Complexation of transition-metal ions, Sn(II), Pb(II) and Al(III) with nucleobase-substituted polyethers and dissociation of adduct ions studied by fast atom bombardment mass spectrometry †

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Metal-ion-complexed dinucleotide analogues were studied by FAB mass spectrometry using tri- and bi-valent transition-metal ions (Cr to Zn), Sn(II), Pb(II) and Al(III). Pairs of thymine nucleobases linked by $(CH_2)_2$-$[O(CH_2)_2]_nO(CH_2)_2$ chains ($n = 1$ **1**, 2 **2**, 3 **3** or 4 **4**) and of adenine nucleobases ($n = 1$ **5** or 4 **6**) co-ordinate to metal ions and form significant $[M + M - H]^+$ and $[M + MCl]^+$ ions. In addition, many transition-metal ions also give $[M + M_2X - 2H]^+$ (X = Cl or NO_3) ions but Cr(III) produces $[M + CrCl_2]^+$ ions. The effect of the spacer chain length is reflected in the ease of formation of $[M + M - H]^+$ and $[M + MX]^+$ ions. Fragmentation of $[M + MX]^+$ and $[M + M_2X - 2H]^+$ ions give $[M + M - H]^+$ ions, suggesting that metal chelation through the nucleobase is more favoured than through the polyether. Complexes of compounds **1–6** with Al(III)–glycerol give abundant $[M + 117]^+$ complex ions (117 = Al + glycerol − 2H). The intensities of these ions decrease with increasing number of ethylene oxide units from **1–4**. The same trend is also observed in **5** and **6**. Bimetallic ions with an unipositive charge are also produced from **1–4**. Dissociation of adduct ions labelled with deuterium confirms the substitution of amide protons with aluminium(III) in the elimination of glycerol.

Hydrogen-bonding interactions are crucial elements for catalysis and molecular recognition in biosystems. Many receptors have been synthesized to investigate the role of these interactions through the recognition of biologically important guests such as nucleobases.[1] Model molecules derived from crown ethers and nucleotide bases can exist with Watson–Crick hydrogen-bonding interactions in a self-assembly process in solution.[2] Gas-phase experiments provide a powerful tool for probing these interactions in the absence of a solvent. The FAB mass spectra of polyethers substituted with nucleobases showed the existence of intramolecular Watson–Crick interactions which are more effective between adenine and thymine than between thymine and thymine.[3]

Metal ions play an important role in biological systems and are often required as cofactors for enzymes. The metal-complexing properties of crown ethers have biological as well as chemical significance.[4] The chelation ability of alkali-metal ions with nucleobase-substituted acylic glymes falls between that of crown ethers and polyethylene glycols.[3] Hydrogen bonds between two nucleobases keep the acylic system in a cyclic form, so as to encapsulate the metal ions more efficiently than their counterparts.

Co-ordination of alkali-metal[3] and alkaline-earth-metal ions[5] with the nucleobases in the selvedge (the high pressure region just above the surface of the sputtered material in desorption experiments) was observed, in addition to complexation with ether oxygens. However, the chelation of alkali-metal ions through a carbonyl group of the nucleobase led to the hydrolysis of nucleobase.[3] When we used alkaline-earth-metal ions for complexation we observed intramolecular covalent bonding of metal between two nucleobases (N–M–N).[5] In the present study, we discuss the interaction of Fe(III), Cr(III), Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Sn(II), Pb(II) and Al(III) with these modified nucleotides and the dissociation of the metal complexes in the first field-free region of a conventional (EB geometry) mass spectrometer.

