

Some neutral three-coordinate complexes of mercury(II) halides and pseudohalides with N-methylnicotinamide

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MS received 28 November 1988; revised 5 September 1989

Abstract. Coordination compounds of mercury(II) chloride, bromide, cyanide and thiocyanate with N-methylnicotinamide, a potentially bidentate ligand, have been prepared. The complexes isolated have 1:1 (metal:ligand) stoichiometry. Molecular weight measurements in molten camphor indicate that the mercury (II) chloride and bromide complexes are monomeric. Based on conductance values, molecular weight determinations and infrared spectral data, it is inferred that in the solid state in all these complexes the metal ion has a coordination number three and is bonded to the N-methylnicotinamide via its pyridine ring nitrogen, and is terminally bonded to the halogen/pseudohalogen.

Keywords. Mercury(II) halide and pseudohalide complexes; N-methylnicotinamide complexes; three-coordinate mercury(II) complexes.

1. Introduction

The characteristic coordination numbers and stereochemical environments of mercury(II) are two-coordinate linear and four-coordinate tetrahedral. In addition to these, octahedral and five-coordination are also known (Cotton and Wilkinson 1977; Eller *et al* 1977; Deane 1978; Hughes 1981; Constable 1982–85). Coordination number three around mercury(II) is known in some systems but the species are mostly anionic, e.g., $[SMe_3][HgI_3]$ and $[NBu_4^+][HgI_3^-]$ which have been established through X-ray structure determinations to contain discrete planar $[HgI_3]^-$ species (Fenn *et al* 1963; Goggin *et al* 1982). The compounds $Na[HgCl_3]$, $Na[HgCl_3] \cdot 2H_2O$ and $[NH_4][HgCl_3]$ appear to have three-coordination around mercury(II), but have in fact distorted octahedral species $[HgCl_6]^{4-}$ containing linear Cl–Hg–Cl skeletons with two Hg–Cl bonds shorter than the other four and have characteristic diagonal coordination for the mercury atom (Grednic 1965). The salt $[NMe_4][HgBr_3]$, on the other hand, contains discretely pyramidal tribromomercurate ion, $[HgBr_3]^-$ (White 1963) which is reported as getting solvated to give four- or five-coordinated species in polar solvents. The compound $[HgL_2(OCIO_3)]ClO_4$, $L = R_3P$ or R_3As , is considered to have a three-coordinate environment around mercury(II) with one perchlorate coordinated to the metal as a monodentate ligand (Naiker *et al* 1981). Crystal structure

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determinations on $[\text{Hg}(\text{PR}_3)(\text{NO}_3)_2]$, where $\text{R} = 2,4,6\text{-trimethylphenyl}$, have established that the bulky ligand forces the mercury(II) to adopt a three-coordinate structure (Alyea *et al* 1979). X-ray analysis of the compound $\text{NH}_4 [\text{HgCl}_2(\text{SCN})]$ has shown that the metal atoms are basically three-coordinate (Dupont *et al* 1983). Some 1:1 complexes, e.g., Ph_3PHgX_2 , PyHgX_2 and PyOHgX_2 ($\text{X} = \text{Cl}, \text{Br}$; $\text{Py} = \text{pyridine}$ or its ring-substituted alkyl or dialkyl derivatives; $\text{PyO} = \text{pyridine N-oxide}$ or its ring-substituted derivatives, are known but these are halogen-bridged dimeric tetrahedral structures in the solid state (Coates and Ridley 1964; Deacon *et al* 1968; Ahuja 1970; Ahuja and Rastogi 1971). $\text{Ph}_3\text{AsOHgCl}_2$, however, has an oxygen-bridged dimeric structure (Branden 1964). The present work describes coordination compounds formed by the interaction of mercury(II) chloride, bromide, cyanide and thiocyanate with N-methylnicotinamide. The complexes isolated have been characterized by molecular conductance, molecular weight and infrared spectral measurements down to 200 cm^{-1} . It is shown that all the complexes isolated have 1:1 (metal:ligand) stoichiometry and are considered neutral species having monomeric three-coordinated environments around mercury(II) in the solid state.

2. Experimental

N-methylnicotinamide was purchased from M/s Ega Chemie, West Germany, and used as such. Mercury(II) chloride, bromide and cyanide complexes were prepared by mixing hot solutions of the mercury(II) salt (10 mmol in 20 ml ethanol) and the ligand (20 mmol in 10 ml ethanol). Preparation of the mercury(II) thiocyanate complex needed boiling of a suspension of the metal thiocyanate in ethanol with an excess of the ligand and filtering of the hot mixture. The complexes which crystallized out on cooling were suction-filtered, washed with ethanol and dried in an air-oven at $\sim 80^\circ\text{C}$. The stoichiometry of the complexes isolated was checked by metal and halogen/pseudohalogen gravimetric estimations.

