

against μ_3 -P, μ_3 -Cl and μ_3 -I atoms, which is accompanied by a conversion of 44 VE to 46 VE cluster species, reveals Re—Re bond elongation in the 46 VE species of about 0.053 (1)–0.094 (1) Å. The electronic structure of the μ_3 -X ligands seems to be a factor of greater influence than the atomic size of X, because in the series of substances of type $\text{Re}_3(\text{CO})_6(\mu_3\text{-H})(\mu_3\text{-X})(\mu\text{-PPh}_2)_3$ [X: Cl > Br > I, Re—Re 2.808 (1) > 2.809 (2) > 2.820 (1) Å], such a steric factor can almost be neglected. In general, the rather rigid phosphido-bridged Re—Re triangles do not show extensive geometrical changes.

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Structure of *trans*-Aquanitrido(1,4,8,11-tetraazacyclotetradecan-5-onato-*N,N',N'',N'''*)technetium(V) Chloride Dihydrate

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Abstract. $[\text{TcN}(\text{C}_{10}\text{H}_{21}\text{N}_4\text{O})(\text{H}_2\text{O})]^+ \cdot \text{Cl}^- \cdot 2\text{H}_2\text{O}$, $M_r = 415.81$, monoclinic, $P2_1/c$, $a = 7.609$ (1), $b = 16.405$ (3), $c = 13.642$ (3) Å, $\beta = 99.57$ (1)°, $V = 1679.2$ (5) Å³, $Z = 4$, $D_x = 1.64$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 1.018$ mm⁻¹, $F(000) = 856$, $T = 298$ K, $R = 0.021$ for 3262 observed reflections. The complex cation displays a distorted octahedral structure, with a water molecule in the *trans* position with respect to the $\text{Tc}\equiv\text{N}$ group and the four N atoms of the ligand in the equatorial position. The degree of pyramidalization of the coordination polyhedron is important [average $\text{N}\equiv\text{Tc}-\text{N}$ angle of 101 (3)°] and the $\text{Tc}-\text{OH}_2$ bond distance is abnormally long (2.560 Å), as a consequence of the strong *trans* influence exerted by the nitrido group. These facts are consistent with an incipient transition from a square pyramidal to octahedral geometry of the coordination polyhedron caused by the incoming water molecule.

Introduction. The application of complexes of metastable technetium-99m in diagnostic nuclear medicine

has stimulated a major development of technetium chemistry.

The chemistry of technetium(V) is largely dominated by $[\text{Tc}\equiv\text{O}]^{3+}$ and *trans*-dioxo $[\text{O}=\text{Tc}=\text{O}]^+$ cores. Throughout this paper the form $[\text{Tc}\equiv\text{O}]^{3+}$ is used to describe the Tc—oxo multiple bond according to the well known bond situation in oxo complexes where the $M-\text{O}$ bond has three components (one σ and two π), out of which two are covalent and one is donor–acceptor ($\text{Tc}\equiv\text{O}$) (Shustorovich, Porai-Koshits & Buslaev, 1975). This formalism is useful to distinguish the bond situation in oxo $[\text{Tc}\equiv\text{O}]^{3+}$ complexes, where Tc—O distances fall in the range 1.61–1.68 Å with stretching frequencies in the range 920–1020 cm⁻¹, from that in dioxo $[\text{O}=\text{Tc}=\text{O}]^+$ complexes where the distances and stretching frequencies occur in the ranges 1.74–1.75 Å and 790–880 cm⁻¹ respectively (Zuckman, Freeman, Troutner, Volkert, Holmes, Van Derveer & Kent Barefield, 1981; Kastner, Lindsay & Clarke, 1982; Jurisson, Aston, Fair, Schlemper, Sharp & Troutner, 1987).

