

terpyridine unit. This results in a short Pt—N3 distance [1.938 (5) Å] and an N2—Pt—N4 *trans* bond angle of only 162.2 (2)°. The remaining bond lengths around the Pt atom are all over 2 Å [2.018 (6), 2.020 (5) and 2.031 (6) Å]. This geometry is entirely consistent with other related Pt(tpy) complexes (Dewan, Lippard & Bauer, 1980; Ratilla, Scott, Moxness & Kostic, 1990; Wong & Lippard, 1977; Jennette, Gill, Sadownik & Lippard, 1976).

The two Pt atoms are bridged by a single pyrazolyl group, resulting in a Pt...Pt separation of 3.432 (1) Å (parallel, by symmetry, with the *y* axis) and an inclination between the two square planes of 47.7 (12)°. This distance is intermediate in the range of Pt^{II}...Pt^{II} separations exhibited by other binuclear tpy complexes, that have been observed as short as 2.9884 Å (Ratilla *et al.*, 1990) and as long as 4.420 Å (Dewan *et al.*, 1980). The Pt atom is displaced out of the terpyridine plane by *ca* 0.2 Å towards the other Pt atom in the same binuclear unit. The bond lengths and angles within each pyridine ring are characteristic of a delocalized aromatic system, ranging from 1.334 (10) to 1.395 (14) Å and from 117.2 (8) to 124.9 (7)°. Similarly, the bond lengths and angles within the pyrazolyl ring range from 1.331 (13) to 1.340 (9) Å and from 105.1 (9) to 110.5 (8)°, thereby

demonstrating the delocalized nature of the π electrons in the five-membered ring.

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Structure of (Benzenethiolato)oxo[N-(2-sulfidophenyl)salicylidene-iminato(2-)-O,N,S]technetium(V)*

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Abstract. [Tc(C₁₃H₉NOS)(O)(C₆H₅S)], C₁₉H₁₄NO₂S₂Tc, *M_r* = 451.2, monoclinic, *P*2₁, *a* = 7.901 (1), *b* = 10.147 (1), *c* = 11.370 (2) Å, β = 93.60 (1)°, *V* = 909.8 (2) Å³, *Z* = 2, *D_x* = 1.646 g cm⁻³, $\lambda(\text{Mo K}\alpha)$ = 0.71073 Å, μ = 1 mm⁻¹, *F*(000) = 452, *T* = 293 K, *R* = 0.055 for 1703 unique reflections. The tridentate dianionic ligand spans three positions in the basal plane, including the phenolic O atom, the neutral N

atom and the thiolate S atom, the fourth position being occupied by the benzenethiolate S atom. The Tc atom lies 0.66 Å above the basal plane towards the O(1) apex and with respect to the mean basal plane the four donor atoms are in a slightly puckered (± 0.12 Å) arrangement.

Introduction. Neutral Tc complexes TcO(SXS)(SR), with ⁻SXS⁻ = dianionic tridentate ligands ⁻S—CH₂CH₂—X—CH₂CH₂—S⁻ (X = O, S) and RS⁻ = monodentate thiolates were obtained by joint action of both the tridentate and the monodentate

* Systematic name: (benzenethiolato)oxo{2-[(2-sulfidophenyl)-iminomethyl]phenolato-O,N,S}technetium(V).

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}/U_{iso}
Tc	3146 (1)	2771	6154 (4)	48 (1)*
S(1)	3103 (5)	1182 (5)	4803 (4)	66 (1)*
S(2)	1641 (6)	1404 (5)	7267 (4)	69 (1)*
O(1)	5080 (9)	2873 (15)	6810 (7)	67 (2)
O(2)	1491 (13)	4132 (11)	6727 (9)	66 (2)
N(1)	3318 (12)	4066 (12)	4696 (9)	48 (2)
C(1)	3875 (6)	2118 (11)	3585 (4)	50 (2)
C(2)	4510	1476	2622	58 (2)
C(3)	5062	2206	1679	65 (2)
C(4)	4979	3579	1701	69 (2)
C(5)	4344	4222	2665	67 (2)
C(6)	3792	3491	3607	47 (2)
C(7)	2724 (14)	5182 (13)	4556 (11)	52 (2)
C(8)	1986 (7)	5982 (7)	5424 (5)	47 (2)
C(9)	1796	7329	5206	66 (2)
C(10)	1024	8130	6014	76 (2)
C(11)	442	7584	7039	61 (2)
C(12)	631	6237	7257	65 (2)
C(13)	1403	5437	6449	44 (2)
C(14)	653 (9)	2399 (8)	8327 (6)	63 (2)
C(15)	-1113	2465	8281	70 (2)
C(16)	-1920	3235	9095	76 (2)
C(17)	-960	3939	9953	98 (2)
C(18)	807	3873	9999	98 (2)
C(19)	1613	3103	9185	76 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected bond lengths (\AA) and bond angles ($^\circ$)

