Notes

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Study of α- and β-Enneatungstosilicates and -germanates

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The heteropolyanions obtained with tungstate and molybdate are very numerous, differing in composition as well as in structure.[1,2] Beside these compounds, polyanions containing B^{III}, Si^{IV}, Ge^{IV}, P^{V}, and As^{V} are very similar. Until now, with the exception of the last two elements (which can form several compounds of varied composition), heteropolyanions have belonged to the 1:11 and 1:12 series, corresponding to the formulas $SiW_{11}O_{39}^{8-}$ and $SiW_{12}O_{40}^{4-}$. Isomers of SiW_{12}[3] and BW_{12} were described a long time ago.[4,5] In both cases, one of the isomers occurs in small amounts and their preparation required fractional crystallizations. In the 1960's, two isomers, denoted α and β, of 12-molybdo polyanions were described.[6-9] For all of these compounds the occurrence of isomers has been proved only for the 1:12 series. This note reports the synthesis and characterization of 9-tungstosilicate and -germanate isomers which are formed before the 1:11 and 1:12 complexes.

By analogy with 1:12 molybdo heteropolyanions, the easily reducible 12-tungstosilicate (or germanate) is named β and the other one α. The 1:9 and 1:11 heteropolyanions which give an α-12-tungsto heteropolyanion in acid solution will be called α and conversely.

Experimental Section

Preparation of Compounds. Sodium α-9-Tungstosilicate. Sodium tungstate (182 g) and 11 g of sodium silicate were dissolved in 200 mL of water. Hydrochloric acid (6 M, 130 mL) was added with stirring. The solution was then boiled for 1 h and concentrated to 300 mL. Eventually, the silica residue was filtered off. A solution of 50 g of anhydrous sodium carbonate in 50 mL of water was added. Then, the lukewarm solution was gently stirred and the sodium salt of the α-9-tungstosilicate precipitated.

Anal. Calcd for $Na_{10}SiW_9O_{34}\cdot18H_2O$: Na, 8.3; W, 58.1; H_2O, 11.6. Found: Na, 8.4; W, 58.4; H_2O, 11.8.

Sodium α-9-Tungstogermanate was prepared in the same way.

Anal. Calcd for $Na_{10}GeW_9O_{34}\cdot18H_2O$: Na, 7.9; W, 56.8; H_2O, 11.1. Found: Na, 8.2; W, 57.1; H_2O, 11.3.

Sodium β-9-Tungstosilicate. Sodium silicate (12 g) was dissolved in 250 mL of cold water and 150 g of sodium tungstate was added. Hydrochloric acid (6 M, 95 mL) was slowly poured into the vigorously stirred solution. The silica was filtered off and the solution was left to stand at room temperature. The sodium salt slowly crystallized after some hours.

Anal. Calcd for $Na_9SiW_9O_{34}H\cdot23H_2O$: Na, 7.3; W, 58.1; H_2O, 14.5. Found: Na, 7.5; W, 57.5; H_2O, 14.5.

Sodium β-9-tungstogermanate was prepared in the same way.

Anal. Calcd for $Na_9GeW_9O_{34}H\cdot23H_2O$: Na, 7.2; W, 57.2; H_2O, 14.3. Found: Na, 7.3; W, 56.9; H_2O, 14.5.

Analytical Procedures. Tungsten was precipitated with cinchonin and weighed as WO_3 after heating the precipitate at 600 °C. Silica and germanium were not titrated. The W/Si and W/Ge ratios were indirectly established by amperometric determination of the amount of tungsten needed to quantitatively make α- or β-SiW_{12} and -GeW_{12}. Sodium determination was carried out by atomic absorption. The number of water molecules was determined by thermogravimetric analysis with the Cahn RG balance using a 5–10-mg sample.

