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# Complexes of Mercury(II) Halides with N-methyl O-ethylthiocarbamate

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Mercury(II) halides have been reported to give complexes of various stoichiometries with thiocarbonylic ligands. Whereas thioureas form complexes having metal to ligand ratios from 1:1 to 1:4 [1–5], with monothiobiureth [6] and thioamides [7–9] 1:2 adducts have been generally obtained. In the complex $Hg(TSC)_2Cl_2$ (where TSC = thiosemicarbazide, $H_2N–CS–NH–NH_2$) the metal is in the center of a distorted tetrahedron formed by two chlorine and two sulfur atoms [10]; however in $Hg(TSC)Cl_2$ thiosemicarbazide acts as a bidentate ligand through the sulfur atom and the nitrogen of the aminic group [11]. A distorted tetrahedral configuration has been found also for $Hg(TC)_2Cl_2$ (where TC = ethylthiocarbamate, $H_2N–CS–OEt$) [12].

As a part of a study on the complexes of O-ethylthiocarbamates with transition metals [13, 14], this paper gives preliminary informations on the adducts obtained by raction of $HgX_2$ (X = Cl, Br, I) with the title ligand (MTC = $CH_3NH–CS–OEt$).

## Experimental

Mercury halides were R. G. commercial products; MTC was prepared as in ref. [14]. Instruments were as in refs. [13, 14]. In taking the $^1H$ NMR spectra of deuterated acetone solutions, benzene was used as an internal standard, owing to the immediate reaction of tetramethylsilane with the complexes.

### *Preparation of the Complexes*

#### *$Hg(MTC)_2X_2$ (X = Cl, Br, I).*

The salt was dissolved in a benzene solution of MTC (molar ratio from 1:3 to 1:4) and the complex isolated by addition of n-pentane. All the compounds are white and soluble in benzene and acetone. $Hg(MTC)_2I_2$ releases ligand molecules giving pale-yellow solutions.

#### *$HgCl_2{\cdot}MTC$*

*Form (A).* A suspension of $HgCl_2$ (1.3 mmol) in a benzene solution (10 ml ) of MTC (1.3 mmol) was heated up to 50 °C. The undissolved residue (110 mg M.p. 131–6 °C; C = 3.7; H = 0.8; N = 1.2) was separated, by cooling the filtrate gave the white flocculent solid. By adding n-pentane to the residual solutions small fractions of $Hg(MTC)_2Cl_2$ were obtained. *Form B.* The compound precipitated by addition of MTC (1.5 mmol) to an acetone solution (2 ml) of $HgCl_2$ (1.5 mmol). It was filtered and washed with an acetone–pentane solution. By adding pentane to the filtrate a mixture of the two forms, richer in (A), was obtained. Either in solution or more slowly in the solid state, the form (A) changes to the form (B). The solids (A) and (B) have quite different IR spectra below 900 $cm^{-1}$.

#### *$HgBr_2{\cdot}MTC$*

By adding pentane to an acetone solution of $HgBr_2$ and MTC (molar ratio 1:1) a small amount of an oily pink product precipitated, which was discarded. The progressive addition of several small fractions of pentane allowed to separate first the form (A) (200 mg) and then the form (B) (220 mg).

#### *$HgI_2{\cdot}MTC$*

$HgI_2$ (1.3 mmol) and MTC (1.3 mmol) were dissolved in acetone (3 ml). By adding pentane an oily product was obtained which gave an orange solid (form A). On standing the solution gave pale-green crystals (form B). The IR spectra of (A) and (B) are identical. The orange form turns to green if heated at about 50 °C.

## Results and Discussion

The IR spectra of the complexes indicate that the ligand coordinates through the sulfur atom. In fact the band assignable as mainly $\nu$(C–N) observed at 1535 $cm^{-1}$ for the pure MTC [14], shifts towards higher frequencies in the complexes. In the 1:2 adducts the position of $\nu$(N–H) and $\nu$(C–N) depends on the halogen, as for $\nu$(C–S) found at 712 $cm^{-1}$ in the chloro-, at 719 $cm^{-1}$ in the bromo- and at 722 $cm^{-1}$ in the iodo-derivative. A medium band, absent in the palladium complexes with MTC [14], has been observed in $Hg(MTC)_2X_2$ at 307 $cm^{-1}$ (X = Cl), 300 $cm^{-1}$ (X = Br), 293 $cm^{-1}$ (X = I), and tentatively assigned as $\nu$(Hg–S). In the Hg–Hal stretching region the 1:2 adducts exhibit a symmetrically split band suggesting a tetrahedral arrangement analogous to that of $Hg(TC)_2Cl_2$ [12]. The 1:1 chloro- and bromo-complexes have been isolated in two forms with different IR spectra. The form (A) of $HgCl_2{\cdot}MTC$, whose $\nu$(Hg–Cl) absorption is observed around 250 $cm^{-1}$, slowly changes either in solid or in solution to the form (B), in which $\nu$(Hg–Cl) falls around 230 $cm^{-1}$. The spectral behaviour, similar to that of the two bromo- derivatives, strongly suggest a polymeric halide-bridged structure in the forms (B).

