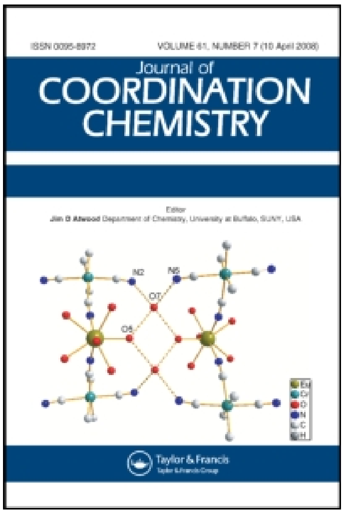


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Formation and coordination of a terdentate dithiocarbazatopyrazoline derivative to technetium(V)

Thomas I. A. Gerber[a]; Eric Hosten[a]; Otto Knoesen[b]; Peter Mayer[c]
[a] Department of Chemistry, Nelson Mandela Metropolitan University, Port Elizabeth, South Africa [b] Department of Radiochemistry, Applied Science and Technology, Pretoria [c] Department of Chemistry, Ludwig-Maximilians University, Münich, Germany

To cite this Article Gerber, Thomas I. A. , Hosten, Eric , Knoesen, Otto and Mayer, Peter(2007) 'Formation and coordination of a terdentate dithiocarbazatopyrazoline derivative to technetium(V)', Journal of Coordination Chemistry, 60: 21, 2369 — 2375, First published on: 13 July 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701266724

URL: http://dx.doi.org/10.1080/00958970701266724

Journal of Coordination Chemistry
Vol. 60, No. 21, 1 November 2007, 2369–2375

Formation and coordination of a terdentate dithiocarbazatopyrazoline derivative to technetium(V)

THOMAS I. A. GERBER*†, ERIC HOSTEN†,
OTTO KNOESEN‡ and PETER MAYER§

†Department of Chemistry, Nelson Mandela Metropolitan University,
Port Elizabeth, South Africa
‡Department of Radiochemistry, Applied Science and Technology, Nuclear Energy
Corporation of South Africa, Pretoria
§Department of Chemistry, Ludwig-Maximilians University, Münich, Germany

(*Received 30 November 2006; revised 17 January 2007; in final form 22 January 2007*)

The potentially terdentate ligand 1-(*S*-methyldithio)-3,5-dimethyl-3-(*S*-methyldithiocarbazato)pyrazoline (H_2mdp) was prepared by the reaction of *S*-methyldithiocarbazate with acetylacetone in an acidic ethanol solution. The neutral complex [TcOCl(mdp)](**1**) was formed by the reaction of (n-Bu_4N)[$TcOCl_4$] with H_2mdp in ethanol at room temperature. Compound **1** has a square-pyramidal geometry with the thiolate, thiocarbonyl and amide donor atoms of the terdentate chelate mdp and chloride forming a square plane, with the oxo oxygen in the apical position.

Keywords: Oxotechnetium(V); Crystal structure; Pyrazoline; Dithiocarbazate

1. Introduction

The coordination chemistry of technetium has received immense interest during the last three decades due to the application of the ^{99m}Tc radionuclide in diagnostic nuclear medicine [1]. Most studies have focused on the +5 oxidation state of the metal, containing the $[TcO]^{3+}$ core, since it is easily obtained by the simple reduction of pertechnetate. Complexes with the $[TcO]^{3+}$ core usually have the distorted octahedral or square-pyramidal geometries with multidentate ligands such as Schiff bases and chelates containing the N_2S_2 donor-atom set [2–6].

We have found that derivatives of dithiocarbazic acids are versatile ligands for the stabilization of the $[TcO]^{3+}$ core. For example, with the bidentate N,S-donor ligands $R_1R_2C{=}N{-}N{=}C(SCH_3)S^-$ (L^1) complexes of the type $[TcOCl(L^1)_2]$ were obtained [7], and with the terdentate $\{(2\text{-}O^-)C_6H_4\}C(CH_3){=}N{-}N{=}C(SCH_3)S^-$ (L^2) the complex

---

*Corresponding author. Email: thomas.gerber@nmmu.ac.za

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701266724

[TcOClL^2] was isolated [8]. Efforts to synthesize the potentially tetradentate ligand H_2ddp were unsuccessful, and the reaction of acetylacetone with two equivalents of *S*-methyldithiocarbazate in ethanol led to the isolation of the pyrazoline derivative H_2mdp.

Reaction of H_2mdp with $[TcOCl_4]^-$ in ethanol led to the production of [TcOCl(mdp)], in which mdp coordinates as a dinegative terdentate chelate *via* a neutral thiocarbonyl, a deprotonated secondary amino nitrogen and a thiolate donor atom.

