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Fast Atom Bombardment Mass Spectrometry of Phthalocyanines

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Fast atom bombardment mass spectra of two series of metal-substituted phthalocyanine derivatives are reported. The first series includes the unsubstituted H_2, Fe, Co, Ni, Cu, Zn, and Pb phthalocyanines. The second series includes the H_2, Be, Mg, Fe, Co, Ni, Cu, Zn, Pt, Pd, and Pb 2,9(10),16(17),23(24)-tetrakis(cumylphenoxy)phthalocyanine compounds. Protonated molecules and molecular ions were observed in the mass spectra with very little or no fragmentation. Oxygen–phthalocyanine adduct ions of the parent molecule were observed, which corroborate ESR analyses. Mass spectrometric evidence for a divalent bismuth phthalocyanine is also presented. The molecular weight of a novel tetra-9,10-phenanthrotetraazaporphyrin was determined, confirming its proposed structure. Several novel liquid sample matrices consisting of a concentrated H_2SO_4/H_3PO_4 mixture, aryl and alkyl phthalates, phosphonates, and sulfonates were used to obtain the fast atom bombardment spectra. For the synthetic chemist, the technique provides a facile method for obtaining molecular weight information of this intractable class of organometallic compounds.

Introduction

Interest in phthalocyanines, long an important class of dye substances, has been renewed because of their semiconductivity.[1] Properties of Langmuir–Blodgett monolayer films of phthalocyanine compounds have been the subject of recent studies.[2] The properties under investigation include electrical conductivity,[3] photovoltaic effects,[4] electrical switching between conducting states,[5] oxidative catalytic activity,[6] and electrochromism.[7] Such properties of phthalocyanine films can be modified by external stimuli such as electrical potential or interaction with chemical vapors.

As novel phthalocyanine compounds are synthesized, a means of facile characterization becomes an important consideration. Analysis and structural characterization of such complex macrocyclic molecules have included multiple instrumental and chemical analyses. Such an analytical problem has already been discussed with respect to synthetic porphyrins,[8] a related class of compounds. The analysis of such large molecules is often complicated by their intractable nature. The presence of impurities (occlusion of solvents), insolubility, involatility, oligomerization or aggregation, and thermal stability are a few of the problems encountered in the analytical characterization of these high molecular weight compounds.

Porphyrins, a class of phthalocyanine-like macrocyclic compounds, have been studied by using the desorption ionization mass spectrometry techniques.[8] Field desorption mass spectrometry (FDMS)[9] is useful for the study of natural porphyrins and provides a high abundance of the molecular ion but very little structural information.[10] When the porphyrin contains labile side chains or is intractible, very little of the molecular ion is observed.[11] The novel desorption ionization techniques, fast atom bombardment (FAB),[12] desorption chemical ionization (DCI),[13] and desorption electron ionization (DEI),[14] have been applied to the characterization of synthetic porphyrins.[8] Molecular ions were obtained for all of the porphyrins studied with FAB. The FAB technique also provided significant structural information on the labile "tails" or side chains.

Special techniques have been used to obtain the electron ionization mass spectra of the phthalocyanines[15] because of their low volatility. High ion source temperatures are necessary, and the spectra of highly substituted phthalocyanines are difficult to obtain.[16] The use of the FDMS technique has been reported for the analysis of a series of phthalocyanines.[17] With these mass spectrometric techniques, the spectra of phthalocyanines exhibit fragment ions, metal ions, metal fragment ions, and doubly charged ions. Because of the high thermal stability of the phthalocyanines,[18] the molecular ion of the unsubstituted phthalocyanine is often seen to be the major ion in the spectra. Highly substituted phthalocyanines give no molecular ions,[16] hampering the use of mass spectroscopy as an analytical technique for molecular weight confirmation. Fragment ions of phthalocyanines have been reported to come from thermal depolymerization, electron ionization induced dissociation, and thermal decomposition of the phthalocyanines.[15] The fragment ions consist primarily of the phthalonitrile species (*m/z* 128) and the loss of CN and HCN from the phthalonitrile species. (Each phthalocyanine nucleus is essentially a phthalonitrile tetramer.)