Lipophilic square-pyramidal complexes containing the $[\text{Tc}\equiv\text{O}]^{3+}$ moiety as $[\text{TcO}(L)]$ ($L = \text{diamino-}$

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dithiolates, amino-oxime ligands) (Bryson, Dewan, Lister-James, Jones & Davison, 1988; Jurisson *et al.*, 1987; Jurisson, Schlemper, Troutner, Canning, Nowotnik & Neirinx, 1986) can cross the blood barrier and this fact seems to indicate that the formation of a square-pyramidal structure containing an apical TcX group (X = O, N) is a favourable feature for obtaining potential radiopharmaceutical agents for brain imaging. On the other hand it is well known that technetium(V) tends to form dioxo-octahedral complexes with neutral or poor π -donor ligands such as in [TcO₂(en)₂]⁺ (en = ethylenediamine) and [TcO₂(cyclam)]⁺ (Kastner *et al.*, 1982; Zuckman *et al.*, 1981).

Baldas and coworkers (Baldas, Bonnyman & Williams, 1986; Baldas, Bass, Bonnyman & Williams, 1984; Baldas & Bonnyman, 1985) have proposed, as an alternative to the [TcO₂]⁺ and [Tc=O]³⁺ groups, the [Tc≡N]²⁺ core which is isoelectronic with [Tc=O]³⁺ and, furthermore, has the property that the nitrido ligand N³⁻ tends to stabilize the metal in high oxidation states (Griffith, 1972). Thenceforward, new technetium nitrido complexes which could be potential radiopharmaceutical agents have been characterized and investigated. Lipophilic square-pyramidal complexes with bi- and tridentate Schiff bases derived from *S*-methyl dithiocarbamate NH₂NHC(=S)SCH₃ and containing the [Tc≡N]²⁺ and [Tc=O]³⁺ moieties were synthesized as potential tracers for brain imaging (Marchi, Duatti, Rossi, Magon, Pasqualini, Bertolasi, Ferretti & Gilli, 1988; Marchi, Rossi, Magon, Duatti, Pasqualini, Ferretti & Bertolasi, 1990). Moreover, a number of monocationic complexes of technetium in low oxidation states, such as [Tc(CNR)₆]⁺ (CNR = alkyl or aryl isonitriles), were synthesized (Abrams, Davison, Jones, Costello & Pang, 1983) in order to obtain new ^{99m}Tc myocardial agents.

Recently, we have reported the synthesis and crystal structure of monocationic octahedral nitrido complexes of technetium(V) with nitrogen-donor ligands such as chelating amines (Marchi, Garuti, Duatti, Magon, Rossi, Ferretti & Bertolasi, 1990) and tetraaza macrocycles (Marchi, Rossi, Magon, Duatti, Casellato, Graziani, Vidal & Riche, 1990). The strong demand for decreasing the positive charge on the [Tc≡N]²⁺ core has promoted the synthesis of monocationic complexes containing a Cl⁻ ion in a *trans* position to the Tc≡N group where chelating amines and cyclam were used. With the mono-oxocyclam ligand (1,4,8,11-tetraaza-cyclotetradecan-5-one) a monocationic octahedral complex is also obtained through deprotonation of an amide group and coordination of an H₂O molecule in a *trans* position to the Tc≡N multiple bond, and this structure is the object of the present investigation.

Experimental. Orange prismatic crystal of dimensions 0.24 × 0.26 × 0.50 mm; Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo *K* α radiation, $\omega/2\theta$ scan ($2 \leq \theta \leq 27^\circ$); cell parameters from 25 reflections in the range $9 \leq \theta \leq 15^\circ$; 3655 reflections collected ($0 \leq h \leq 9$, $0 \leq k \leq 20$, $-17 \leq l \leq 17$), 3262 with $I_o \geq 3\sigma(I_o)$ used in the refinement; three standard reflections monitored every 2 h showed no significant variation during data collection; Lorentz, polarization and absorption corrections (minimum transmission factor = 0.92). Solution by Patterson and Fourier methods, refinement by full-matrix least squares, anisotropic non-H and isotropic H atoms (located in ΔF map), final $R = 0.021$, $wR = 0.030$, weighting scheme $w = 4F_o^2/[\sigma^2(F_o)^2 + (0.04F_o^2)^2]$; maximum $\Delta/\sigma = 0.05$, $S = 1.200$; final difference-map peaks in the range -0.3 – 0.55 e \AA^{-3} . Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); all calculations performed with CAD-4-SDP system of programs (Frenz, 1978) and PARST (Nardelli, 1983).

