Electron Spin Resonance Spectra of a Ti^{IV}–Ti^{III} Mixed-valence Tetranuclear Species $[Ti_4(OR)_{12}O]$

By **Sylviane Sabo, Robert Choukroun,** and **Danièle Gervais,*** Laboratoire de Chimie de Coordination du C.N.R.S. associé a l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse, France

Reduction of $[Ti(OPr^i)_4]$ by $Li[BH_4]$ at room temperature produces the mixed-valence complex $[Ti_4(OPr^i)_{12}O]$ which has been shown by variable-temperature e.s.r. measurements to contain Ti^{III} and Ti^{IV}. The complex is tetranuclear in the solid state, while dinuclear species are observed in solution. The solid complex exhibits singlet–triplet states arising from the interaction between two Ti^{III} atoms. The various transitions $\Delta M_S = 1$ as well as $\Delta M_S = 2$ have been observed.

REDUCED titanium species are currently considered as active intermediates in the mechanism of many reactions of organic and inorganic synthesis, illustrated by Volpin's reduction of dinitrogen as well as by titanium-catalysed hydroboration and hydromagnesiation. However, considering the vast quantity of publications dealing with the organic chemistry of titanium the amount of work which appears to have been carried out in investigating compounds in which the titanium has a valency below four is surprisingly small. In the last fifteen years, several systems containing the cyclopentadienyltitanium(III) moiety have been investigated using e.s.r. techniques, namely $[\{Ti(C_5H_5)_2X\}_2]$,[1,2] $[\{Ti(C_5H_5)X_2\}_2]$,[2,3] $[Ti(C_5H_5)_2X_2]^-$,[4] and bimetallic complexes such as $[Ti(C_5H_5)_2(\mu\text{-}X)_2AlX_2]$ [5] ($X = Cl$, H, CH_3, O_2CR, NR_2, *etc.*). In the dimeric species $[\{Ti(C_5H_5)_2X\}_2]$ and $[\{Ti(C_5H_5)X_2\}_2]$, a d^1–d^1 exchange interaction is evidenced by abnormally low values of the magnetic moments at room temperature [2,5–8] as well as by $\Delta M_S = 2$ transition in the e.s.r. spectra.[8,9] Titanium(III) derivatives without any cyclopentadienyl ligands have been much less investigated. In the alkoxide family, the diamagnetic compounds $[\{Ti(OR)_3\}_n]$ (R = Me or Et) are known.[3,10–12] A phenoxyhydridotrititanium(II,II,III) complex $[Ti_3(OPh)_6H]$ has been obtained by Wilkinson and co-workers,[13] and we have reported the synthesis and properties of an ethoxytitanium(IV,III) mixed-valence tetranuclear hydride complex $[Ti_4(OEt)_{13}H]$, which is diamagnetic.[14]

The present investigation is concerned with a new Ti^{IV}–Ti^{III} mixed-valence species obtained by action of lithium tetrahydroborate on tetraisopropoxytitanium, $[Ti(OPr^i)_4]$.

EXPERIMENTAL

All manipulations were carried out under argon in conventional Schlenk apparatus, using solvents dried over CaH_2 or Na, and degassed before use. E.s.r. measurements were recorded in the temperature range 100—300 K, using a Bruker ER200TT MRDH 10 spectrometer at a microwave frequency of 9.61 GHz. Diphenylpicrylhydrazyl (dpph) was used as external standard.

In a typical run, $[Ti(OPr^i)_4]$ (5.0 g, 18 mmol) was dissolved in ether (50 cm^3) and solid $Li[BH_4]$ (2.35 g, 107 mmol) was added in 0.5 h. A purple colour immediately developed. After 24 h stirring, ether was removed and replaced by pentane. Filtration gave a purple filtrate which was reduced in volume, and acetonitrile added with vigorous stirring. Immediate filtration gave a purple solid which was washed with acetonitrile and dried under vacuum (yield, 25%). This product is a very air-sensitive solid, soluble in common organic solvents. Failure to obtain the product is possible if filtration is not performed quickly. Increased yields can be obtained by irradiation of the reaction mixture $\{[Ti(OPr^i)_4]$, $Li[BH_4]$, ether$\}$ in a quartz tube under a mercury arc lamp (Philips HPK 125), which gives 35% yield {Found: C, 46.5; H, 9.2; Ti, 21.4. Calc. for $C_{36}H_{84}O_{13}Ti_4$: C, 47.2; H, 9.2; Ti, 21.0%, which agrees with $[Ti_4(OC_3H_7)_{12}O]$}.

