Chiral Polytungstometalates $[WM_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ ($X = M = Zn$ or Co^{II}) and their M-Substituted Derivatives. Syntheses, Chemical, Structural and Spectroscopic Study of some D,L Sodium and Potassium Salts†

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Heteropolyanions $[WM_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ ($X = M = Zn$ or Co^{II}) form on ageing concentrated solutions of sodium salts of the well known polyanions $[Zn(H_2O)(ZnW_{11}O_{39})]^{8-}$ and $[Co^{II}(H_2O)(Co^{II}W_{11}O_{39})]^{8-}$. Their high-yield syntheses are reported. An X-ray crystallographic study of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 46H_2O$ [Space group $P2_1/c$, $a = 13.027(4)$, $b = 17.788(5)$, $c = 24.124(4)$ Å, $\beta = 118.94(2)°$, $Z = 2$, $R' = 0.051$ for 3783 reflections] and its high-resolution ^{183}W NMR spectrum (ten lines, one with half the intensity of the others) reveal that the polyanion is isotypical of the earlier described $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anions ($M = Zn$ or Co^{II}) and elucidate the puzzling analytical composition Zn_5W_{19}. However, the lower point-group symmetry $C2$ (instead of $C2h$) points to the existence of enantiomers. This anion and the homologous cobalt(II) anion are always obtained as racemic mixtures. Both parent anions transform into substitution derivatives by replacement of atoms in M positions (two or three for Zn, two only for Co) by transition elements: derivatives of Mn^{II} or Mn^{III}, Fe^{II} or Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn, Pd^{II}, Pt^{II} and V^{IV} are reported. The structures of D,L-$Na_{12}[WCu_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 48H_2O$ and D,L-$K_{12}[WZnV_2O_2(ZnW_9O_{34})_2]\cdot 30H_2O$ are also described and compared. Chemical features, comparative electronic UV–VIS spectra, and ^{183}W NMR spectra of these series are discussed.

The chemistry of tungsten heteropolyanions structurally related to the basic Keggin type has been developed extensively, mainly around the species containing central tetrahedrally co-ordinated atoms such as P, As, Si or Ge.[1] Although these complexes were the earliest known, interest in them has been renewed by the discovery of new structure types,[2] progress in obtaining the predicted isomers,[1,3] the stimulating prospects of their non-aqueous chemistry,[2c,4] and the increasingly successful attempts to explore their catalytic properties.[5] Since the remarkable work of Baker and co-workers on polytungstocobaltates,[6] and that of various authors on the analogous polytungstozincates,[7] few papers have been devoted increasing the chemical knowledge of these families of polyanions. Moreover, all the newly reported compounds contain the complete Keggin cluster, either as dodecatungsten anion or as monosubstituted derivatives (one tungsten replaced by another heteroatom).[8] Also, all papers refer to the α isomers.[1,3a] The study of these highly charged polyanions, isoelectronic with the metatungstate ion $[H_2W_{12}O_{40}]^{6-}$, is thus very incomplete. Simple problems remain to be solved such as the existence and/or structure of so-called 'lacunary' species $[X^{II}W_{11}O_{39}]^{10-}$ and the mediocre yield of $[X^{II}W_{12}O_{40}]^{6-}$ through acidification of monosubstituted $[M^{II}(H_2O)(X^{II}W_{11}O_{39})]^{8-}$ ($X^{II} = Zn$ or Co; $M^{II} = Co$, Ni, Cu or Zn) with simultaneous production of metatungstate. We are interested in these polytungstometalate series, and especially would like to know whether other structure types may exist, similar to the phosphate or silicate series.

The present paper reports our first results with the discovery of very stable heteropolyanions which exhibit the unexpected bulk composition ratio W:Zn (or Co) = 19:5. Announced previously,[9] these anions lead to numerous substituted derivatives whose preparation, structure and properties are also discussed here.

Results and Discussion

Formation, Synthesis and Formulation of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ *and* $[WCo_3(H_2O)_2(CoW_9O_{34})_2]^{12-}$.—The discovery of these polyanions results from observing the ageing of sodium salt solutions of the Keggin type $[Zn(H_2O)(ZnW_{11}O_{39})]^{8-}$ or $[Co^{II}(H_2O)(Co^{II}W_{11}O_{39})]^{8-}$ polyanions. The latter anions are usually prepared by treating acidified sodium tungstate with Zn^{2+} (aq) or Co^{2+} (aq). Using nitric acid and nitrates and the theoretical stoichiometry $WO_4^{2-}:H^+:Zn^{2+}$ (or Co^{2+}) = 11:10:2, the sodium nitrate produced may be extracted with acetone, leaving a dense aqueous solution of the polyanion which behaves differently depending on the heating time of the reagents. Brief heating times result only in an almost saturated solution of the sodium salt of the well known M_2W_{11} anions (evaporation to dryness gives a vitreous, very soluble solid). On the other hand, prolonged heating (1 h at least) favours the formation of needle-like crystals. Also, variously concentrated solutions of the vitreous sodium salts (0.05–0.50 mol dm^{-3}, 0.165–1.65 kg dm^{-3}), kept at room temperature, begin to crystallize after some time (minutes to years) depending greatly on concentration. All these experiments result in isomorphous sodium salts, colourless for the zinc anion, deep olive green for Co, with specific X-ray diffraction diagrams. When converted into potassium salts, the corresponding diffraction diagrams are also specific and differ distinctly from those of the cubic potassium salts of the related Keggin polyanions. However, it is surprising that carefully executed analyses give erratic molar ratios W:Zn (or Co) (3.85–4.13:1 for Zn, 3.80–3.96:1 for Co). This precludes a definitive formulation

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

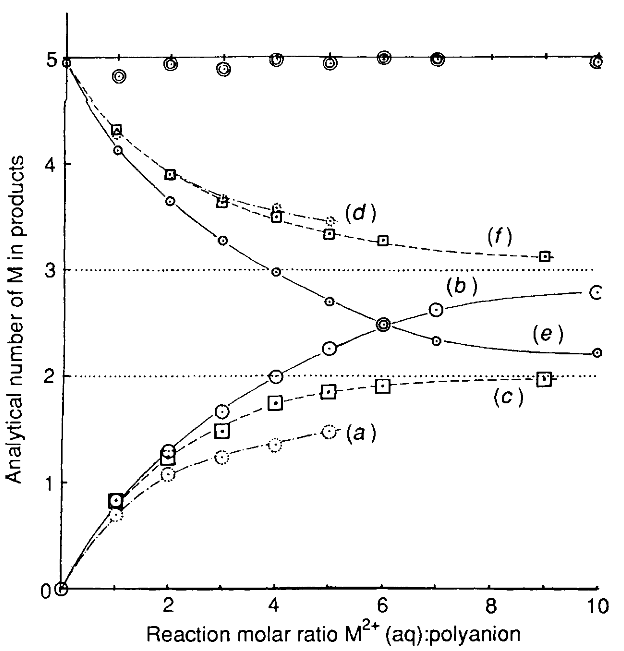

Fig. 1 Analytical composition of products resulting from substitution of Co^{II} in $[H_4Zn_5W_{19}O_{70}]^{12-}$ (circles) and of Zn^{II} in $[H_4Co^{II}{}_5W_{19}O_{70}]^{12-}$ (squares) according to the initial ratio of reagents, temperature and time of reaction. Curves: (*a*)–(*c*), substituted element. (*d*)–(*f*), remaining element. Conditions: 25 °C, 12 h [(*a*), (*d*)], 100 °C, 30 min [(*b*), (*e*); (*c*), (*f*)]. Upper double circles: Zn + Co titrated together in experiments (*b*) and (*e*).

of the novel polyanions. Decisive information was obtained from the high-resolution ^{183}W NMR spectrum of the lithium salt of the novel polytungstozincate which shows ten lines with relative intensities 1:2:2:2:2:2:2:2:2:2 in order of decreasing frequencies (Fig. 5). This corresponds to 19 tungsten atoms. On this basis, the number of zinc or cobalt atoms is close to 5, although always a little lower (4.95 currently, but sometimes as low as 4.6 for the tungstozincate). Accordingly, preparations carried out with the corresponding stoichiometry WO_4^{2-}:HNO_3:$M(NO_3)_2$ = 19:16:5 (M = Zn or Co^{II} rapidly yield pure products in which the molar ratio W:Zn (or Co) of 19:5 is always well defined. This unexpected composition will be elucidated below by a crystallographic structural study.

Numerous preparations carried out while varying the initial composition, pH, concentration, temperature, duration and conditions of the reagent addition show that the present condensed (dimeric) polytungstometallates *do not form directly*, but only after the initial formation of monomers associated with the Keggin structure [adding too rapidly the excess of the zinc (or cobalt) salt results in amorphous precipitates and the separated filtrates yield only the usual cubic salt when they are treated with potassium salts]. Attempts to obtain information on the precursors of the condensation with the help of ^{183}W NMR spectroscopy failed when starting from concentrated Na^+ solutions of $[Zn(H_2O)(ZnW_{11}O_{39})]^{8-}$, because the transformation of this anion into the dimer is too fast in this medium (the solution solidifies entirely after a short time). With concentrated Li^+ solutions, NMR spectra may be obtained. They consist of 12 major intense lines interpretable as two six-line sets (each of intensity ratio 1:2:2:2:2:2, though non-attributable), presumably representative of a mixture of two isomers α, β of the initial Keggin polyanion, as is also observed for numerous $[M(H_2O)(XW_{11}O_{39})]^{q-}$ polyanions,[10,11]

Here, the broadened NMR signals are typical of fast exchanges on the NMR time-scale (Δν ≈ 8–40 compared to usual ≈1–2 Hz). The spectrum of the dimer does not appear after several days, but becomes slightly visible if small amounts of Na^+ are present. So, this cation seems to induce condensation specifically.

A comparable evolution, with slow crystallization, is also observed in aqueous concentrated solutions of sodium salts prepared to obtain the isotypical substituted polyanions $[M^{II}(H_2O)(ZnW_{11}O_{39})]^{8-}$ with M = Mn, Co, Ni or Cu (initial ratio W:M:Zn = 11:1:1). However, here, crystallized salts appear more slowly than for $[Zn(H_2O)(ZnW_{11}O_{39})]^{8-}$ and $[Co^{II}(H_2O)(Co^{II}W_{11}O_{39})]^{8-}$: several days to months for $CoZnW_{11}$, several years for the others. The variously coloured products are identified as substitution derivatives of the parent polytungstozincate. Thus, the molar ratio W:(Zn + M) always approaches the theoretical values of 3.80:1, but the Zn:M ratio is nearly 1:1 (analytical composition $M_{2.5}Zn_{2.5}W_{19}$). Therefore, they are practically equimolar mixtures of di- and tri- substituted anions (respective composition $M_2Zn_3W_{19}$ and $M_3Zn_2W_{19}$). Likewise, sodium salt solutions of $[Co^{II}(H_2O)(Co^{II}W_{11}O_{39})]^{8-}$ treated by addition of an excess of Zn^{2+} (aq) or passed down a cation-exchange resin in mixed form Na^+–Zn^{2+} crystallize as green needles of composition $Zn_2Co_3W_{19}$, considered to be a disubstituted product of the dimeric tungstocobaltate.

