Data collection

Enraf–Nonius CAD-4 diffractometer	1004 observed reflections $[I > 3\sigma(I)]$
$\omega/2\theta$ scans	$R_{int} = 0.025$
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)	$\theta_{max} = 25°$ $h = 0 \to 17$ $k = 0 \to 11$
$T_{min} = 0.68$, $T_{max} = 0.82$	$l = -12 \to 9$
1093 measured reflections	3 standard reflections
1007 independent reflections	frequency: 60 min intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.01$
$R = 0.020$	$\Delta\rho_{max} = 0.19\,(2)$ e Å^{-3}
$wR = 0.025$	$\Delta\rho_{min} = -0.07\,(2)$ e Å^{-3}
$S = 0.389$	Atomic scattering factors
1004 reflections	from *International Tables*
119 parameters	*for X-ray Crystallography*
$w = 1/[\sigma^2(F) + 0.0004F^2 + 1]$	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Sn	0	1/4	0	2.445 (7)
Cl	0.23377 (7)	0.2433 (3)	0.1360 (1)	3.81 (2)
N	0	0.4305 (7)	$-1/2$	4.1 (2)
C1	0	0.4670 (7)	0	2.6 (1)
C2	0.0757 (4)	0.5402 (6)	-0.0102 (5)	3.3 (1)
C3	0.0748 (4)	0.6803 (6)	-0.0122 (5)	4.0 (1)
C4	0	0.751 (2)	0	4.4 (2)
C5	-0.0621 (3)	0.1451 (5)	-0.2199 (4)	2.6 (1)
C6	-0.1776 (4)	0.1804 (6)	-0.3865 (5)	3.2 (1)
C7	-0.2176 (4)	0.1150 (7)	-0.5311 (5)	4.1 (1)
C8	-0.1463 (4)	0.0117 (7)	-0.5128 (5)	4.7 (1)
C9	-0.0320 (4)	-0.0242 (6)	-0.3485 (5)	4.4 (1)
C10	0.0093 (4)	0.0428 (6)	-0.2051 (5)	3.7 (1)
C11	0.0915 (7)	0.344 (1)	-0.3486 (9)	9.9 (3)
C12	0.0621 (6)	0.5147 (9)	-0.5325 (8)	9.3 (2)

Table 2. *Selected geometric parameters* (Å, °)

Sn—Cl	2.598 (1)	C3—C4	1.38 (1)
Sn—Cl	2.144 (8)	C5—C6	1.392 (7)
Sn—C5	2.137 (5)	C5—C10	1.379 (8)
N—C11	1.46 (1)	C6—C7	1.392 (8)
N—C12	1.448 (9)	C7—C8	1.37 (1)
C1—C2	1.392 (7)	C8—C9	1.38 (1)
C2—C3	1.385 (8)	C9—C10	1.383 (8)
Cl—Sn—Cl^i	177.1 (2)	Sn—C1—C2	121.3 (4)
Cl—Sn—Cl	91.5 (1)	Sn—C1—C2^i	121.3 (4)
Cl—Sn—C5	88.4 (1)	C2—C1—C2	117.4 (7)
Cl—Sn—C5^i	90.2 (1)	C1—C2—C3	121.4 (6)
Cl^i—Sn—C1	91.5 (1)	C2—C3—C4	120 (1)
Cl^i—Sn—C5	90.2 (1)	C3—C4—C3	119 (2)
Cl^i—Sn—C5^i	88.4 (1)	Sn—C5—C6	120.2 (4)
Cl^i—Sn—C5^i	119.0 (1)	Sn—C5—C10	122.5 (4)
Cl—Sn—C5	119.0 (1)	C6—C5—C10	117.3 (5)
C5—Sn—C5^i	121.9 (3)	C5—C6—C7	120.7 (6)
C11—N—C11^{ii}	108 (1)	C6—C7—C8	120.9 (6)
C11—N—C12	107.1 (6)	C7—C8—C9	118.8 (6)
C11^{ii}—N—C12	107.1 (6)	C8—C9—C10	120.4 (6)
C12—N—C12^{ii}	110 (1)	C5—C10—C9	121.9 (6)

Symmetry codes: (i) $-x, y, -z$; (ii) $-x, y, -1 - z$.

