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Phosphine derivatives of mercury and cadmium dithiolates: an electrospray mass spectrometric study

Alan M. Bond [a], Ray Colton [a,*], John C. Traeger [a], Justin Harvey [b]

[a] *School of Chemistry, La Trobe University, Bundoora 3083, Australia*

[b] *School of Chemistry, University of Melbourne, Parkville 3052, Australia*

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Abstract

Electrospray mass spectrometry (ESMS) has been used to investigate the ionic species present in solutions of mercury and cadmium diethyldithiocarbamates (dtc) and diethyldithiophosphates (dtp) after reaction with phosphine ligands. After reaction between the dithiolates (S-S) and monodentate ligands, ESMS shows the presence of both $[Hg(S\text{-}S)(PR_3)]^+$ and $[Hg(S\text{-}S)(PR_3)_2]^+$, but only $[Cd(S\text{-}S)(PR_3)_2]^+$. The 1:1 $Cd(S\text{-}S)_2$ phosphine complex observed by NMR methods is thought to be the neutral $Cd(S\text{-}S)_2(PR_3)$. Reaction of all the metal dithiolates with polydentate ligands in solution gives systems which are labile on the NMR timescale, but ESMS shows the presence of $[M(S\text{-}S)(phos)]^+$ in each case. This work emphasises the complementary nature of NMR and ESMS techniques.

Keywords: Electrospray mass spectrometry; Cadmium complexes; Dithiolate complexes; Mercury complexes

1. Introduction

Phosphine derivatives of metal dithiolate complexes have been of interest for some years, particularly for multinuclear magnetic resonance studies. Platinum dithiolates, $Pt(S\text{-}S)_2$, (S-S = dithiocarbamate, dtc, dithiophosphate, dtp etc.) react with monodentate phosphines in a sequential manner

$$Pt(S\text{-}S)_2 + PR_3 \longrightarrow (PR_3)Pt(\eta^1\text{-}S\text{-}S)(\eta^2\text{-}S\text{-}S)$$

$$(PR_3)Pt(\eta^1\text{-}S\text{-}S)(\eta^2\text{-}S\text{-}S) + PR_3 \longrightarrow [(PR_3)_2Pt(\eta^2\text{-}S\text{-}S)]^+ + [S\text{-}S]^-$$

Both types of phosphine complex are square planar and numerous examples have been fully characterised by NMR methods in solution and by X-ray crystallography in the solid state [1–7]. NMR methods are particularly powerful in these systems because ligands on platinum exchange slowly on the NMR timescale so that even when mixtures of complexes are present in solution, their individual spectra can be observed and the complexes can usually be unambiguously identified. Subsequently, this work was extended to include the reactions of bidentate and polydentate phosphine based ligands with platinum dithiolates [8–12].

In contrast, the tetrahedral dithiolates of cadmium and mercury are very labile in solution. Metal–dithiophosphate coupling was not observed in the NMR spectra at any temperature to −100 °C, and mixtures of two dithiophosphate complexes of the same metal gave only an average metal NMR signal. Similarly, in the case of the dithiocarbamates, the lability was demonstrated by mixing different dithiocarbamate complexes and observing only an average ^{113}Cd or ^{199}Hg NMR signal, except in one case where separate ^{199}Hg NMR signals for individual complexes were observed at very low temperature [13]. These dithiolate complexes also react with monodentate phosphine ligands in solution to give complexes of stoichiometry $M(S\text{-}S)_2(PR_3)$ and $M(S\text{-}S)_2(PR_3)_2$ in solution, although they could not be isolated. Even the phosphine ligands are labile on the NMR timescale at room temperature, but cooling allowed observation of metal–phosphine coupling and the metal NMR spectra confirmed the 1:1 and 1:2 stoichiometries of the complexes. The dithiolate ligands were still labile at all temperatures studied, so it was not possible to determine the coordination modes of the anionic ligands from the NMR spectra or other data available at that time. However, importantly, it

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[*] Corresponding author.

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was not possible to coordinate more than two monodentate phosphines to any of the metal dithiolates [13] although three or four phosphines could be coordinated to mercury when other anions were used [14]. This strongly indicates that at least one dithiolate remains coordinated to the metal in the phosphine dithiolate complexes.

Electrospray mass spectrometry (ESMS) is a recently developed technique [15,16] which allows pre-existing ions in solution to be very gently transferred to the gas phase and subsequently examined by conventional mass spectrometric methods. So far, the major impact of the technique has been in the area of biochemistry since it has allowed the observation of the mass spectra of large biomolecules, such as proteins [17–19]. However, in our laboratories we have shown that ESMS is applicable to inorganic and organometallic systems, including the platinum dithiolate phosphine complexes referred to above [20–22]. In particular, we have demonstrated that the technique is a viable alternative to low temperature NMR studies and can be used to identify the components of rapidly exchanging systems [23–25].

