January, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(1), 87—91 (1976) 87

Heteropolytungstates Containing Cobalt(II) or Cobalt(III)

Akitoshi KOMURA, Mutsuo HAYASHI, and Hiroto IMANAGA
Faculty of Technology, Kanazawa University, Kanazawa 920

(Received May 14, 1975)

The reactions of tungstophosphate with cobalt ion and the properties of heteropolytungstates containing cobalt have been investigated. Unsaturated heteropolyanion $PW_{11}O_{39}^{7-}$ produced by the partial degradation of the parent 12-tungstophosphoric acid reacts with cobalt ion to give 11-tungstocobaltophosphate $PCoW_{11}O_{40}H_2^{5-}$. Discussion is given on the presence of cobalt in the heteropolyanion and on the above reaction. Both 12-tungstocobaltate-(II) and -(III) are very resistant to acid, but 11-tungstocobaltophosphates lose cobalt ion in strongly acidic solutions to give the parent 12-acid. Some aspects of the spectra of the heteropolytungstates, in which cobalt(II) and cobalt(III), respectively, are present in the specific site, are discussed.

The characteristic of molybdenum and tungsten is the formation of numerous isopoly and heteropoly acids and their salts. The heteropolyanions containing two different heteroatoms have been reported.[1–3] Baker and Figgis[4] showed that in heteropolyanions an octahedrally coordinated transition metal atom replaces one of the 12 octahedral tungsten atoms of conventional Keggin structure,[5] being simultaneously coordinated to a water molecule (constitutional water). Malic and Weakley[1,2] prepared many ternary heteropolyanions from the solutions containing unsaturated heteropolyanions which were isolated as solid by Tourné and Tourné,[6] and formulated the ternary heteropolyanions. Weakley[7] reported the replacement of the constitutional water by other ligands mainly in the heteropolyanions containing cobalt. On the other hand, there are some ternary heteropolyanions which can not be interpreted on the basis of the Keggin structure.[8] The anions probably formed through addition reactions appear to have the composition X: Z: W or Mo=1: 1: 12, where both X and Z are heteroatoms. The heteropolyanions containing metal heteroatoms form an important class of coordination compounds, but their chemistry remains unclarified. In order to obtain information on heteropoly complexes, we have investigated the chemical and spectroscopic properties of heteropolytungstates containing cobalt, reported by Weakley.[7] The present paper deals with the formation process of the heteropolyanions and the formulation proposed by Baker and Figgis.[4]

Experimental

Dodeca-tungstophosphoric acid was obtained from Wako Pure Chemical Industries Ltd. (Found: P, 1.0; W, 64.4%). Potassium monohydrogen 12-tungstocobaltate(II) was prepared by Baker's method.[9] The cerimetric titration gave 3550 as its equivalent weight. Found: K, 5.3; Co, 1.7; W, 62.0%. Calcd for $K_5HCoW_{12}O_{40}\cdot 24H_2O$: K, 5.5; Co, 1.7; W, 62.4%, equiv. wt, 3534.

Potassium 11-Tungstophosphate. Preparation was carried out by a modification of Tourné's method.[6] To a solution of 12-tungstophosphoric acid (25 g) in water (300 ml) at 90—100 °C was added 0.5 M-potassium bicarbonate dropwise with stirring until a large portion of the precipitate of the resulting potassium 12-tungstophosphate disappeared (the pH of the solution being then about 5). A small quantity of the residual precipitate was filtered off and the pH of the filtrate was adjusted to 5.25 with potassium acetate buffer solution. The filtrate was concentrated to one third of its original volume and then kept at 5 °C for a few days while white crystals formed. These were filtered off, washed with water, and air-dried at room temperature. Found: K, 8.1; P, 1.0; W, 58.6%. Calcd for $K_7PW_{11}O_{39}\cdot 28H_2O$: K, 7.9; P, 0.9; W, 58.5%.

