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NMR Studies of Anionic Cadmium and Mercury 1,1-Dithiolate Complexes

BRENDAN F. ABRAHAMS, GEORGE WINTER
Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052 (Australia)
and DAINIS DAKTERNIEKS
Division of Chemical and Analytical Sciences, Deakin University, Geelong, Vic. 3217 (Australia)

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Abstract

Phosphorus-31, cadmium-113 and mercury-199 NMR data in dichloromethane solution indicate formation of anionic species when additional ligand $S\text{-}S^-$ is added to solutions of $M(S\text{-}S)_2$ [$M = Cd$, Hg; $S\text{-}S^- = S_2CO^iPr$, $S_2P(O^iPr)_2$]. The dithiocarbamate analogue $M[S_2CNEt_2]_3^-$ is formed for $M = Cd$ but when $M = Hg$, the complex $Hg[S_2CNEt_2]_2$ is too weak a Lewis acid to add further dithiolate ligands. Variable temperature NMR experiments have been used to study the exchange processes associated with formation, in solution, of a number of novel dithiolate mixed-ligand complexes.

Introduction

$Cd(exa)_2$ ($exa = S_2COEt$) reacts with additional xanthate ion to form the anionic complex, $Cd(exa)_3^-$ [1]. The crystal structure determination of this complex shows the cadmium atom coordinated by five sulphur atoms (from one monodentate and two bidentate xanthate ligands) in a tetragonal pyramidal geometry [2]. The solid state structures of $Cd(moexa)_3^-$ ($moexa = S_2COCH_2CH_2OCH_3$) [3], $Cd(edtc)_3^-$ ($edtc = S_2CNEt_2$) [4] and $Cd(ipdtp)_3^-$ ($ipdtp = S_2P(OPr^i)_2$) [4] are also known and in each case the cadmium atom is coordinated by three chelating dithiolate ligands with an overall geometry about the cadmium atom which is intermediate between octahedral and trigonal prismatic. Of the corresponding mercury complexes, only $Hg(edtc)_3^-$ has been isolated, although the presence of $Hg(exa)_3^-$ [5] and $Hg(buxa)_3^-$ ($buxa = S_2COBu$) [6] in solution has been established using electrochemical techniques. Very little is known concerning the nature of complexes of the type $M(S\text{-}S)_3^-$ (S-S = xanthate, dithiocarbamate and dithiophosphate) in solution and the possibility of mixed-ligand anionic complexes has not been investigated. The study of such complexes is of interest because xanthate, dithiocarbamate and dithiophosphate ligands exhibit different donor ligand strengths. The use of ^{113}Cd and ^{199}Hg NMR spectroscopy is particularly attractive because of the sensitivity of these nuclei to subtle changes in the coordination sphere of these atoms.

We now report the results of an NMR investigation of the species present in dichloromethane solution from the *in situ* reaction of the dithiolate ion $(S\text{-}S)^-$ with the metal bisdithiolate $M(S\text{-}S)_2$ complexes.

Experimental

Nuclear Magnetic Resonance Spectrometry

NMR spectra were recorded on a Jeol FX 100 spectrometer, ^{113}Cd at 22.04 MHz, ^{199}Hg at 17.76 MHz and ^{31}P at 40.26 MHz using external ^7Li lock. ^{113}Cd spectra were referenced against external 4.5 M cadmium nitrate in water; ^{199}Hg spectra against external 1 M phenylmercuric acetate in DMSO, and ^{31}P spectra against external 85% H_3PO_4. Spectra were recorded with complete proton decoupling. Temperatures were maintained using a Jeol NM 5471 controller.

Preparations

The compounds $Cd(ipdtp)_2$ [7], $Hg(ipdtp)_2$ [7], $Cd(edtc)_2$ [8] $Hg(edtc)_2$ [8], and $Hg(ipxa)_2$ [9] were prepared according to literature methods. $Cd(ipxa)_2$ was prepared from $CdCl_2$ in a similar manner to $Hg(ipxa)_2$ and was recrystallized from methanol.

$Ph_3PCH_2Ph(ipxa)$ was prepared by mixing equimolar quantities of K(ipxa) and Ph_3CH_2PhCl in dichloromethane. The KCl precipitate was filtered off and the solution evaporated to dryness. The solid material was recrystallized from acetone. $Ph_3CH_2Ph(edtc)$ was prepared similarly from Na(edtc). $Bu_4N(ipdtp)$ was prepared by mixing Bu_4NBr with K(ipdtp) in ethanol, the KBr removed by filtration, and evaporating the solution to dryness. The solid material was recrystallized from ethanol.

