

**trans-Bis(hexafluoroantimonato)-
(phthalocyaninato)copper(II)**

Anna S. Gardberg and James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

Correspondence e-mail: iberns@chem.nwu.edu

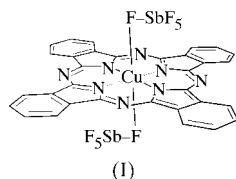
Received 16 October 2000

Accepted 22 January 2001

The title compound, *trans*-bis(hexafluoroantimonato-*F*)-(phthalocyaninato- $\kappa^4 N^{29,30,31,32}$)copper(II), [Cu(SbF₆)₂(C₃₂H₁₆N₈)] or Cu(pc)(SbF₆)₂ (pc is phthalocyaninate), comprises a six-coordinate Cu atom, lying on an inversion center, bonded to four N atoms of a phthalocyanine ring and to F atoms of two *trans* SbF₆⁻ groups. The compound is presumed to consist of a Cu^{II} center and a doubly oxidized phthalocyanine ring, by analogy with Cu(pc)(ReO₄)₂.

Comment

Whereas galvanostatic oxidations of phthalocyanine [H₂(pc)] and metallophthalocyanines normally lead to solid-state structures comprising stacks of partially oxidized macrocycles with counter-ions occupying the adjacent channels (Godfrey *et al.*, 1990; Yakushi *et al.*, 1987), the recently discovered compound *trans*-bis(perrhenato)(phthalocyaninato)copper(II), Cu(pc)(ReO₄)₂, (II) (Gardberg, Doan *et al.*, 2001), prepared by galvanostatic oxidation, is a molecular compound in which the six-coordinate Cu center is bonded to four N atoms of the pc ring and to O atoms of two *trans* ReO₄ groups. EPR (electron paramagnetic resonance) measurements indicate that this is a Cu^{II} compound with a doubly ring-oxidized pc ring. A modification of the synthesis of (II) yielded a few very small crystals of the title compound, Cu(pc)(SbF₆)₂, (I).



From the present single-crystal X-ray diffraction study, compound (I) is found to be analogous with (II), in that it is a molecular complex containing a six-coordinate Cu center (Fig. 1). The Cu atom is at an inversion center and hence lies in the least-squares plane of the pc ligand. The mean deviation from this plane is 0.0196 Å, and the maximum deviation is 0.046 (10) Å for atom C5. The Cu—F bond of (I) makes an angle of 4.7 (3)° with the normal to this plane. The two Cu—N

distances, 1.955 (9) and 1.957 (9) Å, are normal. The largest residual peak, the electron density of which is about half that of a typical F peak, is located 1.21 Å from atom F1 and 1.79 Å from atom Cu1. A search of the April 2000 release of the Cambridge Structural Database (Allen & Kennard, 1993) for structures containing a Cu atom bonded to four equatorial N atoms (with the N—Cu—N' angle constrained to lie between 80 and 100° and the N—Cu—N'' angle constrained to lie between 170 and 190°) and to at least one axial F atom (F—Cu—N angle not constrained) revealed 17 structures. The range of Cu—F bond distances in these structures is 2.22–2.73 Å; the Cu—F distance in (I) is 2.626 (7) Å.

In the structure of (I), the Cu(pc) macrocycles are parallel to one another, with the peripheral benzene rings partially overlapping at a distance of 3.4 Å. This is to be contrasted with the structure of (II), in which the Cu(pc) rings are perpendicular to one another, creating a herring-bone-type packing arrangement. Compound (I) is the second example of an oxidized copper phthalocyanine with a structure that is molecular and that does not comprise stacks of partially oxidized macrocycles. Whether (I) and (II) are isolated examples or whether they are the forerunners of many others remains to be determined.

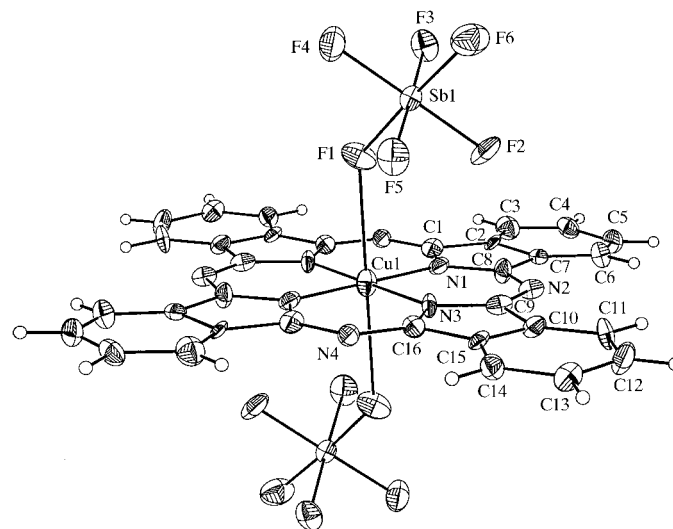


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-labeling scheme. H atoms are displayed as small spheres of arbitrary radii.

