# Synthesis and Properties of Binuclear $[LTiCl_2(\mu\text{-}O)TiCl_2L]^{n+}$ ($n$ = 0, 1, 2; L = 1,4,7-trimethyl-1,4,7-triazacyclononane) Complexes. The Crystal Structure of the Mixed Valence Compound $[L_2Ti_2Cl_4(\mu\text{-}O)]Cl{\cdot}2H_2O$

**Axel Bodner,[a] Beatrice S. P. C. Della Vedova,[a] Karl Wieghardt,*[a] Bernhard Nuber,[b] and Johannes Weiss[b]**

[a] *Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum, FRG*
[b] *Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, FRG*

Three linearly μ-oxo bridged binuclear complexes $[L_2Ti_2Cl_4(\mu\text{-}O)]^{n+}$ ($n$ = 0, 1, 2) have been synthesized and the mixed valence complex $[L_2Ti_2Cl_4(\mu\text{-}O)]Cl{\cdot}2H_2O$ has been characterized by *X*-ray crystallography (L = 1,4,7-trimethyl-1,4,7-triazacyclononane).

A remarkable difference exists between the magnetic properties of linearly μ-oxo bridged binuclear complexes of chromium(III) ($d^3$)[1] and vanadium(III) ($d^2$).[2] For example, in $[(NH_3)_5Cr^{III}\text{–}O\text{–}Cr^{III}(NH_3)_5]^{4+}$ the spins of the two metal ions are strongly intramolecularly antiferromagnetically coupled (S=0 ground state), whereas in $[L(acac)V^{III}\text{–}O\text{–}V^{III}(acac)L]^{2+}$ [L = 1,4,7-trimethyl-1,4,7-triazacyclononane; acac = pentane-2,4-dionato(1−)] the spins of both vanadium(III) ions are fully aligned even at room temperature (S = 2 ground state)[2a] indicating a very strong ferromagnetic exchange coupling. Recently we have reported that in $[LCl_2Ti^{III}\text{–}O\text{–}Ti^{III}Cl_2L]$ the two unpaired electrons of the titanium(III) ($d^1$) ions are uncoupled.[3] Complexes containing the $[Ti^{III}\text{–}O\text{–}Ti^{III}]^{4+}$ core are quite rare[4] and a mixed valence species $[Ti^{III}\text{–}O\text{–}Ti^{IV}]^{5+}$ has not been structurally characterized to date.[5] Here we report the synthesis, magnetic properties, and electrochemistry of complexes $[LCl_2Ti\text{–}O\text{–}TiCl_2L]^{n+}$ ($n$ = 0, 1, 2).

Synthesis of the blue, neutral complex $[LCl_2Ti^{III}\text{–}O\text{–}Ti^{III}Cl_2L]$, (**1**), has been described elsewhere.[3] The mixed valence compound $[L_2Ti_2Cl_4(\mu\text{-}O)]Cl{\cdot}2H_2O$, (**2**), was obtained from a solution of $TiCl_3$ in dry dimethylformamide to which an equimolar amount of L was added under an argon atmosphere at 90 °C. A few drops of water and a small volume of air were added while the solution was still hot. Subsequent cooling to 0 °C produced dark blue crystals of (**2**). Crystals suitable for an *X*-ray analysis† were obtained from a $CH_2Cl_2$ solution of (**2**). The fully oxidized form of (**2**) $[L_2Ti_2Cl_4(\mu\text{-}O)]Cl_2{\cdot}2H_2O$, (**3**), was obtained when a blue solution of (**2**) in MeCN was stirred in the presence of air until the solution was colourless. From the reduced reaction volume colourless crystals of (**3**) precipitated out.

Measurements of the magnetic susceptibility on solid samples of (**1**), (**2**) and (**3**) in the temperature range −193 to 25 °C using the Faraday method gave temperature-independent magnetic moments of 2.35 $\mu_B$ and 1.72 $\mu_B$ per binuclear unit for (**1**)[3] and (**2**), respectively. Complex (**3**) is diamagnetic. For (**1**) the observed value of μ corresponds to 1.66 $\mu_B$ per $Ti^{III}$ centre which indicates that the two $Ti^{III}$ ions are uncoupled. Clearly, (**2**) contains one unpaired electron per binuclear unit.

