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Intense Satellites in the N 1s X-ray Photoelectron Spectra of Certain Metalloporphyrins

Sir:

Satellite features associated with core-electron photoelectron photoionization, as observed in X-ray photoelectron spectroscopy (XPS), have attracted considerable interest over the last 10 years.[1-3] These features, commonly called shake-up satellites but perhaps better called correlation-state structure, following Shirley,[5] arise because photoionization may leave the final system in a valence excited state. This is due physically to the rearrangement of valence electronic structure upon core ionization. The interest in such features in transition-metal compounds has been especially intense,[2,4,6,7] partly because of their intensity in some of these systems and partly because it is felt that they may provide useful information not readily obtained otherwise about the excited-state manifolds of these compounds. Most recently, attention has focused upon satellite structures arising from ligand levels in transition-metal compounds.[8,9] We report here rather striking N 1s satellites in certain metalloporphyrins, satellites which are strongly metal dependent and thus reflect properties of the metals involved.

Weak N 1s satellites are ubiquitous in porphyrins and have been reported by various workers.[10-12] They depend weakly, if at all, on the metal and probably represent a $\pi \rightarrow \pi^*$ transition localized on the porphyrin. We have found quite different behavior, however, in the metal porphyrins containing Zn, Ag, Cd, and Mg and in four metalloporphyrins of trivalent lanthanides (Gd, Ho, Er, and Tm). The lanthanide compounds are believed to contain hydroxide as an axial ligand.[13] N 1s spectra of four of these compounds appear in Figure 1, along with the N 1s spectrum of Ni(OEP) (OEP = octaethylporphyrin) for comparison. Spectra similar to some of those in Figure 1 have appeared previously; in particular, spectra of magnesium porphyrins and of chlorophylls[12] have appeared. The satellites have been attributed to radiation-induced demetalation of the porphyrin. The intensity of the satellite is constant from sample to sample, however, and does not change with time of irradiation. The positions and relative intensities of the satellites shown in Figure 1 appear in Table I.

None of these compounds display any structure on the metal core ionizations. Various sources of the features we observe must be considered. (1) They may be due to the presence of more than one nitrogen-containing species on the sample, due, for instance, to sample degradation. (2) They may be due to irregular geometries of the compounds involved, leading to the presence of more than one electronically distinct type of nitrogen atom. (3) The features are genuine correlation-state structures, due to population of excited final states of the systems involved.

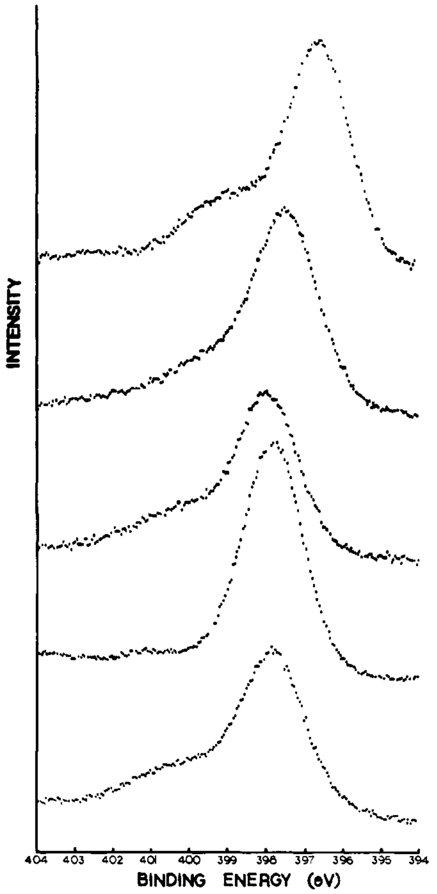

Figure 1. N 1s spectra of (top to bottom): MgTPP, AgOEP, GdOEP, NiOEP, and ZnOEP (TPP = tetraphenylporphyrin, OEP = octaethylporphrin).

Table I. Positions and Intensities of the N 1s Satellites of Several Porphyrins

compound	satellite position, eV from main line	intensity, % of main line
NiOEP	3.1	4.7
ZnOEP	2.3	16.3
AgOEP	2.1	20.6
MgTPP	2.2	29.7
GdOEP	1.7	39

We have eliminated the first possibility by observing the intensity distribution in the N 1s region of several samples of each compound as a function of time of irradiation. In all the cases at hand, the intensities were independent of sample and time of irradiation. We could obtain spectra after as little as 3-min irradiation at 100 K.

The second possibility is hardly likely for such compounds as magnesium porphyrins, in which the geometry is known[14] but cannot be excluded in such compounds as the lanthanide porphyrins, in which the geometry is really quite unknown. The intensities of the features (see Table I) militate against such an explanation, however, since they should be approximately in the ratio of multiples of one-fourth, i.e., 1:3 or 1:1, and these intensity

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ratios are not seen. We are left with the conclusion that the compounds under discussion display intense correlation-state structures on the N 1s ionizations, a unique behavior, to our knowledge.

