RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

July 1974

Translated from *Uspekhi Khimii*, **43**, 1137-1159 (1974)

U.D.C. 541.6; 541.49

Structural Principles in the Chemistry of Heteropolycompounds

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Different types of heteropolycompounds, which are formed in solutions and can be isolated from the latter in a crystalline state, have been analysed and classified on the basis of the results of latest X-ray diffraction studies. The physicochemical and research techniques which have led to the current views on the structures of heteropolycompounds (a large class of complexes) are briefly considered. The possibilities which arise on substitution of one or several metal atoms in the coordination sphere of the heteropolycompound are examined on the basis of structural considerations. The principal trends and problems in the chemistry of heteropolycompounds are discussed. The bibliography includes 191 references.

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I. INTRODUCTION

Various views concerning the structures and nature of heteropolycompounds which have been held until recently are described fairly completely in monographs and other publications [1-4]. The present review considers the current state of the chemistry of heteropolycompounds—a large class of complexes which are formed in solution from whence they can be isolated in the solid state. The physicochemical methods and also certain problems and the principal trends in the chemistry of compounds of this class will be briefly considered.

All the heteropolycompounds examined obey the well known Pauling rules [5], which explain the properties of stable oxide structures. In all cases the fundamental unit of isopolycompounds and heteropolycompounds is the MO_6 octahedron. The octahedra are joined to one another by their vertices, edges, or faces, forming the coordination sphere around the central atom. The outer octahedra of the coordination sphere are distorted, the displacement of the metal atom leading to the formation of shortened (multiple) bonds with the non-delocalised oxygen atoms. The M–O distances are about 1.7 Å for the terminal M=O bonds, 2.0 Å for the M–O–M bridge bonds, and 2.2–2.3 Å for the M–O–X bonds, where X is the central atom; the shortest M=O bond is always in the *trans*-position to the longest bond. We may note that in all the isopolycompounds and heteropolycompounds investigated the number of such non-delocalised atoms does not exceed two [6].

The large number of physicochemical studies on aqueous solutions of these compounds has not unfortunately yielded a corresponding amount of valuable information concerning the forms in which heteropolycompounds exist.

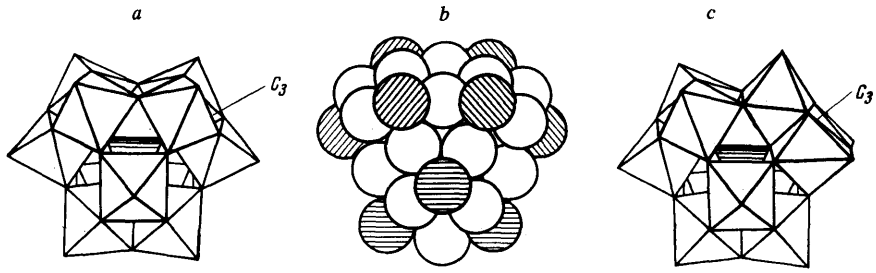


Figure 1. The structure of the anions: *a*) α-$X^{x+}M_{12}O_{40}^{x-8}$; *b*) ditto in the form of close-packed spheres; *c*) β-$X^{x+}M_{12}O_{40}^{x-8}$.

Very often investigators make no assumption concerning the form with which they are dealing in solution. Although the compounds can be isolated in a crystalline form, the number of X-ray diffraction studies is fairly limited, since the large unit cell involves the determination of a large number of parameters. For this reason, work on the complete analysis of the structures of such compounds was not started unil the beginning of the 1960s.

II. STRUCTURAL TYPES OF HETEROPOLYCOMPOUNDS

Heteropolycompounds differ from the usual coordination compounds because they do not contain discrete ligands coordinated to the central atom, since the discrete MO_6^{n-} ion does not exist. Therefore one can regard the coordination sphere as one large ligand [7].

The structure of heteropolycomplexes is represented by an ideal octahedron whose vertices are occupied by oxygen atoms. Molybdenum or tungsten atoms are placed within the octahedron. The ionic radii of molybdenum(VI) and tungsten(VI) are 0.62 and 0.65 Å respectively and the ionic radius of O^{2-} is assumed to be 1.40 Å. [8]

The classification of heteropolycompounds generally adopted at present is based on the coordination number of the central atom and the number of metal atoms forming the coordination sphere [9]; attempts are being made to employ the IUPAC nomenclature for this purpose and this is the nomenclature which we shall adhere to in the present review. The overall formula, for example $H_3PMO_{12}O_{42}.nH_2O$, is usually employed to designate heteropolycompounds, because, as already stated, it is impossible to isolate an individual ligand. Sometimes formulae of the type $SiO_4W_{12}O_{36}^{4-}$ or $AlO_6Mo_6O_{18}^{9-}$ are used to indicate the coordination number of the central atom.

1. The Structure of the Anion $X^{x+}M_{12}O_{40}^{x-8}$ and Its Derivatives

The most familiar and widely investigated structure is the so-called Keggin structure [10]. The anion consists of four M_3O_{13} triplet† forming a tetrahedral cavity in which the central atom is placed (Fig. 1*a*). The general formula of the anion can be written in the form (for the 12 : 1 ratio)

$$X^{x+}M_{12}O_{40}^{x-8} ,$$

where X is the tetrahedrally coordinated central atom, which can be B, Si, P, As, Cr, Mn, Fe, Co, Cu, Zn, Ti, Zr, Ga, or H_2^{2+}. [12] The overall symmetry of the anion is T_d. X-Ray diffraction studies have been made on P^{5+}, As^{5+}, Si^{4+}, Ti^{4+}, and Zr^{4+} dodecamolybdates [8,13-20] and P^{5+}, B^{3+}, Ge^{4+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, and Co^{3+} dodecatungstates [8,13,14,19-25], where the anion is claimed to have the T_d symmetry. We emphasise that the representation of the anion in the form of ideal octahedra does not take into account the fact that the oxygen atoms must be represented by large spheres. For this reason, the representation of the structure in this form (Fig. 1*a*) can create the incorrect impression that there are large open spaces within the anion. In Fig. 1*b* the anion is represented by close-packed spheres (the shaded circles represent terminal oxygen atoms). The structure is characterised by the presence of 12 M=O bonds and 24 M−O−M bridge bonds, twelve of which are almost linear and twelve are angular. The maximum M−O distance is that between the metal atom and the oxygen atom which links three metal atoms to the central atom (sp^3 hybridisation). The length of this bond depends on the size of the central atom. For central atoms of metallic type (for example Co^{III}, d^6), the tetrahedron is appreciably distorted (extended along the C_2 axis) in consequence of the Jahn−Teller effect, although the external coordination shell does not undergo appreciable changes [7]. Incidentally the Co^{3+} ion in $CoW_{12}O_{40}^{5-}$ is atypically in a tetrahedral environment.

Heteropolycompounds are formed immediately at an appreciable rate (faster on heating) in acid solutions on mixing molybdates or tungstates with the salt of the corresponding heteroelement. The acids can be isolated in a free state from highly acidified solutions by extraction with ether and also by ion exchange [1,4]. Certain metal heteropolycompounds are formed with much difficulty, since octahedral coordination is usually characteristic of the metals and the transition to tetrahedral coordination requires additional energy [26].

The large number of different hydrates of the same compound gives rise to difficulties in the preparation of truly homogeneous phases for chemical analysis and physicochemical studies. The exact amount of water is frequently fairly difficult to determine, because it can be zeolitic and is only gradually removed on dehydration [27]. The crystal structures of different hydrates of heteropolycompounds have been examined [2,28].

† The M_3O_{13} triplet, which is found in almost all the known structures of heteropolyanions, is made up of three MO_6 edge-sharing octahedra. It has been detected as a discrete unit in cluster type compounds $M_2^{II}Mo_3O_8$ in which a metal−metal bond is postulated [11]. In the heteropolyanion the M−M distance is about 3.3 Å, which rules out direct d−d interaction. However, it is quite possible in highly reduced forms of heteropolyanions.

