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Structure of the Ionic Polynuclear Tantalum(V) Derivative Bis{tri-μ-chloro-bis[dichloro-(η-pentamethylcyclopentadienyl)tantalum(V)]} 2,3;2,3-Di-μ-chloro-1,1,1,1,1,2,2,2,3,3,3,4,4,4,4,4-hexadecachloro-1,2;3,4-di-μ-oxo-tetratantalate(V),* 2[{Ta(η-C$_5$Me$_5$)Cl$_2$}$_2$-(μ-Cl)$_3$]$^+$.[{TaCl$_5$(μ-O)TaCl$_3$}$_2$(μ-Cl)$_2$]$^{2-}$

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Abstract. $M_r = 3155{\cdot}0$, monoclinic, $P2_1/c$, $a = 16{\cdot}839\ (3)$, $b = 15{\cdot}225\ (4)$, $c = 17{\cdot}065\ (7)$ Å, $\beta = 111{\cdot}18\ (3)^\circ$, $U = 4079{\cdot}5$ Å^3, $Z = 2$, $D_x = 2{\cdot}57$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 12{\cdot}33$ mm^{-1}, $F(000) = 2888$, room temperature, $R = 0{\cdot}050$ for 2087 independent observed reflections. The compound consists of dinuclear monovalent cations and tetranuclear divalent anions. The former have one η^5-C$_5$Me$_5$ group, two terminal Cl atoms and three bridging Cl atoms bonded to each Ta$^{\rm V}$. The anions can be described in terms of a central dinuclear [O=TaCl$_3$(μ-Cl)$_2$Cl$_3$Ta=O]$^{2-}$ unit bonded through the O atoms to two tantalum pentachloride, [TaCl$_5$], molecules. Both in the cations and in the anions the geometry round each Ta atom is that of a distorted octahedron (the C$_5$ rings considered as point ligands); the distortion is greater in the cations, as expected from their greater bridge multiplicity.

Introduction. Cyclopentadienyl Nb and Ta tetrahalides, [(η-C$_5R_5$)MX_4], can be conveniently prepared by means of the reaction between the corresponding metal pentahalide, [MX_5], and tin reagents of the type [(C$_5R_5$)SnR'_3] (Labinger, 1982):

$$[MX_5] + [(\mathrm{C}_5R_5)\mathrm{Sn}R'_3] \rightarrow [(\eta\text{-}\mathrm{C}_5R_5)MX_4] + [\mathrm{Sn}XR'_3]$$

R = H or alkyl group $\quad M$ = Nb or Ta
R' = alkyl group $\quad X$ = halogen.

Reaction of [TaCl$_5$] with [Sn(Bu^n)$_3$(C$_5$Me$_5$)] in refluxing dichloromethane and subsequent recrystallization of

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* Part of this work has been briefly communicated: Green, Overton, Prout & Marín (1983).

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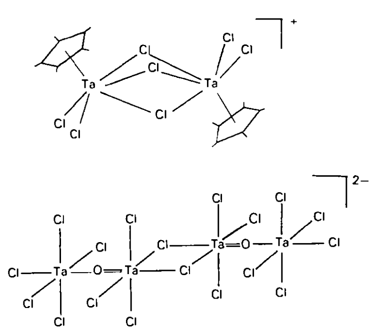
the reaction product, $[Ta(\eta\text{-}C_5Me_5)Cl_4]$ (Maclain, Wood & Schrock, 1979), also afforded a small amount of deep-red crystals,* characterized by X-ray crystallography as the title compound.

