

Heteropolyanions related to $P_2W_{18}O_{62}^{6-}$ containing Heteroatoms of Two Elements

By S. A. MALIK and T. J. R. WEAKLEY*

(Chemistry Department, Dundee University, Dundee, Scotland)

BAKER and his co-workers have described¹ a series of heteropolyanions $XYW_{11}O_{40}H_n^{z-}$, and have shown that the second hetero-atom Y has replaced one tungsten atom in an anion $XW_{12}O_{40}^{y-}$ with the Keggin structure.² We have recently prepared other anions of this series,³ including ones with X = P and Y = Ni^{II} and with X = Ge and Y

= Ni^{II}, Co^{II}, and Co^{III}. Further experiments suggest that the replacement of a tungsten atom in an $XW_{12}O_{40}^{y-}$ anion (X = P, Si, Ge) by an atom of the first transition series is a quite general reaction,⁴ occurring under conditions where the 12-tungstate ion is partly degraded.

The anions $X_2W_{18}O_{62}^{6-}$ (X = P or As) have

structures related to the Keggin structure.⁵ They undergo partial degradation to X_2W_{17} anions in the vicinity of pH 7; one tungsten only is lost although twelve equivalent tungstens of one kind and six of a second kind are present.⁶ We now find that new 17-tungstate heteropolyanions, $X_2YW_{17}O_{62}H_2^{8-}$ ($X = P$ or As ; $Y = Mn^{II}$, Co^{II} , or Ni^{II}) are formed when the pH of a solution containing $X_2W_{18}O_{62}^{6-}$ at 80° is raised to 6 with aqueous potassium acetate in the presence of the Y^{2+} cation. The anions are isolated and analysed as their potassium, rubidium, guanidinium, or dimethylammonium salts. The element Y is always present in the anion. The anions containing manganese(II) are oxidized electrolytically or by peroxodisulphate to manganese(IV) species

which (unlike the others) do *not* lose the Y hetero-atom on treatment with dilute acid. Anions containing cobalt(III) are obtained similarly, but salts free from cobalt(II) cannot be isolated.

The ligand-field spectra of the Y hetero-atoms closely resemble, in band positions and intensities, the spectra of these atoms in anions of the 11-tungstate series.^{3,4} The latter spectra have been interpreted in terms of distorted YO_6 chromophores. We therefore formulate the new anions with 62 oxygen atoms apiece on the assumption that the Y atom has in each case replaced one tungsten atom within an 18-tungstate anion and has not merely attached itself to exterior oxygens.

(Received, September 14th, 1967; Com. 986.)

¹ L. C. W. Baker, V. S. Baker, K. Eriks, M. T. Pope, M. Shibata, O. W. Rollins, J. H. Fang, and L. L. Koh, *J. Amer. Chem. Soc.*, **1966**, **88**, 2329.

² J. F. Keggin, *Proc. Roy. Soc.*, **1934**, *A*, **144**, 75.

³ T. J. R. Weakley and S. A. Malik, *J. Inorg. Nuclear Chem.*, in the press.

⁴ S. A. Malik and T. J. R. Weakley, work in progress.

⁵ B. Dawson, *Acta Cryst.*, **1953**, **6**, 113.

⁶ P. Souchay, *Ann. Chim. (France)*, **1947**, **2**, 203, and references therein.