In the crystalline state there is no direct linkage between the anions. Their packing is achieved via hydrogen bonds or via cations. Water can be completely removed by thermal dehydration (at about 300–400°C), whereupon the structure of the anion is fully retained, its stability increasing with increase of the ionic radius of the central ion [29]. All the heteropolyacids and some of their salts are very soluble in water and in oxygen-containing solvents, which can be explained [7] by the very low crystal lattice energy and by the solvation of the cations. Although the crystal lattice energies of heteropolycompounds are unknown, to a first approximation the lattice energy can be estimated as about 800 kcal mole^{-1} for $K_4SiW_{12}O_{40}$. [29]

There is no reason to doubt at present that the anion with Keggin's structure retains its high symmetry (T_d) in aqueous solutions. An X-ray diffraction study of the heteropolycompounds $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ in aqueous solution [30,31] showed that the results agree with the existence of one form containing twelve tungsten atoms, forming a cubo-octahedron, i.e. the structure which was discovered by Keggin. Similar results were obtained for the dodecamolybdophosphate anion [30].

The determination of the diffusion coefficients of the heteropolyanions $XM_{12}O_{12}^{X-8}$ in solution showed that the anions are almost spherical, their radii are the same, and that the hydrodynamic radius of the anion is equal to the crystallographic radius of the non-solvated anion [7]. This indicates a very low degree of solvation. The addition of alkali to solutions of heteropolyacids leads to the decomposition of the anion and a slight increase of alkalinity leads to the formation of compounds with the ratio M : X = 11 : 1. [4] The formation of 11 : 1 complexes can be regarded as involving a simple elimination of one octahedron (i.e. an M=O group) from the structure of $X^{X+}M_{12}O_{40}^{X-8}$ and the charge of the anion always increases by four units. An X-ray diffraction study [28] of the salt $(NH_4)_7Na_2[GaW_{11}O_{39}(H_2O)].15H_2O$ showed that the Keggin structure persists and that gallium is in the centre of the tetrahedral cavity. The site of one octahedron is occupied by the water molecule. The formation of 11 : 1 compounds probably accounts for the hypothesis of an unjustifiably large number of dissociable protons in the Keggin structure, for example eight in molybdosilicic acid [1]. We shall not consider here the problem of the number of dissociable protons in heteropolyacids and no conclusions will be reached concerning the structure of the anion on the basis of determinations of the number of dissociable protons or the isolation of salts substituted to a high degree. In the light of structural concepts, any departure of the number of dissociable protons in an acid whose anions have the Keggin structure from the value $x - 8$, where x is the positive charge of the central atom, is caused either by the degradation of the anion or by the presence of non-salt-forming hydrogen atoms.

A greater increase in alkalinity leads to other forms with different M : X ratios. Salts containing the pentamolybdophosphate anion have been isolated [32]. The same anion was obtained in a study of multicomponent $PO_4 : MoO_4$ mixture [33], where the sodium salt was isolated and studied by X-ray diffraction [34]. The salt $Na_2H_2Mo_5.P_2O_{39}.10H_2O$ no longer belongs to heteropolycompounds, since in its anion there is no central atom, although its structure consists of five MoO_6 octahedra and two PO_4 tetrahedra. The addition of an excess of alkali (20–28 moles per mole of the anion) leads to the decomposition of the anion into simple MO_4^{2-} and XO_4^{X-8} anions. The stability of the molybdate anions varies in the series Si > (Zr,Ti) > Ge > P > As.

As early as 1941 Jahr [35] and later Chalmers and Sinclair [36] pointed out the possibility that different anions with a tetrahedral arrangement around the central atom can be formed by a simple rotation of one or several M_3O_{13} triplets by 60°, which reduces the T_d symmetry of the anion to C_{3v} or C_{2v}. Recently Yamamura and Sasaki [37] confirmed the possibility of geometrical isomerism for β-$Ba_2SiW_{12}O_{40}$ in the anion of which one W_3O_{13} triplet is rotated by 60° about the C_3 axis (Fig. 1*c*).

Heteropolycompounds with the ratio M : X = 9 : 1 or 18 : 2 have properties close to those of the 12 : 1 compounds. This series of complexes is known only with phosphorous and arsenic central atoms and they are obtained after prolonged boiling from solutions with a high excess PO_4^{3-} or AsO_4^{3-} concentration and a low acidity. An X-ray diffraction study [38] of compounds with the ratio W : P = 9 : 1 showed that the complex is made up of two fragments of the Keggin anion from the structure of which three WO_6 octahedra have been eliminated. The two 9 : 1 fragments share the resulting free vertices of the octahedra, leading to the 18 : 2 structure, which belongs to the point group D_{3h} (Fig. 2*a*). Two XO_4 tetrahedra remain separate. It is easy to imagine the formation of geometrical isomers of $X_2M_{18}O_{62}^{2X-16}$ by a simple rotation of one 9 : 1 fragment by 60°, which leads to the D_{3d} symmetry,

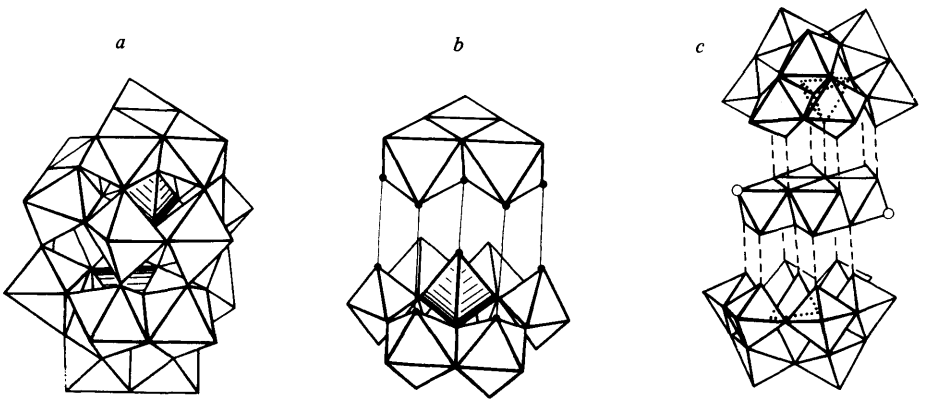


Figure 2. The structure of the anions:
a) $X_2^{X+}M_{18}O_{62}^{2X-16}$; *b*) $H_6PMo_9O_{34}^{3-}$; *c*) $P_2Co_4(H_2O)_2W_{18}O_{68}^{10-}$.

or by a rotation of W_3O_{13} triplets [39]. However, there is yet another possibility of the formation of isomers. The two fragments of the Keggin anion, each of which has lost one M_3O_{13} triplet, can share the free vertices but the two inner XO_4 tetrahedra then have a common oxygen atom (i.e. the X_2O_7 group is present) and the general formula of the anion should be written $X_2M_{18}O_{61}^{2X-14}$. There is no doubt that these geometrical isomers are possible for the molybdenum analogues.

The preparation of salts of octadecatungstodiberyllic acid, the anion of which belongs to the M : X = 18 : 2 series and has the formula $Be_2W_{18}O_{62}^{12-}$, has been described [40]. Goldman and Hargis [41], who studied the kinetics of the reduction of molybdophosphoric acid in the presence of bismuth(III), suggested the formation of a diheteropolycompound with the ratio P : Bi : Mo = 1 : 1 : 18. If this is confirmed by structural studies, the complex will be the first example of diheteropolycompounds with two different heteroelements.

It is interesting to note that a fragment of the Keggin structure was obtained recently for the first time. The anion $PMo_9O_{34}^{9-}$ (C_{3v} symmetry) was detected in the $xPO_4 : yMoO_4$ multicomponent system [33]. The sodium salt was crystallised and investigated by X-ray diffraction [42]. The structure of the anion is illustrated in Fig. 2*b*. It was also shown to persist in aqueous solutions [33].

