in iron loading). The foregoing reactions are accompanied by the formation of 1.5 mol of H_2/g-atom of iron and trace amounts of CO_2 and saturated hydrocarbons. Therefore, several reactions occur in parallel, and the different elementary steps are presently under study, especially in correlation with the reactivity of carbon oxides (CO and CO_2) toward water and hydrogen. This work has shown that chemisorbed CO_2 reacts with H_2 to produce CH_4, and CO reacts with H_2O to produce the water–gas shift reaction.

The Fe(II) species have been characterized by complex formation with NO ($(FeNO)^7$ electron configuration) and CO. Decomposition at mild temperatures leads to location of the ions mainly in accessible sites (supercage, sodalite cavity) whereas a more drastic treatment induces their migration into the inaccessible sites (hexagonal prism). The present method is clearly superior to the conventional exchange ones for the introduction of Fe^{2+} ions into the molecular sieve pores. The advantages of this method are that it does not damage the crystalline structure, permits the location of the ions in more accessible sites, and does not introduce counteranions which can be trapped as impurities during the exchange process.

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Registry No. $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8.

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The Oxidation Product of (β-Phthalocyaninato)chromium(II)

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The oxidation of (β-phthalocyaninato)chromium(II) by molecular oxygen gives a product with a 1:1 ratio of chromium to oxygen atoms. From infrared and Raman spectra, magnetic data, and mass spectra of the product, obtained by reaction of (β-phthalocyaninato)chromium(II) with $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$, it was characterized as an oxo(phthalocyaninato)chromium(IV) dimer.

Introduction

Elvidge and Lever[1] reported that $Cr^{III}PcOH$ (Pc denotes the phthalocyanine moiety) is formed as long purple needles on repeated sublimation of a mixture of $Cr^{II}Pc$ and $Cr^{III}PcOH$, which was obtained by reacting phthalodinitrile with chromium(III) acetate.

By this method Ercolani[2] also obtained a purple-red crystalline compound, which he denoted product I. His compound, however, was sensitive to air which is usually not observed for a phthalocyanine containing chromium in the oxidation state III. On exposure to air, product I changed into a blue-violet product (II) with properties different from those described by Elvidge and Lever[1] for $Cr^{III}PcOH$. Product I could be repeatedly sublimed but remained sensitive to air. It did not contain oxygen. By its composition, magnetic

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moment (4.6 μ_B), IR spectrum, and crystallographic data, Ercolani[2] identified his product I as β-$Cr^{II}Pc$. No definite conclusion was given for product II. He stated only that not all analytical data were in agreement with the formula $Cr^{III}PcOH$.

Meloni, Ocone, and Block[3] prepared $Cr^{II}Pc$ by a different method. Oxidized by air, it formed a product which in its IR spectrum substantially agreed with $Cr^{III}PcOH$ of Elvidge and Lever.[1] The authors therefore formulated their product as $Cr^{III}PcOH$.

Ercolani[4] reported in a subsequent publication that his product II was identical to a sample obtained from Dr. B. P. Block. In this paper Ercolani accepted the formulation as $Cr^{III}PcOH$. However, no explanation was given for the difference in the analytical data of his oxidation product II and Elvidge and Lever's data of $Cr^{III}PcOH$.

Since this question has not been discussed further, a closer study of the reaction of β-$Cr^{II}Pc$ with oxygen was undertaken to establish the nature of the oxidation product.

Experimental Section

β-$Cr^{II}Pc$ was prepared by the method of Meloni, Ocone, and Block[3] from phthalodinitrile and chromium hexacarbonyl in 1-chloronaphthalene. The product was washed with benzene and anhydrous ether and the solvents removed in vacuo at 10^{-3} torr. The purity of the compound was checked by X-ray diffraction measurements. The diffraction pattern did not show any evidence for the presence of the α modification. On sublimation a mixture of both the α and β modification was formed. Therefore all experiments were carried out using the unsublimed compound.

The oxidation product was obtained by reaction of β-$Cr^{II}Pc$ with air or pure oxygen in a desiccator over P_4O_{10} or $CaCl_2$. The reaction was complete after 4 days or, in the case of pure oxygen, in 1 day. Typical analysis results were (in %) as follows: C, 65.9; H, 3.0; N, 19.3; Cr, 8.9. The percentages for CrPcO ($C_{32}H_{16}N_8OCr$) are as follows: C, 66.2; H, 2.8; N, 19.3; Cr, 9.0.

