

Phenoxo-Bridged Dimeric Structure of Technetium(I) Tricarbonyl Complex with Schiff Base Ligand

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Technetium(I) carbonyl complexes such as $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ (salbut = 2-(1-butyl-nitrilomethylidene)phenolato), $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ and $\text{Tc}(\text{CO})_3(\text{salbut})(\text{py})$ (py = pyridine) with Schiff base ligands were synthesized. The dinuclear complex $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ is the first phenoxo-bridged dinuclear technetium complex. From X-ray crystallography, this dinuclear complex was revealed to be a "dimer" composed of two $\text{Tc}(\text{CO})_3(\text{salbut})$ subunits bridged by two oxygen atoms of the salbut ligand. The two $\text{Tc}(\text{CO})_3(\text{salbut})$ subunits are in inversion symmetry each other. Schiff base Hsalbut loses a phenol proton through the ligand exchange reaction and coordinates to the technetium atom as a bidentate ligand with nitrogen and oxygen atoms. Three carbonyl ligands coordinate to the technetium atom in a *facial* configuration. Structures of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ in solvents were investigated by NMR and UV-vis spectroscopy. The mononuclear complex $\text{Tc}(\text{CO})_3(\text{salbut})(\text{solv})$ (solv = solvent molecule) was formed in strong Lewis base solvents like acetonitrile and pyridine. In weak Lewis base solvents like dichloromethane and benzene, on the other hand, the dinuclear $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ complex was stable.

1. Introduction

The complex $(\text{Et}_4\text{N})_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ is a useful starting material for synthesis of technetium(I) carbonyl complexes. After the synthesis of $(\text{Et}_4\text{N})_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ under a mild condition (1 atm and 65 °C),¹ the coordination chemistry of technetium complexes in a +1 oxidation state with carbonyl ligands have attracted considerable interest.² Technetium(I) tricarbonyl complexes are generally six-coordinated in octahedral geometry. The *fac*- $[\text{Tc}(\text{CO})_3]^+$ core is stable toward ligand substitution reactions, whereas the three Cl ligands are easily substituted by other ligands. In recent years, reactions of $[\text{Tc}(\text{CO})_3\text{Cl}_3]^{2-}$ with bidentate ligands are extensively studied to provide a basic insight into *fac*-^{99m}Tc(CO)₃ radiopharmaceuticals with bidentate ligands.³ Technetium(I) carbonyl complexes with various bidentate ligands with N, O and S donor atoms were synthesized by ligand substitution reactions of $(\text{Et}_4\text{N})_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$.⁴⁻⁶

Schiff base ligands with N donor atoms of the imine group and O donor atoms of the phenol group afford stable complexes with various transition metals.⁷⁻¹² Although a number of technetium complexes with a Schiff base imine-phenol ligand in higher oxidation states (+3 to +6) have been reported in the literature,¹³⁻¹⁸ little is known about technetium(I) carbonyl complexes with this ligand.

We have synthesized technetium(I) carbonyl complexes with Hsalbut of a Schiff base imine-phenol bidentate ligand for the first time, and their structures are characterized in this paper. In terms of radiopharmaceutical application, the structure of technetium complexes in solution is to be elucidated, and we investigate further the structure of technetium(I) carbonyl complexes with a salbut ligand also in solution.¹⁹

2. Experimental

2.1. Materials. A potassium salt of pertechnetate (⁹⁹Tc) purchased from Radiochemical Center Amersham was dissolved in 0.8 M aqueous ammonia solution. Hsalbut [2-(1-butyl-nitrilomethylidene)phenol] was synthesized from the reaction of salicylal-

dehyde and 1-butanamine. Hsalbut was identified by ¹H NMR spectroscopy. The starting material $(\text{Et}_4\text{N})_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ was synthesized in a manner described in the literature.¹ Other chemicals and solvents were of reagent grade, and used without further purification.

2.2. Instruments. The elemental analysis was performed by a Yanaco MT-3 CHN recorder. The composition of technetium was determined radiometrically with a liquid scintillation counter (Aloka, LSC-5100). IR spectra were recorded with a KBr pellet method on SHIMADZU FTIR-8600PC. ¹H NMR spectra were recorded on JEOL G5X270 (270 MHz) at room temperature. UV-vis spectra were recorded in acetonitrile or dichloromethane on SHIMADZU Multi Spec-1500 at room temperature.

