the same solvent in a manner analogous to that used for related derivatives (Kataeva *et al.*, 1995).

Crystal data

[CuCl($C_{18}H_{15}PS_3$)]
$M_r = 457.44$
Trigonal
$P3_1$
$a = 12.519\,(2)$ Å
$c = 10.257\,(3)$ Å
$V = 1392.2\,(5)$ Å^3
$Z = 3$
$D_x = 1.637$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 10.0$–$12.5°$
$\mu = 1.741$ mm^{-1}
$T = 173\,(2)$ K
Prism
0.40 × 0.14 × 0.12 mm
Colourless

Data collection

Nicolet R3 diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{\min} = 0.757$, $T_{\max} = 0.811$
4566 measured reflections
3620 independent reflections
2777 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.035$
$\theta_{\max} = 27.56°$
$h = -11 \rightarrow 16$
$k = -16 \rightarrow 13$
$l = -13 \rightarrow 11$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.097$
$S = 1.018$
3620 reflections
217 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 1.1312P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = $-0.054\,(19)$

Table 1. *Selected geometric parameters (Å, °)*

Cu—P	2.2434 (16)	P—S1	2.117 (2)
Cu—Cl	2.3235 (16)	P—S3	2.1745 (19)
Cu—Cl$^{\rm i}$	2.3351 (15)	S1—C1	1.776 (6)
Cu—S3$^{\rm i}$	2.3442 (15)	S2—C11	1.795 (6)
P—S2	2.103 (2)	S3—C21	1.796 (6)
P—Cu—Cl	101.22 (6)	S2—P—Cu	124.41 (8)
P—Cu—Cl$^{\rm i}$	104.53 (6)	S1—P—Cu	119.77 (8)
Cl—Cu—Cl$^{\rm i}$	107.13 (3)	S3—P—Cu	106.89 (7)
P—Cu—S3$^{\rm i}$	123.85 (6)	Cu—Cl—Cu$^{\rm ii}$	109.06 (5)
Cl—Cu—S3$^{\rm i}$	118.09 (6)	C1—S1—P	97.56 (19)
Cl$^{\rm i}$—Cu—S3$^{\rm i}$	100.40 (6)	C11—S2—P	102.23 (19)
S2—P—S1	100.64 (8)	C21—S3—P	102.27 (19)
S2—P—S3	104.41 (8)	C21—S3—Cu$^{\rm ii}$	115.5 (2)
S1—P—S3	96.40 (8)	P—S3—Cu$^{\rm ii}$	103.85 (7)
Cl—Cu—P—S3	−36.04 (8)	Cu—Cl—Cu$^{\rm ii}$—S3	11.82 (7)
P—Cu—Cl—Cu$^{\rm ii}$	13.21 (7)	Cu—P—S3—Cu$^{\rm ii}$	45.34 (8)
P—S3—Cu$^{\rm ii}$—Cl	−33.66 (7)		

Symmetry codes: (i) $-x + y, -x, z - \frac{1}{3}$; (ii) $-y, x - y, \frac{1}{3} + z$.

The absolute structure was determined on the basis of 1478 Friedel pairs. The origin was fixed according to the method of Flack & Schwarzenbach (1988). H atoms were refined using a riding model starting from calculated positions.

Data collection: *P*3 *Software* (Nicolet, 1987). Cell refinement: *P*3 *Software*. Data reduction: *XDISK* in *P*3 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1265). Services for accessing these data are described at the back of the journal.

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Iodo(phthalocyaninato)vanadium(III)

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Abstract

A new vanadium phthalocyanine complex with the formula [VI($C_{32}H_{16}N_8$)], or PcVI (Pc = $C_{32}H_{16}N_8$), has been obtained by the reaction of pure V powder with

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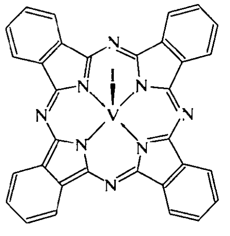
1,2-dicyanobenzene under iodine vapour. The V atom is bonded to one apical iodide ligand and four $N_{isoindole}$ atoms, and has square-pyramidal coordination geometry. The mean V—$N_{isoindole}$ distance is 1.952 (3) Å. The V—I bond has a length of 2.6279 (8) Å and is tilted 1.7 (1)° to the normal of the plane formed by the four $N_{isoindole}$ atoms. The phthalocyaninato ligand is saucer-shaped.

