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Complexes of tetradentate β-keto enamine Schiff bases: an electrospray mass spectrometric study

Terence J. Cardwell, Ray Colton*, Shelly Mitchell and John C. Traeger
Department of Chemistry, La Trobe University, Bundoora 3083 (Australia)

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Abstract

Electrospray mass spectrometry (ESMS) has been used to investigate several types of derivatives of four tetradentate Schiff base ligands. The ES mass spectra of the free ligands give strong peaks due to singly protonated intact ions which are formed by reaction with the acetic acid in the mobile phase used in the spectrometer. In the presence of alkali metal salts, the ES mass spectra show the corresponding adduct ions with one alkali metal attached to each Schiff base. The neutral Schiff base derivatives of Cu(II), Ni(II), Pd(II) and VO(II) all give intact ions corresponding to the singly protonated species in their ES mass spectra. Mixtures of different transition metal Schiff base derivatives give only ions for the protonated starting materials, with no evidence for metal exchange between the complexes. In the presence of alkali metal salts, the transition metal Schiff base complexes act as neutral ligands towards the alkali metals producing ions with one, two and three metal complexes coordinated to the alkali metal. Similar coordination of the transition metal Schiff base complexes to divalent transition metal ions is also observed, but in these cases acetate ions are involved so that the charge on the observed ions is always +1.

Key words: Mass spectrometry, Transition metal complexes; Schiff base complexes

Introduction

Schiff bases and their complexes with transition metals are well known [1–6]. Several compounds have been reported in which the transition metal Schiff base complex acts as a ligand towards alkali and alkali earth metal cations. The solid state structures of [(Co{salen})$_2$Na(THF)$_2$]BPh$_4$ [7] and [(Ni{salen})$_2$-Na(MeCN)$_2$]BPh$_4$ (salen = bis(salicylaldehydecthylenediimine) reveal that the neutral metal complex acts as a bidentate ligand to sodium through the oxygen atoms and the octahedral coordination of the sodium ion is completed by the two solvent molecules [8]. Similar structures are known for (Cu{salen})$_2$NaClO$_4$-(*p*-xylene)] [9] and (Ni{acen})$_2$NaClO$_4$ [10] (acen = *N*,*N*-ethylenebis(acetylacetoneiminato) in which the octahedral coordination about the sodium ion is completed by the bidentate perchlorate ligand, and in [(VO{salen})$_2$Na]BPh$_4$ in which all three oxygen atoms of each vanadium complex are coordinated to sodium [11]. Similar coordination to magnesium occurs in the complex (Cu{salen})Mg(hfacac)$_2$ (hfacac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato) [12]. Transition metal Schiff base complexes can also act as ligands towards other transition metals [13, 14]. For example, reaction between Cu{salen} and other Cu(II) salts yielded species such as (Cu{salen})$_2$CuCl$_2$ and [(Cu{salen})$_2$Cu](ClO$_4$)$_2$. In view of the ionic nature of many of these systems, they appeared to be suitable candidates for study with the new technique of electrospray mass spectrometry (ESMS).

ESMS was developed largely by Fenn and co-workers [15–17] and it provides a way of transferring pre-existing ions from solution to the gas phase and then examining them by conventional mass spectrometric methods. The technique is very soft and the transfer causes minimal fragmentation. ESMS has been widely used in biological applications and in these cases a large molecule such as a protein is multiply-protonated by the mobile phase used in the spectrometer (typically H$_2$O/MeOH/HOAc = 50:50:1%) and the resulting ions are observed in the ES mass spectrum [18–20]. Although we have been exploring the application of ESMS to ionic inorganic and organometallic systems which do not require the protonation step [21–23], there have been some investigations of inorganic systems by ESMS which have

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*Author to whom correspondence should be addressed.

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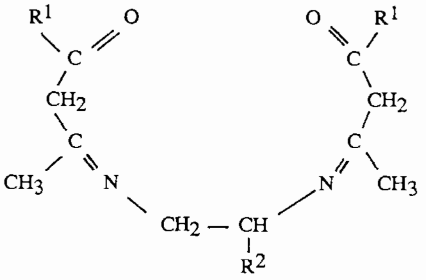


R^1	R^2	
Me	H	$H_2en(AA)_2$
Me	Me	$H_2pn(AA)_2$
CF_3	H	$H_2en(TFA)_2$
CF_3	Me	$H_2pn(TFA)_2$

Scheme 1.

used the protonation method to generate cations from neutral species. Recently β-diketone and mixed β-diketone/acetate derivatives of several lanthanide elements were observed via protonation [24], as were monovalent and divalent metal derivatives of a tripodal monoanionic ligand [25].