2. Experimental

^{99}Tc is a weak β-emitter ($E_\beta = 0.292$ keV, t½ = 212000 years). All manipulations were carried out in a laboratory approved for low-level radioactivity. (n-Bu_4N)[$TcOCl_4$] was prepared by a literature method [9]. All solvents used were purified and dried by standard methods. All other chemicals were obtained commercially and were used without further purification. Scientific instrumentation used is the same as reported elsewhere [10]. Infrared data were obtained using KBr disks and ^{1}H NMR spectra were run in $CDCl_3$.

2.1. *Synthesis*

2.1.1. H_2mdp. A mixture of *S*-methyldithiocarbazate (2.5 g, 20 mmol) [8], acetylacetone (1.0 g, 10 mmol) and hydrochloric acid (10 M, 2 drops) were heated under reflux in ethanol (25 cm^3) for 2 h. Cooling to −15°C precipitated a yellow compound, which was filtered off by suction and washed with cold ethanol. Recrystallization from ethanol gave the product as yellow crystals. Yield = 55% (1.7g); m.p. 115°C. Anal. Calcd for $C_9H_{16}N_4S_4$ (%): C, 35.04; H, 5.23; N, 18.16. Found: C, 35.13; H, 5.33; N, 18.47. ^{1}H NMR (δ, ppm): 3.22 (br s, 1H, NH), 3.15 (br s, 1H, NH), 2.75 (d, 1H, H5), 2.69 (d, 1H, H5), 2.53 (s, 3H, C(9)H_3), 2.69 (s, 3H, C(2)H_3), 2.06 (s, 3H, C(7)H_3), 1.84 (s, 3H, C(4)H_3).

2.1.2. [TcOCl(mdp)] (1). The ligand H_2mdp (33 mg, 107 mmol) in 10 cm^3 ethanol was added to (n-Bu_4N)[$TcOCl_4$] (50 mg, 100 mmol) in 5 cm^3 ethanol, and the mixture was stirred for 30 min at room temperature. A dark brown solution formed with the concomitant formation of a brown precipitate, which was isolated by suction filtration and washed with diethyl ether. The precipitate was dissolved in dichloromethane and layered with n-hexane. After two days at room temperature dark brown crystals were collected, and they were washed with hexane and dried in air. Yield = 59% (27 mg); m.p. 208°C. Anal. Calcd for $C_9H_{14}N_4S_4ClOTc$: C, 23.65; H, 3.09; N, 12.70. Found: C, 23.83; H, 3.21; N, 12.26. Infrared (cm^{-1}): ν(Tc=O) 940, ν(C=N) 1630, ν(C=S) 1145. ^{1}H NMR (δ, ppm): 4.17 (d, 1H, H5), 3.44 (d, 1H, H5), 2.89 (s, 3H, C(9)H_3), 2.64 (s, 3H, C(2)H_3), 2.26 (s, 3H, C(7)H_3), 1.63 (s, 3H, C(4)H_3).

2.2. *X-ray crystallography*

X-ray diffraction studies on **1** were performed at 200(2) K using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods [11] and refined using full-matrix least-squares with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms. All calculations were done with the program SHELX-97 [12]. Further details are given in table 1, with selected bond lengths and angles in table 2.

Table 1. Crystal data and structure refinement for **1**.

Chemical formula	$C_9H_{14}N_4S_4ClOTc$
Formula weight	357.95
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	12.9063 (2)
b	9.3039(1)
c	14.3059 (2)
β	101.502(1)
Volume (Å^3)	1683.34(4)
Z	4
Density (Calcd) (Mg m^3)	1.803
Absorption coefficient (mm^{-1})	1.509
F(000)	912
Crystal size (mm)	0.05 × 0.09 × 0.15
θ range for data collection (°)	3.2–27.5
Index ranges	$-16 \le \le h \le 16$, $-11 \le k \le 12$, $-18 \le \ell \le 18$
Reflections measured	7018
Independent/observed reflections	3854/3178
Data/parameters	3854/237
Goodness-of-fit on F^2	1.05
Final R indices $[I > 2\sigma(I)]$	0.0305, $wR_2 = 0.0795$
Largest diff. peak and hole (e Å^{-3})	0.87, −0.71