Results and Discussion

FeCl₃–Thioglycerol

Relative abundances of metal-containing ions obtained from

$x = 1$ **1**   T =
$x = 2$ **2**
$x = 3$ **3**
$x = 4$ **4**

$x = 1$ **5**   A =
$x = 4$ **6**
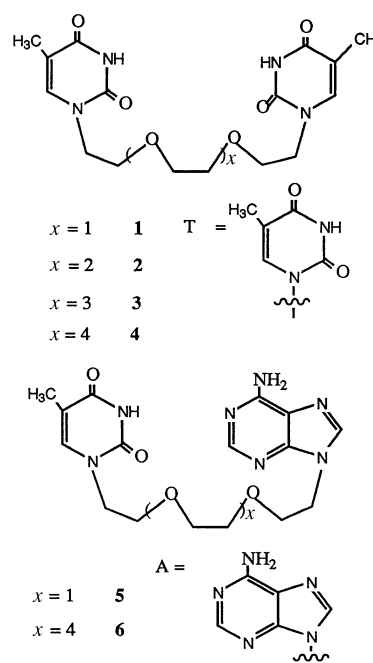
dinucleotide analogues **1–6** using iron(III) chloride and a thioglycerol ($HOCH_2CHOHCH_2SH$) matrix are given in Table 1. The formation of metal-chelated ions such as $[M + Fe - H]^+$, $[M + FeCl]^+$ and $[M + Fe_2Cl - 2H]^+$ indicates reduction of the metal from the +3 to the +2 state in the presence of thioglycerol. Thioglycerol also gives more abundant metal-chelated ions than does glycerol, as we have already observed for the complexation of alkaline-earth-metal ions.[5] The $[M + Fe - H]^+$ ion results from a covalent interaction between the amide nitrogen of the pyrimidine base and a metal ion. Similarly, $[M + Fe_2Cl - 2H]^+$, a unipositive ion, may be formed by the covalent binding of one metal to two pyrimidine bases within the molecule. The other $FeCl^+$ can co-ordinate with the ether oxygens. Polypyridyl and chiral bis(phenanthroline) complexes of ruthenium(II) have been shown to bind covalently to nitrogen

Table 1 Relative abundances of organometallic ions from compounds **1**–**6** with FeCl$_3$–thioglycerol *

	m/z (%)			
Compound	$[M + \text{Fe} - \text{H}]^+$	$[M + \text{FeCl}]^+$	$[M + \text{Fe}_2\text{Cl} - 2\text{H}]^+$	Others
1	14	88	20	582 (5), 583 (7), 637 (5), 787 (3), 841 (8)
2	25	40	22	749 (11), 839 (8)
3	34	12	15	—
4	57	6	21	—
5	22	37	4	556 (15) $[M + \text{Fe}_2\text{Cl}_2 - \text{H}]^+$
6	79	4	3	688 (14) $[M + \text{Fe}_2\text{Cl}_2 - \text{H}]^+$

* m/z 153, $[\text{T·C}_2\text{H}_4]^+$, is the base peak from compounds **1**–**4** and **6**, $[M + \text{H}]^+$ ion that from **5**.

Table 2 Relative abundances of organometallic ions from compounds **1**–**6** with CrCl$_3$–thioglycerol *

	m/z (%)				
Compound	$[M + \text{Cr} - \text{H}]^+$	$[M + \text{CrCl} - \text{H}]^+$	$[M + \text{CrCl}]^+$	$[M + \text{CrCl}_2]^+$	Others
1	22	10	26	18	416 (10), 524 (26), 574 (20)
2	21	10	11	7	460 (5), 568 (14), 618 (12), 745 (6)
3	22	12	10	8	504 (4), 612 (10), 662 (10)
4	24	3	4	8	548 (8), 635 (9), 670 (6), 706 (9)
5	12	4	4	—	—
6	17	5	3	4	665 (6), 715 (3), 930 (3)

* m/z 153, $[\text{T·C}_2\text{H}_4]^+$, is the base peak from compounds **1**–**4** and $[M + \text{H}]^+$ ion that from **5** and **6**.

bases.[6] Complexation of the alkali- and alkaline-earth-metal ions also demonstrated that metal ions can displace amide protons,[3,5] which is not a favourable reaction in solution.[7] Similarly, in the gas phase, metal chelation of alkali-, alkaline-earth- and transition-metal ions by peptides is *via* covalent bonding to amide nitrogens.[8]

