Heteropolyanions Containing Two Different Heteroatoms. Part III.[1] Cobalto(II)undecatungstophosphate and Related Anions

By **T. J. R. Weakley**, Chemistry Department, Dundee University, Dundee DD1 4HN, Scotland

Salts of the heteropolyanions $PCo^{II}W_{11}O_{40}H_2^{5-}$, $AsCo^{II}W_{11}O_{40}H_2^{5-}$, $BCo^{II}W_{11}O_{40}H_2^{7-}$, $BCo^{III}W_{11}O_{40}H_2^{6-}$, and $PZnW_{11}O_{40}H_2^{5-}$ have been prepared. In the case of the first four and of $PNi^{II}W_{11}O_{40}H_2^{5-}$ there is spectroscopic evidence that the constitutional water is present as an actual water molecule and is replaceable by, *e.g.*, a molecule of pyridine or a substituted pyridine. Replacement of water is fast for the cobalt(II) complexes and slow for $BCo^{III}W_{11}O_{40}H_2^{6-}$. Some crystalline salts of derivatives such as $PCo^{II}(C_5H_5N)W_{11}O_{39}^{5-}$ have been prepared.

The diffuse reflectance spectra of the cobalt(II) complexes are cation-dependent in the 17,000—20,000 cm^{-1} region. Salts whose reflectance and solution spectra differ markedly are dichroic; distortion of the CoO_6 chromophore by crystal packing is accompanied by preferential orientation of the heteropolyanion. Such salts should be suitable for *X*-ray studies of the detailed structure of the anion.

HETEROPOLYANIONS of the type $X^{x+}Z^{z+}W_{11}O_{40}H_n^{(14-x-z-n)-}$, in which one tungsten atom of an anion $X^{x+}W_{12}O_{40}^{(8-x)-}$ having the ' Keggin ' structure[2] has been replaced by an atom Z (usually of the first transition series), were first described by Baker and his co-workers.[3] The formation of many anions of this type by the direct reaction of ' unsaturated ' heteropolyanions with transition-metal cations in aqueous solution has been demonstrated.[4-6] In the above general formula *n* is most often 2: that is, the elements of one molecule of constitutional water are present in the anion. Baker and Figgis have shown[7] that in all such cases studied by them an actual water molecule is bonded to the Z atom, in place of the exterior unshared oxygen attached to the tungsten atom which Z replaced, and that the substitution of other ligands for this water is possible. They studied, in particular, the replacement of water by pyridine in $SiCo^{II}(OH_2)W_{11}O_{39}^{6-}$ and by pyridine and ammonia in $SiCo^{III}(OH_2)W_{11}O_{39}^{5-}$.

The present work continues earlier studies[6,8] of anions of the types BZW_{11} and PZW_{11},† and concerns the heteropolyanions $BCo^{II}W_{11}O_{40}H_2^{7-}$, $PCo^{II}W_{11}O_{40}H_2^{5-}$, $AsCo^{II}W_{11}O_{40}H_2^{5-}$, $BCo^{III}W_{11}O_{40}H_2^{6-}$, and $PZnW_{11}O_{40}H_2^{5-}$. The formation of the first two in aqueous solution,[4,5] and some crystallographic data,[9] have been reported previously but analytical results have not been given. The main points of interest are the replacement of constitutional water by other ligands in the anions containing cobalt and in $PNiW_{11}$, and the dependence of the diffuse reflectance spectra of the $XCo^{II}W_{11}$ salts on the cation.

RESULTS AND DISCUSSION

The following properties of the new heteropolyanions require no special comment. The anions (like related anions containing Co, Mn, Ni, and Cu)[6,8] undergo slow degradation by aqueous base. Except for $BCo^{III}W_{11}$, they are all (particularly $BCo^{II}W_{11}$) sensitive to acid, undergoing rapid conversion into $XW_{12}O_{40}^{n-}$ and Co^{2+} or Zn^{2+}. The $BCo^{III}W_{11}$ anion, like $SiCo^{III}W_{11}$ and $GeCo^{III}W_{11}$,[8] can be converted into the hexabasic aqueous acid by cation-exchange. The positions and intensities of the ligand-field spectral bands (Table 1)

TABLE 1

Solution spectra of cobalt in $XCoW_{11}O_{40}H_2^{n-}$ anions: wavenumbers × $10^{-3}/cm^{-1}$ and assignments for O_h symmetry. Molar extinction coefficients in parentheses. Ground states: Co^{II}, $^4T_{1g}(F)$; Co^{III}, $^1A_{1g}$

$BCo^{II}W_{11}O_{40}H_2^{7-}$	7·7 (6), $^4T_{2g}$; 18·3 (49), 18·9, 19·9, $^4T_{1g}(P)$; 26—26·5sh,br (250), C.T.[a]
$PCo^{II}W_{11}O_{40}H_2^{5-}$	7·2 (7·5), $^4T_{2g}$; 14·2sh (4), $^4A_{2g}$; 18·5 (72), 19·7sh, $^4T_{1g}(P)$; ~27sh,br (250), C.T.[a]
$AsCo^{II}W_{11}O_{40}H_2^{5-}$	7·4 (5), $^4T_{2g}$; 14·2sh (2), $^4A_{2g}$; 18·1 (74), 19·6sh, $^4T_{1g}(P)$; ~27sh,br (250), C.T.[a]
$BCo^{III}W_{11}O_{40}H_2^{6-}$	14·6 (58), $^1T_{1g}$; 21·5—22,[b] ?$^1T_{2g}$

[a] Charge transfer, probably Co^{II} to W^{VI}. [b] Inflection on u.v. absorption edge.

