11 568 reflections
781 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1196P)^2 + 3.8543P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ru1—B6	2.057 (9)	Ru1—B3	2.482 (9)
Ru1—B2	2.133 (9)	Ru1—H1	1.69 (8)
Ru1—B4	2.205 (9)	P2—B5	1.941 (10)
Ru1—B7	2.341 (9)	P3—B3	1.928 (9)
Ru1—P1	2.363 (2)	O1—B2	1.401 (11)
Ru1—B5	2.392 (10)	O3—B6	1.410 (10)
Ru1—Cl1	2.482 (2)		
B6—Ru1—P1	120.4 (3)	P1—Ru1—B3	123.0 (2)
B2—Ru1—P1	90.1 (3)	Cl1—Ru1—B3	105.3 (2)
B4—Ru1—P1	150.2 (2)	B6—Ru1—H1	69 (3)
B7—Ru1—P1	104.0 (3)	B2—Ru1—H1	136 (3)
P1—Ru1—B5	166.6 (2)	B4—Ru1—H1	130 (3)
B6—Ru1—Cl1	133.5 (3)	B7—Ru1—H1	100 (3)
B2—Ru1—Cl1	132.8 (2)	P1—Ru1—H1	70 (3)
B4—Ru1—Cl1	81.0 (2)	B5—Ru1—H1	98 (3)
B7—Ru1—Cl1	174.9 (3)	Cl1—Ru1—H1	84 (3)
P1—Ru1—Cl1	80.52 (8)	B3—Ru1—H1	165 (3)
B5—Ru1—Cl1	104.9 (2)		

The title structure was solved by the Patterson method and refined by full-matrix least-squares techniques. The non-H atoms were refined anisotropically to convergence. H atoms on C and O atoms were included in riding positions [phenyl C—H = 0.93 Å, other C—H = 0.97 Å, O—H = 0.82 Å and $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C,O})$]. The cage H atoms and the Ru-bound H atom were located using Fourier methods and refined isotropically. The $CHCl_3$ molecule, modelled as atoms C2*S*, Cl5, Cl6 and Cl7, was refined with an occupancy of 0.20. The C—Cl distances were restrained to be approximately equal (1.68 Å).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1994*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994). Software used to prepare material for publication: *SHELXL*97.

We thank the National Natural Science Foundation of China for support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1032). Services for accessing these data are described at the back of the journal.

References

Crook, J. E., Elrington, M., Greenwood, N. N., Kennedy, J. D., Thornton-Pett, M. & Woollins, J. D. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2407–2415.
Crook, J. E., Elrington, M., Greenwood, N. N., Kennedy, J. D. & Woollins, J. D. (1984). *Polyhedron*, **3**, 901–904.
Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D., Thornton-Pett, M. & Zheng, P. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1717–1718.
Molecular Structure Corporation (1994*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1994*b*). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Yao, H.-J., Fu, J., Jin, R.-S., Wei, J.-D., Chen, J. & Zheng, P.-J. (1995). *Chin. J. Struct. Chem.* **14**, 364–368.
Zsolnai, L. & Huttner, G. (1994). *ZORTEP. A Program for Molecular Graphics*. University of Heidelberg, Germany.

Acta Cryst. (1999). C55, 339-341

$[Ni\{(CH_3)_2SO\}_6]I_4$, a redetermination and reinterpretation

DE-LIANG LONG, HUAI-MING HU, JIU-TONG CHEN AND JIN-SHUN HUANG

State Key Laboratory of Structural Chemistry, Fujan Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China. E-mail: ldl@ms.fjirsm.ac.cn

(*Received 23 June 1998; accepted 9 October 1998*)

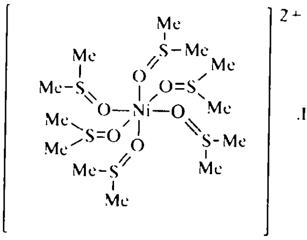
Abstract

The structure of the title polyiodide compound, hexakis(dimethyl sulfoxide-*O*)nickel(II) tetraiodide, $[Ni(C_2H_6OS)_6]I_4$, has been redetermined. The compound comprises discrete $[Ni\{(CH_3)_2SO\}_6]^{2+}$ cations and I_4^{2-} anions. The polyhedron around the six-coordinate Ni atom is a distorted octahedron with the metal atom on a $\bar{3}$ position and six equivalent Ni—O distances of 2.077 (2) Å. The linear uncoordinated centrosymmetric I_4^{2-} polyiodide ion represents a rare example of a tetraiodide ion. It exhibits a central I—I bond of 2.848 (1) Å and two terminal I—I bonds of 3.342 (2) Å.

