

Synthesis and X-ray Data of a Stable in Air Crystalline Modification of Chromium(II) Phthalocyanine (Cr- α -Pc)

C. Ercolani, C. Neri and P. Porta

Received September 20, 1967

When the β modification of chromium(II) phthalocyanine is sublimed under specified conditions, a purple-red microcrystalline product is obtained which, unlike the starting compound, does not react with air. This sublimate has been identified as the α form of chromium(II) phthalocyanine by its analytical data and IR spectrum as well as on the basis of its isomorphism with the α forms of iron(II) and cobalt(II) phthalocyanine. The different stability in air of the two forms of chromium(II) phthalocyanine can be reasonably explained on the basis of their different crystal features.

Introduction

The synthesis and properties of chromium(II)phthalocyanine in its β -form (denoted as Cr- β -Pc)¹ has been described in a recent paper.² This is a purple-red crystalline compound, unstable in air, whose X-ray data have shown it to be isomorphous with the other M- β -Pc compounds, exhaustively studied by Robertson.^{3,4,5} When Cr- β -Pc is exposed to air, it transforms into a red-bluish compound which contains oxygen in a quantity corresponding to one atom per molecule. The uptake of the oxygen atom has been supposed to involve an oxidation of the chromium atom and the probable formula Cr-Pc-OH has been attributed to the oxidation product formed. Previously Elvidge and Lever⁶ reported the synthesis of a chromium(II)-phthalocyanine (Cr-Pc) and of a chromium(III)-phthalocyanine (Cr-Pc-OH), the properties of both of which, including magnetic moments and X-ray data, precluded any possibility to identify them with the above-mentioned compounds. Very recently Meloni *et al.*⁷ described a new method for the synthesis of Cr-Pc. Apparently this form of Cr-Pc coincides with Cr- β -Pc, as it readily transforms, by exposure to air, into a product the elemental analysis of which supports the formula Cr-Pc-OH.⁸

In the present paper we report the synthesis and properties of another type of Cr-Pc, identified as an α form (Cr- α -Pc), a crystalline modification already known for several other metal-phthalocyanines. X-ray data of Cr- α -Pc, together with those of Cr- β -Pc, Cr-Pc-OH and of the α forms of Fe-Pc and Co-Pc are also reported and discussed in order to show the structural difference of Cr- α -Pc from the corresponding β form, its similarity with the α forms of other metal-phthalocyanines prepared in the usual way, and the main crystal features of Cr-Pc-OH.

Experimental Section

Materials. Cr- β -Pc and Cr- α -Pc. The Cr- β -Pc was prepared from chromium(II) acetate and phthalodinitrile.² A sample of Cr- β -Pc was placed in a quartz tube sealed at one end, and a sodium chloride plate was suspended above it. The tube was placed horizontally in an oven, a vacuum of 10^{-2} - 10^{-3} mm was applied and the temperature was then brought to 300-350°C. A purple red sublimate, A, then identified as Cr- α -Pc, condenses on the plate at a temperature roughly estimated to be 300°C. It consisted of a uniform microcrystalline layer (10-15 mg) which differs from Cr- β -Pc in that it is stable to air. It remains purple-red even after prolonged exposure to air and no change in its analytical data is observed. (Calcd: C, 68.08%; H, 2.86%. Found: C, 67.70%; H, 2.68%). When A is heated for three or four hours at 270°-280°C under vacuum (10^{-2} - 10^{-3} mm) it remains completely unchanged, but it is transformed into Cr- β -Pc when sublimed at 400°C and condensed at slightly lower temperature. A sample of the sublimate which condensed on the NaCl plate was used directly to obtain the infrared spectrum, in the region 4000-650 cm^{-1} .

Cr-Pc-OH have been prepared as described in ².

Fe- α -Pc and Co- α -Pc. These two metal phthalocyanines were obtained from the corresponding β forms, prepared according to the method described by Linstead *et al.*⁹ The β metal phthalocyanines were dissolved in conc. H₂SO₄, and the solution was poured onto ice, and the α form precipitated. It was filtered

(1) Pc stands for the phthalocyanine anion, C₂₂H₁₆N₈⁻, and β indicates the crystalline modification.

(2) C. Ercolani, *Ric. Sci.*, 36, 975 (1966), (in English).

(3) J. M. Robertson, *J. Chem. Soc.*, 615 (1935).

(4) R. P. Linstead and J. M. Robertson, *J. Chem. Soc.*, 219 (1937).

(5) J. M. Robertson and L. Woodward, *J. Chem. Soc.*, 219 (1937).

(6) J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.*, 1257 (1961).

(7) E. G. Meloni, L. R. Ocone and B. P. Block, *Inorg. Chemistry*, 424 (1967).