---

† As previously, heteropolyanions will be referred to by abbreviated formulae. The ligand in the unshared co-ordination position of Z in XZW_{11} is water unless specifically designated. The first symbol X denotes the central heteroatom.

[1] Part II, S. A. Malik and T. J. R. Weakley, *J. Chem. Soc.* (*A*), 1968, 2647.

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

[3] 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.

[4] C. M. Tourné, *Compt. rend.*, 1968, *C*, **266**, 702.

[5] C. M. Tourné and G. Tourné, *Bull. Soc. chim. France*, 1969, 1124.

[6] C. M. Tourné, G. F. Tourné, S. A. Malik, and T. J. R. Weakley, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3875.

[7] L. C. W. Baker and J. S. Figgis, *J. Amer. Chem. Soc.*, 1970, **92**, 3794.

[8] T. J. R. Weakley and S. A. Malik, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2935.

[9] C. M. Tourné and G. Tourné, *Compt. rend.*, 1968, *C*, **266**, 1363.

resemble those observed for, *e.g.*, $GeCo^{II}W_{11}$ and $SiCo^{III}W_{11}$ and are interpretable[8] in terms of near-octahedral CoO_6 groups. The assignments are for O_h symmetry, since detailed structural parameters for the CoO_6 groups are not at present available.

The $BCo^{III}W_{11}$–$BCo^{II}W_{11}$ redox potential is *ca.* +0·57 V. The oxidation of $BCo^{II}W_{11}$ is readily effected by H_2O_2 in hot aqueous solution, but attempts to oxidise the $PCo^{II}W_{11}$ and $AsCo^{II}W_{11}$ anions either have no effect (electrolytic oxidation) or result in the decomposition of the anions (peroxodisulphate). The correspondence between the orders of the Co^{III}–Co^{II} and the Mn^{III}–Mn^{II} potentials in the XZW_{11} anions has been noted previously[6] although $BCo^{II}W_{11}$, unlike $BMn^{II}W_{11}$, is not oxidised by molecular oxygen. The relative insensitivity of $BCo^{III}W_{11}$ to reduction makes this anion particularly suitable for ligand-replacement studies (see below).

TABLE 2

Formation constants/l mol⁻¹ at 20 °C of $XCo^{II}(L)W_{11}$ [a] and wavenumbers × 10^{-3}/cm⁻¹ and extinction coefficients of visible absorption maximum

		Pyridine	3-Cyano-pyridine	4-Methyl-pyridine	2-Methyl-pyridine	NCS⁻	Thiourea
$BCo^{II}(L)W_{11}$	K	23	10	20	1·0	*b*	*b*
	ν	18·4	18·8	18·6	18·8		
	ε	155	144	200	150		
$PCo^{II}(L)W_{11}$	K	107	13	140	3·6	3·6	3·1
	ν	18·5	19·1	18·5	18·6	18·2	18·6
	ε	204	218	230	235	261	240
$AsCo^{II}(L)W_{11}$	K	110	8·5	*b*	*b*	*b*	*b*
	ν	18·1	18·4				
	ε	210	255				

[a] Defined for process $XCo^{II}W_{11} + L \rightleftharpoons XCo^{II}(L)W_{11}$. [b] Complex formation not studied quantitatively.

Replacement of Constitutional Water.—This study was begun before Baker and Figgis reported[7] on the $SiCo^{III}W_{11}$ and $SiCo^{III}W_{11}$ anions. Our findings extend theirs and suggest that in all heteropolyanions of the types $XCo^{II}W_{11}$, $XCo^{III}W_{11}$, and $XNi^{II}W_{11}$, at least, a water molecule is bound to the outer (transition metal) heteroatom and is replaceable by other ligands.

$XCo^{II}W_{11}$ *anions in solution.* The interaction of potential ligands and cobalt in the heteropolyanions cannot be studied by potentiometric methods involving variation of the pH because of the limited pH ranges of stability of the anions themselves. However, changes in the position and shape, and an increase in the intensity, of the ligand-field band in the 18,000—20,000 cm⁻¹ region were observed when the following ligands L were present: thiocyanate, thiourea, pyridine, 3-cyanopyridine, 2- and 4-methylpyridine, and 4,4′-bipyridyl. No change was observed with 2,6-dimethylpyridine. In a number of cases the change in the spectrum with [L], at constant $[XCoW_{11}]$, was examined quantitatively; the data in all cases agreed with the formation of 1 : 1 complexes $XCo^{II}(L)W_{11}O_{39}{}^{n-}$ having the formation constants and molar extinction coefficients listed in Table 2. The destabilisation of the pyridine complex upon successive methylation at the 2- and 6-positions must be attributed to crowding between the methyl groups and the four oxygen atoms adjacent to L in the CoO_5L group.