The abundance of the $[M + \text{Fe} - \text{H}]^+$ ion increases with an increase in the length of the alkyl spacer chain between two nucleobases, while the abundance of $[M + \text{FeCl}]^+$ ions declines. A similar trend is observed for **5** and **6** also. These observations suggest that in **1** and **2** there is more intramolecular hydrogen-bonding. This keeps the system in a cyclic form for more effective chelation of the FeCl$^+$ ion by the polyether in **1** and **2** compared to **3** and **4**. These observations also suggest that the displacement of a hydrogen-bonded amide proton requires more energy for the substitution process than a free amide proton. The same phenomenon plays a role in solutions where alkali-metal ions cannot deprotonate amide nitrogens. Since the formation of the $[M + \text{Fe}_2\text{Cl} - 2\text{H}]^+$ ion is a combination of metal chelation through the nucleobase and the polyether chain, there is no such variation in the relative abundances of this ion with an increase in the spacer chain length. However, in **5** and **6**, the substitution of one proton by a metal ion is a major process and this results in the formation of significant amounts of the $[M + \text{Fe}_2\text{Cl}_2 - \text{H}]^+$ ion. The higher proton affinity of adenine[9] present in the complex results in the formation of abundant protonated molecules. In addition, the complexation of metal ions by the matrix is also observed in these spectra. Deuterium oxide exchange experiments with compound **2** show an increase of one and two units in the mass of the $[M + \text{M} - \text{H}]^+$ and $[M + \text{MX}]^+$ ions respectively, and no change in the mass of $[M + \text{M}_2\text{X} - 2\text{H}]^+$ ions. These results indicate that during the substitution processes by metal ions the acidic protons have been eliminated from the nucleobase. From these observations we conclude that the bi- and tri-valent metal ions preferably bind covalently to nucleobases by displacing acidic protons when the system possesses more than one type of chelating site.

CrCl$_3$–Thioglycerol

The interaction of CrCl$_3$ with the dinucleotide analogues **1**–**6** produces ions by the complexation of both Cr$^{\text{III}}$ and Cr$^{\text{II}}$. The latter is due to partial reduction of chromium(III). The $[M + \text{Cr} - \text{H}]^+$ and $[M + \text{CrCl}]^+$ ions have chromium in a +2
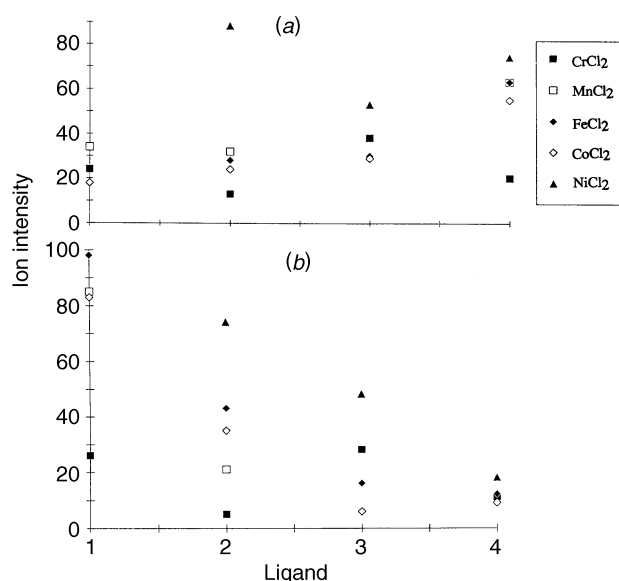
Fig. 1 Relative intensities of the $[M + \text{M} - \text{H}]^+$ (*a*) and $[M + \text{MCl}]^+$ (*b*) ions *vs.* ligand

state, while $[M + \text{CrCl} - \text{H}]^+$ and $[M + \text{CrCl}_2]^+$ ions are nominally Cr$^{\text{III}}$. The relative intensities of the metal-complexed ions obtained are listed in Table 2. Ions due to the complexation of analyte with metal-containing ions derived from matrix species are also observed for Cr$^{\text{III}}$. Bimolecular metal-chelated ions are also formed, but are not as abundant as is found with alkali-metal ions.[3]

Metal-ion complexation of the dinucleotide analogues **1**–**6** has also been studied with CrCl$_2$, MnCl$_2$, FeCl$_2$, CoCl$_2$, NiCl$_2$, Cu(NO$_3$)$_2$, Zn(NO$_3$)$_2$, SnCl$_2$ and Pb(NO$_3$)$_2$ in a thioglycerol matrix. Transition-metal ions and potentially toxic metal ions (Sn$^{\text{II}}$ and Pb$^{\text{II}}$) also produce significant metal-chelated species such as $[M + \text{M} - \text{H}]^+$, $[M + \text{MX}]^+$ and $[M + \text{M}_2\text{X} - 2\text{H}]^+$, just as we observed for Fe$^{\text{III}}$ and Cr$^{\text{III}}$. Copper(II) gives only $[M + \text{M}]^+$ ions in addition to the fragment ions from the ligand. The relative abundances of these metal-chelated ions are given in Table 3. The site of co-ordination of the metal is analogous to that of chromium and iron which displace amide protons. The spectral data collected with equimolar solutions of com-

