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Solid state reactions of chromium(III)-substituted heteropoly tungstates with chromium(III) ammine cations[☆]

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Abstract

The reaction of chromium ammine complexes with chromium-substituted Keggin anions in aqueous solution forms insoluble salts which were then heated to temperatures of 240 and 350°C. The thermal behaviour of the ammine complexes is dominated by a strong exothermic reaction which is interpreted as a linking reaction (condensation) between chromium from the complex ammine cation and the heteropolyanion. Thermal treatment of the title compounds yields products that are soluble in water and could be crystallized as potassium salts in several cases. A chromium-caped Keggin anion is the proposed structure.

Keywords: Ammine complex; Chromium; Keggin anion; Solid state; Tungstate

1. Introduction

The substitution of molybdenum or tungsten in heteropolyanions with the Keggin structure, $[E^eO_4M_{12}O_{36}]^{(8-e)-}$ (e.g. E is Si, P; M is Mo, W), by transition elements is of considerable current interest, from both a theoretical and practical point of view [1–3].

The Keggin anion (Fig. 1a) is formed by four corner-linked M_3O_{13} triplets (each triplet consisting of three edge-linked MO_6 octahedra) which connect to the central tetrahedron EO_4. If the multiple substitution occurs in the same M_3O_{13} group (B-type) or in the corner-linked octahedra (A-type), respectively, different isomers result; additional isomers result from 60° rotation of one triplet [4]. Fig. 1b shows the

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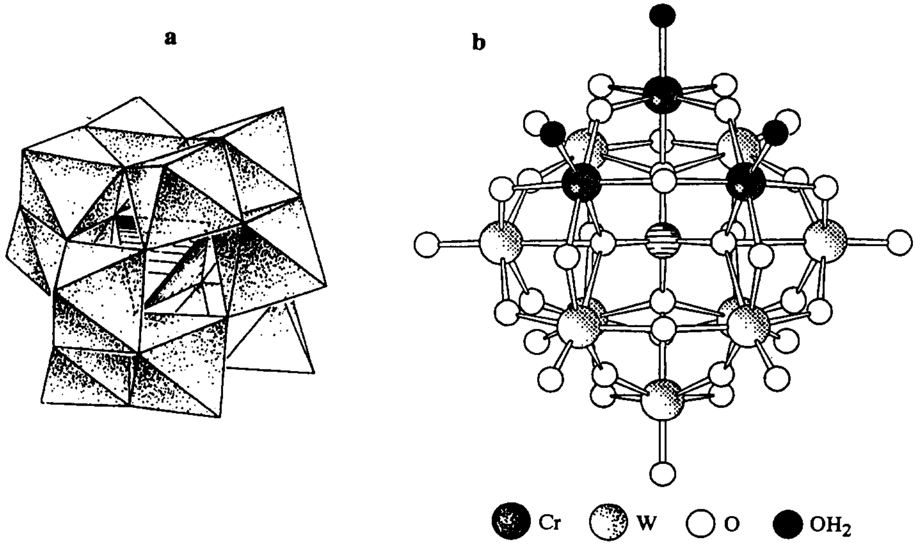

Fig. 1. Structure of the Keggin anion: (a) polyhedral representation of $[\alpha\text{-}SiO_4W_{12}O_{36}]^{4-}$ [4] and (b) SCHAKAL drawing of $[A\text{-}\alpha\text{-}SiO_4W_9Cr_3(OH_2)_3O_{33}]^{7-}$ [6].

structure of $[A\text{-}\alpha\text{-}SiO_4W_9Cr_3(OH_2)_3O_{33}]^{7-}$ where water molecules occupy the terminal oxygen positions in the chromium-substituted octahedra.

Polyoxoanions containing $Cr(OH_2)$ groups should be able to dimerize[a] or to react with complex cations like $[Cr(NH_3)_{6-n}X_n]^{(3-n)+}$ analogous to the chemistry of aquammine complexes (Eq. 1) [5]

$$2\mathit{cis}\text{-}[ML_4(OH_2)(OH)]X_2 \longrightarrow [L_4M(OH)_2ML_4]X_4 + 2H_2O \qquad (1)$$

where M is Cr, Co, Rh, Ir; X is Cl, Br, NO_3; L_4 is $(NH_3)_4$, $(en)_2$.

