Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

Protecting Groups in the Preparation of Thiolate Complexes of Technetium

N. Bryson,[1] J. Lister-James,[1] A. G. Jones,[2] W. M. Davis,[1] and A. Davison*[,1]

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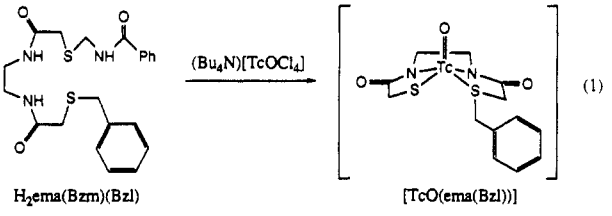
The nitrogen–sulfur ligand $H_2PIC(Acm)$ (*N*-(2-((2-(((acetylamino)methyl)thio)acetyl)amino)ethyl)-2-pyridinecarboxamide) reacted with $(Bu_4N)[TcOCl_4]$ in methanolic solution, yielding the neutral complex [TcO(PIC)] (oxo[*N*-(2-((2-mercaptoacetyl)amino)ethyl)-2-pyridinecarboxamido]technetium(V)) as a red crystalline solid. The thiol-protected derivatives $H_2PIC(Bzm)$ (Bzm = (benzoylamino)methyl) and $H_2PIC(Bzl)$ (Bzl = benzyl) similarly gave [TcO(PIC)] in near-quantitative yield. In contrast, reaction of the unprotected, free-thiol form of the ligand, H_3PIC, with $(Bu_4N)[TcOCl_4]$ in methanol gave a highly colored mixture of reduced technetium species and only traces of the neutral product. The ligand $H_2PYR(Bzm)$ also reacted with $(Bu_4N)[TcOCl_4]$ in methanol, giving a red neutral complex [TcO(PYR)]. The X-ray structure of [TcO(PIC)] was determined. Crystal data for [TcO(PIC)]: $[C_{10}H_{10}N_3O_3STc]$, tetragonal, MW = 349.27, a = 8.010 (0) Å, c = 36.845 (0) Å, space group = $P4_32_12$, Z = 8, R = 0.037, R_w = 0.041.

Introduction

One has only to look at the advances in natural product and peptide synthesis to realize the impact that has been made by the development of organic protecting groups.[3] The concept of easily removable organic functionalities for the masking of heteroatoms can also be helpful in the preparation of inorganic complexes. We have found that the thiol protecting groups, *S*-(benzoylamino)-methyl, *S*-(acetylamino)methyl, and *S*-benzyl, which have been used to prepare polyfunctional ligands containing amide and thiolate functionalities, may not need to be removed prior to metal complexation. In fact, if intermediate or product complexes are reduced by thiols, the use of S-protected ligand can be an advantage.

Not long ago we reported[4] a series of oxotechnetium(V) chelate complexes that were prepared in good yields from the corresponding *S*-(benzoylamino)methyl (*S*-Bzm) protected diamide–thiol–thioether chelates. Reaction of $(Bu_4N)[TcOCl_4]$ with $H_2ema(Bzl)(Bzm)$[5] (Bzl = benzyl) ligand in methanol gave [TcO(ema(Bzl))] (80% yield) by deprotonation of the amides and a metal-induced deprotection of the *S*-Bzm group (eq 1). The



$H_2ema(Bzm)(Bzl)$ [TcO(ema(Bzl))] (1)

use of a metal-cleavable S-protecting group was necessitated by the fact that the product complex was readily reduced by a variety of organic thiols, including the "free-thiol" form of the ligand itself. In addition to the *S*-Bzm group, we have found that *S*-(acetylamino)methyl (*S*-Acm) and *S*-benzyl (*S*-Bzl) protected ligands are also deprotected upon coordination and are useful for the preparation of technetium thiolate complexes in excellent yields. The results of our studies are described below.