The electronic spectra of both (**1**) and (**2**) exhibit one absorption maximum together with a shoulder in the visible region; the wavelengths of these are the same for both complexes. However, the magnitude of the molar extinction coefficient for (**1**) is approximately double that for (**2**). For (**1**): 570 (ε = 520 L $mol^{-1}$ per binuclear unit), 750sh; and for (**2**): 570 (255), 750sh nm.

Deep blue crystals of (**2**) were structurally characterized and shown to consist of the monocation $[L_2Ti_2Cl_4(\mu\text{-}O)]^+$, unco-ordinated chloride ions, and water molecules of crystallization. Figure 1 shows the structure of the cation, which possesses crystallographically imposed $C_i$ symmetry. Both titanium ions are in a distorted octahedral environment of a facially co-ordinated cyclic triamine L, two terminal chloride ligands, and a μ-oxo bridge. The Ti–O–Ti moiety is linear and the two titanium ions are equivalent. The $Ti\text{–}O_{oxo}$ distance at 1.872(1) Å is quite short indicating considerable double-bond character but it is significantly longer than in the organometallic counterparts $[Cp_2Ti]_2(\mu\text{-}O)$ (Cp = $C_5H_5$) [1.838(1) Å] and $[CpTiCl_2]_2(\mu\text{-}O)$ [1.777(1) Å].[6] It is noteworthy that the $Ti\text{–}O_{oxo}$ bonds exert a significant structural *trans* influence. The $Ti\text{–}N_{trans}$ bond distance is longer by 0.101 Å than the average of the two $Ti\text{–}N_{cis}$ bond lengths. However, the structural evidence is insufficient to determine the valencies with certainty as a statistical disorder of the $Ti^{III}Ti^{IV}$ cation would also appear to be delocalized.

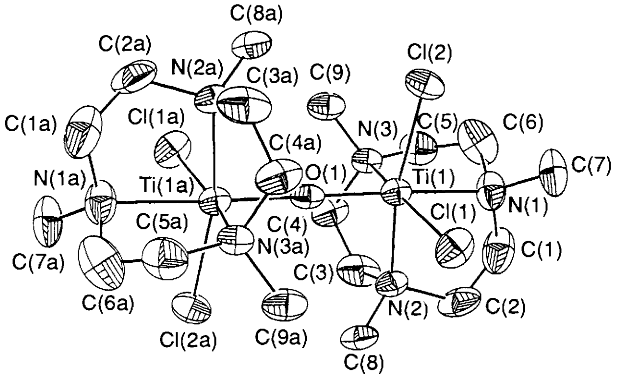

**Figure 1.** Structure of the monocation in crystals of (**2**). Selected bond distances (Å) and angles (°): Ti(1)–Cl(1) 2.319(2), Ti(1)–Cl(2) 2.321(2), Ti(1)–N(1) 2.340(5), Ti(1)–N(2) 2.241(5), Ti(1)–N(3) 2.237(4), Ti(1)–O(1) 1.872(1), Cl(1)–Ti(1)–Cl(2) 95.3(1), Cl(1)–Ti(1)–O(1) 99.8, Cl(2)–Ti(1)–O(1) 99.0(1), Cl(1)–Ti–N(1) 89.6(1), Cl(2)–Ti(1)–N(1) 87.3, O(1)–Ti(1)–N(1) 168.1(1), Cl(1)–Ti(1)–N(2) 90.1(1), Cl(2)–Ti(1)–N(2) 162.9(1), O(1)–Ti(1)–N(2) 96.0(1), N(1)–Ti(1)–N(2) 76.9(2), Cl(1)–Ti(1)–N(3) 163.1(1), Cl(2)–Ti(1)–N(3) 92.9(1), O(1)–Ti(1)–N(3) 93.3(1), N(1)–Ti(1)–N(3) 76.2(2), N(2)–Ti(1)–N(3) 78.0(2), Ti(1)–O(1)–Ti(1′) 180.0(1).

