

Fig. 2. View of the unit cell along the *b* axis.  $\text{Ca}^{2+}$  ions are indicated by stippled spheres.

angles about the central C—C bonds are  $\text{O}(1)\text{—C}(1)\text{—C}(2)\text{—O}(3) = 4.1(3)$  and  $\text{O}(5)\text{—C}(4)\text{—C}(3)\text{—O}(4) = 13.0(3)^\circ$ . Other torsion angles not involving H atoms are listed in Table 2.

The  $\text{Ca}^{2+}$  ion is irregularly surrounded by seven O atoms, including those of two water molecules. Details on the Ca coordination and the extensive hydrogen

bonding of this structure are given in Table 2. The packing of the structure is shown in Fig. 2.

We thank P. van der Sluis for growing and supplying the crystals.

#### References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 KROON, J. (1982). *Molecular Structure and Biological Activity*, edited by J. F. GRIFFIN & W. L. DUAX, pp. 151–163. New York: Elsevier Biomedical.  
 KROON, J., DUSENBERG, A. J. M. & PEERDEMAN, A. F. (1984). *Acta Cryst.* **C40**, 645–647.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of England, Cambridge.  
 SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1984). **C40**, 1544–1546

### Oxo[3,3'-(1,3-propanediyl-diimino)bis(3-methyl-2-butanone oximato)](3-)- $N,N',N'',N'''$ ]technetium(V), $[\text{TcO}(\text{C}_{13}\text{H}_{25}\text{N}_4\text{O}_2)]$

BY C. KAY FAIR, D. E. TROUTNER, E. O. SCHLEMPER, R. K. MURMANN AND M. L. HOPPE

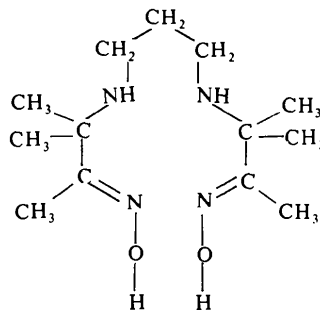
*Department of Chemistry, University of Missouri, Columbia, MO 65211, USA*

(Received 6 February 1984; accepted 10 May 1984)

**Abstract.**  $M_r = 383.4$ , monoclinic, *Pc*,  $a = 6.950(4)$ ,  $b = 11.187(3)$ ,  $c = 11.060(4)$  Å,  $\beta = 104.13(5)^\circ$ ,  $V = 833.8(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.527(1)$  g cm<sup>-3</sup>, *Mo K $\alpha$* ,  $\lambda = 0.7107$  Å,  $\mu = 8.56$  cm<sup>-1</sup>,  $F(000) = 396$ ,  $T = 295(1)$  K, final  $R_F = 2.4\%$  for 2601 unique reflections. The  $\text{Tc}^{\text{V}}$  ion is surrounded by an approximate square pyramid of one multiple-bonded oxygen atom plus four nitrogen atoms from the tetradentate ligand. The distances between the deprotonated N(imino) atoms and the Tc atom [1.917(3), 1.908(3) Å] are much shorter than the N(oxime)—Tc bond distances [2.086(3) and 2.093(4) Å]. The Tc atom is 0.678(1) Å from the  $\text{N}_4$  plane in the direction of the oxo oxygen.

**Introduction.** The family of  $\alpha$ -amine oxime complexes has been studied extensively (e.g. Schlemper & Siripaisarnpipat, 1984) to obtain information about the

resultant intramolecular hydrogen bonds. The propylene-bridged example is shown below.



Upon complexation with a metal, the molecule usually loses one of the hydrogen atoms to form  $[M(\text{pnao-H})]$  with a hydrogen bond between the oxime oxygen atoms.

