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Synthesis and Structural Characterization of Integrally Oxidized, Metal-Free Phthalocyanine Compounds: $[H_2(pc)][IBr_2]$ and $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$

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The first integrally oxidized metal-free phthalocyanine compounds have been synthesized by chemical oxidation. Phthalocyanine (H_2(pc), pc = phthalocyaninato) was oxidized with IBr to afford the compounds $[H_2(pc)][IBr_2]$ (**1**) and $[H_2(pc)]_2[IBr_2]BrAC_{10}H_7Br$ (**2**), whose structures were determined by means of single-crystal X-ray diffraction methods: $[H_2(pc)][IBr_2]$, $P2_1/c$, $a = 8.0272(9)$ Å, $b = 21.258(2)$ Å, $c = 18.1439(2)$ Å, $\beta = 113.975(2)°$, $V = 2828.8(5)$ Å^3, $T = 153$ K, $Z = 4$; $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$, $P\bar{1}$, $a = 8.4724(6)$ Å, $b = 13.5794(10)$ Å, $c = 13.8403(10)$ Å, $\alpha = 90.854(1)°$, $\beta = 103.417(1)°$, $\gamma = 97.049(1)$E°, $V = 1535.61(19)$ Å^3, $T = 153$ K, $Z = 1$. The extended structure of $[H_2(pc)][IBr_2]$ comprises slipped columns of pc rings stacked along the *a* axis in adjacent columns at ~70° to one another. IBr_2^- ions occupy the interstitial columns. The extended structure of $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ comprises slant stacks of pc rings along the crystallographic *a* axis with IBr_2^- ions, Br^- ions, and disordered 1-bromonaphthalene molecules in the adjacent, parallel columns. The overall reaction for the formation of **1** is $2H_2(pc) + 4IBr \rightarrow 2[H_2(pc)][IBr_2] + I_2$, and the overall reaction for the formation of **2** (not including solvent) is $2H_2(pc) + 3IBr \rightarrow [H_2(pc)]_2Br[IBr_2] + I_2$.

Introduction

The discovery of the molecular metal H_2(pc)I[1] proved that oxidized phthalocyanine (pc) compounds need no central metal atom for metallic conduction. Through chemical[1] and electrochemical[2] means, several partially oxidized H_2(pc), H_2(tatbp) (tatbp = triazatetrabenzporphyrinato, $[C_{33}H_{16}N_7]^{2-}$), and H_2(tbp) (tbp = 5,10,15,20-tetrabenzporphyrinato, $[C_{36}H_{16}N_4]^{2-}$) compounds have been synthesized and characterized. Although some integrally oxidized M(pc) (M = metal) compounds have been reported,[3,4] no integrally oxidized H_2(pc) compounds have been described.

We report here the syntheses and structural characterization of two integrally oxidized H_2(pc) compounds, namely $[H_2(pc)][IBr_2]$ (**1**) and $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ (**2**). The structures of these compounds differ from those of conductors such as H_2(pc)I in that they possess slipped, segregated stacks of $[H_2(pc)]^+$ ions rather than uniform columns perpendicular to the stacking axis. The pc planes of $[H_2(pc)][IBr_2]$ in adjacent stacks adopt the herringbone configuration common for neutral M(pc) structures. Those in $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ comprise a slant stack along the crystallographic *a* axis.

Experimental Section

Materials and Equipment. The H_2(pc) starting material was synthesized and purified by a literature method.[5] A diffusion tube was rigorously cleaned and dried at 120 °C before use. 1-Bromonaphthalene was filtered through activated basic alumina, stirred with CaH_2 under vacuum, and then vacuum distilled. IBr (99%) was purchased from Alfa-Aesar and used without further purification.

