

Data collection

Stoe four-circle diffractometer	$R_{\text{int}} = 0.040$
ω scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: none	$h = -9 \rightarrow 13$
8624 measured reflections	$k = -16 \rightarrow 9$
7611 independent reflections	$l = -18 \rightarrow 18$
6331 reflections with $I > 2\sigma(I)$	3 standard reflections every 100 reflections
	intensity decay: 1.52%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$\Delta\rho_{\text{max}} = 1.253 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.134$	$\Delta\rho_{\text{min}} = -1.670 \text{ e } \text{\AA}^{-3}$
$S = 1.044$	Extinction correction: none
7602 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
413 parameters	
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 1.955P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

Ag1—O2	2.386 (3)	Cl2—C1	1.769 (6)
Ag1—P1	2.4120 (12)	P1—C26	1.815 (3)
Ag1—P2	2.4401 (12)	P1—C16	1.825 (3)
Ag1—O1	2.481 (3)	P1—C36	1.826 (4)
N1—O1	1.253 (4)	P2—C46	1.821 (4)
N1—O2	1.259 (4)	P2—C56	1.826 (3)
Cl1—C1	1.777 (6)	P2—C66	1.826 (4)
O2—Ag1—P1	118.35 (8)	N1—O2—Ag1	99.6 (2)
O2—Ag1—P2	109.99 (8)	Cl2—C1—Cl1	111.3 (3)
P1—Ag1—P2	128.67 (4)	C26—P1—Ag1	117.64 (12)
O2—Ag1—O1	51.25 (10)	C16—P1—Ag1	110.01 (12)
P1—Ag1—O1	120.81 (8)	C36—P1—Ag1	111.74 (12)
P2—Ag1—O1	102.06 (8)	C46—P2—Ag1	115.14 (12)
O1—N1—O2	114.1 (3)	C56—P2—Ag1	116.73 (12)
N1—O1—Ag1	95.1 (2)	C66—P2—Ag1	108.82 (12)
O1—N1—O2—Ag1	-1.3 (4)	P1—Ag1—P2—C46	-179.82 (12)
P2—Ag1—P1—C26	-169.02 (12)		

The C atoms of the phenyl rings were refined without any constraints. The H atoms were constrained to parent sites and common isotropic displacement parameters were refined for the H atoms of the same phenyl group [$U_{\text{iso}} = 0.036(5) - 0.046(6) \text{ \AA}^2$] and for the H atoms of the solvent molecule [$U_{\text{iso}} = 0.091(16) \text{ \AA}^2$]. The strongest peaks (0.63 to $1.253 \text{ e } \text{\AA}^{-3}$) and the holes deeper than $-0.61 \text{ e } \text{\AA}^{-3}$ in the final difference Fourier map were situated $0.75 - 1.29 \text{ \AA}$ from the Ag⁺ ion.

Data collection: local program. Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

FB thanks Professor Dr C. Kratky, Institute of Physical Chemistry, University of Graz, Austria, for the use of the diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1123). Services for accessing these data are described at the back of the journal.

References

- Barron, P. F., Dyason, J. C., Healy, P. C., Engelhardt, L. M., Skelton, B. W. & White, A. H. (1986). *J. Chem. Soc. Dalton Trans.* pp. 1965–1970.
- Belaj, F., Trnoska, A. & Nachbaur, E. (1997). *Z. Kristallogr.* **212**, 355–361.
- Ishihara, M., Ohba, S. & Saito, Y. (1987). *Acta Cryst.* **B43**, 160–164.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Ohba, S., Matsumoto, F., Ishihara, M. & Saito, Y. (1986). *Acta Cryst.* **C42**, 1–4.
- Ohba, S. & Saito, Y. (1981). *Acta Cryst.* **B37**, 1911–1913.
- Sheldrick, G. M. (1985). *SHELXS86*. Program for the Solution of Crystal Structures. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93*. Program for Refinement of Crystal Structures. University of Göttingen, Germany.

