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Inorganica Chimica Acta 224 (1994) 137–146

Inorganica Chimica Acta

Multinuclear (^{31}P, ^{77}Se, ^{113}Cd, ^{199}Hg) magnetic resonance, electrospray mass spectrometric and electrochemical studies on the reactions of $M(S_2P\{OEt\}_2)_2$ ($M=Cd$, Hg) with potentially bidentate mixed Group 15/Group 16 and Group 16 donor ligands

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Received by Editor 22 February 1994; received by Publisher 24 May 1994

Abstract

Extensive studies of the labile $Hg(dtp)_2$/dpmSe ($dtp=(S_2P\{OEt\}_2)$; $dpmSe=Ph_2P(Se)CH_2PPh_2$) system by multinuclear magnetic resonance (NMR), electrospray mass spectrometry (ESMS) and electrochemical techniques show that in solution both $Hg(dtp)_2$ itself and the mixed $Hg(dtp)_2$/dpmSe system consist of many competing equilibria with the species being identified as dtp^-, $Hg(dtp)_2$, $[Hg(dtp)_3]^-$, $[Hg_2(dtp)_3]^+$, dpmSe, $Hg(dtp)_2(dpmSe)$, $[Hg(dtp)(dpmSe)]^+$ and $[Hg(dtp)(dpmSe)_2]^+$. NMR studies show that $Hg(dtp)_2$ reacts with dpmSe in 1:1 molar proportions to give products which, at room temperature in dichloromethane solution, are labile with exchange of both types of ligand occurring. Upon cooling to −30 °C the dpmSe ligand becomes chelated and static on the NMR timescale, but the dithiophosphate ligands still undergo rapid exchange. Further cooling causes the exchange of the dithiophosphate ligands to become slow and two species are observed at −100 °C which are identified as $[(\eta^2\text{-dpmSe})Hg(\eta^2\text{-dtp})][S_2P(OEt)_2]$ and $(\eta^2\text{-dpmSe})Hg(\eta^1\text{-dtp})_2$. ESMS studies on solutions of $Hg(dtp)_2$ show the presence of dtp^-, $[Hg(dtp)_3]^-$ and $[Hg_2(dtp)_3]^+$ and, after addition of dpmSe to the solution, ESMS confirmed the presence of $[Hg(dtp)(dpmSe)]^+$. Differential pulse and direct current sampled polarograms re-emphasise the labile nature of this system and provide further evidence of mixed ligand compound formation as well as thermodynamic data. NMR studies on the $Cd(dtp)_2$/dpmSe system show it to be more labile than its mercury analogue and the interpretation of the NMR data is ambiguous. NMR studies on the $M(dtp)_2$/dpmS (or $dpmSe_2$ or $dpmS_2$) systems ($M=Hg$, Cd; $dpmSe_2$ or $dpmS_2=Ph_2P(E)CH_2P(E)Ph_2$; $E=Se$, S) are even less definitive. ESMS confirms the presence in solution of the cations $[(ligand)M(dtp)]^+$ for all the systems studied.

Keywords: Multinuclear NMR; Electrospray mass spectrometry; Electrochemistry; Cadmium complexes; Mercury complexes; Bidentate ligand complexes

1. Introduction

Although the dithiocarbamate complexes of mercury and cadmium and their derivatives have been extensively studied by electrochemical and multinuclear magnetic resonance techniques [1–5] the corresponding dithiophosphates have been relatively neglected. Dakternieks and Graddon [6–8] described the properties of a series of *O*,*O*-dialkyldithiophosphates ($[S_2P(OR)_2]^-$, dtp) of mercury and cadmium and multi-NMR studies have been reported for these complexes and some of their derivatives with phosphine ligands [5]. Previously reported electrochemical work of relevance to this paper is the reversible electrochemical reduction of $Hg(Et_2dtp)_2$ [9] and the reversible oxidation process observed at mercury electrodes for solutions of dpmSe ($dpmSe=Ph_2PCH_2P(Se)Ph_2$) and the reversible reduction of $[Hg(dpmSe)_2]^{2+}$ at mercury [10].

Until recently, it could be argued that NMR and electrochemical techniques are the two most generally

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0020-1693/94/$07.00
SSDI 0020-1693(94)04125-F

useful techniques for the study of species in solution. The new technique of electrospray mass spectrometry (ESMS) provides a third powerful method, provided that the species in solution are ionic [11]. ESMS, unlike other forms of mass spectrometry, allows pre-existing ions in solution to be very gently transferred to the gas phase with minimal fragmentation. The ES technique has been developed mainly by Fenn and co-workers [12–14] and its most common applications have been in the area of mass spectrometric studies of large biomolecules [15–18]. However, recent work in our laboratories as well as from other groups [19–27] has shown that ESMS may advantageously be applied to a wide variety of inorganic and organometallic ionic species. In the cases of non-labile cations and anions, such as $[(P\text{-}P)Pt(R_2dtc)]^+$ (P-P = diphosphine; R_2dtc = dithiocarbamate S_2CNR_2) and $[Cr(CO)_5I]^-$, the intact ions are usually observed without difficulty [19–22]. For labile complexes, fragment 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 observation of the individual species at room temperature and 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 ligand cations [23], phosphine complexes of Hg(II) [24] and mixed tris-(dithiophosphato)zinc(II) anions [25]. ESMS has proved to be particularly successful in the study of cationic dithiocarbamate species, especially labile polynuclear species [28,29].

In this paper we present observations on the reactions of $M(S_2P\{OEt\}_2)_2$ ($M(dtp)_2$; M = Hg, Cd) with the potentially bidentate ligands $Ph_2PCH_2P(E)Ph_2$ (E = S, Se; dpmS, dpmSe) and $Ph_2P(E)CH_2P(E)Ph_2$ ($dpmS_2$, $dpmSe_2$) using multi-NMR, ESMS and electrochemical techniques, as part of our general study of the chemistry of metal dithiolate complexes. It will emerge from this work that the combination of data from the three techniques is required for a complete understanding of the complex solution chemistry and that the individual techniques actually provide complementary information.

