$C_{17}H_{18}Cl_2N^+ \cdot Cl^-$

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1083). Services for accessing these data are described at the back of the journal.

References

Byrn, M. P. & Strouse, C. E. (1991). *J. Am. Chem. Soc.* **113**, 2501–2508.

Camalli, M. & Spagna, R. (1994). *J. Appl. Cryst.* **27**, 861–862.

Chang, A. S., Chang, S. M. & Starnes, D. M. (1993). *Eur. J. Pharmacol.* **247**, 239–248.

Dalpiaz, A., Ferretti, V., Gilli, P. & Bertolasi, V. (1996). *Acta Cryst.* B**52**, 509–518.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Nemeroff, C. B. (1998). *Sci. Am.* **278**, 42–49.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pople, J. A. & Beveridge, D. L. (1970). *Approximate Molecular Orbital Theory*, pp. 63–193, Appendix A. New York: McGraw-Hill.

Robertson, D. W., Jones, N. D., Swartzendruber, J. K., Yang, K. S. & Wong, D. T. (1988). *J. Med. Chem.* **31**, 185–189.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Thewalt, U. & Bugg, C. E. (1972). *Acta Cryst.* B**28**, 82–92.

Welch, W. M., Kraska, A. R., Sarges, R. & Koe, B. K. (1984). *J. Med. Chem.* **27**, 1508–1515.

1:2 Complexes of chloranilic acid with pyrimidine and pyrazine

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## Abstract

The hydrogen-bonded 1:2 complexes of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone) with pyrimidine [(1), $C_6H_2Cl_2O_4 \cdot 2C_4H_4N_2$] and pyrazine [(2), $C_6H_2Cl_2O_4 \cdot 2C_4H_4N_2$] were prepared and their crystal structures determined at room temperature. In both complexes, the chloranilic acid molecules lie

on inversion centres and in each complex, the two components are held together by O—H$\cdots$N hydrogen bonds with short O$\cdots$N distances of 2.615 (2) Å for (1) and 2.590 (4) Å for (2).

Comment

Several hydrogen-bonded complexes in chloranilic acid–amine 1:1 systems were studied by IR, NMR and UV (Issa *et al.*, 1991; Habeeb *et al.*, 1995). Habeeb *et al.* (1995) reported that the hydrogen bonds formed between chloranilic acid and amines vary from an N—H$\cdots$O to an N$\cdots$H—O type with decreasing pK_a values of the amines. Recently, we reported the crystal structure of the 1:2 complex of chloranilic acid and pyridazine (1,2-diazine), where a short hydrogen bond with N$\cdots$O distance 2.582 (3) Å is found and the H atom in the hydrogen bond is located near the centre of N$\cdots$O (Ishida & Kashino, 1999). In the present study, we have prepared the 1:2 complexes of pyrimidine (1,3-diazine) and pyrazine (1,4-diazine), which are isoelectric with pyridazine, and determined the crystal structures at room temperature to investigate the hydrogen bond.

(1)

(2)
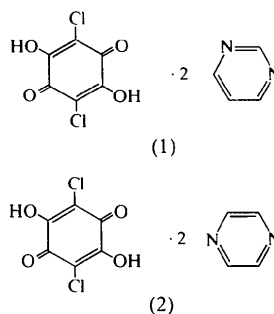
In (1), the two components, $C_4H_4N_2$ and $C_6H_2Cl_2O_4$, are held together by strong O—H$\cdots$N hydrogen bonds [O1—H1 1.07 (4), H1$\cdots$N1 1.57 (4), O1$\cdots$N1 2.615 (2) Å and O1—H1$\cdots$N1 165 (4)°] and stacked in columns along the *a* axis (Fig. 1). In addition, a weak intramolecular O—H$\cdots$O hydrogen bond is observed [H1$\cdots$O2^i 2.33 (4), O1$\cdots$O2^i 2.690 (2) Å and O1—H1$\cdots$O2^i 98 (3)°; symmetry code: (i) $2 - x$, $1 - y$, $1 - z$]. The cell constants and crystal structure are similar to those of the pyridazine complex.

In (2), the two components are also stacked in columns along the *a* axis, but the packing arrangement of the hydrogen-bonded complex is different from (1) as shown in Fig. 2. The hydrogen bond between the two components is strong [O2—H1 1.06 (5), H1$\cdots$N1 1.55 (5), O2$\cdots$N1 2.590 (4) Å and O2—H1$\cdots$N1 165 (5)°], while the intramolecular hydrogen bond is weak [H1$\cdots$O1^i 2.33 (6), O2$\cdots$O1^i 2.693 (4) Å and O2—H1$\cdots$O1^i 98 (4)°; symmetry code: (i) $2 - x$, $-y$, $1 - z$].