TABLE I. Analytical Data (the calculated values are in parentheses) and Infrared Bands.

| Compound | M.p. °C | C% | H% | N% | $\nu$(N–H) | $\nu$(C–N) | $\nu$(Hg–Hal) |
|---|---|---|---|---|---|---|---|
| $Hg(MTC)_2Cl_2$ | 97–8 | 19.0<br>(18.8) | 3.5<br>(3.5) | 5.5<br>(5.5) | 3210m br, 3110mw | 1580s | 252s<br>238s |
| $Hg(MTC)_2Br_2$ | 94–6 | 15.9<br>(16.0) | 3.0<br>(3.0) | 4.8<br>(4.7) | 3230m br, 3105w | 1570s | 174m<br>168m |
| $Hg(MTC)_2I_2$ | 58 | 13.6<br>(13.8) | 2.5<br>(2.6) | 4.0<br>(4.0) | 3260m br, 3100w | 1555s | 143m<br>133m |
| $HgCl_2 \cdot MTC$ (A) | 94–5 | 12.4 | 2.4 | 3.8 | 3220m br, 3180sh, 3130sh, 3080vw | 1608s, 1582s | 250s, 245sh |
| $HgCl_2 \cdot MTC$ (B) | 117 | 12.4<br>(12.3) | 2.4<br>(2.3) | 3.6<br>(3.6) | 3255m br, 3140sh | 1582s | 230br |
| $HgBr_2 \cdot MTC$ (A) | 69–71 | 9.7 | 1.8 | 2.8 | 3240m, 3180sh, 3135sh, 3075w | 1602s, 1575s | 221m, 175m |
| $HgBr_2 \cdot MTC$ (B) | 73–6 | 10.0<br>(10.0) | 1.9<br>(1.9) | 2.9<br>(2.9) | 3220w, 3158vw | 1590s | 211m |
| $HgI_2 \cdot MTC$ (A) | 65–7 | 8.1 | 1.5 | 2.4 | 3300shw, 3270w | 1565s | 152m br, 138sh |
| $HgI_2 \cdot MTC$ (B) | 67–8 | 8.4<br>(8.4) | 1.7<br>(1.6) | 2.4<br>(2.4) | 3300shw, 3270w | 1565s | 152m br, 138sh |

By osmometric data $Hg(MTC)_2Cl_2$ is slightly dissociated in benzene, where the van't Hoff *i* factor is 1.08 for a $10^{-2}$ *M* solution. At the same concentration *i* is 1.24 for $Hg(MTC)_2Br_2$ and 1.65 for $Hg(MTC)_2I_2$. The $^1H$ NMR spectrum of a $5.10^{-2}$ *M* benzene solution of $Hg(MTC)_2Cl_2$ shows one signal for each group of proton; the $O{-}CH_2{-}\underline{CH_3}$ triplet is at 0.70 ppm, the $O{-}\underline{CH_2}{-}CH_3$ quartet at 3.91 ppm and the $N{-}CH_3$ signal at 2.17 ppm. Whereas in the $Pd(MTC)_2X_2$ (X = Cl, Br, I, SCN) complexes the $N{-}CH_3$ resonances appear as sharp doublets, in the mercury complexes these signals are broad indicating some tendency to release ligand. The spectra of $5.10^{-2}$ *M* benzene solutions of the 1:2 bromo- and iodo- adducts have the resonances of the coordinated ligand at the same values of the chloro- complex, along with the signals of the free ligand at 4.4 ppm ($O{-}\underline{CH_2}{-}CH_3$), 1.03 ppm ($O{-}CH_2{-}\underline{CH_3}$) and 2.60 ppm ($N{-}CH_3$). The amount of free ligand, low in the bromo- complex solution, is about 20% for the iodo-complex. Therefore the osmometric and NMR data support the equilibrium $Hg(MTC)_2X_2 \rightleftarrows HgX_2 \cdot MTC + MTC$ in bezene solutions.

In acetone the not-electrolytes 1:2 adducts release ligand molecules in a larger extent than in benzene; *i.e.* for $Hg(MTC)_2Cl_2$ ($10^{-2}$ *M*) $i \simeq 2$. The 1:1 complexes are almost insoluble in benzene, in acetone the polymeric structure is broken. For the forms (A) and (B) of $HgCl_2 \cdot MTC$, not-conductor in this solvent, the osmometric data seem to be in accordance with the monomer. The $^1H$ NMR spectra in acetone of $Hg(MTC)_2X_2$ (X = Cl, Br, I), at 0.1 *M* concentration, show a broad $N{-}CH_3$ signal at about 3 ppm and a weak resonance at 3.10 ppm. The $O{-}CH_2{-}CH_3$ double resonances confirm the presence of either coordinated MTC ($CH_3$ triplet at 1.40 ppm and $CH_2$ quartet at 4.63 ppm) or free MTC (1.29 ppm and 4.48 ppm respectively), whose amount is about 50% in the solution of $Hg(MTC)_2I_2$. However the spectra of the 1:1 adducts in the same solvent could suggest the presence of only coordinated MTC, but further study seems to be required in variable temperature conditions.

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