Non-H atoms were refined anisotropically. H atoms were generated (C—H = 0.95 Å, $B = 5$ Å^2) and were allowed to ride on the parent C atoms.

References

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Harrison, P. G., Molloy, K., Phillips, R. B., Smith, P. J. & Crowe, A. J. (1978). *J. Organomet. Chem.* **160**, 421–434.

Holecek, J., Nadvornik, M., Handlir, K. & Lycka, A. (1983). *J. Organomet. Chem.* **241**, 177–184.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Tse, J. S., Lee, F. L. & Gabe, E. J. (1986). *Acta Cryst.* C42, 1876–1878.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A39, 158–166.

Wharf, I. & Simard, M. G. (1991). *Acta Cryst.* C47, 1605–1609.

Bis(phthalocyaninato)erbium (α1 Phase)

GUIDO OSTENDORP, JAN-PETER WERNER AND HEINER HOMBORG

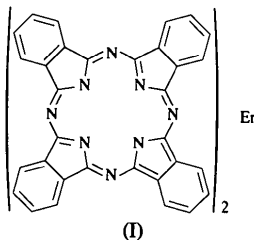*Institut für Anorganische Chemie, Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany*

Abstract

In the title compound, α1-bis(phthalocyaninato)erbium {α1-[Er(Pc)₂], where Pc = $C_{32}H_{16}N_8^{2-/-}$}, Er^{III} is eightfold coordinated by the isoindole N atoms (N$_{iso}$) of the two staggered (41.4°) saucer-shaped Pc ligands. The Er—N$_{iso}$ distance is 2.41 (1) Å; the height of the slightly distorted ErN₈ square antiprism is 2.74 Å. The [Er(Pc)₂] molecules are packed in columns parallel to the tetragonal c axis. In this new tetragonal α1 phase, the disposition of the metal ion is ordered and the Pc rings are structurally equivalent.

Comment

Partially oxidized ('doped') metallophthalocyanines like NiPcI are part of a class of molecular and polymeric materials exhibiting anisotropic metallic behaviour. Quasi-one-dimensional stacks of strongly interacting mainly planar macrocycles with weak interactions between adjacent stacks are formed, leading to the unusual charge-transport properties (Marks, 1990). On the other hand, oxidized metallophthalocyanines like LiPcI with the same architectural design but with a half-filled valence band may be of considerable interest as Mott–Hubbard isolators. Only a few examples of these semiconducting materials have been investigated in detail (Homborg & Teske, 1985; Turek et al., 1987; Maitrot et al., 1987; Guillaud, Al Sadoun, Maitrot, Simon & Bouvet, 1990). The present structure analysis is part of an investigation focused on the electrical properties of half-oxidized metallobisphthalocyanines combining the aforementioned two different ligand-oxidation states in the same molecular building block. The most suitable compounds for these investigations are bisphthalocyanines of tervalent rare earth metal ions {[R(Pc)$_2$], where R = rare earth metal ion, Pc = (C$_{32}$H$_{16}$N$_8$)$^{2-/-}$}, whose polymorphism has been the subject of much debate (Darovskikh, Tsytsenko, Frank-Kamenetskaya, Fundamenskii & Moskalev, 1984; Darovskikh, Frank-Kamenetskaya, Fundamenskii & Golubev, 1986; Darovskikh, Frank-Kamenetskaya & Fundamenskii, 1986; Darovsky, Wu, Lee & Sheu, 1991; de Cian, Moussavi, Fischer & Weiss, 1985; Safarpour Haghighi, Teske & Homborg, 1992). Recently, we found low dimensionality in tetragonal α-[Pr(Pc)$_2$]Br$_{1.5}$ (Safarpour Haghighi, Rath, Rotter & Homborg, 1993) showing a characteristic disorder with the disposition of the Pr ions along two incompletely filled crystallographic positions at a distance of $c/2$. Here we report on a further tetragonal modification (α1 phase) found for crystals of bis[29H,31H-phthalocyaninato-N^{29},N^{30},N^{31},N^{32}]erbium, α1-[Er(Pc)$_2$], (I), obtained by oxidation of [(C$_4$H$_9$)$_4$N][Er(Pc)$_2$].

