

Synthesis, Structure, and Spectroscopic Properties of *fac*-[Tc^ICl(CO)₃(bpy)] (bpy = 2,2'-bipyridine)

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The 1:1 reaction of ((C₂H₅)₄N)₂[*fac*-TcCl₃(CO)₃] with 2,2'-bipyridine (bpy) gave *fac*-[TcCl(CO)₃(bpy)] (**[1]**). The complex **[1]** is characterized on the basis of electronic absorption and ¹H NMR spectra along with single crystal X-ray analysis. The complex **[1]** crystallizes in the orthorhombic space group *Pca*2₁ with *a* = 25.027(3) Å, *b* = 6.5327(7) Å, *c* = 16.679(2) Å, *V* = 2726.9(6) Å³, *Z* = 8, and *R* = 0.0320. In **[1]**, Tc(I) ion is coordinated by three carbonyls with the facial positions, one chloride, and one bpy ligand. The metal-to-ligand charge transfer transition band was observed at 354 nm in CH₃CN solution. The transition energy of the metal-to-ligand charge transfer band for **[1]** is somewhat larger than that for the Re congener.

1. Introduction

Since the discovery of an easily accessible preparation method of six-coordinate octahedral technetium(I) complexes with three carbonyl ligands, *fac*-Tc(CO)₃ unit, the chemistry of the Tc(I) complexes has developed rapidly with respect to the syntheses of the new complexes, besides their radiopharmaceutical applications.¹⁻⁶ It has been known that a number of the second- and third-row transition metal ions with a d⁶ low-spin ground state, Mo(0),⁷ W(0),⁸ Re(I),⁹⁻¹¹ Ru(II),¹² Os(II),¹³ Rh(III),¹⁴ and Ir(III)^{15, 16} having monodentate or polydentate pyridyl ligands exhibit photoluminescence. For example the rhenium tricarbonyl bipyridine complexes *fac*-[ReX(CO)₃(N-N)]^{0 or 1+} (X = halide, pyridine derivatives; N-N = α-diimine) show strong emission in the visible region at room temperature.⁹⁻¹¹ The emission character has been assigned as metal-to-ligand charge transfer phosphorescence except for the π-π* transition of the several complexes.⁹⁻¹¹ The rhenium tricarbonyl α-diimine complexes have been shown the rich electrochemical and photochemical reactions.¹⁷

From the periodical law, it is expected that the iso-electronic d⁶ low-spin Tc(I) complexes with polypyridine ligands have the rich redox, photophysical and photochemical properties. Several *fac*-Tc^I(CO)₃ complexes containing α-diimine ligands such as 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy) have been synthesized,¹⁸⁻²¹ however the information of their structures and the spectroscopic properties is still limited. In this paper, we report the synthesis, crystal structure, and spectroscopic properties of *fac*-[Tc^ICl(CO)₃(bpy)] (**[1]**). The transition energy of the MLCT band in electronic absorption spectrum of *fac*-[TcCl(CO)₃(bpy)] in CH₃CN was observed at shorter wavelength than that of *fac*-[ReCl(CO)₃(bpy)].

2. Experimental Section

Preparation of the Complex. To a solution containing 0.055 g (0.10 mmol) of ((C₂H₅)₄N)₂[*fac*-TcCl₃(CO)₃] in 5 mL of acetonitrile was added a solution of 0.016 g (0.10 mmol) of 2,2'-bipyridine in 5 mL of acetonitrile. The mixture was stirred for 2 h, which gave a yellow solution. The reaction solution was

poured onto a silica-gel column (20 mm × 150 mm). The yellow band eluted with acetonitrile was collected, and then the solution was evaporated to dryness. Recrystallization from acetonitrile/*n*-pentane gave yellow microcrystals. Yield: 0.024 g (65%). Anal. Calcd for [TcCl(CO)₃(bpy)]: C, 41.68; H, 2.15; N, 7.48; Tc, 26.42%. Found: C, 41.22; H, 2.30; N, 7.17; Tc, 26.72. ¹H NMR in CD₃CN; δ = 7.62 (dd, 2H), 8.15 (dd, 2H), 8.38 (d, 2H), 8.94 (d, 2H). IR (KBr, cm⁻¹); 2030, 1927, 1906. UV-vis in CH₃CN, nm (ε/M⁻¹cm⁻¹) 354 (2770).

