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New insights into the constitution of solutions containing labile, polynuclear compounds: an electrospray mass spectrometric study of mercury- and cadmium-rich dithiocarbamato cations

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Abstract

Electrospray mass spectrometry (ESMS) has been used to study the constitution of mercury and mixed mercury/cadmium dithiocarbamato cations in dichloromethane and methanol solutions. In all cases the ions observed are of the form $\{[M(R_2dtc)]^+ + nM(R_2dtc)_2\}$ ($n = 1$–3, M = Hg, Cd), e.g. $[Hg_2(R_2dtc)_3]^+$ ($n = 1$). Addition of $M(R_2dtc)_2$ favours formation of the higher oligomers. Ligand exchange between different mercury dithiocarbamato cations is fast on the NMR timescale, but ESMS shows the individual ions with various ligand combinations. Similarly, reaction of a mercury-rich dithiocarbamato cation with a neutral $Cd(R_2dtc)_2$ complex of a different dithiocarbamate gives global exchange between ligands and metals and ESMS observes individual ions in the complex mixture. Exploratory experiments show that a similar chemistry exists for metal-rich dithiophosphate cationic systems. The order observed in these solutions leads to the suggestion that the $M(R_2dtc)_2$ groups act as ligands towards the $[M(R_2dtc)]^+$ cations and analogies are proposed between these ligand properties and those of the $[MS_4]^{2-}$ (M = Mo, W) anions.

Introduction

All the transition and many main group metals react with the dithiocarbamate ligands, $[S_2CNR_2]^-$ ($[R_2dtc]^-$), to form complexes which have been widely studied and extensively reviewed [1–4]. For some time, we have been investigating the dithiocarbamates of mercury, cadmium, zinc and lead [5–12]. One feature of their chemistry is that solutions in organic solvents show electrochemical oxidation processes at a mercury electrode, although these are not oxidations of the compounds themselves. We have demonstrated that oxidation of the mercury electrode occurs to give, in the case of $Hg(R_2dtc)_2$ compounds, mercury-rich cationic dithiocarbamate complexes such as $[Hg_3(Et_2dtc)_4]^{2+}$ [7, 8, 12]. Other metals give mixed metal–mercury species in solution under similar conditions [10, 11]. It was subsequently discovered that the same polynuclear cationic species may be chemically generated in solution by interaction of the neutral metal dithiocarbamate and mercurous perchlorate [8].

The oligomeric mercury–metal dithiocarbamato complexes have been investigated by chemical, electrochemical and NMR techniques. Although the average stoichiometries of the species in solution have been established, they all show evidence of lability between several species in solution. In the case of the $Hg(Et_2dtc)_2$ system, solutions containing species of average empirical composition $[Hg_3(Et_2dtc)_4](ClO_4)_2$ have been characterised [7], but mercury-199 NMR studies, even at low temperatures, failed to provide definitive structural information. The solid isolated from the solution, $[Hg_5(Et_2dtc)_8](ClO_4)_2$, contained a polymeric mercury-rich cation and when redissolved in dichloromethane, it behaved electrochemically as a mixture of $[Hg_3(Et_2dtc)_4]^{2+}$ and $2Hg(Et_2dtc)_2$ [7]. It appears therefore that the solid which crystallises from the solution of this labile system is simply that which is least soluble under the experimental conditions, and may not necessarily provide information that is directly relevant to the species actually present in solution.

Similar studies of the $Hg(pipdtc)_2$ system (pipdtc = piperidinecarbodithioato) showed that the material in solution appeared to have the empirical formula $[Hg_4(pipdtc)_6]^{2+}$ and the solid isolated from solution was characterised as polymeric $[Hg_2(pipdtc)_3](ClO_4)$

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[12]. Thus, the chemistry of these mercury-rich complexes is complicated and diverse and it was not easy to see how further progress in understanding the solution chemistry could be achieved with existing techniques.

Electrospray mass spectrometry (ESMS) is a new technique which allows pre-existing ions in solution to be transferred to the gas phase with a minimal fragmentation, followed by conventional mass spectrometry. The ES technique has been developed mainly by Fenn and co-workers [13–16] and its most spectacular successes have been in the area of mass spectrometry of large bio-molecules [16, 17] where its use is expanding exponentially [18], although to date there are few applications to inorganic chemistry.

We have begun investigating the use of ESMS in inorganic and organometallic systems. In the cases of non-labile cations and anions, such as phosphonium salts and species such as $[(P\text{-}P)Pt(R_2dtc)]^+$ ($P\text{-}P =$ diphosphine), the intact ions are usually observed without difficulty [19–21]. However with labile complexes, daughter ions formed by loss of one or more ligands may be observed together with the intact ions. Interestingly, in cationic or anionic systems where ligands are exchanging rapidly on the NMR timescale at room temperature, the ESMS technique allows room temperature observation of the individual species present in solution, and it provides a viable alternative to low temperature NMR studies for their characterisation. Examples of labile systems to which this technique has already been applied include Cu(I) mixed phosphine cations [22], mixed phosphine complexes of Hg(II) [23] and mixed tris(dithiophosphato)zinc(II) anions [24].

