

the monomeric molecule resides on the special position *c* of space group *Pccn* (No. 56) and therefore the molecule has a twofold symmetry axis lying along the *c* axis of the unit cell.

The Sn—S(1) bond length corresponds to that of 2.482 (2) Å in Me₂Sn[SP(S)Me₂]₂ (Molloy, Hossain, van der Helm, Zuckerman & Mullins, 1981) and to those of 2.49 (1) and 2.481 (8) Å, respectively, in Ph₂Sn[SP(S)(OEt)₂]₂ (Liebich & Tomassini, 1978). In these compounds the ligands are unsymmetrically chelating, Sn being in a heavily distorted environment. A somewhat shorter bond of 2.4582 (9) Å was found in Ph₃SnSP(S)(OEt)₂, which contains tetrahedral tin (Molloy *et al.*, 1979), while in Ph₂Sn[SP(S)(OR)₂]₂ (*R* = *i*-C₃H₇) with octahedral tin the Sn—S bonds with lengths of 2.689 (1) and 2.678 (1) Å are appreciably longer (Molloy *et al.*, 1980). The Sn—S(2) bond length of 3.130 (1) Å in the present compound is well below the sum of the van der Waals radii of Sn and S (2.16 and 1.80 Å) and is shorter than the analogous bonds in Ph₂Sn[SP(S)(OEt)₂]₂ of 3.20 (1) and 3.23 (1) Å, respectively (Liebich & Tomassini, 1978). Considering the angles at tin, mainly C(1)—Sn—C(1') 133.9 (2)°, being appreciably greater than tetrahedral, one has to assume weak intramolecular interaction between Sn and S(2), extending the primary tetrahedron around Sn [formed by C(1), C(1'), S(1), S(1')] to a heavily distorted octahedron. The two types of Sn—S bonds are each in *cis* positions. In accordance with this view of anisobidentate chelating dithiophosphate ligands the bond distances P—S(1) and P—S(2) are distinctly different.

They lie in the ranges 1.85 to 1.95 Å and 1.99 to 2.19 Å, respectively, which have been found in dithiophosphate complexes and which can be ascribed to P—S bonds with predominant double- and single-bond characters, respectively (Molloy *et al.*, 1981, and references therein). Between the molecules there are no interactions exceeding van der Waals forces.

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Structure of Bis[tetraphenylarsonium] Bis(1,2-dithiooxalato-S,S')zincate(II)

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Abstract. [As(C₆H₅)₄]₂[Zn(C₂O₂S₂)₂], *M_r* = 1072.4, triclinic, *P*1̄, *a* = 10.427 (1), *b* = 12.654 (1), *c* = 18.639 (2) Å, α = 94.55 (1), β = 97.27 (1), γ = 81.48 (1)°, *V* = 2408.0 Å³, *Z* = 2, *D_m* = 1.484 (by flotation), *D_x* = 1.479 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 2.092 mm⁻¹, *F*(000) = 1088, *T* = 293 (1) K, final *R* = 0.044 for 4693 observed reflections. The central Zn ion is tetrahedrally coordinated by the four sulfur atoms from two dithiooxalate ligands

with Zn—S distances in the range 2.304 (2) to 2.334 (2) Å. The dithiooxalate ligands are not planar, having torsion angles along the C—C axes of 31.7 (2)° for S(1)—C(1)—C(2)—S(2) and 43.3 (2)° for S(3)—C(3)—C(4)—S(4), respectively.

Introduction. The major portion of structural work on dithiooxalate (dto) complexes has been done with compounds containing transition-metal central ions in

planar or octahedral coordination spheres formed by the sulfur donor atoms. These coordination geometries also remain in 'mixed-metal' dithiooxalates containing not only transition-metal ions but also main-group or *d*¹⁰ metal ions, respectively, which are linked by dithiooxalate bridges in such a manner that the sulfur atoms contact the more thiophilic ions (Hollander & Coucouvanis, 1974; Hollander, Leitheiser & Coucouvanis, 1977; Gleizes & Verdager, 1984; Trombe, Gleizes & Galy, 1984). Thus, in ZnNi(dto)₂·2·08H₂O the nickel ions are also planar coordinated by four sulfur atoms and the zinc ions octahedrally coordinated by oxygen exclusively (Maury, Gleizes & Galy, 1980). Therefore, for the anion in (Ph₄As)₂[Zn(dto)₂] two questions arise: (i) is the zinc ion coordinated by sulfur atoms only as postulated from vibrational spectra (Coucouvanis & Piltingsrud, 1973), and (ii) is the actual coordination geometry tetrahedral as found in similar compounds such as tetraphenylarsonium (*N,N*-diethyldithiocarbamate)(dimercaptomaleonitrilato)zincate(II) (Leban, Golič, Kirmse, Stach, Abram, Sieler, Dietzsch & Keijzers, 1986)?