Experimental Section

Caution! Technetium-99 is a weak β emitter (β = 0.292 MeV) with a half-life of 2.12×10^5 years. Technetium was obtained as an 0.3 M aqueous solution of NH_4TcO_4 from Du Pont Biomedical Products, Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity. The precautions followed were as detailed previously.[6]

Melting points were obtained with a Melt-Temp apparatus and are uncorrected. Infrared spectra were measured on samples in the form of KBr pellets from 4800 to 400 cm^{-1} on an IBM IR/30S spectrophotometer with a DTGS detector and 2-cm^{-1} resolution. ^1H and ^{13}C NMR spectra were recorded on Bruker WM 250- and 270-MHz spectrometers, respectively, and unless specified, the solvent used was $CDCl_3$. UV–visible spectra were recorded with a Hewlett-Packard 8451A photodiode array spectrophotometer. Conductivity measurements were made on acetonitrile solutions with an Altex RC-16C conductivity bridge. Electrochemical experiments were performed in dry acetonitrile by using TBAP electrolyte, a rotating platinum electrode, and a Princeton Applied Research Model 174 polarographic analyzer. Fast atom bombardment mass spectra were measured on samples dissolved in a 3-nitrobenzyl alcohol matrix by using a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and operating at an accelerating voltage of 8 kV. The FAB gun produced a beam of 6–8-keV xenon neutrals. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

N-(2-Aminoethyl)-2-mercaptoacetamide,[7] (acetylamino)methanol (AcmOH),[8,9] (benzoylamino)methanol (BzmOH),[10] *N*-(2-aminoethyl)-2-((triphenylmethyl)thio)acetamide, *N*-(2-((triphenylmethyl)-thio)acetyl)glycine *N*-hydroxysuccinimide ester,[11] and $(Bu_4N)[TcOCl_4]$[12] were prepared as described previously. All solvents and reagents used were reagent grade and used as received.

***N*-(2-((2-((Triphenylmethyl)thio)acetyl)amino)ethyl)-2-pyridinecarboxamide, $H_2PIC(Tr)$.** To a solution of 2-pyridinecarboxylic acid (0.617 g, 5.0 mmol), *N*-(2-aminoethyl)-2-((triphenylmethyl)thio)acetamide (1.88 g, 5.0 mmol), and *N*-hydroxysuccinimide (0.596 g, 5.0 mmol) in acetonitrile (ACN; 50 mL) was added a solution of DCC (dicyclohexylcarbodiimide; 1.24 g, 5.0 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 5 h and the solvent removed under reduced pressure. The resultant colorless oil was redissolved in CH_2Cl_2 and washed with 5% $NaHCO_3$, 0.5 M H_2SO_4, water, and saturated aqueous NaCl and dried over K_2CO_3. Evaporation of the solvent and crystallization from methanol afforded $H_2PIC(Tr)$ (94%). Mp: 174–176 °C. ^1H NMR: δ 3.00–3.60 (m, 4 H, NCH_2CH_2N), 3.01 (s, 2 H, CH_2STr), 6.19 (br, 1 H, CONH), 7.05 (m, 15 H, aryl), 7.80–8.20 (br, 5 H, pyridyl).

***N*-(2-((2-(((Acetylamino)methyl)thio)acetyl)amino)ethyl)-2-pyridinecarboxamide, $H_2PIC(Acm)$.** The triphenylmethyl-protected compound $H_2PIC(Tr)$ (0.500 g, 1.04 mmol) was dissolved in trifluoroacetic acid (50 mL), and AcmOH (0.093 g, 1.04 mmol) was added. The

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(5) $H_2ema(Bzl)(Bzm)$ = *N*-(2-((2-(((benzoylamino)methyl)thio)acetyl)-amino)ethyl)-2-(benzylthio)acetamide.
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reaction was stirred for 3 h, the solvent was removed under reduced pressure, and the oily residue was triturated with ethyl ether. The resultant white solid was recrystallized from ethyl acetate (50%). Mp: 120–122 °C. Anal. Calcd for $C_{13}H_{18}N_4O_3S$: C, 50.31; H, 5.84; N, 18.05; S, 10.33. Found: C, 50.24; H, 5.80; N, 17.79; S, 9.99. IR ν_{max}: 3287, 3078, 2928, 2851, 1651, 1552, 1209, 916, 773, 686, 646 cm^{-1}. ^{1}H NMR: δ 2.03 (s, 3 H, CH_3), 2.35 (s, 2 H, CH_2S), 3.62 (m, 4 H, NCH_2CH_2N), 4.44 (d, 2 H, SCH_2N), 7.47 (m, 1 H, CONH), 7.66 (tr, 1 H, pyridyl), 7.88 (tr, 2 H, CONH), 8.17 (d, 1 H, pyridyl), 8.6 (d, 2 H, pyridyl).

