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Observations on the Spectra and Structures of Seven- and Eight-co-ordinate Oxalato Complexes of Titanium(III)

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Some time ago [1] $KTi(ox)_2 \cdot 2H_2O$, $NH_4[Ti(ox)_2] \cdot 2H_2O$ and $Ti_2(ox)_3 \cdot 10H_2O$ (ox = oxalate) were prepared according to the method of Stähler [2]. The crystal structure of the decahydrate contains a centrosymmetric dimer, $[Ti_2(ox)_3(H_2O)_6]$ and also four non-bonded water molecules. Each metal atom is seven-co-ordinate pentagonal bipyramidal with two water molecules in axial positions and one in an equatorial plane together with one bridging and one non-bridging oxalate ligand [3]. Further work on the anionic oxalato complexes of titanium(III) led to the preparation of $Cs[Ti(ox)_2(H_2O)_3] \cdot 2H_2O$. The discrete anion contains a seven-co-ordinate pentagonal bipyramidal titanium atom with two non-bridging oxalate ions acting as chelating ligands in the equatorial plane and the three water molecules occupying the remaining equatorial site and the axial sites [4].

We report here the vibrational and electronic spectra of these two molecules which have been examined in the light of their established molecular structures and also report the spectra of $K[Ti(ox)_2] \cdot 2H_2O$.

Experimental

All preparations were carried out under nitrogen in deaerated aqueous solutions. $Ti_2(ox)_3 \cdot 10H_2O$ and $MTi(ox)_2 \cdot 2H_2O$ (M = NH_4, Rb, K) were prepared following ref. 2; $Cs[Ti(ox)_2 3H_2O] \cdot 2H_2O$ following ref. 4. For M = Na the compound was prepared by adding sodium acetate solution to $TiCl_3$ in excess oxalic acid solution.

X-ray Studies

Powder photographs showed that $M[Ti(ox)_2] \cdot 2H_2O$, (M = NH_4, Rb, K) were isomorphous with (for M = K) cell dimensions $a = b = 5.704$, $c = 7.476$ Å. M = Na had cell dimensions of $a = b = 8.057(8)$, $c = 15.165(14)$ Å. Preliminary single crystal studies on the K and Na salts suggest that the two compounds have equivalent structures but that the K crystal is twinned and the structure disordered. Refinement of diffractometer data for the Na salt has not so far proved successful being hampered by the poor quality of the data, disorder between cations and lattice water and merohedral twinning, but it is clear that the structure consists of layers of eight-co-ordinate titanium atoms in the llll square antiprismatic configuration linked by bridging oxalate ligands with alkali cations and lattice water located between the layers (Figure 1).

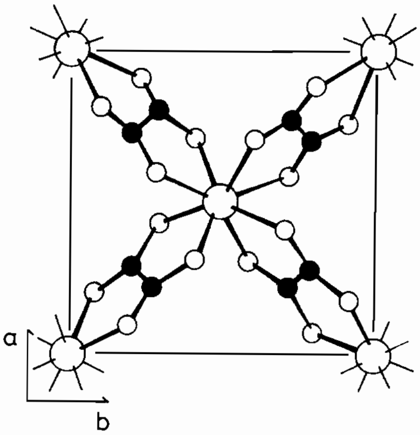

Fig. 1. Proposed structure for $[Ti(ox)_2]_n^{n-}$ (open circles: large Ti, medium O; closed circles: C).

Vibrational Spectra

Infrared spectra were recorded, using Perkin Elmer 457 and Unicam SP200 spectrometers, by the halide disc (KCl) technique. Comparison with mull spectra was made in each case to confirm that structural changes had not been induced in the disc preparation. Bridging oxalato ligands can readily be distinguished from non-bridging co-ordinated oxalate from infrared spectra. Non-bridging coordinated oxalate gives rise to two absorption bands, occurring at about 1280 cm^{-1} (1250 to 1300 cm^{-1}) and 1400 cm^{-1} (1380 to 1430 cm^{-1}) which have been attributed to vibrational modes involving C–O stretch [5]. When only bridging oxalate is present these bands are replaced by two of lower intensity falling between 1300 cm^{-1} and 1380 cm^{-1} [6]. The infrared spectra in the range 1500–1100 cm^{-1} for (I) $[Ti_2(ox)_3(H_2O)_6] \cdot 4H_2O$, (II) $Cs[Ti(ox)_2(H_2O)_3] \cdot 2H_2O$ and (III) $K[Ti(ox)_2] \cdot 2H_2O$ are shown in Figure 2. From the spectra it can be deduced that (I) contains both bridging and non-bridging oxalate ligands, (II) contains only non-bridging oxalate and that (III) contains only bridging oxalate. These observations are in accord with the proposed molecular structures.