Experimental. Title compound prepared by slightly modified method reported by Coucouvanis & Piltingsrud (1973); light yellow crystals grown from acetone solution. Crystal size 0·4 × 0·4 × 0·5 mm. All data collected using Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Mo K α radiation. Cell dimensions from least-squares refinement of 100 reflections in range 9 < θ < 12°; no absorption correction. [Type I triclinic cell, $a = 10\cdot427$ (1), $b = 12\cdot654$ (1), $c = 18\cdot639$ (2) Å, $\alpha = 85\cdot45$ (1), $\beta = 82\cdot73$ (1), $\gamma = 81\cdot48$ (1)°, transformation matrix: $\begin{pmatrix} 100 \\ 010 \\ 001 \end{pmatrix}$.] Three-dimensional diffractometer data; ω - 2θ scan; ω scan width (°) = 0·7 + 0·3 tan θ ; aperture (mm) = 2·4 + 0·9 tan θ ; max. scan time 40 s; $2\theta_{\max}$ 50°; hemisphere ($h \geq 0$) measured; $(\sin \theta/\lambda)_{\max} = 0\cdot6$ Å⁻¹; standard reflections 61 $\bar{1}$, 51 $\bar{3}$, 51 $\bar{7}$; 9104 reflections measured, 8452 unique; $R_{\text{int}} = 1\cdot3\%$; 3759 unobserved reflections [$I < 2\cdot5 \sigma(I)$]. Structure solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Positions for Zn, As and S atoms revealed by best *E* map (CFOM = 2·93); residual atoms O and C estimated from further Fourier map. Final values $R = 0\cdot044$ and $wR = 0\cdot055$ by full-matrix least-squares refinement. Zn, As and S, C, O atoms from dithiooxalate groups refined with anisotropic thermal parameters and C atoms from phenyl rings with isotropic thermal parameters. Positions of phenyl hydrogen atoms calculated and included as fixed-atom contributions in structure factor calculation. Empirical weighting function, $w = W_F \times W_S$, where $W_F(|F_o| < 16\cdot00) = (|F_o|/16\cdot00)^2$, $W_F(|F_o| > 30\cdot00) = 30\cdot00/|F_o|$, $W_S(16\cdot00 < F_o < 30\cdot00) = 1\cdot0$ and

$W_S(\sin \theta < 0\cdot42) = \sin \theta/0\cdot42$, $W_S(\sin \theta > 0\cdot95) = (0\cdot95/\sin \theta)^2$, $W_S(0\cdot42 < \sin \theta < 0\cdot95) = 1\cdot0$, applied to keep $\sum w(\Delta F)^2$ uniform over ranges of $(\sin \theta/\lambda)$ and $|F_o|$; $(\Delta/\sigma)_{\max}$ in final refinement cycle 3·4; $(\Delta/\sigma)_{\text{av}}$ 0·13; $m/n = 21\cdot0$; $S = 1\cdot24$; max. and min. heights in final difference Fourier map 0·49 and $-0\cdot71$ e Å⁻³; isotropic extinction correction (Larson, 1967) taken into account (1·4), atomic scattering and dispersion factors for neutral Zn, As, S, C and O from Cromer & Mann (1968), Cromer & Liberman (1970), and for H atoms from Stewart, Davidson & Simpson (1965); DEC-10 computer at RCU Ljubljana, XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. The final fractional coordinates with U_{eq} (Hamilton, 1959) for non-H atoms are listed in Table 1.* Fig. 1 shows the numbering of the anion [Zn(dto)₂]²⁻ and Fig. 2 the unit-cell contents.

