Metal–Sulphur Stretching Frequencies and Structures of Complexes of Zinc, Cadmium, and Mercury with Thiols

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Assignments of ν_{as}(SMS) and ν_s(SMS) for the complexes $M(SR)_2$ (M = Zn, Cd, Hg; R = Et, Bu^t) and $Hg(SMe)_2$ from infrared and Raman spectroscopy are reported. Comparison of frequencies for the complex $Hg(SBu^t)_2$ containing four-coordinate mercury with those of $Hg(SR)_2$ (R = Me, Et) containing two-coordinate mercury permits assignment of a polymeric structure with linear coordination for the 1:1 complex of Hg(II) with 2,3-dimercaptopropanol (British anti-Lewisite).

Introduction

The dithiol 2,3-dimercaptopropanol $[CH_2(SH)CH(SH)CH_2OH$, British anti-Lewisite, $BALH_3]$ is generally used to remove mercury from the body following inorganic mercury poisoning [1, 2]. A study of the chemistry of Hg(II) and RHg(II) with $BALH_3$ requires assignment of mercury–ligand stretching frequencies for determination of structures of complexes. For organomercury derivatives of $BALH_3$ assignment of structure follows directly from comparison of ν(Hg–S) (IR) with values for model complexes of known structure, e.g. $(PhHg)_2 \cdot$ BALH has the structure PhHg–S~S–HgPh with ν(Hg–S) 353 cm^{-1} [3], similar to that obtained for $PhHgSCH_2CH_2OH$ (343 cm^{-1}) [3], MeHgSMe (333 cm^{-1}) [4], and $MeHgSCH_2CH(NH_3)CO_2 \cdot H_2O$ (325 cm^{-1}) [5].

However, assignment of structure for the Hg(II) derivative, Hg(BALH), from mercury–sulphur stretching frequencies is not straightforward because of a lack of expected correlation between reported assignments and coordination number [ν(M–L) should decrease as coordination number increases [6]] for related model complexes, e.g. $Hg(SMe)_2$ with two-coordinate mercury [7] has ν_{as}(SHgS) 338 cm^{-1} [8, 9], and $Hg(SBu^t)_2$ with four-coordinate mercury [10] has ν_{as}(SHgS) 337 cm^{-1} [8]. In contrast, PhHgCl (coordn. no. 2) has ν(Hg–Cl) 331

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cm^{-1} [11], and $[R_4N]_2[HgCl_4]$ (coordn. no. 4) has ν_{as}(ClHgCl) 228 (R = Et) [12, 13], 225 (R = Me) [14] and ν_s(ClHgCl) 268 (R = Et) [13], 264 cm^{-1} (R = Me) [14]. This anomaly in reported ν_{as}(SHgS) frequencies, together with the surprisingly large difference (152 cm^{-1}) [8] between ν_{as}(SHgS) and ν_s(SHgS) for $Hg(SBu^t)_2$, has prompted reinvestigation of assignments for $Hg(SR)_2$ (R = Me, Et, Bu^t) complexes in association with investigation of Hg(BALH). To assist with assignments for the bis-(alkylthiolato)mercury(II) compounds, spectra of related zinc and cadmium complexes have also been investigated.

Experimental

Preparation of Complexes

The complexes $Hg(SR)_2$ (R = Me, Et) were prepared by the reported method [15] and recrystallized from ethanol. The complex $Hg(SBu^t)_2$ precipitated on addition of the stoichiometric amount of *tert*-butylthiol in ethanol to mercuric acetate in ethanol, and was recrystallized from chloroform. The complexes $M(SR)_2$ (M = Zn, Cd; R = Et, Bu^t) were prepared by the method reported for related zinc mercaptides [16] and Hg(BALH) was prepared from aqueous solution as described previously [2, 3]. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne, and are given in Table I.

TABLE I. Analytical Data for the Complexes.