Discussion. Final atomic positional and thermal parameters are given in Table 1, bond distances and angles are reported in Table 2 and an ORTEPII (Johnson, 1976) view of the asymmetric unit is shown in Fig. 1.*

The crystal consists of [TcN(C₁₀H₂₁N₄O)(H₂O)]⁺ cations and Cl⁻ anions packed together with water molecules by means of a three-dimensional net of hydrogen bonds. The octahedral coordination around the central Tc atom places the four N atoms of the macrocycle in the equatorial plane and the nitrido N atom and the O(1 w) atom of a water molecule at the apical positions. The Tc atom is displaced from the least-squares plane defined by the four N basal atoms by 0.3981 (4) \AA towards the nitrido group.

The bonding situation in this octahedral Tc-nitrido complex can be described using the general scheme already reported for the mononuclear nitrido complexes (Griffith, 1972). If the nitride is placed on the vertical z axis and the equatorial ligands are on the x, y axes, the Tc≡N overlaps will be: N—Tc (σ bond) sp_σ to $4d_{z^2} + 5s$; N=Tc (π bonds) $2p_x$ to $4d_{xz}$ and $2p_y$ to $4d_{yz}$. For the four basal σ bonds, the overlaps would be between the N lone pairs and the ($5s - 4d_{x^2}$), $5p_x$, $5p_y$ and $4d_{x^2-y^2}$ Tc orbitals and for the *trans* Tc—O σ bond the interaction would be between an O lone pair and the $5p_z$ Tc orbital. Tc^V complexes are diamagnetic and thus in a d^2 closed-

* Lists of structure factors, H-atom positional and thermal parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54318 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters ($\times 10^4$) and thermal parameters (\AA^2) with *e.s.d.*'s in parentheses
$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Tc	662.0 (2)	3304.5 (1)	2783.2 (1)	1.854 (3)
O(1)	-2617 (2)	4375.3 (8)	327 (1)	3.57 (3)
N(1)	2121 (2)	2755 (1)	2353 (1)	3.02 (3)
N(2)	-473 (2)	4021.3 (9)	1621 (1)	2.40 (3)
N(3)	2189 (2)	4371.1 (8)	3122 (1)	2.25 (3)
N(4)	1110 (2)	2903.6 (9)	4289 (1)	2.30 (3)
N(5)	-1474 (2)	2448.9 (9)	2665 (1)	2.31 (2)
C(1)	468 (3)	4800 (1)	1533 (1)	3.07 (3)
C(2)	2327 (2)	4751 (1)	2151 (1)	3.01 (3)
C(3)	3920 (2)	4219 (1)	3787 (1)	2.95 (3)
C(4)	3684 (3)	3836 (1)	4770 (1)	3.25 (4)
C(5)	3002 (3)	2965 (1)	4767 (1)	3.14 (4)
C(6)	289 (3)	2079 (1)	4285 (1)	3.03 (4)
C(7)	-1571 (3)	2133 (1)	3683 (1)	2.99 (3)
C(8)	-3184 (2)	2773 (1)	2127 (1)	2.95 (3)
C(9)	-2997 (3)	3101 (1)	1105 (1)	2.98 (4)
C(10)	-1987 (2)	3892 (1)	1013 (1)	2.52 (3)
Cl	-961.6 (7)	3906.8 (3)	5922.8 (3)	3.193 (9)
O(1w)	-1514 (2)	4161.9 (8)	3594.4 (9)	2.90 (2)
O(2w)	-5927 (2)	4152 (1)	-841 (1)	4.83 (4)
O(3w)	-3079 (2)	5627 (1)	2873 (1)	4.65 (4)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

