isolated was established by standard analytical methods. Found: Hg, 57.0; C, 12.2; N, 12.1; S, 18.4. Calculated for  $\text{Hg}_4(\text{hexamethylenetetramine})(\text{NCS})_8$ : Hg, 57.0; C, 12.0; N, 12.0; S, 18.2%. M.p.  $123^\circ\text{C}$ .

Conductivity measurements were carried out on freshly prepared  $\sim 10^{-3}\text{ M}$  solutions in water, methanol, ethanol and DMF at  $25^\circ\text{C}$ . Molecular weight determinations were carried out on  $\sim 0.005\text{ M}$  solutions in distilled water at  $37^\circ\text{C}$  with a Mechrolab Inc. Vapour Pressure Osmometer Model 301 A. Infrared spectra of uncoordinated hexamethylenetetramine and the complex were recorded as Nujol mulls held between sodium chloride plates (rock salt region) and thin polythene sheets ( $650\text{--}200\text{ cm}^{-1}$ ) on a Perkin-Elmer 621 spectrophotometer.

For the determination of the internal standard ratio (ISR) for the integrated absorption intensity (IAI) of the CN stretching band the method of McQuillan *et al.* [3] was adopted. A weighed amount (100 mg) of the complex and a like amount of crystalline AR salicylic acid, used as the internal standard, were ground together thoroughly in an agate mortar. One or two drops of Nujol was then added and the mixture was ground again to obtain a uniform mull which was then transferred to sodium chloride plates for recording the infrared spectrum.

The integrated absorption intensity (IAI) of the  $\nu$ CN band was estimated by adjusting and counting the squares in the  $\nu$ CN band in the compound and the  $1660\text{ cm}^{-1}$  band (due to  $\nu$ CO) in the salicylic acid, the internal standard, using the equation  $\text{IAI} = [(\text{wt of sample peak}) \times (\text{mol wt of sample})] / [(\text{grams of sample}) \times (\text{no. of absorbing groups per molecule})]$ . The internal standard ratio (ISR) value was calculated according to the equation:  $\text{ISR} = \text{IAI complex} / \text{IAI standard}$ .

The complex isolated is freely soluble in water, methanol, ethanol and DMF and behaves as a very strong electrolyte in these solvents ( $\Lambda_M$  values in water, methanol, ethanol and DMF are 870, 240, 525 and  $425\text{ ohm}^{-1}\text{ cm}^2$  respectively).

Hexamethylenetetramine, a heterocyclic system having three fused rings in the chair configuration with four bridge-head nitrogen atoms, is a potentially tetradentate ligand. The chemical and steric equivalence of the four bridge-head nitrogen atoms has been demonstrated by various physicochemical techniques [11]. It may thus act as a mono-, bi-, tri- or tetradentate ligand. The mode of metal-hexamethylenetetramine bonding is usually judged from the splitting of the two strong bands at  $1225$  and  $1000\text{ cm}^{-1}$  assigned to the CN stretching modes and infrared spectroscopy has been successfully used in

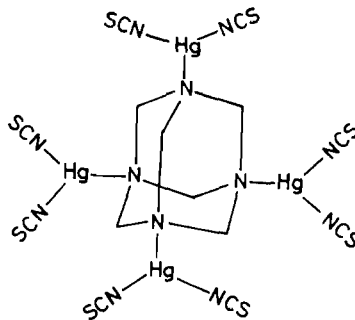
distinguishing the (i) terminal monodentate, and (ii) bidentate hexamethylenetetraamine bridging between two metal ions [12, 13]. Framework molecular models show that (i) this ligand cannot act as a bidentate chelating one, and (ii) all the four donor sites cannot coordinate simultaneously to the same metal ion.

Except for some intensity changes and the slightly lower frequencies of some absorption bands (which provides good evidence for the absence of free ligand, *cf.* coordinated 1,4-dioxane [14]), infrared spectra due to coordinated hexamethylenetetraamine in the complex (Nujol) studied herein are almost superimposable on those of uncoordinated hexamethylenetetraamine (Nujol). These features clearly indicate that the overall symmetry and the chair configuration of uncoordinated hexamethylenetetraamine [11] is retained in this compound, and strongly suggest that the four nitrogen atoms are coordinated to different mercury(II) ions.