Complex	Found %				Calcd. %			
	C	H	S	Hg	C	H	S	Hg
$Zn(SEt)_2$	26.0	5.3	33.3	–	25.6	5.4	34.2	–
$Zn(SBu^t)_2$	39.1	7.4	26.3	–	39.4	7.4	26.3	–
$Cd(SEt)_2$	20.4	4.1	27.3	–	20.5	4.3	27.3	–
$Cd(SBu^t)_2$	33.0	6.2	22.2	–	33.1	6.2	22.1	–
$Hg(SMe)_2$	8.3	2.0	21.4	68.0	8.2	2.1	21.8	68.1
$Hg(SEt)_2$	14.9	3.1	20.1	62.3	14.9	3.1	19.9	62.1
$Hg(SBu^t)_2$	25.2	4.6	16.7	52.6	25.4	4.8	16.9	52.9
Hg(BALH)	11.4	2.1	19.6	60.6	11.2	1.9	19.9	62.1

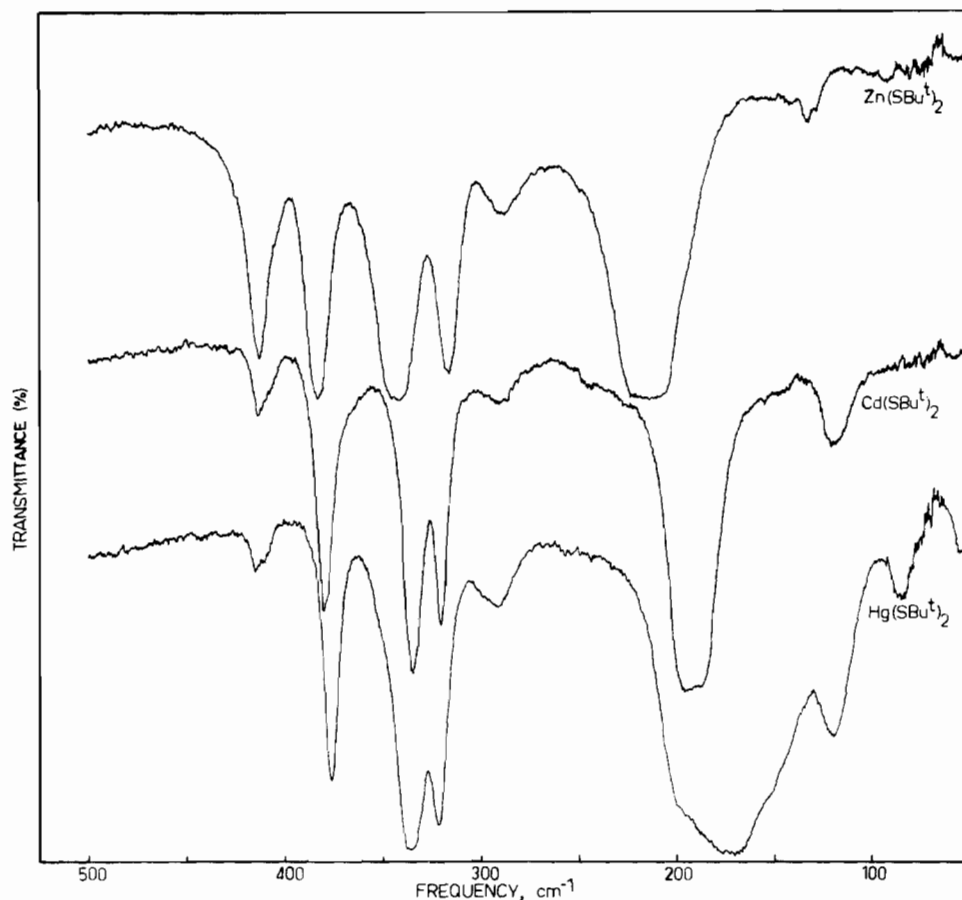Figure 1. Infrared spectra (500–50 cm^{-1}) for complexes M(SBu^t)$_2$ (M = Zn, Cd, Hg).

Physical Measurements

Infrared spectra (4000–400 cm^{-1}) of complexes in Nujol and hexachlorobutadiene mulls were recorded with a Perkin–Elmer 577 spectrometer. Far IR spectra of complexes in Nujol mulls between polythene plates were recorded with Perkin–Elmer 577 (600–200 cm^{-1}) and 180 (500–50 cm^{-1}) spectrometers. Far IR spectra were also examined at −196 °C, but no new features were evident and improvements in resolution were marginal, except where indicated. Raman spectra were measured with a Cary 82 Laser Raman spectrometer over the range 4000–100 cm^{-1} using 514.5 nm excitation. Maximum errors are considered to be 4 cm^{-1} for both IR and Raman spectra.