Potassium 11-Tungstocobalto(II)phosphate. The procedure was based on that for 11-tungstocobalto(II)silicate.[1] A solution of cobalt nitrate (2.2 g) in water (20 ml) was added with stirring to a heated solution (pH 5.3) of 12-tungstophosphoric acid partly degraded in a similar manner to that above. The mixture was concentrated to two thirds of its original volume after being filtered at 60 °C. The solution was kept at 5 °C for a few days while deep red crystals separated. Found: K, 6.8; P, 1.0; Co, 1.6; W, 61.0%. Calcd for $K_5PCoW_{11}O_{40}H_2\cdot 20H_2O$: K, 6.0; P, 0.9; Co, 1.8; W, 61.1%. Weakley[7] gave 15 molecules of water of hydration to the complex.

Pyridinium 11-Tungstocobalto(II)phosphate. This compound was isolated in an attempt to coordinate pyridine to the cobalt atom of potassium 11-tungstocobalto(II)phosphate. Thirty milliliters of 0.1 M-aqueous solution of pyridine was added to a solution of potassium 11-tungstocobalto(II)phosphate (3.34 g) in water (20 ml) with stirring. A pink precipitate which formed immediately was filtered off, washed with an aqueous solution of pyridine and methanol, and air-dried at room temperature. Found: Co, 1.7; W, 64.0%. Calcd for $C_{25}H_{30}N_5PCoW_{11}O_{40}H_2\cdot 5H_2O$: Co, 1.8; W, 62.3%.

Solutions containing cobalt(III) were obtained by constant current electrolysis on a platinum anode placed in a H cell with a fine sintered glass frit separating two compartments. Completion of oxidation was confirmed spectrophotometrically. Electronic and IR spectra were recorded on Hitachi 124 and Nihonbunko DS 301 spectrophotometers, respectively. X-ray powder diffraction data were obtained by use of a Rigaku Denki D-9C X-ray generator with a SG-7 diffractometer. Cu*K*α radiation and a nickel filter were used in all measurements. Differential thermal analytic (DTA) curves were obtained with a Rigaku Denki 8001 at a heating rate of 15 °C/min. The reference material was α-alumina. Potassium was precipitated and weighed as tetraphenylborate. The remaining elements were determined after alkaline decomposition of the hereropolyanions. Cobalt was precipitated as hydroxide, dissolved in hydrochloric acid, and estimated by EDTA titration. Tungsten was precipitated and weighed as trioxide. Phosphorous was separated as magnesium ammonium phosphate and was weighed as magnesium pyrophosphate after a second precipitation.

Results and Discussion

The DTA curves of heteropolytungstates are given in Fig. 1. All the heteropoly salts showed characteristic two endothermic peaks which probably correspond to dehydration. The first large endothermic peak was observed at about 130 °C for all the salts. Ignition of the salts at 175 °C gave 60—80% loss of the water of hydration. All the heteropoly salts lost practically all the water above 400 °C with the change in color. The 12-tungstophosphoric acid showed a prominent exothermic peak at 637 °C. Both 11-tungstophosphate and 11-tungstocobalto(II)phosphate showed a complicated feature at high temperature. The X-ray diffraction pattern showed that 11-tungstophosphate and 11-tungstocobalto(II)phosphate belong to the tetragonal series, a=12.2, c=9.08 Å and a=12.4, c=9.10 Å, respectively; 12-tungstocobaltate(II) is simple cubic (a=10.7 Å). The 12-tungstophosphoric acid was shown to be cubic by Keggin.5)