2. Experimental

2.1. Preparations

All solvents were of Analytical Grade purity or better. $Hg(dtp)_2$ and $Cd(dtp)_2$ were prepared as described previously [5] as were the ligands dpmS, dpmSe, $dpmS_2$ and $dpmSe_2$ [30,31]. The compounds were prepared and isolated by interaction of equimolar quantities of $M(dtp)_2$ and the ligand in CH_2Cl_2 at room temperature. After slow evaporation of the solvent the compounds were recrystallised from CH_2Cl_2/n-hexane.

Proton decoupled NMR spectra in dichloromethane solution were recorded on a JEOL FX 100 spectrometer, ^{31}P at 40.32 MHz, ^{77}Se at 19.02 MHz, ^{113}Cd at 22.04 MHz and ^{199}Hg at 17.76 MHz. The external references were 85% H_3PO_4, 1 M H_2SeO_3 in H_2O, 4.5 M $Cd(NO_3)_2$ in water and 1 M phenylmercury acetate in dimethyl sulfoxide. High frequency positive convention is used for all chemical shifts and external ^7Li lock was used.

Electrospray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer (VG BioTech, Altrincham, Cheshire, UK) using a water/methanol/acetic acid (50:50:1%) mobile phase for positive ion mass spectrometry and water/isopropanol (50:50) in the negative ion mode [32]. The compounds were dissolved in dichloromethane (2 mM) and this solution was then diluted 1:10 with methanol. The diluted solution was directly injected into the spectrometer via a Rheodyne injector equipped 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 3 $\mu l\ min^{-1}$ and 500 $ml\ min^{-1}$, respectively. Voltages on the first skimmer electrode (B1) were varied between 70 V and the minimum possible consistent with retaining a stable ion jet. This varies from time to time but is usually in the range 25–35 V. Pressure in the mass analyser region was usually about 3×10^{-5} torr. The compounds in this study give 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.

Differential pulse and current sampled d.c. polarograms were recorded in acetone (0.1 M Bu_4NPF_6) on a Princeton Applied Research Corp. (PAR) (Princeton NJ) model 174A polarographic analyser. Potentials were measured against an Ag/AgCl (saturated LiCl; 0.1 M Bu_4NPF_6, acetone)) reference electrode. This electrode was frequently calibrated against the ferrocene couple (Fc^+/Fc) and all potentials are reported versus Fc^+/Fc. A drop time of 1 s and a scan rate of 5 $mV\ s^{-1}$ was used for both types of polarographic measurement. For differential pulse polarography, the pulse amplitude was 25 mV. All electrochemical measurements were made at 22 °C on solutions through which nitrogen was bubbled to remove oxygen.

3. Results and discussion

3.1. Reaction of $Hg(dtp)_2$ with dpmSe

3.1.1. NMR spectroscopy

NMR data for this system and all others studied in this paper are summarised in Table 1. Fig. 1 shows the ^{31}P NMR spectra in dichloromethane solution at

Table 1
NMR data

Mixture	Temp. (°C)	$\delta(^{31}P)$ (ppm)	$\delta(^{199}Hg)$ (ppm)	$\delta(^{113}Cd)$ (ppm)	$\delta(^{77}Se)$ (ppm)	Coupling constants (Hz)
$Hg(dtp)_2 + dpmSe$	−100	105.5s	870d			$^1J(Hg,P) = 5780$
		104.4s	815d			$^1J(Hg,P) = 6260$
		102.5s			−1600d	$^1J(Se,P) = 678$
		28.9d			−1570d	$^1J(Se,P) = 685$
		25.3d				$^2J(P,P) = 15–20$
		19.6d				
		16.9d				
$Cd(dtp)_2 + dpmSe$	−70	106.2s				
		28.9d			−1585dd	$^1J(Se,P) = 675$
		−21.6d		392dt		$^3J(Se,P) = 40$
						$^1J(Cd,P) = 1350$
						$^3J(Cd,P) = 60$
$Hg(dtp)_2 + dpmSe_2$	−70	102.4s				$^1J(Se,P) = 720$
		23.3s				
$Cd(dtp)_2 + dpmSe_2$	−80	104.3s				$^1J(Se,P) = 690$
		22.8s				
$Hg(dtp)_2 + dpmS$	22	104.1s				
		35.5s				
		34.2s				
		15.0s,br				
$Cd(dtp)_2 + dpmS$	22	105.5s				
		37.8d				
		34.4s				
		−24.8d				
$Hg(dtp)_2 + dpmS_2$	22	93.8s				
		30.3s				
$Cd(dtp)_2 + dpmS_2$	22	100.0s				
		30.5s				

a series of temperatures for an equimolar mixture of $Hg(dtp)_2$ and dpmSe. At 20 °C (Fig. 1(a)) the spectrum shows a singlet at δ 105.2, a double at δ 29.4 and a very broad resonance at about δ 20. Expansion reveals ^{77}Se satellites for the doublet. The high frequency singlet is due to the dithiophosphate ligands and the lack of ^{199}Hg satellites show that these ligands are labile on the NMR timescale at this temperature. The doublet is due to the selenated phosphorus atom of dpmSe the signal of which is split by coupling to the P(III) atom of the ligand and the broad resonance is attributed to the P(III) atom of dpmSe. This type of spectrum has been observed before [10] and indicates that the dpmSe ligand is moderately labile on the NMR timescale. Thus, at room temperature, competition between the three potentially bidentate ligands for the four tetrahedral coordination sites at mercury leads to exchange of all the ligands. (Note that $Hg(dtp)_2$ itself is labile on the NMR timescale at room temperature [5].) At −30 °C (Fig. 1(b)) the dithiophosphate resonance is still a sharp singlet but the dpmSe signal now consists of two sharp doublets, with the one at higher frequency displaying ^{77}Se satellites and the other having ^{199}Hg satellites. The P,Se coupling (674 Hz) is reduced from the value for the free ligand (732 Hz) [30] indicating coordination of selenium to mercury [31]. The appearance of ^{199}Hg satellites for the other doublet, which is well shifted from the resonance position found for the P(III) atom in free dpmSe, indicates that the phosphorus donor atom of dpmSe is also coordinated to mercury. Thus this spectrum indicates that at −30 °C the observable species in solution is $[(\eta^2\text{-dpmSe})Hg]^{2+}$ with the dpmSe ligand static on the NMR timescale, but with the dithiophosphate ligands still labile. At −70 °C the dithiophosphate resonance is still a singlet but the P(III) resonance of the dpmSe ligand is again broad. Upon further cooling the dithiophosphate resonance begins to broaden as the dithiophosphate ligand exchange begins to slow down and the two signals due to the dpmSe ligand resolve into four signals. At −100 °C (Fig. 1(c)) the dithiophosphate resonance is now resolved into three signals and there are two sets of signals for the dpmSe ligands although their fine structure is not clearly resolved, presumably due to viscosity effects. This spectrum indicates that two major species are present in solution at this temperature and that both contain bidentate dpmSe. As the maximum coordination number of mercury in systems of this type in solution is usually four [5] there are only two possible species, namely $[(\eta^2\text{-dpmSe})Hg(\eta^2\text{-dtp})][S_2P(OEt)_2]$ and $(\eta^2\text{-dpmSe})Hg(\eta^1\text{-dtp})_2$. There are three dithiophosphate resonances in the spectrum as required by