Results

IR and Raman spectra are listed below. Spectra of Hg(SMe)$_2$ are in agreement with those of Iwasaki *et al.* [9] and spectra of Hg(SR)$_2$ (R = Me, Et, Bu^t) extend previously reported data [800–180 cm^{-1} (IR), 800–100 cm^{-1} (Raman)] [8] and are in agree-

ment within these ranges. Spectra generally have sharp well-resolved bands, although Hg(BALH) which is amorphous (X-ray powder diffraction) has broad bands with the IR spectrum poorly resolved below *ca.* 200 cm^{-1}. Far IR spectra of M(SBu^t)$_2$ (M = Zn, Cd, Hg) and M(SEt)$_2$ (M = Zn, Cd, Hg) are shown in Figures 1 and 2 respectively.

Infrared Spectra (4000–50 cm^{-1})

Zn(SBu^t)$_2$

2973 m(sh) and 2961 s and 2943 m(sh), 2924 m, 2896 m, 2864 m, 1456 m(br), 1391 w, 1367 s and 1361 s, 1217 w, 1166 s, 1204 w, 820 w, 573 m, 415 w, 385 m, 344 s, 316 w, 290 w(br), 215 vs(br), 134 w cm^{-1}.

Cd(SBu^t)$_2$

2968 s and 2957 s and 2940 s and 2926 m(sh), 2891 m, 2863 m, 1464 s(sh) and 1456 s, 1391 m, 1365 s, 1218 w, 1163 s and 1145 s(sh), 1027 m, 821 m, 575 s, 411 vw(br), 381 m, 336 s, 322 m, 292 vw, 193 vs(br), 120 w cm^{-1}.
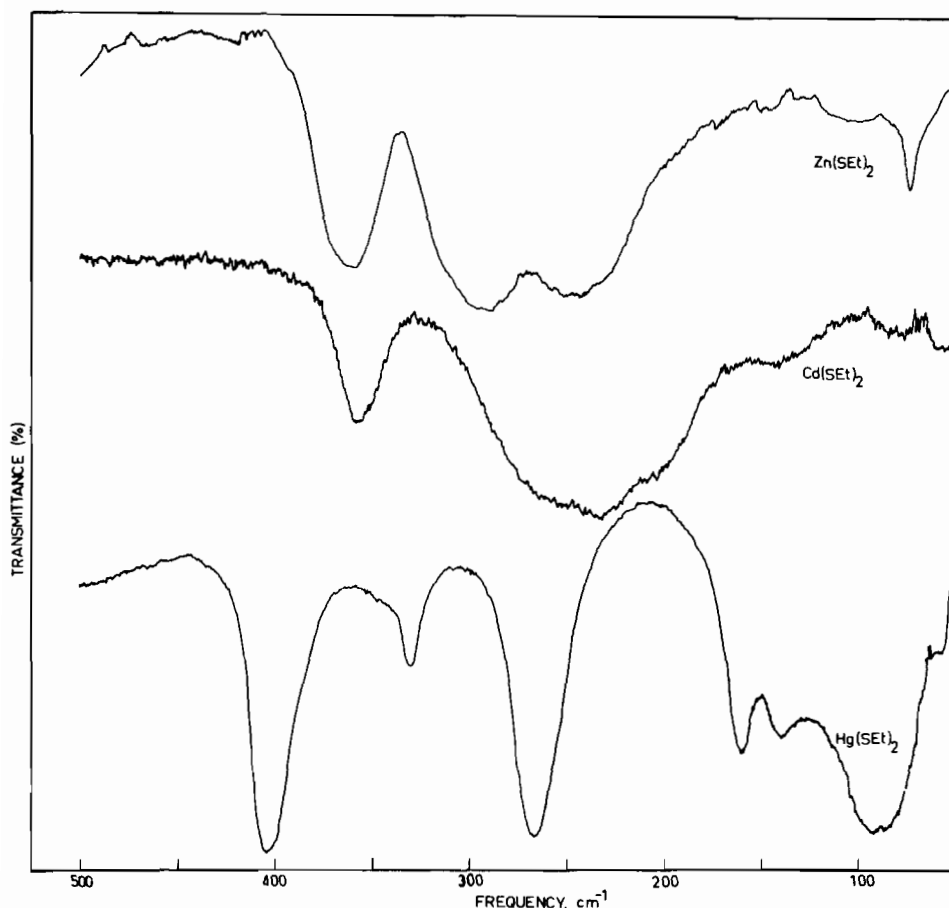
Figure 2. Infrared spectra (500–50 cm^{-1}) for complexes M(SEt)$_2$ (M = Zn, Cd, Hg). The spectrum of Zn(SEt)$_2$ was recorded at −196 °C, At ambient temperature absorptions at *ca.* 290 and *ca.* 245 cm^{-1} for Zn(SEt)$_2$ are poorly resolved. The spectrum of Cd(SEt)$_2$ does not improve on cooling.

