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## X-ray photoelectron spectroscopy of clean and gas-doped films of phthalocyanines

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**Abstract.** Films of a range of phthalocyanines which had been deposited by vacuum sublimation were analysed using x-ray photoelectron spectroscopy (XPS). Spectra of the major peaks were recorded before exposure to NOX ( $\text{NO}_2 + \text{N}_2\text{O}_4$ ), after exposure to 9 vpm NOX in air, after exposure to undiluted NOX and finally after heating the exposed film to 150 °C. The phthalocyanines studied were: metal-free ( $\text{H}_2\text{Pc}$ ), magnesium (MgPc), vanadyl (VOPc), manganese (MnPc), iron (FePc), cobalt (CoPc), nickel (NiPc) and copper (CuPc). The presence of NOX (which would have given rise to new N 1s and O 1s peaks in the XPS spectra) was not detected in any of the films following the exposure to 9 vpm, although slight shifts in the positions of some peaks were observed. All XPS spectra exhibited changes following the exposure of the films to undiluted NOX.  $\text{H}_2\text{Pc}$  clearly suffered severe chemical attack. The effect on the metal phthalocyanines was not so severe, but was different for each metal complex. None of the spectra was restored to the pre-NOX form by heating to 150 °C after exposure to the undiluted NOX. In order to explain the changes in the C 1s XPS spectra which were observed during these experiments, it was found necessary to modify a previous interpretation of the C 1s spectrum.

### 1. Introduction

It is well known that the electrical conductance of films or crystals of phthalocyanine compounds may be increased by many orders of magnitude by exposure to certain gases or vapours (for example [1-4]). Previously we have investigated the effect of NOX ( $\text{NO}_2 + \text{N}_2\text{O}_4$ ) on the IR and UV-visible spectroscopy, and the electrical conductance, of films of phthalocyanine and other organic macrocyclic compounds [5-11].

Here we investigate the effect of NOX on the x-ray photoelectron spectroscopy (XPS) of phthalocyanine films. Metal-free phthalocyanine ( $\text{H}_2\text{Pc}$ ) was studied, together with seven of its metal complexes: magnesium (MgPc), vanadyl (VOPc), manganese (MnPc), iron (FePc), cobalt (CoPc), nickel (NiPc) and copper CuPc (figure 1).

### 2. Experimental details

With the exception of copper, all the metal complexes of phthalocyanine were obtained from Eastman Kodak. Metal-free and copper phthalocyanine were synthesized using standard methods [12].

NOX was obtained from cylinders; the undiluted NOX was obtained from BDH Ltd, and the 9 vpm NOX-in-air was obtained from BOC Special Gases Ltd.

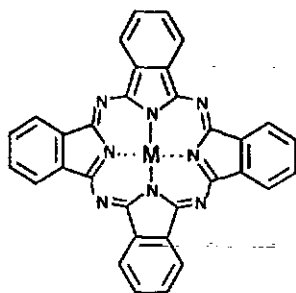


Figure 1. The phthalocyanines studied:  $M \equiv \text{H}_2, \text{Mg}, \text{VO}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$  and  $\text{Cu}$ .

Films of the phthalocyanines were prepared by vacuum sublimation using an Edwards E306A coating unit. The phthalocyanines were deposited from molybdenum boats directly on to cleaned nickel stubs for mounting in the photoelectron spectrometer. It was not possible to transfer the samples from the coating unit to the photoelectron spectrometer without exposing them to air.

Photoelectron spectra were recorded using a VG Scientific ESCALAB Mk II. All spectra were recorded using an unmonochromatized x-ray source with an aluminium anode.

In each case, spectra were recorded from the film: (i) as deposited; (ii) after exposure to 9 vpm NOX for 30 min; (iii) after exposure to undiluted NOX for 5 s; and (iv) after heating the exposed film to  $150^\circ$  for 30 min. The 9 vpm NOX exposures and the heating experiments were performed in a cell within the ESCALAB. The undiluted NOX exposure was performed outside the ESCALAB in a glass vessel contained within a fume cupboard. The set of spectra recorded comprised the carbon 1s region, the nitrogen 1s region, the oxygen 1s region, and the major metal peaks in the cases of the metal complexes.