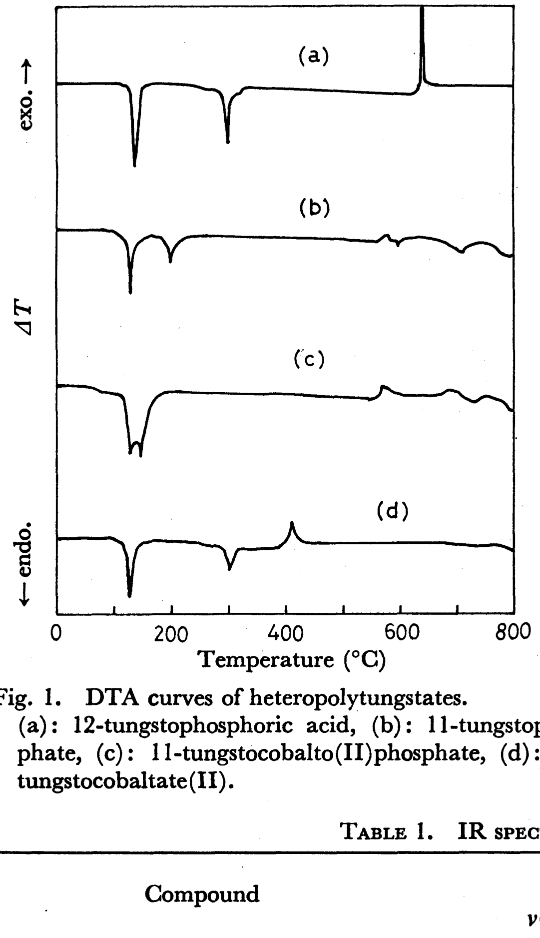

Fig. 1. DTA curves of heteropolytungstates.
(a): 12-tungstophosphoric acid, (b): 11-tungstophosphate, (c): 11-tungstocobalto(II)phosphate, (d): 12-tungstocobaltate(II).

Infrared Spectra. The positions and assignments of the main bands are given in Table 1. All the compounds have strong bands at 740—980 cm^{-1} characteristic of polytungstates. The bands at 880—980 cm^{-1} might be assigned to the independent W–O stretching vibration and the broad bands at 740—820 cm^{-1} to the W–O–W bridge vibrations. Such peaks are also observed in the infrared spectra of several heteropolymolybdovanadates.10) The 12-tungstophosphoric acid having high symmetry Td gives the triply degenerated γ_3 of PO_4 at 1080 cm^{-1}. The band is split into 1085 and 1040 cm^{-1} in 11-tungstophosphate. There is probably a lowering of symmetry from Td in 11-tungstophosphate owing to the lack of one tungsten and the unshared oxygen. The reduction in symmetry of PO_4 should result in the splitting of the degenerate mode γ_3. The complication of the vibration of WO_6 in 11-tungstophosphate can also be attributed to the structural distortion. The splitting of the γ_3 band is also observed in 11-tungstocobaltophosphate where the PO_4 tetrahedron is also distorted because one tungsten atom of 12-tungstophosphate is replaced by cobalt atom. The spectrum of the heteropoly salt with pyridines is similar to that of the potassium 11-tungstocobaltophosphate, except for bands of pyridine at 3060s, 1635m, 1531m, 1482m, 1330w, 1245w, 1200w, and 1165w cm^{-1}. Gill *et al.* distinguished a pyridinium ion from the pyridine coordinated to metals according to infrared spectra.11) Absorption bands of C=C and C=N bonds in the heteropoly salt with pyridine were shifted to higher wave number than those in pure pyridine in agreement with the observation of Murata and Ikeda.12) The infrared spectrum shows that the compound is not a pyridine complex but pyridinium salt.

Reactions. The parent 12-heteropolyanions probably

TABLE 1. IR SPECTRA OF THE HETEROPOLYTUNGSTATESa)

Compound	Assignments			
	$\nu(H_2O)$	$\delta(H_2O)$	ν(P–O)	ν(W–O)
$H_3PW_{12}O_{40}\cdot 29H_2O$	3440s, b	1620m, b	1080s	983s 890s 810s, b
$K_7PW_{11}O_{39}\cdot 28H_2O$	3450s, b	1625m, b	1085m 1040m	950s 900s, b 863s 814s 740s, b
$K_5PCoW_{11}O_{40}H_2\cdot 20H_2O$	3440s, b	1620m, b	1075m 1055m	960s 887s 820s, b 755s
$(pyH)_5PCoW_{11}O_{40}H_2\cdot 5H_2O$	3450s, b	1615m, b	1075m 1057s	955s 890s 820s, b 750s
$K_5HCoW_{12}O_{40}\cdot 24H_2O$	3440s, b	1620m, b		950s 882s, b 745s, b

a) All values in cm^{-1}. Abbreviations; s: strong, m: medium, w: weak, b: broad.

