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***trans*-Dichloro(*O,O'*-diethyldithio-phosphato-*S,S'*)bis(dimethylphenyl-phosphine)technetium(III)**

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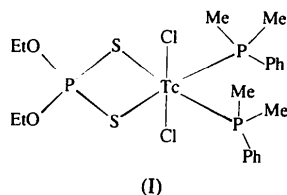
Abstract

The title compound, $[\text{TcCl}_2(\text{C}_4\text{H}_{10}\text{O}_2\text{PS}_2)(\text{C}_8\text{H}_{11}\text{P})_2]$, is formed during the reaction of $[\text{TcNCl}_2(\text{Me}_2\text{PhP})_3]$ with excess sodium diethyldithiophosphate involving cleavage of the technetium–nitrido bond. The Cl ligands are *trans* with respect to each other, with a mean Tc—Cl distance of 2.3545 (6) Å. The diethyldithiophosphate is bonded as a chelate ligand with Tc—S bond lengths of 2.4639 (7) and 2.4787 (6) Å.

Comment

Coordination compounds of technetium with the γ -emitting metastable isotope $^{99\text{m}}\text{Tc}$ (γ energy 140 keV, $t_{1/2} = 6\text{ h}$) are frequently used as tracers in diagnostic nuclear medicine (Clarke & Podbielski, 1987). Knowledge of the coordination chemistry of this man-made element, however, is one of the keystones for the development of new diagnostic agents. These chemical studies are usually carried out with the long-lived isotope ^{99}Tc (weak β -emitter, $E_{\text{max}} = 0.29\text{ MeV}$, $t_{1/2} = 2.12 \times 10^5$ years), which is available in macroscopic amounts.

In the course of our systematic studies of the reactivity of technetium–nitrido compounds, we reacted $[\text{TcNCl}_2(\text{Me}_2\text{PhP})_3]$ with sodium *O,O'*-diethyldithiophosphate (NaEt_2dtp). Surprisingly, cleavage of the $\text{Tc}\equiv\text{N}$ triple bond was observed and the title compound, *trans*-dichloro(*O,O'*-diethyldithiophosphato-*S,S'*)bis(dimethylphenylphosphine)technetium(III), (I),



was formed in 80% yield. This reaction pattern is in contrast to that which was observed for the analogous rhenium compound $[\text{ReNCl}_2(\text{Me}_2\text{PhP})_3]$, which gives the binuclear compound $[\text{ReN}(\text{Me}_2\text{PhP})_3\{\text{S}_2\text{P}(\text{O})\text{OEt}\}]_2$ when refluxed with diethyldithiophosphate (Abram & Ritter, 1993).

$[\text{TcCl}_2(\text{Me}_2\text{PhP})_2(\text{Et}_2\text{dtp})]$ is an air-stable yellow solid which can be crystallized from $\text{CH}_2\text{Cl}_2/2$ -propanol solution. The compound was characterized by elemental and spectroscopic analysis (IR: $\text{P}=\text{S}$ 765 cm^{-1} ; ^1H NMR, broad signals: phenyl 14.8, 13.4 and 5.9; CH_2 0.9; OCH_3 -1.7 ; PCH_3 -32.7 p.p.m. versus TMS). The ^1H NMR signals of the compound are broadened and shifted in the region from 14.8 to -32.7 p.p.m., which is typical for this type of paramagnetic technetium(III) complex.

The coordination sphere of $[\text{TcCl}_2(\text{Me}_2\text{PhP})_2(\text{Et}_2\text{dtp})]$ can best be described as a distorted octahedron with the two Cl ligands in *trans* positions. An ORTEPII diagram (Johnson, 1976) is shown in Fig. 1. Atoms S1, S2, P1 and P2 of the equatorial coordination sphere are coplanar within 0.085 Å. The Tc atom perfectly fits this least-squares plane, with a deviation of only 0.009 Å. Bond distances are in the expected range (Melnik & van Lier, 1987). Significant deviations, for example, due to a structural *trans* effect of the phosphine ligands, could not be observed. Generally, the structure of $[\text{TcCl}_2(\text{Me}_2\text{PhP})_2(\text{Et}_2\text{dtp})]$ is very similar to that of the analogous complex $[\text{TcCl}_2(\text{Me}_2\text{PhP})_2(\text{Me}_2\text{dtp})]$,