Tc—N(1)	1.614 (2)	N(4)—C(5)	1.482 (2)
Tc—N(2)	2.046 (1)	N(4)—C(6)	1.490 (2)
Tc—N(3)	2.109 (1)	N(5)—C(7)	1.496 (2)
Tc—N(4)	2.130 (1)	N(5)—C(8)	1.482 (2)
Tc—N(5)	2.133 (2)	C(1)—C(2)	1.524 (2)
Tc—O(1w)	2.560 (2)	C(3)—C(4)	1.518 (2)
O(1)—C(10)	1.259 (2)	C(4)—C(5)	1.520 (2)
N(2)—C(1)	1.479 (2)	C(6)—C(7)	1.516 (3)
N(2)—C(10)	1.320 (2)	C(8)—C(9)	1.523 (2)
N(3)—C(2)	1.483 (2)	C(9)—C(10)	1.524 (3)
N(3)—C(3)	1.491 (2)		
N(1)—Tc—N(2)	105.45 (7)	C(2)—N(3)—C(3)	115.3 (1)
N(1)—Tc—N(3)	98.97 (7)	Tc—N(4)—C(5)	113.0 (1)
N(1)—Tc—N(4)	99.71 (7)	Tc—N(4)—C(6)	106.1 (1)
N(1)—Tc—N(5)	99.58 (7)	C(5)—N(4)—C(6)	116.1 (1)
N(1)—Tc—O(1w)	175.73 (6)	Tc—N(5)—C(7)	108.2 (1)
N(2)—Tc—N(3)	80.75 (6)	Tc—N(5)—C(8)	113.4 (1)
N(2)—Tc—N(4)	154.70 (6)	C(7)—N(5)—C(8)	114.2 (1)
N(2)—Tc—N(5)	95.82 (6)	N(2)—C(1)—C(2)	109.1 (1)
N(2)—Tc—O(1w)	78.42 (5)	N(3)—C(2)—C(1)	108.6 (1)
N(3)—Tc—N(4)	92.91 (6)	N(3)—C(3)—C(4)	112.6 (1)
N(3)—Tc—N(5)	161.38 (6)	C(3)—C(4)—C(5)	118.5 (1)
N(3)—Tc—O(1w)	79.73 (5)	N(4)—C(5)—C(4)	111.8 (2)
N(4)—Tc—N(5)	82.38 (6)	N(4)—C(6)—C(7)	107.6 (1)
N(4)—Tc—O(1w)	76.35 (6)	N(5)—C(7)—C(6)	109.7 (1)
N(5)—Tc—O(1w)	81.65 (5)	N(5)—C(8)—C(9)	111.8 (1)
Tc—N(2)—C(1)	114.3 (1)	C(8)—C(9)—C(10)	120.1 (1)
Tc—N(2)—C(10)	127.3 (1)	N(2)—C(10)—C(9)	119.0 (1)
C(1)—N(2)—C(10)	118.1 (1)	O(1)—C(10)—C(9)	117.6 (1)
Tc—N(3)—C(2)	105.7 (1)	O(1)—C(10)—N(2)	123.4 (2)
Tc—N(3)—C(3)	113.2 (1)		

shell configuration; the π nitrido-ligand bonds destabilize the d_{yz} and d_{xz} orbitals so that the two paired d electrons of Tc^V are on the d_{xy} orbital. In the bonding scheme, described above, there is competition between the nitrido group and the ligand in the *trans* position for the same σ and π orbitals on the metal