Solubilities and Substituted Derivatives.—The solubility in water of the alkali-metal salts of the parent dimeric polytungstozincate and -cobaltate(II) decreases strongly from Li to Cs. The lithium salts are extremely soluble and evaporated solutions do not crystallize, but become very viscous and finally yield glassy solids. The solubilities at 25 °C of the sodium, potassium and rubidium hydrated salts have been measured for the tungstozincate anion (Na^+, $46H_2O$, 150.1 g dm^{-3}, 24.8 mmol dm^{-3}; K^+, $22H_2O$, 32.22 g dm^{-3}, 5.51 mmol dm^{-3}; Rb^+, $22H_2O$, 5.12 g dm^{-3}, 0.80 mmol dm^{-3}), the homologous tungstocobaltate salts giving comparable values. The alkaline-earth cations precipitate these polyanions as almost insoluble salts (thus, Ca^{2+} in natural water may be determined by turbidity measurements). Addition of a large excess of bivalent transition-metal cations such as Mn^{2+}, Fe^{2+}, . . ., Zn^{2+} to the dimeric polytungstozincate results, successively, in a specific colour change (except for Zn^{2+}) and the formation of a viscous phase which solidifies at the end of addition. The first step is clearly the inclusion of the added cation into the polyanion. Thus, faintly coloured Mn^{2+} (aq) leads to a yellow-brown compound, as observed previously in the preparation of Mn^{II}-substituted polyanions.[12] A quantitative study of such reactions, in the presence of an excess of Li^+ or Na^+ (aq) to prevent subsequent precipitation, shows that the included cation *substitutes partially for* Zn. By studying the reaction of Co^{2+} or Ni^{2+} (aq) by the continuous-variation method (Job's method) and spectrophotometry [equimolar solutions of metal(II) acetate and tungstozincate, 1 mol dm^{-3} $LiNO_3$ or $LiClO_4$ medium, 25 °C, stabilized overnight], the Job plots reveal a maximum for a volume ratio of about 2:3 (experimental 0.65–0.68:1) and consequently the substitution of 2/5 of the total amount of Zn in the anion. In order to make sure that a substitution occurs, the reactions have been studied also by preparative processes involving addition of increasing known amounts of a divalent cation to the sodium salt of the polytungstozincate (or -cobaltate), recovery of the sodium salt ($NaNO_3$ added in excess), recrystallization in the presence of $NaNO_3$, and analysis of the metallic elements. Fig. 1 exemplifies the results obtained by interaction of Co^{2+} (aq) with the polytungstozincate and, inversely, of Zn^{2+} (aq) with the polytungstocobaltate(II). It is clear that an exchange reaction of two divalent elements occurs, but the replacement of the anionic zinc or cobalt is very limited, and requires a large excess of the substituting cation. This involves the precipitation of a sparingly soluble salt which may be redissolved from its aqueous suspension by treatment with a Na^+-saturated cation-exchange resin and recrystallized in the presence of $NaNO_3$. The polytungsto-zincate and -cobaltate(II) behave differently. The former is readily disubstituted at fairly low temperatures (lower than 50 °C) and the trisubstitution of Zn may be achieved by stronger and prolonged heating of the reaction mixtures (even heterogeneous). In contrast, for the latter anion,

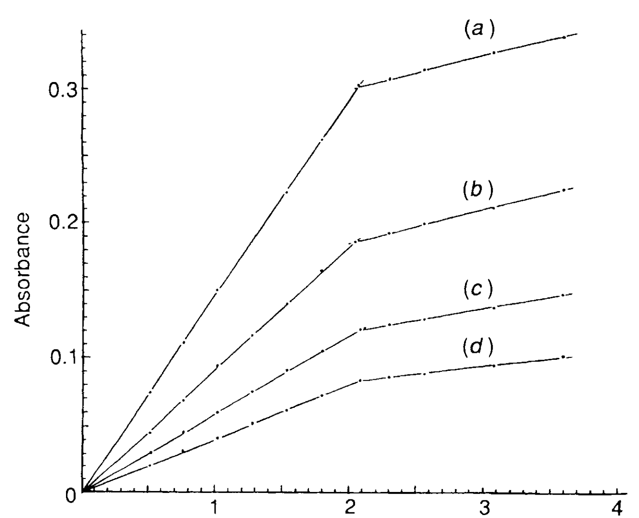

Fig. 2 Titration of $[H_4Zn_5W_{19}O_{70}]^{12-}$ by Fe^{3+} (aq) at 25 °C, pH 5.9 in 0.3 mol dm^{-3} $NaNO_3$, $c = 1.14 \times 10^{-3}$ mol dm^{-3}, monitored by spectrophotometry at (*a*) 440, (*b*) 460, (*c*) 480 and (*d*) 500 nm

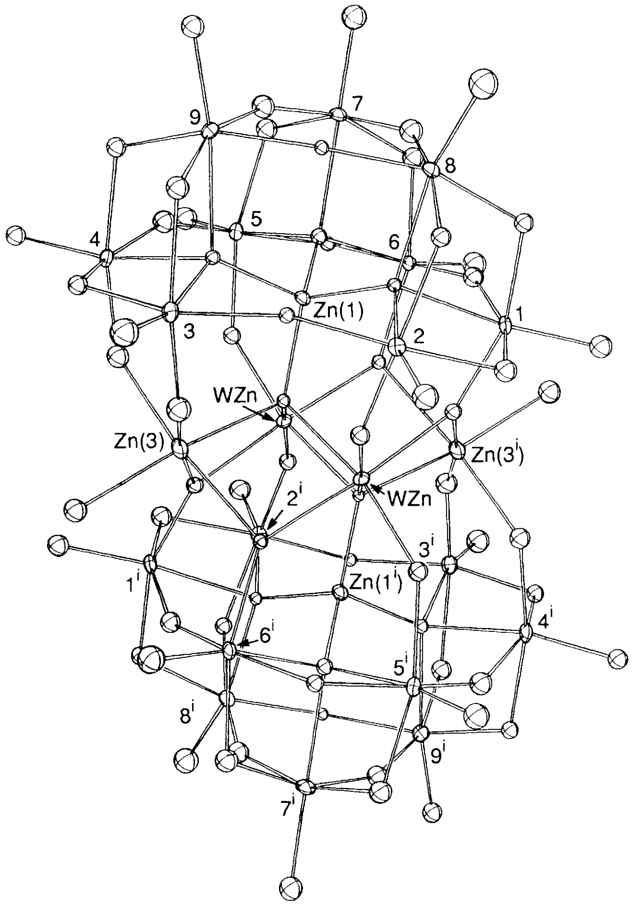

Fig. 3 ORTEP drawing of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ as its sodium salt **1** with 40% ellipsoids. For clarity, metal atoms only are labelled, tungsten atoms numbered; WZn denotes the alternative random occupancy by W or Zn(2). The superscript i refers to inversion-related positions.

two Co atoms only are exchanged under such vigorous conditions.

Other successful disubstitutions have been performed with Pd^{II} (deep brown), Pt^{II} (black), Sn^{II} (brown) on the tungstozincate, while Cd^{II} and Pb^{II} do not lead to conclusive results.

Secondary reactions interfere generally when one tries to insert tri- or tetra-valent elements into the polyanions as described above. Usually, hydrolysis takes place more rapidly than the exchange, making negligible the yield of the expected products (Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Sn^{4+}). Simultaneously, the dimeric polyanion turns into a monomeric Keggin type. Nevertheless, Fe^{3+} (aq) and VO^{2+} (aq) react smoothly and quantitatively, with both parent polyanions, even at room temperature. Fig. 2 shows the clear break point at the substitution of 2/5 of the total Zn. With regard to the hydrolysable cations, we have proof that their derivatives may be obtained indirectly or by very slow evolution of the corresponding Keggin-type polyanions and they will be reported in a later paper. An example of an indirect preparation is given here for the manganese(III) derivative of the polytungstozincate (see the Experimental and the UV–visible electronic spectra sections) which can be obtained by oxidation of manganese(II) species.

Stability.—Aqueous solutions of these novel polyanions are remarkably stable. Variously concentrated solutions of the polytungstozincate have been kept unaltered at room temperature for 20 years. A slight, insoluble, red-wine-coloured deposit begins to appear after about 2 years from non-buffered sodium salt solutions of the cobalt(II) parent. In addition, the visible absorption spectra of the latter anion in buffered dilute solutions (0.20–1.67 mmol dm^{-3}) show a slow, uniform, limited decrease in intensity with time. The more dilute the solution, the lower is the absorption limit. However, when such an aged solution is evaporated to dryness the initial solid may be entirely recovered. Redissolved in water, this gives a spectrum exactly identical in intensity to that of a fresh original solution, suggesting that the phenomenon is some kind of reversible transformation. We are not able to determine it further. We only exclude a simple reverse route to the Keggin-like $[Co(H_2O)(CoW_{11}O_{39})]^{8-}$ because recovery by very rapid evaporation does not yield, even partially, the vitreous sodium salt of the latter.

The pH domain of stability of the parent polyanions extends from about 6.0 to about 10.0 without substantial change (except for the slow transformation) as determined by spectrophotometry and acid–base titration. Outside this range, the complexes transform, especially slowly in basic media. Thus, the elemental analyses of Co and Zn require a high basicity and prolonged heating to arrive at the complete distintegration of the anions. Titration of a 0.4 mmol dm^{-3} solution with a dilute strong acid indicates an equivalence point at about pH 3.5 and 8.5 mol H^+ for 1 mol of polyanion. With the polytungstocobaltate, the solution turns blue-green and after extraction of the Co^{2+} (aq) formed (Na^+ cationic resin) the visible spectrum is that of $[CoW_{12}O_{40}]^{6-}$. Using potassium salts, hexagonal potassium salts of $[CoW_{12}O_{40}]^{6-}$ and $[ZnW_{12}O_{40}]^{6-}$ are recovered on crystallization. Thus, the equivalence point corresponds to the conversion into the Keggin-like species. However, the acidic treatment of more concentrated solutions (5–10 mmol dm^{-3}) is more complex. It gives a lower yield of Keggin species and, in addition, involves the formation of undefined amorphous precipitates and of hydrated WO_3.

Crystal and Molecular Structure of Anions.—The homogeneous family of the novel polyanions give well crystallized series of isomorphous sodium and/or potassium salts respectively. Three salts containing the parent anion $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ **1** and the corresponding WCu_3 **2** and $WZnV_2O_2$ **3** anions were crystallographically studied by X-ray crystallography. The crystallographic data are listed in Table 1, atomic coordinates in Table 2, and selected atomic distances in Table 3 for the anions and Table 4 for the cations. The molecular view of the isotypical anions (Fig. 3) shows that their structure is analogous to that of the tetrametallopolytungstophosphates [or -arsenates(V)] earlier reported and formulated as $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$.[13]

Table 1 Crystallographic data for three dimeric metallopolytungstozincates[a]

Salt	**1**	**2**	**3**
Formula	$Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 46H_2O$	$Zn_{0.25}Na_{11.50}[WCu_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 48H_2O$[b]	$K_{12}[WZnV_2O_2(ZnW_9O_{34})_2]\cdot 30H_2O$[b]
M	6 047.90	6088.97	5920.34
a/Å	13.027(4)	13.108(5)	17.911(7)
b/Å	17.788(5)	17.857(2)	13.298(3)
c/Å	24.124(4)	24.165(8)	21.412(9)
β/°	118.94(2)	119.26(3)	116.94(3)
U/Å^3	4892(2)	4934(4)	4547(5)
D_c/g cm^{-3}	4.105	4.113	4.324
D_m/g cm^{-3}	4.07(2)	4.09(1)	4.35(3)
F(000)	5424	5458	5200
Data collection			
Scan	ω–4θ/3	ω–4θ/3	ω–3θ/2
Range/°	$2 < \theta < 21$	$2 < \theta < 20$	$2 < \theta < 20$
Crystal size/mm	0.21 × 0.16 × 0.34	0.14 × 0.20 × 0.35	0.12 × 0.20 × 0.23
μ/cm^{-1}	250	247	269
Transmission coefficient	0.60–1.00	0.32–1.00	0.36–1.00
Unique data measured	5298	4593	4221
Data used [$F > 3\sigma(F)$]	3783	3637	3125
Parameters	353	366	321
R	0.039	0.052	0.048
R'	0.051	0.042	0.045
Goodness of fit		1.10	1.11
Largest peak in difference map/ e Å^{-3}	1.02	0.51	1.06

[a] Details in common: space group $P2_1/c$; $Z = 2$; Mo-Kα radiation (λ = 0.710 69 Å); Enraf-Nonius CAD 4F diffractometer; full-matrix least-squares refinement on F; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)$, $\sigma(F_o) = \sigma(I)/(2|F_o|L_p)$, goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where L_p = Lorentz polarization, N_o and N_v = number of observations and variables. [b] Exact hydration of the samples specifically prepared for the crystallographic study (see footnote *a*, Table 1).