In this paper we report ES mass spectra for four Schiff base ligands, the structures (one tautomeric form) of which are shown in Scheme 1. ES mass spectra are also reported for solutions containing their complexes with monovalent and divalent metal ions and also for solutions containing the transition metal Schiff base complex acting as a ligand to other metal ions to form polynuclear metal complexes.

Experimental

The four Schiff bases and their complexes with VO(II), Ni(II), Pd(II) and Cu(II) were prepared by literature methods [1]. The alkali metal salts of the Schiff bases were prepared in solution by addition of the metal halide to a methanol/aqueous solution of the ligand. Solutions of the compounds (2 mM) were prepared in methanol and then diluted 1:10 with methanol for mass spectrometric examination.

Electrospray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer (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 l min^{-1} and 100 ml min^{-1} respectively. Pressure in the mass analyser region was usually about 3×10^{-5} torr. The compounds in this study gave strong signals in their ES mass spectra and typically 8–12 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 via collisional activation 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.

Results and discussion

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

The free ligands

Figure 1 shows the positive ion ES mass spectrum at a B1 voltage of 40 V for a methanol solution of $H_2\{en(TFA)_2\}$. The base peak at *m/z* 333 corresponds to the singly protonated species $[H_3\{en(TFA)_2\}]^+$ which is formed by reaction with the acetic acid in the mobile phase. There is no evidence for the doubly protonated species $[H_4\{en(TFA)_2\}]^{2+}$ at *m/z* 167. At higher collisional energies (B1 = 80 V) the base peak is at *m/z* 180 and is assigned to an ion formed by loss of one ketonic side arm and a nitrogen to give the olefin derivative (m/z 180) as shown in Scheme 2. Loss of a phosphino group from diphosphine ligands to give similar olefin complexes has been observed previously in ES mass spectra [2]. The other free Schiff bases

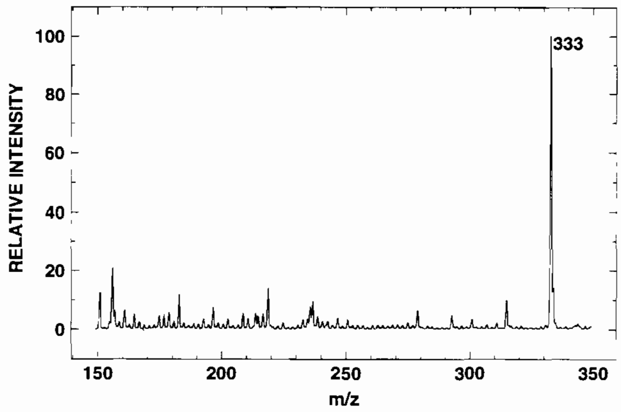
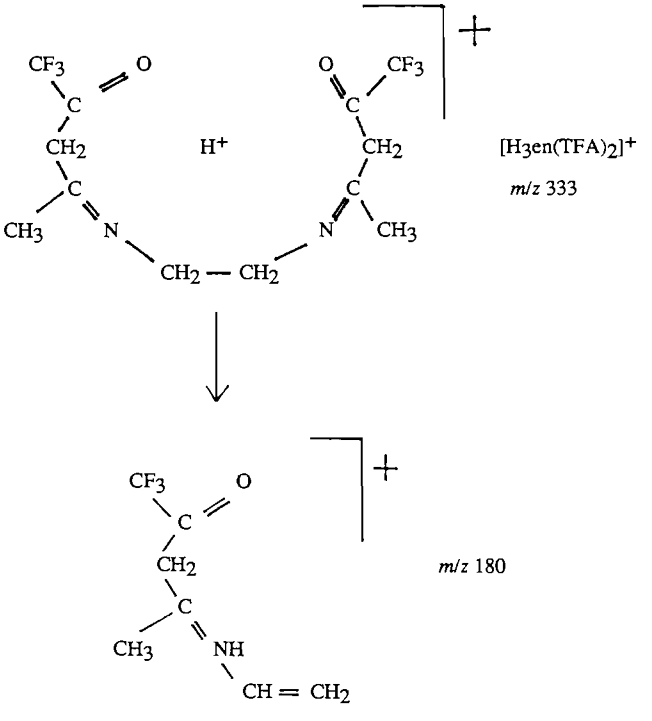


Fig. 1 Positive ion ES mass spectrum (B1 = 40 V) of a solution of $H_2\{en(TFA)_2\}$



Scheme 2.

give analogous ES mass spectra and all data are summarised in Table 1.