RESULTS AND DISCUSSION

Reaction of $Li[BH_4]$ in ether with $[Ti(OPr^i)_4]$ gives a purple solution from which a purple solid has been isolated. This solid is a very air-sensitive compound, and decomposes with mild heating or in solution within a few hours; all attempts to crystallize failed; this compound does not contain any tetrahydroborate. The hypothesis of having obtained a hydride complex can be rejected on the basis of reaction with CCl_4 (no detectable $CHCl_3$),[13,14] and no ν(Ti-H) vibration is observed in the i.r. spectrum.[15]

Conductivity data indicate a non-ionic complex. The u.v. spectra in cyclohexane solution show two *d–d* forbidden transitions at 595 (ε *ca.* 10 dm^3 mol^{-1} cm^{-1}) and 488 nm (ε *ca.* 30), a shoulder at 350 nm (ε *ca.* 150) and a charge-transfer ligand→metal transition at 230 nm (ε *ca.* 7 500).

Due to experimental limitations particularly related to the extreme air-sensitivity of the complex, it proved impossible to obtain magnetic measurements on pure samples. Some decomposition into $[Ti_2(OR)_6O]$ is always observed. Nevertheless, if the amount of diamagnetic impurity is taken into account, the presence of one electron per two titanium atoms is found in agreement with e.s.r. spectral results.

E.S.R. Spectra.—The *X*-band e.s.r. spectrum of a benzene solution of the compound shows a strong signal at $g = 1.96$; this value is in the usual range of g values for an unpaired electron in a titanium(III) species, either in monomeric or dimeric form.[1]

When increasing the sensitivity, hyperfine features attributed to coupling to ^{47}Ti (7.75% abundance, $I = \frac{5}{2}$)

and ^{49}Ti (5.51% abundance, $I = \frac{7}{2}$) nuclei can be seen. Only the outermost lines of the expected sextet and octet are observed with hyperfine coupling 11.3 G* {*cf.* 13.1 G for $[\{Ti(C_5H_5)_2Cl\}_2]$ [1]} (Figure 1).

Cooling the solution from room temperature to 100 K leads to a gradual decrease and broadening of the signal around $g = 1.96$, as well as an increasing formation of a sharp singlet at $g = 3.98$ (very intense as soon as the solution is frozen). This phenomenon is reversible. Spectra of the solid compound give similar features to the frozen solution (Figure 2).

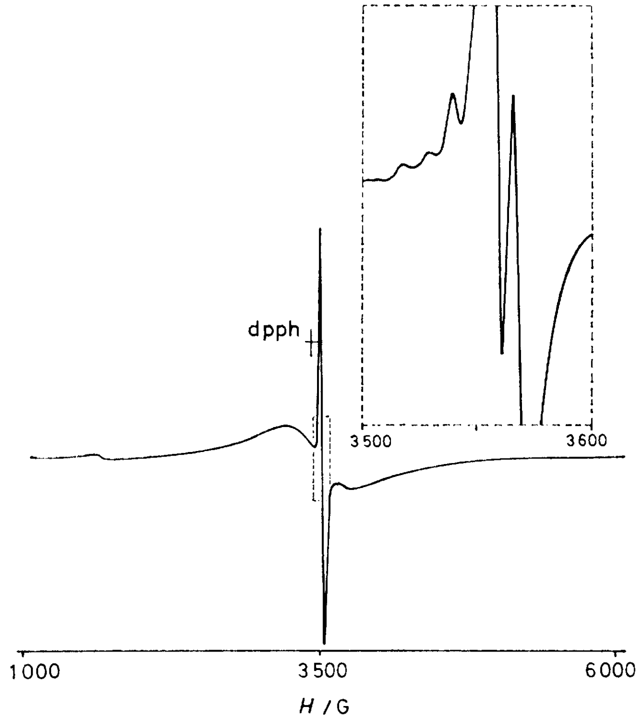

FIGURE 1 The e.s.r. spectrum of a benzene solution at 293 K

The presence of this low-field line at $H = 1\,725$ G ($g = 3.98$) is attributed to a $\Delta M_S = 2$ transition due to the singlet–triplet states arising from the magnetic dipole–dipole interactions of two titanium(III) atoms. In the area of the $\Delta M_S = 1$ transitions, various broad peaks can be observed in the range 2 300—4 800 G, symmetrically arranged on both sides of a central line ($g = 1.95$). They correspond to the $|-1\rangle \rightarrow |0\rangle$ and $|0\rangle \rightarrow |+1\rangle$ transitions; the additional central line is identified as a double quantum transition.

