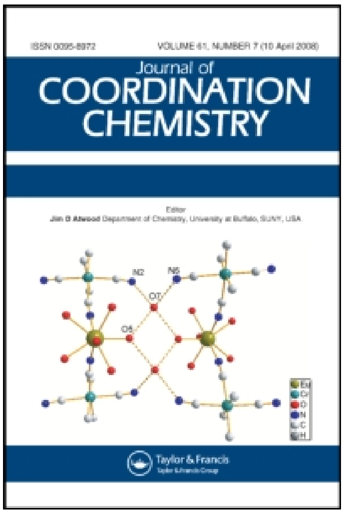

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Technetium(V) complexes of dithiocarbazate derivatives

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The neutral complex [TcOCl(hdc)] (**1**) (hdc = *S*-methyl-β-*N*-(2-hydroxyphenylethylidene) dithiocarbazate) was prepared by reaction of (n-Bu_4N)[$TcOCl_4$] with an equimolar amount of H_2hdc in ethanol/dichloromethane at room temperature. With a fourfold mol excess of H_2hdc in methanol/acetone, the '3 + 2' complex [TcO(hdc)(adc)] (**2**) (adc = *S*-methyl-β-*N*-(prop-2-ylidene)dithiocarbazate) was isolated. Adc was formed by ketone exchange between solvent acetone and the hydroxyacetophenone fragment of hdc. Compounds **1** and **2** were characterized by infrared spectroscopy, ^{1}H NMR spectrometry, elemental analysis and single-crystal X-ray crystallography. Complex **1** has square-pyramidal geometry with the SNO-donor atoms of the tridentate chelate hdc and chloride forming a square plane, with the oxo oxygen atom in the apical position. Complex **2** has a distorted octahedral geometry, with an S_2N_2 donor set in the equatorial plane and the oxo and phenolate oxygen atoms in *trans* apical positions.

Keywords: Oxotechnetium(V); Crystal structures; Dithiocarbazate derivatives

1. Introduction

Current interest in the coordination chemistry of technetium is due to the application of the ^{99m}Tc radionuclide in diagnostic imaging agents in nuclear medicine [1]. Also, the easy generation of ^{99m}Tc from the readily available ^{99}Mo/^{99m}Tc generator set [2] has made its use in radiopharmaceuticals very convenient and practical. The element displays diversified chemical behaviour, with oxidation states ranging from -1 to $+7$. Since the product of the radionuclide generator is pertechnetate, most studies have focussed on technetium(V) complexes containing the $[TcO]^{3+}$ core, which is easily obtained by reduction of $[TcO_4]^-$. Complexes containing the $[TcO]^{3+}$ core usually have square-pyramidal or distorted octahedral geometries, and contain multidentate ligands such as Schiff bases and tetradentate chelates containing the N_2S_2 donor atom set [3–7]. One approach to develop stable technetium(V) complexes has been the '3 + 1' concept of ligand permutation [8], which is based on the ligation of a dinegative tridentate chelate in combination with a monodentate uninegative thiolate to produce a

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square-pyramidal oxotechnetium(V) complex. However, these '3 + 1' complexes were found to be relatively unstable *in vitro* and *in vivo* [9]. Kinetic stability was improved somewhat by '3 + 2' six-coordinated oxotechnetium(V) complexes [10].

The number and diversity of nitrogen-sulfur chelating agents used in the preparation of complexes of technetium, and its third row congener rhenium, have increased markedly during the last few years, and derivatives of dithiocarbazic acids have also been used to stabilize the $[MO]^{3+}$ (M = Tc, Re) core [2, 3, 11]. Here, we report the synthesis and structures of two oxotechnetium(V) complexes, square-pyramidal [TcOCl(hdc)] and the '3 + 2' distorted octahedral [TcO(hdc)(adc)] (hdc = *S*-methyl-β-*N*-(2-hydroxyphenylethylidene)dithiocarbazate; adc = *S*-methyl-β-*N*-(prop-2-ylidene) dithiocarbazate).