The Zn atom is coordinated by all four sulfur atoms from both dithiooxalate ligands in the form of a slightly distorted tetrahedron. The dihedral angle between the best planes through the two five-membered non-planar chelate rings is 86·8 (6)°. The Zn—S bond distances are in the range 2·304 (2) to 2·334 (2) Å (Table 2). Such differences are also found in another tetrahedral Zn complex containing the unsaturated vicinal disulfido ligand disulfidomaleonitrile (mnt), (Ph₄As)₂[Zn(mnt)₂] (Stach, Kirmse, Sieler, Abram, Dietzsch, Böttcher, Hansen, Vergossen & Keijzers, 1986). Here the Zn—S bond distances vary between 2·320 (2) and 2·240 (2) Å; the dihedral angle between the chelate rings is 83·9°. The distances and most angles in the dithiooxalate ligands (Table 2) do not differ significantly from those in the planar nickel(II) chelate K₂[Ni(dto)₂] which contains two terminal dithiooxalate ligands only (Coucouvanis, Baenziger & Johnson, 1973). However, whereas these are quite planar, the distortion of the ligands in the compound under study is rather large. The torsion angles along the C—C bond for S atoms are 31·7 (2) and 43·3 (2)°, respectively. It seems that terminal dithiooxalate ligands are essentially planar only if coordinated to transition-metal ions independently of the actual coordination geometry and the existence of further ligands in the coordination sphere. On the other hand, terminal dithiooxalate ligands deviate considerably from planarity in complexes of *d*¹⁰ or main-group metal ions. For instance, in (Ph₄As)₄[(dto)₂In(μ -dto)In(dto)₂] two different kinds of terminal dto ligands are found having S—C—C—S

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles and calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42660 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

torsion angles of 17 and 49°, respectively (Golič, Bulc & Dietzsch, 1982).

The geometry of the $[(C_6H_5)_4As]^+$ cations is tetrahedral, in good agreement with other determinations (e.g. Cowie & Bennett, 1976).

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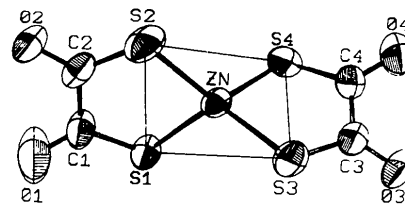


Fig. 1. The anion $[Zn(dto)_2]^{2-}$.

Table 1. Final fractional coordinates ($\times 10^4$; for Zn, As $\times 10^5$) and equivalent isotropic temperature factors U_{eq} ($\text{\AA}^2 \times 10^3$; for Zn, As $\text{\AA}^2 \times 10^4$)