It is difficult to provide an incisive discussion of the correlation-state structures we observe without having calculations on the electronic structures of at least some of the molecules at hand. Magnesium porphyrin has been discussed in some detail by Maggiora and co-workers.[14,15] According to these calculations, all the molecular orbitals within several electronvolts on either side of the highest occupied orbital of magnesium porphyrin are of porphyrin π type, containing essentially no Mg $3p_z$ contribution. It is most likely, thus, that any low-lying excited states of the core-ionized species would derive from excitation from a filled π orbital to an empty π orbital. The calculations furthermore show that the π system of magnesium porphyrin has little electron density on Mg. Thus, the Mg $3p_z$ orbital is essentially decoupled from the porphyrin in the ground state and lower excited states of magnesium porphyrin.

The results outlined in the last paragraph leave only one role for the Mg in promoting the appearance of low-lying correlation-state structure: the strong perturbation which comes from core ionization of a nitrogen atom causes Mg $3p_z$ amplitude to be mixed into the upper filled and lower virtual orbitals of the core-hole state as part of the electronic rearrangement of the system. Magnesium $3p_z$ amplitude can appear in many of the core-hole state π orbitals (to be precise, those arising from a_1, a_2, or e orbitals of magnesium porphyrin) because the perturbation breaks the symmetry of the system. Satellites then arise because the various final states must be superimposed so as to give the original electronic structure.

The extension of the arguments applied to magnesium porphyrin to other compounds is rather difficult because many virtual levels are available and may be mixed into the electronic structure by the perturbation caused by photoionization. Thus, further discussion of the other systems must await the appearance of more calculational data.

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Dogger Bank Itch. The Allergen Is (2-Hydroxyethyl)dimethylsulfonium Ion

Sir:

We report the isolation, structure elucidation, and synthesis of the causative agent of Dogger Bank itch,[1,2] an eczematous allergic contact dermatitis caused by exposure to the marine bryozoan, *Alcyonidium gelatinosum* (L.).[3-6] These marine animals[7] were kept and reextracted with ethanol (96%) to give an inactive residue and active extracts as demonstrated by patch tests on sensitized volunteers,[8] a bioassay which has been used all through the isolation procedure. Evaporation of the combined extracts followed by partition between water and ether proved the activity to be entirely concentrated in the aqueous phase. Sephadex G-10 gel chromatography with water as eluant gave rise to a salt fraction (~0.7% C) displaying almost the entire activity.

In order to reduce the amount of salt, the active gel filtration fraction was extracted with absolute ethanol after freeze-drying. The supernatant held most of the activity and left, on evaporation, a sample which was subjected to repeated ion-exchange chromatography (Dowex 50W-X8). Still the allergen appeared associated with the salt fraction after elution with hydrochloric acid. The carbon content had, however, risen to 7% and cutaneous patch tests revealed an exceedingly high activity. Noise-decoupled 67.889-MHz ^{13}C NMR in D_2O virtually only exhibited three signals at δ 42.3, 56.0, and 57.5 ppm. These signals could be traced back in the earlier active fractions. The signals appeared with integrals roughly 2:1:1, respectively, and with off-resonance decoupling identified themselves as belonging to methyl groups and two magnetically different methylene groups, respectively. The same solution subjected to 270-MHz ^{1}H NMR gave rise to signals at δ 3.9 (br s) and 4.3 (br s) ppm integrating in the ratio 3:2.[9] Elemental analyses of this fraction (lyophilized) gave a C to S ratio of 0.6617 as compared to a calculated value of 0.6668 for $C_4H_{11}O_2S$. High-resolution electron-impact mass spectrometry at 200 °C only gave substantial fragments at m/e 78.0145 (C_2H_6OS, calcd 78.0139) and 62.9951 (CH_3OS, calcd 62.9904). Loss of a methyl group from m/e 78 producing m/e 63 was substantiated by a metastable peak at m/e 50.88. This spectrum was identical with a spectrum of dimethyl sulfoxide.

For comparative purposes the ^{13}C and ^{1}H NMR spectra of sulfocholine[10] ((2-hydroxyethyl)dimethylsulfonium ion) were recorded. In this case the methyl group signals were found at δ 27.7 and 2.96 (s) ppm, the methylene group adjacent to sulfur at δ 48.7 and 3.55 (m), and the methylene group bearing the hydroxyl at δ 58.2 and 4.13 (m) ppm. Clearly the allergen bears a group more deshielding than the sulfonium entity. After this was taken into account, the spectra of the trimethylsulfoxonium ion[11] were recorded, the methyl groups appearing at δ 42.3 and 3.93 in the ^{13}C and ^{1}H NMR spectra, respectively.

From the above-mentioned data it is concluded that the Dogger Bank itch producing allergen must be (2-hydroxyethyl)dimethylsulfoxonium ion. This structure assignment was further substantiated by field desorption (FD) MS measurements. At 80 °C ion source temperature, three significant ions were observed at m/e 108 (25%), 90 (25%), and 78 (100%), assigned to the molecular ions of methyl (2-hydroxyethyl) sulfoxide, methyl vinyl sulfoxide and dimethyl sulfoxide respectively, which were thought to be formed thermally from the allergen precursor. At 200 °C the pattern was m/e 108 (15%), 90 (30%), and 78 (100%). As expected, the EI-MS at the latter temperature was more complicated, m/e 90 (3%), 78 (88%), 63 (100%), 61 (17%), and 50 (95%)/52 (30%), representing methylchloride molecular ion. The structure of one of the key ions, m/e 90, was strongly supported

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