2. Experimental

^{99}Tc is a weak β-emitter ($E_\beta = 0.292$ MeV, $t_{1/2} = 212{,}000$ years). All manipulations were carried out in a laboratory approved for low-level radioactivity. $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ was prepared by a literature method [13]. H_2hdc was synthesized as reported earlier [14]. All solvents were purified and dried by standard methods. All other chemicals were obtained commercially and used without further purification. Scientific instrumentation used is the same as reported elsewhere [15]. IR data were obtained using KBr disks and ^{1}H NMR spectra were run in $CDCl_3$.

2.1. *Synthesis*

2.1.1. [TcOCl(hdc)] (1). To an ethanol solution (10 cm^3) of H_2hdc (35 mg, 146 µmol) was added dropwise 70 mg of $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ (140 µmol) in 10 cm^3 of ethanol, and the mixture was stirred for 60 min at room temperature. The colour of the solution gradually turned brown, and after stirring was stopped, the solution was filtered and left to evaporate slowly at room temperature. After two days dark orange crystals were collected by filtration, washed with cold ethanol and *n*-hexane, and dried under vacuum. Yield 72% (29 mg), m.p. 158°C. Anal. Calcd for $C_{10}H_{10}N_2O_2S_2Cl$ Tc (%): C, 30.89; H, 2.59; N, 7.21. Found: C, 31.01; H, 2.64; N, 7.23. IR (cm^{-1}): ν(Tc=O) 985; ν(C=N) 1600, 1525. ^{1}H NMR (δ, ppm): 8.37 (d, 1H, *H*2), 7.69 (t, 1H, *H*4), 7.52 (d, 1H, *H*5), 7.20 (t, 1H, *H*3), 2.36 (s, 3H, C(8)H$_3$), 2.82 (s, 3H, C(10)H$_3$). UV-Vis{$CHCl_3$, $\lambda(\varepsilon, M^{-1}\,cm^{-1})$}: 285 (18500), 352 (8900), 457 (3100).

2.1.2. [TcO(hdc)(adc)] (2). A mixture of $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$ (50 mg, 100 µmol) in 5 cm^3 of methanol and 96 mg of H_2hdc (400 µmol) in 5 cm^3 of acetone was stirred at room temperature for 30 min. The colour of the solution changed to brown, with the concomitant formation of a fine brown precipitate. The solution was reduced in volume to 30 cm^3, filtered, and the precipitate dissolved in dichloromethane and layered with *n*-hexane. After 48 h at room temperature dark brown crystals were collected by filtration, washed with cold methanol and *n*-hexane, and dried under vacuum. Yield 64% (32 mg), m.p. 213°C. Anal. Calcd for $C_{15}H_{19}N_4O_2S_4$Tc (%): C, 35.01; H, 3.72;

N, 10.91. Found: C, 35.12; H, 3.66; N, 10.72. IR (cm^{-1}): ν(Tc=O) 930; ν(C=N) 1568, 1522; ν(Tc–N) 436; ν(Tc–O) 376; ν(Tc–S) 301. ^{1}H NMR (δ, ppm): 7.76 (d, 1H, *H*7), 7.32 (t, 1H, *H*9), 6.99 (t, 1H, *H*8), 6.54 (d, 1H, *H*10), 3.13 (s, 3H, C(13)H_3), 2.75 (s, 3H, C(15)H_3), 2.64 (s, 3H, C(2)H_3), 2.02 (s, 3H, C(4)H_3), 1.80 (s, 3H, C(5)H_3). Electronic spectrum {$CHCl_3$, $\lambda(\varepsilon, M^{-1}cm^{-1})$}: 279 (17500), 335sh, 463sh. Conductivity (DMF, 10^{-3} M, 25°C): 18 $\mu S\,cm^{-1}$.

