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Ligand- and Metal-Exchange Reactions on Substituted Lacunary Heteropolytungstates

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Conditional ligand-exchange equilibrium constants are reported for several reactions of iron(III)-containing heteropolytungstates:

$$\mathrm{XFe^{III}(OH_2)W_{11}O_{39}}^{m-} + \mathrm{L} \rightleftarrows \mathrm{XFe^{III}(L)W_{11}O_{39}}^{n-} + \mathrm{H_2O}$$

$$\mathrm{X'_2Fe^{III}(OH_2)W_{17}O_{61}}^{7-} + \mathrm{L} \rightleftarrows \mathrm{X'_2Fe^{III}(L)W_{17}O_{61}}^{p-} + \mathrm{H_2O}$$

$$\mathrm{X = B, Si, Ge, P(V), As(V);\ X' = P(V), As(V);\ L = SO_3^{2-}, Fe(CN)_6^{4-}}$$

Less successful attempts to measure such equilibrium constants for L = $S_2O_3^{2-}$, SCN^-, and thiourea are described. The results are compared to data reported on aquo–iron(III) substitution reactions. Preparations of air-stable potassium or guanidinium salts are given for L = SO_3^{2-}, SCN^-, and $Fe(CN)_6^{4-}$. The hexacyanoferrate(II) derivatives of $BFe^{III}W_{11}O_{39}^{6-}$ and $AsFe^{III}W_{11}O_{39}^{4-}$ cannot be isolated. Some aspects of the infrared and UV–visible spectra and their incidence on possible bonding modes are discussed. Satisfactory data for metal-exchange reactions of the type

$$\mathrm{XM^{III}W_{11}O_{39}}^{m-} + \mathrm{M^{4+}(aq)} \rightleftarrows \mathrm{XM^{IV}W_{11}O_{39}}^{(m-1)-} + \mathrm{M^{3+}(aq)}$$

and

$$\mathrm{X'_2M^{III}W_{17}O_{61}}^{7-} + \mathrm{M^{4+}(aq)} \rightleftarrows \mathrm{X'_2M^{IV}W_{17}O_{61}}^{6-} + \mathrm{M^{3+}(aq)}$$

$$\mathrm{X, X'\ as\ above}$$

have been obtained for M^{3+} = In and M^{4+} = V (in VO^{2+} form) only. The values of these constants are 1–2 orders of magnitude smaller than those found for the analogous exchange reactions

$$\mathrm{XM^{II}W_{11}O_{39}}^{(m+1)-} + \mathrm{M^{3+}(aq)} \rightleftarrows \mathrm{XM^{III}W_{11}O_{39}}^{m-} + \mathrm{M^{2+}(aq)}$$

and

$$\mathrm{X'_2M^{II}W_{17}O_{61}}^{8-} + \mathrm{M^{3+}(aq)} \rightleftarrows \mathrm{X'_2M^{III}W_{17}O_{61}}^{7-} + \mathrm{M^{2+}(aq)}$$

Introduction

Most metal ions of radius <90 pm react with monolacunary heteropolyanions of Keggin- or Dawson-type structure[1] to fill the lacuna. The polyanion then functions as a pentadentate ligand.[2]

The general formulas of such monosubstituted heteropolyanions are $XM(L)M'_{11}O_{39}^{n-}$ (X (central heteroatom) = B, Si, Ge, P, As, Zn, Co, Fe, Ga, Al, etc.; M = most transition elements, group 3A elements, etc.; M′ = Mo, W; L = ligand completing the hexacoordination of M) and $X'_2M(L)M'_{17}O_{61}^{p-}$ (X′ = P, As; M, M′, L as above). They will, whenever feasible, be abbreviated, e.g. to $XM(L)M'_{11}$.

Usually the outer ligand L is a water molecule, which may be more or less deprotonated, depending on M and on the pH.[2a,c] Baker and Figgis first recognized that this aquo ligand can be replaced by ligands like pyridine and pyrazine.[2a] Landis recently reported quantitative data[3] on several $XM(L)W_{11}$ complexes, confirming the existence of $XW_{11}M\text{–}L\text{–}MW_{11}X$ "dumbbell" complexes. Some time before Weakley[2b] reported formation constants for the exchange reaction of several $XCo(OH_2)W_{11}$ polyanions with a number of, mainly nitrogen-bonding, ligands and isolated solid salts containing the substituted ligand. The formation constants of a number of metal-insertion reactions have also been measured;[4] they are of the order of 10^4–10^6 mol^{-1}. Likewise, exchange equilibrium constants have been estimated for reactions of the type $XZW_{11} + Z' \rightleftarrows XZ'W_{11} + Z$. The magnitude of such equilibrium constants is largely determined by the charge of Z and Z′; it ranges from 1 to 10 for XZW_{11}, Z and Z′ bivalent (exceptional values of ca. 200 for Z′ = Ni^{2+} are caused by differences in protonation of the oxygen atoms that surround Ni),[6] to >10^4 for XZW_{11}, Z bivalent and Z′ trivalent.[5b] No data have been published for reactions where Z is trivalent and Z′ tetravalent or higher valent.

