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Laser Microprobe Mass Spectrometry (LMMS) of Intracrystalline Crown Ether and Cryptand Complexes in Layer Silicates

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Abstract. Laser microprobe mass spectrometry (LMMS) allows the characterisation of organic inclusions in mineral materials. The complexes are detected as cationized or protonated molecules, arising from the intact desorption or from recombination within the laser generated microplasma. The results obtained sustain the interpretation from other techniques concerning the nature of the cation-ligand association and the proton exchange of the cryptand for acidic Cu^{2+}-ions.

Key words. Macrocyclic complexes, laser microprobe mass spectrometry (LMMS), LAMMA 500, phyllosilicates, crown ethers, cryptands, intercalation.

1. Introduction

Macrocylic compounds, such as crown ethers and cryptands, can be intercalated in homoionic 2 : 1 layer silicates (smectites and vermiculites), yielding very stable intracrystalline polydentate coordination complexes [1–4]. It has been shown previously by IR- and UV-spectroscopic techniques that the coordination between interlayer cations (alkali or alkaline-earths) and macrocyclic ligands involves the replacement of the natural hydration shell [5, 6]. Results from X-ray diffraction (XRD) indicated that the interlayer cations are partially or totally included into the cavity hole of the intercalated ligands, depending on the relative size of the ion *vs.* the cavity [2, 3].

The current literature includes several reports on the successful application of the laser microprobe mass analyser (LAMMA) for elemental and organic characterization of clay minerals [7], organic derivatives of silicates [8] and interlayer complexes [9]. This paper attempts a study of the nature of the intracrystalline association between metal ions and the macrocyclic ligands in homoionic montmorillonite samples by LMMS.

An intriguing, and as yet controversial, aspect of the technique concerns the detection of intact organic compounds from a matrix: it apparently depends on the surface availability of the targets and/or the composition (organic *vs.* inorganic) of the surrounding material. On the one hand, Wieser *et al.* [10] have reported that crown ether complexes are suitable

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for LMMS analysis, at least as pure compounds. Indeed, embedded samples (organic matrix) did not allow for the detection of the macrocyclic ligands. On the other hand, by the selection of appropriate experimental conditions, the method offers the possibility to largely discriminate the organic *vs.* the mineral components within the analysed microvolume. For the former ones, ionisation using a low (threshold) laser energy is a prerequisite and under these conditions, elemental and cluster ions only yield a minor contribution whereas irradiation of the sample at high power density clears the organic information from the microprobe mass spectra [11]. Consequently, the analysis of crown ether complexes within a mineral layered matrix represents an interesting test case to assess the potential of LMMS as an organic microprobe in the field of inclusion research.

2. Experimental

The host matrix unit of 2 : 1 layer silicates (e.g. montmorillonite) consists of two sets of tetrahedral Si/O layers, 'sandwiching' an octahedral M/O, OH-layer (M = Al, Mg). This is illustrated in Figure 1. The isomorphous substitution of the cations in the layers yields a negative charge on the mineral, which is balanced by hydrated cations in the interlayer space.

The submicrometer fraction of the Wyoming montmorillonite (Upton, USA), supplied by Ward's Natural Science Establishment Inc., was used. Homoionic samples were obtained by treatment of the mineral material with 0.5–1N KCl, NaCl or $CuCl_2$. The solids were extensively washed with distilled water to remove the excess of chlorides and

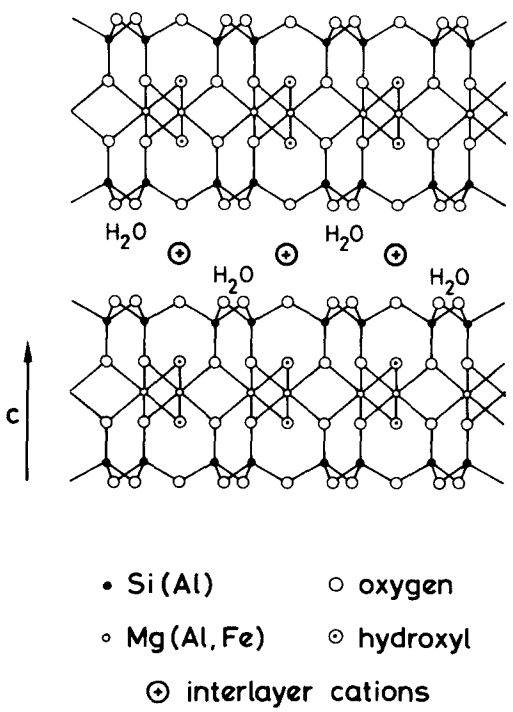


Fig. 1. Structure of 2 : 1 charged phyllosilicates.