Fast atom bombardment mass spectrometry (FABMS), which provides an additional tool in the arsenal of analytical techniques used for characterization, has proven to be a very useful analytical method in the organometallic chemist's

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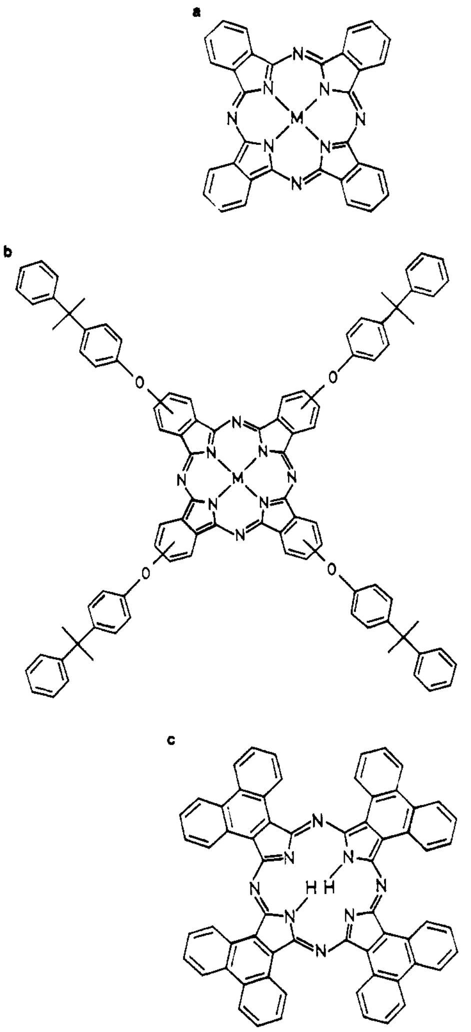

Figure 1. General structures: (a) the phthalocyanines; (b) 2,9-(10),16(17),23(24)-tetrakis(cumylphenoxy)phthalocyanine; (c) tetra-9,10-phenanthrotetraazaporphyrin.

repertoire.[19,20] In FAB, a primary beam of energetic atoms is directed at a solid surface, film, or liquid matrix, which sputters or desorbs secondary neutrals and ions from the sample surface; the secondary ions are analyzed mass spectrometrically. The liquid matrix in which the sample is dissolved provides a renewable source of intact molecular sample species, while molecular films and solids are subject to radiation damage from the energetic primary beam.[21] The FAB mass spectra of involatile and intractable middle molecules have yielded both molecular weight and structural information,[22] and many of the major fragmentations in the FAB mass spectra are similar to those observed by chemical ionization.[23]

The characterization of phthalocyanines has not been investigated by FABMS. This paper reports the FAB mass spectra of two series of phthalocyanines. The first series of phthalocyanines consists of phthalocyanine complexes, MPc, where M equals H_2, Fe, Co, Ni, Cu, Zn, and Pb; the general structure of these is shown in Figure 1a. The second series consists of peripherally substituted tetrakis(cumylphenoxy)phthalocyanine complexes (MTPc), where M equals H_2, Be, Mg, Fe, Co, Ni, Cu, Zn, Pd, Pt, Bi, and Pb; the general structure of these phthalocyanine complexes is shown in Figure 1b. A third, structurally related compound, tetra-9,10-phenanthrotetraazaporphyrin (H_2TPTAP), was analyzed to confirm its molecular weight; the proposed structure is shown in Figure 1c.

Table I. Ion Species Observed in the Fast Atom Bombardment Mass Spectra of H_3PO_4

m/z	rel abund[a]	frag ion stoich	*m/z*	rel abund[a]	frag ion stoich
19	20	$[H_3O]^+$	65	40	$[H_2PO_2]^+$
47	100	$[PO]^+$	81	45	$[H_2PO_3]^+$
48	25	$[HPO]^+$	82	10	$[H_3PO_3]^+$
64	20	$[HPO_2]^+$	99	90	$[(H_3PO_4)H]^+$

