

O3—N3	1.252 (3)	C7—C8	1.404 (4)
O4—N3	1.227 (3)	C7—C11	1.388 (3)
O5—N3	1.254 (3)	C8—C9	1.383 (5)
N1—C1	1.328 (3)	C9—C10	1.395 (4)
N1—C12	1.351 (3)	C11—C12	1.441 (3)
N2—C10	1.323 (3)		
O1—Cu—O2'	93.14 (7)	Cu—N2—C11	112.8 (2)
O1—Cu—N1	92.04 (8)	C10—N2—C11	118.4 (2)
O1—Cu—N2	171.99 (8)	O3—N3—O4	120.3 (3)
O2'—Cu—N1	173.94 (7)	O3—N3—O5	120.7 (3)
O2'—Cu—N2	92.65 (8)	O4—N3—O5	119.0 (3)
O3'—Cu—O1	90.78 (8)	N1—C1—C2	122.3 (3)
O3'—Cu—O2'	97.63 (8)	C1—C2—C3	119.4 (3)
O3'—Cu—N1	85.44 (8)	C2—C3—C4	120.1 (2)
O3'—Cu—N2	82.96 (8)	C3—C4—C5	124.8 (3)
O3'—Cu—O5	172.72 (8)	C3—C4—C12	116.4 (3)
O5—Cu—O1	96.22 (8)	C5—C4—C12	118.7 (2)
O5—Cu—O2'	84.01 (8)	C4—C5—C6	120.7 (2)
O5—Cu—N1	92.30 (8)	C5—C6—C7	121.8 (3)
O5—Cu—N2	89.89 (8)	C6—C7—C8	124.5 (3)
N1—Cu—N2	82.52 (8)	C6—C7—C11	118.7 (3)
O1—P—O2	116.2 (1)	C8—C7—C11	116.7 (3)
Cu—O1—P	134.9 (1)	C7—C8—C9	119.6 (3)
Cu—O2'—P'	123.0 (1)	C8—C9—C10	119.0 (3)
Cu—N1—C1	129.7 (2)	N2—C10—C9	122.4 (3)
Cu—N1—C12	111.9 (2)	N2—C11—C7	123.9 (2)
C1—N1—C12	118.4 (2)	N1—C12—C4	123.4 (2)
Cu—N2—C10	128.8 (2)	N1—C12—C11	116.5 (2)
N2—C11—C12	116.1 (2)	C4—C12—C11	120.0 (2)
C7—C11—C12	120.0 (2)		

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

The displacement parameters for the H atoms range from 2.6 (5) to 5.1 (7) Å².

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro{2-[2-(dimethylamino)ethyl- iminomethyl]phenol}triphenyl- tin(IV) Benzene Hemisolvate, [SnCl(C₆H₅)₃(C₁₁H₁₆N₂O)].0.5C₆H₆

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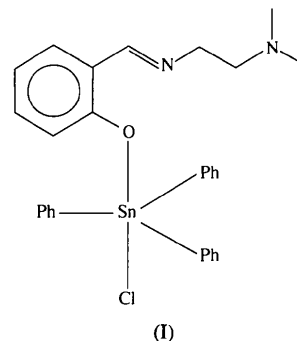
(Received 1 August 1995; accepted 10 October 1995)

Abstract

The coordination geometry of the Sn atom in the title compound is trigonal bipyramidal, with the *ipso* C atoms of the phenyl groups in equatorial and the Cl and O atoms in apical positions. The ligand is bonded to the Sn atom through the phenolic O atom; the hydroxy H atom is shifted towards the imino N atom to give rise to a zwitterion, *i.e.* 2-[2-(dimethylamino)ethyliminomethyl]-phenolate.

