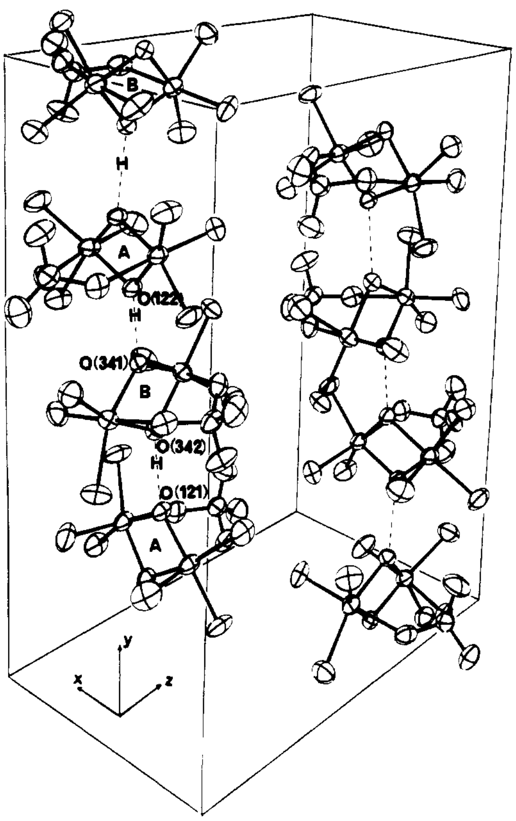

Figure 2. Molecular arrangement of the two independent molecules in the unit cell.

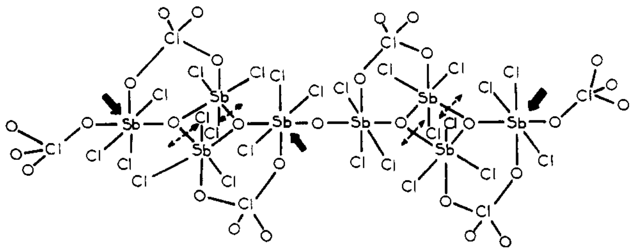

Figure 3. Hypothetical structure for $Sb_8Cl_{24}(O_5)(ClO_4)_6$, showing the attack of water (dark arrows) and breaking of bonds (broken arrows) leading to $Sb_2Cl_6(OH)(O)(ClO_4)$.

The other significant stretchnig modes of SbCl and SbO bonds range from 200 to 550 cm^{-1}, and they are assigned as follows: 539 and 445 (R) and 545 and 455 (IR) to ν(Sb–O) ring, 424 and 305 (R and IR) to ν(SbCl), and 240 (R) and 230 (IR) to ν(Sb–O) (oxygen of ClO_4).

The structure of the compound $Sb_8Cl_{24}O_5(ClO_4)_6$ remains a challenging problem which could be approached by comparison with the structure of the $Sb_2Cl_6(OH)(O)(ClO_4)$ complex and with the use of spectroscopic data.

The only differences between their spectra are for $Sb_8Cl_{24}O_5(ClO_4)_6$ the lack of a broad band characteristic of an OH bond between 2100 and 3350 cm^{-1} and the presence of lines at 1295 (R), 1280 (IR), 1035 (R), 1020 (IR), 726 (R), and 712 cm^{-1} (IR), which describe the stretching modes of an unidentate ClO_4 group.

The coexistence of unidentate and bidentate ClO_4 groups in $Sb_8Cl_{24}(O)_5(ClO_4)_6$ as in the tin complex[15] allows us to imagine a basic skeleton composed of octahedrally surrounded antimony atoms linked to each other through tricoordinate and bicoordinate oxygen atoms as in the Sb_2O_5 frame.[29] The completion of the atomic arrangement around Sb is ensured by uni- and bidentate perchlorato groups and chlorine atoms as shown in Figure 3. This model is particularly in agreement with the two Raman lines observed at 242 and 233 cm^{-1} and assigned to Sb–O stretching vibrations between the metal and, respectively, the bidentate and monodentate perchlorates.

Acknowledgment. We thank the CNRS for financial support. M.C. is grateful to the French Foreign Office for the grant of a fellowship.

