Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Witiak, D. T. (1970). *Medicinal Chemistry*, edited by A. Burger, pp. 1643–1668. New York: John Wiley.

Acta Cryst. (1998). C**54**, 1750–1752

Hexakis(μ-*N*-ethylthiourea-*S*)tetrakis[iodocopper(I)] Monohydrate

Chaveng Pakawatchai,[a] Yupa Thanyasirikul,[a] Tapanee Saepae,[a] Suwaluk Pansook,[a] Hoong-Kun Fun[b]† and Kandasamy Chinnakali[b]‡

[a]*Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai 90112, Thailand, and* [b]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: chaveng@ratree.psu.ac.th*

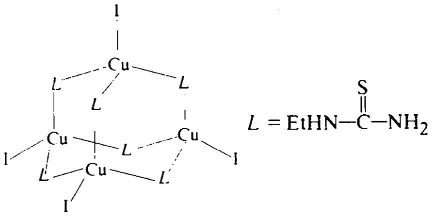
(*Received 6 January 1998; accepted 3 August 1998*)

Abstract

In the title compound, $[Cu_4I_4(N\text{-ethylthiourea})_6]\cdot H_2O$ (*N*-ethylthiourea = $C_3H_8N_2S$), a hexanuclear copper(I) cluster complex, the Cu atoms have tetrahedral coordination. Four such tetrahedra share corners to form a tetrahedral assembly. This cage structure results in the formation of four six-membered Cu—S—Cu—S—Cu—S rings all in the chair conformation.

Comment

Reactions between copper(I) halides and thiourea (tu) or substituted thioureas frequently generate a variety of complexes which have unpredictable stoichiometry and stereochemistry. The substituted thiourea ligands generally coordinate to the Cu atom through the S atom as terminal ligands or bridging ligands or both. Terminal coordination is reported in the complexes $[Cu(dmtu)_3Cl]$ (dmtu = *N*,*N*′-dimethylthiourea) (Girling & Amma, 1971) and $[Cu(detu)_3I]$ (detu = diethylthiourea) (Fun *et al.*, 1998), whereas in the complexes $[Cu(tu)_2Cl]$ (Spofford & Amma, 1968), $[Cu(tu)_3Cl]$ (Okaya & Knobler, 1964) and $[Cu_2(etu)_4Cl_2]$ (etu = ethylenethiourea) (Battaglia *et al.*, 1976), the ligands have both terminal and bridging coordination. The crystal structure determination of the title compound, (I), was carried out to establish the coordination environment.



(I)

The stoichiometric ratio of CuI and *N*-ethylthiourea in the title complex (I) is 1:1.5. Each Cu atom is coordinated tetrahedrally by three S atoms and an I atom. Four such tetrahedra are held together by corner sharing at sulfur positions to form a tetrahedral array. This arrangement defines four six-membered Cu_3S_3 rings, all adopting a chair conformation. In these rings, the substituent I atoms occupy equatorial positions and of the three $C(NH_2)(NHCH_2CH_3)$ substituents, one is in an axial position and the remaining two are in equatorial positions. The Cu—I distances vary from 2.623 (2) to 3.081 (2) Å and the Cu—S distances range from 2.259 (3) to 2.386 (3) Å. The overall complex has an adamantane-like cluster structure with *N*-ethylthiourea as bridging and I as terminal ligands. Similar adamantane structures have been reported for $Cu_4(tu)_6(NO_3)_4\cdot 4H_2O$ and $Cu_4(tu)_9(NO_3)_4\cdot 4H_2O$, with trigonal planar Cu atoms in the former, but with three tetrahedral and one trigonal planar Cu atom in the latter (Griffith *et al.*, 1976). For the sulfate analogue, structures have been reported for $[Cu_4(tu)_6](SO_4)_4\cdot 2H_2O$ (Declercq *et al.*, 1978), $[Cu_8(tu)_{15}](SO_4)_4\cdot xH_2O$ (Declercq *et al.*, 1978) and $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$ (Bott *et al.*, 1998).

The geometry of short N—H···O and N—H···I intra- and intermolecular contacts is given in Table 2. The water in the structure comes from the undried ethanol solvent.