(I)

The title compound crystallizes in the same space group ($P4/nnc$) as the Pr compound, with only slightly different cell parameters; it differs in the ordered disposition of the Er ions. The quasi-one-dimensional character of the structure along [001] is realised by infinite columns of the molecules, as shown by the

packing diagram viewed down the a axis in Fig. 1. The packing diagram viewed down the c axis in Fig. 2 shows that the channels formed by adjacent molecular stacks, being filled in most other cases with 'dopants' such as polyhalides, are considered to be empty, in accordance with the elemental analysis, although there is still a small residual electron density located within the channels, probably due to the presence of a very small amount of an as yet unknown impurity. Together with the relatively large e.s.d.'s for the fractional atomic z coordinates, this seems to indicate a characteristic disorder often found in crystals of this class of molecular (semi)conductors.
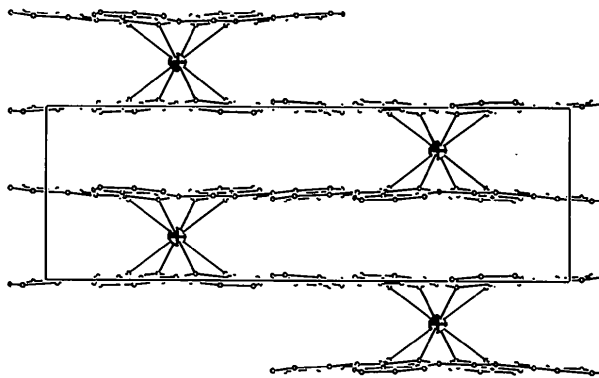

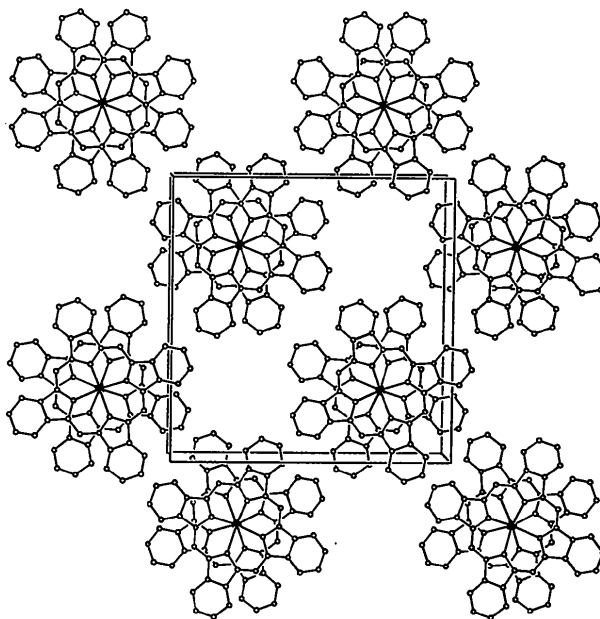Fig. 1. View of the crystal packing along the a axis. H atoms have been omitted for clarity.

Fig. 2. View of the crystal packing approximately along the c axis. H atoms have been omitted for clarity.
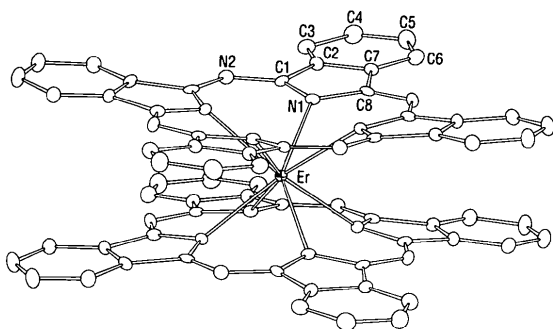
Fig. 3. *ORTEP*II (Johnson, 1976) view of the [Er(Pc)]$_2$ molecule. Displacement ellipsoids are drawn at the 75% probability level; H atoms have been omitted for clarity.