Registry No. $Sb_8Cl_{24}O_5(ClO_4)_6$, 82135-08-8; $Sb_2Cl_6(OH)(O)(ClO_4)$, 82113-01-7; $SbCl_5$, 7647-18-9; Cl_2O_6, 12442-63-6.

Supplementary Material Available: Tables of structure factors, bond distances and angles for unit B, and positional and thermal parameters for $Sb_2Cl_6(OH)(O)(ClO_4)$ (15 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
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Synthesis and Molecular and Crystal Structure of Tetrakis(tetraphenylarsonium) Tetrakis(dithiooxalato-*S*,*S'*)(μ-*trans*-dithiooxalato)diindate(III), $[(C_6H_5)_4As]_4[(O_2C_2S_2)_2In(SOC_2SO)In(S_2C_2O_2)_2]$

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Although 1,2-dithiooxalate (dto) is among the classical sulfur ligands,[2] in the last years much work has been done on the coordination chemistry and characterization of this ligand showing some interesting points. Thus, the dithiooxalate has the highest ligand field strength of all known geminal and vicinal dithio ligands.[3] Coucouvanis and co-workers have shown that the presence of four donor atoms in the dithiooxalate dianion and the possibilities of charge delocalization on any two of these atoms result in a multifunctional ligand with unique coordination properties.[4] X-ray structure determinations and other studies demonstrate the ability of the ligand to coordinate to the central metal ion by two sulfur or two oxygen donor atoms, respectively.[4d,f,h] Further, dithiooxalate may coordinate simultaneously to more than one metal ion in polynuclear complexes that form when various parent dithiooxalate complexes react with coordinately unsaturated species. If $M(PR_3)_2^+$ cations (M = Cu, Ag) are used, surprisingly, in the cases of iron or tin tris(dithiooxalates) a ligand reorganization from S,S chelation to O,O chelation to the central metal ion was found and confirmed by X-ray structure analysis.[4f,h] At present there is no evidence for such bridging dithiooxalate in the trans form proposed in few cases from infrared studies.[4e,g] In the $(Ph_4As)_4[In_2(dto)_5]$ complex salt

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(1) (a) Edvard Kardelj University of Ljubljana. (b) Karl Marx University of Leipzig.

(2) For example: (a) Jones, H. O.; Tasker, H. S. *J. Chem. Soc.* **1909**, *95*, 1904. (b) Robinson, C. S.; Jones, H. O. *Ibid.* **1912**, *101*, 62. (c) Cox, E. G.; Wardlaw, W.; Webster, K. C. *Ibid.* **1935**, 1475.

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Table I. Crystallographic Data, Data Collection, and Refinement Summary

formula	$C_{106}H_{80}As_4In_2O_{10}S_{10}$	β, deg	95.75 (1)
mol wt	2363.52	γ, deg	100.10 (2)
space group	$P\bar{1}$	V, Å^3	2500 (2)
a, Å	10.743 (1)	Z	1
b, Å	12.882 (2)	d_{obsd},[a] g cm^{-3}	1.59 (2)
c, Å	18.478 (2)	d_{calcd}, g cm^{-3}	1.570
α, deg	92.47 (2)	temp, K	293 (1)

diffractometer	CAD-4 automatic, four-circle
scan method	ω–2θ
2θ scan width, deg	0.8 + 0.2 tan θ
aperture, mm	2.4 + 0.9 tan θ
ref reflctns	217, $\bar{4}4\bar{5}$, 327
bkgd	one-fourth of the scan time at each of the scan limits
radiation	Mo K$\bar{\alpha}$ (λ = 0.7107 Å)
monochromator	graphite crystal
scan rate, deg min^{-1}	
min	1.8
max	20.1
max scan time, s	40
$2\theta_{max}$, deg	50
measd reflctns	9346 ($\pm h, +k, \pm l$)
avgd reflctns	8770
obsd reflctns [$I_o > 1.5\sigma(I_o)$]	5192
intens control	in each case after 192 reflctns
orientation control	in each case after 384 reflctns

final refinement cycle	
scale factor (k)	1.001
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.077
$R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$	0.093
av shift/error	0.015
max shift/error	1.129
data (m)-to-variable (n) ratio	12.9
$[\Sigma w(\Delta F)^2/(m-n)]^{1/2}$	2.28
no. of contributing reflctns	7671
final diff map	
max $\Delta\rho$, e Å^{-3}	0.6
isotropic extinction cor	−0.6 (none)

[a] Density was determined by the flotation method using a solution of carbon tetrachloride and chlorobenzene.

we now find a compound possessing one dithiooxalate dianion that acts as a symmetric quadridentate bridging ligand linking two indium ions.