2. Experimental

2.1. Synthesis

We prepared several heteropolyanions $[A\text{-}\alpha\text{-}SiO_4W_{12-n}Cr_n(OH_2)_nO_{36-n}]^{(4+n)-}$ ($n = 1$–3)[b] as polycrystalline free acids as well as salts of $[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_5(OH_2)]^{3+}$ and $[Cr(NH_3)_5Cl]^{2+}$, respectively (Table 1). The principal synthesis is given

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[a] Multiply aluminum(III)-or chromium(III)-substituted Keggin anions form in alkaline aqueous solution after several hours of refluxing dimerized spezies (publication in preparation).

[b] The different heteropoly anions $[A\text{-}\alpha\text{-}SiO_4W_{12-n}Cr_n(OH_2)_nO_{36-n}]^{(4+n)-}$ are abbreviated as SiW_{12}, $SiW_{11}Cr$, $SiW_{10}Cr_2$, SiW_9Cr_3.

Table 1
Analytical data; selected stoichiometric numbers for prepared salts

	W	Cr	H_2O	NH_3	NH_y[a]
$[Cr(NH_3)_6]H[SiO_4W_{12}O_{36}]\cdot 8H_2O$ $[Cr(NH_3)_6][SiW_{12}]$	12	1	8	6	–
$[Cr(NH_3)_6]_{1.5}H_{.5}[SiO_4W_{11}Cr(OH_2)O_{35}]\cdot 14H_2O$ $[Cr(NH_3)_6][SiW_{11}Cr]$	11	2.5	15	9	4[b]
$[Cr(NH_3)_6]_{1.5}H_{1.5}[SiO_4W_{10}Cr_2(OH_2)_2O_{34}]\cdot 12H_2O$ $[Cr(NH_3)_6][SiW_{10}Cr_2]$	10	3.5	14	9	–
$[Cr(NH_3)_6]H_4[SiO_4W_9Cr_3(OH_2)_3O_{33}]\cdot 9H_2O$ $[Cr(NH_3)_6][SiW_9Cr_3]$	9	4	12	6	5[c]
$[Cr(NH_3)_5(OH_2)]H_4[SiO_4W_9Cr_3(OH_2)_3O_{33}]\cdot 12H_2O$ $[Cr(NH_3)_5(OH_2)][SiW_9Cr_3]$	9	4	15	5	3[d]
$[Cr(NH_3)_5Cl]H_3[SiO_4W_9Cr_3(OH_2)_3O_{33}]\cdot 8H_2O$ $[Cr(NH_3)_5Cl][SiW_9Cr_3]$	9	4.5	11	5	4[e]

[a] NH_3 and/or NH_4^+ per anion after thermal treatment, heating rate 5 K min^{-1}, held for 30 min at: [b] 320°C; [c] 240°C; [d] 280°C; [e] 285°C.

below for $[Cr(NH_3)_6]H_4[SiO_4W_9Cr_3(OH_2)_3O_{33}]\cdot nH_2O$[c]

$K_3H_4[A\text{-}\alpha\text{-}SiO_4W_9Cr_3(OH_2)_3O_{33}]\cdot nH_2O$ — obtained by slight modification of the method in Ref. [7]

$\downarrow$ ion exchange (H^+-form) LEWATIT S 100

$H_7[A\text{-}\alpha\text{-}SiO_4W_9Cr_3(OH_2)_3O_{33}]$ (pH 1.8)

$\downarrow$ $+[Cr(NH_3)_6](NO_3)_3$ — Added as diluted aqueous solution (pH 3.50) [8]

$[Cr(NH_3)_6]H_4[SiO_4W_9Cr_3(OH_2)_3O_{33}]\cdot nH_2O$ — Precipitate repeatedly suspended in warm water (60°C) and filtered, air dried

2.2. Thermal characterization

A Netzsch simultaneous thermoanalyser STA 429 was used for the DTA and TG investigation; mini sample holder system, Pt/PtRh10, Pt crucible, sample mass 15–25 mg, α-Al_2O_3 reference, $\beta = 5$ K min^{-1}, 100 ml Ar min^{-1} (Air Liquide).