### 3. Results and discussion

Niwa *et al* [13] investigated the XPS of a number of phthalocyanine and porphyrin compounds, including  $\text{H}_2\text{Pc}$  and  $\text{CuPc}$ . They assumed that the unresolved C 1s region of  $\text{H}_2\text{Pc}$  and  $\text{CuPc}$  was composed of two peaks (C1 and C2), where the larger peak at 284.8 eV (C1) was attributed to carbon bonded to carbon and/or hydrogen, and peak C2 was attributed to the carbon atoms which were bonded to nitrogen atoms. Associated with C1 and C2 were shake-up satellites (C3 and C4 respectively), which were assumed to be arranged such that C3 was exactly superimposed upon C2, thus giving three distinct components to the experimental spectrum. This did not give a very satisfactory agreement with either the expected C2/C1 ratio (8/24) in phthalocyanine, or the calculated peak-to-satellite distance (about 3 to 4 eV). They found the C2/C1 ratio to be higher than 1/3 (0.40 for  $\text{H}_2\text{Pc}$  and 0.43 for  $\text{CuPc}$ ). The possibility of surface contamination was considered unlikely since this would have reduced the ratio.

By assuming each satellite peak to be about 3 to 4 eV to higher binding energy of its parent peak (i.e. within the range quoted by Niwa), we found a good fit to our experimental data; C3 was no longer superimposed upon C2, and the experimental spectrum was formed from four distinct components (figure 2(a)). Measuring the area

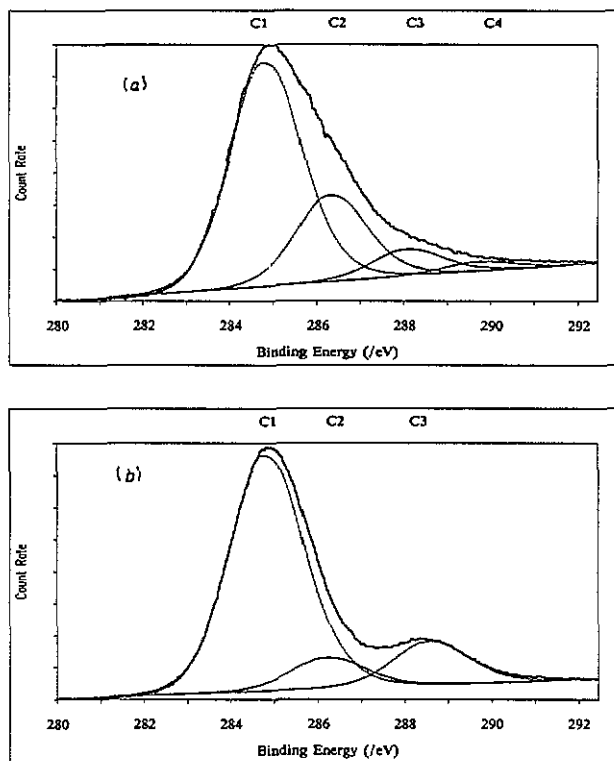


Figure 2. The C 1s x-ray photoelectron spectra of a VOPc film: (a) before exposure to NOX (top); and (b) after exposure to undiluted NOX. The experimental spectrum is shown as a dark trace, and its components elucidated by curve-fitting are shown as light traces labelled C1-C4. (C4 is too weak to be observed in (b)).

of these peaks gave, in most cases a reasonable agreement with the expected C2/C1 ratio. In addition, a satisfactory C2/N1 ratio was obtained in most cases.

The binding energies from all the major peaks for all of the compounds resulting from the experimental regime described earlier have been summarized in table 1. All binding energies have been referenced to peak C1 at 284.8 eV. Table 2 gives the atomic percentages of the components of each film after each process. The values were calculated from the measured peak areas using atomic sensitivity factors given by Wagner *et al* [14]. The forms of the carbon 1s, nitrogen 1s and oxygen 1s spectra were similar for all the compounds studied; therefore the spectra of only one compound (VOPc) have been given (figure 3).