Here we report (1) the preparation of new solid salts in which the aquo ligand of $XFe^{III}(OH_2)W_{11}$ and $X'_2Fe^{III}(OH_2)W_{17}$ has been completely displaced, (2) values of ligand-exchange equilibrium constants for reactions of $XFe^{III}(OH_2)W_{11}$ and $X'_2Fe^{III}(OH_2)W_{17}$ polyanions with $Fe(CN)_6^{4-}$ and SO_3^{2-} and attempts to measure such exchange equilibrium constants for SCN^-, $S_2O_3^{2-}$, and thiourea ligands, and (3) values of the metal-exchange equilibrium constants for the reaction of $XIn(OH_2)W_{11}$ and $X'_2In(OH_2)W_{17}$ polyanions with VO^{2+}. In all three cases X = B, Si, Ge, P(V), As(V) and X′ = P(V), As(V).

Experimental Section

Only the α isomers of both lacunary and substituted heteropolytungstates, prepared according to published procedures,[1b,2c,4b] were used; analytical grade $VOSO_4$ and (potassium salts of) exchange ligands were used as received. Analytical methods and instrumentation have been described.[2c] In addition, sulfite was determined iodometrically and gravimetrically as $SrSO_3$; $Fe(CN)_6^{4-}$ was also determined iodometrically (back-titration at pH 8 by As(III)); thiocyanate was weighed as CuSCN. Analytical data are given in Table I.

Preparations. $\mathbf{K_9XFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}\cdot \mathit{m}H_2O}$ (X = Si, Ge). To a warm (60 °C) solution of 8.0 g (ca. 0.0025 mol) of K_5XFe^{III}-

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Table I. Analytical Data of Ligand-Substituted Iron(III)-Containing Heteropolytungstates

	anal. found (calcd)					
compd	% K or $C(NH_2)_3$	% Fe^{III}	% W	% ligand[a]	% H_2O	% yield
$K_9SiFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}\cdot 23H_2O$	9.54 (9.49)	1.534 (1.506)	55.18 (54.53)	5.63 (5.71)	11.12 (11.18)	65
$K_9GeFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}\cdot 33H_2O$	9.14 (8.95)	1.434 (1.420)	51.49 (51.42)	5.44 (5.39)	15.09 (15.12)	60
$K_8PFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}\cdot 21H_2O$	8.71 (8.60)	1.538 (1.536)	55.47 (55.62)	5.81 (5.83)	10.45 (10.41)	35
$K_{11}P_2Fe^{III}[Fe^{II}(CN)_6]W_{17}O_{61}\cdot 29H_2O$	8.04 (7.99)	1.041 (1.037)	57.79 (58.05)	3.97 (3.94)	9.74 (9.71)	70
$K_{11}As_2Fe^{III}[Fe^{II}(CN)_6]W_{17}O_{61}\cdot 32H_2O$	7.92 (7.78)	1.019 (1.011)	56.41 (56.56)	3.80 (3.84)	10.50 (10.43)	60
$K_6SiFe^{III}(SCN)W_{11}O_{39}\cdot 10H_2O$	7.29 (7.32)	1.749 (1.743)	63.02 (63.14)	1.786 (1.813)	5.59 (5.63)	60
$K_6GeFe^{III}(SCN)W_{11}O_{39}\cdot 10H_2O$	7.27 (7.22)	1.727 (1.720)	62.45 (62.27)	1.770 (1.788)	5.53 (5.63)	50
$K_5PFe^{III}(SCN)W_{11}O_{39}\cdot 10H_2O$	6.21 (6.17)	1.769 (1.763)	63.58 (63.86)	1.818 (1.834)	5.74 (5.69)	30
$[C(NH_2)_3]_5AsFe^{III}(SCN)W_{11}O_{39}\cdot 8H_2O$	9.28 (9.16)	1.689 (1.703)	61.84 (61.66)	1.750 (1.771)	4.32 (4.40)	60
$K_7BFe^{III}(SCN)W_{11}O_{39}\cdot 9H_2O$	8.62 (8.54)	1.738 (1.741)	63.24 (63.06)	1.792 (1.811)	5.09 (5.06)	55
$K_8P_2Fe^{III}(SCN)W_{17}O_{61}\cdot 18H_2O$	6.34 (6.37)	1.138 (1.136)	63.87 (63.60)	1.179 (1.182)	6.60 (6.60)	75
$K_8As_2Fe^{III}(SCN)W_{17}O_{61}\cdot 20H_2O$	6.32 (6.21)	1.098 (1.108)	62.10 (62.03)	1.160 (1.153)	7.10 (7.15)	70
$K_7SiFe^{III}(SO_3)W_{11}O_{39}\cdot 9H_2O$	8.52 (8.43)	1.714 (1.720)	62.08 (62.30)	2.516 (2.467)	4.99 (5.00)	50
$K_7GeFe^{III}(SO_3)W_{11}O_{39}\cdot 9H_2O$	8.48 (8.32)	1.709 (1.697)	61.13 (61.46)	2.410 (2.433)	4.93 (4.93)	40
$K_6PFe^{III}(SO_3)W_{11}O_{39}\cdot 8H_2O$	7.29 (7.35)	1.756 (1.750)	63.10 (63.36)	2.499 (2.508)	4.60 (4.52)	30
$[C(NH_2)_3]_6AsFe^{III}(SO_3)W_{11}O_{39}\cdot 6H_2O$	10.99 (10.84)	1.671 (1.679)	61.01 (60.81)	2.411 (2.407)	3.26 (3.25)	55
$K_8BFe^{III}(SO_3)W_{11}O_{39}\cdot 10H_2O$	9.74 (9.52)	1.684 (1.700)	61.24 (61.54)	2.451 (2.436)	5.55 (5.48)	50
$K_9P_2Fe^{III}(SO_3)W_{17}O_{61}\cdot 20H_2O$	7.07 (7.02)	1.120 (1.114)	62.70 (62.36)	1.589 (1.598)	7.09 (7.19)	70
$K_9As_2Fe^{III}(SO_3)W_{17}O_{61}\cdot 21H_2O$	7.01 (6.88)	1.088 (1.091)	61.20 (61.07)	1.577 (1.564)	7.41 (7.39)	60

[a] Percentages refer to SCN^-, SO_3^{2-}, and $Fe(CN)_6^{4-}$ content, respectively.