Acta Cryst. (1998). **C54**, 728–732

8-Methylaminoquinolinium Salts of Tetrachlorodimethylstannate(IV) and Tetrachlorodiphenylstannate(IV)

ALAN HAZELL,^a LIAN EE KHOO,^b JIEXIANG OUYANG,^b BERNHARD J. RAUSCH^a AND ZARA MIRAVENT TAVARES^a

^aDepartment of Chemistry, Aarhus University,

Langelandsgade 140, DK-8000 Århus C, Denmark, and

^bSchool of Science, National Institute of Education, 469 Bukit Timah Road, Singapore 259756. E-mail: ach@kemi.aau.dk

(Received 21 October 1997; accepted 9 January 1998)

Abstract

The title compounds, (C₁₀H₁₁N₂)₂[SnCl₄(CH₃)₂] and (C₁₀H₁₁N₂)₂[SnCl₄(C₆H₅)₂], have been prepared from the reaction of 8-methylaminoquinoline with diorganotin dichlorides. In the methyl compound, the Sn atom is coordinated to two methyl groups, which are *trans* with respect to each other [Sn—C 2.102 (5) and 2.103 (4) Å], and to four Cl atoms [Sn—Cl 2.442 (1), 2.461 (1), 2.894 (1) and 3.098 (1) Å]. The two long Sn—Cl bonds are *trans* to the short ones and their Cl atoms are hydrogen bonded to the N—H groups of the 8-methylaminoquinolinium cations. The Sn—CH₃ bonds are bent away from the short Sn—Cl bonds so that the CH₃—Sn—CH₃ angle is 155.7 (2)°. A correlation between the C—Sn—C angle and the Sn—Cl bond lengths was observed. The anion of the phenyl compound is close to being octahedral and has exact twofold symmetry; the phenyl groups are *trans* with respect to each other [Sn—C 2.143 (2) Å] and Sn—Cl distances are in the range 2.497 (1)–2.672 (1) Å. Two Cl atoms are hydrogen bonded to N—H groups of the cations.

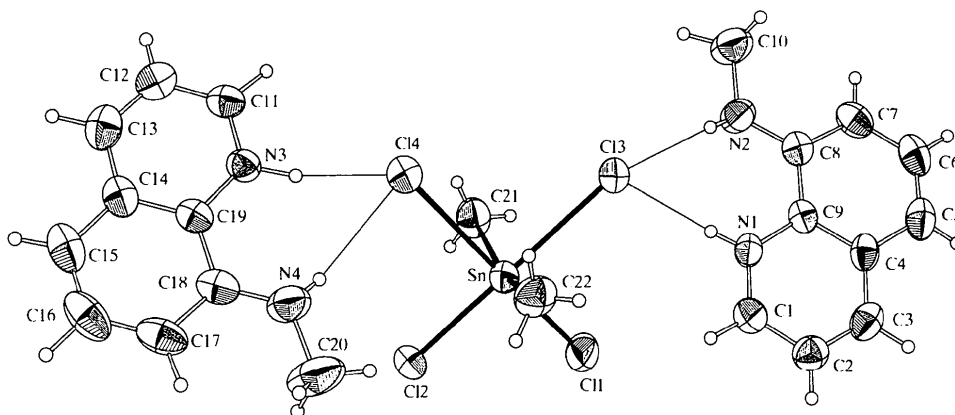
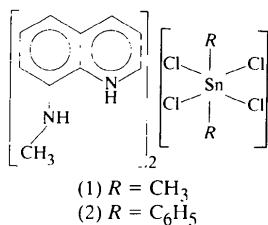


Fig. 1. The structure and hydrogen bonding for compound (1), with 50% probability ellipsoids for non-H atoms.

