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Macrobicyclic d-metal tris-dioximates obtained by cross-linking with p-block elements

Part II. FAB mass spectrometry of macrobicyclic boron-containing iron(II) dioximates

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Abstract

Gas-phase fragmentation pathways for clathrochelate alicyclic iron(II) dioximates $FeD_3(BOH)_2$ (where D^{2-} = cyclohexanedion-1,2-dioxime, 4-methylcyclohexanedion-1,2-dioxime, cycloheptanedion-1,2-dioxime, cyclooctanedion-1,2-dioxime) have been studied by the FAB mass spectrometry method. The most intensive peaks in the spectra belong to protonated molecular ions $[M+H]^+$. The detachment of dioximate fragments is the main pathway of fragmentation of complexes in the gas phase. The intensity of the peaks caused by the complexes fragmentations with the detachment of cross-linking groups is much lower. The detachment of the apical hydroxyl group and boron-containing fragments is mainly characteristic of seven- and eight-membered dioximes. Substituent introduction into the cyclohexane ring and ring enlargement to seven results in a noticeable destabilization of the clathrochelate framework. Transition to a less stressed eight-membered dioxime stabilizes this framework.

Introduction

Compounds with ligands, which are formed and exist only in complexes are well known. Macrobicyclic boron-containing d-metal dioximates which are representatives of a relatively new class of compounds with an encapsulated metal ion (i.e. the metal ion rigidly fixed in the macrobicyclic ligand cavity) belong to such compounds [1, 2]. Such a structure gives rise to a number of extraordinary properties of the metal ion sufficiently isolated from the environmental factors. Furthermore, the structure peculiarities of complexes with encapsulated metal ions (also called clathrochelates) provide a high selectivity of complex formation reactions.

Among macrobicyclic boron-containing iron(II) dioximates $FeD_3(BR)_2$, where D^{2-} = dianion of the corresponding dioxime, R = F, OH, alkyl, alcoxyl, complexes with alicyclic dioximes are of the greatest interest because they possess the highest stability and permit iron(II) to be quantitatively bound in dilute aqueous solutions to clathrochelate $FeD_3(BOH)_2$ complexes.

We have already studied in detail the kinetics and mechanism of template synthesis and decomposition of macrobicyclic $FeD_3(BOH)_2$ complexes, where D^{2-} = dianions of cyclohexanedion-1,2-dioxime (nioxime, H_2Nx), 4-methylcyclohexanedion-1,2-dioxime (4-methylnioxime, H_24MNx) and cycloheptanedion-1,2-dioxime (heptoxime, H_2Gx) in water solutions [3, 4].

We have used fast atom bombardment (FAB) mass spectrometry of macrobicyclic iron(II) complexes to obtain information on the pathways of fragmentation of these compounds in the gas phase. The FAB-MS data were compared with the available data on the stability of macrobicyclic complexes in solutions.

Experimental

The complexes $FeNx_3(BOH)_2$, $Fe(4MNx)_3(BOH)_2$, $FeGx_3(BOH)_2$ and $FeOx_3(BOH)_2$ (Ox^{2-} = dianion of cyclooctanedion-1,2-dioxime, octoxime) were synthesized by the methods described in refs. 5–7.

FAB mass spectrometry

A high-resolution double-focusing mass spectrometer MX-1310 (electrostatic and magnetic sectors) was used in the work. The construction of the FAB ion source is described in ref. 8. The substance to be investigated was dissolved in a mixture of chlo-

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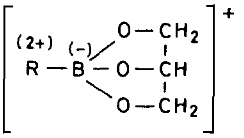
roform or acetone and glycerol. A sample of 5–10 μl of the solution was bombarded by the argon atom beam with an energy of 3.5 KeV. The mass number scale calibration in the mass spectrometer under FAB conditions was performed against the peaks of glycerol cluster ions of the composition $[(\mathrm{Gl})_n + \mathrm{H}]^+$, where $n = 1$–12. The analyzer peak resolution under FAB conditions was usually 10 000.

The relative intensities of the isotope peaks of molecular and fragment ions were calculated from the data on the abundance of natural isotopes of all the elements forming part of these ions. The composition of molecular or fragment ions in experimental mass spectra is confirmed by comparing the isotope peak series of these ions with the calculated ones.