Table I. Half-Wave Potentials Measured against a Saturated Calomel Electrode at 25 °C and Numbers of Electrons of α- and β-Enneatungstosilicates and -germanates

	pH 4.7		pH 8.5	
	$E_{1/2}$, V	n	$E_{1/2}$, V	n
α-SiW_9	−0.78	4	−1.12	2
			−1.20	2
			−1.27	4
β-SiW_9	−0.80	2	−1.12	2
	−0.90	2	−1.22	2
			−1.37	4
α-GeW_9	−0.78	2	−1.13	2
	−0.86	2	−1.25	2
			−1.38	4
β-GeW_9	−0.80	2	−1.13	2
	−0.90	2	−1.25	2
			−1.42	4

Results

Polarograms. Half-wave potentials of the polyanions are given in Table I. They are relatively similar. However, since the number of involved electrons at pH 4.7 is different, isomers can be easily distinguished. In every case, the use of a linear variation of the potential applied to a stationary drop proves that redox systems are fast.

Stabilities and Relation between 1:9 and 1:11 Heteropolyanions. At equilibrium, the protometric titration curves of the 9-tungstosilicates show that it is impossible to define a range of pH in which they could be quantitatively formed. As a result, both compounds are metastable and can only be obtained owing to the low solubility of their sodium salts. The fresh aqueous solutions of these salts have a pH of 9–10 which corresponds to the best conditions of occurrence in solution.

Ultracentrifugation of fresh solutions, treated by the Archibald method, gives a molar weight of about 2800. This result proves that the polyanions are monomers in solution.

These solutions spontaneously change. For basic or not very acid pH, the polyanions XW_9 give the species XO_3^{2-} and WO_4^{2-} and the 11-tungsto heteropolyanion. The final composition of the solution and the rate of transformation depend on the pH: the lower the pH, the greater the proportion of XW_{11}. It is worth pointing out that there is no isomerization of β-SiW_9 and β-GeW_9 into α isomers as opposed to compounds of both the 1:11 and 1:12 series.[10]

The transformation of SiW_9 into SiW_{11} can be studied by polarography and by protometric titration of a mixture of α- or β-SiW_9 and $2WO_4^{2-}$. The titration curves show an equivalent point for six H_3O^+ added per α-SiW_9 and five H_3O^+ per β-SiW_9. The polarograms of the final solution prove the formation of α-SiW_{11} and of a β-11-tungstosilicate (short name β_1-SiW_{11}) by the schemes

$$\alpha\text{-}SiW_9O_{34}^{10-} + 2WO_4^{2-} + 6H_3O^+ \rightarrow \alpha\text{-}SiW_{11}O_{39}^{8-} + 9H_2O \qquad (1)$$

$$\beta\text{-}SiW_9O_{34}H^{9-} + 2WO_4^{2-} + 5H_3O^+ \rightarrow \beta_1\text{-}SiW_{11}O_{39}^{8-} + 8H_2O \qquad (2)$$

β_1 is used because two other isomers of the 1:11 series (β_2, β_3), easily recognizable from their polarograms, can be obtained from β_1.[10]

The rates of eq 1 and 2 can be compared by having both isomers reacting simultaneously with tungstate in a competitive way: about 15% of β_1-SiW_{11} and 85% of α-SiW_{11} are formed.

Discussion

α- and β-9-tungstophosphate and -arseniate with properties similar to those of 9-tungstosilicates have also been obtained.[10]

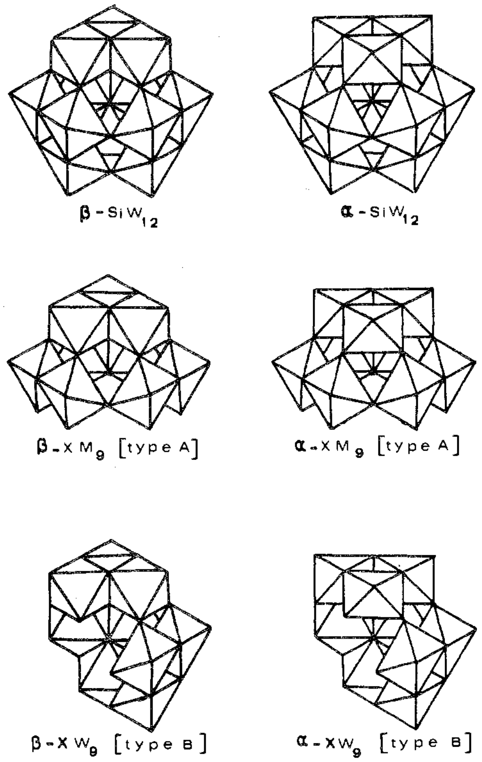

Figure 1. Idealized structures of α and β isomers of dodecatungstosilicates and type A or B ennea heteropolyanions. The central tetrahedron has been omitted for clarity.