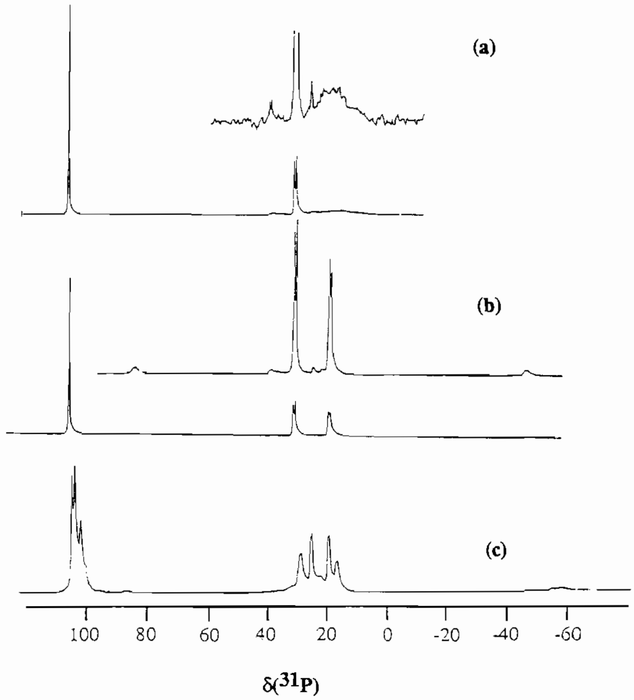

Fig. 1. ^{31}P NMR spectra of a dichloromethane solution containing $Hg(dtp)_2$ and dpmSe (1:1) as a function of temperature: (a) 20, (b) −30, (c) −100 °C.

this interpretation of the data. These ^{31}P NMR spectra provide an interesting example of change from fast to slow exchange average spectra which is then repeated as the two different ligands have independent exchange rates which become slow on the NMR timescale at different temperatures.

Full confirmation of the interpretation of the ^{31}P NMR data is provided by the ^{199}Hg and ^{77}Se NMR spectra. At −30 °C the ^{199}Hg NMR spectrum consists of a doublet (J = 6300 Hz) due to splitting by the phosphorus atom of the coordinated dpmSe ligand, but coupling to the P(Se) atom is not resolved, although the peaks are rather broad. This spectrum confirms that at this temperature only one (average) species exists in the solution with the dpmSe ligands coordinated and the dithiophosphate ligands being labile on the NMR timescale. At about −80 °C the ^{199}Hg NMR spectrum consists of two doublets and at −100 °C they are well defined. This spectrum confirms that at these temperatures there are two distinguishable mercury species each containing a chelated dpmSe ligand (^{31}P NMR data). Coupling to the P(Se) and dithiophosphate ligands is not resolved so that an unambiguous assignment of the mercury doublets to the two proposed species is not possible.

The ^{77}Se NMR spectra also support the conclusions reached above. At −30 °C the spectrum consists of one doublet (due to phosphorus coupling) with different chemical shift and reduced coupling constant compared with the free ligand confirming selenium coordination to mercury [26], but the signal to noise ratio is not sufficient to show ^{199}Hg satellites. The spectrum confirms that only one type of compound with chelated dpmSe exists in solution at this temperature. At −100 °C there are two doublets each indicating chelated dpmSe ligands, thus confirming the conclusions from the ^{31}P and ^{199}Hg NMR spectral data.

When $Hg(dtp)_2$ is reacted with two mole equivalents of dpmSe the ^{31}P NMR spectrum shows the system to be completely labile at room temperature with both kinds of ligand rapidly exchanging, but as the solution is cooled to −80 °C resonances assigned to coordinated dpmSe appear, together with other resonances which could be assigned to either free dpmSe or to Se-bonded dpmSe [10]. However, only one set of signals (with ^{199}Hg satellites) due to P-bonded dpmSe is observed even at −100 °C and the ^{199}Hg NMR spectrum at −100 °C is only one doublet. The conclusion is that additional dpmSe enhances the lability (that is, the rate of ligand exchange) of the system and it is not possible to determine the species present in solution from the NMR spectra.

3.1.2. *Electrospray mass spectrometry*

Peaks in the ES mass spectra are identified by the m/z value for the most intense peak in the isotopic mass distribution. In all cases the agreement between experimental and calculated isotopic mass distribution was excellent.

The mass spectra of a solution of $Hg(dtp)_2$ in methanol/dichloromethane were examined by both positive and negative ion ESMS. The negative ion mass spectrum showed the presence of peaks at m/z 757 and 185 assigned to $[Hg(dtp)_3]^-$ and dtp^-, respectively. Confirmation of the identity of the peak at m/z 757 was obtained by adding dtp^- to the $Hg(dtp)_2$ solution and observing a greatly enhanced signal. The positive ion ES mass spectrum of a solution of $Hg(dtp)_2$ showed a peak at m/z 957 assigned to $[Hg_2(dtp)_3]^+$. This species has been observed previously by ESMS from the reaction between $Hg(dtp)_2$ and $Hg_2(ClO_4)_2$ [29]. The observation of these species in the mass spectra can be rationalised in terms of the existence of the following equilibria in solution.

$$Hg(dtp)_2 \rightleftharpoons [Hg(dtp)]^+ + dtp^- \qquad (1)$$

$$[Hg(dtp)]^+ + Hg(dtp)_2 \rightleftharpoons [Hg_2(dtp)_3]^+ \qquad (2)$$

$$dtp^- + Hg(dtp)_2 \rightleftharpoons [Hg(dtp)_3]^- \qquad (3)$$

The ion $[Hg(dtp)]^+$ was not observed (and nor was the analogous $[Hg(dtc)]^+$ [29]) and this is believed to be due to formation of the neutral Hg(dtp)(OAc) by reaction with the acetate ion contained in the mobile phase.

