Molecular Structure of Diperchloratotetraphenylporphinatotin(IV)

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X-ray diffraction data and NMR spectra of diperchloratotetraphenylporphinatotin(IV), $Sn(tpp)(ClO_4)_2$, provide evidence for a monodentate perchlorato group coordinated to the Sn(IV) atom. The molecule $Sn(tpp)(ClO_4)_2$ displays an octahedral coordination geometry for the tin atom and its crystal belongs to the monoclinic space group $P2_1/n$ with a = 11.241(3), b = 14.644(3), c = 12.173(3) Å, β = 111.18(2)°, and Z = 2. The structure was solved by direct method, 3996 unique reflections having I > $3\sigma(I)$ measured with an automated diffractometer were used to refine the crystal structure to a conventional R factor 0.0431. The tin(IV) ion is centered on a planar tpp moiety. The geometry at the octahedral coordination centre of the $Sn(tpp)(ClO_4)_2$ molecule has Sn-O(perchlorate) = 2.181 Å and Sn-N = 2.073 Å.

INTRODUCTION

As a hard base, the perchlorate ion shows little tendency to form complexes with metal ions. Accordingly, it is used commonly as an inert anion in with complexes of metallic ions in aqueous solution or as a supporting electrolyte in electrochemical experiments. However, when no other donor is present to compete, the perchlorate ion exercises a donor capacity and can function as a unidentate or bidentate ligand.

Binding of perchlorate to Co(III),[1] Co(II),[2] Ni(II),[3] Zn(II),[4] Fe(III),[5] Sb(V),[6] Cu(II),[7] and Sn(II)[8] is well known. So far only $[Sn_3O_2Cl_4(ClO_4)_4]_2$, a tin(IV) perchlorate complex, with coexisting unidentate and bridging bidentate ClO_4, has been prepared and studied by X-ray diffraction.[9] Diperchloratotetraphenylporphinatotin(IV), $Sn(tpp)(ClO_4)_2$, is the second example of perchlorate bound to Sn(IV). As $Sn(tpp)(ClO_4)_2$ is the normal starting material for most tin(IV) tpp bis(acido) complexes,[10] it is important to determine its structure precisely. We report herein the structure of $Sn(tpp)(ClO_4)_2$ derived form X-ray diffraction and ^{1}H, ^{13}C and [35]Cl NMR measurements.

EXPERIMENTAL SECTION

Preparation of Complex

This complex was prepared as previously reported[10,11] and crystals were grown by diffusion of CH_2Cl_2 vapor into a toluene solution.

Crystal Data

$C_{44}H_{28}N_4O_8Cl_2Sn$, M = 930.3, monoclinic, space group $P2_1/n$, a = 11.241(3), b = 11.644(3), c = 12.173(3) Å, β = 111.18(2)°, Z = 2, V = 1868.5(8) Å^3, D_c = 1.654 g cm^{-3}, μ = 0.891 mm^{-1}, F(000) = 936. Intensities were collected for a crystal of dimensions 0.6 x 0.5 x 0.2 mm on a Siemens R 3m/v diffractometer. The structure was solved by direct method (see Table 1 for pertinent crystal information and details of data collection). All non-hydrogenic atoms were refined with anisotropic thermal parameters, where all hydrogen atoms were refined isotropically and included in the structure factor calculation. The final agreement factors were R = 0.0431 and Rw = 0.0508 for 324 variables and 3996 unique reflections with I > $3\sigma(I)$. The GOF is 1.70. An asymmetric unit contains only half the molecule and the tin atom lies at a crystallographic center of inversion.

NMR Spectra

[1]H and ^{13}C nmr spectra were recorded at 300 and 75.46 MHz, respectively, using a Varian VXR-300 spectrometer. The [35]Cl resonances in $Sn(tpp)(ClO_4)_2$ and perchloric acid were measured at 29.407 MHz on a Bruker MSL-300 spectrometer.