Comment

As a continuation of our attempts to coax potentially *N,N'*-bidentate ligands to form adducts with diorganotin dihalides (Hazell *et al.*, 1997), we now report that the reaction of 8-methylaminoquinoline with $R_2\text{SnCl}_2$ ($R = \text{CH}_3$ and C_6H_5) yielded, instead of adducts, the 8-methylaminoquinolinium salts of tetrachlorodimethylstannate(IV) and tetrachlorodiphenylstannate(IV).



In $(\text{C}_{10}\text{H}_{11}\text{N}_2)_2[\text{SnCl}_4(\text{CH}_3)_2]$, (1), the Sn atom is coordinated to two methyl groups, which are *trans* with respect to each other, and four Cl atoms (Fig. 1). There are two short Sn—Cl bonds and two very long Sn—Cl bonds, each of which is *trans* to a short Sn—Cl bond; the Sn—CH₃ bonds are bent away from the short Sn—Cl bonds. The geometry is intermediate between that expected for a regular $(\text{CH}_3)_2\text{SnCl}_4^{2-}$ anion and that of $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2\text{Cl}^-$, but is closer to that of $(\text{CH}_3)_2\text{SnCl}_4^{2-}$. Comparison with related dimethyltin tetrachlorides shows (Fig. 2) that as the Cl⁻ ions are removed, the remaining Sn—Cl bonds get shorter and the CH₃—Sn—CH₃ angle gets narrower, *i.e.* the diagram shows the reaction path for $(\text{CH}_3)_2\text{SnCl}_4^{2-} \rightarrow (\text{CH}_3)_2\text{SnCl}_2 + 2\text{Cl}^-$.

The two N atoms of the 8-methylaminoquinolinium cation are involved in N—H...Cl hydrogen bonds to the Cl atoms of the long Sn—Cl bonds.

In $(\text{C}_{10}\text{H}_{11}\text{N}_2)_2[\text{SnCl}_4(\text{C}_6\text{H}_5)_2]$, (2), the anion is close to being octahedral and has exact twofold symmetry with the phenyl groups *trans* with respect to each other. The Cl1 and Cl2 atoms are both involved in

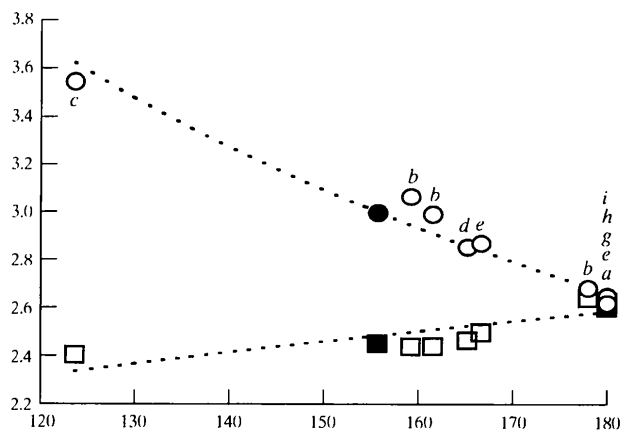


Fig. 2. Sn—Cl distances (Å) versus the CH₃—Sn—CH₃ angle (°) for $(\text{CH}_3)_2\text{SnCl}_4^{2-}$. Short bonds are represented by open squares, long ones by open circles, and the values for (1) by filled squares and circles [REFCODES (Allen *et al.*, 1991): (a) CEZFES, (b) DERTUPI0, (c) DMSNCL01, (d) FUPTER, (e) GEKDEF, (f) KUVGOX, (g) PYMCSN, (h) ZEXJOB, (i) ZIKHUW].

two N—H...Cl hydrogen bonds (Fig. 3). The shortest Sn—Cl bond being that to Cl3, which is not involved in hydrogen bonding, while the longest is to Cl1, which is *trans* with respect to the shortest bond. The phenyl rings are twisted so that the angle between the rings is 77.1 (2)°. These bond distances and angles are similar to those found in the only other $\text{Ph}_2\text{SnCl}_4^{2-}$ structure reported, with *N*-(4-hydroxybenzalidene)-4-methoxyanilinium cations (Teoh *et al.*, 1992), in which the anion differs in having a centre of symmetry, so that the phenyl groups are coplanar.