In all cases there was little change in the binding energies of the C 1s (C2) peaks following exposure to 9 ppm or undiluted NOX ( $C2 = 286.20 \pm 0.20$  eV for all complexes under all conditions), although changes in the peak areas were apparent. Carbon bound to  $NO_2$  is reported [15] to give a C 1s binding energy of 286.6 eV (assuming C 1s for hydrocarbon to be at 284.8 eV). If the  $NO_2$  had become formally bonded to the phthalocyanine ring carbons then the main C 1s peak (C1) would have been diminished, and a new peak due to C- $NO_2$  would have been expected at about 1.8 eV to higher binding energy. However, although C1 was diminished in nearly all cases, a new peak at 286.6 eV was not observed in any of the films, indicating that chemical nitration had not taken place.

Table 1. The binding energies from the major peaks in the photoelectron spectra of the phthalocyanine films referenced to the carbon peak C1 at 284.8 eV.

Pc	Peak	Binding energy (eV)			
		Pre NOX	9 vpm NOX	Undil. NOX	NOX/ heat
H <sub>2</sub>	C2	286.25	286.20	286.25	—
	C3	288.10	287.95	287.90	—
	C4	290.10	289.70	289.55	—
	N1	399.05	399.15	399.85	—
	N2	—	—	407.45	—
	O	533.25	533.65	533.45	—
Mg	C2	286.20	286.20	286.25	286.00
	C3	287.85	287.80	287.95	287.40
	C4	289.05	289.00	289.75	289.10
	N1	398.95	398.95	399.10	399.60
	N2	—	—	406.85	407.60
	O	533.85	533.55	532.45	533.20
	Mg	1303.75	1303.85	1305.45	1305.60
VO	C2	286.15	286.15	286.20	286.15
	C3	287.85	287.80	288.55	287.90
	C4	289.70	289.65	—	289.25
	N1	399.15	399.00	400.30	399.80
	N2	—	—	406.70	406.60
	O1	531.05	531.10	531.20	530.80
	O2	—	—	532.45	532.15
	V	516.75	516.40	517.50	517.50
Mn	C2	286.35	286.35	286.35	286.35
	C3	288.25	288.25	288.25	288.15
	C4	289.95	289.95	289.95	289.85
	N1	399.20	399.40	399.80	399.35
	N2	—	403.00	407.00	407.05
	O	531.20	531.90	532.90	532.85
	Mn	642.50	642.70	642.80	642.65
Fe	C2	286.10	286.15	286.10	286.15
	C3	287.80	287.85	287.85	287.95
	C4	289.60	289.60	289.45	289.60
	N1	399.30	399.35	399.45	399.40
	N2	—	—	407.35	407.60
	O	—	—	533.05	533.40
	Fe	709.40	709.65	711.45	712.60
Co	C2	286.15	286.15	286.00	286.05
	C3	287.95	288.00	287.80	287.65
	C4	289.75	289.80	289.45	289.40
	N1	399.05	399.40	399.45	399.30
	N2	—	—	406.85	407.10
	O	533.45	533.50	532.75	532.70
	Co	781.15	781.50	781.35	781.40
Ni	C2	286.20	286.20	286.15	286.15
	C3	287.90	287.90	287.70	287.70

Table 1. Continued.

Pc	Peak	Binding energy (eV)			
		Pre NOX	9 vpm NOX	Undil. NOX	NOX/heat
	C4	289.40	289.40	289.40	289.40
	N1	399.40	399.40	399.55	399.25
	N2	—	—	406.85	406.85
	O	533.00	533.00	532.85	532.95
	Ni	856.20	856.20	856.15	856.05
Cu	C2	286.10	286.15	286.10	286.15
	C3	287.95	287.95	287.90	287.90
	C4	289.65	289.85	289.75	289.70
	N1	399.55	399.40	399.30	399.50
	N2	—	—	407.60	—
	O	533.85	533.70	533.40	533.40
	Cu	935.85	935.70	935.50	935.90

In every film except CuPc a shoulder or small peak became apparent at about 3.0 to 3.5 eV on the high binding energy side of the main C 1s peak, as shown in figures 2(b) and 3(a) for VOPc. Since, in all cases, the C2 peak was decreased by a greater proportion than the C1 peak, the apparently new feature was in fact due mainly to the improved resolution of the peak C3 (figure 2).