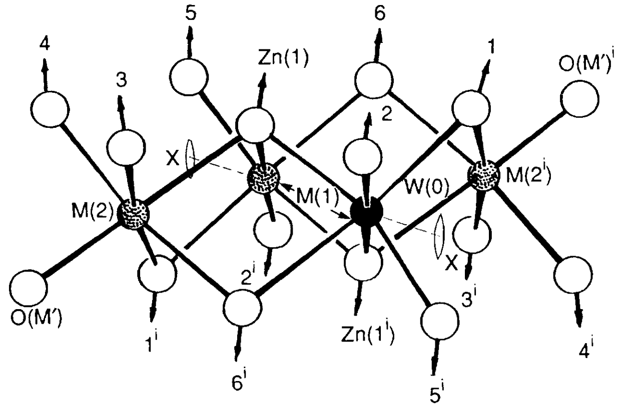

Fig. 4 The bridging atoms of the M(1) (W and Zn, Cu or Zn) and M(2) sites (Zn, Cu or V) in one of enantiomers of compounds **1**–**3** respectively. The two-fold axis (XX) of symmetry relates W(1), (2), (3), ... to W(6^i), W(5^i), W(4^i), ... respectively in the molecular structure.

Like these anions, they contain similar α-B-$[ZnW_9O_{34}]^{12-}$ fragments of the Keggin-type polyanion $[ZnW_{12}O_{40}]^{6-}$ from which a triad of edge-sharing octahedra is removed (except for six oxygens, shared with the three adjacent triads). Two $[ZnW_9O_{34}]^{12-}$ units are also linked through a system of four coplanar metal atoms in such a way that the latter are octahedrally co-ordinated in a close-packed arrangement. These four sites, however, differ in their connectivities (Fig. 4). Two M(1) sites, related by an inversion symmetry, are each surrounded by six oxygens belonging to $[ZnW_9O_{34}]^{12-}$ units. Here, each is found randomly occupied either by a tungsten atom or by another one, Zn in **1** or **3**, Cu in **2**. Accordingly, although crystallographically equivalent, they are not in terms of molecular structure. The two other M(2) sites remain equivalent and contain Zn in **1**, Cu in **2**, or V in **3**. For these atoms, five surrounding oxygens belong to $[ZnW_9O_{34}]^{12-}$ units, the sixth one being a 'free' ligand, the exact nature of which depends on the oxidation state of the metal atom (usually an aqua-ligand for Zn^{II} or Cu^{II}, an oxo-ligand for V^{IV}). These oxygenated ligands can easily be distinguished through their different bond lengths with the metal atoms. Thus, 2.17 and 2.08 Å for Zn–O(Zn) and Cu–O(Cu) respectively indicate an aqua-ligand and 1.62 Å for V–O(V) an oxo-ligand (probably multiply bonded).

The anions exhibit the crystallographic symmetry 1 taking into account the positional disorder in the M(1) sites. As in the homologous polytungstophosphates, they show an almost exact non-crystallographic symmetry $2/m$. However the true molecular structure corresponds to the existence of two enantiomers, which differ in the alternative positions of W and Zn (or Cu) in the M(1) sites, retaining only a two-fold axial symmetry. This agrees with the NMR results (see below). The crystals are always obtained as racemics and no optical activity was ever detected in their aqueous mother solutions. The chiral character of the anions does not involve a significant distortion either in the ZnW_9O_{34} units or in the four M positions. No anomalously high thermal parameters are observed to distinguish the M(1) site occupied by W [labelled W(0) in one enantiomer, instead of WZn or WCu, see NMR section]. Crystallographically, all atomic positions of both enantiomers coincide in racemic crystals and both M(1) octahedra appear geometrically identical. The fairly regular octahedra may be explained by the metal atoms close packed between oxygens of rigid ZnW_9O_{34} fragments. Note that W is found in such an arrangement for the first time. Knowledge of the real situation would require to work on a pure enantiomer, unfortunately still unavailable.

Comparing the homologous interatomic distances in the three anions, only small discrepancies are found, because they contain the same ZnW_9O_{34} fragment. The major ones concern the environment of the four bridging atoms (see below). Comparing with the similar tungsto-phosphate and -arsenate anions, clear differences appear for the XW_9O_{34} units, whose rigid framework practically retains the structure and dimensions of the parent complete cluster $[XW_{12}O_{40}]^{n-}$. Thus, in triads of edge-sharing WO_6 octahedra, the tungsten atoms are clearly

Table 2 Atomic coordinates for compounds **1** and **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 46H_2O$							
W(1)	0.382 59(11)	0.221 38(7)	0.461 45(6)	O(67)	0.469 2(19)	0.219 6(12)	0.666 7(10)
W(2)	0.613 68(11)	0.223 88(8)	0.443 58(6)	O[6,WZn,Zn(3)]	0.401 6(17)	0.045 3(11)	0.560 1(9)
W(3)	0.894 25(11)	0.134 03(8)	0.560 53(6)	O(7)	0.651 8(20)	0.310 5(13)	0.754 6(10)
W(4)	0.910 35(11)	0.056 91(8)	0.685 42(6)	O(78)	0.584 9(19)	0.301 0(13)	0.622 4(10)
W(5)	0.653 41(11)	0.057 82(8)	0.714 26(6)	O(79)	0.781 7(19)	0.240 9(12)	0.703 9(10)
W(6)	0.409 60(11)	0.132 54(7)	0.609 08(6)	O(8)	0.615 8(22)	0.426 6(14)	0.559 2(11)
W(7)	0.633 92(11)	0.240 03(7)	0.698 30(6)	O(89)	0.764 9(17)	0.297 3(11)	0.604 0(9)
W(8)	0.608 31(12)	0.327 29(7)	0.553 21(6)	O(9)	0.981 5(19)	0.318 3(12)	0.718 0(10)
W(9)	0.893 73(11)	0.242 81(7)	0.671 17(6)	O[WZn,Zn(3),Zn(1)]	0.597 6(17)	0.033 3(11)	0.533 4(9)
Zn(1)	0.639 3(3)	0.127 5(2)	0.574 7(2)	O[Zn(3)][a]	0.141 4(19)	0.107 4(13)	0.467 2(10)
WZn[b]	0.486 5(2)	0.039 1(1)	0.437 9(1)	Na(1)	0.326 9(12)	0.248 3(8)	0.286 1(6)
Zn(3)	0.268 4(3)	0.032 9(2)	0.462 3(2)	Na(2)	0.344 3(12)	0.439 9(8)	0.302 9(6)
O(1)	0.237 6(19)	0.247 2(13)	0.412 8(10)	Na(3)	0.242 4(14)	0.381 0(9)	0.679 2(7)
O(12)	0.437 3(19)	0.238 0(13)	0.401 2(10)	Na(4)	0.791 9(13)	0.091 1(8)	0.318 0(7)
O(16)	0.379 9(19)	0.196 9(12)	0.537 3(10)	Na(5)	0.044 0(13)	0.228 8(8)	0.403 4(7)
O(18)	0.440 8(18)	0.320 6(12)	0.497 2(10)	Na(6)	0.621 4(17)	0.449 2(11)	0.434 4(9)
O[128Zn(1)]	0.570 9(17)	0.212 9(11)	0.518 5(9)	AQ(1)[c]	0.434 3(25)	0.164 5(17)	0.254 9(13)
O[1,WZn,Zn(3)]	0.379 8(17)	0.117 0(11)	0.447 7(9)	AQ(2)	0.213 2(24)	0.137 3(16)	0.272 3(12)
O(2)	0.619 6(19)	0.247 6(13)	0.374 4(10)	AQ(3)	0.762 6(23)	0.444 4(16)	0.710 9(12)
O(23)	0.769 8(17)	0.199 7(11)	0.500 7(9)	AQ(4)	0.462 8(21)	0.346 6(14)	0.289 3(11)
O(28)	0.625 8(18)	0.325 9(12)	0.477 4(9)	AQ(5)	0.214 7(26)	0.337 7(17)	0.304 3(13)
O(2,WZn)	0.578 9(18)	0.120 6(12)	0.429 8(9)	AQ(6)	0.202 6(22)	0.248 6(15)	0.672 2(12)
O(3)	0.992 1(20)	0.146 5(13)	0.532 3(10)	AQ(7)	0.229 1(19)	0.054 1(13)	0.695 3(10)
O(34)	0.992 6(18)	0.081 4(12)	0.635 4(9)	AQ(8)	0.624 5(22)	0.066 2(15)	0.333 6(11)
O(39)	0.955 5(19)	0.230 8(12)	0.616 5(10)	AQ(9)	0.980 4(21)	0.131 8(14)	0.327 6(11)
O[349Zn(1)]	0.806 1(17)	0.137 6(11)	0.616 6(9)	AQ(10)	0.961 5(33)	0.323 8(21)	0.344 9(17)
O[3,Zn(3)]	0.815 3(19)	0.051 6(13)	0.520 1(10)	AQ(11)	0.849 3(24)	0.202 8(15)	0.391 5(12)
O(4)	1.025 9(18)	0.013 5(12)	0.760 6(10)	AQ(12)	0.313 8(29)	0.346 8(20)	0.605 0(15)
O(45)	0.802 6(19)	0.067 6(13)	0.719 5(10)	AQ(13)	0.928 6(27)	0.032 4(17)	0.427 4(14)
O(49)	0.974 7(18)	0.161 0(12)	0.726 1(9)	AQ(14)	0.423 9(28)	0.438 4(19)	0.408 3(14)
O[4,Zn(3)]	0.164 1(19)	0.019 4(13)	0.367 0(10)	AQ(15)	0.300 2(30)	0.442 8(20)	0.505 7(15)
O(5)	0.684 5(21)	0.003 3(13)	0.779 2(11)	AQ(16)	0.099 5(29)	0.274 0(19)	0.508 1(15)
O(56)	0.485 8(18)	0.071 8(11)	0.686 0(9)	AQ(17)	0.903 8(43)	0.349 6(29)	0.509 8(22)
O(57)	0.674 7(19)	0.157 1(12)	0.756 3(10)	AQ(18)	0.757 1(31)	0.413 5(20)	0.399 5(16)
O[567Zn(1)]	0.593 4(18)	0.139 5(12)	0.637 8(9)	AQ(19)	0.489 1(30)	0.479 1(19)	0.673 4(15)
O(5,WZn)	0.390 1(18)	0.018 2(12)	0.350 7(9)	AQ(20)	0.075 0(34)	0.460 7(22)	0.381 3(17)
O(6)	0.269 8(21)	0.134 9(14)	0.603 3(11)				
(*b*) $K_{12}[WZnV_2O_2(ZnW_9O_{34})_2]\cdot 30H_2O$							
W(1)	0.320 23(8)	0.518 19(10)	0.570 79(7)	O(57)	0.241 8(13)	0.804 5(16)	0.315 2(11)
W(2)	0.266 30(9)	0.315 35(10)	0.476 75(7)	O[567Zn(1)]	0.304 8(12)	0.668 6(13)	0.400 4(10)
W(3)	0.258 25(9)	0.311 75(10)	0.300 84(8)	O(5,WZn)	0.548 2(12)	0.327 1(15)	0.613 3(11)
W(4)	0.297 55(8)	0.514 44(10)	0.237 23(7)	O(6)	0.398 4(12)	0.841 8(14)	0.562 0(11)
W(5)	0.354 39(9)	0.752 07(10)	0.341 04(7)	O(67)	0.251 5(14)	0.805 6(17)	0.444 0(12)
W(6)	0.365 09(8)	0.754 05(10)	0.496 39(7)	O(6,WZn,V)	0.464 9(13)	0.673 6(15)	0.524 0(11)
W(7)	0.183 04(8)	0.737 05(10)	0.358 15(7)	O(7)	0.098 2(13)	0.814 5(16)	0.328 1(11)
W(8)	0.137 24(8)	0.506 52(11)	0.431 87(7)	O(78)	0.154 3(14)	0.644 8(16)	0.413 3(12)
W(9)	0.124 21(8)	0.499 37(11)	0.253 08(7)	O(79)	0.149 1(14)	0.639 5(17)	0.288 8(12)
Zn(1)	0.321 0(2)	0.524 2(2)	0.406 4(2)	O(8)	0.036 5(13)	0.508 5(16)	0.423 9(11)
WZn[b]	0.479 8(1)	0.401 0(1)	0.531 0(1)	O(89)	0.112 7(13)	0.478 5(15)	0.338 7(11)
V	0.528 1(3)	0.606 6(3)	0.621 6(2)	O(9)	0.023 9(13)	0.511 7(16)	0.196 4(11)
O(1)	0.341 2(12)	0.543 9(14)	0.654 1(10)	O[WZn,V,Zn(1)]	0.437 7(11)	0.482 8(14)	0.443 5(10)
O(12)	0.301 2(14)	0.375 9(17)	0.569 7(12)	O(V)	0.486 5(12)	0.670 8(14)	0.662 3(10)
O(16)	0.327 4(13)	0.655 2(15)	0.536 5(11)	K(1)	0.257 6(7)	0.505 6(9)	0.742 1(6)
O(18)	0.198 1(12)	0.537 9(14)	0.528 9(10)	K(2)	0.349 9(5)	0.761 2(6)	0.664 4(4)
O[128Zn(1)]	0.270 3(12)	0.475 2(14)	0.460 7(11)	K(3)	0.264 8(9)	0.508 6(11)	0.021 7(8)
O(1,WZn,V)	0.432 1(12)	0.492 5(15)	0.579 3(11)	K(4)	0.508 9(7)	0.547 9(8)	0.788 2(16)
O(2)	0.250 9(18)	0.184 4(22)	0.501 6(16)	AQ(1)[c]	0.043 4(22)	0.252 5(27)	0.312 7(19)
O(23)	0.237 5(12)	0.298 3(14)	0.379 6(10)	AQ(2)	0.047 2(27)	0.186 7(33)	0.174 2(23)
O(28)	0.154 3(13)	0.364 1(16)	0.456 3(12)	AQ(3)	0.071 1(26)	0.546 6(31)	0.052 8(22)
O(2,WZn)	0.385 4(15)	0.312 1(18)	0.498 9(13)	AQ(4)	0.131 6(27)	0.432 2(33)	0.605 0(23)
O(3)	0.233 8(15)	0.191 8(18)	0.269 4(13)	AQ(5)	0.149 5(29)	0.303 8(34)	0.088 5(24)
O(34)	0.268 6(15)	0.369 7(17)	0.219 6(12)	AQ(6)	0.180 7(24)	0.731 8(29)	0.047 3(20)
O(39)	0.141 4(14)	0.358 0(17)	0.247 9(12)	AQ(7)	0.170 6(36)	0.789 6(44)	0.155 3(31)
O[349Zn(1)]	0.256 8(12)	0.471 4(14)	0.314 5(10)	AQ(8)	0.143 8(24)	0.093 3(29)	0.363 0(20)
O(3,V)	0.373 1(12)	0.312 2(15)	0.357 1(11)	AQ(9)	0.378 5(18)	0.279 4(21)	0.175 2(15)
O(4)	0.305 7(12)	0.535 1(14)	0.160 1(10)	AQ(10)	0.429 6(29)	0.416 1(36)	0.065 4(25)
O(45)	0.310 7(12)	0.652 1(15)	0.270 6(11)	AQ(11)	0.493 5(16)	0.640 1(18)	0.264 1(13)
O(49)	0.175 2(12)	0.533 1(14)	0.195 9(10)	AQ(12)	0.290 8(21)	0.018 2(24)	0.392 8(18)
O(4,V)	0.595 7(11)	0.519 2(14)	0.697 9(10)	AQ(13)	0.422 8(21)	0.099 0(25)	0.337 5(18)
O(5)	0.382 2(13)	0.839 7(15)	0.294 5(11)	AQ(14)	0.052 2(20)	0.179 1(23)	0.443 6(17)
O(56)	0.392 6(12)	0.823 9(14)	0.429 8(10)	AQ(15)	0.089 7(18)	−0.029 7(22)	0.231 7(16)