Table 3 Relative abundances of metal-containing ions from compounds **1–6**

(*a*) Bivalent transition-metal ions

m/z (%)

MX$_2$	Compound	$[M + M - H]^+$	$[M + MX]^+$	$[M + M_2X - 2H]^+$	Others
CrCl$_2$	**1**	15	22	—	524 (9), 574 (8), 783 (3)
	2	14	8	—	745 (3), 871 (2)
	3	16	6	5	662 (6)
	4	20	3	6	706 (4), 757 (2)
	5	23	25	—	—
	6	28	—	—	—
MnCl$_2$	**1**	13	100	26	581 (7), 634 (7), 839 (6), 928 (2)
	2	16	36	24	748 (7), 837 (6)
	3	23	20	16	669 (3), 722 (4)
	4	41	8	21	713 (5), 766 (4), 891 (2)
	5	28	64	—	—
	6	88	—	—	—
FeCl$_2$	**1**	9	91	24	547 (3), 583 (7), 637 (5), 841 (7)
	2	18	32	14	627 (5), 749 (7), 839 (4)
	3	27	11	13	671 (3), 725 (3)
	4	68	7	32	715 (5), 769 (6)
	5	17	41	—	—
	6	60	—	—	687 (18)
CoCl$_2$	**1**	13	72	25	589 (11), 646 (5), 847 (6)
	2	10	19	8	633 (4), 752 (4)
	3	21	7	10	677 (2), 734 (2)
	4	46	4	21	721 (5), 778 (5)
	5	16	25	—	—
	6	45	—	—	694 (15)
NiCl$_2$	**1**	10	38	—	587 (9), 789 (3)
	2	15	19	—	751 (4)
	3	20	11	—	—
	4	33	6	8	719 (3)
	5	25	26	—	433 (20)
	6	25	—	—	—
Cu(NO$_3$)$_2$	**1**	26	—	—	499 (9), 561 (5)
	2	16	—	—	—
	3	12	—	—	—
	4	13	—	—	—
Zn(NO$_3$)$_2$	**1**	26	34	—	537 (26)
	2	29	11	—	757 (10)
	3	21	—	—	—
	4	25	—	—	—

(*b*) SnCl$_2$ and Pb(NO$_3$)$_2$—thioglycerol

m/z (%)

Compound	$[M + Sn - H]^+$	$[M + SnCl]^+$	$[M + Pb - H]^+$	$[M + PbNO_3]^+$	Others from Sn^{II}	Pb^{II}
1	99	37	65	11	851 (6)	840 (22)
2	55	15	45	11	813 (12)	884 (19), 910 (9), 930 (8)
3	50	13	38	7	—	930 (13)
4	77	20	49	4	—	—
5	6	—	20	—	—	788 (6)
6	9	—	57	—	—	758 (12)

pounds **1–4** and these transition-metal ions (with an excess of MX$_2$) show the relative affinity of the metal ions towards the ligands as a function of the number of ethylene oxide units. The relative abundances of $[M + M - H]^+$ ion [Fig. 1(*a*)] and $[M + MX]^+$ ion [Fig. 1(*b*)] from each metal ion can be used as a probe of the affinity of metal ions towards the nitrogen base itself as the number of polyethylene oxide units between them is increased. This is an alternative to the affinity towards a polyether chain and the effect of hydrogen bonding between two nucleobases on the elimination of HX.

Fragmentation of metal-complexed ions. The $P^+ = [M + M - H]^+$ ions, on collisionally activated decomposition (CAD) (M = Fe or Cr), in which the metal ion is covalently bonded to the nucleobase, undergo fragmentation to produce ions corresponding to $[P - CH_3]^+$, $[P - 43]^+$ and $[P - 152]^+$.