Alkali metal derivatives

When alkali metal salts were added to a solution of H$_2${en(TFA)$_2$} the ES mass spectra were all dominated by a single peak which in each case was assigned to the ion [H$_2$M{en(TFA)$_2$}]$^+$ (M = Li, Na, K, Cs). There was no evidence for ions of the type [HM$_2${en(TFA)$_2$}]$^+$. The other Schiff bases gave similar ES mass spectra and data are summarised in Table 1. At higher B1 voltages the alkali metal salts of H$_2${pn(TFA)$_2$} showed collisionally activated decompositions giving ions of the type [HM(TFA)NHCH=CH(CH$_3$)]$^+$ (M = Na, K), analogous to those produced by the protonated ligand. However, the alkali metal derivatives of the other Schiff bases are considerably more robust and did not show this fragmentation.

Transition metal derivatives

The ES mass spectrum of Cu{pn(TFA)$_2$} at B1 = 40 V (Fig. 2(a)) is dominated by a peak at *m/z* 408 which is due to the protonated ion [HCu{pn(TFA)$_2$}]$^+$ Although this is analogous to [H$_3${pn(TFA)$_2$}]$^+$, on the basis of known crystal structures [7–14] it is expected to have the structure shown in Scheme 3 with copper coordinated to the two oxygen and the two nitrogen atoms on the ligand and with the proton on one oxygen, or more likely, hydrogen bonded between the two oxygen atoms. Similar protonation has been observed for neutral complexes of a uninegative tripodal oxygen ligand [25]. At higher collisional energies (B1 = 110 V) [HCu{pn(TFA)$_2$}]$^+$ undergoes not only the same type of fragmentation as the protonated free ligand (Table 2) to give [Cu(TFA)NHCH=CH$_2$]$^+$ (*m/z* 242) but also loss of an additional CH$_2$ group to give [Cu(TFA)N=CH$_2$]$^+$ (*m/z* 228). In addition there is a strong peak at *m/z* 338 (corresponding to loss of CF$_3$H). Cu{en(TFA)$_2$} gives a similar ES mass spectrum, including loss of CF$_3$H from [HCu{en(TFA)$_2$}]$^+$ in the collisionally enhanced mass spectrum. Cu{en(AA)$_2$} and Cu{pn(AA)$_2$} complexes also give intact protonated derivatives in their ES mass spectra, but in the collisionally enhanced decomposition mass spectra there is no evidence of a peak corresponding to loss of CH$_4$ from the protonated precursor ion, but they do give fragment ions analogous to those discussed for Cu{pn(TFA)$_2$}. The difference between CF$_3$H and CH$_4$ elimination presumably reflects the great difference (~620 kJ mol^{-1}) in the heats of formation of these compounds. All ESMS data are summarised in Table 2.

TABLE 1 ES mass spectrometric data for Schiff base derivatives of monovalent cations

Mixture	Ions at low B1 voltage (*m/z*)	Ions at high B1 voltage (*m/z*)
H$_2${en(TFA)$_2$} + H$^+$	[H$_3${en(TFA)$_2$}]$^+$ (333)	[H$_2$(TFA)NHCH=CH$_2$]$^+$ (180)
H$_2${en(AA)$_2$} + H$^+$	[H$_3${en(AA)$_2$}]$^+$ (225)	[H$_2$(AA)NHCH=CH$_2$]$^+$ (126)
H$_2${pn(TFA)$_2$} + H$^+$	[H$_3${pn(TFA)$_2$}]$^+$ (347)	[H$_2$(TFA)NHCH=CH(CH$_3$)]$^+$ (194)
H$_2${pn(AA)$_2$} + H$^+$	[H$_3${pn(AA)$_2$}]$^+$ (239)	[H$_2$(AA)NHCH=CH(CH$_3$)]$^+$ (140)
H$_2${en(TFA)$_2$} + LiOH	H$_2$Li{en(TFA)$_2$}]$^+$ (339)	
H$_2${en(TFA)$_2$} + NaCl	[H$_2$Na{en(TFA)$_2$}]$^+$ (355)	
H$_2${en(TFA)$_2$} + KCl	[H$_2$K{en(TFA)$_2$}]$^+$ (371)	
H$_2${en(TFA)$_2$} + CsBr	[H$_2$Cs{en(TFA)$_2$}]$^+$ (465)	
H$_2${pn(TFA)$_2$} + NaCl	[H$_2$Na{pn(TFA)$_2$}]$^+$ (369)	[HNa(TFA)NHCH=CH(CH$_3$)]$^+$ (216)
H$_2${pn(TFA)$_2$} + KCl	[H$_2$K{pn(TFA)$_2$}]$^+$ (385)	[HK(TFA)NHCH=CH(CH$_3$)]$^+$ (232)
H$_2${pn(AA)$_2$} + NaCl	[H$_2$Na{pn(AA)$_2$}]$^+$ (261)	
H$_2${pn(AA)$_2$} + KCl	[H$_2$K{pn(AA)$_2$}]$^+$ (277)	