The addition of water-miscible polar organic solvents to aqueous solutions of the potassium ($BCo^{II}W_{11}$, $PCo^{II}W_{11}$) or trialkylammonium ($AsCo^{II}W_{11}$) salts, or to solutions of the sodium or lithium salts prepared by ion-exchange, also resulted in spectral changes in the 18,000—20,000 cm⁻¹ region. The organic solvents included methanol, ethanol, 1,2-dihydroxyethane, 1,4-dioxan, dimethyl sulphoxide, *NN*-dimethylformamide, and acetonitrile. The change in spectrum with solvent composition continued up to the point where precipitation of the solute began [usually over 50% (v/v) organic component]. This is illustrated in Figure 1 for $PCo^{II}W_{11}$ in aqueous acetonitrile. When, as in this case, the spectra at different solvent compositions crossed, small deviations from ' isosbestic ' behaviour were noted; it is uncertain whether slight decomposition of the anion occurred or whether the spectra of the two absorbing species present were slightly solvent-dependent, but dilution with water appeared to reverse the spectral changes quantitatively. Similar observations were made for the previously reported[8,10] $GeCo^{II}W_{11}$ and $SiCo^{II}W_{11}$ anions. For each anion, the biggest spectral changes occurred in aqueous acetonitrile, and the extents of the changes generally depended on the central heteroatom in the order P > Si, B; P > As; Si > Ge, for a given solvent. The very water-soluble lithium salt of $PCo^{II}W_{11}$ is sparingly soluble (0·005—0·01M) in several polar organic solvents, and the spectra are shown in Figure 2. These observations strongly suggest the co-ordination of a molecule of the organic species to cobalt in place of water, the heteropolyanion remaining otherwise intact. Unfortunately, no stable heteropolyanions are known in which all the oxygen atoms of a $Co^{II}O_6$ group are shared with molybdenum or tungsten, but no dependence of spectrum on solvent composition was observed for the well-shielded CoO_4 group in $CoW_{12}O_{40}{}^{6-}$.

Cobalto(II)*undecatungstoborate in solution.* The absorbance at the wavenumbers stated in Table 3 increases linearly with [L] at constant $[BCo^{III}W_{11}]$ until the concentrations are equal and thereafter remains constant, when L is ammonia, pyridine, or 4-methylpyridine. Stable, kinetically inert complexes $BCo^{III}(L)W_{11}O_{39}{}^{6-}$ are formed. By ion-exchange, solutions of the corres-

---

[10] V. E. Simmons, Ph.D. Thesis, Boston University, 1963.

ponding hexabasic free acids can be obtained, in which aquation is slow (half-life over one week at room temperature). When L is anionic or is 2-methylpyridine the plots of absorbance against [L] are continuous curves and are interpretable in terms of similar 1 : 1 complexes with the absorption maxima and extinction coefficients given in Table 3. There was no evidence of complexing with 2,6-dimethylpyridine. The absorption maxima are in the order of the spectrochemical series for L; shifts to higher wavenumbers are accompanied by a broadening of the band, and when L is cyanide or ammonia a shoulder is visible on the low-wavenumber side. For the ligand 4,4′-bipyridyl (LL) it appears from the absorbance data that at high [LL] : [Co] ratios a stable complex $BCo(LL)W_{11}$ is formed, with one end of the ligand free, while at lower ratios there exists a less stable binuclear complex in which two heteropolyanions are linked by the double-ended ligand. Baker and Figgis state[7] that related heteropolyanions form similar dinuclear complexes with pyrazine.

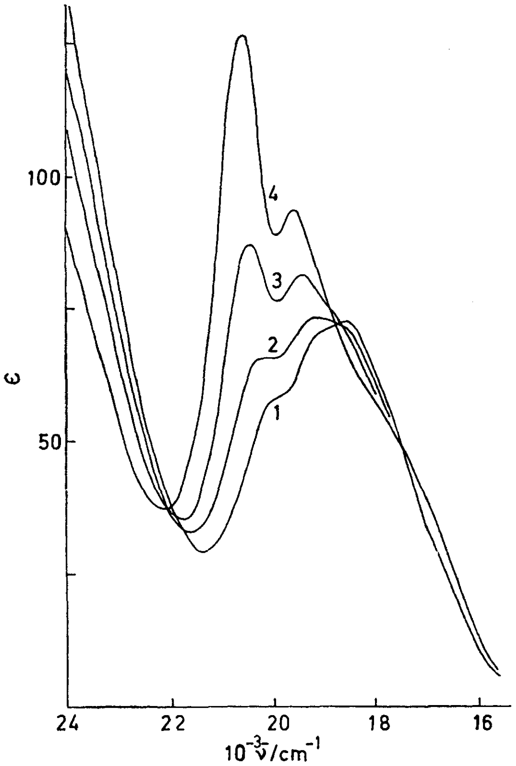

FIGURE 1 Spectrum of sodium cobalto(II)undecatungstophosphate in: 1, water; 2, 8% acetonitrile; 3, 20% acetonitrile; and 4, 72% acetonitrile

TABLE 3

Formation constants/l mol^{-1} at 20 °C for $BCo^{III}W_{11} + L \rightleftharpoons BCo^{III}(L)W_{11}$ and wavenumbers × $10^{-3}/cm^{-1}$ and extinction coefficients of $^1T_{1g}$ band of $BCo^{III}(L)W_{11}$

	CN^-	NO_2^-	NH_3	4-Methyl-pyridine	2-Methyl-pyridine	Pyridine	N_3^-
K	—	250	Large	Large	40	Large	32
ν	17·4	16·5	16·0	16·0	16·0	15·9	14·5
ε	32	62	37	60	56	54	230

In contrast to the $XCo^{II}W_{11}$ systems, the replacement of water in $BCo^{III}W_{11}$ is slow and can conveniently be followed with a conventional spectrophotometer. The second-order rate constants for the reaction of this anion with pyridine and with nitrite are respectively *ca.* 0·1 and 0·02 l mol^{-1} s^{-1} at 20 °C. The anation of $BCo^{III}W_{11}$ and its relatives [unlike that of most other cobalt(III) aquo-complexes][11] is not expected to proceed *via* an ion-pair and may therefore be of mechanistic interest. We hope to study these reactions further.