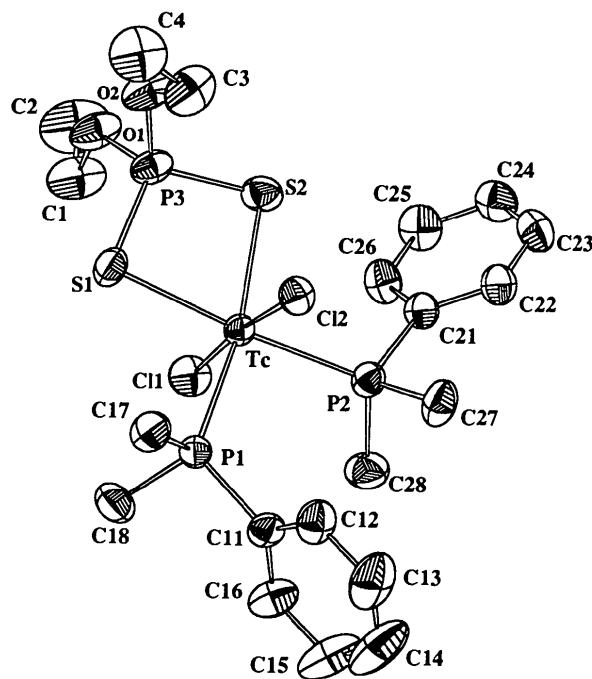


Fig. 1. ORTEPII plot (Johnson, 1976) of $[\text{TcCl}_2(\text{Me}_2\text{PhP})_2(\text{Et}_2\text{dtp})]$ showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

which was obtained from the reaction of [TcCl₃-(Me₂PhP)₃] with ammonium *O,O'*-dimethyldithiophosphate (Lorenz, Schmidt, Hiller, Abram & Hübener, 1993).

Experimental

Crystal data

[TcCl₂(C₄H₁₀O₂PS₂)-
(C₈H₁₁P)₂]

M_r = 631.39

Monoclinic

C2/c

a = 32.885 (3) Å

b = 8.983 (2) Å

c = 19.043 (2) Å

β = 101.49 (1)°

V = 5513 (1) Å³

Z = 8

D_x = 1.519 Mg m⁻³

Data collection

Enraf-Nonius CAD-4
diffractometer

ω/2θ scans

Absorption correction:

ψ scans

T_{min} = 0.974, *T_{max}* =
0.999

16 374 measured reflections

7314 independent reflections

6117 observed reflections

[*I* > 2σ(*I*)]

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0271

wR(*F*²) = 0.0753

S = 1.068

7312 reflections

271 parameters

H atoms refined using a
riding model

Mo *Kα* radiation

λ = 0.7107 Å

Cell parameters from 25
reflections

θ = 9.38–12.36°

μ = 1.057 mm⁻¹

T = 208 (2) K

Needle

0.7 × 0.2 × 0.2 mm

Yellow

R_{int} = 0.0275

θ_{max} = 28.96°

h = -44 → 44

k = -12 → 1

l = -25 → 25

3 standard reflections
monitored every 200
reflections

intensity decay: none

w = 1/[σ²(*F_o*²) + (0.0342*P*)²
+ 4.1514*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = -0.005

Δρ_{max} = 0.488 e Å⁻³

Δρ_{min} = -0.559 e Å⁻³

Atomic scattering factors
from *International Tables
for Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