Hg(SBu^t)$_2$

2973 s and 2960 s and 2948 s and 2940 s and 2920 m(sh), 2893 m, 2860 m, 1462 s and 1454 s, 1390 w, 1363 s, 1218 w, 1163 s and 1143 m(sh), 1025 m, 816 w, 756 vw, 573 m, 416 vw, 377 m, 336 s and 322 m, 292 vw, 172 vs(br) and 119 m(sh), 84 vw, and 53 vw cm^{-1}.

Zn(SEt)$_2$ (ambient temperature)

2959 m, 2924 s, 2867 w, 1446 w, 1373 vw, 1263 vs, 1052 w, 1031 w, 968 s, 764 m, 653 s, 361 m, *ca.* 285 s(vbr) and *ca.* 240 s(vbr, sh), and 83 w cm^{-1}. At −196 °C (500–50 cm^{-1}): 361 m, *ca.* 292 s(vbr) and *ca.* 248 s(vbr), and 76 w cm^{-1}.

Cd(SEt)$_2$

2958 m, 2923 m, 2864 w, 1445 m, 1372 w, 1260 s, 1051 vw, 1028 vw, 970 m, 765 m, 651 m, 358 m, *ca.* 260 s(vbr, sh) and *ca.* 233 s(vbr) and *ca.* 205 s(vbr, sh) cm^{-1}.

Hg(SEt)$_2$

2977 m(sh) and 2956 s and 2926 m(sh), 2860 w, 1445 s, 1367 m, 1308 vw, 1261 s and 1240 w(sh), 1045 vw, 1026 vw, 971 w and 952 vs(sh), 769 m, 654 w, 405 s(br), 332 w, 268 s(br), 161 m, 140 m(sh) and 90 s cm^{-1}.

Hg(SMe)$_2$

2980 vw, 2918 s, 2828 vw, 1420 w(br), 1312 w(sh) and 1307 w, 945 s(br), 696 m, 337 vs, 296 m, 204 m, *ca.* 110 s(vbr), 72 s, and 56 s cm^{-1}.

Hg(BALH)

3329 m(vbr), 2900 vw and 2872 vw(sh), 1449 w, 1408 m, 1302 vw, 1262 w, 1229 vw, 1046 m, 1005 m, 967 w(sh), 892 w, 864 vw, 655 vw, 555 vw, 521 vw, 454 vw, 405 vw, *ca.* 348 m(vbr), *ca.* 104 m(vbr) cm^{-1}.

Raman Spectra (4000–100 cm^{-1})
Zn(SBu^t)$_2$

2981 vs, 2968 vs, 2944 s, 2932 vs, 2904 vs, 2872 s, 2777 w, 2725 w and 2714 m, 1481 vw,

1466 s and 1452 s and 1442 s, 1394 vw, 1369 vw, 1220 s, 1169 s, 1038 m and 1029 m, 933 m, 823 vs, 583 vs, 418 vw, 402 m, 391 s, 342 m, 327 w, 311 m, 238 vw, 198 vs, 136 w cm^{-1}.