The interplanar angles between the rings in chloranilic acid and diazines are 12.4 (7), 52.4 (3) and 52.4 (4)°

Fig. 1. *ORTEP*-3 (Farrugia, 1997) packing diagram of (1) viewed down the *a* axis and atomic numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of an arbitrary radius. Hydrogen bonds are indicated by dashed lines.
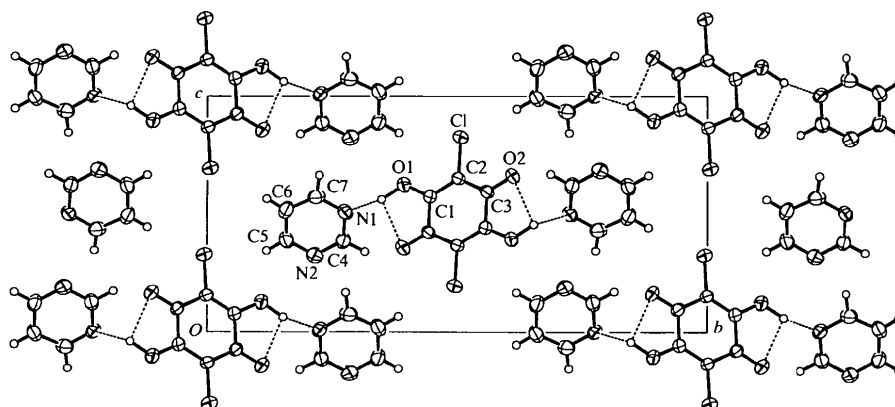

Fig. 2. *ORTEP*-3 (Farrugia, 1997) packing diagram of (2) viewed down the *a* axis and atomic numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of an arbitrary radius. Hydrogen bonds are indicated by dashed lines.
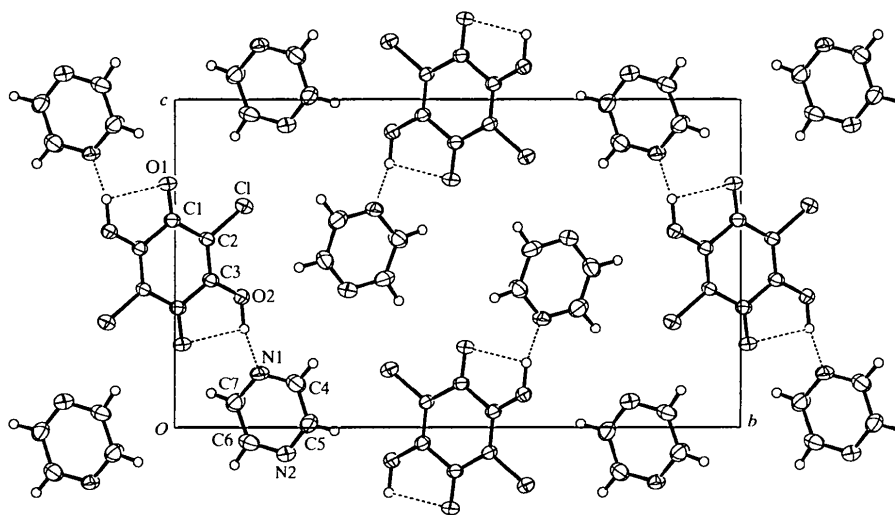
for pyridazine, pyrimidine and pyrazine complexes, respectively. The H atoms in the hydrogen bonds in (1) and (2) are located at the O-atom site as one may expect from the lower pK_a values of pyrimidine (1.3) and pyrazine (0.7) compared with that of pyridazine (2.3), but long O—H bonds are observed. The large displacement parameters of H atoms [U_{iso} 0.15 (1) and 0.12 (1) Å^2 for (1) and (2), respectively] can be attributed to the positive effective charge of the acid-H atom and disorder of H atoms in the hydrogen bonds (Tanogaki *et al.*, 1993).

Experimental

Crystals of the title complexes were prepared by slow evaporation from solutions of chloranilic acid with pyrimidine and pyrazine (molar ratio 1:2) in CH_3CN at room temperature.

Compound (1)

Crystal data

$2C_4H_4N_2 \cdot C_6H_2Cl_2O_4$
$M_r = 369.16$
Monoclinic
$P2_1/c$
$a = 3.952 (1)$ Å
$b = 19.95 (1)$ Å
$c = 9.551 (4)$ Å
$\beta = 96.60 (3)°$
$V = 747.9 (5)$ Å^3
$Z = 2$
$D_x = 1.639$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.9–11.4°$
$\mu = 0.462$ mm^{-1}
$T = 296$ K
Prismatic
$0.40 \times 0.25 \times 0.15$ mm
Dark brown

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans

1319 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.031$

Absorption correction:
ψ scan (North et al., 1968)
$T_{min} = 0.86$, $T_{max} = 0.93$
3518 measured reflections
1771 independent reflections