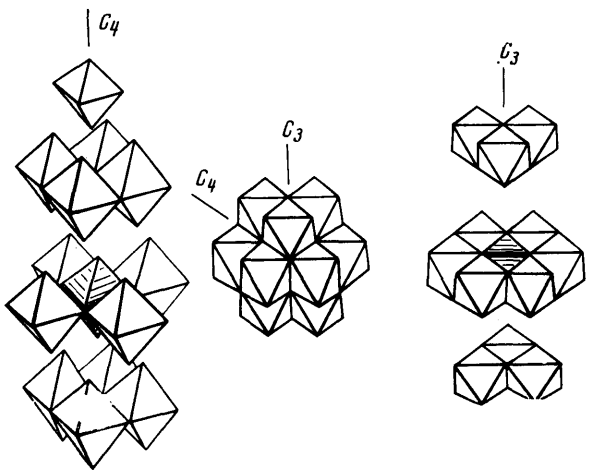


Figure 3. The structure of the $X^{X+}M_{12}O_{38}^{X-4}$ anion and its resolution along the C_4 and C_3 axes.

Another complex in which there is a fragment of the Keggin anion is $P_2Co_4(H_2O)_2W_{18}O_{68}^{10-}$ (point group C_{2h}), which has unique characteristics and whose structure has been determined [43] (Fig. 2*c*). The nickel and copper complexes belong to the same type and phosphorus can be replaced by arsenic(V). The characteristic features are the high molecular weight (4729) and the presence of the planar Co_4 group which is made up of CoO_6 octahedra in one plane; the two water molecules (represented by circles) cannot be replaced by other ligands, since they are thoroughly screened by the oxygen atoms of the neighbouring WO_6 groups. The Co_4 plane separates the two fragments of the Keggin anion from the structure of which a W_3O_{13} triplet has been eliminated. The anion may be of interest for the investigation of magnetic interactions since similar tetranuclear manganese(II), cobalt(II), nickel(II), and copper(II) complexes are unknown.

2. The Structure of the Anion $X^{X+}M_{12}O_{38}^{X-4}$ and Its Derivatives

The next group of heteropolycompounds comprises complexes whose structures are based on an octahedral arrangement around the central atom. Any of these structures can be represented as a fragment of the highly symmetrical (O_h symmetry) heteropolyanion (12 : 1) $X^{X+}M_{12}O_{38}^{X-4}$ (Fig. 3) formed by the addition of twelve MO_6 octahedra to all twelve edges of the central XO_6 octahedron [9]. This hypothetical ion would have a very low negative charge and for a high-valent central atom such as either Mo^{VI} or W^{VI} would have a zero or positive charge. However, in the case of vanadium the overall charge of the anion becomes $x - 16$; this structure has been proposed [44] for the anion $MnV_{13}O_{39}^{9-}$, the thirteenth VO_6 octahedron occupying the site between the four VO_6 octahedra on the C_4 axis (Fig. 3*a*). A preliminary X-ray diffraction study showed that the structure has tetragonal symmetry. The structure of the compound $MnV_{14}O_{40}^{8-}$ (D_{4h} symmetry), in which the fourteenth vanadium atom is in the *trans*-position relative to the thirteenth vanadium atom, was determined recently [45].

A known group of heteropolycompounds with an octahedral arrangement around the central atom comprises hexamolybdenum and hexatungsten compounds [12] (M : X = 6 : 1) with the general formula $X^{X+}M_6O_{24}^{X-12}$, where X^{X+} = Te^{6+}, I^{7+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Rh^{3+}, Ga^{3+}, or Ni^{2+}. The structures of tellurium(IV) and chromium(III) hexamolybdates, which belong to this class, have been determined by Evans [46] and Perloff [47]. An incomplete X-ray diffraction study [25] confirmed this structure for the $NiW_6O_{24}^{10-}$ anion. The elimination of two M_3O_{13} triplets from the hypothetical ion on the C_3 axis (Fig. 3) leads to a structure consisting of seven octahedra, one of which is the central XO_6 octahedron. All the octahedra share their edges and are located in the same plane. The structure has the D_{3d} symmetry (Fig. 4*a*). The central XO_6 octahedron undergoes a slight trigonal distortion. The heteropolycompounds of triply-charged ions contain six protons firmly linked to the oxygen atoms of the central XO_6 octahedron. For this reason, the formula of the anion can be written as $X(OH)_6M_6O_{18}^{X-6}$.

The inclusion of six protons in the formula of the anions aroused a majory controversy, because these are non-salt-forming protons. Baker and coworkers [48,49] and then Rollins and Earley [50] had to resort to the hypothesis that dimeric forms of the anion exist in order to reduce the number of oxygen atoms and hence diminish the atomic charge of six units. However, in hexamolybdogallate(III) three water molecules are removed at a fairly high temperature, which indicates their unusual situation [51]. Subsequently Baker and coworkers [25] had to abandon these views, particularly since the ^1H NMR spectra of salts of 6 : 1 heteropolycompounds revealed the presence of six hydroxy-groups [52]. On the basis of this example, we should like to emphasise yet again the necessity for a critical approach to the interpretation of the results and also the desirability of employing several physicochemical methods to confirm one's conclusions.

Fig. 4*b* illustrates the structure of $CrMo_6O_{24}^{9-}$ with close-packed oxygen atoms (the terminal atoms are represented

by shaded circles), the metal ions being distributed within the octahedral cavities formed. The $Co_2Mo_{10}O_{38}^{8-}$ ion, whose structure has been determined by Evans and Showell[53], is related to these 6:1 complexes. The anion is formed from two $CoMo_6O_{24}^{9-}$ groups after two MoO_6 octahedra have been removed. By combining two 5:1 fragments and rotating one of them through 180° in relation to the other about the edges of the central octahedron (Fig. 5*a*), one obtains an anion with D_2 symmetry, which is consequently capable of having optical isomers. Quite recently these two isomers were isolated with the aid of the tristetramminecobalt ion[54]. In all probability this anion as well as the anions with the 2:18 ratio (Fig. 2*a*) are the only examples of true diheteropolycompounds.

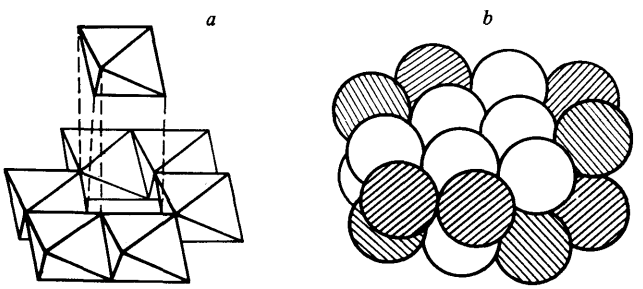


Figure 4. The structure of the anions: *a*) $X^{X+}M_6O_{24}^{X-12}$; *b*) ditto in the form of close-packed spheres.

Other examples of an octahedral arrangement about the central atom are provided by the manganese(IV) and nickel (IV) 9:1 complexes[55] whose structures are obtained by the removal of three octahedra from the six octahedra located in a plane perpendicular to the C_3 axis of the hypothetical anion $XM_{12}O_{38}$ (Fig. 3), which leads to the D_3 symmetry of the anion (Fig. 5*b*). Baker and Weakley[56] showed by cryoscopic measurements in Na_2SO_4 that the anion is monomeric. The acid prepared by ion exchange proved to be fairly unstable, but the number of its dissociable protons was found to be close to the calculated value.

3. The anions $X^{X+}W_{10}O_{36}H_2^{X-10}$

Peacock and Weakley[57] obtained a series of lanthanide heteropolytungstates with the ratio W:Ln = 10:1. It is interesting that all the lanthanides have the same coordination number, which is fairly unusual for this series of elements. The structure of decatungstocerate(IV) was determined[58] (Fig. 6). It contains the residues of two $W_6O_{19}^{2-}$ anions[59] and resembles the $W_{10}O_{32}^{4-}$ anion[60] (Fig. 7), the two halves of which make an angle of 45°. The heteropolycompounds XW_8O_{28}, where X = Ce^{IV}, Th^{IV}, or U^{IV}, have been isolated for elements with high coordination numbers[61,62], but subsequently their formulae were written as $XW_{10}O_{36}$,[63] and they probably belong to the same structural type.