Cd(SBu^t)$_2$

2975 vs, 2960 vs, 2942 vs, 2920 vs, 2902 vs, 2868 vs, 2778 w, 2725 w(sh) and 2715 m, 1477 vw, 1464 m, 1439 m, 1395 vw, 1371 w, 1216 s, 1167 m and 1142 w(sh), 1031 m, 932 w, 821 s, 584 s, 410 vw, 385 m, 335 m, 318 s, 294 vw, 216 w, 191 vs, 106 s cm^{-1}.

Hg(SBu^t)$_2$

2972 s, 2959 m, 2950 m, 2935 m, 2930 m, 2915 m, 2895 s, 2860 m, 2773 vw, 2712 w, 1476 vw, 1463 w and 1459 w, 1440 w, 1393 vw, 1370 w, 1212 s, 1164 m, 1144 w(br), 1027 m, 931 w, 818 s, 579 m, 410 m, 382 vs, 336 m, 322 vs, 293 w, 188 vs cm^{-1}.

Zn(SEt)$_2$

2962 s(sh) and 2929 vs, 2871 s, 2728 w, 1450 m and 1435 m(sh), 1375 w, 1264 m and 1245 w(sh), 1057 m, 1037 w, 975 m, 770 vw, 700 vw, 662 vs, 370 vw(br), 287 vw(br, sh) and 198 vs cm^{-1}.

Cd(SEt)$_2$

2958 s(sh) and 2922 vs, 2867 s, 2724 w, 1449 m and 1438 w(sh), 1376 vw, 1315 vw, 1262 m, 1053 m, 1029 vw, 972 w, 767 vw, 695 vw, 654 s, 362 vw, 239 vw(sh) and 187 s(br) cm^{-1}.

Hg(SEt)$_2$

2975 w(sh) and 2958 s, 2938 s(sh) and 2926 s, 2860 w, 2715 vw, 1460 w, 1451 w, 1441 w, 1370 w, 1264 s, 1241 vw, 1048 m, 1030 vw, 974 m, 774 vw, 697 w, 658 vs, 394 vs, 335 w, 245 vs, 151 s cm^{-1}.
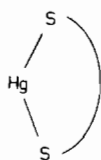
Hg(SMe)$_2$

2980 vw, 2910 m, 2828 vw, 1426 vw(br), 1382 vw (br), 1310 w and 1304 w, 952 vw(br), 697 m, 338 vw, 297 vs, 178 cm^{-1}.

Hg(BALH)

2909 m(br), 1465 vw, 1417 vw, 1273 vw, 1070 vw (vbr), 1015 vw, 897 vw, 737 w, 660 vw, 620 vw, 56 vw, 531 vw, 458 vw, 408 w, ca. 298 s(br), 185 w(br) cm^{-1}.

Discussion

The cyclic structure (I) usually drawn [2, 17] for Hg(BALH) is unlikely as it requires non-linear two-coordinate mercury which is unknown, in contrast with many cases of linear two-coordination [18].


I

A polymeric structure would be more consistent with the amorphous nature and low solubility of Hg(BALH). Crystal structure determinations of complexes Hg(SR)$_2$ show either linear [R = Me, Et; with Hg(SMe)$_2$ also having weak intermolecular Hg···S interactions (see below)] [7, 19] or tetrahedral (R = Bu^t, II) [10] geometry for mercury.
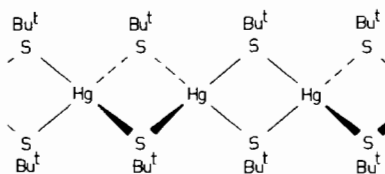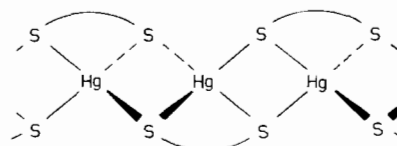

II

With these structures as models, possible polymeric structures for Hg(BALH) involving linear or tetrahedral mercury are (III) and (IV) respectively.
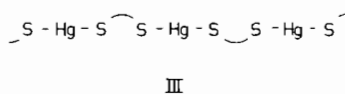
III

IV

More complex structures involving tetrahedral mercury can also be envisaged.