2.2. *X-ray crystallography*

X-ray diffraction studies of **1** and **2** were performed at 200(2) K using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods [16] and refined using full-matrix least-squares with all non-hydrogen atoms anisotropic and hydrogens included in calculated positions, riding on their carrier atoms. All calculations were done with the program SHELX-97 [17]. Further details are given in table 1, with selected bond lengths and angles in table 2.

3. Results and discussion

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

Table 1. Crystal data and structure refinement for **1** and **2**.

Chemical formula	$C_{10}H_{10}N_2O_2S_2ClTc$	$C_{15}H_{19}N_4O_2S_4Tc$
Formula weight	388.78	514.60
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
Unit cell dimensions		
a (Å)	9.0652(2)	14.6408(1)
b (Å)	14.5229(2)	14.9279(1)
c (Å)	20.3103(4)	20.5425(2)
α (°)		111.0294(7)
β (°)		102.2485(4)
γ (°)		92.0712(4)
Volume (Å^3)	2673.91(9)	4064.13(6)
Z	8	8
Density (Calcd) ($Mg\,m^{-3}$)	1.931	1.682
Absorption coefficient (mm^{-1})	1.582	1.137
F(000)	1536	2080
Crystal size (mm^3)	0.01 × 0.04 × 0.07	0.08 × 0.13 × 0.18
θ range for data collection (°)	3.3–27.5	3.2–27.5
Index ranges	$-11 \le h \le 11$, $-18 \le k \le 18$, $-26 \le l \le 26$	$-19 \le h \le 19$, $-19 \le k \le 19$, $-26 \le l \le 26$
Reflections measured	5727	33821
Independent/observed reflections	3057/2270	18340/14813
Data/parameters	3057/165	18340/937
Goodness-of-fit on F^2	1.06	1.03
Final *R* indices [$I > 2\sigma(I)$]	0.0308, $wR_2 = 0.0711$	0.0336, $wR_2 = 0.0871$
Largest diff. peak and hole (e Å^{-3})	0.69, −0.63	0.80, −0.92

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

1			
Tc–O(2)	1.641(2)	Tc–O(1)	1.956(2)
Tc–S(1)	2.2536(9)	Tc–N(1)	2.054(2)
Tc–Cl	2.3364(8)	N(1)–N(2)	1.412(3)
C(7)–N(1)	1.322(3)	N(2)–C(9)	1.287(4)
C(1)–O(1)	1.347(3)	S(1)–C(9)	1.759(3)
O(2)–Tc–Cl	106.16(6)	O(2)–Tc–O(1)	116.20(8)
O(2)–Tc–S(1)	110.11(7)	O(2)–Tc–N(1)	105.48(8)
N(1)–N(2)–C(9)	113.4(2)	N(2)–N(1)–C(7)	113.0(2)
N(1)–C(7)–C(6)	120.7(2)	S(1)–Tc–N(1)	81.76(6)
C(9)–S(1)–Tc	97.8(1)	N(1)–Tc–O(1)	85.79(8)
2			
Tc–O(2)	1.666(2)	Tc–O(1)	2.007(2)
Tc–S(1)	2.310(1)	Tc–S(3)	2.327(1)
Tc–N(2)	2.246(2)	Tc–N(4)	2.154(2)
N(2)–C(3)	1.290(4)	C(1)–N(1)	1.282(4)
C(1)–S(1)	1.762(3)	C(14)–S(3)	1.756(3)
N(3)–C(14)	1.288(4)	N(4)–C(12)	1.309(3)
O(1)–C(6)	1.337(3)	N(1)–N(2)	1.413(3)
O(2)–Tc–S(1)	104.4(1)	O(2)–Tc–S(3)	99.6(1)
O(2)–Tc–N(2)	83.6(1)	O(2)–Tc–N(4)	94.8(1)
O(1)–Tc–O(2)	156.5(1)	Tc–O(1)–C(6)	122.0(2)
S(1)–Tc–S(3)	92.50(3)	N(2)–Tc–N(4)	107.1(1)
C(1)–N(1)–N(2)	115.0(2)	O(1)–Tc–N(4)	78.2(8)
N(4)–Tc–S(3)	78.5(6)	S(1)–Tc–N(2)	80.8(1)