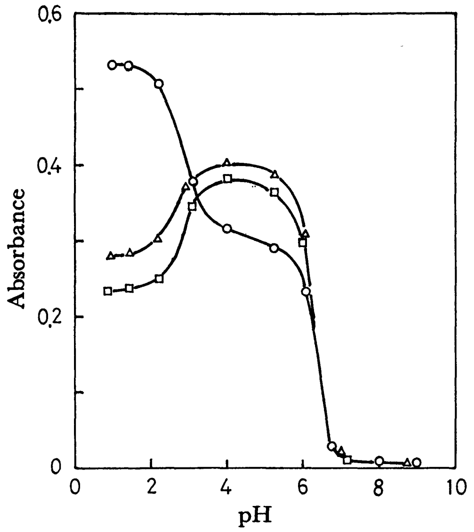

Fig. 2. Relation between the absorbance of 12-tungstophosphate solution and the pH.
The concentration of 12-tungstophosphate is 10^{-5} M. ○: 264 nm, △: 247 nm, □: 235 nm.

undergo gradual degradation on alkalization.[6] The 12-tungstophosphoric acid exihibits a characteristic intense absorption band ($\varepsilon=5.2\times10^4$ l mol^{-1}cm^{-1}) at 264 nm in acidic solutions. The position of the absorption maximum shifts to shorter wavelength with an increase in pH, no maximum being observed above pH 7. Figure 2 shows the relation between the absorbance of 12-tungstophosphate solution and the pH at different wavelengths. The absorbances show abrupt changes at pH 2.7 and 6.2, a distinct plateau occurring in the 3.5—6 pH region. This suggests that the parent 12-tungstophosphoric acid is transformed into a certain species in this region, and further decomposes into other species above pH 7 (ultimately to WO_4^{2-} and PO_4^{3-}). On the basis of the measurement of pH on rapid neutralization, Schwarzenbach *et al.* presumed the initial process of the degradation as follows.[13]

$$PW_{12}O_{40}^{3-} + 9/2\,OH^- \rightleftharpoons PW_{11}O_{39}^{7-} + 1/12H_2W_{12}O_{40}^{6-} + 13/6H_2O \quad (1)$$

In equilibrium (1) the metatungstate $H_2W_{12}O_{40}^{6-}$ may be some other species. The equilibrium can explain the fact that an aqueous solution of 12-tungstophosphoric acid contains 3–4 titratable H$^+$ per molecule. Tourné and Tourné isolated solid potassium 11-tungstates by the partial degradation of 12-heteropolyanions.[6] A hydrolysis product which we isolated from the weakly acidic solution of 12-tungstophosphate could also be formulated as potassium 11-tungstophosphate according to the analytical data. The latter compound seems to be further decomposed by base into species such as $P_2W_{19}O_{69}^{14-}$, $(PW_9O_{34}^{9-})_n$, *etc.*[14] On the other hand, 12-tungstocobaltate(II) seems to be considerably resistant to the degradation. Its spectrum showed no change at all on alkalization up to pH 7 though the anion decomposed completely above pH 10.5. The 11-tungstophosphate reacts with cobalt ion under weakly acidic conditions.[6] The stoichiometry of the reaction was examined spectrophotometrically by the molar ratio method (Fig. 3). An inflection in the absorbance occurred at a heteropolyanion: cobalt ratio of 1: 1. This indicates the formation of a complex of stoichiometry 1 heteropolyanion: 1 cobalt. As shown in Fig. 4, a similar result was also obtained when the parent 12-acid was allowed to react with cobalt ion at pH 5.2 (whereas no reaction occurred in 0.1 M-hydrochloric acid). This implies that equilibrium (1) lies sufficiently to the right or that the reaction is fairly rapid. We isolated a ternary heteropoly salt from the solution which might contain 11-tungstophosphate and cobalt ion. The analytical data agreed with the values calculated for 11-tungstate rather than for 12-tungstate. The formation of the complex is probably a simple reaction as follows.