In this paper we report ESMS studies on cadmium and mercury dithiolates with monodentate phosphine ligands and compare the results with those obtained earlier by NMR studies. We then extend the application of ESMS to reactions of the dithiolates with bidentate phosphine ligands, the products of which are too insoluble to allow NMR studies, and to dithiolate derivatives with polydentate phosphine ligands in which even the phosphine ligands are too labile for NMR studies to be informative.

2. Experimental

Mercury and cadmium dithiolates were prepared by literature methods [13]. All the phosphines were commercial samples (Strem) and were used without further purification. All solvents were of Analytical grade or better. Milligram quantities of the metal dithiolate and the phosphine were dissolved in the minimum amount of dichloromethane and the solution then diluted with methanol to give an approximately 2 mM solution of the complex. This solution was then diluted 1:10 with methanol and this solution was used for mass spectral studies.

Positive ion electrospray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer (VG Bio Tech, Altrincham, Cheshire, UK) using a water/methanol/acetic acid (50:50:1%) mobile phase. The diluted solution prepared as described above was directly injected into the spectrometer via a Rheodyne injector with a 10 μl loop. A Phoenix 20 micro LC syringe pump delivered the solution to the vaporisation nozzle of the electrospray ion source at a flow rate of 5 μl min^{-1}. Nitrogen was used as both a drying gas and for nebulisation, with flow rates of approximately 4 l min^{-1} and 500 ml min^{-1}, respectively. Pressure in the mass analyser region was typically about 3×10^{-5} torr. The compounds in this study gave moderately strong signals in the ES mass spectra and typically 9–12 signal averaged spectra were required to give an acceptable signal to noise ratio.

3. Results and discussion

3.1. NMR studies

NMR studies on solutions containing $M(S\text{-}S)_2$ ($M = Cd,Hg$; $S\text{-}S = S_2CNEt_2$, dtc and $S_2P(OEt)_2$, dtp) and added PBu_3 or $Pcyl_3$ ($Pcyl_3 = P(c\text{-}C_6H_{11})_3$) have been reported previously [13]. 1:1 and 1:2 phosphine complexes were identified from observation of the metal NMR spectra, but the dithiolate ligands were still labile even at low temperatures. Products with PPh_3 and dpe (dpe $= Ph_2PCH_2CH_2PPh_2$) were not sufficiently soluble for NMR studies to be undertaken.

In this work we have reacted the metal dithiolates with P_2P' ($Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$), P_3 ($CH_3C(CH_2PPh_2)_3$) and P_3P' ($P(CH_2CH_2PPh_2)_3$) and investigated the ^{31}P NMR spectra of the mixtures in dichloromethane solution. All the mixtures were extremely labile in solution, and at the lowest accessible temperatures (about −100 °C) even the polyphosphine ligands were still exchanging rapidly and no metal/phosphine coupling was observed. However, the ^{31}P resonances of the mixtures were shifted to higher frequencies compared with the free ligands (exact position depending upon the proportions of reactants) indicating that interaction with the metal centres was occurring. No structural information about the products could be deduced from the NMR spectra. Presumably the increased lability in these systems compared with the monodentate phosphine mixtures arises from the fact that there are increasing numbers of potential donor atoms. Even with the monodentate phosphines, addition of excess phosphine enhances lability [13].

3.2. ESMS studies

All peaks in the ES mass spectra are identified by the most abundant mass in the isotopic mass distribution. In all cases the experimental and calculated isotopic mass distributions were in excellent agreement.

The first mixtures investigated by ESMS were those with monodentate phosphines for which NMR information is available for comparison. Fig. 1 shows the positive ion ES mass spectrum of a solution containing $Hg(dtc)_2$ and PBu_3. There are two significant peaks in

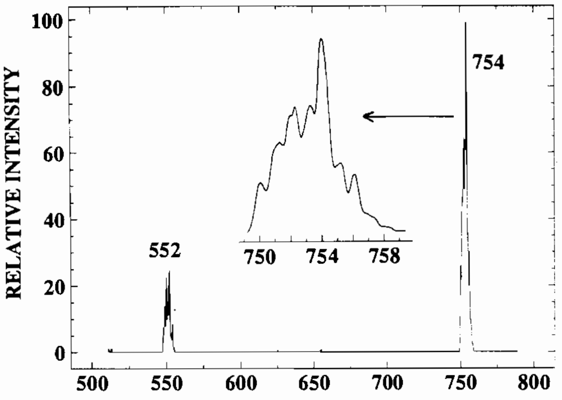

Fig. 1. Positive ion ES mass spectrum of a methanol solution of $Hg(dtc)_2$ and PBu_3.