Nickelo(II)*undecatungstophosphate*. Baker and Figgis observed[7] the replacement of water at nickel(II) in $XNiW_{11}$ anions, but did not say which ones they studied. In this work, we examined the previously reported[8] $PNiW_{11}$ anion, whose spectrum was interpreted in terms of a slightly distorted NiO_6 octahedron. In the presence of potential ligands in aqueous solution, small changes in the position of the $^3T_{1g}(P)$ band (23,700 cm^{-1} in pure water) and in the position and shape of the $^3T_{1g}(F)$ band (baricentre 13,300 cm^{-1} in water) were observed, the wavenumber of the $^3T_{1g}(P)$ band increasing in the following order of ligands: thiourea (23,100 cm^{-1}), thiocyanate, 88% dimethyl sulphoxide, water, 80% dioxan, and 1,2-dihydroxyethane, 76% acetonitrile, pyridine (24,100 cm^{-1}), for a ten-fold or greater excess of ligand. The intensification of this band permitted the formation constant of $PNi(py)W_{11}O_{39}^{5-}$ to be estimated as 700—1000 l mol^{-1}. The band intensities in all other cases were scarcely altered. In aqueous pyridine the $^3T_{2g}$ band was shifted from 8200 to 8500 cm^{-1}; the effects of other

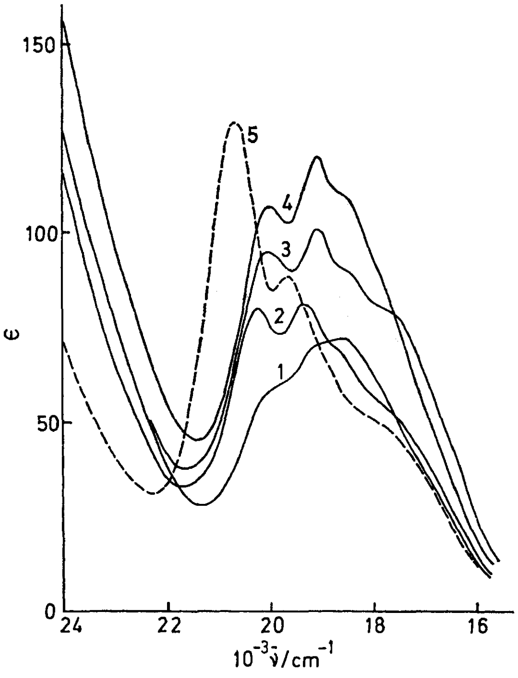

FIGURE 2 Spectrum of lithium cobalto(II)undecatungstophosphate in: 1, water; 2, dihydroxymethane; 3, dimethyl sulphoxide; 4, *NN*-dimethylformamide; and 5 (ε/2), acetonitrile

[11] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, pp. 193—207.

ligands on this weak band, in a spectral region where water is beginning to absorb, were not examined.

Solid salts. Several crystalline salts in which water co-ordinated to cobalt or nickel had been replaced by ammonia or pyridine were prepared. Analysis indicated the formulae $Ba_3BCo^{III}(NH_3)W_{11}O_{39},26H_2O$, $(pyH)_6BCo^{III}(py)W_{11}O_{39},6H_2O$, $(pyH)_5PNi(py)W_{11}O_{39},5H_2O$, $(pyH)_5PCo^{II}(py)W_{11}O_{39},6H_2O$, and $(pyH)_5AsCo^{II}(py)W_{11}O_{39},8H_2O$. The first was isomorphous with $Ba_3BCo^{III}W_{11}O_{40}H_2,26H_2O$. The diffuse reflectance spectra of the first three closely resembled the solution spectra in the presence of excess of ligand, confirming that the ligand was not merely trapped in the interanionic spaces containing lattice water. The reflectance spectra of the cobalt(II) complexes differed somewhat from the spectra in aqueous pyridine, particularly in showing more structure in the 17,000—20,000 cm^{-1} region. This may result from a distortion of the chromophore owing to crystal packing forces (see below). It was not possible to obtain crystalline salts of less stable complexes; for example, when the potassium salt of $BCo^{II}W_{11}$ was recrystallised from aqueous KSCN, the well-washed product contained no thiocyanate.