The molecular structure of α1-[Er(Pc)$_2$] (with the atomic labelling scheme) is presented in Fig. 3. The Er ion is on a special crystallographic position (2b) located inside the distorted square antiprism formed by the eight isoindole N atoms (N$_{iso}$ = N1 in Fig. 3) of the two staggered macrocycles (with a staggering angle of 41.4°). Both halves of the sandwich-like molecule are structurally equivalent, thus no integral formal oxidation number can be assigned to either of them. The eight Er—N$_{iso}$ bonds are equidistant [2.41 (1) Å] in contrast to, for instance, the strongly varying Nd—N distances (2.47–2.62 Å) in α-[NdPc^{2-}Pc$^-$] (Darovskikh, Frank-Kamenetskaya & Fundamenskii, 1986). The Er ion is in the centre of the square-antiprismatic coordination polyhedron, while in other known oxidized bisphthalocyanines, the R ion is displaced towards one of the ligands (probably the less oxidized one). The intramolecular distance between the squares formed by the four coordinating N$_{iso}$ atoms of each Pc ligand is 2.74 Å, much smaller than in α-[NdPc^{2-}Pc$^-$] (3.14 and 3.45 Å). This leads to a distinct alternation of short intra- and long intermolecular distances of the N$_{iso}$ planes oriented parallel to [110]. The Pc ligands are not planar but distorted in a saucer-shaped fashion, almost like in α-[NdPc^{2-}Pc$^-$], as indicated by the increase of the intramolecular distance between planes formed by, for example, the outermost C atoms C4 or C5. The result is the typical biconcave lense structure of the molecule as found in bisphthalocyanines of quadrivalent metal ions (Safarpour Haghighi, Teske & Homborg, 1992). The isoindole rings are rotated by *ca* 1.1° about axes lying in the plane of the Pc ligand. Although there is a distinct distortion of the Pc ligand, its molecular geometry (inner bond lengths and angles) compares closely with that of many other metallophthalocyanines (Mossoyan-Deneux, Benlian, Pierrot, Fournel & Sorbier, 1985).

Very recently, the crystal structures of the tetragonal α-phases of oxidized bisphthalocyanines of neodymium and praseodymium have been determined (Darovsky, Keserashvili, Harlow & Mutikainen, 1994), whose remarkable ratio of the $R(1)/R(2)$ site occupancy coeffi-

cients, approximately 1:2.7, is close to that found for α-[Pr(Pc)$_2$]Br$_{1.5}$ mentioned above. While we have shown a correlation between the content of tribromide and the population of the Pr(2) site, this has now been interpreted in terms of a disordered superstructure caused by the presence of a triple-decker complex [R_2(Pc)$_3$]. Although the syntheses of the less soluble [R_2(Pc)$_3$] complexes have been reported (Sokolova, Lomova, Morozov & Berezin, 1994; Takahashi, Itoh, Tomita, Nojima, Kasuga & Isa, 1993) and structures have been confirmed for porphyrines and mixed porphyrines/phthalocyanines (Chabach, Lachkar, de Cian, Fischer & Weiss, 1992), we exclude the presence of [R_2(Pc)$_3$] in our α-phases due to the synthetic procedure based on the very soluble precursor [(C$_4$H$_9$)$_4$N][R(Pc)$_2$].

Experimental

The title compound was prepared by anodic oxidation of a solution of [(C$_4$H$_9$)$_4$N][Er(Pc)$_2$] in dichloromethane in the presence of [(C$_4$H$_9$)$_4$N]PF$_6$ as supporting electrolyte.