(8) A. sample of Cr-Pc-OH, kindly provided by Dr. B. P. Block (7), has shown to have an X-ray powder pattern perfectly identical to that of the Cr-Pc-OH obtained by exposure to air of Cr- β -Pc (2).

(9) P. A. Barrett, C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

off, washed with water and then ethanol, and dried under vacuum. (Fe- α -Pc requires: C, 67.61%; H, 2.84%. Found: C, 67.46%; H, 2.81%. Co- α -Pc requires: C, 67.24%; H, 2.82%. Found: C, 67.00%; H, 2.57%). From now on we will indicate these metastable forms as Fe- α II-Pc and Co- α II-Pc respectively, following the nomenclature used by Honigmann *et al.*¹⁰ For the α form of Cu-Pc (Cu- α II-Pc).

I.R. Spectra. The I.R. spectra were obtained with Beckmann IR7 spectrometer. The following absorption bands were observed on A: 1611 (m-s), 1586 (w), 1494 (s), 1476 (s), 1460 (m-w), 1416 (s), 1335 (vs), 1288 (vs), 1190 (w), 1166 (vs), 1120 (vs), 1087 (vs), 1066 (m), 1001 (vw), 945 (w), 901 (s), 881 (vw), 867 (vw), 803 (vw), 769 (w), 754 (vs), 727-722 (vs).

X-Ray Spectra. The X-ray spectra were obtained on all samples with a Debye powder camera, 114.6 mm in diameter, using CuK α (Ni-filtered) radiation ($\lambda = 1.5418 \text{ \AA}$). The positions of the lines were read visually to an accuracy of 0.005 cm, using a Norelco measuring device and the intensities were estimated visually. The indices of the diffraction lines were assigned according to Ito's method.¹¹ The same wavelength of CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) was used in the calculations. The agreement between the experimental and calculated d values is excellent, their differences being not larger than 1%.

X-ray powder spectra taken on all the above-mentioned compounds are reported in Table I and the results of their interpretation are summarised in Table

II. It is worth noting that the experimental values of the density for Fe- α II-Pc, Co- α II-Pc and Cr-Pc-OH, picnometrically determined, agree fairly well with the values of the densities calculated on the basis of the cell parameters. It was not possible to measure the density neither of Cr- β -Pc, owing to its instability in air, nor of A, because the method used for its preparation provides too small quantities of the product (10-15 mgs).

Results and Discussion

The infrared spectrum of A, taken in the region 4,000-650 cm^{-1} , shows that all the bands characteristic of the β form² are absent. A comparison of the spectrum of A with those of the α forms of several metal phthalocyanines studied by Sidorov and Kotlyar.¹² is indicative but does not lead to conclude unequivocally that compound A is a metastable form (*i.e.*, an α form) of Cr-Pc. As it is known¹² in the IR-region the α forms have only very weak characteristic absorptions, which are therefore of limited diagnostic value. More significant is the frequency of the very intense band which is present in both the α and the β forms and is assigned to the out-of-plane bending vibration of the C-H bonds in the aromatic rings. This absorption appears in the range 720-730 cm^{-1} for the α forms, and is found at slightly higher frequencies in the β forms. Compound A does indeed have this band at 725 cm^{-1} , while for Cr- β -Pc the band appears at 733 cm^{-1} .

A comparison of the powder spectra reported in Table I shows that A has a spectrum very similar to

Table I.