Other metal-containing ions are observed due to consecutive losses of C$_2$H$_4$O units from $[P - 152]^+$ ions. These fragmentations suggest that the metal is in multiple co-ordination with the polyether, and on the elimination of neutral (Thy − H) + (C$_2$H$_4$) (152 mass units), the metal ion migrates to the polyether chain. Further fragmentation involves losses of C$_2$H$_4$O units. The difference in the *m/z* values of metal-containing fragment ions obtained from $[M + Cr - H]^+$ and $[M + Fe - H]^+$ ions corresponds to the difference in the atomic weights of the metals.

The dissociation of the $[M + MCl]^+$ ion gives an abundant ion due to dehydrohalogenation. Further fragmentation of this ion is similar to the fragmentation of the $[M + M - H]^+$ ion. The labile group of the metal complex is replaced in a nucleophilic substitution by an acidic proton of the nucleobase. The CAD of the $[M + Fe_2Cl - 2H]^+$ ion also shows the formation

Table 4 Relative intensities of ions obtained from compounds **1–4** using AlCl$_3$–glycerol–CF$_3$CO$_2$H–water *

	m/z (%)					
Compound	$[M + H]^+$	$[M + 117]^+$	$[M + 139]^+$	$[M + 141]^+$	$[M + Al − 2H]^+$	Others
1	35	51	8	13	5	409 (5), 411 (9), 597 (12), 599 (7), 621 (6), 713 (5), 715 (3)
2	21	27	5	9	4	437 (9), 641 (4), 643 (3), 719 (6)
3	21	21	5	5	2	—
4	12	13	4	7	6	—
5	100	20				616 (12)
6	100	13				879 (10)

* In compounds **1–4** *m/z* 153, $[T \cdot C_2H_4]^+$, is the base peak.

of the $[M + Fe − H]^+$ ion followed by loss of 152 mass units. This fragmentation process indicates that the metal-ion affinity is greater towards the nucleobase than towards the ether. The dissociation of complex ions between transition-metal ions and ribonucleoside monophosphates also gave [nucleobase + M^{2+} − H]$^+$ ions in which the base was deprotonated and bound to the metal ion directly.[10]

Dissociation of the $P^+ = [M + M − H]^+$ ion of Pb^{II} and Sn^{II} from compounds **1** and **4** gives $[P − NHCO]^+$, $[P − 152]^+$ followed by loss of C$_2$H$_4$O units. The same adduct ions, derived from Co^{II}, Mn^{II} and Fe^{II}, produce $[P − 152]^+$ and $[P − 2(152)]^+$ ions in high abundance. However, the $[M + Zn − H]^+$ ion of **4** produces the $[P − 152]^+$ ion as the major process. Fragmentation of $[M + Cu]^+$ yields abundant $[P − NHCO]^+$ and $[P − 152]^+$ ions. The dissociation of $[M + MX]^+$ and $[M + M_2X − 2H]^+$ is similar to that of the corresponding ions derived from Fe^{III} and Cr^{III}. The site of metal complexation is preferentially with the nucleobase and is analogous to the chelation of Fe^{III} and Cr^{III}.

AlCl$_3$–Glycerol–CF$_3$CO$_2$H–water

As reported in our earlier studies [11,12] a metal–matrix mixture of AlCl$_3$–glycerol (glyc)–CF$_3$CO$_2$H–water generates ions at *m/z* 117 ([Al + glyc − 2H]$^+$), 209 ([Al + 2 glyc − 2H]$^+$), 231 ([Al + CF$_3$CO$_2$H + glyc − 2H]$^+$) and 233 ([2Al + 2 glyc − 5H]$^+$) along with species produced by substitution of the hydroxy proton of these ions by 116 mass units *i.e.* [Al + glyc − 3H] and 114 mass units (CF$_3$CO$_2$H) in addition to the ions from glycerol matrix. The mass spectra of compounds **1–6** recorded using AlCl$_3$, glycerol, CF$_3$CO$_2$H and water show ions due to $[M + H]^+$, $[M + 117]^+$, $[M + 139]^+$, $[M + 141]^+$, $[M + Al − 2H]^+$ and $[M + 45]^+$, *i.e.* $[(M − H) + AlF]^+$. Relative abundances of these ions are listed in Table 4. The $[M + 117]^+$ ion shows an increase of three mass units during D$_2$O-exchange experiments. An increase of two units is due to the nucleobase and one unit from the glycerol hydroxy group.