$(OH_2)W_{11}O_{39}\cdot 14H_2O$ in 100 mL of water is added 16.0 g (0.038 mol) of solid $K_4Fe(CN)_6$. The solution turns blue immediately. It is stirred for 10 min. The sought salt separates, after cooling the solution to 2 °C, on addition of 10–20 mL of methanol. The precipitate is filtered off and washed with a 1:1 (v/v) methanol/water mixture. It may be recrystallized from an aqueous 0.1 M solution of the ligand.

$K_8PFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}\cdot 21H_2O$. A procedure similar to the preceding preparation is used. The starting materials are 10.0 g (0.0031 mol) of $K_4PFe^{III}(OH_2)W_{11}O_{39}\cdot 14H_2O$ and 20.0 g (0.047 mol) of $K_4Fe(CN)_6$.

$K_{11}X'_2Fe^{III}[Fe^{II}(CN)_6]W_{17}O_{61}\cdot nH_2O$ (X' = P(V), As(V)). To a hot (80 °C) solution of 10.0 g (ca. 0.0020 mol) of $K_7X'_2Fe^{III}(OH_2)W_{17}O_{61}\cdot \sim 21H_2O$ in 100 mL of water is added 13.0 g (0.031 mol) of $K_4Fe(CN)_6$. The blue solution is stirred for 10 min. The sought salt separates on cooling the solution to 2 °C. The precipitate is filtered off, washed with ice-cold water, and recrystallized from a 0.1 M aqueous solution of $K_4Fe(CN)_6$.

$K_6XFe^{III}(SCN)W_{11}O_{39}\cdot 10H_2O$ (X = Si, Ge). To a warm (60 °C) solution of 10.0 g (0.0031 mol) of $K_5XFe^{III}(OH_2)W_{11}O_{39}\cdot 14H_2O$ in 100 mL of water is added 10.0 g (0.103 mol) of solid KSCN. The solution turns red rapidly; it is stirred at 60 °C for 10 min and then cooled rapidly to 2 °C. The sought salt separates on adding 10 mL of methanol to the cold solution. It is not recrystallized.

$K_5PFe^{III}(SCN)W_{11}O_{39}\cdot 10H_2O$. A procedure similar to the preceding preparation is used. The starting materials are 12.0 g (0.0037 mol) of $K_4PFe^{III}(OH_2)W_{11}O_{39}\cdot 14H_2O$ and 15.0 g (0.155 mol) of KSCN.

$K_7BFe^{III}(SCN)W_{11}O_{39}\cdot 9H_2O$. A procedure similar to the preceding preparation is used. The starting materials are 10.0 g (0.0031 mol) of $K_6BFe^{III}(OH_2)W_{11}O_{39}\cdot 14H_2O$ and 10.0 g (0.103 mol) of KSCN. The stirring time is 5 min. The sought salt precipitates on cooling the solution to 2 °C. Again, it is not recrystallized.

$K_8X'_2Fe^{III}(SCN)W_{17}O_{61}\cdot pH_2O$ (X' = P(V), As(V)). A procedure similar to the preceding preparation is used, but with a stirring time of 10 min. The starting materials are 10.0 g (0.0020 mol) of $K_7X'_2Fe^{III}(OH_2)W_{17}O_{61}\cdot \sim 21H_2O$ and 8.0 g (0.083 mol) of KSCN.

$[C(NH_2)_3]_5AsFe^{III}(SCN)W_{11}O_{39}\cdot 8H_2O$. A 4.0-g (0.0013-mol) sample of $[C(NH_2)_3]_4AsFe^{III}(OH_2)W_{11}O_{39}\cdot 10H_2O$ is dissolved in 100 mL of warm (70 °C) water. The solution turns red rapidly on addition of 4.0 g (0.042 mol) of solid KSCN. It is stirred for 5 min at 70 °C. Then 3 g (0.025 mol) of guanidinium nitrate is added. The sought salt separates on cooling the solution to 2 °C. It is not recrystallized.

$K_7XFe^{III}(SO_3)W_{11}O_{39}\cdot 9H_2O$ (X = Si, Ge). A procedure similar to that of $K_6XFe^{III}(SCN)W_{11}O_{39}\cdot 10H_2O$ is used. The starting materials are 10.0 g (0.0031 mol) of $K_5XFe^{III}(OH_2)W_{11}O_{39}\cdot 14H_2O$ and 15.0 g (0.125 mol) of $KHSO_3$. The resulting salt is orange.

$K_6PFe^{III}(SO_3)W_{11}O_{39}\cdot 8H_2O$. A procedure similar to the preceding preparation is used. The starting materials are 12.0 g (0.0037 mol) of $K_4PFe^{III}(OH_2)W_{11}O_{39}\cdot 14H_2O$ and 15.0 g (0.125 mol) of $KHSO_3$.