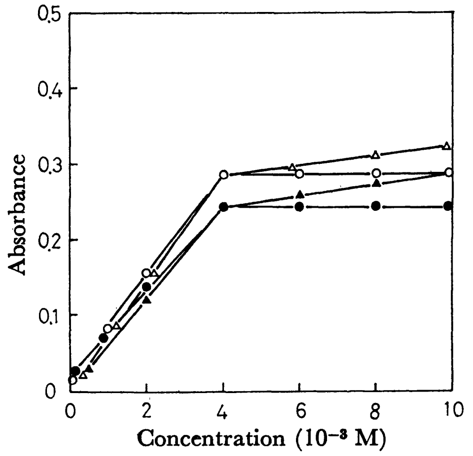

Fig. 3. Absorbances of the solutions containing 11-tungstophosphate and cobalt ion.
Circle; the concentration of cobalt ion is 4×10^{-3} M and that of 11-tungstophosphate is shown on the abscissa. Triangle; the concentration of 11-tungstophosphate is 4×10^{-3} M and that of cobalt ion is shown on the abscissa. Open: 540 nm, close: 511 nm.

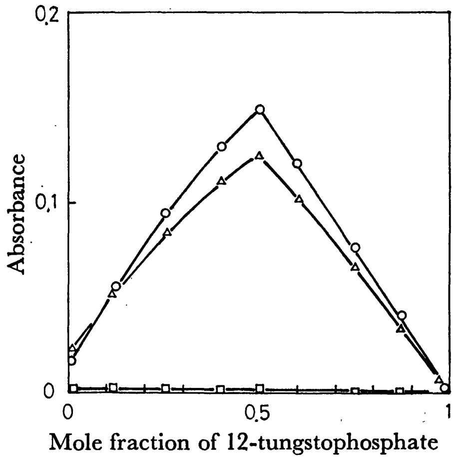

Fig. 4. Continuous variations plots of the reaction of 12-tungstophosphate with cobalt ion.
Total concentration were 4×10^{-3} M. ○: pH 5.2, 540 nm. △: pH 5.2, 511 nm. □: in 0.1 M-HCl, 540 nm.

$$Co(H_2O)_6^{2+} + PW_{11}O_{39}^{7-} \longrightarrow PCoW_{11}O_{40}H_2^{5-} + 5H_2O \quad (2)$$

Absence of the complex in 0.1 M-HCl can be interpreted in terms of equilibria (1) and (2). If we suppose that 11-tungstophosphate remains unchanged when it is dissolved in water, we can estimate the stability constant of the complex, using the molar absorption coefficient (ε) of the species participating in the formation of the complex. The ε values at 540 nm were 75 for 11-tungstocabalto(II)phosphate, 0 for 11-tungstophosphate, and 3.0 l mol^{-1}cm^{-1} for cobalt ion. The stability constant of 11-tungstocobalto(II)phosphate was estimated to be log $K=5$ at 25 °C.

If 11-tungstocobalto(II)phosphate has the structure of the type proposed by Baker and Figgis,[4] an oxygen atom, probably of a water molecule (or hydroxide ion[15]), should occupy a coordination position of cobalt pointing to the exterior of the heteropoly part. It was difficult to determine from the analytical data whether a water or hydroxide ion occupied the sixth coordination position of the cobalt atom (the charge of anion is different in the two cases). If the above formulation is correct, the water or hydroxide ion coordinated to cobalt should be replaceable by other ligands in aqueous solution. Weakley reported spectrophotometrical indications of the replacement of the constitutional water by other ligands, with the isolation of pyridine complexes.[7] We attempted to replace the water or hydroxide ion with monodentate ligands such as thiocyanate, chloride, ammonia, and pyridine, but could not confirm the formation of any new complex. In the presence of pyridine, an increase in the intensity of the d-d band of 11-tungstocobalto(II)phosphate was observed, but the molar ratio plot at pH 5 was linear until about 5 molar ratio of pyridine to the heteropolytungstate. In larger excess of pyridine, the solid probably corresponding to the pyridinium salt of 11-tungstocobalto(II)phosphate was obtained in disagreement with the results of Weakley.[7] With the other ligands, there were no spectral changes, molar ratio plots at pH 5 being straight lines parallel to the abscissa (molar ratio). Since the replacement at only one of 6 coordination positions of cobalt causes no significant change in the spectrum, it might be difficult to examine spectrophotometrically the replacement of the constitutional water.

