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Observations on the Presence of Oligomeric Species in the Positive Ion Fast Atom Bombardment Mass Spectra of Mixed Ligand Complexes of Magnesium

PETER R. ASHTON, DAVID E. FENTON*

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

RAGHU NANDAD PRASAD*, MITHLESH JINDAL and MAMTA JAIN

Department of Chemistry, University of Rajasthan, Jaipur-302004, India

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Abstract

Attention is drawn to the occurrence of oligomeric ions in the FAB-MS of a group of mixed ligand complexes of magnesium; possible mechanisms of formation are suggested.

Introduction

The determination of the nature of metal complexes bearing mixed ligands can be problematic, particularly in the absence of X-ray crystallographic information. We have attempted to use positive-ion Fast Atom Bombardment mass spectrometry (FAB-MS) to help in the characterisation of a group of mixed ligand complexes of magnesium, $MgLL'\cdot 2H_2O$, where HL and HL′ represent salicylaldehyde (Hsal), 2-hydroxyacetophenone (Hhap), 2-hydroxyproprio-phenone (Hhpp), pentane-2,4-dione (Hacac), 1-phenylbutane-1,3-dione (Hbzac) and 1,3-diphenyl-propane-1,3-dione (Hdbzm). Preliminary information from chemical analysis, NMR and IR spectroscopy and thin layer chromatography had suggested discrete species [1]. The FAB-MS of the mixed ligand complexes showed the presence of oligomeric species in which the mixed ligand content was retained. To our knowledge this represents a unique example of this phenomenon.

Results and Discussion

The mixed ligand complexes were prepared by the reaction of magnesium chloride with a mixture of the appropriate ligands in 1:1:1 molar ratio in ethanol at pH *ca.* 8.5 [1]; the pH adjustment was made using ammonia solutions. Thin layer chromatographs of the magnesium complexes silica gel G using benzene:petrol ether (1:1) as the solvent gave single spots for the mixed complexes with R_f values intermediate to those for the corresponding symmetric bis-complexes. The FAB-MS were recorded using a 3-nitrobenzyl alcohol (NOBA) matrix.

A notable feature of the gas-phase MS of alkaline earth metal β-diketonates is the presence of polymeric species [2–6]. The origin of these species has caused concern: MacDonald and Shannon suggested that ionisation and fragmentation of neutral polymers might occur at the ion source but that the possibility of ion–neutral molecule reactions should not be discounted [2]. Later papers considered the possibility of reaction upon evaporation of the metal complex, and the existence of gas phase polymeric precursors [4, 5]. A high pressure MS study concerning metal β-diketonates in general led to the proposition that there was a reaction of the fragment ion with the neutral monomer leading to the polymeric species [6]. Both homo- and hetero-metallic polymers have been noted, the latter arising in analyses of mixtures of metal β-diketonate complexes [2]. The peaks present in the FAB-MS of the mixed ligand species $MgLL'\cdot 2H_2O$ although not all were present in all of the spectra, can be assigned to $Mg(lig)^+$, Mg(lig), $NOBA^+$, $Mg_2(lig)_3^+$, $Mg_2(lig)_4$, M'^+ ($M'l$ = H, Na), and $Mg_3(lig)_5^+$ where (lig) refers to L, L′, or mixtures thereof. The spectrum of Mg(hpp)(hap) is given in Fig. 1 as a representative example.

It is interesting to speculate on the origin of the oligomers. X-ray structural determinations have shown that $Mg(acac)_2\cdot 2H_2O$ [7] and $Mg(dbzm)_2\cdot$ 2DMP [8] are monomeric, whereas anhydrous $Mg(acac)_2$ has a trimeric structure [9]. It is unlikely in the present study that an oligomeric species will be generated from $MgLL'\cdot 2H_2O$ in the preparation of the NOBA matrix. A second possibility is to consider the availability of ion–neutral molecule interactions leading to aggregation.

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*Authors to whom correspondence should be addressed.