Physical Measurements. The electronic absorption spectrum was recorded with JASCO V-550 UV/Vis spectrophotometer, and the infrared spectrum was recorded with PERKIN-ELMER 983G spectrophotometer with KBr pellet at room temperature. The ¹H NMR spectrum was recorded with JEOL G5X270 in CD₃CN at the probe temperature. The residual proton signal of the solvent molecule (δ = 1.93) was used as the reference. The elemental analysis (C, H, N) were recorded with Yanaco MT-3 CHN recorder.

X-ray Crystal Structure Determinations. Single-crystal X-ray diffraction experiment for **[1]** was performed on a Rigaku Mercury CCD diffractometer with a graphite-monochromatized Mo Kα radiation (λ = 0.71070 Å). Crystallographic data are summarized in Table 1. The structure was solved by direct

TABLE 1: Crystal Data for *fac*-[TcCl(CO)₃(bpy)] (**[1]**)

formula	C ₁₃ H ₈ N ₂ O ₃ ClTc
fw	372.67
crystal system	orthorhombic
space group	<i>Pca</i> 2 ₁
<i>a</i> /Å	25.027(3)
<i>b</i> /Å	6.5327(7)
<i>c</i> /Å	16.679(2)
<i>V</i> /Å ³	2726.9(6)
<i>Z</i>	8
<i>T</i> /K	173.2
λ/Å	0.7107
d _{calc} /g cm ⁻³	1.815
μ(Mo Kα)/cm ⁻¹	12.48
<i>R</i> (wR2)	0.0320 (0.0730)
GOF	1.019

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methods and was refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms. All H atoms were located at calculated positions. All calculations were performed by using the teXsan crystallographic software package.

3. Results and Discussion

Preparation of the Complex. Treatment of a colorless acetonitrile solution of $((C_2H_5)_4N)_2[fac-TcCl_3(CO)_3]^6$ with 1 molar equivalent of bpy gave a yellow solution. The purification of the complex was succeeded by using silica-gel column chromatography eluted with acetonitrile. The elemental analytical result and the radio activity measurement with a liquid scintillation counter are in good agreement with the formula $[TcCl(CO)_3(bpy)]$. Characterization of the complex is performed on the basis of IR and 1H NMR spectra, besides the X-ray crystallographic determination (vide supra). Previously, several *fac*- $Tc^I(CO)_3$ complexes *fac*- $[TcX(CO)_3(L-L)]$ ($X = Cl, Br, I, L-L = phen^{18}; X = Br,^{19} CH_3CN,^{21} L-L = bpy$) were synthesized by the reaction of $[TcX(CO)_5]$ ($X = Cl, Br, I, CH_3CN$) with α -diimine ligands. For example, *fac*- $[Tc(CO)_3(bpy)(CH_3CN)]^+$ was prepared by the reaction of $[Tc(CO)_5(CH_3CN)]^+$ with bpy in a 1:1 molar ratio in refluxing CH_3CN for 4h.²¹ It is noted that the synthetic condition to produce *fac*- $[TcCl(CO)_3(bpy)]$ is much milder than that to synthesize *fac*- $[Tc(CO)_3(bpy)(acetonitrile)]^+$. The labile nature of the chloride ions for *fac*- $[TcCl_3(CO)_3]^{2-}$ is responsible for the easier substitution on the technetium center.