Crystal data

[Er(C$_{32}$H$_{16}$N$_8$)$_2$]	Mo $K\alpha$ radiation
$M_r = 1192.32$	$\lambda = 0.71069$ Å
Tetragonal	Cell parameters from 25
$P4/nnc$	reflections
$a = 19.907 (5)$ Å	$\theta = 8.00–17.00°$
$c = 6.430 (5)$ Å	$\mu = 1.709$ mm^{-1}
$V = 2548.1 (22)$ Å^3	$T = 293 (2)$ K
$Z = 2$	Prismatic
$D_x = 1.554$ Mg m^{-3}	0.3 × 0.3 × 0.1 mm
	Black

Data collection

Enraf–Nonius CAD-4-Turbo four-circle diffractometer	$R_{int} = 0.0315$
	$\theta_{max} = 20.00°$
ω scans	$h = -19 \rightarrow 19$
Absorption correction:	$k = 0 \rightarrow 19$
ψ scans	$l = 0 \rightarrow 6$
$T_{min} = 0.96$, $T_{max} = 0.99$	3 standard reflections
2288 measured reflections	monitored every 300
605 independent reflections	reflections
462 observed reflections	frequency: 250 min
[$I > 2\sigma(I)$]	intensity decay: 10%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0478$	$\Delta\rho_{max} = 1.625$ e Å^{-3}
$wR(F^2) = 0.1831$	$\Delta\rho_{min} = -0.368$ e Å^{-3}
$S = 1.370$	Extinction correction: none
604 reflections	Atomic scattering factors
94 parameters	from *International Tables*
H atoms refined using a	*for Crystallography* (1992,
riding model	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.1055P)^2$	6.1.1.4)
$+ 37.1169P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Er	1/4	1/4	3/4	0.0311 (8)
N1	0.2851 (6)	0.3432 (6)	0.9631 (17)	0.036 (3)
N2	0.1808 (6)	0.4047 (6)	0.9883 (22)	0.042 (3)
C1	0.2479 (9)	0.4002 (7)	0.9824 (22)	0.039 (4)
C2	0.2890 (7)	0.4583 (7)	1.0024 (26)	0.038 (4)
C3	0.2766 (9)	0.5243 (8)	1.0124 (27)	0.053 (5)
C4	0.3322 (9)	0.5666 (9)	1.0289 (32)	0.066 (6)
C5	0.3963 (9)	0.5434 (8)	1.0333 (31)	0.063 (5)
C6	0.4077 (9)	0.4774 (8)	1.0206 (29)	0.056 (5)
C7	0.3546 (7)	0.4338 (7)	1.0054 (24)	0.040 (4)
C8	0.3502 (8)	0.3605 (8)	0.9846 (21)	0.040 (4)

Table 2. *Selected geometric parameters* (Å, °)

Er—N1	2.410 (11)	C2—C7	1.39 (2)
N1—C8	1.35 (2)	C3—C4	1.40 (2)
N1—C1	1.36 (2)	C4—C5	1.36 (2)
N2—C1	1.34 (2)	C5—C6	1.34 (2)
N2—C8^i	1.36 (2)	C6—C7	1.37 (2)
C1—C2	1.42 (2)	C7—C8	1.47 (2)
C2—C3	1.34 (2)		
N1^{ii}—Er—N1^i	79.4 (6)	C3—C2—C7	121.2 (14)
N1^{ii}—Er—N1^{iii}	71.1 (3)	C7—C2—C1	104.8 (12)
N1^i—Er—N1^{iii}	140.4 (6)	C2—C3—C4	116.6 (16)
N1^{ii}—Er—N1^{iv}	82.9 (6)	C5—C4—C3	122.9 (16)
N1^{iii}—Er—N1^v	110.7 (5)	C6—C5—C4	119.5 (17)
N1^{iv}—Er—N1^v	146.3 (6)	C5—C6—C7	119.7 (17)
C8—N1—C1	107.4 (13)	C6—C7—C2	120.1 (14)
C1—N2—C8^i	123.3 (12)	C2—C7—C8	107.0 (12)
N2—C1—N1	126.9 (14)	N1—C8—N2^{vi}	127.8 (13)
N1—C1—C2	111.9 (14)	N1—C8—C7	108.7 (14)

Symmetry codes: (i) $\frac{1}{2}-y,x,z$; (ii) $\frac{1}{2}-y,\frac{1}{2}-x,\frac{3}{2}-z$; (iii) $x,\frac{1}{2}-y,\frac{3}{2}-z$; (iv) $\frac{1}{2}-x,\frac{1}{2}-y,z$; (v) $\frac{1}{2}-x,y,\frac{3}{2}-z$; (vi) $y,\frac{1}{2}-x,z$.

