APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 660–669 (2000)

NOTE

Modeling chromium sulfate complexes in relation to chromium tannage in leather technology: a computational study†

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Structures that may lead to polynuclear chromium complexes to cross-link the collagen fibrils in chromium tanning processes are modeled. Pathways are suggested to the olation reaction. The role of sulfate as a facilitator has been demonstrated. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: chromium sulfate; collagen; complexation; olation; tanning

Coordination of protein carboxyl groups to chromium is the main reaction in chrome tannage. The usual treatment is to introduce Cr^{3+} salts into the hide, after pickling during which the pH is adjusted to a pH of approximately 3, and then to allow the collagen–chromium complex cross-linking reaction to occur.[1] It was Gustavson[2] who first recognized the fact that chromium tanning consists of building carboxyl groups of collagen as ligands into the chromium complexes. He also showed that thermal stability depends on favorable stereochemical conditions at the moment of chrome tannage.[3] Theis showed that thermal stability is related to swelling of protein at the moment of tannage.[4] Spacing between main protein chains varies from 10 Å in the dry state to 17 Å in the swollen condition, and bridging by single Cr atoms would be unlikely.[4]

Un-ionized acid does not form a stable coordination compound with chromium, so that the pH of tannage will govern the extent of coordination of carboxyl groups. In the chromium sulfate liquors normally used in practice, the precipitation point governs the optimum tanning point, but if the pH of the precipitation is raised by masking agents the coordination of more carboxyl groups can be promoted by a higher pH value. According to Bowes and Kenten[5] (in terms of the percentage of carboxylic groups on collagen) the main acid residues are aspartic acid (5%) and glutamic acid (11.3%), which have pK values of 3.76 and 4.2 respectively. It has been shown that carboxyl groups become partly displaced by hydroxyl groups at high pH values,[6–9] so that the bond between protein and chromium may be broken by raising the pH value too far. At 6.6 and above there exists the danger of over-neutralization.

The chromium cation Cr^{3+} in aqueous solutions occurs as the hydrated hexaquochromium ion, $Cr(H_2O)_6{}^{3+}$. Water held by this ion can be exchanged for other ions. An ^{18}O-enriched water exchange reaction has been carried out to find out the strength of the bond between the water molecules and chromium in aqueous solution. A surprisingly high lifetime, 54 h (when compared with Al^{3+}, Li^{+}, Mg^{2+}, Bi^{3+}) is found, and the existence of six water molecules linked directly to the Cr^{3+} ion in aqueous solution is confirmed.

As early as 1910 Bjerrum[10] suggested the formation of μ-bridges between the chromium atoms. In this reaction, called 'olation', hydroxy groups are built in the internal sphere of the complexes upon aging or heating, and form Cr–OH–Cr links. Chrome tanning liquor consists of chromium atoms linked by olation. According to some investigators the loss of a proton may cause oxolation (deprotonation) and formation of oxygen bridges (Cr–O–Cr). Further reaction results in formation of a complex with two ol bridges. The influence of sulfate is suggested to make olation easier. Kawamura and Wada,[11] and later Indubala

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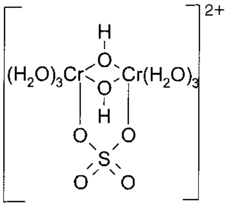
† Presented at the XIIIth FECHEM Conference on Organometallic Chemistry, held 29 August–3 September 1999, Lisbon, Portugal.

Contract/grant sponsor: Bogazici University Research Funds; Contract/grant number: 00B502.



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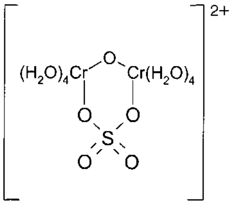


2

and Ramaswamy,[12] have isolated three components of sulfate liquor of 33% basicity, namely $[Cr(H_2O)_5SO_4]^+$ and another two that are binuclear complexes of total charge 2+ with a Cr: SO_4 ratio of 2:1. IR determinations have confirmed the presence of the ions **1** and **2**.[12]

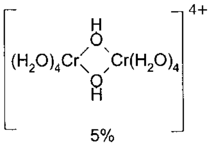
Stiasny and Koningfeld[13] have observed a greater tendency for sulfates to olate than chlorides, and have attributed this to formation of six-membered rings. This has been confirmed by Shuttleworth,[14] who has produced evidence that chlorides and nitrates form stable di-ol and tri-ol bridges involving two chromium atoms at 33% and 50% basicity and four chromium atoms at 66% basicity, all complexes being soluble. Addition of sulfate, followed by boiling, is said to cause an enlargement of the molecule.

