The Titanium(IV) Complex of a Hexadentate Tricatechol Ligand: Synthesis, Crystal Structure and Electrochemistry

F. Ekkehardt Hahn,*[a] Stefan Rupprecht[a] and Klaus Heinrich Moock[b]

[a] *Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, Germany*

[b] *Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstraße 34–36, D-1000 Berlin 33, Germany*

The tricatechol ligand, tripace, forms an octahedral complex with Ti^{IV}; the complex possesses a protonated central nitrogen atom in the 'in' conformation and is stable towards reduction up to $E_{1/2} = -1.02$ V *vs.* standard calomel electrode.

The nearly ideal radiophysical properties of the metastable nuclide ^{99m}Tc ($t_{1/2} = 6.02$ h, $E_\gamma = 140.6$ keV[1]) have made this isotope the most commonly used nuclide for the imaging of internal organs.[2] We reported the synthesis of the siderophore-like hexadentate tricatechol ligand tripace,[3] which is capable of reducing the nuclide-generator produced $[^{99m}TcO_4]^-$ (presumably to Tc^{VI}[4]) and to bind the reduced ^{99m}Tc.[5]

The species formed from $^{99}Mo/^{99m}Tc$-generator eluate and tripace cannot be investigated by standard methods owing to the short half-life of ^{99m}Tc. We have, therefore, studied the coordination chemistry of tripace[6] with another highly oxidized transition metal and report the molecular structure of $[HNEt_3][Ti(tripace)]\cdot 1.5MeCN$ and the electrochemical behaviour of this complex.

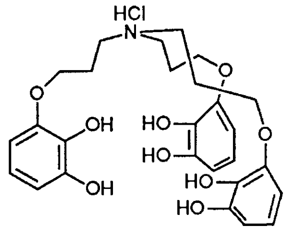
The ligand tripace reacts in the presence of $[HNEt_3][MeCO_2]$ in ethanol with $Ti(OEt)_4$ to give orange $[HNEt_3][Ti(tripace)]$, which was fully characterized by elemental analysis, ^1H NMR and ^{13}C NMR spectroscopy.† The salt can be crystallized from acetonitrile to give orange prisms of $[HNEt_3][Ti(tripace)]\cdot 1.5MeCN$.

The structure analysis‡ of $[HNEt_3][Ti(tripace)]\cdot 1.5MeCN$ (Fig. 1) shows the anion to contain a hexacoordinated Ti^{IV} in the centre of a distorted octahedron made up from six catechol oxygens. The structure is similar to the structures of metal catechoylamides like $K_3[V(trencam)]$[7] and $Na_3[Fe(bicapped trencam)]$.[8] In these derivatives as well as in the $[Ti(tripace)]^-$ anion, the central nitrogen atom is in the 'in' conformation. The striking difference between the metal complexes of catechoylamides and the $[Ti(tripace)]^-$ anions is the fact that the central nitrogen in the latter derivative is protonated.

The hydrogen atom bound to N(1)[NH(1)] was found in a difference Fourier map and its positional parameters refined in the least-squares procedure to give an N(1)–HN(1) distance of 1.05(6) Å. The N(1)–HN(1) vector is not pointed towards any of the catechol oxygen atoms as judged by the angles at N(1), the HN(1)–O distances and N(1)–HN(1)–O angles [HN(1)–O 2.22(6)–2.38(6) Å, N(1)–HN–(1)–O 129(4)–145(4)°]. This vector points towards the titanium atom [HN(1) · · · Ti 2.87(6) Å, N(1)–HN(1)–Ti 170(4)°].

The protonation of N(1) is significant for ^{99m}Tc derivatives. If the reaction of $[^{99m}TcO_4]^-$ with tripace does indeed give Tc^{VI} complexes, then these derivatives would be monocationic, owing to the protonated central amine. One major complication in the application of cationic ^{99m}Tc complexes concerns the *in vivo* reduction of the metal centre, giving a complex with different charge and biodistribution than the original monocation.[9] We have, therefore, studied the electrochemical properties of $[HNEt_3][Ti(tripace)]$ to see if the ligand is capable of stabilizing highly oxidized transition metals.