Syntheses. Single crystals of both $[H_2(pc)][IBr_2]$ (**1**) and $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ (**2**) grew in a diffusion tube that consisted of two compartments separated by a glass frit. The tube was

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protected from light and fitted with septa and balloons of air. The temperature of the hot arm was maintained at 160(6) °C; the cold arm was not heated. Each arm contained 15 mL of 1-bromonaphthalene. IBr (0.44 g, 2.1 mmol) was added to the cold arm, and $H_2(pc)$ (0.0198 g, 0.04 mmol) was added to the hot arm. Dark blue, needle-shaped crystals of **1** and dark maroon, thick platelike crystals of **2** grew in the hot arm of the apparatus. The crystals were separated manually, and the determination of the I:Br ratio of each crystal by energy dispersive spectroscopy provided a check of the visual identification. The I:Br ratios found were 0.34:0.66 for $[H_2(pc)][IBr_2]$ (**1**) (expected ratio: 0.33:0.67) and 0.17:0.83 for $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ (**2**) (expected ratio: 0.20:0.80). Insufficient material was available for CHN analysis. Raman: 163 cm^{-1} (expected[6] value for IBr_2^-: 168 cm^{-1}). Both compounds are air- and light-stable.

General Crystallographic Details. X-ray diffraction data from single crystals of **1** and **2** were collected on a Bruker SMART 1000 CCD diffractometer with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data for **1** were collected by an ω scan of 0.3° in groups of 606 frames each at φ settings of 0°, 90°, 180°, and 270°, followed by 50 more frames at $\varphi = 0°$ to determine the extent of possible crystal decay. Data for **2** were collected by an ω scan of 0.25° in groups of 727 frames each at φ settings of 0°, 90°, 180°, and 270°, followed by 50 more frames at $\varphi = 0°$. The exposure times for both collections were 15 s/frame. Intensity data were collected with the program SMART.[7] Cell refinement and data reduction were carried out with the use of the program SAINT,[7] face-indexed absorption corrections were carried out with the program XPREP,[8] and the frame variations were further corrected with the use of the program SADABS.[8] The structures were solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL of the SHELXTL-PC suite of programs.[8]

The $C_{10}H_7Br$ solvent in **2** is disordered and lies on an inversion center. To account for the observed pattern of electron density, the solvent molecule was modeled with a half-occupied, idealized C_{10} skeleton; a half-occupied Br atom was allowed to refine independently of the naphthalene group.

The final refinements for **1** and **2** included anisotropic displacement parameters for all atoms except the C atoms in the solvent of **2**. The positions of the hydrogen atoms were fixed by geometry ($C-H = 0.95$ Å, $N-H = 0.88$ Å) and were not varied. Further details are provided in Table 1 and in the Supporting Information.

Results and Discussion

Syntheses. The reaction of $H_2(pc)$ and IBr in 1-bromonaphthalene affords crystals of both $[H_2(pc)][IBr_2]$ (**1**) and $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ (**2**). The oxidation of $H_2(pc)$ ($E_0 = 714(4)$ mV) by I_2 is known,[1] and IBr is a stronger oxidant than I_2.[9] The IBr_2^- ion is usually synthesized by the reaction of I^- with Br_2.[10] Here, though, the formation of the IBr_2^- ion may be the result of the heterolytic dissociation of IBr[9]

$$3IBr \rightleftharpoons I_2Br^+ + IBr_2^-$$

or of a series of reactions, such as

$$2IBr + 2H_2(pc) \rightarrow 2[H_2(pc)]^+ + I_2 + 2Br^-$$

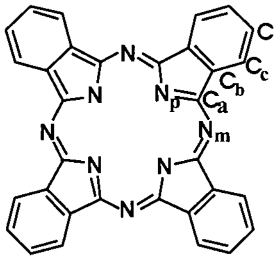
$$Br^- + IBr \rightarrow IBr_2^-$$

Table 1. Crystallographic Data for $[H_2(pc)][IBr_2]$ (**1**) and $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ (**2**)

param	$[H_2(pc)][IBr_2]$	$[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$
empirical formula	$C_{32}H_{18}Br_2IN_8$	$C_{74}H_{43}Br_4IN_{16}$
fw	801.26	1602.78
a, Å	8.0272(9)	8.4724(6)
b, Å	21.258(2)	13.5794(10)
c, Å	18.143(2)	13.8403(10)
α, deg	90	90.854(1)
β, deg	113.975(2)	103.417(1)
γ, deg	90	97.049(1)
V, Å^3	2828.8(5)	1535.61(19)
T, K	153	153
Z	4	1
d_{calc}, g/cm^3	1.881	1.733
space group	$P2_1/c$	$P\bar{1}$
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	39.97	31.86
R_1,[a] wR_2[b]	0.0469, 0.1179	0.0409, 0.1164