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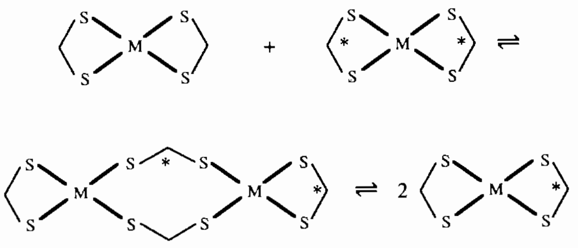
Results and Discussion

Formation of [Cd(ipdtp)$_3$]$^-$

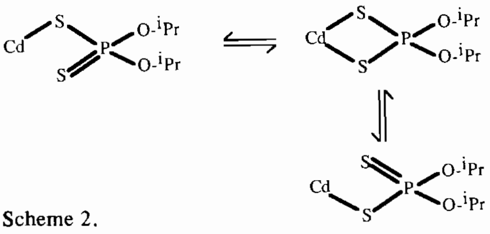
The ^{113}Cd spectrum of a dichloromethane solution of Cd(ipdtp)$_2$ and NBu$_4$(ipdtp) in a 1:1 mole ratio recorded at room temperature shows a single sharp resonance at 329 ppm. Cooling the solution to –20 °C causes the signal to broaden and at –50 °C it becomes a quartet. The magnitude of the coupling constant, 64 Hz, is consistent with two-bond coupling, ^2J-(Cd–P). The position of the quartet varies with temperature. At –70 °C the resonance occurs at 284 ppm and at –95 °C it occurs at 269 ppm. The absence of *J*(Cd–P) coupling above –50 °C indicates intermolecular dithiophosphate exchange which is rapid on the NMR time scale.

The observation of a quartet in the ^{113}Cd spectrum points to the cadmium atom being coordinated by three equivalent dithiophosphate ligands and confirms the formation of Cd(ipdtp)$_3^-$. The ^{31}P spectrum recorded at –50 °C shows a single resonance at 105.7 ppm (cf. 109.5 ppm at 30 °C for K(ipdtp) [7]) accompanied by unresolved ^{113}Cd and ^{111}Cd satellites. NMR data are presented in Table 1. Interestingly, *J*(Cd–P) coupling is not observed for Cd(ipdtp)$_2$, the resonance remaining a singlet [δ(^{113}Cd) 452.7 ppm, δ(^{31}P) 100.39 ppm] even at –90 °C. Although molecular weight data indicate that Cd(ipdtp)$_2$ is essentially dimeric, even in dilute solution [10], it is likely that there is a monomer–dimer equilibrium which causes rapid ligand exchange and precludes *J*(Cd–P) coupling. Scheme 1 shows an exchange process whereby two monomers exchange ligands through a dimeric intermediate.

In Cd(ipdtp)$_3^-$ the three ligands are equivalent which implies either that the dithiolate ligands are static bidentate and the cadmium atom six coordinate or that there is a rapid intramolecular monodentate–bidentate ligand exchange process as depicted in Scheme 2. In such an exchange process at least one sulphur atom from each ligand is always coordinated to the cadmium atom and ensures that *J*(Cd–P) coupling is maintained.



Scheme 1.



Scheme 2.

Formation of [Cd(edtc)$_3$]$^-$

The ^{113}Cd spectrum of a dichloromethane solution of Cd(edtc)$_2$ and Ph$_3$PCH$_2$Ph(edtc) in a 1:1 mole ratio recorded at room temperature consists of a single broad resonance at 296 ppm ($w_{1/2}$ 130 Hz). At –50 °C there are two resonances at 366 and 250 ppm. The resonance at 250 ppm, although broad, is more intense and better resolved than the one at 366 ppm. Cooling the solution to –90 °C sharpens both

TABLE 1. NMR data for various cadmium dithiolate complexes in dichloromethane solution