***N*-(2-(((2-(((Benzoylamino)methyl)thio)acetyl)amino)ethyl)-2-pyridinecarboxamide, H_2PIC(Bzm).** This compound was prepared by using BzmOH in trifluoroacetic acid, similar to the procedure described above. Recrystallization from ACN gave analytically pure material (88%). Mp: 139–142 °C. Anal. Calcd for $C_{18}H_{20}N_4O_3S$: C, 50.08; H, 5.37; N, 15.04; S, 8.61. Found: C, 50.14; H, 5.48; N, 15.00; S, 8.63. IR ν_{max}: 3286, 3063, 2929, 2851, 1649, 1603, 1544, 1333, 1275, 1233, 693 cm^{-1}. ^{1}H NMR: δ 3.31 (m, 6 H, NCH_2CH_2N and CH_2S), 4.57 (d, 2 H, SCH_2N), 7.4–7.7 (m, 4 H, aromatic), 7.89 (m, 2 H, aromatic), 8.05 (m, 2 H, aromatic), 8.26 (t, 1 H, aromatic), 8.68 (d, 1 H, aromatic), 8.96 (tr, 1 H, CONH), 9.24 (tr, 1 H, CONH).

***N*-(2-((2-(Benzylthio)acetyl)amino)ethyl)-2-pyridinecarboxamide, H_2PIC(Bzl).** To a degassed solution of *N*-(2-aminoethyl)-2-thioacetamide (2.50 g, 18.66 mmol) in ethanol (100 mL) was added 4.37 M methanolic sodium methoxide (4.3 mL, 18.8 mmol) and benzyl chloride (2.1 mL, 18.3 mmol). The mixture was heated at reflux for 2 h and filtered hot through a bed of diatomaceous earth. Removal of the solvent gave an oily residue, which was redissolved in 1:1 DMF/ACN. To this were added 2-pyridinecarboxylic acid (2.3 g, 18.7 mmol), *N*-hydroxysuccinimide (1.8 g, 8.69 mmol), and, subsequently, a solution of DCC (3.86 g, 18.71 mmol) in 10 mL of ACN, and the solution was stirred overnight. The solvent was removed and the residue partitioned between 5% $NaHCO_3$ and CH_2Cl_2. The organic layer was washed with brine, dried over K_2CO_3, and evaporated to give a pale yellow oil. Recrystallization from methanol afforded white needles (56%). Mp: 110–111 °C. Anal. Calcd for $C_{17}H_{19}N_4O_3S$: C, 62.02; H, 5.77; N, 12.75; S, 9.73. Found: C, 62.03; H, 5.83; N, 12.73; S, 9.81. IR ν_{max}: 3315, 3088, 1659, 1559, 1526, 1431, 695 cm^{-1}. ^{1}H NMR: δ 2.82 (s, 2 H, SCH_2Ph), 3.06 (4-line m, 2 H, NCH_2CH_2N), 3.11 (4-line m, 2 H, NCH_2CH_2N), 3.30 (s, 2 H, CH_2SBzl), 6.84 (m, 6 H, aryl and CONH), 7.04 (m, 1 H, pyridyl), 7.44 (m, 1 H, pyridyl), 7.79 (d, 1 H, pyridyl), 7.97 (br tr, 1 H,CONH), 8.18 (d, 1 H, pyridyl).

***N*-(2-(2-Pyridinyl)ethyl)-*N'*-(2-((triphenylmethyl)thio)acetyl)glycinamide, H_2PYR(Tr).** A solution of *N*-(2-((triphenylmethyl)thio)acetyl)-glycine succinate ester (2.96 g, 6.06 mmol) and 2-(2-aminoethyl)pyridine (0.730 mL, 6.06 mmol) dissolved in CH_2Cl_2 was stirred for 30 min and filtered through Celite. The filtrate was washed with 5% $NaHCO_3$ and saturated aqueous NaCl and dried over K_2CO_3. The solvent was evaporated and the residue crystallized from absolute ethanol (88%). Mp: 147–148 °C. ^{1}H NMR: δ 2.6–3.8 (br m, 8 H, NCH_2CH_2N and NCH_2CH_2), 6.50 (br, 1 H, CONH), 7.01 (m, 19 H, aryl and pyridyl), 7.80 (br, 1 H, CONH).