n	cluster ion stoich[a,b]	*x*
2	$[(H_3PO_4)_nH - (H_2O)_x]^+$	0-2
3	$[(H_3PO_4)_nH - (H_2O)_x]^+$	0-3
4	$[(H_3PO_4)_nH - (H_2O)_x]^+$	0-4
5	$[(H_3PO_4)_nH - (H_2O)_x]^+$	0-5
6	$[(H_3PO_4)_nH - (H_2O)_x]^+$	1-6
7	$[(H_3PO_4)_nH - (H_2O)_x]^+$	2-7
8	$[(H_3PO_4)_nH - (H_2O)_x]^+$	2-7
9	$[(H_3PO_4)_nH - (H_2O)_x]^+$	3-8
10	$[(H_3PO_4)_nH - (H_2O)_x]^+$	3-8
11	$[(H_3PO_4)_nH - (H_2O)_x]^+$	4-9
12	$[(H_3PO_4)_nH - (H_2O)_x]^+$	6-10
13	$[(H_3PO_4)_nH - (H_2O)_x]^+$	7-10

[a] The relative abundances of the ions vary with time. [b] The relative abundances of the clusters decrease monotonically as *n* increases.

Experimental Section

The FAB spectra were obtained on a VG Analytical ZAB-2F double-focusing mass spectrometer (Manchester, U.K.) fitted with an Ion Tech saddle field gun (Teddington, U.K.). Xenon was used as the fast-atom beam, and a resolving power of greater than 1000 was used for all studies.

Both series of phthalocyanines were synthesized by methods previously described in the literature.[2,24]

The phthalocyanine solvents used as the liquid matrices were obtained from commercial sources and were used without further purification. The phosphoric acid was reagent grade 85% (Matheson, Coleman, and Bell), the sulfuric acid was concentrated (Ultrex, J. T. Baker), and the aryl and alkyl phthalates, phosphates, and sulfonates were obtained from Scientific Polymer Products.

Results and Discussion

Matrix Studies. The phthalocyanines are insoluble in the liquid matrices (solvents) commonly used for FAB of organometallics such as glycerol,[12] thioglycerol,[8] 18-crown-6 cyclic ether,[25] carbowax-200,[20] sulfolane, and others.[19] The series of unsubstituted phthalocyanines (Figure 1a) are soluble in concentrated sulfuric acid; however, they tend to decompose in this medium. These phthalocyanines were found to be soluble yet suffered no appreciable decomposition in a matrix consisting of 1 part concentrated sulfuric acid to 2 parts 85% phosphoric acid; they have no appreciable solubility in 85% H_3PO_4 alone. The H_2SO_4/H_3PO_4 matrix used for the unsubstituted phthalocyanines gives rise to a series of cluster ions, whose nature seems to depend on several factors. Initially, the most predominant types of cluster ions were those of protonated acid clusters, $[H(H_3PO_4)_n]^+$, $[H(H_2SO_4)_n]^+$, and $[H(H_3PO_4)_x(H_2SO_4)_{n-x}]^+$ ($n = 1$–15; $x = 1$ to $n - 1$), which occur every 98 mass-to-charge (*m/z*) units. After continuous fast atom bombardment, the abundance of the protonated acid clusters decreased, and several series of clusters arose consisting of a loss of one to three H_2O molecules from a protonated acid

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Table II. Ion Species Observed in the Fast Atom Bombardment Mass Spectra of H_2SO_4

m/z	rel abund[a]	frag ion stoich	*m/z*	rel abund[a]	frag ion stoich
19	20	$[H_3O]^+$	66	10	$[H_2SO_2]^+$
32	20	$[S]^+$	81	20	$[HSO_3]^+$
48	40	$[SO]^+$	82	10	$[H_2SO_3]^+$
49	20	$[HSO]^+$	99	100	$[(H_2SO_4)H]^+$
65	50	$[HSO_2]^+$			

n	cluster ion stoich[a,b]	*x*
1	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-2
2	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-2
3	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-3
4	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-3
5	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-3
6	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-3
7	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-3
8	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-3
9	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0-3
10	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0, 1
11	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0, 1
12	$[(H_2SO_4)_nH + (H_2O)_x]^+$	0, 1

[a] The relative abundances of the ions vary with time. [b] The relative abundances of the clusters decrease monotonically as *n* increases.