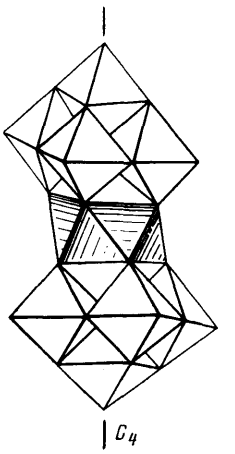


Figure 6. The structure of the $X^{X+}W_{10}O_{36}^{X-12}$ anion.

4. The Structure of the $X^{4+}Mo_{12}O_{42}^{8-}$ Anion

The anion of the 12:1 molybdoceric acid $CeMo_{12}O_{42}^{8-}$ belongs to the last known type of heteropolycomplexes. On the basis of the undoubtedly high number of dissociable protons and the high ionic radius of Ce^{4+}, Baker et al.[64] suggested that the structure of the anion should differ

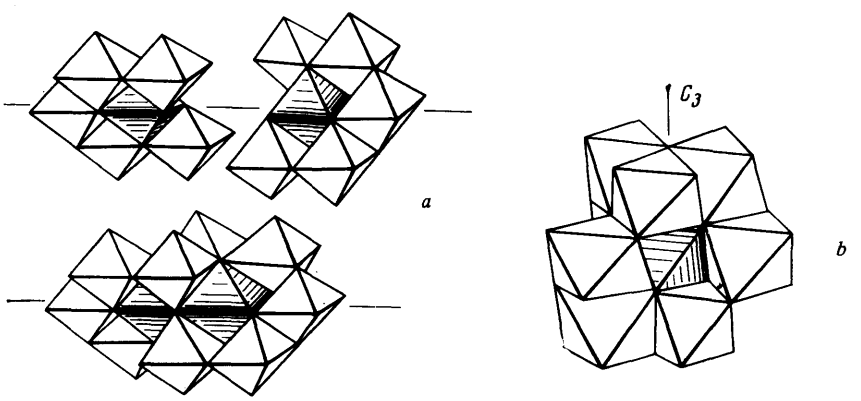


Figure 5. The structures of the anions: *a*) $Co_2Mo_{10}O_{38}^{8-}$; *b*) $X^{4+}Mo_9O_{32}^{6-}$.

significantly from the Keggin structure. A preliminary X-ray diffraction study[65] revealed two characteristic features of this anion: an eicosahedral arrangement about the central atom and face-sharing of pairs of MO_6 octahedra (Fig. 8) (T_i symmetry), observed for the first time in the structures of isopolycompounds and heteropolycompounds. The similarity of the properties[66] and X-ray diffraction data[67] show that the individual heteropolymolybdenum acids of quadrivalent cerium, thorium, uranium, and neptunium[68] have the same structures.

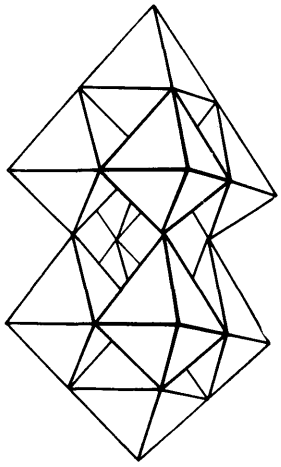


Figure 7. The structure of the $W_{10}O_{32}^{4-}$ anion.

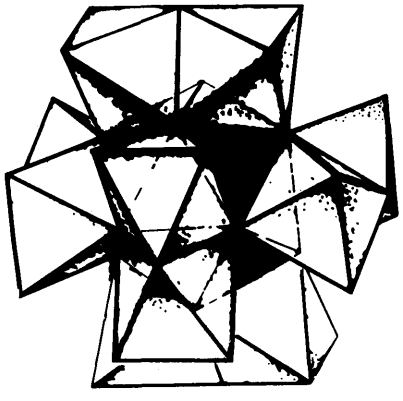


Figure 8. The structure of the $X^{4+}Mo_{12}O_{42}^{8-}$ anion.

5. Other Anions

Flynn and Stucky[69] made an X-ray diffraction study of the salt $Na_{12}[Mn(Nb_6O_{19})_2].5H_2O$. The anion consists of two isopolyanions $Nb_6O_{19}^{8-}$ coordinated to the Mn^{4+} ion (Fig. 9), so that the oxygen atoms form an octahedron about the Mn^{4+} ion and the overall symmetry of the anion becomes D_{3d}. However, in this case not all the Nb atoms are joined to the Mn^{4+} ion, and although its structure resembles $CeW_{10}O_{36}$ (Fig. 6), the complex is not intermediate between isopolycompounds and heteropolycompounds.

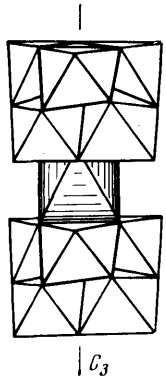


Figure 9. The structure of the $Mn^{4+}(Nb_6O_{19})_2^{12-}$ anion.

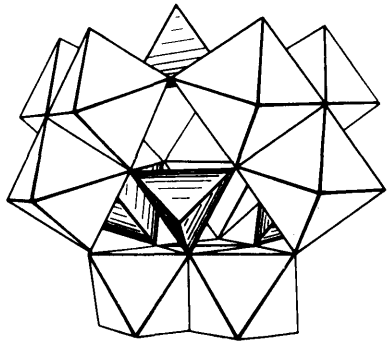


Figure 10. The structure of the $As_4Mo_{12}O_{50}^{8-}$ anion.

In 1973 Nishikawa and Sasaki[70] determined the crystal structure of $(NH_4)_4H_4As_4Mo_{12}O_{50}.4H_2O$ (Fig. 10). The anion has the T_d symmetry and resembles the Keggin structure turned inside out. The four Mo_3O_{13} triplets are joined via their vertices, forming the anion $Mo_{12}O_{46}^{20-}$ to which four AsO_4 tetrahedra are linked. At the centre of the anion there is a cavity (radius 1.43 Å) formed by eighteen oxygen atoms.

III. METHODS FOR THE INVESTIGATION OF HETEROPOLYCOMPOUNDS

There is at present no well founded theory which would account for the mechanism of the formation of heteropolycompounds, apart from a few hypotheses[71]. It is very difficult even to determine whether the process takes place in stages, the intermediate forms being fairly stable and long lived, or whether the intermediate compounds are unstable and the process can have a chain mechanism.

At any rate the intermediate compounds have not been isolated and characterised in the case of heteropolycompounds unless of course one formally includes among these the 6 : 1 compound (Fig. 4) as an intermediate before the formation of the 9 : 1 complex (Fig. 5*b*) with an octahedral arrangement about the central atom.

Moreover even for isopolycompounds it is not evident how the complex structure is produced by a simple addition of MoO_6 octahedra to the pre-existing framework. For example, it is regarded as fully proved that acidification of the MoO_4^{2-} ion [72] does not lead to the formation of intermediate species (the heptamolybdate anion [73] $Mo_7O_{24}^{6-}$ is formed at once and only then the octamolybdate anion [74] $Mo_8O_{26}^{4-}$ and the structure of the latter is not obtained by the simple addition of a single MoO_6 octahedron to the heptamolybdate framework but involves a rearrangement of the anion), but the causes of this are unknown.

In studies on the relaxation of isopolymolybdate solutions [75,76] it has been suggested that acidification of MoO_4^{2-} results in a rapid transition of molybdenum from tetrahedral configuration to an octahedral configuration with subsequent condensation of the octahedra.