***N*-(2-(2-Pyridinyl)ethyl)-*N'*-(2-(((benzoylamino)methyl)thio)-acetyl)glycinamide, H_2PYR(Bzm).** To the triphenylmethyl derivative H_2PYR(Tr) (2.51 g, 5.07 mmol) in trifluoroacetic acid was added BzmOH (0.78 g, 5.17 mmol), and the reaction mixture was stirred for 3 h. Evaporation of the solvent gave a yellow oil, which was redissolved in CH_2Cl_2, washed with 5% $NaHCO_3$ and saturated aqueous NaCl, and dried over K_2CO_3. The solvent was removed at reduced pressure and the residual solid crystallized from acetonitrile (65%). Mp: 138–139 °C. Anal. Calcd for $C_{19}H_{22}N_4O_3S$: C, 59.08; H, 5.70; N, 14.50; S, 8.30. Found: C, 59.16; H, 5.77; N, 14.46; S, 8.36. IR ν_{max}: 3339, 3360, 3273, 3088, 2964, 2931, 1645, 1569, 1534, 1277, 1249, 711, 688 cm^{-1}. ^{1}H NMR: δ 2.93 (tr, 2 H, CH_2CH_2N), 3.30 (s, 2 H, $COCH_2S$), 3.62 (q, 2 H, CH_2CH_2N), 3.90 (d, 2 H, $COCH_2N$), 4.67 (d, 2 H, SCH_2N), 7.10 (m, 3 H, pyridyl and CONH), 7.41 (m, 3 H, aryl), 7.60 (m, 2 H, aryl), 7.80 (m, 2 H, pyridyl), 7.8. (br, 1 H, CONH), 8.47 (m, 1 H, pyridyl).

Oxo[*N*-(2-((2-mercaptoacetyl)amino)ethyl)-2-pyridinecarboxamido]-technetium(V), [TcO(PIC)]. Method 1. To $(Bu_4N)[TcOCl_4]$ (208 mg, 0.42 mmol) dissolved in methanol (5 mL) was added ligand H_2PIC(Acm) (0.64 mmol). The reaction mixture was stirred for 10 min and then allowed to stand undisturbed overnight. X-ray-quality red crystalline plates that formed were filtered out, washed with cold methanol, and dried (90%). Mp: 245 °C. Anal. Calcd for $C_{10}H_{10}N_3O_3STc$: C, 34.20; H, 2.87; N, 11.96; S, 9.13. Found: C, 34.11; H, 2.90; N, 11.92; S, 9.11. IR ν_{max}: 1657, 1633, 966 cm^{-1}. ^{1}H NMR: δ 4.0 (m, 2 H, NCH_2CH_2N), 4.12 (AB, J(AB) = 17 Hz, 1 H, CH_2S), 4.22 (AB, J(AB) = 17 Hz, 1 H, CH_2S), 4.26 (m, 1 H, NCH_2CH_2N), 5.28 (m, 1 H, NCH_2CH_2N), 7.92 (tr, 1 H, pyridyl), 8.23 (d, 1 H, pyridyl), 8.37 (tr, 1 H, pyridyl), 9.17 (d, 1 H, pyridyl). ^{13}C NMR: δ 38.76, 54.41, 55.18, 125.07, 128.68, 144.11, 152.14, 153.31, 171.50, 185.72. Electronic spectrum [λ_{max}, nm (ϵ, cm^{-1} M^{-1})]: 300 (sh, 7300), 400 (sh, 1800), 500 (104). FAB$^+$ MS: m/z 352, 703. $E_{1/2}$(red) = −0.55 V irrev. Conductivity in CH_3CN: Λ = 11.9 Ω^{-1} m^2 mol^{-1}.

Table I. Crystal Data for [TcO(PIC)]

empirical formula	$C_{10}H_{10}N_3O_3STc$
fw	349.27
cryst syst	tetragonal
a, Å	8.010 (2)
c, Å	36.845 (7)
V, Å^3	2364 (2)
Z	8
space group	$P4_32_12$ (No. 96)
T, °C	23
λ(Mo Kα (graphite monochromated)), Å	0.71069
ρ(calcd), g/cm	1.96
μ, cm^{-1}	13.39
No. of reflcns measd	2179
transm factors	1.0, 0.87
R, R_w	0.037, 0.041

Method 2. To $(Bu_4N)[TcOCl_4]$ (208 mg, 0.42 mmol) dissolved in 10% CH_2Cl_2 in methanol (5 mL) was added ligand H_2PIC(Bzm) (0.64 mmol). Evaporation of the solvent and crystallization of the residue gave a red crystalline product, which was indistinguishable from authentic [TcO(PIC)].

Method 3. To $(Bu_4N)[TcOCl_4]$ (29 mg, 0.058 mmol) dissolved in methanol (5 mL) was added ligand H_2PIC(Bzl) (23 mg, 0.067 mmol). On warming, the ligand dissolved to give a green solution, which was further heated at reflux. The green color slowly changed to red over 2 h, and then the solution was allowed to cool. The complex precipitated from the reaction mixture in quantitative yield.