Both positive and negative ion ESMS were used to investigate the interaction between $Hg(dtp)_2$ and dpmSe.

Positive ion ESMS unambiguously confirms the presence of $[(dpmSe)Hg(dtp)]^+$ in a solution containing equimolar quantities of dpmSe and $Hg(dtp)_2$, thereby supporting the NMR results. Fig. 2(a) shows the ES mass spectrum for such a solution and it is dominated by the peak at *m/z* 849 due to the intact ion $[(dpmSe)Hg(dtp)]^+$. Fig. 2(b) shows the comparison between experimental and calculated isotopic mass distributions and provides unambiguous confirmation of the assignment. Addition of further dpmSe to the solution gave rise to an ES mass spectrum still having $[(dpmSe)Hg(dtp)]^+$ as the base peak, but an additional peak was observed at *m/z* 1313, due to the ion $[(dpmSe)_2Hg(dtp)]^+$. This complex was not identified by the NMR studies since mixtures of this composition are too labile. ESMS data for this mixture and others studied are summarised in Table 2.

Negative ion ESMS was also used to monitor the reaction between $Hg(dtp)_2$ and dpmSe. As noted above, the negative ion ES mass spectrum of $Hg(dtp)_2$ shows peaks at *m/z* 757 and 185 due to $[Hg(dtp)_3]^-$ and dtp^-, respectively. As dpmSe is added, a small quantity at a time, the peak at *m/z* 757 decreases relative to that at *m/z* 185 and at approximately 1:1 molar proportions only the latter peak is observed. These observations indicate that at 1:1 molar proportions there is a negligible amount of $Hg(dtp)_2$ available to form the $[Hg(dtp)_3]^-$ ion and this is consistent with the known reactivity of $Hg(dtp)_2$ towards phosphine ligands.

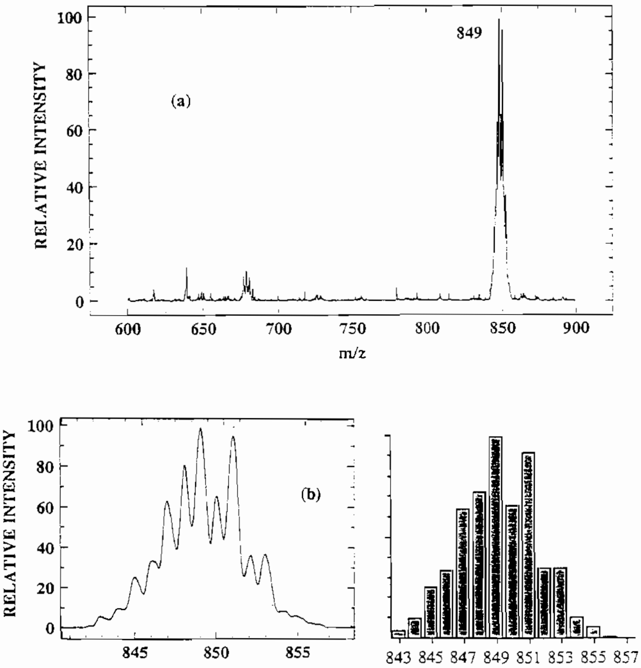

Fig. 2. (a) ES mass spectrum of a dichloromethane/methanol solution containing $Hg(dtp)_2$ and dpmSe (1:1). (b) Comparison of experimental and calculated isotopic mass distributions.

Table 2
Positive ion electrospray mass spectrometric data

Mixture	Ions (*m/z*)
$Hg(dtp)_2 + dpmSe$	$[(dpmSe)Hg(dtp)]^+$ (849); $[(dpmSe)_2Hg(dtp)]^+$ (1313)
$Cd(dtp)_2 + dpmSe$	$[(dpmSe)Cd(dtp)]^+$ (761)
$Hg(dtp)_2 + dpmS$	$[(dpmS)Hg(dtp)]^+$ (803)
$Cd(dtp)_2 + dpmS$	$[(dpmS)Cd(dtp)]^+$ (715)
$Hg(dtp)_2 + dpmSe_2$	$[(dpmSe_2)_2Hg]^{2+}$ (643); $[(dpmSe)Hg(dtp)]^+$ (849); $[(dpmSe_2)Hg(dtp)]^+$ (929)
$Cd(dtp)_2 + dpmSe_2$	$[(dpmSe_2)Cd(dtp)]^+$ (841)
$Hg(dtp)_2 + dpmS_2$	$[(dpmS_2)Hg(dtp)]^+$ (835)
$Cd(dtp)_2 + dpmS_2$	$[(dpmS_2)Cd(dtp)]^+$ (747)

3.1.3. *Electrochemical studies*

Previous studies of the oxidative electrochemistry of dpmSe at a mercury electrode [10] can be summarised as

$$Hg + 2dpmSe \rightleftharpoons [Hg(dpmSe)_2]^{2+} + 2e^- \quad \text{(process 1)} \qquad (4)$$

The electrochemical reduction of $Hg(dtp)_2$ at a mercury electrode [9] revealed two reversible responses which were attributed to the reactions

$$3Hg(dtp)_2 + 2e^- \rightleftharpoons Hg + 2[Hg(dtp)_3]^- \quad \text{(process 2)} \qquad (5)$$

$$2[Hg(dtp)_3]^- + 4e^- \rightleftharpoons 2Hg + 6[dtp]^- \quad \text{(process 3)} \qquad (6)$$

Overall

$$Hg(dtp)_2 + 2e^- \rightleftharpoons Hg + 2[dtp]^- \qquad (7)$$

Although these systems have been well characterised by electrochemical and spectroscopic techniques, the mixed $Hg(dtp)_2$/dpmSe system has not been previously investigated by electrochemical methods.

