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Molecular Weight and Mercury-199 NMR Studies on Mercury-rich Cations Produced from Mercury(II) Dithiocarbamates

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Abstract

The mercury-rich dithiocarbamate cations $[Hg_3(R_2dtc)_4]^{2+}$ and $[Hg_4(pipdtc)_6]^{2+}$ (R = Et, Bz; pip = piperidyl; dtc = dithiocarbamate) have been shown by a polarographic method to be partially dissociated at the $\sim 2 \times 10^{-4}$ M concentration level in dichloromethane solution. However, for approximately 10^{-2} M solutions of $[Hg_3(R_2dtc)_4]^{2+}$ in dichloromethane, mercury-199 NMR studies over a wide temperature range are more consistent with the presence of higher oligomers such as $[Hg_6(R_2dtc)_8]^{4+}$.

Introduction

Mercury(II) dithiocarbamate complexes $Hg(R_2dtc)_2$ (R = alkyl or aryl group) have been known for many years. A number of reports have appeared concerning their chemical, physical, spectroscopic and electrochemical properties [1–7]. Structural studies [8–12] reveal that they may be monomeric or dimeric in the solid state. In dilute solution (10^{-3}–10^{-4} M) in organic solvents they are predominantly monomeric, but may be partly associated in more concentrated solutions [13, 14].

In a recent paper [15] we described how the oxidation of a mercury electrode in the presence of $Hg(Et_2dtc)_2$ gave in solution a complex with the empirical formula $[Hg_3(Et_2dtc)_4]^{2+}$. The solid isolated from solutions was shown by X-ray crystallography to be $[Hg_5(Et_2dtc)_8](ClO_4)_2$ which redissolves in CH_2Cl_2 to behave as a mixture of $[Hg_3(Et_2dtc)_4]^{2+}$ and $2Hg(Et_2dtc)_2$. Mercury-199 NMR signals were not observed for $[Hg_3(Et_2dtc)_4]^{2+}$ but the average mercury-199 chemical shift for $[Hg_3(Et_2dtc)_4]^{2+}$ was calculated from exchange reactions involving addition of free $[Et_2dtc]^-$ [15]. We have also found that $Hg(Bz_2dtc)_2$ (Bz = benzyl) gives behaviour exactly analogous to that of $Hg(Et_2dtc)_2$, but that oxidation of the mercury electrode in the presence of $Hg(pipdtc)_2$ (pip = piperidyl) produces in solution a mercury-rich product with the different empirical formula $[Hg_4(pipdtc)_6]^{2+}$, and the isolated solid was shown by X-ray crystallography to be polymeric $[Hg_2(pipdtc)_3]^+$ [16].

In this paper we describe a polarographic method to determine the molecular weights of the mercury-rich species in solution and mercury-199 NMR spectra for these new classes of mercury-rich cations are reported for the first time.

Results and Discussion

Electrochemical Studies

It has been shown [15, 16] that the polymeric mercury-rich cations are generated by exhaustive oxidation of mercury electrodes in the presence of the appropriate $Hg(dtc)_2$ according to eqns: (1) and (2) although these studies do not preclude multiples or fractions of these formulations.

$$Hg + 2Hg(R_2dtc)_2 \longrightarrow [Hg_3(R_2dtc)_4]^{2+} + 2e^- \qquad (1)$$

(R = Et, Benzyl)

$$Hg + 3Hg(pipdtc)_2 \longrightarrow [Hg_4(pipdtc)_6]^{2+} + 2e^- \qquad (2)$$

We have also shown [15, 16] that reduction of the polymeric cations produces elemental mercury and $Hg(dtc)_2$ which is then further reduced according to eqns. (3) and (4)

$$[Hg_3(R_2dtc)_4]^{2+} + 2e^- \rightleftharpoons Hg + 2Hg(R_2dtc)_2 \qquad (3a)$$

$$Hg(R_2dtc)_2 + 2e^- \rightleftharpoons Hg + 2R_2dtc^- \qquad (3b)$$

$$[Hg_4(pipdtc)_6]^{2+} + 2e^- \rightleftharpoons Hg + 3Hg(pipdtc)_2 \qquad (4a)$$

$$Hg(pipdtc)_2 + 2e^- \rightleftharpoons Hg + 2pipdtc^- \qquad (4b)$$

The concentration of $Hg(dtc)_2$ at the electrode surface generated by processes (3a) and 4(a), and hence the limiting currents for the reduction of $Hg(dtc)_2$

