538. *Charge Transfer from Inorganic Ions to Titanium*(IV)

By M. L. REYNOLDS

MANY titanium(IV) compounds and complexes with inorganic ions show absorption spectra which may be attributed to charge transfer from the inorganic ion to the titanium(IV) ion.[1-3] The brown colour of solutions containing iron(II) and titanium(IV) has been investigated,[2] and interactions between titanium(III) and titanium(IV) in hydrochloric [3] and sulphuric [4] acids have been described. A number of solid sulphates containing titanium(IV) and bivalent cations of the first transition series have been prepared.[5] The manganese, iron, and cobalt compounds are yellow, blue, and red-brown, respectively, whereas the other double sulphates are colourless. The absorption spectra recorded in this work are discussed in terms of the oxidation potentials of the couples involved. In the course of the work several new interactions were observed.

Solution Spectra.—The nature of the titanium(IV) species present in aqueous solutions is uncertain. Titanium(IV) solutions (0·1—5 mM) in 2N-sulphuric or 2N-perchloric acid show continuous absorption at wavelengths below 320 mμ, and there are well defined points of inflexion in the absorption curves at 265 and 270 mμ, respectively. Titanium(IV) solutions containing bisulphite show a discrete peak at 385 mμ and appear yellow. The optical density at 385 mμ of a 30 mM-titanium sulphate solution in 2N-sulphuric acid containing 0·36M-sodium hydrogen sulphite is 0·52. Since the extinction coefficient would be of the order of 10^4 if the transition were electronically allowed, the amount of complex formation appears to be only some 0·2%.

Solutions containing iron(II) and titanium(IV) sulphates are brown in colour and the absorption which commences at about 600 mμ continues into the ultraviolet. No absorption peak is observed since the spectrum merges with the absorption of the titanium sulphate complexes. Beukenkamp and Herrington [2] suggests that the species responsible for the absorption contains iron and titanium in the molar ratio of 2 : 1. The present author (see following Note) has shown that a 1 : 1 species is also present, and that the interaction occurs in perchlorate as well as in sulphate solutions.

A similar interaction occurs in green solutions containing vanadyl and titanium(IV) sulphates. In addition to the ligand-field absorption of the vanadyl ion at 740 mμ, continuous absorption occurs at wavelengths below 480 mμ. No visible absorption is observed in solutions containing titanium(IV) sulphate and any of the other bivalent ions of first-row transition metals which are stable in its presence. However, any absorption in the ultraviolet would be masked by the absorption of titanium sulphate complexes as mentioned above.

Solid Spectra.—In this work the series of compounds $MSO_4,Ti(SO_4)_2$ were prepared and investigated [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)]. Examination of the *d*-values of the *X*-ray diffraction photographs and of the infrared absorption frequencies of these compounds shows that structurally the compounds fall into two groups, *viz.*, those containing nickel, copper, or zinc, and those containing manganese, iron, or cobalt. The magnetic susceptibilities at room temperature of the iron and cobalt compounds are $31·0 \times 10^{-6}$ and $24·2 \times 10^{-6}$ electromagnetic c.g.s. units, respectively, giving effective magnetic moments of 5·36 and 4·73 B.M. Whereas the susceptibility of the iron compound indicates that the iron is octahedrally co-ordinated and bivalent, the susceptibility of the cobalt compound could arise with either octahedral or tetrahedral co-ordination of the bivalent ion. The reflection spectra of all the compounds show broad absorption maxima at about

---

[1] R. A. Ford, Photospectrometry Group Bulletin, 1958, **11**, 282; A. L. Companion and R. E. Wyatt, *J. Phys. and Chem. Solids*, 1963, **24**, 1025; O. T. Zimmerman, Ph.D. Thesis, Purdue, 1958.

[2] J. Beukenkamp and K. D. Herrington, *J. Amer. Chem. Soc.*, 1960, **82**, 3025.

[3] C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 1327.

[4] Ya G. Goroshchenko and M. M. Godneva, *Russ. J. Inord. Chem.*, 1961, **6**, 745.

[5] A. D. Damodaron and V. G. Neurganokar, *J. Sci. Ind. Res., India*, 1961, **19***B*, 364; S. Z. Haider and N. Begum, *J. Inorg. Nuclear Chem.*, 1961, **16**, 365; S. M. Mehta and S. R. Patel, *J. Amer. Chem. Soc.*, 1951, **73**, 224.

290 and 370 mμ which in the case of the manganese and cobalt compounds continue into the visible region of the spectrum. The cobalt and iron compounds also have absorption bands at 550 mμ.

Discussion.—Visible and ultraviolet absorption is observed in a number of very different systems containing titanium(IV) ions. It is suggested that in all cases this is due to charge transfer to titanium(IV). In solutions of sulphate and perchlorate, which are normally oxidising ligands, the absorption occurs at very high energies. Bisulphate, a more powerful reducing agent, gives rise to absorption at lower energy. The absorption observed with inorganic cations may be correlated with the oxidation potentials involved and the proximity of the cation to the titanium(IV) ion. In solution, titanium(IV) has been observed to interact with only ferrous and vanadyl ions, and it is significant that the oxidation potentials of these two ions are considerably lower than any of the other ions studied (see Table).