The following discussion is related to all of these compounds. In the first part, this discussion attempts to propose structures for α- and β-9-tungsto heteropolyanions. Then, in the second part, formation paths of 1:12 and 2:18 heteropolyanions will be proposed.

(1) Every 1:9 polyanion gives 1:11 and 1:12 heteropolyanions by very fast reactions. Therefore, it may be assumed that no important changes in structure occur. This suggests that 1:9 polyanions have an open structure deriving from α-1:12 or β-1:12 structures. Such an assumption is confirmed by vibration spectra of the α-SiW_{12}, α-SiW_{11}, and α-SiW_9 anions.[11] Deltcheff and Thouvenot have found that the general appearances of the spectra are similar. However, in the stretching region, a significant decrease of frequencies with respect to the sequence SiW_{12}–SiW_{11}–SiW_9 occurs; it is correlated to the progressive decrease of the polyanion cohesion.

The structures of α- and β-12 heteropolyanions, solved by crystallography,[12-18] are shown in Figure 1. Four W_3O_{13} groups are associated around a central tetrahedron XO_4. The α isomer has the T_d symmetry and the idealized β isomer has the C_{3v} symmetry. The 1:12 structures can be converted into 1:9 structures in two ways: by removing three W from three different W_3O_{13} groups (in this paper this structure will be named "type A"); by removing three W from the same W_3O_{13} group (this structure will be named "type B").

There are many possible geometric isomers for the type A-XM_9, depending on the fact that the withdrawn tungsten atoms belong to adjacent (most probable case) or nonadjacent sites. One of them has been already described: the α-9-molybdophosphate $PMo_9O_{34}H_6^{3-}$.[19] Its structure[20,21] shows that the three vacant metallic sites actually are adjacent.

The properties of α- and β-9-tungstosilicates and -germanates described in this note (and the analogous polyanions obtained with P^V and As^V) can be compared with those of A-α-PMo_9: A-α-PMo_9 is formed in acid solution and dimerizes into α-P_2Mo_{18}; our complexes are obtained in basic solution and they do not dimerize into α- or β-X_2W_{18} in acid solution though X_2W_{18} are well-known with P^V and As^V. Therefore, it is most unlikely that their structures are of the same type as A-α-PMo_9. One can thus assume that they have a type B structure. The B-β-XW_9 (C_s symmetry) differs from the B-α-XW_9 (C_{3v} symmetry) by rotating one of the three remaining W_3O_{13} groups (Figure 1). It is worth pointing out that there is a special X–O bond with the oxygen bound only to the central X atom. A p_π–d_π overlap is probably a stabilizing factor and it can lead, even for the α isomer, to an important deformation of the central tetrahedron. As a matter of fact, if the central atom is boron, no 1:9 heteropolyanion has been obtained.[22] Boron has no d orbital available.

Table II. Types (A or B) of the Known Enneamolybdo and -Tungsto Heteropolyanions

	Si^{IV}	Ge^{IV}	P^V	As^V
Mo	B	B	A, B	A, B
W	B[a]	B[a]	B[a]	B[a]

[a] Two isomers α and β are known.