Complex	δ(^{113}Cd) (ppm)	δ(^{31}P) (ppm)	J(^{113}Cd–^{31}P) (Hz)	Temperature (°C)
Cd(ipxa)$_2$ [a]	223			20
Cd(ipdtp)$_2$	450s	100.2		20
	453s	100.4		–90
Cd(edtc)$_2$	383			20
Cd(ipxa)$_3^-$	329			20
	311			–90
Cd(ipxa)$_2$(ipdtp)$^-$	320	104.6	54	–65
Cd(ipxa)$_2$(edtc)$^-$	341			–40
Cd(ipdtp)$_3^-$	329s			20
	269q	104.5	68	–95
Cd(ipdtp)$_2$(ipxa)$^-$	310t	105.4	59	–65
Cd(ipdtp)$_2$(edtc)$^-$	337t	105.1	49	–100
Cd(edtc)$_3^-$	250			–95
Cd(edtc)$_2$(ipdtp)$^-$	346d	103.5	35	–100

s, singlet; d, doublet; t, triplet. [a] Spectrum recorded on methanol solution.

resonances considerably with the resonance at 250 ppm being approximately twice as intense as the higher frequency resonance which has shifted to 376 ppm. The resonance at 376 ppm is attributed to $Cd(edtc)_2$ and the resonance at 250 ppm to $Cd(edtc)_3^-$. This assignment is supported by the S_2C region of the ^{13}C spectrum, recorded at –90 °C, which indicates the presence of two types of coordinated dithiocarbamates (202.7, 201.3 ppm) as well as uncoordinated dithiocarbamate (191.2 ppm). This implies that $Cd(edtc)_3^-$ is substantially dissociated. This is in agreement with the results of Nieuwpoort and co-workers [8] who established through electrochemical and conductivity studies that $Cd(edtc)_3^-$ shows some degree of dissociation in solution. The observation of a single ^{113}Cd resonance at room temperature indicates that rapid intermolecular dithiocarbamate ligand exchange occurs, resulting in an average resonance for $Cd(edtc)_2$ and $Cd(edtc)_3^-$.

Formation of [Cd(ipxa)$_3$]$^-$

The ^{113}Cd spectrum of a dichloromethane solution of $Cd(ipxa)_2$ and $Ph_3PCH_2Ph(ipxa)$ in a 1:1 mole ratio recorded at room temperature shows a broad resonance at 329 ppm ($w_{1/2}$ 60 Hz). As the temperature is lowered to –40 °C the resonance sharpens; at –60 °C the signal starts to broaden again and at –90 °C it has $w_{1/2}$ of 180 Hz. The observation of a single ^{13}C resonance, (227.2 ppm) in the S_2C region of the spectrum recorded at –90 °C shows that all xanthate ligands in solution are coordinated and equivalent. These observations are consistent with the formation of $Cd(ipxa)_3^-$. Whilst it is difficult to identify the factors responsible for the sharpening and subsequent broadening of the ^{113}Cd resonance, it is likely that they arise from changes in the rate of intramolecular monodentate–bidentate and intermolecular ligand exchange processes.

Mixed Cadmium Xanthate and Dithiophosphate Anionic Complexes

The ^{113}Cd spectrum of a dichloromethane solution of $Cd(ipdtp)_2$ and $Ph_3PCH_2Ph(ipxa)$ in a 1:1 mole ratio recorded at room temperature shows a single broad resonance at 338 ppm ($w_{1/2}$ 70 Hz). Cooling the solution to –10 °C causes further broadening of the signal in addition to the appearance of a weaker signal at 316 ppm. At –40 °C a doublet [327 ppm, ^2J(Cd–P) 59 Hz], a triplet [321 ppm, ^2J(Cd–P) 61 Hz], and a quartet [296 ppm, ^2J(Cd–P) 63 Hz] are observed. Cooling of the solution to –65 °C results in a shift to lower frequency of each of these resonances as well as in the appearance of a singlet at 316 ppm. The chemical shift positions of the quartet and the singlet correspond to resonances previously assigned to $Cd(ipdtp)_3^-$ and $Cd(ipxa)_3^-$ respectively. The stoichiometry of the reactants and the close proximity of the triplet to the resonances for $Cd(ipdtp)_3^-$ and $Cd(ipxa)_3^-$ suggest that the triplet results from formation of $Cd(ipdtp)_2(ipxa)^-$. The doublet is assigned to $Cd(ipdtp)(ipxa)_2^-$. At –90 °C resolution of the singlet, doublet and triplet resonances deteriorate considerably whilst the quartet remains sharp.