2.3. X-ray crystallographic data collection and refinement of structure. A single crystal of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ was subjected to X-ray crystallography. The diffraction data were collected at 173 K using a Rigaku Mercury CCD diffractometer with MoK α graphite monochromator radiation ($\lambda = 0.71070$ Å). The structure was solved by direct methods²⁰ and expanded using Fourier techniques.²¹ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final discrepancy factors: $R_1 = 0.044$, $wR_2 = 0.141$ for all reflections. All of the calculations were made using the CrystalStructure crystallographic software package.^{22, 23} More information on crystal data and structure refinement is summarized in Table 1.

2.4. Synthesis of [2-(1-butyl-nitrilomethylidene)phenolato]-acetone-tricarbonyltechnetium(I), $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$. The starting material $(\text{Et}_4\text{N})_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ (100 μmol) was dissolved in acetonitrile (10 mL). To the solution, Hsalbut (100 μmol) in acetonitrile and triethylamine (50 μL) were added. The yellow reaction mixture was stirred for 12 h at room temperature. The solution was condensed to 3 mL and then subjected to silicagel column chromatography (20 mm Φ \times 150 mm, Wakogel C-200). By elution with acetonitrile, the yellow fraction containing $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ was collected. Evaporation of the solution gave yellow precipitate of $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ (60 μmol , 60%). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_4\text{Tc}$: C, 48.00; H, 4.28; N, 7.00; Tc, 24.73. Found: C, 47.44; H, 4.08; N, 6.83; Tc, 24.60%. IR (cm⁻¹, KBr): $\nu(\text{CO})$

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TABLE 1: The Crystallographic Data of [Tc(CO)₃(salbut)]₂

Formula	C ₂₈ H ₂₈ N ₂ O ₈ Tc ₂
Formula weight	714.54
Crystal size / mm ³	0.15 × 0.10 × 0.10
Crystal system	triclinic
Space group	P-1 (No. 2)
<i>a</i> / Å	7.897(4)
<i>b</i> / Å	9.263(4)
<i>c</i> / Å	11.547(5)
α / degree	104.441(5)
β / degree	106.708(5)
γ / degree	105.647(5)
<i>V</i> / Å ³	728.4(6)
<i>Z</i> value	1
<i>D</i> (calc) / g cm ⁻³	1.626
μ / cm ⁻¹	9.90
Radiation	MoK α (0.71070 Å)
Temp / K	173
2 θ range / degree	6.2 – 55.0
Reflections measured	13110
Reflections observations	3305
<i>R</i> ₁ ^a	0.044
<i>wR</i> ₂ ^b	0.141
Goodness of fit indicator	1.010
Max shift / error in final cycle	0.064

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2}$$

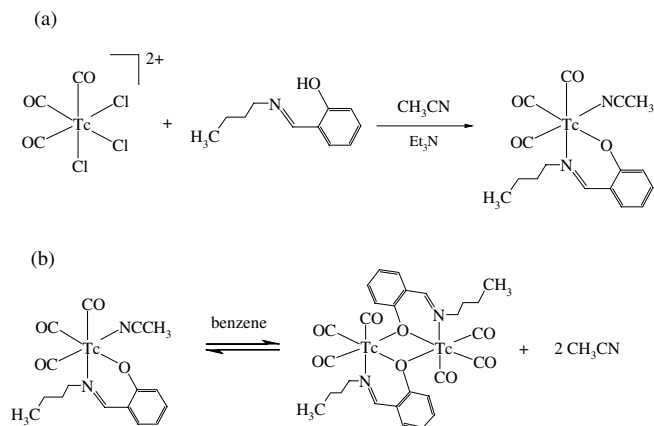
2025, 1923, 1899. ¹H NMR (δ , CD₃CN): 0.96 (t, 3H; CH₃), 1.35 (sext, 2H; CH₂), 1.85 (quint, 2H; CH₂), 3.87 (br, 2H; CH₂), 6.47 (ddd, 1H; phenyl), 6.63 (dd, 1H; phenyl), 7.12 (dd, 1H; phenyl), 7.18 (ddd, 1H; phenyl), 8.13 (s, 1H; N=CH).

