Preparative and Vibrational Spectroscopic Studies of Anilinium Salts Containing the \([\text{Hg}_2\text{Cl}_6]^{2-}\), \([\text{Hg}_2\text{Cl}_4\text{X}_2]^{2-}\), \([\text{CdHgl}_6]^{2-}\), \([\text{CdHgl}_4\text{Br}_2]^{2-}\) and \([\text{CdHgBr}_4\text{I}_2]^{2-}\) Ions (X = Br, I)

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Z. Naturforsch. 46b, 1532–1538 (1991); received March 1, 1991

Trihalogenomercurates, Cadmium(II)–Mercury(II) Hetero-dinuclear Complexes, IR Spectra, Raman Spectra

Synthetic procedures are described that allow access to anilinium salts containing the complex anions \([\text{Hg}_2\text{Cl}_6]^{2-}\), \([\text{Hg}_2\text{Cl}_4\text{X}_2]^{2-}\) (X = Br, I), \([\text{CdHgl}_6]^{2-}\), \([\text{CdHgBr}_4\text{I}_2]^{2-}\) and \([\text{CdHgBr}_4\text{I}_2]^{2-}\). Isolated dimeric structures are proposed for the new complexes in the solid state, using X-ray powder patterns, Far-IR and Raman spectra. The spectral detail is greatly enhanced in measurements at low temperature (≈ 100 K).

1. Introduction

Homo- and hetero-dinuclear/polynuclear transition metal complexes occupy an important position in modern inorganic chemistry [1]. The impetus for the study of these complexes derives from the interest in connection with magnetic exchange interactions [2], electron transfer between metal ions [3], catalysis [4] and materials chemistry [5] and from their significance as models for biological systems [6]. In contrast to the great number of studies concerning dinuclear transition metal complexes, little is known about the corresponding non-transition-metal complexes.

Our objective in these laboratories is to synthesize hetero-dinuclear and hetero-polynuclear halogeno complexes of the group 12 metals. A necessary prerequisite in this approach, however, is a better understanding of the chemistry of mononuclear and homo-dinuclear/polynuclear Zn(II), Cd(II) and Hg(II) complexes with one (simple halogeno complexes) or more (mixed) different types of halogeno ligands. Our interest in such species is threefold: (i) to redress the lack of characterized [7, 8] hetero-dinuclear halogeno complexes of these metals; (ii) to study the stability and structure of mixed halogenometallate anionic complexes, as such anions have received little attention [9–11]; (iii) to investigate the possibility of using dinuclear or trinuclear halogeno complexes as “building-blocks” [12] for the assembly of higher nuclearity aggregates, as there still is no systematic synthetic approach available to prepare larger and larger halogeno-bridged complexes.

The present paper describes our progress toward objectives i and ii, i.e. the synthesis and spectroscopic characterization of salts containing the anions \([\text{Hg}_2\text{Cl}_6\text{X}_2]^{2-}\) (X = Br, I), \([\text{CdHgI}_4\text{Br}_2]^{2-}\), \([\text{CdHgI}_6\text{Br}_2]^{2-}\) and \([\text{CdHgI}_6\text{Br}_2]^{2-}\); we also report here the preparation and study of a salt containing the \([\text{Hg}_2\text{Cl}_6]^2-\) ion. In the past we [13, 14], and others [11, 15–22], have reported the reactions of MX₂ (M = Cd, Hg; X = Cl, Br, I) with X⁻ to give anions of various degrees of condensation.

2. Experimental

The solvents were distilled prior to use. The salts AnHX (An = aniline; X = Cl, Br, I) were prepared as described elsewhere [23] and recrystallized from EtOH/Et₂O. The complexes (An₂H)₂[CdI₄] [24], (An₂H)[CdI₂An] [24], (AnH₂)[CdBr₂An] [25] and (AnH₂)[Hg₂I₆] [13] were available from previous work.