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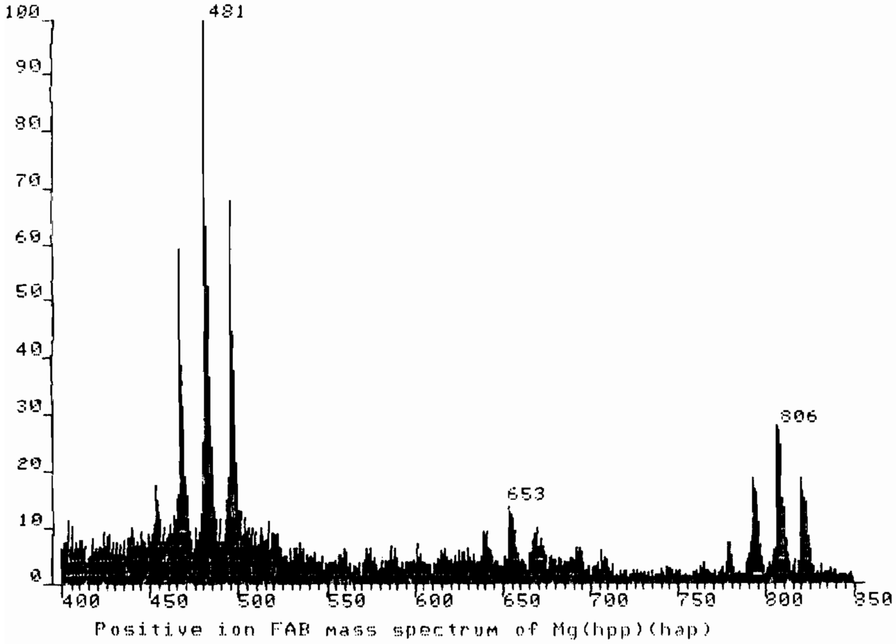

Fig. 1. The FAB-MS of Mg(hpp)(hap) from 400–850 amu. The peak patterns are assigned as:

$Mg_2L_3^+$	495	$Mg_2L_4Na^+$	667	$Mg_3L_5^+$	817[a]
$Mg_2L_2L'^+$	481	$Mg_2L_3L'Na^+$	653	$Mg_3L_4L'^+$	803
$Mg_2LL'^+_2$	467	$Mg_2L_2L'_2Na^+$	639	$Mg_3L_3L'^+_2$	789
$Mg_2L'^+_3$	453	$Mg_2LL'_3Na^+$	625	$Mg_3L_2L'^+_3$	775
		$Mg_2L'_4Na^+$	611	$Mg_3LL'^+_4$	761
				$Mg_3L'^+_5$	747

[a]The principal peak for the $Mg_3(lig)_5^+$ cluster consistently appears at M + 3 amu.

$$\mathrm{MgLL'} \longrightarrow \mathrm{MgL^+},\ \mathrm{MgL'^+}$$

$$\mathrm{MgLL'} + \mathrm{MgL^+} \longrightarrow \mathrm{Mg_2L_2L'^+}$$

$$\mathrm{MgLL'} + \mathrm{MgL'^+} \longrightarrow \mathrm{Mg_2LL'^+_2}$$

The presence of any symmetric species—whether from minor impurity or an equilibrium established in the matrix—would generate further combinations and the $Mg_2(lig)_3^+$ peak pattern would be complete.

$$\mathrm{MgL_2} + \mathrm{MgL^+} \longrightarrow \mathrm{Mg_2L_3^+}$$

$$\mathrm{MgL'_2} + \mathrm{MgL'^+} \longrightarrow \mathrm{Mg_2L'^+_3}$$

$$\mathrm{MgL_2} + \mathrm{MgL'^+} \longrightarrow \mathrm{Mg_2L_2L'^+}$$

$$\mathrm{MgL'_2} + \mathrm{MgL^+} \longrightarrow \mathrm{Mg_2LL'^+_2}$$

Once the $Mg_2(lig)_3^+$ species have been formed further ion–neutral molecule reactions would generate the $Mg_3(lig)_5^+$ series. The $Mg_2(lig)_4,M'^+$ species are then available by fragmentation of $Mg_3(lig)_5^+$ with accompanying addition of M'^+. Although such species seem unlikely, cationisation from adventitious sodium has been seen to provide a mechanism for formation in numerous instances [10].