2.5. Synthesis of bis[μ -{2-(1-butylnitrimethylidene) phenolato-1:2 κ^2 O}]-hexacarbonylditechnetium(I), [Tc(CO)₃(salbut)]₂. The reaction product Tc(CO)₃(salbut)(CH₃CN) (80 μ mol) was dissolved in benzene (3 mL). Slow evaporation of the solution gave pale yellow crystals of [Tc(CO)₃(salbut)]₂ (68 μ mol, 85%). Anal. Calcd for C₂₈H₂₈N₂O₈Tc₂: C, 46.36; H, 3.83; N, 4.07; Tc, 27.55. Found: C, 46.76; H, 3.90; N, 3.90; Tc, 27.30%. IR (cm⁻¹, KBr): ν (CO) 2024, 1920, 1885. ¹H NMR (δ , CD₂Cl₂): 0.99 (t, 6H; CH₃), 1.42 (sext, 4H; CH₂), 1.73 (quint, 4H; CH₂), 4.10 (br, 4H; CH₂), 6.88 (m, 4H; phenyl), 7.36 (m, 4H; phenyl), 8.36 (s, 2H; N=CH).

2.6. Synthesis of [2-(1-butylnitrimethylidene)phenolato]-pyridinetricarbonyltechnetium(I), Tc(CO)₃(salbut)(py). The reaction product [Tc(CO)₃(salbut)]₂ (60 μ mol) was dissolved in pyridine (1 mL). The solution was stirred for 12 h at room temperature. Evaporation of the solution gave Tc(CO)₃(salbut)(py) (57 μ mol, 95%). Anal. Calcd for C₁₉H₁₉N₂O₄Tc: C, 52.06; H, 4.37; N, 6.39; Tc, 22.58. Found: C, 51.66; H, 4.28; N, 6.53; Tc, 22.30%. IR (cm⁻¹, KBr): ν (CO) 2018, 1914, 1880. ¹H NMR (δ , CD₃CN): 0.98 (t, 3H; CH₃), 1.38 (sext, 2H; CH₂), 1.78 (quint, 2H; CH₂), 3.95 (br, 2H; CH₂), 6.43 (ddd, 1H; phenyl), 6.74 (dd, 1H; phenyl), 7.12 (dd, 1H; phenyl), 7.16 (ddd, 1H; phenyl), 7.41 (m, 3H; py), 8.13 (s, 1H; N=CH), 8.62 (m, 2H; py).

3. Results and Discussion

The reaction of (Et₃N)₂[Tc(CO)₃Cl₃] and Hsalbut in acetonitrile gave a complex Tc(CO)₃(salbut)(CH₃CN) as shown in Scheme 1 (a). When triethylamine was absent in the reaction



Scheme 1. (a) Preparation of Tc(CO)₃(salbut)(CH₃CN); (b) formation of [Tc(CO)₃(salbut)]₂ by dimerization of Tc(CO)₃(salbut)(CH₃CN).

mixture, this reaction hardly proceeded. The addition of a base was necessary for dissociation of the phenol proton of Hsalbut. In this reaction, three Cl ligands of [Tc(CO)₃Cl₃]²⁺ are replaced by one bidentate salbut ligand and one acetonitrile molecule of a monodentate ligand.