Comment

In recent years, polyiodides have been the focus of increasing interest due to the high conductivity and non-linear optical properties of many of their salts with sulfur-rich compounds (Wanka *et al.*, 1996; Truong *et al.*, 1993), their ability to introduce partial oxidation into hydrocarbon donor molecules to stabilize mixed valence in metal complexes (Niebling *et al.*, 1996), and their rich and varied structural chemistry. In this area, I_3^-, I_5^- and I_7^- are normally used for the synthesis of these compounds. In contrast, the formation of isolated I_4^{2-} ions was indicated by theoretical calculations to be disfavoured (Sæthre *et al.*, 1988). $[Co(NH_3)_6I_3I_4]$

(Tebbe, 1977) and $Cu(NH_3)_4I_4$ (Dubler & Linowsky, 1975) are among the few examples characterized by X-ray structure determination. While using I_2 as an oxidant to prepare nickel(III) dithiolene complexes for non-linear optical studies (Long *et al.*, 1998), we obtained the nickel(II) tetraiodide salt (I).



(I)

The structure of (I) was reported recently by Reibenspies & Kim (1996), who described the iodine components as I^- and I_2. We have now redetermined the structure to greater precision but, more importantly, we present another interpretation of the structure wherein the cations are as described in the previous study but the iodine component consists solely of I_4^{2-} dianions (Fig. 1).

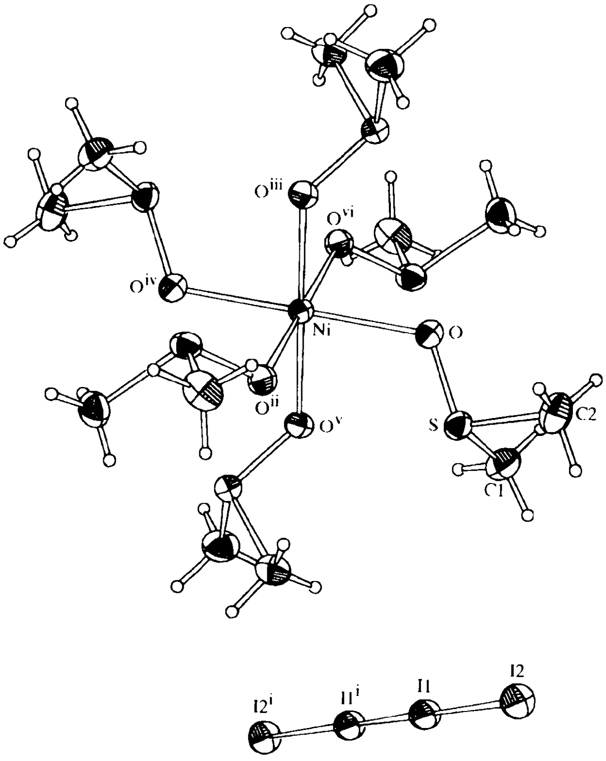


Fig. 1. View of the title molecule. Displacement ellipsoids are shown at the 30% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry codes: (i) $-x, -y, -1-z$; (ii) $-x+y, 1-x, z$; (iii) $1-y, 1+x-y, z$; (iv) $\frac{2}{3}-x, \frac{4}{3}-y, -\frac{2}{3}-z$; (v) $y-\frac{1}{3}, \frac{1}{3}-x+y, -\frac{2}{3}-z$; (vi) $x+\frac{2}{3}-y, \frac{1}{3}+x, -\frac{2}{3}-z$.]

