A Seven-Coordinate Mixed-Dithiolate Complex of Niobium(V): Synthesis and Structure of $(PPh_4)[Nb(SCH_2CH_2S)_2(SCH_2CH_2SCH_2CH_2S)]$

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Introduction

The chemistry of discrete metal thiolates is currently a subject of intense interest.[1] We have reported that the homoleptic ethane-1,2-dithiolate (edt) complex of niobium (A)$[Nb(edt)_3]$ (A = PPh_4, NEt_4, $Li(thf)_4$) (**1**)[2] undergoes an unusual isomerization to give (A)[NbS(edt)(tpdt)] (**2**) (tpdt = $SCH_2CH_2SCH_2CH_2S$) at 70–100 °C in the presence of a trace amount of water or methanol via a C–S bond cleavage of an edt ligand.[3,4] This finding prompted us to synthesize the tpdt analogue of the complex **1** in order to examine the behavior of the tpdt ligand at the Nb(V) center. Thus we investigated the reaction between $NbCl_5$, Li_2(tpdt), and PPh_4Br to find that the homoleptic tpdt complexes such as $[Nb(tpdt)_3]^-$ and $[Nb(tpdt)_2]^+$ could not be isolated. Instead, a facile C–S bond cleavage of the tpdt ligand took place to give $(PPh_4)[Nb(edt)_2(tpdt)]$ (**3**), (PPh_4)[NbS(edt)(tpdt)] (**2**), and (PPh_4)[NbO(edt)(tpdt)] (**4**). This contrasts with the reaction of $MoCl_5$ with H_2(tpdt), which was reported to yield a homoleptic tpdt complex, $Mo(tpdt)_2$.[5] In this paper we describe the isolation and X-ray structure of the seven-coordinate mixed-dithiolate complex **3** and its reaction with H_2(edt) to generate **1** (A = PPh_4).

Experimental Section

All manipulations were carried out under an argon atmosphere using dry solvents and conventional Schlenk techniques. Acetonitrile was distilled over CaH_2 under Ar before use. 3-Thiapentane-1,5-dithiol, H_2(tpdt), was used as purchased from Aldrich Chemicals Ltd., and its lithium salt was prepared by adding butyllithium to H_2(tpdt) in THF and isolated straightforwardly as a white powder.

^1H NMR spectra were recorded on JEOL GX-400 spectrometers. NMR data are listed in ppm downfield from TMS, while coupling constants are quoted in hertz. Infrared spectra were recorded on Jasco DS-402G and Hitachi FIS-3 spectrometers, and Raman spectra were obtained on a Jasco R-800 spectrometer equipped with a He–Ne laser, NEC GLG 5800. For UV–visible spectra, Jasco UVIDEC-5A and Jasco Ubest-30 spectrometers were used.

An acetonitrile solution (40 mL) of $NbCl_5$ (1.9 g, 7.0 mmol) was added to a mixture of Li_2(tpdt) (3.7 g, 23 mmol) and PPh_4Br (2.6 g, 6.3 mmol) in the same solvent (80 mL), and the resultant mixture was stirred for 2 h at room temperature. The solution turned vermilion immediately, and white powders (LiCl and LiBr) precipitated. After removal of the precipitates, the solution was concentrated in vacuo to ca. 40 mL and was stored at −20 °C overnight to give an orange solid. Careful recrystallization of this orange solid from acetonitrile produced first (PPh_4)[NbS(edt)(tpdt)] (**2**) as orange crystals (1.2 g, 1.6 mmol, 23%) and then (PPh_4)[NbO(edt)(tpdt)] (**4**) as yellow crystals (0.98 g, 1.3 mmol, 19%). As the solution phase was further concentrated, $(PPh_4)[Nb(edt)_2(tpdt)]$ (**3**) was obtained as red crystals (0.54 g, 0.70 mmol, 10%). The full characterization of **2** was reported in ref 3. Spectroscopic and analytical data etc. for **3** and **4** are as follows.