In both 8-methylaminoquinolinium compounds, the C—N_{sp³} bonds of the cations show considerable double-bond character [C—N 1.366 (5) and 1.344 (6) Å in the methyl compound, and 1.369 (2) Å in the phenyl compound] and the C—N—CH₃ angles [122.0 (4), 123.2 (5) and 120.3 (2)°] are all larger than the ideal tetrahedral angle. The C—N distances are similar to that

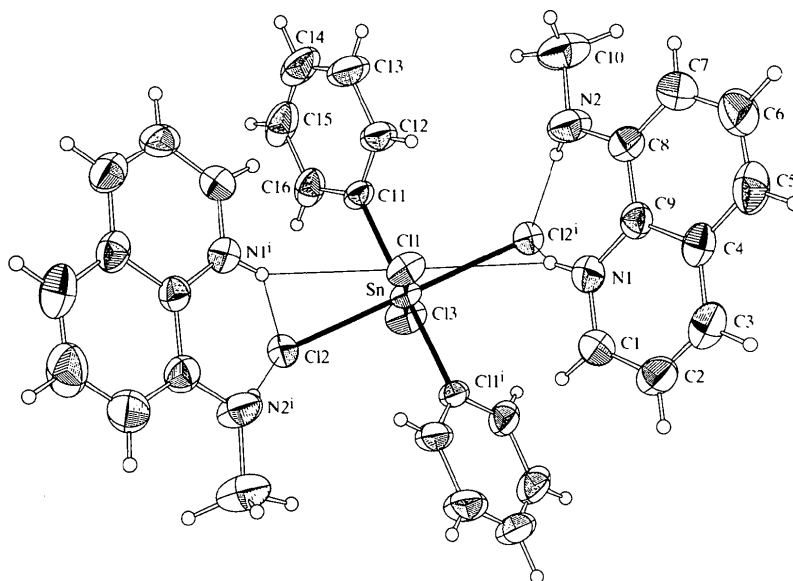


Fig. 3. The structure and hydrogen bonding for compound (2), with 50% probability ellipsoids for non-H atoms. For symmetry operator (i), see Table 5.

in 8-aminoquinolinium chloride [1.358 (6) Å], but considerably shorter than that observed when 8-aminoquinoline is coordinated to tin (Bengtson *et al.*, 1996).

Experimental

8-Methylaminoquinoline was prepared according to the method of Deady & Yusoff (1976). An equimolar mixture of 8-methylaminoquinoline (0.4 g, 2.5 mmol) and dimethyltin dichloride in 6 ml of chloroform was heated to boiling for 5 min on a hotplate. On cooling, 5 ml of petroleum ether (313–333 K) was added to the mixture which was then allowed to stand in a freezer for 1 h. A red solid (0.36 g, 47% yield, m.p. 363–381 K) was isolated from the mixture. Recrystallization of this solid from $CH_3OH/CHCl_3$ (1:5) yielded needle-shaped red crystals of compound (1) (m.p. 423–427 K) with satisfactory chemical analyses. Adopting the above procedure and using diphenyltin dichloride, compound (2) was obtained in 46% yield (m.p. 431–435 K, satisfactory chemical analyses).

Compound (1)

Crystal data

$(C_{10}H_{11}N_2)_2[SnCl_4(CH_3)_2]$	Mo $K\alpha$ radiation
$M_r = 608.99$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 6627 reflections
$P2_1/n$	$\theta = 1.4$ – 29.4°
$a = 7.1020$ (4) Å	$\mu = 1.441$ mm $^{-1}$
$b = 12.7094$ (6) Å	$T = 296$ K
$c = 28.213$ (2) Å	Plate
$\beta = 92.076$ (1) $^\circ$	$0.50 \times 0.30 \times 0.16$ mm
$V = 2544.9$ (2) Å 3	Red
$Z = 4$	
$D_x = 1.589$ Mg m $^{-3}$	
D_m not measured	