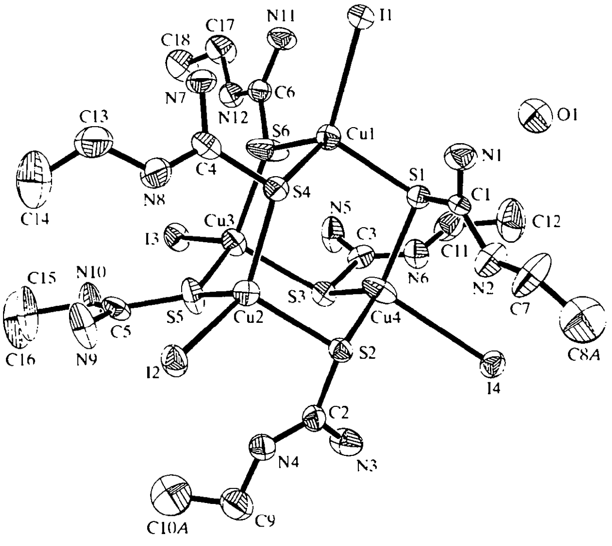


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. The H atoms have been omitted for clarity.

---

† On sabbatical leave at: Department of Chemistry, Prince of Songkla University, Hat Yai, Thailand.

‡ On leave from: Department of Physics, Anna University, Chennai 600 025, India.

Experimental

N-Ethylthiourea (0.35 g, 3.3 mmol) was dissolved in ethanol (50 ml) with continuous stirring. CuI (0.25 g, 1.3 mmol) was added and the solution was kept warm for 3 h, after which time it was filtered and allowed to cool to room temperature. Slow evaporation of this solution yielded colourless crystals.

Crystal data

$[Cu_4I_4(C_3H_8N_2S)_6]\cdot H_2O$
$M_r = 1404.84$
Orthorhombic
$P2_12_12_1$
$a = 11.1794\ (9)$ Å
$b = 18.505\ (2)$ Å
$c = 22.409\ (2)$ Å
$V = 4635.7\ (8)$ Å^3
$Z = 4$
$D_x = 2.013$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 34 reflections
$\theta = 5.403–12.535°$
$\mu = 4.775$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped
0.34 × 0.26 × 0.16 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scan (Sheldrick, 1990)
$T_{min} = 0.292$, $T_{max} = 0.466$
7124 measured reflections
6864 independent reflections
3634 reflections with $I > 2\sigma(I)$

$R_{int} = 0.034$
$\theta_{max} = 27.5°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 24$
$l = -1 \rightarrow 29$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.092$
$S = 0.794$
6863 reflections
404 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.581$ e Å^{-3}
$\Delta\rho_{min} = -0.665$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (3)

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

I1—Cu1	2.679 (2)	Cu2—S5	2.332 (4)
I2—Cu2	2.767 (2)	Cu2—S2	2.344 (3)
I3—Cu3	2.623 (2)	Cu3—S5	2.300 (4)
I4—Cu4	3.081 (2)	Cu3—S6	2.346 (4)
Cu1—S6	2.262 (4)	Cu3—S3	2.386 (3)
Cu1—S1	2.351 (3)	Cu4—S3	2.259 (3)
Cu1—S4	2.358 (3)	Cu4—S1	2.273 (3)
Cu2—S4	2.307 (3)	Cu4—S2	2.274 (3)
S6—Cu1—S1	107.3 (2)	S5—Cu3—I3	118.66 (10)
S6—Cu1—S4	106.5 (2)	S6—Cu3—I3	115.38 (10)
S1—Cu1—S4	104.72 (11)	S3—Cu3—I3	112.60 (10)
S6—Cu1—I1	118.91 (10)	S3—Cu4—S1	117.78 (13)
S1—Cu1—I1	109.82 (9)	S3—Cu4—S2	113.97 (13)
S4—Cu1—I1	108.70 (10)	S1—Cu4—S2	114.65 (12)
S4—Cu2—S5	113.72 (13)	S3—Cu4—I4	103.70 (10)
S4—Cu2—S2	107.35 (12)	S1—Cu4—I4	103.34 (9)
S5—Cu2—S2	103.93 (13)	S2—Cu4—I4	100.27 (9)
S4—Cu2—I2	111.88 (10)	Cu4—S1—Cu1	103.12 (13)
S5—Cu2—I2	110.85 (10)	Cu4—S2—Cu2	101.60 (12)
S2—Cu2—I2	108.62 (9)	Cu4—S3—Cu3	107.92 (14)
S5—Cu3—S6	107.4 (2)	Cu2—S4—Cu1	113.26 (14)
S5—Cu3—S3	99.03 (13)	Cu3—S5—Cu2	117.04 (14)
S6—Cu3—S3	101.3 (2)	Cu1—S6—Cu3	122.83 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.86	2.22	3.011 (13)	152
N5—H5*A*···O1^{i}	0.86	2.27	3.014 (13)	145
N1—H1*B*···I1	0.86	2.88	3.729 (9)	170
N2—H2*A*···I4	0.86	2.95	3.799 (11)	171
N3—H3*A*···I4^{ii}	0.86	3.02	3.833 (11)	159
N3—H3*B*···I4	0.86	2.87	3.711 (11)	168
N4—H4*A*···I2	0.86	2.95	3.810 (11)	174
N5—H5*B*···I3	0.86	2.91	3.753 (11)	169
N6—H6*A*···I4	0.86	2.99	3.816 (9)	163
N7—H7*A*···I4^{iii}	0.86	3.01	3.811 (10)	156
N7—H7*B*···I1	0.86	2.92	3.735 (10)	158
N8—H8*A*···I2	0.86	2.86	3.719 (11)	175
N9—H9*A*···I1^{iv}	0.86	3.01	3.762 (12)	148
N9—H9*B*···I2	0.86	2.78	3.635 (12)	171
N10—H10*A*···I3	0.86	2.85	3.691 (11)	168
N11—H11*A*···I2^{iii}	0.86	2.96	3.746 (9)	153
N11—H11*B*···I1	0.86	2.79	3.643 (10)	174
N12—H12*A*···I3	0.86	2.85	3.711 (10)	177