[a] Oxygen of an aqua-ligand. [b] Scattering factor $(f\mathrm{w} + f\mathrm{z}_\mathrm{n})/2$. [c] Water molecules of crystallization, AQ.

Table 3 Selected bond lengths and interatomic distances (Å) in anions **1**–**3**

	1	**2**	**3**		**1**	**2**	**3**
(*a*) W–O, σ = 0.02 Å							
W(1)–O(1)	1.73	1.66	1.68	W(5)–O(57)	1.99	1.98	1.96
W(1)–O(12)	1.93	1.96	1.92	W(5)–O[567Zn(1)]	2.17	2.14	2.17
W(1)–O(16)	1.89	1.98	1.99	W(5)–O(5,WM^{I})	1.94	1.89	1.89
W(1)–O(18)	1.95	1.99	1.97	W(6)–O(6)	1.76	1.67	1.71
W(1)–O[128Zn(1)]	2.16	2.19	2.19	W(6)–O(16)	1.95	1.87	1.86
W(1)–O(1,WM,M′)	1.88	1.90	1.96	W(6)–O(56)	1.95	1.95	1.95
W(2)–O(2)	1.76	1.77	1.76	W(6)–O(67)	1.97	1.98	1.95
W(2)–O(12)	2.03	1.98	1.97	W(6)–O[567Zn(1)]	2.15	2.14	2.16
W(2)–O(23)	1.87	1.87	1.92	W(6)–O(6,WM,M′)	1.92	1.87	1.93
W(2)–O(28)	1.96	1.95	1.96	W(7)–O(7)	1.78	1.71	1.70
W(2)–O[128Zn(1)]	2.14	2.14	2.16	W(7)–O(57)	1.92	1.99	1.91
W(2)–O(2,WM)	1.88	1.93	1.96	W(7)–O(67)	1.93	1.95	1.92
W(3)–O(3)	1.72	1.72	1.71	W(7)–O(78)	1.95	1.94	1.93
W(3)–O(23)	1.95	1.95	1.89	W(7)–O(79)	1.86	1.80	1.86
W(3)–O(34)	1.88	1.93	1.99	W(7)–O[567Zn(1)]	2.21	2.20	2.15
W(3)–O(39)	2.09	2.10	1.97	W(8)–O(8)	1.77	1.74	1.73
W(3)–O[349Zn(1)]	2.16	2.13	2.15	W(8)–O(18)	1.93	1.92	1.90
W(3)–O(3,M′)	1.79	1.78	1.86	W(8)–O(28)	1.95	1.99	1.95
W(4)–O(4)	1.74	1.70	1.74	W(8)–O(78)	1.89	1.92	1.93
W(4)–O(34)	2.01	1.97	1.98	W(8)–O(89)	1.88	1.83	1.88
W(4)–O(45)	1.95	1.93	1.94	W(8)–O[128Zn(1)]	2.16	2.17	2.21
W(4)–O(49)	2.07	2.11	1.97	W(9)–O(9)	1.77	1.74	1.66
W(4)–O[349Zn(1)]	2.11	2.16	2.17	W(9)–O(39)	1.86	1.86	1.92
W(4)–O(4,M′^{I})	1.79	1.75	1.84	W(9)–O(49)	1.91	1.86	1.88
W(5)–O(5)	1.71	1.72	1.75	W(9)–O(79)	1.97	2.03	1.99
W(5)–O(45)	1.89	1.87	1.89	W(9)–O(89)	1.94	2.01	1.95
W(5)–O(56)	1.96	1.95	1.95	W(9)–O[349Zn(1)]	2.26	2.27	2.16
(*b*) WM–O, σ = 0.02 Å							
WM–O(2,WM)	1.95	1.90	1.92	WM–O[WM,M′,Zn(1)^{I}]	2.02	2.03	2.03
WM–O(1,WM,M′)	2.06	2.09	2.02	WM–O(5,WM)	1.89	1.91	1.90
WM–O[WM,M′,Zn(1)]	2.05	2.05	2.00	WM–O(6,WM,M′^{I})	2.08	2.17	2.10
(*c*) M′–O, σ = 0.02 Å							
M′–O(6,WM,M′)[a]	2.16	2.07	2.07	M′–O(3,M′^{I})[b]	2.02	2.10	1.94
M′–O(1,WM,M′)[b]	2.23	2.22	2.16	M′–O[WM,M′,Zn(1)^{I}][c]	2.07	2.00	2.12
M′–O(4,M′)[a]	2.04	2.07	1.92	M′O(M′)[c,d]	2.17	2.08	1.62
(*d*) Zn(1)–O, σ = 0.02 Å							
Zn(1)–O[128Zn(1)]	1.94	1.94	1.89	Zn(1)–O[567Zn(1)]	1.90	1.95	1.94
Zn(1)–O[349Zn(1)]	1.91	1.90	1.91	Zn(1)–O[WM,M′,Zn(1)]	1.89	1.93	1.95
(*e*) W ··· W(WM), σ = 0.002 Å							
W(1) ··· W(2)	3.241	3.246	3.241	W(3) ··· W(9)	3.299	3.315	3.288
W(1) ··· W(6)	3.754	3.761	3.766	W(4) ··· W(5)	3.734	3.721	3.730
W(1) ··· W(8)	3.286	3.291	3.285	W(4) ··· W(9)	3.321	3.333	3.279
W(1) ··· WM	3.662	3.701	3.677	W(5) ··· W(6)	3.240	3.251	3.244
W(2) ··· W(3)	3.728	3.731	3.704	W(5) ··· W(7)	3.259	3.275	3.258
W(2) ··· W(8)	3.250	3.265	3.274	W(5) ··· WM^{I}	3.647	3.639	3.621
W(2) ··· WM	3.653	3.636	3.639	W(6) ··· WM^{I}	3.732	3.769	3.714
W(3) ··· W(4)	3.223	3.229	3.238				
(*f*) WM ··· WM^{I}, σ = 0.004 Å							
WM ··· WM^{I}	3.163	3.160	3.175				
(*g*) Zn(1) ··· W(WM)(M′), σ = 0.004 Å							
Zn(1) ··· W(1)	3.549	3.571	3.527	Zn(1) ··· W(7)	3.619	3.649	3.588
Zn(1) ··· W(2)	3.469	3.463	3.503	Zn(1) ··· W(8)	3.585	3.613	3.579
Zn(1) ··· W(3)	3.501	3.488	3.472	Zn(1) ··· W(9)	3.625	3.647	3.583
Zn(1) ··· W(4)	3.472	3.480	3.455	Zn(1) ··· WM	3.312	3.300	3.319
Zn(1) ··· W(5)	3.508	3.488	3.502	Zn(1) ··· WM^{I}	3.329	3.326	3.346
Zn(1) ··· W(6)	3.471	3.506	3.508	Zn(1) ··· M′	3.380	3.338	3.486
(*h*) M′ ··· W(WM), σ = 0.005 Å							
M′ ··· W(1)	3.672	3.676	3.572	M′ ··· W(6)	3.573	3.597	3.532
M′ ··· W(3^{I})	3.533	3.544	3.582	M′ ··· WM	3.169	3.173	3.207
M′ ··· W(4^{I})	3.555	3.557	3.596	M′ ··· WM^{I}	3.193	3.211	3.235

[a–c] A same letter designates *trans* bonds. [d] O(M′) is an aqua-ligand in compounds **1** and **2**, an oxo-ligand in **3**. Symmetry code: I $1 - x, -y, 1 - z$.

nearer each other in the zincate anions (3.26 Å) and presumably in tungstocobaltates[8c] than in phosphate anions[13b] (mean 3.45 Å, to be compared to 3.406 and 3.413 Å in $[PW_{12}O_{40}]^{3-}$).[14] In contrast, the long distances between adjacent tungsten atoms belonging to different triads do not vary significantly within all the series (3.70–3.73 Å). To date, no structural data have been

Table 4 Selected interatomic distances (Å) between the cations and near oxygens for anions **1**–**3**