(AnH₂)₂[Hg₂Cl₆] (1) and (AnH₂)₂[Hg₂Cl₄Br₂] (2)

Equimolar quantities of HgCl₂ and AnHX (X = Cl for 1; X = Br for 2) were stirred with acetone (typically 10 mmol, 120 ml) at room temperature until a clear solution was obtained. Diethyl ether was added until the onset of turbidity. The solutions were then cooled to 0 °C to yield white microcrystals. The precipitates were collected by fil-

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tration, washed with cold EtOH and Et₂O, and dried in vacuo, yields ca. 50%.

\((AnH)\sub{2}[HgClI_2]\) (3)

For the preparation of this salt, equimolar amounts of HgCl₂ and AnHI were stirred together in hot acetone, using a quantity of solvent just sufficient to cause complete dissolution. After cooling and overnight storage at room temperature, the resulting pale yellow needles were isolated as above; yield ca. 40%. The product was recrystallized from boiling EtOH.

\((AnH)\sub{2}[CdI_4Br]\) (4)

Method A: Equimolar quantities (10 mmol) of (An₂H)₃[CDI₄] and HgI₂, each dissolved in the minimum volume of hot acetone, were mixed and stirred at ~40 °C for 30 min. The flask was stored in a freezer for 2 days. The yellow powder thus obtained was collected by filtration, washed with MeCN and Et₂O, and dried in air. The yield was ca. 60%. Recrystallization can be effected from boiling acetone.

Method B: This complex was also prepared by mixing a hot solution of (An₂H)[CDI₄An] in acetone and an ethanolic slurry of (An₂H)₃[HgI₄] in the molar ratio 2:1. The mixture was boiled to dissolve the solid material and then for 1 h under reflux. The homogeneous solution was allowed to cool slowly, whereupon a yellow precipitate formed, which was isolated as above; yield ca. 70%. The IR spectrum and X-ray powder pattern of this product were identical with those of the salt prepared by Method A.

\((AnH)\sub{2}[CdHgI_3Br]\) (5) and \((AnH)\sub{2}[CdHgBrI_2]\) (6)

Employing (An₃H)₃[CDI₄] – HgBr₂ and (An₃H)₃[CdBr₃An] – HgI₂ as starting materials, the previously detailed Method A yielded the pale yellow compounds 5 and 6, respectively. Yields of ca. 45–50% have routinely been obtained. Complex 5 was recrystallized from EtOH.

Reactions of 2 and 3 with 2,2’-bipyridine (bpy)

To a stirred solution of 2 (5.0 mmol) in warm MeCN was added a solution of bpy (5.0 mmol) in MeCN. A white precipitate formed immediately which was filtered off, washed with MeCN and Et₂O (not added to the filtrate), and dried at 80 °C; the yield was ca. 50% based on total available Hg. Detailed characterization of the solid (metal, halogens, C, H and N analyses, IR spectrum, Raman spectrum) proved this to be the known monomeric, pseudotetrahedral complex [HgClBr(bpy)] (and not an equimolar mixture of [HgCl₂(bpy)] and [HgBr₂(bpy)] [9]). The filtrate of the above reaction was allowed to slowly concentrate by evaporation at room temperature to give white microcrystals of (An₃H)₃[HgClBr] [26]; the yield was ca. 40% based on total available Hg. Using 10.0 mmol of bpy, i.e. molar ratio Hg:bpy = 1:1, the above reaction yielded again [HgClBr(bpy)] in a nearly 100% yield (based on Hg). Et₂O was added to the filtrate to initiate crystallization. After overnight storage in a freezer, the white precipitate was collected by filtration, washed with Et₂O, and dried in vacuo, yield ca. 80% based on total available An. Characterization of the solid (H⁺ and Cl⁻ analyses, IR spectral comparison with authentic material) proved this material to be AnHCl.

Using 3 as starting complex and similar experimental conditions, the 2:1 reaction with bpy yielded the known [9] complex [HgClI(bpy)] and (An₃H)₃[HgCl₄I] [26], while the 1:1 reaction gave [HgClI(bpy)] and AnHCl.