In this paper we report results of the application of ESMS to solutions of mercury- and cadmium-rich dithiocarbamato cationic species. It will emerge that the technique provides new insights into the constitution of these solutions and reveals previously unsuspected complexity, and order, in these systems. It is also shown that similar complex cationic chemistry exists for mercury- and cadmium-rich dithiophosphate cations.

Results and discussion

All peaks in the ES mass spectra are identified by the most abundant *m/z* value within the isotopic mass distribution. In all cases the agreement between experimental and calculated isotopic mass distribution is excellent.

Dithiocarbamate systems

ES mass spectral data are summarised in Table 1. A solution of empirical composition $[Hg_3(Et_2dtc)_4](ClO_4)_2$ was generated in dichloromethane by the interaction of $Hg(Et_2dtc)_2$ and $Hg_2(ClO_4)_2$ as described previously [8]. Elemental mercury was removed by filtration and after suitable dilution, the solution was injected into the electrospray mass spectrometer. Figure 1(a) shows the resulting mass spectrum at a low ion source energy, B1 voltage = 30 V (see 'Experimental'). The peak at *m/z* 846 corresponds to $[Hg_2(Et_2dtc)_3]^+$ and that at *m/z* 1343 is due to $[Hg_3(Et_2dtc)_5]^+$. Figure 1(b) shows the ES mass spectrum of the same solution at a higher ion source energy (B1 = 50 V). The relative intensities of the peaks are markedly different showing that $[Hg_3(Et_2dtc)_5]^+$ readily loses a $Hg(Et_2dtc)_2$ fragment by collisionally activated decomposition within the ion source to give the daughter ion at *m/z* 846 No peaks were observed at lower *m/z* values (to *m/z* 200) corresponding to doubly charged cations. Thus the first result of this ESMS study is to confirm that the solution containing species stoichiometrically equivalent to $[Hg_3(Et_2dtc)_4](ClO_4)_2$ is in fact a mixture of compounds, as deduced from electrochemical studies, but the identities of components are surprising. Previous studies [7, 8] have shown this system to be labile on the NMR timescale and this suggested that addition of further $Hg(Et_2dtc)_2$ should increase the concentration of $[Hg_3(Et_2dtc)_5]^+$ (*m/z* 1343), since this can be regarded as $[Hg_2(Et_2dtc)_3]^+ + Hg(Et_2dtc)_2$. In fact, addition of extra $Hg(Et_2dtc)_2$ does increase the relative intensity of the peak at *m/z* 1343, but it also gives rise to a new peak at *m/z* 1840 (Fig. 1(c)) which is due to $[Hg_4(Et_2dtc)_7]^+$ (i.e. $[Hg_3(Et_2dtc)_5]^+ + Hg(Et_2dtc)_2$). This peak is always weak at low ion source energies and disappears when the B1 voltage exceeds 40 V, but no new peaks appear in the mass spectrum. This shows that $[Hg_4(Et_2dtc)_7]^+$ is very unstable towards loss of $Hg(Et_2dtc)_2$ units to give the ions at *m/z* 846 and 1343. Since the relative intensities of the peaks vary with B1 voltage, these observations also emphasise that the relative intensities of peaks in the ES mass spectra are not a measure of the relative concentrations of the species in solution. At a stoichiometric composition of $[Hg_3(Et_2dtc)_4](ClO_4)_2 + 2Hg(Et_2dtc)_2$ (which is equivalent to $[Hg_5(Et_2dtc)_8](ClO_4)_2$) the ES mass spectrum shows only the same three peaks. A sample of solid $[Hg_5(Et_2dtc)_8](ClO_4)_2$, prepared as described previously [7], was dissolved in dichloromethane and after suitable dilution was injected into the electrospray mass spectrometer. Its ES mass spectrum also showed the same three peaks at *m/z* 846, 1343 and 1840.