Fe- α -Pc				Co- α -Pc				A (Cr- α -Pc)				Cr- β -Pc		Cr-Pc-OH			
I ^a	d _{exp.}	d _{calcd.}	hkl	I ^a	d _{exp.}	d _{calcd.}	hkl	I ^a	d _{exp.}	d _{calcd.}	hkl	I ^a	d _{exp.}	I ^a	d _{exp.}	d _{calcd.}	hkl
vs	12.70	12.80	200	vs	12.40	12.70	200	vs	12.55	12.60	200	vs	12.41	vs	12.72	12.82	001
		12.60	002			12.31	002			12.50	002						
m	9.00	8.99	202	m	8.79	8.82	202	m	8.93	8.91	202	vs	9.59	s	7.02	7.05	201
vvw	6.37	6.37	400					w	6.30	6.31	400	w	8.41	m	6.41	6.41	002
s	5.69	5.69	402	m	5.60	5.64	402	s	5.66	5.64	402	m	7.07	m	5.97	5.98	010
vw	4.03	4.03	602					v	3.99	3.99	602	vw	5.72	s	5.13	5.16	301
s	3.71	3.71	111	w	3.69	3.68	111	m	3.71	3.70	111	w	4.89			5.11	202
s	3.58	3.59	112	w	3.56	3.56	112	s	3.56	3.56	112	m	4.77	s	4.91	4.88	210
								s	3.43	3.43	310	m	4.17	w	4.50	4.56	211
				m	3.34	3.32	312	m	3.29	3.31	312	w	3.86	w	4.27	4.27	003
vw	3.21	3.19	800	s	3.20	3.18	800	vw	3.16	3.16	800	s	3.75	vs	3.81	3.81	203
vw	3.10	3.09	802					w	3.06	3.06	802	w	3.52	vw	3.53	3.53	402
vw	3.00	2.99	606	v	2.93	2.94	606	w	2.97	2.96	606	s	3.38	m	3.15	3.15	104
vw	2.88	2.85	315	v	2.82	2.82	315	w	2.84	2.83	315	m	3.18	vw	2.99	2.99	020
				v	2.53	2.55	712	v	2.69	2.71	514	m	2.93	vw	2.77	2.75	221
vw	2.54	2.55	712	v	2.53	2.55	712	vw	2.53	2.54	712	w	2.77	w	2.58	2.58	602
								vw	2.49	2.48	1002	w	2.71	vw	2.06	2.06	620
vw	2.37	2.37	1004					vw	2.34	2.34	1004	vw	2.34	vw	1.73	1.73	820
v	2.20	2.22	912					vw	2.21	2.21	912	vw	2.29				
v	2.09	2.10	0012					v	2.08	2.08	0012	vw	2.23				
vw	2.00	2.01	718					w	2.00	2.00	718	vw	2.15				
				v	1.75	1.76	423	v	1.78	1.79	0014	vw	2.09				
				v	1.66	1.65	426	v	1.75	1.76	423	w	1.92				
								v	1.72	1.72	620	vw	1.80				
								v	1.66	1.65	426	vw	1.70				
								v	1.54	1.54	825	w	1.66				
								v	1.42	1.42	1026	vw	1.60				

^a vs = verystrong; s = strong; m = medium; w = weak; vw = veryweak; vvw = veryveryweak.

(10) B. Honigmann, H. Lennè and R. Schrodol, *Z. Krist.*, **122**, 185 (1965).

(11) T. Ito, X-ray Studies on Polymorphism, Maruzen Co., Ltd., Tokyo, 187 (1950).

(12) A. N. Sidorov and I. P. Kotlyar, *Optika i Spektroskopiya*, **11**, 175 (1961).

those of Fe- α II-Pc and Co- α II-Pc, whereas it is completely different from those of Cr- β -Pc and Cr-Pc-OH. The occurrence of a greater number of diffraction lines in the spectrum of A, with respect to those of Fe- α II-Pc and Co- α II-Pc indicates a higher degree of crystallinity probably due to the different methods of preparation.

Despite the small differences found in the powder spectra of A, Fe- α II-Pc and Co- α II-Pc, consisting in the lack of some reflexions in the spectra of the latter two compounds and in the different intensity of some other reflexions, the calculations by Ito's method performed on the three above-mentioned spectra led to the same interpretation in terms of unit-cell data (which exhibit only very small differences in their dimensions) and of crystal system and space group, indicating that A is isomorphous with Fe- α II-Pc and Co- α II-Pc, and hence that A is also a metastable crystalline modification, which will be hereafter indicated as Cr- α -Pc. As regards the crystal system and the relative space group, to which Cr- α -Pc, Fe- α II-Pc and Co- α II-Pc belong, an uncertainty exists mainly due to the poor resolution of the reflexions as given by the powder method. In fact, if the crystals are monoclinic with a β angle slightly different from 90° it is not possible to discriminate between positive and negative reflexions of the same class in the X-ray powder patterns. Therefore, considering the number of molecules contained in the unit cell, as deduced from the calculated density, and the systematic absences, the most probable space groups are the orthorhombic C_{cc2} (if $\beta = 90^\circ$) or alternatively the monoclinic $C_{2/c}$ (if $\beta \cong 90^\circ$).

From the evidence presented it can be concluded that, when Cr- β -Pc is sublimed under specified conditions, it is transformed to Cr- α -Pc, so that chromium(II)phthalocyanine, like many other metal phthalocyanines, can occur in at least two crystalline modifications. It may be mentioned here that X-ray data and stability to air rule out any possibility also for Cr- α -Pc to be identified with the Cr-Pc described by other authors.⁶

It is worthwhile to point out that of all the metal phthalocyanines for which both an α and a β form are known, Cr-Pc is the only one to have a form stable in air (α) and a form sensitive to air (β). On the assumption that the chromium atom in the isolated molecule would be sensitive to oxidation by air we must conclude that the different behaviour of the metal must be in some way associated with the different arrangement of the molecules in the crystal lattice of the two polymorphs.