Oxo[*N*-(2-(2-pyridinyl)ethyl)-*N'*-(2-mercaptoacetyl)glycinamido]-technetium(V) Hydrate, [TcO(PYR)]·H_2O. To ligand H_2PYR(Bzm) (131 mg, 0.416 mmol) in methanol (3 mL) was added a solution of $(Bu_4N)[TcOCl_4]$ (208 mg, 0.416 mmol) in methanol (2 mL) to give a dark red solution. Celite was added to the reaction mixture, which was stirred and filtered. The filtrate was cooled to −20 °C; the dark red crystals that precipitated were filtered and dried (58.5 mg, 38%). Mp: 180–182 °C. Anal. Calcd for $C_{11}H_{14}N_3O_4STc$: C, 34.50; H, 3.65; N, 10.96; S, 8.37. Found: C, 34.95; H, 3.69; N, 11.02; S, 8.38. IR ν_{max}: 1647, 1620, 964 cm^{-1}. ^{1}H NMR: δ 2.81 (m, 1 H, NCH_2CH_2), 3.31 (m, 1 H, NCH_2CH_2), 3.63 (m, 1 H, NCH_2CH_2), 3.89 (m, 1 H, NCH_2CH_2), 4.09 (AB, J(AB) = 14 Hz, 1 H, CH_2S), 4.15 (AB, J(AB) = 14 Hz, 1 H, CH_2S), 4.50 (d, J = 18 Hz, 1 H, $COCH_2N$), 5.30 (d, J = 18 Hz, 1 H, $COCH_2N$), 7.65 (d, 2 H, pyridyl), 8.11 (tr, 1 H, pyridyl), 9.57 (d, 1 H, pyridyl). ^{13}C NMR: δ 37.03, 39.38, 39.61, 56.92, 124.22, 127.35, 142.47, 154.71, 162.18, 185.00, 185.98. Electronic spectrum [λ_{max}, nm (ϵ, cm^{-1} M^{-1})]: 263 (sh, 19800), 330 (6600), 564 (168). FAB$^+$ MS: m/z 366, 731. $E_{1/2}$(red): no wave observed. Conductivity: Λ(CH_3CN) = 2.75 Ω^{-1} m^2 mol^{-1}.

Crystal Structure of Oxo[*N*-(2-((2-mercaptoacetyl)amino)ethyl)-2-pyridinecarboxamido]technetium(V), [TcO(PIC)]. X-ray data were collected from a red crystal at room temperature on a Enraf-Nonius CAD4F-11 k-geometry diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Details of the data collection and reduction were similar to those described elsewhere.[13] A total of 2719 reflections ($+h,+k,\pm l$) were collected in the range $3° < 2\theta < 55°$, with the 1975 having $I > 3\sigma(I_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (164 variables) using the TEXSAN crystallographic software package.[14] The structure was solved and refined in space group $P4_32_12$ to a final R = 0.037 and R_w = 0.041. The alternate hand of the molecule was then refined to convergence in space group $P4_12_12$ to a final R = 0.054 and R_w = 0.061, thus ensuring $P4_32_12$ as the correct choice. Hydrogen atoms were refined from their calculated positions (d_{C-H} = 0.95 Å) and were assigned isotropic thermal parameters equal to 50% of the B_{equiv} value of the atom to which they were bonded. The largest peak on the final difference-Fourier map was 1.18 e Å^{-3}. No absorption correction was applied. Crystal data are given in Table I, and final positional parameters are given in Table II.

Results and Discussion

The ligands H_2PIC(R) (R = Acm, Bzm, Bzl) and H_2PYR-(Bzm) were prepared by using standard techniques of peptide

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(14) TEXSAN-TEXRAY Structure Analysis Package. Molecular Structure Corp., 1985.

