A novel technetium(IV) complex of a tetradentate Schiff base ligand was synthesized from the reaction of H_dmsalen [dmsalen; N,N'-ethylenebis(3,5-dimethylsalicylideniminato)] and trans-$^9$Tc IV Cl$_2$[(PPh$_3$)$_2$; triphenylphosphin]. The complex $^{99}$Tc IV Cl$_2$(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.

![Graph](image_url)

Figure 1. Cyclic voltammogram of 1.9 mM trans-Tc IV Cl$_2$(dmsalen). Counter electrode, platinum wire; working electrode, glassy carbon; reference electrode, Ag/Ag$^{+}$ [0.01 M AgNO$_3$/CH$_3$CN containing 0.1 M (C$_4$H$_9$)$_4$NClO$_4$]; supporting electrolyte, 0.1 M (C$_4$H$_9$)$_4$NClO$_4$. A single crystal (0.20×0.20×0.06 mm$^3$) of Tc IV Cl$_2$(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 MoK$\alpha$ radiation ($\lambda = 0.71070$ 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) 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. Crystal data: formula = C$_{20}$H$_{22}$Cl$_2$N$_2$O$_2$Tc, fw = 490.31, orthorhombic, space group Pnma (No. 33), $a = 13.309(4)$ Å, $b = 11.760(3)$ Å, $c = 12.880(3)$ Å, $V = 2015(1)$ Å$^3$, $Z = 4$. $D_{calcd}$ 1.662 g/cm$^3$, $R_I = 0.024$, $R_w = 0.064$ for 3404 unique reflections ($I > 2\sigma(I)$).

The ORTEP drawing of Tc IV Cl$_2$(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.$^{1-6}$

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Notes

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), 3/2.$^3$ but little is known for Tc(IV). We have synthesized a novel technetium(IV) complex of a tetradentate Schiff base ligand for the first time using $^{99}$Tc (T$_{1/2} = 2.1 \times 10^5$ y). In this note, the crystal structure of trans-Tc IV Cl$_2$(dmsalen) is reported together with a redox property of the complex.

The Tc IV Cl$_2$(dmsalen) complex was synthesized in a manner described below. An ethanol solution (10 mL) of H_dmsalen (110 µmol) was added to suspensions of trans-Tc IV Cl$_2$(PPh$_3$)$_2$ (105 µmol)$^9$ 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 CH$_2$Cl$_2$, and then charged on a silica gel column (6 cm × 20 cm). The product was eluted with CH$_2$Cl$_2$. The effluent containing the complex was filtered, and the dark purple crystals were obtained by concentration, the solvent being slowly evaporated to dryness. Yield 16.0 µmol (15%).

The magnetic moment of Tc IV Cl$_2$(dmsalen) was measured by the Evans method$^7$ at 293 K in DCI solvent to determine the oxidation state of Tc. The observed value of 3.82 $\mu$B indicates that spin state is $^3$S$^1 = 3/2$. 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 CH$_3$CN solution. Cyclic voltammograms were recorded with a Yanaco cyclic voltammetric analyzer P-1000 equipped with a standard three-electrode configuration at 298 K. Figure 1 shows the cyclic voltammogram of Tc IV Cl$_2$(dmsalen) observed in CH$_3$CN. 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.
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 IV O(salen)Cl and Tc IV N(dmsalen), and trans-[Tc III (acacen)(PPh 3 ) 2 ]PF 6 [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 Cl 2 (dmsalen) is extremely shorter than that of Tc IV O(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 Cl 2 (dmsalen), while an oxo ligand is at the trans position in Tc IV O(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 Cl 2 (dmsalen) is shorter than that in Tc IV O(salen)Cl.

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

<table>
<thead>
<tr>
<th>Bond length/Å</th>
<th>Bond angle/degree</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc–O</td>
<td>Tc–N</td>
<td>Tc–Cl</td>
</tr>
<tr>
<td>trans-Tc IV Cl 2 (dmsalen)</td>
<td>1.96</td>
<td>2.06</td>
</tr>
<tr>
<td>Tc IV O(salen)Cl</td>
<td>1.99</td>
<td>2.02</td>
</tr>
<tr>
<td>Tc IV N(dmsalen)</td>
<td>2.04</td>
<td>2.07</td>
</tr>
<tr>
<td>[Tc III (acacen)(PPh 3 ) 2 ]PF 6</td>
<td>2.02</td>
<td>2.06</td>
</tr>
</tbody>
</table>

The N imine–Tc–N imine angle of trans-Tc IV Cl 2 (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 Cl 2 (dmsalen) is comparable with that of Tc IV O(salen)Cl and Tc IV N(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 Cl 2 (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 Cl 2 (dmsalen) is the same as that of Tc IV O(salen)Cl and Tc IV N(dmsalen). 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 Cl 2 (dmsalen) is shorter than that in Tc IV O(salen)Cl.

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