RESULTS AND DISCUSSION

The skeletal framework of the $Sn(tpp)(ClO_4)_2$ molecule, with C_{2h}-2/m symmetry in the crystal is illustrated

Table 1. Crystal Data

Formula	$C_{44}H_{28}N_4O_8Cl_2Sn$
M_r	930.3
Space group[a]	$P2_1/n$
$a/\text{Å}$	11.241(3)
$b/\text{Å}$	14.644(3)
$c/\text{Å}$	12.173(3)
$\beta/\deg$	111.18(2)
$V/\text{Å}^3$	1868.5(8)
Z	2
$D_c/\text{g cm}^{-3}$	1.654
F(000)	936
μ/cm^{-1}	8.91
R^b	0.0431
R_w^c	0.0508
GOF	1.70
A^c	1
B^c	5.0×10^{-4}
Crystal size/mm^3	0.5 x 0.2 x 0.6
Data collected	5943
$2\theta_{max}$	60
Temperature/K	296
Data used	3996
Discrimination	$I > 3\sigma(I)$

[a] The monoclinic space group $P2_1/n$ was used in the data collection
and refinement; the atomic coordinates (Table 2) are given in this
space group.
[b] $R = [\Sigma||F_o|-|F_c||/|F_o|]$
[c] $R_w = [(\Sigma w(||F_o|-|F_c||^2/\Sigma w|F_o|^2)^{1/2}]$; $w = A/(\sigma^2 F_o + BF_o^2)$

in Fig. 1. The view of the molecule $Sn(tpp)(ClO_4)_2$, as
shown in Fig. 1, is nearly parallel to the perchlorate-tin

bond and perpendicular to the mean plane of the macro-
cycle. A convenient notation for carbon atoms of the four
chemical types in the porphinato skeleton is displayed in
Fig. 2. The C(2), C(5) and C(3), C(4) atoms of a pyrrole
ring are designated C_α and C_β respectively and methine
carbon C_{meso} and C_p for a phenyl carbon atom that is
bonded to the core. The average bond lengths in the por-
phinato moiety are $N\text{-}C_\alpha = 1.388(4)$, $C_\alpha\text{-}C_\beta = 1.437(5)$,
$C_\alpha\text{-}C_m = 1.411(4)$, $C_\beta\text{-}C_\beta = 1.346(5)$ and $C_m\text{-}C_p =$
1.496(4) Å. Average bond angles are $Sn(1)\text{-}N(1)\text{-}C(2) =$
$125.7(2)°$, $C_\alpha\text{-}N\text{-}C_\alpha = 108.2(3)°$, $N\text{-}C_\alpha\text{-}C_\beta = 107.2(3)°$, $N\text{-}$
$C_\alpha\text{-}C_m = 126.6(3)°$, $C_\alpha\text{-}C_\beta\text{-}C_\beta = 108.5(3)°$, $C_\alpha\text{-}C_m\text{-}C_\alpha =$
$125.3(3)°$, $C_\beta\text{-}C_\alpha\text{-}C_m = 125.2(3)°$ and $C_\alpha\text{-}C_m\text{-}C_p =$
$117.0(3)°$. Figure 2 also shows the structural radii, $Sn...C_\alpha$
and $Sn...C_{meso}$. The $Sn...N$ distance is 2.073 Å, close to the
value 2.098 Å for $Sn(tpp)Cl_2$[12] and 2.08(6) Å for both
$Sn(tpp)(C_6H_5CO_2)_2$ and $Sn(tpp)(2\text{-}OH\text{-}C_6H_4CO_2)_2$.[13]
"Radial Strain" reaches its minimum as the distance from
metal to coordinated nitrogen is only ~ 2.01 Å.[14] As $Sn...N$
$= 2.073$ Å is longer than 2.01 Å, the tin(IV) atom is
centered in a highly expanded porphinato core defined by
the four nitrogen atoms and the entire $C_{20}N_4$ porphine
skeleton of the required C_{2h} symmetry.

The dihedral angles between the mean plane of the
porphine skeleton and the planes of the four phenyl groups
are 66, 66, 64.1 and 64.1°.