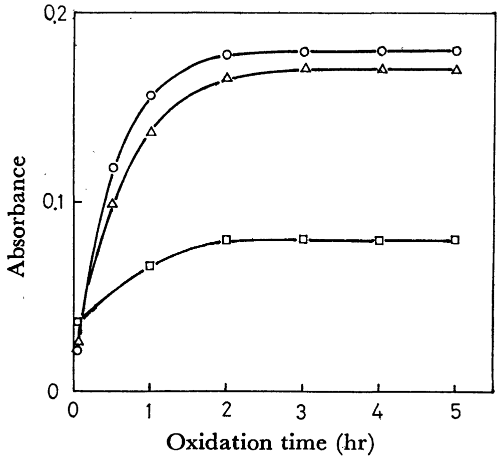

Fig. 5. Variations of the absorbance of the heteropolytungstates containing cobalt with oxidation time.
△: 5×10^{-4} M 11-tungstocobalto(II)phosphate in borate buffer (pH 5), 457 nm. □: the same as above, 540 nm. ○: 7.5×10^{-4} M 12-tungstocobaltate(II) in 0.1 M-sulfuric acid, 390 nm, absorbance (1/5).

It is known that the transition elements in heteropolyanions can be oxidized to higher oxidation states, with only the change in oxidation number of the elements apart from the charge of anions. We carried out the electrolytic oxidation of 11-tungstocobalto(II)phosphate and 12-tungstocobaltate(II). The complete oxidation of the cobalt(II)-anions could be confirmed spectrophotometrically (Fig. 5). When the oxidized solutions were left to stand, 11-tungstocobalto(III)phosphate was slowly reduced to 11-tungstocobalto(II)phosphate, whereas 12-tungstocobaltate(III) was stable and isolated as pure crystals by Baker and McCutcheon.[9] The electrolysis of 11-tungstocobalto(II)phosphate with phosphate as a buffer solution gave solutions with higher absorbance than those in the case of borate buffer solution, and gave variable molar absorption coefficients depending upon the concentration of the original 11-tungstocobalto(II)phosphate. Other heteropolyanions besides 11-tungstocobalto(III)phosphate might be formed by the electrolysis of 11-tungstocobalto(II)phosphate in the presence of excess phosphate.

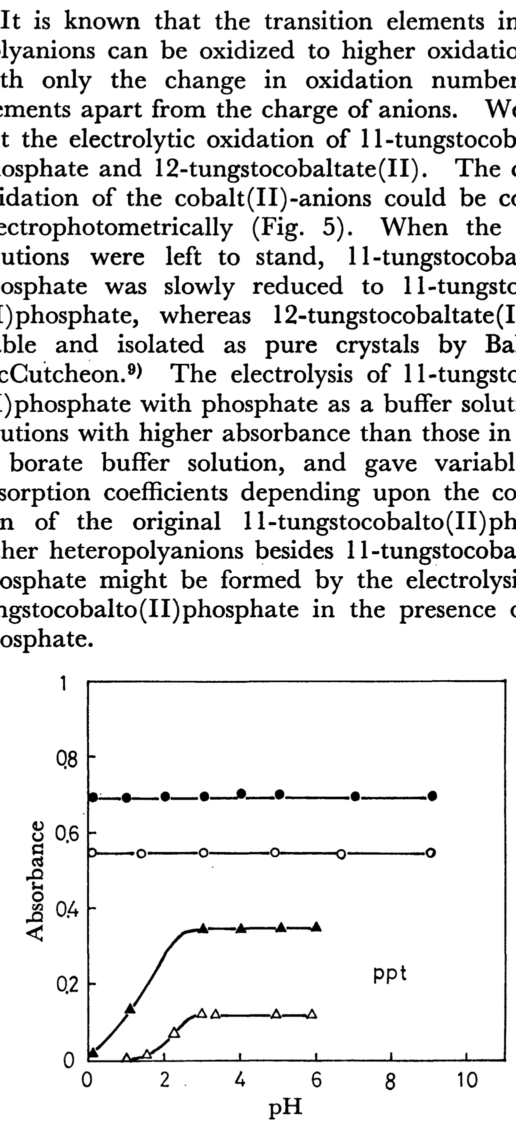

Fig. 6. Variations of the absorbance of the heteropolytungstates with pH.
▲: 10^{-3} M 11-tungstocobalto(III)phosphate, 457 nm. △: 2×10^{-3} M 11-tungstocobalto(II)phosphate, 540 nm. ●: 5×10^{-4} M 12-tungstocobaltate(III), 390 nm. ○: 3×10^{-3} M 12-tungstocobaltate(II), 624 nm.