Oxygen-18 was purchased from Prochem (London). Two samples were used for the preparation containing 99% $^{18}O_2$ or a mixture of 48% $^{16}O^{18}O$ in 46% $^{16}O_2$ and 1.7% $^{18}O_2$. The oxygen was contained in 100-mL break-seal flasks. These were fused to the reaction vessel and the β-CrPc was added under nitrogen in a glovebox. After the reaction vessel was evacuated (10^{-3} torr) and sealed off, the break seal was opened and the sample allowed to react with the oxygen for 5 days.

IR spectra in the 250–4000-cm^{-1} region were recorded on a Perkin-Elmer Model 457 in Nujol mulls and CsI pellets. Both sample preparations gave the same results. The Raman spectra were obtained on a Coderg T 800 spectrometer equipped with a Spectra Physics 165–03 argon ion laser. The excitation wavelength was 488 nm. KBr pellets were used rotated at 3000 rpm to prevent laser heating of the sample.

Thermograms were recorded on a Mettler Thermoanalyzer. The X-ray diagrams were obtained with a Debye powder camera of 57.3-mm radius and Cu Kα radiation.

The mass spectra were recorded on a Varian MAT 731. The temperature of the sample was 400 °C, the source temperature 300 °C, and the electron energy 100 eV.

For taking the electronic spectra, powdered samples were brought in between quartz plates. The spectra were recorded with a Cary 14 spectrophotometer.

The magnetic moment was measured with a Gouy balance consisting of a Sartorius microanalytical balance, Type 4104, and a Bruker B-E10C8 magnet.

Results

When β-$Cr^{II}Pc$ is exposed to air, its purple lustre starts to disappear slowly, and the volume of the sample increases due to the reaction with oxygen. The oxygen uptake, followed by the increase in weight with time, was studied in air and pure oxygen at atmospheric pressure. The results are depicted in Figure 1.

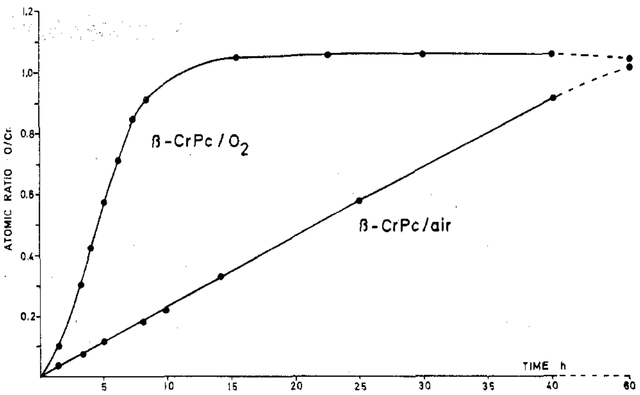


Figure 1. Oxygen uptake at atmospheric pressure of β-$Cr^{II}Pc$ in air and oxygen as a function of time at room temperature (25 °C).

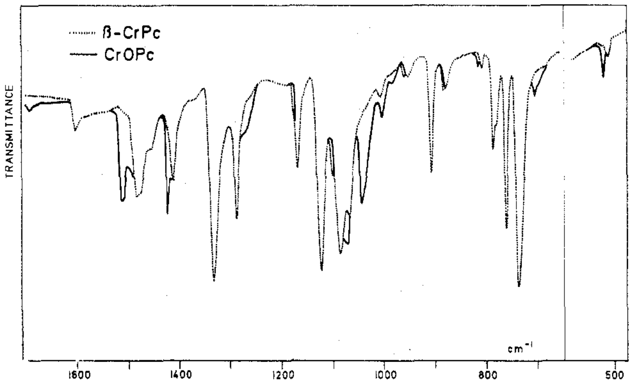


Figure 2. Infrared spectra of β-$Cr^{II}Pc$ and its oxidation product. Additional absorptions of the oxidation product are drawn in heavy lines.

The initial rate of gas uptake was approximately one-fifth as fast as in pure oxygen, consistent with the lower concentration of oxygen in air. The final increase in weight was found to be slightly higher than expected for a product with a 1:1 ratio of Cr to O atoms. Most probably this was caused by adsorption of oxygen at the surface of the sample. As is evident from Figure 1, the oxygen uptake is sufficiently slow to allow handling of β-$Cr^{II}Pc$ in the open air for short times like that required for pressing pellets, for example.

The oxidation product was a voluminous, deep blue powder. It was slightly soluble in polar organic solvents. When this compound was dissolved in concentrated sulfuric acid and precipitation was done afterward with H_2O, a different product was obtained.