C3	0.66055 (10)	0.7269 (4)	0.6783 (2)	0.0677 (8)
C4	0.68739 (11)	0.8203 (4)	0.7312 (2)	0.0764 (9)
C11	0.62524 (6)	0.8605 (2)	0.28477 (11)	0.0378 (4)
C12	0.59969 (7)	0.9784 (3)	0.29498 (15)	0.0495 (6)
C13	0.57113 (10)	1.0345 (3)	0.2375 (2)	0.0732 (9)
C14	0.56799 (12)	0.9741 (5)	0.1708 (2)	0.0940 (13)
C15	0.59304 (13)	0.8578 (4)	0.1597 (2)	0.0858 (11)
C16	0.62170 (9)	0.8010 (3)	0.21632 (13)	0.0554 (6)
C17	0.68517 (7)	0.9498 (3)	0.40579 (13)	0.0473 (5)
C18	0.70283 (7)	0.7063 (3)	0.32228 (14)	0.0535 (6)
C21	0.53961 (6)	0.4185 (2)	0.40235 (11)	0.0349 (4)
C22	0.49933 (7)	0.4396 (3)	0.41263 (12)	0.0414 (5)
C23	0.47906 (7)	0.3274 (3)	0.44172 (13)	0.0476 (5)
C24	0.49854 (8)	0.1938 (3)	0.46131 (13)	0.0477 (5)
C25	0.53814 (8)	0.1703 (3)	0.45030 (14)	0.0499 (6)
C26	0.55869 (7)	0.2809 (3)	0.42123 (13)	0.0447 (5)
C27	0.53271 (7)	0.7176 (3)	0.34885 (14)	0.0503 (6)
C28	0.56974 (8)	0.4888 (3)	0.27797 (12)	0.0531 (6)

Table 2. Selected geometric parameters (Å, °)

Tc—Cl1	2.3531 (6)	Tc—S2	2.4787 (6)
Tc—Cl2	2.3559 (6)	P3—O2	1.570 (2)
Tc—P1	2.4237 (6)	P3—O1	1.576 (2)
Tc—P2	2.4397 (6)	P3—S2	1.9969 (9)
Tc—S1	2.4639 (7)	P3—S1	1.9984 (8)
Cl1—Tc—Cl2	174.09 (2)	Cl2—Tc—S2	92.00 (2)
Cl1—Tc—P1	90.91 (2)	P1—Tc—S2	168.73 (2)
Cl2—Tc—P1	85.97 (2)	P2—Tc—S2	93.80 (2)
Cl1—Tc—P2	86.43 (2)	S1—Tc—S2	80.04 (2)
Cl2—Tc—P2	88.98 (2)	O2—P3—O1	95.70 (9)
P1—Tc—P2	97.24 (2)	O2—P3—S2	114.08 (8)
Cl1—Tc—S1	92.10 (2)	O1—P3—S2	113.92 (8)
Cl2—Tc—S1	92.86 (2)	O2—P3—S1	113.70 (8)
P1—Tc—S1	88.98 (2)	O1—P3—S1	114.27 (8)
P2—Tc—S1	173.62 (2)	S2—P3—S1	105.41 (3)
Cl1—Tc—S2	92.02 (2)		

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software* and *SDP* (Frenz, 1983). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Tc	0.63620 (1)	0.61629 (2)	0.44273 (1)	0.02830 (5)
Cl1	0.66109 (2)	0.40913 (6)	0.38848 (3)	0.04564 (13)
Cl2	0.60716 (2)	0.82962 (6)	0.48531 (3)	0.03872 (11)
P1	0.66122 (2)	0.78359 (6)	0.36090 (3)	0.03245 (11)
P2	0.56885 (2)	0.56262 (6)	0.36685 (3)	0.03434 (11)
P3	0.67971 (2)	0.51596 (6)	0.59513 (3)	0.03963 (12)
S1	0.70270 (2)	0.64716 (7)	0.52775 (3)	0.04189 (12)
S2	0.62249 (2)	0.46326 (7)	0.54382 (3)	0.04367 (13)
O1	0.70765 (6)	0.3771 (2)	0.62273 (8)	0.0529 (4)
O2	0.68163 (6)	0.5867 (2)	0.67110 (8)	0.0541 (4)
C1	0.71739 (11)	0.2660 (3)	0.57296 (15)	0.0685 (8)
C2	0.71633 (15)	0.1191 (4)	0.6027 (2)	0.0949 (13)

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Heptacoordinate Cu^{II} in catena-Poly[aquabis(benzimidazole-*N*³)copper(II)- μ -adipato-*O,O'*:*O''*,*O'''*]

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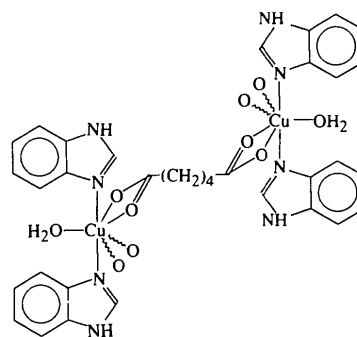
Abstract