Strakhov[15] states that coupling of chromium compounds by collagen is greater when half the coordination points belong to more active ligands than water, and explains the greater fixation by albumins of chromium sulfate than of chloride liquors.

Shuttleworth[16] has worked on reaction velocities of olation and found that the hexaquochromium salts olate according to a bimolecular reaction, nitrate being faster than chloride and sulfate the slowest, presumably owing to ligand competition. Slabbert[17] demonstrated that at least 10 ionic and nonionic complexes are present in 33% basic chromium sulfate solution. The six compounds present in highest concentration and of determined structure are **3**–**8**.

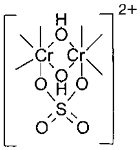
3 $[Cr(H_2O)_5SO_4]^+$ 10%

4 $[Cr(H_2O)_6]^{3+}$ 9%



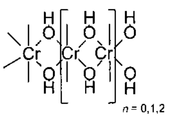
5%

5



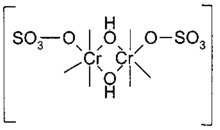
32%

6



20%

7



11%

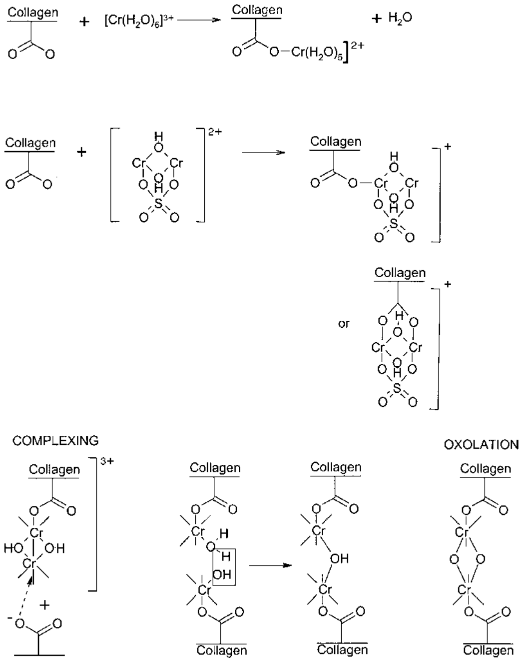
8

Chromium compounds are frequently reported as generally stable. Reactions of chromium complexes (mostly exchange reactions) are characterized by their particular slowness. The ligand exchange in chromium complexes is the fundamental principle of chromium tannage theory. Essential for this theory is the acceptance of the Cr^{3+}–collagen carboxylic group complex as the most stable among the complexes known, and weakly bound masking ligands give way to carboxyls.

Chrome tanning may be defined as the control of four competing reactions:

(1) entry of OH groups;
(2) binding of ion in the first sphere of the complex to make it susceptible to masking;
(3) masking reaction—entry of organic acid residue;
(4) reaction of protein carboxyl group;

Cross-linking may be the fifth reaction. It is probably still proceeding during piling of the leather after tanning.



Scheme 1

Lasek[18] in his chrome tanning theory stresses the part the sulfate ion plays in the formation of polynuclear complexes from the binuclear ones, with previously built-in collagen carboxyls.

Masking agents enter complexes, if they are sufficiently ionized at low pH. When the organic acid used for the masking is weak, a higher pH facilitates its reaction, as its ionization increases. The increase in pH of the tanning liquor is a reason for the increase in the basicity of the chromium complexes and their oxolation as an aging effect (deprotonation), whereas the coordination affinity of the sulfate residues remains unchanged. In this reaction step the masking agent remains coordinated with chromium; the reactivity of the protein increases, however, and the carboxyls enter the complex.

According to Harlan and Feairheller,[19] the following reaction types can take place as the carboxyl ion attached to collagen enters the complexes:

(1) entry of two carboxyl ions into the same chromium complex;
(2) olation with elimination of water and formation of a linkage between two complexes (Scheme 1).