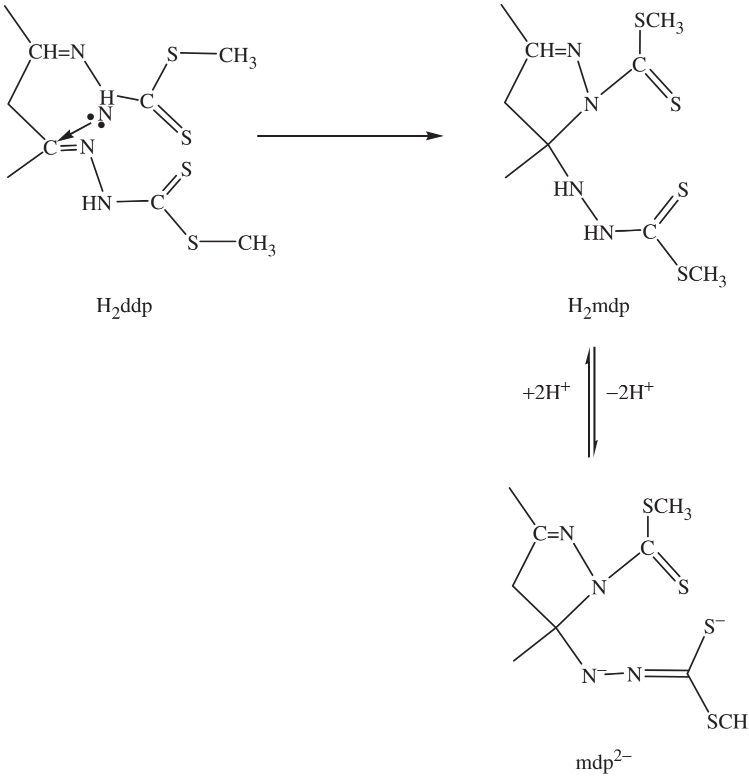
Table 2. Selected bond lengths (Å) and angles (°) for **1**.

1			
Tc–O	1.661(2)	Tc–N(2)	1.949(2)
Tc–S(1)	2.280(1)	Tc–S(3)	2.334(1)
Tc–Cl	2.386(1)	C(1)–S(1)	1.749(3)
C(1)–N(1)	1.281(4)	C(8)–S(3)	1.718(3)
C(8)–N(4)	1.316(3)	N(1)–N(2)	1.396(3)
C(6)–N(3)	1.276(3)	N(3)–N(4)	1.416(3)
C(5)–C(6)	1.483(4)	C(3)–N(4)	1.503(3)
C(2)–S(2)	1.803(5)	C(3)–N(2)	1.473(3)
O–Tc–Cl	105.74(7)	O–Tc–N(2)	104.73(9)
O–Tc–S(1)	111.45(8)	O–Tc–S(3)	113.96(8)
S(1)–Tc–N(2)	81.20(6)	N(2)–Tc–S(3)	90.59(6)
C(1)–S(1)–Tc	96.54(9)	C(8)–S(3)–Tc	112.60(9)
C(1)–N(1)–N(2)	113.2(2)	N(1)–N(2)–C(3)	110.1(2)
N(4)–C(3)–C(5)	98.9(2)	S(3)–C(8)–N(4)	124.6(2)
N(1)–C(1)–S(2)	121.0(2)	C(6)–N(3)–N(4)	107.1(2)

3. Results and discussion

3.1. *Description of the structure*

The structure of **1** is illustrated in figure 1. It consists of a discrete, monomeric, neutral oxotechnetium(V) complex [TcOCl(mdp)] packed with no intermolecular contacts shorter than the sum of the van der Waal's radii. The coordination geometry around the technetium is square-pyramidal; the S_2N-donor atoms of the terdentate dinegative mdp ligand lie on the equatorial plane along with the chloride, with the oxo oxygen at the apical position. The equatorial plane is strictly planar, and the technetium atom is displaced from this plane by 0.697(1) Å towards the oxo oxygen atom. This displacement leads to the non-orthogonal angles O–Tc–S(1) = 111.45(8)°, O–Tc–Cl = 105.74(7)°, O–Tc–N(2) = 104.73(9)° and O–Tc–S(3) = 113.96(8)°. The two 'bite' angles of mdp, S(1)–Tc–N(2) = 81.20(6)° and N(2)–Tc–S(3) = 90.59(6)°, contribute considerably to the distortion of the pyramid. The dithiocarbazate parts of the ligand backbone are reasonably planar, with the torsion angles C(1)N(1)N(2)C(3) = 178.0(2)°, C(9)S(4)C(8)N(4) = −180.0(2)° and N(3)N(4)C(8)S(3) = −177.2(2)°.