The structure of Tc(CO)₃(salbut)(CH₃CN) was characterized by ¹H NMR and IR spectroscopy. The spin multiplicity of signals of methylene protons at α -position of imine nitrogen was triplet for free Hsalbut. Meanwhile, the signal was multiplet in the spectrum of Tc(CO)₃(salbut)(CH₃CN), as a result of the constraint of a rotation of the methylene group through coordination of the imine N atom to the Tc atom in the complex. A difference of spin multiplicity in ¹H NMR spectra is also observed for signals of aromatic hydrogens. Four aromatic hydrogens of free Hsalbut show multiple signals. In the spectrum of Tc(CO)₃(salbut)(CH₃CN), two signals of dd and two signals of ddd were observed. This result indicates that the O atom of the phenol group coordinates to the Tc atom. The salbut coordinates to the Tc atom in a fashion of the bidentate chelate through one N donor atom of the imine group and one O donor atom of the phenol group. The IR spectrum of Tc(CO)₃(salbut)(CH₃CN) showed a pattern typical of a *facial* arrangement of three CO ligands. Absorption peaks for stretching of carbonyl ligands were observed at 2025, 1923 and 1899 cm⁻¹. The highest energy peak arises from symmetrical stretching of three carbonyl ligands. Peaks at lower wave numbers (1923 and 1899 cm⁻¹) are due to unsymmetrical stretching modes.²⁴ An acetonitrile molecule would coordinate to the sixth coordination site. The central Tc atom acts as a chiral center. Two enantiomeric forms of Tc(CO)₃(salbut)(CH₃CN) are expected, although these have not been isolated here.

The dinuclear complex [Tc(CO)₃(salbut)]₂ was obtained in a quantitative yield from a benzene solution of Tc(CO)₃(salbut)(CH₃CN). The dimerization of Tc(CO)₃(salbut)(CH₃CN) should occur in the benzene solution (Scheme 1b). The dimeric complex [Tc(CO)₃(salbut)]₂ was also obtained from a dichloromethane solution of Tc(CO)₃(salbut)(CH₃CN). In the ¹H NMR spectrum for the CD₂Cl₂ solution of Tc(CO)₃(salbut)(CH₃CN), two singlet signals originated from the imine proton were observed at 7.93 and 8.36 ppm. This result indicates that both monomeric and dimeric complexes are present in the solution. The signal at higher chemical shift is assigned to [Tc(CO)₃(salbut)]₂, and the lower one to Tc(CO)₃(salbut)(CH₃CN).

The structural determination of [Tc(CO)₃(salbut)]₂ by X-ray crystallography was carried out for the pale yellow prism single crystal obtained from a benzene solution. The ORTEP drawing of [Tc(CO)₃(salbut)]₂ is shown in Figure 1. Selected bond distances and angles are listed in Table 2. The dinuclear complex is composed of two Tc(CO)₃(salbut) subunits bridged by the O atoms of phenoxo groups of the salbut ligand. These subunits are enantiomeric. The inversion center is located at the center of the Tc₂O₂ ring. Each Tc atom is six-coordinated in

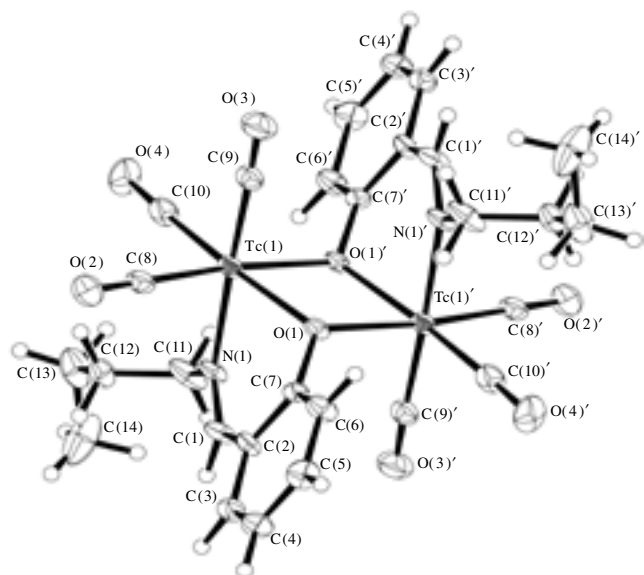


Figure 1. ORTEP drawing of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ (50% probability level).