In all probability the tendency of molybdenum, tungsten, and vanadium to form shortened M=O bonds, leading to a weakening of the M–O bonds in the *trans*-position, is responsible for the interaction of several octahedra. The formation of these double bonds leads to certain differences in the structures. A structure of the type XMo_6O_{24} has been suggested for the heptamolybdate (Fig. 4), but the structure of the isopolymolybdate is such (C_{2v} symmetry) that all the molybdenum atoms in it are equivalent, i.e. all the MoO_6 octahedra undergo identical distortions, whereas in the XMo_6O_{24} structure all the bonds in the XO_6 octahedron are equivalent and in MoO_6 they are different.

Furthermore, in many instances the molybdenum analogues of $XO_4W_{12}O_{36}^{X-8}$ do not exist, because the Mo–O bonds are weaker than the W–O bonds, and the $Mo_{12}O_{36}$ framework cannot maintain the X^{X+} ion in a tetrahedral arrangement. Although many examples of anions with the same structures have been observed in the chemistry of molybdenum and tungsten, in certain cases the heteropolyanions are different, for example the structure of cerium heteropolytungstate differs appreciably from that of the dodecamolybdocerate ion (Figs. 6 and 8).

The formation of heteropolycompounds is largely determined by the ability of the metal ions, comprising the coordination sphere, to polymerise and the structure of the complex depends on the nature of the central atom. However, cases are known where the conditions of the synthesis determine the coordination number of the central atom. For example, depending on the proportions of the initial reactants, the acidity of the solution, and time, it is possible to obtain complexes with the ratios M : GaIII = 6 : 1 (D_{3d} symmetry of the anion) and 12 : 1 (T_d symmetry) having octahedral and tetrahedral arrangements about the central atom [77].

The thermodynamics of the formation of polynuclear species having different shapes (the compact hexaniobate [78] $Nb_6O_{19}^{8-}$, the swollen heptamolybdate [73,79] $Mo_7O_{24}^{6-}$, or the loose bulky paratungstate [80] $W_{12}O_{42}^{12-}$) is virtually unknown. For this reason, studies [81–83] undertaken to determine the activity and osmotic coefficients of anions belonging to the 6 : 1 and 12 : 1 series merit attention.

There are many equilibrium states in the chemistry of solutions, which involves a time factor since equilibrium is very frequently established slowly, particularly in the case of molybdenum. It is sometimes impossible to compare the results of different studies, since the experiments were carried out under different conditions which are difficult to compare. Moreover it has been shown that the concentration and composition of the supporting electrolyte are very important and that the electrolyte can in turn influence the charge and dimensions of the anion. Therefore the results of studies in which the concentration of the supporting electrolyte did not exceed 3 M proved to be promising.

The existence of heteropolycompounds with the Keggin structure in different forms in equilibrium with one another, one of which (the metastable form) is converted into the other (the stable form), is well known. This equilibrium is influenced by the state of the initial tungsten and molybdenum ions, as shown clearly for dodecatungstosilicic and dodecatungstogermanic acids [84]. Depending on the sequence in which the solutions of the initial reactants are mixed, different forms are obtained:

$$\mathrm{Si(Ge)} + \mathrm{WO_4^{2-}} \xrightarrow{(H+)} \alpha\text{-isomer (11 : 1 or 12 : 1)},$$

$$\mathrm{WO_4^{2-}} + \mathrm{H^+} \rightarrow \mathrm{HW_6O_{21}^{5-}} \xrightarrow{\mathrm{Si(Ge)}} \beta\text{-isomer (11 : 1 or 12 : 1)},$$

and in the case of silicon the conversion of the β-form into the α-form is very slow even on heating.

Much importance was attributed earlier to results obtained by certain methods which are not theoretically well founded. For example, diffusion coefficients were measured for many years [85] and then linked to the ionic weight of the polymeric form on the basis of the familiar Riecke relation. It was not until 1960 that Baker and Pope [86] published the results of a fairly simple but clear-cut experiment in which it was shown that the diffusion coefficients of the isomorphous anions $SiW_{12}O_{40}^{4-}$ (ionic weight 2875) and $SiMo_{12}O_{40}^{4-}$ (ionic weight 1820) are equal. This of course led to the conclusion (which was apparent previously) that the diffusion coefficients depend only on the ionic radius but not on the ionic weight.

Arbitrary interpretation of the results of thermogravimetric analysis and of other methods led to the assertion that heteropolyacids with the Keggin structure have a large number of dissociable protons [1] and doubts were actually cast on the results of X-ray diffraction analysis. In this connection it is useful to consider briefly the methods used to investigate heteropolycompounds. Evidently none of the individual methods can provide an unambiguous answer as to the nature of the existing forms of heteropolycompounds.

The first method used to determine the stoichiometric coefficients of the complex formation reaction products was quantitative analysis. More than 100 year ago, Marignac [87] carried out a major crystallographic and quantitative analytical study of complex compounds which were subsequently called heteropolycompounds. Here we must emphasise the importance of chemical analysis in relation to compounds where one of the metal atoms forming the coordination sphere is substituted by another metal atom, since in this case incorrect conclusions have been reached concerning the structures of the resulting compounds. For example, Baker and McCutcheon [88] reported the discovery of a new class of compounds, which they called diheteropolycomplexes, with the ratios M : X : Y = 12 : 1 : 1, where Y is a transition metal. Subsequently other studies were published [89], where the preparation of similar compounds was claimed. However, later these views were revised [28,90] and evidence was obtained showing that the second heteroatom substitutes one tungsten (or molybdenum) atom in the coordination sphere, the Keggin structure remaining unchanged. The discrepancy between the analytical results for the 11 : 1 and 12 : 1 compounds is

very small (11 : 1 = 12 : 1.09) and therefore the results of chemical analysis alone may prove to be unreliable.

In the potentiometric determination of the number of dissociable protons in heteropolyacids it is always necessary to take into account the possibility of the decomposition of the anion on increase of pH. Souchay [3] was able to show that a slight increase of the alkalinity of a solution of heteropolyacids leads to the formation of the anions of unsaturated heteropolyacids:

$$PMo_{12}O_{40}^{3-} + OH^- \rightarrow PMo_{11}O_{39}^{7-} + MoO_4^{2-} \text{ (or } Mo_6O_{24}^{6-}).$$

Therefore, in order to avoid the decomposition of the anion, Keller et al. [91] determined spectrophotometrically the degree of ionisation of heteropolyacids. These results show that the number of dissociable protons in heteropolyacids with the Keggin structure is small.

The spectrophotometric method (the molar ratio and isomolar series procedures) and also the method based on the variation of the pH of solutions as a function of the amount of heteroatoms introduced are widely used to determine the stoichiometric coefficients in complex formation reactions [92]. However, the interpretation of the results is fairly difficult and frequently indefinite so that it is difficult to determine reliably the equivalence point for high ratios such as 12 : 1. For this reason, the conclusions based on these data must be approached with much caution.

The method of salt cryoscopy, based on the decrease of the $Na_2SO_4.10H_2O \rightarrow Na_2SO_4 + 10H_2O$ transition temperature in the presence of various ions, is frequently used to determine the degree of condensation [56,77,93-95]. It was shown with the aid of this method that the hexamolybdochromate, hexamolybdoaluminate, and hexamolybdogallate ions as well as the 11 : 1 : 1 complexes (Co–Ga, Mn–Ga, Cr–Ga) are monomeric and that decomposition products are absent. A recent thermodynamic examination of this method [96] showed that it has a reasonable theoretical basis. The method involves a number of difficulties: (1) the necessity to know the exact H^+ and HSO_4^- concentrations, since they contribute to Δt and (2) the impossibility of extrapolation to infinite dilution when Δt varies with concentration. The application of certain methods requires extrapolation to infinite dilution in order to create nearly ideal conditions. Analysis of light scattering and ultracentrifugation data showed [97-99] that large anions bind the counterions from the salt medium to a considerable extent. In solutions where concentration influences the position of equilibrium, such extrapolation is impossible. Light scattering and equilibrium ultracentrifugation as well as sedimentation (methods which supplement one another) make it possible to establish the effective ionic weight of the anion in solution, usually the dominant ion, provided that the solutions are monodisperse and provided that the degree of polymerisation of the solutes is not influenced by dilution. Light scattering data [97] showed that, in solutions with the W : P = 12 : 1 and 9 : 1 ratios, there are monomeric and dimeric species respectively, i.e. W : P = 18 : 2. The results of sedimentation [100] and ultracentrifugation [101] studies on dodecamolybdophosphoric acid showed that it is fairly unstable and forms an anion with the ratio Mo : P = 11 : 1.

