Monomeric, Tetranuclear Three-coordinate Mercury(II)

I S AHUJA* & C L YADAVA
Chemistry Department, Banaras Hindu University, Varanasi 221 005
and
RAGHUVIR SINGH
School of Chemistry, University of Hyderabad, Hyderabad 500 134
Received 25 March 1982; revised 14 May 1982; accepted 21 June 1982

A 4:1 complex formed by the interaction of mercury(II) thiocyanate with hexamethylenetetramine (a potentially tetradentate ligand) has been prepared and characterized by molecular conductance, molecular weight and IR spectral measurements. The complex is tentatively assigned a monomeric tetranuclear structure with a three-coordinate environment of three nitrogen atoms around each mercury(II) in the solid state. Three-coordination though exhibited in many metal(II) complexes is rather rare for mercury(II) and has been reported in a few systems but the species are mostly anionic or cationic. Some mercury(II) complexes have recently been reported which are shown to be neutral, monomeric mononuclear species with a three-coordinate planar environment around mercury(II). The formation of a 4:1 coordinate compound by the interaction of mercury(II) thiocyanate with hexamethylenetetramine (Hmta), a potentially tetradentate ligand, is reported in this note. The compound is considered as the first example of a novel monomeric tetranuclear structure with a three-coordinate environment around each mercury(II) in the solid state.

Mercury(II) thiocyanate-Hmta complex was prepared by boiling an ethanolic solution of K₂Hg(SCN)₄ [obtained by dissolving freshly prepared Hg(SCN)₂ in KNCS] and the ligand in excess. The mixture was filtered hot and the complex which crystallized out on cooling the filtrate was suction-filtered, washed with ethanol, ether and finally dried in vacuo. [Found: Hg, 57.0; NCS, 33.1%; Calc. for Hg₄(NCS)₄Hmta: Hg, 57.0; NCS, 33.1%]; m.p. 123°.

This compound is freely soluble in water, methanol, ethanol and DMF and behaves as a very strong electrolyte in these solvents (Å values in water, methanol, ethanol and DMF are 870, 240, 525 and 425 ohm⁻¹ cm² mol⁻¹, respectively, for 10⁻⁴ M solutions.

Hexamethylenetetramine is a potentially tetradeinate ligand and the chemical and steric equivalence of its four nitrogen atoms has been demonstrated by various physico-chemical techniques. The IR spectra of complexes of Hmta in which it acts as a bidentate bridging ligand display well defined splitting of the fundamentals of νCN bands of the uncoordinated ligand at 1225 and 1000 cm⁻¹. However, in complexes in which Hmta molecule(s) act as monodentate ligand(s) both these νCN bands suffer only very minor splitting in closely spaced doublets or triplets. Apart from these the IR spectrum due to coordinated Hmta (terminal monodentate or bidentate bridging) does not suffer any significant change from that of the uncoordinated ligand, thereby, supporting the view that the chair configuration of uncoordinated Hmta is retained in all such complexes. Although it is a potentially tetradentate ligand, molecular models show that all the four donor sites of Hmta cannot coordinate simultaneously to the same metal ion. These can, however, coordinate to four different metal ions resulting in a tetranuclear structure. Tetradentate Hmta would be anticipated to have the same symmetry as the uncoordinated molecule and its IR spectrum would not suffer any splitting of the νCN bands and would be closely similar to that of the uncoordinated Hmta. Such an expectation is realised in the complex synthesized presently, thus indicating its tetranuclear structure. The tetranuclear nature of the present species is further supported by molecular weight determination of this compound at 37° carried out on a Mechrolab Inc. Vapour Pressure Osmometer Model 301 A by calibrations using raffinose in the range 0.005 M – 0.10 M and the ΔΛ readings recorded at three minute intervals. The observed values 1030, 1035 and 1042 correspond to the tetranuclear species [Hg₄Hmta]⁻ (calculated for [Hg₄(NCS)₄Hmta] 1404; calculated for [Hg₄Hmta] 940), thereby, indicating that the NCS groups are dissociated in aqueous solution. The somewhat higher values of the observed molecular weights may be due to the partial recombination of NCS groups with the Hg₄Hmta species. It is thus clear that the species present in solid state is [Hg₄(NCS)₄Hmta] while in aqueous solutions it is [Hg₄Hmta]⁻.

In addition to the ligand bands IR spectrum of the 4:1 mercury(II) thiocyanate-Hmta complex shows absorption bands at 2055, 815, 462 and 924 cm⁻¹. These bands are assigned to νCN (2055), νCS (815), δNCS (462) and 2 × δNCS (924) due to coordinated thiocyanate groups and their frequencies are consistent with those normally associated with terminally N-bonded NCS groups. Mercury(II) having a 'soft' character normally forms Hg-SCN bondings. From the above considerations the
complex isolated in the present study is tentatively assigned a monomeric tetranuclear structure(I) with a three-coordinate environment of three nitrogen atoms around mercury(II) in the solid state. The tetranuclear character of the species [Hg₄Hmta]⁺ is also retained in aqueous solution as is obvious from the molecular weight determinations. The complex reported herein is the first example of a neutral, monomeric, tetranuclear, three-coordinate mercury(II) in the solid state.

We thank Mr V N Mulay, Microanalyst, B H U, for molecular weight determinations.

REFERENCES
7 Geary W J, Coord chem Rev, 7 (1971) 81.