Data collection

Siemens SMART CCD diffractometer	6333 independent reflections
ω rotation scans with narrow frames	4583 reflections with $I > 3\sigma(I)$
Absorption correction: numerical (XPREP; Siemens, 1995)	$R_{int} = 0.038$
$T_{min} = 0.501, T_{max} = 0.779$	$\theta_{max} = 29.4^\circ$
12 315 measured reflections	$h = -9 \rightarrow 9$
	$k = 0 \rightarrow 17$
	$l = 0 \rightarrow 38$

Refinement

Refinement on F	$\Delta\rho_{max} = 0.45$ e Å $^{-3}$
$R = 0.034$	$\Delta\rho_{min} = -0.58$ e Å $^{-3}$
$wR = 0.048$	Extinction correction:
$S = 1.324$	B–C type 1, Lorentzian isotropic (Becker & Coppens, 1974)
4583 reflections	Extinction coefficient:
393 parameters	63 (12)
All H atoms refined	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
$w = 1/[\{\sigma_c(F^2) + 1.03F^2\}^{1/2} - F]^2$	
$(\Delta/\sigma)_{max} = 0.005$	

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

	$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j a_i a_j$			
	x	y	z	U_{eq}
Sn	0.11200 (4)	0.23333 (2)	0.35246 (1)	0.0431 (2)
Cl1	0.27758 (18)	0.10995 (8)	0.30231 (4)	0.0673 (7)
Cl2	0.12579 (17)	0.37799 (8)	0.29468 (3)	0.0602 (6)
Cl3	0.09557 (16)	0.06545 (8)	0.42151 (3)	0.0565 (6)
Cl4	-0.10353 (16)	0.38357 (8)	0.41784 (3)	0.0598 (6)
N1	0.1929 (4)	-0.1469 (2)	0.3722 (1)	0.040 (2)
N2	0.3245 (5)	-0.1357 (3)	0.4678 (1)	0.054 (2)
C1	0.1333 (5)	-0.1471 (3)	0.3272 (1)	0.046 (2)
C2	0.1238 (6)	-0.2404 (3)	0.3021 (1)	0.049 (2)

C3	0.1771 (5)	-0.3313 (3)	0.3239 (1)	0.050 (2)
C4	0.2414 (5)	-0.3327 (3)	0.3716 (1)	0.042 (2)
C5	0.2974 (6)	-0.4250 (3)	0.3955 (2)	0.055 (2)
C6	0.3574 (6)	-0.4200 (3)	0.4415 (2)	0.058 (2)
C7	0.3664 (5)	-0.3250 (3)	0.4663 (1)	0.052 (2)
C8	0.3130 (5)	-0.2302 (3)	0.4448 (1)	0.042 (2)
C9	0.2503 (4)	-0.2356 (3)	0.3963 (1)	0.038 (2)
C10	0.3742 (9)	-0.1280 (5)	0.5178 (2)	0.070 (3)
N3	-0.1705 (4)	0.6214 (3)	0.4222 (1)	0.042 (2)
N4	-0.2837 (6)	0.5481 (3)	0.3312 (1)	0.063 (2)
C11	-0.1170 (5)	0.6516 (3)	0.4654 (1)	0.048 (2)
C12	-0.1256 (6)	0.7551 (3)	0.4784 (2)	0.055 (2)
C13	-0.1915 (5)	0.8276 (4)	0.4462 (2)	0.056 (2)
C14	-0.2518 (5)	0.7975 (3)	0.4002 (1)	0.048 (2)
C15	-0.3215 (6)	0.8703 (4)	0.3658 (2)	0.061 (3)
C16	-0.3779 (6)	0.8340 (4)	0.3225 (2)	0.069 (3)
C17	-0.3657 (6)	0.7272 (4)	0.3100 (1)	0.061 (3)
C18	-0.2957 (5)	0.6509 (3)	0.3419 (1)	0.049 (2)
C19	-0.2391 (4)	0.6894 (3)	0.3880 (1)	0.041 (2)
C20	-0.3385 (11)	0.5055 (7)	0.2850 (2)	0.095 (5)
C21	-0.3425 (7)	0.2827 (4)	0.3958 (2)	0.057 (3)
C22	-0.1679 (7)	0.1867 (5)	0.3375 (2)	0.063 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (1)

