

The Heteropoly-12-niobomanganate(IV) Anion

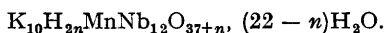
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IN contrast to the large number of heteropoly-molybdates and -tungstates, very few heteropoly-anions of Group V elements have been reported, and none has been well characterized. We report here the first discrete heteropoly-niobate anion with a high (12:1) niobium to central atom ratio.

Lapitskii¹ has described niobate complexes of divalent iron, cobalt, nickel, and copper, and of cerium(III), with niobium to central atom ratios ranging from 4:1 to 1:1. We have examined some of these compounds, together with a similar nioboferrate(III), and although solutions of these materials contain complex anions, the solute species do not appear to be monodisperse.²

Potassium 12-niobomanganate(IV) was prepared by adding a solution of manganese(II) sulphate and ammonium peroxydisulphate to a hot (80°) solution of potassium hexaniobate. After filtration and cooling, the heteropoly-salt separated as bright orange octahedral crystals, which were then recrystallized from water. Treatment of a solution of the salt with the potassium form of a strong acid cation-exchange resin showed the manganese to be anionic. A complete analysis of the crystals is in good agreement with the composition $5K_2O, MnO_2, 6Nb_2O_5, 22H_2O$, and the compound is provisionally formulated as



The anion is extremely inert towards analytical reducing agents, and we have so far been unable to carry out an accurate determination of the oxidation state of the manganese. However, comparisons with the well-established³⁻⁵ 9-molybdomanganate(IV) anion, $[MnMo_9O_{32}]^{6-}$, strongly suggest that the manganese in the compound is also quadrivalent. The heteropoly-molybdate has

an asymmetric structure containing a trigonally distorted MnO_6 octahedron.⁴ The electronic absorption spectrum of the molybdate shows bands at 20,600 ($\epsilon = 370$), 21,300 ($\epsilon = 387$), and 25,500 cm^{-1} ($\epsilon = 180$). The first two bands have been assigned to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition, split by the trigonal distortion.⁵ The spectrum of the heteropoly-12-niobomanganate(IV) anion, at pH 7, is very similar, with bands at 20,750 ($\epsilon = 386$) and 21,900 cm^{-1} ($\epsilon = 398$) followed by charge-transfer absorption. If the above assignment is correct, this spectrum suggests that the trigonal distortion in the niobate is even more pronounced than in the molybdate. Preliminary e.s.r. measurements of frozen solutions of both heteropoly-compounds at 77° K and 9.2 KMc showed virtually identical broad asymmetric signals with $g = 3.8$. This further demonstrates the similarity of the manganese oxidation state and environment in these two compounds.⁶ A more complete investigation of the magnetic properties is in progress.

Dilute solutions of the potassium salt in pure water have a pH between 9 and 10, and the anion appears to be stable within the pH range 6.5 to 11.0. This stability contrasts with that of heteropoly-molybdates and -tungstates which are usually stable only in neutral or acidic solutions.

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Note added in proof. It has recently come to our attention that C. M. Flynn, jun. (University of Illinois), has independently prepared some other salts of this heteropoly-anion.

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² R. R. Riesenman, B. W. Dale, and M. T. Pope, unpublished results.

³ R. D. Hall, *J. Amer. Chem. Soc.*, 1907, **29**, 692.

⁴ J. L. T. Waugh, D. P. Shoemaker, and L. C. Pauling, *Acta Cryst.*, 1954, **7**, 438.

⁵ L. C. W. Baker and T. J. R. Weakley, *J. Inorg. Nuclear Chem.*, 1966, **28**, 447.

⁶ L. S. Singer (*J. Chem. Phys.*, 1955, **23**, 379) has observed e.s.r. signals at $g = 4$ from powdered trischelate chromium(III) complexes. The high apparent g -value is due to the random orientation of the d^3 ions coupled with a large zero field splitting of the $S = \pm \frac{3}{2}$ and $S = \pm \frac{1}{2}$ states.