Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

trans-Bis(5,5-diphenylhydantoinato)bis(2-phenylethylamine)copper(II)

Takashiro Akitsu* and Yasuaki Einaga

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan

Correspondence e-mail:
akitsu@chem.keio.ac.jp

Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.007 Å
R factor = 0.047
wR factor = 0.152
Data-to-parameter ratio = 11.7

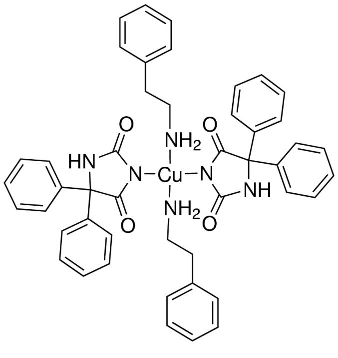
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 15 March 2004
Accepted 29 March 2004
Online 9 April 2004

The title compound, $[Cu(C_{15}H_{11}N_2O_2)_2(C_8H_{11}N)_2]$, has its metal atom in a square-planar *trans*-CuN_4 coordination environment; the Cu^{II} atom lies on a center of symmetry. The 5,5-diphenylhydantoinate and 2-phenylethylamine ligands behave as monodentate ligands and bind through their N atoms. The crystal structure is stabilized by N—H···O═C intermolecular hydrogen bonds [N···O = 2.864 (3) Å].

Comment

We are investigating thermochromic compounds in a broad study on photofunctional materials (Sato, 2003). An example of a class of such materials is the class of tetrachlorocuprate(II) complexes, which are also photochromic. The property is related to a change from a square planar to a distorted tetrahedral geometry (Riley *et al.*, 1998). Copper(II) complexes with *N*-substituted ethylenediamines also exhibit thermochromism (Narayanan & Bhadbhade, 1998) and photochromism (Takahashi *et al.*, 2002). The electronic states of (distorted) square-planar CuN_4 chromophores have been satisfactorily assigned for the amine complexes of copper 5,5-diphenylhydantoinate (Akitsu, Komorita & Urushiyama, 2001). The present study details the structure of the 2-phenylethylamine complex, (I).



(I)

In (I) (Fig. 1), the Cu atom exists in a square-planar CuN_4 coordination geometry; it lies on an inversion center. The 2-phenylethylamine and 5,5-diphenylhydantoinate groups function as monodentate ligands. Similar complexes commonly adopt a square-planar coordination geometry (Akitsu, Komorita & Kushi, 2001; Akitsu *et al.*, 2003). The five-membered ring of the 5,5-diphenylhydantoinate group is planar, and the carbonyl O atoms lie in the plane. The C1—N1—C2 angle of 108.7 (2)° indicates the sp^2 character of the deprotonated N1 atom; the O1—C1—N1 and O2—C2—N1

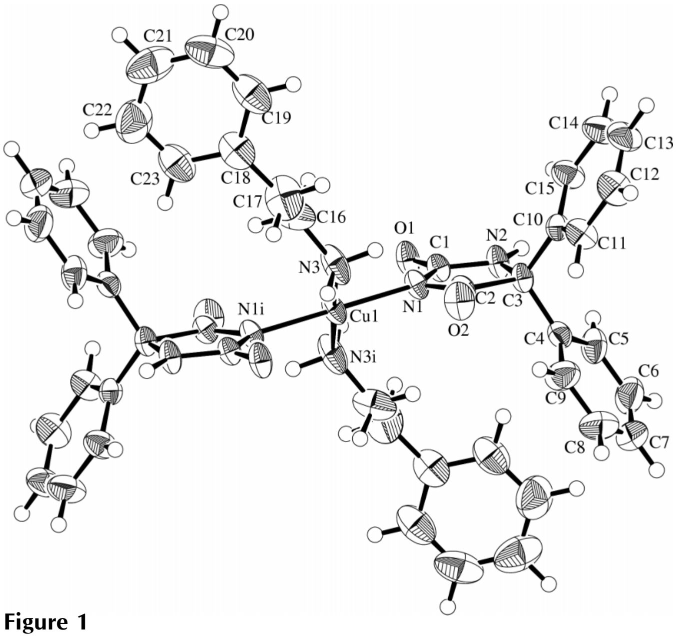


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

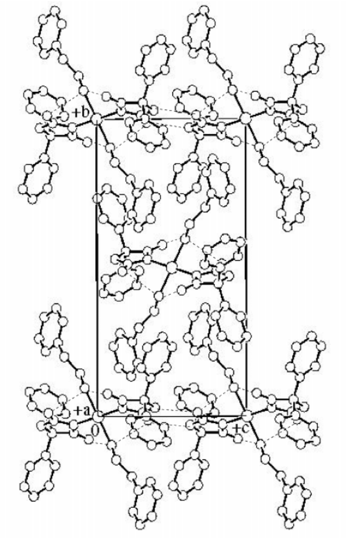


Figure 2
A molecular packing diagram of (I), viewed down the crystallographic *a* axis. Dashed lines represent hydrogen bonds.

