Complexes in solution formed by an organometallic tripodal oxygen ligand with monovalent, divalent and trivalent metal ions: an electrospray mass spectrometric study

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Abstract

Electrospray mass spectrometry (ESMS) has been used to observe mass spectra for solutions of a wide variety of metal salts of the uni-negative tripodal oxygen donor ligand $[(C_5H_5)Co\{P(O)(OEt)_2\}_3]^-$, abbreviated to L^-. In aqueous/methanol solutions the sodium salt gives peaks in the ES mass spectrum corresponding to species containing one, two and three ligand moieties showing that the trimeric structure known to occur in the solid state and in benzene solution is partially retained even in aqueous media. The species observed are all monocations generated by addition of protons (from the mobile phase) or sodium ions to L^-, L_2^{2-} or L_3^{3-}. Addition of NaL to KCl solution gives ions corresponding to almost global exchange of Na^+ and K^+, but CsCl does not give any ions with more than one Cs^+, although the oligomeric units are retained with additional H^+ and Na^+ coordinated. In contrast, Li^+ competes successfully with Na^+ for coordination to L^-, and the peak intensities of the dimeric and trimeric oligomers are greatly reduced. These observations are in accord with known stability constant data of these metals with L^-. The Group 2 metals react with a deficiency of L^- to give the protonated species $[HML(OAc)]^+$ (the acetate is derived from the mobile phase) and with sufficient L^- present the ES mass spectra show peaks due to the ions $[HML_2]^+$. Group 3 metals and the lanthanides give the ions $[ML(OAc)]^+$ and $[HML(OAc)_2]^+$ with a deficiency of L^-, and exclusively $[ML_2]^+$ with an excess of L^- present. ESMS provides a convenient method for the qualitative analysis of mixtures of lanthanide and Group 3 elements after complexing with L^-.

Introduction

The tripodal oxygen ligand $[(C_5H_5)Co\{P(O)(OEt)_2\}_3]^-$ (L^-), Structure 1,
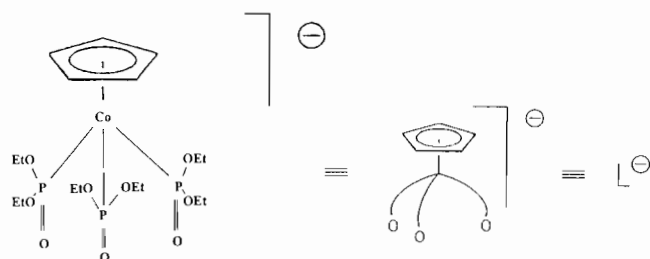
has been shown to be a versatile ligand forming coordination complexes with a large number of monovalent, divalent and trivalent metals, but somewhat more surprisingly it also bonds to low oxidation state organometallic fragments [1–12]. The coordination complexes are thermodynamically very stable, mainly as a result of a favourable entropy term [13]. The structures of a number of derivatives of this ligand in the solid state have been determined by X-ray crystallography and the sodium salt has been shown to have a unique trimeric structure in which each ligand is bidentate to one sodium ion with the third oxygen bridging to another sodium ion and the trimeric structure is retained in benzene solution (molecular weight determinations) [14]. The aggregation into trimeric units buries the three sodium ions in a hydrophobic cavity that is surrounded by lipophilic cyclopentadienyl rings and 18 ethoxy groups. This explains why the sodium salt has the remarkable properties of being soluble in both water and pentane. However, even in coordinating solvents like water this sodium salt, NaL, does not behave like a 1:1 electrolyte but still tends to aggregate (conductivity measurements). All efforts to follow the dynamics of the aggregation of NaL by ^1H, ^{13}C and ^{31}P NMR, UV–Vis and IR spectroscopies have been unsuccessful.

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With the availability of the new technique of electrospray mass spectrometry (ESMS) we hoped to gain detailed insights into the aggregation behaviour and coordination chemistry of this unusual tripodal oxygen ligand.

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 largely developed by Fenn and coworkers [15–17] and its most common applications so far have been in the area of mass spectrometric studies of large bio-molecules [18–20]. In these studies the neutral molecules are multiply protonated by the mobile phase $(H_2O/MeOH/HOAc = 50:50:1\%)$ which is used to introduce the species into the electrospray source, and the protonated cations are observed in the mass spectrum. In a similar manner, high molecular weight poly(ethyleneglycols) have been observed at relatively low m/z values by multiple sodium additions [21]. A recent paper [22] reported the ES mass spectra of β-diketone and mixed β-diketone/acetate complexes of some of the lanthanide elements which were observed via ligand exchange and protonation of the neutral complexes by the mobile phase.

Recent work in our laboratories [23] has shown that ESMS may advantageously be applied to a wide variety of ionic inorganic and organometallic species which do not necessarily depend upon protonation by the mobile phase for observation of their mass spectra. Typical species investigated include phosphonium salts, cationic dithiolate and phosphine complexes of several metals, such as $[(P\text{-}P)Pt(S\text{-}S)]^+$ (P-P = diphosphine, S-S = dithiocarbamate etc.) [24–29], as well as organometallic systems [30–32].