an equimolar amount of H_2hdc in ethanol to form the stable dark red complex [TcOCl(hdc)] (**1**). However, in methanol/acetone, $[TcOCl_4]^-$ reacts with four equivalents of H_2hdc to produce the '3 + 2' complex [TcO(hdc)(adc)] (**2**). The hdc chelate participates in a tautomeric equilibrium in solution and acts as a tridentate dianionic S^-,N,O^- ligand [14], by coordination of the phenolate oxygen, thiolate sulfur and imino nitrogen atoms. The ligand adc is formed by ketone exchange between solvent acetone and the hydroxyacetophenone fragment of hdc. This exchange possibly occurs after coordination of a second molecule of H_2hdc, since the process will be promoted by the dissociated protons of the H_2hdc ligands. In fact, this exchange can be prevented in the absence of acetone, and the complex [ReO(hdc)(Hhdc)] was synthesized by the reaction of $[ReOCl_4]^-$ with two equivalents of H_2hdc in dichloromethane [18]. Here the Hhdc ligand acts as a bidentate N,S^- chelate with an uncoordinated OH group. Complexes **1** and **2** are insoluble in water and non-polar solvents, and are weakly soluble in DMF, acetonitrile, DMSO and chloroform. They are non-electrolytes in DMF.

In the IR spectra of **1** and **2** Tc = O stretching frequencies appear as sharp strong bands at 985 and 930 cm^{-1}, respectively. The relatively high value for **1** is typical of a square pyramidal complex of technetium(V), with a vacant coordination site *trans* to the oxo oxygen [19]. In addition, the value of ν(Tc=O) for **2** falls within the range observed for octahedral technetium(V) complexes with a phenolate oxygen *trans* to the oxo group [20]. The stretching frequency of the non-coordinated C=N group of hdc in **1** appears at 1600 cm^{-1}, with the coordinated C=N group at 1525 cm^{-1}. In **2** these values are 1568 and 1522 cm^{-1}, respectively. The presence of the coordinated chloride

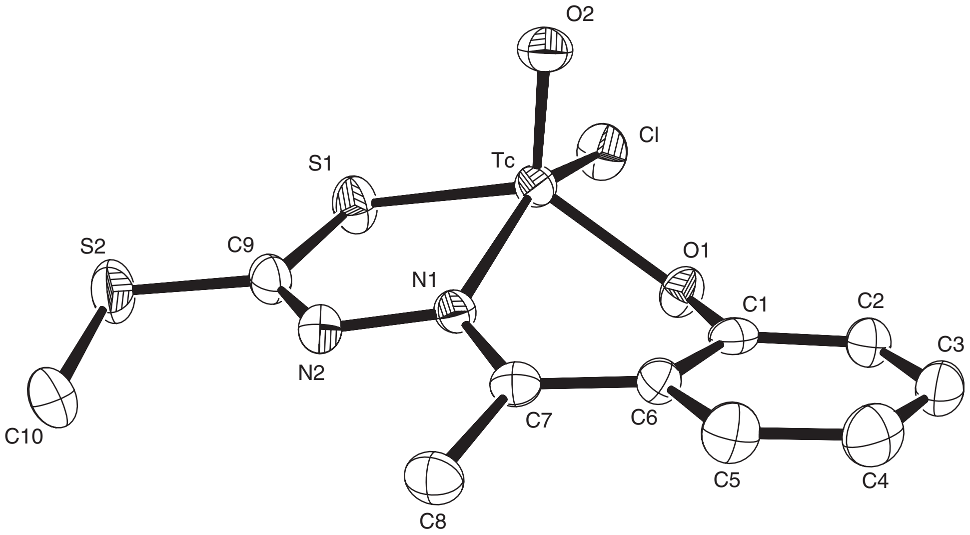

Figure 1. An ORTEP view of [TcOCl(hdc)] (**1**) showing the atom labelling scheme and 40% probability ellipsoids.

in **1** is established by ν(Tc–Cl) at 315 cm^{-1}, and ν(C–O) appears at 1229 cm^{-1}. The latter frequency occurs at 1252 cm^{-1} in **2**, thereby implying a weaker Tc–O bond than in **1**.