Na–O, mean σ = 0.03 Å

	1	**2**		**1**	**2**
Na(1)–O(12)	2.44	2.46	Na(4)–O(7$^{\rm II}$)	2.46	2.45
Na(1)–AQ(1)	2.40	2.40	Na(4)–AQ(3$^{\rm III}$)	2.50	2.51
Na(1)–AQ(2)	2.39	2.39	Na(4)–AQ(7$^{\rm IV}$)	2.60	2.57
Na(1)–AQ(4)	2.46	2.43	Na(4)–AQ(8)	2.42	2.30
Na(1)–AQ(5)	2.34	2.37	Na(4)–AQ(9)	2.46	2.45
Na(1)–AQ(6$^{\rm III}$)	2.42	2.45	Na(4)–AQ(11)	2.52	2.70
Na(2)–AQ(3$^{\rm IV}$)	2.42	2.36	Na(4)–AQ(13)	2.58	2.72
Na(2)–AQ(4)	2.39	2.40	Na(5)–O(1)	2.44	2.50
Na(2)–AQ(5)	2.49	2.46	Na(5)–O(M′)	2.60	2.63
Na(2)–AQ(7$^{\rm III}$)	2.29	2.34	Na(5)–AQ(9$^{\rm IX}$)	2.35	2.31
Na(2)–AQ(14)	2.23	2.27	Na(5)–AQ(10$^{\rm IX}$)	2.13	2.17
Na(2)–AQ(19$^{\rm V}$)	2.43	2.46	Na(5)–AQ(11$^{\rm IX}$)	2.45	2.47
Na(3)–AQ(1$^{\rm V}$)	2.41	2.45	Na(5)–AQ(16)	2.41	2.32
Na(3)–AQ(2$^{\rm VI}$)	2.47	2.60	Na(6)–O(28)	2.41	2.52
Na(3)–AQ(6)	2.40	2.42	Na(6)–AQ(14)	2.36	2.26
Na(3)–AQ(12)	2.46	2.53	Na(6)–AQ(15$^{\rm V}$)	2.32	2.44
Na(3)–O(5$^{\rm VII}$)	2.39	2.37	Na(6)–AQ(18)	2.38	2.43
Na(3)–AQ(22)	—	2.39	Na(6)–AQ(19$^{\rm V}$)	2.62	3.13

K–O	**3**	K–O	**3**
K(1)–O(1)	2.93(2)	K(2)–AQ(11$^{\rm II}$)	2.81(3)
K(1)–O(3$^{\rm I}$)	2.76(3)	K(3)–O(2$^{\rm VII}$)	2.73(3)
K(1)–O(5$^{\rm II}$)	2.86(2)	K(3)–O(4)	2.73(2)
K(1)–O(57$^{\rm II}$)	3.05(2)	K(3)–O(6$^{\rm II}$)	2.92(2)
K(1)–AQ(4)	2.94(4)	K(3)–O(67$^{\rm II}$)	2.93(3)
K(1)–AQ(12$^{\rm I}$)	3.02(3)	K(3)–AQ(10)	2.93(5)
K(1)–AQ(13$^{\rm I}$)	3.06(3)	K(3)–AQ(12$^{\rm VIII}$)	3.02(4)
K(1)–AQ(15$^{\rm I}$)	2.93(3)	K(4)–O(1)	3.07(2)
K(2)–O(1)	2.90(2)	K(4)–O(5$^{\rm II}$)	2.77(2)
K(2)–O(4$^{\rm II}$)	2.81(2)	K(4)–O(4,V)	3.00(2)
K(2)–O(5$^{\rm II}$)	2.90(2)	K(4)–O(V)	3.02(2)
K(2)–O(6)	2.90(2)	K(4)–AQ(9$^{\rm V}$)	2.92(3)
K(2)–O(16)	2.94(2)	K(4)–AQ(10$^{\rm V}$)	2.85(5)
K(2)–O(45$^{\rm II}$)	2.90(2)	K(4)–AQ(11$^{\rm V}$)	2.73(3)
K(2)–O(V)	2.74(2)	K(4)–AQ(13$^{\rm I}$)	2.96(3)
K(2)–AQ(6$^{\rm II}$)	2.93(4)		

Symmetry codes: I $-x, 1-y, z$; II $x, \frac{3}{2}-y, \frac{1}{2}+z$; III $x, \frac{1}{2}-y, \frac{1}{2}+z$; IV $1-x, -y, 1-z$; V $1-x, 1-y, 1-z$; VI $x, \frac{1}{2}-y, \frac{3}{2}+z$; VII, $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; VIII $x, \frac{1}{2}-y, -\frac{1}{2}+z$; IX $-1+x, y, z$.

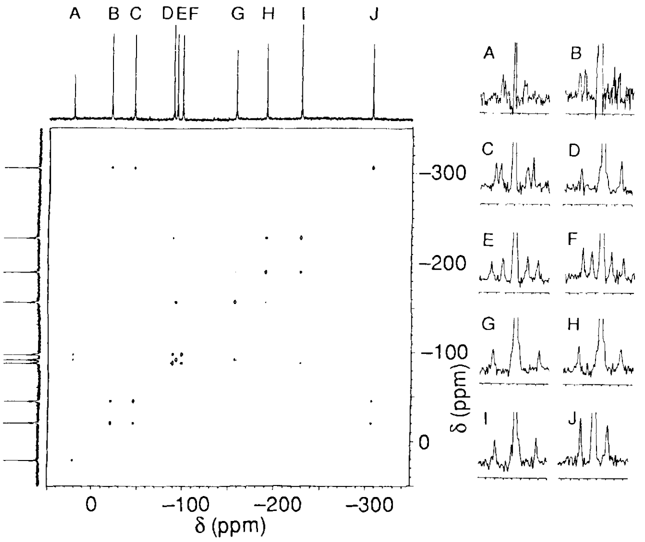

Fig. 5 Tungsten-183 NMR spectrum and two-dimensional COSY plot of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ as its lithium salt. Insets show the coupling signals (expanded scale, 1 division = 5 Hz). Note the enlargements due to non-resolved weak couplings.

reported on $[ZnW_{12}O_{40}]^{6-}$ and those presented here are the first ones on polytungstozincates. Regarding the interatomic distances between the M(1) atoms, they are noticeably reduced in zincate anions (about 3.16 against 3.31 and 3.46 Å in phosphate and arsenate respectively). This is not due to the presence of one W, since a shorter distance has been found (Fe · · · Fe 3.10 Å) between equivalent sites in $[H_6Fe^{III}_4Cu_2W_{18}O_{70}]^{10-}$ reported by Wasfi *et al.*[15] and evidently isomorphous with our compounds in the sodium salt form (converted into space group $P2_1/c$, $a = 13.079$, $b = 17.772$, $c = 24.148$ Å, $\beta = 119.27°$). Its formula rewritten to be similar to that of our series would be $[Fe_2Cu_2(H_2O)_2(FeW_9O_{34})_2]^{12-}$ (the analysis given by the authors is more consistent with the presence of 12 Na^+: calc. 4.95 instead of 4.15% Na; found 4.95%).

We are interested in a comparison of this iron(III) anion with our Cu-containing tungstozincate **2**, because a Jahn–Teller distortion might be expected for the copper octahedra of the M(2) sites. It is surprising that no *trans* metal-to-ligand bond elongation appears clearly (the Cu–OH_2 bond is usually longer than Cu–O) neither in the cuprotungstoferrate nor in the cuprotungstozincate. Moreover, the corresponding M(2)–Zn octahedra in **1** undergo practically the same distortions as M(2)–Cu in **2**. The greatest M(2)–O bond lengths occur rather when the oxygen is linked to three metal atoms. So, the asymmetry of the M(2) octahedra is mostly due to the bonding mode and stacking of the bridging atoms between the XW_9O_{34} units and secondarily to a specific influence of the metal atoms. Therefore, the distribution of Fe and Cu in M(1) and M(2) sites respectively, as given by Wasfi, does not seem anomalous, in spite of unexpected elongated *trans* bond lengths (2.27, 2.29 Å) in M(2)–Fe octahedra. By contrast, Jahn–Teller distortions appear strikingly in $[Cu_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$.[16]

The Na^+ cations of compounds **1** and **2** are surrounded by five to seven neighbouring oxygens (usually six) belonging chiefly to water molecules (Table 4). They associate by means of two or three bridging water oxygens as described by Wasfi *et al.*[15] for cuprotungstoferrate [Fig. 4 in ref. 15, in which successive Na-(5), -(3), -(1), -(4), -(2) correspond to Na-(5), -(4), -(2), -(1), -(3) in our salts]. In addition, we found a sixth Na linked to Na(2) through two water molecules at the middle of the cationic chain. No such arrangement exists in **3**, wherein the cations K^+ are connected chiefly to anionic oxygens. In the three salts, numerous hydrogen bonds between water molecules and anionic oxygen or aqua-ligands are deduced from significantly short O · · · O distances.

^{183}W *NMR Spectra.*—The NMR spectrum of the lithium salt of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ contains ten lines extended over an exceptionally wide frequency range (Table 5, Fig. 5). The first signal A is shifted downfield from the reference (+21.1 ppm). This has never before been observed for Keggin-type polyanions nor their derivatives, but only for $[W_7O_{24}]^{6-}$ (ref. 17) and $[W_6O_{19}]^{2-}$ (ref. 18) or their derivatives.[19] Its intensity, half that of the others, leads logically to assignment to the single bridging W located in a M(1) site [here, it will be labelled W(0), instead of WZn which denotes '$W_{0.5}Zn_{0.5}$']. The nine other signals, of the same intensity, shifted upfield, refer to nine pairs of both ZnW_9O_{34} fragments (each line for a pair related by the molecular two-fold axis symmetry as discussed in the crystallographic study). Like the crystals, the solutions are racemic and the spectra of enantiomers are identical. Consequently, the assignment of lines to tungsten atoms localized according to the crystal structure cannot be unique. It is discussed below assuming the single bridging W(0) to be a neighbour of W(1) and W(2). The corresponding tungsten framework is represented in Fig. 6. The off-diagonal signals in the two-dimensional correlation spectroscopy (COSY) plot (Fig. 5) and quite different ^2J(W–O–W) strongest couplings, representative of corner-sharing octahedra[20] (Fig. 5, insets) allow us to assign the line set D–I to the six tungstens W(1)–W(6) forming a 'belt'.

Table 5 ^{183}W NMR chemical shifts and coupling constants for the enantiomers of $[WZnM^{II}_2(H_2O)_m(ZnW_9O_{34})_2]^{12-}$ (m = 2 for M = Zn, undetermined but presumed to be 0 for Pd and Pt)

	Assignment		δ (±0.1 ppm)			
Line	Enantiomer **I**	Enantiomer **II**	M = Zn	Pd	Pt	^2J[W(i)–O–W(j)] ±0.2 Hz for enantiomer **I** (M = Zn)
A	W(0)*	W(0)*	20.9	21.3	21.6	W(1), 11.2; W(2), 13.8
B	W(7)W(9)	W(8)W(9)	−19.8	−22.7	−28.8	W(9), W(7), W(8), 15.4; W(3), W(4), W(5), W(6), <2.5
C			−45.0	−45.9	−44.2	
D	W(6)	W(1)	−87.8	−89.6	−89.2	W(1), 23.1; W(5), 4.0; W(7) <2.5
E	W(2)	W(5)	−92.3	−93.3	−92.1	W(0), 13.8; W(3), 26.5; W(1), W(8), <2.5
F	W(1)	W(6)	−97.5	−98.5	−95.2	W(0), 11.1; W(6), 23.1; W(2), W(8), <2.5
G	W(3)	W(4)	−156.8	−156.6	−150.9	W(2), 26.5; W(4), 4.1; W(9), <2.5
H	W(4)	W(3)	−190.2	−190.7	−188.3	W(5), 23.8; W(3), 4.1; W(9), <2.5
I	W(5)	W(2)	−228.7	−228.2	−224.4	W(4), 23.8; W(6), 4.0; W(7), <2.5
J	W(8)	W(7)	−306.8	−305.2	−297.2	W(7), W(9), 15.4; W(1), W(2) <2.5

* Molecular labelling, WZn in-crystal labelling.

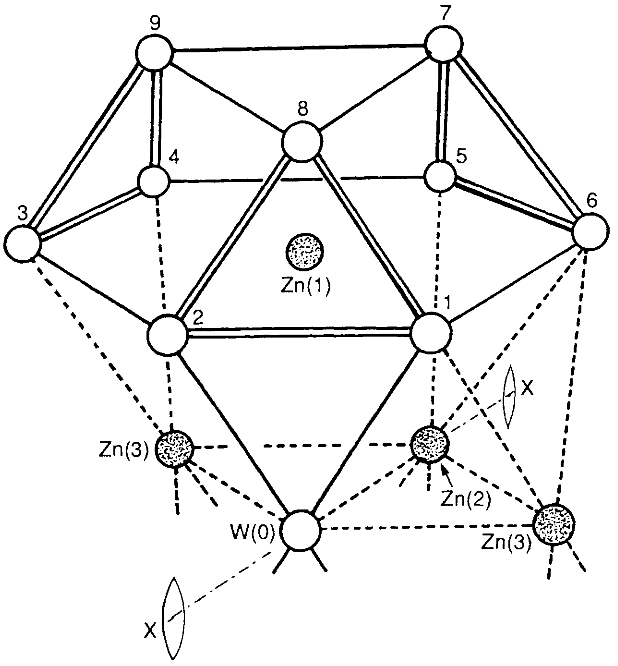

Fig. 6 Partial framework of metal atoms in one of enantiomers of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$. Full lines connect neighbouring W atoms: single ones for corner-sharing WO_6 octahedra, double for edge-sharing WO_6. Broken lines indicate other connections.