Experimental. Approximately spherical single crystal (∅ *ca* 0·20 mm) supplied by Dr J. C. Green (Inorganic Chemistry Laboratory, Oxford) and mounted in a glass capillary and sealed under nitrogen (the compound is very air and moisture sensitive). Enraf–Nonius CAD-4F diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions obtained from the setting angles of 25 accurately centered reflections. 6200 independent reflections with $2\theta \leq 46°$ in the *hkl* range (−17,0,0)-(17,15,17) measured. ω–2θ scan technique. Three standard reflections monitored every 3600 s, intensity variation within ±5%. Data corrected for Lorentz, polarization and absorption effects (North, Phillips & Mathews, 1968), absorption correction range 1·2–1·9. 2087 reflections considered observed $[I \geq 3\sigma(I)]$ and used in subsequent calculations. Structure solved by Patterson and Fourier techniques and refined by full-matrix least squares using F's. C and O isotropic, Ta and Cl anisotropic; H placed geometrically and included in the refinement with fixed contributions to F_c. In the final cycles each reflection given a weight computed from a Chebyshev series with three parameters: 14·3, 19·6 and 6·7 (Carruthers & Watkin, 1979). Final $R = 0{\cdot}050$ and $R_w = 0{\cdot}065$. $(\Delta/\sigma)_{\max} = 0{\cdot}15$. Final Fourier difference map showed no feature greater than −0·41 and +0·50 e Å^{-3}. Atomic scattering factors taken from Cromer & Mann (1968), and allowance was made for the real and imaginary components of anomalous dispersion in the case of the Ta and Cl atoms (*International Tables for X-ray Crystallography,* 1974). All computations carried out on the in-house VAX 11/750 computer, using the Oxford *CRYSTALS* package (Watkin & Carruthers, 1981).

Discussion. Final atomic coordinates, and bond distances and angles are given in Table 1† and 2. The crystal structure is built up of $[\{(\eta\text{-}C_5Me_5)TaCl_2\}_2(\mu\text{-}Cl)_3]^+$ cations and $[\{Cl_5Ta(\mu\text{-}O)TaCl_3\}_2(\mu\text{-}Cl)_2]^{2-}$ anions (I); thus the number of cations is required to be twice the number of anions to preserve electrical neutrality.



(I)

The asymmetric unit consists of one cation and half an anion in the relative disposition shown in Fig. 1. In the cation, three bridging Cl atoms bind two Ta atoms at the distances shown in Table 2. One of the Cl atoms is quite symmetrically placed between the metal atoms. In addition to the bridging Cl atoms there are two terminal Cl atoms and one pentamethylcyclopentadienyl group on each Ta. The average Ta—Cl(terminal) distance is 2·325 (8) Å which, as expected, is considerably shorter than the average Ta—Cl(bridge) distance, 2·57 Å. The carbon rings bind the metal

Table 1. *Atomic coordinates and isotropic temperature factors* (Å^2)