Vibrational spectra eliminate the cyclic structure (I) as IR and Raman spectra differ (Table II) whereas I, with C$_1$ symmetry, is expected to have all skeletal vibrations both IR and Raman active. IR active ν_{as}(SHgS) and Raman active ν_s(SHgS) skeletal modes are consistent with both III and IV which have centres of symmetry.

We find that Hg(SBu^t)$_2$ has ν_{as}(SHgS) at 172 cm^{-1} rather than the reported value (337 cm^{-1})*, and thus Hg(SBu^t)$_2$ with tetrahedral mercury(II) has both ν_{as}(SHgS) and ν_s(SHgS) *below* the values for Hg(SR)$_2$ (R = Me, Et) which have linear mercury. Assignment

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*Biscarini *et al.* [8] measured IR spectra in the region 3000–180 cm^{-1} and thus would be unaware of the strong, broad, absorption at 172 cm^{-1}.

TABLE II. Metal–Ligand Vibrations (cm^{-1}).[a]

Complex	ν_{as}(SMS)	ν_s(SMS)
Zn(SBu^t)$_2$	215 vs, br	(198 vs)
Cd(SBu^t)$_2$	193 vs, br	(191 vs)
Hg(SBu^t)$_2$	172 vs, vbr;	(188 vs);
	[337 vs][b]	[(185 vs)][b]
Zn(SEt)$_2$	ca. 248 s, vbr[c]	(198 vs)
Cd(SEt)$_2$	260–200 s, vbr[d]	(187 s, br)
	(239 vw)	
Hg(SEt)$_2$	405 s, br;	(394 vs);
	[268 s][b]	[(246 s)][b]
Hg(SMe)$_2$	337 vs; (338 vw)	(297 vs); 296 m
	[338 vs][b,e]	[(298 m)][b]; [(295 s)][e]
Hg(BALH)	ca. 348 m, vbr	(ca. 298 s, vbr)
		ca. 185 w(br)

[a] Raman values in parentheses ( ). Previous assignments in parentheses [ ]. Abbreviations: v, very; s, strong; m, medium; w, weak; br, broad. [b] From reference 8. [c] Spectrum obtained at −196 °C (Figure 2). [d] Strong, very broad, absorption in this range does not permit assignment of ν_{as}(SCdS) (Figure 2). [e] From reference 9.

of ν_{as}(SHgS) in the infrared spectrum is apparent from both the intensity and broadness of the absorption at 172 cm^{-1}, and comparison with spectra of the analogous zinc and cadmium complexes (Figure 1). As expected for a series of closely related complexes [6] ν(SMS) frequencies follow the order Zn > Cd > Hg with increase in atomic weight of the central metal (Table II), e.g. a similar trend is found for tetrahedral coordination in [Et$_4$N]$_2$[MCl$_4$], with ν_{as}(ClMCl) [12] 271 (Zn), 260 (Cd), and 228 cm^{-1} (Hg). Assignment of ν_{as}(SHgS) as 172 cm^{-1} is also consistent with ν_s(SHgS) 188 cm^{-1}, whereas the previous assignment [8] has these modes 152 cm^{-1} apart. The absorption of Hg(SBu^t)$_2$ at 336 cm^{-1}, previously assigned as ν_{as}(SHgS), is now attributed to a mode of the SBu^t group, and this assignment is supported by observation of similar absorption in spectra of M(SBu^t)$_2$ (M = Zn, Cd) (Figure 1). Tetrahedral CdS$_4$ coordination proposed for Cd(SBu^t)$_2$ has been observed in distorted form in Cd(SCH$_2$CH$_2$OH)$_2$ [20] and [Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$](SO$_4$)$_2$·2H$_2$O [21]. Distorted trigonal bipyramidal cadmium atoms (CdS$_4$O) are also present in both structures, and distorted octahedral (CdS$_3$O$_3$) in the latter.