recovered from the suspensions by filtering through Millipore membranes. Films of 3–5 mg cm^{-2} were used to intercalate the macrocyclic compounds from dilute methanol solutions according to a procedure described elsewhere [2, 4]. Crown ethers (15-crown-5: 15C5 and dibenzo-18-crown-6: DB18C6) and C(222) cryptand were supplied by PCR Research Chemical and Merck (Kryptofix 222), respectively.

IR spectra were recorded from film samples with a Perkin Elmer 580 B double beam spectrophotometer. X-ray diffraction (XRD) data were obtained using a Phillips PW 1010 diffractometer (Cu anode, Ni filter).

Laser microprobe mass analysis was performed using the transmission type LAMMA 500® (Leybold-Heraeus, Koln, FRG). The output of a high power pulsed Nd : YAG laser beam is frequency quadrupled (λ : 266 nm, τ = 15 ns) and focused into a micrometer size spot of which the actual diameter depends on the selected microscope objective (typically 2 μm for the 32× lens). A visible He-Ne pilot laser (collinear with the Nd : YAG) allows the selection of the sample area of interest. Either positive or negative ions may be continuously extracted into a time-of-flight mass spectrometer (MS), equipped with an electrostatic reflector to improve peak shape and MS resolution. The signals from the open Cu-Be secondary electron multiplier (17 dynodes) are stored in a 100 MHz transient recorder (Biomation 8100) with 2K memory, interfaced to a Digital LSI-11 MINC microcomputer. Additional details on the instrument are provided by Vogt *et al.* [12].

The samples were powdered and supported on a Formvar coated TEM grid and for organic compounds, the analysis was performed in the desorption mode (at low power density). The final adjustment of the laser focus (by microscope lens position), laser output attenuation and MS-voltage settings were selected to optimize the MS peak shape, intensity and MS resolution ($M/\Delta M >$ measured m/z). In order to sample at least 10 points within each mass peak, the accelerating voltage was typically 1.5–2 kV for a range up to m/z 400. The laser energy on the sample typically ranged from 10 to 100 nJ, yielding a power density of 10^7–10^8 W cm^{-2}. The m/z scale was externally calibrated using the average of 20 spectra from carbon foil (thickness 25 nm), which was perforated with about the same energy as used for the organic analysis. It provided a reliable mass scale (within 0.1%), but a significant shift may occur due to the variations on the time delay between the laser trigger and the transient recorder start.

3. Results and Discussion

For the investigation by LMMS of intracrystalline complexes obtained by the adsorption of macrocyclic compounds on Na^+, K^+ and Cu^{2+}-montmorillonites, we selected samples which have been well characterized by other methods (IR, XRF and chemical analysis). Table I summarises the data, concerning the increase of the basal space (Δd_L), resulting from the insertion of the macrocyclic compounds into the silicate, as well as the adsorbed quantities, derived from chemical analysis. Since the exchange capacity of montmorillonite for cations is in the range of 90 meq/100 g, it can be assumed that a fraction of the interlamellar cations remains unassociated because of the steric hindrance by the intercalated ligands. However, to a major part, complex formation in a 1 : 1 stoichiometry applies [3, 4].

The IR spectra (Figure 2) reveal that the characteristic absorption of the macrocyclic compounds is changed upon their intercalation in different montmorillonites. This is due to the coordination with interlamellar cations [5]. For the cryptand C(222), the band at about 3100 cm^{-1} is interpreted as arising from the protonation of the ligand, induced by