Similar experiments were carried out with the $Hg(pipdtc)_2$ system. As noted earlier, this system is qualitatively similar to the diethyldithiocarbamate system in that it forms mercury-rich species upon electrochemical oxidation at a mercury electrode, or by

TABLE 1 ES mass spectral data

Mixture	Ions observed (*m/z*)
$[Hg_3(Et_2dtc)_4](ClO_4)_2$	$[Hg_2(Et_2dtc)_3]^+$ (846); $[Hg_3(Et_2dtc)_5]^+$ (1343)
$[Hg_3(Et_2dtc)_4](ClO_4)_2 + Hg(Et_2dtc)_2$	$[Hg_2Et_2dtc)_3]^+$ (846); $[Hg_3(Et_2dtc)_5]^+$ (1343); $[Hg_4(Et_2dtc)_7]^+$ (1840)
$[Hg_5(Et_2dtc)_8](ClO_4)_2$	$[Hg_2(Et_2dtc)_3]^+$ (846); $[Hg_3(Et_2dtc)_5]^+$ (1343); $[Hg_4(Et_2dtc)_7]^+$ (1840)
$[Hg_4(pipdtc)_6](ClO_4)_2$	$[Hg_2(pipdtc)_3]^+$ (882), $[Hg_3(pipdtc)_5]^+$ (1403)
$Cd(Et_2dtc)_2 + Hg_2(ClO_4)_2$	$[Cd_2(Et_2dtc)_2(OAc)]^+$ (581); $[Cd_2(Et_2dtc)_3]^+$ (670), $[CdHg(Et_2dtc)_3]^+$ (758), $[Hg_2(Et_2dtc)_3]^+$ (846), $[Cd_3(Et_2dtc)_5]^+$ (1078); $[Cd_2Hg(Et_2dtc)_5]^+$ (1166); $[CdHg_2(Et_2dtc)_5]^+$ (1254); $[Hg_3(Et_2dtc)_5]^+$ (1343); $[Cd_4(Et_2dtc)_7]^+$ (1488), $[Cd_3Hg(Et_2dtc)_7]^+$ (1576); $[Cd_2Hg_2(Et_2dtc)_7]^+$ (1664), $[CdHg_3(Et_2dtc)_7]^+$ (1752)
$[Hg_5(Et_2dtc)_8](ClO_4)_2 + Hg(chx_2dtc)_2$	$[Hg_2(Et_2dtc)_3]^+$ (846), $[Hg_2(Et_2dtc)_2(chx_2dtc)]^+$ (954), $[Hg_2(Et_2dtc)(chx_2dtc)_2]^+$ (1062), $[Hg_3(Et_2dtc)_5]^+$ (1343), $[Hg_3(Et_2dtc)_4(chx_2dtc)]^+$ (1451), $[Hg_3(Et_2dtc)_3(chx_2dtc)_2]^+$ (1559); $[Hg_3(Et_2dtc)_2(chx_2dtc)_3]^+$ (1667)
$[Hg_5(Et_2dtc)_8](ClO_4)_2 + Cd(Pr_2dtc)_2$	$[Cd_2(Et_2dtc)_3]^+$ (670), $[Cd_2(Et_2dtc)_2(Pr_2dtc)]^+$ (698), $[Cd_2(Et_2dtc)(Pr_2dtc)_2]^+$ (726), $[Cd_2(Pr_2dtc)_3]^+$ (754), $[CdHg(Et_2dtc)_2(Pr_2dtc)]^+$ (786), $[CdHg(Et_2dtc)(Pr_2dtc)_2]^+$ (814), $[CdHg(Pr_2dtc)_3]^+$ (842); $[Hg_2(Et_2dtc)(Pr_2dtc)_2]^+$ (902); $[Hg_2(Pr_2dtc)_3]^+$ (930); $[Cd_3(Et_2dtc)_5]^+$ (1078); $[Cd_3(Et_2dtc)_4(Pr_2dtc)]^+$ (1106), $[Cd_3(Et_2dtc)_3(Pr_2dtc)_2]^+$ (1134); $[Cd_3(Et_2dtc)_2(Pr_2dtc)_3]^+$ (1162), $[Cd_3(Et_2dtc)(Pr_2dtc)_4]^+$ (1190), $[Cd_3(Pr_2dtc)_5]^+$ (1218), $[Cd_2Hg(Et_2dtc)_2(Pr_2dtc)_3]^+$ (1250), $[Cd_2Hg(Et_2dtc)(Pr_2dtc)_4]^+$ (1278); $[Cd_2Hg(Pr_2dtc)_5]^+$ (1307), $[CdHg_2(Et_2dtc)_2(Pr_2dtc)_3]^+$ (1340), $[CdHg_2(Et_2dtc)(Pr_2dtc)_4]^+$ (1367), $[CdHg_2(Pr_2dtc)_5]^+$ (1395), $[Hg_3(Et_2dtc)(Pr_2dtc)_4]^+$ (1455); $[Hg_3(Pr_2dtc)_5]^+$ (1483)
$Pb(Et_2dtc)_2 + Hg_2(ClO_4)_2$	$[Hg_2(Et_2dtc)_3]^+$ (846), $[Hg_3(Et_2dtc)_5]^+$ (1343)
$Cd(Et_2dtp)_2 + Hg_2(ClO_4)_2$	$[Cd_2(Et_2dtp)_3]^+$ (781); $[CdHg(Et_2dtp)_3]^+$ (869); $[Hg_2(Et_2dtp)_3]^+$ (957), $[Cd_3(Et_2dtp)_5]^+$ (1263); $[CdHg_2(Et_2dtp)_4(OAc)]^+$ (1313), $[Cd_2Hg(Et_2dtp)_5]^+$ (1351); $[Hg_3(Et_2dtp)_4(OAc)]^+$ (1401); $[CdHg_2(Et_2dtp)_5]^+$ (1439), $[Hg_3(Et_2dtp)_5]^+$ (1527)