Comment

As part of our study on the synthesis of metallophthalocyanines, we obtained a new vanadium phthalocyanine with the formula PcVI (Pc = $C_{32}H_{16}N_8$).



PcVI

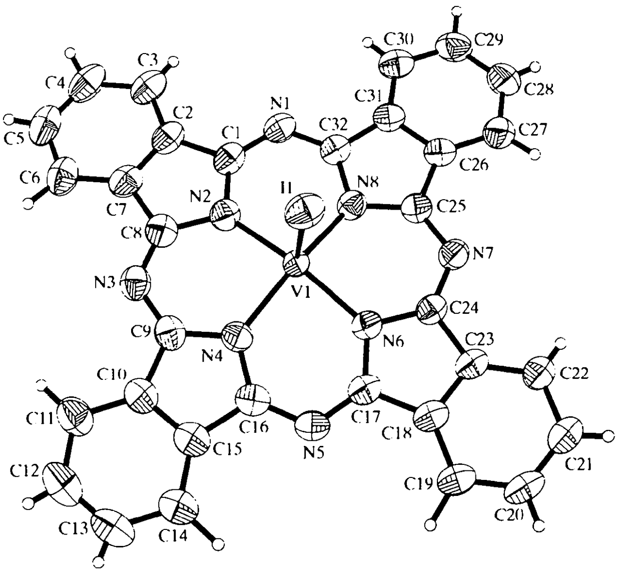


Fig. 1. The molecular structure of PcVI, showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

The crystal structure consists of discrete molecules (Fig. 1). The five-coordinate V atom is bonded to the four isoindole N atoms of the phthalocyaninato ligand and one terminal iodide ligand, in a square-pyramidal coordination sphere. The V^{III} atom is displaced 0.322 (2) Å above the N_4 plane in the direction of the iodide ligand. In PcVO this displacement is 0.575 (1) Å (Ziolo *et al.*, 1980); in other related vanadium porphinate complexes it ranges from 0.48 (Pettersen, 1969) to 0.638 (1) Å (Piarulli *et al.*, 1996). However, in these other structures the V atom is multiply-bonded by the apical O or N atom, in contrast to the bonding motif of the iodide in PcVI. As a result, the mean V—N distance of 1.952 (3) Å for PcVI is also the smallest in such square-pyramidal complexes. For instance, in PcVO the mean V—N distance is 2.026 (7) Å (Ziolo *et al.*, 1980). Moreover, the iodide ligand in PcVI takes part in an I···H intermolecular interaction with a peripheral H atom in a neighbouring molecule. The I1···H30^i [symmetry code: (i) $1-x$, $-y$, $-z$] distance is 3.15 (6) Å [C30^i—H30^i = 0.867 (8), I1···C30^i = 3.992 (3) Å and C30^i—H30^i···I1 = 164.4 (2)°]. This gives pairs of face-to-face but stepped PcVI molecules in the crystal, and is also the reason for the 1.7 (1)° tilt of the V—I bond with respect to the normal to the N_4 plane.

The phthalocyaninato ligand is saucer-shaped. The largest deviations from the N_4 plane are observed for C4 and C5 [0.48 (1) and 0.46 (1) Å, respectively], on the opposite side to V and I. The dihedral angles between the isoindole planes (defined by N2, C1–C8; N4, C9–C16; N6, C17–C24 and N8, C25–C32) and the N_4 plane are 6.3 (2), 3.7 (2), 2.1 (2) and 3.9 (2)°, respectively. In PcVO, the analogous dihedral angles are 2.0, 5.4, 6.5 and 9.4° (Ziolo *et al.*, 1980). The mean C—N_4, C—$N_{azamethine}$ and C—C bond lengths in the phthalocyanine ligand are 1.380 (3), 1.317 (3) and 1.399 (5) Å, respectively. These distances are similar to those observed in other metallophthalocyanine complexes.