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generated by processes (3b) and (4b), is determined by the diffusion coefficients of the polymeric cations, not the diffusion coefficients of $Hg(dtc)_2$ themselves. This provides a means of estimating the approximate molecular weight of a species in solution using d.c. polarographic techniques [17–19]. If the limiting currents for processes (3b) and (4b) are compared with those for the reduction of the original solutions of $Hg(dtc)_2$ themselves, the ratio of the limiting currents will provide an estimate of the ratio of the diffusion coefficients of the polymeric cations to those of $Hg(dtc)_2$ using the Ilkovic equation [19]. Diffusion coefficients (D) are related to molecular weights (M) by the Stokes–Einstein equation [18, 19].

$$D_1/D_2 = (M_2/M_1)^{1/3} \qquad (5)$$

where 1 and 2 refer to the mercury-rich cations and $Hg(dtc)_2$ respectively. This comparison of the limiting currents does not provide highly accurate estimates of the average molecular weights because small errors in the measurement of the ratios of the limiting currents leads to large variations in the calculated molecular weight and because of approximations involved in using charged non-spherical molecules, but it is quite sufficient to distinguish between possible oligomers of a species of large molecular weight.

Comparison of the diffusion controlled limiting currents described above for 5×10^{-4} M solutions of $Hg(Bz_2dtc)_2$ and the $[Hg_3(Bz_2dtc)_4]^{2+}$ generated from it by oxidation of a mercury electrode in dichloromethane (0.1 M Bu_4NClO_4) demonstrates that the reduction wave for $Hg(Bz_2dtc)_2$ in the latter case is only 86% (average of many determinations) of the former. This gives a ratio of diffusion coefficients of 1.35 leading to an approximate molecular weight for the mercury-rich species of 1840. The molecular weight of $[Hg_3(Bz_2dtc)_4]^{2+}$ is 1690 and thus the species in solution at this concentration is mainly $[Hg_3(Bz_2dtc)_4]^{2+}$ rather than $[Hg_6(Bz_2dtc)_8]^{4+}$ or other oligomers. The result for the similar $[Hg_3(Et_2dtc)_4]^{2+}$ species is a ratio of 92% between the diffusion currents leading to an average molecular weight of about 800, compared with that of about 1200 for $[Hg_3(Et_2dtc)_4]^{2+}$. In this case there is probably some dissociation, but higher oligomers are even more definitely excluded for this compound at this concentration. Similar comparisons of the diffusion controlled limiting currents of $Hg(pipdtc)_2$ and $[Hg_4(pipdtc)_6]^{2+}$ demonstrate that the latter is 90% of the former which leads to an approximate molecular weight for the mercury-rich species of 987. The molecular weight of $[Hg_4(pipdtc)_6]^{2+}$ is 1764 and hence there is considerable dissociation in this case.

Mercury-199 NMR Studies of the Mercury-rich Species

In earlier studies [15] mercury-199 NMR signals could not be observed for solutions of $[Hg_3(Et_2dtc)_4](ClO_4)_2$ produced by oxidative controlled potential electrolysis at a mercury pool electrode in dichloromethane, because the solutions were too dilute. Considerable problems result when the electrolysis is performed at the higher concentrations necessary for the detection of mercury-199 NMR signals. In the case of the $Hg(Et_2dtc)_2$ system for example, although some $[Hg_3(Et_2dtc)_4]^{2+}$ is generated, unidentified precipitates are also formed and the oxidation is not quantitative. However, pure concentrated solutions of $[Hg_3(R_2dtc)_4](ClO_4)_2$ and $[Hg_4(pipdtc)_6](ClO_4)_2$ have now been synthesized from the reaction of $Hg(dtc)_2$ with mercury(I) perchlorate.