Diffuse Reflectance Spectra and Anion Orientation.—The solution spectra of all salts of a given $XCo^{II}W_{11}$ anion are identical. However, the reflectance spectra in the region of the 17,000—20,000 cm^{-1} band [$^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$ in O_h symmetry] are cation-dependent, and in some cases differ markedly from the solution spectra. Such reflectance spectra are here termed 'abnormal.' The effect is most apparent for the $PCo^{II}W_{11}$ and $BCo^{II}W_{11}$ anions and is illustrated in Figures 3 and 4. The positions of the $^4T_{2g}$ and $^4A_{2g}$ bands (near 7000 and 14,000 cm^{-1} respectively) are slightly cation-dependent but no splitting or intensification of the bands is observed. Salts of very large cations (*e.g.*, Et_4N^+ or Ph_3MeN^+) invariably have abnormal reflectance spectra, but are generally virtually insoluble and microcrystalline, and impossible to purify; in some cases (Me_4N^+ salts of $SiCo^{II}W_{11}$ and $GeCo^{II}W_{11}$) larger crystals can be grown by the slow interdiffusion of solutions of the component ions, but the material so obtained does not appear homogeneous. Figures 3 and 4 and Table 4 and the present discussion refer to recrystallisable salts which gave satisfactory analyses.

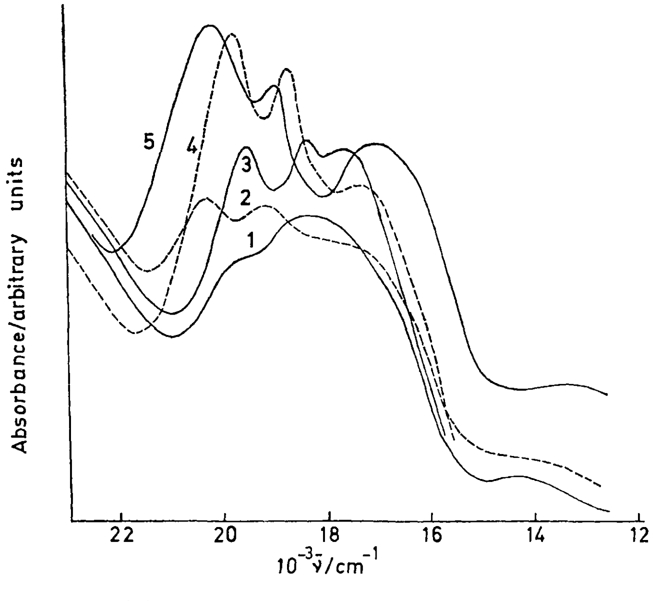

FIGURE 3 Diffuse reflectance spectra of salts of cobalto(II)-undecatungstophosphate at 80 K. 1, Potassium; 2, guanidinium; 3, dimethylammonium; 4, caesium; 5, triethylammonium

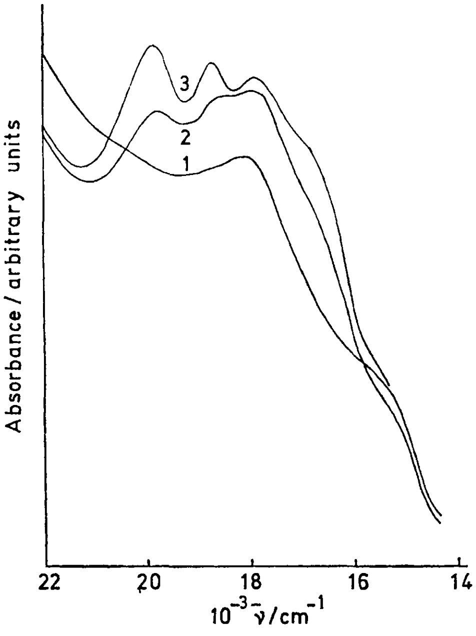

FIGURE 4 Diffuse reflectance spectra of salts of cobalto(II)-undecatungstoborate at 80 K. 1, Potassium sodium; 2, potassium; 3, caesium

TABLE 4

Diffuse reflectance *d–d* spectra of salts of $XCo^{II}W_{11}$ anions: wavenumbers × 10^{-3}/cm^{-1}

$BCo^{II}W_{11}$	K_6Na	7·2 is not here; 8·2; 15·6sh; 18·0,[a] 20·3sh
	K_7	7·9; 15·6sh; 18·0,[a] 18·6, 19·85
	Cs	7·6; 17·7, 18·5, 19·55[a]
	NH_4	7·7; ~15sh; 17·6, 18·7, 19·8[a]
$PCo^{II}W_{11}$	K	7·2; ~14·5w; 18·7,[a] 19·7sh
	Rb	7·25; ~14sh,w; 18·7,[a] 19·8
	Cs	7·3; 17·7, 18·45,[a] 19·55
	CH_6N_3	7·45; 13·8w; 17·8sh, 19·5, 20·2[a]
	Me_2NH_2	7·4; 17·3, 18·8, 19·9[a]
	Et_3NH[b]	7·2; ~13·5w; 17·1, 19·05, 20·2[a]
	Me_4N	7·1; ~13·5w; 17·1, 18·95, 20·0[a]
$PCo^{II}(py)W_{11}$	pyH	7·55; ~17·5sh,w, ~18·5sh,w, 19·0,[a] 19·9
$AsCo^{II}W_{11}$	Me_3NH	7·0; 13·6sh,w; 17·55sh, 18·6,[a] 19·5
	Et_3NH	7·0; 13·1w; 17·0sh,br, 18·75,[a] 19·8
$AsCo^{II}(py)W_{11}$	pyH	7·5; ?15sh,w; 18·35,[a] 19·7

[a] Most intense *d–d* peak. [b] Spectra of Et_3NH, Et_2NH_2, and Me_3NH salts very similar.