Comment

Triorganotin halides and pseudohalides form complexes with α -amino acids (Khoo, Goh, Eng, Walen & Hazell, 1995), picolinic acid (Gabe, Lee, Khoo & Smith, 1985) and Schiff bases (Hazell, Goh & Khoo, 1994). For Schiff base derivatives of *ortho*-hydroxy phenols in particular, a zwitterionic conformation results owing to coordination by the phenolic O atom, whose proton is transferred to the imino N atom. In a continuation of studies of these Schiff base complexes of triorganotin halides, a study of the title complex, (I), was initiated, with 2-[2-(dimethylamino)ethyl]iminomethylphenol as a ligand, a Schiff base having a substituent with the potential to accept the hydroxy proton on complexation.



The coordination of the Sn atom is trigonal bipyramidal with the *ipso* C atoms of the phenyl groups in equatorial positions and the phenol O and the Cl atoms

occupying axial positions. The ligand lies roughly in the plane defined by C7, Sn and O19. The phenyl groups are twisted out of the equatorial plane by differing amounts (63.3, 23.1 and 54.8° for the rings containing C1, C7 and C13, respectively). This is very similar to the arrangement in the related ethyl *N*-salicylidene-glycinate compound (Lee, Gabe, Khoo, Eng & Smith, 1990). Other similar features are the large spread of the C—Sn—C angles [112.8 (2), 121.6 (2) and 125.1 (2)° *cf.* 113.9 (3), 119.6 (3) and 125.6 (3)°], the very small C7—Sn—O19 angle [81.8 (1) *cf.* 81.5 (3)°] and the large Sn—O—C angle [135.9 (3) *cf.* 133.5 (5)°]. The narrowing of the Sn—C—C angle together with the widening of the Sn—O—C angle tilts the ligand so as to increase the distance between H21 and Sn from 2.3 Å (for C—Sn—C = 90° and Sn—O—C = 109.5°) to 3.34 (5) Å. The Sn—Cl [2.546 (1) Å] and Sn—O [2.256 (3) Å] distances are in the ranges found in the Cambridge Structural Database (Allen, Davies, Galloy, Johnson, Kennard, Macrae, Mitchell, Smith & Watson, 1991) for similar compounds [Sn—Cl 2.438–2.569 Å, mean value 2.506 (11) Å, and Sn—O 2.102–2.569 Å, mean value 2.371 (21) Å]. The spread of values is very large, strong (short) Sn—O bonds being associated with weak (long) Sn—Cl bonds [$r(\text{Sn—Cl}) = 3.695 - 0.502 \times r(\text{Sn—O})$]. The mean Sn—C distance is 2.142 (4) Å. C—C, C—O, C—N and C—H distances have expected values.

The phenol H atom is shifted to the imine N atom and forms an N—H···O hydrogen bond: N···O = 2.619 (6) Å, N—H = 0.85 (5), O···H = 1.99 (5) Å, and N—H···O = 131 (4)°, *cf.* the values found for the 2:1 complex of methyl *N*-(2-hydroxybenzylidene)alaninate with dimethyltin dichloride (Hazell, Goh & Khoo, 1994) of 2.628 (4) (N···O), 0.81 (4) (N—H), 1.98 (4) Å (O···H), and 137 (4)° (N—H···O). The complex crys-

tallizes with one benzene molecule of crystallization, situated on a symmetry centre, for every two molecules of complex. Unlike in some transition metal complexes (Root, Hoeschele, Cornman, Kampf & Pecoraro 1993; Anderson, Crespo, Jennings, Lough, Ferguson & Puddephat, 1991), the amine N atom is not involved in coordination with the Sn atom and there is no intermolecular hydrogen bonding with the phenol proton.

Experimental

Preparation of the ligand was according to the method described by Shukla, Bharadwaj, Hall & Whitmire (1994). 3.85 g (10 mmol) of recrystallized triphenyltin chloride in 20 ml of benzene was added to a solution of 1.92 g (10 mmol) of 2-[2(dimethylamino)ethyl]salicylideneamine in 10 ml of benzene. The mixture was warmed on a water bath for *ca* 10 min. On cooling, hexane (5 ml) was added and the mixture was allowed to stand at room temperature overnight. On filtration, 3.66 g (63%) of a yellow solid was obtained. Elemental analysis (USM, Malaysia): calculated for C₂₉H₃₁ClN₂O₂Sn (found after drying *in vacuo*) C 60.28 (60.97), H 5.42 (5.10), N 4.85% (4.50%). Recrystallization from a 1:1 benzene–hexane solvent gave the title adduct, m.p. 351–353 K.