	x	y	z	U_{eq}
Zn	1491 (7)	23308 (5)	25911 (4)	501 (4)
S(1)	-204 (2)	3332 (1)	1578 (1)	62 (1)
S(2)	-730 (2)	3681 (2)	3362 (1)	76 (1)
C(1)	-1101 (8)	4459 (5)	1936 (4)	72 (4)
C(2)	-1013 (7)	4709 (5)	2775 (4)	63 (4)
O(1)	-1828 (12)	5079 (6)	1568 (4)	156 (7)
O(2)	-1214 (6)	5642 (4)	2977 (4)	92 (4)
S(3)	-785 (2)	751 (1)	2484 (1)	61 (1)
S(4)	2267 (2)	1506 (1)	2858 (1)	62 (1)
C(3)	656 (7)	-137 (5)	2574 (3)	56 (3)
C(4)	1880 (7)	245 (5)	2994 (4)	64 (4)
O(3)	737 (6)	-1064 (4)	2341 (3)	79 (3)
O(4)	2520 (7)	-367 (5)	3423 (4)	114 (5)
As(1)	36181 (6)	81391 (4)	2523 (3)	443 (3)
C(10)	4980 (6)	8318 (5)	1015 (3)	48 (1)
C(11)	5867 (7)	7448 (5)	1235 (4)	59 (2)
C(12)	6878 (8)	7592 (6)	1784 (4)	70 (2)
C(13)	6975 (8)	8606 (6)	2098 (4)	72 (2)
C(14)	6087 (8)	9466 (6)	1896 (4)	71 (2)
C(15)	5105 (7)	9337 (5)	1351 (4)	60 (2)
C(20)	4337 (5)	7787 (4)	-644 (3)	45 (1)
C(21)	5659 (6)	7777 (5)	-674 (4)	58 (1)
C(22)	6137 (8)	7558 (6)	-1350 (4)	72 (2)
C(23)	5292 (8)	7358 (7)	-1959 (5)	77 (2)
C(24)	3990 (7)	7357 (6)	-1928 (4)	65 (2)
C(25)	3499 (6)	7558 (5)	-1263 (4)	56 (1)
C(30)	2709 (6)	7011 (5)	459 (3)	53 (1)
C(31)	1893 (7)	7191 (6)	1002 (4)	66 (2)
C(32)	1226 (9)	6366 (7)	1154 (5)	84 (2)
C(33)	1360 (11)	5435 (9)	774 (6)	104 (3)
C(34)	2180 (12)	5227 (9)	237 (7)	112 (3)
C(35)	2848 (9)	6048 (7)	73 (5)	86 (2)
C(40)	2474 (5)	9462 (4)	176 (3)	43 (1)
C(41)	2204 (6)	9942 (5)	-478 (3)	53 (1)
C(42)	1390 (7)	10909 (6)	-523 (4)	65 (2)
C(43)	832 (7)	11385 (5)	84 (4)	59 (2)
C(44)	1079 (7)	10882 (5)	729 (4)	62 (2)
C(45)	1906 (6)	9930 (5)	778 (4)	57 (1)
As(2)	63809 (5)	70497 (4)	47458 (3)	410 (3)
C(50)	5511 (5)	6664 (4)	3814 (3)	46 (1)
C(51)	4501 (7)	7385 (5)	3512 (4)	58 (2)
C(52)	3895 (8)	7169 (6)	2819 (4)	70 (2)
C(53)	4353 (8)	6224 (6)	2432 (4)	70 (2)
C(54)	5362 (8)	5521 (6)	2734 (4)	72 (2)
C(55)	5953 (7)	5714 (6)	3438 (4)	62 (2)
C(60)	5110 (5)	7899 (4)	5283 (3)	45 (1)
C(61)	4017 (7)	7435 (5)	5384 (4)	58 (2)
C(62)	3103 (8)	7996 (6)	5802 (4)	74 (2)
C(63)	3276 (8)	9009 (6)	6108 (4)	73 (2)
C(64)	4360 (7)	9456 (6)	6002 (4)	67 (2)
C(65)	5298 (6)	8896 (5)	5592 (3)	51 (1)
C(70)	7802 (5)	7785 (4)	4619 (3)	39 (1)
C(71)	8550 (6)	8157 (5)	5232 (3)	51 (1)
C(72)	9642 (7)	8616 (5)	5150 (4)	58 (1)
C(73)	10007 (7)	8680 (5)	4465 (4)	60 (2)
C(74)	9261 (6)	8292 (5)	3861 (4)	58 (1)
C(75)	8152 (6)	7848 (4)	3932 (3)	46 (1)
C(80)	7138 (5)	5844 (4)	5289 (3)	44 (1)
C(81)	8103 (6)	5107 (5)	5006 (4)	56 (1)
C(82)	8700 (7)	4266 (6)	5419 (4)	67 (2)
C(83)	8360 (7)	4167 (6)	6090 (4)	67 (2)
C(84)	7426 (8)	4912 (7)	6371 (5)	78 (2)
C(85)	6799 (7)	5760 (6)	5971 (4)	63 (2)

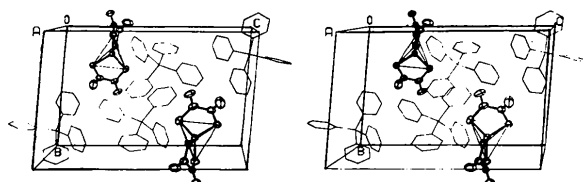


Fig. 2. Unit cell of $[(C_6H_5)_4As]_2[Zn(S_2C_2O_2)_2]$.

Table 2. Interatomic distances (\AA) and angles ($^\circ$) for the anion $[Zn(dto)_2]^{2-}$

Coordination tetrahedron			
Zn-S(1)	2.318 (2)	S(1)-Zn-S(2)	95.6 (1)
Zn-S(2)	2.304 (2)	S(1)-Zn-S(3)	116.2 (1)
Zn-S(3)	2.334 (2)	S(1)-Zn-S(4)	115.0 (1)
Zn-S(4)	2.310 (2)	S(2)-Zn-S(3)	116.2 (1)
		S(2)-Zn-S(4)	120.3 (1)
		S(3)-Zn-S(4)	95.2 (1)
Dithiooxalate ligands			
Ligand 1			
C(1)-C(2)	1.566 (11)	S(1)-C(1)-C(2)	120.5 (5)
C(1)-S(1)	1.723 (7)	S(1)-C(1)-O(1)	122.8 (7)
C(1)-O(1)	1.199 (11)	O(1)-C(1)-C(2)	116.7 (7)
C(2)-S(2)	1.734 (7)	S(2)-C(2)-C(1)	120.7 (5)
C(2)-O(2)	1.207 (8)	S(2)-C(2)-O(2)	123.1 (6)
		O(2)-C(2)-C(1)	116.1 (6)
Ligand 2			
C(3)-C(4)	1.531 (10)	S(3)-C(3)-C(4)	119.0 (4)
C(3)-S(3)	1.735 (6)	S(3)-C(3)-O(3)	123.2 (5)
C(3)-O(3)	1.214 (7)	O(3)-C(3)-C(4)	117.7 (6)
C(4)-S(4)	1.748 (8)	S(4)-C(4)-C(3)	119.8 (5)
C(4)-O(4)	1.222 (10)	S(4)-C(4)-O(4)	123.9 (6)
		O(4)-C(4)-C(3)	116.3 (7)