For Ta and Cl, $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}/U_{iso}
Ta(1)	−0·2890 (1)	0·0942 (1)	0·0174 (1)	0·0268
Ta(2)	−0·4341 (1)	0·2240 (1)	−0·1604 (1)	0·0276
Cl(11)	−0·3686 (6)	0·0803 (6)	0·1039 (5)	0·0409
Cl(12)	−0·2996 (7)	−0·0539 (6)	−0·0164 (6)	0·0472
Cl(13)	−0·4496 (5)	0·0839 (5)	−0·0939 (5)	0·0305
Cl(14)	−0·3518 (5)	0·2494 (5)	−0·0039 (5)	0·0326
Cl(15)	−0·2869 (6)	0·1370 (6)	−0·1209 (5)	0·0436
Cl(21)	−0·4491 (7)	0·1539 (7)	−0·2858 (5)	0·0486
Cl(22)	−0·3460 (7)	0·3343 (7)	−0·1774 (6)	0·0466
C(11)	−0·1318 (8)	0·1071 (15)	0·0477 (12)	0·0493 (104)
C(12)	−0·1417 (8)	0·0387 (16)	0·0963 (12)	0·0587 (117)
C(13)	−0·1739 (8)	0·0689 (14)	0·1546 (10)	0·0316 (84)
C(14)	−0·1834 (8)	0·1596 (14)	0·1415 (11)	0·0390 (92)
C(15)	−0·1577 (8)	0·1841 (15)	0·0751 (11)	0·0490 (106)
C(111)	−0·0923 (28)	0·1061 (26)	−0·0210 (23)	0·0659 (127)
C(121)	−0·1081 (32)	−0·0528 (21)	0·0887 (29)	0·0848 (151)
C(131)	−0·1865 (32)	0·0146 (25)	0·2243 (24)	0·0792 (148)
C(141)	−0·2105 (27)	0·2250 (22)	0·1955 (22)	0·0585 (117)
C(151)	−0·1491 (24)	0·2764 (18)	0·0442 (20)	0·0444 (94)
C(21)	0·5899 (9)	0·2167 (15)	−0·1921 (14)	0·0284 (79)
C(22)	−0·5492 (9)	0·2605 (14)	−0·1143 (14)	0·0249 (75)
C(23)	−0·5164 (9)	0·3403 (15)	−0·1324 (15)	0·0371 (89)
C(24)	−0·5383 (9)	0·3438 (15)	−0·2201 (15)	0·0403 (94)
C(25)	−0·5824 (9)	0·2680 (14)	−0·2565 (14)	0·0231 (72)
C(211)	−0·6442 (27)	0·1335 (22)	−0·2059 (26)	0·0635 (125)
C(221)	−0·5638 (28)	0·2347 (28)	−0·0338 (20)	0·0614 (117)
C(231)	−0·4786 (28)	0·4177 (24)	−0·0724 (23)	0·0686 (132)
C(241)	−0·5240 (30)	0·4217 (24)	−0·2700 (25)	0·0715 (134)
C(251)	−0·6247 (27)	0·2505 (28)	−0·3501 (17)	0·0633 (124)
Ta(3)	0·1716 (1)	0·0915 (1)	0·3008 (1)	0·0467
Ta(4)	0·0797 (1)	0·0845 (1)	0·4736 (1)	0·0358
Cl(31)	0·2926 (9)	0·0303 (12)	0·3971 (11)	0·0955
Cl(32)	0·2301 (10)	0·0967 (11)	0·1981 (9)	0·0908
Cl(33)	0·1156 (10)	−0·0482 (8)	0·2625 (8)	0·0870
Cl(34)	0·0441 (8)	0·1518 (9)	0·2135 (8)	0·0708
Cl(35)	0·2181 (9)	0·2312 (10)	0·3499 (10)	0·0870
Cl(41)	0·1881 (7)	−0·0021 (8)	0·5626 (7)	0·0514
Cl(42)	−0·0439 (6)	0·1602 (7)	0·3977 (6)	0·0479
Cl(43)	0·0016 (6)	0·0531 (6)	0·5820 (5)	0·0404
Cl(44)	0·1353 (9)	0·2082 (9)	0·5497 (8)	0·0806
O(34)	0·1238 (16)	0·0872 (16)	0·3946 (15)	0·0508 (68)

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* Adventitious water or oxygen, or tantalum chloride oxide impurities in $[TaCl_5]$ are the possible sources of the oxygen necessary for the formation of the anions.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39782 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms at an average distance of 2·48 Å for Ta(1), and 2·46 Å for Ta(2); the corresponding Ta—C_5-plane perpendicular distances are 2·18 (2) and 2·15 (2) Å, respectively, and the torsion angle C_5Me_5—Ta(1)—Ta(2)—C_5Me_5 is 120 (1)° (where C_5Me_5 refers to the centroid of each pentamethylcyclopentadienyl group).

The *trans* influence of the C_5Me_5 groups causes the Ta—Cl bonds *trans* to them to be relatively long [2·690 (8) Å and 2·674 (10) Å for Ta(1)—Cl(13) and Ta(2)—Cl(15), respectively]. If the bridging Cl atoms are assumed to act as three-electron donors, a 16-electron structure results for the metal atoms.

The detailed structures of the cyclopentadienyl Nb and Ta tetrahalides, $[(\eta\text{-}C_5R_5)MX_4]$ (R = H or Me, M = Nb or Ta, X = halogen), are not known, but their non-monomeric nature has been established (Bunker, De Cian, Green, Moreau & Singanporia, 1980). It is likely, in view of the results obtained for the Ta derivative described in the present paper, that they are ionic in nature and their true formulation is $[\{(\eta\text{-}C_5R_5)MX_2\}_2(\mu\text{-}X)_3]^+.X^-$.