Table 1. *Positional parameters for non-hydrogen atoms*

$$B_{eq} = \frac{1}{3}[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma) B(1,2) + ac(\cos\beta) B(1,3) + bc(\cos\alpha) B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Tc	0.0000	0.71770 (2)	0.0000	2.115 (4)
O(1)	-0.3216 (5)	0.5476 (3)	-0.1356 (3)	4.41 (8)
O(2)	-0.3383 (5)	0.7430 (3)	-0.2313 (4)	4.36 (8)
O(3)	-0.0930 (5)	0.7709 (3)	0.1158 (3)	3.52 (7)
N(1)	-0.1389 (5)	0.5549 (3)	-0.0605 (3)	2.84 (7)
N(2)	-0.1576 (5)	0.7852 (3)	-0.1714 (3)	2.91 (7)
N(3)	0.2058 (5)	0.6050 (3)	0.0638 (3)	2.97 (7)
N(4)	0.1813 (5)	0.8308 (3)	-0.0409 (3)	2.82 (7)
C(1)	-0.0476 (5)	0.4591 (3)	-0.0091 (4)	2.93 (9)
C(2)	-0.0907 (6)	0.8800 (4)	-0.2132 (4)	2.90 (8)
C(3)	0.1504 (6)	0.4763 (4)	0.0736 (4)	3.24 (9)
C(4)	0.1121 (6)	0.9182 (4)	-0.1418 (4)	3.01 (8)
C(5)	-0.148 (1)	0.3406 (5)	-0.0364 (6)	6.1 (2)
C(6)	-0.2125 (8)	0.9455 (5)	-0.3236 (5)	4.3 (1)
C(7)	0.3009 (8)	0.3945 (5)	0.0309 (5)	4.4 (1)
C(8)	0.1443 (8)	0.4470 (5)	0.2056 (5)	4.7 (1)
C(9)	0.2488 (7)	0.9212 (5)	-0.2321 (4)	4.1 (1)
C(10)	0.0995 (9)	1.0450 (4)	-0.0903 (5)	4.6 (1)
C(11)	0.4144 (6)	0.6341 (5)	0.1178 (4)	3.8 (1)
C(12)	0.3946 (6)	0.8378 (5)	0.0206 (5)	3.8 (1)
C(13)	0.4428 (7)	0.7662 (5)	0.1398 (5)	3.9 (1)

Complexes of Tc–pnao have been prepared recently (Troutner, Volkert, Hoffman & Holmes, 1984) and are under active investigation as possible radiopharmaceuticals for measurement of regional cerebral blood flow. Complexes for this purpose are prepared with 6.0h <sup>99m</sup>Tc at concentrations of ~10<sup>-8</sup> mol dm<sup>-3</sup>. Characterization by radiochemical methods indicated the complexes were neutral and lipophilic. In order to elucidate the structure of the uncharged species, the complex was prepared in milligram quantities using the longer lived isomer, 0.21 My <sup>99m</sup>Tc.

**Experimental.** Crystals obtained by scaling up the tracer level preparative method (Troutner *et al.*, 1984) and recrystallization by slow evaporation from CH<sub>3</sub>OH/H<sub>2</sub>O solution. Rectangular, 0.3 × 0.2 × 0.2 mm; Enraf–Nonius CAD-4 diffractometer; 24 reflections (2θ = 16–37°) used for lattice parameters; empirical (ψ-scan) absorption correction (*T* = 0.921–1.00); *hkl* range (roughly 2/3 of sphere): *h* = -8 to 8, *k* = -13 to 13, *l* = -13 to 13. 4094 *hkl* with 2θ < 50°. 3 standards measured every 2 h of X-ray exposure (4% range); 2712 unique reflections; *R*<sub>int</sub> (merging) = 1.6%; 111 unobserved reflections [*I* < 2σ(*I*)]. Tc atom located by direct methods, all other atoms by difference Fourier techniques; positional parameters and isotropic temperature factors refined for all H atoms except H(OO). Temperature factor for H(OO) fixed at 8.0 Å<sup>2</sup>. 287 parameters refined. Σ*w*(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup> minimized, *w*<sup>-1</sup> = (σ<sub>counting</sub> + 0.05 *F*<sub>o</sub><sup>2</sup>)/4*F*<sub>o</sub><sup>2</sup>. *R* = 2.4%, *R*<sub>w</sub> = 3.3%, *S* = 1.18. Reversal of direction of polar axis gave significantly higher *R* factor. Max. Δ/σ in last cycle = 0.14; Δρ(max.) on final difference Fourier map = 1.02 e Å<sup>-3</sup>; scattering factors including *f*' and *f*''

values from *International Tables for X-ray Crystallography* (1974). Computations on PDP 11/34 computer using Enraf–Nonius (1979) *SDP-Plus* programs. The atom positional parameters are listed in Table 1.\*

**Discussion.** [TcO(pnao-3H)] (Fig. 1) is the first example of a pnao complex with a metal in an oxidation state higher than three. All other known pnao complexes (Hussain & Schlemper, 1979*a*; Liss & Schlemper, 1975; Schlemper, Hussain & Murmann, 1981; Murmann & Schlemper, 1973; Schlemper, LaPlaca & Hamilton, 1971; Hussain & Schlemper, 1979*b*; Schlemper & Siripaisarnpipat, 1984) retain the amine protons. The deprotonation which occurs in this complex has, however, been postulated for other related Tc complexes (Ravert, Burns, Heindel, Kramer & Epps, 1983; Kramer, Epps, Burns, Johnson, Raganathan & Ravert, 1983). The loss of protons increases the planarity of the ligand. The carbon atoms attached to the nitrogen atoms in [TcO(pnao-3H)] all lie in a plane parallel to the plane of the four nitrogen atoms whereas in the other pnao complexes these atoms are puckered considerably.