Data collection: *CAD-4/PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4/PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

References

Chabach, D., Lachkar, M., de Cian, A., Fischer, J. & Weiss, R. (1992). *New J. Chem.* **16**, 431–433, and references therein.

Cian, A. de, Moussavi, M., Fischer, J. & Weiss, R. (1985). *Inorg. Chem.* **24**, 3162–3167.

Darovskikh, A. N., Frank-Kamenetskaya, O. V. & Fundamenskii, V. S. (1986). *Sov. Phys. Crystallogr.* **31**, 534–537.

Darovskikh, A. N., Frank-Kamenetskaya, O. V., Fundamenskii, V. S. & Golubev, A. M. (1986). *Sov. Phys. Crystallogr.* **31**, 165–168.

Darovskikh, A. N., Tsytsenko, A. K., Frank-Kamenetskaya, O. V., Fundamenskii, V. S. & Moskalev, P. N. (1984). *Sov. Phys. Crystallogr.* **29**, 273–276.

Darovsky, A., Keserashvili, V., Harlow, R. & Mutikainen, I. (1994). *Acta Cryst.* B50, 582–588.

Darovsky, A., Wu, L. Y., Lee, P. & Sheu, H. S. (1991). *Acta Cryst.* C47, 1836–1838.

Enraf-Nonius (1993). *CAD-4/PC Software.* Version 1.2. Enraf-Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf-Nonius, Delft, The Netherlands.

Guillaud, G., Al Sadoun, M., Maitrot, M., Simon, J. & Bouvet, M. (1990). *Chem. Phys. Lett.* **167**, 503–506.

Homborg, H. & Teske, Chr. L. (1985). *Z. Anorg. Allg. Chem.* **527**, 45–61.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Maitrot, M., Guillaud, G., Boudjema, B., Andre, J.-J., Strzelecka, H., Simon, J. & Even, R. (1987). *Chem. Phys. Lett.* **133**, 59–62.

Marks, T. J. (1990). *Angew. Chem.* **102**, 886–908; *Angew. Chem. Int. Ed. Engl.* **29**, 857–888.

Mossoyan-Deneux, M., Benlian, D., Pierrot, M., Fournal, A. & Sorbier, J. P. (1985). *Inorg. Chem.* **24**, 1878–1882.

Safarpour Haghighi, M., Rath, M., Rotter, H. W. & Homborg, H. (1993). *Z. Anorg. Allg. Chem.* **619**, 1887–1896.

Safarpour Haghighi, M., Teske, Chr. L. & Homborg, H. (1992). *Z. Anorg. Allg. Chem.* **608**, 73–80.

Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.

Sokolova, T. N., Lomova, T. N., Morozov, V. V. & Berezin, B. D. (1994). *Russ. J. Coord. Chem.* **20**, 603–606.

Takahashi, K., Itoh, M., Tomita, Y., Nojima, K., Kasuga, K. & Isa, K. (1993). *Chem. Lett.* pp. 1915–1918.

Turek, T., Petit, P., Andre, J.-J., Simon, J., Even, R., Boudjema, B., Guillaud, G. & Maitrot, M. (1987). *J. Am. Chem. Soc.* **109**, 5119–5121.

Potassium Hydrogen Phthalate Hemiperhydrate

BENSON M. KARIUKI

Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, England

WILLIAM JONES

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England

Abstract

The crystal structure of the title compound, K$^+$.(HO$_2$C—C$_6$H$_4$—CO$_2$)$^-$.0.5H$_2$O$_2$, is layered with eight O atoms around the cation. Anion–anion and anion–hydrogen