Physical measurements

Elemental analyses were performed at the Microanalytical Laboratory, University of Liverpool, England or at Galbraith Laboratories, Knoxville, Tennessee, U.S.A. To estimate the molecular weights of some representative solids the Rast camphor method was used [9, 27]. Room- and liquid nitrogen-temperature IR and Far-IR spectra were obtained using a Bruker IFS 113v Fourier transform spectrophotometer, with the samples studied as pressed discs in KBr (4000–500 cm⁻¹) and polyethylene (500–40 cm⁻¹). A 6-μm Mylar beamsplitter, a Glowbar source and a DTGS detector with polyethylene windows were used for the Far-IR region, while a KBr beamsplitter and a DTGS detector with KBr windows were employed in the mid-IR region. Room-temperature Raman spectra of the powdered solids were recorded on a SPEX 1403 spectrometer using the 514.5 nm line of a Spectra-Physics Ar⁺ laser; a spinning sample-cell was used to avoid thermal degradation of the coloured compounds. Signal recording was performed using photon counting with an integration time of 0.5 s, using a 2 cm⁻¹ slit width. Low-temperature (ca. 100 K) Raman spectra were recorded on a Coderg T 800 triple monochromator spectrometer employing d.c. amplification and using Ar⁺ (514.5 nm) laser excitation; a Coderg Cryocirc cryostat cooled with liquid nitrogen was used. X-ray powder patterns were obtained using a Ri-
gaku Miniflex diffractometer in the range $4 < 2\theta < 70^\circ$; a Cu anticathode ($\lambda_{\text{CuK}_{\alpha}} = 1.5418$ Å) was employed as the source of X-ray primary beam.

3. Results and Discussion

The Experimental Section lists six complexes in order of time of their preparation. The formation of some representative compounds can be summarized in eq. (1)–(3):

$$2\text{HgCl}_2 + 2\text{AnHBr} \xrightarrow{\text{acetone-ether}} (\text{AnH})_2[\text{Hg}_2\text{Cl}_4\text{Br}_2] \quad (1)$$

$$2(\text{AnH})[\text{Cd}_{1}\text{An}] + (\text{AnH})[\text{Hg}_{1}\text{I}_4] \xrightarrow{\text{acetone-ethanol}} (\text{AnH})_2[\text{Cd}_{1}\text{Hg}_{1}\text{I}_4] + 6\text{An} \quad (2)$$

$$2(\text{AnH})[\text{CdBr}_{1}\text{An}] + \text{HgI}_2 \xrightarrow{\text{acetone-40^\circ C}} (\text{AnH})_2[\text{CdHgBr}_{4}\text{I}_2] + 2\text{An} \quad (3)$$

The easy formation (even from starting materials containing coordinated An) and good yields of 4, 5 and 6 indicate that these hetero-metallic complexes are the thermodynamically preferred products in Cd(II)/Hg(II)/X⁻ reaction systems (in organic solvents). The driving force for this interaction seems to be the great affinity of Hg(II) for iodide and bromide [28]; in agreement with this no reaction between [CdCl₄]²⁻ and HgX₂ (X = Cl, Br, I) took place under a variety of experimental conditions. The tendency to form these species apparently increases with increasing softness [29] of the halide ion which is bound to Cd(II), the iodo complex 4 being formed most readily.

Colors, analytical data and molecular weights for the complexes are given in Table I. Solid-state molecular weight determination for representative complexes indicates their dimeric nature. The isolated compounds are microcrystalline or powder-like, stable under atmospheric conditions and readily soluble only in DMF and DMSO. We had hoped to structurally characterize one of the complexes by X-ray crystallography, but were thwarted on numerous occasions by twinning problems or lack of single crystals. Thus, the characterization of the complexes was based on spectroscopic techniques.

X-ray powder diffraction patterns indicate that each solid represents a definite compound, which is not contaminated with starting materials.

The complexes have IR spectra (4000–300 cm⁻¹) indicative of the absence of coordinated An and of the existence of AnH⁺ ions involved in hydrogen bonding [24, 25].