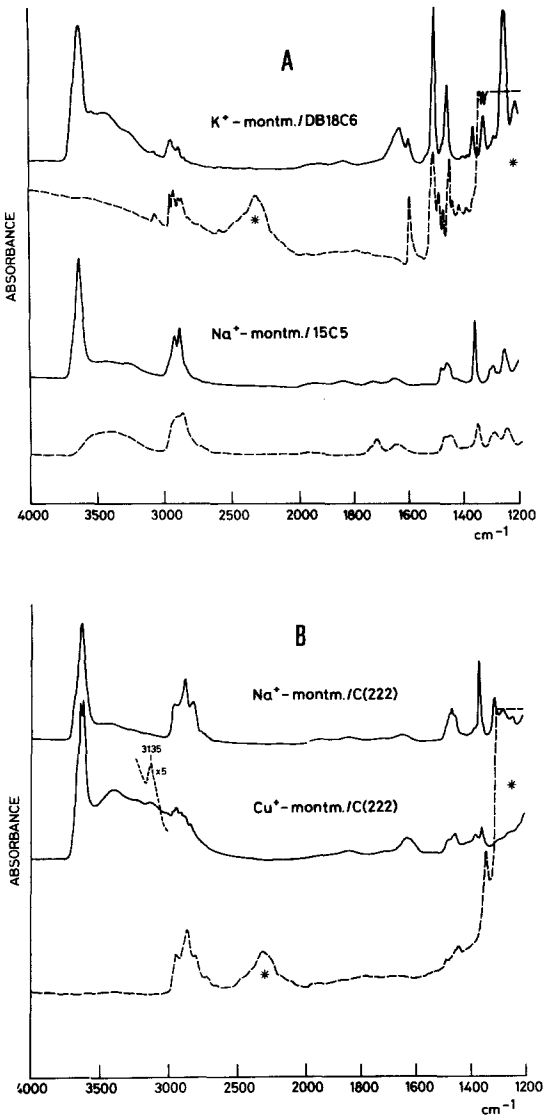


Fig. 2. IR spectra of some crown ethers (A) and cryptand (B) complexes in montmorillonite. The broken lines refer to the results for the ligands, measured as pure products (15C5) or in Fluorolube oil (C(222) and DB18C6). Asterisks indicate the spectral contribution of the Fluorolube oil.

the acidic nature of a transition metal cation, such as, e.g., Cu^{2+} [5]. As will be shown later, the results from LMMS support this explanation.

3.1. CROWN ETHERS

The inclusion complexes 15C5/Na-mont. and DB18C6/K-mont. were selected for LMMS investigation. In both cases, the fit between the size of the cation and the size of the cavity ensures the formation of stable complexes with alkali-cations [13].

Table I. Survey of the adsorbed ligands and effect on the basal space (Δd_L)

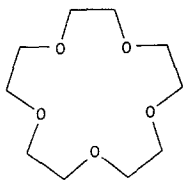
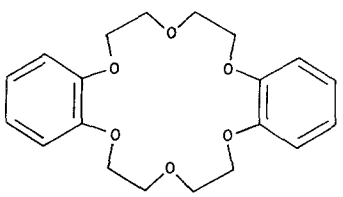
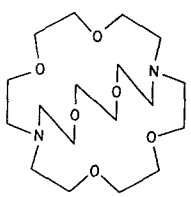
Macrocyclic ligand	Cation in interlayer	Adsorbed (mmole/g)	Δd_L (Å)
 15-crown-5 (15C5)	Na^+	0.70	4.1
 dibenzo-18-crown-6 (DB18C6)	K^+	0.50	8.0
 cryptand C(222)	Na^+ Cu^{2+}	0.68 0.45	7.9 6.9

Figure 3 illustrates a typical LMMS mass spectrum, recorded in the positive ion detection mode for the 15C5/Na-mont. complex (m/z range: 40–250). The base peak is found at $m/z = 243$ and clearly points to the cationized ligands $(15C5.Na)^+$. There is no significant signal arising from the protonated molecule. However, it is not known to what extent these entities are released intact from the solids or alternatively, recombination between neutral ligands and co-desorbed Na^+ cations is involved. Table II includes a list of the signals in the lower mass range and provides a tentative structural assignment. The mass peak at $m/z = 56$, is due to Fe in the silicate. The ions at m/z 89, 87, 71 and 45 are shared with electron impact MS(EI-MS), applied to the pure crown ether 15C5 [14, 15]. The fairly intense peak at m/z 67 (66%) can be associated with cationized ethylene oxide:

These ions may issue from the fragmentation of the parent species by consecutive loss of several ethylene oxide – and/or dioxane-units (see Figure 4). Weak peaks are detected at m/z 199, 155 and 111, which are easily rationalized using the same mechanisms. The resulting structures are then consistent with the interpretation of EI-MS results for pure crown ethers [16]. However, it has to be recognised that the series of peaks at m/z 67, 89, 111 and 155 can be associated also with the ions at m/z 45 by multiple cation exchange. In particular when a relatively high laser energy power density is applied to the sample, this