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma F_o^2$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for all data; $w^{-1} = \sigma^2(F_o^2) + (pF_o^2)^2$ for $F_o^2 \geq 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$; $p = 0.04$ for **1** and 0.06 for **2**.

Table 2. Average Bond Lengths (Å) and Angles (deg) for $[H_2(pc)][IBr_2]$ (**1**) and $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ (**2**)[a]



bond or angle	**1**	**2**
I−Br	2.7087(15)	2.6986(4)
N_p-C_a	1.368(14)	1.370(11)
N_m-C_a	1.335(15)	1.332(16)
C_a-C_b	1.453(7)	1.454(5)
C_b-C_b	1.401(7)	1.402(4)
C_b-C_c	1.391(7)	1.396(5)
C_c-C_d	1.387(8)	1.389(5)
C_d-C_d	1.390(9)	1.399(7)
C−Br (solvent)		1.881(3)
Br−I−Br	179.28(3)	180
$C_a-N_p-C_a$	108.4(1.1)	108.5(1.2)
$C_a-N_m-C_a$	124.1(1.8)	124(2)
$N_m-C_a-N_p$	127.2(1.8)	127(2)
$N_p-C_a-C_b$	109.4(1.3)	109.3(1.3)
$N_m-C_a-C_b$	123.4(1.1)	123.7(1.7)
$C_a-C_b-C_c$	132.3(1.2)	132.2(1.5)
$C_a-C_b-C_b$	106.3(9)	106.4(1.0)
$C_b-C_b-C_c$	121.4(6)	121.3(6)
$C_b-C_c-C_d$	116.9(6)	117.1(3)
$C_c-C_d-C_d$	121.7(7)	121.6(6)
C−C−Br (solvent)		120(14)

[a] The error estimate in parentheses of a given quantity is equal to the larger of the standard deviation of a single observation as estimated from the group or of the largest estimated standard deviation of a group member.

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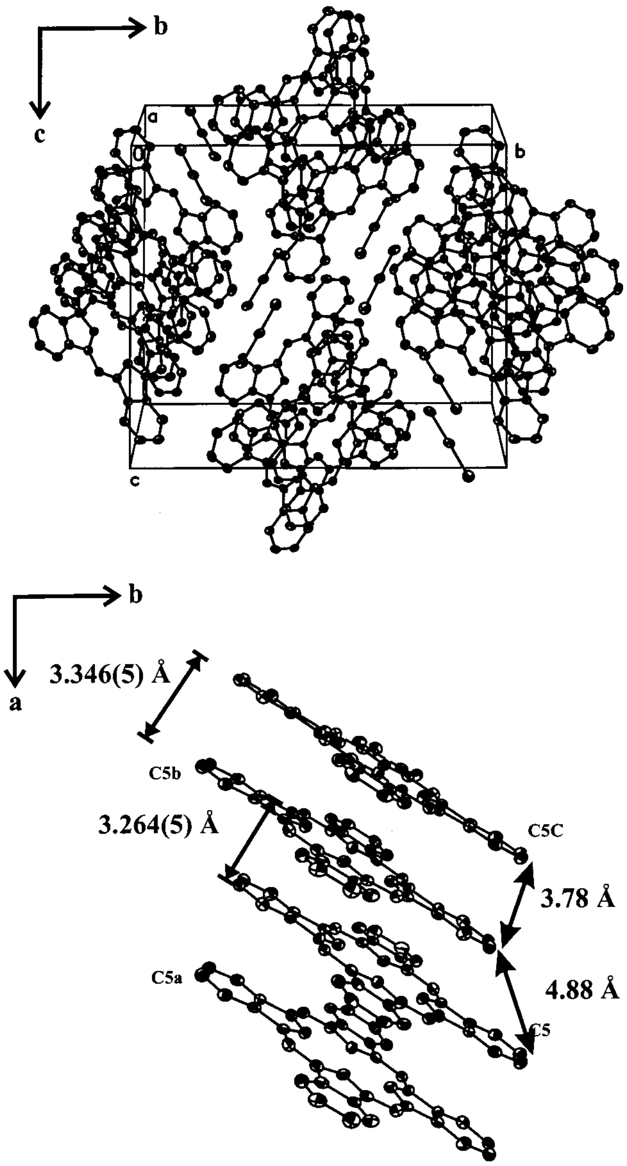