The previous assignment [8] of ν(SHgS) modes for Hg(SR)$_2$ (R = Me, Et) does not correlate well with crystal structures and physical properties of these complexes. Although the structure determinations do not give accurate interatomic distances [7, 19], they do indicate the presence of weak intermolecular Hg$\cdots$S interactions in Hg(SMe)$_2$ but not in Hg(SEt)$_2$ [10, 19]. Bradley and Kunchur [7, 10, 19] comment that this is consistent with melting points of Hg(SR)$_2$ complexes, e.g. R (m.p.) [15]: Me (175 °C), Et

(76 °C), Pr^n (71 °C). The melting point of Hg(SMe)$_2$ is actually higher than that of four-coordinate Hg(SBu^t)$_2$ (159–160 °C) [22]. With stronger intermolecular Hg$\cdots$S bonding in Hg(SMe)$_2$ than Hg(SEt)$_2$, weaker Hg–S bonding and thus lower ν(SHgS) modes are expected for Hg(SMe)$_2$, in contrast with the previous assignment [8] (Table II).*

In addition the value of ν_{as}(SHgS) previously assigned for Hg(SEt)$_2$, 268 cm^{-1}, is similar to ν_{as}(SMS) for M(SEt)$_2$ (M = Zn, Cd) which are assumed to have tetrahedral coordination as their spectra exhibit strong absorption attributable to ν(SMS) in regions similar to spectra of tetrahedral complexes M(SBu^t)$_2$ (M = Zn, Cd, Hg) (Table II, Figures 1 and 2). The IR spectrum of Zn(SEt)$_2$ has two strong, broad, absorptions (ca. 292 and ca. 248 cm^{-1}) in the range 350–50 cm^{-1} (Figure 2). The lower value is considered to be ν_{as}(SZnS) as it is similar to ν_{as}(SZnS) for Zn(SBu^t)$_2$ (215 cm^{-1}) which has ν_s(SZnS) identical with that of Zn(SEt)$_2$ (198 cm^{-1}, Table II). For Cd(SEt)$_2$ ν_{as}(SCdS) is in the range 260–200 cm^{-1} where the IR spectrum has strong absorption consisting of several unresolved absorptions (Figure 2). Comparison of these spectra (Figure 2) indicate that the absorption at 268 cm^{-1} for Hg(SEt)$_2$ may be a thiol absorption, occurring at ca. 292 cm^{-1} for Zn(SEt)$_2$ and ca. 260 cm^{-1} for Cd(SEt)$_2$. A strong absorption at 405 cm^{-1} in the IR spectrum of Hg(SEt)$_2$ has no analogue in spectra of the Zn and Cd complexes, and is higher than ν_{as}(SHgS) for Hg(SMe)$_2$, and thus may be ν_{as}(SHgS). The Raman spectrum has a strong band at 394 cm^{-1} not present in the Zn and Cd complexes. This is a more suitable value for ν_s(SHgS) than the previous value of 246 cm^{-1} if ν_{as}(SHgS) is reassigned to 405 cm^{-1}. However, possible analogues of 246 cm^{-1} as a thiol band in the Raman spectra of Zn(SEt)$_2$ (287 cm^{-1}) and Cd(SEt)$_2$ (239 cm^{-1}) are only of low intensity. Thus, some uncertainty remains over the assignment for Hg(SEt)$_2$, but the present values are more consistent with structural data.

As Hg(BALH) has ν_{as}(SHgS) and ν_s(SHgS) near the values for Hg(SR)$_2$ (R = Me, Et) and well above the values for tetrahedral mercury in Hg(SBu^t)$_2$, we conclude that this complex has the polymeric structure (III) with linear coordination for mercury. The possibility that small regions of the amorphous polymer contain higher coordination numbers for

*Lowering of metal–ligand modes by weak intermolecular bonding is illustrated by mercuric bromide: in the vapour phase HgBr$_2$ (linear) has ν_{as} 293 [23] and ν_s 220 cm^{-1} [24], whereas solid HgBr$_2$ [linear, with four additional weak Hg$\cdots$Br interactions 3.23 Å [25] (sum of van der Waals radii 3.45 or 3.68 Å depending on the value chosen for the radius of mercury) [18] has ν_{as} 249 [11, 26] and ν_s 184 cm^{-1} [27].

mercury cannot be definitely discounted because of the poor quality of its IR spectrum below *ca.* 200 cm^{-1} and the presence of a weak Raman absorption at 185 cm^{-1}.

Acknowledgments

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