The $^4T_{1g}(P)$ band in the abnormal spectra is split by 2000—3000 cm^{-1}. It is split by a similar amount in the diffuse reflectance spectra of Co^{2+} in distorted-octahedral sites in a number of oxide and silicate host materials;[12-14] for example, in $Co_{2-x}Mg_xGeO_4$ the CoO_6 group has been compressed along a trigonal axis, while in Co-doped Mg_2SiO_4 and $MgCaSiO_4$ it has point symmetry C_i and C_s.[13] The ${}^4T_{1g}(P)$ band is also split in the spectra of Co^{2+}–MnF_2[15] and of $CoCl_2,6H_2O$[16] (by 3500 cm^{-1} in the latter), the ligand fields having symmetries D_{2h} and C_{2h} respectively. In a number of the present abnormal reflectance spectra there are indications of more than three bands in the 17,000—20,000 cm^{-1} region (the ${}^4A_{2g}$ band, where identifiable, always lies below 16,000 cm^{-1}); transitions to ligand-field components of the free-ion ${}^2G$, ${}^2P$, and ${}^2H$ states, gaining intensity from spin-allowed transitions through spin–orbit coupling, may lie in this region.[16,17] The nature of the distortion of the CoO_6 [actually $CoO_5(OH_2)$] chromophores in the $XCo^{II}W_{11}$ anions cannot be deduced from the abnormal reflectance spectra alone, nor can the maxima be assigned. The distortion should, however, cause the transitions to the components of the ${}^4T_{1g}(P)$ state to be polarised.[15-17] In agreement with this, the $XCo^{II}W_{11}$ salts whose reflectance spectra show the biggest band splittings are all markedly dichroic, and moreover seem from their crystal morphology and complex *X*-ray powder patterns to be of low symmetry. Apparently the preferred mode of packing of the anions in these salts induces both a distortion of the CoO_6 groups and an alignment of their axes. The question of the orientation of the anions must now be considered.

An XW_{12} anion with the Keggin structure[2] has T_d overall symmetry. The derived XZW_{11} anion has C_s symmetry; the ZO_6 group presumably has micro-symmetry close to C_{4v}, like the WO_6 group it replaces. However in many crystalline salts the Z positions are disordered, with the result that *X*-rays 'see' an array of $X(Z_{1/12}W_{11/12})_{12}$ anions. Consequently the structural parameters of the WO_6 and ZO_6 groups cannot be separately determined. Evans, in a recent review,[18] has stressed the need for studies of disorder-free XZW_{11} salts of low crystal symmetry. Certain of the $XCo^{II}W_{11}$ salts having abnormal reflectance spectra, in particular $(Et_3NH)_5PCo^{II}W_{11}O_{40}H_2,2H_2O$ (see below), should be suitable provided that structural parameters appropriate to the undistorted anion in solution are not required.

Some crystal data were obtained during the present work, and illustrate the discussion just given. $K_6NaBCo^{II}W_{11}O_{40}H_2,14H_2O$ is cubic, $a = 21{\cdot}53$ Å, $Z = 8$ (powder diffraction), and is isomorphous with the disordered cubic ($Fm3m$) salts previously studied by Baker and his co-workers[3] and by Evans.[18] The anions form two interpenetrating face-centred cubic arrays, like the ions in KCl. Each anion is inverted with respect to its six neighbours; since inversion of the anion brings the set of heavy atoms almost into self-coincidence, the odd-order reflections are weak or absent. $K_5PCo^{II}W_{11}O_{40}H_2,15H_2O$ and $K_5PZnW_{11}O_{40}H_2,15H_2O$ are tetragonal, $a = 14{\cdot}22$, $c = 12{\cdot}46$ Å and $a = 14{\cdot}29$, $c = 12{\cdot}64$ Å respectively, $Z = 2$. These results agree with those of Tourné and Tourné.[9] The reflections with odd Σh in the *X*-ray powder patterns are weak or absent, suggesting that the anion at the cell centre is inverted with respect to those at the corners as in (cubic) $H_3PW_{12}O_{40},5H_2O$ studied by Keggin.[2] These $XCo^{II}W_{11}$ salts have normal reflectance spectra. The absorption in the $PCo^{II}W_{11}$ salt is unpolarised; the Z atom positions must be disordered in this salt and in the zinc isomorph. The cobalt positions are also disordered in $Ba_3BCo^{III}W_{11}O_{40}H_2,26H_2O$; single-crystal measurements show that the unit cell is tetragonal, $a = 12{\cdot}38$, $c = 18{\cdot}34$ Å, $Z = 2$, space group $P4nc$ or $P4/mnc$, possibly isomorphous with $H_5BW_{12}O_{40},31H_2O$ and $(NH_4)_5BW_{12}O_{40},26H_2O$ ($P4/mnc$).[19]