It is clear that at room temperature intermolecular xanthate and dithiophosphate ligand exchange is rapid on the NMR time scale and this is responsible for the single time-average resonance at 338 ppm. Observation of J(Cd–P) coupling at –40 °C indicates that intermolecular dithiophosphate ligand exchange is slow relative to the NMR time scale at this temperature. Therefore broadening of the resonances (apart from the quartet) as the temperature is lowered to –90 °C is not associated with intermolecular dithiophosphate exchange. Figure 1 shows the changes in the ^{113}Cd spectra as the temperature is lowered.

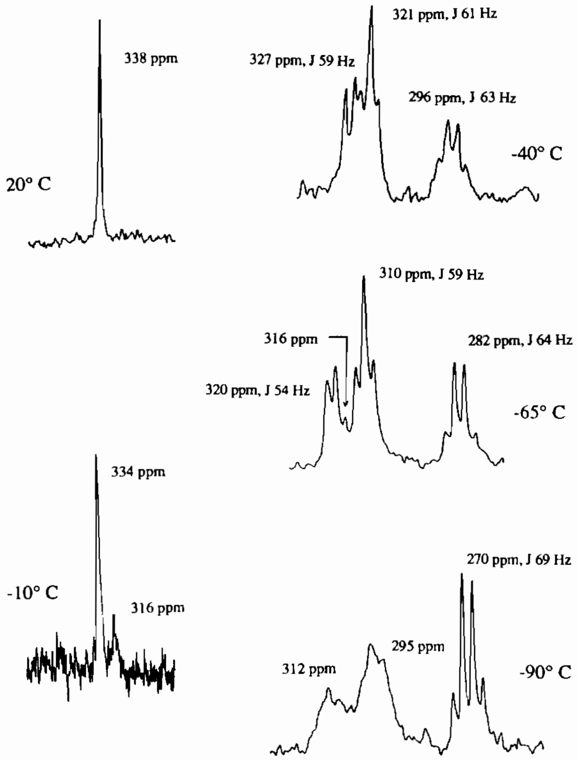


Fig. 1. Variable temperature ^{113}Cd NMR spectra for $Cd(ipdtp)_2 + (Ph_3PhCH_2P)^+(ipxa)^-$ in dichloromethane solution.

There are three main resonances (106.0, 105.1 and 104.6 ppm) in the ^{31}P spectrum recorded at –65 °C. The resonance at 106.0 ppm is assigned to $Cd(ipdtp)_3^-$, and on the basis of relative intensities, the resonances at 105.1 and 104.6 ppm are assigned to $Cd(ipdtp)_2(ipxa)^-$ and $Cd(ipdtp)(ipxa)_2^-$ respectively. The narrow range of the dithiophosphate resonances in the ^{31}P spectra results in most of the cadmium satellites being obscured by other resonances.

Mixed Cadmium Dithiophosphate and Dithiocarbamate Anionic Complexes

The ^{113}Cd spectrum of a dichloromethane solution containing a 1:1 molar ratio of Cd(ipdtp)$_2$ and Ph$_3$PCH$_2$Ph(edtc) recorded at room temperature shows a single resonance at 352 ppm. As the solution is cooled this resonance broadens and other broad but less intense resonances appear. At –100 °C there are three main resonances which are all sharp; a quartet at 262 ppm, J(Cd–P) 69 Hz; a triplet at 337 ppm, J(Cd–P) 47 Hz which is more intense than the other two signals and a doublet at 349 ppm, J(Cd–P) 35 Hz.

The quartet corresponds to the resonance previously assigned to Cd(ipdtp)$_3^-$. Given the ratio of the reactants the relatively high intensity of the triplet suggests that it is due to the formation of Cd(ipdtp)$_2$(edtc)$^-$ whilst the intensity of the doublet suggests that it may be assigned to the complex Cd(ipdtp)(edtc)$_2^-$. The ^{31}P spectrum of the solution at –100 °C is consistent with the presence of these species (Table 1).

Mixed Cadmium Xanthate and Dithiocarbamate Anionic Complexes

The ^{113}Cd spectrum of a dichloromethane solution of Cd(edtc)$_2$ and Ph$_3$PCH$_2$Ph(ipxa) in a 1:1 mole ratio, recorded at room temperature, shows a single weak resonance at 363 ppm. At –40 °C two sharp and intense resonances are observed at 370 and 341 ppm. The spectrum changes very little as the solution is cooled to –70 °C except for the emergence of a weak resonance at 251 ppm. At –90 °C, however the resonance at 341 ppm broadens considerably while the other two (at 376 and 250 ppm) remain relatively sharp. The signals at 250 and 376 ppm at –90 °C are assigned to Cd(edtc)$_2$ and Cd(edtc)$_3^-$ respectively whilst the origin of the resonance at 341 ppm is not immediately obvious.