Crystal data

[SnCl(C₆H₅)₃(C₁₁H₁₆N₂O)].
0.5C₆H₆
M_r = 616.80
Monoclinic
*P*2₁/*c*
a = 17.0989 (22) Å
b = 10.4699 (18) Å
c = 17.7115 (24) Å
 β = 109.721 (8)°
V = 2984.8 (8) Å³
Z = 4
D_x = 1.372 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
Cell parameters from 30 reflections
 θ = 10.06–14.60°
 μ = 0.973 mm⁻¹
T = 294 K
Tabular
0.56 × 0.48 × 0.34 mm
Yellow

Data collection

Huber four-circle diffractometer
 $\omega/2\theta$ scans
Absorption correction:
by integration from crystal shape
T_{min} = 0.603, *T_{max}* = 0.705
5444 measured reflections
5254 independent reflections

3489 observed reflections
[*I* > 3σ(*I*)]
R_{int} = 0.019
 θ_{max} = 25°
h = -20 → 19
k = 0 → 12
l = 0 → 21
2 standard reflections monitored every 50 reflections
intensity decay: <1%

Refinement

Refinement on *F*
R = 0.033
wR = 0.042
S = 0.968

(Δ/σ)_{max} = 0.10
 $\Delta\rho_{\text{max}}$ = 0.62 (7) e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.33 (7) e Å⁻³
Extinction correction: none

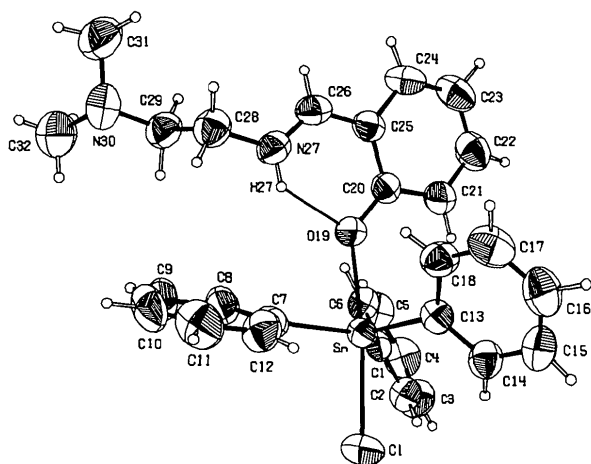


Fig. 1. ORTEP (Johnson, 1976) plot of the title compound (excluding solvent). Displacement ellipsoids are plotted at the 50% probability level.