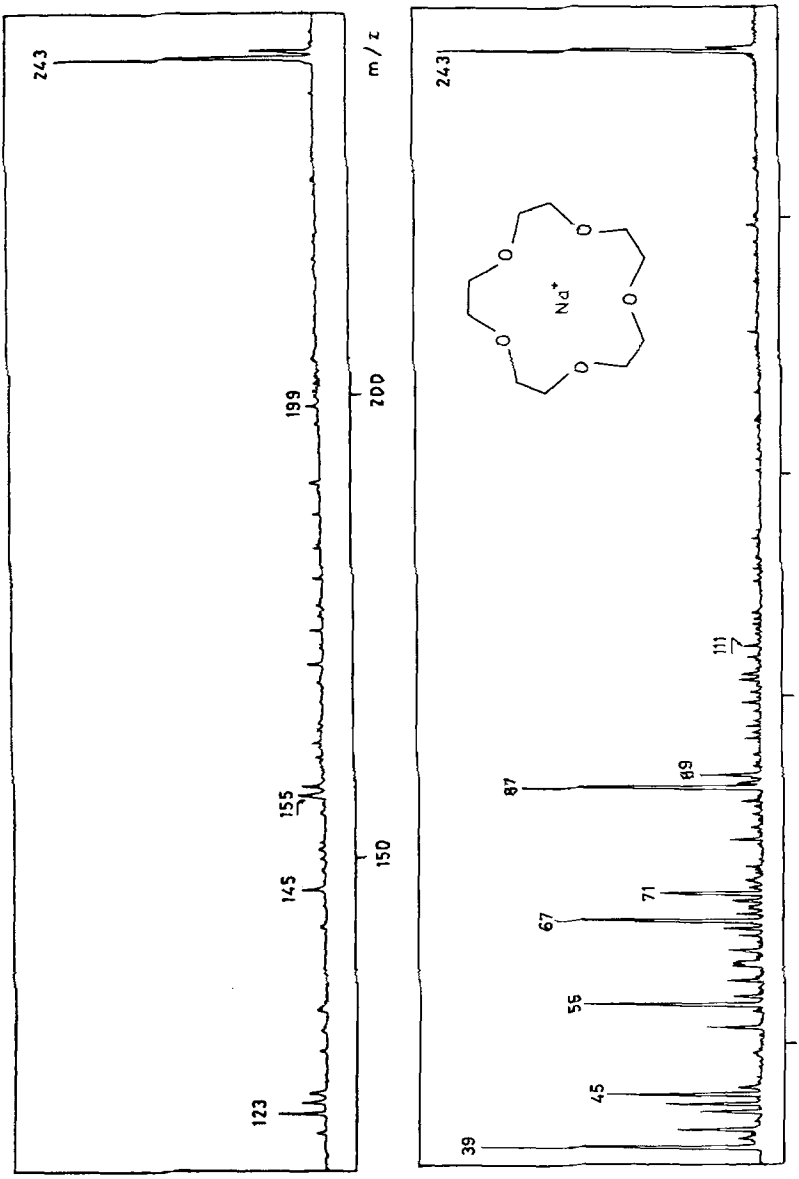
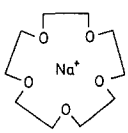
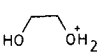
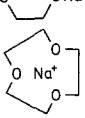


Fig. 3. LMMS mass spectra in the positive ion detection mode for the 15C5/Na^+-montmorillonite complex. The relative abundance of the lower m/z range signals *vs.* the parent peak depends on the locally applied laser energy.

Table II. Assignment of fragment ions in the positive LAMMA mass spectrum of the 15C5/Na-montmorillonite complex.

m/z	Relative intensity (%)	Fragment ion
45	48	
56	59	Fe^+
67	66	
71	28	
87	73	
89	21	
243	100	
61*		
63		
95		
111		
155		

* Relative intensity too irreproducible to be quantitatively estimated (less than 10%).

phenomenon is often encountered in LMMS: the different hydrogens, bonded to the carbon atoms, may be replaced by alkali cations by statistical recombination within the microplasma.

Anyway, the discussion about the lower *m/z*-range fragment ions does not affect the point of major interest: all these complexes, when incorporated in a lamellar silicate type matrix, are readily detected. In contrast, according to Wieser *et al.* [10], crown ethers, embedded in a purely organic matrix, do not yield cationized molecules in LMMS. Apparently, our data indicate that the local mineral environment favours the measurement of the particular macrocyclic ligands.