It has been shown that bidentate sulfate groups remain in the final complexes after leather curing and dyeing. Their apparent significance for improving the stability of complexes has been recognized.

In this study the possible structures that may lead to polynuclear chromium complexes to cross-link the collagen fibrils in chromium tanning are modeled. The aim is to bring insight to the olation reaction and to investigate the role of the sulfate ion.

METHOD AND COMPUTATIONS

A theoretical approach using quantum chemical calculations was taken. The strategy has been

(a) to start with the modeling of the hexaquochromium ion;
(b) to determine the tendency of hydroxy, sulfate, formate and acetate ions to replace water molecules in the complex-forming reaction;
(c) to model the possible complexes (mononuclear and binuclear) in solution and write possible reactions for their formation;
(d) to explain the formation of the olated complexes.

All the species of interest were modeled using the HyperChem[20] series of programs and their heats of formation, ΔH_f, were obtained. The ZINDO/1 method[21] was used and the geometry of all the structures was optimized. The heats of reaction were calculated as $\Delta H_R = \Delta H_f$ (products) $-\Delta H_f$ (reactants), negative values showing the liberation of energy during the reaction.

RESULTS AND DISCUSSION

Calculations were carried out for possible structures that may lead to polynuclear chromium complexes to cross-link the collagen fibrils in chrome tanning. The heats of formation for the species are listed in Tables 1 and 2.

A negative free energy change, ΔG, is associated with reactions that favor the formation of products when equilibrium is reached. Heat of reaction and entropy change are the two components that contribute to the free energy change ($\Delta G = \Delta H - T\Delta S$). A negative value for ΔH_R will contribute to making ΔG negative and will favor the formation of products. The entropy change is expected to be positive since cross-linking through polynuclear chromium complexes renders the system more orderly. Temperature, T, is not high (*ca* 351 °C) because leather tanning is not carried out at high temperatures. $T\Delta S$ is more or less constant and a large value of ΔH will determine whether or not the formation of the products will be favored.

Fennen[22] has used the DFT method to calculate the structure of an olated dinuclear chromium complex model (the only quantum mechanical work found in the literature for similar complexes) and reports the dimensions of the chromium complex to give a good fit to the positions of reactive sites in the collagen model.

Water molecules held by $Cr(H_2O)_6^{3+}$ ion are easily exchanged by hydroxyl groups. Takenouchi has reported on the stability of the hexaquo complexes of chromium, and that they change to hydroxo complexes at $pH > 3$.[23] The entry of the first hydroxyl group into the complex, expelling a water molecule, is the most exothermic; introduction of the second |hydroxyl is less exothermic than the first, and that of the last hydroxyl is the least exothermic (Eqns [1] [2] [3]).

The total heat of reaction calculated for the

Table 1 Structures, formulas and heats of formation for the complexes calculated.