In this paper we present some ESMS observations on the species formed in solution by the interaction of NaL with various metal cations in aqueous methanol solutions. Although we observe the trivalent $[ML_2]^+$ species, as expected, it has emerged that the ML and ML_2 complexes are also observable via protonation by the mobile phase.

Experimental

The compound $Na_3L_3 \cdot 2H_2O$ (NaL) was prepared as described previously [4]. About 1–2 mg of salts of the metals to be investigated were dissolved in water or methanol (1 ml) and a few drops of a solution NaL in methanol were added. This mixed solution was then diluted 1:10 with methanol for the ESMS investigations.

Electrospray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer (VG Bio-Q, VG Bio-Tech, Altrincham, Ches., UK) using a water/methanol/acetic acid (50:50:1%) mobile phase. The diluted solutions of the compounds, prepared as described above, were injected directly 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 μl min^{-1}. Nitrogen was used as both a drying gas and for nebulisation with flow rates of approximately 3 and 100 ml min^{-1}, respectively. Pressure in the mass analyser region was usually about 3×10^{-5} torr. The compounds in this study give strong signals in their ES mass spectra and typically 4–8 signal averaged spectra were required to give a good signal to noise ratio. Increasing the voltage on the first skimmer electrode (B1) may induce fragmentation caused by collisions with solvent molecules in the region of the nozzle where the pressure is close to atmospheric. Measurements were made at a B1 voltage of 40 V unless stated otherwise.

Fragmentation may also be studied via tandem mass spectrometry. Ions of a particular m/z value (i.e. the peak maximum in an isotopic mass distribution) can be selected and passed through a collision cell into a second mass analyser. Collision activated decomposition (CAD) mass spectra of the selected precursor ions can be obtained by admitting argon to the collision cell to a pressure that gave an approximately 50% reduction in the parent ion abundance, usually with an accelerating voltage of 200 V.

Results and discussion

Peaks in the ES mass spectra are identified by the most intense m/z value in the isotopic mass distribution, in all cases the experimental and calculated isotopic mass distribution agreed well.

NaL and derivatives with monovalent metals

All data for derivatives of monovalent metal ions with the ligand L^- are given in Table 1.

Figure 1 shows the ES mass spectrum of a solution of NaL dissolved in methanol. The mass spectrum consists of three families of peaks at widely different m/z ranges and under the prevailing experimental conditions the peaks around m/z 1100 are the strongest and those at the highest m/z values are much weaker, but easily observable. In the lowest m/z range (Fig. 1(a)) peaks identified as $[H_2L]^+$, $[HNaL]^+$ and $[Na_2L]^+$ are observed at m/z 537, 559 and 581, respectively. The additional peak at m/z 513 will be discussed below. The diprotonated ligand cation has been identified previously in chemical reactions [14]. The strong peaks in the intermediate m/z range are assigned to species containing two ligand moieties, $[H_2NaL_2]^+$ (1095), $[HNa_2L_2]^+$ (1117) and $[Na_3L_2]^+$ (1139) (Fig. 1(b)). In the context of this paper such species will be referred

TABLE 1. ESMS data for complexes of L^- with Group 1 elements

Mixture	Ions $(m/z)^a$
NaL	$[H_2L]^+$(537); $[HNaL]^+$(559); $[Na_2L]^+$(581); $[H_2NaL_2]^+$ (1095); $[HNa_2L_2]^+$(1117); $[Na_3L_2]^+$(1139); $[H_2Na_2L_3]^+$(1653); $[HNa_3L_3]^+$(1675); $[Na_4L_3]^+$(1697)
KCL + NaL	$[HKL]^+$(575); $[NaKL]^+$(597); $[K_2L]^+$(613); $[H_2KL_2]^+$(1111); $[HNaKL_2]^+$(1133); $[HK_2L_2]^+$(1149); $[Na_2KL_2]^+$(1155); $[NaK_2L_2]^+$(1171); $[H_2NaKL_3]^+$(1669); $[HNa_2KL_3]^+$(1691); $[Na_3KL_3]^+$(1713); $[Na_2K_2L_3]^+$(1729); $[NaK_3L_3]^+$(1745)
CsBr + NaL	$[HCsL]^+$(669); $[NaCsL]^+$(691); $[H_2CsL_2]^+$(1205); $[HNaCsL_2]^+$(1227); $[Na_2CsL_2]^+$(1249); $[H_2NaCsL_3]^+$(1763); $[HNa_2CsL_3]^+$(1785); $[Na_3CsL_3]^+$(1807)
LiCl + NaL	$[HLiL]^+$(543); $[Li_2L]^+$(549); $[LiNaL]^+$(565); $[H_2LiL_2]^+$(1079); $[HLi_2L_2]^+$(1085); $[Li_3L_2]^+$(1091); $[Li_2NaL_2]^+$(1107)