the mass spectrum which are due to $[Hg(dtc)(PBu_3)]^+$ (*m/z* 552) and $[Hg(dtc)(PBu_3)_2]^+$ (*m/z* 754). In contrast, the ES mass spectrum of a mixture of $Cd(dtc)_2$ and PBu_3 gave only one peak assignable to a cadmium phosphine complex at *m/z* 666, which is due to $[Cd(dtc)(PPh_3)_2]^+$. Analogous results were obtained with $Pcyl_3$ and PPh_3; in each case the ES mass spectrum of the mixture of $Hg(dtc)_2$ and the phosphine gave peaks due to $[Hg(dtc)(PR_3)]^+$ and $[Hg(dtc)(PR_3)_2]^+$, whilst those of $Cd(dtc)_2$ and the phosphines gave only a peak due to $[Cd(dtc)(PR_3)_2]^+$. The dithiophosphate complexes behaved similarly and all data are summarised in Table 1. The signal to noise ratio in the ES mass spectrum of the cadmium complexes with monodentate phosphines was always inferior to that of the corresponding mercury compound. Occasionally an additional peak corresponding to oxidation of the phosphine to phosphine oxide was also detected, especially for cadmium complexes. This oxidation has been noted before [24] and probably occurs within the ion source.

There is an apparent conflict between the NMR data, which clearly identified both 1:1 and 1:2 phosphine complexes for the dithiolates of both metals, and the ESMS data which detects only the 1:2 complex for cadmium. However, a limitation of ESMS is that it can detect only ionic species, and the difference in the ES mass spectra of the two metals is an indication that the 1:1 complexes for the two metals have different compositions. In a recent study [26] it was shown that the interaction of $Hg(dtp)_2$ with dpmSe (dpmSe = $Ph_2P(Se)CH_2PPh_2$) gave a labile system in solution, but at very low temperatures two species, $Hg(dtp)_2(dpmSe)$ and $[Hg(dtp)(dpmSe)]^+$, were identified by a combination of ^{31}P, ^{77}Se and ^{199}Hg NMR spectroscopies. The presence of the ionic species was confirmed by ESMS, but the neutral molecule cannot be detected by this technique. We suggest that in the present work, the 1:1 complexes between $Cd(S\text{-}S)_2$ and PR_3 ligands are neutral $Cd(S\text{-}S)_2(PR_3)$ molecules, most likely of the form $Cd(\eta^1\text{-}S\text{-}S)(\eta^2\text{-}S\text{-}S)(PR_3)$, which would not be detected by ESMS. The mercury dithiolates react with the monodentate phosphines (1:1) to give the peaks due to the ionic $[Hg(S\text{-}S)(PR_3)]^+$ in their ES mass spectra, but it is not possible to determine the concentration of these species, and there may well be neutral $Hg(dtp)_2(PR_3)$ present in the solution also. It will be recalled that the dithiolate ligands are too labile to determine this point by NMR methods.

In these solutions there is competition between the dithiolate and phosphine ligands for the four coordination sites at the metal centre, and the suggested explanation for the observed data is consistent with the previously determined preferences of the metal for these types of ligands. Competitive NMR studies have shown that, in general, phosphines are much less strongly bound to cadmium than to mercury [27] and that cadmium prefers to bond to sulfur rather than phosphorus [28,29], so the retention of two dithiolate ligands by cadmium in these 1:1 mixtures would not be surprising.

When two moles of monodentate phosphine are added per mole of metal dithiolate, both metals give peaks in the ES mass spectra corresponding to $[M(S\text{-}S)(PR_3)_2]^+$, but again there may also be neutral species present, such as $M(\eta^1\text{-}S\text{-}S)_2(PR_3)_2$, which remain undetected. Reaction of the metal dithiolates with the diphosphine, dpe, led in each case to the observation in the ES mass spectra of the ion $[M(S\text{-}S)(dpe)]^+$ as the only metal containing species (Table 1). These particular complexes are rather insoluble in dichloromethane and other organic solvents, so NMR studies could not be carried out to investigate the lability of the dithiolate ligands, and it is not possible to decide whether complexes of the type $M(\eta^1\text{-}S\text{-}S)_2(dpe)$ are also present in the solution, as might be the case for cadmium. An excess of dpe did not lead to the observation of the $[M(dpe)_2]^{2+}$ ion, suggesting that one dithiolate is retained by the metal even in the presence of excess chelating phosphine.

The other phosphines reacted with the metal dithiolates were tridentate and quadridentate ligands. In each case the ES mass spectrum of the reaction mixture gave a very strong peak for the ion $[M(S\text{-}S)(phos)]^+$ (Table 1). Addition of further phosphine did not lead to the observation of the ions $[M(phos)_2]^{2+}$, again suggesting that one dithiolate is always retained by the metal. The retention of the second dithiolate ligand becomes less favourable as the number of phosphine donor atoms increases, so it is likely that $[M(S\text{-}S)(phos)]^+$ is the only metal species present in these solutions. The lability of these systems in solution on the NMR timescale is therefore due to rapid exchange between coordinated and pendant phosphine groups of the polyphosphine ligand, probably accompanied by $\eta^1 \rightleftharpoons \eta^2$ coordination of the remaining dithiolate ligand.