Sn—C21	2.103 (4)	Sn—C12	2.461 (1)
Sn—C22	2.102 (5)	Sn—C13	2.894 (1)
Sn—C11	2.442 (1)	Sn—C14	3.098 (1)
C21—Sn—C22	155.7 (2)	C14—Sn—C21	82.0 (2)
C11—Sn—C22	100.0 (2)	C11—Sn—C12	93.70 (4)
C12—Sn—C22	97.9 (2)	C11—Sn—C13	87.05 (3)
C13—Sn—C22	82.3 (2)	C11—Sn—C14	178.10 (5)
C14—Sn—C22	79.0 (2)	C12—Sn—C13	179.16 (9)
C11—Sn—C21	98.5 (2)	C12—Sn—C14	88.07 (3)
C12—Sn—C21	96.5 (1)	C13—Sn—C14	91.19 (3)
C13—Sn—C21	83.0 (1)		

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$) for (1)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—HN1...C13	0.83 (4)	2.31 (4)	3.126 (3)	168 (4)
N2—HN2...C13	0.78 (4)	2.50 (5)	3.275 (4)	172 (4)
N3—HN3...C14	1.00 (4)	2.09 (4)	3.063 (3)	165 (3)
N4—HN4...C14	0.79 (5)	2.66 (5)	3.429 (4)	167 (5)

Compound (2)*Crystal data* $(\text{C}_{10}\text{H}_{11}\text{N}_2)_2[\text{SnCl}_4(\text{C}_6\text{H}_5)_2]$ $M_r = 733.13$

Monoclinic

 $C2/c$ $a = 13.7689 (6) \text{\AA}$ $b = 12.0870 (5) \text{\AA}$ $c = 18.7926 (8) \text{\AA}$ $\beta = 92.641 (1)^\circ$ $V = 3124.2 (2) \text{\AA}^3$ $Z = 4$ $D_x = 1.559 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Siemens SMART CCD diffractometer

 ω rotation scans with narrow framesAbsorption correction: numerical (*XPREP*; Siemens, 1995) $T_{\min} = 0.680$, $T_{\max} = 0.851$

21 740 measured reflections

4104 independent reflections

3600 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.021$ $\theta_{\text{max}} = 29^\circ$ $h = -18 \rightarrow 18$ $k = 0 \rightarrow 15$ $l = 0 \rightarrow 26$ *Refinement*Refinement on F^2 $R = 0.020$ $wR = 0.033$ $S = 1.198$

3600 reflections

252 parameters

All H atoms refined

 $w = 1/[\sigma_c(F^2) + 1.03F^2]^{1/2}$
 $- |F|]^2$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$

Extinction correction:

B—C type 1, Lorentzian

isotropic (Becker &

Coppens, 1974)

Extinction coefficient:

 $3.5 (4) \times 10^2$ Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)