and consequently, since the $\text{Tc}\equiv\text{N}$ bond is very strong, the ligand in the *trans* position is either weakly coordinated or, more frequently, absent entirely. Accordingly, the $\text{Tc}\equiv\text{N}$ (nitrido) complexes, owing to the very strong *trans* influence of the N^{3-} group, are mainly characterized by a square pyramidal Tc^V penta-coordination (Marchi *et al.*, 1988, and references therein). However, some structures of Tc^V nitrido complexes with an unusual pseudo-octahedral geometry have recently been reported, *i.e.* $\text{Tc}(\text{NCS})_2(\text{MeCN})(\text{PPh}_3)_2$ (Baldas, Bonnyman & Williams, 1984), $[\text{Tcn}(\text{bpy})_2\text{Br}]^+$ ($\text{bpy} = 2,2'$ -bipyridyl) (Archer, Dilworth, Kelly & McPartlin, 1989), $[\text{TcN}(\text{en})_2\text{Cl}]^+$ ($\text{en} = \text{ethylenediamine}$) and $[\text{TcN}(\text{tad})\text{Cl}]^+$ ($\text{tad} = 1,5,8,12$ -tetraazadodecane) (Marchi, Garuti *et al.*, 1990); $\text{TcN}(\text{L}')(\text{H}_2\text{O})$ ($\text{H}_2\text{L}' = 1,4,8,11$ -tetraazacyclotetradecane-5,7-dione) (Marchi, Rossi *et al.*, 1990). The present compound displays what can be called a pseudo-octahedral Tc^V coordination which is characterized by the very short $\text{Tc}\equiv\text{N}$ distance [1.614 (2) \AA], the umbrella deformation of the octahedron [$\text{N}\equiv\text{Tc}-\text{N}$ (*cis*) angle = 101 (3) $^\circ$, on average] and the long $\text{Tc}-\text{O}$ (*trans*) bond distances [2.560 (2) \AA] which are a consequence of the *trans* weakening caused by the multiple $\text{Tc}\equiv\text{N}$ bond. Experimental data are in agreement with the idea that the *trans* influence exerted by the $\text{Tc}\equiv\text{N}$ multiple bond must be much greater than that exerted by the isoelectronic $\text{Tc}\equiv\text{O}$ group (Shustorovich *et al.*, 1975; Marchi, Garuti *et al.*, 1990). The present $\text{Tc}-\text{O}$ (*trans*) bond distance of 2.560 (2) \AA is much longer than the corresponding $\text{Tc}-\text{O}$ distances observed in bonds *trans* to the $\text{Tc}\equiv\text{O}$ multiple bonds in Tc^V octahedral oxo complexes; in particular, it is longer than that of 2.282 (2) \AA with a *trans* water molecule (Jurisson, Lindoy, Dancey, McPartlin, Tasker, Uppal & Deutsch, 1984) and that of

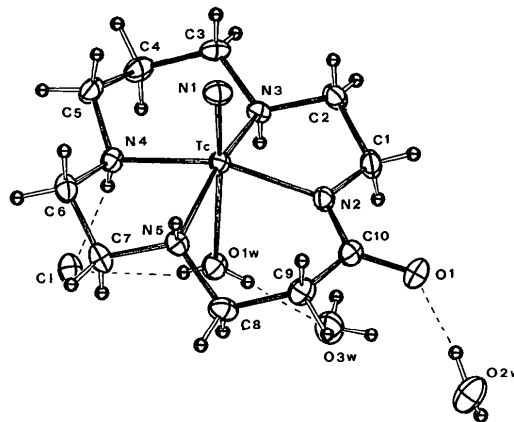


Fig. 1. An ORTEP (Johnson, 1976) view of the asymmetric unit displaying the thermal ellipsoids at 40% probability.

2.359 (8) Å formed with the *trans* ketonic O atom of the salicylaldehyde ligand (Duatti, Marchi, Magon, Deutsch, Bertolasi & Gilli, 1987). The *trans* weakening of the Tc—OH₂ bond caused by the nitrido group is still more pronounced in the strictly similar structure of TcN(L')H₂O (H₂L' = 1,4,8,11-tetraazacyclotetradecane-5,7-dione) (Marchi, Rossi *et al.*, 1990) where Tc—OH₂ distances were found to be 2.688 (4) and 2.947 (4) Å in the two independent molecules of the asymmetric unit. The most interesting feature of these compounds is, therefore, their ability to form a variety of Tc—O bonds which are abnormally long and can be considered as secondary bonds, *i.e.* intermediate between true bonds and van der Waals contacts. Analysis of the overall coordination geometries shows that the lengthening of the Tc—OH₂ bond is associated with the increasing pyramidalization of the Tc coordination polyhedron, measured by the N≡Tc—L_{cis} mean angle, α , which is 101° in the present compound and 104 and 105° in the other related Tc^V nitrido tetraaza macrocyclic complex (Marchi, Rossi *et al.*, 1990), while in typical square-pyramidal complexes α values fall in the range 105–108° (Marchi *et al.*, 1988; Baldas, Bonnyman, Pojer, Williams & Mackay, 1981; Baldas *et al.*, 1986). Fig. 2 shows a scatterplot of Tc—OH₂ distances *versus* α angles, which can be considered to represent, making allowance for the very few data available, the incipient transition from pseudo-octahedral to square-pyramidal geometry (and *vice versa*) of the coordination around the Tc(N)²⁺ moiety. The dashed line connecting the points on the figure might be considered to map the hypothetical reaction pathway or reaction coordinate (Bürgi & Dunitz, 1983) of this coordination variation.