Diagnostic low-frequency vibrational data, which give an insight into the structure and the bonding in the solid state, are reported in Tables II and IV. Only features at ≤ 300 cm⁻¹ are listed, since it was clear that no fundamentals of the complex anions occurred above this wavenumber. A marked enhancement of detail is obtained if the spectra are measured at low temperature and, thus, we base our discussion on those obtained at ca. 100 K. Since the bending, twisting, rocking and ring deformation vibrational modes of the complex anions lie in a region where the lattice modes also occur [9], we will confine our assignments and relevant discussion to the stretching frequency region only. Assignments of the bands in Tables II and IV have been made by noting: (i) the frequencies of the internal modes of AnH⁺; (ii) bands principally dependent on halogen; (iii) the variation in

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>[%]</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
<th>Cd</th>
<th>Hg</th>
<th>Mol. Wt. a</th>
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<td>white</td>
<td>Calcd</td>
<td>17.97</td>
<td>2.01</td>
<td>3.49</td>
<td>26.52</td>
<td>3.54</td>
<td>17.93</td>
<td>50.01</td>
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<td></td>
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<td>Found</td>
<td>17.64</td>
<td>2.09</td>
<td>3.54</td>
<td>26.40</td>
<td>3.60</td>
<td>17.80</td>
<td>49.43</td>
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<tr>
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<td>Calcd</td>
<td>16.17</td>
<td>1.81</td>
<td>3.14</td>
<td>15.91</td>
<td>17.93</td>
<td>45.02</td>
<td>874 (891.1)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Found</td>
<td>15.91</td>
<td>1.69</td>
<td>3.03</td>
<td>16.04</td>
<td>17.80</td>
<td>45.87</td>
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<td>1.64</td>
<td>2.84</td>
<td>14.39</td>
<td>25.76</td>
<td>40.73</td>
<td>957 (985.1)</td>
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<td>1.70</td>
<td>2.74</td>
<td>14.38</td>
<td>26.00</td>
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<td>11.41</td>
<td>1.28</td>
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<td>8.90</td>
<td>15.89</td>
<td>1214 (1262.7)</td>
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<td></td>
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<td>Found</td>
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<td>1.36</td>
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<td>17.16 b</td>
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<td>2.44</td>
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<td>off-white</td>
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<td>1.50</td>
<td>2.61</td>
<td>29.74</td>
<td>23.62</td>
<td>18.66</td>
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<tr>
<td></td>
<td></td>
<td>Found</td>
<td>13.50</td>
<td>1.47</td>
<td>2.60</td>
<td>29.44</td>
<td>24.00</td>
<td>18.40 b</td>
<td></td>
<td></td>
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</table>

a Calculated values for dimers are in parentheses; b no data available.
Table II. Low-frequency vibrational assignments\(^a\) (cm\(^{-1}\)) of the mercury(II)-halogen stretching modes for the 
\([\text{Hg}_2\text{Cl}_6]\)\(^2^-\) and 
\([\text{Hg}_2\text{Cl}_4\text{X}_2]\)\(^2^-\) ions in the solid state.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(\text{Hg-Cl})_h)</th>
<th>(v(\text{Hg-Br})_h)</th>
<th>(v(\text{Hg-I})_h)</th>
<th>(v(\text{HgCl})_b)</th>
</tr>
</thead>
</table>
| (AnH)\(_2\)[Hg\(_2\)Cl\(_6\)] | IR: 291s, 281 vs, 273 vs, 267 m  
Raman: 295 m, 279 s, 272 m, 268 sh |  |  |  |
| (AnH)\(_2\)[Hg\(_2\)Cl\(_4\)Br\(_2\)] | IR: 299 m, 289 vs  
Raman: 300 w, 285 mb | 196 m, 178 vsh\(^b\)  
194 s, 176 w |  |  |
| (AnH)\(_2\)[Hg\(_2\)Cl\(_4\)I\(_2\)] | IR: 293 m, 279 vs  
Raman: 299 w, 277 mb |  | 152 m, 137 m  
150 m, 135 vsh | 209 m, 184 vsh, 176 m  
212 mb, 187 m, 182 w, 174 w |

\(^a\) At ca. 100 K; \(^b\) possibly overlapping with the symmetric breathing mode of the Hg\(_2\)Cl\(_2\) ring [15]. \(\text{vs} = \) very strong, \(\text{s} = \) strong, \(\text{m} = \) medium, \(\text{w} = \) weak, \(\text{b} = \) broad, \(\text{sh} = \) shoulder, \(v(\text{Hg-X})\) is the stretching vibration of the terminal Hg-X bond, \(v(\text{HgCl})_b\) is the stretching vibration of the Hg-Cl bond in the bridging HgClHg group.