Fig. 3 shows differential pulse voltammograms for pure solutions of dpmSe and $Hg(dtp)_2$ and mixtures thereof in acetone (0.1 M Bu_4NPF_6). For reversible processes, the peak potential, E_p, obtained from differential pulse polarograms is closely related to the reversible half-wave potential, $E^r_{1/2}$, and therefore has thermodynamic significance. Fig. 3(a) is the differential pulse polarogram of a 0.5 mM solution of dpmSe in acetone (0.1 M Bu_4NPF_6) and shows a well defined reversible response (process 1, Eq. (4)) with a peak potential of -0.493 V versus Fc^+/Fc. The reason for the apparent slight discrepancy in potential (about 50 mV) with previous studies [10] may be due to the different electrolyte used, although further studies would be required to identify the origin of the differences. Fig. 3(e) is the corresponding polarogram of a 0.5 mM

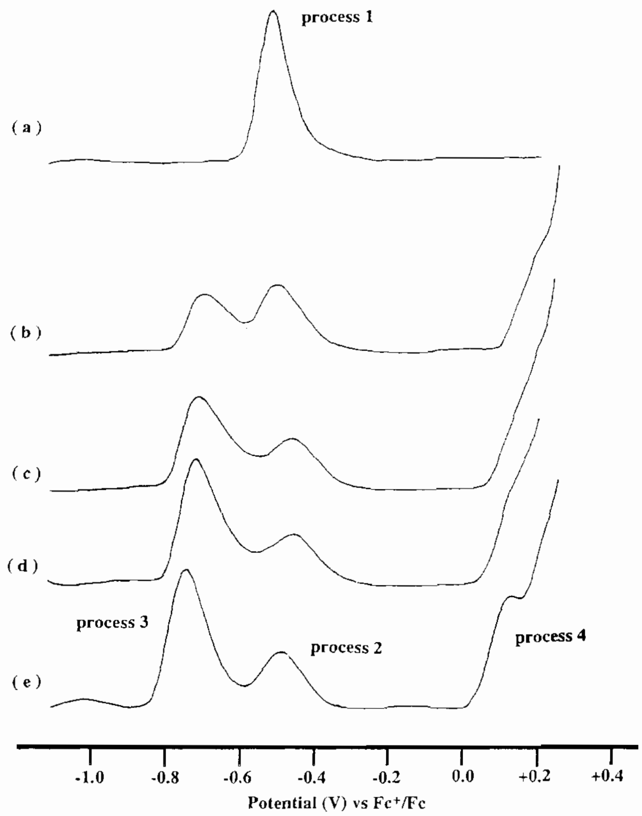

Fig. 3. Differential pulse polarograms for the $Hg(dtp)_2$/dpmSe system at different molar ratios: (a) dpmSe, (b) dpmSe:$Hg(dtp)_2$ = 2:1, (c) 1:1, (d) 1:2, (e) $Hg(dtp)_2$.

solution of $Hg(dtp)_2$ and it shows a number of responses. The well defined processes 2 and 3 with $E_p{}^2$ and $E_p{}^3$ at -0.483 and -0.734 V versus Fc^+/Fc, respectively, have been characterised previously [9] and correspond to the reactions in Eqs. (5) and (6). Process 4 which occurs at the mercury oxidation limit has been observed previously [9], but not identified. However, since that report was made, analogous complexes with the dithiocarbamate ligand have been well characterised [29,33,34] by a variety of techniques (including electrochemistry) as mercury-rich cationic dithiocarbamate species, and the analogous cationic mercury dithiophosphate ions themselves have been identified by electrospray mass spectrometry [29]. By analogy, therefore, process 4 is identified as the oxidation of the mercury electrode in the presence of dithiophosphate ligand. Other minor processes seen in Fig. 3(e) at about -1.0 V versus Fc^+/Fc have been previously attributed to adsorption phenomena [9]. All electrochemical data are summarised in Table 3.

Fig. 3(b)–(d) shows differential pulse polarograms for various molar proportions of dpmSe and $Hg(dtp)_2$. The solutions were prepared such that the total bulk concentration of all electroactive species remains constant for these and subsequent measurements, although the concentrations of the individual components vary. For example, the 2:1 molar ratio solution was prepared by adding 2.5 ml of 0.5 mM $Hg(dtp)_2$ to 5.0 ml of 0.5 mM dpmSe. The data summarised in Table 3 and Fig. 3 show that the total responses of the mixtures are not simply the summation of the processes for the initial components of the mixtures. For example, the process at most negative potential is shifted significantly from the potential of process 3, and although it is obviously derived from process 3 it is modified by the addition of dpmSe. It is therefore denoted as $E_p{}^3{}_{mix}$. Processes 1 and 2 for the individual compounds have very similar peak potentials, but in the mixtures only one response, $E_p{}^{1,2}{}_{mix}$, is seen at more positive potentials than either of the processes observed for the individual components.

Process 3 is well resolved from processes 1 and 2. Table 3 shows the shift in peak potential for process 3 from dilution of $Hg(dtp)_2$ alone, which would occur during the addition of dpmSe solution, calculated on the basis of previous studies [9]. The present data in Table 3 show that for the mixture the potential shift of $E_p{}^3{}_{mix}$ is much greater than can be attributed to mere dilution of $Hg(dtp)_2$. This may be interpreted as being due to the additional lowering of the concentration of $[Hg(dtp)_3]^-$ via the following equilibria.

$$[Hg(dtp)_3]^- + dpmSe \rightleftharpoons Hg(dtp)_2(dpmSe) + dtp^- \quad (8)$$

$$Hg(dtp)_2(dpmSe) \rightleftharpoons [Hg(dtp)(dpmSe)]^+ + dtp^- \quad (9)$$

Table 3 shows the predicted [9,10] changes in potential based on concentration effects for processes 1 and 2. Whereas for process 2, $E_p{}^2$ becomes more negative with decreasing concentration of $Hg(dtp)_2$ and process 1 is essentially independent of the concentration of dpmSe, within the concentration range studied the average response, $E_p{}^{1,2}{}_{mix}$, for the mixture shifts to considerably more negative potentials as the molar concentration of dpmSe increases. This is also consistent with a decrease in the concentration of $[Hg(dtp)_3]^-$ in solution according to the equilibria in Eqs. (5) and (8). The average process, represented by $E_p{}^{1,2}{}_{mix}$, corresponds to a combination of the overall equations

$$Hg(dtp)_2(dpmSe) + 2e^- \rightleftharpoons Hg + 2dtp^- + dpmSe \quad (10)$$

$$[Hg(dtp)(dpmSe)]^+ + 2e^- \rightleftharpoons Hg + dtp^- + dpmSe \quad (11)$$

$$[Hg(dtp)(dpmSe)_2]^+ + 2e^- \rightleftharpoons Hg + dtp^- + 2dpmSe \quad (12)$$