Table II. Final Positional Parameters for [TcO(PIC)][a]

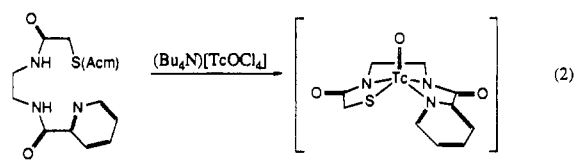
atom	x	y	z
Tc	0.97047 (5)	−0.01134 (5)	0.81726 (1)
S	0.7699 (2)	0.1874 (2)	0.81538 (5)
O1	1.1327 (5)	0.0376 (6)	0.7917 (1)
O21	0.5803 (6)	−0.1611 (6)	0.7524 (1)
O51	1.0854 (6)	−0.3749 (5)	0.8904 (1)
N1	0.8069 (6)	−0.1408 (6)	0.7893 (1)
N2	0.9808 (6)	−0.2304 (5)	0.8412 (1)
N3	1.0281 (5)	0.0531 (5)	0.8711 (1)
C1	0.6344 (8)	0.0995 (8)	0.7808 (2)
C2	0.6706 (8)	−0.0797 (8)	0.7725 (2)
C3	0.8467 (8)	−0.3204 (8)	0.7867 (2)
C4	0.9101 (8)	−0.3763 (8)	0.8235 (2)
C5	1.0510 (7)	−0.2453 (7)	0.8748 (2)
C6	1.0775 (6)	−0.0776 (6)	0.8919 (2)
C7	1.1394 (7)	−0.0554 (8)	0.9263 (2)
C8	1.1473 (8)	0.1055 (8)	0.9405 (2)
C9	1.0974 (7)	0.2363 (8)	0.9193 (2)
C10	1.0381 (7)	0.2085 (6)	0.8849 (2)

[a] Numbers in parentheses are errors in the last significant digit.

Table III. FABMS$^+$ of Green Intermediate

m/z	assignment
352	$[TcO(PIC)]^+$
442	$[TcO(PIC(Bzl))]^+$
478	$[TcOCl(PIC(Bzl))]H^+$
514	$[TcOCl_2(PIC(Bzl))]H_2^+$
550	$[TcOCl_3(PIC(Bzl))]H_3^+$

synthesis in conjunction with a new method for the interchanging of the *S*-triphenylmethyl and *S*-aminomethyl protecting groups reported previously.[4] The complexes [TcO(PIC)] and [TcO(PYR)] were subsequently prepared by ligand exchange. Reaction of 1 equiv of $H_2PIC(Acm)$ with $(Bu_4N)[TcOCl_4]$ in methanol was rapid and produced a bright red solution from which red crystals of [TcO(PIC)] precipitated on standing (eq 2). Several



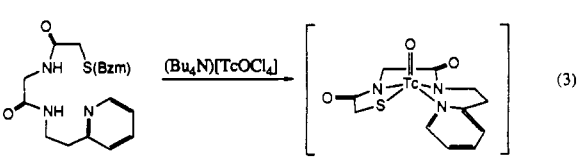
(2)

$H_2PIC(Acm)$ [TcO(PIC)]

of the crystals isolated from the reaction mixture were suitable for X-ray diffraction, and a structural characterization was performed (vide infra). Under identical conditions, the ligand $H_2PIC(Bzm)$ reacted with $(Bu_4N)[TcOCl_4]$ to give comparable results.

Reaction of the *S*-Bzl-protected ligand $H_2PIC(Bzl)$ with $(Bu_4N)[TcOCl_4]$ proceeded differently, producing a bright green solution on mixing of the reagents in methanol. The reaction did not proceed any further upon standing at room temperature but was complete with clean conversion to [TcO(PIC)] after 2 h at reflux. An FAB$^+$ mass spectrum of the intermediate green solution showed several ions containing the "TcO^{3+}" core, chloride, and both the protected and unprotected N_3S chelates (see Table III). As yet, we do not know if all of the species observed in the mass spectrum are actually contained in the mixture or, rather, that they are formed in the matrix of the mass spectrometer.

The complex [TcO(PYR)] was prepared from $H_2PYR(Bzm)$ and $(Bu_4N)[TcOCl_4]$ in methanol and yielded a dark red crystalline solid (eq 3).



(3)

$H_2PYR(Bzm)$ [TcO(PYR)]

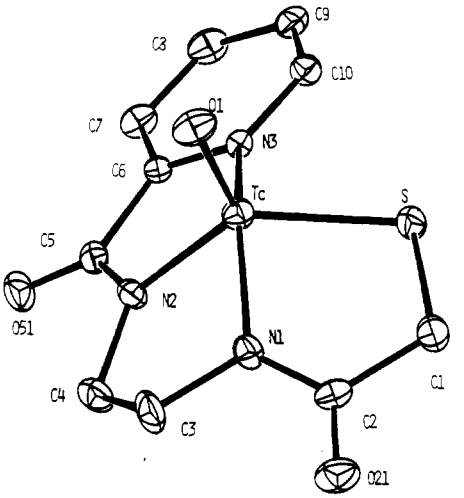


Figure 1. ORTEP drawing of [TcO(PIC)] showing 30% probability ellipsoids.