In contrast, $K_7BCo^{II}W_{11}O_{40}H_2,11H_2O$ is dichroic (deep red to colourless rhombs) with an abnormal reflectance spectrum. Well-separated single crystals could not be obtained, but the powder pattern agreed with a tetragonal cell, $a = 21{\cdot}1$, $c = 10{\cdot}6$ Å, $Z = 4$. The triethylammonium salts of the $PCo^{II}W_{11}$, $AsCo^{II}W_{11}$, and $PZnW_{11}$ anions are isomorphous (*X*-ray powder patterns and crystal morphology). The first two have abnormal reflectance spectra; the splitting of the ${}^4T_{1g}(P)$ band is particularly large for the $PCo^{II}W_{11}$ salt (Figure 3). A single-crystal *X*-ray study of $(Et_3NH)_5PCo^{II}W_{11}O_{40}H_2,2H_2O$ shows that the unit cell is orthorhombic, $a = 21{\cdot}65$, $b = 14{\cdot}78$, $c = 20{\cdot}79$ Å, $Z = 4$. The crystals are generally elongated parallel to *a*, with prominent {011} faces, and are strongly dichroic (deep red to pale green) with maximum absorption when the electric vector is parallel to *a*. The space group is $Pna2_1$ or $Pnam$, with four or eight asymmetric units respectively per unit cell. In neither case is it necessary to assume that there is disorder. The former space group implies that the distortion of the CoO_6 group (evident from the reflectance spectrum) has eliminated the mirror plane of the free anion. The latter requires the asymmetric unit to be the half-anion, the anion mirror-plane coinciding with a space-group mirror-plane [parallel to (001)]. One possible packing arrangement would then have the anions centred at 0,0,0; $0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$; and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, with the local axes of symmetry of the CoO_6 groups lying in the mirror-planes and all making the same small angle with the [100] direction. The crystals are air-stable, and ones suitable for microspectrophotometry can be grown without difficulty, although we were unable to grow large enough crystals of this salt (diluted with the zinc isomorph) to obtain the polarised transmission spectrum with the apparatus available.

There is no evidence so far that the Z atom positions may be completely ordered, or that the ZO_6 groups are distorted as a result of crystal packing, in any salts of

---

[12] D. Reinen, *Theoret. Chim. Acta*, 1967, **8**, 260.

[13] O. Schmitz-Dumont and C. Friebel, *Monatsh.*, 1967, **98**, 1583.

[14] H. Kasper, *Z. anorg. Chem.*, 1968, **363**, 213.

[15] R. F. Blunt, *J. Chem. Phys.*, 1966, **44**, 2317.

[16] J. Ferguson, *J. Chem. Phys.*, 1960, **32**, 533.

[17] J. Ferguson, D. L. Wood, and K. Knox, *J. Chem. Phys.*, 1963, **39**, 881.

[18] H. T. Evans, jun., *Perspectives Structural Chem.*, 1971, **4**, 1.

[19] O. Kraus, *Z. Krist.*, 1933, **91**, 402.

other XZW_{11} anions. For example, $(Et_3NH)_5PNiW_{11}O_{40}H_2,H_2O$ has a normal reflectance spectrum (similar to that of the potassium salt and to the solution spectrum) and lacks dichroism; the crystal is of low symmetry (morphology and powder pattern) but is not isomorphous with the $PCo^{II}W_{11}$, $AsCo^{II}W_{11}$, and $PZnW_{11}$ salts.

EXPERIMENTAL

The instruments and analytical methods used have been described.[1,8] All new analytical data are in Table 5. General methods for preparing salts of XZW_{11} anions (X = B, Si, Ge, P, or Zn; Z = bivalent transition element) have been discussed and exemplified elsewhere.[6] The procedures for the potassium salts of the $BCo^{II}W_{11}$, $PCo^{II}W_{11}$, and $PZnW_{11}$ anions closely followed those for the salts of the $BMn^{II}W_{11}$, $PMn^{II}W_{11}$, and $PNiW_{11}$ anions.[6,8] Other salts were obtained by metathesis, and were recrystallised from water (70 °C). In the preparation of the $BCo^{II}W_{11}$ ion a three- to five-fold excess of H_3BO_3 was needed to avoid contamination of the product by the $Co^{II}Co^{II}W_{11}$ anion; addition of KCl to the reaction mixture gave both the K_7 and the K_6Na salts, which were obtained pure by repeated recrystallisation from hot 2% aqueous KCl and NaCl, respectively. The $BCo^{III}W_{11}$ anion was obtained by oxidation with H_2O_2 or $Na_2S_2O_8$ in hot aqueous solution, and was isolated and purified as the barium salt. Pyridinium salts of pyridine derivatives [*e.g.*, $(C_5H_6N)_5PCo^{II}(C_5H_5N)W_{11}O_{39},6H_2O$] were prepared by treating a hot solution of a salt of the aquo-complex with a concentrated aqueous solution of pyridine whose pH had been adjusted to 5·5 with acetic acid, and were recrystallised from a hot 0·1% aqueous solution of pyridine. $Ba_3BCo^{III}(NH_3)W_{11}O_{39},26H_2O$ separated on filtering and cooling a hot aqueous solution of $Ba_3BCo^{III}W_{11}O_{40}H_2,26H_2O$ containing about 1·1 times the calculated amount of ammonia.

Cobalto(II)*undecatungstoarsenate*.—The pH of a solution containing $Na_2WO_4,2H_2O$ (66 g, 0·2 mol) and $Na_2HAsO_4,7H_2O$ (6·3 g, 0·02 mol) in water (150 ml) was adjusted to 5·5. The solution was heated to 95 °C and a concentrated solution of $Co(OAc)_2,4H_2O$ (5·1 g, 0·02 mol) was added dropwise. The deep red solution was filtered hot, and was treated with a concentrated solution of triethylammonium or trimethylammonium chloride. Small purple-red dichroic crystals separated on cooling, a by-product [20] $AsCo_2^{II}W_9O_{34}^{5-}$ remaining in solution, and were recrystallised from hot water. Attempts to prepare the guanidinium and the very soluble potassium salts appeared to result in some decomposition of the anion.