For compound **2** the $[M + 141]^+$ ion is observed even in experiments carried out with acetic acid in place of CF$_3$CO$_2$H. We thus confirm that the CF$_3$CO$_2$H is not involved in the formation of the $[M + 141]^+$ ion. Therefore, the $[M + 141]^+$ ion must be formed from aluminium and glycerol. The mass of the $[M + 141]^+$ ion remains the same during the D$_2$O exchange. This indicates that two exchangeable protons are involved in the substitution of Al^{III} at pyrimidine nitrogen (NH) to form the $[M + 141]^+$ ion, *i.e.* $[(M − 2H) + (2Al + glyc − 3H)]^+$. This bimetallic complex ion $[M + 2Al + glyc − 5H]^+$ is formed by the bonding of Al^{III} to two nitrogens (N^3) of the nucleobases and one hydroxy of a glycerol unit. The other aluminium ion is also attached to the glycerol along with the remaining two hydroxy groups as proposed for structure **a**. The *ab initio* energy-minimized structure is in agreement with the proposed structure **a**. Similar substitution reactions were observed with alkali-metal and alkaline-earth-metal ions for these dinucleotide analogues.[3,5] Reactions of Al^{III}–glycerol give ions due to metal-insertion reactions by substituting exchangeable protons
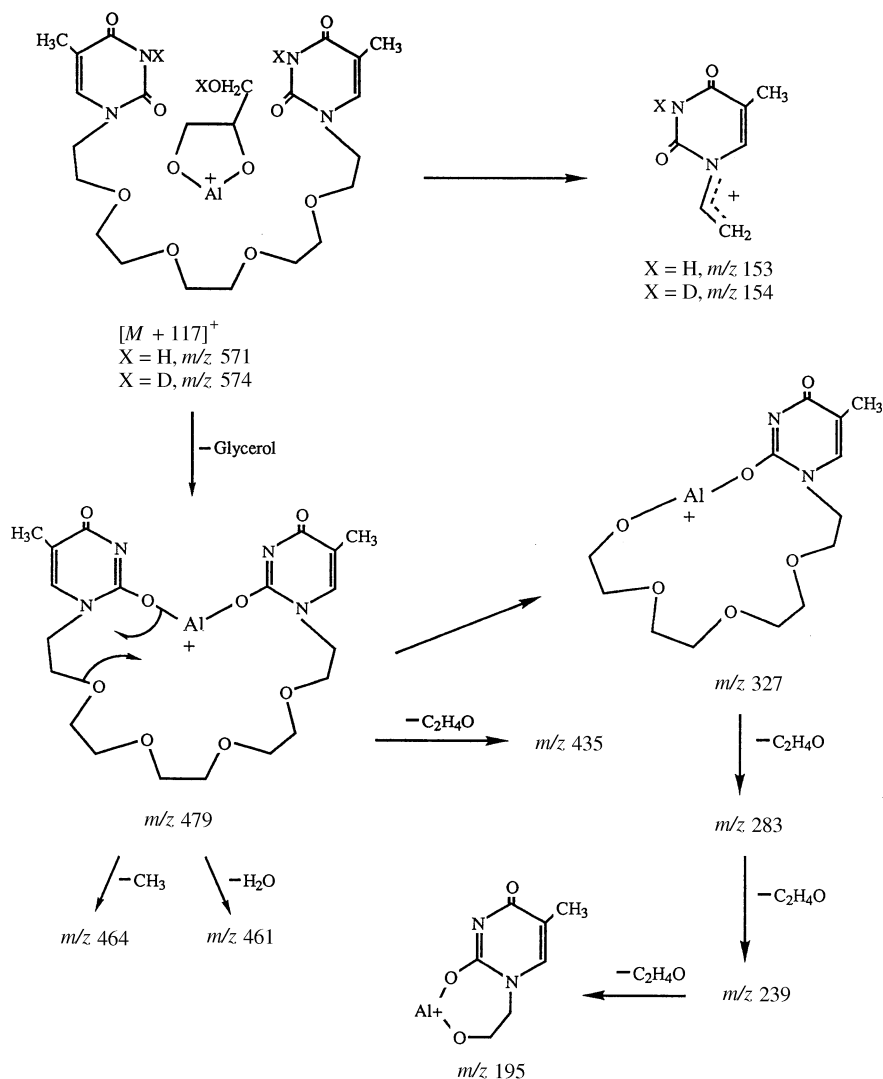