$K_8BFe^{III}(SO_3)W_{11}O_{39}\cdot 10H_2O$. A procedure similar to the preceding preparation is used. The starting materials are 10.0 g (0.0031 mol) of $K_6BFe^{III}(OH_2)W_{11}O_{39}\cdot 14H_2O$ and 15.0 g (0.125 mol) of $KHSO_3$. The stirring time is 5 min. The salt precipitates on cooling the solution to 2 °C. It is not recrystallized, like all sulfito-ligand salts reported here.

$K_9X'_2Fe^{III}(SO_3)W_{17}O_{61}\cdot \sim 20H_2O$ (X' = P(V), As(V)). A procedure similar to the preparation of $K_8X'_2Fe^{III}(SCN)W_{17}O_{61}\cdot pH_2O$ salts is used. The starting materials are 10.0 g (0.0020 mol) of $K_7X'_2Fe^{III}(OH_2)W_{17}O_{61}\cdot \sim 21H_2O$ and 6.0 g (0.050 mol) of $KHSO_3$. The salt precipitates on cooling the solution to 2 °C.

$[C(NH_2)_3]_6AsFe^{III}(SO_3)W_{11}O_{39}\cdot 6H_2O$. A procedure similar to the preparation of $[C(NH_2)_3]_5AsFe^{III}(SCN)W_{11}O_{39}\cdot 8H_2O$ is used. The starting materials are 4.0 g (0.0013 mol) of $[C(NH_2)_3]_4AsFe^{III}(OH_2)W_{11}O_{39}\cdot 10H_2O$ and 6.0 g (0.050 mol) of $KHSO_3$. The stirring time is 10 min. The sought salt separates on cooling the solution to 2 C.

Techniques. We define the conditional ligand-exchange equilibrium constant K'_{lig} for the reaction $XFe^{III}(OH_2)W_{11} + L \rightleftarrows XFe^{III}(L)W_{11} + H_2O$ as $K'_{lig} = [XFe^{III}(L)W_{11}]/[XFe^{III}(OH_2)W_{11}][L]$.

Similarly, we define the conditional metal ion exchange equilibrium constant K'_{met} for the reaction $XM^{III}(OH_2)W_{11} + VO^{2+}(aq) \rightleftarrows XV(O)W_{11} + M^{3+}(aq)$ as $K'_{met} = [XV(O)W_{11}][M^{3+}]/[XM^{III}(OH_2)W_{11}][VO^{2+}]$.

The fact that only one ligand or metal ion is exchangeable under the chosen conditions simplifies the choice of suitable measuring methods; these may be spectroscopic, as the $XFe^{III}(L)W_{11}$ anion generally exhibits an electronic absorption spectrum that is distinctly different from that both of the $XFe^{III}(OH_2)W_{11}$ anion and of L. The last two usually do not absorb appreciably in the region of the absorption maximum of $XFe^{III}(L)W_{11}$.

We opted for the molar ratio variation method (using the linear plotting variant of Momoki et al.[7]) and for the continuous isomolar variation ("Job plot") method, adapted from Likussar and Boltz' treatment.[8]

The first method performs well when small values of exchange equilibrium constants are measured (below ca. 150); the latter for larger values (over 100). The applicability of both methods was checked in the overlapping range. The obtained values agree well (see Table II).

Use of the first method is sometimes restricted by the high ligand concentrations that are required (up to 4 M). This necessitates the use of $S_2O_5^{2-}$ salts as a HSO_3^- source. The actual free ligand concentration was carefully checked.[9] The polyanion concentration was 1.00×10^{-3} M. Total concentration for the Job plot measurements

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Table II. Conditional Ligand-Exchange Equilibrium Constants (K'_{lig})[a]

initial polyanion	method[b]	pH	K'_{lig}	std dev[c]
	Sulfito Ligand			
$K_5SiFe(OH_2)W_{11}O_{39}$	Job	3.85	148	17
	mrv	3.85	153	15
	mrv	5.70	157	14
	mrv	6.40	82	5
	mrv	6.55	67	6
	mrv	6.80	40	4
$K_5GeFe(OH_2)W_{11}O_{39}$	mrv	3.90	48	5
	mrv	5.70	32	3
$K_6BFe(OH_2)W_{11}O_{39}$	mrv	5.70	48	4
	mrv	6.80	50	4.5
$K_4PFe(OH_2)W_{11}O_{39}$	Job	4.00	146	12
	mrv	4.00	141	14
	mrv	5.30[e]	112	10
$(gua)_4As(OH_2)W_{11}O_{39}$[d]	mrv	5.30[f]	38	4
$K_7P_2Fe(OH_2)W_{17}O_{61}$	mrv	5.50	77	10
$K_7As_2Fe(OH_2)W_{17}O_{61}$	mrv	5.30	194	27
	Hexacyanoferrate(II) Ligand			
$K_5SiFe(OH_2)W_{11}O_{39}$	Job	4.00	2328	87
	Job	5.30	4082	57
$K_5GeFe(OH_2)W_{11}O_{39}$	Job	4.00	1842	38
	Job	5.30	2629	49
$K_6BFe(OH_2)W_{11}O_{39}$	dissociation at any pH, precipitation of Prussian Blue			
$K_4PFe(OH_2)W_{11}O_{39}$	Job	4.00	3437	75
$(gua)_4AsFe(OH_2)W_{11}O_{39}$[d]	dissociation at any pH, precipitation of Prussian Blue			
$K_7P_2Fe(OH_2)W_{17}O_{61}$	Job	5.30	2890	150
$K_7As_2Fe(OH_2)W_{17}O_{61}$	Job	5.30	2269	50