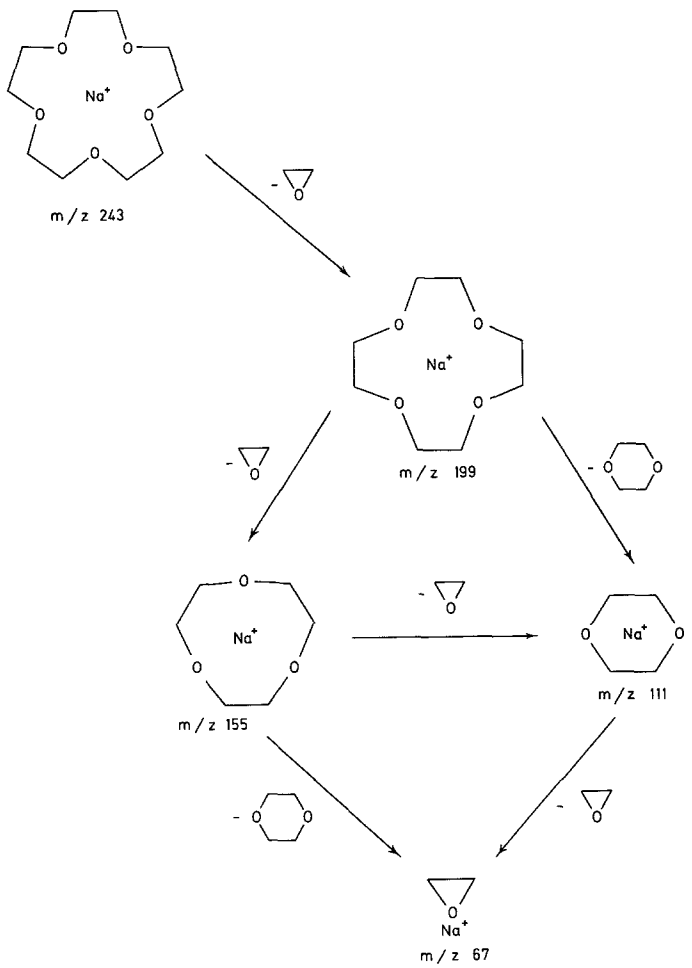


Fig. 4. Tentative scheme for the mass spectral fragmentation of the crown ether complex 15C5/Na^+.

We also compared these results to those obtained for the pure complex, i.e. $(15C5/Na)^+Cl^-$. The samples were prepared by the method described by Pedersen [17]. The base peak in the corresponding positive mass spectrum is found at m/z 243 and points to the cationized molecules. The absence of additional fragment ions is not considered as a highly relevant feature. Indeed, it may be partly related to a significant difference in the locally applied power density on the sample surface during laser irradiation, a parameter which escapes external (macroscopic) control. However, it does not affect the major conclusion *viz.* the parent ions $(15C5/Na)^+$ are easily detected by LMMS from pure products as well as from complexes within the intracrystalline space of the phyllosilicates.

The results for the intercalation complex of dibenzo-18-crown-6 in mortmorillonite, saturated with K^+ ions (DB16C6/K^+-mont.) confirm that the most intense signal in the positive LMMS spectrum issues from the cationized molecules. In agreement with the former data, the same species also yields the base peak on analysis of the pure ionic $(DB18C6/K^+)SCN^-$, obtained by homogeneous reaction of DB18C6 with KSCN [17].