The ^{113}Cd spectrum at room temperature of a dichloromethane solution of Cd(ipxa)$_2$ and Ph$_3$PCH$_2$Ph(edtc) in a 1:1 mole ratio is a singlet at 342 ppm. At –50 °C the spectrum shows an intense, sharp, resonance at 342 ppm and two less intense resonances, which are also sharp, at 375 and 316 ppm. The resonances at 316 and 375 ppm arise from Cd(ipxa)$_3^-$ and Cd(edtc)$_2$ respectively whilst the resonance at 342 ppm may be due to either Cd(edtc)$_2$(ipxa)$^-$ or Cd(ipxa)$_2$(edtc)$^-$ or to an average between both. Cooling the solution further results in broadening of the resonances which have been assigned to xanthate containing species.

The presence of relatively high concentrations of Cd(edtc)$_2$ in the solutions of Cd(edtc)$_2$ + edtc$^-$ indicates that formation of Cd(edtc)$_3^-$ is not strongly favoured. In contrast, Cd(ipxa)$_2$ and Cd(ipdtp)$_2$ readily incorporate an additional dithiolate ligand to form Cd(ipxa)$_3^-$ and Cd(ipdtp)$_3^-$ respectively which suggests that Cd(ipxa)$_2$ and Cd(ipdtp)$_2$ are better Lewis acids than Cd(edtc)$_2$. Accordingly it is likely that the formation of Cd(ipxa)$_2$(edtc)$^-$ is more favourable than the formation of Cd(edtc)$_2$(ipxa)$^-$ and the resonance at 342 ppm is tentatively assigned to the former species.

Formation of [Hg(ipdtp)$_3$]$^-$

The room temperature ^{199}Hg spectrum of a dichloromethane solution containing an equimolar ratio of Hg(ipdtp)$_2$ and NBu$_4$(ipdtp) shows a sharp resonance at 452 ppm. This resonance is significantly different from that for Hg(ipdtp)$_2$ and is assigned to Hg(ipdtp)$_3^-$. The ^{31}P spectrum recorded at room temperature shows a singlet at 102.4 ppm [cf. 95.4 ppm for Hg(ipdtp)$_2$].

Cooling the solution to –100 °C results in the appearance of a quartet in the ^{199}Hg spectrum at 486 ppm with a coupling constant of 127 Hz, which is consistent with two bond coupling, ^2J(Hg–P) (see Table 2). The corresponding ^{31}P resonance is accompanied by ^{199}Hg satellites with a coupling constant corresponding to that observed in the ^{199}Hg spectrum.

TABLE 2. NMR data for various mercury dithiolate complexes in dichloromethane solution

Complex	$\delta(^{199}$Hg) (ppm)	$\delta(^{31}$P) (ppm)	$J(^{199}$Hg–^{31}P) (Hz)	Temperature (°C)
Hg(ipxa)$_2$	142s			20
Hg(ipdtp)$_2$	345s	95.4		20
Hg(edtc)$_2$	177 [ref. 7]			20
Hg(ipxa)$_3^-$	398			20
Hg(ipxa)$_2$(ipdtp)$^-$	431	103.8		–95
Hg(ipxa)$_2$(edtc)$^-$	421			–105
Hg(ipdtp)$_3^-$	452s	102.4		20
	486q	102.4	127	–100
Hg(ipdtp)$_2$(ipxa)$^-$	456t	102.8	102	–95
Hg(ipdtp)$_2$(edtc)$^-$	460t	102.7	126	–100

s, singlet; d, doublet; t, triplet.

Observation of a quartet in the ^{199}Hg spectrum indicates that the three dithiophosphate ligands in Hg(ipdtp)$_3^-$ are equivalent. Absence of coupling above −90 °C probably results from a rapid intermolecular dithiophosphate ligand exchange.