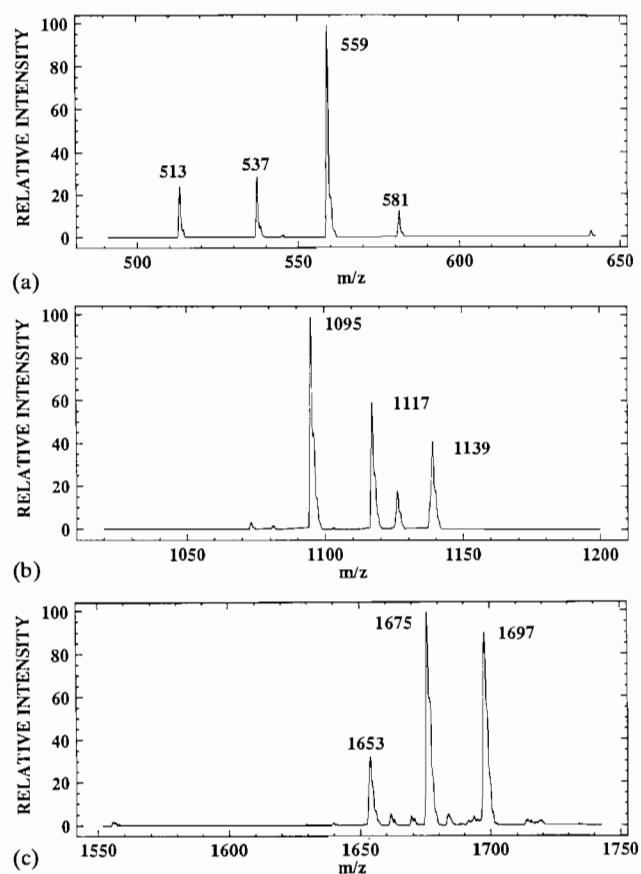^{a}Peaks due to species derived from NaL are observed in all cases, in addition to the species listed.

Fig. 1. Positive ion ES mass spectra (B1 = 40 V) at different m/z ranges for a solution of NaL: (a) m/z 500–650 (monomers), (b) 1050–1200 (dimers), (c) 1550–1750 (trimers).

to as dimers, indicating two ligand (L^-) units, rather than referring to the number of metal atoms in the molecule (which varies from 3 to 5 for the dimers). The peak at 1126 is assigned to $[FeL_2]^+$; it is a frequent impurity and is thought to arise from interaction of the solution with the steel evaporation nozzle in the

ion source under electrospray conditions. Figure 1(c) shows the peaks at highest m/z values which are assigned to species containing three ligand units, $[H_2Na_2L_3]^+$ (1653), $[HNa_3L_3]^+$ (1675) and $[Na_4L_3]^+$ (1697). No peaks were observed at higher m/z ranges. These ES mass spectra show the surprising result that the trimeric units found in the solid state and in non-aqueous solvents persist even in acidic aqueous media.

Figure 2 shows the effects on the ES mass spectra of the low m/z species caused by varying the ion source energy (B1 voltage). At B1 = 30 V (Fig. 2(a)) only $[H_2L]^+$ (537) and $[HNaL]^+$ (559) are observed but at B1 = 40 V (Fig. 2(b)) an extra peak at m/z 513 appears, as well as the peak at m/z 581 due to $[Na_2L]^+$. As the B1 voltage is increased to 60 V (Fig. 2(c)) two new peaks appear at m/z 445 and 491 and the relative intensities of the original peaks at m/z 537 and 559 are greatly diminished, although the relative intensity of m/z 581 increases. Finally at B1 = 80 V (Fig. 2(d)) the peak at m/z 445 dominates, but the peak at m/z 581 remains. Inspection of the m/z values reveals that m/z 513 = 559 − 46, 491 = 537 − 46 and 445 = 491 − 46 suggesting a common fragmentation pattern which is loss of EtOH, formed from an OEt group and a proton. This was confirmed by tandem mass spectrometry. Ions of mass 559 were selected from the first mass analyser and passed through the collision cell containing argon, under an accelerating voltage of 200 V. Only one product ion was observed at m/z 513. In contrast, when ions of m/z 537 were selected in the same manner, they gave two product ions at m/z 491 and 446. This experiment confirms that the fragmentation pattern does involve elimination of EtOH from both original ions. $[HNaL]^+$ (559) can only lose one EtOH moiety since it is only singly protonated, but $[H_2L]^+$ (537) can undergo the process twice. $[Na_2L]^+$, with no protons, cannot undergo this elimination at all and so it remains unaffected by varying the ion source energy, thus its
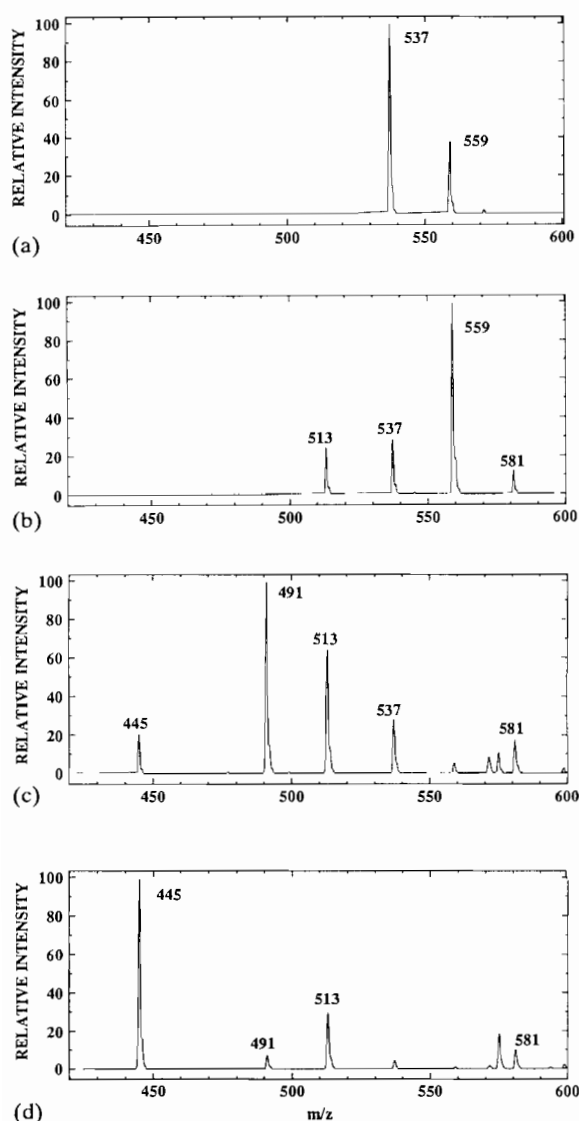
Fig. 2. Positive ion ES mass spectra at different ion source energies (B1 voltages) for a solution of NaL: B1 = 30 (a), 40 (b), 60 (c), 80 (d) V.