Thus, starting from W(0) (signal A), corner-coupled to the pair W(1) and W(2), E and F are attributed to these atoms, but equivocally. One can distinguish between the two possible attributions using the fact that the ^2J coupling constants are very sensitive to the bond angles. Comparing the angles W(1)–O[1,WZn,Zn(3)]–WZn and W(2)–O(2,WZn)–WZn in the crystal [wherein WZn corresponds to W(0) in the enantiomer chosen], we found 136.8 ± 1 and 144.5 ± 1.2° respectively. Assuming that such substantial differences for the anions also exist in solution, F corresponds to W(1) (^2J = 11.1 ± 0.2 Hz) and E to W(2) (^2J = 13.8 ± 0.2 Hz). Note that this interpretation would be similar putting W(0) in the symmetrical M(1) crystal site near W(5) and W(6) (the second enantiomer), since the homologous angles W(6)–O[6,WZn,Zn(3)]–WZn and W(5)–O(5,WZn)–WZn are found to be 137.8 ± 1.1 and 144.4 ± 1.2° respectively. Also, this bond-angle difference is not fortuitous, as it is found for both copper and vanadium derivatives (means 137 and 145° for Cu, 134.5 and 142° for V) and for the equivalent atomic positions in the cuprotungstoferrate [133 and 145°, Table 3, (j), in ref. 15]. The coupling constants ^2J are clearly stronger (21–26.5 Hz) between the tungstens of the other corner-sharing octahedra (mean bond angle 153.5°). After that, the signals and tungstens of the 'belt' are easily correlated (Table 5). Note that only two weak couplings may be detected and measured between edge-sharing tungsten octahedra of the 'belt', but none with the trio W(7), W(8) and W(9). The correlation of the latter with signals B, C and J is thus problematic. The following approach may however be attempted, based on the great difference in chemical shifts. As described earlier for the similar tungstophosphates, two $WZn_2(ZnW_9O_{34})$ groups sharing W and Zn of M(1) sites may be considered in the tungstozincate. Each one, taken separately, derives from a β-$[XW_{12}O_{40}]^{n-}$ structural type, a rotational isomer of the Keggin type. Its WZn framework has nearly a local reflection symmetry whose mirror plane would pass through W(0),W(8) and the middle of the segment Zn(2)–Zn(3) (molecular labelling, see Fig. 6). The distances between the metal atoms and the almost equal magnitudes of the weak couplings W(3)–W(4) and W(5)–W(6) support this view. Accordingly, line J is attributed to W(8) located at the same side as W(0), and the neighbouring peaks B and C to the almost equivalent W(7) and W(9) (not ascribed individually).

Confirmation of this interpretation (and eventually more complete information) was looked for in the ^{183}W NMR spectra of the diamagnetic palladium(II) and platinum(II) disubstituted derivatives. These are very similar to that of the parent anion, with minor changes only in the chemical shifts (the major deviations concern the lines B and J shifted by about 9 ppm for the Pt-substituted complex) (Table 5). The weak couplings remain also undetected as do the expected couplings ^2J(W–O–Pt) (the ^{195}Pt NMR signal is considerably broadened and difficult to observe). Regarding the weak undetected couplings, for all the anions, the corresponding signals are certainly hidden in the base of the lines and the constants are estimated to be smaller than 2.5 Hz. It is the first time that such small values have been found in Keggin-type edge-sharing trioctahedra subgroups (usual range 5–10 Hz).[10] Indeed, this appears to be related to the shrinkage of W ··· W distances and the decrease in the W–O–W angles (mean 3.26 Å and 110–115° respectively) compared to those of $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$, for example (3.43 Å, mean 123°, ^2J = 5.8–9.0 Hz).[13b]

UV–Visible Electronic Spectra.—As usual for Keggin-type polyanions, the present dimers show an intense, broad absorption band attributed to oxygen-to-tungsten charge transfer in both XW_9O_{34} units. The molar absorption coefficients exceeds 10^5 dm^3 mol^{-1} cm^{-1} in the 43 500–46 500 cm^{-1} region. From about 30 000 cm^{-1} into the 'blue' region, it interferes with a less intense band (ε = 100–3000 dm^3 mol^{-1} cm^{-1}), best revealed by logarithmic scale plotting as a shoulder extending very often into the visible spectrum. Such a band has been previously observed for $[M(H_2O)(XW_{11}O_{39})]^{q-}$ anions

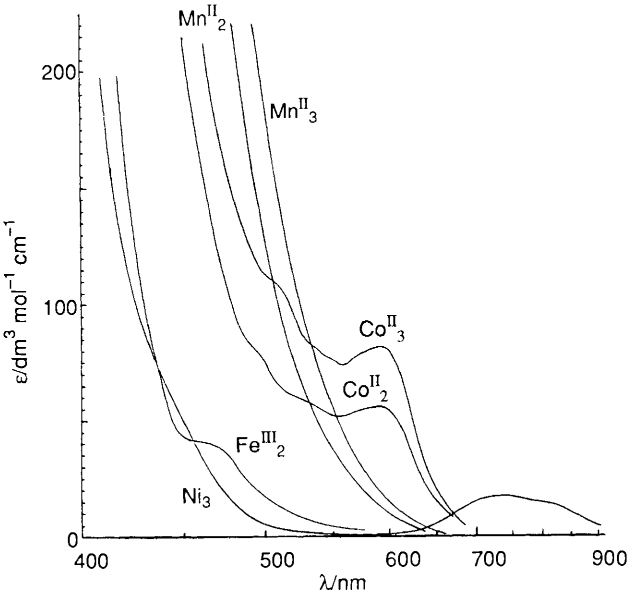

Fig. 7 Visible absorption spectra of some M_2- and M_3-substituted derivatives of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ supporting the existence of trisubstituted anions

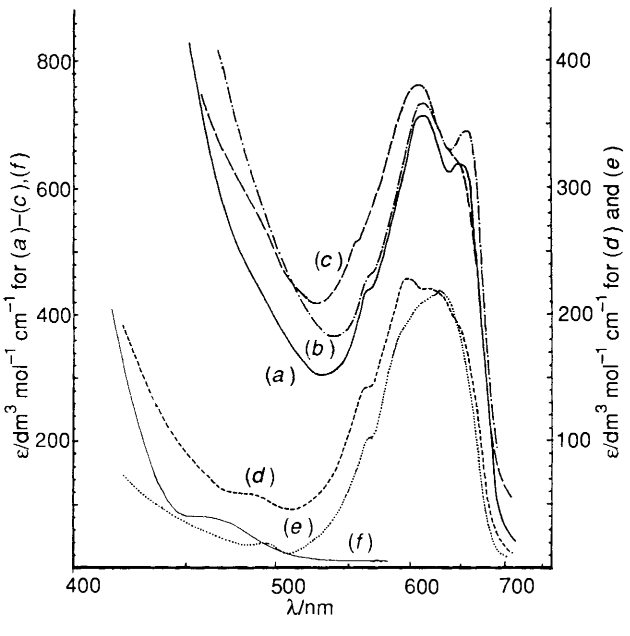

Fig. 8 Visible absorption spectra of $[WCo^{II}_3(H_2O)_2(Co^{II}W_9O_{34})_2]^{12-}$ (*a*) and its Mn^{II}_2- (*b*) and Fe^{III}_2 (*c*)-substituted derivatives compared with those of $[Co^{II}(H_2O)(Co^{II}W_{11}O_{39})]^{8-}$ (*d*) and $[Co^{II}W_{12}O_{40}]^{6-}$ (*e*). The spectrum of the Fe^{III}_2-substituted derivative of polytungstozincate is reported, (*f*) to show the identical inflection like that in (*c*), due to Fe^{III}. Note that the left scale corresponds to ε for one tetrahedral cobalt(II) chromophore.

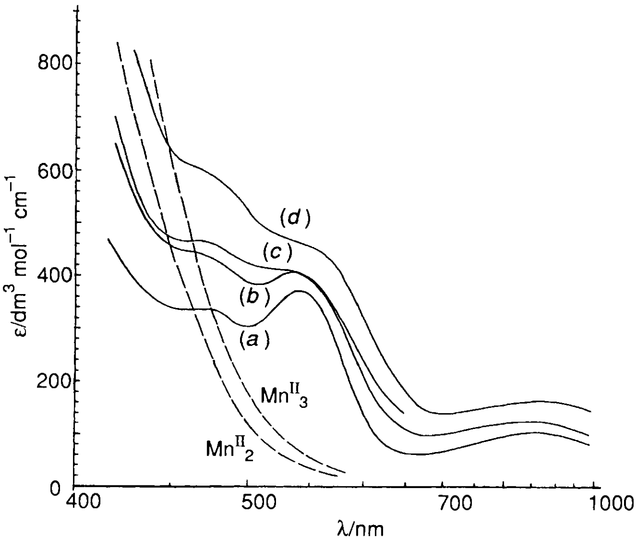

Fig. 9 Visible absorption spectra of various Mn^{II}- and Mn^{III}-substituted compounds derived from the dimeric polytungstozincate. Analytical composition of bridging atoms: (*a*) $Zn_{3.57}Mn^{II}_{0.30}Mn^{III}_{1.13}$, (*b*) $Zn_{3.02}Mn^{III}_{1.98}$, (*c*) $Zn_{2.64}Mn^{III}_{2.36}$ and (*d*) $Zn_{2.00}Mn^{III}_{3.01}$.

(M = Co^{II}, Mn^{II} or Cu^{II}) and attributed to oxygen-to-metal charge transfer (interpretation as d–d transitions was indeed impossible).[12] Here, we found it more clearly, with greater intensity and width, depending on the M atoms, related apparently to oxidation power. Thus, not seen for the parent tungstozincate, it appears weakly in Ni- or Cu-substituted anions, but remarkably strong and broad for derivatives of Co^{II} and Mn^{II}. The yellowish shade of the present polyanions certainly results from the large extension of this band in the visible region. At 400 nm, *e.g.*, ε reaches 1670 and 1200 for the Mn^{II}_3 and Mn^{II}_2 anions, 1400 and 840 for Co^{II}_3 and Co^{II}_2, 540 for Fe^{II}_2 and 100 dm³ mol⁻¹ cm⁻¹ for Cu_2. Note that the charge-transfer absorption of manganese(II) anions exceeds that of the corresponding manganese(III) species (Fig. 9).

The usual electronic d–d visible absorption bands typical of M atoms in an octahedral ligand field are observable for the metallotungstozincates. The exceptional magnitude of the molar absorption coefficient results from the number of substituted M atoms (two or three) and also, sometimes, depending on M, from the overlap by the extended charge-transfer band ascribed to those atoms (see Fig. 7). Regarding the various tungstocobaltates(II), the visible part of the spectra is dominated by the absorption of the tetrahedrally co-ordinated Co^{II}, as seen for $[Co^{II}(H_2O)(Co^{II}W_{11}O_{39})]^{8-}$ and $[Co^{II}W_{12}O_{40}]^{6-}$. The absorption coefficient based on the concentration of these cobalt(II) chromophores is however noticeably larger for the present dimer (Fig. 8). The substituted polyanions therefore exhibit the same deep green colour as the parent anion. In both series, substituted reducing atoms lead to deeply coloured complexes like Fe^{II} (blue-black), V^{IV} (deep brown) or Pt^{II} (black), which involve an intervalence transfer band W–O–M in the visible region.