Formation of [Hg(ipxa)$_3$]$^-$

The ^{199}Hg NMR spectrum recorded at room temperature of a dichloromethane solution containing Hg(ipxa)$_2$ and Ph$_3$PCH$_2$Ph(ipxa) in an equimolar ratio shows a single sharp resonance at 398 ppm. This resonance is significantly different from the chemical shift of Hg(ipxa)$_2$ (142 ppm) and is interpreted with the formation of Hg(ipxa)$_3^-$. Cooling the solution to −100 °C causes the resonance to broaden ($w_{1/2}$ 300 Hz) but without change in the resonance position. The ^{13}C spectrum shows a single resonance in the S$_2$*C* region of the spectrum in the 20 to −100 °C temperature range. Addition of excess ipxa$^-$ to the solution does not result in any further change to the ^{199}Hg spectrum so that the resonance at 398 ppm must be the result of a single species rather than being a time-average signal for Hg(ipxa)$_2$ and Hg(ipxa)$_3^-$.

Formation of [Hg(edtc)$_3$]$^-$

The room temperature ^{199}Hg spectrum of a dichloromethane solution of Ph$_3$PCH$_2$Ph(edtc) and Hg(edtc)$_2$ in a 1:1 mole ratio shows a single resonance at 148 ppm. Cooling the solution to −40 °C results in a very broad resonance at 158 ppm. At −90 °C a single sharp ^{199}Hg resonance is observed at 174 ppm. At room temperature the ^{13}C spectrum shows a single resonance in the S$_2$*C* region at 201.2 ppm. At −90 °C there are two resonances (191.2 and 201.1 ppm) in the S$_2$*C* region, the resonance at lower frequency corresponding to that for uncoordinated edtc$^-$.

The chemical shift of Hg(edtc)$_2$ has been reported [7] to be at 177 ppm however we find that the shift is very dependent on the concentration and temperature and have observed values between 155 ppm for a dilute solution at room temperature to 202 ppm for a concentrated solution at −90 °C. The similarity in the chemical shifts of the resonances from the Hg(edtc)$_2$ + edtc$^-$ and the Hg(edtc)$_2$ solutions suggest that Hg(edtc)$_3^-$ is not formed in any appreciable quantity. This is in agreement with Niewpoort *et al.* [8] who showed electrochemically that solutions of Hg(edtc)$_3^-$ disproportionate almost completely to Hg(edtc)$_2$ and edtc$^-$. Addition of an excess of edtc$^-$ causes no change in the ^{199}Hg spectrum.

Mixed Mercury Xanthate and Dithiophosphate Anionic Complexes

The room temperature ^{199}Hg spectrum of an equimolar solution of Hg(ipdtp)$_2$ and Ph$_3$PCH$_2$Ph(ipxa) in dichloromethane shows a single sharp resonance at 431 ppm. Cooling the solution causes broadening of the signal and a slight change in the chemical shift position. At −70 °C three distinct broad resonances are observed at 474, 449 and 427 ppm in an approximate ratio of 1:3:1. Cooling to −95 °C results in the observation of a quartet at 486 ppm, a triplet at 456 ppm and a broad resonance at 431 ppm in the same relative intensities as were observed at −70 °C. The quartet is due to Hg(ipdtp)$_3^-$ whilst the triplet is assigned to Hg(ipdtp)$_2$(ipxa)$^-$. The broad resonance at 431 ppm is likey to be due to Hg(ipxa)$_2$(ipdtp)$^-$. There is no evidence for a resonance assignable to Hg(ipxa)$_3^-$.

A single sharp resonance is observed in the ^{31}P spectrum in the 20 to −70 °C temperature range. At −95 °C, broad, less intense resonances merge with the base of a reasonably sharp signal at 102.8 ppm. It is likely that this main resonance is due to a combination of Hg(ipdtp)$_3^-$ and Hg(ipdtp)$_2$(ipxa)$^-$. The broad resonances are probably due to Hg(ipxa)$_2$(ipdtp)$^-$ and ^{199}Hg satellites of the major resonances.

To assist in the identification of the complexes the ligand ratio was changed. The room temperature ^{199}Hg spectrum of a 1:1 mole ratio solution of Hg(ipxa)$_2$ and NBu$_4$(ipdtp) in dichloromethane shows a single resonance at 414 ppm. Cooling the solution causes considerable broadening of this resonance until at −90 °C three distinct resonances are observed at 453, 428 and 405 ppm with an intensity ratio of approximately 1:3:1. While all three signals are broad, the resonance at 453 ppm appears to show some coupling resulting in a poorly defined triplet [*J*(Hg–P) 112 Hz]. The three resonances at 453, 428 and 405 ppm are assigned to Hg(ipdtp)$_2$(ipxa)$^-$, Hg(ipxa)$_2$(ipdtp)$^-$ and Hg(ipxa)$_3^-$ respectively.