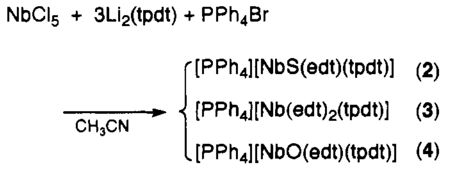
$(PPh_4)[Nb(edt)_2(tpdt)]$ (3). Mp: 164–168 °C dec. UV/vis (λ_{max} (ϵ), DMF): 318 nm (6000), 435 (7100). Far-IR (Nujol mull): 341 (m), 325 (s), 307 cm^{-1} (m) (Nb–S). Raman: 341 (s), 310 cm^{-1} (w). Anal. Calcd for $C_{32}H_{36}S_7PNb$: C, 49.98; H, 4.37; S, 29.19. Found: C, 50.00; H, 4.74; S, 28.69.

(PPh_4)[NbO(edt)(tpdt)] (4). The crystals contain acetonitrile as solvent of crystallization. Mp: 142–146 °C dec. ^1H NMR (400 MHz, CD_3CN, room temperature): δ 7.6–7.9 (m, 20H, Ph), 3.69 (m, 2H, tpdt), 3.48 (m, 2H, tpdt), 3.25 (m, 2H, tpdt), 3.01 (s, 4H, edt), 2.26 (m, 2H, tpdt). UV/vis (λ_{max} (ϵ), CH_3CN): 268 nm (28 000), 276(30 000), 288(27 000), 402(17 000). IR (KBr): 886 cm^{-1} (Nb=O). Far-IR (Nujol mull): 334 (s), 316 cm^{-1} (m) (Nb–S). Raman: 317 cm^{-1} (s). Anal. Calcd for **4**·CH_3CN, $C_{32}H_{35}NS_5OPNb$: C, 52.38; H, 4.81; N, 1.91; S, 21.85. Found: C, 52.51; H, 4.96; N, 1.66; S, 21.71. The crystal structure and chemical characteristics of **4** will be published elsewhere.

X-ray Structure Analysis of 3. A suitable single crystal of **3** was mounted in a thin-walled glass capillary and sealed under Ar. The intensity data were collected at 20 °C up to $(\sin\theta)/\lambda = 0.55$ Å^{-1} with Mo Kα radiation on a Rigaku automated four-circle diffractometer. No significant decomposition of the crystal occurred during the data collection. The intensity measurements were corrected for Lorentz and polarization effects, while no absorption corrections were applied, since the crystal dimensions (0.3 × 0.5 × 0.6 mm) were reasonably uniform. Crystal data are summarized in Table I. The niobium atom was located by the heavy-atom method using a SHELX-86 program. Subsequent refinements and difference Fourier calculations, using the UNICS-Osaka software package, led to the location of the remaining atoms. All non-hydrogen atoms were assigned anisotropic thermal parameters, and hydrogen atoms were included in the structure factor calculations. The structure was refined to $R = 0.063$ and $R_w = 0.069$ by block-diagonal least-squares methods for 3616 reflections. The positional and isotropic thermal parameters are given in Table II. All computations were performed on an ACOS 930 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Results and Discussion

From the reaction of $NbCl_5$ with 2–3 equiv of Li_2(tpdt) and PPh_4Br in CH_3CN at room temperature or in an ice bath, we isolated **2** (23%), **3** (10%), and **4** (19%) as red, orange, and yellow crystals, respectively. The yields of **3** as crystals from different batches remained relatively constant (9–11%), while those of **2** and **4** varied from 19 to 30% and from 17 to 21%. The formation of the oxo complex **4** was probably due to a trace amount of water remaining in the CH_3CN solution. Note that hydrolysis of Li_2(tpdt) regenerated H_2(tpdt) cleanly and formation of H_2(edt) was not detected. Therefore, the observed C–S bond cleavage of the tpdt ligand must be promoted by the Nb(V) metal center.



$$NbCl_5 + 3Li_2(tpdt) + PPh_4Br \xrightarrow[CH_3CN]{} \left\{ \begin{array}{ll} [PPh_4][NbS(edt)(tpdt)] & (\mathbf{2}) \\ [PPh_4][Nb(edt)_2(tpdt)] & (\mathbf{3}) \\ [PPh_4][NbO(edt)(tpdt)] & (\mathbf{4}) \end{array} \right.$$

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(1) (a) Dance, I. G. *Polyhedron* **1986**, 1037–1104. (b) Mueller-Westerhoff, U. T.; Vance, B. *Comprehensive Coordination Chemistry*; Vol. 2, Chapter 16.5. (c) The homoleptic benzenethiolate complexes of Nb(V) and Ta(V) have been reported. In this case, C–S bond cleavage was not observed: Koo, S.-M.; Bergero, R.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 4844–4846.