reaction with Hg(I), but the overall stoichiometry is slightly different [12]. The ES mass spectrum of a solution formed by reacting $Hg(pipdtc)_2$ with $Hg_2(ClO_4)_2$ shows a strong peak assigned to $[Hg_2(pipdtc)_3]^+$ (*m/z* 882) and a weak peak due to $[Hg_3(pipdtc)_5]^+$ (*m/z* 1403). Addition of $Hg(pipdtc)_2$ to the solution increased the relative intensity of the peak at *m/z* 1403. Thus the $Hg(pipdtc)_2$ system produces the same types of ions in solution as the $Hg(Et_2dtc)_2$ system, even though previous studies had indicated some differences between them.

Before proceeding further it is worth considering the above results and their relationship to previous studies. It is known that these systems are labile and equilibrium concentrations of species are readily altered by changing the conditions. For example, solutions which behave electrochemically as $[Hg_3(Et_2dtc)_4]^{2+}$ crystallise to give $[Hg_5(Et_2dtc)_8]^{2+}$ and $Hg(ClO_4)_2$.

$$2[Hg_3(Et_2dtc)_4](ClO_4)_2 \longrightarrow [Hg_5(Et_2dtc)_8](ClO_4)_2 + Hg(ClO_4)_2$$

When the solid $[Hg_5(Et_2dtc)_8](ClO_4)_2$ is redissolved, it behaves electrochemically as a mixture of $[Hg_3(Et_2dtc)_4]^{2+}$ and $Hg(Et_2dtc)_2$.

$$[Hg_5(Et_2dtc)_8](ClO_4)_2 \longrightarrow [Hg_3(Et_2dtc)_4](ClO_4)_2 + 2Hg(Et_2dtc)_2$$

Thus the conclusion was that $[Hg_3(Et_2dtc)_4]^{2+}$ is the thermodynamically favoured species and there were no previous indications to suggest that $[Hg_3(Et_2dtc)_4]^{2+}$ itself is in fact a mixture of single charged species. All of the ions detected by ESMS are of the form $\{[Hg(Et_2dtc)]^+ + nHg(Et_2dtc)_2\}$ and these can be rationalised by equilibria such as

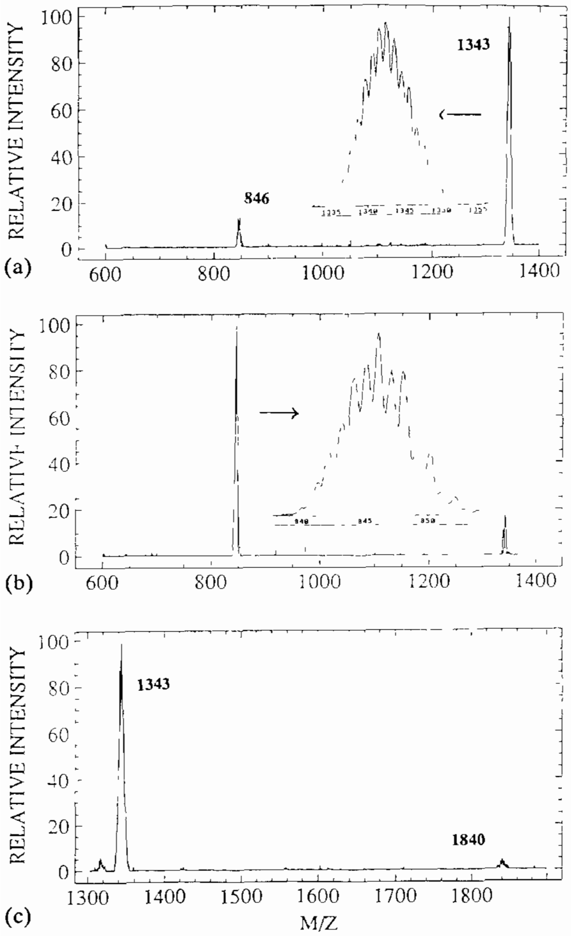

Fig 1. (a) ES mass spectra of a solution of composition $[Hg_3(Et_2dtc)_4](ClO_4)_2$ at a B1 voltage of 30 V. (b) Same solution at B1 = 50 V. (c) Same solution after addition of $Hg(Et_2dtc)_2$, B1 = 30 V

$$[Hg_3(Et_2dtc)_4]^{2+} \rightleftharpoons [Hg(Et_2dtc)]^+ + [Hg_2(Et_2dtc)_3]^+$$