Cyclic voltammograms (CV) of an acetonitrile solution of $[HNEt_3][Ti(tripace)]$ (10 mmol dm^{-3}) in tetraethylammonium hexafluorophosphate (0.1 mol dm^{-3}) are shown in Fig. 2. At 20 °C only an irreversible reduction is observed. At lower temperatures (−35 °C) the corresponding oxidation wave appears. However, the electrochemical process at −1.02 V



$H_6tripace\cdot HCl$

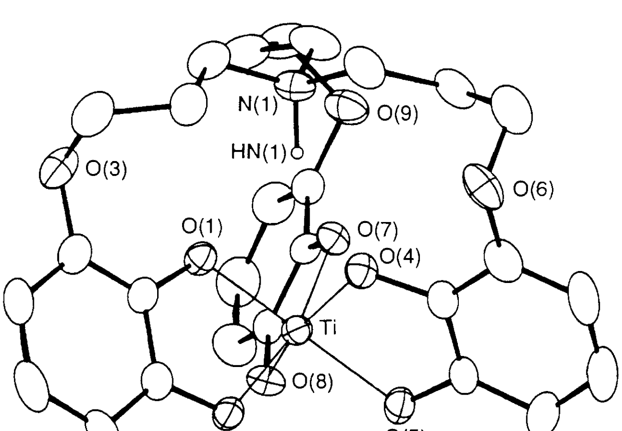


Fig. 1 ORTEP drawing of the $[Ti(tripace)]^-$ anion in $[HNEt_3][Ti(tripace)]\cdot 1.5MeCN$. Selected bond length (Å): Ti–O in the range from 1.979(3) to 1.939(3), N(1)–HN(1) 1.05(6). Selected bond angles (°): O(1)–Ti–O(2) 80.3(1), O(4)–Ti–O(5) 80.0(1), O(7)–Ti–O(8) 80.2(1).

---

† *Selected spectroscopic data* for solvent free $[HNEt_3][Ti(tripace)]$: ^1H NMR (CD_3SOCD_3), δ 1.15 (t, 9H, CH_3), 1.97 (br m, 6H, $CH_2CH_2CH_2$), 3.07 (q, 6H, CH_3CH_2), 3.35 (br m, 6H, NCH_2CH_2), 3.76 (br m, 6H, OCH_2), 5.92 (dd, 3H, Ar–H), 6.13 (dd, 3H, Ar–H) 6.27 (t, 3H, Ar–H), 7.89 (s, 1H, *H*N-tripace), 8.90 (s, 1H, $HNEt_3^+$); ^{13}C NMR (CD_3SOCD_3), δ 8.53 (Me), 23.3 ($CH_2CH_2CH_2$), 45.8 ($HNCH_2Me$), 49.8 (NCH_2CH_2), 70.8 (OCH_2), 107.1, 111.5, 116.1, 141.9, 153.6, 160.3 (Ar). Satisfactory elemental analysis for $[HNEt_3][Ti(tripace)]\cdot 1.5$ MeCN was obtained.

‡ *Crystal data* for $[HNEt_3][Ti(tripace)]\cdot 1.5MeCN$: $C_{36}H_{48.5}N_{3.5}O_9Ti$, orange prisms, $M = 722.2$, monoclinic space group $P2_1/c$ (no. 14), $a = 12.798(6)$, $b = 21.717(7)$, $c = 14.078(9)$ Å, $\beta = 112.00(4)°$, $U = 3628(6)$ Å^3, $D_m = 1.30$, $D_c = 1.32$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71073$ Å), μ(Mo-Kα) = 2.78 cm^{-1}. 6142 Reflections collected at −100(5) °C on a four-circle diffractometer in the 2θ-range between 2 and 48°. Redundant and systematically absent data were removed leaving 5690 unique reflections. The structure was solved by heavy atom methods, and refined [Ti, O, N, C anisotropic; HN(1) found in difference Fourier map and refined with fixed isotropic temperature factor, other Hs in calculated positions unrefined with fixed $B_{eq} = 1.3$ B_{eq} of the parent atom] to $R = 0.0454$, $R_w = 0.0446$ for 2536 reflections [$F_o^2 \geqslant 3\sigma(F_o^2)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