Experimental Section

Preparation of $(Ph_4As)_4[In_2(dto)_5]$. $InCl_3$ (prepared from 115 mg (1 mmol) In metal) in ethanol was allowed to react with 892 mg (4.5 mmol) K_2dto[2a] in 50 mL water obtaining a yellow complex solution which was extracted with 90 mL dichloromethane containing 1.26 g (3 mmol) Ph_4AsCl. Concentration of the dried organic phase to a volume of 25 mL, addition of anhydrous ether to the first cloudiness and cooling to −10°C effected the crystallization of the complex salt. Recrystallization by dissolving in 20 mL nitromethane, addition of ether and cooling in the same manner gave yellow crystals.[5]

X-ray Crystallography. Crystals suitable for diffraction studies were grown from a concentrated nitromethane solution of the complex salt covered with a layer of ether and stored at 0 °C over some days. The investigated crystal had the shape of a thin plate with the dimensions 0.05 mm × 0.5 mm × 0.3 mm.

The cell parameters were obtained by least squares from the θ values of 45 high-order reflections in the range $9° < \theta < 18°$ measured on an Enraf-Nonius CAD-4 diffractometer. Details of the data collection and reduction are given in Table I. The linear absorption coefficient μ was 20.22 cm^{-1}. Therefore, no absorption correction was made.

The structure was solved by direct methods using MULTAN 77.[6] The best E map (CFOM = 2.41) revealed the positions for In, As, and O and partially for C atoms. From the subsequent Fourier maps the residual C atoms were estimated. The refinement of all atom positions including the anisotropic temperature factors gave final $R = 0.077$ and $R_w = 0.093$. Refinement was carried out with use of the empirical weighting function $w = w_{F_o}w_S$, where $w_{F_o}(F_o < 23.00) = (F_o/23.00)^2$, $w_{F_o}(F_o > 34.00) = (34.00/F_o)^{1.5}$, $w_{F_o}(23.00 < F_o < 34.00) = 1.0$, $w_S(\sin\theta < 0.29) = ((\sin\theta)/0.29)^{1.5}$, $w_S(\sin\theta > 0.35) = (0.35/\sin\theta)^{1.5}$, and $w_S(0.29 < \sin\theta < 0.35) = 1.0$. The positions of the phenyl hydrogen atoms were calculated and have been included as fixed atom contributions in the structure calculation. Scattering factors for the non-hydrogen atoms were taken from Cromer and Mann,[7] anomalous-dispersion corrections from Cromer and Liberman,[8] and H atom scattering factors from Steward et al.[9] All calculations were performed on the CDC Cyber 172 computer of RRC Ljubljana with the XRAY system.[10]

Table II. Final Atomic Coordinates of the Anion

atom	x/a	y/b	z/c
In	0.044 05 (6)	0.937 41 (5)	0.334 46 (4)
S(1)	−0.171 76 (25)	0.815 96 (24)	0.312 76 (18)
S(2)	0.134 60 (24)	0.770 46 (22)	0.312 63 (19)
S(3)	0.009 28 (27)	1.002 33 (24)	0.206 25 (15)
S(4)	0.260 75 (28)	1.059 24 (23)	0.344 49 (16)
S(5)	0.074 09 (33)	0.931 48 (25)	0.596 94 (15)
O(1)	−0.213 84 (96)	0.637 45 (96)	0.237 06 (87)
O(2)	0.008 02 (94)	0.587 58 (69)	0.262 55 (65)
O(3)	0.134 3 (11)	1.182 45 (80)	0.174 94 (58)
O(4)	0.357 14 (87)	1.122 94 (81)	0.227 89 (59)
O(5)	0.084 65 (72)	0.912 63 (62)	0.458 36 (39)
C(1)	−0.134 8 (11)	0.706 2 (10)	0.271 10 (71)
C(2)	0.001 17 (96)	0.677 08 (92)	0.279 55 (59)
C(3)	0.135 1 (11)	1.105 78 (94)	0.210 25 (58)
C(4)	0.259 3 (11)	1.097 22 (78)	0.255 77 (68)
C(5)	0.043 94 (97)	0.959 53 (82)	0.508 25 (58)