Figure 6 shows the stability of the heteropolyanions towards acid and base. Both 12-tungstocobaltates are stable in wide pH range below 9 regardless of the oxidation state of cobalt. This does not mean that the anions remain actually unchanged. The anions probably undergo partial degradation at higher pH, but cobalt ions are still present in approximately tetrahedral environment. The 11-tungstocobalto(III)phosphate is slightly more stable towards acid than 11-tungstocobalto(II)phosphate, but both lose cobalt ion in strongly acidic solutions to give the parent 12-acid. On the other hand, all heteropolyanions are decomposed by strong alkali.

Electronic Spectra. The positions, intensities, and assignments of the absorption maxima are given in

Table 2. Visible spectra of the heteropolyanions[a)]

Compound	ν_{max} (10^3 cm^{-1})	Assignments
11-tungstocobalto(II)-phosphate	14.1(2)	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$
	18.5(75)	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$
	19.0(75)	
	19.8sh	
11-tungstocobalt(III)-phosphate	13.9(140)	$^1A_{1g}\rightarrow{}^1T_{1g}$
	21.9(340)	$^1A_{1g}\rightarrow{}^1T_{2g}$
12-tungstocobaltate(II)	16.0(180)	$^4A_2(F)\rightarrow{}^4T_1(P)$
	16.8sh	
	17.7sh	
12-tungstocobaltate(III)	25.7(1060)	$^5E\rightarrow{}^5T_2$

a) Molar absorption coefficients (l mol^{-1} cm^{-1}) are given in parentheses.

Table 2. The spectra assignments for 11-tungstocobaltophosphates are made on the basis of O_h symmetry, though the true site symmetry around cobalt is probably lower.[1,16)] The spectrum of 11-tungstocobalto(II)phosphate differs distinctly from that of 12-tungstocobaltate(II) having Td symmetry, resembling that of the well-known cobalt(II) aqua-ion, except in intensity.[1)] This is also the case for the corresponding cobalt(III) complex. When metal heteroatoms are present in octahedral sites, the spectra should resemble those of the corresponding aqua-ions, the ligand-field parameters being of similar magnitude.[1)] Thus, a comparison of the spectra presents evidence supporting the view that cobalt atom in 11-tungstocobaltophosphates is present in essentially octahedral site. In the 12-heteropolyanions, tungsten or molybdenum atoms are effectively in tetragonal oxide environments.[17)] When cobalt replaces a single tungsten, it is to be expected that the CoO_6 group will also be distorted. The splitting of the second band in the 11-tungstocobalto(II)phosphate spectrum might be attributed to the lower site symmetry around cobalt atom. Thus the ε value for 11-tungstocobalto(II)phosphate is 15 times as great as that for the cobalt(II) aqua-ion. The remarkable band in the spectrum of 11-tungstocobalto(III)phosphate is also 5—15 times as intense as the corresponding bands for the cobalt(III) aqua-ion and centrosymmetric 6-molybdocobaltate(III).[1,18,19)] The spectrum of 11-tungstocobalto(III)phosphate indicates that the cobalt(III) is certainly of low-spin and the ligand-field stabilization energy is less even than in the cobalt(III) aqua-ion.[16)] The latter is also the case for the corresponding cobalt(II) complex. The 12-tungstocobaltate(III) seems to be the first compound containing cobalt(III) in any tetrahedral site.[20)] The band of 25700 cm^{-1} was assigned tentatively to the transition $^5E\rightarrow{}^5T_2$. The ε value is *ca.* 50 times as great as that for 6-molybdocobaltate(III) with cobalt(III) in octahedral site. The heteropolyanions all show an intense absorption in the ultraviolet (Fig. 7). This is characteristic of polytungstates, and is to be ascribed to charge transfer from oxygen to tungsten.[16)] The ultraviolet absorption band for 12-tungstophosphate is shifted 2—3 kK to higher energies in 11-tungstophosphate and 11-tungstocobalto(II)-phosphate, with decreasing ε value. In heteropolyanions containing cobalt, a broad, relatively weak band ($\varepsilon \sim 220$) is superimposed on the ultraviolet absorption edge (spectra 5 and 6 in Fig. 7). This has been ascribed by Malik and Weakley[16)] to the charge transfer between cobalt and polytungstate, either from cobalt(II) to tungsten or from oxygen to cobalt(III). The charge transfer from oxygen to cobalt(III) should result in a stabilization of the (III) oxidation state of cobalt.