TABLE 2: Selected Bond Distances (Å) and Angles (degree) of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$

Distances			
Tc(1)-O(1)	2.144(3)	Tc(1)-O(1)'	2.183(3)
Tc(1)-N(1)	2.177(4)	Tc(1)-C(8)	1.911(5)
Tc(1)-C(9)	1.919(5)	Tc(1)-C(10)	1.902(5)
O(1)-Tc(1)'	2.183(3)	Tc(1)-Tc(1)' ^a	3.408(2)
Angles			
O(1)-Tc(1)-O(1)'	76.1(1)	N(1)-Tc(1)-O(1)	81.7(1)
Tc(1)-O(1)-C(7)	119.9(2)	C(8)-Tc(1)-O(1)	98.4(2)
C(9)-Tc(1)-O(1)	94.5(2)	C(10)-Tc(1)-O(1)	172.9(2)
Tc(1)-O(1)-Tc(1)'	104.2(2)	N(1)-Tc(1)-O(1)'	83.8(1)
C(8)-Tc(1)-O(1)'	173.5(2)	C(9)-Tc(1)-O(1)'	96.7(2)
C(10)-Tc(1)-O(1)'	96.9(2)	Tc(1)-O(1)-Tc(1)'	103.9(1)
C(8)-Tc(1)-N(1)	92.0(2)	C(9)-Tc(1)-N(1)	176.0(2)
C(10)-Tc(1)-N(1)	96.5(2)	Tc(1)-N(1)-C(1)	123.5(3)
Tc(1)-N(1)-C(11)	120.9(3)	N(1)-C(1)-C(2)	126.4(4)
O(1)-C(7)-C(2)	122.0(4)	O(1)-C(7)-C(6)	119.3(4)

^aInteratomic distance

octahedral geometry. The three carbonyl ligands are arranged in a *facial* configuration. An anionic salbut ligand coordinates to the Tc atom as a bidentate chelate through the N and O atoms. The oxygen atom of the bridging phenoxy group coordinates to the sixth coordination site. The proton dissociation makes the phenoxy group a very strong donor, and the O atom of the phenoxy group coordinates to two Tc atoms forming a bridge between them.

The central unit of the dinuclear complex $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ is a four-membered Tc_2O_2 ring with the Tc(1)-O(1)-Tc(1)' angle of 103.9 degree and the O(1)-Tc(1)-O(1)' angle of 76.1 degree. The two Tc atoms and the two O atoms are fairly in the same plane. The distance of the Tc(1)-O(1) bond (2.144 Å) is shorter than that of the Tc(1)-O(1)' bond (2.183 Å). The distance between the two Tc atoms is as long as 3.404 Å, and the Tc-Tc bond does not exist in this dinuclear complex. A typical metal-metal bond distance in dinuclear technetium complexes with Tc_2O_2 units is known to be in the range from 2.331 to 2.401 Å.²⁵⁻²⁸

The structure of Tc(I) complex with the salbut ligand were investigated in a variety of solvents. The UV-vis spectrum of

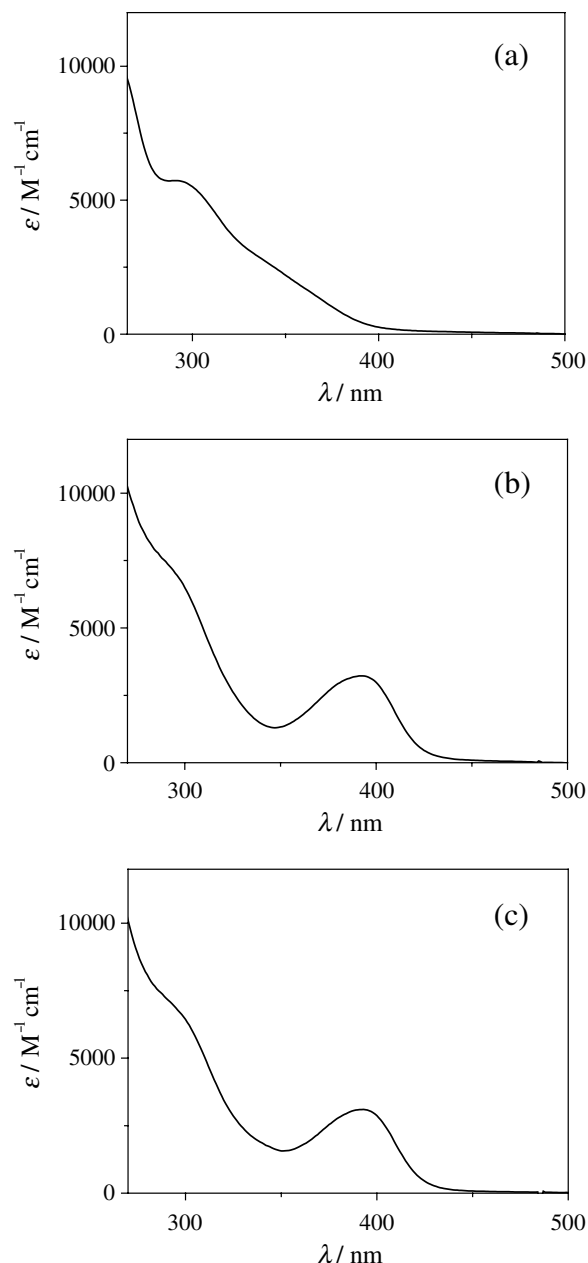
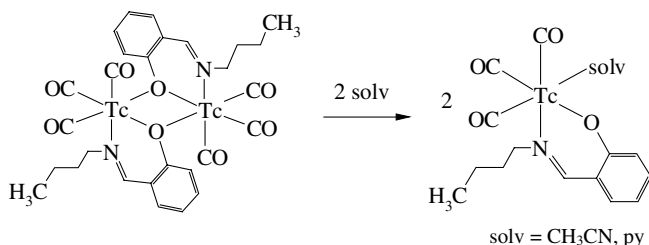