The IR spectrum is shown in Figure 2. When comparison was made to the spectrum of β-$Cr^{II}Pc$, the following additional bands appeared: 1695 (vw), 1510 (m), 1420 (m), 1271 (m), 1041 (s), 810 (w), 701 (w), 519 (w) cm^{-1}. The spectrum did not show the bands at 878 (w), 956 (w), 1095 (sh), and 1173 (sh) cm^{-1} which are characteristic of the β modification.[5] The spectrum was essentially identical to that reported by Ercolani[2] for his product II. Also the Debye–Scherrer diagram was the same as that reported by Ercolani et al.[4]

The electronic spectra of β-$Cr^{II}Pc$ and the oxidation product are presented in Figure 3. In the spectrum of the oxidation product, bands were detected at 755 (sh), 720, 660 (sh), 490, and 380 nm. The spectra are similar to those observed for metal phthalocyanines in the solid state.[6] Compared to solution spectra, the bands are broader and shifted to the red. On oxidation this effect is enhanced.

A typical thermogram obtained at a heating rate of 6 °C/min in helium (flow rate 10 L/h) is depicted in Figure 4. Weight loss started at 200 °C and became more pronounced at higher temperatures. No indication of a reversible oxygen desorption was found at lower temperatures. Above 500 °C the minor noncharacteristic deflections in the DTA curve suggest the superposition of the endothermic sublimation

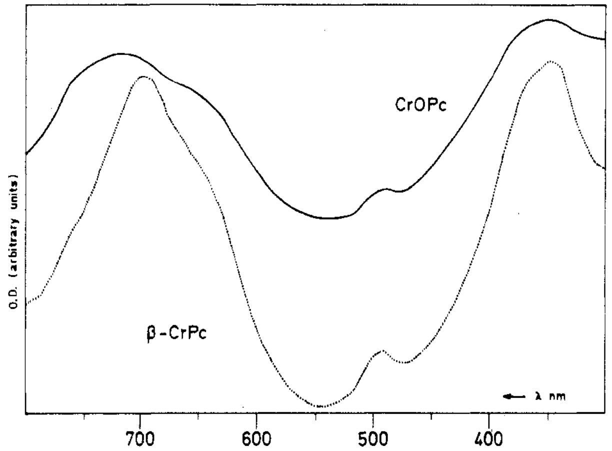


Figure 3. Solid-state absorption spectra of β-$Cr^{II}Pc$ and its oxidation product.

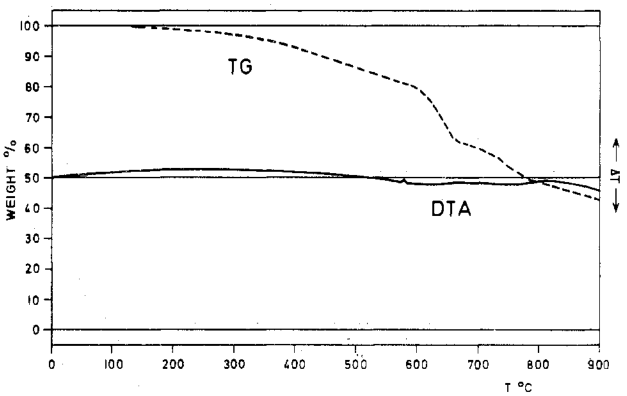


Figure 4. TGA and DTA curves of the oxidation product of β-$Cr^{II}Pc$.

by an exothermic decomposition. At 900 °C a residue of about 40% of the initial weight remained.

Attempts to purify the compound by sublimation at temperatures below 380 °C and 10^{-3} torr were not successful. As in the thermogravimetric experiments, the sample sublimed only in part, and a black residue was obtained. During the sublimation process, a white material deposited in the cool trap held at liquid nitrogen temperature. From an analysis the material was identified to be a mixture of phthalimide and phthalodinitrile formed most probably by oxidative cleavage of the phthalocyanine ring. The sublimation product was a mixture of $Cr^{II}Pc$ in the α and β modification.

The oxygen-dependent vibrations were characterized by their shift in the IR and Raman spectra on isotopic substitution (Figure 5). β-$Cr^{II}Pc$ was oxidized by either $^{16}O^{18}O$ or $^{18}O_2$. As a result the band at 1041 cm^{-1} found in the $^{16}O_2$ oxidation product was shifted in both cases by 44 cm^{-1} in the IR and Raman spectra. In the $^{16}O^{18}O$ sample the relative intensities of the 1041 and 997 cm^{-1} bands were consistent with the isotopic composition of the oxygen gas applied.

No isotopic shifts were observed below 1000 cm^{-1}. The oxidation product obtained with oxygen-18 showed no isotopic exchange when left in the open air for 1 year.