Oxidation potentials of divalent cations [6] (volts).

VO^{2+}	Mn^{2+}	Fe^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
−1·00	−1·50	−0·77	−1·82	Not measurable	

Solid hydrated ferrous titanium sulphates are brown, but the anhydrous compounds are blue. Transitions, therefore, require less energy as the two cations come closer together whereas interactions between titanium(IV) and manganese(II) or cobalt(II), which have considerably greater oxidation potentials, are observed only in the anhydrous solids. Oxidation states of +3 are rare or unknown for nickel, copper, and zinc, and interactions are not observed between titanium(IV) and these cations. The absorption band at 550 mμ observed in the cobalt compound is attributed to a ligand-field transition (cf. the absorption band at 520 mμ of anhydrous cobalt sulphate). The anhydrous sulphates of the other cations are colourless.

Experimental.—*Materials.* Titanium sulphate solutions were prepared from titanyl sulphate dihydrate; other reagents were AnalaR grade. The double sulphates were prepared by heating equimolar quantities of the two constituents in 80% sulphuric acid until precipitation occurred, usually at about 250°.

X-*Ray diffraction* (Cu K_α radiation). The observed *d*-values were:

$MnSO_4,Ti(SO_4)_2$: 5·5w, 4·1s, 3·8s, 3·15s, 2·70w, 2·40m, 2·10w, 2·00w, 1·90m, 1·80m, 1·75m, 1·62m, 1·45m.

$FeSO_4,Ti(SO_4)_2$: 5·5m, 4·25, 3·8s, 3·5s, 3·25s, 2·97s, 2·65s, 2·40m, 2·05m, 1·84m, 1·57s, 1·45w.

$CoSO_4,Ti(SO_4)_2$: 5·5m, 4·3s, 3·8s, 3·5, 3·20s, 3·00m, 2·65m, 2·40m, 1·87m, 1·57m, 1·45w.

$NiSO_4,Ti(SO_4)_2$: 5·5w, 4·75s, 4·05s, 3·75s, 3·25s, 3·00s, 2·50s, 2·32m, 2·17m, 2·10m, 2·00m, 1·95m, 1·80w, 1·75m, 1·65s, 1·61w, 1·59m, 1·47m.

$CuSO_4,Ti(SO_4)_2$: 5·5w, 4·8s, 4·1s, 3·75s, 3·4s, 3·10s, 3·00w, 2·60, 2·55, 2·45ms, 2·25ms, 2·00ms, 1·90w, 1·80ms, 1·74m, 1·68m, 1·63w, 1·59m, 1·45ms.

$ZnSO_4,Ti(SO_4)_2$: 5·5m, 4·7m, 4·1s, 3·75s, 3·4s, 3·25s, 2·65w, 2·58w, 2·42m, 2·00m, 1·90m, 1·82m, 1·76m, 1·64m, 1·59m, 1·45ms.

Infrared spectra. The samples were examined as Nujol mulls with a Unicam S.P. 100 spectrophotometer.

$MnSO_4,Ti(SO_4)_2$: 395, 422, 433, 460, 470, 595, 608, 635, 663, 673, 692, 740, 789, 860, 920, 1030, 1128, 1145, 1260, 1315 cm.$^{-1}$.

$FeSO_4,Ti(SO_4)_2$: 395, 430, 465, 610, 662, 672, 690, 725, 785, 870, 950, 1030, 1080, 1120, 1145, 1255, 1305 cm.$^{-1}$.

$CoSO_4,Ti(SO_4)_2$: 390, 425, 438, 460, 595, 608, 665, 676, 695, 740, 840, 910, 1035, 1145, 1260, 1315 cm.$^{-1}$.

$NiSO_4,Ti(SO_4)_2$: 385, 420, 485, 575, 603, 633, 665, 680, 695, 720, 775, 920, 955, 1015, 1055, 1090, 1155, 1235, 1300 cm.$^{-1}$.

$CuSO_4,Ti(SO_4)_2$: 390, 420, 480, 595, 626, 665, 672, 680, 720, 785, 915, 1010, 1062, 1090, 1150, 1235, 1300 cm.$^{-1}$.

$ZnSO_4,Ti(SO_4)_2$: 385, 420, 480, 580, 605, 628, 663, 695, 720, 790, 920, 1000, 1055, 1090, 1155, 1235, 1300 cm.$^{-1}$.

---

[6] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, New Jersey, 1952, pp. 340—345.

Visible and ultraviolet spectra. Reflection spectra were determined, on samples diluted ten times by weight with magnesium oxide, with a Beckman DK-2A instrument.

The author thanks Dr. A. W. Evans who first described the preparation of $Fe(SO_4)_2,Ti(SO_4)_2$, and Dr. D. J. Machin of Manchester University who measured the magnetic susceptibilities.

BRITISH TITAN PRODUCTS LIMITED, BILLINGHAM, CO. DURHAM.
[Present address: 6 NOTTINGHAM ROAD, BRISTOL 7.]

[*Received, August 13th*, 1964.]