	x	y	z	U_{eq}
Sn	1/2	-0.00667 (1)	3/4	0.0325 (1)
C11	1/2	-0.22776 (4)	3/4	0.0413 (3)
C12	0.53184 (3)	-0.01181 (3)	0.88774 (2)	0.0430 (2)
C13	1/2	0.19988 (5)	3/4	0.0538 (3)
N1	0.3542 (1)	-0.2644 (1)	0.6067 (1)	0.048 (1)
N2	0.5329 (1)	-0.2489 (1)	0.5417 (1)	0.057 (1)
C1	0.2695 (1)	-0.2631 (2)	0.6380 (1)	0.055 (1)
C2	0.1921 (1)	-0.3250 (2)	0.6108 (1)	0.055 (1)
C3	0.2045 (1)	-0.3888 (2)	0.5529 (1)	0.054 (1)
C4	0.2938 (1)	-0.3914 (1)	0.5186 (1)	0.046 (1)
C5	0.3094 (2)	-0.4551 (2)	0.4575 (1)	0.064 (1)
C6	0.3970 (2)	-0.4504 (2)	0.4277 (1)	0.074 (1)
C7	0.4718 (1)	-0.3822 (2)	0.4543 (1)	0.062 (1)
C8	0.4613 (1)	-0.3166 (1)	0.5134 (1)	0.045 (1)
C9	0.3706 (1)	-0.3246 (1)	0.5468 (1)	0.039 (1)
C10	0.6221 (2)	-0.2325 (2)	0.5045 (2)	0.074 (1)
C11	0.6535 (1)	-0.0174 (1)	0.7368 (1)	0.037 (1)
C12	0.6928 (1)	-0.0957 (2)	0.6928 (1)	0.048 (1)
C13	0.7924 (1)	-0.0992 (2)	0.6835 (1)	0.067 (1)
C14	0.8528 (2)	-0.0230 (2)	0.7173 (1)	0.075 (2)
C15	0.8152 (1)	0.0553 (2)	0.7609 (1)	0.068 (1)
C16	0.7154 (1)	0.0580 (2)	0.7717 (1)	0.050 (1)

Table 5. Selected geometric parameters (\AA , $^\circ$) for (2)

Sn—C11	2.672 (1)	Sn—C13	2.497 (1)
Sn—C12	2.606 (1)	Sn—C11	2.143 (2)
C11—Sn—C12	88.63 (1)	C12'—Sn—C11	90.31 (4)
C11—Sn—C13	180	C12—Sn—C13	91.37 (1)
C11—Sn—C11	86.53 (4)	C13—Sn—C11	93.47 (4)
C12—Sn—C12'	177.27 (3)	C11—Sn—C11'	173.05 (8)
C12—Sn—C11	89.52 (4)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.Table 6. Hydrogen-bonding geometry (\AA , $^\circ$) for (2)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—HN1...C11	0.81 (2)	2.62 (2)	3.313 (1)	145 (2)
N1—HN1...C12'	0.81 (2)	2.87 (2)	3.432 (2)	128 (2)
N2—HN2...C12'	0.83 (2)	2.47 (2)	3.298 (2)	176 (2)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

The data collection nominally covered a hemisphere of reciprocal space by combining three sets of exposures with $\varphi = 0, 88$ and 180° . The methyl compound decayed in the beam; however, 93% of the reflections were collected before decay set in, as indicated by scaling of batches of exposures from common reflections, and only these were retained for the refinement.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to

solve structures: *SIR92* (Altomare *et al.*, 1994) in *KRYSTAL* (Hazell, 1995); program(s) used to refine structures: modified *ORFLS* (Busing *et al.*, 1962) in *KRYSTAL*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) in *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

We are indebted to Nanyang Technological University (Grants No. RP18/96KLE and RG76/94) and to the Carlsberg Foundation for the diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1224). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–147.
- Bengtson, A., Goh, N. K., Hazell, A., Khoo, L. E., Ouyang, J. & Petersen, K. R. (1996). *Acta Chem. Scand.* **50**, 1020–1024.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- Deady, L. W. & Yusoff, N. I. (1976). *J. Heterocycl. Chem.* **13**, 125–126.
- Hazell, A. (1995). *KRYSTAL. An Integrated System of Crystallographic Programs*. Aarhus University, Denmark.
- Hazell, A., Thong, K. F., Ouyang, J. & Khoo, L. E. (1997). *Acta Cryst.* **C53**, 1226–1228.
- Siemens (1995). *SMART, SAINT and XPREP. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Teoh, S.-G., Teoh, S.-B., Yeap, G.-Y. & Declercq, J.-P. (1992). *Polyhedron*, **11**, 2351–2356.