Table III. Ion Species Observed in the Fast Atom Bombardment Mass Spectra of Butyl Benzyl Phthalate

m/z	rel abund[a]	ion stoich
27	20	$[C_2H_3]^+$
29	25	$[C_2H_5]^+$
39	15	$[C_3H_3]^+$
41	20	$[C_3H_5]^+$
57	15	$[C_4H_9]^+$
77	20	$[C_6H_5]^+$
91	100	$[C_7H_7]^+$
105	15	$[C_6H_4COH]^+$
149	90	$[C_6H_4(CO)_2OH]^+$
181	15	$[C_6H_4COC_6H_5]^+$?
205	40	$[C_6H_4(CO)COOC_4H_9]^+$
313	40	$[M + H]^+$
369	10	$[M + 57]^+$
403	25	$[M + 91]^+$
417	5	$[M + 105]^+$
517	5	$[M + 205]^+$
625	5	$[2M + H]^+$

[a] The relative abundances of the ions vary with time.

cluster. The FAB spectra of the neat H_3PO_4 is quite similar to that of the mixed acid matrix, consisting of protonated acid clusters and ion peaks corresponding to the loss of water from these clusters. Table I lists the series of ions observed in a FAB spectrum of 85% H_3PO_4. The relative ion abundances of the series of cluster ions change with time as observed by others from a glycerol matrix.[26] The FAB spectra of the neat H_2SO_4 differs slightly in that H_2O adduct ions of the protonated acid clusters are observed; clusters resulting from loss of water are not observed in significant abundance. Table II shows the ions observed in a FAB spectrum of neat H_2SO_4.

The tetrakis(cumylphenoxy)phthalocyanines were discovered to be soluble in a number of different alkyl and aryl phthalates (e.g., dimethyl, diethyl, diisobutyl, butyl benzyl phthalate), alkyl and aryl phosphates (tricresyl, tributyl, etc.), and alkyl sulfonates. Butyl benzyl phthalate was chosen as the liquid matrix for this second series of phthalocyanines because of its higher boiling point and hence its lower vapor pressure and longer duration in the FAB ion source. Other phthalates, phosphates, and sulfonates were investigated and proved acceptable albeit somewhat more volatile than the butyl benzyl phthalate, and hence ion signal duration was shorter. The fragment ions of the butyl benzyl phthalate matrix (*m/z* 77, 149, etc.) could mask any fragment ions of the cumylphenoxy side chains. Tributyl phosphate was used as a sample matrix to determine if any fragment ions of the cumylphenoxy side chains were present in the FAB mass spectra. Tables III and IV list the ions observed in the FAB spectra of butyl benzyl phthalate and tributyl phosphate.

Table IV. Ion Species Observed in the Fast Atom Bombardment Mass Spectra of Tributyl Phosphate

m/z	rel abund[a]	ion stoich
27	10	$[C_2H_3]^+$
29	15	$[C_2H_5]^+$
39	10	$[C_3H_3]^+$
41	20	$[C_3H_5]^+$
57	25	$[C_4H_9]^+$
99	80	$[H_4PO_4]^+$
155	20	$[H_3(C_4H_9)PO_4]^+$
211	25	$[H_2(C_4H_9)_2PO_4]^+$
267	100	$[M + H]^+$
523	15	$[2M + H]^+$

[a] The relative abundances of the ions vary with time.

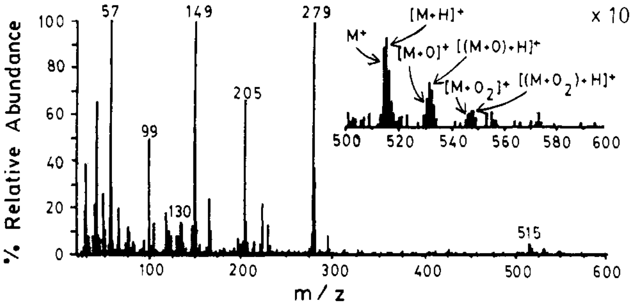

Figure 2. Fast atom bombardment mass spectrum of metal-free phthalocyanine in a matrix of neat H_2SO_4. The inset of the molecular ion region is magnified by a factor of 10.