The ^{31}P spectrum of this solution consists of a single broad resonance at −90 °C but at −100 °C the spectrum shows two dominant resonances at 103.8 and 102.6 ppm which are assigned to Hg(ipxa)$_2$(ipdtp)$^-$ and Hg(ipdtp)$_2$(ipxa)$^-$ respectively.

Mixed Mercury Dithiophosphate and Dithiocarbamate Complexes

The ^{199}Hg spectrum of a dichloromethane solution of Hg(ipdtp)$_2$ and Ph$_3$PCH$_2$Ph(edtc) in a 1:1 mole ratio recorded at room temperature shows a single broad resonance at 372 ppm. Cooling the solution to −50 °C causes the resonance to broaden further and shift to 429 ppm. At −90 °C the spectrum is dominated by a broad resonance ($w_{1/2}$ 300 Hz) at 454 ppm. A poorly defined quartet, of much lower intensity, at 483 ppm is also observed. Cooling the solution to −100 °C causes the broad resonance to become a triplet [δ(^{199}Hg) 460 ppm *J*(Hg–P) 126 Hz]. The quartet indicates the presence of Hg(ipdtp)$_3^-$ while the triplet is consistent with the formation of Hg(ipdtp)$_2$(edtc)$^-$.

The ^{31}P spectrum shows a single resonance in the dithiophosphate region which shifts from 103.3 to

102.7 ppm as the solution is cooled to –90 °C. At –100 °C ^{199}Hg satellites appear with a coupling constant corresponding to that derived from the ^{199}Hg triplet resonance. No ^{31}P resonance due to $Hg(ipdtp)_3^-$ was observed, although it may be obscured by the $Hg(ipdtp)_2(edtc)^-$ resonance.

The ^{199}Hg spectrum of a dichloromethane solution of $Hg(edtc)_2$ and $NBu_4(ipdtp)$ in a 1:1 mole ratio recorded at room temperature shows a single broad resonance at 208 ppm ($w_{1/2}$ 140 Hz). Cooling the solution to –50 °C results in the appearance of a very broad resonance at 185 ppm ($w_{1/2}$ 300 Hz) and a very weak resonance at 435 ppm. At –80 °C both resonances sharpen and the higher frequency resonance becomes a triplet, J(Hg–P) 117 Hz. The singlet resonance at 219 ppm (–100 °C) is due to $Hg(edtc)_2$ whilst the triplet is assigned to $Hg(ipdtp)_2(edtc)^-$. Cooling to –100 °C causes no further significant change to the spectrum. The weak Lewis acidity of $Hg(edtc)_2$ was demonstrated earlier by the dissociation of $Hg(edtc)_3^-$. It is therefore not surprising there is no evidence for $Hg(edtc)_2(ipdtp)^-$ in mixtures of $Hg(edtc)_2$ and $NBu_4(ipdtp)$.

Mixed Mercury Xanthate and Dithiocarbamate Anionic Complexes

The ^{199}Hg spectrum of a dichloromethane solution of $Hg(ipxa)_2$ and $Ph_3PCH_2Ph(edtc)$ in an equimolar ratio, recorded at room temperature shows a single resonance at 348 ppm. Cooling the solution to –70 °C causes the resonance to broaden and shift to 398 ppm. At –105 °C the spectrum shows a very broad resonance at 421 ppm and a weaker resonance at 163 ppm, the latter being due to $Hg(edtc)_2$. The broad resonance at 421 ppm may be due to $Hg(ipxa)_3^-$ or $Hg(ipxa)_2(edtc)^-$ or an exchange average between both.

Conclusions

Cadmium bisdithiolates easily incorporate another dithiolate ligand into their coordination spheres to form anionic complexes, $Cd(S\text{-}S)_3^-$. In mixtures involving more than one type of dithiolate ligand, scrambling reactions produce a number of new mixed-ligand species in solution. Mercury dithiolates behave similarly with the exception of $Hg(edtc)_2$ which appears to be a remarkably weak Lewis acid and consequently there is little tendency to add a further dithiolate ligand. Similar trends have already been noted with the addition of phosphines to these complexes [7]. These observations imply that dithiocarbamate ligands effectively transfer more electron density to the metal centre than do xanthates and dithiophosphates.

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