3489 reflections
470 parameters
All H-atom parameters
refined

$$w = 1/\{[\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|\}$$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Sn	0.75602 (2)	0.02748 (3)	0.89608 (2)	0.0450 (2)
Cl	0.77174 (9)	-0.01999 (14)	0.76095 (8)	0.0666 (10)
C1	0.7603 (3)	-0.1714 (4)	0.9258 (3)	0.047 (2)
C2	0.7369 (3)	-0.2643 (5)	0.8671 (4)	0.060 (3)
C3	0.7353 (4)	-0.3926 (6)	0.8870 (5)	0.077 (5)
C4	0.7576 (4)	-0.4295 (7)	0.9651 (5)	0.081 (4)
C5	0.7820 (4)	-0.3400 (6)	1.0238 (4)	0.075 (4)
C6	0.7837 (3)	-0.2117 (5)	1.0054 (3)	0.056 (3)
C7	0.8610 (3)	0.1538 (5)	0.9295 (3)	0.051 (3)
C8	0.9338 (3)	0.1269 (7)	0.9909 (4)	0.069 (3)
C9	1.0007 (4)	0.2107 (10)	1.0095 (5)	0.091 (3)
C10	0.9944 (6)	0.3218 (9)	0.9688 (7)	0.101 (5)
C11	0.9215 (6)	0.3524 (7)	0.9076 (7)	0.099 (7)
C12	0.8558 (4)	0.2671 (6)	0.8888 (4)	0.073 (4)
C13	0.6408 (3)	0.1253 (4)	0.8426 (3)	0.050 (3)
C14	0.5848 (3)	0.0890 (6)	0.7696 (3)	0.062 (3)
C15	0.5098 (4)	0.1519 (7)	0.7360 (4)	0.075 (4)
C16	0.4916 (4)	0.2557 (7)	0.7733 (5)	0.081 (4)
C17	0.5469 (4)	0.2954 (7)	0.8451 (5)	0.080 (5)
C18	0.6205 (4)	0.2309 (5)	0.8803 (4)	0.064 (4)
O19	0.7559 (2)	0.0799 (3)	1.0196 (2)	0.054 (2)
C20	0.7042 (3)	0.0669 (5)	1.0595 (3)	0.047 (2)
C21	0.6389 (3)	-0.0214 (6)	1.0394 (3)	0.064 (3)
C22	0.5882 (4)	-0.0324 (7)	1.0847 (4)	0.075 (4)
C23	0.5981 (4)	0.0433 (6)	1.1510 (4)	0.077 (4)
C24	0.6584 (4)	0.1323 (6)	1.1710 (4)	0.070 (4)
C25	0.7128 (3)	0.1466 (5)	1.1271 (3)	0.051 (3)
C26	0.7754 (3)	0.2417 (5)	1.1503 (3)	0.059 (4)
N27	0.8294 (3)	0.2658 (4)	1.1166 (3)	0.055 (3)
C28	0.8953 (4)	0.3622 (6)	1.1458 (4)	0.067 (4)
C29	0.9750 (4)	0.3016 (6)	1.2011 (4)	0.068 (4)
N30	1.0386 (3)	0.3961 (5)	1.2347 (3)	0.080 (3)
C31	1.0287 (7)	0.4502 (10)	1.3071 (6)	0.107 (6)
C32	1.1208 (5)	0.3369 (13)	1.2551 (7)	0.119 (5)
C33	0.5794 (6)	0.4789 (15)	1.0495 (6)	0.113 (6)
C34	0.5207 (11)	0.3908 (13)	1.0372 (7)	0.129 (12)
C35	0.4409 (7)	0.4070 (12)	0.9852 (8)	0.117 (8)

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

Sn—C1	2.546 (1)	C15—C16	1.361 (9)
Sn—C1	2.143 (5)	C16—C17	1.369 (9)
Sn—C7	2.145 (5)	C17—C18	1.377 (8)
Sn—C13	2.138 (5)	O19—C20	1.313 (5)
Sn—O19	2.256 (3)	C20—C21	1.400 (7)
C1—C2	1.381 (7)	C20—C25	1.425 (6)
C1—C6	1.394 (7)	C21—C22	1.370 (8)
C2—C3	1.391 (8)	C22—C23	1.378 (9)
C3—C4	1.362 (10)	C23—C24	1.345 (8)
C4—C5	1.357 (9)	C24—C25	1.407 (7)
C5—C6	1.385 (8)	C26—N27	1.282 (7)
C7—C8	1.378 (8)	N27—C28	1.471 (7)
C7—C12	1.375 (8)	C28—C29	1.522 (8)
C8—C9	1.389 (9)	C29—N30	1.442 (7)
C9—C10	1.353 (12)	N30—C31	1.464 (10)
C10—C11	1.385 (12)	N30—C32	1.466 (10)
C11—C12	1.385 (10)	C33—C34	1.326 (16)
C13—C14	1.377 (7)	C35—C35'	1.335 (15)
C13—C18	1.395 (7)	C34—C35	1.375 (16)
C14—C15	1.385 (8)		
Cl—Sn—C1	92.1 (1)	Sn—C13—C18	120.6 (4)
Cl—Sn—C7	92.0 (1)	C13—C14—C15	121.4 (6)
Cl—Sn—C13	92.9 (1)	C14—C15—C16	120.1 (6)