angles of 124.9 (3) and 126.2 (3)°, respectively, also reflect electron delocalization in the π-conjugated system. Intramolecular hydrogen bonds (Table 2) serve to stabilize the square-planar geometry. Adjacent molecules are linked by intermolecular hydrogen bonds along the crystallographic *b* axis (Fig. 2). Such a hydrogen-bonding pattern is also found in the above-mentioned related complexes.

Experimental

The reaction of copper(II) acetate (0.454 g, 2.50 mmol), 5,5-diphenylhydantoin (1.26 g, 5.00 mmol) and 2-phenylethylamine (0.606 g, 5.00 mmol) in ethanol (100 ml) at 323 K for 1 h gave a red–violet compound. Prismatic crystals were obtained by the slow evaporation of a methanol–chloroform (4:1 *v*/*v*) solution in a hexane vapor at 278 K; the yield was about 20%. Analysis found: C 68.04, H 5.61, N 10.30%; calculated for $C_{46}H_{44}CuN_6O_4$: C 68.34, H 5.49, N 10.40%. IR (Nujol mull): 1647 cm^{-1} (amide band). UV–vis (diffuse reflectance): 20 100 cm^{-1} [log$F(R_d)$ 0.36] with a shoulder around 16 700 cm^{-1} (0.24).

Crystal data

$[Cu(C_{15}H_{11}N_2O_2)_2(C_8H_{11}N)_2]$
$M_r = 808.42$
Monoclinic, $P2_1/c$
$a = 11.050$ (9) Å
$b = 18.502$ (10) Å
$c = 9.916$ (5) Å
$\beta = 95.08$ (5)°
$V = 2019$ (2) Å^3
$Z = 2$

$D_x = 1.330$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.4$–13.0°
$\mu = 0.59$ mm^{-1}
$T = 297$ (1) K
Prism, red–violet
0.70 × 0.50 × 0.30 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.708$, $T_{max} = 0.837$
5357 measured reflections
4643 independent reflections
4635 reflections with $I > 2\sigma(I)$

$R_{int} = 0.034$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 24$
$l = -12 \rightarrow 5$
3 standard reflections every 150 reflections
intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.152$
$S = 1.03$
4635 reflections
259 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 2.676P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.979 (2)	Cu1—N3	2.026 (3)
N1—Cu1—N3	91.4 (1)	Cu1—N3—C16	118.3 (3)
N1—Cu1—N3^i	88.6 (1)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H13···O2	0.95	2.24	2.901 (4)	126
N3—H12···O1^i	0.95	2.15	2.872 (3)	132
N2—H1···O1^{ii}	0.95	1.92	2.864 (3)	172

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 2 - z$.

Initial measurements on smaller crystals were not successful, owing to weak diffraction, and a somewhat large crystal was then used in the measurements. All H atoms were placed in calculated positions, with C—H and N—H = 0.95 Å, and included in the final cycles of refinement using a riding model, with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR*92 (Altomare *et* *al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

This work was supported by Grant-in-Aid for the 21st Century COE program 'KEIO Life Conjugate Chemistry' from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References

Akitsu, T., Komorita, S. & Kushi, Y. (2001). *Inorg. Chim. Acta*, **315**, 18–25.

Akitsu, T., Komorita, S. & Tamura, H. (2003). *Inorg. Chim. Acta.* **348**, 25–32.

Akitsu, T., Komorita, S. & Urushiyama, A. (2001). *Bull. Chem. Soc. Jpn*, **74**, 851–860.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

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

Molecular Structure Corporation (2001). *TEXSAN.* Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.

Narayanan, B. & Bhadbhade, M. M. (1998). *J. Coord. Chem.* **46**, 1115–123.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta* Ctyst. A**25**, 351–359.

Rigaku (1999). *WinAFC Diffractometer Control Software*. Rigaku Corporation, Tokyo Japan.

Riley, M. J., Neill, D., Bernhardt, P. V., Byriel, K. A. & Kennard, C. H. L. (1998). *Inorg. Chem.* **37**, 3635–3639.

Sato, O. (2003). *Acc. Chem. Res.* **36**, 692–700.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Takahashi, K., Nakajima, R., Gu, Z.-Z., Yoshiki, H., Fujishima, A. & Sato, O. (2002). *Chem. Commun.* pp. 1578–1579.