$$2[Hg_2(Et_2dtc)_3]^+ \rightleftharpoons [Hg(Et_2dtc)]^+ + [Hg_3(Et_2dtc)_5]^+$$

etc. which minimise the charge on each cation, and addition of extra $Hg(Et_2dtc)_2$ to the system would obviously favour the higher members of the series. $[Hg(Et_2dtc)]^+$ itself is not observed in the ES mass spectrum, but we believe there are good reasons for this. The cation is effectively coordinatively unsaturated and would readily acquire an acetate ligand from the mobile phase used in the ES mass spectrometer to give neutral $Hg(Et_2dtc)(OAc)$ which would be undetected in this experiment. Addition of acetate (or substitution by acetate for other anionic ligands) is a common phenomenon in ESMS. For example, species such as $[Hg(PPh_3)_2]^{2+}$ appear in the ES mass spectrum as the mono cations $[Hg(PPh_3)_2(OAc)]^+$ [23]. As noted above, uncharged species, such as $Hg(Et_2dtc)_2$ itself, are not detected so the true complexity of the solutions is probably even greater than revealed by ESMS.

Analogous reasoning may be applied to explain the $Hg(pipdtc)_2$ system which gave slightly different stoichiometry for its mercury-rich cation in both solution (electrochemistry) and the solid state (crystallography) [12]. It also gives ions of the type $\{[Hg(pipdtc)]^+ + nHg(pipdtc)_2\}$ (i.e. $[Hg_2(pipdtc)_3]^+$ and $[Hg_3(pipdtc)_5]^+$), but there is a noticeable decrease in the relative intensities of the peak due to $[Hg_3(pipdtc)_5]^+$ which suggests that the equilibria favour $[Hg(pipdtc)]^+$ and $[Hg_2(pipdtc)_3]^+$ rather than the higher members, both in solution and in the solid state, presumably for steric reasons.

It will be seen that all the cations observed throughout this paper can be regarded as $\{[M(R_2dtc)]^+ + nM(R_2dtc)_2\}$ (M = Hg, Cd) and it appears that the $[M(R_2dtc)]^+$ moiety is the fundamental species and the additional $M(R_2dtc)_2$ groups act as ligands towards this cation.

The above concept is usefully extended to rationalise the mercury/cadmium dithiocarbamate system where we have shown [9] that mixed mercury/cadmium cationic species are generated by the interaction of $Cd(Et_2dtc)_2$ and one mole of $Hg_2(ClO_4)_2$, or alternatively they may be prepared via the mercury electrode oxidation process occurring in $Cd(Et_2dtc)_2$ solutions. Electrochemical measurements have also shown rapid exchange of dithiocarbamate ligands occurs between cadmium and mercury and the average empirical formula of the material in solution was deduced to be $[Cd_2Hg(Et_2dtc)_4](ClO_4)_2$, analogous to the mercury-rich solution of composition $[Hg_3(Et_2dtc)_4](ClO_4)_2$.

Figure 2(a)–(c) shows the ES mass spectra for such a solution at mass ranges which have been selected to overlap in order to show the relative intensities of all related peaks. The peaks in the lower mass range at *m/z* 581, 670, 758 and 846 correspond to $[Cd_2(Et_2dtc)_2(OAc)]^+$, $[Cd_2(Et_2dtc)_3]^+$, $[CdHg(Et_2dtc)_3]^+$ and $[Hg_2(Et_2dtc)_3]^+$, respectively. In the intermediate mass range the strong peaks at *m/z* 1078, 1166, 1254 and 1343 are assigned to $[Cd_3(Et_2dtc)_5]^+$, $Cd_2Hg(Et_2dtc)_5]^+$, $[CdHg_2(Et_2dtc)_5]^+$ and $[Hg_3(Et_2dtc)_5]^+$, respectively. The weak peaks in the higher mass range are assigned to $[Cd_4(Et_2dtc)_7]^+$ (*m/z* 1488), $[Cd_3Hg(Et_2dtc)_7]^+$ (*m/z* 1576), $[Cd_2Hg_2(Et_2dtc)_7]^+$ (*m/z* 1664) and $[CdHg_3(Et_2dtc)_7]^+$ (*m/z* 1752). A peak due to $[Hg_4(Et_2dtc)_7]^+$ (*m/z* 1839) was not detectable for this solution since the concentration of mercury was only half that of cadmium, so the concentration of this species would be very low. These results show that exactly the same types of cation (i.e. $\{[M(dtc)^+ + nM(dtc)_2\}$), and no significant quantities of other metal containing species, are generated in the