$$\mathrm{Mg_2L_3^+} + \mathrm{MgL_2} \longrightarrow \mathrm{Mg_3L_5^+}$$

$$\mathrm{Mg_2L_2L'^+} + \mathrm{MgL_2} \longrightarrow \mathrm{Mg_3L_4L'^+}$$

$$\mathrm{Mg_2L_2L'^+} + \mathrm{MgLL'} \longrightarrow \mathrm{Mg_3L_3L'^+_2}\ \text{etc.}$$

$$\begin{tikzcd}
\mathrm{Mg_3(lig)_5^+} \arrow[r] & \mathrm{Mg_2(lig)_4} \arrow[d, "\mathrm{M'^+}"] & + \mathrm{Mg(lig)^+} \\
& \mathrm{Mg_2(lig)_4M'^+} &
\end{tikzcd}$$

There is not, at this time, a wide literature concerning the FAB-MS of coordination complexes [11] and so although it is not possible to be more precise about the above mechanisms we feel that it is appropriate to draw attention to the phenomenon of oligomerisation and ligand redistribution observed here. Furthermore we have noted that oligomerisation is not restricted to this class of complexes but is also prevalent in the FAB-MS of metal complexes of functionally substituted macrocycles and even with such species as *N,N'*-ethylenebis(salicylideneaminato)copper(II), Cu(salen) [12].

Experimental

The mixed ligand complexes were prepared by the method of ref. 1. The MS were recorded using a Kratos MS 80RF mass spectrometer (accelerating voltage 4 kV; resolution 1500) coupled to a DS55 data system. The atom gun was an adapted saddle-field source (Ion Tech Ltd) operated at *ca.* 6 eV and a tube current of *ca.* 2 mA. Xenon was used to provide the primary beam of atoms and the samples were mixed with a small amount of 3-nitrobenzyl-alcohol matrix on a stainless steel probe. Spectra were recorded in the positive-ion mode at a scan speed of 30 s per decade.

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References

1 M. Jindal, *Ph.D. Thesis*, University of Rajasthan, 1987; R. N. Prasad and M. Jindal, *Synth. React. Inorg. Met.-Org. Chem.*, *17*, 635 (1987).
2 C. G. MacDonald and J. S. Shannon, *Aust. J. Chem.*, *19*, 1545 (1966).
3 J. Macklin and G. Dudek, *Inorg. Nucl. Chem. Lett.*, *2*, 403 (1968).
4 J. E. Schwarzberg, R. E. Sievers and R. W. Moshier, *Anal. Chem.*, *42*, 1828 (1970).
5 R. Belcher, C. R. Cranley, J. R. Majer, W. I. Stephen and P. C. Uden, *Anal. Chim. Acta*, *60*, 109 (1972).
6 S. M. Schildcrout, *J. Phys. Chem.*, *80*, 2834 (1976).
7 B. Morosin, *Acta Crystallogr.*, *22*, 315 (1967).
8 F. J. Hollander, D. H. Templeton and A. Zalkin, *Acta Crystallogr., Sect. B*, *29*, 1289 (1973).
9 E. Weiss, J. Kopf, T. Gardein, S. Corbelin, U. Schumann, M. Kirilov and G. Petrov, *Chem. Ber.*, *118*, 3529 (1985).
10 J. R. Chapman, 'Practical Organic Mass Spectrometry', Wiley-Interscience, Chichester, 1985.
11 M. I. Bruce and M. J. Liddell, *Appl. Organomet. Chem.*, *1*, 191 (1987).
12 P. R. Ashton, D. E. Fenton and D. J. Winter, unpublished results.