Table III. Terminal (T) and bridging (B) stretching modes expected for 
\([\text{Hg}_2\text{Cl}_4\text{X}_2]\)\(^2^-\) (X = Br, I) ions of various structures.
band frequency and the appearance of new bands in the spectra of 4, 5 and 6, and (iv) extensive literature reports [7—11, 13—16, 30, 31]. As has been found previously [11], the Raman scattering ability of the stretching metal-halogen modes increases markedly in the sequence: Cl < Br < I. Consequently, the $v(\text{Hg-Cl})$, and $v(\text{HgBr})$ modes in 1, 2 and 3 are rather broad and of lower Raman intensity than those of the corresponding bromide or iodide modes.

The IR spectrum of the solid 1 shows four bands in the region appropriate to terminal Hg-Cl stretching; in the bridging stretch region two relatively strong bands carry two shoulders. The Raman spectrum also shows four terminal stretches, but is less rich in the bridging region than the IR spectrum, showing only one prominent band and two weak features. This number (totally 15) of IR- and Raman-active stretching vibrations is, of course, much greater than that to be expected for a monomeric $[\text{HgCl}_3]$ ion of any shape [32]. It is not in accordance with predictions for: (i) a centrosymmetric $D_{2h}$ dimeric anion $[\text{Hg}_2\text{Cl}_6]^2-$ which, based on tetrahedral geometry around the metal, should show [32] four IR-active ($B_{1u} + B_{2u} + 2B_{3u}$) and four Raman-active ($2A_g + B_{1g} + B_{2g}$) modes, i.e. totally 8 stretching fundamentals, and (ii) a structure consisting of infinite sheets of edge-shared $[\text{HgCl}_6]$ octahedra with AnH$^+$ ions on axes between the sheets [16] or a double-rutile chain structure [16]; in both of these structures a smaller number of stretching modes is expected [16]. To make sure that the multiplicity of bands is not simply the result of factor-group effects in the solid we recorded the spectra in solution; the solvents used were dichloromethane and acetone. The striking similarity between low-frequency vibrational spectra of solid 1 and its solutions leaves no doubt that the structure of this complex is the same in both states. Tetra-n-butylammonium trichloromercurate(II) is known [15] from a single-crystal X-ray study to exist as the discrete, not-centrosymmetric, unsymmetrically doubly chloride-bridged $[\text{Hg}_2\text{Cl}_6]^2-$ anions and $[\text{NBu}_{4}]^+ cations, the anion being formed by two tetrahedra sharing an edge. The spectra Goggin and his co-workers [15] reported for $(\text{NBu}_{4})_2[\text{Hg}_2\text{Cl}_6]_2$ resemble very much those of our AnH$^+$ salt 1. An isolated $[\text{Hg}_2\text{Cl}_6]^2-$ anion lacking a centre of symmetry should show four terminal and four bridging stretching modes, all IR- and Raman-active, i.e. a total of 16 vibrations. Thus there can be little doubt that the anion of 1 is of similar structure as the anion in $(\text{NBu}_{4})_2[\text{Hg}_2\text{Cl}_6]_2$. The wavenumbers and separation of bands due to HgCl bridge vibrations differ somewhat between the two salts and this may suggest that bond lengths and asymmetries in the bridges vary with hydrogen bonding present in 1 and crystal packing.