Table 3
Differential pulse polarographic data for 0.5 mM $Hg(Et_2dtp)_2$ and 0.5 mM dpmSe and mixtures thereof in acetone (0.1 M Bu_4NPF_6) at 22 °C, pulse amplitude = 25 mV, drop time = 1.0 s

Reactant ratio dpmSe: $Hg(Et_2dtp)_2$	Experimental values for pure compounds[a]			Theoretical potentials for pure compounds as a function of concentration[b]			Experimental values for mixtures[c]		Difference between experimental and theoretical values	
	E_p^1 dpmSe (mV)[d]	E_p^2 $Hg(dtp)_2$ (mV)[d]	E_p^3 $Hg(dtp)_2$ (mV)[d]	$(E_p^1)_t$ (mV)[d]	$(E_p^2)_t$ (mV)[d]	$(E_p^3)_t$ (mV)[d]	$E_p^{1,2}{}_{mix}$ (mV)[d]	$E_p^3{}_{mix}$ (mV)[d]	$E_p^{1,2}{}_{mix} - (E_p^2)_t$ (mV)[d]	$E_p^3{}_{mix} - (E_p^3)_t$ (mV)[d]
1:0	−493			−493						
2:1				−493	−497	−706	−495	−679	2	27
1:1				−493	−492	−716	−443	−697	49	19
1:2				−493	−488	−724	−436	−706	52	18
0:1		−483	−734		−483	−734				

[a] E_p^1, E_p^2 and E_p^3 are the differential pulse polarographic peak potentials for processes 1, 2 and 3, respectively.

[b] $E_p^3{}_{mix}$ is the differential pulse polarographic peak potential of modified process 3, after mixing. $E_p^{1,2}{}_{mix}$ is the differential pulse polarographic peak potential of modified processes 1 and 2 after mixing.

[c] $(E_p^1)_t$, $(E_p^2)_t$ and $(E_p^3)_t$ are theoretically calculated differential pulse polarographic peak potentials of processes 1, 2 and 3 as a function of concentration [9,10].

[d] All potentials are reported relative to the Fc^+/Fc redox couple.

in combination with Eqs. (1)–(9). That is, the electrochemical data at room temperature are entirely consistent with a completely labile system in which the rates of exchange are fast on the voltammetric timescale.

Process 4, which involves oxidation of the electrode mercury to form mercury-rich dithiophosphate cationic species, diminishes in height as dpmSe is added to a solution of $Hg(dtp)_2$. These data are consistent with the lowering of the concentration of $Hg(dtp)_2$ in the solution both by dilution and complexation with dpmSe.

Fig. 4 shows current sampled d.c. polarograms over the potential range encompassing processes 1, 2 and 3. The total current (corrected for change in concentration) is approximately constant, confirming that all species generated in the reaction mixtures are electrochemically active. The resolution of the d.c. technique is not sufficient to accurately define the $E_{1/2}$ potentials of the individual processes in the mixtures.

3.2. Other reactions in similar systems

The reactions of $Cd(dtp)_2$ with dpmSe and both $Hg(dtp)_2$ and $Cd(dtp)_2$ with the ligands $dpmSe_2$, dpmS and $dpmS_2$ have also been investigated by NMR and ESMS techniques. These reaction mixtures are more labile than the $Hg(dtp)_2$/dpmSe system, so the amount of information which can be extracted from NMR studies is reduced.

3.2.1. NMR studies

The ^{31}P NMR spectrum of an equimolar mixture of $Cd(dtp)_2$ and dpmSe in dichloromethane at 20 °C shows a sharp dithiophosphate ligand resonance at δ 106 without cadmium satellites and two relatively sharp doublets at δ 29.3 and −21.9 due to the dpmSe ligand, again with no sign of cadmium satellites. The conclusion to be drawn from this spectrum is that both types of ligand are exchanging rapidly on the NMR timescale at this temperature. At −30 °C the only observable difference is that the resonance at about δ −22 is

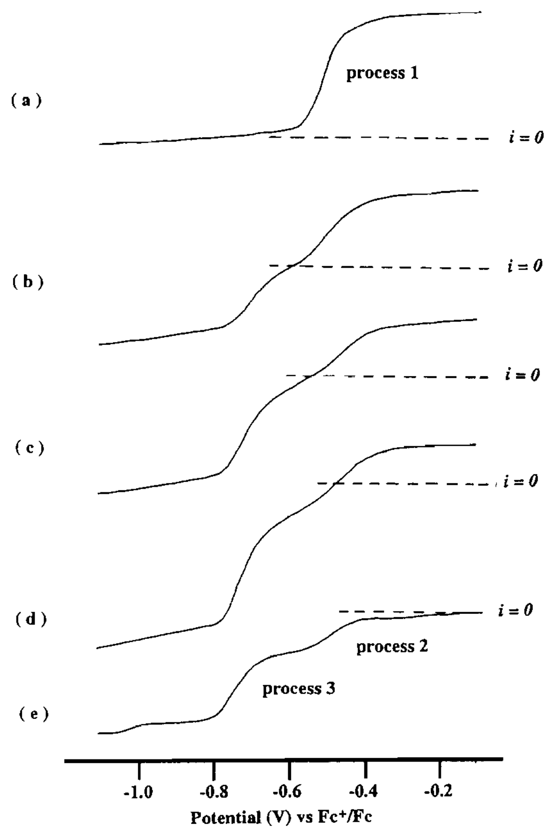

Fig. 4. Current sampled d.c. polarograms for the $Hg(dtp)_2$/dpmSe system at different molar ratios: (a) dpmSe, (b) dpmSe:$Hg(dtp)_2$ = 2:1, (c) 1:1, (d) 1:2, (e) $Hg(dtp)_2$.

broadened. At −50 °C this resonance is again sharp and cadmium satellites for it become visible, whilst the resonance at δ 29.3 shows ^{77}Se satellites with a coupling constant reduced from that of the free ligand, indicating selenium coordination to cadmium. Even at −70 °C the dithiophosphate ligand resonance remains relatively sharp, but slightly broadened compared with the room temperature spectrum, and no cadmium satellites can be discerned. These spectra suggest that at these temperatures the dpmSe ligand is chelated and static on the NMR timescale, but the dtp ligands are still exchanging rapidly, indicating that overall the Cd(dtp)$_2$/dpmSe system is more labile than the corresponding mercury system.

