A Mixed Valence Binuclear Complex of Vanadium(IV) and Vanadium(V). X-Ray Crystal Structure of $(NH_4)_3[V_2O_3(\text{nitrotriacetate})_2]\cdot 3H_2O$

By MASATO NISHIZAWA, KEN HIROTSU,† SHUN'ICHIRO OOI,† and KAZUO SAITO*

(*Chemistry Department, Faculty of Science, Tohoku University, Sendai* 980, *Japan; and* †*Chemistry Department, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka* 558, *Japan*)

Summary A deep blue mixed valence complex $[VO(nta)\text{-}O\text{-}VO(nta)]^{3-}$ (nta = nitrilotriacetate) was found to be in equilibrium with $[V^{IV}O(nta)(H_2O)]^-$ and $[V^VO_2(nta)]^{2-}$ in aqueous solution; the crystal structure of its ammonium salt trihydrate has been determined.

ADDUCT formation between vanadium(IV) and vanadium(V) complexes has been reported for various ligands.[1,2] The electronic interaction between the vanadium ions seems very weak, and a linkage through the *trans* (apical) site has been suggested.[2] We have synthesised a deeply coloured binuclear complex containing nitrilotriacetate (nta^{3-}), studied its e.s.r. spectra in aqueous solution, determined its structure by X-ray crystallography, and found a characteristic interaction between the two vanadium ions.

Blue crystals of $Ba[V^{IV}O(nta)(H_2O)]_2\cdot 4H_2O$ were obtained by mixing $V^{IV}OSO_4$, $H_3(nta)$, and $Ba(OH)_2$ in aqueous solution, centrifuging, evaporating at 50 °C, and adding ethanol. This was converted into the potassium salt by cation exchange, and treated with KNO_2. Yellow crystals of $K[V^VO_2(nta)]\cdot 3H_2O$ were formed on addition of ethanol. Aqueous solutions of the former and latter potassium salts were mixed, and the resulting deep blue solution was treated with NH_4ClO_4 and ethanol to give deep blue crystals with the composition $(NH_4)_3[V_2O_3(nta)_2]\cdot 3H_2O$.

This complex showed i.r. absorption due to the V=O stretching vibration at 947 cm^{-1} (KBr disc) (*cf.* 975, and 920 and 890 cm^{-1} for the V^{IV} and the V^V complexes, respectively), and its electronic spectra showed peaks (aqueous solution, pH 3—5) at 583 (240), 750 (380), and 1000 nm (350) (ϵ in cm^{-1} dm^3 mol^{-1} in parentheses). Spectrophotometry in aqueous solution indicated that this complex is in equilibrium with the V^{IV} and V^V complexes [equation (1)], with a formation constant K of 20 dm^3 mol^{-1} at 25 °C (I = 1·0 M).

$$[V^{IV}O(nta)(H_2O)]^- + [V^VO_2(nta)]^{2-} \rightleftharpoons [VO(nta)\text{-}O\text{-}VO(nta)]^{3-} + H_2O \qquad (1)$$

An aqueous solution of $K[V^{IV}O(nta)(H_2O)]$ gave 8 hyperfine peaks in its e.s.r. spectrum (Figure 1a), with g_0 and $|a_0|$ values of 1·978 and 100 × 10^{-4} cm^{-1}, respectively. A 0·01 M solution of $(NH_4)_3[V_2O_3(nta)_2]$ gave a similar pattern, but a 0·02 M solution containing 0·08 M $[V^VO_2(nta)]^{2-}$ gave the pattern shown in Figure 1c. When the peaks due to the V^{IV} complex were subtracted, 15 hyperfine peaks remained (Figure 1b), from which g_0 and $|a_0|$ were found to be 1·981 and 52 × 10^{-4} cm^{-1}, respectively. The e.s.r. spectra of crystalline V_2O_5 have been examined by several authors,[3] and 15 or 29 hyperfine peaks observed depending on the direction of magnetic field. These peaks indicate delocalisation of an electron, arising from the inevitable V^{IV} impurity,