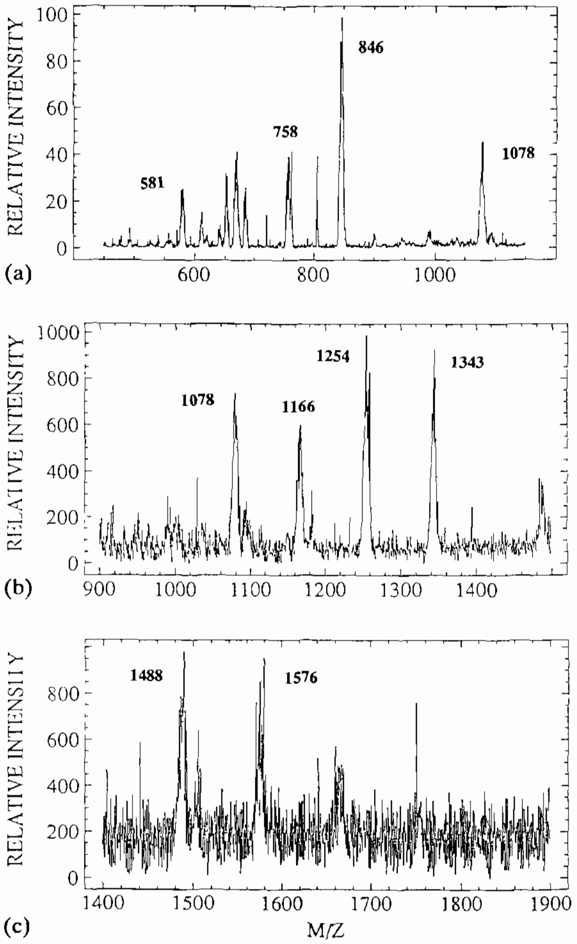

Fig. 2. ES mass spectra of a solution of composition $[Cd_2Hg(Et_2dtc)_4](ClO_4)_2$ (B1 = 30 V) at different *m/z* ranges: (a) dimetal species; (b) trimetal species; (c) tetrametal species.

mixed metal system and that mercury and cadmium are interchangeable in the metal-rich dithiocarbamate cations. It should be emphasised that these systems undergo exchange at room temperature at rates which are fast on the NMR timescale and there would be little prospect of identifying all these species in solution by multi-NMR methods.

We have shown by multi-NMR methods [25] that rapid ligand exchange occurs between different $Hg(R_2dtc)_2$ or $Cd(R_2dtc)_2$ compounds. The above results suggest that a great deal of information may be gained if ligand exchange reactions are investigated in the metal-rich dithiocarbamate cations by using ESMS. In studies of exchange reactions it was convenient to use solid $[Hg_5(Et_2dtc)_8](ClO_4)_2$ as the source of the metal-rich cations.

Figure 3 shows the ES mass spectrum of a dichloromethane solution of $[Hg_5(Et_2dtc)_8](ClO_4)_2$ to which has been added some $Hg(chx_2dtc)_2$ ($chx_2dtc = (c\text{-}C_6H_{11})_2dtc$). Figure 3(a) covers the *m/z* range appropriate for the dimercury species and peaks assigned to

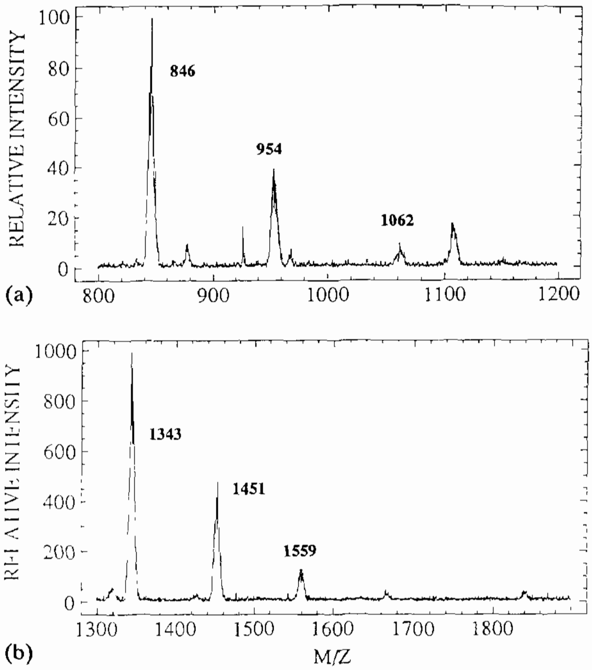

Fig. 3. ES mass spectra of a solution of $[Hg_5(Et_2dtc)_8](ClO_4)_2$ with added $Hg(chx_2dtc)_2$ (B1 = 30 V) at different *m/z* ranges: (a) dimetal species, (b) trimetal species.

