

09.4-32 STRUCTURAL CHEMISTRY OF NITRIDO COMPLEXES OF TECHNETIUM. By G.A. Williams, Australian Radiation Laboratory, Lower Plenty Road, Yallambie, Victoria, Australia, 3085.

The nitrido ligand (N^{3-}) is a powerful π -electron donor which may act as a terminal or bridging ligand and which tends to stabilise metals in high oxidation states. With terminal nitrido ligands, the formal metal-nitrogen bond order corresponds to a triple bond, and crystal structure determinations of nitrido complexes manifest extremely short metal-nitrogen bond lengths and the distinct *trans*-effect of the π -bonded nitrogen ligand. Previous work has shown that mononuclear nitrido complexes are most readily formed by the metals molybdenum, ruthenium, tungsten, rhenium and osmium, with osmium forming the most extensive and stable series of nitrido complexes.

We reported the first nitrido complex of technetium in 1981, and the crystal structure determination of $[TcN(S_2CNEt_2)_2]$ confirmed the presence of a short $Tc \equiv N$ bond of length 1.604(6) Å. Since 1981, we have determined the crystal structures of six mononuclear nitrido complexes of technetium containing $Tc \equiv N$ bonds.

$Tc \equiv N$ bond distances range from 1.581(5) and 1.596(6) Å in the technetium(VI) complexes of the air-stable tetraphenylarsonium salts of the $[TcNCl_4]^-$ and $[TcNBr_4]^-$ anions, to 1.623(4) Å in the square-pyramidal technetium(V) nitrido complex of the 8-quinolinethiol ligand, $[TcN(C_9H_6NS)_2]$, and 1.629(4) Å in the distorted octahedral technetium(V) complex $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$. In this latter compound, the strong *trans* influence of the nitrido ligand is evident in the exceptionally long $Tc-N$ bond distance of 2.491(4) Å to the CH_3CN ligand.

09.4-33 NEODYMIUM HEXAMETHYLPHOSPHORAMIDE (HMPA) COMPLEX WITH THIOCYANATE: A COMPOUND CONTAINING TWO DIFFERENT COORDINATION POLYHEDRA FOR TWO INDEPENDENT Nd(III) IONS. By C.A. de Simone, E.E. Castellano, Instituto de Física e Química de São Carlos, Univ. de São Paulo, C.P. 369, 13560, São Carlos, SP, Brazil, G. Vicentini and L.B. Zinner, Instituto de Química Fundamental, Univ. de São Paulo, C.P. 20.780, São Paulo, SP, Brazil.

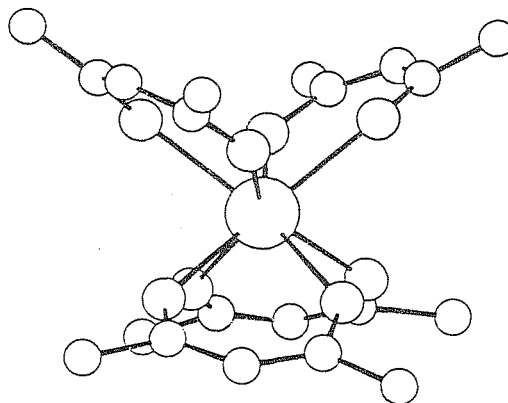
The crystal structure of the title complex, $[Nd(NCS)_3(HMPA)_3][Nd(NCS)_3(HMPA)_4]$ was determined by three-dimensional X-Ray diffraction methods and refined anisotropically to $R=0.038$. The compound crystallizes in the trigonal system, space group $R\bar{3}(n^0 146)$, with $a=b=19.947(3)$; $c=20.106(3)$ Å; $V=6928(4)$ Å³, $M=1891.4$; $Z=3$; $D_c=1.360$ g cm⁻³; $\lambda(MoK\alpha)=0.71073$ Å; $\mu=1.4$ mm⁻¹; $F(000)=2922$.

There are two independent Nd^{3+} ions, both located on the three-fold axis. The one sited on the unit cell origin is coordinated to the nitrogen atoms of three symmetry related NCS^- anions which are below the $(x,y,0)$ plane and to the oxygen atoms of three symmetry related HMPA groups located above the mentioned plane. The coordination polyhedron is a slightly distorted octahedron, ($Nd-N=2.44(1)$ Å and $Nd-O=2.351(7)$ Å). The other Nd^{3+} ion ($z=0.5025(1)$) is coordinated to the nitrogen atoms of three symmetry related NCS^- anions located above the $(x,y,0.5)$ plane, to the oxygen atoms of three symmetry related HMPA groups which are below that plane ($Nd-N=2.523(9)$ Å and $Nd-O=2.366(6)$ Å) and to the oxygen atom of an HMPA group located on the three-fold axis ($Nd-O=2.38(1)$ Å). The coordination number is in this case seven and the polyhedron is a slightly distorted capped trigonal antiprism of crystallographic point symmetry C_{3v} .

09.4-34 TETRAKISACETYLACETONATOTHORIUM(IV), COMPARATIVE RESULTS ON STRUCTURES IN DIFFERENT CRYSTAL ENVIRONMENTS. By J. H. Birkett and A. J. Smith, Department of Chemistry, University of Sheffield, SHEFFIELD S3 7HF, England.

Allard, B. (Acta Chem. Scand., 1976, A30, 461-467) has reported the structure of ThA_4 , the title compound; he describes the metal coordination as dodecahedral. We have redetermined the structure of ThA_4 (to a slightly better R than Allard) and, whilst our atom parameters are in broad agreement with his, we find the metal coordination to be clearly square antiprismatic. These two polyhedra have usually been distinguished by the fit of certain least-squares planes and the dihedral angles between them. We examine quantitative aspects of the use of these criteria and conclude that they are inadequate for choosing a 'best-fit' polyhedron. We present a procedure for fitting an idealised polyhedron with n degrees of freedom to a set of experimental points. By using spherical polar coordinates, differential bond length effects are eliminated. The method is of general applicability. We can now compare the structure of the ThA_4 with those of related compounds. Of particular interest are the adducts $2ThA_4 \cdot C_6H_6$ (Lenner, M., Acta Cryst., 1978, B34, 3770-3772) and $2ThA_4 \cdot C_6H_5NH_2$ (Reeves, P. R. and Smith, A. J., 2nd I.C.L.A., Lisbon, April 1987, to be published in Inorg. Chim. Acta) where the ThA_4 moieties are distorted by the presence of the included molecules. The ϕ angle of the antiprism varies very little but the dihedral angles between the ligand planes and the equatorial plane (of the antiprism) show considerable variety. These angles are about 30° for ThA_4 and for two ligands in each ThA_4 in the adducts, but the other two ligands are opened up to about 40° . They are close to 20° for CeA_4 (Titze, H., Acta Chem. Scand., 1969, 23, 399-408).

Other related compounds will also be discussed.



The ThA_4 Molecule