A halogen-bridged $[\text{Hg}_2\text{Cl}_4\text{X}_2]^2-$ ($X = \text{Br}, \text{I}$) species can belong to either $D_{2h}, C_{2v}, C_{2h}, C_5$ or $C_1$ point groups [9, 10]. Regardless of the molecular symmetry, these species give rise to 8 stretching modes (4 terminal and 4 bridging). Table III conveniently summarizes the expected number of terminal and bridging stretching modes and their activities. In $D_{2h}$ and $C_{2h}$ structures the mutual exclusion selection rule for the IR and Raman bands should be valid. From Table II it can be easily inferred that in both 2 and 3 a complete coincidence of the IR and Raman bands is observed and therefore the two centrosymmetric structures $D_{2h}$ and $C_{2h}$ can be ruled out. The structures with $C_{2v}$ and $C_1$ molecular symmetries can be easily differentiated from the $C_1$ structure, since in the former 4 bridging and 2 terminal mercury-chloride stretching modes are to be observed in the IR and Raman, whereas only 2 terminals must be detected for the mercury-bromide or -iodide modes. In the $C_1$ structure, 2 bridging and 3 terminal mercury-chloride stretching modes and 2 bridging and 1 terminal mercury-bromide or -iodide stretches must

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**Table IV. Low-frequency vibrational assignments (cm$^{-1}$) of the metal-halogen stretching modes for the $[\text{CdHgI}_6]^{2-}$, $[\text{CdHgI}_4\text{Br}_2]^{2-}$ and $[\text{CdHgBr}_4\text{I}_2]^{2-}$ ions in the solid state.**

| Compound | $v(\text{Cd-Br})$ | $v(\text{Hg-Br})$ | $v(\text{Cd-I})$ | $v(\text{Hg-I})$ | $v(\text{CdBr})$ | $v(\text{HgBr})$ | $v(\text{CdI})$ | $v(\text{HgI})$
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</thead>
<tbody>
<tr>
<td>$(\text{AnH})_2[\text{CdHgI}_6]$</td>
<td>IR 167 s, 142 b</td>
<td>IR 152 m, 135 m</td>
<td>IR 121 m, 110 w</td>
<td>IR 97 m</td>
<td>IR 167 w, 149 s</td>
<td>IR 155 w, 139 s</td>
<td>IR 128 w, 116 s</td>
<td>IR 105 s</td>
</tr>
<tr>
<td>$(\text{AnH})_2[\text{CdHgI}_4\text{Br}_2]$</td>
<td>IR 197 s, 178 s</td>
<td>IR 169 s, 150 s</td>
<td>IR 124 m, 112 w</td>
<td>IR 96 m</td>
<td>Raman 193 w, 175 m</td>
<td>Raman 167 w, 154 vs</td>
<td>Raman 130 w, 118 s</td>
<td>Raman 103 s</td>
</tr>
<tr>
<td>$(\text{AnH})_2[\text{CdHgBr}_4\text{I}_2]$</td>
<td>IR 207 vs, 187 s</td>
<td>IR 153 sb, 139 m</td>
<td>IR 153 sb, 144 m</td>
<td>133 mb</td>
<td>Raman 206 w, 196 m</td>
<td>Raman 156 sb, 143 s</td>
<td>Raman 168 w, 156 sb</td>
<td>137 s</td>
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</table>

*At ca. 100 K; b it may be due to a $v(\text{Hg-Br})$ mode; c it may be due to a $v(\text{Cd-I})$ mode; d overlapping.*
be observed. The number of terminal and bridging stretching modes and the absence of \( \nu(\text{HgX})_b \) (\( X = \text{Br}, \text{I} \)) bands point towards a structure with a \( C_2v \) or \( C_s \) symmetry.