N(2)—C(19) and C(19)—O(1) bond distances of 1.320 (2) and 1.259 (2) Å clearly indicate that the negative charge of the ligand is delocalized among the atoms of the deprotonated amide fragment N(2)—C(19)—O(1). The Tc—N distances with the

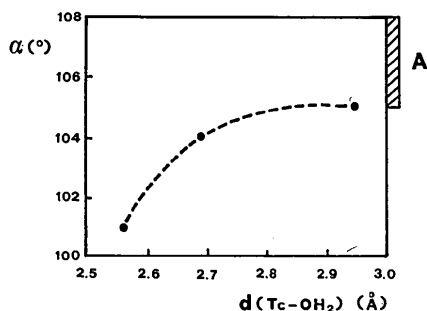


Fig. 2. Scatter plot of mean pyramidal angle N≡Tc—N(*cis*), α , *versus* *trans*-OH₂ bond distances, $d(\text{Tc—OH}_2)$, for pseudo-octahedral (Tc≡N)²⁺ complexes. 'A' shows the range of α for square-pyramidal complexes for which $d(\text{Tc—OH}_2)$ is infinite.

Table 3. Puckering parameters

Ring	Q (Å)	φ (°)	θ (°)	Conformation
Tc, N(2), C(10), C(9), C(8), N(5)	0.511 (2)	46.5 (2)	124.6 (2)	² H ₁ / ² E
Tc, N(4), C(5), C(4), C(3), N(3)	0.635 (2)	25 (5)	1.75 (1)	¹ C ₄
Tc, N(3), C(2), C(1), N(2)	0.471 (2)	50.92 (2)		³ T ₂
Tc, N(5), C(7), C(6), N(4)	0.476 (2)	-74.2 (2)		⁴ E

Table 4. Hydrogen-bond parameters (Å, °)

D—H...A	Symmetry operation	Symmetry			
		D...A	H...A	D—H	D—H...A
N(4)—H(N4)...Cl	i	3.366 (2)	2.58 (4)	0.79 (2)	170 (2)
N(3)—H(N3)...Cl	ii	3.310 (2)	2.54 (2)	0.84 (2)	153 (1)
N(5)—H(N5)...Cl	iii	3.325 (2)	2.48 (2)	0.87 (2)	162 (1)
O(1w)—H(12w)...Cl	i	3.162 (1)	2.40 (3)	0.80 (3)	160 (2)
O(3w)—H(32w)...Cl	ii	3.325 (2)	2.58 (2)	0.86 (2)	146 (1)
O(2w)—H(21w)...O(1)	i	2.772 (2)	1.89 (2)	0.89 (2)	172 (2)
O(2w)—H(22w)...O(1)	iv	2.795 (2)	2.03 (3)	0.77 (3)	178 (3)
O(1w)—H(11w)...O(3w)	i	2.788 (2)	2.02 (2)	0.77 (2)	177 (2)
O(3w)—H(31w)...O(2w)	iv	2.773 (2)	1.95 (3)	0.84 (3)	167 (2)

Symmetry code: (i) x, y, z ; (ii) $-x, -y, 1-z$; (iii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iv) $-1-x, 1-y, -z$.

macrocyclic N atoms are within the normally observed range. Their differences can be ascribed to the different basicities of the coordinated atoms. The hard Tc^V cation forms a stronger bond with the negatively charged N(2) [Tc—N = 2.046 (1) Å] than with the neutral N(3), N(4) and N(5) atoms [Tc—N = 2.12 (1) Å, on average]. In other words, the differences in bond distances can be imputed to the different hybridization around the aminic sp^3 N atoms and around the amidic sp^2 N(2) atom.