The ^1H NMR spectra of both **1** and **2** are sharp and well-resolved, and illustrate the diamagnetism of the complexes. Signals of the ring protons of the hdc chelate in **1** are shifted markedly downfield relative to the corresponding proton signals in complex **2**. Also, as expected, the singlet signals of the methyl protons $CH_3C{=}N$ appear further downfield than the signals of the methyl groups attached to the sulfur atoms. There are no signals that can be ascribed to NH and OH in the spectra, illustrating the tridentate dianionic and bidentate monoanionic coordination modes of hdc and adc, respectively, in the complexes.

The structure of **1** is illustrated in figure 1. It consists of a discrete, monomeric and neutral oxotechnetium(V) complex [TcOCl(hdc)] packed with no intermolecular contacts shorter than the sum of van der Waals radii. The coordination geometry around technetium is square pyramidal; the SNO-donor atoms of the terdentate dinegative hdc ligand lie on the equatorial plane along with chloride, with the oxo O(2) at the apical position. The equatorial plane is strictly planar, and the technetium atom is displaced from this plane by 0.710(1) Å towards the oxo oxygen atom. This displacement leads to the non-orthogonal angles O(2)–Tc–S(1) = 110.11(7)°, O(2)–Tc–N(1) = 105.48(8)°, O(2)–Tc–O(1) = 116.20(8)° and O(2)–Tc–Cl = 106.16(6)°. The two 'bite' angles of hdc, S(1)–Tc–N(1) = 81.76(6)° and N(1)–Tc–O(1) = 85.79(8)°, contribute considerably to the distortion of the pyramid. The S(1)C(9)N(2)N(1)C(7)C(6) fragment of the chelate is reasonably planar, with torsion angles S(1)C(9)N(2)N(1) = 1.1(3)° and N(2)N(1)C(7)C(6) = 178.4(2)°. The backbone of the hdc chelate is reasonably planar, with torsion angles S(1)C(9)N(2)N(1) = 1.1(3)°, N(2)N(1)C(7)C(6) = 178.4(2)° and C(7)C(6)C(1)O(1) = 2.0(4)°. Coordination of the sp^2-hybridized N(1) decreases the N(2)–N(1)–C(7) bond angle to 113.0(2)°. The existence of the hdc ligand in the dianionic thio-enolate form is manifested by the N(2) = C(9) double bond,

