A New Kind of Metal Incorporation in Porphyrins during Mass Spectrometric analysis: Cation Exchange beween Lithium Halide or Transition-metal Halide Surfaces and Metalloporphyrins in Field Desorption

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Under conditions normally used for cationisation field desorption, cations from some metal salts replace central metal ions in representative porphyrin complexes. Lithium ions replace weakly bound central metal cations, such as Cd, but not more strongly bound ions such as Cu. The transition-metal cations, on the other hand, not only replace weakly bound metals in the metalloporphyrin complex, but can also replace cations normally considered 'strongly bound.' Cation-exchange reactions in field desorption are thus more general than those found in electron ionization and define a limit of usefulness of the cationisation field desorption technique.

CATIONISATION and field desorption (F.D.) combined as a technique for molecular-weight identification [equation (1)] is in some respects analogous to the common form of chemical ionization [C.I., equation (2)]. In the common form of cationisation the molecule B is converted to an

$$Li^+X^- + B \longrightarrow LiB^+ + X^- \text{ (or } X + e^-) \quad (1)$$

$$AH^+ + B \longrightarrow BH^+ + A \quad (2)$$

ion LiB^+ by acting as a Lewis base towards the metal ion, Li^+, a Lewis acid [equation (1)]. Analogously, in C.I. the molecule B is converted to an ion BH^+ by acting as a Brönsted–Lowry base towards an acid AH^+ [equation (2)]. The hard acid Li^+ has been most commonly used for cationisation–F.D. experiments, because Li^+ ions are easily desorbed and because the cationised products LiB^+ are stable, even from such non-polar molecules as alkanes.[1] Other alkali-metal ions have also been studied and suggested as possible candidates for analytical applications.[2] Since metal-containing ions are observed in the spectra of organic compounds ionized by field ionization at transition-metal salt surfaces,[3] and since selectivity is found for some classes of organic compounds in secondary-ion mass spectrometry experiments using transition-metal ions sputtered by Ar^+,[4,5] the concept of cationisation may be expended. Cationisation reactions thus include not only equation (1) but also the displacement equation (3), in which B is ionized by

$$MX_n + B \longrightarrow B(MX_{n-1})^+ + X^- \text{ (or } X + e^-) \quad (3)$$

addition of a monopositive $MX_{n-1}{}^+$ fragment instead of Li^+. In exploring the practical limitations of this idea, we have uncovered an unusually general exchange reaction when B has a formula containing both a metal ion and an anionic ligand [*e.g.* equation (4)].

$$MX_n + M'L \longrightarrow ML + M'X_n \quad (4)$$

A partial analogy exists between this exchange and previously observed exchanges in the mass spectrometer. Electron ionization (E.I.) techniques have often been used in the analysis of free-base porphyrin (H_2por) and metalloporphyrin [M(por)] compounds.[6-8] The main characteristic peaks in E.I. spectra of a free-base porphyrin are due to the molecular ion M^+, ions resulting from cleavage of side chains on the porphyrin macrocycle, and the doubly charged molecular ion. The spectra of metalloporphyrins are similar; the major difference from the spectra of the free base is an increase in ion currents due to fragmentation of side chains.[7,8] In addition to these characteristic peaks, the spectrum of a free-base porphyrin has often been found to include an isotope cluster at $[M + \text{metal} - 2]^+$, corresponding to M(por), of significant but irreproducible intensity.[9] This reaction is presumed to be a scavenging of metal by free-base molecules in the stainless steel source, equation (5).

$$H_2\text{por} + M \longrightarrow M(\text{por}) + 2H_{(\text{adsorbed})} \quad (5)$$

Incorporation of metal from the source housing is not seen in the published spectra of metalloporphyrins. Demetallation is observed, however; the E.I. spectra of thallium and mercury(II) porphyrins contain ions corresponding to both free-base porphyrins H_2por^+ and dehydroporphyrins por^{+}.[10,11] The observation of metal exchange in E.I. mass spectra is reported in personal communications among numerous persons but is not apparently recorded in the literature.[12]

EXPERIMENTAL

The metalloporphyrins were prepared from the free base (Strem Chemicals) according to established procedures [13-15] and their purity prior to mass spectral studies confirmed by electronic spectra.[14,15] The field-desorption experiments were carried out with a Dupont 21-492B mass spectrometer using Co emitters; the advantages of metal dendrites for cationisation have been noted previously.[16] The emitter was coated with metal halide by dipping in a 2 mol dm^{-3} aqueous solution and evaporating the water. Then a solution of the metal chelate in either benzene or methylene chloride was deposited on the emitter by dropwise addition. The solvent was rapidly evaporated and the probe positioned in the mass spectrometer source, under conditions in which it was shown that essentially no metal exchange had occurred between the chelate and the previously deposited salt (by removing the chelate in organic solvents and checking its electronic spectrum). (The visible spectra of the magnesium, cadmium, and lead porphyrins differ significantly from those of the copper and cobalt porphyrins and the free base.[14,15])

RESULTS AND DISCUSSION

Table 1 lists combination of salts and metalloporphyrins in which exchange of metal was observed. Besides cationised molecular ions, the only peaks observed in the spectra were, as expected, those due to the molecular ion $M(por)^+$, the exchange product, $M'(por)^+$, the free base, H_2por^+, and the dehydroporphyrin por^+.