The DSC measurements were made under identical conditions on a Setaram DSC 92.

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[c] Continuing former studies on the substitution of the central tetrahedral position EO_4 in the Keggin anion by trivalent metal ions like Al^{3+} and Fe^{3+} [9], we report now for the first time the synthesis of the free acids as solid, polycrystalline powders with heteropoly anions being substituted in the periphery. Preparation and characterization is given in more detail in Ref. [10].

2.3. Oven experiments

Samples of 0.3–1.5 g were heated in an oven (5 K min^{-1}) in air to temperatures obtained from the STA curves, held there for 30 min, and characterized by IR, EPR spectra, powder X-ray analysis and chemical analysis.

2.4. Chemical analysis

For tungsten and chromium, samples were heated with excess NaOH and H_2O_2 to ensure complete decomposition and oxidation to chromium (VI). The metals were determined with an ICP Spectro Flame. Ammonia was determined according to Kjeldahl's method and additionally as nitrogen with an Elementar Analysator C H N S 932 LECO. For chloride, Schöningers method was used followed by titration with $Hg(ClO_4)_2$. Water was determined by weight loss at 570°C ($H_2O + NH_3$).

3. Results

The DTA curves for the complex salts of chromium-substituted Keggin anions exhibit as a distinguishing feature a broad exothermic signal between 240 and 400°C (Fig. 2, curves a–c), which is not observed for the chromium ammine complexes alone (Fig. 3)[d] or for complex salts of *non*-substituted Keggin anions (Fig. 2, curve d).

The characteristic exothermic effect is also not observed for the free acids of the differently substituted anions. The appearance of the exothermic signal is obviously due to the existence of the $Cr(OH_2)$ groups in the heteropolyanion as well as the complex chromium cations. Therefore the results have to be interpreted in terms of a condensation reaction. The exothermic reaction is not dominated by the thermal degradation of the cation itself and no reaction takes place between the heteropoly anions (no exothermic effect for the free acids). From an inspection of the numerical values of the initiation temperatures, we conclude that the condensation takes place more readily according to the sequence: triply-, di-, mono-chromium-substituted Keggin anion (Table 2) and hexammine, aquopentammine, chloro-pentammine (Table 3, Fig. 4). The unexpected large enthalpy values have been proved by separate measurements using DSC equipment, confirming their magnitude and general course.

The enthalpy values for different substitution degrees follow the general tendency of the onset temperatures which seems to be coincident with the idea of an increasing number of water ligands of $Cr(OH_2)$ in the heteropoly anion favouring the condensation reaction. A more detailed discussion of the enthalpy values is complicated because

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[d] The homologous complexes of Co(III), Rh(III), Ir(III), being much more sensitive to redox reactions between ligands and central atom than the Cr(III) compounds, also show a generally endothermic decomposition [11].