The bond distances and angles for the non-hydrogen atoms are given in Table 2. The coordination around the Tc atom is approximately square pyramidal with the Tc atom 0.678 (1) Å above the plane of the four N atoms. The Tc–O distance of 1.679 (3) Å is similar to that in other monooxo Tc complexes [1.610 (4) to 1.672 (8) Å] (Cotton, Davison, Day, Gage & Trop, 1979; DePamphilis, Jones, Davis & Davison, 1978; Smith, Byrne, Cotton & Sekutowski, 1978; Jones,

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms and equations of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39465 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

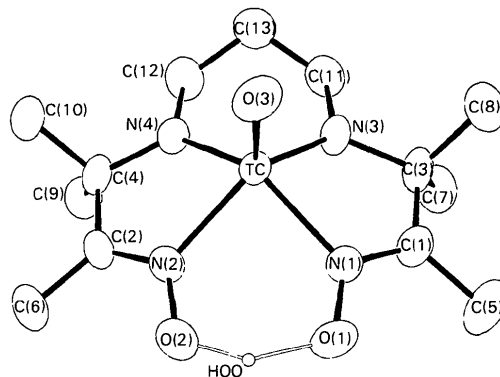


Fig. 1. The [TcO(pnao-3H)] molecule showing the thermal ellipsoids (50% probability level) and the atom labeling.

Table 2. Bond distances (Å) and angles (°) for non-hydrogen atoms

Numbers in parentheses are e.s.d.'s in the least significant digits.

Tc—O(3)	1.679 (3)	C(1)—C(3)	1.467 (7)
Tc—N(1)	2.093 (4)	C(1)—C(5)	1.492 (7)
Tc—N(2)	2.086 (3)	C(2)—C(4)	1.500 (6)
Tc—N(3)	1.908 (3)	C(2)—C(6)	1.496 (6)
Tc—N(4)	1.917 (3)	C(3)—C(7)	1.548 (6)
O(1)—N(1)	1.339 (4)	C(3)—C(8)	1.507 (6)
O(2)—N(2)	1.354 (4)	C(4)—C(9)	1.538 (6)
N(1)—C(1)	1.304 (5)	C(4)—C(10)	1.539 (6)
N(2)—C(2)	1.288 (5)	C(11)—C(13)	1.502 (7)
N(3)—C(3)	1.502 (5)	C(12)—C(13)	1.509 (6)
N(3)—C(11)	1.463 (5)		
N(4)—C(4)	1.473 (5)		
N(4)—C(12)	1.474 (5)		
O(2)—N(2)—C(2)	119.0 (3)	N(2)—Tc—N(3)	139.0 (1)
Tc—N(3)—C(3)	118.6 (3)	N(2)—Tc—N(4)	77.0 (1)
Tc—N(3)—C(11)	125.6 (3)	N(3)—Tc—N(4)	92.7 (2)
C(3)—N(3)—C(11)	115.4 (3)	Tc—N(1)—O(1)	123.0 (3)
Tc—N(4)—C(4)	120.3 (2)	Tc—N(1)—C(1)	116.0 (3)
Tc—N(4)—C(12)	124.8 (3)	O(1)—N(1)—C(1)	120.4 (4)
C(4)—N(4)—C(12)	114.9 (3)	Tc—N(2)—O(2)	122.5 (2)
N(1)—C(1)—C(3)	116.5 (4)	Tc—N(2)—C(2)	118.0 (3)
N(1)—C(1)—C(5)	119.3 (5)	N(3)—C(3)—C(8)	110.3 (4)
C(3)—C(1)—C(5)	124.2 (5)	C(1)—C(3)—C(7)	109.5 (4)
N(2)—C(2)—C(4)	114.9 (3)	C(1)—C(3)—C(8)	109.3 (4)
N(2)—C(2)—C(6)	121.0 (4)	C(7)—C(3)—C(8)	110.4 (4)
C(4)—C(2)—C(6)	124.2 (4)	N(4)—C(4)—C(2)	107.5 (3)
N(3)—C(3)—C(1)	107.4 (4)	N(4)—C(4)—C(9)	111.5 (4)
N(3)—C(3)—C(7)	109.9 (4)	N(4)—C(4)—C(10)	111.6 (4)
O(3)—Tc—N(1)	108.6 (1)	C(2)—C(4)—C(9)	108.3 (4)
O(3)—Tc—N(2)	110.5 (1)	C(2)—C(4)—C(10)	109.1 (4)
O(3)—Tc—N(3)	110.2 (2)	C(9)—C(4)—C(10)	108.7 (4)
O(3)—Tc—N(4)	110.1 (1)	N(3)—C(11)—C(13)	111.3 (4)
N(1)—Tc—N(2)	85.7 (1)	N(4)—C(12)—C(13)	111.0 (3)
N(1)—Tc—N(3)	77.8 (2)	C(11)—C(13)—C(12)	112.9 (4)
N(1)—Tc—N(4)	141.0 (1)		