Cl—Sn—O19	173.7 (1)	C15—C16—C17	119.6 (6)
O19—Sn—C1	90.5 (2)	C16—C17—C18	120.7 (6)
O19—Sn—C7	81.8 (1)	C13—C18—C17	120.6 (6)
O19—Sn—C13	90.6 (2)	Sn—O19—C20	135.9 (3)
C1—Sn—C7	125.1 (2)	O19—C20—C21	123.8 (4)
C1—Sn—C13	121.6 (2)	O19—C20—C25	119.6 (4)
C7—Sn—C13	112.8 (2)	C21—C20—C25	116.6 (4)
C2—C1—C6	117.4 (5)	C20—C21—C22	121.0 (6)
Sn—C1—C2	121.4 (4)	C21—C22—C23	122.0 (6)
Sn—C1—C6	121.1 (4)	C22—C23—C24	119.1 (6)
C1—C2—C3	121.0 (6)	C23—C24—C25	121.3 (6)
C2—C3—C4	120.6 (7)	C24—C25—C26	119.3 (5)
C3—C4—C5	119.4 (7)	C20—C25—C24	120.1 (5)
C4—C5—C6	121.0 (7)	C20—C25—C26	120.6 (5)
C1—C6—C5	120.6 (6)	C25—C26—N27	126.6 (5)
C8—C7—C12	118.1 (5)	C26—N27—C28	124.0 (5)
Sn—C7—C8	122.8 (4)	N27—C28—C29	110.7 (5)
Sn—C7—C12	119.2 (4)	C28—C29—N30	111.5 (5)
C7—C8—C9	120.7 (7)	C29—N30—C31	109.5 (6)
C8—C9—C10	120.4 (8)	C29—N30—C32	109.8 (7)
C9—C10—C11	120.2 (7)	C31—N30—C32	109.4 (7)
C10—C11—C12	118.8 (8)	C34—C33—C35'	118.9 (9)
C7—C12—C11	121.8 (8)	C33—C34—C35	123.3 (9)
C14—C13—C18	117.5 (5)	C33'—C35—C34	117.6 (10)
Sn—C13—C14	121.9 (4)		

D—H...A	D—H	H...A	D...A	D—H...A
O19—H27...N27	0.85 (5)	1.99 (5)	2.619 (6)	131 (4)

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

Cell dimensions were determined from reflections measured at $\pm 2\theta$. Data were corrected for background, Lorentz and polarization effects, and for absorption. H atoms were located from a difference electron-density map. Non-H atoms were refined anisotropically and H atoms isotropically using a modification of *ORFLS* (Busing, Martin & Levy, 1962).

Data collection: *MAD* (Allibon, 1995). Cell refinement: *MAD*. Data reduction: *KRYSTAL* (Hazell, 1995). Program(s) used to solve structure: *SIR92* (Altmore, Cascarano, Giocovazzo, Guagliardi, Burla, Polidori & Camalli, 1994); *KRYSTAL*. Program(s) used to refine structure: *KRYSTAL*. Molecular graphics: *ORTEPII* (Johnson, 1976); *KRYSTAL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(triphenylphosphine)iminium Nitrito-(phthalocyaninato)zincate Hydrate