$[Hg_2(Et_2dtc)_3]^+$ (*m/z* 846), $[Hg_2(Et_2dtc)_2(chx_2dtc)]^+$ (*m/z* 954) and $[Hg_2(Et_2dtc)(chx_2dtc)_2]^+$ (*m/z* 1062) can be seen. A peak due to $[Hg_2(chx_2dtc)_3]^+$ (*m/z* 1170) is not observed and the peak at *m/z* 1107 is not identified. Figure 3(b) covers the mass range for trimercury species and peaks due to $[Hg_3(Et_2dtc)_5]^+$ (*m/z* 1343), $[Hg_3(Et_2dtc)_4(chx_2dtc)]^+$ (*m/z* 1451), $[Hg_3(Et_2dtc)_3(chx_2dtc)_2]^+$ (*m/z* 1559) and $[Hg_3(Et_2dtc)_2(chx_2dtc)_3]^+$ (*m/z* 1667) are observed together with a peak at *m/z* 1840 which is due to $[Hg_4(Et_2dtc)_7]^+$. No peak due to $[Hg_3(chx_2dtc)_5]^+$ (*m/z* 1773) was detected. Addition of further $Hg(chx_2dtc)_2$ did not significantly alter the relative intensities of the peaks, so the decrease in relative intensities as the proportion of dicyclohexyldithiocarbamate increases in the cation is apparently real and may be related to steric effects similar to those discussed earlier.

In an attempt to illustrate the existence of completely global exchange between metals and ligands, $[Hg_5(Et_2dtc)_8](ClO_4)_2$ was reacted with an excess of $Cd(n\text{-}Pr_2dtc)_2$ in dichloromethane solution. The ES mass spectrum of this solution is shown in Fig. 4; Fig. 4(a) shows the *m/z* region appropriate for dimetal species and Fig. 4(b) that for trimetal species and data are summarised in Table 1. Almost all of the possible combinations of metal and ligand are observed for the dimetal species $[(Cd, Hg)_2(Et_2dtc)_x(Pr_2dtc)_{3-x}]^+$, the exceptions being $[CdHg(Et_2dtc)_3]^+$ (*m/z* 758) and $[Hg_2(Et_2dtc)_3]^+$ (*m/z* 846) which are obscured by much stronger peaks, and the peak due to $[Cd_2(Et_2dtc)_3]^+$

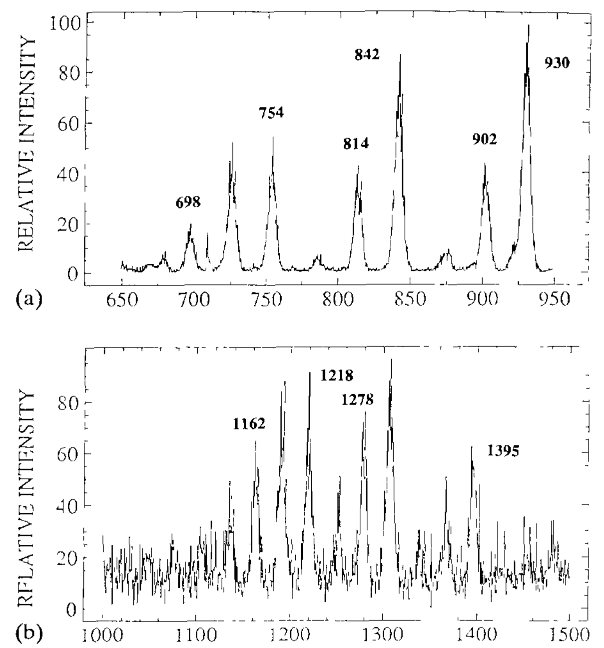

Fig. 4 ES mass spectra of a solution of $[Hg_5(Et_2dtc)_8](ClO_4)_2$ with added $Cd(n\text{-}Pr_2dtc)_2$ (B1 = 30 V) at different *m/z* ranges (a) *m/z* 650–950; (b) *m/z* 1000–1500.

(*m/z* 670) is very weak due to the relatively low concentration of diethyldithiocarbamate. The signal to noise ratio in Fig. 4(b) is worse than in Fig. 4(a) because the ion current is divided between twenty-four possible trimetal species. Fourteen of these species can be clearly identified (Table 1) and the remainder are expected to be weak because they contain large proportions of mercury or diethyldithiocarbamate (or both) which are the least abundant components in the solution, but there is no reason to doubt their existence in the solution.

Electrochemical studies of the oxidation processes which occur when solutions of $Pb(Et_2dtc)_2$ are oxidised at a mercury electrode suggest the formation of mixed lead/mercury cations [10]. However the solids which crystallised from these solutions were $[Hg_5(Et_2dtc)_8](ClO_4)_2$ and $Pb(ClO_4)_2$, suggesting that the dithiocarbamate ligand preferred to coordinate to mercury. ESMS experiments with solutions of $Pb(Et_2dtc)_2$ and $Hg_2(ClO_4)_2$, similar to those described above for the cadmium system, confirmed the different behaviour of the lead/mercury system. The only species observed in the ES mass spectrum were $[Hg_2(Et_2dtc)_3]^+$ and $[Hg_3(Et_2dtc)_5]^+$, showing that the mixed lead/mercury species postulated on the basis of electrochemical experiments are short lived and are only detectable at the mercury electrode–$Hg(Et_2dtc)_2$ solution interface.