Tc—S(1)	2.225 (5)	S(1)—C(1)	1.82 (1)
Tc—S(2)	2.265 (5)	S(2)—C(14)	1.79 (1)
Tc—O(1)	1.661 (7)	O(2)—C(13)	1.36 (1)
Tc—O(2)	2.037 (11)	N(1)—C(6)	1.44 (1)
Tc—N(1)	2.126 (11)	N(1)—C(7)	1.23 (1)
		C(7)—C(8)	1.43 (1)
S(1)—Tc—S(2)	87.5 (2)	Tc—N(1)—C(6)	116.9 (9)
S(1)—Tc—O(1)	109.2 (4)	Tc—N(1)—C(7)	128.8 (8)
S(2)—Tc—O(1)	106.7 (4)	C(6)—N(1)—C(7)	112.3 (11)
S(1)—Tc—O(2)	136.9 (3)	S(1)—C(1)—C(2)	120.6 (3)
S(2)—Tc—O(2)	82.3 (3)	S(1)—C(1)—C(6)	119.4 (3)
O(1)—Tc—O(2)	113.9 (5)	N(1)—C(6)—C(1)	115.8 (11)
S(1)—Tc—N(1)	84.8 (6)	N(1)—C(6)—C(5)	123.8 (10)
S(2)—Tc—N(1)	151.1 (5)	N(1)—C(7)—C(8)	127.0 (12)
O(1)—Tc—N(1)	102.1 (8)	C(7)—C(8)—C(9)	118.5 (6)
O(2)—Tc—N(1)	84.5 (8)	C(7)—C(8)—C(13)	121.4 (6)
Tc—S(1)—C(1)	99.0 (4)	O(2)—C(13)—C(8)	124.4 (5)
Tc—S(2)—C(14)	107.3 (4)	O(2)—C(13)—C(12)	115.5 (5)
Tc—O(2)—C(13)	127.5 (7)	S(2)—C(14)—C(15)	118.7 (3)
		S(2)—C(14)—C(19)	121.3 (3)

ligands on appropriate oxotechnetium(V) precursors (Pietzsch, Spies & Hoffmann, 1989). This synthetic route was applied to tridentate Schiff bases, which, in combination with monothioles, yields neutral oxotechnetium(V) complexes. Thus, the reaction of tridentate ONS and ONO Schiff bases with benzenethiols or alkylthiols (RSH) and tetrachlorooxotechnetium(V) or Tc^{V} gluconate leads to complexes $\text{TcO}(\text{ONS})(\text{SR})$ and $\text{TcO}(\text{ONO})(\text{SR})$, respectively (Pietzsch, Spies, Hoffmann & Scheller, 1990). Here we report the structure of $\text{TcOL}(\text{SR})$ [$\text{H}_2\text{L} = N$ -(2-mercaptophenyl)salicylideneimine and $\text{RSH} = \text{benzenethiol}$].

Experimental. (Benzenethiolato)oxo[N -(2-sulfidophenyl)salicylideneimino(2-)- O,N,S]technetium(V) was prepared by the addition of an EtOH solution of 2-(salicylideneimino)benzenethiol and benzenethiol (1:1 molar ratio) to $\text{Bu}_4\text{N}(\text{TcOCl}_4)$ in chloroform and was recrystallized from $\text{CHCl}_3/\text{MeOH}$. Its composition was determined by elemental analysis, infrared and ^1H NMR spectra (Pietzsch, Spies, Hoffmann & Scheller, 1990). The complex crystallizes as red-brown right parallelepipeds ($0.08 \times 0.12 \times 0.16$ mm).

Unit-cell parameters were determined from the angular settings of 50 reflections ($20 < 2\theta < 30^\circ$) measured on a Nicolet $R3m/V$ four-circle diffractometer, with graphite-monochromated $\text{Mo K}\alpha$ radiation at room temperature. Intensities of reflections with $-11 < h < 11$, $0 < k < 14$, $0 < l < 15$ (up to $2\theta = 50^\circ$) were measured by ω - 2θ scan mode; scan rate from 1.5 to 15°min^{-1} in 2θ ; ratio of total background time to scan time 0.5; numbers of parameters refined 76; $wR = 0.059$ [unit weight was assigned to each reflection; a weighting scheme of the type $w = (\sigma^2|F_o| + K|F_o|^2)^{-1}$ did not improve the