TABLE 1

Exchange products of metalloporphyrins under cationisation–F.D. conditions

Salt	Chelate	Ions observed
LiCl	Cd(tpp)	$LiCd(tpp)^+$, $Li(tpp)^+$, $Li_2(tpp)^+$, $H_2(tpp)^+$, $LiH_2(tpp)^+$
LiCl	Mg(tpp)	$LiMg(tpp)^+$, $Li(tpp)^+$, $H_2(tpp)^+$, $LiH_2(tpp)^+$
$CoCl_2$	Cd(tpp)	$Cd(tpp)^+$, $Co(tpp)^+$, $H_2(tpp)^+$
$CoCl_2$	Zn(tpp)	$Zn(tpp)^+$, $Co(tpp)^+$, $H_2(tpp)^+$
$CoCl_2$	Cu(tpp)	$Cu(tpp)^+$, $Co(tpp)^+$, $H_2(tpp)^+$
$CoCl_2$	Mg(tpp)	$Mg(tpp)^+$, $Co(tpp)^+$
$CoCl_2$	Pb(tpp)	$Pb(tpp)^+$, $Co(tpp)^+$
CuCl	Mg(tpp)	$Mg(tpp)^+$
$CoCl_2$	Cu(oep)	$Cu(oep)^+$, $Co(oep)^+$

tpp = Tetraphenylporphyrin, oep = octaethylporphyrin.

Our results may be summarized as follows. First, cation-exchange reactions occurred in most 'weak'[17] metalloporphyrins whether or not the new metal porphyrin bond was stronger than the old bond. Those chelates in which the central metal is so large as to distort the macrocycle, such as cadmium,[17] can be expected to have easily replaceable metal; and likewise, those complexes which are unstable because the central metal is small, and therefore a hard acid, like magnesium, should be susceptible to this reaction. In these cases even a cation which would form a weaker bond to the porphyrin macrocycle than the original cation exchanges. There are, however, differences among the types of exchange products observed.

'Stronger'[17] metalloporphyrin complexes show more selectivity; they do not exchange with lithium, but some do exchange with the Co^{2+} cation.

Now it should be recognized that the metal exchange here in no way corresponds to the type of metallation or metal exchange observed during electron impact experiments. That type of exchange in porphyrins and other complexes, as we and others have observed for more than ten years, is with the stainless steel of the source housing, so that iron complexes are observed in addition to, or in place of, the metal complexes actually introduced into the source. In F.D., however, we observe only miniscule peaks corresponding to an exchange with metal from the source, the principal exchange being with the metal whose salt is introduced on the emitter. On the other hand, the unstable porphyrin does not, under our conditions, exchange with the metal until the field is applied, since the porphyrin, washed from the emitter with an organic solvent, has the visible spectrum characteristic of the unstable porphyrin and not of its product from exchange with either the cation of the salt on the emitter or metal from the housing.

Consequently, the reaction is field-induced; it requires heating, probably to supply some mobility to surface species. It takes place entirely on the surface because no detectable current due to metal ions leaving the emitter surface is detected, and no reaction takes place far from the path of field ions to the cathode since no reaction with the source housing is observed. We have no evidence to preclude the involvement of emitter surfaces as catalyst.

This study presents one limit to the previously unexplored area of cationisation with transition-metal ions or complexes of them. Information from secondary-ion mass spectrometry of adsorbed organics suggests that transition-metal cationisation exhibits specificity in some cases and is therefore a complex subject deserving of careful exploration. It is advisable at the very outset to illustrate the limit of this group of techniques, as we have done here in establishing the limits of exchange in place of cationisation. The cation exchange complements the anion exchange recently found by Röllgen and Ott[18] which similarly points out a limitation of field desorption and field ionization: alkali halides on emitters often exchange halide with alkyl halides ionized on such surfaces [equation (6)].

$$\begin{aligned} RX + M^+X'^- &\longrightarrow RX' + M^+X^- \qquad (6) \\ RX' &\longrightarrow \text{field ions} \end{aligned}$$

This new kind of metal exchange in field desorption, aside from its inherent interest, may have some analytical value for ligand analysis when it is necessary to move an analyte from a region of heavy interference to a relatively clean part of the mass spectrum, but much work needs to be done to determine what range of metals can be exchanged in many other types of chelate compounds. Cationisation itself may be useful in the analysis of metal chelates generally, although we have also observed some surprises even with lithium and simple metal chelates. Reference to Table 2 illustrates one of these. Sometimes two lithium cations are attached, and sometimes only one, to nickel dithiophosphate complexes. Our experience at this point is that multiple cationisation (with reduction of the metal ion, since the charge of the

TABLE 2

Cationised products of representative chelates

Salt	Chelate	Ions observed
LiCl	Cu(tpp)	M^+; $(M + Li)^+$
LiCl	Cu(oep)	M^+; $(M + Li)^+$
LiCl	Zn(tpp)	M^+; $(M + Li)^+$
LiCl	Mg(tpp)	M^+; $(M + Li)^+$
LiCl	Cd(tpp)	M^+; $(M + Li)^+$
LiCl	Pb(tpp)	M^+; $(M + Li)^+$
LiCl	$Ni(dmtp)_2$	M^+; $(M + Li)^+$; $(M + 2\,Li)^+$
LiCl	$Ni(detp)_2$	M^+; $(M + Li)^+$
LiCl	$Ni(dctp)_2$	M^+; $(M + Li)^+$
LiCl	$Cr(detp)_3$	M^+; $(M + Li)^+$
LiCl	$Pd(dptc)_2$	M^+; $(M + Li)^+$

dmtp = *OO'*-Dimethyl dithiophosphate, detp = *OO'*-diethyl dithiophosphate, dctp = *OO'*-dicyclohexyl dithiophosphate, dptc = dphenyldithiocarbamate.

ion remains +1) occurs with small alkyl groups in dithiophosphate complexes but not large ones. In spite of such complications, cationisation still appears useful for identifying molecular weight, since in all cases we have observed an [M + Li] peak whether or not [M + 2Li] is also present, and the spacing due to accretion of Li units is easily recognized.

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