[a] For definition of K'_{lig}, see text. [b] Job = continuous isomolar variation method. mrv = molar ratio variation method. [c] Based on at least 10 series of measurements made between 16.5×10^3 and 22.5×10^3 cm^{-1} (SO_3^{2-}) or 11.5×10^3 and 15.0×10^3 cm^{-1} ($Fe(CN)_6^{4-}$). [d] gua = guanidinium ion, $C(NH_2)_3^+$. [e] Starts to decompose slowly after 1 day at pH > 4.0. [f] Starts to decompose slowly after 1 day at pH $\leqslant$4.5.

was ca. 0.04 M. Equilibrium was reached rapidly, but not instantaneously, at room temperature for the ligand-exchange reactions and was reached after 1–3 days for the metal-exchange experiments.

The exchange equilibrium constants were measured at 297.0 ± 0.5 K on acetate- or succinate-buffered solutions of constant ionic strength (1 M; expressed as acetate), except at high ligand concentations (corresponding to >1 M acetate in ionic strength). Series of plots, each constructed from data obtained at a particular wavelength, yielded values for the exchange constants that were averaged to the tabulated value.

The pH was adjusted to maximize the ligand-exchange constants; in some cases results are reported for the full stability range of the substituted polyanion (pH 2.5–6.5). The pH of the metal-exchange solutions was fixed at 3.0 ± 0.1 to prevent hydrolysis of the liberated indium(III). A few milligrams of hydroxylamine hydrochloride was added to each solution to suppress the oxidation of vanadium(IV) to vanadium(V).

Results

The data obtained for the ligand-exchange reactions with $Fe(CN)_6^{4-}$ and HSO_3^- are assembled in Table II, and those for the metal-exchange reactions with VO^{2+} in Table III.

The values found for the ligands SCN^-, $S_2O_3^{2-}$, and thiourea are not tabulated for the following reasons:

(1) Although the exchange equilibrium constants for SCN^- are fairly high (all equal ca. 100), the calculated values are unsatisfactorily reproducible (deviations up to 30% occur); the SCN^- complexes are not stable in solution, and the characteristic red color begins to fade after a few minutes, in the absence of a large excess of SCN^-.

(2) The complexes $XFe^{III}(S_2O_3)W_{11}$ are also unstable. Exchange takes place (the solution turns orange-yellow), but after a few minutes a fine precipitate of sulfur appears: both $S_2O_3^{2-}$ and SCN^- are oxidized by Fe^{3+} under these conditions. This redox reaction is to some extent reduced when a mixed solvent like Me_2SO/water is used, but the obtained data are erratic.

Table III. Conditional Metal-Exchange Equilibrium Constants K'_{met}[a] for the Reaction $XIn(OH_2)W_{11} + VO^{2+}(aq) \leftrightarrows XV(O)W_{11} + In^{3+}(aq)$

initial polyanion	pH	K'_{met}	std dev[c]	method[b]
$K_5SiIn(OH_2)W_{11}O_{39}$	3.1	100	10	Job, mrv
$K_5GeIn(OH_2)W_{11}O_{39}$	3.1	190	20	Job
$K_6BIn(OH_2)W_{11}O_{39}$	3.2	430	30	Job
$K_4PIn(OH_2)W_{11}O_{39}$	3.0	850	50	Job
$K_7P_2In(OH_2)W_{17}O_{61}$	3.2	400	50	Job
$K_7As_2In(OH_2)W_{17}O_{61}$	3.1	350	40	Job

[a] For definition of K'_{met}, see text. [b] Job = continuous isomolar variation method. mrv = molar ratio variation method. [c] Based on at least 10 series of measurements made between 22.0×10^3 and 24.5×10^3 cm^{-1}.

(3) The exchange reactions with thiourea are slow and yield small and variable exchange constants of ca. 3–5. Side reactions occur before equilibrium is established.

The electronic absorption spectra in the near UV–visible region show for the $XFe^{III}(SCN)W_{11}$ complexes a broad band centered at ca. 21.5×10^3 cm^{-1} (ϵ = ca. 5500 at pH 5.3) and for the sulfito-ligand complexes a distinct shoulder on the tail of the W ← O charge-transfer (CT) (and Fe ← O CT) band at ca. 28×10^3 cm^{-1}. The hexacyanoferrate(II)–ligand complexes exhibit a broad band, the barycenter of which varies from 13.9×10^3 cm^{-1} ($\epsilon = 1500$) for $SiFe^{III}[Fe^{II}(CN)_6]W_{11}$ to 12.8×10^3 cm^{-1} ($\epsilon = 2400$) for $As_2Fe^{III}[Fe^{II}(CN)_6]W_{17}$ (both at pH 5.30).

Metal-exchange experiments with other $XM^{III}W_{11}$ polyanions (M = Al, Ga, Fe, Rh) conducted at pH 3.0 show that VO^{2+} replaces M^{3+}, but the reaction rates are very low, no equilibrium being established after 6 months at room temperature in most cases. The estimated exchange constants are largest for M(III) = Al (K'_{met} = ca. 100). Similarly, exchange reactions of the type $XMW_{11} + M' \rightleftarrows XM'W_{11} + M$ (M, M′ trivalent ions of Fe, Cr, Rh, Al, Ga, In) take place, but they are very slow, even at higher temperatures; no equilibrium is reached after 6 months at 60 °C. Furthermore, sometimes partial decomposition of the polyanion occurs.

