

X-ray Crystallographic Determination of the Structure of *trans*-Dichloro[*N,N'*-ethylenebis(3,5-dimethylsalicylideneiminato)]technetium(IV)

Tsutomu Takayama,* Ryouji Koudo, Tsutomu Sekine, and Hiroshi Kudo

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

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A novel technetium(IV) complex of a tetradentate Schiff base ligand was synthesized from the reaction of H₂dmsalen [dmsalen; *N,N'*-ethylenebis(3,5-dimethylsalicylideneiminato)] and *trans*-⁹⁹Tc^{IV}Cl₄(PPh₃)₂ [PPh₃; triphenylphosphine]. The complex ⁹⁹Tc^{IV}Cl₂(dmsalen), the structure of which was determined by X-ray crystallography, has an octahedral coordination geometry. The dmsalen ligand coordinates to the technetium atom through two N and two O atoms of the tetradentate ligand in the equatorial plane. Two chloro ligands are in the *trans* apical position with an average Tc-Cl bond length of 2.35 Å.

Technetium complexes with Schiff base ligands attract interest not only for application in nuclear medicine,¹ but also in coordination chemistry because the flexibility of Schiff base ligands in geometry and coordination sites makes it possible to synthesize several types of technetium complexes differing in the chemical properties.² Schiff base complexes of technetium reported so far are in oxidation states of Tc(III), Tc(V) and Tc(VI),³⁻⁷ but little is known for Tc(IV). We have synthesized a technetium(IV) complex with a tetradentate Schiff base ligand for the first time using ⁹⁹Tc (*T*_{1/2} = 2.1 × 10⁵ y). In this note, the crystal structure of *trans*-Tc^{IV}Cl₂(dmsalen) is reported together with a redox property of the complex.

The Tc^{IV}Cl₂(dmsalen) complex was synthesized in a manner described below. An ethanol solution (10 mL) of H₂dmsalen (110 μmol) was added to suspensions of *trans*-Tc^{IV}Cl₄(PPh₃)₂ (105 μmol)⁸ in benzene (50 mL). This mixture was stirred for 3 h at 60°C. The color of the mixture gradually turned from green to brown. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in CH₂Cl₂, and then charged on a silica gel column (φ 2 cm × 20 cm). The product was eluted with CH₂Cl₂. The effluent with a purple band in the column was collected, and the dark purple crystals were obtained by concentration, the solvent being slowly evaporated to dryness. Yield 16.0 μmol (15%). Anal. Found: C, 48.35; H, 4.30; N, 5.81; Tc, 19.91%. Calcd for C₂₀H₂₂Cl₂N₂O₂Tc: C, 48.79; H, 4.50; N, 5.69; Tc, 20.11%. UV-vis spectrum {EtOH, λ_{max}/nm (ε/M⁻¹cm⁻¹): 262 (2.22 × 10⁵), 345 (7.19 × 10⁴), 456 (7.47 × 10³).

The magnetic moment of TcCl₂(dmsalen) was measured by the Evans method⁹ at 293 K in CDCl₃ solvent to determine the oxidation state of Tc. The observed value of 3.82 μ_B indicates that spin state is *S* = 3/2. The result indicates that Tc of this complex is in the +4 oxidation state with three unpaired electrons.

A stability of the complex toward oxidation-reduction reactions was examined by cyclic voltammetry in a CH₃CN solution. Cyclic voltammograms were recorded with a Yanaco voltammetric analyzer P-1000 equipped with a standard three-electrode configuration at 298 K. Figure 1 shows the cyclic voltammogram of Tc^{IV}Cl₂(dmsalen) observed in CH₃CN. This complex showed two quasi-reversible redox waves at +0.825 V and -0.522 V, suggesting that this Tc(IV) complex is stable toward the addition and removal of one electron.