Figure 2. UV-vis spectra of (a) $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ in dichloromethane, (b) $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ in acetonitrile and (c) $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ in acetonitrile.

$[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ in dichloromethane is shown in Figure 2a. The dinuclear structure is retained in dichloromethane solution. When $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ is dissolved in acetonitrile, the UV-vis spectrum (Figure 2b) is different from that in dichloromethane. The metal-to-ligand charge transfer (MLCT) absorption peak appeared at 393 nm. The spectrum of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ in acetonitrile resembles that of $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ in acetonitrile quite well (Figure 2c). Furthermore, the ^1H NMR spectrum of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ in CD_3CN was the same as that of $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ observed in CD_3CN . The result indicates that $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ is formed in the acetonitrile solution of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ as a result of substitution of the bridging phenoxy group by the CH_3CN ligand. Only the monomeric $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ complex is present in the acetonitrile solution.

When $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ was dissolved in pyridine, $\text{Tc}(\text{CO})_3(\text{salbut})(\text{py})$ was formed. In the ^1H NMR spectrum of $\text{Tc}(\text{CO})_3(\text{salbut})(\text{py})$, signals of pyridine coordinating to Tc are observed at 7.21 ppm and 8.42 ppm. The other signals are similar to that of $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$ with the six-coordinated monomeric structure.

Strong Lewis bases such as acetonitrile and pyridine act as a



Scheme 2. Reaction of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ in acetonitrile or pyridine.

monodentate ligand, and substitute the bridging O atom of the $\text{Tc}(\text{CO})_3(\text{salbut})$ subunit. In these solvents, mononuclear complexes with neutral charge were formed (Scheme 2). The molecular formula of these mononuclear complexes can be written as $\text{Tc}(\text{CO})_3(\text{salbut})(\text{solv})$.

On the contrary, no structural change of $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ was observed in dichloromethane and benzene solvents. These solvents are a very weak Lewis base and should be irrelevant to the ligand substitution reaction.

4. Conclusions

Three technetium(I) carbonyl complexes, $\text{Tc}(\text{CO})_3(\text{salbut})(\text{CH}_3\text{CN})$, $\text{Tc}(\text{CO})_3(\text{salbut})(\text{py})$ and $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$, were synthesized in the present work. The phenoxo-bridged dinuclear complex $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ is revealed to be composed of two enantiomeric $\text{Tc}(\text{CO})_3(\text{salbut})$ subunits bridged by a phenoxo group.

In solution, the Lewis basicity of the solvents is a key factor in determining the structure of technetium(I) carbonyl complexes with salbut. In strong Lewis base solvents like acetonitrile and pyridine, dinuclear $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ changes its structure to a mononuclear $\text{Tc}(\text{CO})_3(\text{salbut})(\text{solv})$. In weak Lewis base solvents like dichloromethane or benzene, on the other hand, dinuclear $[\text{Tc}(\text{CO})_3(\text{salbut})]_2$ is stable.