(2) (a) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 86–87. (b) Tatsumi, K.; Matsubara, I.; Sekiguchi, Y.; Nakamura, A.; Mealli, C. *Inorg. Chem.* **1989**, *28*, 773–780.

(3) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1358–1359.

(4) There are examples of C–S bond rupture in Nb thiolate complexes: (a) Skripkin, Yu. V.; Eremenko, I. L.; Pasynskii, A. A.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285–292. (b) Seela, J. L.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1258–1260. (c) Coucouvanis, D.; Al-Ahmd, S.; Kim, C. G.; Koo, S.-M. *Inorg. Chem.* **1992**, *31*, 2996–2998 and references therein.

(5) Hyde, J.; Magin, L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 204–205.

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Table I. Crystallographic Data for $(PPh_4)[Nb(edt)_2(tpdt)]$ (3)

formula	$C_{32}H_{36}PS_7Nb$
fw	768.94
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	14.031(2)
b, Å	9.140(2)
c, Å	28.030(4)
β, deg	107.28(1)
V, Å^3	3432(1)
Z	4
d_{calc}, g/cm^3	1.488
μ, cm^{-1}	8.19
T, °C	20
radiation	Mo Kα (graphite monochromator, $\lambda = 0.710\,69$ Å)
scan mode	$\theta/2\theta$
no. of unique data	3616 ($\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)$)
final no. of variables	371
R (R_w)^a	0.063 (0.069)

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in $(PPh_4)[Nb(edt)_2(tpdt)]$ (3) with Esd's in Parentheses

atom	x	v	z	B_{eq},^{a} Å^2
Nb	0.12562(6)	0.75715(10)	0.13224(3)	3.0
S1	0.27926(18)	0.6031(4)	0.15524(10)	3.6
S2	0.07682(21)	0.5185(4)	0.17763(11)	3.8
S3	0.02456(19)	0.6172(4)	0.06087(10)	3.7
S4	0.04918(23)	0.9816(4)	0.09110(14)	5.3
S5	0.25073(19)	0.8479(4)	0.09268(11)	3.8
S6	−0.04057(18)	0.8009(4)	0.15189(10)	3.7
S7	0.19026(19)	0.8411(4)	0.21904(10)	4.0
C1	0.2765(8)	0.4881(13)	0.2071(5)	4.6
C2	0.1828(10)	0.3948(14)	0.1934(5)	5.7
C3	−0.0074(9)	0.4157(14)	0.1275(5)	5.0
C4	0.0221(9)	0.4285(14)	0.0803(5)	5.1
C5	0.1261(12)	1.0678(18)	0.0584(7)	8.8
C6	0.1860(11)	0.9738(16)	0.0429(6)	6.7
C7	−0.0039(10)	0.8720(24)	0.2133(6)	9.6
C8	0.0876(10)	0.9196(21)	0.2361(6)	8.8
P	0.52570(16)	0.3611(3)	0.10211(9)	2.3
C11	0.5656(7)	0.5455(10)	0.1212(4)	2.8
C12	0.6679(7)	0.5639(11)	0.1475(4)	3.4
C13	0.7001(8)	0.6974(12)	0.1686(4)	4.1
C14	0.6339(10)	0.8116(12)	0.1640(4)	4.6
C15	0.5345(9)	0.7944(11)	0.1368(5)	4.4
C16	0.5015(7)	0.6620(11)	0.1156(4)	3.3
C21	0.6300(6)	0.2709(10)	0.0904(4)	2.6
C22	0.6812(6)	0.1620(13)	0.1237(5)	4.1
C23	0.7648(9)	0.0988(14)	0.1152(6)	5.5
C24	0.7975(8)	0.1424(13)	0.0763(5)	4.8
C25	0.7494(8)	0.2513(14)	0.0450(5)	4.7
C26	0.6653(8)	0.3143(12)	0.0518(5)	3.9
C31	0.4192(7)	0.3482(11)	0.0480(4)	2.7
C32	0.4215(7)	0.2650(12)	0.0073(4)	3.6
C33	0.3344(8)	0.2434(14)	−0.0325(4)	4.4
C34	0.2456(8)	0.3020(14)	−0.0300(4)	4.4
C35	0.2428(7)	0.3853(13)	0.0103(4)	3.8
C36	0.3278(7)	0.4074(11)	0.0497(4)	3.2
C41	0.4949(6)	0.2762(10)	0.1535(4)	2.4
C42	0.4156(8)	0.1777(11)	0.1453(4)	3.4
C43	0.3940(9)	0.1165(12)	0.1862(5)	4.3
C44	0.4478(9)	0.1504(12)	0.2336(4)	4.3
C45	0.5269(8)	0.2471(13)	0.2413(4)	4.0
C46	0.5498(7)	0.3114(12)	0.2014(4)	3.5