Conductivity measurements were made on freshly prepared $\sim 10^{-3}\text{ M}$ solutions in absolute methanol at 25°C with a Phillips conductivity bridge Model PR 9500. Molecular weight determinations were carried out by the Rasts' method in camphor. Infrared spectra of the uncoordinated N-methylnicotinamide and its complexes with mercury(II) halides and pseudohalides were recorded as nujol mulls supported between sodium chloride plates on a Perkin-Elmer 621 spectrophotometer. The $650\text{--}200\text{ cm}^{-1}$ region spectra were recorded as nujol mulls held between caesium iodide plates on a Perkin-Elmer spectrophotometer Model 225 equipped with caesium iodide optics.

3. Results and discussion

The complexes isolated in the present study (table 1) are quite stable, have sharp melting points and are fairly soluble in absolute methanol in which they behave as non-electrolytes ($\Lambda_M \sim 10\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) (Geary 1971). The mercury(II) chloride, bromide, cyanide and thiocyanate complexes with N-methylnicotinamide have 1:1 (metal:ligand) stoichiometry. In the preparation of these complexes, the reactants (metal and ligand) have been used in 1:2 molar ratio. However, the species isolated in the solid state have a 1:1 ratio. It is just possible that the species formed in solution

Table 1. Analytical data.

Compound	M.P. (°C)	Mol. wt.		Mercury (%)		Anion (%)	
		Found	Calc.	Found	Calc.	Found	Calc.
HgLCl ₂	221	367	407	49.4	49.0	17.2	17.4
HgLBr ₂	205	486	497	40.2	40.2	32.2	32.2
HgL(CN) ₂	196	Insoluble		51.2	51.2	—	—
HgL(SCN) ₂	144	Reacts with camphor		44.0	44.2	25.4	25.6

L = N-methylnicotinamide

Table 2. Characteristic infrared bands (cm⁻¹)

Compound	ν NH	ν CO	ν C=N ν C=C	ν CN	Ring vibrations	Other bands
L	3330	1640	1599	1130	1000 607 399	
HgLCl ₂	3350	1660	1600	1125	1028 632 430	ν Hg-Cl 290
HgLBr ₂	3358	1645	1600	1110	1030 630 423	ν Hg-Br 230
HgL(CN) ₂	3360	1630	1595	1120	1027 624 415	ν CN 2180 ν Hg-C 430 δ Hg C N 327
HgL(SCN) ₂	3350	1640	1596	1115	1030 631 420	ν CN 2136 ν CS 695 δ SCN 455 ν Hg-SCN 300

L = N-methylnicotinamide

on mixing the reactants may have a 1:2 ratio and be soluble in the medium, but the solid crystallizing out on cooling may invariably be in 1:1 ratio thereby suggesting greater stability for the 1:1 compounds. It may be pointed out that only the most stable species exist either in solution or in solid state. Hence the possibility of attachment/bonding of the second ligand molecule to mercury(II) leading to a 1:2 metal:ligand ratio in the solid state is ruled out in the present study.

N-methylnicotinamide, a pyridine derivative with an amide group in the β -position in the ring, possesses two potential donor sites: (i) the pyridine ring nitrogen, and (ii) the carbonyl oxygen. Significant absorption bands due to the amide group in N-methylnicotinamide are ν NH, ν CO and ν CN (table 2). The carbonyl stretching frequency undergoes a significant negative shift because of coordination through the carbonyl oxygen in complexes of amides and other carbonyl donors with metal salts (Paul *et al* 1966; Paul and Chadha 1969). The ν NH, ν CO and ν CN modes of the uncoordinated N-methylnicotinamide remain either unperturbed or undergo slight positive shifts in the mercury(II) halide and pseudohalide complexes with this ligand. These features clearly indicate that the amide group is inert towards coordination. On

the other hand, the pyridine ring vibrations of the ligand at 1000, 607 and 399 cm^{-1} undergo significant positive shifts. These frequency shifts (table 2) indicate conclusively that coordination of N-methylnicotinamide takes place via the pyridine ring nitrogen only (Gill *et al* 1961) to the mercury(II) ions studied.