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

The ethyl C8 and C10 atoms of the ligand were found to be disordered. The occupancies of the disordered positions C8*A*/C8*B* and C10*A*/C10*B* were initially refined and later fixed as 0.55/0.45 and 0.60/0.40, respectively. All the disordered atoms were refined isotropically without any restraints. H atoms were fixed geometrically and allowed to ride on the atoms to which they were attached. The H atoms of the water molecule could not be located.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1983).

The authors acknowledge Prince of Songkla University of Thailand for a research grant. The authors also thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. HKF thanks the Royal Thai Ministry of University Affairs for a grant under its Foreign Expert Invitation programme. KC thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1242). Services for accessing these data are described at the back of the journal.

References

Battaglia, L. P., Corradi, A. B., Nardelli, M. & Vidoni Tani, M. E. (1976). *J. Chem. Soc. Dalton Trans.* pp. 143–146.
Bott, R. C., Bowmaker, G. A., Davis, C. A., Hope, G. A. & Jones, B. E. (1998). *Inorg. Chem.* **37**, 651–657.
Declercq, J. P., Kamara, R., Moreaux, C., Dereppe, J. M., Germain, G. & Van Meerssche, M. (1978). *Acta Cryst.* **B34**, 1036–1037.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Fun, H.-K., Razak, I. A., Pakawatchai, C., Khaokong, C., Chantrapromma, S. & Saithong, S. (1998). *Acta Cryst.* **C54**, 453–456.
Girling, R. L. & Amma, E. L. (1971). *Inorg. Chem.* **10**, 335–340.

Griffith, E. H., Hunt, G. W. & Amma, E. L. (1976). *J. Chem. Soc. Chem. Commun.* pp. 432–433.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Okaya, Y. & Knobler, C. (1964). *Acta Cryst.* **17**, 928–930.
Sheldrick, G. M. (1990). *SHELXTL/PC. Structure Determination Software Programs.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XSCANS. Diffractometer Control Program.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spofford, W. A. III & Amma, E. L. (1968). *J. Chem. Soc. Chem. Commun.* pp. 405–407.

Acta Cryst. (1998). C**54**, 1752-1753

trans-Carbonyl(pentafluorophenyl-*C*)bis[(pentafluorophenyl)diphenylphosphine-*P*]iridium(I)

JOHN FAWCETT, ERIC G. HOPE AND LEE A. PECK

Department of Chemistry, University of Leicester, Leicester LE1 7RH, England. E-mail: jxf@leicester.ac.uk

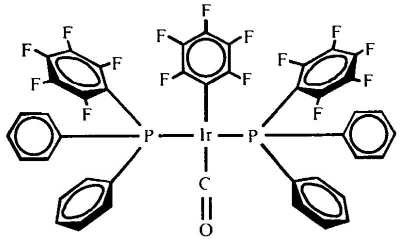
(Received 26 March 1998; accepted 8 June 1998)

Abstract

In *trans*-$[Ir(C_6F_5)\{P(C_6F_5)(C_6H_5)_2\}_2(CO)]$, the Ir—P and Ir—C distances are comparable to those of the triphenylphosphine analogue. F···F interactions appear to dominate the configuration, resulting in virtually eclipsed $C_6F_5(Ir)$ and $C_6F_5(P)$ rings.