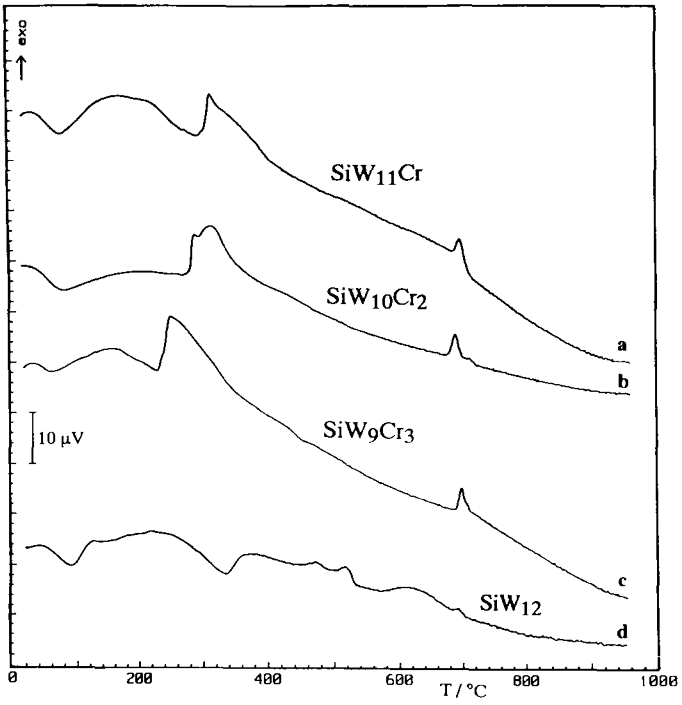

Fig. 2. DTA curves of $[Cr(NH_3)_6]^{3+}$ salts of different substituted Keggin anions; sample mass in mg: a, 17.5; b, 17.0; c, 15.0; d, 25.0.

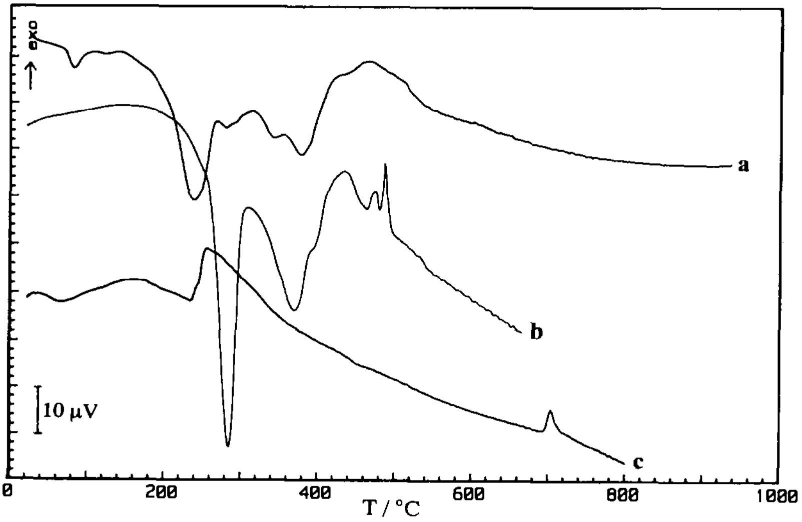

Fig. 3. DTA curves of different ammine chromium chlorides: a, $[Cr(NH_3)_6]Cl_3$ (15.3 mg); b, $[Cr(NH_3)_5Cl]Cl_2$ (12.6 mg); compared with: c, $[Cr(NH_3)_6][SiW_9Cr_3]$ (15.0 mg).

Table 2
Thermal data of the exothermic region for $[Cr(NH_3)_6][SiW_{12-n}Cr_n]$ ($n = 1$–3)

	$T_{on}^{ex}/°C$	$\Delta H/J g^{-1}$
$SiW_{11}Cr$	306	164
$SiW_{10}Cr_2$	284	218
SiW_9Cr_3	240	279

Table 3
Thermal data of the exothermic region for different chromium ammine cations with triply-substituted anion $[SiW_9Cr_3]$ (see Fig. 4)

	$T_{on}^{ex}/°C$	$\Delta H/J g^{-1}$
$[Cr(NH_3)_6]$	240	279
$[Cr(NH_3)_5(OH_2)]$	272	143
$[Cr(NH_3)_5Cl]$	286	309