This structural hypothesis may be checked with mixed heteropolyanions α- or β-$SiW_{12-x}Mo_xO_{40}^{4-}$ (x = 1, 2, or 3) prepared from α- or β-SiW_9 by Fruchart. The visible absorption spectra of reduced derivatives are characterized by intervalence-transfer bands between reduced and unreduced metallic centers. These spectra can only be interpreted by a type B structure (i.e., Mo atoms are in the same group M_3O_{13}) but not by a type A one.[23]

(2) Table II summarizes the known ennea heteropolyanions with M = W or Mo. We propose the paths

$$\left.\begin{array}{c} X + M \rightarrow B\text{-}\beta\text{-}XM_9 \rightarrow \beta\text{-}XM_{11} \\ \downarrow \\ B\text{-}\alpha\text{-}XM_9 \rightleftharpoons \alpha\text{-}XM_{11} \end{array}\right\} \rightarrow \left\{\begin{array}{l} XM_{12} \\ \text{or} \\ A\text{-}XM_9 \rightarrow X_2M_{18} \end{array}\right.$$

leading to 1:12 and 2:18 polyanions.

Until now, the first product obtained by gradual acidification of tungstate and XO_4^{2-} is the B-β-XW_9. In contrast, the B-α-9-tungstosilicate and -germanate can only be obtained by hydrolysis of the α-11-tungstosilicate and -germanate.

Both B-XM_9 can be transformed by adding MO_4^{2-}. The reaction gives XM_{11} (α or β) and, in more acid solution, XM_{12}. If this latter is very stable (Si and Ge), the reaction stops. If it is not very stable (P) or unstable in aqueous solution (As), the polyanion A-XM_9 can be formed and dimerizes. The two paths seem to occur simultaneously in the P–Mo and As–Mo systems.[24] Until now, we have been unable to observe the polyanions A-PW_9 and A-AsW_9. This may be explained by an equilibrium state with strongly prevailing dimerization.

Conclusion

This work gives evidence of a new type of 1:9 heteropolyanion: two isomers, α and β, of enneatungstosilicates and -germanates have been isolated in basic solution. The β isomer appears as the first step in the synthesis of heteropolyanion species. These compounds, labeled type B, are different from the previously mentioned ennea heteropolyanions obtained in acid solution, labeled type A. Structural differences between these complexes have been proposed.

Registry No. Sodium α-9-tungstosilicate, 62682-79-5; sodium α-9-tungstogermanate, 62682-77-3; sodium β-9-tungstosilicate, 62682-78-4; sodium β-9-tungstogerminate, 62682-76-2; sodium tungstate, 13472-45-2; sodium silicate, 1344-09-8; sodium germanate, 12025-19-3.

References and Notes

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Electron Spin Resonance Spectra and Spin-Hamiltonian Parameters for Trigonal-Bipyramidal Nickel(I) and Copper(II) Complexes

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The ESR spectra of five-coordinate trigonal-bipyramidal copper(II) complexes have been far less investigated than those of complexes which can be considered as derived from octahedral or tetrahedral stereochemistries.[2] The data for other d^9 ions are still scarcer. In particular no ESR data have been reported up to now in the literature for trigonal-bipyramidal nickel(I) complexes, although several well-documented and relatively stable compounds of this kind have been recently synthesized and characterized.[3,4] In all reported cases of trigonal-bipyramidal copper(II) complexes[5-7] the observed pattern exhibited $g_{\parallel} = 2.0023 = g_e < g_{\perp}$ suggesting that the unpaired electron had to be placed in an orbital which was mainly metal d_{z^2}. However both positive and negative deviations of $g_{\parallel}$ from g_e were observed. In particular $g_{\parallel}$ values sensibly lower than g_e were observed in the frozen-solution spectra of $[CuX(Me_6tren)]^+$ (where Me$_6$tren is tris(2-dimethylaminoethyl)amine and X = Br, I),[7] with higher deviations for the iodide as compared to the bromide derivative. On the other hand $g_{\parallel}$ values slightly higher than g_e were reported for some complexes[5,6] in which all donor atoms had low spin–orbit coupling constants.