Table IV. Selected Bond Angles and Distances for [TcO(PIC)][a]

	Bond Lengths (Å)		
Tc–O1	1.653 (4)	Tc–N2	1.966 (4)
Tc–S	2.263 (1)	Tc–N3	2.102 (4)
Tc–N1	1.963 (4)		
	Bond Angles (deg)		
O1–Tc–S	112.0 (2)	S–Tc–N2	132.2 (1)
O1–Tc–N1	110.6 (2)	S–Tc–N3	90.7 (1)
O1–Tc–N2	115.8 (2)	Tc–S–C1	100.0 (2)
O1–Tc–N3	107.9 (2)	Tc–N3–C6	126.6 (4)
S–Tc–N1	83.2 (2)	Tc–N3–C10	114.1 (3)

[a] Numbers in parentheses are errors in the last significant digit.

Both [TcO(PIC)] and [TcO(PYR)] are nonconducting and stable to air and moisture. Their infrared spectra show strong absorptions at ca. 965 cm^{-1}, characteristic of the multiply bonded oxo group. The carbonyl stretches of the coordinated amido groups were observed between 1657 and 1620 cm^{-1}. Positive mode fast atom bombardment (FAB$^+$) mass spectra of both complexes were very clean and gave strong molecular ion peaks at MH^+ (100%) and weak ion peaks corresponding to M_2H^+ (ca. 1%). The higher mass ion is presumably formed in the mass spectrometer and not due to dimeric impurities in the sample.[4,15]

The ^1H NMR spectra of the [TcO(PIC)] and [TcO(PYR)] complexes are complicated slightly by the asymmetry of the monoxo core. As a result, each set of geminal protons on the ligand are observed as diastereotopic pairs ($J(AB)$ = ca. 17 Hz) and the NCH_2CH_2N units as set of four multiplets. The ^{13}C NMR spectra are straightforward and consistent with the formulations.

The structure of [TcO(PIC)] was determined by X-ray crystallography, and an ORTEP drawing is shown in Figure 1. Selected bond distances and angles are found in Table IV. The technetium center is five-coordinate in a square-pyramidal geometry with an oxo ligand at the apical position and the N_3S chelate occupying the basal plane. The Tc–N1(amido) and Tc–N2(amido) bond distances (1.963 (4) and 1.966 (4) Å) are slightly shorter than observed for a similar complex with a "$TcON_2S_2$" coordination sphere.[4] As a consequence of the chelate ring in [TcO(PIC)] the Tc–N3(pyridine) bond distance is slightly shorter than those observed for the complexes *trans*-$[TcO_2(4\text{-}Bu^tpy)_4](CF_3SO_3)$ (2.146 (7) Å[16] and [TcO(py)(SAr)$_3$] (2.205 Å).[17] The short reach of the five-membered ring is also responsible for an angled approach of the pyridyl group to the metal (Tc–N3–C6 = 126.6°

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and Tc-N3-C10 = 114°). The Tc—S and Tc=O1 distances are unexceptional.[18]

The neutral complexes [TcO(PIC)] and [TcO(PYR)] react rapidly with a variety of thiol compounds to give highly colored polar complexes, which remained bound to silica or alumina on chromatography and thus could not be adequately purified for detailed analysis. Similar results were obtained upon treating the complexes with inorganic reducing agents, such as stannous chloride, stannous tartrate, and sodium dithionite. It is exactly for this reason that the desired neutral complexes [TcO(PIC)] and [TcO(PYR)] could not be satisfactorily prepared from the unprotected thiol forms of the ligands. Indeed, attempts to prepare [TcO(PIC)] from reaction of $(Bu_4N)[TcOCl_4]$ and 1 equiv of H_3PIC (having an -SH group) gave only traces of the neutral product, with the remainder of the technetium as a mixture of highly colored species that no longer showed a Tc=O stretch in the infrared region. In this latter reaction it is likely that the thiol has caused a reduction of the metal center. In contrast, the thiol of the ligands $H_2PIC(Bzm)$ and $H_2PIC(Acm)$ is masked by the protecting group and this stops unwanted redox chemistry from occurring.