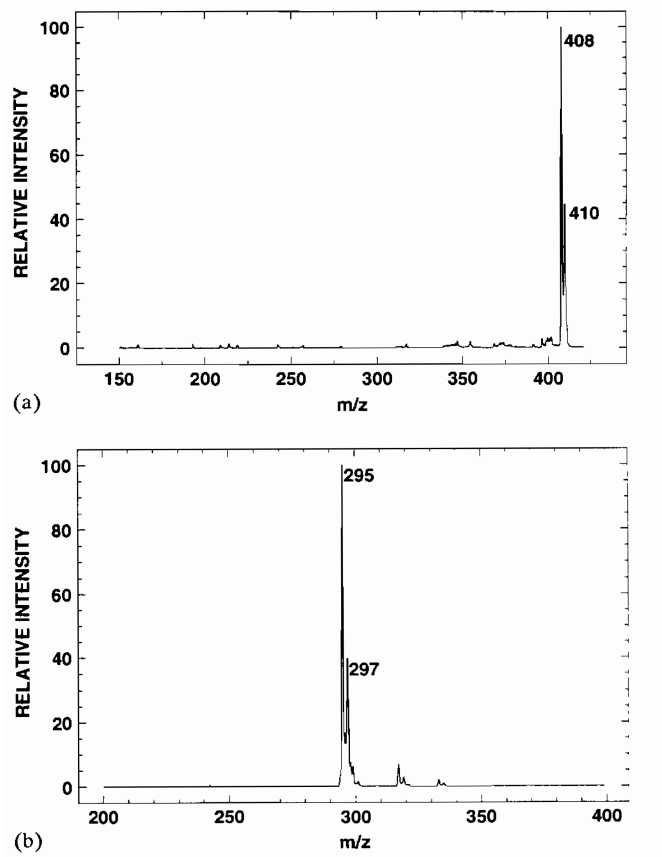
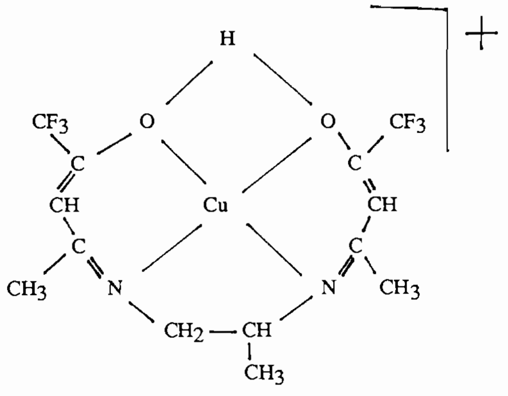


Fig 2. Positive ion ES mass spectra (B1 = 40 V) of a solution of (a) Cu{pn(TFA)$_2$}, (b) Ni{pn(AA)$_2$}.



Scheme 3

At low collision energies (B1 = 40 V) the nickel complexes of the four Schiff bases all give ES mass spectra which show peaks due to the singly protonated intact cations, exactly analogous to those of copper and Fig. 2(b) shows the ES mass spectrum of a solution of Ni{pn(AA)$_2$}. The peak at *m/z* 295 is due to the protonated ion [HNi{pn(AA)$_2$}]$^+$, the weaker peaks at *m/z* 317 and 333 are due to [NaNi{pn(AA)$_2$}]$^+$ and [KNi{pn(AA)$_2$}]$^+$, respectively (see below). However, the pattern of peaks observed in the collisionally enhanced mass spectra is different to that of the copper complexes. Only one nickel containing peak is observed in the decomposition of both [HNi{en(TFA)$_2$}]$^+$ and [HNi{pn(TFA)$_2$}]$^+$ which corresponds to loss of CF$_3$H. A weak signal due to [Ni{(AA)NHCH=CH$_2$]$^+$ (*m/z* 183) is observed in the decomposition of [HNi{en(AA)$_2$}]$^+$, but for [HNi{pn(AA)$_2$}]$^+$ unidentified peaks occur at *m/z* 194 and 182. The palladium complexes of the Schiff bases behave similarly to those of nickel. At low collision energies all give the intact singly protonated ion. At high collision energies [HPd{en(TFA)$_2$}]$^+$ and [HPd{pn(TFA)$_2$}]$^+$ both lose CF$_3$H, but no other palladium containing ions were observed in any of the ES mass spectra.