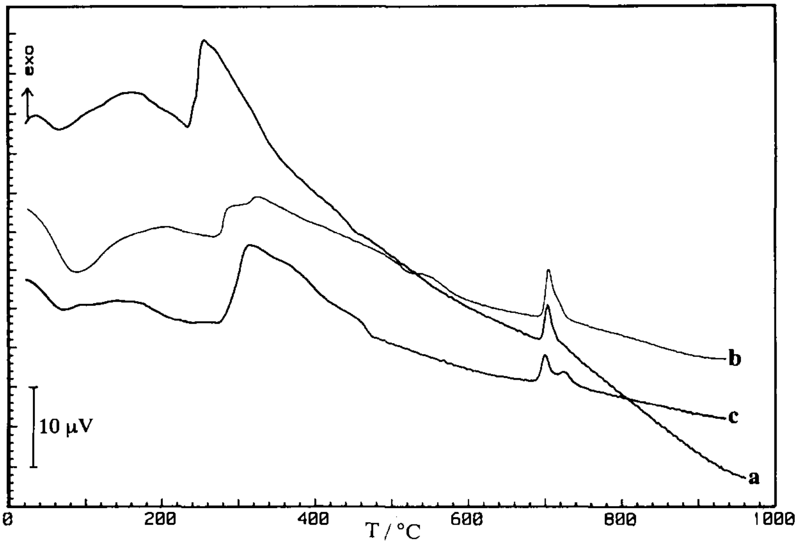

Fig. 4. The influence of different cations on the exothermic region for: a, $[Cr(NH_3)_6][SiW_9Cr_3]$ (15.0 mg); b, $[Cr(NH_3)_5OH_2][SiW_9Cr_3]$ (24.5 mg); c, $[Cr(NH_3)_5Cl][SiW_9Cr_3]$ (20.0 mg).

of the overlapping of the exothermic condensation and other enthalpy contributions caused by the endothermic decomposition reactions, e.g. of the cation.

The attribution of the exothermic signal to the reaction between the $Cr(OH_2)$ groups of the heteropolyanion and the ammine chromium cation is further evidenced by the non-dependence of the gas atmosphere (Fig. 5). If the cation degradation alone was the main process in this temperature region, an influence of the gas atmosphere would be observed.

All thermal processes up to 450°C are accompanied by mass losses due to simultaneous reactions (dehydration, condensation, NH_3 loss). The absence of a plateau in the TG curves indicates the existence of different reaction products. Furthermore, the NH_3 content changes continuously for different heating rates and tempering times. As a consequence, characterization of the thermally treated samples becomes more difficult.

The thermal decomposition of the water-insoluble complex salts in air was run in an oven at different temperatures, held for 30 min; this gave compounds which are readily soluble in water and surprisingly stable in alkaline solution. The addition of KCl or CsCl gives precipitates in low yields which were recrystallized several times in warm water. Fig. 6 shows the IR spectra for the products of the main steps of the preparation and gives further evidence for the linking between chromium of the ammine complexes and chromium in the polyoxoanion. The different bands for W–O vibrations (700–1000 cm^{-1}) [12] have not changed, indicating the retention of the Keggin anion during the whole process. The region for the N–H deformation modes (1250–1400 cm^{-1}) shows a decrease (NH_3 loss) and a shift for $\delta_s(NH)$, 1320 cm^{-1} to 1290 cm^{-1}, and

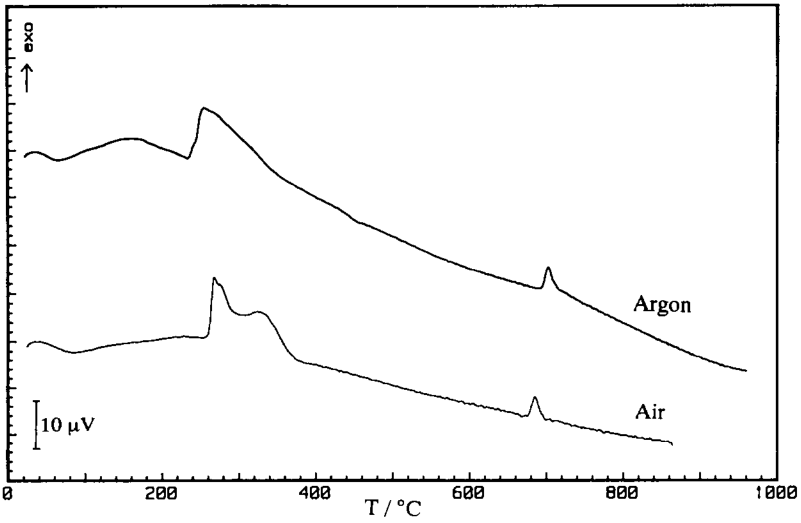

Fig. 5. DTA curves for $[Cr(NH_3)_6][SiW_9Cr_3]$ (15.0 mg) in different atmospheres.