$\theta_{max} = 27.49°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 25$
$l = -12 \rightarrow 12$
3 standard reflections
every 97 reflections
intensity decay: 2.53%

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.083$
$S = 1.65$
1691 reflections
130 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: $2.1(5) \times 10^{-6}$
Scattering factors from International Tables for Crystallography (Vol. C)

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

C1—C2	1.731 (2)	N1—C4	1.328 (3)
O1—C1	1.288 (2)	N1—C7	1.332 (3)
O2—C3	1.223 (2)	N2—C4	1.321 (3)
C1—C2	1.357 (2)	N2—C5	1.334 (3)
C1—C3ⁱ	1.529 (3)	C5—C6	1.375 (3)
C2—C3	1.435 (2)	C6—C7	1.364 (3)
O1—C1—C2	123.2 (2)	C1—C3ⁱ—C2ⁱ	118.1 (1)
O1—C1—C3ⁱ	117.4 (2)	N1—C4—N2	125.5 (2)
C2—C1—C3ⁱ	119.4 (2)	N2—C5—C6	122.3 (2)
C1—C2—C1	120.2 (1)	C4—N1—C7	117.6 (2)
C1—C2—C3	117.3 (1)	C4—N2—C5	116.2 (2)
C1—C2—C3	122.5 (2)	C5—C6—C7	117.3 (2)
O2—C3—C1ⁱ	117.7 (2)	N1—C7—C6	121.1 (2)
O2—C3—C2	124.2 (2)		

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

Compound (2)

Crystal data

2C₄H₄N₂·C₆H₂Cl₂O₄
$M_r = 369.16$
Monoclinic
$P2_1/n$
$a = 3.8283(7)$ Å
$b = 18.514(5)$ Å
$c = 10.795(3)$ Å
$\beta = 94.48(2)°$
$V = 762.8(3)$ Å^3
$Z = 2$
$D_x = 1.607$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.9–11.5°$
$\mu = 0.453$ mm^{-1}
$T = 296$ K
Needle
$0.50 \times 0.15 \times 0.10$ mm
Dark red

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans
Absorption correction: ψ scan (North et al., 1968)
$T_{min} = 0.93$, $T_{max} = 0.96$
2054 measured reflections
1799 independent reflections

877 reflections with $I > 2\sigma(I)$
$R_{int} = 0.090$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 4$
$k = 0 \rightarrow 24$
$l = -13 \rightarrow 13$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.065$
$wR(F^2) = 0.061$
$S = 1.37$
1731 reflections
130 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.00004|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.00$ e Å^{-3}
$\Delta\rho_{min} = -0.90$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: $2.8(3) \times 10^{-6}$
Scattering factors from International Tables for Crystallography (Vol. C)

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

C1—C2	1.733 (4)	N1···C4	1.326 (6)
O1—C1	1.219 (4)	N1—C7	1.329 (5)
O2—C3	1.298 (5)	N2—C5	1.320 (6)
C1—C2	1.443 (6)	N2—C6	1.340 (6)
C1—C3ⁱ	1.517 (5)	C4—C5	1.387 (6)
C2—C3	1.356 (5)	C6—C7	1.378 (6)
O1—C1—C2	124.3 (4)	C1ⁱ—C3—C2	119.2 (4)
O1—C1—C3ⁱ	117.7 (4)	N1—C4—C5	120.6 (5)
C2—C1—C3ⁱ	118.0 (4)	N2—C5—C4	122.8 (5)
C1—C2—C1	116.5 (3)	C4—N1—C7	117.7 (4)
C1—C2—C3	120.8 (4)	C5—N2—C6	115.6 (4)
C1—C2—C3	122.8 (4)	N2—C6—C7	122.4 (5)
O2—C3—C1ⁱ	117.9 (4)	N1—C7—C6	120.8 (5)
O2—C3—C2	122.8 (4)		

Symmetry code: (i) $2 - x, -y, 1 - z$.

Refined distances: O—H 1.07 (4) and 1.06 (5) Å, and C—H 0.92 (2)–1.00 (3) and 0.93 (4)–0.96 (4) Å for (1) and (2), respectively.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structures: *SIR92* (Altomare et al., 1993); program(s) used to refine structures: *TEXSAN for Windows*; software used to prepare material for publication: *TEXSAN for Windows*.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). J. Appl. Cryst. 26, 343.
Farrugia, L. J. (1997). ORTEP-3 for Windows. University of Glasgow, Scotland.
Habeeb, M. M., Alwakil, H. A., El-Dissouky, A. & Fattab, H. A. (1995). Pol. J. Chem. 69, 1428–1436.
Ishida, H. & Kashino, S. (1999). Acta Cryst. C55, 1149–1152.
Issa, Y. M., Darwish, N. A. & Hassib, H. B. (1991). Egypt. J. Chem. 34, 87–93.
Molecular Structure Corporation (1990). MSC/AFC Diffractometer Control Software. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1997). *TEXSAN for Windows* (Version 1.03) and *Single Crystal Structure Analysis Software* (Version 1.04). MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Tanogaki, M., Kawata, T., Ohba, S., Iwata, Y. & Shibuya, I. (1993). *Acta Cryst.* B49, 1031–1039.