The Ni^{II} centre lies on a $\bar{3}$ site and is coordinated by six symmetry equivalent dimethyl sulfoxide molecules, with Ni—O distances of 2.077 (2) Å. The coordination polyhedron around the Ni atom is a distorted octahedron flattened in the direction of the threefold axis so that its two axial O_3 faces [$OO^{iii}O^{ii}$ and $O^{vi}O^{v}O^{iv}$; symmetry codes: (ii) $-x+y, 1-x, z$; (iii) $1-y, 1+x-y, z$; (iv) $\frac{2}{3}-x, \frac{4}{3}-y, -\frac{2}{3}-z$; (v) $y-\frac{1}{3}, \frac{1}{3}-x+y, -\frac{2}{3}-z$; (vi) $x+\frac{2}{3}-y, \frac{1}{3}+x, -\frac{2}{3}-z$] have much longer O···O distances than the remaining edges in the equatorial region.

The linear uncoordinated centrosymmetric I_4^{2-} polyiodide ion exhibits a central I1—I1($-x, -y, -1-z$) distance of 2.848 (1) Å and a terminal I1—I2 bond of 3.342 (2) Å. These I—I separations are comparable to corresponding respective values of 2.802 (1) and 3.342 (1) Å found in $Cu(NH_3)_4I_4$ (Dubler *et al.*, 1975), where both terminal I atoms have weak coordination to Cu centres, forming a ladder structure. The closest Ni···I contact is 5.21 Å indicating that there are no significant interactions between the Ni and I atoms in this structure.

Experimental

Crystals of (I) were obtained from a solution of $Na_2Ni(mnt)_2$ (mnt = maleonitriledithiolate) in dimethyl sulfoxide into which I_2 had been sublimed.

Crystal data

$[Ni(C_2H_6OS)_6]I_4$
$M_r = 1035.08$
Trigonal
$R\bar{3}$
$a = 11.8241$ (5) Å
$c = 19.8441$ (11) Å
$V = 2402.7$ (2) Å^3
$Z = 3$
$D_x = 2.146$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3245 reflections
$\theta = 2.24$–$25.00°$
$\mu = 4.874$ mm^{-1}
$T = 293$ (2) K
Block
0.30 × 0.15 × 0.10 mm
Deep brown

Data collection

Siemens SMART CCD diffractometer
Area-detector scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.483$, $T_{max} = 0.614$
3994 measured reflections

944 independent reflections
854 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25°$
$h = -14 \rightarrow 11$
$k = -9 \rightarrow 14$
$l = -23 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.041$
$S = 1.131$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: none

943 reflections
69 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0125P)^2 + 4.788P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	1/3	2/3	−1/3	0.0294 (2)
I1	0	0	−0.42824 (2)	0.05254 (13)
I2	0	0	−0.25984 (2)	0.05009 (12)
S	0.29182 (7)	0.41669 (7)	−0.25930 (4)	0.0378 (2)
O	0.3912 (2)	0.5581 (2)	−0.27545 (9)	0.0374 (4)
C1	0.3264 (4)	0.3198 (3)	−0.3153 (2)	0.0496 (8)
C2	0.3498 (4)	0.3834 (4)	−0.1833 (2)	0.0549 (9)

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

Ni—O	2.077 (2)	S—O	1.521 (2)
I1—I1^{i}	2.848 (1)	S—C1	1.784 (4)
I1—I2	3.342 (1)	S—C2	1.780 (4)
O—Ni—O^{ii}	92.37 (7)	O—S—C2	104.5 (2)
O^{iv}—Ni—O	180	O—S—C1	106.0 (2)
O—Ni—O^{v}	87.63 (7)	C1—S—C2	98.5 (2)
I1^{i}—I1—I2	180	Ni—O—S	118.9 (1)

Symmetry codes: (i) $-x, -y, -1-z$; (ii) $-x+y, 1-x, z$; (iv) $\frac{2}{3}-x, \frac{4}{3}-y, -\frac{2}{3}-z$; (v) $y-\frac{1}{3}, \frac{1}{3}-x+y, -\frac{2}{3}-z$.