Experimental

The crystals of PcVI were obtained by the reaction of pure V powder with 1,2-dicyanobenzene and iodine. The reagents, in 1:4:1 molar ratio, were mixed together and pressed into pellets, which were sealed in an evacuated glass ampoule. This was heated to 473 K for 1 d, yielding red–violet crystals.

Crystal data

[VI($C_{32}H_{16}N_8$)]
M_r = 690.37
Monoclinic
$P2_1/n$
a = 13.135 (3) Å
b = 10.309 (2) Å
c = 19.363 (4) Å
β = 99.99 (3)°
V = 2582.17 (97) Å^3
Z = 4
D_x = 1.7759 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 5–15°
μ = 1.621 mm^{-1}
T = 293 (2) K
Parallelepiped
0.35 × 0.30 × 0.25 mm
Red–violet

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans

R_{int} = 0.039
θ_{max} = 30.1°

Absorption correction:
empirical *via* ψ scan
(Sheldrick, 1990)
$T_{\min} = 0.526$, $T_{\max} = 0.667$
14 419 measured reflections
7156 independent reflections
4395 reflections with
$I > 2\sigma(I)$

$h = 0 \rightarrow 18$
$k = -14 \rightarrow 14$
$l = -23 \rightarrow 24$
2 standard reflections
every 50 reflections
intensity decay: 1.324%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.039$
7156 reflections
443 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 2.7268P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.028$
$\Delta\rho_{\max} = 1.387$ e Å^{-3}
(0.51 Å from V1)
$\Delta\rho_{\min} = -0.864$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

I1—V1	2.6279 (8)	V1—N4	1.951 (3)
V1—N8	1.947 (3)	V1—N2	1.960 (3)
V1—N6	1.951 (3)		
N8—V1—N6	89.11 (14)	N4—V1—N2	88.92 (14)
N8—V1—N4	160.50 (14)	N8—V1—I1	98.70 (10)
N6—V1—N4	87.76 (14)	N6—V1—I1	97.90 (10)
N8—V1—N2	88.00 (14)	N4—V1—I1	100.80 (10)
N6—V1—N2	161.57 (14)	N2—V1—I1	100.52 (10)

Data collection: *Kuma Diffractometer Software* (Kuma, 1997). Cell refinement: *Kuma Diffractometer Software*. Data reduction: *Kuma Diffractometer Software*. Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *SHELXTL* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1259). Services for accessing these data are described at the back of the journal.

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Barium Terephthalate, a Three-Dimensional Coordination Polymer with 7:7 Cation–Anion Connectivity

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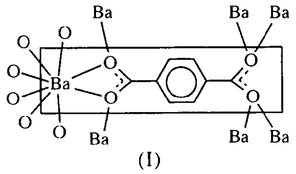
Abstract

Barium terephthalate, $[\mathrm{Ba}\{1,4\text{-}\mathrm{C_6H_4(COO)_2}\}]_n$, forms a three-dimensional coordination network polymer with 7:7 connectivity between the barium cations and terephthalate dianions. Each Ba atom is eight-coordinate and uses all eight oxygen lone pairs of the ligand.

Comment

The synthesis of crystalline metal coordination polymers by use of multi-functional ligands is of much recent interest, however, control of their dimensionality to achieve three-dimensional networks is often thwarted by ligation of ancillary ligands such as water. Compounds based on polybenzoate ligands are often highly hydrated and thus frequently form only one-dimensional chain or two-dimensional sheet structures. Use of hydrothermal methods may assist loss of ancillary ligands, as shown in the case of manganese trimesate $[\mathrm{Mn_3(TMA)_2}]$ (Gutschke *et al.*, 1996). We have also found that the use of larger cations, such as barium or lead, which have higher coordination numbers, also promotes higher dimensionality (Chui & Williams, 1998). We report herein the structure of barium terephthalate, $[\mathrm{Ba}\{1,4\text{-}\mathrm{C_6H_4(COO)_2}\}]$, (I), which was crystallized at room temperature under aqueous conditions, but surprisingly is composed solely of barium cations and terephthalate anions.



(I)

The polymer network is three-dimensional and is, we believe, the first example of an ionic structure showing 7:7 connectivity between cations and counter-anions. The asymmetric unit consists of one barium cation and one terephthalate dianion. Each terephthalate ligand has

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