The vanadium(IV) complexes VO{en(AA)$_2$} and VO{pn(AA)$_2$} both form the singly protonated ions which are observed in the ES mass spectra as the intact ions [HVO{en(AA)$_2$}]$^+$ and [HVO{pn(AA)$_2$}]$^+$ at *m/z* 290 and 304, respectively. However, if the solutions are treated with NOBF$_4$ before injection into the mass spectrometer, then the corresponding vanadium(V) non-protonated ions [VO{en(AA)$_2$}]$^+$ and [VO{pn(AA)$_2$}]$^+$ are observed at *m/z* 289 and 303, respectively.

Attempted transmetallation reactions

A number of mixtures of two different transition metals with different Schiff bases, such as Cu{en(TFA)$_2$} and Ni{en(AA)$_2$}, were examined to determine whether metal exchange occurred between the complexes at room temperature on the time scale of several minutes. However, in all cases the only ions observed were those of the singly protonated original reactants and no evidence was found for metal exchange.

Transition metal Schiff base complexes as ligands to alkali metals

Figure 3 shows the ES mass spectrum (B1 = 30 V) of a methanol solution of Ni{pn(AA)$_2$} to which has been added a small amount of aqueous KCl solution. The three peaks at *m/z* 923, 627 and 333 are assigned to [K(Ni{pn(AA)$_2$})$_3$]$^+$, [K(Ni{pn(AA)$_2$})$_2$]$^+$ and [KNi{pn(AA)$_2$}]$^+$, respectively. The weaker peaks at *m/z* 907, 611 and 317 are the corresponding sodium ions formed by adventitiously introduced sodium. At B1 = 40 V the relative intensity of the peak at *m/z* 923 is much reduced, whilst that of the peak at *m/z* 627 is increased; no additional peaks are observed in the ES mass spectrum. This result indicates that the tris complex readily loses a complete metal Schiff base ligand to form the bis complex. Although alkali metal complexes with two coordinated transition metal Schiff base complexes are known [7–11] this mass spectrum presents the first evidence for tris(complexes). Presumably in this complex the metal Schiff base is acting as a conventional neutral bidentate oxygen ligand to