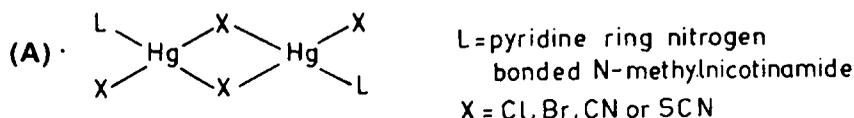
The 1:1 mercury(II) chloride and bromide complexes with N-methylnicotinamide may be postulated as (i) polymeric, 6-coordinated structures with only bridging halogens, (ii) 4-coordinated halogen-bridged dimeric tetrahedral structures, thus permitting two types of metal-halogen frequencies – (a) terminal, and (b) bridging (bridging M–X bonds absorb at $\sim 70\text{ cm}^{-1}$ lower frequencies than the terminal M–X bonds), or (iii) monomeric three-coordinate structures with only terminal halogens. Molecular weight determinations as carried out by the Rasts' method in molten camphor, show that the 1:1 mercury(II) chloride and bromide complexes with N-methylnicotinamide are monomeric. Low frequency infrared absorption bands observed at 290 cm^{-1} in the chloro- and 230 cm^{-1} in the bromo-complexes are assigned to $\nu\text{Hg-Cl}$ and $\nu\text{Hg-Br}$ modes, respectively, consistent with the exclusive presence of terminally-bonded mercury(II)-halogen bonds in several mercury(II) halide complexes shown to have three-coordinated environments (Ahuja and Singh 1980; Ahuja *et al* 1980, 1988) around mercury(II). From considerations of their molecular weights and the frequency of Hg–X bonds the 1:1 mercury(II) chloride and bromide complexes with N-methylnicotinamide are thus tentatively taken as neutral species with a monomeric three-coordinated environment of one nitrogen (from the pyridine ring nitrogen bonded N-methylnicotinamide molecule) and two halogens around mercury(II) in the solid state. Although the results obtained by the Rasts' method are not very accurate, they are of practical value (errors upto 5% may be considered negligible) and give some idea of the molecular nature of the compounds. The compounds under investigation could be postulated to be 4-coordinated dimeric or 6-coordinated polymeric structures in the solid state and these may get dissociated in molten camphor presumably to form monomeric three-coordinated structures. The mercury-halogen bonds are, however, consistent with the presence of only terminal bonds and are in good agreement with 3-coordinated structures.

In addition to the ligand bands modified slightly on account of coordination, the infrared spectrum of the 1:1 mercury(II) cyanide complex with N-methylnicotinamide shows absorption bands at 2180, 430 and 327 cm^{-1} which are assigned to the νCN , $\nu\text{Hg-C}$ and $\delta\text{Hg C N}$ modes, respectively, due to coordinated cyano groups. These frequencies are significantly lower than those of the corresponding modes in mercury(II) cyanide. Mercury(II) cyanide has a linear cyanide-bridged polymeric chain structure (Hvoslef 1958) in the solid state and absorbs at 2193, 442 and 341 cm^{-1} due to νCN , $\nu\text{Hg-C}$ and $\delta\text{Hg C N}$ modes, respectively (Jones 1957). The frequency of νCN suffers a significant negative shift when the cyano bridges break down and mercury(II) cyanide complexes with terminal cyano groups absorb at lower frequencies (Jain and Rivest 1970; Ahuja and Singh 1973; Ahuja and Rao 1975) than pure mercury(II) cyanide, while bridging cyano groups absorb at higher energies ($> 2200\text{ cm}^{-1}$) (Dows *et al* 1961; Nakamoto 1986). Moreover, complexes having both terminal and bridging cyano groups exhibit two bands in each of the νCN , $\nu\text{Hg-C}$ and $\delta\text{Hg C N}$ regions (Ahuja and Garg 1972) – the one appearing at higher wavenumbers being assigned to the bridging cyano groups and the other at lower wavenumbers to the terminal cyano groups. The observed frequencies of νCN , $\nu\text{Hg-C}$ and $\delta\text{Hg C N}$ in the 1:1 mercury(II) cyanide complex with N-methylnicotinamide

(table 2) strongly suggest the exclusive presence of terminally bonded cyano groups and the complex is assigned a monomeric, three-coordinated structure with terminal cyano groups and a nitrogen of the organic ligand molecule around mercury(II) in the solid state.

The infrared spectrum of the 1:1 mercury(II) thiocyanate complex with N-methylnicotinamide shows additional absorption bands at 2136, 695, 455 and 300 cm^{-1} which are assigned to the νCN , νCS , δSCN and $\nu\text{Hg-SCN}$ modes, respectively, due to coordinated thiocyanato groups. The frequencies of these modes are consistent with the exclusive presence of terminally S-bonded thiocyanato groups (Ahuja and Garg 1972) and the complex under investigation is assigned a monomeric three-coordinated structure in the solid state. It may be pointed out that the frequency of $\nu\text{Hg-S}$ of $\text{Hg}(\text{SCN})_2$ (Cooney and Hall 1969) suffers only a small negative shift in the mercury(II) thiocyanate complex studied herein. This may be attributed to the fact that there are two sets of anti-bonding π -orbitals localized on the sulphur atom which along with the vacant d orbitals of the sulphur atom can accept electron density from the filled non-bonding d orbitals of the mercury atom thus resulting in strengthening of the Hg-S bond.

One could postulate halogen/pseudohalogen-bridged dimeric, 4-coordinate tetrahedral structures (A) or six-coordinated polymeric octahedral structures with only bridging halogen/pseudohalogen groups for these 1:1 complexes. However, such



structures are ruled out as the infrared spectra of the compounds under investigation indicate the exclusive presence of terminally bonded halogen/pseudohalogen groups. The tentative stereochemistry of the mercury(II) complexes in the present study has been arrived at from a comparison of the metal ligand and metal-halogen/pseudohalogen frequencies with those of compounds of established structures. However, X-ray studies would lend more conclusive support for the structures of these compounds.

Acknowledgement

We thank the Council of Scientific and Industrial Research for the award of a Fellowship to ST.

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