Ion exchange is used not only for preparative purposes (for the synthesis of heteropolyacids in a free state) but also permits an indirect determination of the ionic charge and also the stability of heteropolyanions. However, the determination of the charge of the anion yields no information about its structure, since the anion, which can formally have a large charge, frequently binds counterions from the supporting electrolyte and its overall effective charge does not exceed −6.

The origin of the absorption bands in the ultraviolet spectra of heteropolycompounds has been hardly considered [102-108]. There is no doubt that the absorption bands with extinction coefficients of the order of 10^4-10^5 are due to electron transfer from orbitals localised mainly at oxygen atoms to orbitals localised at the metal atoms forming the coordination sphere. The nature of the ultraviolet spectrum changes appreciably as a function of the structure of the anion and its symmetry [107]. A decrease of symmetry leads to the splitting of the absorption bands [104]. The similarity of the ultraviolet spectra constitutes satisfactory confirmation that the structures of the anions are the same [105]. A purely qualitative employment of ultraviolet spectra enabled Strickland [106] to detect isomeric forms of the dodecamolybdosilicate anion and to investigate the kinetics of their interconversion.

The absorption spectra of aqueous solutions in the region of $d-d$ transitions have been used to investigate the coordination and also to determine the degree of oxidation of both the central atom and of the metal ions entering into the coordination sphere [109,110]. $Na_3CrO_6Mo_6O_{18}.H_6$ (D_{3d}), the luminescence spectra of which are observed even at room temperature, has unusual spectroscopic properties [111]. This phenomenon is unknown for other chromium(III) complexes. On the basis of the calculated and experimental absorption bands in the visible spectra of solutions of dodecamolybdouranic and dodecamolybdoneptunic acids, it was shown that uranium [67] and neptunium [68] in these compounds are in the +4 oxidation state. It is noteworthy that in all instances the absorption bands due to the metal ion in the coordination sphere are appreciably more intense than in the spectra of the usual complexes. Comparison of the absorption spectra of solutions of compounds of the type $MXW_{11}O_{40}H_2^{n-}$ with the reflection spectra of crystalline specimens shows that the environment of the metal ions in the structure of the anion remains unaltered [109]. The study of the absorption spectra of lanthanide heteropolytungstates [59] permitted the determination of the coordination of the Ln ion.

The hyperchromic effect observed in the reduction of one or several metal atoms forming the coordination sphere, i.e. the formation of heteropolyblues, is due to the valence change $MV \rightarrow MVI$, [112] since the usual $d-d$ transitions have much lower extinction coefficients at $\nu \simeq 10-14\,000\ cm^{-1}$. This effect has been used in analytical practice for the quantitative determination of certain elements.

Redox titration and also magnetic measurements have been used for the direct determination of the degree of oxidation and the site of the metal ion in the heteropolycompound.

An anomalous magnetic behaviour of certain heteropolycomplexes was pointed out [28] in 1966. When two cobalt atoms (bivalent and tervalent) were present in the heteropolyanion, an intense intraionic paramagnetic interaction was observed and the magnetic susceptibility of the compound changed by only 13% between −143° and +23°C. This was also noted [89] for the complex $FeNiW_{11}O_{40}H_3^{6-}$. Quite recently these complexes as well as certain others [113] were used to investigate the spin–spin interaction between the paramagnetic ions forming part of the structure of the anion. It was emphasised that the heteropolyanions constitute a very interesting and convenient model in which the second metal atom always occupies a site with the same arrangement of oxygen atoms around it. It has been shown for the 12 : 1 copper heteropolycompound,

which is a convenient model for the investigation of electron transfer processes in copper-containing enzymes, that copper retains its tetrahedral environment in the transition $Cu^{2+} \rightarrow Cu^{+}$.[114]

The polarographic method has been used widely to investigate heteropolycompounds[84,115-124]. The conditions governing the formation of different $XM_{12}O_{40}^{X-8}$ isomers have been determined polarographically[84,117]. The electronic structures of the reduced forms (the so called heteropolyblues) are analogous to the structures of the tungsten bronzes, but there is one difference: the reduced forms are discrete (i.e. they do not give rise to polymeric species) and are soluble in water. The magnetic[121] and spectroscopic properties of reduced heteropolycompounds[108] have been investigated and it has been shown that the first electrons added are located at specific molybdenum or tungsten atoms and that as a result of further reduction the electrons introduced are located in the common delocalised orbital of the coordination sphere. Examination of the bonds in the anion with the Keggin structure (the formation of π-bonds in the coordination sphere so that the structure becomes a π-conducting system)[118] has shown that the reduction of the heteropolyanion may be compared with the reduction of polycyclic aromatic hydrocarbons with formation of the corresponding anions.

An increase of the number of electrons introduced leads to a shift of the region of stability of the heteropolyanion towards higher pH values[117]. It has been shown by X-ray diffraction that the reduced forms retain the Keggin structure[125]. In the general case 12-heteropolyphosphate anions are reduced more readily than the silicon analogues, since the charge of the latter is higher. Heteropolymolybdates have a higher oxidising capacity than heteropolytungstates.

The energies of the first charge-transfer band, observed in the ultraviolet spectra of heteropolyacids, have been correlated[103] with the reduction half-wave potential and it has been shown that the lower the first vacant antibonding orbital the higher the oxidising capacity of the heteropolyanion. The reduction of the heteropolyanions XMo_6O_{24} (D_{3d}) leads to their decomposition[124]. This example and also data for the reduction of the anions[120] $XMo_{12}O_{42}^{8-}$ (T_h) indicate differences between the structures of the anions and the environments of the molybdenum atoms. There is no unanimous view concerning the mechanism of the reduction process. Moreover it is quite probable that the employment of chemical reducing agents frequently used in analytical practice ($SnCl_2$, ascorbic acid, etc.) can lead to irreversible processes and the formation of unknown compounds with the initial heteropolycompounds. These phenomena and also the fact that, with increase of the number of electrons introduced, the maximum of the valence-change bands shifts towards shorter wavelengths, will undoubtedly affect the interpretation of the results. For this reason, studies[126] in which the reduction of heteropolyacids by an $SnCl_2$ solution was investigated quantitatively are not fortuitous.

^1H NMR has been widely used to determine the proton groups within the structure of heteropolycompounds[52,127-130]. It has been shown that acid protons in heteropolyacids with the Keggin structure are present in the form of H_3O^+.[127-129] Moreover, it has been established that such acids have a small number of dissociable protons. In contrast to these acids, some of the protons in heteropolymolybdoceric(IV), heteropolymolybdothoric, heteropolymolybdouranic, and heteropolymolybdoneptunic acids are present as H_3O^+ and some are present as OH^- groups, the number of dissociable protons in the acids being eight[68,129]. It has been shown for metatungstic acid, which gives rise to the anion $H_2W_{12}O_{40}^{8-}$ (T_d symmetry), that there are two protons in the tetrahedral cavity. In aqueous solutions the signal due to these protons is displaced towards lower fields by 1.0–1.4 p.p.m., relative to the water signal. This indicates a pronounced insulation of these two protons by the polytungstate shell, which can be clearly seen from Fig. 1*b*.[131]

NMR spectroscopy involving heavy nuclei (^{17}O, ^{31}P, and many others which have non-zero spins) yields valuable information about the molecular and electronic structure of the heteropolyanion[132]. The effect of the metal entering into the coordination sphere on the oxygen atoms has been traced, for example, on the basis of the chemical shifts in ^{17}O NMR of both simple and mixed heteropolyacids. The ^{27}Al NMR spectra of aluminium heteropolytungstate clearly indicate a tetrahedral arrangement of atoms around aluminium.

