

LASER RAMAN SPECTROSCOPIC EVIDENCE FOR THE EXISTENCE OF OXOPEROXOTITANATE(IV) IN AQUEOUS SOLUTION CONTAINING 'TITANYL' MOIETY AND THE SYNTHESIS OF AN UNUSUAL PEROXOTITANATE(IV) COMPLEX, POTASSIUM OXOPEROXODICHLOROTITANATE(IV) MONOHYDRATE, $K_2[TiO(O_2)Cl_2].H_2O$

MIHIR K. CHAUDHURI and BIMALENDU DAS

Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India.

ABSTRACT

Laser Raman spectrum of an yellow solution obtained from the reaction of freshly prepared TiO_2 with potassium chloride, hydrogen peroxide and hydrochloric acid at pH 6, adjusted by the addition of KOH solution, showed a distinct polarized signal at 970 cm^{-1} due to $\nu(Ti=O)$ in addition to the expected modes of peroxide (O_2^{2-}). This provides an evidence for the existence of oxoperoxotitanate(IV). Treatment of this solution with ethanol led to the synthesis of light yellow micro-crystalline potassium oxoperoxodichlorotitanate(IV) monohydrate, $K_2[TiO(O_2)Cl_2].H_2O$. The identity of the compound was established from chemical analyses, magnetic susceptibility and EPR measurements at ambient temperatures, and IR and laser Raman spectroscopic studies. A distorted octahedral structure of the complex $[TiO(O_2)Cl_2]^{2-}$ with $-Ti-O-Ti-$ interactions has been suggested on the basis of the spectroscopic results. The results suggest that a monomeric oxoperoxotitanate(IV) species formed in solution undergoes polymerization during its isolation in the solid form. The unusual oxoperoxotitanate(IV) species has been accounted for in terms of the interaction of π_g^* orbital of O_2^{2-} with a d -orbital of the metal.

INTRODUCTION

ALBEIT both titanium and vanadium form complexes with hydrogen peroxide. Studies on the peroxo chemistry of titanium are far less exhaustive than those of the vanadium. Peroxo complexes of titanium(IV) are intrinsically important because such compounds not only serve as model systems¹ but also act as reagents and catalysts² in organic synthesis. It was reported³ that a solution of titanyl sulphate in concentrated sulphuric acid reacted with an excess of hydrogen peroxide to afford a dark red compound which analysed as $Ti(O_2)SO_4.3H_2O$. It was further reported that both the peroxide (O_2^{2-}) and the sulphate occurred as chelated ligands with the metal centre being

hexa-co-ordinated containing two co-ordinated water molecules. Making use of a similar preparative method, a few more compounds were obtained from the solutions of titanium(IV), hydrogen peroxide and certain dibasic acids such as oxalic, malonic and maleic acids. It is believed that the peroxo(oxolato) species is probably the best characterized of these derivatives. In addition there are also a few well-defined molecular titanium(IV)-peroxo complexes⁴ such as (dipic) $Ti(O_2).2H_2O$. The X-ray structure determination showed that the compound $[Ti(dipic)(OH_2)(O_2)]$ occurs in an orthorhombic form⁵. Quite interesting are also the results of electronic structure calculations on dioxygen complexes from which it has been shown⁶ that for $Ti(\text{porph})O_2$ an η^2 structure,

[i.e. the peroxide being bonded in a chelated (C_2) manner] is favourable.

Though solid peroxo complex of both titanium and vanadium can be synthesized from aqueous solutions, there exists a very significant difference in the types of the compounds obtained thereof. Thus, while the peroxo-vanadium chemistry is dominated by oxo-peroxo species⁷⁻¹⁰, peroxo-titanium chemistry in contrast presents a different story. Indeed examples of oxoperoxotitanates(IV) are very sparse. To the best of our knowledge, $K_2[TiO(O_2)_2(dipic)_2]$ (dipic = dipicoline)¹¹ is one of the very few reported examples. A few non-peroxo complexes containing TiO^{2+} moiety, e.g. $TiOCl_4^{2-}$,¹² $TiOF_5^{3-}$,¹³ TiO (phthalocyanine)¹⁴ and TiO (porphyrin)¹⁵ are, however, known. Nevertheless, it is generally accepted that oxotitanates(IV) are rarely encountered^{16,17}.