The satellite peaks, C3 and C4, would be expected to alter in proportion with C1 and C2 respectively, but it can be seen that in all cases, with the exception of H<sub>2</sub>Pc and CuPc, the peak C3 apparently increased following exposure to undiluted NOX. It is noted that the position of C3 (about 3 eV to the high binding energy side of the C1 peak) is close to the position expected for carbon bonded to oxygen.

All films contained at least a small amount of oxygen prior to exposure, gained during deposition and/or during transport from the coating unit to the ESCALAB. In some cases a small increase in the height of the O 1s peak was apparent following exposure to 9 vpm NOX. In all cases there was a very large increase in the size of the O 1s peak following exposure to undiluted NOX.

In the case of nitrogen, the N 1s peak from the phthalocyanine ring occurred at  $399.25 \pm 0.30$  eV (pre-NOX), and  $399.75 \pm 0.6$  eV (undiluted NOX). The N 1s from NO<sub>2</sub> would be expected at about 407 eV. None of the films studied exhibited such a peak following exposure to 9 vpm NOX, but all films did exhibit this peak following exposure to undiluted NOX ( $407.15 \pm 0.45$  eV) (N2 in tables 1 and 2). As noted previously, the O 1s peak was greatly enhanced. However, the O/N2 ratio was  $4.2 \pm 0.8$  instead of the expected 2.0. A possible explanation is as follows. At room temperature the reactive gas is N<sub>2</sub>O<sub>4</sub> which decays by heterolytic fission to NO<sub>2</sub><sup>+</sup>NO<sub>2</sub><sup>-</sup> at the surface. The NO<sub>2</sub><sup>+</sup> is the species responsible for nitration, or for oxidizing the organic material to its radical cation [16]; the NO<sub>2</sub><sup>-</sup> can react with surface-bound dioxygen by electron exchange releasing NO<sub>2</sub> from the surface with O<sub>2</sub> remaining surface bound. The gross effect in the region of this surface reaction is therefore (Pc,NO<sub>2</sub>)<sup>+</sup>;O<sub>2</sub><sup>-</sup>, thus leading to an O/N2 ratio of 4.

The observed increase in binding energy of the metal 2p<sub>3/2</sub> levels in FePc and VOPc following exposure to undiluted NOX are consistent with the changes Fe(II) → Fe(III) and V(IV)O → V(V)O. In the case of MgPc, the pre-NOX Mg1s binding energy