It is interesting that high-resolution ^1H NMR spectra make it possible to follow the *trans*-influence of the central atom X via the inner oxygen atom on the ligand Y in the heteropolyanions $XW_{11}CoO_{39}Y$, where Y is pyrazine[133]. ^1H NMR spectra in organic media[134] have shown that $XMo_{12}O_{40}^{X-8}$ exhibits a lower tendency towards the formation of hydrogen bonds than does ClO_4^-. This indicates yet again the low negative charge density (-4 over a sphere with $r = 5.6$ Å) on the surface of the anion.

The present authors' Mössbauer spectroscopic data indicate an effect by the molybdate and tungstate spheres on the iron(III) nucleus in the $SiM_{11}O_{39}Fe(H_2O)^{5-}$ ions, which have the same structures. This is correlated with ESR data for the same complexes[135]. ESR has been used to investigate the reduced $PW_{10}V_2^{IV}O_{40}^{5-}$ anions. It was shown that two vanadium(V) atoms are reduced to vanadium(IV) and that they occupy two non-equivalent positions in the structure of the anion, because the local crystal fields of the anion are directed at different angles with respect to the magnetic field[136].

Vibrational spectroscopy has not been widely used to investigate the molecular structures of heteropolyanions in view of their fairly considerable complexity, although a number of studies dealing with this problem have been published[137-143]. Vibrational spectroscopy can be very useful for the identification of the structures of new hitherto unknown compounds, since each type of structure of heteropolycompounds gives rise to fairly characteristic spectra in consequence of the differences in the structure of the anion. The employment of Raman spectroscopy, particularly with a laser source, permits the identification of the species present in solution, as has been done for vanadium, molybdenum, and tungsten isopolycompounds[142] and also heteropolyacids with T_h (Kazanskii et al.[141]) and T_d (Kazanskii[143]) symmetries. It was established that the structure of the heteropolyacids found in crystalline specimens persists also in aqueous solutions. Raman and infrared spectroscopy of the ether adducts of certain heteropolyacids[140] confirmed the retention of the structure of the anions in ether without any decomposition. The effect of the charge of the central atom X^{X+} is clearly shown in the Raman spectra of the heteropolyanions $XM_{12}O_{40}^{X-8}$ (i.e. there are *trans*- and *cis*-effects on the positions of the vibrational bands A_1 of the terminal M=O and bridging M–O–M groups). With decrease of x, the stability of the terminal M=O bonds falls[143].

Together with ^1H NMR, infrared spectroscopy is frequently used to investigate the nature of the water in heteropolycompounds[144,145].

Among other methods, which are purely qualitative, mention may be made of dialysis, which is used to determine the dimensions of the anions, and of chromatography, which has been employed to separate certain heteropolycompounds [146].

Interesting prospects arise in connection with the application of X-ray electronic spectroscopy to the study of the electronic structures of heteropolyanions. X-Ray electronic spectra of the inner $3d_{3/2}$ and $3d_{5/2}$ electrons of heteropolymolybdates and normal molybdates have been obtained [147]. The changes in charge distribution in the valence shell, occurring when the valent state of the atom is altered, influence all the inner levels and the results indicate a decrease of the positive charge on the molybdenum atoms in heteropolycomplexes compared with MoO_4^{2-}. According to X-ray electronic spectra [148], the binding energy of phosphorus $2p$ electrons is higher in $PW_{12}O_{40}^{3-}$ than in $PMo_{12}O_{40}$. This indicates a decrease of the positive charge in $PMo_{12}O_{40}$, which is correlated with results obtained from ^{31}P NMR chemical shifts and the vibrational spectra of these heteropolyanions [143,148].

Presumably much information about the electronic structures and charge distribution within and on the surface of heteropolyanions will be obtained from the photoelectronic spectra of the outer valence energy levels.

IV. PRINCIPAL TRENDS IN THE CHEMISTRY OF HETEROPOLYCOMPOUNDS

Apart from continued interest in the theoretical problems of the molecular electronic structure, the present state of the chemistry of heteropolycompounds is also characterised by the development of the synthesis of mixed and diheteropolycomplexes. Since the coordination sphere is made up of metal and oxygen atoms, heteropolycomplexes can serve as model compounds for the investigation of the chemistry of metal oxides. A wide range of physical methods can be used to investigate heteropolycompounds in a crystalline form, in aqueous and non-aqueous solutions, and in the recently discovered [133] gaseous state.

Many mixed compounds (sometimes one or several molybdenum atoms in molybdate coordination sphere are substituted by tungsten or vanadium) and diheteropolycomplexes (as defined by Baker), in which one atom of the coordination sphere is replaced by some other metal atom (usually a transition metal atom), have been obtained. They must be distinguished from true diheteropolycomplexes in which two atoms of the complex-forming agent are surrounded by the same atoms, which form the coordination sphere (cf. Figs. 2*a* and 5*a*).

We assigned to mixed compounds the complexes in the coordination spheres of which molybdenum, vanadium, or tungsten may be present jointly in the highest oxidation states in proportions of 11 : 1. The formation of these compounds is due to the general tendency of the ions of these elements to link up into polymeric structures. The resulting compounds are mainly complexes having the Keggin structure. Other known types are the mixed molybdotungstates $(NH_4)_4NiMo_{6-n}W_nH_6$, where $n = 0-6$ (Kokorin and Dimant [149]); the acids have been obtained from these salts in a free state.

We may quote several examples where one or several tungsten (or molybdenum) atoms in the coordination sphere are replaced by a vanadium atom. Much work has been done in this field by Kokorin and coworkers [150-168], who investigated the conditions governing the formation of heteropolycomplexes with different degrees of substitution of M by vanadium atoms. The corresponding acids were isolated, for example $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$, and $H_6PMo_9V_3O_{40}$, which decompose at different rates with increase of pH. The synthesis of vanadomolybdenum acids with substitution of up to ten molybdenum atoms, for example of the anion $PV_{10}Mo_2O_{40}^{13-}$, was reported recently [161].

Studies on the electron diffraction patterns of decamolybdotrivanadogermanic acid and of the powder diffraction patterns of hexamolybdohexatungstophosphoric acid [163] confirmed the retention of the Keggin structure in the substituted complexes.

Apart from studies on theoretical problems of mixed heteropolyacids (bond strengths, electronic and molecular structures, oxidation–reduction properties etc.) much effort has been devoted to the determination of the number of dissociable protons in these acids in both aqueous and non-aqueous media. A parallel is frequently drawn with the initial acids ($H_{x-8}XO_4$), although these analogies have no theoretical basis. It is clear from structural considerations that, following the substitution of one molybdenum atom by a vanadium(V) atom, the charge of the anion should increase by -1, since the structure of the anion persists, i.e. the number of oxygen atoms in the anion remains 40. The fact that the number of dissociable protons in the acids is sometimes inconsistent with this suggests instability of the anion, the occurrence of additional equilibria, and changes in the degree of dissociation of protons as the dielectric constant of the solvent is varied.

On the other hand, when a highly charged ion (for example, Zr^{4+}, Ti^{4+}, Th^{4+}, or Nb^{5+}) is introduced into a solution of heteropolyacids, the so called "ternary" complexes are formed. It has been claimed on the basis of spectrophotometric data only [169,170] that phosphorus, niobium, and oxygen form a "central molecule" (a niobium phosphate the composition of which varies with the medium and the pH) surrounded by a molybdate coordination sphere. Later the formation of a zirconium molybdophosphate complex of the same type was postulated [171]. However, subsequently it was shown [172] on the basis of the infrared spectra of solid complexes containing zirconium, titanium, and thorium that the ions of these elements substitute molybdenum in the coordination sphere with formation of mixed heteropolycomplexes. Heteropolycomplexes in which molybdenum is substituted by niobium, for example $PMo_{10}Nb_2O_{40}^{5-}$, have also been obtained and characterised [29]. Dodecamolybdovanadoselenic acid $H_6SeMo_{10}V_2O_{40}.xH_2O$ was obtained by extraction with ether and partly characterised [173].