The S-deprotection reactions described here that lead to [TcO(PIC)] and [TcO(PYR)] are more simply described as dealkylation reactions. Dealkylation of thioether ligands coordinated to transition metals is well documented.[19] Indeed, we have also characterized intermolecular and intramolecular thioether dealkylations on technetium(V) complexes in which amines and water effect an S_N2 attack on the electrophilic carbon α to the coordinated thioether.[4] The *S*-Acm- and *S*-Bzm-protected ligands described in the present study were synthesized to be very reactive toward S-deprotection (S-dealkylation). Unlike the benzyl group that is removed by a nucleophilic attack of water, the (acetylamino)methyl and (benzoylamino)methyl groups can be eliminated as their respective *N*-methylene amide cations, $H_2C=NHCOCH_3^+$ or $H_2C=NHCOPh^+$, which are quenched by reaction with the solvent. This elimination reaction was rapid enough that technetium complexes of the *S*-Acm- and *S*-Bzm-protected ligands were not observed.

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Supplementary Material Available: Tables SI-SVI, listing complete crystallographic data and collection parameters, final positional and thermal parameters, temperature factor expressions, and complete bond distances and angles (12 pages); a listing of observed and calculated structure factor data (19 pages).

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Contribution from the Department of Chemistry,
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Synthesis and Structural Characterization of Mixed-Metal Chloro Chalcogenido Cluster Complexes of Molybdenum and Nickel $[Mo_3Ni_2X_4Cl_4\{P(C_2H_5)_3\}_5]$ (X = S, Se)

Taro Saito,* Yoshimichi Kajitani, Tsuneaki Yamagata, and Hideo Imoto

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Condensation of $[Mo_3X_4Cl_4(PEt_3)_n(MeOH)_{5-n}]$ (X = S, n = 3; X = Se, n = 5) with $Ni(cod)_2$ formed pentanuclear mixed-metal cluster complexes $[Mo_3Ni_2X_4Cl_4\{P(C_2H_5)_3\}_5]$ (**1**, X = S; **2**, X = Se). X-ray structure determination of **1** has shown that the cluster framework is a square pyramid consisting of three molybdenum and two nickel atoms. A sulfido ligand quadruply bridges the square base of Mo_2Ni_2, and three triply bridging sulfido ligands cap the triangles of Mo_3 and Mo_2Ni. A triply bridging chloro ligand is on the triangular face of $MoNi_2$, and another chloro ligand bridges the basal molybdenum atoms to which terminal chloro ligands are also bonded. One triethylphosphine ligand is coordinated to each of the five metals. Crystal data for $[Mo_3Ni_2S_4Cl_4\{P(C_2H_5)_3\}_5]\cdot CHCl_3$: $C_{31}H_{76}Cl_7Mo_3Ni_2P_5S_4$, triclinic, space group $P\bar{1}$ with a = 14.628 (4) Å, b = 18.095 (8) Å, c = 10.594 (2) Å, α = 93.68 (4)°, β = 98.01 (4)°, γ = 91.22 (3)°, V = 2770 (2) Å^3, Z = 2, R = 0.046, and R_w = 0.041. Selected bond distances (Å) and angles (deg): Mo-Mo(av), 2.677; Mo-Ni(av), 2.586; Ni(1)-Ni(2), 2.710(1); Mo(2)-Mo(3)-Ni(1), 90.23 (3); Mo(3)-Mo(2)-Ni(2), 89.80(3); Mo(2)-Mo(1)-Mo(3), 61.20 (2); Ni(1)-Mo(1)-Ni(2), 65.54 (4); Mo(2)-Mo(1)-Ni(2), 62.05 (3). ^{31}P NMR spectra of the complexes can be interpreted as AA'MXX' systems, and all the couplings among the phosphorus nuclei have been determined by simulation.

Introduction

The triangular metal framework is ubiquitous in the polyhedral cluster compounds,[1] and some trinuclear cluster complexes are good starting materials for the preparation of larger polyhedra.[2] This has been demonstrated in the syntheses of tetrahedral,[3] square-pyramidal,[4] trigonal-prismatic,[5] bitetrahedral,[6] bicapped-tetrahedral,[7] and octahedral clusters.[8] Our contribution to the area was the preparation of $[M_6S_8(PEt_3)_6]$ (M = Mo,[9] W[10]), which may be regarded as molecular models for the superconducting Chevrel phases.[11] We have now found that trinuclear molybdenum chalcogenido clusters condense with a zerovalent nickel complex to form square-pyramidal mixed-metal cluster complexes.[12]

* To whom correspondence should be addressed at the Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan.

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