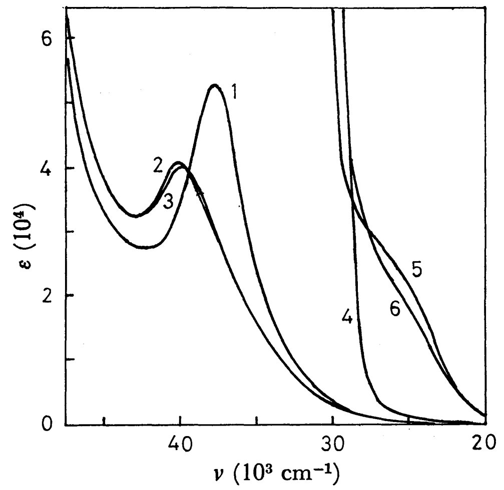

Fig. 7. Ultraviolet absorption spectra of the heteropolyanions. 1,4: 12-tungstophosphoric acid. 2: 11-tungstophosphate. 3,5: 11-tungstocobalto(II)phosphate. 6: 12-tungstocobaltate(II). Ordinate: 4,5,6 (100ε).

References

1) T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2935 (1967).

2) C. M. Tourné, G. F. Tourné, S. A. Malik, and T. J. R. Weakley, *ibid.*, **32**, 3875 (1970).

3) R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc., A*, **1971**, 1836.

4) L. C. W. Baker and J. S. Figgis, *J. Amer. Chem. Soc.*, **92**, 3794 (1970).

5) J. F. Keggin, *Proc. Roy. Soc. Ser. A*, **144**, 75 (1934).

6) C. M. Tourné and G. F. Tourné, *Bull. Soc. Chim. Fr.*, **1969**, 1124.

7) T. J. R. Weakley, *J. Chem. Soc., Dalton*, **1973**, 341.

8) R. A. Chalmers, *Proc. Soc. Analyt. Chem.*, **1966**, 157.

9) L. C. W. Baker and T. P. McCutcheon, *J. Amer. Chem. Soc.*, **78**, 4503 (1956).

10) G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem.*, **7**, 437 (1968).

11) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

12) K. Murata and S. Ikeda, *Anal. Chim. Acta*, **51**, 489 (1970).

13) G. Schwarzenbach, G. Geier, and J. Littler, *Helv. Chim. Acta*, **45**, 2601 (1962).

14) C. M. Tourné, A. Revel, and G. F. Tourné, *Chem. Abstr.*, **80**, 55394p (1974).

15) R. Ripan and M. Puscasiu, *Z. Anorg. Allg. Chem.*, **380**, 102 (1971).

16) S. A. Malik and T. J. R. Weakley, *J. Chem. Soc., A*, **1968**, 2647.

17) G. M. Varga, E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9**, 662 (1970); J. W. Linnett, *J. Chem. Soc.*, **1961**, 3796.

18) D. Sutton, "Electronic Spectra of Transition Metal Complexes," McGraw-Hill Publishers, New York, N. Y. (1968), p. 103.

19) Y. Shimura, H. Ito, and R. Thuchida, *Nippon Kagaku Zasshi* **75**, 560 (1954).

20) L. C. W. Baker and V. E. Simmons, *J. Amer. Chem. Soc.*, **81**, 4744 (1959).