m/z 595
a
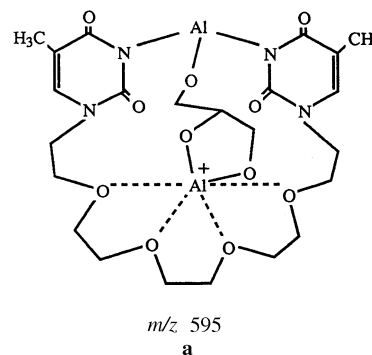
with α-amino acids, peptides and glycols also.[11,12] The high-resolution mass measurements made on the $[M + 141]^+$ ion at *m/z* 507 from **1** fit with the proposed elemental composition C$_{19}$H$_{25}$Al$_2$N$_4$O$_9$ (calc. 507.12521, obs. 507.12310; Δ 4.1 ppm).

The other adduct ion, corresponding to $[M + 139]^+$, shows an increase of one mass unit during D$_2$O experiments. This ion is not observed when CF$_3$CO$_2$H is changed to acetic acid. Hence, this ion must be formed by the substitution of Al^{III} with one amide proton of one nucleobase and CF$_3$CO$_2$H, $[(M − H) + Al + (CF_3CO_2H − H)]^+$. The exact mass measurement on the $[M + 139]^+$ ion at *m/z* 505 from compound **1** gives the elemental composition C$_{18}$H$_{21}$AlF$_3$N$_4$O$_8$ with an error of 4.9 ppm (calc. 505.11268, obs. 505.11019). The characteristic loss of CF$_2$CO$_2$ (94 mass units) from the $[M + 139]^+$ ion can yield $[M + 45]^+$ ions in which AlF$^+$ is bonded to a N$_3$ of the thymine moiety. Finally, the formation of the $[M + Al − 2H]^+$ ion from $[M + 117]^+$ can be accounted for by the elimination of glycerol in a substitution process.

Compounds **5** and **6** also yield $[M + 117]^+$ ions. Owing to their higher proton affinity, they did not form cluster ions as did **1–4** with aluminium ions. Instead the formation of $[M + H]^+$ ions predominates in the spectrum. Loss of adenine (135 mass units) from the protonated bimolecule is consistent with previous reports.[3,5] The accurate mass measurements on the $[M + 117]^+$ ion at *m/z* 483 from **1** gives a deviation Δ 2.6 ppm from the elemental composition C$_{19}$H$_{28}$AlN$_4$O$_9$ (calc. 483.16716, obs. 483.16843).

Mass spectra recorded with equimolar concentrations of compounds **1–4** yield the gradual decrease in the abundances of $[M + 117]^+$ ions with an increase in the spacer between the two nucleobases. The competitive metal chelation of Al^{III} with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and **4** with six ethylene glycol units produces the $[M + 117]^+$ ions in 5:1 ratio respectively. Especially in **4**, the hydrogen-bonding interactions are not strong enough to keep the system in a cyclic form to make it more effective in metal chelation.

Fragmentation of ionic complexes. The CAD of the $[M + 117]^+$ ions of compounds **1–3** leads to similar fragment ions. Hence, only the fragmentation of ions obtained from **3** is discussed. The dissociation of $[M + 117]^+$ ions gives ions cor-

H3C—...NX   XN...—CH3
XOH2C
O   O
+
Al

[M + 117]+
X = H, m/z 571
X = D, m/z 574

X N ... CH3
+
CH2
X = H, m/z 153
X = D, m/z 154

− Glycerol

H3C ... Al+ ... CH3
m/z 479

Al+ ... CH3
m/z 327

−C2H4O → m/z 435

−C2H4O
m/z 283

−CH3 → m/z 464   −H2O → m/z 461

−C2H4O
m/z 239

−C2H4O

Al+ ... CH3
m/z 195

Scheme 1 The collisionally activated dissociation of the $[M + 117]^+$ ion from compound **3**

responding to $[M + Al - 2H]^+$, followed by the elimination of water and 152 mass units. Then, an abundant ion due to consecutive losses of C_2H_4O units, which is the characteristic elimination of neutral C_2H_4O from crown ethers[13] is observed from $[M - 244]^+$ ions. In addition, they form ions at m/z 153 and 110. The fragmentation pathway for this ion is established by the dissociation of the $[M - D_2 + 118]^+$ ion at m/z 574. All deuteriums are lost in the elimination of glycerol to give $[M + Al - 2H]^+$. The only ion at m/z 154 contains one D due to the thymines' exchangeable protons. The remaining fragmentation of this labelled ion is similar to that of the unlabelled ion. These fragmentation pathways, by substituting the groups attached to the metal ion (Scheme 1), suggest covalent bonding of the metal ion through the nucleobase.