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Bis[(thiényl-2)-2 glyoxylato]cuivre(II) et Diaquabis[(thiényl-2)-2 glyoxylato]cuivre(II)

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Abstract. [Cu(C₆H₃O₃S)₂], (1), $M_r = 373.8$, triclinic, space group $P\bar{1}$, $a = 5.073$ (2), $b = 8.199$ (1), $c = 8.770$ (2) Å, $\alpha = 61.89$ (2), $\beta = 82.28$ (2), $\gamma = 81.36$ (2)°, $V = 317.2$ (3) Å³, $Z = 1$, $D_x = 1.96$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.7107$ Å, $\mu = 21.3$ cm⁻¹, $F(000) = 187$, $T = 295$ K, $R = 0.062$ for 1045 unique reflections. [Cu(C₆H₃O₃S)₂(H₂O)₂], (2), $M_r = 409.9$, monoclinic, space group $P2_1/c$, $a = 8.425$ (2), $b = 11.532$ (4), $c = 7.348$ (1) Å, $\beta = 92.93$ (2)°, $V = 713.0$ (5) Å³, $Z = 2$, $D_x = 1.91$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.7107$ Å, $\mu = 19.1$ cm⁻¹, $F(000) = 414$, $T = 295$ K, $R = 0.044$ for 2736 unique reflections. For both compounds, the 2-(2-thienyl)glyoxylato ligands are distributed in two conformations, which correspond to 180° rotations about the C(O)–C(ring) bond. In (1), the Cu coordination is a nearly square-planar centrosymmetrical arrangement [Cu–O = 1.965 (4) and 1.899 (3) Å]. In (2), the coordination is a centrosymmetric octahedral arrangement [Cu–O = 1.955 (2), 2.029 (2) and 2.290 (2) Å].

Introduction. De nombreux travaux démontrent le rôle modulateur du cuivre dans l'organisme. Des complexes de cuivre se sont révélés des agents anti-inflammatoires, anti-épileptiques, anti-cancéreux (Sorenson, Kishore, Pezeshk, Oberley, Leuthauser & Oberley, 1984). La recherche de coordinats capables d'améliorer le caractère anti-inflammatoire et anti-arthritique propre au

cuivre par formation de complexes actifs et peu toxiques nous a déjà conduit à étudier un complexe dont les coordinats sont le groupe salicylidène et un vecteur sucre (Arnaud & Sabbagh, 1983). Neuf autres complexes sont en cours d'étude, choisis en fonction des propriétés pharmacophores de leurs coordinats. Ces complexes étant généralement très stables, il est nécessaire d'en connaître la structure afin de mieux appréhender leur mode d'action au niveau des récepteurs physiologiques. Parmi les complexes étudiés, le diaquabis[(thiényl-2)-2 glyoxylato]cuivre(II) est intéressant par la présence dans le coordinat d'un hétérocycle aromatique soufré porté par un groupe glyoxylique, éléments structuraux pouvant être en relation avec les propriétés anti-inflammatoires. Nous avons également étudié le complexe anhydre pour lequel nous avons rencontré les mêmes problèmes de conformation lors de la détermination de la structure.

Partie expérimentale. Cristallisation: (1) dans le méthanol, (2) dans l'eau; parallélépipède taillé: (1) 0,25 × 0,20 × 0,05 mm; (2) 0,50 × 0,50 × 0,20 mm; diffractomètre Nonius CAD-4; monochromateur de graphite; paramètres de maille affinés par moindres carrés utilisant 25 réflexions [(1) 12,84 ≤ 2θ ≤ 43,66°; (2) 20,74 ≤ 2θ ≤ 59,12°]. Balayage ω–½θ. Lp correction, absorption ignorée. Réflexions de contrôle 122 pour (1), 242 pour (2); variation maximale autour de la valeur