intensity relative to the peaks at m/z 537 and 559 increases as the B1 voltage is increased.

The ES mass spectra of the NaL solutions could be interpreted either as showing that monomers, dimers and trimers are present simultaneously in the solution, or alternatively that the main species are trimers and the observed dimers and monomers are fragments formed by collisions within the ion source. In an attempt to resolve this point, ES mass spectra covering the m/z range for monomers and dimers were acquired at different B1 voltages. If the monomers were indeed product ions of the dimers then it might be expected that their relative intensities would increase with B1 voltage, at least for lower values of B1 voltage. As the B1 voltage was increased, the intensities of the peaks for $[H_2NaL_2]^+$ (1095) and $[HNa_2L_2]^+$ (1117) relative

to that of $[Na_3L_2]^+$ (1139) decreased rapidly until at B1 = 80 V the ES mass spectrum was dominated by the peak due to $[Na_3L_2]^+$ (1139). The peaks due to $[H_2L]^+$ and $[HNaL]^+$ (but not $[Na_2L]^+$) also decreased and no new peaks appeared. These spectra suggest that since $[Na_3L_2]^+$ withstands high ion source energies, breakdown of dimer units to monomers is not a facile process in the gas phase and that $[H_2NaL_2]^+$ (1095) and $[HNa_2L_2]^+$ (1117) probably fragment by loss of EtOH, as was found for the monomers. The experiment is not conclusive, but on balance it favours the concept that the solution contains a mixture of monomers, dimers and trimers in equilibrium rather than just trimers.

The ES mass spectrum of a solution of KCl to which has been added some NaL also gives three families of peaks corresponding to species containing one, two or three ligand units. All of the species previously identified in the ES mass spectrum of a solution of NaL itself are observed in the mixed solution, but most other possible species containing potassium are also detected. There are however some interesting effects as can be seen in Fig. 3(a) which shows the ES mass spectrum in the region associated with monomeric species containing one ligand. The dominant peak at m/z 575 is assigned to $[HKL]^+$ and there is also a product ion at m/z 529 formed by collisional activation within the ion source resulting in loss of EtOH (corresponding to m/z 513 derived from $[HNaL]^+$). Although there was more potassium in the solution than there was sodium, the peak due to $[K_2L]^+$ (m/z 613) is weaker
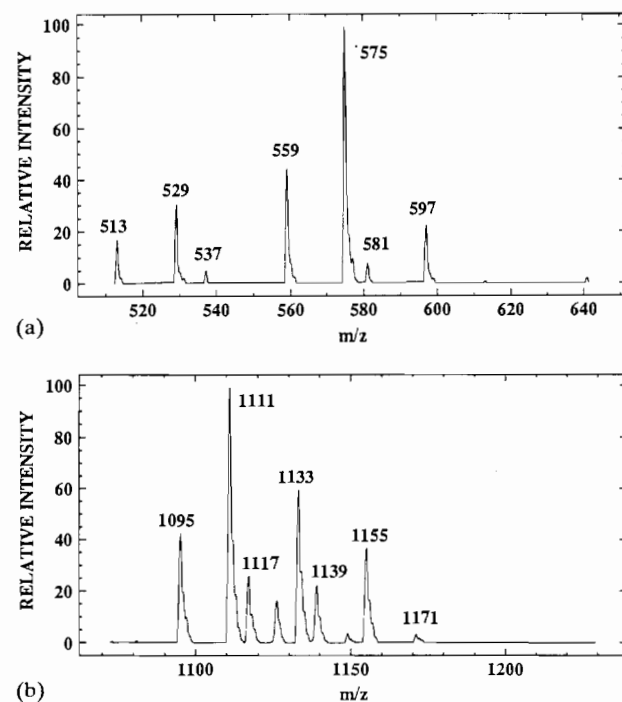