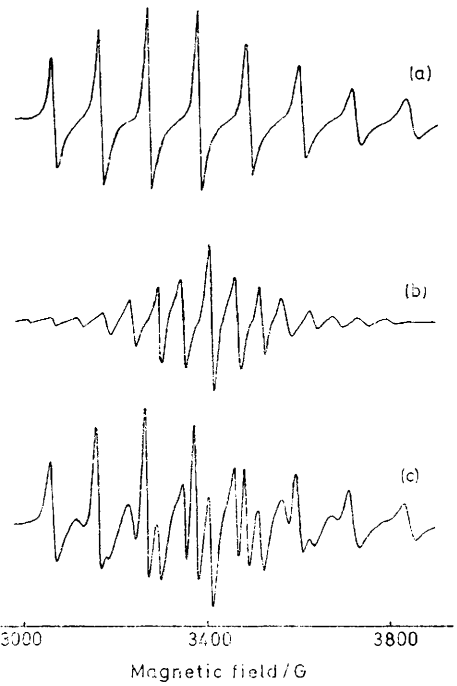

FIGURE 1. (a) E.s.r. spectrum of $K[V^{IV}O(nta)(H_2O)]$ in aqueous solution at room temperature; (b) difference spectrum in which the component of (a) is subtracted from that in (c); (c) e.s.r. spectrum of 0·02 M $K[V^{IV}O(nta)(H_2O)]$ containing 0·08 M $K_2[V^VO_2(nta)]$ in water–methanol (1 : 1 v/v) at room temperature.

between 2 and 4 V atoms, respectively (amorphous V_2O_5 gave only 8 signals). The present binuclear complex anion must have a delocalised electron in aqueous solution.

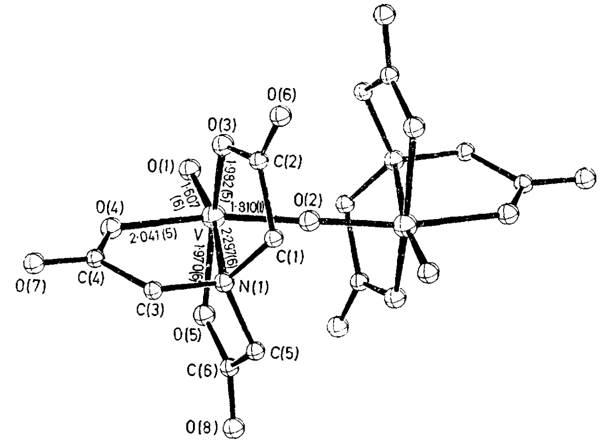

Figure. 2. *X*-Ray structure of the binuclear complex anion in $(NH_4)_3[V_2O_3(nta)_2]\cdot 3H_2O$.

Single crystals of $(NH_4)_3[V_2O_3(nta)_2]\cdot 3H_2O$ are monoclinic, space group $C2/c$, with cell dimensions $a = 17\cdot993(8)$, $b = 9\cdot862(5)$, $c = 15\cdot134(8)$ Å, $\beta = 107\cdot7(1)°$, and $Z = 4$. Its structure was determined from 1300 diffractometer data (Mo-K_α radiation) and refined to R 0·065. The structure of the binuclear anion is shown in Figure 2. It has crystallographic C_i ($\bar{1}$) symmetry, so the V–O–V′ segment is linear. The V atoms have a distorted octahedral co-ordination. The V–O(1) bond length (1·607 Å) resembles the V^{IV}=O (1·56—1·63 Å[4]) rather than the V^{V}=O length (1·62—1·66 Å[5]) in VO_2^+ complexes. The short V–O(2) bond (1·810 Å) indicates multiple bond character, but it is longer than the V^{V}=O bond.‡

All the information clearly indicates that the two vanadium ions in the binuclear complex are equivalent to each other, both in the crystalline state and in aqueous solution at room temperature. The interaction between vanadium ions through the basal site of the V=O unit seems to be much more marked than that through the apical site. Such a difference may be related to the remarkable regioselectivity for these two co-ordination sites in substitution reactions of oxovanadium(IV) complexes in aqueous solution.[6]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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