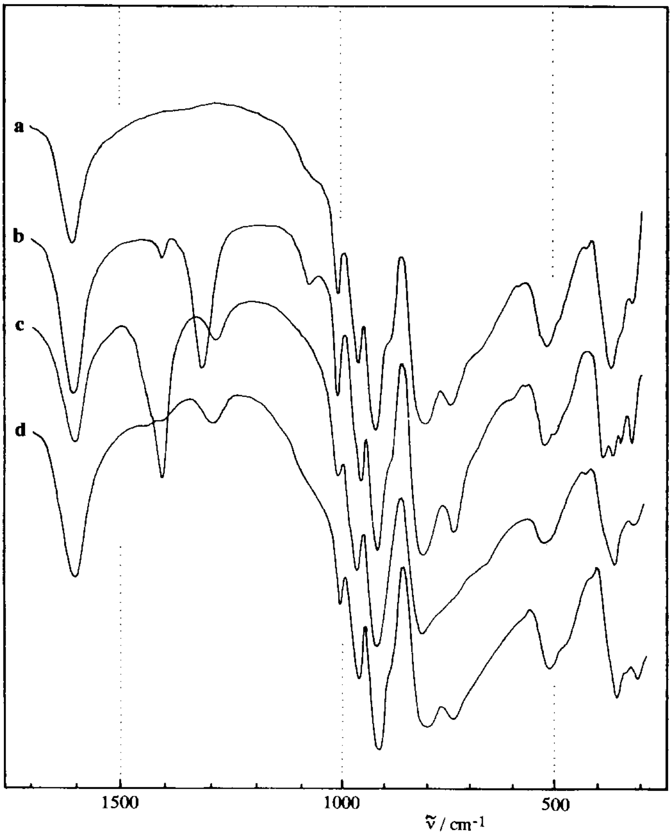

Fig. 6. IR spectra of: a, potassium salt of SiW_9Cr_3; b, $[Cr(NH_3)_5Cl][SiW_9Cr_3]$; c, thermally treated b at 285°C for 30 min; and d, recrystallized potassium salt after dissolving c in water.

a simultaneous increase for $\delta_s(NH_4^+)$, 1400 cm^{-1}. The observed bending mode δ_s(M–OH), 1075 cm^{-1}, belongs to bridging OH groups between Cr–O polyhedra of the Keggin anion which disappears during the thermal treatment. This is explained as a H^+ transfer to NH_3. From the spectra of the recrystallized potassium salts, we conclude that NH_3 remains bound to chromium and in the region for Cr–O vibration modes (500–700 cm^{-1}), some broadening occurs. We believe this broadening to be due to the presence of additional Cr–O vibration modes. Fig. 7 proposes a possible structure for the Keggin anion caped by $Cr(OH)_x(NH_3)_y$ octahedra. The linking occurs via OH groups, in the case shown by faces; linking by common edges is also imaginable. The terminal positions should be occupied by NH_3 molecules.

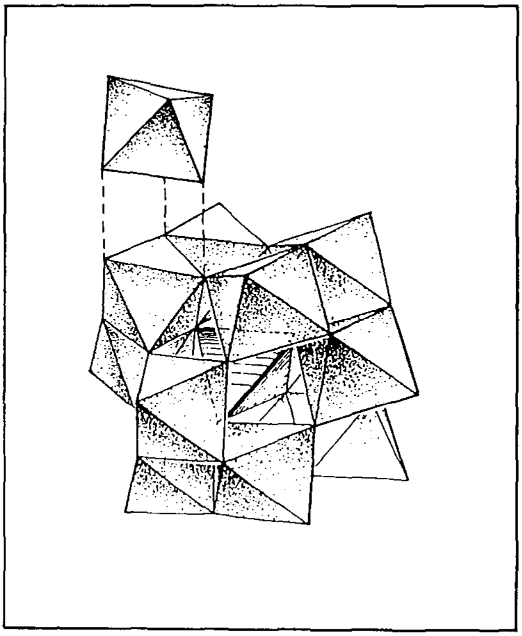

Fig. 7. Possible structure for the Keggin anion caped by a $Cr(OH)_x(NH_3)_y$ octahedron.

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