At −70 °C the ^{77}Se NMR spectrum is a doublet of doublets with the larger coupling constant of 674 Hz significantly smaller than that for free dpmSe, indicating selenium coordination to cadmium. It is ambiguous whether the smaller coupling of 40 Hz is to a dithiolate phosphorus atom or to the other phosphorus of the dpmSe ligand. Unfortunately, the signal to noise ratio of the spectrum is not sufficient to allow observation of cadmium satellites. At −70 °C the ^{113}Cd NMR spectrum is a doublet of triplets ($^1J=1350$ Hz, $^3J=60$ Hz), the larger coupling being to the phosphine of dpmSe and the smaller couplings due to two of the other three phosphorus atoms present. Since there is obviously coupling to a least one dithiophosphate ligand it must be assumed that the weak cadmium satellites for the dithiophosphate ^{31}P resonance are lost in the foot of the peak. Only one observable species is present in the solution at low temperature, in contrast to the mercury system, but the NMR data are ambiguous and cannot distinguish between (η^2-dpmSe)Cd(η^1-dtp)$_2$ and [(η^2-dpmSe)Cd(η^2-dtp)]$^+$ (corresponding to the mercury complexes) or indeed fast exchange between them.

At all temperatures over the range 30 to −100 °C, the ^{31}P NMR spectrum of a 1:1 mixture of Hg(dtp)$_2$ and dpmSe$_2$ consisted of two singlets at about δ 105 (dithiophosphate) and another at δ 29 with ^{77}Se satellites (J(P,Se) = 728 Hz). The coupling constant is slightly reduced from the value observed for the free ligand but no definitive information about any compound formation can be deduced from this data. Similar results were obtained for a solution of Cd(dtp)$_2$ and dpmSe$_2$ and data are summarised in Table 1.

The mixtures of M(dtp)$_2$ and dpmS and dpmS$_2$ are also labile over the temperature range studied and in the absence of any suitable magnetic isotope for sulfur, even less information about the species present in solution can be deduced from their NMR spectra. Data are summarised in Table 1.

3.2.2. ESMS studies

The ES mass spectrum of a solution containing equimolar quantities of Cd(dtp)$_2$ and dpmSe, or alternatively a solution of an isolated sample of (dpmSe)Cd(dtp)$_2$, gives a strong peak at m/z 761 which is due to the intact ion [(dpmSe)Cd(dtp)]$^+$, confirming the presence of this ion in the solution. However, ESMS can provide no information about whether the neutral (dpmSe)Cd(dtp)$_2$ is also present. In all the other systems examined, ESMS provides positive proof of the existence of the corresponding cationic species [(ligand)M(dtp)]$^+$ as detailed in Table 2. In the case of the Hg(dtp)$_2$/dpmSe$_2$ system, the ES mass spectrum gives a strong peak with the correct isotopic mass distribution at m/z 929 assigned to the intact ion [(dpmSe$_2$)Hg(dtp)]$^+$ but also another due to [(dpmSe)Hg(dtp)]$^+$ (m/z 849). This is believed to be formed by collisionally activated decomposition within the ion source as its relative intensity increases with increasing collisional energy. In addition, a weaker peak is also observed for [(dpmSe$_2$)$_2$Hg]$^{2+}$ (m/z 643), which has previously been characterized by interaction of Hg(ClO$_4$)$_2$ with dpmSe$_2$ [10].

4. Conclusions

It has been known for some time that Hg(dtp)$_2$ is labile on the NMR timescale and low temperatures are required to observe mercury–phosphorus coupling [5], but the mechanism of exchange was not understood. The ESMS studies described in this paper show the charged species dtp$^-$, [Hg(dtp)$_3$]$^-$ and [Hg$_2$(dtp)$_3$]$^+$ are involved in the equilibria.

The spectroscopic, mass spectrometric and electrochemical data for the Hg(dtp)$_2$/dpmSe system, which is the least labile system studied, are all consistent with global exchange reactions and equilibria represented by Eqs. (1)–(12), i.e. many species (depending upon relative concentrations) are present in these seemingly innocuous solutions. Each of the following have been identified by at least one of the techniques used: dtp$^-$, Hg(dtp)$_2$, [Hg(dtp)$_3$]$^-$, [Hg$_2$(dtp)$_3$]$^+$, dpmSe, Hg(dtp)$_2$(dpmSe), [Hg(dtp)(dpmSe)]$^+$ and [Hg(dtp)(dpmSe)$_2$]$^+$.

Only the Hg(dtp)$_2$/dpmSe (1:1) system could be unambiguously characterised by multinuclear magnetic resonance studies. This system provides a nice example of the complementary information provided by the NMR, ESMS and electrochemical techniques. The NMR spectroscopy provides much more structural information than ESMS on solutions containing equimolar quantities of Hg(dtp)$_2$ and dpmSe, although that knowledge is difficult to obtain. The combination of ^{31}P, ^{199}Hg and ^{77}Se NMR spectra is necessary to identify the two species in solution at low temperature as [(η^2-dpmSe)Hg(η^2-dtp)][S$_2$P(OEt)$_2$] and (η^2-dpmSe)Hg(η^1-dtp)$_2$. These NMR spectra have to be acquired at low temperature to reduce the rate of exchange on the NMR timescale, and for ^{199}Hg and ^{77}Se NMR spectra lengthy acquisition times are necessary. In contrast, although ESMS can detect only the ionic species in solution, this is done at room temperature within a few minutes. However, ESMS cannot determine the coordination modes of the ligands in the cation, nor can it detect neutral species in the solution. In the presence of additional dpmSe, the system is too labile to observe the slow exchange NMR spectra, and so ESMS provides the only information in this situation, successfully identifying $[Hg(dtp)(dpmSe)_2]^+$. The electrochemical studies confirm the lability of the system and provide some information on the thermodynamics of compound formation and, as with ESMS, the data is readily obtainable at room temperature.