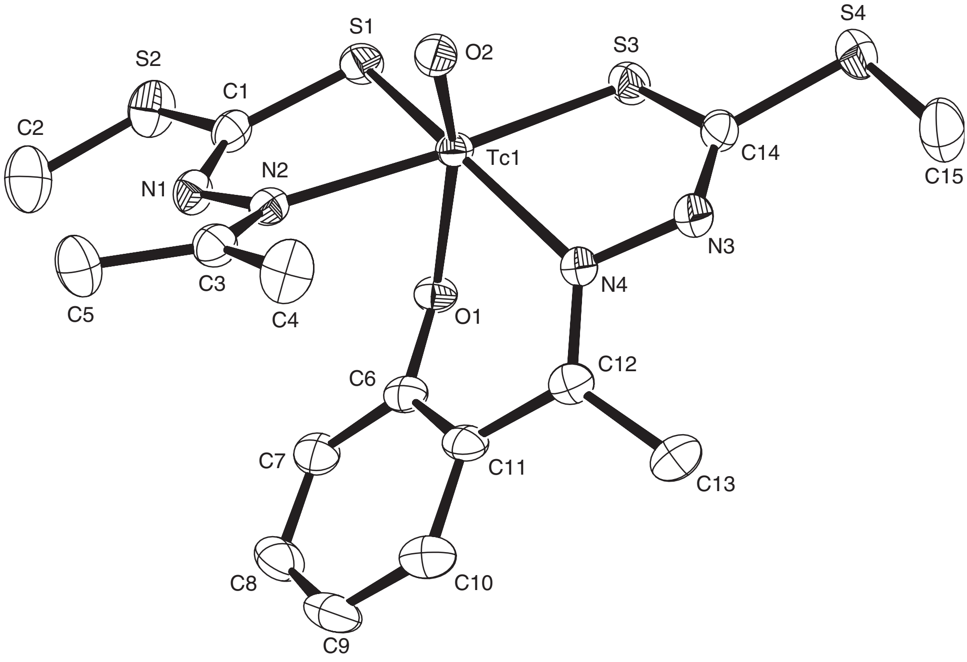

Figure 2. Molecular structure and atom numbering scheme for [TcO(hdc)(adc)] (**2**). Hydrogen atoms have been omitted for clarity.

equal to 1.287(4) Å, and the C(9)–S(1) single bond, equal to 1.759(3) Å. The Tc = O distance of 1.641(2) Å implies some triple bond character and is typical of neutral square pyramidal oxotechnetium(V) complexes [19].

In **2**, four molecules of the compound exist in the asymmetric unit. These have different orientations in the lattice, but they have comparable bond distances and angles. The molecular structure of the complex is shown in figure 2, and selected average bond lengths and angles of the four molecules of **2** are listed in table 2. The coordination geometry around technetium is highly distorted octahedral; the sulfur and nitrogen atoms of the uninegative bidentate ligand adc and dinegative tridentate hdc lie on the equatorial plane, with the phenolate O(1) of the tridentate ligand *trans* to the O(2) oxo atom in apical positions. The O(1)–Tc–O(2) axis is non-linear [156.5(1)°], and technetium is displaced from the mean equatorial plane by 0.036(1) Å towards O(2), resulting in the nonorthogonal angles O(2)–Tc–S(1) = 104.4(1)°, O(2)–Tc–S(3) = 99.5(1)°, O(2)–Tc–N(2) = 84.5(1)° and O(2)–Tc–N(4) = 95.2(1)°. The two 'bite' angles of hdc, O(1)–Tc–N(4) = 78.23(8)° and N(4)–Tc–S(3) = 78.53(6)°, are practically equal and considerably smaller than those in **1**. The 'bite' angle of adc [S(1)–Tc–N(2)] equals 80.82(6)°. In the $N_2O_2S_2$ polyhedron the technetium atom is 1.285 Å from the O(1)N(4)S(3) plane and 1.124 Å from the O(2)N(2)S(1) one, the dihedral angle being 13.46°. Dihedral angles N(2)–N(1)–C(1)–S(1) and N(4)–N(3)–C(14)–S(3) equal 0.2(4) and 1.7(3)°, respectively. In adc the bond angle C(1)–N(1)–N(2) = 115.0(2)°, and double bonds exist between C(1) and N(1) [1.282(4) Å] and C(3) and N(2) [1.290(4) Å]. In hdc the two double bonds N(3)–C(14) = 1.288(4) Å and N(4)–C(12) = 1.309(3) Å and the C(14)–S(3) single bond [1.756(3) Å] illustrate the dianionic nature of the ligand. The axial Tc–O(1) bond [2.007(2) Å] is, as expected, longer than in **1** [1.956(2) Å], illustrating the *trans* influence of the oxo group. There are significant differences in the distances between technetium and the equatorial donor atoms of the two chelates: Tc–S(1) = 2.310(1), Tc–S(3) = 2.327(1), Tc–N(2) = 2.246(2), Tc–N(4) = 2.154(2) Å. These differences can be ascribed to steric effects and to different electronic properties of the substituents in the dithiocarbazate backbones of the chelates.