The structure was solved by direct methods and expanded using Fourier techniques. All H atoms were found in difference Fourier maps and refined isotropically.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SMART* and *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

This research was supported by grants from the National Natural Science Foundation of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1277). Services for accessing these data are described at the back of the journal.

References

Dubler, E. & Linowsky, L. (1975). *Helv. Chim. Acta*, **58**, 2604–2609.

Long, D.-L., Cui, Y., Chen, J.-T., Cheng, W.-D. & Huang, J.-S. (1998). *Polyhedron*, **17**, 3969–3975.

Niebling, U., Moldenhauer, J., Ludwig, T., Schweitzer, D. & Strunz, W. (1996). *Solid State Commun.* **97**, 837–842.

Reibenspies, J. H. & Kim, J. S. (1996). *Z. Kristallogr.* **211**, 418.

Sæthre, L. J., Gropen, O. & Sletten, J. (1988). *Acta Chem. Scand. Ser. A*, **42**, 16–26.

Sheldrick, G. M. (1996). *SADABS. Absorption Correction Program*. University of Göttingen, Germany.

Siemens (1994). *SHELXTL*. Release 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Tebbe, K. F. (1977). In *Homoatomic Rings, Chains and Macromolecules of Main Group Elements*, edited by A. L. Rheingold. New York: Elsevier.

Truong, K. D., Grenier, P., Houde, D. & Bandrauk, A. D. (1993). *Synth. Met.* **57**, 3968–3973.

Wanka, S., Beckmann, D., Wasnitza, J., Balthes, E., Schweitzer, D., Strunz, W. & Keller, H. J. (1996). *Phys. Rev. B: Condens. Matter*, **53**, 9301–9309.

Acta Cryst. (1999). C55, 341–343

Di-μ-iodo-1:2κ^4*I*-bis(quinoline)-1κ*N*,2κ*N*-bis(triphenylphosphine)-1κ*P*,2κ*P*-dicopper(I)

QIONG-HUA JIN,[a] YU-XIAN WANG[a] AND XIU-LAN XIN[b]

[a]*Department of Chemistry, Capital Normal University, Beijing 100037, People's Republic of China, and*
[b]*Department of Chemical Engineering, Beijing Institute of Light Industry, Beijing 100037, People's Republic of China.*
E-mail: jinqh@mailhost.cnu.edu.cn

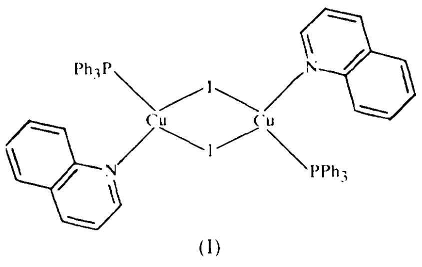
(*Received 8 June 1998; accepted 12 October 1998*)

Abstract

The title compound, $[CuI(PPh_3)(C_9H_7N)]_2$ or $[Cu_2I_2(C_9H_7N)_2(C_{18}H_{15}P)_2]$, is an inversion-symmetric dimer with two Cu atoms each tetrahedrally coordinated to two I, one N and one P atom. The diamond-shaped central Cu_2I_2 group has longer I···I [4.351 (1) Å] and shorter Cu···Cu distances [3.144 (1) Å] than the $X\cdots X$ (X = Br, I) and Cu···Cu distances found in the related compounds $[CuBr(PPh_3)(C_9H_7N)]_2$ and $[CuI(C_9H_7N)_2]_2$.

Comment

Recently, we obtained the group *IB* metal complexes $[CuBr(PPh_3)(C_9H_7N)]_2$ [(II); Jin, Long *et al.*, 1998] and $[CuI(PPh_3)(phen)]$ (Jin, Xin *et al.*, 1998), where phen is 1,10-phenanthroline, which have found use in our work on the synthesis of Mo(W)–Cu(Ag)–S compounds (Hou *et al.*, 1996). We report here the structure of another such Cu^{I} complex, namely, $[CuI(PPh_3)(C_9H_7N)]_2$, (I).



(I)