The mercury-199 NMR spectrum of a solution of $[Hg_3(Et_2dtc)_4](ClO_4)_2$ in dichloromethane at room temperature (Fig. 1(a)) consists of a singlet at ~δ 307 ppm ($w_{1/2}$ ~50 Hz) indicating that the species is undergoing moderately fast exchange. This position is very close to that calculated previously [15] from exchange studies (δ 315 ± 4 ppm). On lowering the temperature (Fig. 1(b) and (c)), the resonance broadens further and gradually shifts to higher frequency and at −60 °C almost no signal is visible. At −70 °C (Fig. 1(d)) three sharp singlets of equal

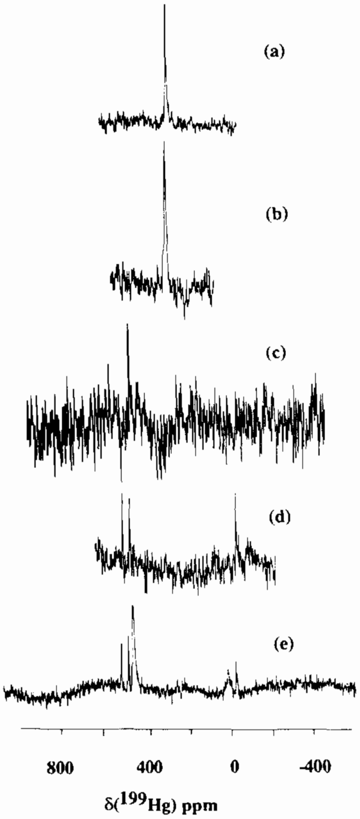
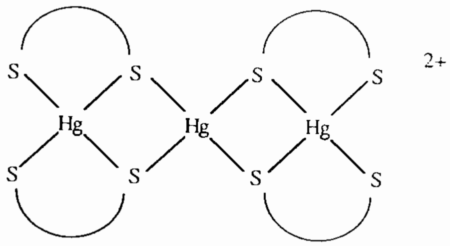


Fig. 1. Mercury-199 NMR spectra of a dichloromethane solution of $[Hg_3(Et_2dtc)_4]^{2+}$ at (a) 0 (b) −20 (c) −50 (d) −70 (e) −90 °C.

intensity are visible at δ 543, δ 509 and δ −27 ppm. At −80 ℃ the NMR spectrum contains a total of five resonances, the three singlets observed previously at −70 ℃ and two new broad signals at δ 485 and δ 14 ppm with relative intensities approximately 2:1, with the more intense resonance at higher frequency. At −90 ℃ (Fig. 1(e)) the intensity of the three singlets decreases with respect to the two broad signals and no further significant changes occur in the appearance of the spectrum at temperatures between −90 and −110 ℃. It should be noted that none of the resonances correspond to that of $Hg(Et_2dtc)_2$ at low temperature (δ 145). The signal at room temperature is at approximately the exchange average of the signals at low temperatures. These changes in the NMR spectrum with temperature are reversible and are accompanied by a colour change from deep yellowish/green at room temperature to very pale yellow at −90 ℃. No precipitation is observed at −90 ℃, despite the high concentration of compound in solution.

The mercury-199 NMR spectra at low temperatures for solutions of $[Hg_3(Et_2dtc)_4]^{2+}$ indicate that there are at least two mercury containing species present. A linear structure based on the $[Hg_3(Et_2dtc)_4]^{2+}$ formulation such as **I** could easily account for the 2:1 intensity spectrum but there is considerable difficulty in proposing a reasonable structure based on $[Hg_3(Et_2dtc)_4]^{2+}$ which would give three non-equivalent mercury atoms. One possibility that might be considered is the weak coordination of a perchlorate anion, as in **II**. However this was ruled out by chlorine-35 NMR spectroscopy which showed the chlorine reasonance of the perchlorate ion to remain sharp over the whole temperature range. Any coordination of the perchlorate ion would broaden its signal considerably, since chlorine-35 is a highly quadrupolar nucleus.



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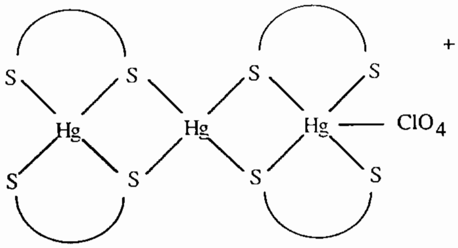

II

It is important to note that the concentrations of the solutions used to determine the molecular weight of the mercury-rich species in solution by electrochemical methods were 5×10^{-4} M, whilst those used for mercury-199 NMR studies were approximately 10^{-2} M, so it is not unreasonable to suggest that further polymerization may occur at the higher concentrations, especially as it is known that this occurs with the simple mercury dithiocarbamates themselves, as noted earlier. Indeed, there is direct evidence for concentration dependence effects, since the oxidation processes of mercury in the presence of both $Hg(Bz_2dtc)_2$ and $Hg(pipdtc)_2$ vary with changes in concentration [15, 16].