Results and discussion

When considering the processes of ion formation from the liquid phase in the FAB method, it is necessary to take into account the fact that the energy of an ionizing argon atom beam is rather unevenly distributed among the liquid phase molecules [9]. This results in the formation of comparable quantities of intact molecular and fragment ions.

Formed by coupling of clathrochelate and dissociated glycerol proton, ions of $[M+\mathrm{H}]^+$ composition yield the most intensive peaks in the FAB-MS of macrobicyclic iron(II) dioximates (Table 1). The interaction between the neutral molecules of the complexes and the matrix molecules followed by proton detachment from the tribasic alcohol seems hardly probable in our case since the usual solvates in FAB as well as adducts with glycerol of the type



where R^{2+} is the double-charged semiclathrochelate residue, are absent from the mass spectrum (such type adducts were found for triols in ref. 10). This is due to the fact that the boron atom in macrobicyclic complexes is in a tetrahedral environment and is not capable of forming chelates with polyalcohols typical to trigonal environment. We did not study the hydrolytic stability of the complexes in glycerol for long periods of time (more than 3–4 h). However, the absence of strong solvolysis product signals from the mass spectra indicates that polyols can be successfully used as highly polar solvents which do not destruct macrobicyclic boron-containing iron(II) dioximates.

The excited complex molecules, which have obtained (in a series of collisions) [9] an energy sufficient for valence bond rupture, undergo fragmentation which proceeds for all the complexes under consideration by similar schemes.

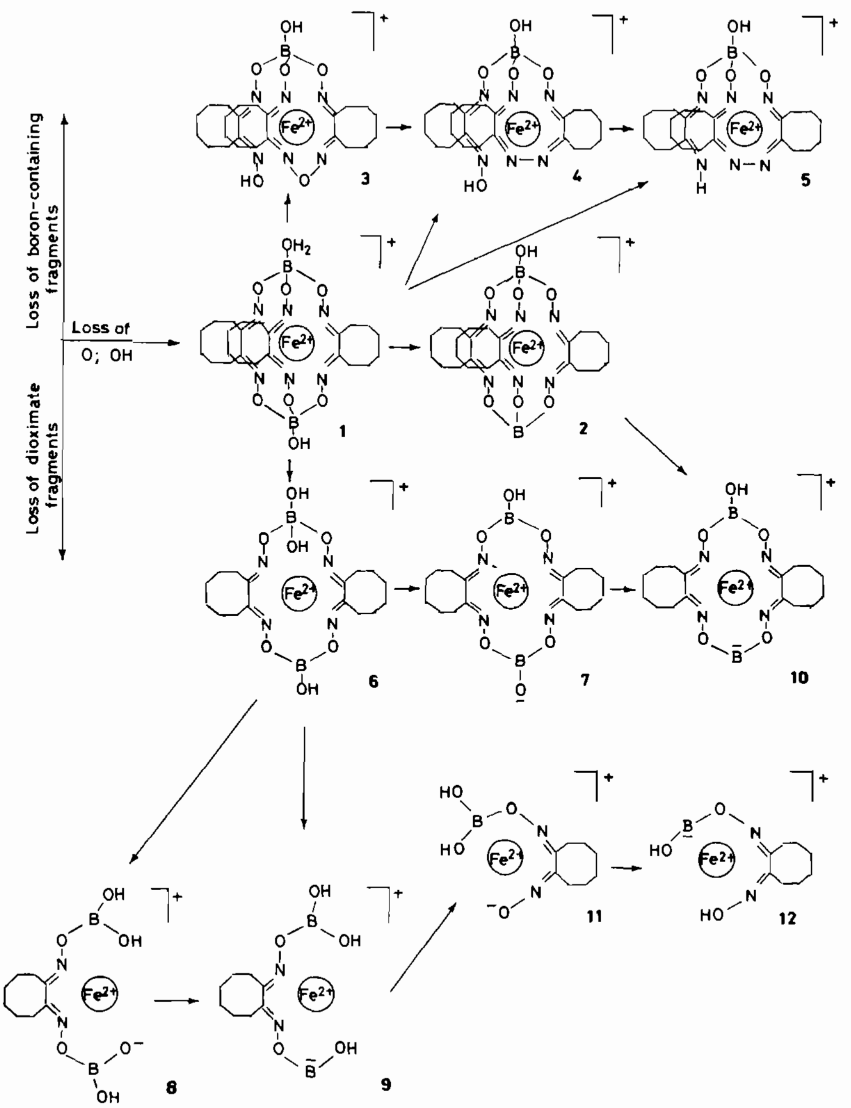
Scheme 1 demonstrates the relationship between fragment ion structures. As an example the degradation products of $\mathrm{FeOx_3(BOH)_2}$ are given. While elaborating this scheme some suppositions were used.