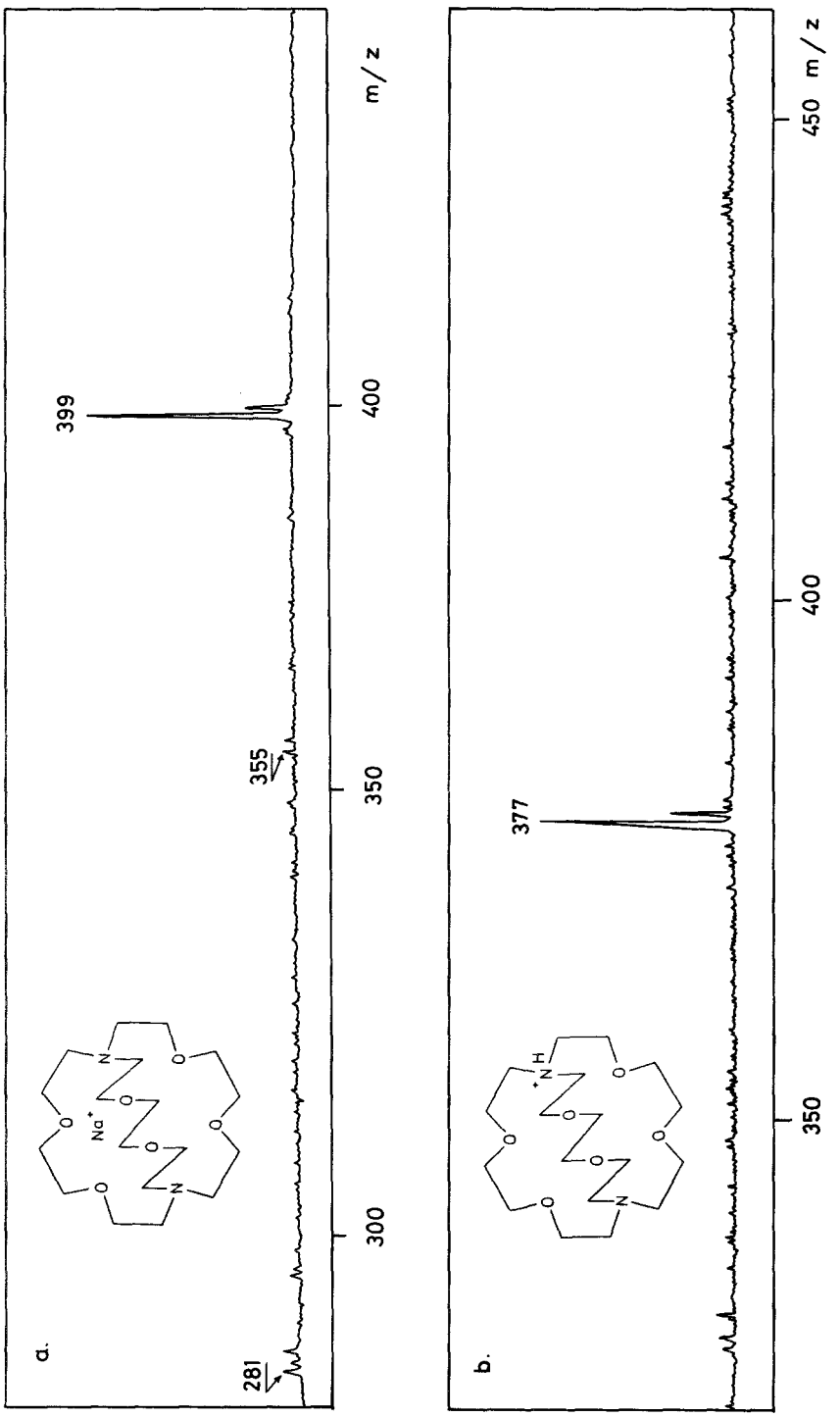


Fig. 5. LMMS mass spectra in the positive ion detection mode for cryptand C(222)/Na^+-montmorillonite (a) and C(222)Cu^{2+}-mont. (b).

3.2. CRYPTAND COMPLEXES

We also studied the interlamellar complexes of the cryptand C(222) in montmorillonite, saturated by alkali or transition metal cations. This ligand yields quite stable complexes with these cations, whereas the crown ethers do not form interlayer coordination complexes with the cations of transition metals [2, 3]. LMMS has been applied to the study of the intercalation complexes of C(222) with Na^+ – and Cu^{2+}–montmorillonite.

An example of the results obtained is illustrated in Figure 5. For the C(222)/Na-mont. sample, the base peak is detected at $m/z = 339$. Obviously, it has to be assigned to the cationized cryptand: $(M+Na)^+$.