In addition to the ligand bands indicating that hexamethylenetetraamine is acting as a tetradentate ligand, the infrared spectrum of this complex shows absorption bands at 2055, 815, 462, 350 and 924  $\text{cm}^{-1}$ . These additional bands are assigned as  $\nu\text{CN}$  (2055  $\text{cm}^{-1}$ ),  $\nu\text{CS}$  (815  $\text{cm}^{-1}$ ),  $\delta\text{NCS}$  (462  $\text{cm}^{-1}$ ),  $\nu\text{Hg-NCS}$  (350  $\text{cm}^{-1}$ ) and  $2 \times \delta\text{NCS}$  (924  $\text{cm}^{-1}$ ) due to coordinated thiocyanate groups. Mercury(II), being a 'soft' character, normally forms Hg-SCN bonding and absorbs at  $\sim 2100$ , 720, 420 and 320  $\text{cm}^{-1}$  due to  $\nu\text{CN}$ ,  $\nu\text{CS}$ ,  $\delta\text{SCN}$  and  $\nu\text{Hg-SCN}$  modes, respectively, due to terminal Hg-SCN bondings in the mercury(II) thiocyanate complexes [5-10]. The observed frequencies due to the fundamental modes of the NCS groups are consistent with those normally associated with terminally N-bonded NCS groups [2]. The Hg-NCS bonding in the present compound has been further confirmed by the internal standard ratio (ISR) for the integrated absorption intensity (IAI) of the  $\nu\text{CN}$  band. The internal standard ratio ISR defined as (CN stretching absorption area per mol of thiocyanate ion): (1660  $\text{cm}^{-1}$  absorption area per mol of salicylic acid) measured for a nujol mull prepared from a mixture of the mercury(II) thiocyanate-hexamethylenetetraamine complex and salicylic acid, 1.66, is also consistent with Hg-NCS bonding [3] in the compound investigated herein. The ISRs for S-bonded thiocyanato compounds fall in the range 0-0.6:1 while for the N-bonded thiocyanato complexes the values are  $>1.5:1$  in salicylic acid as the internal standard [3]. It is thus clear that the NCS groups are exclusively N-bonded to mercury (*i.e.*, Hg-NCS) in this complex. Molecular models of the 4:1 mercury(II) thiocyanate-hexamethylenetetraamine also support the linear N-bonded NCS groups to mercury(II). Based on the considerations of the fundamental frequencies due to coordinated hexamethylenetetraamine (indicating its

tetradentate behaviour retaining the chair configuration of the uncoordinated molecule) and the fundamental frequencies due to coordinated NCS groups the complex reported in this study is tentatively assigned a monomeric, tetranuclear structure with a three-coordinate planar environment of three nitrogen atoms (one from hexamethylenetetraamine and two from terminally N-bonded NCS groups) around the mercury(II) in the solid state.

The tetranuclear nature of the complex is also supported by the molecular weight determinations of this compound in aqueous solutions. The observed values 1030, 1035 and 1042 correspond with the species  $(\text{Hg}_4 \text{ hexamethylenetetraamine})^{8+}$  (calculated for  $\text{Hg}_4 \text{ hexamethylenetetraamine}(\text{NCS})_8$ : 1404; calculated for  $(\text{Hg}_4 \text{ hexamethylenetetraamine})^{8+}$ : 940) that is, the NCS groups are dissociated in aqueous solutions. The somewhat higher values of the observed molecular weight may be due to partial recombination of NCS groups with the  $(\text{Hg}_4 \text{ hexamethylenetetraamine})^{8+}$  species.



The complex reported herein seems to be the first example of Hg-NCS bonding. The tentative stereochemistry and the Hg-NCS bonding has been arrived at from a comparison of the metal-hexamethylenetetraamine and metal-thiocyanate frequencies with those of compounds of established structures. However, unambiguous characterization of this compound should be based on complete crystal structure determinations.

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