Final coordinates and thermal parameters for all
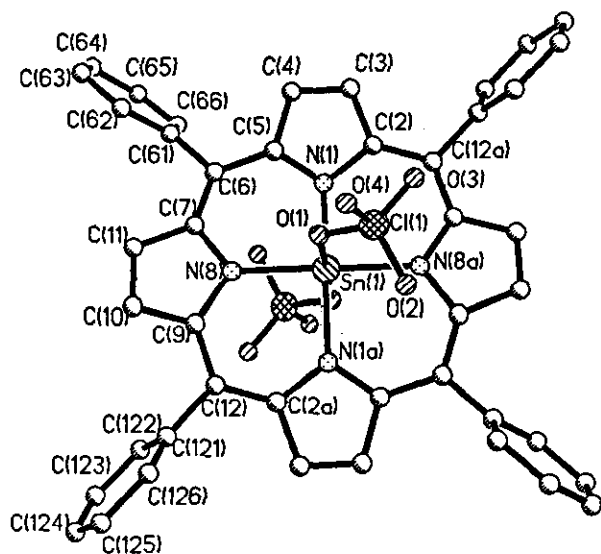atoms except hydrogen for $Sn(tpp)(ClO_4)_2$ are listed in

Fig. 1. Molecular configuration and scheme of labeling
atoms (hydrogen atoms omitted) in
$Sn(tpp)(ClO_4)_2$. An atom denoted 'a' in the
parentheses has been derived according to the in-
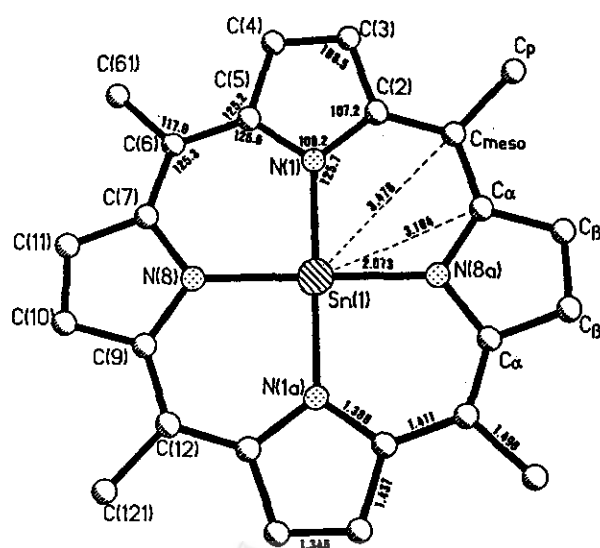version symmetry.

Fig. 2. Diagram of the carbon-nitrogen skeleton in the
phorphinato core with the same relative orienta-
tion as Fig. 1. Values of the principal radii (Å),
bond lengths (Å) and angles (deg) are shown on
the diagram.

Table 2. Final Positional Parameters (x 10^4) and Isotropic Thermal Parameters (x $10^3Å^2$) for Atoms in Sn(tpp)(ClO4)2 (with Estimated Standard Deviations (esd) in Parentheses)

Atom	X	Y	Z	$U_{(iso)}$
Sn(1)	0	5000	5000	23(1)
Cl(1)	3112(1)	5341(1)	5699(1)	39(1)
C(7)	-1442(3)	6406(2)	3071(3)	28(1)
C(11)	-2050(3)	7282(2)	2955(3)	34(1)
C(10)	-1889(3)	7587(2)	4046(3)	35(1)
C(9)	-1199(3)	6910(2)	4883(3)	27(1)
O(3)	3225(3)	4537(3)	5111(4)	81(2)
O(2)	3278(3)	5179(3)	6878(3)	86(2)
O(1)	1760(2)	5677(2)	5088(2)	41(1)
O(4)	3930(3)	6021(2)	5570(3)	58(1)
N(1)	-218(2)	4527(2)	3334(2)	26(1)
N(8)	-907(2)	6207(2)	4267(2)	27(1)
C(2)	302(3)	3728(2)	3087(3)	27(1)
C(3)	37(3)	3717(2)	1840(3)	32(1)
C(4)	-650(3)	4465(2)	1359(3)	31(1)
C(5)	-812(3)	4986(2)	2289(3)	26(1)
C(6)	-1429(3)	5840(2)	2151(3)	27(1)
C(61)	-2214(3)	6126(2)	922(3)	30(1)
C(62)	-1929(4)	6898(3)	411(3)	38(1)
C(63)	-2704(4)	7139(3)	-742(3)	49(1)
C(64)	-3743(4)	6613(3)	-1362(3)	55(2)
C(65)	-4027(4)	5858(4)	-852(4)	59(2)
C(66)	-3250(4)	5601(3)	284(3)	44(1)
C(12)	-953(3)	6939(2)	6096(3)	28(1)
C(121)	-1512(3)	7726(2)	6537(3)	28(1)
C(122)	-2831(3)	7795(3)	6193(3)	37(1)
C(123)	-3369(3)	8529(3)	6580(3)	40(1)
C(124)	-2604(4)	9173(3)	7316(3)	42(1)
C(125)	-1300(4)	9099(3)	7677(4)	47(1)
C(126)	-745(3)	8382(3)	7288(4)	41(1)