Fig. 3. Positive ion ES mass spectra (B1 = 40 V) at different m/z ranges for a solution of KCl to which has been added some NaL: (a) m/z 510–640 (monomers), (b) 1070–1200 (dimers).

than that due to $[Na_2L]^+$ (m/z 581). A similar trend is apparent within the family of peaks for species containing two ligand groups, Fig. 3(b). The strongest peak within this series is that due to $[H_2KL_2]^+$ (m/z 1111), but that assigned to $[HK_2L_2]^+$ (m/z 1149) is much weaker than that for $[HNa_2L_2]^+$ (m/z 1117) and similarly the peak for $[NaK_2L_2]^+$ (m/z 1171) is much weaker than that due to $[Na_3L_2]^+$ (m/z 1139) whilst that due to $[K_3L_2]^+$ is not observed at all. In the series of peaks due to the trimeric species the same trends are apparent, the intensities of the peaks due to species with larger numbers of potassium ions are very weak and $[K_4L_3]^+$ is not observed. There is a large excess of cations (H^+, Na^+ and K^+) over L^- in this solution and this pattern of intensities is consistent with the known [13] stability constants for complexes of these cation with L^- in 90% methanol/water, H^+ having the largest and K^+ the smallest stability constant.

This pattern of stability is emphatically confirmed by the ES mass spectra of a solution containing CsBr and NaL. At low m/z values the strongest peak is at m/z 669 which is due to $[HCsL]^+$ (there is also a peak at m/z 623 caused by loss of EtOH) and there is a weak peak due to $[NaCsL]^+$ (m/z 691), together with the usual peaks due to NaL itself. In the intermediate m/z range the only Cs containing species detected were $[H_2CsL_2]^+$ (m/z 1205), $[HNaCsL_2]^+$ (1227) and $[Na_2CsL_2]^+$ (1249). These peaks were as intense as those in the m/z range 1095–1139 identified previously for NaL solutions, but no signals for species containing two caesium ions were detected. The same situation pertained in the m/z region associated with the trimeric species, strong signals are observed for $[H_2NaCsL_3]^+$ (m/z 1763), $[HNa_2CsL_3]^+$ (1785) and $[Na_3CsL_3]^+$ (1807), but no signals were observed for species containing two caesium ions. In this case more CsBr was added to the original solution, but ions containing two caesium moieties could still not be detected, proving that their absence is due to a thermodynamic preference for sodium or protons to coordinate to L^- rather than caesium, and that the absence of multiple caesium ions is not merely a concentration effect.

The stability constant for the interaction of Li^+ with L^- is greater than that for Na^+ [13], so a different pattern of ions might be expected for a solution containing LiCl and NaL. At the low m/z range peaks due to $[HLiL]^+$ (m/z 543) (also $543 - 46 = 497$), $[Li_2L]^+$ (549) and $[LiNaL]^+$ (565) are the most intense peaks and all the usual ions containing Na^+ give very weak signals, indicating that the L^- ligand prefers coordination with lithium. There is also a strong signal at m/z 609 for a singly charged species containing lithium which appears to be due to $[HLi_2L(OAc)]^+$. Protonated species containing both L^- and acetate are frequently observed for M^{2+} and M^{3+} complexes, as described

below. For the lithium containing solutions, signals in the intermediate m/z range, which in previous spectra were the most intense signals, are now very weak and the most intense peak in this region is that at m/z 1126 which is thought to be due to $[FeL_2]^+$ impurity. Nevertheless, peaks due to $[H_2LiL_2]^+$ (1079), $[HLi_2L_2]^+$ (1085), $[Li_3L_2]^+$ (1091) and $[Li_2NaL_2]^+$ (1098) are identified. Interestingly, no peaks at all are observable for this solution in the m/z range 1600–1800, the region associated with species containing three ligands groups. It is obvious from these results that not only does lithium compete successfully with sodium for coordination to the L^- ligands, but it also causes the trimeric species to be broken down completely and the relative concentration of the dimeric species to be greatly reduced. Presumably this arises because lithium is usually four-coordinate, whereas in the trimeric Na_3L_3, sodium is six-coordinate and so this trimeric structure cannot be stabilised with lithium as the cation.