Qualitatively, one finds the following order of stability of $XM^{III}W_{11}$ anions: at pH 4–5, Fe $\simeq$ Cr > Al > Ga > Rh > In; at pH 2, Fe $\simeq$ Cr $\simeq$ Rh > In > Ga > Al. The same order is found from exchange experiments (Job plots) with bivalent metal ion containing heteropolytungstates.

The solid salts containing a hexacyanoferrate(II), sulfito, or thiocyanato ligand are stable in air. They are crystalline and soluble in water, but in solution the hetero ligand is partially replaced by water, in the absence of free ligand. X-ray powder diffractograms show that the potassium salts of the sulfito- and thiocyanato-ligand-containing polyanions are isostructural with aquo-ligand salts that contain the same number of potassium atoms.[2c] E.g., $K_6XFe^{III}(L)W_{11}$ salts are approximately centered tetragonal, type Q_b;[4b] $K_7XFe^{III}(L)W_{11}$ salts possess a face-centered cubic crystal symmetry.[4b] The potassium salts of hexacyanoferrate(II)-containing polytungstates are not isomorphous with analogous aquo-ligand salts. They also contain much more water of crystallization, indicative of a more open structure.

Discussion

Ligand-Exchange Reactions. The ligand-exchange equilibrium constants reported so far concern mainly ligands that bind through nitrogen,[2b] besides thiourea and thiocyanate.[2b] We chose to study the two last-mentioned ligands, others that may bind through sulfur, and hexacyanoferrate(II) for the following reasons:

(1) The resulting complex should have an electronic absorption spectrum as different as possible from that of both the aquo-ligand complex and the free ligand. Ligands bound to iron(III) via sulfur often exhibit appropriate CT spectra.

(2) For at least some sulfur-containing ligands it should prove possible to determine whether they are effectively S bonded to iron(III).

(3) As the trivalent state of the "addendum" atom (here Fe(III)) is stabilized with respect to the divalent state in heteropolytungstates,[2b,11,12] coordination through sulfur should be hampered less by reduction processes.

The stabilization of Fe(III) results indeed in the formation of iron(III)–mono(sulfito) complexes that are stable both in solution and as solid salts. The thiocyanato complexes are stable in the solid state only, whereas no complexes could be isolated with the ligands thiosulfate or thiourea. These are too good reducing agents.

As a large outward shift of small trivalent ions like iron(III) within the polytungstate framework, necessary for a change to tetracoordination instead of pentacoordination, is quite improbable, the coordination of the exchanged ligands is almost certainly unidentate.

Infrared spectra of sulfito-ligand compounds show S–O stretching absorption bands at 1110–1130 and at ca. 1060 cm^{-1} that are indicative of S bonding[13,14] (peaks below 1000 cm^{-1} that might be due to SO_3 are swamped by heteropolyanion bands). Such sulfur coordination has been proposed for mono(sulfito)– and bis(sulfito)–aquo–iron(III) complexes.[15,16]

The relative slowness of the exchange reaction for other sulfur-containing ligands is probably largely due to the availability of a single exchange site that prevents the formation of favorable transition states;[16] it suggests that these ligands are also bound through sulfur to iron(III), as does the position of the maximum of the electronic absorption spectrum for $S_2O_3^{2-}$ and thiourea (ca. 27.0×10^3 cm^{-1}).

Considering the sensitivity of iron(III)–sulfito complexes to internal redox reactions, it is not surprising that no formation constants have been reported so far. For SCN^- the formation constant of $Fe(H_2O)_5(SCN)^{2+}$ (ca. 100)[17] is quite close to the exchange constants found here (also ca. 100). In the aquo complex SCN^- also is a unidentate ligand, but iron(III)–thiourea complexes contain bidentate ligands as in $Fe(H_2O)_2[H_2NCSNH_2]_2^{3+}$,[18] conferring to these species a much higher stability ($\log \beta_2 = 8.44$),[18] compared to that of the unidentate complexes reported here.

Weakley's data, especially those concerning $XCo^{II}(L)W_{11}$ (L = pyridine, various methylpyridines) complexes, show that the exchange constants are, again, close to those measured for exchange reactions on aqueous Co^{2+}.[17] The values of the exchange constants involving the hexacyanoferrate(II) ion are rather low. No comparable formation constants have been reported, as Prussian Blue type compounds tend to be very insoluble because of their three-dimensional Fe^{III}–NC–Fe^{II}–CN–Fe^{III} through-bonding network.[19] Such type of bonding is naturally absent here (cf. high solubility of these complexes), although linear $XW_{11}Fe^{III}$–NC–Fe^{II}–CN–$Fe^{III}W_{11}X$ bonds cannot be excluded, in the absence of conclusive interpretation of the IR data (specifically the attribution of several bands in the 2200–2000-cm^{-1} range).[13] The considerable variation of the exchange constant values with changes in central atom (and pH) does not follow identical patterns for the SO_3^{2-} and $Fe(CN)_6^{4-}$ ligands. Nevertheless, at similar pH, the value of the constant generally increases with the charge/size ratio of the central atom. The latter influences both the iron(III)–$O(H_2)$ bond length, and thus the exchangeability of the aquo ligand, and the retention of the iron atom itself (cf. dissociation of $BFeW_{11}$ and $AsFeW_{11}$ in the presence of $Fe(CN)_6^{4-}$).[2c] The influence of the central atom also manifests itself in the electronic absorption spectra; witness the gradual shift of the barycenter of the low-energy CT band mentioned above for the $Fe(CN)_6^{4-}$ ligand complexes. Weakley[2b] found a similar dependency for $XCo^{II}(L)W_{11}$ polyanions.