Typical mass spectra are shown in Figure 6. The fragmentation pattern was similar to that of the oxygen-free metal phthalocyanines.[7] A group of peaks at mass numbers between 578 and 582 in the mass spectrum of the oxidation product with $^{16}O_2$, for example, was observed to have the same characteristic structure as that of $Cr^{II}Pc^+$ shifted by 16 mass units to higher numbers. This group was therefore assigned to originate from $CrPcO^+$.

The same observations were made for the product obtained by reaction with $^{18}O_2$. In this case a shift by 18 mass units

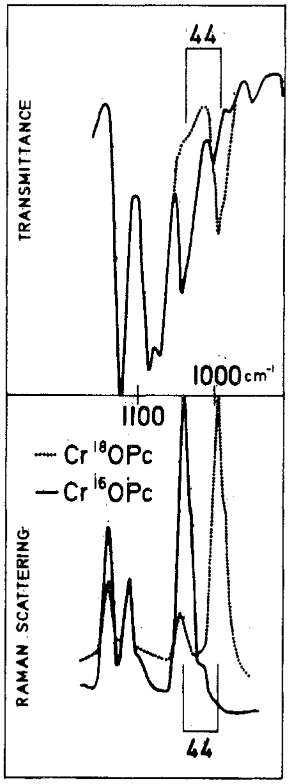


Figure 5. Isotopic shift observed in the IR and Raman spectra of the oxidation products obtained with $^{16}O_2$ and $^{18}O_2$.

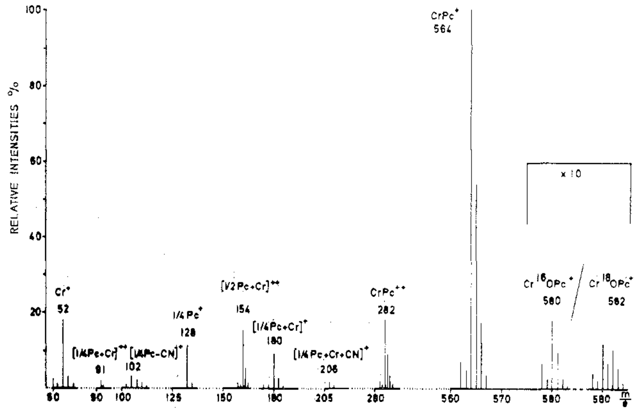


Figure 6. Mass spectra of $Cr^{16}OPc$ and $Cr^{18}OPc$.

was observed. The intensity distribution of this group of peaks, however, was somewhat different. Most probably this was caused by isotopic exchange with ^{16}O in the ion source of the mass spectrometer.

If $Cr^{III}PcOH$ were the result of the oxidation reaction, a shift by 17 mass units of this particular group of peaks would then be expected. In the spectra a group of peaks of this kind could not be found ruling out the presence of $Cr^{III}PcOH$ or a mixture of CrPcO and $Cr^{III}PcOH$. Peak groups of $CrPcO_2$ or dimers could not be detected.

The magnetic moment of the oxidation product was found to be 1.9 μ_B at room temperature and 1.6 μ_B at liquid nitrogen temperature.

Discussion

The formulation of the oxidation product as $Cr^{III}PcOH$ is not in accordance with the following observations. (1) The IR spectrum lacks the characteristic bands of the OH– vibrations. These bands, for example, were readily detected at 3440 and 1620 cm^{-1} in the IR spectrum of the hydroxy-bridged sulfonated phthalocyaninatochromium.[8] (2) The oxidation

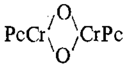
Table I. Metal–Oxygen Stretching Frequencies (cm^{-1}) of Oxophthalocyaninato Transition-Metal Complexes

TiOPc	VOPc	CrOPc	MnOPc	MoOPc
978[11]	1017[11]	1041	1096[14,a]	975[13]
965[6]	1004[6]			
	1003[12]			

[a] MnOPcpy (py = pyridine).

product was formed in the absence of water. (3) In the mass spectrum the species $Cr^{III}PcOH^+$ or characteristic fragments thereof were not observed.

