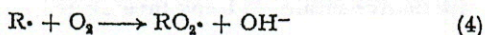


We now report that $1 \times 10^{-3} \text{ M}$ titanium(III) chloride complexed with an excess of tartaric acid (0.1 M) at pH 7.0 reacts with oxygenated water (*ca.* $1.0 \times 10^{-3} \text{ M}$) in a rapid-flow c.s.r. system² to exhibit a relatively narrow singlet $\Delta H_{pp} = 0.16 \text{ mT}$, 20–50 ms after mixing. A g -value of 2.0134 ± 0.0002 is determined relative to the tartrate ketyl trianion $^{-}\text{O}_2\text{C}\overset{\cdot}{\text{C}}(\text{O}^{-})\text{CHOHCO}_2^{-}$, $g = 2.0042$ with $a_{\text{CNOH}}(1) 0.266 \text{ mT}$. The latter species can be generated under virtually identical spectrometer conditions by allowing the titanium(III) solution to react with basic 0.0125 M hydrogen peroxide solution instead of oxygenated water in a consecutive experiment. The same mixing cell-cavity configuration is maintained throughout the sequence.

When the initial titanium(III) tartrate solution is adjusted to pH 9.0–9.5, a less intense second singlet appears at $g = 2.0145$. Its intensity is sharply increased when metal ion solutions are deliberately partially hydrolysed, indicating probable dimeric complexes containing superoxide ligands. The first singlet is still 3 times more intense at pH 9.0.

In order to assign the signal at $g = 2.0134$ to a titanium(III) dioxygen complex, it is necessary to eliminate possible peroxy radicals $\text{ROO}\cdot$ that would arise through capture of the ketyl in a full 'Fenton' sequence, equation (4).



During our initial work² we measured peroxide yields for the reaction of $2 \times 10^{-3} \text{ M}$ titanium(III) tartrate with $1 \times 10^{-3} \text{ M}$

oxygenated water over the pH range 8–12, obtaining a conversion of oxygen into peroxide of 75% at pH 9.0. In these experiments we acidified after mixing and assayed the peroxy titanium(IV) complex at pH 0.8 ($\lambda_{\text{max}} 405 \text{ nm}$, $\epsilon 830$). In agreement with Kristine and Shepherd³ we observed promptly the yellow peroxy titanium(IV) tartrate complex ($\lambda_{\text{max}} 348 \text{ nm}$) at pH 8–10.5. Clearly, in the light of these studies on two electron reduction, it is kinetically unlikely that the $g = 2.0134$ signal is due to an alkylperoxy species. Such peroxy radicals, in any event, normally give broad signals at g_{iso} values of 2.0150–2.0165.⁴

In further experiments we have allowed titanium(III) to form a complex with sodium gluconate at pH 7.0–9.0, observing an analogous singlet at $g = 2.0128$ on reaction with 1 equiv. of oxygen. Now the g value is relative to the gluconate 2-ketyl radical $(\text{HOCH}_2)(\text{CHOH})_3\overset{\cdot}{\text{C}}(\text{O}^{-})\text{CO}_2^{-}$, $g = 2.0042$, $a_{\text{CNOH}}(1) 0.66 \text{ mT}$.⁵ Attempts to generate the $\text{Ti}(\text{edta})\text{O}_2^{-}$ species by flowing aqueous dioxygen against 1 mM $\text{Ti}(\text{edta})\text{H}_2\text{O}^{-}$ gave no signal over the pH range 4–9.

Comparison of the observed g values (2.0134, 2.0128) with approximate g_{av} values derived from data on anisotropic superoxide complexes in the solid state⁶ lends support to the assignment of the signals to titanium(III) dioxygen complexes.

The authors thank the National Science and Engineering Research Council of Canada for financial support.

(Received, 9th June 1980; Com. 619.)

¹ F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, 1975, 8, 384; J. P. Collman, *ibid.*, 10, 265.

² P. West and P. Premovic, *J. Chem. Soc., Chem. Commun.*, 1977, 876.

³ F. J. Kristine and R. E. Shepherd, *J. Chem. Soc., Chem. Commun.*, 1980, 132.

⁴ R. W. Fessenden and R. N. Schuler, *J. Chem. Phys.*, 1963, 39, 2417.

⁵ P. R. West and R. C. Catton, unpublished observations.

⁶ B. R. McGarvey and E. L. Tepper, *Inorg. Chem.*, 1969, 8, 498; Y. Chimura, M. Beppu, S. Yoshida, and K. Tomara, *Bull. Chem. Soc., Japan*, 1977, 50, 691; J. Latour, J. Marchon, and M. Nakajima, *J. Am. Chem. Soc.*, 1979, 101, 3974.

Co-ordination Polymers of Rhodium(1+) with Di-isocyanonaphthalene (1,4 and 1,5) Linkages

By AVI EFRATY,* IRENE FEINSTEIN, FELIX FROLOW, and ALEXANDER GOLDMAN

(Departments of Organic Chemistry and Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel)

Summary The template polymerization of tetragonal rhodium(1+) with 1,4- and 1,5-di-isocyanonaphthalenes gives two-dimensional co-ordination polymers with a stacked layers arrangement; the powder X-ray diffractometric traces of these polymers are presented and discussed.

The isomers 1,4- and 1,5-di-isocyanonaphthalene¹ can be regarded as non-chelating bidentate ligands capable of forming stereochemically rigid linkages between metal nuclei with a bridge span of *ca.* 12 Å. Viewing the terminal isocyanide-to-metal bonds as vectors suggests that the terms 'colinear' (1,4) and 'parallel' (1,5) may be used to describe the bridging geometries of these ligands. Compared with the colinear (1,4) ligand, a displacement of 2.42 Å between the parallel vectors in 1,5-di-isocyno-

naphthalene requires a slightly longer bridge span (*ca.* 0.2 Å). The co-ordination properties of these bridging ligands were ascertained for a tetragonal rhodium(1+) system.

Di-isocyanonaphthalenes (1,4 and 1,5) react with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in CH_2Cl_2 solution to afford quantitative yields of insoluble green polycrystalline polymers which analyse as $[\text{Rh}(\text{bridge})_2^+\text{Cl}^-]_n$. These polymers readily absorb water, and therefore, unless rigorously dried *in vacuo*, are best formulated as $[\text{Rh}(\text{bridge})_2^+\text{Cl}^- \cdot x\text{H}_2\text{O}]_n$ ($x = 0-5$). A single strong $\nu(\text{NC})$ at $2040 \pm 5 \text{ cm}^{-1}$ in their i.r. spectra may suggest the presence of terminally co-ordinated isocyanides in a symmetric environment.

Two-dimensional models of the $[\text{Rh}(\text{bridge})_2]_n$ network which depict the template polymerization of tetragonal Rh^{I} with 1,4-di-isocyanonaphthalene [Figure (A)] and