The existence of the mdp ligand in the dianionic thiocarbonyl-amido-thiolate form is manifested by the intraligand bond angles and metal-donor atom bond distances. The bond angle N(1)–N(2)–C(3) = 110.1(2)° is indicative of the sp^3 hybridization of the N(2) atom, and the Tc–N(2) bond length of 1.949(2) Å is typical of the metal amide bond. Tc–N(amine) bond lengths typically occur in the range 2.12–2.22 Å [13, 14]. The bond distances C(3)–N(2) = 1.473(3) Å and N(1)–N(2) = 1.396(3) Å are typical values of

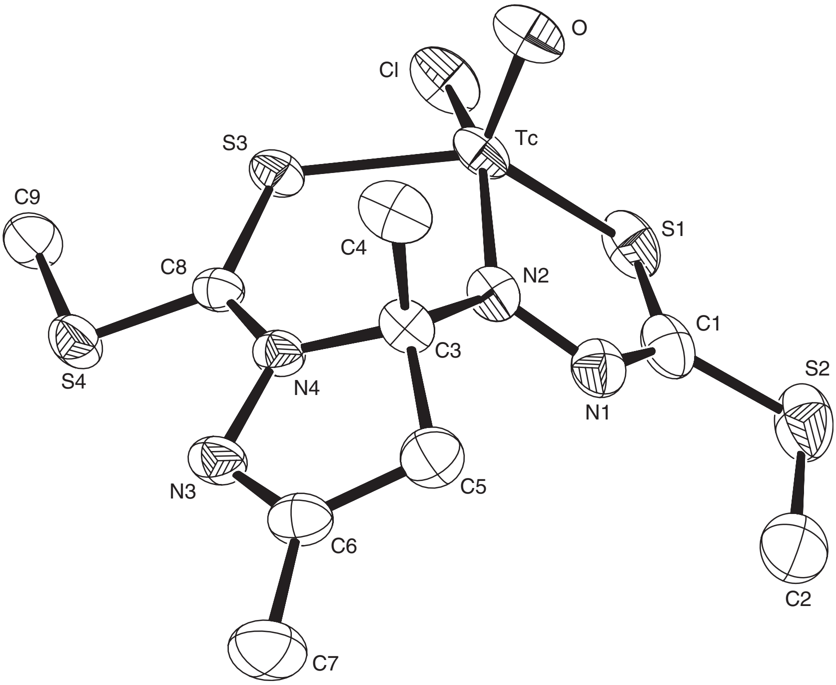


Figure 1. An ORTEP view of [TcOCl(mdp)] (**1**) showing the atom labelling scheme and 40% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

single bonds. The C(1)–N(1) bond is double [1.281(4) Å], and C(1)–S(1) is a single bond [1.749(3) Å]. The Tc–S(1) bond length of 2.280(1) Å falls within the range normally observed for technetium(V)-thiolate sulfur bonds [15]. On the other hand, the Tc–S(3) bond length [2.334(1) Å] is significantly longer, and intimates the coordination of a neutral thiocarbonyl sulfur atom S(3). Also, the C(8)–S(3) bond length [1.718(3) Å] is considerably shorter than the C(1)–S(1) one [1.749(3) Å], and shows the double bond character of this bond. The coordinated mdp ligand thus carries negative charges on atoms S(1) and N(2), with S(3) being a neutral donor atom. Although steric and angular constraints of the mdp ligand play a role, there is an unusually large difference in the bond angles Tc–S(1)–C(1) = 96.54(9)° and Tc–S(3)–C(8) = 112.60(9)°, indicating differences in the hybridization of the two sulfur donor atoms. The Tc = O [1.661(2) Å] and Tc–Cl [2.386(1) Å] are typical for these bonds in square-pyramidal technetium(V) complexes [2–8].

In the pyrazole ring the only double bond is N(3)–C(6) = 1.276(3) Å. The N(3)–C(6)–C(7) = 121.1(3)° and N(4)–C(3)–C(4) = 108.5(2)° bond angles show sp^2 and sp^3 hybridization of the C(6) and C(3) carbons respectively. The ring approximates an envelope conformation, with the N(1) atom involved in an intramolecular hydrogen bond to C(5)H [N(1) · C(5)H(5A) = 2.645(4) Å].

3.2. *Synthesis*

Attempts to synthesize the potentially tetradentate S_2N_2-donor ligand H_2ddp by the reaction of acetylacetone with two equivalents of *S*-methyldithiocarbazate in ethanol were unsuccessful, and instead led to the isolation of the potentially terdentate pyrazoline derivative H_2mdp. General method for the synthesis of pyrazoline derivatives include the reaction of hydrazine derivatives with α,β-unsaturated carbonyls [16], and the 1,3-dipolar cyclo-addition reaction of α,β-unsaturated esters, amides or nitriles with diazomethane or trimethylsilyldiazomethane [17].