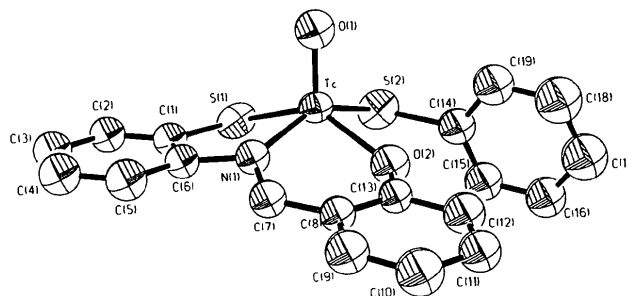


Fig. 1. ORTEP (Johnson, 1965) drawing of $[\text{TcOL}(\text{SC}_6\text{H}_5)]$ with atom-numbering scheme [$L = N$ -(2-mercaptophenyl)salicylideneimine(2-)].

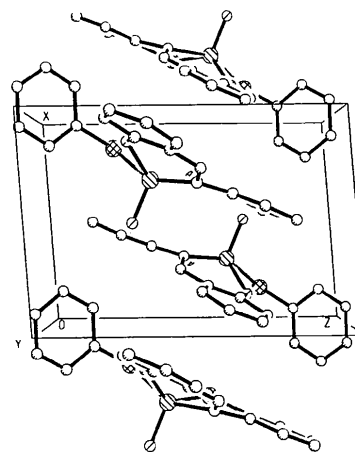


Fig. 2. Packing of $[\text{TcOL}(\text{SC}_6\text{H}_5)]$ within the unit cell [$L = N$ -(2-mercaptophenyl)salicylideneimine(2-)].

Table 3. Some relevant structural data in oxotechnetium(V) square-pyramidal complexes containing sulfur ligands

Complex	Core	Tc=O	Tc—S	Δ	Reference
[TcO(SCH ₂ C(O)S) ₂] ⁻	TcOS ₄	1.67	2.32	0.79	De Pamphilis, Jones, Davis & Davison (1978)
[TcO(SCH ₂ CH ₂ S) ₂] ⁻	TcOS ₄	1.64	2.31	0.76	Smith, Byrne, Cotton & Sekutowski (1978)
[TcO{SCH(CO ₂ Me)CH(CO ₂ Me)S ₂ }] ⁻	TcOS ₄	1.67	2.30	0.78	Bandoli, Nicolini, Mazzi, Spies & Münze (1984)
[Tc ₂ O ₂ (H ₂ ema) ₄] ²⁻	TcOS ₄	1.64	2.34	0.73	Bryson <i>et al.</i> (1989)
[TcO(tbt) ₂ (py)]	TcOS ₂ N	1.66	2.28	0.67	De Vries, Jones & Davison (1989)
[TcO(SCH ₂ CH ₂ O) ₂] ⁻	TcO ₂ S ₂	1.66	2.29	0.72	Jones, De Pamphilis & Davison (1981)
[TcO(abt) ₂]	TcOS ₂ N ₂	1.73	2.30	0.72	Bandoli & Gerber (1987)
[TcO(ema)]	TcOS ₂ N ₂	1.68	2.30	0.77	Jones <i>et al.</i> (1982)
[TcO{SC ₂ H ₄ N(Me)C ₂ H ₄ N(Me)C ₂ H ₄ S}] ⁺	TcOS ₂ N ₂	1.65	2.26	0.77	Faggiani <i>et al.</i> (1988)
[TcO(Et ₂ tcb) ₂] ⁺	TcOS ₂ N ₂	1.65	2.32	0.69	Abram <i>et al.</i> (1989)
[TcO(NetTMDADT)]	TcOS ₂ N ₂	1.68	2.28	0.76	Mahmood <i>et al.</i> (1990)
[TcO(L,L-ECD)]	TcOS ₂ N ₂	1.67	2.30	0.73	Edwards <i>et al.</i> (1990)
[TcOCL ₁]	TcO ₂ SNCl	1.62	2.33	0.70	Tisato <i>et al.</i> (1987)
Present complex	TcO ₂ S ₂ N	1.66	2.25	0.66	

Abbreviations

tibt	2,4,6-triisopropylbenzenethiolate(1-)
py	pyridine
abt	2-aminobenzenethiolate(2-)
ema	<i>N,N'</i> -ethylenebis(2-mercaptoacetamide)
Et ₂ tcb	<i>N-(N,N</i> -diethylthiocarbamoyl)benzamidinate(1-)
NetTMDADT	4- <i>N</i> -ethyl-2,2,9,9-tetramethyl-4,7-diaza-1,10-decanedithiolate(3-)
L,L-ECD	L,L isomer of <i>N,N'</i> -ethylenebiscysteine
L ₁	<i>N</i> -(2-mercaptophenyl)salicylideneiminato(2-)

model]; largest shift/e.s.d.: 0.012. Collected reflections were corrected for Lorentz and polarization effects, no corrections for absorption or extinction were made. Two standard reflections were monitored throughout the data collection and showed random variation in their intensities. Data reduction yielded 1703 unique reflections with $R_{\text{int}} = 0.019$ for the averaging of equivalent reflections; 1371 of these with $I > 3\sigma(I)$ were used in the structure solution and refinement.