Dithiophosphate systems

The oxidative electrochemistry of metal dithiophosphate systems at mercury electrodes or their reaction with $Hg_2(ClO_4)_2$ have not been investigated, so there is little indication in the literature of the existence of mercury-rich dithiophosphate systems analogous to the dithiocarbamates. However, since the general chemistry of mercury and cadmium dithiophosphates closely resembles that of the dithiocarbamates [1, 2], it seems reasonable to expect metal-rich cationic complexes to exist. In order to investigate this possibility, the ES mass spectrum of a solution generated by reacting $Cd(Et_2dtp)_2$ with one mole of $Hg_2(ClO_4)_2$ in dichloromethane was examined. It shows families of peaks similar to those observed in the mixed dithiocarbamate system. Thus peaks at *m/z* 781, 869 and 957 are due to $[Cd_2(Et_2dtp)_3]^+$, $[CdHg(Et_2dtp)_3]^+$ and $[Hg_2(Et_2dtp)_3]^+$, respectively, and at higher *m/z* values peaks are observed for all members of the series $[Cd_xHg_y(Et_2dtp)_5]^+$ ($x+y=3$). Relevant data are presented in Table 1. Some additional peaks are noted which contain acetate replacing a dithiophosphate ligand and these are also detailed in Table 1. The ES mass spectrum demonstrates that an extensive chemistry of metal-rich dithiophosphate cations does indeed exist.

Conclusions and general discussion

The results presented in this paper confirm that ES mass spectrometry is a powerful technique for investigating labile ionic species in solution, and especially well suited to the study of charged polynuclear species in solution.

The ES mass spectral data presented here gives information on the species in the solutions which reveals a complexity, and order, which was previously unsuspected. The formulae of all the cations observed are of the general type $\{[M(R_2dtc)]^+ + nM(R_2dtc)_2\}$ ($n = 1$–3) and since adjacent members in each series differ by the addition of a neutral $M(R_2dtc)_2$ unit, the concept arises of $M(R_2dtc)_2$ units behaving as neutral ligands adding to the $[M(R_2dtc)]^+$ cations. Similar structural characteristics are known for octahedral tris(dithiocarbamates) in compounds such as $[Co_2(R_2dtc)_5]^+$ [26–28] and analogous rhodium [29], ruthenium [30] and osmium [31] compounds, which in the solid state are linked together by various arrangements of shared sulfur atoms, and which may be regarded as a neutral metal tris(dithiocarbamate) coordinated to a metal(III) bis(dithiocarbamato) cation.

It is tempting to draw analogies between the ligand-like behaviour of the tetrahedral $M(R_2dtc)_2$ unit and the well known coordination chemistry of the tetrahedral $[MS_4]^{2-}$ anions (M = Mo, W) [32, 33]. These anions give rise to much polynuclear chemistry in which they can act as the central unit, as in $[Cl_2Fe(MoS_4)FeCl_2]^{2-}$ [34], or as peripheral ligands as in $[(WS_4)WS(WS_4)]^{2-}$ [35]. Both tetrahedral species have the same arrangement of sulfur atoms about the central metal, and on the basis of the evidence presented here, both give rise to polynuclear systems. A major difference is the lability of the mercury and cadmium dithiocarbamates, but interesting possibilities also arise with non-labile dithiocarbamates.

Experimental

The mercury, cadmium and lead dithiocarbamates [6–12], cadmium dithiophosphates [25] and $[Hg_5(Et_2dtc)_8](ClO_4)_2$ [8] were prepared as described previously [6–12, 25].

Electrospray mass spectra were recorded by using a VG Bio-Q triple quadrupole mass spectrometer (VG Bio-Tech, Altrincham, Ches., UK) with a water/methanol/acetic acid (50:50:1%) mobile phase. The compounds were dissolved in AR grade dichloromethane or methanol (2 mM) and a portion of this solution was diluted 1:10 with methanol. The diluted solution was injected directly into the spectrometer via a Rheodyne injector using a Phoenix 20 micro LC syringe pump to deliver the solution to the vaporisation nozzle of the electrospray ion source at a flow rate of 3 μl min^{-1}. Voltages at the first skimmer electrode (B1) were varied between 100 V and the minimum possible consistent with retaining a stable ion jet. This varies from time to time but is usually in the range 25–30 V. Increasing the B1 voltage enhances the formation of daughter ions by collisions with solvent molecules within the ion source. It should be noted that increasing the concentration of solute does not increase the signal intensity for weak peaks, in fact it usually causes signal suppression.

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