Crystal Structure. X-ray structural analysis for [1] reveals that two independent molecules exist, yet nearly identical. One of the complex molecules is shown in Figure 1, and selected bond distances and angles of [1] are listed in Table 2. Three CO ligands face a Tc octahedron and two nitrogen atoms of a bpy ligand and one chlorine atom occupy the other coordinating sites of the technetium atom. The complex molecule has an approximate C_s symmetry. The Tc atom adopts a slightly distorted octahedral geometry with C2-Tc1-N1 = 169.35(16), C3-Tc1-N2 = 173.26(16), C15-Tc2-N3 = 173.27(15), C16-Tc2-N4 = 173.72(17), C11-Tc1-C1 = 177.97(14), and C12-Tc2-C14 = 178.32(13)°. The bond angles of N1-Tc1-N2 and N3-Tc2-N4 are 75.25(12) and 75.35(12)°, which are much smaller than 90° with the angle of the regular octahedron, because of the bite angle of the chelating bpy ligand. The bond distances of Tc-C 1.906(4)-1.978(5) Å are in the ranges of the known Tc^I complexes containing Tc-CO bond.²² The Tc-N bond distances of [1] are 2.167(3)-2.187(3) Å. These values are ca. 0.1 Å longer than those observed in the technetium polypyridine complexes, $[Tc^{III}(bpy)_3]^{3+}$ (Tc-N = 2.077(10) Å)²³ and the Tc-N distance (2.075(6) Å) of the external nitrogen of the tpy ligand in Tc(I) complex $[TcCl(tpy)(py)_2]$ (tpy = 2,2':6':2''-terpyridine, py = pyridine).²⁴ This long Tc-N distance of [1] is due to the strong

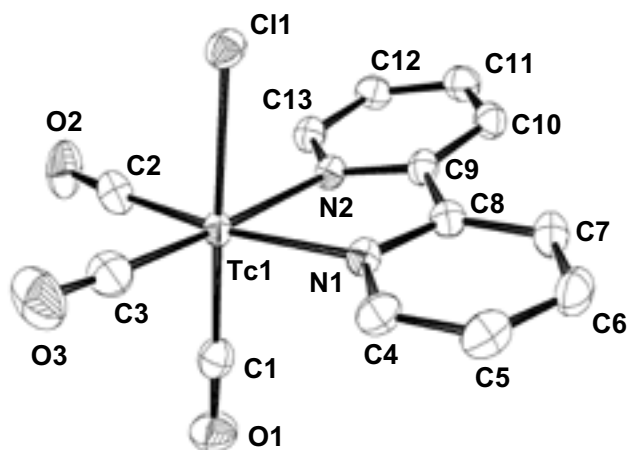


Figure 1. An ORTEP drawing of one of the two independent complex molecules of [1]. Hydrogen atoms are omitted for clarity.

TABLE 2: Selected Bond Distances(Å) and Angles (deg) for *fac*- $[TcCl(CO)_3(bpy)]$ ([1])

Distances			
Tc1-C1	1.906(4)	Tc2-C14	1.978(5)
Tc1-C2	1.914(5)	Tc2-C15	1.911(4)
Tc1-C3	1.939(5)	Tc2-C16	1.918(5)
Tc1-N1	2.187(3)	Tc2-N3	2.178(3)
Tc1-N2	2.167(3)	Tc2-N4	2.174(3)
Tc1-Cl1	2.4958(10)	Tc2-Cl2	2.4663(12)
C1-O1	1.138(5)	C14-O4	1.069(5)
C2-O2	1.143(6)	C15-O5	1.150(5)
C3-O3	1.133(5)	C16-O6	1.150(5)
Angles			
C1-Tc1-C2	89.5(2)	C14-Tc2-C15	88.84(17)
C1-Tc1-C3	89.23(19)	C14-Tc2-C16	88.02(18)
C2-Tc1-C3	89.0(2)	C15-Tc2-C16	87.94(18)
C1-Tc1-N1	93.51(16)	C14-Tc2-N3	93.41(15)
C1-Tc1-N2	96.66(16)	C14-Tc2-N4	93.40(15)
C2-Tc1-N1	169.35(16)	C15-Tc2-N3	173.27(15)
C2-Tc1-N2	94.27(16)	C15-Tc2-N4	98.20(14)
C3-Tc1-N1	101.21(17)	C16-Tc2-N3	98.47(16)
C3-Tc1-N2	173.26(16)	C16-Tc2-N4	173.72(17)
N1-Tc1-N2	75.25(12)	N3-Tc2-N4	75.35(12)
Cl1-Tc1-C1	177.97(14)	C12-Tc2-C14	178.32(13)
Cl1-Tc1-C2	92.50(14)	C12-Tc2-C15	92.11(13)
Cl1-Tc1-C3	91.11(14)	C12-Tc2-C16	93.40(15)
Cl1-Tc1-N1	84.45(9)	C12-Tc2-N3	85.48(9)
Cl1-Tc1-N2	82.88(9)	C12-Tc2-N4	85.09(9)
Tc1-C1-O1	179.0(4)	Tc2-C14-O4	172.9(4)
Tc1-C2-O2	174.5(4)	Tc2-C15-O5	178.7(4)
Tc1-C3-O3	176.9(4)	Tc2-C16-O6	179.0(5)