An initial sharpened Patterson map (*SHELXTL-Plus* with PATT option[#]) was used to derive the position of the Tc atom. Successive difference Fourier syntheses were used to locate the positions of the non-H atoms. The structure was refined by full-matrix least-squares methods and, due to the limited number of data, the phenyl rings were treated as rigid bodies (C—C 1.395 Å) and only Tc and S atoms were refined anisotropically. H atoms were included in the structure-factor calculation in idealized positions (C—H = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than that of the atom to which they were bonded. The model refined smoothly (the structure is pseudocentrosymmetric and in LS option[#] a damping factor of 100 was used) to the final residual $R = 0.055$ with goodness of fit $S = 1.48$.

The complex is chiral in a noncentrosymmetric space group and the solution given corresponds to the enantiomer with the smaller R factor ($R = 0.055$ for the solution reported and $R = 0.058$ for the other enantiomer). A large e.s.d. value (0.19) of Roger's η

parameter (0.58) indicates that the absolute configuration cannot be determined (Rogers, 1981). A final difference Fourier map had no peaks of higher intensity than 0.8 e \AA^{-3} with valley -0.5 e \AA^{-3} .

Neutral-atom scattering factors were taken from the usual source, those for heavy atoms were corrected for real and imaginary anomalous-dispersion components (*International Tables for X-ray Crystallography* (1974, Vol. IV).

Final positional parameters are given in Table 1,* while bond lengths and angles are reported in Table 2. The molecular structure and the crystallographic numbering scheme are given in Fig. 1; a unit-cell plot is shown in Fig. 2.

All computations were made with *SHELXTL-Plus* (Siemens Nicolet, 1989) on a Digital MicroVAX 3300 computer.

Discussion. This compound represents a member of the wide family of oxotechnetium(V) square-pyramidal complexes containing S donor atoms (Table 3). The compound is related to TcOCL₁ in Table 3 (Tisato, Refosco, Mazzi, Bandoli & Nicolini, 1987), from which it is formally derived by exchange of the chlorine with the benzenethiolate anion.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55045 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE0080]

The tridentate dianionic ligand spans three positions in the basal plane, *via* the charged phenolic O atom, the neutral N atom and the charged thiolate S atom, the fourth position being occupied by the benzenethiolate S atom. The Tc atom, as usual (Table 3), lies above the basal plane towards the O(1) apex (0.66 Å) and with respect to the mean basal plane the four donor atoms are in a slightly puckered (± 0.12 Å) arrangement (Table 2), similar to other compounds of this type (Bryson, Brenner, Lister-James, Jones, Dewan & Davison, 1989; Faggiani, Lock, Epps, Kramer & Brune, 1988; Mahmood, Haplin, Baidoo, Sweigart & Lever, 1990). The angle between the Tc—O(1) bond direction and the normal to the basal plane is 177.2° and the benzenethiolate mean plane is approximately normal (102.4°) to the same plane. There is nothing remarkable about the bond lengths and angles (Bandoli, Mazzi, Roncari & Deutsch, 1982; Clarke & Fackler, 1982; Davison & Jones, 1982; Melnik & Van Lier, 1987).

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Structure of $(\eta^5\text{-Cyclopentadienyl})(\eta^6\text{-1,3,5-trimethylbenzene})\text{iron-7,7,8,8-Tetracyano-}p\text{-quinodimethane (1/2)}$

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Abstract. $[\text{Fe}(\text{C}_9\text{H}_{12})(\text{C}_5\text{H}_5)](\text{C}_{12}\text{H}_4\text{N}_4)_2$, $M_r = 649.5$, monoclinic, $P2_1/m$, $a = 7.914$ (2), $b = 30.983$ (3), $c = 6.629$ (1) Å, $\beta = 102.38$ (1)°, $V = 1588$ Å³, $Z = 2$, D_x

$= 1.36$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 4.22$ mm⁻¹, $F(000) = 696$, $T = 295$ K, $R = 0.042$ for 2587 observed reflections. The crystal structure of the