A third type of compound, tetra-9,10-phenanthrotetraazaporphyrin, was analyzed with concentrated H_2SO_4 as the matrix.

Unsubstituted Phthalocyanines. The metal-free unsubstituted phthalocyanine, H_2Pc, was observed to produce both a molecular ion at *m/z* 514 and a protonated molecule at *m/z* 515 as determined by isotopic ion abundances. Fragment ions of H_2Pc were not observed when the sample was analyzed in an H_2SO_4/H_3PO_4 matrix. When H_2Pc was analyzed in neat H_2SO_4, ion peaks were observed at *m/z* 129 (protonated phthalonitrile) and at *m/z* 130 (phthalonitrile + 2 H). Because these ion peaks were not observed in the acid mixture, they probably result from decomposition of the phthalocyanine in the neat H_2SO_4. A FAB spectrum of H_2Pc in the neat H_2SO_4 is shown in Figure 2. The inset in Figure 2 shows the molecular ion region magnified including several adduct ions that were observed in the FAB spectra. A cluster of ions was seen at *m/z* 530, 531, and 532; these correspond to the attachment of an oxygen atom to give the adduct ion species $[H_2Pc + O]^+$, $[(H_2Pc + O) + H]^+$, and $[H_2Pc + H_2O]^+$ as determined by isotopic ion abundances. another cluster of ions was observed at *m/z* 546 and 547. These ions correspond to dioxygen–phthalocyanine adduct ions of the following stoichiometry: $[H_2Pc + O_2]^+$ and $[(H_2Pc + O_2) + H]^+$. These results support the oxygen–phthalocyanine interaction that has been established from ESR spectra of phthalocyanines.[27]

The metal-bound phthalocyanines with the exception of the lead-containing species give a combination of both a molecular

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Table V. Ions Observed in the Fast Atom Bombardment Mass Spectra of Phthalocyanines (MPc)[a]

M	mol wt	ions obsd
H_2	514	$[H_2Pc]^+$, $[H_2Pc + H]^+$, $[H_2Pc + O]^+$, $[(H_2Pc + O) + H]^+$, $[H_2Pc + H_2O]^+$, $[H_2Pc + O_2]^+$, $[(H_2Pc + O_2) + H]^+$
Fe	568	$[FePc]^+$, $[FePc + H]^+$, $[FePc + O]^+$, $[(FePc + O) + H]^+$, $[FePc + H_2O]^+$, $[FePc + O_2]^+$, $[(FePc + O_2) + H]^+$
Co	571	$[CoPc]^+$, $[CoPc + H]^+$, $[CoPc + O]^+$, $[(CoPc + O) + H]^+$, $[CoPc + H_2O]^+$, $[CoPc + O_2]^+$, $[(CoPc + O_2) + H]^+$, $[Pc + 3 H]^+$
Ni	570	$[NiPc]^+$, $[NiPc + H]^+$, $[NiPc + O]^+$, $[(NiPc + O) + H]^+$, $[NiPc + H_2O]^+$, $[NiPc + O_2]^+$, $[(NiPc + O_2) + H]^+$
Cu	575	$[CuPc]^+$, $[CuPc + H]^+$, $[CuPc + O]^+$, $[(CuPc + O) + H]^+$, $[CuPc + H_2O]^+$, $[CuPc + O_2]^+$, $[(CuPc + O_2) + H]^+$
Zn	576	$[ZnPc]^+$, $[ZnPc + H]^+$, $[ZnPc + O]^+$, $[(ZnPc + O) + H]^+$, $[ZnPc + H_2O]^+$, $[ZnPc + O_2]^+$, $[(ZnPc + O_2) + H]^+$
Pb	720	$[Pc + 3 H]^+$

[a] The liquid matrix was a 2:1 mixture of 85% phosphoric acid and concentrated sulfuric acid.