Table III. Distances (Å) and Angles (Deg) in the InS_5O Octahedron

In–S(1)	2.544 (3)	In–S(4)	2.554 (3)
In–S(2)	2.544 (3)	In–S(5)	2.638 (4)
In–S(3)	2.560 (3)	In–O(5)	2.334 (7)
S(1)–In–S(2)	85.17 (9)	S(3)–In–S(4)	85.81 (9)
S(1)–In–S(3)	89.70 (10)	S(4)–In–O(5)	87.55 (19)
S(1)–In–S(5)	85.83 (10)	S(4)–In–S(5)	96.65 (10)
S(1)–In–O(5)	97.18 (19)	O(5)–In–S(5)	74.01 (22)
S(2)–In–S(4)	94.01 (9)	S(3)–In–S(5)	98.06 (10)
S(2)–In–O(5)	86.07 (22)		

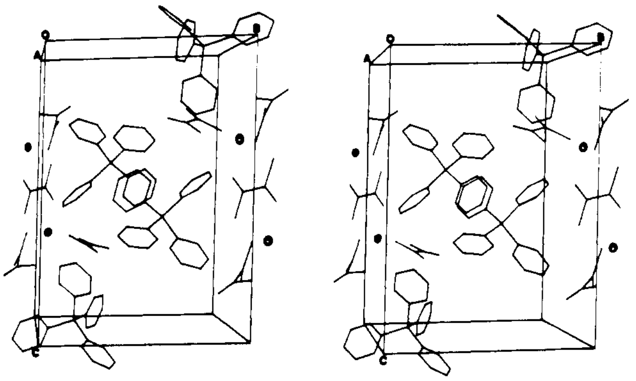

Figure 1. Stereoview of the molecular packing showing the contents of one unit cell (the lines between the donor atoms and the central metal ion are omitted).

Description and Discussion

The final positional parameters of the atoms of the anion are listed in Table II. The unit cell contains one molecule

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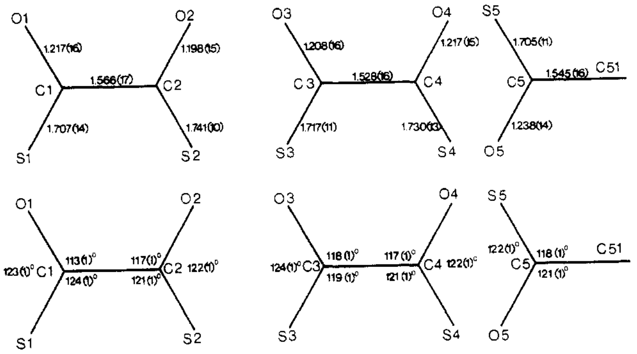

Figure 2. Dimensions and angles within the three different dithiooxalate ligands.

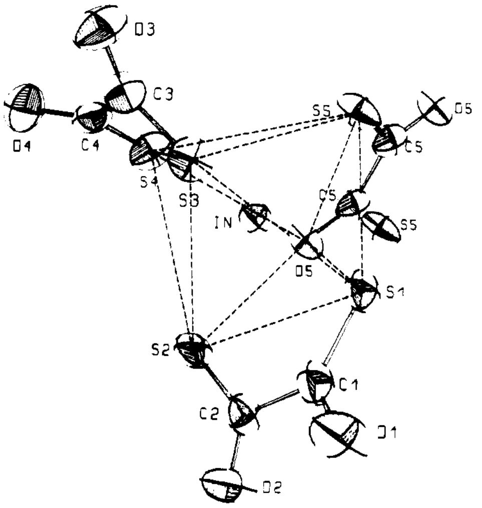

Figure 3. Arrangement of three dithiooxalate ligands around the indium ion causing a distorted octahedral InS_5O polyhedron.

as shown in Figure 1. Interatomic distances and angles of the anion with their estimated standard deviations are listed in Table III and are shown in Figure 2. The numbering scheme of the anion $[(O_2C_2S_2)_2In(SOC_2SO)In(S_2C_2O_2)_2]^{4-}$ is shown in Figures 3 and 4.