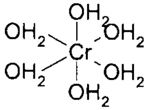
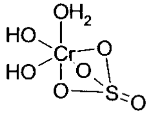
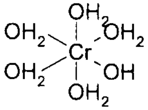
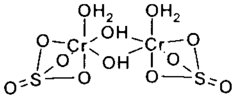
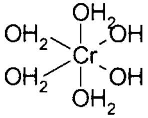
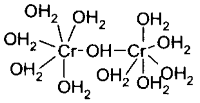
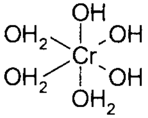
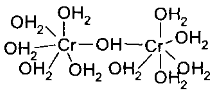
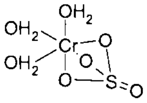
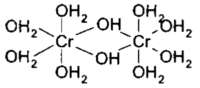
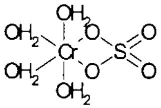
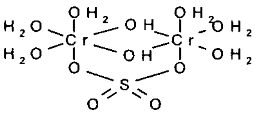
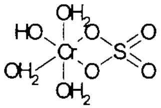
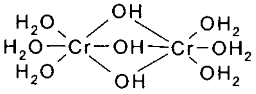
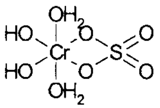
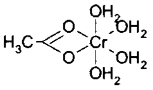
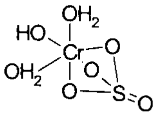
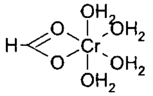
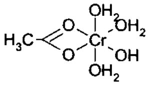
Structure	Formula	ΔH_f (kcal/mol^{-1})	Structure	Formula	ΔH_f (kcal/mol^{-1})
	$[Cr(H_2O)_6]^{3+}$	−803.60		$[Cr(SO_4)(OH)_2(H_2O)_3]^-$	−770.26
	$[Cr(OH)(H_2O)_5]^{2+}$	−1053.80		$[Cr(SO_4)_2(OH)_2(H_2O)_2]$	−1017.97
	$[Cr(OH)_2(H_2O)_4]^+$	−1087.56		*trans*-$[Cr_2(OH)(H_2O)_{10}]^{5+}$	−1312.63
	$[Cr(OH)_3(H_2O)_3]$	−1050.42		*cis*-$[Cr_2(OH)(H_2O)_{10}]^{+5}$	−1319.48
	$[Cr(SO_4)(H_2O)_3]^+$	−687.0206		$[Cr_2(OH)_2(H_2O)_8]^{4+}$	−1273.22
	$[Cr(SO_4)(H_2O)_4]^+$	−977.40		$[Cr_2(SO_4)(OH)_2(H_2O)_6]^{2+}$	−1647.31
	$[Cr(SO_4)(OH)(H_2O)_3]$	−975.63		$[Cr_2(OH)_3(H_2O)_6]^{3+}$	−1296.75
	$[Cr(SO_4)(OH)_2(H_2O)_2]^-$	−853.57		$[Cr(CH_3COO)(H_2O)_4]^{2+}$	−1851.08
	$[Cr(SO_4)(OH)(H_2O)_2]$	−698.58		$[Cr(HCOO)(H_2O)_4]^{2+}$	−1257.62
				$[Cr(CH_3COO)(OH)(H_2O)_4]^+$	−1869.76

Table 1 continued.

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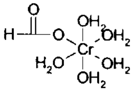
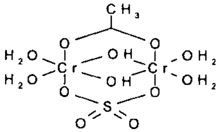
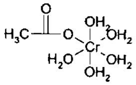
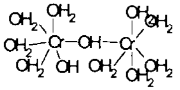
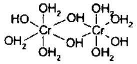
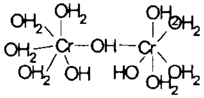
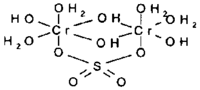
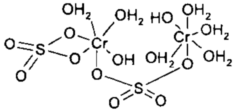
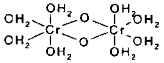
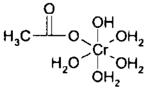
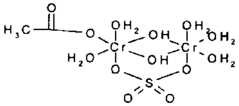
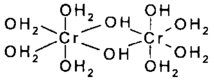
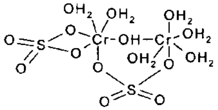
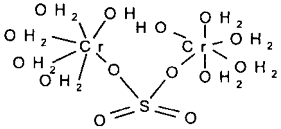
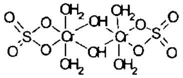
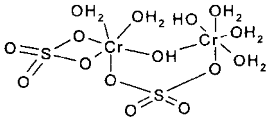
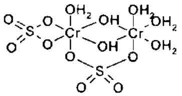
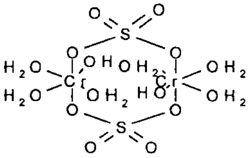
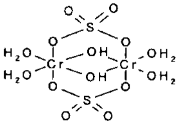
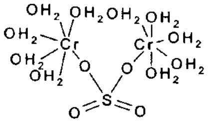
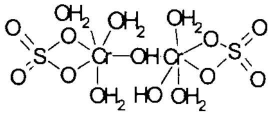
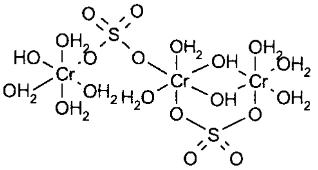
	$[Cr(HCOO)(H_2O)_5]^{2+}$	−1487.98		$[Cr_2(SO_4)(CH_2COO)(OH)_2(H_2O)_4]$	−2735.1306
	$[Cr(CH_3COO)(H_2O)_5]^{2+}$	−2091.04		$[Cr_2(OH)_2(H_2O)_9]^{4+}$	−1533.4430
	$[Cr_2(OH)_4(H_2O)_6]^{2+}$	−1739.39		$[Cr_2(OH)_2)(H_2O)_8]^{3+}$	−1770.8342
	$[Cr_2(SO_4)(OH)_4(H_2O)_4]$	−1714.37		$[Cr_2(SO_4)_2(OH)_2(H_2O)_6]$	−2040.1223
	$[Cr_2O_2(H_2O)_8]^{2+}$	−1746.48		$[Cr(CH_3COO)(OH)(H_2O)_4]^{+}$	−2136.3990
	$[Cr_2(SO_4)(CH_3COO)(OH)_2(H_2O)_4]^{2+}$	−2861.7587		$[Cr_2OH)_3(H_2O)_7]^{4+}$	−1490.9
	$[Cr_2(SO_4)_2(OH)(H_2O)_6]^{1+}$	−2081.3942		$[Cr_2(SO_4)(OH)_2(H_2O)_8]^{2+}$	−2044.3297
	$[Cr_2(SO_4)_2(OH)_2(H_2O)_4]$	−1601.1565		$[Cr_2(SO_4)_2(OH)_2(H_2O)_5]$	−2081.39
	$[Cr_2(SO_4)_2(OH)_2(H_2O)_4]$	−1771.7587		$[Cr_2(SO_4)_2(OH)_2(H_2O)_6]$	−2320.2615
	$[Cr_2(SO_4)(OH)_2(H_2O)_4]$	−2117.2098			
	$[Cr_2(SO_4)(H_2O)_{10}]^{4+}$	−1877.8649			