Some explanations were put forward for interpreting this behavior, but since these were based on solution spectra,[7] the nature of low-symmetry components of the ligand field could not be assessed. In order to eliminate these inconveniences we resolved to study the single-crystal ESR spectra of chromophores possessing as high symmetry as possible, however not less than C_3. The only suitable examples of copper(II) complexes, to the best of our knowledge, are $CuX(Me_6tren)X$ and $Cu(NH_3)_2Ag(SCN)_3$ whose x-ray structures have been reported[8,9] and the copper atoms have been found to possess C_3 and D_3 site symmetry, respectively. We wish to report now the ESR spectra of $CuX(Me_6tren)X$ doped into the isomorphous zinc salts and the variable-temperature spectra of $Cu(NH_3)_2Ag(SCN)_3$. Further, unpublished work of our laboratory[10] has shown that the d^9 ion nickel(I) has C_3 site symmetry in the trigonal-bipyramidal complexes NiX(np$_3$) (X = Cl, Br, I; np$_3$ = tris(2-diphenylphosphinoethyl)amine) and we wish to report here their powder ESR spectra.

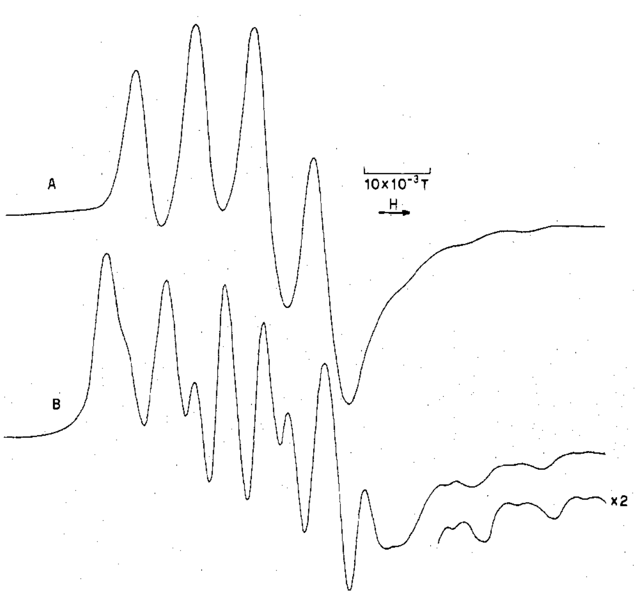

Figure 1. Polycrystalline powder ESR spectra of the CuX(Me$_6$tren)X complexes doped into the zinc isomorphous salts: A, X = Br; B, X = I.

Table I. Spin-Hamiltonian Parameters for Trigonal-Bipyramidal Copper(II) and Nickel(I) Complexes

	$g_{\parallel}$[b]	$g_{\perp}$[b]	$A_{\parallel}$[a,b]	$A_{\perp}$[a,b]
CuBr(Me$_6$tren)Br	1.956 (1)	2.182 (1)	+80 (5)	−100 (5)
CuI(Me$_6$tren)I				
Site 1	1.895 (1)	2.226 (1)	+97 (5)	−103 (5)
Site 2	1.922 (1)	2.189 (1)	+99 (5)	−107 (5)
$Cu(NH_3)_2Ag(SCN)_3$				
296 K	2.006 (1)	2.201 (2)		
233 K	2.004 (1)	2.201 (2)		
183 K	2.002 (1)	2.201 (2)		
133 K	2.001 (1)	2.201 (2)		
4.2 K	1.998 (1)	2.199 (2)		
NiCl(np$_3$)	2.001 (1)	2.210 (4)		
NiBr(np$_3$)	2.004 (4)	2.184 (4)		
NiI(np$_3$)	2.004 (4)	2.151 (4)		

[a] All hyperfine coupling constants in units 10^{-4} cm^{-1}. [b] The values in parentheses are the estimated errors.

Experimental Section

All of the compounds were prepared as previously described.[4,11,12] $Cu(NH_3)Ag(SCN)_3$ and NiX(np$_3$) were used undiluted, since attempts to prepare suitable diamagnetic hosts were unsuccessful. For the Me$_6$tren complexes about 1% copper-doped powders of the zinc complexes were obtained by slow evaporation of 1-butanol solutions. Powder and single-crystal spectra were recorded with a Varian E-9 spectrometer equipped with X band; variable-temperature spectra were recorded using an Oxford Instruments continuous-flow liquid helium cryostat and a Varian variable-temperature assembly.