---

† *Crystal data* for (**2**), μ-oxobis[dichloro(1,4,7-trimethyl-1,4,7-triazacyclononane)titanium]chloride·dihydrate $[(C_9H_{21}N_3)_2Ti_2Cl_4(\mu\text{-}O)]Cl$: $M$ = 613.6, orthorhombic, *Pnaa* ($D_{2h}^{10}$, No. 56), $a$ = 9.752(6), $b$ = 14.601(7), $c$ = 22.24(2) Å, $U$ = 3166.7 Å$^3$; $Z$ = 4; $D_c$ = 1.47 g $cm^{-3}$. Crystal dimensions, 0.28 × 0.46 × 0.46 $mm^3$, Mo-$K_\alpha$ (0.7107 Å), $T$ = 22 °C, Synthex R3 diffractometer. Data were reduced and the structure was solved using the SHELXTL PLUS program package. Hydrogen atoms were included at calculated positions with a fixed isotropic thermal parameter of 0.08 Å$^2$; μ(Mo-$K_\alpha$) = 10.4 $cm^{-1}$; unique reflections 5182; reflections with $I > 2.5\,\sigma(I)$ = 2117; 157 refined parameters; $R$ = 0.072. Attempts to refine the crystal structure in the acentric space group yielded similar $R$ values but gave some unreasonable bond distances within the cation. The above space group is therefore considered to be the correct one. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Cyclic voltammetry (CV) shows that (**1**), (**2**), and (**3**) are interconvertible in solution by one-electron transfer processes. The cyclic voltammogram of (**2**) in MeCN {0.1 M [TBA]$PF_6$ (TBA = tributylammonium) supporting electrolyte} at a Pt electrode in the potential range +0.80 to −0.80 V *vs.* Ag;AgCl (saturated LiCl in EtOH) shows two reversible one-electron waves at $E^1_{1/2}$ +0.52 V and $E^2_{1/2}$ −0.38 V *vs.* Ag/AgCl at scan rates 20—200 mV $s^{-1}$. The cyclic voltammograms of (**2**) and (**3**) are identical under the same experimental conditions. Coulometric measurements of (**2**) dissolved in $CH_2Cl_2$ at constant potentials of +0.90 V and −0.70 V *vs.* Ag/AgCl show that (**2**) is oxidized to (**3**) or reduced to (**1**) by 1.0 ± 0.1 electron, respectively. The redox couples are assigned as in equation (1).

$$\underset{\textbf{(1)}}{\mathrm{Ti^{III}\text{–}O\text{–}Ti^{III}}} \xrightleftharpoons{E^2_{1/2}} \underset{\textbf{(2)}}{\mathrm{Ti^{III}\text{–}O\text{–}Ti^{IV}}} \xrightleftharpoons{E^1_{1/2}} \underset{\textbf{(3)}}{\mathrm{Ti^{IV}\text{–}O\text{–}Ti^{IV}}} \qquad (1)$$

From the $E^1_{1/2}$ and $E^2_{1/2}$ values a comproportionation constant, $K_c$ of $5.2 \times 10^{15}$ may be calculated for the equilibrium shown in equation (2).

$$[\mathrm{Ti^{III}{}_2O}] + [\mathrm{Ti^{IV}{}_2O}] \rightleftharpoons 2\,[\mathrm{Ti^{III}Ti^{IV}O}],\ K_c \qquad (2)$$

*Received, 17th April 1990; Com. 0/01665I*

## References

1 E. Pedersen, *Acta Chem. Scand.*, 1972, **26**, 333; J. Glerup, *ibid.*, 3775.

2 (a) P. Knopp, K. Wieghardt, B. Nuber, J. Weiss, and W. S. Sheldrick, *Inorg. Chem.*, 1990, **29**, 363; (b) S. G. Brand, N. Edelstein, C. J. Hawkins, G. Shalimoff, M. R. Snow, and E. R. T. Tiekink, *ibid.*, 434.

3 A. Bodner, S. Drüeke, K. Wieghardt, B. Nuber, and J. Weiss, *Angew. Chem.*, 1990, **102**, 60; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 68.

4 B. Honold, U. Thewalt, M. Herberhold, H. G. Alt, L. B. Kool, and M. D. Rausch, *J. Organomet. Chem.*, 1986, **314**, 105.

5 C. G. Young, *Coord. Chem. Rev.*, 1989, **96**, 89.

6 U. Thewalt and D. Schomburg, *J. Organomet. Chem.*, 1977, **127**, 169.