^{a} B_{eq} is the mean of the principal axes of the thermal ellipsoid.

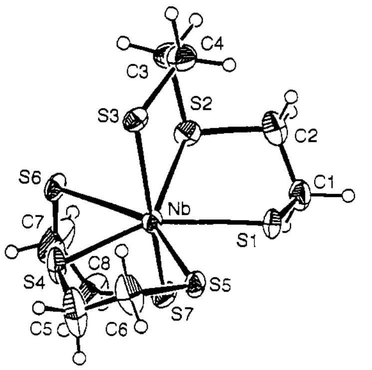

Figure 1. Structure of the complex anion in **3** shown with 50% probability ellipsoids.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $(PPh_4)[Nb(edt)_2(tpdt)]$ (3) with Esd's in Parentheses

	Bond Lengths		
Nb–S1	2.494(3)	Nb–S2	2.714(4)
Nb–S3	2.446(4)	Nb–S4	2.440(4)
Nb–S5	2.481(4)	Nb–S6	2.581(4)
Nb–S7	2.454(4)		
	Bond Angles		
S1–Nb–S2	75.2(1)	S1–Nb–S3	99.4(1)
S2–Nb–S3	78.4(1)	S4–Nb–S5	77.2(1)
S6–Nb–S7	80.3(1)	S1–Nb–S5	68.4(1)
S2–Nb–S6	69.8(1)	S4–Nb–S6	70.9(1)
S3–Nb–S7	158.5(1)		

An interesting aspect of the reaction is formation of the seven-coordinate mixed-dithiolate complex **3**, in which the central Nb metal is surrounded solely by S donors. The X-ray-derived structure of **3** is shown in Figure 1, and selected metric parameters are listed in Table III. The coordination geometry at Nb is best described as a distorted pentagonal bipyramid. The thioether-type sulfur of tpdt occupies an equatorial site with a long Nb–S2 distance of 2.714(4) Å, which may be compared with the corresponding Nb–S distance of 2.740(4) Å in **2**.[3] The Nb–S(thiolate) bond lengths are diverse, ranging from 2.440 to 2.581 Å. Their average of 2.483 Å is somewhat longer than in known alkanethiolate (and alkanedithiolate) Nb complexes: **1** (A = NEt_4, 2.450 Å), **2** (2.461 Å), $(PPh_4)[Nb(S)(S^tBu)_4]$ (2.38 Å),[4c] $(PPh_4)[Nb(SCH_2CH_2CH_2S)_3]$ (2.441 Å),[6] and (NEt_4)[Nb-(norbornane-*exo*-2,3-dithiolate)$_3$] (2.439 Å).[7] The elongation is probably due to the steric congestion in the seven-coordinated geometry. The equatorial sulfur atoms are not exactly coplanar, and S1 (0.206 Å), S2 (−0.228 Å), and S6 (0.184 Å) depart notably from the least-squares plane, while Nb sits right on the plane. Another significant distortion is the axial S3–Nb–S7 angle of 158.5(1)°.