Table 3. Anisotropic Thermal Parameters (x $10^3Å^2$) of the Atoms in the Crystals[a]

Atom	Anisotropic Parameters[b]					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	25(1)	22(1)	18(1)	6(1)	3(1)	1(1)
Cl(1)	26(1)	42(1)	43(1)	-1(1)	5(1)	6(1)
C(7)	28(1)	30(1)	23(1)	4(1)	4(1)	4(1)
C(11)	39(2)	33(2)	27(2)	11(1)	8(1)	7(1)
C(10)	41(2)	29(2)	34(2)	13(1)	10(1)	2(1)
C(9)	28(1)	24(1)	27(1)	6(1)	7(1)	1(1)
O(3)	52(2)	50(2)	142(4)	-1(2)	34(2)	-24(2)
O(2)	50(2)	148(4)	44(2)	-24(2)	-3(1)	30(2)
O(1)	27(1)	42(1)	46(1)	1(1)	4(1)	10(1)
O(4)	38(1)	54(2)	81(2)	-11(1)	21(1)	6(2)
N(1)	28(1)	28(1)	19(1)	8(1)	4(1)	0(1)
N(8)	29(1)	25(1)	22(1)	6(1)	5(1)	1(1)
C(2)	29(1)	27(1)	23(1)	2(1)	6(1)	-5(1)
C(3)	38(2)	31(2)	25(1)	3(1)	8(1)	-6(1)
C(4)	37(2)	33(2)	21(1)	1(1)	8(1)	-3(1)
C(5)	29(1)	25(1)	21(1)	4(1)	5(1)	2(1)
C(6)	28(1)	27(1)	23(1)	2(1)	6(1)	2(1)
C(61)	31(1)	34(2)	23(1)	6(1)	5(1)	3(1)
C(62)	44(2)	38(2)	28(2)	4(1)	6(1)	8(1)
C(63)	59(2)	50(2)	32(2)	12(2)	9(2)	18(2)
C(64)	56(2)	68(3)	29(2)	16(2)	0(2)	9(2)
C(65)	44(2)	81(3)	35(2)	-8(2)	-6(2)	-2(2)
C(66)	43(2)	48(2)	32(2)	-8(2)	3(1)	7(2)
C(12)	29(1)	25(1)	26(1)	4(1)	7(1)	-3(1)
C(121)	31(1)	26(1)	27(1)	6(1)	10(1)	-1(1)
C(122)	32(2)	42(2)	32(2)	1(1)	7(1)	-6(1)
C(123)	33(2)	52(2)	37(2)	14(2)	13(1)	5(2)
C(124)	50(2)	39(2)	42(2)	16(2)	22(2)	0(2)
C(125)	50(2)	35(2)	55(2)	1(2)	16(2)	-17(2)
C(126)	32(2)	37(2)	51(2)	1(1)	12(2)	-15(2)

[a] Numbers in parentheses are the estimated standard deviations.
[b] The form of anisotropic thermal parameter is
$$exp[-2\pi^2(u_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2u_{12}hka^*b^* + 2u_{13}hla^*c^* + 2u_{23}klb^*c^*)].$$

Tables 2 and 3, respectively. Table 4 gives the individual bond angles in the Sn(tpp)(ClO4)2 molecule with their estimated standard deviations. Coordinate bond lengths, polyhedral edge lengths and the angles subtended at the tin atom of Sn(tpp)(ClO4)2 are also given. In this molecule the coordination polyhedron is an octahedron.

The bridging Cl-O bonds are longer than the terminal ones (i. e., mean value of 1.51 Å compared to 1.40 Å). For comparison in the compound [Sn3O2Cl4(ClO4)4]2[7a,9] these distances are 1.46 and 1.33 Å, respectively, and in the compound [Cl3SnOClO3]2- [8] they are 1.43 and 1.40 Å.