The most remarkable aspect of these analyses concerns the results for the C(222)/Cu^{2+}-mont. sample. Indeed, the corresponding species, $(M+Cu)^+$, has to be detected at $m/z = 439$ and 441 with a relative peak intensity ratio of 3 : 1, reflecting the natural isotope abundance of ^{63}Cu vs. ^{65}Cu. However, these signals are quite small and the base peak is due to the protonated molecules at $m/z = 377$. This observation is particularly relevant in view of the interpretation of the results from IR-spectroscopy which point to the formation of protonated ligands $(M+H)^+$ in the interlamellar cavity of the silicate. Indeed, the absorption band at about 3160 cm^{-1} (see Fig. 2b) for the complex C(222)/Cu^{2+}-mont. can be assigned to the ν(N–H) vibration of the protonated cryptand [5]. This phenomenon is explained by an intracrystalline proton transfer reaction, involving the dissociation of water molecules induced by the acidic Cu^{2+} cations (see Figure 6).

It has to be stressed again that the LMMS results alone, evaluated as such, do not allow for definitive conclusions: as a matter of fact, protonation and cationisation have to be considered as competitive processes during recombination. In a strict way, it cannot be excluded that the actually detected ligands (C(222) H^+) issue from C222/Cu^{2+}-entities in the solid state by proton uptake of released neutral cryptands on the descorption step. Only the combination with the IR results enables us to consider the explanation that the proton transfer occurs in the montmorillonite sample itself. The LMMS spectra may be interpreted consistently and hence, the laser microprobe provides an indirect but valuable and additional indication about the chemical nature of the intercalated complex.

4. Conclusion

LMMS can be successfully applied to the analysis of inclusion complexes between organic macrocyclic ligands (crown ethers and cryptands) and intracrystalline cations of some charged phyllosilicates. The base peak of the microprobe mass spectrum is due to the combination of the intercalated organic and the interlamellar ions. In the case of the bicyclic amine cryptand C(222), the detection of the protonated molecules by LMMS apparently sustains the interpretation of the IR results : the acidic nature of the transition metal cations (Cu^{2+}) yields an exchange reaction and coordination with hydrogen.

In general, it has to be recognised that the LAMMA 500 does not allow the unambiguous determination of the exact nature of the complex within the solid sample. As a matter of fact the possibility of recombination between organics, released as neutrals, and co-desorbed charged species (cations, protons) has to be considered as well and the detected ligand ion species may be different from the entity which has been originally present in the analysed material. Nevertheless the microprobe still yields useful information to sustain or check the tentative interpretation issuing from other techniques.

An additional point of interest concerns the observation that the macrocyclic organic

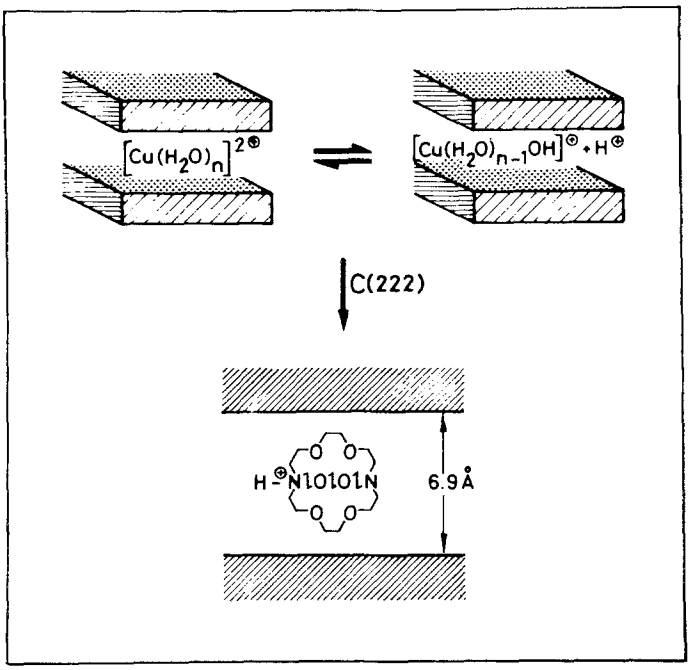


Fig. 6. Coordination of the cryptand C(222) by intracrystalline proton exchange of acidic Cu^{2+}-hydrated cations.

molecules can be readily detected from a montmorillonite matrix. It has been reported [10] previously that crown ether complexes could not be measured by LMMS from embedded samples and that surface-availability is a prerequisite for the generation of molecular or adduct ions from an organic matrix [18]. Apparently, our results now indicate that the inorganic nature of the matrix and/or the layered structure of the silicate allows us to largely reduce the drastic limitations, imposed by sample morphology and hindrance to the release of organic targets by the surrounding material. Consequently the data for the montmorillonite test case clearly reflect the merits of LMMS for the characterisation of organic inclusions within mineral solids.

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