(i) Taking into account that the $[M+\mathrm{H}]^+$ ion produces the most intensive signal in mass spectra reflecting a strong protonoacceptor ability [11] of the complex molecules, the protonated molecular ion has been chosen as a parent particle alternatively with M.

(ii) The single act of ion degradation consist of detachment of only one functional group.

TABLE 1. The most abundant ionic species arising from unimolecular decomposition

Species number	Ionic species	$\mathrm{FeNx_3(BOH)_2}$	$\mathrm{Fe(4MNx)_3(BOH)_2}$	$\mathrm{FeGx_3(BOH)_2}$	$\mathrm{FeOx_3(BOH)_2}$
1	$[M\mathrm{H}]^+$	533(100)	574(100)	575(100)	617(100)
2	$[M\mathrm{H}-\mathrm{H_2O}]^+$	515(33)	557(40)	557(49)	599(52)
3	$[M\mathrm{H}-\mathrm{BO(OH)}]^+$			531(10)	573(10)
4	$[M\mathrm{H}-\mathrm{BO_2(OH)}]^+$			515(16)	557(16)
5	$[M\mathrm{H}-\mathrm{BO_3(OH)}]^+$	457(13)		499(16)	541(10)
6	$[M\mathrm{H}-(\mathrm{D\text{-}O})]^+$	409(18)	437(42)	437(27)	465(21)
7	$[M\mathrm{H}-\mathrm{H_2D}]^+$	392(8)	420(42)	420(33)	448(33)
8	$[M\mathrm{H}-2(\mathrm{D\text{-}O})]^+$	285(12)	299(100)	299(72)	313(29)
9	$[M\mathrm{H}-(\mathrm{D\text{-}O})-\mathrm{D}]^+$		283(46)	283(30)	297(12)
10	$[M\mathrm{H}-\mathrm{H_2O}-\mathrm{D}]^+$	375(15)	403(66)	403(60)	431(19)
11	$[M\mathrm{H}-\mathrm{B(OH)(D\text{-}O)D}]^+$	241(5)		255(26)	269(10)
12	$[M\mathrm{H}-\mathrm{B(OH)D_2}]^+$		239(48)	239(73)	253(31)
13	$[\mathrm{D_2(OH)(BOH)_2}]^+$		381(24)		409(9)
14	$[\mathrm{D_2(BOH)}]^+$		336(28)		



Scheme 1.

(iii) The fragmentation in gas phase is not followed by ion–ion or ion–molecule reactions.

The most heavy fragment ions are formed as a result of heterolytic bond rupture and detachment of the apical substitutent (group OH^- or, more likely, H_2O) from the cross-linking boron-containing group.

$$[FeD_3(BOH)_2+H]^{+,*} \longrightarrow [FeD_3B(BOH)]^+ + H_2O \quad (1)$$

In accordance with $FeD_3(BOH)_2$ complex dissociation processes in aqueous solutions, which occur in two stages of detachment of cross-linking boric acid molecules followed by the decomposition of protonated $Fe(H_2D)_3^{2+}$ tris-dioximate [3, 4], one could expect a stronger fragmentation of complexes excited in the gas phase by the same route. However, the intensities of the peaks of the fragment ions formed by reaction (2). are low in the mass spectra

$$[FeD_3(BOH)_2+H]^{+,*} \longrightarrow [FeD_2(D\text{-}O)(BOH)+H]^+ + BO(OH) \quad (2)$$

of $FeGx_3(BOH)_2$ and $FeOx_3(BOH)_2$, and these ions are quite absent from the spectra of complexes with six-membered dioximes.