DePamphilis & Davison, 1981; Thomas, Estes, Elder & Deutsch, 1979). The longer pair of Tc—N distances [2.086 (3), 2.093 (4) Å] are comparable to other reported Tc—N distances [2.088 (3) to 2.259 (4) Å] (Kastner, Lindsay & Clarke, 1982; Thomas *et al.*, 1979; Zuckman *et al.*, 1981; Franklin, Howard-Lock & Lock, 1982). The other pair of Tc—N distances [1.917 (3), 1.908 (3) Å] are much shorter, which would indicate multiple-bond character in the Tc—N(imino) bonds.

The O...O distance of 2.420 (5) Å is in the range of short interactions which often have a single H-atom position. The O—H distances of 1.16 (8) and 1.35 (8) Å are similar to those in other reported structures (Schlemper, LaPlaca & Hamilton, 1971); Saarinen, Korvenranta & Näsäkkälä, 1979). The H(OO) atom did not refine well; if the temperature

factor was allowed to vary an ever-increasing value resulted. With *B* fixed at 8.0 Å<sup>2</sup> the positional parameters converged. A difference map calculated without inclusion of the H(OO) atom indicated the possibility of a disordered H atom. If suitable crystals can be obtained, we plan to use neutron diffraction in the near future to clarify this problem.

Partial support (CKF and EOS) of this work by the National Science Foundation (CH No. 81-06795) is gratefully acknowledged.

## References

- COTTON, F. A., DAVISON, A., DAY, V. W., GAGE, L. D. & TROP, H. S. (1979). *Inorg. Chem.* **18**, 3024–3029.
- DEPAMPHILIS, B. V., JONES, A. G., DAVIS, M. A. & DAVISON, A. (1978). *J. Am. Chem. Soc.* **100**, 5570–5571.
- Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft.
- FRANKLIN, K. J., HOWARD-LOCK, H. E. & LOCK, C. J. (1982). *Inorg. Chem.* **21**, 1941.
- HUSSAIN, M. S. & SCHLEMPER, E. O. (1979a). *Inorg. Chem.* **18**, 1116–1121.
- HUSSAIN, M. S. & SCHLEMPER, E. O. (1979b). *Inorg. Chem.* **18**, 2275–2282.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JONES, A. G., DEPAMPHILIS, B. V. & DAVISON, A. (1981). *Inorg. Chem.* **20**, 1617–1618.
- KASTNER, M. E., LINDSAY, M. J. & CLARKE, M. J. (1982). *Inorg. Chem.* **21**, 2037–2040.
- KRAMER, A. V., EPPS, L. A., BURNS, H. D., JOHNSON, A. N., RAGANATHAN, N. & RAVERT, H. T. (1983). *J. Nucl. Med.* **24**, P127.
- LISS, I. B. & SCHLEMPER, E. O. (1975). *Inorg. Chem.* **14**, 3035–3039.
- MURMANN, R. K. & SCHLEMPER, E. O. (1973). *Inorg. Chem.* **12**, 2625–2631.
- RAVERT, H. T., BURNS, H. D., HEINDEL, N. D., KRAMER, A. V. & EPPS, L. A. (1983). *J. Nucl. Med.* **24**, P10.
- SAARINEN, H., KORVENRANTA, J. & NÄSÄKKÄLÄ, E. (1979). *Cryst. Struct. Commun.* **8**, 359–362.
- SCHLEMPER, E. O., HUSSAIN, M. S. & MURMANN, R. K. (1981). *Acta Cryst.* **B37**, 234–237.
- SCHLEMPER, E. O., LAPLACA, S. J. & HAMILTON, W. C. (1971). *J. Chem. Phys.* **54**, 3990–4000.
- SCHLEMPER, E. O. & SIRIPAISARNPIPAT, S. (1984). *Inorg. Chem.* **23**, 330–334, and references cited therein.
- SMITH, J. E., BYRNE, E. F., COTTON, F. A. & SEKUTOWSKI, J. C. (1978). *J. Am. Chem. Soc.* **100**, 5571–5572.
- THOMAS, R. W., ESTES, G. W., ELDER, R. C. & DEUTSCH, E. (1979). *J. Am. Chem. Soc.* **101**, 4581–4585.
- TROUTNER, D. E., VOLKERT, W. A., HOFFMAN, T. J. & HOLMES, R. A. (1984). *Int. J. Appl. Radiat. Isot.* In the press.
- ZUCKMAN, S. A., FREEMAN, G. M., TROUTNER, D. E., VOLKERT, W. A., HOLMES, R. A., VAN DERVEER, D. G. & BAREFIELD, E. K. (1981). *Inorg. Chem.* **20**, 2386–2389.