The most important feature for the present purpose is the location of the perchlorate ions relative to the tin atom. The Sn-O(1) distance 2.18(1) Å indicating a well defined bonding interaction is the first direct evidence of a pure monodentate perchlorate ligand in the tin(IV) perchlorate complex. For comparison a distance 2.16(2) Å between the tin and perchlorate oxygen atom was observed in [Sn3O2Cl4(ClO4)4]2[9] and a distance 2.91(1) Å was found in

[Cl3SnOClO3]2-.[8]

Proton chemical shifts (ppm) and tin-proton coupling constant (J/Hz) for the Sn(tpp)(ClO4)2 complex in acetone-d_6 at 28 ± 2°C are shown as follow: δ_H 7.99 (12H, m, meta-H, para-H); 8.40 (8H, m, ortho-H) and 9.58 [8H, d, ^4J(Sn-H) = 18.6 Hz, β-pyrrole]. Arnold[10] have reported the ^1H NMR parameter for the β-pyrrole as 9.56 ppm [8H, d, ^4J(Sn-H) = 18 Hz] which are close agreement with our results. Carbon-13 spectra were assigned with the aid of the DEPT technique. The ^{13}C NMR parameters are: δ 148.6 ppm (C_α, ^2J(Sn-C) = 9 Hz); 135.2 ppm (C_β, ^3J(Sn-C) = 36 Hz); 123.7 ppm (C_{meso}, ^3J(Sn-C) = 26 Hz); 140.4 ppm (C_p, C_p is a phenyl carbon atom that is bonded to the core, i.e., C-61, C-121); 135.6 ppm (ortho-C); 128.5 ppm (meta-C) and 130.2 ppm (para-C). The line width at half height ($\nu_{1/2}$) of the ^{35}Cl resonance in 2 M HClO4 aqueous solution

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Table 4. Bond Lengths and Bond Angles in the $Sn(tpp)(ClO_4)_2$ Molecule[a]

(a) Bond Lengths

Type	Length/Å	Type	Length/Å
Sn(1)-O(1)	2.181(3)	C(2)-C(12a)	1.398(4)
Sn(1)-N(1)	2.072(3)	C(3)-C(4)	1.346(5)
Sr(1)-N(8)	2.075(2)	C(4)-C(5)	1.431(5)
Sn(1)-O(1a)	2.181(3)	C(5)-C(6)	1.411(4)
Sn(1)-N(1a)	2.072(3)	C(6)-C(61)	1.496(4)
Sn(1)-N(8a)	2.075(2)	C(61)-C(62)	1.383(5)
Cl(1)-O(3)	1.408(4)	C(61)-C(66)	1.377(5)
Cl(1)-O(2)	1.399(4)	C(62)-C(63)	1.404(5)
Cl(1)-O(1)	1.512(2)	C(63)-C(64)	1.375(6)
Cl(1)-O(4)	1.402(3)	C(64)-C(65)	1.361(8)
C(7)-C(11)	1.436(5)	C(65)-C(66)	1.395(5)
C(7)-N(8)	1.390(4)	C(12)-C(121)	1.503(5)
C(7)-C(6)	1.397(5)	C(12)-C(2a)	1.398(4)
C(11)-C(10)	1.350(5)	C(121)-C(122)	1.391(5)
C(10)-C(9)	1.433(4)	C(121)-C(126)	1.389(5)
C(9)-N(8)	1.381(4)	C(122)-C(123)	1.395(6)
C(9)-C(12)	1.400(5)	C(123)-C(124)	1.369(6)
N(1)-C(2)	1.388(4)	C(124)-C(125)	1.374(6)
N(1)-C(5)	1.379(4)	C(125)-C(126)	1.391(6)
C(2)-C(3)	1.437(5)		

