The Crystal Structure of Tetrakis-(*NN*-diethyldithiocarbamato)titanium(IV), an Eight-co-ordinated Titanium Compound

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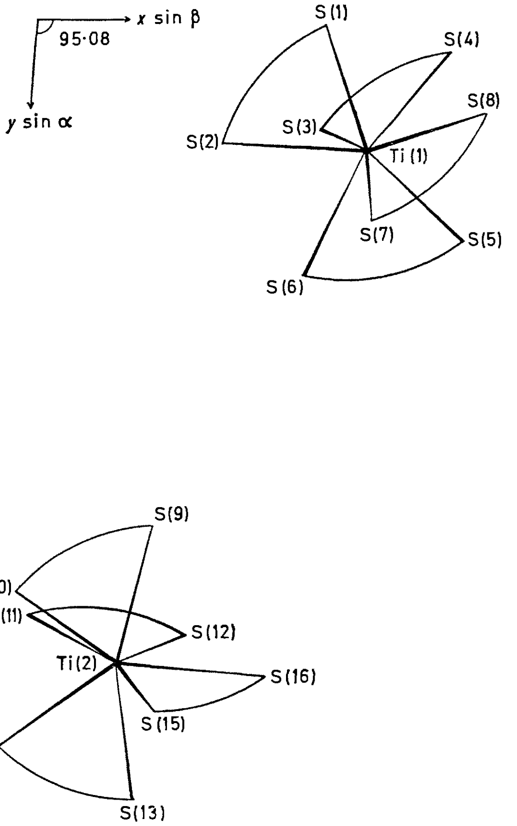
Summary The crystal structure of tetrakis-(*NN*-diethyldithiocarbamato)titanium(IV) contains eight-co-ordinated (dodecahedral) titanium and the vanadium and zirconium analogues are isomorphous.

EIGHT-CO-ORDINATED complexes of titanium proved by *X*-ray structural analysis are rare.[1] Although tetrakis-(*N*-ethylsalicylaldiminato)zirconium(IV) contains eight-co-ordinated zirconium, the titanium analogue prefers a distorted *cis*-octahedral structure with two bidentate and two unidentate ligands.[2] Recent structural determinations have shown that the tetrakis-*NN*-diethyldithiocarbamato-complexes $Th(S_2CNEt_2)_4$ and $NEt_4[Np(S_2CNEt_2)_4]$ are eight-co-ordinated,[3] but a complex containing a unidentate dithiocarbamate group is known, $Ru(NO)(S_2CNEt_2)_3$,[4] and the comparatively small size of the titanium atom left the structure of titanium dithiocarbamates open to doubt. Although i.r. and variable temperature n.m.r. spectra were consistent with an eight-co-ordinated tetrachelated structure,[5] they did not constitute a proof of the structure and in view of current interest in the configurations of 8-co-ordinated structures we have carried out a single-crystal *X*-ray structure determination of tetrakis-(*NN*-diethyldithiocarbamato)titanium(IV), $Ti(S_2CNEt_2)_4$ which proves that it is a tetra-chelated complex.

Red crystals from benzene–cyclohexane solution were found to be triclinic with $a = 11·435$, $b = 18·408$, $c = 15·382$ Å, $\alpha = 96·39$, $\beta = 91·62$, $\gamma = 95·08°$; $Z = 4$; $U = 3168$ Å^3, $D_m = 1·33$, $D_c = 1·34$ g cm^{-3}. Successful refinement of the structure proved the space group to be $P\bar{1}$. The intensities of 3637 reflections greater than background ($2\theta = 0$—86°) were recorded with a General Electric XRD6 diffractometer using Cu-K_α radiation ($\lambda = 1·5418$ Å). No absorption corrections have been applied. The co-ordinates of titanium atoms were determined from sharpened and unsharpened Patterson syntheses and the lighter atoms (except hydrogen) from subsequent Fourier syntheses. Block-diagonal least-squares refinement has reduced the *R*-factor to 0·106 (with anisotropic temperature factors for all atoms) and refinement is being continued. The co-ordination of the two titanium atoms in the asymmetric unit, viewed down the *c* axis, is shown in the Figure.

The titanium co-ordination is a very good approximation to dodecahedral (maximum deviation from planarity of the two interlocking trapezoids for the two dodecahedra is 0·11 Å). Chelation is along the *m* dodecahedral edges, following the notation of Hoard and Silverton[6] (D_{2d} isomer). The shape of the dodecahedra are specified by the parameters[6] (mean values):—Ti–S_A 2·606 ± 0·003, Ti–S_B 2·522 ± 0·003 Å, θ_A 35·13 ± 0·06, θ_B 77·53 ± 0·07°, Ti–S_A/Ti–S_B 1·03, *a* 2·999 ± 0·004, *b* 3·642 ± 0·003, *g* 3·297 ± 0·003, *m* 2·840 ± 0·003 Å, (*cf.* most favourable parameters for the dodecahedron,[6] M–A:M–B 1·03, θ_A 35·2, θ_B 73·5°).

The slightly longer Ti–S_A than Ti–S_B bonds is not unexpected[6] and may be explained in terms of a minimization of ligand repulsive energy from closed shell interactions and also the greater ability of the sulphur atoms in the B positions to act as π-donors with the titanium atom using its vacant d_{xy} orbital.[7] The Ti–S bond lengths are not remarkably long (0·08 and 0·17 Å longer than the sum of the covalent radii[8]). It has been suggested[3] that the highly distorted structures of $Th(S_2CNEt_2)_4$ and $NEt_4[Np(S_2CNEt_2)_4]$ might be due to a maximization of inter-ligand S ··· S distances (the 'bite,' *m*, is 2·7—2·9 Å whereas the other S ··· S distances are 3·60—4·10 Å). It might be expected therefore that the titanium complex would have an even more distorted structure and the relatively undistorted structure found, with shorter S ··· S inter-ligand contacts, indicates that there must be some other explanation for the distortion of the thorium and neptunium complexes. However, the dodecahedral structure of $Ti(S_2CNEt_2)_4$ is very similar to that of $Ti(NO_3)_4$.[9]



FIGURE

The dithiocarbamate ligands are very nearly planar (except for the β-carbon atoms of the ethyl groups) and co-planar with the trapezoids of the dodecahedra. The short C–N bond length (1·34 ± 0·01Å) indicates considerable double bond character, as is normally found in dithiocarbamate complexes.

The compounds $V[S_2CNEt_2]_4$ and $Zr[S_2CNEt_2]_4$ are isomorphous with $Ti[S_2CNEt_2]_4$ (a single-crystal study of the zirconium complex has been carried out). The approximately D_{2d} symmetry of the vanadium complex is consistent with the e.s.r. parameters ($g_{\parallel} = 1{\cdot}956$, $g_{\perp} = 1{\cdot}985$ for powder samples of a matrix of $V(S_2CNEt_2)_4$ (7%) in $Ti(S_2CNEt_2)_4$, indicating a d_{xy} ground state. The interesting case of vanadium dithiocarbamates[10] will be discussed fully in a later publication.

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