Table VI. Ions Observed in the Fast Atom Bombardment Mass Spectra of Tetrakis(cumylphenoxy)phthalocyanines (MTPc)[a]

M	mol wt	ions obsd	M	mol wt	ions obsd
H_2	1354	$[H_2TPc]^+$, $[H_2TPc + H]^+$	Cu	1415	$[CuTPc]^+$, $[CuTPc + H]^+$
Be	1361	$[BeTPc]^+$, $[BeTPc + H]^+$	Zn	1416	$[ZnTPc]^+$, $[ZnTPc + H]^+$
Mg	1376	$[MgTPc]^+$, $[MgTPc + H]^+$	Pt	1458	
Mn	1407	$[MnTPc]^+$, $[MnTPc + H]^+$	Pd	1547	
Fe	1408	$[FeTPc]^+$, $[FeTPc + H]^+$	Pb	1560	$[PbTPc]^+$, $[PbTPc + H]^+$, $[TPc + 3 H]^+$
Co	1411	$[CoTPc]^+$, $[CoTPc + H]^+$	Bi	1561	$[BiTPc]^+$, $[BiTPc + H]^+$, $[TPc + 3 H]^+$
Ni	1410	$[NiTPc]^+$, $[NiTPc + H]^+$			

[a] The liquid matrix was butyl benzyl phthalate.

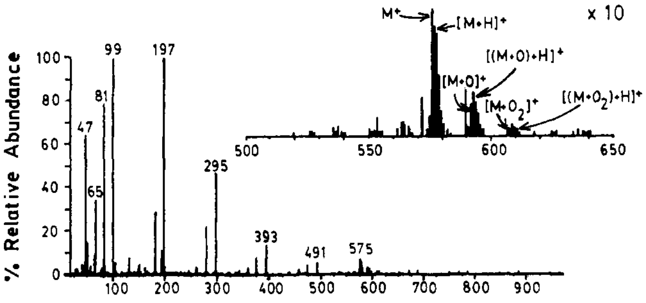

Figure 3. Fast atom bombardment mass spectrum of copper phthalocyanine in a matrix of H_2SO_4/H_3PO_4. The inset of the molecular ion region is magnified by a factor of 10.

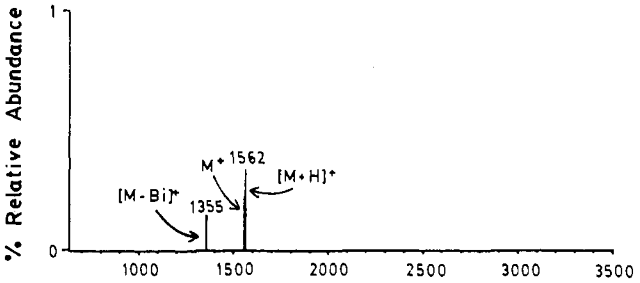

Figure 4. Fast atom bombardment mass spectrum of bismuth 2,9-(10),16(17),23(24)-tetrakis(cumylphenoxy)phthalocyanine in a butyl benzyl phthalate matrix.

ion, $[MPc]^+$, and a protonated molecule, $[MPc + H]^+$, evidenced by the isotopic abundances. Table V lists the molecular weights and the ions observed for the unsubstituted phthalocyanines. Because of its large size, the lead ion lies outside the plane of the phthalocyanine ring structure.[28] The lead ion is subject to attack and displacement in an acid solution; this demetalation reaction has been studied.[29] The CuPc and the ZnPc gave noticeably stronger and more stable ion abundances than the other $[MPc + H]^+$ species. A spectrum of CuPC in the H_2SO_4/H_3PO_4 matrix is shown in Figure 3. The spectra of the cobalt and lead phthalocyanines exhibit the loss of the metal from the ring, and they give rise to a cluster of ion peaks at *m/z* 513–515. Especially in the case of the PbPc spectra, which show no molecular ion, the ion at *m/z* 515 appears to be the predominant species corresponding to the $[Pc + 3 H]^+$ species. In all of the metal-bound phthalocyanines that give a molecular ion (FePc, CoPc, NiPc, CuPc, ZnPc), a cluster of peaks is observed at 16–18 *m/z* units above the molecular ion. These ions correspond to the adduct ion species $[MPc + O]^+$, $[(MPc + O) + H]^+$, and $[MPc + H_2O]^+$ as determined by isotopic ion abundances. The dioxygen-phthalocyanine adduct ion and the protonated dioxygen-phthalocyanine species also were observed at 32 and 33 *m/z* units above the molecular ions. The inset in Figure 3 shows the molecular and adduct ion region magnified for the CuPc species.