X-ray studies^{3,4,5} have shown that the stacking of the molecules in the crystal of the β form of several metal phthalocyanines is of the type reported in Figure 1a. The only report of a crystal structure of an α form has been that published on Pt-Pc by Robertson and Woodward,¹³ who however were not aware of the existence of polymorphs in the class of the phthalocyanine compounds. B. Honigmann *et al.*¹⁰ have recently found that Cu- α II-Pc is isomorphous with Pt- α -Pc, which has a structure of the type shown in Figure 1b. It can be seen from the figure that the difference in the polymorphs lies essentially in the orientation of the

molecules with respect to the crystallographic axes, whereas the perpendicular distance between the planes of the molecules remains, to a first approximation, the same. The inclination of the molecules in the α forms makes them more superimposed one to the other than they are in the β forms, so that atoms of the same nature, which occupy exactly equivalent positions in neighbouring molecules, approach more than in the β forms. The distance which separates the metal atoms (in the direction coincident with the b axis), for example, comes to be about 3.8 Å for the α form, much shorter than that found in the β form (4.7-4.8 Å). Thus, for the α forms it can not be excluded that the metal atom of a certain molecule feels the influence of the metal atoms lying in adjacent molecules above and below the molecular planes, resulting in some metal-metal interaction.

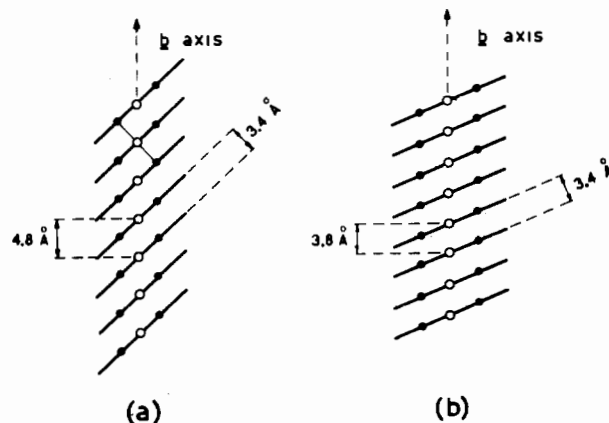


Figure 1. Schematic representation of the arrangement of the molecules in the β (a) and α (b) polymorphs of the metal phthalocyanines.

On the basis of the above considerations, schematically represented in Figure 1, the shorter distance between the metal atoms, responsible of the probable metal-metal interaction, and the different stacking of the molecules (which makes the metal more protected from external agents) can be suggested as two factors both predominantly influencing the different behaviour in air of the Cr- α -Pc with respect to Cr- β -Pc.

It should be emphasized that the two metastable forms of Copper phthalocyanine studied by Honigmann,¹⁰ *i.e.*, Cu- α I-Pc and Cu- α II-Pc (previously denoted α and γ), obtained on slightly varying the experimental procedure, show very similar crystal features. Crystal data also show that the same similarity is observed for Fe- α II-Pc and Co- α II-Pc studied by us and the two corresponding metastable forms reported by Ashida,¹⁴ even though these compounds are prepared using completely different methods. It seems possible to deduce from the above observations that the existence of several crystalline modifications for each metal phthalocyanine can be

(13) J. M. Robertson and L. Woodward, *J. Chem. Soc.*, 36 (1940).

(14) M. Ashida, N. Uyeda and E. Suito, *Bull. Chem. Soc. Japan*, 39, 2616 (1966).

Table II.

Samples	a(Å)	b(Å)	c(Å)	V(Å ³)	d _{calcd.}	d _{exp.}	n	M.W.	β
Fe-α-Pc	25.5±0.1	3.77±0.02	25.2±0.1	2425	1.56	1.59	4	568	90°
Co-α-Pc	25.4±0.1	3.77±0.02	24.6±0.1	2358	1.60	1.60	4	571	90°
Cr-α-Pc	25.3±0.1	3.76±0.02	25.0±0.1	2374	1.58		4	564.5	90°
Cr-β-Pc	19.7±0.1	4.85±0.02	14.8±0.1	1225	1.53		2	564.5	120°
Cr-Pc-OH	16.9±0.1	5.98±0.02	12.8±0.1	1297	1.49	1.47	2	583	90°

seen as follows: the β form is the thermally more stable one and is characterized by a well defined and peculiar disposition of the molecules in the crystal lattice; on the other hand more than one metastable form can exist, the probability of formation being highly dependent on the experimental conditions used. However, on the basis of the data collected so far, the crystallographic evidence suggests that these metastable forms have practically identical unit cell parameters which

probably corresponds to a slightly different arrangement of the molecules in the crystal.

Table II also provides some information about the oxidation product of Cr-β-Pc. It can be seen from the results in the Table II that in the formation of Cr-Pc-OH from Cr-β-Pc a large expansion of the cell volume occurs; particularly, the increase of the *b* axis by about 1.1 Å appears to account for the introduction of the OH group on the metal.