The peaks at m/z values corresponding to products of reactions (3) and (4) were found in the mass spectra of the $FeOx_3(BOH)_2$, $FeGx_3(BOH)_2$ and $FeNx_3(BOH)_2$ complexes. These products, however, cannot be formed by hydrolysis reaction but only in the gas phase with homolytic N–O bond rupture.

$$[FeD_3(BOH)_2+H]^{+\cdot *} \longrightarrow$$
$$[FeD(D\text{-}O)_2(BOH)+H]^+ + BO_2(OH) \quad (3)$$
$$[FeD_3(BOH)_2+H]^{+\cdot *} \longrightarrow$$
$$[Fe(D\text{-}O)_3(BOH)+H]^+ + BO_3(OH) \quad (4)$$

Practically all the fragment ions in the mass spectra of the complexes studied yield sets of peaks, whose intensity ratios indicate the presence of boron-containing fragments in these species. On the basis of the composition of fragment ions determined from the *m/z* mass number values of the maxima of the isotope peak series of these ions (Table 1), one can assert that the formation of fragment ions in the gas phase involves generally a detachment of dioximate fragments from the 'parent' molecule or ion.

$$[FeD_3(BOH)_2+H]^{+\cdot *} \longrightarrow$$
$$[FeD_2O(BOH)_2+H]^+ + (D\text{-}O) \quad (5)$$
$$[FeD_3(BOH)_2+H]^{+\cdot *} \longrightarrow$$
$$[FeD_2(BO)(BOH)]^+ + H_2D \quad (6)$$
$$[FeD_3(BOH)_2+H]^{+\cdot *} \longrightarrow$$
$$[FeDO(BOH)+H]^+ + B(OH)D(D\text{-}O) \quad (7)$$
$$[FeD_3(BOH)_2+H]^{+\cdot *} \longrightarrow$$
$$[FeD(BOH)+H]^+ + B(OH)D_2 \quad (8)$$

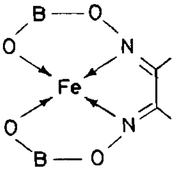
In this case, the total intensity of the peaks of fragment ions formed by the detachment of dioximate fragments, with both borate ions remaining (eqns. (5) and (6)), is higher than that of ions which 'have lost' fragments of both types (eqns. (7) and (8)). This may indicate the borate fragments are detached after the dioximate fragments. Probably, the detachment of a borate fragment requires a higher complex species excitation energy.

Another interesting peculiarity of fragmentation is non-selective bond rupture in the B–O–N chain, which takes place probably due to the homolytic character of bond rupture involving the formation of ion radicals in the gas phase. However, as was noted, the O–N bond rupture proves to be more favoured.

Among fragment ions which do not contain any iron ion, the fragments $D_2(BOH)^+$ and $D_2O(BOH)_2{}^+$ yield intensive peaks; they manifest themselves clearly in the mass spectrum of the complex $Fe(4MNx)_3(BOH)_2$ and are formed by eqns. (8) and (9).

$$[FeD_3(BOH)_2+H]^{+\cdot *} \longrightarrow$$
$$Fe^{2+} + (D\text{-}O)^{2-} + D_2(OH)(BOH)_2{}^+ \quad (9)$$

The results of the FAB-MS study of macrobicyclic boron-containing iron(II) dioximates in the gas phase indicate a change of the energetics of bond rupture in a molecule of complexes as compared to aqueous solutions. A fragment having three conjugated five-membered chelate rings is more stable in the gas phase



The formation of these rings produces a considerable energy gain when two dioximate fragments are detached. It should be noted that in the mass spectra of macrobicyclic cobalt tris-dimethylglyoximates obtained by the electron impact method the main process in fragmentation is also the detachment of dioximate fragments [12]. The more likely detachment of the boron-containing cross-linking fragment in dissociation in aqueous solutions appears to be associated with the high hydration energy of this fragment.

In the alicyclic dioxime series one can trace the effect of substituents and ring size on the fragmentation of the corresponding clathrochelate complexes. As is evident from Table 1, the intensity of the peak which corresponds to the detachment of the hydroxyl group from the framework increases slightly with increase in ring size. The detachment of boron-containing cross-linking fragments is mainly characteristic of seven- and eight-membered dioximes.

Fragmentation involving the detachment of dioxime chelate rings is quite insignificant for nioximate and the most favoured for 4-methylnioximate; it decreases further with increasing ring size. Consequently, one can assert that the introduction of a substituent into the cyclohexane ring and an increase of ring size to seven result in a noticeable destabilization of the clathrochelate framework. The subsequent transition to an eight-membered dioxime, which is less stressed than the seven-membered one, decreases the framework stress and stabilizes the framework.

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