The dissociation of the $[M + 141]^+$ ion from compound **3** on CAD produces more abundant ions at m/z 500 and 479. The ion at m/z 479 is due to the formation of $[M + Al - 2H]^+$. Loss of 152 mass units from the ion at m/z 479 is also observed. The dissociation of $[M + Al + CF_3CO_2H - 2H]^+$ from **3** at m/z 593 gives ions corresponding to loss of CF_2CO_2 and CF_3CO_2H followed by elimination of 152 mass units to form other fragment ions.

Conclusion

Transition-metal ions and potentially toxic metal ions (Pb^{II} and Sn^{II}) complex with nucleobase-derived polyether glymes. Fragmentation of these adduct ions showed that there is a greater affinity of the metals towards the nucleobase than towards the polyether chain. Hydrogen-bond interactions play a major role in the complexation of MX^+ ions with these nucleotide-modified systems, which may be helpful to probe Watson–Crick interactions. Chelation of bi- or tri-valent metal ions with tautomeric forms of carbonyl oxygens may allow the metal ion to interact both with the polyether chain and/or only with the nucleobase.

The formation of $[M + 117]^+$ ions also showed that cyclic systems chelate with the metal ions more strongly, as observed in the competitive complexation reactions of 18-crown-6 and compound **4**. The formation of abundant adduct ions with aluminium(III) decreases as the length of the spacer increases, which is another indication of the existence of intramolecular recognition through hydrogen bonding. The fragmentation of the $[M + 117]^+$ ion produced a $[M + Al - 2H]^+$ ion, which involved the substitution of exchangeable protons. This is consistent with the dissociation of $[M + 117]^+$ ions derived from α-amino acids, peptides and glycols.[11,12] Our study demonstrates that metal chelation with modified dinucleotide analogues may be useful both to probe biologically relevant interactions and to mimic the mechanism by which far larger systems operate.

Experimental

Spectra were measured on a Kratos (Manchester, UK) Concept 1S EB geometry instrument equipped with a FAB gun

(Ion Tech, Teddington, UK). Samples were prepared by dissolving the analyte and metal chlorides in a thioglycerol matrix for recording the spectra with transition-metal ions, Sn^{II} and Pb^{II}. For aluminium(III), compounds **1–6** were mixed in a matrix mixture containing $AlCl_3$ in glycerol, CF_3CO_2H and water. For each sample 1 μl of prepared solution was loaded on to the 1 mm wide stainless-steel FAB probe tip and bombarded with fast xenon atoms generated at 6–8 kV using an ion current of 0.5–1 mA. The source housing pressure was $1–2 \times 10^{-5}$ Torr. The secondary-ion beam was accelerated to 8 kV. The system was calibrated with 2,4,6-tris(perfluoroheptyl)-1,3,5-triazine. The spectra recorded, 6–10 scans for each run, were averaged and the background was subtracted from spectra using a Kratos MACH 3/DART data system running on a SUN SPARC Station 10. Helium was used to reduce the main beam intensity by 45–50% in the first field-free region of the (EB geometry) mass spectrometer to obtain the CAD spectra. High-resolution mass measurements were made at 10 000 resolving power and 8 kV accelerating voltage. Spectra were obtained with equimolar concentrations of **1–4** (0.5 mg) using $AlCl_3$ (2–3 mg), glycerol (25-30 mg), CF_3CO_2H (2 μl) and water (2 μl).

Energy minimization of ion **a** was carried out using the Hartree-Fock method at the STO-3G level using the SPARTAN *ab initio* program running on a Silicon Graphics Power Indigo 2 Extreme computer. The initial geometry of the molecule was estimated using the Sybyl/x force field.

The preparation of compounds **1–6** was described in our previous work.[3] Matrices (thioglycerol and glycerol), metal chlorides and nitrates, CF_3CO_2H and D_2O were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

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