For the sulfito ligand the exchange constants increase slowly up to a pH of ca. 5.5 and then drop off rapidly; probable reasons for this are (1) bonding is to SO_3^{2-} rather than to HSO_3^- (see below) and (2) While the aquo ligand is only very slighty protonated below pH 3, it is rapidly deprotonated above pH 5.5;[2c] in most cases, at pH 6.5–7, the exchange involves in fact the more strongly bound hydroxo or oxo ligand. Protonation of the oxygen atoms surrounding the iron(III) is weak and hardly varies with pH; it thus has little influence on the exchange equilibrium.

Solid Salts. The analytical data for the sulfito-ligand salts indicate that the ligand is present in SO_3^{2-} form. This has also been found for the mono(sulfito)–aquo–iron(III) ion in solution[16] and for solid $(NH_4)_2[Fe(SO_3)OH]$[20a] and $Na_5[Fe(SO_3)_4]\cdot 2H_2O$.[20b] The crystal isomorphism deduced from powder diffractograms shows that the sulfito and thiocyanato ligands are too small to prevent the potassium ions from playing their structure-determining role.[2c] The much larger $Fe(CN)_6^{4-}$ ligand introduces a considerable lowering in symmetry and a general lack of isomorphism.

Metal-Exchange Reactions. Few tetravalent (or higher valent) ions are suitable for use in simple exchange reactions of the type $XM^{III}W_{11} + M^{4+}(aq) \rightleftarrows XM^{IV}W_{11} + M^{3+}(aq)$, mainly because of hydrolysis problems. We limited ourselves to V^{4+} in VO^{2+} form (V^{4+}-substituted heteropolytungstates are well-known[1]) and to $XInW_{11}$ and $XAlW_{11}$ heteropolytungstates, which are at pH 3 less stable than most other $XM^{III}W_{11}$ polytungstates.[2c]

Equilibrium for these reactions is slow to establish, in contrast to the almost instantaneous $M^{2+} \rightleftarrows M^{3+}$ replacement. The difference may be due to the fact that here the tetravalent ion is introduced as a quasi lower valent oxyanion and to sterically imposed less favorable transition states. The results for $XAlM_{11}$ are unsatisfactorily reproducible and are not discussed further.

The exchange constants are small compared to those found for the analogous $M^{2+} \rightleftarrows M^{3+}$ exchange (usually $>10^4$),[5b] for reasons that are not very clear. The short V=O double bond in VO^{2+}, which probably is maintained within the polytungstate framework,[1a,23] implies diminished bonding to the innermost oxygen, that forms part of the central tetrahedron. The tungsten–outer oxygen bonds have a similar character, but the electrostatic effect of the metal charges is more favorable for tungsten(VI). The role of the charge/size ratio

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of the central atom is clear from the figures in Table III. Only the result for $BInW_{11}$ falls somewhat out of line, unless we postulate a significant distortion of the BO_4 central tetrahedron, extrapolating the results obtained for the less symmetric h-$BW_{12}O_{40}$ isomer to the even less symmetric $BW_{11}O_{39}$ anion.[21,22] This line of reasoning is corroborated by the relative order of stability exposed above. Rhodium(III) is the only outer heteroelement present in $M\overset{\cdot\cdot}{-}O$ form[2c] at pH 5 (but not at pH 2); at pH 5 $XRh(O)W_{11}$ polytungstates are less stable than the (aquo–) iron(III) and (aquo–) chromium(III) homologues but not at pH 2. Possible preferential solvation effects should not be discounted, however.[23] The inversion of the order of stability with change of pH for group 3A elements has been explained previously.[2c] Another possible reason for the small exchange constant values is the low degree of delocalization of the single d electron on V(IV) over the polyanion, due to unfavorable overlap with the bridging oxygens' 2p orbitals.[22,23] This effect is more pronounced in polytungstates than in polymolybdates.[23] The argument is subject to caution, however.[23] Data on the homologous heteropolymolybdates are needed to judge its validity.

Conclusions

Keggin- and Dawson-type heteropolytungstate anions are convenient pentadentate ligands for many transition and group 3A elements, whose octahedral coordination is completed by a single, usually aquo, ligand. Exchange of this "sixth" ligand can be studied with simple techniques. The coordination approximates that of the corresponding aquo ion. For $XFe^{III}(OH_2)W_{11}$ and $X_2Fe^{III}(OH_2)W_{17}$ anions the conditional equilibrium exchange constants are for several ligands generally similar to those found for the substitution of a single ligand on the aquo ion, inasfar as such figures are available. The stabilization of higher oxidation states of the metal heteroatom in polytungstates leads to the obtention of air-stable mono(sulfito)-iron(III) derivatives. The exchange equilibrium between a trivalent heteroatom and vanadium(IV) present as $VO^{2+}(aq)$ is slow to establish; reproducible results have been obtained for the $In^{3+} \rightleftarrows V^{4+}$ exchange only. The exchange constants are much smaller than those generally found for $M^{2+} \rightleftarrows M^{3+}$ exchange, for reasons that are not yet completely clear.