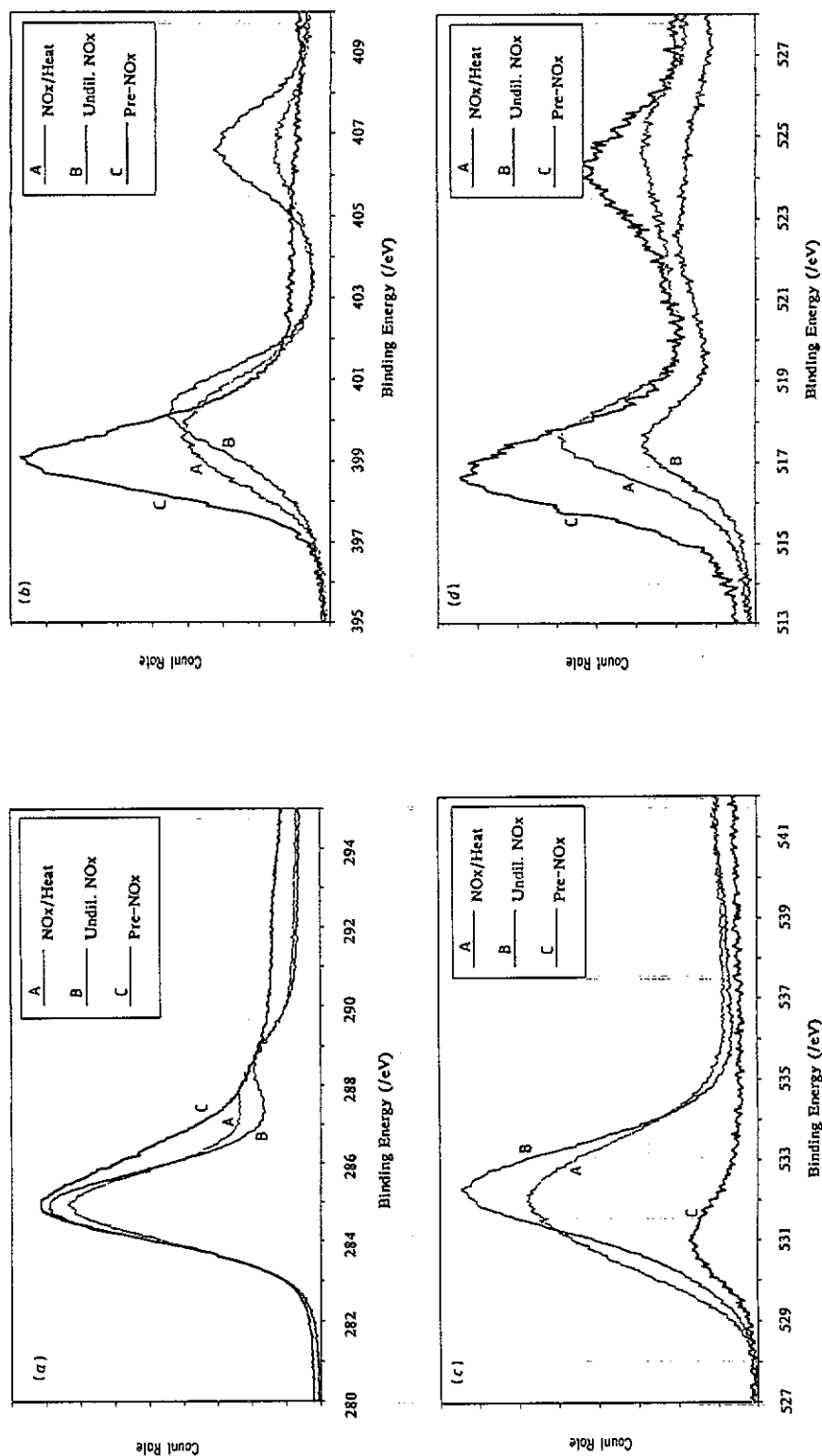


Figure 3. (a) C 1s, (b) N 1s, (c) O 1s and (d) V 2p x-ray photoelectron spectra of a VOPc film before exposure to NOx (dark traces), after exposure to undiluted NOx (medium density traces) and after heating the NOx-exposed film to 150°C for 30 min (light traces). The two main peaks in (d) are due to the V  $2p_{3/2}$  (516.75 eV) and V  $2p_{1/2}$  (524.15 eV) electrons. The small, broad peak at around 522.5 eV (medium-density trace) is due to O 1s excited by x-ray satellites.

Table 2. The atomic percentages of the components of each phthalocyanine calculated from the measured peak areas using sensitivity factors given by Wagner *et al* [14].