Perhaps two $[Hg_3(Et_2dtc)_4]^{2+}$ species, each with a unique central mercury atom, could combine at low temperatures to give a species containing six mercury atoms arranged about an octahedron, with bridging dithiocarbamate ligands linking the structure. It is easy to visualize how 1:1:1 (actually 2:2:2) and 2:1 (actually 4:2) NMR spectra may be obtained, with the unique mercury atoms of the two trimeric units being *cis* or *trans* in the octahedral arrangement respectively. Of course these structures are entirely speculative, but there is no further information that can be obtained to identify the two species which are shown by the NMR spectra to exist at low temperatures.

The mercury-199 NMR spectrum of $[Hg_3(Bz_2dtc)_4]^{2+}$ exhibits a singlet at room temperature and on lowering the temperature changes in the spectrum are observed which are analogous to those described for the diethyldithiocarbamate system, except that at approximately −90 ℃ only two resonances of relative intensity 2:1 are observed. The mercury-199 NMR spectrum for $[Hg_4(pipdtc)_6]^{2+}$ is a singlet over the whole accessible temperature range, although it does shift to higher frequency at lower temperatures. Thus, no information is available from NMR studies on the structure of this complex in solution, since the data indicate that either the mercury atoms are equivalent in the structure in solution or that the complex is labile at all temperatures. All NMR data are given in Table 1.

Experimental

Materials

All solvents and reagents used were of AR grade or better. The electrochemical supporting electrolyte tetrabutylammonium perchlorate, Bu_4NClO_4, was obtained wet with water from Southwestern Analytical Chemicals and was dried under vacuum at 70 ℃. Microanalyses were by AMDEL, Melbourne.

TABLE 1. Mercury-199 NMR data

Compound	δ (^{199}Hg) (ppm)	Temperature (℃)
$Hg_3(Et_2dtc)_4]^{2+}$	307	25
	543(1)	−90
	509(1)	
	485(2)	
	14(1)	
	−27(1)	
$[Hg_3(Bz_2dtc)_4]^{2+}$	269	25
	366(1)	−50
	313(1)	
	−136(1)	
	532(2)	−90
	−21(1)	
$[Hg_4(pipdtc)_6]^{2+}$	278	25

Preparations

Hg(R$_2$dtc)$_2$

These were prepared by a slight modification of the literature method [1, 2] by stirring 1:2 molar proportions of $Hg[NO_3]_2$ and the appropriate Na[dtc] salt in water. The resulting precipitate was filtered, dried and then purified by Soxhlet extraction into dichloromethane. The compounds were characterized by their known mercury-199 NMR spectra [5–7].

$[Hg_3(R_2dtc)_4](ClO_4)_2$ (R = Et, Bz) and $[Hg_4(pipdtc)_6](ClO_4)_2$

Addition of solid $Hg_2[ClO_4]_2 \cdot 4H_2O$ (0.3 mmol) to a dichloromethane solution (30 cm^3) of $Hg(R_2dtc)_2$ (0.60 mmol) with stirring for approximately 12 h resulted in a colour change (yellow to yellow/green) and the deposition of elemental mercury. The solution was filtered and the solids were characterized by microanalytical data. The cations were also generated electrochemically as described previously [15, 16].

Instrumentation

Voltammetric measurements were made with a Princeton Applied Research Corp. (PAR) (Princeton, NJ) Model 174A polarographic analyser with a dropping mercury electrode.

Mercury-199 and chlorine-35 NMR spectra were recorded at 17.76 and 9.70 MHz respectively on a JEOL FX 100 spectrometer. Mercury chemical shifts were referenced against 1 M phenylmercury acetate in Me_2SO_4 [20], high frequency positive convention is used. A JEOL NM 5471 controller was used for temperature control, and temperatures in the probe were measured with a calibrated platinum resistance thermometer.

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