TABLE 2 ES mass spectrometric data for transition metal Schiff base derivatives

Compound or mixture	Ions at low B1 voltage (*m/z*)	Ions at high B1 voltage (*m/z*)
$\mathrm{Cu\{en(TFA)_2\}}$	$\mathrm{[HCu\{en(TFA)_2\}]^+}$ (394)	(324)[a]; $\mathrm{[Cu(TFA)NHCH{=}CH_2]^+}$ (242), $\mathrm{[Cu(TFA)N{=}CH_2]^+}$ (228)
$\mathrm{Cu\{en(AA)_2\}}$	$\mathrm{[HCu\{en(AA)_2\}]^+}$ (286)	$\mathrm{[Cu(AA)NHCH{=}CH_2]^+}$ (188); $\mathrm{[Cu(AA)N{=}CH_2]^+}$ (174)
$\mathrm{Cu\{pn(TFA)_2\}}$	$\mathrm{[HCu\{pn(TFA)_2\}]^+}$ (408)	(338)[a]; $\mathrm{[Cu(TFA)NHCH{=}CH(CH_3)]^+}$ (256), $\mathrm{[Cu(TFA)NHCH{=}CH_2]^+}$ (242)
$\mathrm{Cu\{pn(AA)_2\}}$	$\mathrm{[HCu\{pn(AA)_2\}]^+}$ (300)	$\mathrm{[Cu(AA)NHCH{=}CH(CH_3)]^+}$ (202); $\mathrm{[Cu(AA)NHCH{=}CH_2]^+}$ (188)
$\mathrm{Ni\{en(TFA)_2\}}$	$\mathrm{[HNi\{en(TFA)_2\}]^+}$ (389)	(319)[a]
$\mathrm{Ni\{en(AA)_2\}}$	$\mathrm{[HNi\{en(AA)_2\}]^+}$ (281)	$\mathrm{[Ni(AA)NHCH{=}CH_2]^+}$ (183)
$\mathrm{Ni\{pn(TFA)_2\}}$	$\mathrm{[HNi\{pn(TFA)_2\}]^+}$ (403)	(333)[a]
$\mathrm{Ni\{pn(AA)_2\}}$	$\mathrm{[HNi\{pn(AA)_2\}]^+}$ (295)	(194); (182)
$\mathrm{Pd\{en(TFA)_2\}}$	$\mathrm{[HPd\{en(TFA)_2\}]^+}$ (437)	(367)[a]
$\mathrm{Pd\{en(AA)_2\}}$	$\mathrm{[HPd\{en(AA)_2\}]^+}$ (329)	
$\mathrm{Pd\{pn(TFA)_2\}}$	$\mathrm{[HPd\{pn(TFA)_2\}]^+}$ (451)	(381)[a]
$\mathrm{Pd\{pn(AA)_2\}}$	$\mathrm{[HPd\{pn(AA)_2\}]^+}$ (343)	
$\mathrm{VO\{en(AA)_2\}}$	$\mathrm{[HVO\{en(AA)_2\}]^+}$ (290)	$\mathrm{[VO(AA)NHCH{=}CH_2]^+}$ (191)
$\mathrm{VO\{pn(AA)_2\}}$	$\mathrm{[HVO\{pn(AA)_2\}]^+}$ (304)	$\mathrm{[VO(AA)NHCH{=}CHCH_3]^+}$ (205)
$\mathrm{VO\{en(AA)_2\}+NOBF_4}$	$\mathrm{[VO\{en(AA)_2\}]^+}$ (289)	
$\mathrm{VO\{pn(AA)_2\}+NOBF_4}$	$\mathrm{[VO\{pn(AA)_2\}]^+}$ (303)	

[a] (*m/z*) is the ion formed by elimination of $\mathrm{CF_3H}$ from the intact precursor ion

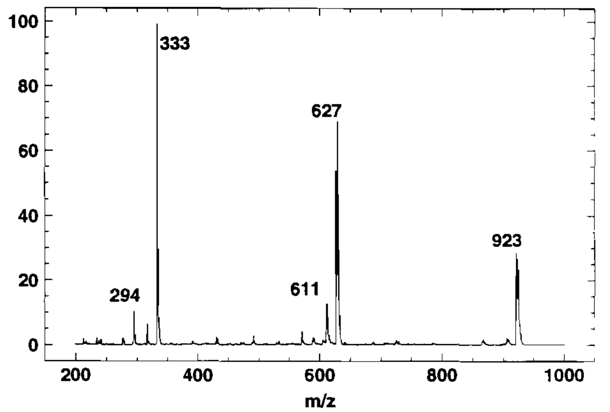


Fig 3 Positive ion ES mass spectrum (B1 = 40 V) of a solution of $\mathrm{Ni\{pn(AA)_2\}}$ to which has been added a little KCl solution

give a normal octahedral potassium complex. Addition of NaCl and CsBr to solutions of $\mathrm{Ni\{pn(AA)_2\}}$ gave the corresponding sodium and caesium ions. When lithium salts were added to $\mathrm{Ni\{pn(AA)_2\}}$, only the mono and bis(metal chelate) complexes were observed in the ES mass spectrum, which is consistent with the usual four coordination of the small lithium ion. In contrast, when the alkali metal ions were added to solutions of $\mathrm{Cu\{en(TFA)_2\}}$, only mono and bis(metal complexes) were observed with no evidence for any tris complexes in the solutions. This difference is ascribed to the steric effect of the relatively bulky $\mathrm{CF_3}$ groups in the $\mathrm{Cu\{en(TFA)_2\}}$ ligand rather than the change from copper to nickel as the transition metal. To confirm this interpretation, the potassium complexes with $\mathrm{Cu\{en(AA)_2\}}$ and $\mathrm{Ni\{pn(TFA)_2\}}$ were examined. $\mathrm{[K(Cu\{en(AA)_2\})_3]^+}$ (*m/z* 894) was observed, but $\mathrm{[K(Ni\{pn(TFA)_2\})_3]^+}$ (*m/z* 1248) was not. All data are summarised in Table 3.