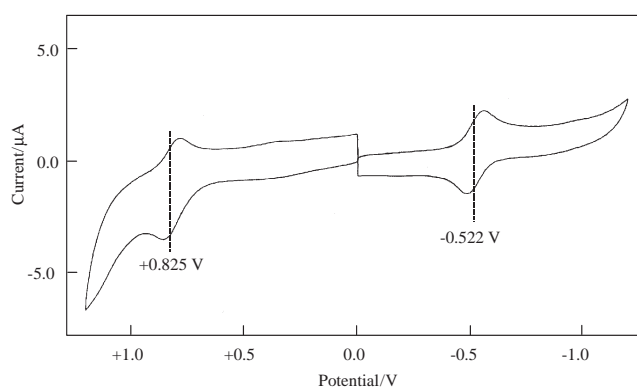


Figure 1. Cyclic voltammogram of 1.9 mM *trans*-Tc^{IV}Cl₂(dmsalen). Counter electrode, platinum wire; working electrode, glassy carbon; reference electrode, Ag/Ag⁺ [0.01 M AgNO₃/CH₃CN containing 0.1 M (C₄H₉)₄NClO₄]; supporting electrolyte, 0.1 M (C₄H₉)₄NClO₄.

A single crystal (0.20 × 0.20 × 0.06 mm³) of Tc^{IV}Cl₂(dmsalen) was subjected to X-ray crystallography. The diffraction data were collected at 160 K using a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71070 Å). A total of 27007 reflections was collected in the range 6.2 < 2θ < 55.0 degrees. The structure of the complex was solved by the direct method (SIR92). All remaining non-hydrogen atoms were refined by the full-matrix least-squares method (SHELXL-97)¹⁰ with anisotropic thermal parameters. The coordinates of the hydrogen atoms were deduced from the difference Fourier map and refined using isotropic temperature factors. All of the calculations were made using the teXsan crystallographic software package.¹¹ Crystal data: formula = C₂₀H₂₂Cl₂N₂O₂Tc, fw = 490.31, orthorhombic, space group *Pna*2₁ (No. 33), *a* = 13.309(4) Å, *b* = 11.760(3) Å, *c* = 12.880(3) Å, *V* = 2015(1) Å³, *Z* = 4, *D*_{calcd} 1.662 g/cm³, *R*₁ = 0.024, *R*_w = 0.064 for 3404 unique reflections (*I* > 2σ(*I*)).

The ORTEP drawing of Tc^{IV}Cl₂(dmsalen) is shown in Figure 2 with thermal ellipsoids at the 30% probability level. The technetium atom is in an octahedral coordination geometry. Two chloro ligands are *trans* to each other in the axial position. The tetradentate dmsalen ligand coordinates to the technetium atom through two nitrogen atoms of imine and two anionic oxygen atoms of phenol in the equatorial plane. The symmetrical coordination of the dmsalen ligand in the equatorial plane is the same as that in technetium complexes of salen type ligands reported previously.³⁻⁶

*Corresponding author. E-mail: takayama@mail.cc.tohoku.ac.jp. FAX: +81-22-217-6596.

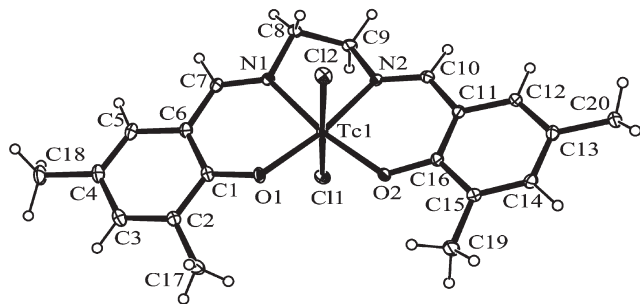


Figure 2. ORTEP diagram of *trans*-Tc^{IV}Cl₂(dmsalen). Selected bond lengths (Å): Tc1–Cl1, 2.352(1); Tc1–Cl2, 2.3465(9); Tc1–O1, 1.968(2); Tc1–O2, 1.960(2); Tc1–N1, 2.067(2); Tc1–N2, 2.061(3). Selected bond angles (degree): O1–Tc1–O2, 100.1(1); N1–Tc1–N2, 81.1(1); O1–Tc1–N1, 89.1(1); O2–Tc1–N2, 89.7(1); Cl1–Tc1–Cl2, 174.73(3).