TABLE 5

Analytical data for $M_x[XZ(L)W_{11}O_{39}],nH_2O$

Anion	M	n	Found (Required)/% Cation or N	Z	W	Loss on ignition
$BCo^{II}(H_2O)W_{11}O_{39}^{7-}$	K_6Na	14	K 6·96 (7·24) Na 0·80 (0·71)	1·84 (1·82)	61·4 (62·3)	8·3 (8·3)
	K_7	12	8·46 (8·50)	1·85 (1·83)	62·5 (62·1)	7·2 (7·3)
	Cs	9	24·7 (24·3)	1·59 (1·54)	53·2 (52·9)	4·6 (4·7)
	NH_4	12	2·97 (3·18)	1·94 (1·92)	65·6 (65·6)	13·3 (13·5)
$BCo^{III}(H_2O)W_{11}O_{39}^{6-}$	Ba	26	11·4 (11·4)	1·62 (1·63)	56·0 (56·0)	13·4 (13·4)
	K	15	7·53 (7·25)	1·87 (1·82)	62·3 (62·4)	8·8 (8·9)
$BCo^{III}(C_5H_5N)W_{11}O_{39}^{6-}$	C_5H_6N	6	2·74 (2·90)	1·82 (1·74)	59·8 (59·9)	20·8 (21·0)
$BCo^{III}(NH_3)W_{11}O_{39}^{6-}$	Ba	26	10·9 (11·4) [a]	1·63 (1·62)	56·1 (56·0)	—
$PCo^{II}(H_2O)W_{11}O_{39}^{5-}$	K	15	6·09 (6·07)	1·80 (1·83)	63·8 (62·8)	9·0 (8·9) [b]
	Cs	3	19·8 (19·1)	1·71 (1·70)	58·3 (58·2)	4·2 (4·2)
	$C(NH_2)_3$	4	6·60 (6·70)	1·88 (1·88)	65·6 (64·7)	13·7 (18·8) [c]
	Me_2NH_2	3	2·12 (2·30)	1·91 (1·94)	67·0 (66·6)	11·2 (11·3)
	Et_2NH_2	2	2·12 (2·21)	1·86 (1·86)	64·3 (64·0)	14·6 (14·7)
	Me_3NH	1	2·16 (2·28)	1·93 (1·92)	66·0 (65·9)	12·2 (12·2)
	Et_3NH	2	2·04 (2·13)	1·77 (1·80)	61·6 (61·6)	18·0 (17·9) [d]
	Me_4N	2	2·09 (2·20)	1·86 (1·85)	—	14·6 (14·6)
$PCo^{II}(C_5H_5N)W_{11}O_{39}^{5-}$	C_5H_6N	5	2·52 (2·54)	1·80 (1·78)	61·7 (61·2)	18·8 (18·4)
$AsCo^{II}(H_2O)W_{11}O_{39}^{5-}$	Me_3NH	4	2·19 (2·21)	1·94 (1·86)	64·1 (63·8)	13·7 (13·6)
	Et_3NH	3	2·07 (2·08)	1·73 (1·73)	60·1 (60·5)	— [e]
$AsCo^{II}(C_5H_5N)W_{11}O_{39}^{5-}$	C_5H_6N	8	2·41 (2·47)	1·79 (1·73)	58·5 (59·4)	19·6 (19·5)
$PZn(H_2O)W_{11}O_{39}^{5-}$	K	16	6·45 (6·04)	2·02 (2·01)	62·7 (62·3)	9·7 (9·4) [f]
	$C(NH_2)_3$	4	6·54 (6·70)	2·08 (2·09)	62·3 (64·6)	13·7 (13·7)
	Et_3NH	1	2·03 (2·13)	1·99 (1·99)	62·1 (61·5)	18·0 (17·8)
$PZn(C_5H_5N)W_{11}O_{39}^{5-}$	C_5H_6N [g]	4	2·44 (2·55)	1·99 (2·00)	61·8 (61·5)	17·6 (17·9)
$PNi(H_2O)W_{11}O_{39}^{5-}$	Et_3NH	1	2·03 (2·13)	1·78 (1·79)	61·8 (61·7)	19·6 (20·0)
$PNi(C_5H_5N)W_{11}O_{39}^{5-}$	C_5H_6N	5	2·52 (2·54)	1·77 (1·78)	61·5 (61·2)	18·2 (18·4)

[a] N 0·43 (0·39). [b] P 0·96 (0·96). [c] P 1·00 (0·99). [d] P 0·97 (0·94). [e] As 2·19 (2·22). [f] P 1·01 (0·96). [g] Not recrystallised.

I thank Dr. H. T. Evans for an advance copy of his review (ref. 18) and Mr. J. Loco for single-crystal *X*-ray measurements.

[2/1639 *Received*, 11*th July*, 1972]

[20] H. T. Evans, jun., J. S. Showell, T. J. R. Weakley, G. F. Tourné, and C. M. Tourné, *J.C.S. Chem. Comm.*, accepted for publication.