The anions $[\{Cl_5Ta(\mu\text{-}O)TaCl_3\}_2(\mu\text{-}Cl)_2]^{2-}$ are centrosymmetric tetranuclear species (see Fig. 2) and can be described in terms of a central dinuclear $[O{=}TaCl_3(\mu\text{-}Cl)_2Cl_3Ta{=}O]^{2-}$ unit and two terminal $TaCl_5$ molecules bonded to the O atoms through dative

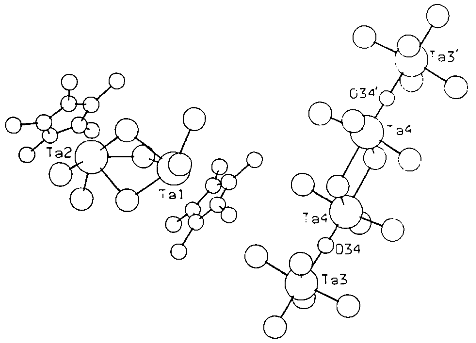

Fig. 1. Structures of the cation $[\{(\eta\text{-}C_5Me_5)TaCl_2\}_2(\mu\text{-}Cl)_3]^+$ and the anion $[\{Cl_5Ta(\mu\text{-}O)TaCl_3\}_2(\mu\text{-}Cl)_2]^{2-}$ showing their relative disposition in the crystal.

Table 2. *Bond distances* (Å) *and bond angles* (°)