Derivatives with divalent metals

All data for derivatives of divalent metal ions with the ligand L^- are given in Table 2. The ES mass spectrum of a solution containing $Ca(OAc)_2$ and a deficiency NaL is dominated by peaks due to ions with one L^- group. The base peak at m/z 635 is assigned to $[HCaL(OAc)]^+$, there is another peak at m/z 695 due to $[H_2CaL(OAc)_2]^+$ and a third intense peak at m/z 653 which is unidentified. Weak peaks are observed in the region associated with species containing two L^- groups. Addition of further NaL greatly enhances the relative intensities of the dimer species, and the unidentified peak at m/z 653 is now very weak. Peaks are observed for $[HCaL_2]^+$ (1111) and $[NaCaL_2]^+$ (1133) as well as those observed for NaL itself, but the relative intensities of the sodium (non-calcium) ions are interesting. The peak assigned to $[Na_3L_2]^+$ (1139) is the strongest and that assigned to $[H_2NaL_2]^+$ (m/z 1095) is the weakest, which is the reverse of the relative intensities observed for NaL itself (Fig. 1(b)). We believe this arises because of the greater stability constants for the calcium species [13] which ensures most of the L^- is coordinated to Ca^{2+}, leaving a large excess of sodium ions over the remaining L^- which therefore forms the sodium-rich dimer species.

A solution of $Sr(NO_3)_2$ and NaL gave very similar results with peaks being observed for $[HSrL(OAc)]^+$ (m/z 683), $[H_2SrL(OAc)_2]^+$ (743), $[HSrL_2]^+$ (1159) and $[NaSrL_2]^+$ (1181). A solution of $Ba(ClO_4)_2$ and NaL gave the corresponding ions containing barium, but interestingly the ES mass spectrum of the solution also showed peaks due to the dimeric species containing only sodium, as well as that due to $[HBaL(OAc)]^+$, which indicates that barium does not compete well with sodium for its second L^- group. Barium is the only

TABLE 2. ESMS data for complexes of L^- with Group 2 and divalent transition metal elements

Mixture	Ions (m/z)
$Mg(OAc)_2 + NaL$	$[HMgL(OAc)]^+(619)$; $[HMgL_2]^+(1095)$; $[NaMgL_2]^+(1117)$
$Ca(OAc)_2 + NaL$	$[HCaL(OAc)]^+(635)$; $[H_2CaL(OAc)_2]^+(695)$; $[HCaL_2]^+(1111)$; $[NaCaL_2]^+(1133)$
$Sr(NO_3)_2 + NaL$	$[SrL]^+(623)$; $[HSrL(OAc)]^+(683)$; $[H_2SrL(OAc)_2]^+(743)$; $[HSrL_2]^+(1159)$; $[NaSrL_2]^+(1181)$
$Ba(ClO_4)_2 + NaL$	$[BaL]^+(673)$; $[HBaL(OAc)]^+(733)$; $[H_2BaL(OAc)_2]^+(793)$; $[HBaL_2]^+(1209)$; $[NaBaL_2]^+(1231)$

Group 2 metal to show this equilibrium and it simply demonstrates the decreasing overall stability constants in Group 2 as the metal size increases.

Magnesium has been left to last in the discussion of Group 2 metal complexes since there is some ambiguity in the ES mass spectra because Mg^{2+} (most abundant isotope ^{24}Mg) has the same mass as HNa^{2+} (within the resolution of our instrument). However, the general behaviour of the other Group 2 elements considerably helps in the mass spectral assignments for the magnesium system. At low m/z values the ES mass spectrum of a solution containing $Mg(OAc)_2$ and a deficiency NaL gave a strong peak at m/z 619 which is unambiguously assigned to $[HMgL(OAc)]^+$ and weaker peaks in the m/z region associated with dimeric species. Upon addition of more NaL, peaks at m/z 1095, 1117 and 1139 dominate the mass spectrum and their intensities are similar but increase slightly with increasing m/z value. The peak at 1095 could be $[H_2NaL_2]^+$ or $[HMgL_2]^+$, that at 1117 could be $[HNa_2L_2]^+$ or $[NaMgL_2]^+$ whilst that at 1139 is unambiguously due to $[Na_2L_2]^+$. Since the peak at m/z 619 almost disappears upon addition of the extra NaL, the Mg^{2+} clearly reacts with further L^-, as expected. The calculated isotopic mass distribution patterns for dimeric species containing magnesium have three weak components at higher m/z value than the main peak, due to the combined effects of carbon-13, magnesium-25 and magnesium-26, whilst those without magnesium have only two weak peaks above the main one due solely to carbon-13, because sodium is monoisotopic. The peaks at m/z 1095 and 1117 show three weak peaks at higher m/z values whilst that at 1139 shows only two. It is therefore concluded that the peaks at 1095 and 1117 are mainly due to $[HMgL_2]^+$ and $[NaMgL_2]^+$, respectively, and that the relatively high intensity of the peak for $[Na_3L_2]^+$ (1139) arises for the same reasons as discussed for the calcium system. However, small quantities of $[H_2NaL_2]^+$ and $[HNa_2L_2]^+$ would not be detected.

Derivatives with trivalent metals

All data for derivatives of trivalent metal ions with the ligand L^- are given in Table 3.