Table 1 continued.

Structure	Formula	ΔH_f(kcal/mol^{-1})
	$[Cr_2(SO_4)_2(OH)_2(H_2O)_5]$	−2022.22
	$[Cr_3(SO_4)_2(OH)_3(H_2O)_9]$	−2786.2233

stepwise exchange (-1057.95 kcal mol^{-1}) is of the same order as the heat of reaction calculated for the one-step complexation of three hydroxyl groups reaction (Eqn [4]).

Shuttleworth[16] has studied the kinetics of olation and deolation and has pointed out that alkali added to make the basic liquor is absorbed extremely rapidly by the normal commercial type of chromium tanning liquor.

The sulfate ion, being divalent, does not form a monodentate complex with the chromium ion in mononuclear complexes. It prefers to be bidentate rather than tridentate and easily replaces water molecules (Eqns [5] and [6]).

There is IR evidence that the sulfate group coordinates as a bidentate ligand.[23] Comparison of monodentate with bidentate complexation of acetate and formate ions with the chromium ion shows their preference for being monodentate (Eqns [7]–[10]).

The affinity order among monodentate ligands seems to be hydroxy > acetate > formate > water, in accordance with the literature. The formation of formate and acetate complexes from hexaquochromium complexes has been studied and possible structures have been discussed on the basis of spectral and stoichiometric characteristics.[24]

Table 2 Formulas and heats of formation for the complexing ligands.