An average bond length between the anionic oxygen atoms and the technetium atom is 1.96 Å. The Tc–O bond length is short compared with that of other technetium complexes with Schiff base ligands such as Tc^VO(salen)Cl [salen; *N,N'*-ethylenebis(salicylideneimine)],⁴ Tc^VN(dmsalen),⁶ and *trans*-[Tc^{III}(acacen)(PPh₃)₂]PF₆ [acacen; *N,N'*-ethylenebis(acetylacetonato)]⁵ (Table 1). The fact indicates the strong σ donation of the dmsalen ligand to the Tc(IV) atom through the anionic oxygen atoms. The Tc–Cl bond length of *trans*-Tc^{IV}Cl₂(dmsalen) is extremely shorter than that of Tc^VO(salen)Cl. This is due to a difference of the ligand species at the *trans* position of the chloro ligand. Two chloro ligands are at the *trans* position each other in *trans*-Tc^{IV}Cl₂(dmsalen), while an oxo ligand is at the *trans* position in Tc^VO(salen)Cl. The electron donation of the chloro ligand is weaker than that of the oxo ligand, and the Tc–Cl bond length of *trans*-Tc^{IV}Cl₂(dmsalen) is shorter than that in Tc^VO(salen)Cl.

TABLE 1: Selected Bond Lengths and Bond Angles of Technetium Complexes with Tetradentate Schiff Base Ligands

	Bond length/Å		Bond angle/degree		Ref.	
	Tc–O	Tc–N	Tc–Cl	N–Tc–N		O–Tc–O
<i>trans</i> -Tc ^{IV} Cl ₂ (dmsalen)	1.96	2.06	2.35	81.1	100.1	This work
Tc ^V O(salen)Cl	1.99	2.02	2.53	81.9	79.6	4
Tc ^V N(dmsalen)	2.04	2.07	–	79.6	87.8	6
[Tc ^{III} (acacen)(PPh ₃) ₂]PF ₆	2.02	2.06	–	82.8	99.6	5

The N_{imine}–Tc–N_{imine} angle of *trans*-Tc^{IV}Cl₂(dmsalen) is comparable with that of other technetium complexes with Schiff base ligands as listed in Table 1. The O–Tc–O angle of *trans*-Tc^{IV}Cl₂(dmsalen) is comparable with that of [Tc^{III}(acacen)(PPh₃)₂]PF₆, but larger than that of Tc^VO(salen)Cl and Tc^VN(dmsalen). The difference in the O–Tc–O angle is attributed to a difference in the location of the technetium atom relative to the equatorial coordination plane. The technetium atom of *trans*-Tc^{IV}Cl₂(dmsalen) is on the O–N–N–O plane defined by two coordinating nitrogen atoms and two coordinating oxygen atoms. This structural feature of *trans*-Tc^{IV}Cl₂(dmsalen) is the same as that of [Tc^{III}(acacen)(PPh₃)₂]PF₆, while in Tc(V)-oxo and Tc(V)-nitrido complexes the technetium atom is displaced toward the oxo or nitrido ligand from the O–N–N–O plane.^{4–6}

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References

- (1) G. Bandoli, A. Dolmella, M. Porchia, F. Refosco, and F. Tisato, *Coord. Chem. Rev.* **214**, 43 (2001).
- (2) F. Refosco, F. Tisato, and U. Mazzi, *J. Chem. Soc. Dalton Trans.* 611 (1988).
- (3) H.-J. Pietzsch, U. Abram, R. Kirmase, and K. Kohler, *Z. Chem.* **27**, 265 (1987).
- (4) S. Jurisson, L. F. Lindoy, K. P. Dancy, M. McPartlin, P. A. Tasker, D. K. Uppal, and E. Deutsch, *Inorg. Chem.* **23**, 227 (1984).
- (5) S. Jurisson, K. P. Dancy, M. McPartlin, P. A. Tasker, and E. Deutsch, *Inorg. Chem.* **23**, 4743 (1984).
- (6) T. Takayama, T. Sekine, and H. Kudo, *J. Radioanal. Nucl. Chem.* **255**, 97 (2003).
- (7) J. R. Dilworth, P. Jobanputra, R. M. Thompson, D. C. Povey, C. M. Acher, and J. D. Kelly, *J. Chem. Soc. Dalton Trans.* 1251 (1994).
- (8) G. Bandoli, D. A. Clemente, and U. Mazzi, *J. Chem. Soc. Dalton Trans.* 125 (1976).
- (9) D. F. Evans, *J. Chem. Soc.* 2003 (1959).
- (10) G. M. Sheldrick, *Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).
- (11) Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1999).