Of concern to us, as a sequel to our efforts in the field of peroxotitanate(IV) chemistry¹⁸, was to generate an oxoperoxotitanate(IV) in solution followed by isolation in the solid state which has now been achieved. This article presents an account of the results of such studies including the synthesis and characterization of potassium oxoperoxodichlorotitanate(IV) monohydrate, $K_2[TiO(O_2)Cl_2].H_2O$.

EXPERIMENTAL

The chemicals used were all reagent grade products. IR spectrum was recorded on a Perkin Elmer (model 983) spectrophotometer separately in KBr and Nujol media. Laser Raman spectrum was recorded on a SPEX Ramalog (model 1403) spectrometer. The 5145 Å laser line from the Spectra-Physics (model 165) argon laser was used as the excitation source. The scattered light at 90° was detected using a cooled RCA 31034 photomultiplier tube followed by photon count processing system. The spectra of the solution and of the solid were recorded at ambient temperatures. The spectra were recorded either in a quartz capillary or in the form of a pressed

pellet. The EPR spectrum of the solid was recorded on a similar instrument used earlier¹⁹. The pH of the reaction solution was measured with a Systronics (type 335) digital pH meter, and also with pH indicator (BDH) paper. Magnetic susceptibility was measured by the Gouy method, using $Hg[Co(SCN)_4]$ as the calibrant.

Evidence for the existence of oxoperoxotitanate(IV) complex containing 'titanyl' moiety, and synthesis of potassium oxoperoxodichlorotitanate(IV) monohydrate, $K_2[TiO(O_2)Cl_2].H_2O$

An amount of 1 g (12.5 mmol) of freshly prepared TiO_2 was mixed well with 9.4 g (126.17 mmol) of potassium chloride in a beaker with the molar ratio of Ti:KCl being maintained at 1:10. To this was added 25 cm³ (220.5 mmol) of 30% H_2O_2 with stirring, and the reaction container was placed in an ice-water bath. The whole was stirred for ≈ 10 min. An amount of 15 cm³ of 9 M HCl was added to the resultant mixture to get a clear deep red solution. Drop-wise addition of KOH solution (30% w/v) to the above mixture, until the reaction solution attained a pH of 6, changed the colour of the solution to yellow. Laser Raman spectrum of a sample of the above solution was recorded at ambient temperatures and the spectrum exhibited, in addition to the expected modes of peroxide (O_2^{2-}), a distinct polarized signal at 970 cm⁻¹ assignable to $\nu(Ti=O)$ showing the existence of oxoperoxotitanate(IV) containing TiO^{2+} moiety.

The yellow solution thus obtained was treated with a small amount of precooled ethanol until light yellow precipitate just began to appear. The whole was kept in an ice-water bath for ≈ 30 min, and the compound was separated by filtration, washed twice with ethanol, and finally dried *in vacuo* over concentrated sulphuric acid. The yield of $K_2[TiO(O_2)Cl_2].H_2O$ was 2.5 g (76%).

Elemental analyses

Titanium content in the compound was

estimated gravimetrically as TiO_2 , after precipitation with cupferron²⁰. The peroxide content was determined by redox titration with standard potassium permanganate solution²¹ in the presence of boric acid. Chloride was estimated by Volhard's method²². Potassium was determined by the methods described earlier^{10, 18}. Anal. Calcd for $\text{K}_2[\text{TiO}(\text{O}_2)\text{Cl}_2] \cdot \text{H}_2\text{O}$, K, 29.65; Ti, 18.25; O_2^{2-} (active oxygen), 12.16; Cl, 26.99%. Found: K, 29.5; Ti, 18.3; O_2^{2-} (active oxygen), 12.1; Cl, 26.9%.