Since vibrational spectroscopy cannot differentiate between \( C_2v \) and \( C_s \) symmetry structures, the reactivity of complexes 2 and 3 with the well-known bridge-breaking chelating ligand bpy has been investigated [9] in both 1:1 and 1:2 molar ratios. If a \( C_2v \) structure is present in the 1:1 reaction, the products will be [HgClX(bpy)] and [HgCl₃X]²⁻ (\( X = \text{Br}, \text{I} \)); on the other hand if the solids possess a \( C_s \) structure, the main product will be the least soluble complex [HgX₂(bpy)] with [HgCl₄]²⁻ as the side product. If a \( C_2v \) structure is present in the 1:2 reaction, the products will be [HgClX(bpy)] and AnHCl; on the other hand if 2 and 3 have a \( C_s \) structure, the main product will be a mixture of [HgCl₂(bpy)] and [HgX₂(bpy)] with AnHCl as the side product, provided that no secondary exchange reactions take place. The products obtained from these reactions (eq. (4) and (5)) indicate that complexes 2 and 3 have a structure with \( C_2v \) symmetry.

\[
\begin{align*}
\text{(AnH)}_2[Hg_2Cl_4X_2] + \text{bpy} & \quad \text{MeCN} \quad \sim 50 \degree C \\
[HgClX(bpy)] + (\text{AnH})_2[HgCl_3X] & \\
(\text{AnH})_2[Hg_2Cl_4X_2] + 2 \text{bpy} & \quad \text{MeCN} \quad \sim 50 \degree C \\
2[HgClX(bpy)] + 2 \text{AnHCl} & 
\end{align*}
\]

(4)

The spectra of 4, 5 and 6 are rather crowded in the region 210–90 cm⁻¹, making their assignment rather difficult. Additionally, it should be noted that generally the \( \nu(\text{CdI})_b \), \( \nu(\text{HgI})_b \), and \( \nu(\text{CdBr})_b \) modes appear in the same spectral region [7, 8, 11]. Thus, the actual structures of the complex anions of 4, 5 and 6 can not be unambiguously deduced from the vibrational spectra. However, judging from: (i) the result of the molecular weight determination for 4 (Table I); (ii) the appearance of both \( \nu(\text{CdI})_b \) and \( \nu(\text{HgI})_b \) bands in the spectra of 4 and 5; (iii) the appearance of \( \nu(\text{HgBr})_b \) and \( \nu(\text{CdBr})_b \) in 5 and 6, respectively, and (iv) the presence of a \( \nu(\text{HgBr})_b \) mode in 6, we suggest that these salts contain the dimeric anions shown in Fig. 1 with metals in tetrahedral coordination, the pairs of tetrahedra are sharing an edge.

Dimeric structures for 5 and 6 other b and c (Fig. 1) are unlikely to occur since in both cases this would imply a complete reorganization of the halo ligands previous to the complex formation; to produce such an effect it would be necessary to consider that the M–X (M = Cd, Hg; X = Br, I) bonds are essentially ionic which is not the case.

Contreras and Seguel [8] inferred from vibrational spectra that (Me₄N)₂[CdHgI₄Br₂] and (Me₄N)₂[CdHgBr₄I₂] contain isolated dimeric anions having the same structures with those proposed by our study. Their spectra resemble those we have reported here; however, neither the number of the bands nor the relative intensities correspond very well.

4. Concluding comments

From the variety of coordination structures adopted by trihalogenomercurates(II) [9, 13–17, 19, 20] it seems that the energy differences between different ligand arrangements about mercury are very slight [15]. In the absence of hydrogen bonding, ionic forces between the cations and halides of the complex anions are the important features dic-
tating the structures with small cations (e.g. the alkali metals); with cations of large diameter the optimum packing arrangements preclude structures with continuous chain-polymer anions. In the presence of hydrogen bonding (as in 1, 2 and 3), the nature of hydrogen bonds (intramolecular or intermolecular) may also be an important factor.

The HgX₂/CdY₂ (X, Y = halogens) reaction system seems to be a source of a variety of new hetero-complexes. In addition to complexes 4, 5 and 6 mentioned above, other members of this family with different structures are under investigation and will be described in due course.

We wish to thank Prof. Dr. H. O. Desseyn for providing some instrumental facilities and for helpful discussions.

[26] Th. F. Zafiropoulos and S. P. Perlepes, manuscript in preparation concerning synthesis and characterization of the pseudotetrahedral mixed halogenometallate(II) ions [HgX₂Y₂]²⁻ (X, Y = halogens).