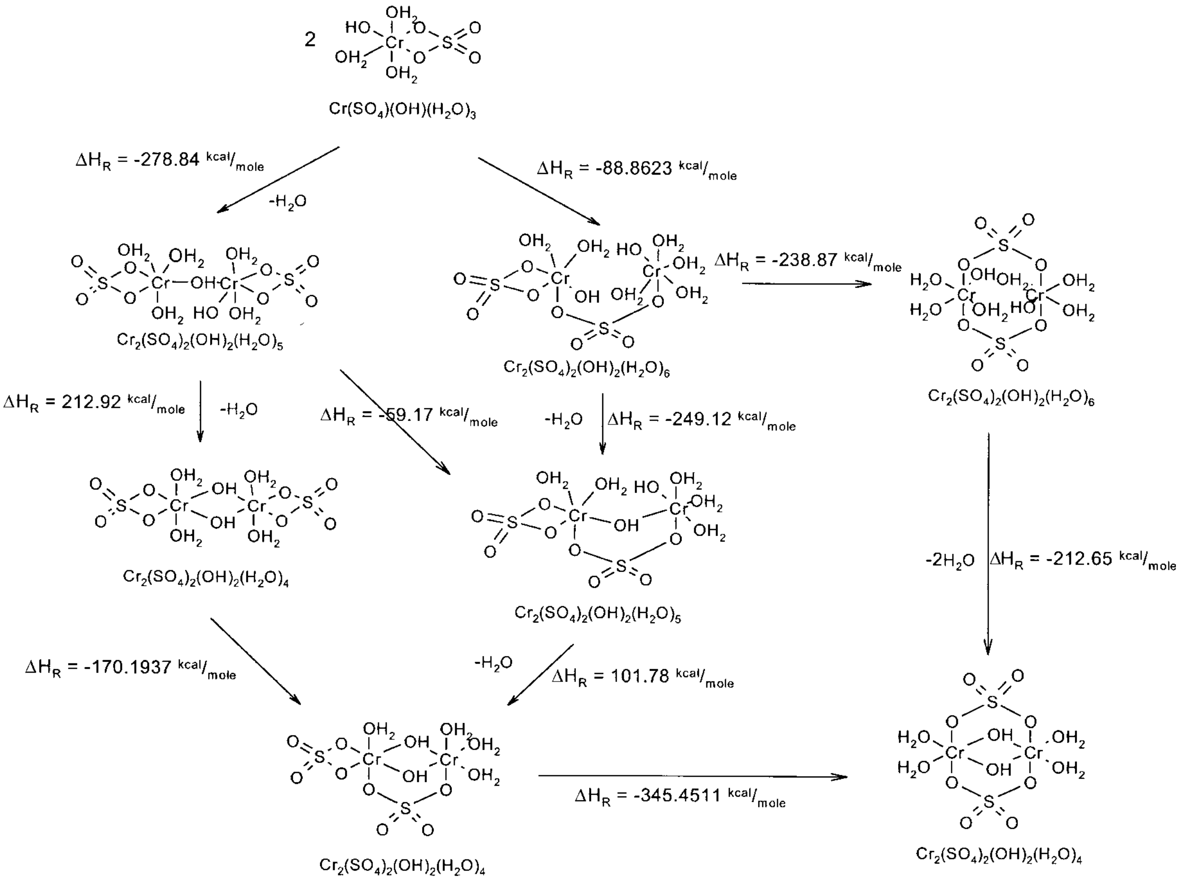
Formula	ΔH_f (kcal mol^{-1})
H_2O	−207.85
OH^-	62.26
SO_4^{2-}	138.21
CH_3COO^-	−1019.04
$HCOO^-$	−462.80

Olation through reactions of $Cr(OH)_n(H_2O)_{6-n}$ seem unlikely, since their reactions give positive heats of reaction. The di-μbridges are shown by $Cr < (OH)_2 > Cr$.

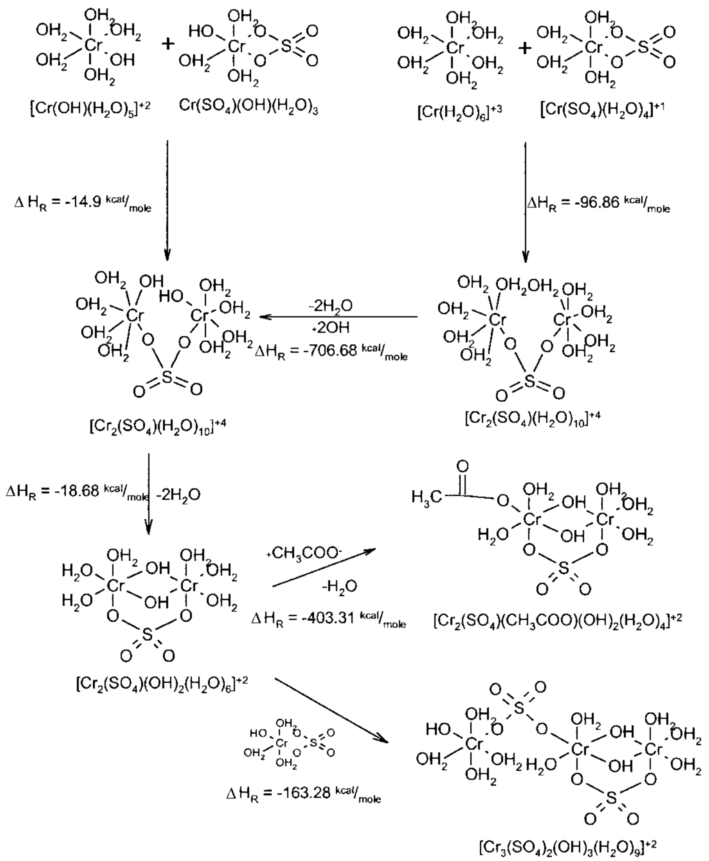
Olation reactions with $Cr(H_2O)_3(OH)(SO_4)$ as one of the reactants are shown in Schemes 2 and 3 with the heats of reaction given on the arrows. Two $Cr(OH)(SO_4)(H_2O)_3$ complexes react with each other through different pathways and form the dimer in Scheme 2. In Scheme 3, a set of reactions leads to the olation of the $Cr(OH)(SO_4)(H_2O)_3$ complex with $Cr(OH)(H_2O)_5{}^{2+}$ or $Cr(H_2O)_6{}^{3+}$ complexes, which is followed by the replacement of a water molecule by acetate or further growth to a trichromium complex.