Ta(1)–Cl(11)	2·334 (8)	Ta(2)–C(24)	2·480 (14)
Ta(1)–Cl(12)	2·319 (10)	Ta(2)–C(25)	2·533 (14)
Ta(1)–Cl(13)	2·690 (8)		
Ta(1)–Cl(14)	2·560 (8)	C–C*	1·39 (2)
Ta(1)–Cl(15)	2·461 (9)	C–C†	1·40 (2)
Ta(2)–Cl(21)	2·321 (9)	$C–CH_3$‡	1·53 (2)
Ta(2)–Cl(22)	2·326 (9)	Ta(3)–Cl(31)	2·30 (1)
Ta(2)–Cl(13)	2·475 (8)	Ta(3)–Cl(32)	2·30 (1)
Ta(2)–Cl(14)	2·556 (8)	Ta(3)–Cl(33)	2·32 (1)
Ta(2)–Cl(15)	2·674 (10)	Ta(3)–Cl(34)	2·32 (1)
Ta(1)–C(11)	2·515 (14)	Ta(3)–Cl(35)	2·32 (1)
Ta(1)–C(12)	2·503 (15)		
Ta(1)–C(13)	2·470 (13)	Ta(3)–O(34)	2·03 (2)
Ta(1)–C(14)	2·432 (13)	Ta(4)–O(34)	1·76 (2)
Ta(1)–C(15)	2·481 (14)	Ta(4)–Cl(41)	2·32 (1)
Ta(2)–C(21)	2·482 (14)	Ta(4)–Cl(42)	2·323 (9)
Ta(2)–C(22)	2·406 (12)	Ta(4)–Cl(43)	2·672 (9)
Ta(2)–C(23)	2·400 (13)	Ta(4)–Cl(43′)	2·49 (1)
		Ta(4)–Cl(44)	2·29 (1)
Cl(11)–Ta(1)–Cl(12)	93·4 (4)	Cl(31)–Ta(3)–O(34)	85·7 (8)
Cl(11)–Ta(1)–Cl(13)	77·3 (3)	Cl(32)–Ta(3)–Cl(33)	93·4 (6)
Cl(11)–Ta(1)–Cl(14)	82·6 (3)	Cl(32)–Ta(3)–Cl(34)	92·8 (5)
Cl(11)–Ta(1)–Cl(15)	147·2 (3)	Cl(32)–Ta(3)–Cl(35)	93·5 (6)
Cl(12)–Ta(1)–Cl(13)	78·4 (3)	Cl(32)–Ta(3)–O(34)	178·1 (8)
Cl(12)–Ta(1)–Cl(14)	150·6 (3)	Cl(33)–Ta(3)–Cl(34)	89·7 (5)
Cl(12)–Ta(1)–Cl(15)	92·6 (4)	Cl(33)–Ta(3)–Cl(35)	173·0 (5)
Cl(13)–Ta(1)–Cl(14)	72·3 (3)	Cl(33)–Ta(3)–O(34)	87·5 (8)
Cl(13)–Ta(1)–Cl(15)	72·4 (3)	Cl(34)–Ta(3)–Cl(35)	89·0 (5)
Cl(14)–Ta(1)–Cl(15)	76·6 (3)	Cl(34)–Ta(3)–O(34)	88·9 (8)
Ta(1)–Cl(13)–Ta(2)	91·6 (3)	Cl(35)–Ta(3)–O(34)	85·6 (8)
Ta(1)–Cl(14)–Ta(2)	92·8 (3)	Ta(3)–O(34)–Ta(4)	178·4 (15)
Ta(1)–Cl(15)–Ta(2)	92·3 (3)	O(34)–Ta(4)–Cl(41)	93·7 (9)
Cl(21)–Ta(2)–Cl(22)	94·6 (4)	O(34)–Ta(4)–Cl(42)	95·9 (9)
Cl(21)–Ta(2)–Cl(13)	91·8 (3)	O(34)–Ta(4)–Cl(43)	169·9 (9)
Cl(21)–Ta(2)–Cl(14)	150·5 (3)	O(34)–Ta(4)–Cl(43′)	93·1 (8)
Cl(21)–Ta(2)–Cl(15)	77·7 (3)	O(34)–Ta(4)–Cl(44)	102·5 (9)
Cl(22)–Ta(2)–Cl(13)	149·0 (3)	Cl(41)–Ta(4)–Cl(42)	169·4 (4)
Cl(22)–Ta(2)–Cl(14)	83·8 (3)	Cl(41)–Ta(4)–Cl(43)	85·0 (3)
Cl(22)–Ta(2)–Cl(15)	79·3 (3)	Cl(41)–Ta(4)–Cl(43′)	88·0 (4)
Cl(13)–Ta(2)–Cl(14)	76·0 (3)	Cl(41)–Ta(4)–Cl(44)	91·9 (5)
Cl(13)–Ta(2)–Cl(15)	72·4 (3)	Cl(42)–Ta(4)–Cl(43)	84·8 (3)
Cl(14)–Ta(2)–Cl(15)	73·0 (3)	Cl(42)–Ta(4)–Cl(43′)	86·9 (3)
Cl(31)–Ta(3)–Cl(32)	92·6 (6)	Cl(42)–Ta(4)–Cl(44)	90·5 (5)
Cl(31)–Ta(3)–Cl(33)	89·7 (6)	Cl(43)–Ta(4)–Cl(43′)	76·9 (3)
Cl(31)–Ta(3)–Cl(34)	174·6 (5)	Cl(43)–Ta(4)–Cl(44)	87·6 (4)
Cl(31)–Ta(3)–Cl(35)	91·0 (6)	Cl(43′)–Ta(4)–Cl(44)	164·4 (4)
		Ta(4)–Cl(43)–Ta(4′)	103·1 (3)

The average C–C–C and CH_3–C–C angles are 108 (2) and 126 (2)°, respectively. The prime refers to the equivalent position $-x, -y, 1 - z$.

* Average value for the C_5 ring bonded to Ta(1).

† Average value for the C_5 ring bonded to Ta(2).

‡ Average value for the two C_5Me_5 groups.