Although stability constant data are not available for the interaction of trivalent metals with L^-, simply on a consideration of charge interactions it would be expected that two L^- ligands would be coordinated very readily to give octahedral $[ML_2]^+$ species. This has been confirmed by the isolation of the Group 13 metal (Al, Ga, In, Tl) trivalent derivatives [4] and similar complexes have been prepared for several trivalent transition metals [14]. These compounds are ideally suited for examination by ESMS and their observation is expected not to depend upon any protonation by the mobile phase.

The ES mass spectrum of a solution formed by addition of a small amount of NaL to a Group 13 metal compound was always dominated by the peak due to the intact $[ML_2]^+$ ion. As a typical example, Fig. 4 shows the mass spectrum of a solution of NaL and $NBu_4[GaBr_4]$. Quite clearly the trivalent metal coordinates with all the available L^- ligand, and in fact the next most intense peak at m/z 1126 is assigned to the previously mentioned impurity $[FeL_2]^+$. Increasing the B1 voltage to 100 V caused no collisionally activated decompositions, showing that these simple ions are very stable.

Complexes of the Group 3 metals scandium, yttrium and lanthanum were also examined. In these cases, when a small amount of NaL was added, peaks assigned to $[ML(OAc)]^+$ and $[HML(OAc)_2]^+$ as well as those due to $[ML_2]^+$ were observed, but addition of further NaL gave $[ML_2]^+$ as the dominant peak and the only one containing the Group 3 metal ion. There were no peaks in the higher m/z region. Since cationic complexes of these metals were so easy to observe, a number of other lanthanide metal complexes were examined, including Ce(III), Nd(III), Gd(III), Dy(III) and Tb(III). In all cases the ion $[ML(OAc)]^+$ and $[HML(OAc)_2]^+$, as well as $[ML_2]^+$, were observed with a deficiency of NaL, but additional NaL then gave $[ML_2]^+$ as the only ion containing the lanthanide ion.
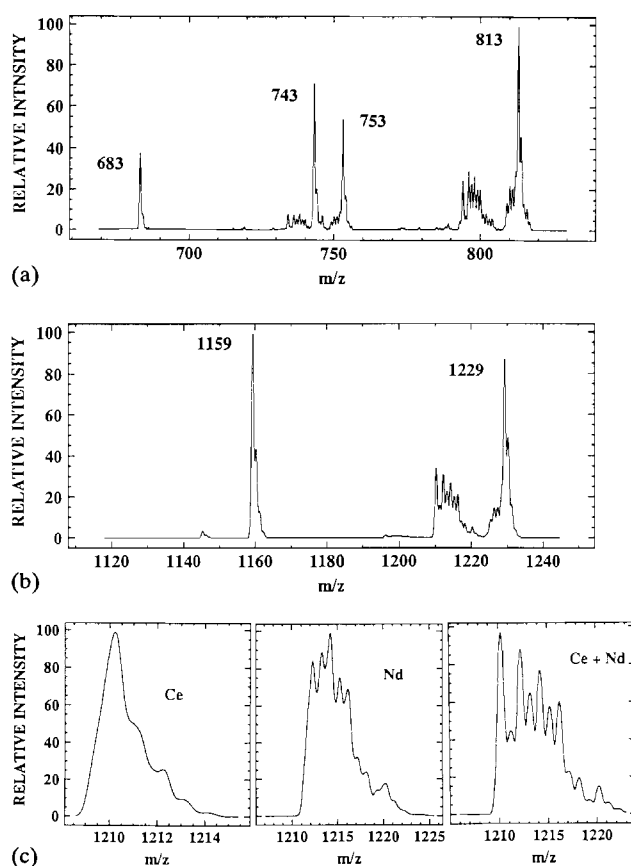
The uniform behaviour of the Group 3 and lanthanide metal ions towards reaction with NaL suggests that this reagent may be used in conjunction with ESMS as the basis for, at least, a qualitative analysis of mixtures of

TABLE 3. ESMS data for complexes of L⁻ with Group 3, Group 13, trivalent transition and lanthanide elements