Zachariasen, W. H. (1967). *Acta Cryst.* 23, 558–564.

Bis(*epi*-globulyloxy)(phthalocyaninato)-silicon,† a new photosensitizer for the photodynamic therapy of cancer

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Abstract

The structure of bis(*epi*-globulyloxy)(phthalocyaninato)-silicon, $C_{62}H_{66}N_8O_2Si$ or $[Si(C_{32}H_{16}N_8)(C_{15}H_{25}O)_2]$, has been assigned. The Si atom is coordinated to the N atoms of the phthalocyanine ring and bridges the two *epi*-globulyloxy moieties through two Si—O bonds, which are almost perpendicular to the phthalocyanine plane. The molecule displays a pseudo-centrosymmetric character relative to silicon, but the two apical ligands break the symmetry.

Comment

In recent publications (Decréau, Chanon & Julliard, 1998, 1999), we described the binding of steroid moieties on silicon and aluminium phthalocyanines, leading to new efficient photosensitizers against human melanoma cells in the photodynamic therapy of cancer (Decréau, Verrando *et al.*, 1998). The binding of sesquiterpenoid moieties was also performed in order to reach a higher solubility, to decrease the stacking aggregation of the phthalocyanine (PHC) rings, and to increase the molecular recognition for the liposome-

† Alternative name: (1a,2,3,4,4a,5,6,7,7a,7b-decahydro-1,1,4,7-tetra-methyl-1*H*-cycloprop[*e*]azulen-4-olato-*O*)(phthalocyaninato-$N^{29},N^{30},$-N^{31},N^{32})silicon.

delivered new photosensitizers. It was then achieved by reacting the *epi*-globulol alcoholate with dichloro-silicon phthalocyanine, (1) (Decréau, Julliard *et al.*, 1999), leading to bis(*epi*-globulyloxy)(phthalocyaninato)silicon, (2), in 65% yield. The *in vitro* photodynamic activity of (2) was higher than that of (1) (Decréau, 1998). The structure of (2) has been assigned here by X-ray crystallography analysis.
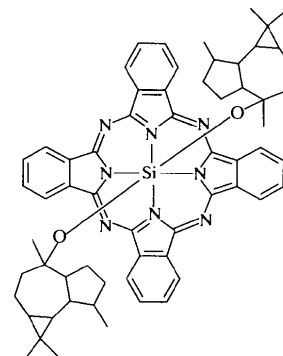
(2)

The core of photosensitizer (2) is composed of two *epi*-globulol moieties, each of which is connected to the silicon phthalocyanine *via* an Si—O bond. The Si atom lies in the middle of the phthalocyanine cavity and exhibits an octahedral geometry with the two bridging O atoms in apical positions. Each *epi*-globulol is composed of a seven-membered ring to which three- and five-membered rings are fused. The molecular structure of (2) shows that these units are related by a pseudo-twofold axis parallel to the O—Si—O direction, conferring a centrosymmetric character on the structure. However, the relative orientation of the seven- or five-membered rings breaks this symmetry; the C54–C58 and the C39–C43 cycles point in the same direction (Fig. 1). The geometrical parameters of (2) show that the PHC macrocycle is essentially planar, as previously described in the case of other metallophthalocyanines (Mooney *et al.*, 1975; Silver *et al.*, 1998; Brewis *et al.*, 1998).

The most interesting geometrical parameters involve the inner Si atom of (2). The average Si—O bond length is 1.696 (3) Å and the average Si—N distance is 1.919 (6) Å; nevertheless, two Si—N bonds are observed at 1.906 (3) and 1.934 (3) Å. The O—Si—O bridge is almost linear [175.4 (2)°], and the Si—O—C angles are 148.0 (3) and 148.4 (3)°. These parameters can be compared to those of silicon phthalocyanine (Si-PHC) bearing two trimethylsiloxy groups, (3) (Mooney *et al.*, 1975), two ferrocenylcarboxylate groups, (4) (Silver *et al.*, 1998), or two Frechet's dendritic groups, (5) (Brewis *et al.*, 1998), or to those of compounds containing two silicon phthalocyanine moieties, (6), *e.g.* oligomerized silicon phthalocyanines (Si-PHC-O)$_n$ (n = 2, x), where the PHC units are connected to each other *via* a μ-oxo bridge. So the Si—O and Si—N bond lengths display