The conformation of the macrocycle can be described using puckering coordinates (Cremer & Pople, 1975). The parameters regarding the rings formed by chelation are reported in Table 3. They show that the consequence of the oxidation at the C(10) atom is the conformational change of the six-membered ring, containing C(10) itself, from the characteristic 'chair' to a mixed 'half-chair/envelope', while the conformation of the adjacent five-membered ring changes from 'envelope' to 'twist'.

The crystal packing is determined by a complex network of hydrogen bonds, see Table 4, involving O(1) atoms, Cl⁻ anions, the three water molecules and all the aminic H atoms. In most octahedral Tc complexes the Cl⁻ anion is found to occupy the *trans* position with respect to the Tc—X (X = O, NR, N) multiple bond instead of a water molecule as is to be expected in view of the greater basicity of the Cl⁻ ion with respect to water. The fact that in the present compound the Cl⁻ anion is not coordinated in a *trans* position to the Tc≡N nitrido group is to be imputed to two concomitant causes, the weakening of the *trans* Tc^V—Cl⁻ bond produced by the nitrido N³⁻ group (Shustorovich *et al.*, 1975) and the possibility of crystal segregation of the Cl⁻ anion by

a set of hydrogen bonds between the N—H groups of three cation complexes and two water molecules.

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Structure of Bis(1-ethyl-3-*p*-nitrophenyltriazene 1-oxide)nickel(II)

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Abstract. $C_{16}H_{18}N_8NiO_6$, $M_r = 477.08$, monoclinic, $P2_1/c$, $a = 9.200$ (1), $b = 8.658$ (1), $c = 12.654$ (1) Å, $\beta = 98.82$ (1)°, $V = 996.0$ (2) Å³, $Z = 2$, $D_x = 1.591$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 1.726$ mm⁻¹, $F(000) = 492$, $T = 295$ K, $R = 0.0438$ for 1398 unique reflections with $I > 3\sigma(I)$. The molecule displays square-planar N_2O_2 coordination about Ni^{II} . Ligand phenyl rings are stacked 3.426 (2) Å apart.

Introduction. 1-Alkyl(aryl)-3-(*X*-phenyltriazene) 1-oxides {henceforth abbreviated as $H[R(Ar);X]$ } belong to a wide class of ligands forming 'inorganic' (carbon-free) chelate rings (Haiduc & Silaghi-Dumitrescu, 1986). To date, three molecular structures of the free ligands, *i.e.* $H[Me;4-CONH_2]$ (Kuroda & Wilman, 1985), $H[\varphi;2-OH]$ (Samanta,

De, Sarkar, Saha & Talapatra, 1985) and $H[\varphi;2-CO_2H]$ (Sarkar, Khalil, Saha & Talapatra, 1983) have been reported. Of the metal complexes of these ligands the structures of $Pd[\varphi;H]_2$ (Meyer, 1965), $Co[Me;2-Cl]_2$, $Ni[Me;2-Cl]_2$ (Dwivedi & Srivastava, 1971, 1976), $Ni[Me;2-Cl,6-Me]_2$, $Ni[Me;2-Cl,6-Me]_2-C_6H_6$ (Rajasekharan, Varughese & Manoharan, 1979) and $Ru[Et;4-Me]_2Cl_2$ (Bhattacharya, Chakravorty, Cotton, Mukherjee & Schwotzer, 1984) are known. In addition, the structure of a dinuclear copper complex of the 3,3'-dimethoxy-4,4'-benzidine based ligand has been published (Hodgson, 1983).

Recently, we reported the formation of both high-spin and low-spin complexes of Co^{II} , together with the molecular structure of the low-spin, square-planar $Co[Et;H]_2$ (Rudolf, Wolny, Ciunik & Chmielewski, 1988). In contrast the Ni^{II} complexes