Figure 1. Views of $[H_2(pc)][IBr_2]$ (**1**).

The overall reaction for the formation of **1** is

$$2H_2(pc) + 4IBr \rightarrow 2[H_2(pc)][IBr_2] + I_2$$

and the overall reaction for the formation of **2** (not including solvent) is

$$2H_2(pc) + 3IBr \rightarrow [H_2(pc)]_2Br[IBr_2] + I_2$$

Crystal Structures. Bond lengths and angles for **1** and **2** are summarized in Table 2. The bond lengths in these oxidized pc systems are not significantly different from those in unoxidized pc systems, presumably because of the delocalized nature of the HOMO on the pc ring.[11]

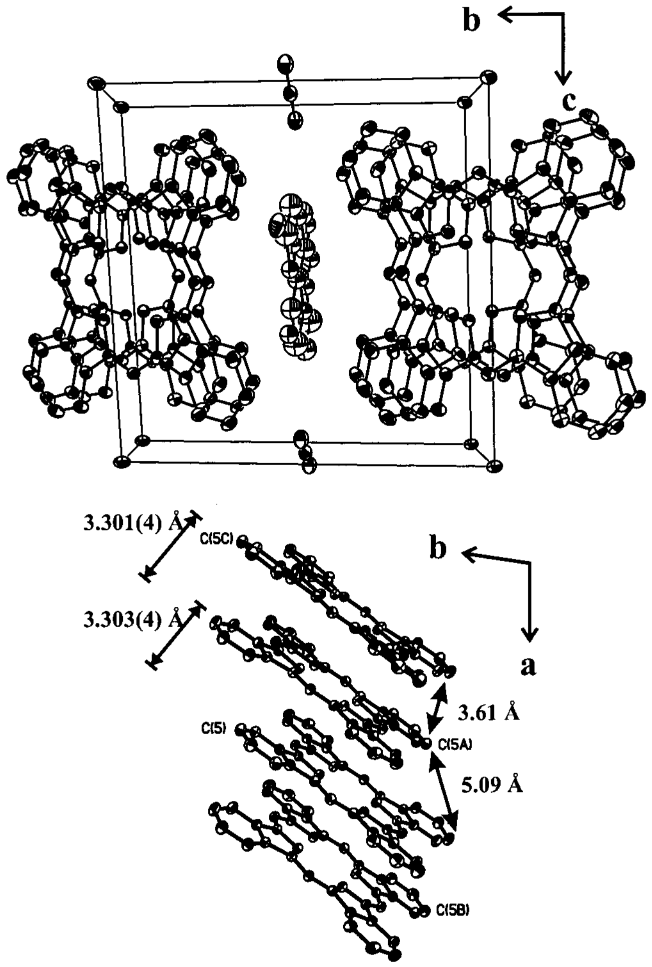

Figure 2. Views of $[H_2(pc)]_2[IBr_2]Br{\cdot}C_{10}H_7Br$ (**2**).