Transition metal Schiff base complexes as ligands to divalent metal ions

The ES mass spectrum of a solution of $\mathrm{Cu\{en(TFA)_2\}}$, to which some $\mathrm{Zn(OAc)_2}$ had been added, shows not only the peaks previously described for solutions of $\mathrm{Cu\{en(TFA)_2\}}$ alone, but also some additional peaks assigned to Zn(II) complexes of $\mathrm{Cu\{en(TFA)_2\}}$. These complexes are identified as $\mathrm{[Zn(Cu\{en(TFA)_2\})_2(OAc)]^+}$ (*m/z* 911), $\mathrm{[HZn(Cu\{en(TFA)_2\})(OAc)_2]^+}$ (*m/z* 578) and $\mathrm{[Zn(Cu\{en(TFA)_2\})(OAc)]^+}$ (*m/z* 518). There is no evidence for a peak at *m/z* 229.5 corresponding to the simple $\mathrm{[Zn(Cu\{en(TFA)_2\})_2]^{2+}}$ ion, but instead the monoacetate adduct is observed at *m/z* 911. There have been previous examples in ESMS of dications forming a monoanion adduct in the gas phase [23, 25]. The species $\mathrm{[HZn(Cu\{en(TFA)_2\})(OAc)_2]^+}$ is simply

TABLE 3 ES mass spectrometric data for complexes of transition metal Schiff base derivatives with alkali metals

Mixture	Ions at low B1 voltage (*m/z*)
$\mathrm{Ni\{pn(AA)_2\}}$ + LiOH	$[\mathrm{Li(Ni\{pn(AA)_2\})_2}]^+$ (595), $[\mathrm{LiNi\{pn(AA)_2\}}]^+$ (301)
$\mathrm{Ni\{pn(AA)_2\}}$ + NaCl	$[\mathrm{Na(Ni\{pn(AA)_2\})_3}]^+$ (907), $[\mathrm{Na(Ni\{pn(AA)_2\})_2}]^+$ (611), $[\mathrm{NaNi\{pn(AA)_2\}}]^+$ (317)
$\mathrm{Ni\{pn(AA)_2\}}$ + KCl	$[\mathrm{K(Ni\{pn(AA)_2\})_3}]^+$ (923), $[\mathrm{K(Ni\{pn(AA)_2\})_2}]^+$ (627), $[\mathrm{KNi\{pn(AA)_2\}}]^+$ (333)
$\mathrm{Ni\{pn(AA)_2\}}$ + CsBr	$[\mathrm{Cs(Ni\{pn(AA)_2\})_3}]^+$ (1017), $[\mathrm{Cs(Ni\{pn(AA)_2\})_2}]^+$ (721), $[\mathrm{CsNi\{pn(AA)_2\}}]^+$ (427)
$\mathrm{Cu\{en(TFA)_2\}}$ + LiOH	$[\mathrm{Li(Cu\{en(TFA)_2\})_2}]^+$ (793), $[\mathrm{LiCu\{en(TFA)_2\}}]^+$ (400)
$\mathrm{Cu\{en(TFA)_2\}}$ + NaCl	$[\mathrm{Na(Cu\{en(TFA)_2\})_2}]^+$ (809), $[\mathrm{NaCu\{en(TFA)_2\}}]^+$ (416)
$\mathrm{Cu\{en(TFA)_2\}}$ + KCl	$[\mathrm{K(Cu\{en(TFA)_2\})_2}]^+$ (825), $[\mathrm{KCu\{en(TFA)_2\}}]^+$ (432)
$\mathrm{Cu\{en(TFA)_2\}}$ + CsBr	$[\mathrm{Cs(Cu\{en(TFA)_2\})_2}]^+$ (919), $[\mathrm{CsCu\{en(TFA)_2\}}]^+$ (526)

TABLE 4. ES mass spectrometric data for complexes of transition metal Schiff base derivatives with divalent transition metals