trans influence of the Tc-C bonds. The Tc-Cl bond distances (2.4663(12) and 2.4958(10) Å) are somewhat shorter than those of $[Tc^I Cl(tpy)(py)_2]$ (2.518 Å),²⁴ however the values are similar to that observed in $[Tc^I Cl(CN-tBu)_2(CO)_3]^+$ (2.496(2) Å).²² Therefore, it can be said that the Tc-Cl distance in [1] is normal as the *trans* position of the Tc-C bond of the carbonyl ligand.

Compared with the bond distances (Mn-C = 1.794(5) – 1.812(4) Å, Mn-N = 2.044(3) – 2.062(3) Å, Mn-Cl = 2.399(1), 2.404(1) Å) of the Mn congeners *fac*- $[MnX(CO)_3(bpy)]$ ($X = Cl, I$),^{25, 26} the bond distances around the Tc atom of [1] is somewhat larger than those of the Mn complexes. This difference is due to the difference of the ionic radii between Mn and Tc ions. While the bond lengths and angles around the Tc atom are very similar to the structurally characterized iso-electronic Re(I) tricarbonyl bipyridine complexes²⁷⁻³⁰ owing to the similarity of the ionic radii of Tc and Re ions.

Spectroscopic Properties. The 1H NMR spectrum of [1] in CD_3CN at room temperature showed typical diamagnetic behavior and the only one set of the signals for bpy ligand were observed at 7.62, 8.15, 8.38, and 8.94 ppm. The positions of the signals are shift to down field compared with the position of the signals of free bpy ligand in CD_3CN . This observation suggests that the complex retains the structure in CD_3CN . In the IR spectrum, three strong absorption peaks of the carbonyls and the peaks from the bpy ligand were observed. The CO stretching bands are shown at 2030, 1927, and 1906 cm^{-1} . The positions of the CO stretching peaks are similar to those of *fac*- $[TcBr(CO)_3(bpy)]$ (2033, 1944, 1929 cm^{-1}).¹⁹ This result suggests that the structure of [1] is very similar to that of *fac*- $[TcBr(CO)_3(bpy)]$. In the UV-vis absorption spectrum for [1] in

CH₃CN, the band at 354 nm was observed. It is known that the band of MLCT transition ($\text{Re} \rightarrow \pi^*_{\text{bpy}}$) for *fac*-[ReCl(CO)₃(bpy)] was shown at 371 nm.³¹ Thus, we assign the band at 354 nm for [1] as the metal-to-the ligand charge transfer from Tc to the π^* orbital of the bpy ligand. This band of [1] appears at somewhat shorter wavelength than that of the Re analogue, *fac*-[ReCl(CO)₃(bpy)].

4. Conclusion

In the present study, the 1:1 reaction of *fac*-[TcCl₃(CO)₃] with 2,2'-bipyridine was found to give *fac*-[TcCl(CO)₃(bpy)] in good yield. The transition energy of the MLCT band for [1] is somewhat larger than that of *fac*-[ReCl(CO)₃(bpy)] which is known to give the strong MLCT emission in the visible region. Because of the similarity of the structural and spectroscopic properties between [1] and the Re analogue, it is expected that *fac*-[TcCl(CO)₃(bpy)] has the rich redox and photoluminescent properties.

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