The rhenium analogues of complexes **1** and **2** were recently reported in the literature [18]. The complex [ReOCl(hdc)] was synthesized from (n-Bu$_4$N)[ReOCl$_4$] and an equimolar amount of H$_2$hdc in dichloromethane, and the molecular structure of the iodo analogue shows square pyramidal geometry around the metal. [ReO(hdc)(adc)] was prepared from Na[ReO(gluconate)$_2$] and equimolar quantities of H$_2$hdc and Hadc in methanol/water [18]. Ketone exchange between acetone and the salicylaldehyde substituent of H$_2$hdc was also observed in the latter synthesis.

Supplementary data

CCDC-609357 (for **1**) and CCDC-609358 (for **2**) contain crystallographic data for this paper. 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; email: deposit@ccdc.cam.ac.uk].

References

[1] W.A. Volkert, T.J. Hoffman. *Chem. Rev.*, **99**, 2269 (1999).
[2] J. Steigman, W.C. Eckelman. *The Chemistry of Technetium in Medicine*, Nuclear Science Publications NAS-NS-3204, National Academy Press, Washington DC (1992).
[3] G. Bandoli, U. Mazzi, B.E. Wilcox, S. Jurisson, E. Deutsch. *Inorg. Chim. Acta*, **95**, 217 (1984).
[4] T.I.A. Gerber, H.J. Kemp, J.G.H. du Preez, G. Bandoli, A. Dolmella. *Inorg. Chim. Acta*, **202**, 191 (1992).
[5] G. Grummon, R. Rajagopalan, G.J. Palenik, A.F. Kosiol, D.L. Nosco. *Inorg. Chem.*, **34**, 1764 (1995).
[6] S.Z. Lever, K.E. Baidoo, A. Mahmood. *Inorg. Chim. Acta*, **176**, 184 (1990).
[7] A. Davison, A. Jones, C. Orvig, M. Sohn. *Inorg. Chem.*, **20**, 1629 (1981).
[8] X. Chen, F.J. Femia, J.W. Babich, J. Zubieta. *Inorg. Chim. Acta*, **307**, 154 (2000).
[9] B. Nock, T. Maina, D. Yannoukakos, I.C. Pirmettis, M.S. Papadopoulos, R. Chiotellis. *J. Med. Chem.*, **42**, 1066 (1999).
[10] X. Chen, F.J. Femia, J.W. Babich, J. Zubieta. *Inorg. Chim. Acta*, **307**, 149 (2000).
[11] J.G.H. du Preez, T.I.A. Gerber, O. Knoesen. *Inorg. Chim. Acta*, **130**, 9 (1987).
[12] F. Mevellec, A. Roucoux, N. Noiret, H. Patin. *J. Chem. Soc., Dalton Trans.*, 3603 (2001).
[13] F.A. Cotton, A. Davison, V.W. Day, L.D. Gage, H.S. Trop. *Inorg. Chem.*, **18**, 3024 (1979).
[14] J.G.H. du Preez, T.I.A. Gerber, O. Knoesen. *J. Coord. Chem.*, **16**, 285 (1987).
[15] T.I.A. Gerber, Z.R. Tshentu, P. Mayer. *J. Coord. Chem.*, **56**, 1357 (2003).
[16] 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).
[17] G.M. Sheldrick. *SHELX-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[18] F. Mevellec, A. Roucoux, N. Noiret, H. Patin. *Inorg. Chim. Acta*, **332**, 30 (2002).
[19] A.G. Jones, B.V. DePamphilis, A. Davison. *Inorg. Chem.*, **20**, 1617 (1981).
[20] J.E. Smith, E.F. Byrne, F.A. Cotton, J.C. Sekutowsky. *J. Am. Chem. Soc.*, **100**, 5571 (1978).