Upon consideration of all the experimental results, the formulation of the oxidation product as $(CrPcO)_x$ (x denotes an integer) is suggested. Oxidation of the phthalocyanine ring is not likely since ring oxidation drastically changes the electronic absorption spectrum. Ring-oxidated compounds are brown[9] in contrast to the blue or green appearance of the metal phthalocyanines investigated in this study. The following structural arrangements are consistent with the general formula above: (i) PcCr–O–O–CrPc (two phthalocyanine units are linked by a peroxo group), (ii) –O–Cr(Pc)–O–Cr(Pc)– or



(Phthalocyanine units are linked by oxygen bridges involving Cr–O–Cr single bonds. The first example describes a polymeric structure.), (iii) PcCr═O (the oxygen atom is double-bonded to a tetravalent chromium ion). If described by (i), two oxygen-dependent vibrations are expected in the IR spectrum of the oxidation product involving the O–O and the Cr–O stretches. Both vibrations should appear in the 800–1200 and 300–500-cm^{-1} spectral range, respectively.[10]

If the band at 1041 cm^{-1} is assigned to a O–O stretching vibration, three discernible bands are expected, originating from the $^{16}O-^{16}O$, $^{16}O-^{18}O$, and $^{18}O-^{18}O$ stretching vibrations. However, the number and position of the oxygen-dependent vibrations observed in the IR and Raman spectra marked by their shift on isotopic substitution clearly indicate that this is not the case.

Similar arguments rule out formulation (ii). The Cr–O–Cr bridge is characterized by the Cr–O single bond and hence has a stretching frequency expected to be around 400 cm^{-1}. No oxygen-dependent vibrations were observed below 1000 cm^{-1}.

The strong intensity of the band at 1041 cm^{-1} in the Raman spectrum suggests a stretching type vibration. The isotopic shift of such a vibration, calculated for Cr–O on substitution of ^{16}O by ^{18}O, is 45 cm^{-1} which compares well with the experimentally observed shift of 44 cm^{-1}. This result supports formulation (iii) where the oxygen atom is attached to the chromium ion by a double bond. The frequency of 1041 cm^{-1} is expected to be in this range since in the series of oxophthalocyaninato complexes of the first transition row, the metal–oxygen stretching frequency increases with increasing atomic number. This is evident from an inspection of Table I where some of the frequencies reported in the literature are summarized and compared to the value found in this work.

The magnetic moment (spin-only value) of the tetravalent ion in (iii) (d^2 configuration) is 2.9 μ_B in the high-spin case. The experimental value, however, measured at room temperature, is 1.9 μ_B and is temperature dependent pointing to the presence of antiferromagnetic coupling between the chromium ions. It could easily occur, for example, via the oxo bridges of structure (ii).

Structure (ii), however, seems to be less likely in view of the vibrational band at 1041 cm^{-1}. The Cr–O–Cr bridge in (ii) is characterized by the Cr–O single bond and hence has a stretching frequency expected to be below 1000 cm^{-1}. The Mn–O–Mn vibration in $(MnPc)_2O$, for example, was assigned to be at 860 cm^{-1}.[15] However, no oxygen-dependent vibrations were observed below 1000 cm^{-1} in the spectra of CrPcO. In addition, a polymeric structure is not in agreement with the large expansion of the lattice on oxidation.[4]

Coupling between chromium atoms is also possible in structure (iii) if a dimeric formulation is considered. In this case, one CrPcO molecule is closely placed on top of another, thus forming a double sheet with the oxygen atoms protruding on the outside. In this way two chromium atoms are sufficiently close to enable interaction between the atoms, and, at the same time, sufficient space is provided between neighboring dimers in the lattice to account for the large increase of the unit cell volume on oxidation. The strong Cr–Cr interaction may prevent further oxidation. For instance, α-$Cr^{II}Pc$ is stable against molecular oxygen, in contrast to the less closely packed β modification.[4]

In transition-metal porphyrins stabilization of lower valencies can also be accomplished by axial coordination of pyridine bases.[17] Hence it is not surprising that in $Cr^{II}pyTPP$ (TPP = tetraphenylporphyrin) the chromium is oxidized only to Cr(III) by molecular oxygen.[18,19]

In the dimeric structure of (iii) where two CrPcO sheets are closely placed together, strong interaction of the adjacent phthalocyanine rings is expected. Such an interaction is indicated by the pronounced red shift observed in the electronic spectrum of CrPcO and additional bands in the IR spectrum when compared to that of β-$Cr^{II}Pc$. The band at 1510 cm^{-1}, for example, is also present in $SnPc_2$ (1508 cm^{-1}) but is missing in the spectra of SnPc and $SnPcX_2$ (X = F, Cl, Br, OH).[16]

In view of these results we tentatively formulate the oxidation product of β-$Cr^{II}Pc$ by molecular oxygen as an oxo(phthalocyaninato)chromium(IV) dimer. During the reaction of O_2 with $Cr^{II}Pc$, the oxygen molecule is split, and the oxygen atoms form double bonds to one chromium atom each. The chromium is thereby oxidized to the oxidation state IV.

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Registry No. β-$Cr^{II}Pc$, 14285-60-0; CrPcO, 68682-95-1; O_2, 7782-44-7.

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