$[H_2(pc)][IBr_2]$ (1). The asymmetric unit of **1** contains one $[H_2(pc)]^+$ ring and one IBr_2^- group. The extended structure (depicted in Figure 1) comprises slipped columns of eclipsed pc rings stacked along the *a* axis with pc rings in adjacent columns (related by a glide plane) at ~70° to one another. The normal to the pc planes makes a ~35° angle with the *a* axis. IBr_2^- ions occupy the interstitial columns. The pattern of pc rings within a stack is ···A′ABB′···, with the pairs A and A′ as well as the pairs B and B′ related by a center of symmetry at 0, 0, 1/2 and A and B related by a center of symmetry at 1/2, 0, 1/2. The A−A′ and B−B′ interplanar distance (defined by the perpendicular distance between the least-squares planes of the 24-atom porphyrazine cores) is 3.346(5) Å; the distance between the centers is 3.78 Å. The interplanar distance between A and B is 3.264(5) Å, whereas the distance between the centers is 4.88 Å.

The bond lengths in the pc ring of **1** are normal for H_2-(pc).[12,13] The 24-atom core of the ring is flat, with an average deviation of 0.021(13) Å. The peripheral benzene rings are nearly in the plane of the core, the maximum deviation being 0.097(6) Å. The IBr_2^- ion is essentially linear, with an Br−I−Br angle of 179.28(3)°. The I−Br distances, 2.7076(8) and 2.7097(8) Å, are normal.[6,13]

This structure differs from that of the phthalocyanine/trihalide molecular metals (e.g., $[H_2(pc)]_3[I_3]$)[1,5] in several respects. The pc rings of $[H_2(pc)]_3[I_3]$ are crystallographically constrained to lie in the *aa* plane of their tetragonal unit cell, so they are strictly perpendicular to the stacking axis, which

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is also the unique axis. The two rings in the cell are not eclipsed but are rotated 40° relative to one another. They are evenly spaced, whereas the distances separating the eclipsed rings in **1** alternate, albeit only slightly (3.346(5) vs 3.264(5) Å). In this respect, the stacking in **1** resembles that found in neutral phthalocyanine compounds.[12] Yet another difference is the ordering of the trihalide anions—elongated displacement ellipsoids indicate that the I_3^- ion in [H_2(pc)]$_3$[I_3] is ordered within each column but disordered with respect to the anions in neighboring columns, whereas the IBr_2^- ions in **1** are well-ordered.

[H_2(pc)]$_2$[IBr_2]Br·$C_{10}H_7Br$ (2). The asymmetric unit of **2** contains one pc ring, half of an IBr_2^- ion at the 1/2, 0, 1/2 inversion center, and half of a Br^- ion at 0, 0, 0. The extended structure of **2** (depicted in Figure 2) comprises slant stacks of pc rings along the crystallographic *a* axis with IBr_2^- ions, Br^- ions, and disordered 1-bromonaphthalene molecules in the adjacent, parallel columns. The plane of the pc ring makes a ~39° angle to the *a* axis and (in contrast with **1**) is parallel to the rings in adjacent columns. The pattern of pc rings within a stack is essentially that seen in **1** and is again ···A′ABB′···, with the pairs A and A′ as well as the pairs B and B′ related by a center of symmetry at 0, 0, $^1/_2$ and A and B related by a center of symmetry at $^1/_2$, 0, $^1/_2$. The A′—A and B—B′ interplanar distance is 3.301(4) Å; the distance between the centers is 3.61 Å. The interplanar distance between A and B is 3.303(4) Å, whereas the distance between the centers is 5.09 Å. As in **1**, the pc rings within each stack are eclipsed.

The bond lengths in the pc ring of **2** are normal for H_2(pc). The 24-atom core of the ring is flat, with an average deviation of 0.018(17) Å. The peripheral benzene rings are distorted from planarity, with a maximum deviation of 0.280(4) Å. The linear IBr_2^- ion has a crystallographically imposed center of symmetry. The I—Br distance is 2.6986(4) Å.

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Supporting Information Available: X-ray crystallographic files in CIF format for [H_2(pc)][IBr_2] (**1**) and [H_2(pc)]$_2$[IBr_2]Br·$C_{10}H_7Br$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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