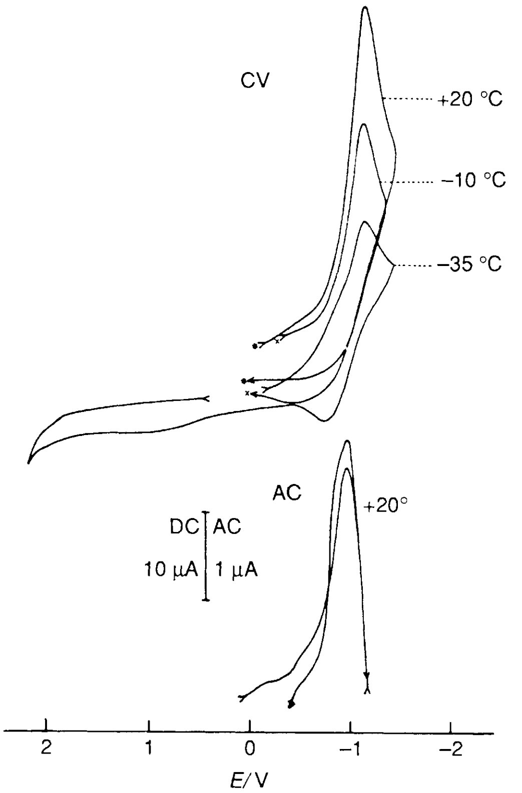


Fig. 2 Cyclic voltammograms (CV) and AC reduction of $[HNEt_3]$-[Ti(tripace)] at different temperatures (SCE = standard calomel electrode)

(*vs.* SCE) is at best quasi-reversible. Experiments with AC techniques give a quasi-reversible reduction at $E_{1/2} = -1.03$ V (Fig. 2). Since the reduction of $[Ti(tripace)]^-$ is not reversible, the number of electrons in the reduction step could not be determined by coulometric methods. However, based on chemical and electrochemical analogies,[10] a one-electron reduction can be proposed. The shift of the Ti^{IV}/Ti^{III} reduction potential [+0.30 V *vs.* SCE for $Ti(OH)_3{}^+/Ti^{3+}$][11] by 1.32 V shows the remarkable ability of tripace to stabilize highly oxidized transition metals.

Received, 31st July 1990; Com. 0/03489D

References

1 H. Münzel in *Gmelin Handbook of Inorganic Chemistry, Technetium, Supplement Volume 1*, ed. H. K. Kugler and C. Keller, Springer Verlag, Heidelberg, 1982, p. 26 ff.
2 T. C. Pinkerton, C. P. Desiletes, D. J. Hoch, V. Mikelsons and G. M. Wilson, *J. Chem. Ed.*, 1985, **62**, 965.
3 K. N. Raymond, G. Müller and B. F. Matzanke in *Topics in Current Chemistry*, ed. F. L. Boschke, Springer Verlag, Heidelberg, 1984, vol. 123, pp. 49–102.
4 L. A. deLearle, R. C. Haltiwanger and C. G. Pierpont, *J. Am. Chem. Soc.*, 1989, **111**, 4324.
5 F. E. Hahn and S. Rupprecht, *Chem. Ber.*, 1991, **124**, in the press.
6 B. Wolff and A. Weiss, *Angew. Chem.*, 1986, **98**, 173.
7 A. R. Bulls, C. G. Pippin, F. E. Hahn and K. N. Raymond, *J. Am. Chem. Soc.*, 1990, **112**, 2627.
8 T. M. McMurry, M. W. Hossaini, T. M. Garrett, F. E. Hahn, Z. E. Reyes and K. N. Raymond, *J. Am. Chem Soc.*, 1987, **109**, 7196.
9 J. R. Kirchhoff, W. R. Heinemann and E. Deutsch, *Inorg. Chem.*, 1988, **27**, 3608.
10 B. A. Borgias, S. R. Cooper, Y. B. Koh and K. N. Raymond, *Inorg. Chem.*, 1984, **23**, 1009.
11 V. R. Evans, *The Corrosion and Oxidation of Metals*, Arnold London, 1960, p. 900.