Pc	Proc	Atomic percentages							Metal
		C1	C2	C3	C4	N1	N2	O	
H <sub>2</sub>	Pre	46.8	22.1	6.7	2.5	21.4	—	0.5	—
	9 vpm	46.4	22.5	6.7	3.2	20.7	—	0.5	—
	Undil.	23.1	7.2	4.2	1.8	5.8	13.0	44.8	—
Mg	Pre	48.1	20.2	6.2	2.2	20.2	—	1.1	1.9
	9 vpm	46.8	20.2	6.3	2.5	20.9	—	1.6	1.8
	Undil.	45.6	13.5	6.7	1.6	12.4	3.9	15.5	0.7
	Heat	36.1	23.6	8.9	3.6	13.5	1.7	11.7	0.8
VO	Pre	47.6	18.6	6.2	2.2	20.8	—	2.2	2.5
	9 vpm	46.3	19.0	7.1	3.0	20.4	—	2.1	2.2
	Undil.	47.1	5.8	8.4	0.0	9.8	5.1	5.2	17.3
	Heat	43.5	7.8	8.9	2.8	10.5	2.4	7.1	14.5
Mn	Pre	51.5	16.9	4.9	1.2	20.6	—	2.8	2.1
	9 vpm	50.9	16.7	4.7	0.8	20.6	—	4.0	2.3
	Undil.	45.2	10.0	6.8	1.9	8.4	5.1	21.0	1.4
	Heat	44.8	12.3	6.7	1.7	9.5	3.8	18.9	2.3
Fe	Pre	51.3	19.0	5.5	2.3	19.1	—	0.4	2.4
	9 vpm	51.0	17.7	5.6	2.6	20.4	—	0.6	2.2
	Undil.	44.3	12.6	6.5	3.2	10.1	4.7	17.3	1.3
	Heat	36.6	20.1	7.9	3.4	10.8	3.3	16.1	1.6
Co	Pre	48.8	20.5	5.7	1.8	19.6	—	1.6	2.0
	9 vpm	47.0	21.7	5.8	2.0	19.8	—	1.7	2.0
	Undil.	39.4	13.8	8.6	3.5	8.7	4.1	21.1	0.8
	Heat	42.7	13.9	8.7	3.3	10.1	2.9	17.6	0.9
Ni	Pre	49.5	20.1	5.1	2.7	20.0	—	0.6	2.0
	9 vpm	50.3	19.4	4.6	2.3	20.6	—	0.8	2.0
	Undil.	46.7	15.8	7.2	2.8	11.4	2.8	12.2	1.1
	Heat	48.4	16.5	7.5	2.8	12.6	1.4	9.6	1.2
Cu	Pre	45.7	23.3	6.9	1.8	19.3	—	1.1	1.9
	9 vpm	48.1	22.8	5.4	1.5	19.5	—	0.9	2.0
	Undil.	38.4	18.6	6.3	2.1	12.1	3.3	17.8	1.5
	Heat	35.2	20.1	7.2	2.7	13.0	1.4	18.7	1.5

corresponds to that observed in solid MgO, in which the magnesium is divalent. It is known that magnesium can become six-coordinate; the increase in the Mg1s binding energy following exposure to undiluted NOX suggests the presence of an axially-bound oxygen-rich ligand such as O<sub>2</sub> or NO<sub>2</sub>. There were no major shifts in the binding energies of the 2p<sub>3/2</sub> levels of the remaining metal complexes, although the lack of a substantial binding energy shift does not necessarily rule out the possibility of an increase in the oxidation state.

Following exposure to undiluted NOX, the percentages of the metals and ring nitrogens (N1) were approximately halved, and the C2 percentages were reduced by varying



proportions, while the C1 percentages were reduced to a lesser extent. These results are consistent with the model suggested earlier, where the extra layer of oxygen-rich ligands centred on the metal ion would lead to physical screening of (i.e. reducing the observed photoelectron emission from) the metal, the N1 nitrogen atoms and the carbons (C2) bonded to them more than the benzene carbons (C1).

In the case of H<sub>2</sub>Pc, severe chemical attack clearly occurred following exposure to undiluted NOX. Peaks due to the presence of nickel (from the supporting stub) were observed after, but not before, exposure. This did not occur for any of the other films.

Finally, each film was heated to 150°C for 30 min in the ESCALAB after the exposure to undiluted NOX, to discover whether any of the changes could be reversed by heating.

Following heating, H<sub>2</sub>Pc showed evidence of further severe chemical attack. The metal complexes all exhibited a rise in the C2, N1 and metal percentages compared with these percentages following exposure to undiluted NOX. All except CoPc and NiPc exhibited a fall in C1. All complexes exhibited a fall in the percentage of N2, and all but CuPc exhibited a fall in the percentage of O. In the metal complexes (except CoPc and NiPc) the percentage rise in N1 was less than the percentage rise in C2, but partial restoration of N1, C2 and the metal percentages, together with the decrease in the percentage of oxygen and N2 implies that some of the screening layer mooted earlier may have been removed by heating.

### Acknowledgment

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