The special case of the manganese-(II) and -(III) derivatives of the tungstozincate deserves mention because the visible absorption spectra furnish a rapid check of products used for magnetic studies. The manganese(III) derivatives are obtained by oxidizing previously prepared corresponding metal(II) species with MnO_4^- as reported before.[12] The manganese(III)-trisubstituted anion is better defined. One needs to start with reagents containing about 2.6 Mn^{II} per anion (a mixture of di- and tri-substituted anions) which are obtainable through one or two exchange reactions. The MnO_4^- oxidizes the anionic Mn^{II} to give Mn^{III} which replaces the remaining bridging Zn. The excess precipitates as hydroxides of Mn^{III} and Mn^{IV}. The resulting solution is brown. However, on working with reagents having a lower content in Mn^{II}, a complicated and non-reproducible mixture of anions is obtained, whose bridging metal atom composition may be one of the following: $WZnMn^{II}Mn^{III}$, $WZnMn^{III}_2$, $WMn^{II}_2Mn^{III}$, $WMn^{II}Mn^{III}_2$ or WMn^{III}_3 (the influence of factors such as temperature, concentrations and addition rates of reactants is not yet clearly understood). Nevertheless, after numerous trials, the Mn^{III}-disubstituted anion has been reliably prepared, and its spectrum is used as reference in this series. Its garnet-red aqueous solution exhibits the absorption bands due to manganese(III) transitions in an octahedral environment, comparable to those of

Table 6 Analytical results (theoretical in parentheses) and formulations of the dimeric polytungsto-zincate and -cobalates(II) and their derivatives prepared in this work

		Analysis (%)				
Salt	Colour	W	Zn	M	Cation	Total H_2O[a]
$Na_{12}[Zn_5W_{19}O_{68}]\cdot46H_2O$	Colourless	57.5 (58.1)	5.30 (5.45)		4.50 (4.60)	13.8 (13.8)
$K_{12}[Zn_5W_{19}O_{68}]\cdot23H_2O$	Colourless	60.2 (60.35)	5.50 (5.65)		8.20 (8.10)	7.1 (7.15)
$Na_{12}[Zn_3Mn^{II}_2W_{19}O_{68}]\cdot48H_2O$	Brown-yellow	57.0 (57.95)	3.30 (3.25)	1.90 (1.80)	4.30 (4.60)	14.3 (14.3)
$Na_{12}[Zn_2Mn^{II}_3W_{19}O_{68}]\cdot56H_2O$	Brown-yellow	57.1 (56.6)	2.25 (2.10)	2.60 (2.65)	4.55 (4.45)	16.3 (16.3)
$K_{11}[Zn_2Mn^{III}_3W_{19}O_{69}]\cdot27H_2O$	Red-brown	60.1 (60.15)	2.35 (2.25)	2.90 (2.85)	7.50 (7.40)	8.4 (8.4)
$K_{12}[Zn_3Mn^{III}_2W_{19}O_{69}]\cdot28H_2O$	Red-brown	59.1 (59.50)	3.20 (3.35)	2.10 (1.85)	7.80 (8.00)	8.7 (8.6)
$Na_{12}[Zn_2Fe^{II}_3W_{19}O_{68}]\cdot39H_2O$	Black	58.8 (59.65)	2.55 (2.25)	2.70 (2.85)	4.50 (4.70)	12.1 (12.0)
$Na_{12}[Zn_3Fe^{III}_2W_{19}O_{69}]\cdot49H_2O$	Light yellow	57.1 (57.60)	3.20 (3.25)	2.00 (1.85)	4.30 (4.55)	14.5 (14.5)
$Na_{11}[Zn_2Fe^{III}_3W_{19}O_{69}]\cdot44H_2O$	Yellow	58.2 (58.80)	2.35 (2.20)	2.95 (2.80)	4.10 (4.25)	13.3 (13.3)
$Na_{12}[Zn_3Co^{II}_2W_{19}O_{68}]\cdot45H_2O$	Brownish red	58.2 (58.40)	3.25 (3.30)	1.90 (1.95)	4.40 (4.60)	13.6 (13.5)
$Na_{12}[Zn_3Ni_2W_{19}O_{68}]\cdot48H_2O$	Yellow		3.45 (3.25)	1.90 (1.95)	4.40 (4.55)	14.2 (14.3)
$Na_{12}[Zn_2Ni_3W_{19}O_{68}]\cdot48H_2O$	Yellow	58.3 (57.95)	2.20 (2.15)	2.95 (2.90)	4.50 (4.55)	14.4 (14.3)
$Na_{12}[Zn_2Cu_3W_{19}O_{68}]\cdot49H_2O$ *	Yellow-green	57.2 (57.65)	2.45[b] (2.15)	3.00 (3.15)	3.86[b] (4.55)	14.6 (14.6)
$K_{12}[Zn_3Pd^{II}_2W_{19}O_{68}]\cdot38H_2O$	Deep brown		3.05 (3.20)	3.40 (3.45)		11.2 (11.1)
$K_{12}[Zn_3V^{IV}_2W_{19}O_{70}]\cdot26H_2O$	Brown	60.2 (60.05)	3.90 (3.35)	1.75 (1.75)	6.0 (6.8)	8.2 (8.05)
			Co			
$Na_{12}[Co_5W_{19}O_{68}]\cdot47H_2O$	Deep green	57.8 (58.35)	4.70 (4.90)		4.40 (4.60)	14.0 (14.1)
$K_{12}[Co_5W_{19}O_{68}]\cdot24H_2O$		60.0 (60.5)	4.90 (5.10)		8.10 (8.10)	7.5 (7.5)
$Na_{12}[Co_3Mn^{II}_2W_{19}O_{68}]\cdot43H_2O$		58.3 (59.0)	3.05 (3.00)	1.85 (1.85)	4.60 (4.65)	13.1 (13.1)
$Na_{12}[Co_3Fe^{III}_2W_{19}O_{69}]\cdot38H_2O$		61.0 (59.75)	2.85 (3.00)	1.80 (1.90)	4.55 (4.70)	11.7 (11.7)
$Na_{12}[Co_3Ni_2W_{19}O_{68}]\cdot49H_2O$		57.0 (57.90)	3.05 (2.95)	2.00 (1.95)	4.25 (4.55)	14.1 (14.6)
$Na_{12}[Co_3Zn_2W_{19}O_{68}]\cdot47H_2O$		58.2 (58.00)	2.95 (2.95)	2.15 (2.15)	4.35 (4.60)	14.2 (14.0)

[a] Determined by ignition at 600 °C; subjected to small variations according to the samples. [b] Contains cationic Zn^{2+} (see crystallographic study).

$[Mn^{III}(H_2O)(ZnW_{11}O_{39})]^{7-}$ (note, however, that in the dimer, Mn^{III} bears a ligand OH, according to the analysis). Fig. 9 shows the visible spectra of several mixtures.

Conclusion

Dimeric heteropolyanions built by bridging of Keggin-type fragments α-B-$[XW_9O_{34}]^{p-}$ with four metallic elements (X having a complete tetrahedral co-ordination XO_4) have been prepared, belonging to three series. They have been studied respectively for X = P^V or As^V, first discovered, for X = Fe^{III}, and here for X = Zn or Co^{II}. They might be associated with the analogous dimers made from Dawson-type units $[P_2W_{15}O_{56}]^{12-}$.[2b] The three series are however unequally represented. Thus, the dimeric tungstoferrates are mainly illustrated by the well defined $[Fe_2Cu_2(H_2O)_2(FeW_9O_{34})_2]^{12-}$ whose described synthesis gives a poor yield (another compound containing Fe^{III} and Co^{II}, prepared by the same author, seems to be homologous to this,[21] but its stoichiometry does not agree well with the analytical composition and has not been confirmed). Although being the first described and several times reported, the dimeric tungsto-phosphates(V) and -arsenates(V) known so far contain mainly Zn, Co^{II} or Cu^{II} as bridging atoms. Yet Mn^{II}, Ni^{II}, VO^{2+}, for example, may be included similarly, integrally or partially (our attempts show however that the exchanges are very slow and often limited), and the study of such polyanions remains to be completed. In comparison, the specific features of the dimeric tungsto-zincates and -cobaltates(II) are (*i*) the presence of one W^{VI} as a bridging atom which causes the chirality of all the parent and derived anions, (*ii*) the exceptional ease and variety of substitutions of Zn and Co^{II} as bridging atoms. Thus, other members than those reported here are being investigated successfully (especially with hydrolysis-sensitive ions such as Al^{3+}, Ga^{3+}, Cr^{3+}, Ti^{4+}, Sn^{4+} and Sn^{2+}), though requiring careful or time-consuming procedures. We have been concerned first with the zincate series which was shown to allow more facile and extended substitutions, and therefore the cobaltate series has so far received less attention. We are now completing our study of the latter. Regarding the free oxygenated ligands of the M(2) metal atoms, they cannot be exchanged, as in the tungstophosphate series. Here, due to the larger diversity of the bridging M(2) atoms, they are found, from analysis and structures, to be more or less protonated, depending on the oxidation state of the M(2) atoms. Thus, divalent elements bear aqua-ligands, trivalent Fe or Mn hydroxo-ligands, and quadrivalent vanadium oxo-ligands (Table 6). Unfortunately we have not been able to elucidate the interesting case of the derivatives of Pd^{II} and Pt^{II} (a square configuration is expected), because, till now, we have not obtained suitable crystals.

Interesting redox and various associated magnetic properties are expected for this novel series, analogous to the ferromagnetism observed in $[Co^{II}_2(H_2O)_2(PW_9O_{34})_2]^{10-}$ (ref. 8*c*) and the antiferromagnetism in $[Fe^{III}_2Cu_2(H_2O)_2(Fe^{III}W_9O_{34})_2]^{12-}$.[15]

Finally there is no reason to believe that similar series based on X = Al, Ga, Si or Ge should not exist between X^{II} = Zn or Co and X^V = P or As. Their dimers are also produced from α-B Keggin fragments which require prolonged ageing in a moderately basic medium. Such experiments are actually successful in the tungsto-gallate and -germanate systems, although the reaction proceeds very slowly. Other conditions should be investigated in order to reach a higher efficiency.

Experimental

Preparations of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot46$–$48H_2O$ *and* $Na_{12}[WCo^{II}_3(H_2O)_2(Co^{II}W_9O_{34})_2]\cdot46$–$48H_2O$.—A solution of $Na_2WO_4\cdot2H_2O$ (127 g, 0.38 mol) in water (350 cm^3), heated at 80–85 °C and vigorously stirred, was treated with 14 mol dm^{-3} nitric acid (25 cm^3, 0.35 mol) until the precipitate formed dissolved entirely. A solution of zinc nitrate hexahydrate (29.8 g, 0.10 mol) in water (100 cm^3) was then added with continuous stirring and heating at 90–95 °C (not boiling). The addition was carried out first in small aliquots (*ca.* 3–4 cm^3), giving a white precipitate which redissolves rapidly (until about 2/3 of the zinc nitrate solution is added), then dropwise, more and more slowly, in such a way that the mixture remained clear till the end. The process requires 2–3 h. The final pH was about 7.5. If necessary, the solution is filtered (a possible slight turbidity might not be filterable). A first crystallization as fine needles occurred on moderate cooling (to about 40 °C), affording a first crop. The liquid was evaporated to half volume and left unstirred, covered, at 50 °C. Overnight, needle-like crystals appeared and were left to grow for 3–4 d. Thus 90–95 g of the product (yield 65–68%) was initially separated. The resulting cold filtrate was shaken with an equal volume of acetone to extract the major part of the sodium nitrate produced (two layers). The dense lower layer was diluted with an equal volume of water, heated to 50 °C, and left again at this temperature. Supplementary amounts of product were recovered. The process was repeated until the filtrate no longer crystallized at room temperature. Currently, a total yield of 85–90% is reached. Although each fraction recovered is pure, they can be recrystallized from water together to obtain an homogeneously hydrated product. A similar procedure can be carried out using different reagents (HCl or acetic acid and chloride or acetate). The nitric acid medium allows however the best separation of the sodium salt formed.

The preparation of the cobalt(II) homologue is identical. The solution is initially emerald-green, but turns olive-green on prolonged heating, indicating formation of the expected polyanion. A pink precipitate eventually appears, readily separated. The yield varies between 50 and 80%.