The title compound, [Cu(C₆H₈O₄)(C₇H₆N₂)₂(H₂O)], has been synthesized and its crystal structure determined by single-crystal X-ray diffraction at room temperature. The seven-coordinate Cu^{II} complexes adopt a C₂ elongated tetragonal pyramidal geometry with double-capped base. The Cu atoms are located on the twofold axes and are connected by bridging tetradentate adipate ions to form polymeric chains. In the base of the coordination polyhedron, the two short Cu—N bonds are 2.007 (2) Å in length and the two short Cu—O bonds are 2.010 (2) Å. The length of the apical Cu—H₂O bond is 2.245 (4) Å; the lengths of the two long semicoordinate Cu—O bonds, which complete the seven coordination, are 2.930 (2) Å. The intermolecular hydrogen bonds and geometry of the carboxylate group are discussed.

Comment

This work forms part of a continuing study of Cu^{II} complexes with benzimidazole and dicarboxylic acids (Tosik & Bukowska-Strzyżewska, 1992). A fragment of the polymeric structure of the title compound, (I), is shown in Fig. 1. The structure represents the first example of a seven-coordinate alkylcarboxylate Cu^{II} complex (Orpen *et al.*, 1989).

Each Cu atom and H₂O molecule are located on the twofold axis. The Cu atoms are connected by bridging tetradentate adipate ions to form polymeric chains. Two N atoms, one from each benzimidazole molecule, and two O atoms, one from each adipate ion, form short Cu—N and Cu—O bonds of lengths 2.007 (2) and 2.010 (2) Å, respectively. Along with this deformed square coordination, the Cu—H₂O bond of 2.245 (4) Å



(I)

forms an elongated pyramid. The observed short Cu—N and Cu—O bonds are distinctly longer than the average literature data for Cu^{II} of coordination number 5, and the long Cu—H₂O bond is somewhat shorter [according to Orpen *et al.* (1989), average short Cu—N = 1.966, average short Cu—O = 1.962, and average long Cu—H₂O = 2.331 Å]. Two long semicoordinate Cu—O bonds of 2.930 (2) Å complete the Cu coordination environment, forming an elongated tetragonal pyramid with a double-capped base. Thus, Cu^{II} heptacoordination is formed by the mutually perpendicular square coordination (four short bonds) and the triangular coordination (three long bonds). The carboxylate groups, in a similar manner to carboxylate groups in the only other known Cu^{II} adipate complex (Pajunen & Nasakkala, 1977), form four-membered almost planar chelate rings with two distinctly different C—O bonds and two distinctly different Cu—O bonds.

An interesting feature of this structure is the three-dimensional hydrogen-bond system formed by O...O and O...N contacts (Table 3, Fig. 2). The neighbouring

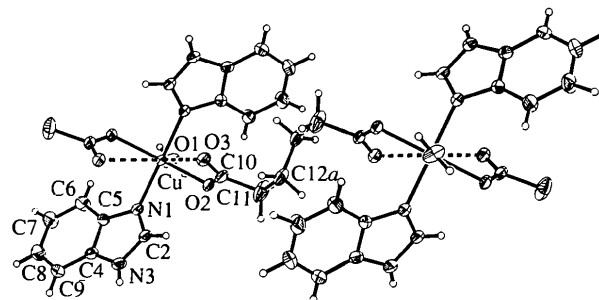


Fig. 1. A fragment of the polymeric structure of (I). For clarity, atom C12b (with an occupancy factor of 0.19) is omitted. Displacement ellipsoids are at the 30% probability level.

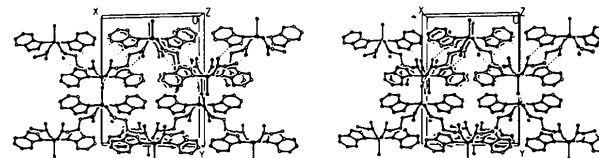


Fig. 2. Stereoview of the crystal packing of (I) viewed along [001]. H atoms have been omitted and hydrogen bonds are shown as dotted lines.