Two indium atoms and five dithiooxalate groups form a dimer containing an $In_2S_{10}O_2C_2$ skeleton. Either indium ion is coordinated to two dithiooxalate ligands in cis arrangement. The fifth dithiooxalate acts as a symmetric quadridentate bridging ligand linking both $In(S_2C_2O_2)_2$ units. This ligand represents the first authentic example of a coordinated dithiooxalate in trans arrangement. Thus, the indium atoms are coordinated by five sulfur atoms and one oxygen atom, causing a distorted octahedral coordination sphere as shown in Figure 3. While four In-S distances are practically equal, having an average value of 2.551 (3) Å (see Table III), the fifth sulfur atom, belonging to the bridging ligand, has a longer distance (2.638 (4) Å). This value lies near the average In-S bond length 2.604 (8) Å in the octahedral tris(maleonitriledithiolato)indate(III) trianion, $[In(S_2C_2(CN)_2)_3]^{3-}$, the only other In(III) complex with a 1,2-dithio ligand whose structure has been determined by X-ray analysis.[11] The In-O distance is 2.334 (7) Å. This value is significantly larger than the Sn-O distance to the bridging cis dithiooxalate in the complex $K[Sn[dto(Cu(P(tol)_3)_2)](dto)_2]\cdot 2C_3H_6O$,[4h] which is 2.158 (4) Å. As expected, the angles in the octahedron vary significantly from a minimum value of 74° for O(5)-In-S(5) to a maximum value of 98° for S(3)-In-S(5) (see Table III).

There are three types of dithiooxalate ligands in the molecule. In contrast to the nearly planar bridging trans dithiooxalate containing the inversion center of the whole molecule, the other four terminal ligands deviate more or less from the planarity and can be divided into two groups as to be seen from the torsion angles along the C-C bond. These angles have the values 11° for O(1)-C(1)-C(2)-O(2) and 17° for S(1)-C(1)-C(2)-S(2) in the one ligand type and 41° for O(3)-C(3)-C(4)-O(4) and 49° for S(3)-C(3)-C(4)-S(4) in the other one causing to angles of 15 and 45°, respectively, between the thiocarboxylic units in the ligands. Hitherto, such strong distortions of the coordinated dithiooxalate ligands have not been found in other complexes. Despite of this fact, in all three types of ligands the C-C, C-O, and C-S distances and the S-C-O angles also are similar to those found in some other dithiooxalate compounds.[4d,h,12-15] In the structure there are two different types of tetraphenylarsonium cations whose geometry is tetrahedral, in good agreement with earlier determinations,[16] and is not further discussed.

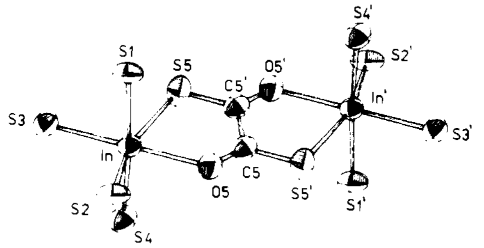

Figure 4. Central part of the anion $[In_2(dto)_5]^{4-}$ with a planar dto bridge in trans arrangement containing the inversion center of the molecule.

The $(Ph_4As)_4[In_2(dto)_5]$ complex shuts a gap because, despite the usually extensive coordination chemistry of indium with dithiolate ligands,[17] surprisingly no indium dithiooxalate complexes have been reported.

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Registry No. $(Ph_4As)_4[In_2(dto)_5]$, 79725-63-6.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (Table IV), atomic coordinates and anisotropic temperature factors of all atoms (Table V), and atomic coordinates of the generated phenyl hydrogen atoms (Table VI) (41 pages). Ordering information is given on any current masthead page.

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Chromium Oxide Trifluoride ($CrOF_3$). Preparation and Properties

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Chromium trioxide reacts with chlorine monofluoride at 0 °C to produce chromyl fluoride.[2a] When the interaction of