Metal-substituted Derivatives of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$.—(*i*) M = Mn, Co, Ni *or* Cu. To a solution of the sodium salt of the parent polyanion, heated and vigorously stirred (typically 30 g, 0.005 mol in 100 cm^3 ml of water), was added at once a concentrated solution containing a 8–12 fold molar excess of the substituting divalent cation (nitrate, chloride or acetate). Moderate heating (50 °C) and a minimal excess of this reagent favours disubstitution (composition Zn_3M_2). Temperatures near the boiling point, a large excess of M^{II}, and, chiefly, a long heating period are required for the more extended substitution. A coloured viscous phase was formed initially, which transformed more or less rapidly to a solid precipitate, while the solution became colourless. The solid recovered by filtration was treated immediately according to one of the following procedures. (*a*) Poured into a concentrated solution of sodium nitrate (120–150 g in 600 cm^3 of water), the mixture boiled and stirred during 20–30 min. The resulting coloured solution was filtered and left to cool at room temperature. The sodium salt crystallized slowly as needles and was separated when the solution became practically colourless. It was rapidly washed with chilled water (30 cm^3). (*b*) The solid was suspended in water (250 cm^3) in the presence of a Na^+-saturation cation-exchange resin (50–60 g) until it dissolved. The coloured solution was filtered, moderately heated (50–60 °C) after addition of sodium nitrate (25–30 g), and left to crystallize at room temperature as above. Obtaining a well defined compound requires monitoring of the divalent components Zn and M. First the total (Zn + M) was checked. If it exceeded 5.0 mol dm^{-3}, another exchange with sodium nitrate was carried out. Generally, the molar ratio M/(Zn + M) was found to be between 2:5 and 3:5. To obtain the trisubstituted compounds, supplementary treatments with metal salt were necessary. The disubstitution is achieved more readily (see above), but must also be checked.

(*ii*) M = Pd *or* Pt. To a solution or a suspension of the parent polyanion (sodium salt; 15 g, 0.0025 mol in 75 cm^3 of water) heated at 50–60 °C and stirred, was added, dropwise (but rather rapidly), a solution of the chloro complex of M, in a slight molar excess for Pd ($K_2[PdCl_4]$, 1.8 g, 0.0055 mol, 10% molar excess) or the stoichiometric ratio for Pt ($K_2[PtCl_4]$, 2.08 g, 0.005 mol). With Pd^{II}, the reaction mixture rapidly yielded a deep brown solution. Powdered KCl (6–7 g) was added and the resulting brown precipitate separated by filtration. It was redissolved and again precipitated with KCl, filtered off, and washed rapidly with chilled water–methanol (1:1, 15 cm^3). After analysis, a new treatment with $K_2[PdCl_4]$ (amount calculated from the stoichiometric deficiency) was carried out, if the substitution was incomplete. With Pt^{II} the reaction was continued for 30–45 min, giving a black solution. A black, soluble salt was obtained which precipitated from the luke-warm solution on addition of powdered potassium nitrate. It does not need to be recrystallized (the ^{183}W NMR spectrum reveals a unique tungsten compound).

(*iii*) *Iron-*(II) *and -*(III) *derivatives.* The iron(II) derivative was obtained as in (*i*) using iron(II) chloride in the presence of N_2H_5Cl (0.5 g), under air-free conditions. The blue-black salt is very sensitive to oxidation by air and the samples contain small amounts of Fe^{III}.

The disubstituted iron(III) anion was prepared at room temperature, adding dropwise a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (3.3 g, 0.008 mol in 30 cm^3 water) to a stirred solution of the parent tungstozincate (sodium salt, 24 g, 0.004 mol, 150 cm^3 of water). A light yellow solution resulted. Solid sodium acetate (*ca.* 8–10 g) was added, then methanol until the liquid became turbid. The sodium salt crystallized overnight, at 0 °C, as a lemon-yellow microcrystalline powder. It was filtered off and washed with chilled methanol–water (3:1).

The trisubstitued polyanion was obtained by heating (60–65 °C) and adding 3 molar equivalents of iron(III) (nitrate, 0.012 mol). The yellow-brown compound was precipitated as the potassium salt. In both cases the yield exceeds 90%.

(*iv*) *Manganese*(III) *derivatives.* The trisubstituted derivative is more easily prepared. A crude Mn^{II}-substituted compound was first prepared which contains at least 2.6 equivalents Mn per anion [see (*i*)]. This compound (12 g, 2 mmol) was dissolved in water (100 cm^3) at 60 °C and treated dropwise with a solution of $KMnO_4$ (0.214 g, 1.35 mmol, 25 cm^3 water, one drop of 50% H_2SO_4). The deep brown solution was stirred and heated for 20 min, then filtered to remove a brown precipitate. Solid KCl (15 g) was added to the filtrate at 50 °C resulting in the rapid crystallization of the potassium salt. It was filtered off, washed with a cold solution (5–10 cm^3) of 1 mol dm^{-3} KCl, then with chilled water (5 cm^3).

(*v*) *Oxovanadium*(IV) *derivative.* The sodium salt (12.1 g, 0.002 mol) of the parent anion was transformed into the potasssium salt by dissolution in water (100 cm^3) at 80 °C and addition of solid KCl (8–10 g). The mixture was kept at 0 °C overnight where upon the potassium salt separated. This crude salt was dissolved in water (120 cm^3) at 80–85 °C, N_2H_5Cl (0.1 g) added, then a solution of $VO(SO_4) \cdot 5H_2O$ (1.5 g, 0.006 mol, 20 cm^3 of water) containing N_2H_5Cl (0.05 g) and buffered with potassium acetate (0.6 g). A red-brown colour developed immediately. An ochre precipitate appeared toward the end of the addition (excess of vanadium). After filtration, the warm solution was poured into a solution (60–75 cm^3) of KCl saturated at 80 °C, giving a brown crystalline powder. It was kept at 5 °C overnight, filtered and the solid recrystallized likewise after redissolution in the minimum of water. The final product was washed with chilled methanol–water (1:4) and dried in air. Yield: 80–85%.

Metal-substituted Derivatives of $[WCo_3(H_2O)_2(CoW_9O_{34})_2]^{12-}$.—Similar procedures were carried out for this polyanion substituted by Mn^{II}, Fe^{III}, Ni^{II} and Zn^{II} only. Other substituting atoms were used successfully, but several problems remain for the purification and the analysis of the products is not satisfactory. No difficulty was encountered in the preparation of the disubstituted iron(III) anion, at room temperature (see above for the tungstozincate). With the divalent elements, however, a greater excess and a longer heating period are necessary. This is sufficient for Mn^{II} and Zn^{II}, but not for Ni^{II}. The latter gave a viscous phase which hardened as a gum on cooling. When kneaded with the mother solution in a mortar, it transformed into a fine powder which separated well. It was subjected to the usual cation exchange with Na^+. Analysis showed that insufficient substitution occurs and the treatment with a nickel salt has to be repeated twice to reach complete disubstitution.

Analysis.[22,23]—The alkali-metal cations were determined as usual (sodium flame spectrophotometry, K as tetraphenylborate). Because of the stability in basic media, analysis of metal atoms of anions must be performed in > 1.0 mol dm^{-3} NaOH, heating overnight at 50–60 °C. Some metallic elements precipitate as hydroxides, sometimes in oxidized form (Mn, Co, Fe, Ni and Pd) and may be separated for titration by conventional methods; W, Zn and V remain in solution. Tungsten was precipitated in a strongly acidic medium in the presence of cinchonine. Zinc was determined preferably by gravimetry with 8-hydroxyquinoline,[22] although titration with ethylenediaminetetraacetate (edta) may be used, provided that the polyanion is destroyed at pH 14, excess of edta added at this pH, followed by a careful decrease of the pH to 10.5, is necessary for the back-titration of edta. Various mixtures of two metallic elements (Zn + M) or (Co + M) may be titrated also using edta complexometry, as described for Zn, but adding in succession edta then NaOH. Specific methods were applied to analyse Mn (spectrophotometry of MnO_4^-), Mn^{III} (reduction), Fe (reduction to Fe^{II} and oxidimetry), Co (biamperometry), Ni and Pd (dimethylglyoxime) and Cu (salicylaldoxime). The analytical results are collected in Table 6.

X-Ray Structure Determination.—Crystals of the three compounds (Table 1) were obtained by slow evaporation in air of aqueous solutions almost saturated at room temperature. They exhibit well developed faces. The sodium salts of **1** and **2** were elongated and mounted in the direction of the *a* axis. They show ten prismatic faces, six {100} and four {011}. The potassium salt of **3** usually grew as thin rhombic platelets. Obtaining the most equidimensional crystals suitable for structure determination required very slow evaporation of a deep layer of solution. After mounting, the crystals were coated with a paraffin oil film to prevent incidental dehydration. Crystal parameters, data collection and results are listed in Table 1.

The intensities were corrected for Lorentz-polarization and absorption. The latter was based on a good knowledge of the crystal morphology (face indexing and dimensions) refined by the use of ψ-scan data (14–18 planes).[24] A framework of 12 selected non-equivalent positions of the heaviest atoms (11 only in **3**) was determined by a direct method approach (MULTAN).[25] In the three centrosymmetric structures (**1** and **2** are isomorphous, **3** is not) no atom occupies the centre of symmetry. Therefore, the odd number of W, Zn or Cu atoms was only consistent with a partial occupancy factor for some of them. The first refinement and Fourier map of **1**[26] allowed us to assign unambiguously 11 independent positions to nine tungsten and two zinc atoms, one Zn being surrounded by the nine W at about 3.5 Å. The twelfth peak showing an intermediate intensity between those of W and Zn was interpreted as an alternate equal occupancy of W and Zn. A scattering factor corresponding to '$W_{0.5}Zn_{0.5}$' was thus attributed to this position. The subsequent refinement confirmed the validity of this hypothesis. Atomic positions in compound **2** were attributed on the basis of those found for **1** taking into account that the copper complex is derived from **1** without exchange of the interior Zn atoms. Thus, two peaks exterior to the ZnW_9 framework were ascribed to Cu and '$W_{0.5}Cu_{0.5}$'. For **3** the Fourier map reveals the analogous '$W_{0.5}Zn_{0.5}$' site and the vanadium site. After these steps, alternate difference syntheses and full-matrix least-squares refinements on F[26] allowed the location of the anionic oxygen atoms. Sodium cations and water molecules of crystallization were distinguished with the help of the number of neighbours and interatomic distances (Na–O distances are usually near 2.4 Å and hydrogen-bond distances about 2.8 Å). The whole of the Na$^+$ and almost all water molecules were located in **1** and **2**. In the latter a partially occupied Zn^{2+} cation site was identified on the same basis. In contrast, in **3**, only four independent K$^+$ sites were well characterized. The remaining two K atoms are certainly disordered and no peak attributed to water molecules was found to be consistent with partially occupied potassium sites. As often reported in structural studies of hydrated salts of polyanions, a number of cations and/or water molecules are not detected, being randomly distributed in interanion voids (see, *e.g.*, note 13 in ref. 16). Here, only few atoms remain undetected.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths.

NMR Spectra.—Lithium salts of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ and its palladium(II) and platinum(II) disubstituted derivatives were prepared by cation exchange, either from sodium salts passed through a Li$^+$-form cation-exchange resin, or potassium salts treated with stoichiometric amounts of $LiClO_4$ in a few cm^3 of water. After filtration, the solutions were evaporated to dryness. In both cases, solid samples were taken, redissolved in water, brought to crystallization through addition of sodium nitrate or potassium chloride, and the products checked using their X-ray powder diffractogram. The latter and analysis of essential metal components confirmed that the anions were not altered. Solutions containing lithium salts (12–18 g) dissolved in water–deuterium oxide (*ca.* 0.3–0.45 mol dm^{-3}, pH 7.0; 4–4.5 cm^3) were used to measure the ^{183}W NMR spectra of polyanions. The one-dimensional spectra were recorded at 15.0046 MHz with 15 mm diameter sample tubes (Spectrometer Bruker WP360), the two-dimensional COSY spectrum as described earlier[10] at 16.671 MHz with 10 mm diameter tubes (Bruker MSL400). The temperature was 305 K, the reference $Na_2WO_4 \cdot 2H_2O$, 2 mol dm^{-3} in D_2O at 302 K.

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