The $[TcOCl_4]^-$ anion is a common starting material for the preparation of technetium(V) complexes, and it reacts rapidly and under mild conditions with H_2mdp in ethanol to give **1** in good yield. The complex is insoluble in water and non-polar solvents, and is weakly soluble in DMF, DMSO, acetonitrile and chloroform.

3.3. *Spectroscopic characterization*

In the infrared spectrum of **1** the Tc=O stretching frequency appears as a sharp strong band at 940 cm^{-1}, which falls in the lower end of the range [930–960 cm^{-1}] observed for this vibration in square-pyramidal technetium(V) complexes [3–8]. The stretching frequencies of the uncoordinated C=N groups of mdp appear as a broad strong peak around 1630 cm^{-1}. A peak of medium intensity at 1145 cm^{-1} is assigned to C(8) = S(3), and there are no peaks in the region 2550–2650 cm^{-1} that can be ascribed to ν(S–H). The four methyl groups in **1** are clearly distinguishable as three-proton singlets in the NMR spectrum in the range 1.60–2.90 ppm, and the two geminal H(5) protons, one which is involved in a hydrogen bond with N(1), appears as two one-proton doublets at 3.44 and 4.17 ppm.

Examples of metal coordination compounds of pyrazolines are scarce in the literature. Results obtained from the reaction of the pyrazoline, prepared from acetylacetone and 4-methyl-3-thiosemicarbazide, with Cu(II) and Zn(II) suggest that the ring undergoes ring-opening back to the *bis*-thiosemicarbazone upon coordination to the transition metal, accompanied by oxidation of the central methylene group when the reactions are carried out in air [19].

Supplementary material

CCDC-621678 contains the crystallographic data for **1**. These data can be obtained at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

References

[1] W.A. Volkert, T.J. Hoffman. *Chem. Rev.*, **99**, 2269 (1999).
[2] T.I.A. Gerber, H.J. Kemp, J.G.H. du Preez, G. Bandoli, A. Dolmella. *Inorg. Chim. Acta*, **202**, 191 (1992).
[3] S.Z. Lever, K.E. Baidoo, A. Mahmood. *Inorg. Chim. Acta*, **176**, 184 (1990).
[4] A. Davison, A. Jones, C. Orvig, M. Sohn. *Inorg. Chem.*, **20**, 1629 (1981).
[5] G. Bandoli, U. Mazzi, B.E. Wilcox, S. Jurisson, E. Deutsch. *Inorg. Chim. Acta*, **95**, 217 (1984).
[6] G. Grummon, R. Rajagopalan, G.J. Palenik, A.F. Kosiol, D.L. Nosco. *Inorg. Chem.*, **34**, 1764 (1995).
[7] J.G.H. du Preez, T.I.A. Gerber, O. Knoesen. *Inorg. Chim. Acta*, **132**, 241 (1987).

[8] J.G.H. du Preez, T.I.A. Gerber, O. Knoesen. *J. Coord. Chem.*, **16**, 285 (1987).
[9] F.A. Cotton, A. Davison, V.W. Day, L.D. Gage, H.S. Trop. *Inorg. Chem.*, **18**, 3024 (1979).
[10] T.I.A. Gerber, E. Hosten, P. Mayer, Z.R. Tshentu. *J. Coord. Chem.*, **59**, 243 (2006).
[11] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giocovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Crystallogr.*, **32**, 115 (1999).
[12] G.M. Sheldrick. *SHELX-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[13] A.G. Jones, B.V. DePamphilis, A. Davison. *Inorg. Chem*, **20**, 1617 (1981).
[14] A. Marchi, L. Marvelli, M. Cattabriga, R. Rossi, M. Neves, V. Bertolasi, V. Ferretti. *J. Chem. Soc., Dalton Trans.*, **1937** (1999).
[15] J. Baldas, J. Bonnyman, G.A. Williams. *Inorg. Chem.*, **25**, 150 (1986).
[16] F.M. Abd El Latif, A.S. Maghraby, M.A. Barsy, M.Z.A. Badr, D. Dopp. *Coll. Czec. Chem. Comm.*, **59**, 247 (1994).
[17] G.A. Whitlock, E.M. Carreira. *Helv. Chim. Acta*, **83**, 2007 (2000).
[18] J.H. Ahn, H. Kim, S.K. Kang, J.D. Ha, E.K. Yum, D.K. An, J. Choi, S.S. Kim. *Bull. Korean Chem. Soc.*, **26**, 467 (2005).
[19] S.C. Davies, M.C. Durrant, D.L. Hughes, A. Pezeshk, R.L. Richards. *J. Chem. Res.*, **3**, 100 (2001).