RESULTS AND DISCUSSION

An existence of 'titanyl' species in aqueous solution was of concern for a long time. However, it was recently shown^{23, 24} that titanium(IV) can exist as a 'titanyl' species in solution under an appropriate condition. Our interest in the chemistry of peroxo-metal compounds^{10, 25-27} in general and peroxotitanates(IV)^{18, 28} in particular led us to investigate the possibility of existence of oxoperoxotitanate(IV) species in solution. We were also interested in isolating such a species in the solid state. It was observed that the reaction of a sample of freshly prepared TiO_2 (obtained by dissolving a commercial variety of TiO_2 in aqueous HF followed by precipitation with aqueous ammonia) with potassium chloride, aqueous HCl and hydrogen peroxide afforded a deep red solution. The pH of the medium, when raised to 6 by adding KOH, produced a yellow solution characteristic of the formation of a peroxotitanate(IV) in the reaction medium. The laser Raman spectrum of the solution showed, in addition to the expected modes of peroxide (O_2^{2-}), a distinct polarized signal at 970 cm^{-1} which undoubtedly owes its origin to $\nu(\text{Ti}=\text{O})$ ^{23, 24}. This, therefore, provided a clear evidence of the formation of an oxoperoxotitanate(IV) species in solution. Thus, it may be inferred that oxoperoxotitanate(IV) complex containing a true 'titanyl' moiety is capable of being formed under appropriate experimental conditions. The other aim was to isolate such a species in the solid

form. In order to achieve this the yellow solution, on being treated with a small amount of pre-cooled ethanol (vide experimental), afforded a light yellow micro-crystalline product in a very good yield. The product on being isolated, purified, dried, and analysed revealed the stoichiometry of $\text{K}:\text{Ti}:\text{O}_2^{2-}:\text{Cl}$ as 2:1:1:2. The compound did not permit molar conductance measurement owing to its insolubility in both water and in common organic solvents. The product is EPR silent. This as well as the result of magnetic susceptibility measurement, which evidenced the diamagnetic nature of the product, lend a clean support to the occurrence of titanium(IV) in the aforesaid product.

The compound was quite stable for a prolonged period and its stability was ascertained by chemical estimation of peroxide content from time to time. The importance of chemical determination of active oxygen content in such compounds has already been emphasized^{10, 18, 25} and the results obtained herein ensures the presence of one peroxide per titanium(IV) centre. Although the IR spectrum of the compound is straightforward, the observed bands and their positions are very informative. The significant features of the spectrum are the absorptions originating from the presence of coordinated peroxide (O_2^{2-}) at $860\text{ (vs)}\text{ cm}^{-1}$ assigned to $\nu(\text{O}-\text{O})\nu_1$, at 600(s) and at $535\text{(s)}\text{ cm}^{-1}$ attributed to the complementary ν_3 and ν_2 modes, respectively, of $\nu(\text{Ti}-\text{O}_2)$ vibrations^{10, 18, 25, 29}, and at 470 cm^{-1} due to $\nu(\text{Ti}-\text{Cl})$ ³⁰. Another important feature of the spectrum is the appearance of a medium intensity band at 720 cm^{-1} and the clear absence of any absorption in the 970 cm^{-1} region. This shows that the terminal oxo group of the 'titanyl' moiety which was present in the complex formed in solution has now lost its identity in the corresponding solid compound owing to the formation of an oxo-bridged (μ -oxo) species through $-\text{Ti}-\text{O}-\text{Ti}-$ interactions. The IR signature at $720\text{(m)}\text{ cm}^{-1}$ arising from $\nu(-\text{Ti}-\text{O}-\text{Ti}-)$ ³¹ modes attest to the above contention. Two additional bands at 1640(s) and at $3460\text{(m)}\text{ cm}^{-1}$ are typical of those, arising from the occurrence of un-coordinated water^{32, 33}

Considering the results of chemical analyses, magnetic susceptibility, EPR measurements and IR spectroscopic studies, it appears logical to assign $K_2[TiO(O_2)Cl_2].H_2O$ as the formula of the compound. It may be pointed out, in line with the assumptions of Hoffman *et al.*³⁴, that an interaction of the occupied π_g^* orbital of the peroxide O_2^{2-} ligand with the d -orbitals of the central titanium atom would explain the expansion of coordination sphere and in turn account for the formation of the oxoperoxotitanate species. A similar π_g^*-3d interaction was also proposed by Swalen and Ibers³⁵ for the oxoperoxochromate, $CrO(O_2)_2$. The complex $[TiO(O_2)Cl_2]^{2-}$ species might have a distorted octahedral structure which it has attained through $-Ti-O-Ti-$ interactions with the contiguous titanium centres in the crystal lattice. The insoluble nature of the compound adduces support for the polymeric nature of the aforementioned complex ion. It may be mentioned that thermodynamically polymerization during solid formation might not be a very favoured process; however, such a phenomenon could be operative if it is aided by the conductive entropy of the process. Although the occurrence of a polymeric species containing lattice water is not very common, there have been definite cases where this has really happened. The compound, potassium pentafluoromanganate (III) monohydrate, $K_2MnF_5.H_2O$ ³³, for instance, is a good example of this type and this has also been confirmed by X-ray crystallography³⁶.