Tetrakis(cumylphenoxy)phthalocyanines. The FAB spectra of the tetrakis(cumylphenoxy)phthalocyanines show a cluster of ions in the region of the molecular ion, but little or no fragmentation. A protonated molecule (*m/z* 1355) and a molecular ion (*m/z* 1354) are observed for the metal-free tetrakis(cumylphenoxy)phthalocyanine, H_2TPc. Other ions that were observed were assigned to the butyl benzyl phthalate matrix. The region between *m/z* 313 (protonated butyl benzyl phthalate) and *m/z* 1354 is free of ion signals except for matrix adduct ions. Fragment ions of H_2TPc were not observed with the tributyl phosphate sample matrix.

The metal-bound tetrakis(cumulphenoxy)phthalocyanines, BeTPc, MgTPc, MnTPc, FeTPc, CoTPc, NiTPc, CuTPc, ZnTPc, PbTPc, and BiTPc, show a cluster of ions corresponding to $[MTPc]^+$ and $[MTPc + H]^+$. Table VI lists the molecular weights and the ions observed. It has been shown by vapor pressure osmometry measurements of toluene solutions that the MTPc compounds often exist in solution as dimeric species.[2] The exceptions to this are PbTPc, which is monomeric, and CuTPc, NiTPc, PtTPc, and PdTPc, which form progressively larger oligomeric aggregates ranging from 2.7 to 4.1 molecular units in size. The CuTPc and NiTPc species exhibit relatively lower molecular ion abundances than the other metals, and only the FAB spectra of PtTPc and PdTPc do not yield a molecular ion cluster. Dimers or larger aggregates were not observed in the FAB mass spectra of the tetrakis(cumylphenoxy)phthalocyanines.

The lead- and bismuth-containing tetrakis(cumylphenoxy)phthalocyanines demetalate under FAB conditions to give

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a fragment corresponding to the metal-free tetrakis(cumylphenoxy)phthalocyanines (m/z 1355). Again, as in the case of the unsubstituted lead phthalocyanine, this likely is due to the size of the lead and bismuth ions and hence their ease of displacement from their location above the plane of the phthalocyanine nucleus.

The observation of a protonated BiTPc molecule at m/z 1562 is of particular importance because it establishes evidence of a Bi(II) compound. Previous to this study, the only evidence for the existence of this compound was an elemental analysis.[29] A FAB spectrum of BiTPc is shown in Figure 4.

Tetra-9,10-phenanthrotetraazaporphyrin. A sample of this compound was presented as an unknown in order to obtain molecular weight information, confirming a novel synthesis.[30] This compound, H_2TPTAP, was run in a neat sulfuric acid matrix as this was the only solvent in which the sample dissolved. A molecular ion at m/z 914 and a protonated molecule (m/z 915) were observed in the FAB mass spectra. No fragment ions were observed. In addition, like the underivatized phthalocyanines, an isotope cluster was observed at m/z 930 corresponding to an oxygen adduct ion. Elemental analyses of this compound were confused by the presence of oxygen until the samples were degassed by heating in vacuo. Exposure to air resulted in readsorption of oxygen according to elemental analysis.[29]

Conclusion

In general, FAB provides a rapid technique for the confirmation of the molecular weight of different series of substituted and unsubstituted phthalocyanines. Fragmentation of the phthalocyanines by FAB is minimal, yielding little structural information. This is in contrast to the FAB results on the "tailed" porphyrins and meso-substituted tetraphenylporphines.[8] However, these phthalocyanines are structurally simple relative to the tailed porphyrins. Because there is no perceptible fragmentation, and sometimes a meager abundance of the molecular ion, the FAB technique is not readily amenable to evaluation of a complete unknown. However, as shown in the case of the tetra-9,10-phenanthrotetraazaporphyrin, FAB can provide evidence confirming proposed identities of phthalocyanines and structurally similar compounds.