Mixture	Ions at low B1 voltage (*m/z*)
$\mathrm{Cu\{en(TFA)_2\}}$ + $\mathrm{Cu(OAc)_2}$	$[\mathrm{Cu(Cu\{en(TFA)_2\})_2(OAc)}]^+$ (910); $[\mathrm{HCu(Cu\{en(TFA)_2\})(OAc)_2}]^+$ (575), $[\mathrm{Cu(Cu\{en(TFA)_2\})(OAc)}]^+$ (515)
$\mathrm{Cu\{en(TFA)_2\}}$ + $\mathrm{Ni(NO_3)_2}$	$[\mathrm{Ni(Cu\{en(TFA)_2\})_2(NO_3)}]^+$ (905), $[\mathrm{HNi(Cu\{en(TFA)_2\})(OAc)_2}]^+$ (570), $[\mathrm{Ni(Cu\{en(TFA)_2\})(OAc)}]^+$ (510)
$\mathrm{Cu\{en(TFA)_2\}}$ + $\mathrm{Zn(OAc)_2}$	$[\mathrm{Zn(Cu\{en(TFA)_2\})_2(OAc)}]^+$ (911); $[\mathrm{HZn(Cu\{en(TFA)_2\})(OAc)_2}]^+$ (578); $[\mathrm{Zn(Cu\{en(TFA)_2\})(OAc)}]^+$ (518)
$\mathrm{Ni\{pn(AA)_2\}}$ + $\mathrm{Cu(OAc)_2}$	$[\mathrm{Cu(Ni\{pn(AA)_2\})_2(OAc)}]^+$ (712), $[\mathrm{HCu(Ni\{pn(AA)_2\})(OAc)_2}]^+$ (476), $[\mathrm{Cu(Ni\{pn(AA)_2\})(OAc)}]^+$ (416)
$\mathrm{Ni\{pn(AA)_2\}}$ + $\mathrm{Ni(NO_3)_2}$	$[\mathrm{Ni(Ni\{pn(AA)_2\})_2(OAc)}]^+$ (707); $[\mathrm{HNi(Ni\{pn(AA)_2\})(OAc)_2}]^+$ (471), $[\mathrm{Ni(Ni\{pn(AA)_2\})(OAc)}]^+$ (411)
$\mathrm{Ni\{pn(AA)_2\}}$ + $\mathrm{Zn(OAc)_2}$	$[\mathrm{Zn(Ni\{pn(AA)_2\})_2(OAc)}]^+$ (714), $[\mathrm{HZn(Ni\{pn(AA)_2\})(OAc)_2}]^+$ (477), $[\mathrm{Zn(Ni\{pn(AA)_2\})(OAc)}]^+$ (417)

the protonated version of the 1:1 $\mathrm{Cu\{en(TFA)_2\}}$ adduct of $\mathrm{Zn(OAc)_2}$. No doubt the unprotonated form is also present in the solution, but it is unobservable by this technique. The large number of (identified) peaks in this spectrum and the recognition that uncharged species are not observed by the ES technique illustrates the great complexity of these apparently simple solutions. However, since the mixing experiments described above showed the transition metal Schiff base complexes to be kinetically inert, we can be sure that zinc and copper are not scrambled in this solution, i.e. the species listed above are zinc complexes of $\mathrm{Cu\{en(TFA)_2\}}$ and not copper complexes of $\mathrm{Zn\{en(TFA)_2\}}$. Exactly analogous ions were observed in the ES mass spectra of solutions containing $\mathrm{Cu\{en(TFA)_2\}}$ with added $\mathrm{Ni(NO_3)_2}$ and $\mathrm{Cu(OAc)_2}$ and also for solutions of $\mathrm{Ni\{pn(AA)_2\}}$ to which was added $\mathrm{Zn(OAc)_2}$, $\mathrm{Ni(NO_3)_2}$ and $\mathrm{Cu(OAc)_2}$. Although $\mathrm{Ni(NO_3)_2}$ was added to the Schiff base complexes, with one exception the ions observed in the ES mass spectra after the addition of $\mathrm{Ni(NO_3)_2}$ were acetate adducts with the acetate being derived from the mobile phase. All data are summarised in Table 4.

Conclusions

This work confirms that, in principle, any ligand which contains an oxygen atom, or any metal complex of that ligand, may be examined by ESMS. If the original compound is neutral then the species is observed as the singly protonated ion, if the compound has a single positive charge it is observed as the intact ion and multiply-charged cations are usually observed as acetate adducts. Systems which illustrate these observations include metal β-diketone complexes [24], metal complexes of tripodal monoanionic ligand [25] as well as these Schiff base complexes.

This work also illustrates the utility of ESMS to investigate the chemistry of labile polynuclear complexes. Previous investigations of the complexes formed between transition metal Schiff base complexes and other cations have depended upon isolation of solid compounds and the determination of their structures by X-ray crystallography. However, the nature of the solids isolated does not always give a true indication of the species present in solution, especially in the case of labile systems Most of the transition metal complexes studied here are paramagnetic so NMR methods are not applicable and we believe there is no technique other than ESMS which can yield such detailed information on the species present in these solutions.

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