In order to get further support concerning the formula and the proposed structure of the complex, laser Raman spectrum of the solid was recorded at ambient temperatures. The spectrum showed signals at 860, 650, 605, 530, 520, 480, and 460 cm^{-1} . The bands at 860, 605 and 530 cm^{-1} complement the corresponding IR absorptions owing to $\nu(O-O)\nu_1$, $\nu(Ti-O_2)\nu_3$, and $\nu(T-O_2)\nu_2$, respectively¹⁸ and conform to the occurrence of a chelated peroxide (O_2^{2-}) ligand coordinated to the metal centre in a triangular bidentate (C_{2v}) manner. The signal at 480 cm^{-1} is related to that observed at 470 cm^{-1} in the IR spectrum of the compound

and is assignable to $\nu(Ti-Cl)$. Here again, like in the IR spectrum, no $\nu(Ti=O)$ mode could be observed. However, signals at 650, 520 and 460 cm^{-1} due to $\nu(-Ti-O-Ti-)^{17}$ vibrations support the proposition that the complex ion in the solid state does not have a monomeric structure with a terminal $Ti=O$ ('titanyl') unit, instead the complex species polymerizes (through $-Ti-O-Ti-$ interactions) during the process of isolation in the solid state from solution.

In conclusion, we note that like vanadium, the hitherto unreported formation of oxoperoxotitanate(IV) complex in solution containing a 'titanyl' moiety is evidenced. The complex species formed in solution, under the present experimental conditions, polymerizes in the process of its isolation in the solid form via μ -oxo bridges in the crystal lattice. In addition, a distorted octahedral structure of the complex ion $[TiO(O_2)Cl_2]^{2-}$, through $-Ti-O-Ti-$ interactions involving contiguous titanium atoms, is in agreement with the available data. In this way further insight into the chemistry of oxoperoxotitanates(IV) may be gained.

ACKNOWLEDGEMENTS

The authors thank CSIR, New Delhi, for financial support and the reviewer for helpful comments.

3 June 1988; Revised 6 February 1989

1. Guillard, R., Latour, M. J., Lecompte, L., Marchon, J. C., Protas, J. and Ripoll, D., *Inorg. Chem.*, 1978, 17, 1228.
2. Katsuki, T. and Sharpless, K. B., *J. Am. Chem. Soc.*, 1980, 102, 5974.
3. Jere, G. V. and Patel, C. C., *Nature (London)*, 1962, 194, 471.
4. Schwarzenbach, D., *Helv. Chim. Acta*, 1972, 55, 2990; *Inorg. Chem.*, 1970, 9, 2371.
5. Manohar, H. and Schwarzenbach, D., *Helv. Chim. Acta*, 1974, 57, 1086.
6. Rohmer, M. M., Barry, M., Dedieu, A. and Veillard, A., *Int. J. Quantum Chem. (Quantum Biol. Symp.)*, 1977, 4, 337.