The other systems examined provide a study in diminishing returns from NMR spectroscopy, so that only limited information is available from NMR studies of the $Cd(dtp)_2$/dpmSe system and effectively no information on complex formation is available from NMR spectroscopy for the dpmS and $dpmS_2$ systems with either $Hg(dtp)_2$ or $Cd(dtp)_2$. However, the information available from positive ion ESMS is essentially the same for all the systems examined and the cations $[(ligand)M(dtp)]^+$ are always observed.

While there is some variation in solvent used for the different techniques, the general conclusions are believed not to be solvent dependent. This conclusion is supported by limited electrochemical studies in the different solvents used and is consistent with the detailed data in acetone reported in this paper.

This series of compounds helps to confirm the rapidly growing impression that for solutions containing ionic components, ESMS is a powerful new technique for the inorganic chemist. We have shown previously [23–25] that ESMS can be used to observe ionic species in solutions which are rapidly exchanging on the NMR timescale at room temperature. However, in all those cases the static NMR spectra were observable at low temperatures so ESMS merely confirmed the earlier NMR conclusions. In this work ESMS is used for the first time to characterize mixed ligand systems, most of which are too labile for NMR techniques, even at low temperatures. Fortunately as the $Hg(dtp)_2$/dpmSe system can be fully characterised by multi-NMR methods, it provides an internal test for ESMS. The fact that ESMS readily confirms the presence of $[(dpmSe)Hg(dtp)]^+$, already identified by NMR methods, adds credence to the similar results for the other solutions which are too labile for NMR to be able to study adequately.

Acknowledgements

We thank La Trobe University for an SCAEF major equipment grant which assisted in the purchase of the electrospray mass spectrometer. J.H. thanks the Commonwealth Government for an Australian Postgraduate Research Award. The financial support of the Australian Research Council is gratefully acknowledged.

References

[1] A.M. Bond, R. Colton, M.L. Dillon, J.E. Moir and D.R. Page, *Inorg. Chem., 23* (1984) 2883.

[2] A.M. Bond, R. Colton, M.L. Dillon, A.F. Hollenkamp and J.E. Moir, *Inorg. Chem., 24* (1985) 1591.

[3] A.M. Bond, R. Colton, A.F. Hollenkamp and J.E. Moir, *Inorg. Chem., 25* (1986) 1519.

[4] A.M. Bond, R. Colton, A.F. Hollenkamp, B.F. Hoskins and K. McGregor, *J. Am. Chem. Soc., 109* (1987) 1969.

[5] A.M. Bond, R. Colton, D. Dakternieks, M.L. Dillon, J. Hauenstein and J.E. Moir, *Aust. J. Chem., 34* (1981) 1393.

[6] D.R. Dakternieks and D.P. Graddon, *Aust. J. Chem., 23* (1970) 1989.

[7] D.R. Dakternieks and D.P. Graddon, *Aust. J. Chem., 23* (1970) 2521.

[8] D.R. Dakternieks and D.P. Graddon, *Aust. J. Chem., 24* (1970) 2077.

[9] A.M. Bond, A.T. Casey and J.R. Thackeray, *J. Electrochem. Soc., 120* (1973) 1502.

[10] A.M. Bond, R. Colton and J. Ebner, *Inorg. Chem., 27* (1988) 1697.

[11] X. Xu, S.P. Nolan and R.B. Cole, *Anal. Chem., 66* (1994) 119.

[12] M. Yamashita and J.B. Fenn, *J. Phys. Chem., 88* (1984) 4451.

[13] M. Yamashita and J.B. Fenn, *J. Phys. Chem., 88* (1984) 4671.

[14] C.M. Whitehouse, M. Yamashita, J.B. Fenn and R.N. Dreyer, *Anal. Chem., 57* (1985) 675.

[15] J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong and C.M. Whitehouse, *Science, 246* (1989) 64.

[16] J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong and C.M. Whitehouse, *Mass Spectrom. Rev., 9* (1990) 37.

[17] R.D. Smith, J.A. Loo, C.G. Edmonds, C.J. Barinaga and H.R. Udseth, *Anal. Chem., 62* (1990) 882.

[18] R.D. Smith, R.J. Loo, R.R. Ogorzalek-Loo, M. Busman and H.R. Udseth, *Mass Spectrom. Rev., 10* (1991) 359.

[19] R. Colton and J.C. Traeger, *Inorg. Chim. Acta, 201* (1992) 153.

[20] R. Colton, J.C. Traeger and V. Tedesco, *Inorg. Chem., 31* (1992) 3865.

[21] R. Colton, J.C. Traeger and J. Harvey, *Org. Mass. Spectrom., 27* (1992) 1030.

[22] I. Ahmed, A.M. Bond, R. Colton, M. Jurcevic, J.C. Traeger and J.N. Walter, *J. Organomet. Chem., 447* (1993) 59.

[23] R. Colton, B.D. James, I.D. Potter and J.C. Traeger, *Inorg. Chem., 32* (1993) 2626.

[24] R. Colton and D. Dakternieks, *Inorg. Chim. Acta, 208* (1993) 173.

[25] T.J. Cardwell, R. Colton, N. Lambropoulos, J.C. Traeger and P.J. Marriott, *Anal. Chim. Acta, 280* (1993) 239.

[26] J.M. Curtis, P.J. Derrick, A. Schnell, E. Constantin, R.T. Gallagher and J.R. Chapman, *Inorg. Chim. Acta, 201* (1992) 153.

[27] S.R. Wilson, A. Yasmin and Y. Wu, *J. Org. Chem., 57* (1992) 6941.

[28] A.M. Bond, R. Colton, A. D'Agostino, J. Harvey and J.C. Traeger, *Inorg. Chem., 32* (1993) 3952.
[29] A.M. Bond, R. Colton, J. Harvey and J.C. Traeger, *Inorg. Chim. Acta, 212* (1993) 233.
[30] S.W. Carr and R. Colton, *Aust. J. Chem., 34* (1981) 35.
[31] R. Colton and P. Panagiotidou, *Aust. J. Chem., 40* (1987) 13.
[32] R.F. Straub and R.D. Voyksner, *J. Am. Soc. Mass. Spectrom., 4* (1993) 578.
[33] A.M. Bond, R. Colton, A.F. Hollenkamp, B.F. Hoskins and K. McGregor, *J. Am. Chem. Soc., 109* (1987) 1969.
[34] A.M. Bond, R. Colton, A.F. Hollenkamp and K. McGregor, *Inorg. Chim. Acta, 168* (1990) 233.