We shall not consider the numerous studies (see the references in Spitsyn and Torchenkova's paper [174]) in which the preparation of two heteropolycompounds in solution is reported without proof of their individuality. Of the latest studies, we shall mention the isolation of salts of heteropolycompounds, in which rhenium(VI), for example, substitutes a molybdenum atom in 12 : 1 and 18 : 2 molybdophosphate anions. The free acids have been obtained from these salts by ion exchange [175]. We may note that the unsaturated heteropolyacid $H_6[CrW_{11}O_{39}H_3]$ was recently obtained in solution, although unsaturated heteropolyacids with the Keggin structure [176] are not usually formed in a free state. However, one may postulate the formation of a diheteropolycomplex the central cavity of which contains two protons.

Heteropolytungstate complexes with phosphorus(III) and arsenic(III) have been obtained [177]. The X-ray diffraction

study being carried out should reveal certain structural features of these compounds.

It was shown[28] in 1966 that the coordination sphere of the anion with the Keggin structure (Fig. 1) or the Dawson structure (Fig. 2*a*) can incorporate one transition metal atom (usually belonging to the 3*d* group) with simultaneous displacement of one molybdenum or tungsten atom and the formation of a new complex having the general formula

$$[H_hM^{m+}O_6X^{x+}O_4(\text{Mo or W})_{11}O_{30}]^{m+x+h-14}.$$

On the other hand, if the sixth coordination site of the transition element is occupied by another ligand, then

$$[Y^{y-}M^{m+}O_5X^{x+}O_4(\text{Mo or W})_{11}O_{30}]^{m+x-y-13}$$

or

$$\{Y^{y-}M^{m+}O_5[(P^{5+} \text{ or } As^{5+})O_4]_2(\text{Mo or W})_{17}O_{48}\}^{m-y-10}$$

where Y is a monodentate ligand which occupies the site of a non-delocalised oxygen atom; this can be ammonia, pyridine, pyrazine, a halide ion, etc. For a bidentate ligand, there is a possibility of the binding of two anions via this ligand and of the formation of a compound heteropolycomplex in the form of a dumbell whose molecular weight exceeds 6000. The existence of such complexes, which may incorporate a wide range of ligands and different metal atoms, greatly extends the range of complexes under consideration. The inclusion of the metal ion M^{m+} in the coordination sphere via five oxygen atoms leads to a possible overlapping of different atomic orbitals, which is reflected in unusual values of the Racah parameters and unusual magnetic properties and electrical conductivities of the anionic framework. From the standpoint of the investigation of the spectroscopic properties of the injected heteroatom (Baker's definition), these heteropolycomplexes constitute a very convenient model, since the metal ion always has the same environment and only a change in the type of ligand and also the influence of the coordination sphere can affect the spectra. The existence of this new group of compounds has been demonstrated by the following methods: (1) by the analysis of the recrystallised pure products in which the ratios Y : M : X : Mo(W) were 1 : 1 : 1 : 11 (this must be confirmed by determining the molecular weight from the results of crystal-chemical studies); (2) by ion-exchange experiments, which showed that the resin in the K^+-form does not contain M^{m+}; (3) by determining the degree of oxidation of M^{m+} by oxidation-reduction titration; (4) by magnetic measurements; (5) by cryoscopy in $Na_2SO_4.10H_2O$; (6) by studying the absorption spectra of both solutions and solid heteropolycomplexes in the region of $d-d$ transitions; (7) by polarography; (8) on the basis of the isomorphism of the crystals.

The central atom X^{x+} can be P^{5+}, Sr^{4+}, Ge^{4+}, H_2^{2+}, Co^{2+}, B^{3+}, Fe^{3+}, and Zn^{2+} and the metal M entering into the coordination sphere[178-187] can be Co^{2+}, Co^{3+}, Ga^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Mn^{3+}, Cr^{3+}, and Al^{3+}; the molybdenum analogues are less stable. Complexes with doubly charged metal ions are stable at pH ~ 4, but the corresponding acids have not been obtained, since, on being passed through a cation exchanger in the H^+-form, they split off M^{2+} and only the initial 12 : 1 heteropolyacids were produced. For triply and more highly charged ions, the new heteropolycompounds are fairly stable in acid media, M^{3+} ions are not split off in the presence of the cation exchanger, and for this reason the acids have been obtained in a free state. Derivatives of the $X_2MW_{17}O_{61}^{n-}$ anion, in which $X = P^{5+}$ or As^{5+} and one tungsten atom is substituted by a metal ion (Mn^{2+}, Co^{3+}, Ni^{2+}, or Zn^{2+}), have also been investigated; the properties of these compounds are analogous to those of the complexes $MXW_{11}O_{40}^{n-}$.

Apart from the above data for the formation of the new class of heteropolycompounds which have the Keggin structure and the reactions in which they are synthesised (these can be classified as complex formation reactions), we shall consider cases where the second heteroatom cannot enter the inner sphere and remains on the surface of the anion. When conditions for the formation of anions of the type $XW_{11}O_{39}^{n-}$ or $XW_{17}O_{61}^{n-}$ are created (pH ~ 4–6) and the solution contains a cation with a large radius, for example a lanthanide ion (Ln radius = 1.0 Å), a complex with the ratio An : Ln = 2 : 1 is formed. The $XW_{11}O_{39}^{n-}$ anion provides four electron-donating sites, which are produced following the elimination of one metal atom from the coordination sphere; the lanthanide ion can retain two anions. The coordination number of the lanthanide is 8. On the basis of structural considerations, it is difficult to expect other possibilities in the formation of the complex apart from the manganese(IV) complex (Fig. 9), in which the Nb_6O_{19} ligands provide bridging oxygen atoms as electron-donating atoms. It is quite likely that the formation of compounds of this type is not typical for heteropolyanions having the Keggin structure and a low charge. All other oxygen atoms in the structure of the 12 : 1 anion (T_d) are sterically unsuitable for the formation of compound heteropolycomplexes.

The formation of complexes by the dodecamolybdocerate ion with the cations of lanthanide elements, thorium, niobium, tantalum, and other metals has also been established[67,188-191]. For example, the interaction of erbium chloride with molybouranic acid[67] led to the formation of a complex with the ratio Er : An = 2 : 1. However, compounds with the ratio Er : An = 4 : 3 were isolated in a solid state. It was shown that MO_6 is not split off in this case. The structural features of the $UMo_{12}O_{42}^{8-}$ anion are such that on the surface there are three terminal oxygen atoms of the three combined octahedra, which can make up the coordination polyhedron around the Er^{3+} ion. The erbium ion tends to "saturate" its coordinating capacity by forming complicated structures. This is also observed for $XW_{11}O_{39}^{n-}$ (An). The An : Ln = 1 : 1 complex has not been isolated, although its stability constant is much higher than that of the complex $LnAn_2$. In this case, as in many others, the problem must be solved by X-ray diffraction. With the introduction of modern diffractometer and high-speed computers, one may hope that these problems will be successfully solved.

In a brief review we naturally could not cover many literature sources, since our aim was to write a critical review and not a simple compilation of research results. Here we have presented general relations based on the latest X-ray diffraction studies, on which the understanding of many problems in the chemistry of heteropolycompounds depends.

In addition we endeavoured to show that, although heteropolycompounds were discovered more than a hundred years ago, their chemistry constitutes a fruitful and interesting field for both physicochemical research and for the investigation of new synthetic possibilities.

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