7. Vuletic, N. and Djordjevic, C., *J. Chem. Soc.*, 1973, 1137.
8. Campbell, N. J., Capparelli, M. V., Griffith, W. P. and Skapski, A. C., *Inorg. Chim. Acta*, 1983, 77, L215.
9. Mimoun, H., Saussine, L., Daire, E., Postel, M., Fischer, J. and Weiss, L., *J. Am. Chem. Soc.*, 1983, 105, 3101.
10. Chaudhuri, M. K. and Ghosh, S. K., *Inorg. Chem.*, 1984, 23, 534; *J. Chem. Soc., Dalton Trans.*, 1984, 507.
11. Schwarzenbach, D., *Inorg. Chem.*, 1970, 9, 2391.
12. Feltz, A., *Z. Chem.*, 1967, 7, 158.
13. Dehnicke, K., Pausewang, G. and Rudorff, W., *Z. Anorg. Allg. Chem.*, 1969, 366, 64.
14. Taube, R., *Z. Chem.*, 1963, 3, 194; Block, B. P. and Meloni, E. G., *Inorg. Chem.*, 1965, 4, 111.
15. Dwyer, P. N., Puppe, L., Buchler, J. W. and Scheidt, W. R., *Inorg. Chem.*, 1975, 14, 1782.
16. Clark, R. J. H., *The chemistry of titanium and vanadium*, Elsevier, Amsterdam, 1968.
17. Wiegardt, K., Quilitzsch, U., Weiss, J. and Nuber, B., *Inorg. Chem.*, 1980, 19, 2514.
18. Chaudhuri, M. K. and Das, B., *Inorg. Chem.*, 1986, 25, 168.
19. Chaudhuri, M. K., Ghosh S. K. and Subramanian, J., *Inorg. Chem.*, 1984, 23, 4439.
20. Vogel, A. I., *A text book of quantitative inorganic analysis*, Longmans, Green and Co., New York, 1962, p. 544.
21. Vogel, A. I., *A text book of quantitative inorganic analysis*, Longmans, Green and Co., New York, 1962, p. 295.
22. Vogel, A. I., *A text book of quantitative inorganic analysis*, Longmans, Green and Co., New York, 1962, p. 266.
23. Graetzel, M. and Rotzinger, E. P., *Inorg. Chem.*, 1985, 24, 2320.
24. Comba, P. and Merbach, A., *Inorg. Chem.*, 1987, 26, 1315.
25. Chaudhuri, M. K. and Islam, N. S., *J. Indian Chem. Soc.*, 1985, 62, 815; Chaudhuri, M. K. and Ghosh, S. K., *Inorg. Chem.*, 1982, 21, 4020.
26. Bhattacharjee, M. N., Chaudhuri, M. K. and Dutta Purkayastha, R. N., *J. Chem. Soc., Dalton Trans.*, 1985, 409.
27. Bhattacharjee, M., Chaudhuri, M. K. and Dutta Purkayastha, R. N., *Inorg. Chem.*, 1986, 25, 2354.
28. Chaudhuri, M. K. and Das, B., *Polyhedron*, 1985, 4, 1449.
29. Griffith, W. P., *J. Chem. Soc.*, 1964, 5248; Griffith, W. P. and Wickins, T. D., *J. Chem. Soc.*, 1967, 590; 1968, 397.
30. Jenkins, L. S. and Willey, G. A., *J. Chem. Soc., Dalton Trans.*, 1979, 1697.
31. Coutts, R. S. P. and Wailes, P. C., *Inorg. Nucl. Chem. Lett.*, 1967, 3, 1.
32. Curtis, N. F., *J. Chem. Soc. (A)*, 1968, 1584.
33. Bhattacharjee, M. N., Chaudhuri, M. K., Dasgupta, H. S. and Khathing, D. T., *J. Chem. Soc., Dalton Trans.*, 1981, 2587.
34. Hoffman, R., Chen, M. M. L. and Thorr, D. L., *Inorg. Chem.*, 1977, 16, 503.
35. Swalen, J. D. and Ibers, J. A., *J. Chem. Phys.*, 1962, 37, 17.
36. Edwards, A. J., *J. Chem. Soc.*, 1971, 2653.

ANNOUNCEMENT

NATIONAL SYMPOSIUM ON STRUCTURE AND BONDING IN INORGANIC MATERIALS

The above Symposium will be held during May 23–25, 1989 and is organized by the Shivaji University, Kolhapur.

The tentative themes of the Symposium are: 1. Synthesis, analysis and structure of ceramic bulk superconducting materials and related compositions; 2. Techniques of solid state physics and chemistry, 3. Oxygenation, fluxional chemistry, mixed valence, geochemistry of oxide minerals and characterization

of mixed oxides. 4. Ferrites, catalysts and semi-conducting materials of oxidic composition. 5. The novel coordination compounds in solid state studies. 6. Teaching of theoretical and experimental aspects of superconductivity.

Further particulars may be had from: Dr C. K. Bhaskare, Convener, National Symposium on Structure and Bonding in Inorganic Materials, Shivaji University, Kolhapur 416 004.