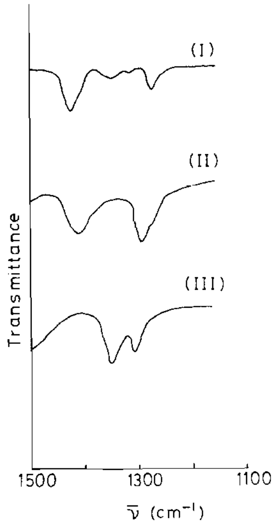

Figure 2. Infrared spectra.

Electronic Spectra (Diffuse Reflectance)

Diffuse reflectance spectra were plotted with a Beckman D.U. and a Unicam (SP800) Spectrophotometer. Low intensity bands attributed to *d* electron transitions were obtained in the region 16,000 to 5000 cm^{-1}. The first two compounds show the expected two bands for seven-co-ordinate Ti(III) in a pentagonal bipyramidal environment [7] for $A_1 \leftarrow E_1$ and $E_2 \leftarrow E_1$. Simple crystal field calculations [8] show the relative frequencies of the bands in the two compounds to be entirely consistent with the structures found. Thus the position of the $A_1 \leftarrow E_1$ band (at about 12,400 cm^{-1}), depending largely on the axial ligands, is expected to be relatively insensitive to whether the oxalate is bridging or not and so it proves (12,400, 12,500 in (I) and (II) respectively). The other band $E_2 \leftarrow E_1$ is much lower in (I) than in (II) (9300 cm^{-1} vs. 10,500 cm^{-1}) because of the lesser contribution of the bridging oxalate to the field. With a simple crystal field theory the difference can be shown to be consistent with differences in Ti–O bond lengths.

(III) shows two bands at 12,300 cm^{-1} and 6800 cm^{-1} and clearly has a different structure from (I) and (II). As it is unlikely that the complex could be seven-co-ordinate and not be pentagonal bipyramidal [7], an eight co-ordinate structure seemed possible. The spectrum is consistent with a square antiprismatic structure, but not with a dodecahedral structure [9, 10]. The ratio of 1.81 between the observed band frequencies, which are attributed to $E_3 \leftarrow A_1$ and $E_2 \leftarrow A_1$ transitions, when compared with a graph of energy levels plotted as functions of the angle θ between the Ti–O bonds and the unique axis [9] gives a θ value of about 55.2°. This is less than values calculated for the hard sphere (59.3°) and the most favoured polyhedron (57.3°) and that found in the eight-co-ordinate, llll square antiprismatic molecule $Nb(dpm)_4$ {dpm = 2,2,6,6-tetramethyl-3,5-heptane dionate} (57.0°), but is consistent with the preliminary X-ray results.

Conclusion

There are thus three distinct structural types proposed for the oxalato complexes of titanium(III); the partially bridged dimeric structure of $[Ti_2(ox)_3(H_2O)_6]\cdot 4H_2O$, the unbridged structure of $Cs[Ti(ox)_2(H_2O)_3]\cdot 2H_2O$, both of these containing seven-co-ordinate titanium(III) and the fully bridged eight-co-ordinate structure of $K[Ti(ox)_2]\cdot 2H_2O$. It has been found that the vibrational and electronic spectra of the compounds can readily be interpreted on the basis of these structures. The llll isomeric structure proposed for (III) from the X-ray study is relatively rare for eight-co-ordinate molecules but is particularly well suited to structures with large normalised bites {= 1.25 in (III)} [10].

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