Acta Cryst. (1998). **C54**, 732–734

Bis(di-2-pyridylmethanediol-*N,O,N'*)-copper(II) Diperchlorate

GUANG YANG,^a MING-LIANG TONG,^a XIAO-MING CHEN^a
AND SEIK WENG NG^b

^aDepartment of Chemistry, Zhongshan University,
Guangzhou 510275, People's Republic of China, and

^bInstitute of Postgraduate Studies and Research, University
of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail:
cedc03@zsu.edu.cn

(Received 3 November 1997; accepted 6 January 1998)

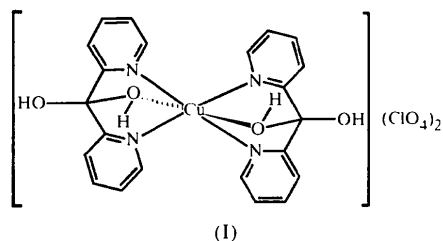
Abstract

Di-2-pyridyl ketone reacts with diaquatetrakis(betaine)-dicopper tetraperchlorate in water to form centrosymmetric bis(di-2-pyridylmethanediol)copper(II) diper-

chlorate, $[Cu(C_{11}H_{10}N_2O_2)_2](ClO_4)_2$, whose metal atom is *N,O,N'*-chelated by the two di-2-pyridylmethanediol ligands in an elongated octahedral CuN_4O_2 geometry. The hydroxyl groups are hydrogen bonded to the perchlorate anion.

Comment

Di-2-pyridyl ketone (hereafter DPK) functions either as a bidentate *N,N'*-donor or as a tridentate *N,O,N'*-donor towards metal ions, depending on the reaction medium used in the synthesis of the complexes (Deveson *et al.*, 1996), and several mononuclear and polynuclear transition metal–DPK complexes have been reported (Wang *et al.*, 1986; Sommerer *et al.*, 1993). The ligand undergoes alcoholysis to the acetal, $[(NC_5H_4)_2C(OR)(OH)]$ (*R* = alkyl), whose existence has been documented through its metal complexes (Bayers *et al.*, 1985; Baggio *et al.*, 1993; Papadopoulos *et al.*, 1996; Tangoulis *et al.*, 1996). The $[(NC_5H_4)_2C(OH)_2]$ homologue is trapped in the title complex, (I), which was obtained in the attempt to prepare a copper–DPK–betaine complex.



The title complex consists of bis(di-2-pyridylmethanediol)copper(II) cations and perchlorate anions. The Cu^{II} atom, which is located at an inversion centre, is chelated by the *N, O* and *N'* atoms of the ligand, being surrounded by four *N* and two *O* atoms in an elongated octahedral CuN_4O_2 environment. The distortion arises from the deviation of the $N1-Cu1-N2$ [$88.2(1)^\circ$] and $O1-Cu1-N1$ [$74.7(1)^\circ$] angles from the idealized 90° value. The $Cu-N$ bond lengths [$2.009(2)$ and $2.010(2)$ Å] are similar to those [$1.994(5)$ – $2.098(5)$ Å] found in the di-2-pyridyl ketal complexes of nickel(II) and copper(II) (Wang *et al.*, 1986).

The title complex is structurally different from bis-(di-2-pyridyl-1-hydroxymethoxy)cobalt(III) perchlorate trihydrate, where the Co^{III} atom is coordinated by a pair of the tridentate ligands, with the two $Co-O$ bonds in a *cis* arrangement (Tong *et al.*, 1998). In contrast, in the present case, the two $Cu-O$ bonds [$2.454(2)$ Å], being in a *trans* arrangement, significantly exceed the $Cu-N$ bond distances, a feature which can be attributed to the Jahn–Teller effect, which usually manifests itself in d^9 metal systems. The hydroxyl groups are both involved as donors in hydrogen bonds with the perchlorate anion (Table 2).