Registry No. $K_5SiFe^{III}(OH_2)W_{11}O_{39}$, 81553-20-0; $K_5GeFe^{III}(OH_2)W_{11}O_{39}$, 81553-10-8; $K_9SiFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}$, 84774-67-4; $K_9GeFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}$, 84774-69-6; $K_4PFe^{III}(OH_2)W_{11}O_{39}$, 81553-16-4; $K_8PFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}$, 84774-65-2; $K_{11}P_2Fe^{III}[Fe^{II}(CN)_6]W_{17}O_{61}$, 84750-80-1; $K_{11}As_2Fe^{III}[Fe^{II}(CN)_6]W_{17}O_{61}$, 84774-63-0; $K_7P_2Fe^{III}(OH_2)W_{17}O_{61}$, 81553-24-4; $K_7As_2Fe^{III}(OH_2)W_{17}O_{61}$, 81552-73-0; $K_6SiFe^{III}(SCN)W_{11}O_{39}$, 84774-61-8; $K_6GeFe^{III}(SCN)W_{11}O_{39}$, 84774-60-7; $K_5PFe^{III}(SCN)W_{11}O_{39}$, 84750-81-2; $K_7BFe^{III}(SCN)W_{11}O_{39}$, 84750-78-7; $K_6BFe^{III}(OH_2)W_{11}O_{39}$, 81552-94-5; $K_8P_2Fe^{III}(SCN)W_{17}O_{61}$, 84835-84-7; $K_8As_2Fe^{III}(SCN)W_{17}O_{61}$, 84835-83-6; $(gua)_5AsFe^{III}(SCN)W_{11}O_{39}$, 84750-83-4; $(gua)_4AsFe^{III}(OH_2)W_{11}O_{39}$, 81571-91-7; $K_7SiFe^{III}(SO_3)W_{11}O_{39}$, 84809-55-2; $K_7GeFe^{III}(SO_3)W_{11}O_{39}$, 84809-54-1; $K_6PFe^{III}(SO_3)W_{11}O_{39}$, 84774-70-9; $K_8BFe^{III}(SO_3)W_{11}O_{39}$, 84774-59-4; $K_9P_2Fe^{III}(SO_3)W_{17}O_{61}$, 84848-77-1; $K_9As_2Fe^{III}(SO_3)W_{17}O_{61}$, 84835-82-5; $(gua)_6AsFe^{III}(SO_3)W_{11}O_{39}$, 84774-72-1; $K_5SiIn(OH_2)W_{11}O_{39}$, 81553-61-9; $K_5GeIn(OH_2)W_{11}O_{39}$, 81553-46-0; $K_6BIn(OH_2)W_{11}O_{39}$, 81553-00-6; $K_4PIn(OH_2)W_{11}O_{39}$, 81553-59-5; $K_7P_2In(OH_2)W_{17}O_{61}$, 81553-63-1; $K_7As_2In(OH_2)W_{17}O_{61}$, 81552-83-2; $K_4Fe(CN)_6$, 13943-58-3; KSCN, 333-20-0; $KHSO_3$, 7773-03-7; VO^{2+}, 20644-97-7.

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Trifluoroacetyl Derivatives of *N*,*N*-Dimethylhydrazine, Urea, and Thiourea. Reaction of Hexafluoroacetylacetone with *N*,*N*-Dimethylhydrazine

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Trifluoroacetyl chloride was reacted in the presence of CsF with $(CH_3)_2NNH_2$, $H_2NC(S)NH_2$, and $H_2NC(O)NH_2$ to give $CF_3C(O)NHN(CH_3)_2$, $CF_3C(O)NHC(S)NHC(O)CF_3$ and $CF_3C(O)NHC(S)NH_2$, and $CF_3C(O)NHC(O)NH_2$, respectively. With $(C_2H_5)_3N$ as base, $CF_3C(O)NHN(CH_3)_2$ was also formed with $(CH_3)_2NNH_2$. Hexafluoroacetylacetone gave $CF_3C(=NN(CH_3)_2)CH=C(OH)CF_3$ with $(CH_3)_2NNH_2$.

Introduction

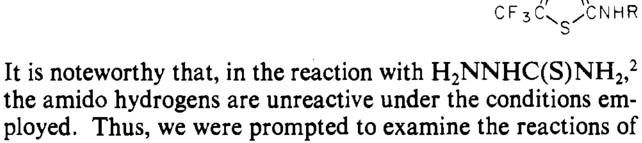
Studies of the reactions of trifluoroacetyl halides with amines[1] or substituted hydrazines[2,3] have shown that formation of the trifluoroacetamide derivative with concomitant loss of HX is the typical behavior.

$$CF_3C(O)X + RR'NH \xrightarrow{\text{solv}} CF_3C(O)NRR' + HX$$

$$R = R' = H;\ R = H,\ R' = \text{alkyl};$$
$$R = H,\ R' = H_2NNHC(S)$$

$$CF_3C(O)X + H_2NNHP_3N_3F_5 \rightarrow CF_3C(O)NHNHP_3N_3F_5 + HX$$

However, in some cases, elimination of HX occurs with subsequent intramolecular addition to the carbonyl function followed by elimination of water by heating in the presence of H_2SO_4 to form interesting heterocycles,[4,5] viz.



It is noteworthy that, in the reaction with $H_2NNHC(S)NH_2$,[2] the amido hydrogens are unreactive under the conditions employed. Thus, we were prompted to examine the reactions of $CF_3C(O)Cl$ with an unsubstituted amide $(NH_2C(O)NH_2)$ and

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