Comment

It has been shown that a σ-pentafluorophenyl ligand can markedly influence the tendency of low-valent metal complexes to undergo oxidative addition reactions (Bennett, Bruce & Goodfellow, 1973; Bennett, Bruce & Gardner, 1973; Rausch & Moser 1974). We have been investigating crystallographically the steric and electronic effects of F atoms in arylphosphine and -phosphite ligands (Atherton *et al.*, 1995, 1997), and during this work obtained crystals of the title compound, (1).



(1)

The structural features of this complex can be directly compared to those of *trans*-carbonyl(pentafluorophenyl)bis(triphenylphosphine)iridium(I), (2) (Clearfield *et al.*, 1975). The Ir coordination environments are very similar: Ir—P distances of 2.305 (1) and 2.304 (1) Å in (1), *cf.* 2.326 (4) and 2.305 (5) Å in (2), $Ir—C_{carbonyl}$ 1.863 (5) Å in (1), *cf.* 1.891 (17) Å in (2), and $Ir—C_{aryl}$ 2.092 (4) Å in (1), *cf.* 2.090 (16) Å in (2). The $Ir—C_{aryl}$ distances suggest little π overlap between the ligand and the metal centres, indicating that the reduced reactivity of these pentafluorophenyl derivatives towards oxidative addition reactions is predominately a steric effect. This is in marked contrast to the results of our work on fluorophenylimido molybdenum dimers (Fawcett *et al.*, 1994; Bhattacharyya *et al.*, 1997), which showed that the introduction of the $-N(C_6F_5)$ ligand had a significant electronic influence on the metal centres.

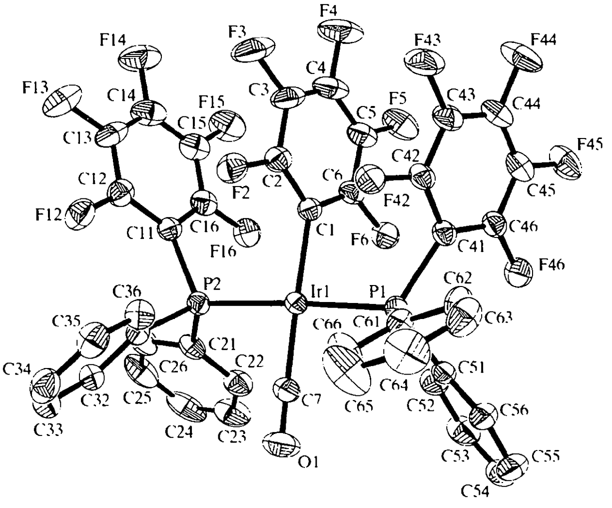


Fig. 1. The molecular structure of the title compound, showing the atom-numbering scheme and 30% displacement ellipsoids. H atoms have been omitted for clarity.

In the structure determination of (2), the atoms in the pentafluorophenyl ring were seen to have large displacement parameters, affording unusual C—C and C—F bond lengths. In (1), the metal-bound pentafluorophenyl ring is well defined and the average C—C [1.378 (17) Å] and C—F [1.348 (6) Å] distances are virtually identical to the corresponding distances in the P-bound pentafluorophenyl rings [1.378 (15) and 1.340 (7) Å, respectively]. In contrast to the staggered arrangement of the phosphine aryl groups in (2) and in most *trans*-bis(phosphine) metal complexes, in (1), the phosphine aryl groups are eclipsed and both of the $C_6F_5(P)$ rings and the $C_6F_5(Ir)$ ring line up, presumably as a result of interactions between the F atoms, resulting in very small C41—P1—Ir1—C1 and C11—P2—Ir1—C1 torsion angles [3.7 (2) and 7.1 (2)°, respectively]. There is slight bending of the P1—Ir1—P2 axis [175.4 (1)°]