Water, oxygen, and dioxygen adduct ions were observed for the unsubstituted phthalocyanines, providing corroborating evidence of an oxygen–phthalocyanine interaction from ESR analyses.[27] Because the metal-free as well as the metal-bound phthalocyanines show these oxygen adduct species, one may conclude that there is no significant oxygen–metal interaction. Instead, this observation implies that the oxygen interaction is with the aromatic macrocycle. Furthermore, the peripherally substituted tetrakis(cumylphenoxy)phthalocyaninces do not show such adducts. This may indicate a much weaker interaction of the oxygen on the macrocyclic backbone of the peripherally substituted species.

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Registry No. H_2Pc, 574-93-6; FePc, 132-16-1; CoPc, 3317-67-7; NiPc, 14055-02-8; CuPc, 147-14-8; ZnPc, 14320-04-8; PbPc, 15187-16-3; H_2TPc, 93530-40-6; BeTPc, 93530-41-7; MgTPc, 93530-42-8; MnTPc, 93530-43-9; FeTPc, 93530-44-0; CoTPc, 93530-45-1; NiTPc, 93530-46-2; CuTPc, 93530-47-3; ZnTPc, 93530-48-4; PtTPc, 93530-49-5; PdTPc, 93530-50-8; PbTPc, 93530-51-9; BiTPc, 93530-52-0.

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Crystal and Molecular Structure of Chloro(phthalocyaninato)gallium(III), Ga(Pc)Cl, and Chloro(phthalocyaninato)aluminum(III), Al(Pc)Cl

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A single-crystal X-ray diffraction analysis has been carried out on the title compounds to provide a structural basis for the observed conductivity upon doping and the photoconductivity. Ga(Pc)Cl (Pc = phthalocyaninato dianion, $C_{32}H_{20}N_8^{2-}$) crystallizes in the triclinic space group $P\bar{1}$ with the following: $a = 9.301$ (3), $b = 11.272$ (1), $c = 13.143$ (3) Å; $\alpha = 105.46$ (2), $\beta = 105.61$ (2), $\gamma = 96.80$ (2)°; $V = 1252.8$ Å^3. For $Z = 2$ and fw = 617.7 the calculated density is 1.64 g/cm^3. Automated diffractometer intensity data (Enraf-Nonius CAD4) were used to solve the structure. Refinement led to $R_F = 0.036$ and $R_{wF} = 0.042$ for all 3483 unique reflections with $2.8° < 2\theta < 46°$ (Mo Kα radiation). Square-pyramidal coordination exists about Ga with Cl occupying the apex (Ga–Cl = 2.217 (1) Å) and N(1)–N(4) the basal positions: Ga–N(1) = 1.979 (4), Ga–N(2) = 1.981 (4), Ga–N(3) = 1.983 (4), Ga–N(4) = 1.9988 (4) Å. Gallium is 0.439 (1) Å above the least-squares plane formed by N(1)–N(4). The Pc ring is essentially planar; packing gives an interleaved slipped–stacked array in the crystal with an interplanar distance of 3.34 Å. Al(Pc)Cl also crystallizes in the triclinic space group $P\bar{1}$ with the following: $a = 13.776$ (6), $b = 13.775$ (4), $c = 14.059$ (5) Å; $\alpha = 98.36$ (3), $\beta = 108.60$ (3), $\gamma = 90.16$ (3)°; $V = 2498.2$ Å^3. For $Z = 4$ and fw = 579.0 the calculated density is 1.54 g/cm^3. Disorder gave rise to high overall R values: $R_F = 0.137$ and $R_{wF} = 0.164$ for 9454 unique reflections with $2.8° < \theta < 140°$ (Cu Kα radiation). The coordination geometry is square pyramidal as for Ga(Pc)Cl. Bond distances for the nondisordered molecule containing Al(1) are Al(1)–Cl(1) = 2.179 (6), Al(1)–N(1) = 1.961 (12), Al(1)–N(2) = 1.962 (13), Al(1)–N(3) = 1.966 (12), and Al(1)–N(4) = 2.018 (12) Å. Al(1) is 0.410 (6) Å above the basal plane formed by N(1)–N(4).

Introduction

There has recently been considerable interest in group 3 and 4 phthalocyanines because of the high conductivity of partially oxidized derivatives,[2–4] interesting cofacial polymeric structures,[3–7] and the thermal and hydrolytic robustness of these

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