Experimental

Single crystals of the title compound grew at the anode of an electrolytic cell that consisted of two compartments separated by a glass frit. The Cu(pc) starting material was synthesized by metallation of very pure H₂(pc) (Thompson *et al.*, 1993) with CuCl₂·xH₂O (99.9999%, dehydrated), followed by repeated sublimation. The cell was protected from light, kept purged with dry N₂ and maintained at 403 (5) K. Each half-cell contained a 1-chloronaphthalene solution of [N(*n*-Bu)₄][SbF₆] (20 ml, 0.0125 M); the solution in the anode compartment was saturated with Cu(pc). A 3.00 μA current was passed through the cell *via* Pt electrodes for one month, during which

time the initially blue solution turned green. A few small crystals of (I) grew on the anode, amid several long needles of $[\text{Cu}(\text{pc})]_3\text{[SbF}_6\text{]}_2\cdot\text{C}_{10}\text{H}_7\text{Cl}$ (Gardberg, Brazis *et al.*, 2001). Semi-quantitative energy dispersive spectroscopy indicated that the small crystals contained Cu and Sb, but no Cl. They were air- and light-stable, but there was not enough material for CHN analysis.

Crystal data

$[\text{Cu}(\text{SbF}_6)_2(\text{C}_{32}\text{H}_{16}\text{N}_8)]$	$Z = 1$
$M_r = 1047.57$	$D_x = 2.142 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.596(4) \text{ \AA}$	Cell parameters from 1358 reflections
$b = 9.150(5) \text{ \AA}$	$\theta = 2.26\text{--}21.71^\circ$
$c = 10.724(5) \text{ \AA}$	$\mu = 2.410 \text{ mm}^{-1}$
$\alpha = 92.528(9)^\circ$	$T = 153(2) \text{ K}$
$\beta = 101.917(9)^\circ$	Prism, purple
$\gamma = 99.127(9)^\circ$	$0.10 \times 0.06 \times 0.04 \text{ mm}$
$V = 812.3(7) \text{ \AA}^3$	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	7294 measured reflections
$0.3^\circ \omega$ scans	2880 independent reflections
Absorption correction: numerical face-indexed correction [<i>XPREP</i> and <i>SADABS</i> , both in <i>SMART</i> (Bruker, 1999)]	1855 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.815$, $T_{\max} = 0.920$	$R_{\text{int}} = 0.085$
	$\theta_{\text{max}} = 25.09^\circ$
	$h = -10 \rightarrow 10$
	$k = -10 \rightarrow 10$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.064$	$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$wR(F^2) = 0.150$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.343$	$\Delta\rho_{\text{max}} = 2.49 \text{ e \AA}^{-3}$
2880 reflections	$\Delta\rho_{\text{min}} = -1.16 \text{ e \AA}^{-3}$
250 parameters	

H-atom positions were idealized and were refined with a riding model in which the C–H distance was constrained to be 0.95 \AA .

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT+* (Bruker, 2000); data reduction: *SAINT+*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*.

This work was supported by the MRSEC program of the National Science Foundation (DMR-0076097) at the Materials Research Center of Northwestern University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1164). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Bruker (2000). *SMART* (Version 5.054) and *SAINT+* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
- Gardberg, A. S., Brazis, P., Kannewurf, C. R. & Ibers, J. A. (2001). In preparation.
- Gardberg, A. S., Doan, P. E., Hoffman, B. M. & Ibers, J. A. (2001). *Angew. Chem.* **113**, 250–252; *Angew. Chem. Int. Ed. Engl.* **40**, 244–246.
- Godfrey, M. R., Newcomb, T. P., Hoffman, B. M. & Ibers, J. A. (1990). *J. Am. Chem. Soc.* **112**, 7260–7269.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Thompson, J. A., Murata, K., Miller, D. C., Stanton, J. L., Broderick, W. E., Hoffman, B. M. & Ibers, J. A. (1993). *Inorg. Chem.* **32**, 3546–3553.
- Yakushi, K., Sakuda, M., Hamada, I., Kuroda, H., Kawamoto, A., Tanaka, J., Sugano, T. & Kinoshita, M. (1987). *Synth. Met.* **19**, 769–774.