

tions of disulphides in boiling solvents, precautions must be taken against the effect of even diffused light causing intrusion of radical activity.

E. R. COLE

Department of Applied Organic Chemistry,
University of New South Wales,
Kensington, Sydney.

Yttrium and Rare Earth Vanadates

THE diffraction pattern for yttrium vanadate, YVO_4 , has been reported by Broch¹ and appears in the A.S.T.M. *Index to the X-ray Powder Data File* (4-0457). The patterns for the rare earth vanadates do not appear in the A.S.T.M. *Index* and apparently have not been previously reported in the literature. In this work, the vanadates of the rare earths from praseodymium to erbium, excepting promethium, have been successfully prepared by heating equimolar powder mixtures of the rare earth oxides, 99.9 per cent, and vanadium pentoxide, C.P., at 950° C. These compounds all have the same tetragonal structure as yttrium vanadate. The reaction product of lanthanum oxide and vanadium pentoxide does not have this structure and has not been identified.

The failure of lanthanum to form an isomorphous structure can be explained on the basis of ionic radius because its radius is about 15 per cent larger than that of yttrium, whereas the other rare earth ions investigated all fall within about 10 per cent of yttrium in the trivalent state. These observations are in general agreement with the rules for the formation of isomorphous structures. A calcium uranium vanadate having this structure could not be formed either. The instability of the calcium uranium compound must be attributed to some other cause, however, because the radii of divalent calcium, trivalent yttrium and tetravalent uranium are all quite close.

The effect of the lanthanide contraction is apparent in the diffraction patterns of these rare earth vanadates. In Table 1 the Goldschmidt radii of the trivalent rare earth ions and yttrium are shown along with the interplanar spacings from the diffraction patterns for the (200) and the (400) planes. The interplanar spacings for the (004) planes are also given, but this reflexion is quite weak and the values should be taken as very tentative.

Table 1. EFFECT OF LANTHANIDE CONTRACTION ON INTERPLANAR SPACINGS

Element	Goldschmidt radius (Å)	d_{200} (Å)	d_{400} (Å)	d_{004} (Å)
39 Y	1.06	3.55	1.78	1.57
57 La	1.22	—	—	—
59 Pr	—	3.65	1.83	1.64
60 Nd	1.15	3.64	1.82	1.60
62 Sm	1.13	3.62	1.81	1.59
63 Eu	1.13	3.61	1.80	1.59
64 Gd	—	3.58	1.80	—
65 Tb	1.09	3.56	1.79	—
66 Dy	1.07	3.55	1.78	—
67 Ho	1.05	3.55	1.78	1.59
68 Er	1.04	3.53	1.77	1.58

The changes in h_{200} or in d_{004} respectively reflect changes in the 'a' and 'c' dimensions of the unit cell. It appears that the 'a' dimension shows a regular decrease from the largest to the smallest ion in the rare-earth series, but the 'c' dimension seems to be relatively insensitive to the rare earth radius, except for praseodymium. Whatever variations do occur in the unit cell dimensions do not seem to be great enough to establish a definite trend in the c/a ratio as indicated by the ratio d_{004}/d_{400} . Final conclusions on these points should be based on more precise X-ray work.

All diffraction patterns were obtained using a General Electric XRD-3 unit with a goniometer and nickel filtered copper radiation. Peak positions were established by estimating 2θ to the nearest 0.02 degrees on both sides of the maximum at a height of 2/3 peak maximum and averaging. The yttrium vanadate pattern, run using

Table 2

d Å	I/I_0	hk	d Å	I/I_0	hk
4.71	11	101	1.59	14	420
3.55	100	200	1.57	9	303, 004
2.86	3	211	1.48	19	332
2.66	57	112	1.43	14	204, 323
2.51	19	220	1.39	8	501, 431
2.35	8	202	1.33	10	224, 413
2.22	15	301	1.27	13	512
2.01	9	103	1.14	8	532
1.88	9	321	1.12	6	523
1.83	59	312	1.115	10	—
1.78	19	400	—	—	—

potassium bromide as an internal standard, is shown in Table 2.

This pattern shows a large variation from Broch's intensities and some differences in the interplanar spacing values. The large number of intense lines reported by Broch suggests the possibility of an over-exposure which would have made the line intensities and diffraction angles difficult to measure. No compounds other than YVO_4 were found in X-ray and DTA studies of the V_2O_5 - Y_2O_3 system. Both yttrium and the rare earth vanadates displayed unusual thermal stability for vanadates; heating these compounds to 1,600° C did not result in any detectable change. The colour of the vanadates corresponds fairly closely to reported² colours of the trivalent ions of the rare earths. $PrVO_4$, $NdVO_4$, and $SmVO_4$ are intensely coloured yellow-green, blue-violet, and yellow respectively. $TbVO_4$, $HoVO_4$, and $ErVO_4$ are brownish-yellow, and the remainder are colourless or nearly colourless.

J. R. GAMBINO
C. J. GUARE

Advanced Technology Laboratories,
General Electric Co.,
Schenectady, New York.

¹ Broch, E., *Z. Phys. Chem.*, **20**, 345 (1933).

² Remy, H., *Treatise on Inorganic Chemistry*, **2**, 484 (Elsevier Pub. Co., 1950).

Cobalt Complexes of Polyglycines

THE binding of cobalt to proteins and polypeptides has been shown to occur in a number of cases, particularly under conditions of high alkalinity, where ligation occurs with amide groups in addition to the terminal functions¹.

In the course of our investigations on the chemical reactions of the polyglycines I and II², we noticed a difference in the ability of these isomers to form complexes with metals, particularly cobalt. The structures of the polyglycines³ differ in that polyglycine I (prepared from piperazine-2,5-dione and water at 180° for 6 h) is an almost fully extended β -polypeptide, whereas polyglycine II (prepared by precipitating polyglycine I from a solution in a strong electrolyte) is a folded structure having a 3-fold screw axis, the chains being packed in a hexagonal array. In both structures a large proportion of the terminal groups would be available for co-ordination with a cobalt ion.

The uptake of cobalt from solution in excess of concentrated ammonium hydroxide was followed using a radioactive tracer technique using cobalt-60. Polyglycine I (degree of polymerization (DP) about 12) absorbed 3.2 moles cobalt per mole polymer, whereas polyglycine II (DP about 12) only absorbed 1.1 moles cobalt per mole polymer. From the shape of the absorption isotherms, the accessibility of cobalt into the polyglycine II lattice appears to be limited by electrical or diffusion phenomena characteristic of the uptake of dye by a natural or synthetic polypeptide. No irregularities were found in the case of polyglycine I.

These results suggest that a cobalt (III) ion, possibly also co-ordinated by ammonia molecules, cannot be readily accommodated by the three-fold screw axis, but can be fitted into the more extended polyglycine I structure. X-ray diffraction photographs of the polymers