Evidently, the two edt ligands are not equivalent in the solid complex, and the solid-state structure appears to be retained in solution at low temperatures. In the −40 °C ^{1}H NMR spectra in CD_3CN, the edt protons give rise to a singlet (3.65 ppm (4H)) and multiplets with an A_2B_2 pattern (3.32 ppm (2H), 3.10 ppm (2H)): the former may be assigned to the equatorial edt and the latter to edt chelating an axial site and an equatorial site. These signals coalesce at ca. 10 °C and reappear as a singlet (3.53 ppm (8H)) upon raising the temperature to 70 °C. The activation barrier to equilibration of the two edt ligands is estimated to be $\Delta G = 13.2$ kcal/mol. On the other hand, resonances for tpdt protons are observed as multiplets at −40 °C (3.41 ppm (2H), 3.26 ppm (4H), 2.68 ppm (2H)), which become two triplets at 70 °C (3.35 ppm (4H, $J_{HH} = 5.96$ Hz), 3.11 ppm (4H, broad)). Formation of the seven-coordinate complex indicates that familiar six-coordinate dithiolate complexes of d^0 metals[2,6–8] are capable of taking up a seventh ligand if steric demands allow it.

The UV–visible and CV spectra of **3** deserve comment. The two absorption bands (435 and 318 nm) arising from S-to-Nb charge-transfer transitions are systematically at lower wavelengths

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(6) Tatsumi, K.; Matsubara, I.; Sekiguchi, Y.; Nakamura, A.; Mealli, C. *Inorg. Chem.* **1989**, *28*, 773–780.

(7) Tatsumi, K.; Matsubara, I.; Inoue, Y.; Nakamura, A.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1989**, *111*, 7766–7777.

(8) (a) Cowie, M.; Bennett, M. *Inorg. Chem.* **1976**, *15*, 1584–1589, 1589–1595, and references therein. (b) Rao, Ch. P.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 428–439.

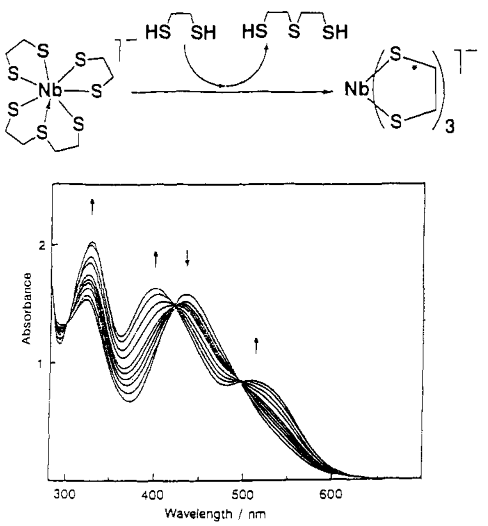

Figure 2. Change in the UV–visible spectra during the reaction of **3** with H_2(edt) leading to formation of **1**.

relative to the corresponding absorptions (523 and 386 nm) for the six-coordinate complex (PPh_4)[Nb(edt)$_3$] (**1**).[2] The observed single well-defined Nb(V)/Nb(IV) redox reaction occurs at −1.67 V, which is 0.42 V more negative than that of **1**.[2] These UV–visible and CV data indicate that, in going from **1** to **3**, low-lying vacant Nb d orbitals are destabilized by coordination of the seventh sulfur donor at Nb.

Complex **3** reacts smoothly with H_2(edt) in CH_3CN to give **1**, and the change in UV–visible spectra during this reaction is shown in Figure 2. By monitoring the spectra, we found that the reaction obeys a second-order kinetics, $r = k[\mathbf{3}][\mathrm{edt}]$, with the rate constant being $k = 2.5 \times 10^{-4}\ \mathrm{s^{-1}\ M^{-1}}$. Treatment of either **2** or **4** with H_2edt also gave rise to **1**, while formation of **3** was not detected. In contrast, **1** does not react with H_2(tpdt) (1–3 equiv) at room temperature. We also examined the reaction system (1:2:1:1) $NbCl_5/Li_2edt/Li_2tpdt/PPh_4Br$ in CH_3CN to find that the major product is **1** (44% yield) and only small amounts of **2** (3.2%), **3** (1.4%), and **4** (3.2%) are formed. Furthermore, no interconversion among **2**, **3**, and **4** occurs under the reaction conditions employed. Therefore the three complexes are probably generated via three independent pathways in the reaction of $NbCl_5$ with Li_2(tpdt), the mechanism of which still needs to be elucidated.

Supplementary Material Available: Complete listings of thermal parameters, atomic parameters of H atoms, bond distances and angles, and experimental details for **3** and two figures showing crystal and molecular structures and atom numbering for **3** (8 pages). Ordering information is given on any current masthead page.