Mixture	Ions (m/z)
$Al_2(SO_4)_3 + NaL$	$[AlL_2]^+$ (1097)
$NBu_4[GaBr_4] + NaL$	$[GaL_2]^+$ (1139)
$InCl_3 + NaL$	$[InL_2]^+$ (1185)
$pyH[TlCl_4] + NaL$	$[TlL_2]^+$ (1275)
$ScCl_3 + NaL$	$[ScL(OAc)]^+$ (639); $[HScL(OAc)_2]^+$ (699); $[ScL_2]^+$ (1115)
$Y(NO_3)_3 + NaL$	$[YL(OAc)]^+$ (683); $[HYL(OAc)_2]^+$ (743); $[YL_2]^+$ (1159)
$LaCl_3 + NaL$	$[LaL(OAc)]^+$ (733); $[HLaL(OAc)_2]^+$ (793); $[LaL_2]^+$ (1209)
$Ce_2(SO_4)_3 + NaL$	$[CeL_2]^+$ (1210)
$Nd_2(SO_4)_3 + NaL$	$[NdL_2]^+$ (1214)
$Gd(NO_3)_3 + NaL$	$[GdL(OAc)]^+$ (752); $[HGdL(OAc)_2]^+$ (812); $[GdL_2]^+$ (1228)
$TbCl_3 + NaL$	$[TbL(OAc)]^+$ (753); $[HTbL(OAc)_2]^+$ (813); $[TbL_2]^+$ (1229)
$Dy_2(SO_4)_3 + NaL$	$[DyL(OAc)]^+$ (757); $[HDyL(OAc)_2]^+$ (817); $[DyL_2]^+$ (1233)
$Fe(NO_3)_3 + NaL$	$[FeL(OAc)]^+$ (650); $[FeL_2]^+$ (1126)
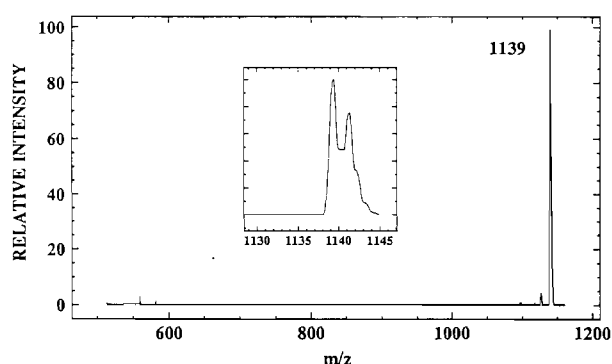
Fig. 4. Positive ion ES mass spectrum (B1 = 40 V) for a solution of $NBu_4[GaBr_4]$ to which has been added some NaL.

Fig. 5. Positive ion ES mass spectra (B1 = 40 V) at different m/z ranges for a solution of Y(III), Ce(III), Nd(III), Gd(III) and Tb(III) to which has been added some NaL: (a) m/z 670–830, (b) 1120–1240, (c) comparison of isotopic mass distributions for $[CeL_2]^+$, $[NdL_2]^+$ and for the mixture of these cations shown in (b).

Group 3 and lanthanide metals in extracts from ores such as monazites. A synthetic mixture was prepared containing Y(III), Ce(III), Nd(III), Gd(III) and Tb(III). This mixture was selected to give some metals whose isotopic mass distributions are dominated by one isotope (Y, Tb) and others which have a wide range of isotopes, and also to include ions whose isotopic mass distributions would overlap (Ce, Nd and Gd, Tb). Sufficient NaL was added so that both low m/z mixed acetate species and simple $[ML_2]^+$ species were present in the solution and Fig. 5 shows the ES mass spectra at different m/z ranges. In Fig. 5(a) the sharp peaks at m/z 683 and 743 are due to $[YL(OAc)]^+$ and $[HYL(OAc)_2]^+$ and those at m/z 753 and 813 are the corresponding terbium ions. The broad envelopes covering m/z values 734–741 and 793–804 are overlapping signals for corresponding cerium and neodymium ions whilst the gadolinium ions are observed as the broad envelopes at slightly lower m/z values than the terbium complexes. Figures 5(b) shows the m/z region appropriate for the $[ML_2]^+$ ions and Fig. 5(c) shows the comparison between the experimental isotopic mass distributions for $[CeL_2]^+$ and $[NdL_2]^+$ and the isotopic mass distribution for the

mixture of the two ions shown in Fig. 5(b). It is obvious from these ES mass spectra that mixtures of lanthanides can be identified by using ESMS and the ligand L⁻.

The method is sensitive, so good signal to noise ratios are achieved at low concentrations.

Since $[FeL_2]^+$ is thought to be responsible for the impurity peak frequently observed at m/z 1126, NaL was reacted with $Fe(NO_3)_3$ and a strong ES mass spectrum was obtained with the characteristic peak at m/z 1126 being dominant.

General conclusions

Although many of the compounds investigated here have previously been isolated as pure compounds, in this paper they were all prepared in solution from the sodium salt NaL so that in fact ESMS has been used to investigate competitive exchange reactions of L^- between sodium and the various metals. Fortunately, stability constant data are available for the Group 1 and Group 2 metals with L^- and the ESMS data are nicely consistent with that information. It is therefore not a major extrapolation to suggest that ESMS may become a very convenient method for investigating trends in stability constants between other ligands and a variety of metals.

One of the more remarkable findings in this paper is the retention of at least some of the trimeric oligomers of NaL in acidic aqueous media. Obviously the very high stability constant of the sodium salt is partly responsible for their existence in the solution, since similar trimers containing three or four of the larger Group 1 metals do not appear to exist. Similar overall effects of decreasing stability constants as a function of increasing metal ion size are also apparent with the Group 2 metal ions.

The multiple charging of the L^- ligand by either protons or metal ions is reminiscent of the seminal work by Fenn and coworkers on the formation of multi(sodium) ions of poly(ethyleneglycol) [21]. That work provided one of the first examples of high molecular weight species being rendered observable in accessible m/z ranges by multicharging. The difference here is that only single charge cationic species are observed, but their formation depends upon adduct formation with several metal cations or protons.

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