These observations may be explained by the presence of a Ti^{III}–Ti^{III} species without any axial symmetry and the only signal observed at low field corresponds to the turning point $H_{min.} = 1\,725$ G. Moreover, in solution at room temperature (when increasing the sensitivity), a supplementary peak can be observed at $g = 1.95$. This line may be ascribed to a Ti^{IV}–Ti^{III} species, in agreement with cryoscopic measurements and with formulae such as $[Ti_2(OR)_7]$ and/or $[Ti_2(OR)_5O]$ bridged by alkoxy-groups {cryoscopic measurements in C_6H_6 solution give a molecular weight in the range 400—450: $[Ti_2(OR)_7]$,*M* 509; $[Ti_2(OR)_5O]$,*M* 407}. When cooling the solution, or in the solid state, such moieties interact and form another species containing four titanium atoms, of which two are trivalent and two tetravalent, with the formula $[Ti_4(OR)_{12}O]$ (in agreement with analytical data, but in the absence of *X*-ray crystal determination, no definitive molecular structure can be ascertained). In this arrangement, the trivalent d^1 titanium atoms are linked to one another by OR bridges. Coupling may occur and explains the triplet state, resulting in a $\Delta M_S = 2$ transition at low field as well as $|-1\rangle \rightarrow |0\rangle$ and $|0\rangle \rightarrow |+1\rangle$ transitions in the field of $\Delta M_S = 1$. Transitions $\Delta M_S = 2$ have rarely been observed in titanium chemistry. In fact, two papers only have mentioned this phenomenon. They are concerned with $[\{Ti(C_5H_5)(O_2CR)_2\}_2]$ [2] and $[Ti(C_5H_4Me)_2]$-pyrimidine-2,4-dithiolate.[8] None refers to mixed-valence derivatives.

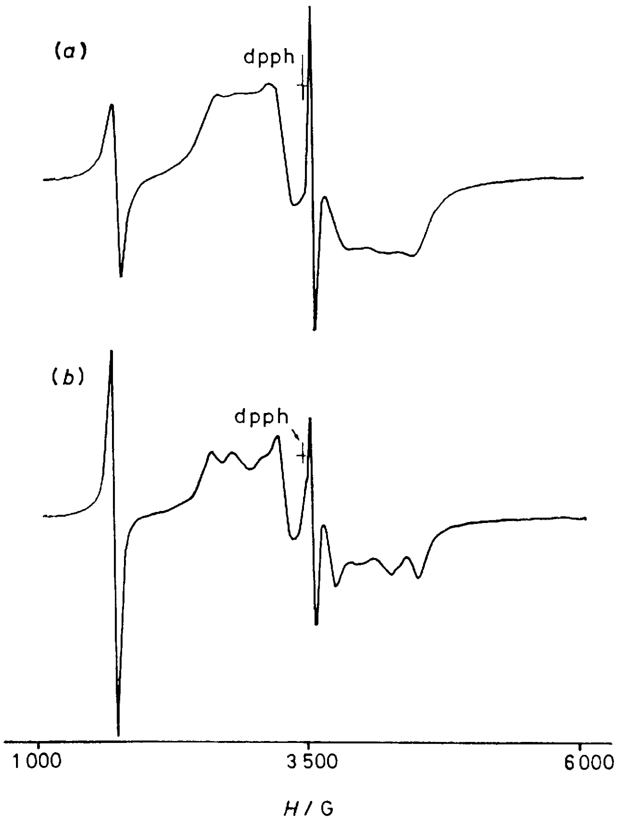

FIGURE 2 The e.s.r. solid-state spectra showing the $\Delta M_S = 2$ transition: (*a*) 293 K and (*b*) 120 K

We thank Mr. H. Biasini for technical assistance in e.s.r. measurements.

[1/591 *Received, 13th April,* 1981]

---

* Throughout this paper: 1 G = 10^{-4} T.

REFERENCES

[1] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.
[2] R. S. P. Coutts, R. L. Martin, and P. C. Wailes, *Aust. J. Chem.*, 1973, **26**, 941.
[3] M. F. Lappert and A. R. Sanger, *J. Chem. Soc. A*, 1971, 1314.
[4] J. G. Kenworthy, J. Myatt, and M. C. R. Symons, *J. Chem. Soc. A*, 1971, 1020.

[5] J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1979, 45.

[6] R. L. Martin and G. Winter, *J. Chem. Soc.*, 1965, 4709.

[7] R. S. P. Coutts, R. L. Martin, and P. C. Wailes, *Aust. J. Chem.*, 1973, **26**, 2101.

[8] L. C. Francesconi, D. R. Corbin, D. N. Hendrickson, and G. C. Stucky, *Inorg. Chem.*, 1978, **18**, 3074.

[9] R. S. P. Coutts, Ph. D. Thesis, University of Melbourne, 1972.

[10] D. W. Mac Corquodale and H. Adkins, *J. Am. Chem. Soc.*, 1928, **50**, 1938.

[11] A. N. Nesmeyanov, O. V. Nogina, and R. K. Freidlina, *Izv. Akad. Nauk. Sci. SSSR., Otd. Kim. Nauk.*, 1956, 355.

[12] R. W. Adams, E. Bishop, R. L. Martin, and G. Winter, *Aust. J. Chem.*, 1966, **19**, 207.

[13] A. Flamini, D. J. Cole-Hamilton, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 454.

[14] S. Sabo and D. Gervais, *C. R. Acad. Sci., Ser. C*, 1980, **291**, 207.

[15] J. E. Bercaw and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1969, **91**, 7301.