Table 1
Positive ion ESMS data for phosphine dithiolate complexes

Mixture	Ions observed (*m/z*)
$Hg(dtc)_2+PBu_3$	$[Hg(dtc)(PBu_3)]^+$(552); $[Hg(dtc)(PBu_3)_2]^+$(754)
$Hg(dtc)_2+Pcyl_3$	$[Hg(dtc)(Pcyl_3)]^+$(630); $[Hg(dtc)(Pcyl_3)_2]^+$(910)
$Hg(dtc)_2+PPh_3$	$[Hg(dtc)(PPh_3)]^+$(612); $[Hg(dtc)(PPh_3)_2]^+$(874)
$Cd(dtc)_2+PPh_3$	$[Cd(dtc)(PPh_3)_2]^+$(786)
$Hg(dtc)_2+dpe$	$[Hg(dtc)(dpe)]^+$(748)
$Cd(dtc)_2+dpe$	$[Cd(dtc)(dpe)]^+$(660)
$Hg(dtc)_2+P_3$	$[Hg(dtc)(P_3)]^+$(974)
$Hg(dtc)_2+P_2P'$	$[Hg(dtc)(P_2P')]^+$(884)
$Cd(dtc)_2+P_2P'$	$[Cd(dtc)(P_2P')]^+$(796)
$Hg(dtc)_2+P_3P'$	$[Hg(dtc)(P_3P')]^+$(1020)
$Cd(dtc)_2+P_3P'$	$[Cd(dtc)(P_3P')]^+$(932)
$Hg(dtp)_2+PBu_3$	$[Hg(dtp)(PBu_3)]^+$(589); $[Hg(dtp)(PBu_3)_2]^+$(791)
$Cd(dtp)_2+PBu_3$	$[Cd(dtp)(PBu_3)_2]^+$(703)
$Hg(dtp)_2+Pcyl_3$	$[Hg(dtp)(Pcyl_3)]^+$(667); $[Hg(dtp)(Pcyl_3)_2]^+$(947)
$Cd(dtp)_2+Pcyl_3$	$[Cd(dtp)(Pcyl_3)_2]^+$(859); $[Cd(dtp)(Pcyl_3)(Pcyl_3O)]^+$(875)
$Hg(dtp)_2+PPh_3$	$[Hg(dtp)(PPh_3)]^+$(649); $[Hg(dtp)(PPh_3)_2]^+$(911)
$Cd(dtp)_2+PPh_3$	$[Cd(dtp)(PPh_3)_2]^+$(823)
$Hg(dtp)_2+dpe$	$[Hg(dtp)(dpe)]^+$(785)
$Cd(dtp)_2+dpe$	$[Cd(dtp)(dpe)]^+$(697); $[Cd(dtp)(dpeO)]^+$(713)
$Hg(dtp)_2+P_3$	$[Hg(dtp)(P_3)]^+$(1011)
$Cd(dtp)_2+P_3$	$[Cd(dtp)(P_3)]^+$(923); $[Cd(dtp)(P_3O)]^+$(939)
$Hg(dtp)_2+P_2P'$	$[Hg(dtp)(P_2P')]^+$(921)
$Cd(dtp)_2+P_2P'$	$[Cd(dtp)(P_2P')]^+$(833)
$Hg(dtp)_2+P_3P'$	$[Hg(dtp)(P_3P')]^+$(1057)
$Cd(dtp)_2+P_3P'$	$[Cd(dtp)(P_3P')]^+$(969); $[Cd(dtp)(P_3P'O)]^+$(985)

4. Conclusions

This work serves to emphasise the complementary nature of multi-NMR and ESMS studies, particularly in very labile systems. Neither technique alone is able to fully characterise all the species present in these seemingly simple solutions, but the combination of both methods provides useful additional information. In the case of the reaction of the metal dithiolates with PBu_3 and $Pcyl_3$, earlier NMR measurements unambiguously characterised 1:1 and 1:2 phosphine complexes, but could give no information on the dithiolate coordination except to imply retention of at least one dithiolate. ESMS confirms directly the presence of $[M(S\text{-}S)(PR_3)_2]^+$ and $[Hg(S\text{-}S)(PR_3)]^+$, and implies the presence of $Cd(S\text{-}S)_2(PR_3)$. In this work we have utilised the lower solubility requirements of ESMS, compared to NMR, to investigate the products of the reactions of the dithiolates with PPh_3 and dpe. NMR can provide little information on the mixtures containing the metal dithiolates with the polydentate ligands, but ESMS has identified the cationic products in these reactions.

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