(b) Angles

Angle	Value/deg	Angle	Value/deg
O(1)-Sn(1)-N(1)	89.1(1)	Sn(1)-N(8)-C(7)	126.1(2)
O(1)-Sn(1)-N(8)	86.0(1)	Sn(1)-N(8)-C(9)	125.3(2)
N(1)-Sn(1)-N(8)	89.9(1)	C(7)-N(8)-C(9)	108.4(2)
O(1)-Sn(1)-O(1a)	180.0(1)	N(1)-C(2)-C(3)	107.2(3)
N(1)-Sn(1)-O(1a)	90.9(1)	N(1)-C(2)-C(12a)	125.9(3)
N(8)-Sn(1)-O(1a)	94.0(1)	C(3)-C(2)-C(12a)	126.9(3)
O(1)-Sn(1)-N(1a)	90.9(1)	C(2)-C(3)-C(4)	108.5(3)
N(1)-Sn(1)-N(1a)	180.0(1)	C(3)-C(4)-C(5)	107.9(3)
N(8)-Sn(1)-N(1a)	90.1(1)	N(1)-C(5)-C(4)	108.2(3)
O(1a)-Sn(1)-N(1a)	89.1(1)	N(1)-C(5)-C(6)	126.6(3)
O(1)-Sn(1)-N(8a)	94.0(1)	C(4)-C(5)-C(6)	125.2(3)
N(1)-Sn(1)-N(8a)	90.1(1)	C(7)-C(6)-C(5)	125.3(3)
N(8)-Sn(1)-N(8a)	180.0(1)	C(7)-C(6)-C(11)	117.6(3)
O(1a)-Sn(1)-N(8a)	86.0(1)	C(5)-C(6)-C(61)	117.0(3)
N(1a)-Sn(1)-N(8a)	89.9(1)	C(6)-C(61)-C(62)	122.0(3)
O(3)-Cl(1)-O(2)	112.1(3)	C(6)-C(61)-C(66)	118.7(3)
O(3)-Cl(1)-O(1)	106.3(2)	C(62)-C(61)-C(66)	119.3(3)
O(2)-Cl(1)-O(1)	107.3(2)	C(61)-C(62)-C(63)	119.6(3)
O(3)-Cl(1)-O(4)	110.7(2)	C(62)-C(63)-C(64)	120.3(4)
O(2)-Cl(1)-O(4)	112.7(2)	C(63)-C(64)-C(65)	119.9(4)
C(1)-Cl(1)-O(4)	107.3(2)	C(64)-C(65)-C(66)	120.3(4)
C(11)-C(7)-N(8)	107.5(3)	C(61)-C(66)-C(65)	120.5(4)
C(11)-C(7)-C(6)	126.4(3)	C(9)-C(12)-C(121)	116.8(3)
N(8)-C(7)-C(6)	126.1(3)	C(9)-C(12)-C(2a)	125.6(3)
C(7)-C(11)-C(10)	108.0(3)	C(121)-C(12)-C(2a)	117.4(3)
C(11)-C(10)-C(9)	108.4(3)	C(12)-C(121)-C(122)	119.1(3)
C(10)-C(9)-N(8)	107.6(3)	C(12)-C(121)-C(126)	121.7(3)
C(10)-C(9)-C(12)	125.3(3)	C(122)-C(121)-C(126)	119.2(3)
N(8)-C(9)-C(12)	126.9(3)	C(121)-C(122)-C(123)	119.9(3)
Sn(1)-O(1)-Cl(1)	127.5(2)	C(122)-C(123)-C(124)	120.3(4)
Sn(1)-N(1)-C(2)	125.7(2)	C(123)-C(124)-C(125)	120.0(4)
Sn(1)-N(1)-C(5)	125.9(2)	C(124)-C(125)-C(126)	120.6(4)
C(2)-N(1)-C(5)	108.2(3)	C(121)-C(126)-C(125)	119.9(3)

[a] The number in parentheses following a parameter value is the estimated standard deviation in units of the least significant digit.

is about 2 Hz. This value compares with a line width 21 Hz of the ^{35}Cl resonance in a 1.8×10^{-2} M $Sn(tpp)(ClO_4)_2$ solution. *The variation in line width between Cl in the free perchlorate ion and in the monodentate perchlorato group coordinated to the Sn(IV) atom in* $Sn(tpp)(ClO_4)_2$ *is interpreted in terms of the environmental difference. The perchlorate ion has tetrahedral symmetry and tumbles quickly in aqueous solution resulting in a narrow line. Because in the tin system the perchlorate is bonded to the complex through O(1) (shown in Fig. 1.) leading to lower symmetry from* T_d *to locally* C_{3v}, *the reorientational motion becomes slower.*

SUPPLEMENTARY MATERIAL

Lists of atomic coordinates, thermal parameters of H atoms and structural factors are available upon request from the authors.

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