References

- (1) R. Alberto, R. Schibli, and P. A. Schubiger, *Polyhedron* **15**, 1079 (1996).
- (2) R. Alberto, R. Schibli, R. Waibel, U. Abram, and A. P. Schubiger, *Coord. Chem. Rev.* **192**, 901 (1999).
- (3) S. Mundwiler, M. Kündig, K. Ortner, and R. Alberto, *Dalton Trans.* 1320 (2004).
- (4) R. Alberto, R. Schibli, A. P. Schubiger, U. Abram, H.-J. Pietzsch, and B. Johannsen, *J. Am. Chem. Soc.* **121**, 6076 (1999).
- (5) W. Wang, B. Spingler, and R. Alberto, *Inorg. Chim. Acta* **355**, 386 (2003).
- (6) H. Braband, and U. Abram, *J. Organomet. Chem.* **689**, 2066 (2004).
- (7) P. G. Cozzi, *Chem. Soc. Rev.* **33**, 410 (2004).
- (8) T. Katsuki, *Chem. Soc. Rev.* **33**, 437 (2004).
- (9) J. D. Bois, J. Hong, E. M. Carreira, and M. W. Day, *J. Am. Chem. Soc.* **118**, 915 (1996).
- (10) W. A. Herrmann, M. U. Rauch, and G. R. J. Artus, *Inorg. Chem.* **35**, 1988 (1996).
- (11) A. Hori, T. Ozawa, H. Yoshida, Y. Imori, Y. Kuribayashi, E. Nakano, and N. Azuma, *Inorg. Chim. Acta* **281**, 207 (1998).
- (12) A. Duatti, A. Marchi, S. A. Luna, G. Bandoli, U. Mazzi, and F. Tisato, *J. Chem. Soc. Dalton Trans.* 867 (1987).
- (13) S. Jurisson, K. Dancey, M. McPartlin, P. Tasker, and E. Deutsch, *Inorg. Chem.* **23**, 4743 (1984).
- (14) T. Takayama, R. Koudo, T. Sekine, and H. Kudo, *J. Nucl. Radiochem. Sci.* **4**, 1 (2003).
- (15) T. Takayama, T. Sekine, and H. Kudo, *J. Radioanal. Nucl. Chem.* **255**, 97 (2003).
- (16) H. J. Pietzsch, U. Abram, R. Kirmase, and K. Kohler, *Z. Chem.* **27**, 265 (1987).
- (17) J. R. Dilworth, P. Jobanputra, R. M. Thompson, D. C. Povey, C. M. Archer, and J. D. Kelly, *J. Chem. Soc. Dalton Trans.* **8**, 1251 (1994).
- (18) T. Takayama, Y. Abe, T. Sekine, and H. Kudo, *Radiochim. Acta* **92**, 265 (2004).
- (19) S. S. Jurisson and J. D. Lydon, *Chem. Rev.* **99**, 2205 (1999).
- (20) SIR92: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, and M. J. Camalli, *Appl. Cryst.* **27**, 435 (1994).
- (21) DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- (22) CrystalStructure 3.6.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MS (2000-2004). 9009 New Trails Dr. The Woodlands TX 77381 USA.
- (23) CRYSTALS Issue 10: D. J. Watkin, C. K. Prout, J. R. Caruthers, and P. W. Betteridge, *Chemical Crystallography Laboratory*, Oxford, UK, 1996.
- (24) T. P. Ortiz, J. A. Marshall, L. A. Emmert, J. Yang, W. Choi, A. L. Costello, and J. A. Brozik, *Inorg. Chem.* **43**, 132 (2004).
- (25) K. E. Linder, J. C. Dewan, and A. Davison, *Inorg. Chem.* **28**, 3820 (1989).
- (26) G. Anderegg, E. Müller, K. Zollinger, and H. B. Burgi, *Helv. Chim. Acta* **66**, 1593 (1983).
- (27) H. B. Burgi, G. Anderegg, and P. Blauenstein, *Inorg. Chem.* **20**, 3829 (1981).
- (28) R. Alberto, G. Anderegg, and A. Albinati, *Inorg. Chim. Acta* **178**, 125 (1990).