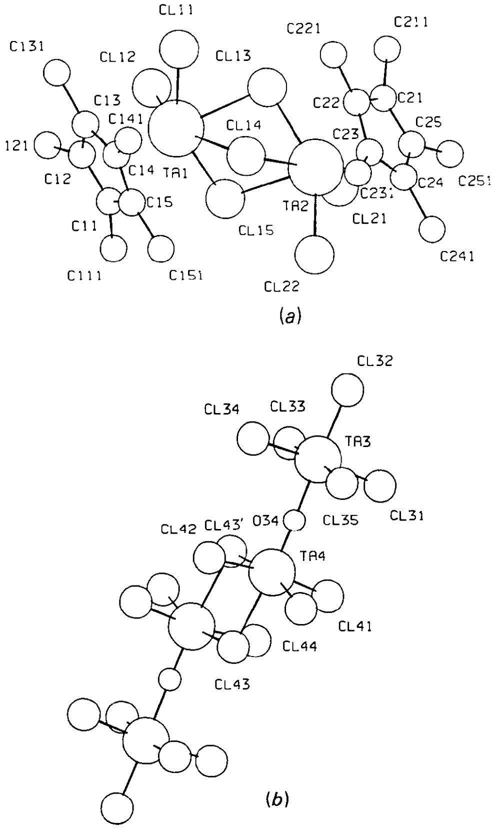

Fig. 2. Structure and atom labelling of (*a*) the cation and (*b*) the anion.

bonds [Ta(3)—O(34) = 2·03 (2) Å]. The Ta—O distance in the central unit [1·76 (2) Å] indicates a double-bond interaction; the O bridges are thus unsymmetrical, although essentially linear [Ta(3)—O(34)—Ta(4) = 178·4 (15)°] (Prout & Daran, 1979).

As a result of the *trans* influence of the oxo groups, the Cl atoms *trans* to the Ta(4)—O(34) and Ta(4')—O(34') bonds show a relatively weak interaction with Ta(4) and Ta(4'), respectively [the corresponding bond distance is 2·672 (9) Å]. Accordingly, the Cl atoms *trans* to the Ta(3)—O(34) and Ta(3')—O(34') dative bonds show relatively short Ta—Cl distances at 2·30 (1) Å.

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Bis[(*N,N'*-diethyldithiocarbamato)bis(diphenylphosphinito)platinato-*O,O'*]cobalt(II) Chloroform (1/2), $Co[(C_{12}H_{10}OP)_2Pt(C_5H_{10}NS_2)]_2.2CHCl_3$

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Abstract. $M_r = 1789{\cdot}11$, triclinic, $P\bar{1}$, $a = 11{\cdot}31$ (3), $b = 14{\cdot}085$ (4), $c = 24{\cdot}701$ (8) Å, $\alpha = 80{\cdot}20$ (3), $\beta = 76{\cdot}73$ (3), $\gamma = 66{\cdot}32$ (2)°, $V = 3493{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$, $D_m = 1{\cdot}65$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 49{\cdot}13$ cm^{-1}, $F(000) = 1754$, $T = 291$ K, $R = 0{\cdot}0914$ for 3979 unique observed reflections. The molecule has the Co atom at the centre with the Pt atoms and the associated ligands either side of it. The coordination about each Pt atom is square-planar, with Pt—S 2·38, Pt—P 2·25 Å, and tetrahedral about the Co atom, with Co—O 1·95–1·97 Å.

Introduction. The crystal-structure determination was undertaken as part of a wider study of the metal complexes of sulphur ligands. The reaction of $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ with some first-row transition-metal acetylacetonates, in this case cobalt, yielded the heterobimetallic complex whose structure is reported here. The structure analysis was undertaken to confirm the proposed tetrahedral coordination about the Co atom and the square-planar environment of the Pt atoms. To the best of our knowledge this structure is the first of its kind to be reported.

Experimental. The preparation of, and the spectral and magnetic data for the blue compound $Co[(OPPh_2)_2Pt(S_2CNEt_2)]_2$ have been previously reported (Allan, Milburn, Stephenson & Veitch, 1983). Recrystallization from $CHCl_3$ produced the compound $Co[(OPPh_2)_2Pt(S_2CNEt_2)]_2.2CHCl_3$ whose X-ray structure analysis is reported here. D_m measured by flotation in chloroform and 1,3-dibromopropan-2-ol. Crystals: dark-blue needles, dimensions 0·4 × 0·4 × 0·2 mm. They decomposed in air through loss of solvent and the

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