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Abstract

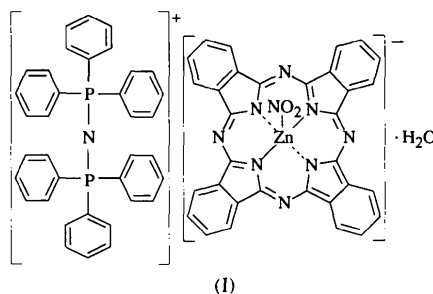
^b(PNP)[Zn(ONO)Pc²⁻].H₂O [Pc²⁻ = (C₃₂H₁₆N₈)²⁻] has been prepared from zinc phthalocyanine and bis-(triphenylphosphine)iminium nitrite [(PNP)NO₂] in acetone. The Zn atom has tetragonal pyramidal coordination geometry with the Zn atom displaced out of the center (Ct) of the four inner N atoms (N_{iso}) of the non-planar Pc ligand toward the nitrite ligand [Zn—Ct = 0.469 (3) Å]. The nitrite ion is monodentate O-coordinated [Zn—O = 2.059 (3) Å]. The average Zn—N_{iso} distance is 2.032 Å. Pairs of weakly overlapping anions are present. The cation adopts a bent conformation [^b(PNP): P1—N(K) = 1.576 (2), P2—N(K) = 1.582 (2) Å; P1—N(K)—P2 = 141.12 (13)°].

Comment

The nitrite ion is a very versatile ligand with rich chemistry and bonding characteristics. These properties derive from the fact that it can function as a ligand in up to nine different crystallographically confirmed ways (Hitchman & Rowbottom, 1982; Burmeister, 1990). Of great interest are the widespread reactions of the nitrite ion with hemoproteins in assimilatory and dissimilatory nitrite reductases reducing the nitrite ion to ammonia (Coleman, Cornish-Bowden & Cole, 1978) and nitri-

ous oxide, nitric oxide or dinitrogen (Johnson, Thomson, Walsh, Barber & Greenwood, 1980). Furthermore, the nitrite–nitrosyl conversions have become important processes in mild nitrosyl-assisted oxidations of organic substrates (Ercolani, Paoletti, Pennesi & Rossi, 1991; Hubbard, Zoch & Elcesser, 1993). As part of our systematic investigation of the mode of ligand binding and catalytical reactivity of the nitrite ion with structurally related metallophthalocyanines, we report an X-ray study of a five-coordinate zinc complex salt, (I).

Only a few examples of metallophthalocyanines with this coordination geometry have been reported (Fischer, Templeton, Zalkin & Calvin, 1970; Palmer *et al.*, 1985; Assmann, Ostendorp & Homborg, 1995).



ORTEPII (Johnson, 1976) diagrams with labeling schemes for the [Zn(ONO)Pc²⁻]⁻ anion (*a*) and the ^b(PNP)⁺ cation (*b*) are shown in Fig. 1. The geometric data for the cation and the Pc ligand are close to usual values (Safarpour Haghighi, Franken & Homborg, 1994; Assmann, Franken & Homborg, 1995; Mossoyandeneux, Benlian, Pierrot, Fournel & Sorbier, 1985). The cation adopts the bent conformation: the P1/P2—N(K) distances are 1.576 (2)/1.582 (2) Å, the P1—N(K)—P2 angle is 141.12 (13)°. The average values for the unique chemical classes of distances and angles in the ZnPc core and the perpendicular displacements of each atom from the 'best' N_{iso} plane (N_{iso}: N1–N4) are given in Fig. 2. The Pc ligand has a non-planar 'saucer-like' conformation. However, the pyrrole and benzene rings are essentially planar.

The Zn atom is displaced 0.469 (3) Å out of the N_{iso} plane toward the nitrite ligand. The average Zn—N_{iso} distance is 2.032 Å. The nitrite ligand is coordinated *via* the O atom to zinc in the monodentate nitrito arrangement (type II), which is the preferred method of nitrite coordination to this metal ion (Hitchman & Rowbottom, 1982). The Zn—O distance is 2.059 (3) Å. The Zn—O vector is essentially collinear with the Zn—Ct vector, where Ct is the center of the N_{iso} plane. The distortion is <1° for the O—Ct vector. The non-bonded O atom is *trans* to the Zn atom.

The anions are close together forming partially overlapping 'dimers' related by an inversion center. The closest atomic approach between the anions is 3.294 (5) Å for the distance between C8 of one