$Cr(H_2O)_3(OH)(SO_4)$ can react to start the formation of the binuclear complex through a sulfate link or more exothermically it can expel a water molecule and become binuclear through an OH link. As can be seen from Scheme 2, olation is facilitated by the existence of a sulfate bridge between the chromium ions. The sulfate anion, being bidentate, holds the two chromium ions in close proximity. Olation increases the stability of chromium sulfate complexes. The formation of a second —OH— bridge between the chromium ions is more endothermic in the absence of a sulfate bridge. Alternatively, the two sulfate bridges may be formed first and then olation may follow.

Comparison of Schemes 2 and 3 shows that the presence of one sulfate group per chromium ion renders the olation reaction more exothermic than that with one sulfate group per two chromium ions.



Scheme 2 A schematic representation of a set of reactions for the olation of two $Cr(OH)(SO_4)(H_2O)_3$ complexes.



Scheme 3 A schematic representation of a set of reactions for the olation of the $Cr(OH)(SO_4)(H_2O)_3$ complex with $Cr(OH)(H_2O)_5^{2+}$ or $Cr(H_2O)_6^{3+}$ complexes.

$$\mathrm{Cr(H_2O)_6}^{3+} + \mathrm{OH^-} \rightarrow \mathrm{Cr(OH)(H_2O)_5}^{2+} + \mathrm{H_2O} \qquad -\,520.31\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [1]$$

$$\mathrm{Cr(OH)(H_2O)_5}^{2+} + \mathrm{OH^-} \rightarrow \mathrm{Cr(OH)_2(H_2O)_4}^{+} + \mathrm{H_2O} \qquad -\,304.67\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [2]$$

$$\mathrm{Cr(OH)_2(H_2O)_4}^{+} + \mathrm{OH^-} \rightarrow \mathrm{Cr(OH)_3(H_2O)_3} + \mathrm{H_2O} \qquad -\,232.97\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [3]$$

$$\mathrm{Cr(H_2O)_6}^{3+} + \mathrm{3OH^-} \rightarrow \mathrm{Cr(OH)_3(H_2O)_3} + \mathrm{3H_2O} \qquad -\,1066.15\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [4]$$

$$\mathrm{Cr(H_2O)_6}^{3+} + \mathrm{SO_4}^{2-} \rightarrow \mathrm{Cr(SO_4)(H_2O)_3}^{+} + \mathrm{3H_2O} \qquad -\,645.18\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [5]$$

$$\mathrm{Cr(H_2O)_6}^{3+} + \mathrm{SO_4}^{2-} \rightarrow \mathrm{Cr(SO_4)(H_2O)_4}^{+} + \mathrm{2H_2O} \qquad -\,727.71\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [6]$$

$$\mathrm{Cr(H_2O)_6}^{3+} + \mathrm{CH_3COO^-} \rightarrow \mathrm{Cr(CH_3COO)(H_2O)_4}^{2+} + \mathrm{2H_2O} \qquad -\,444.14\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [7]$$

$$\mathrm{Cr(H_2O)_6}^{3+} + \mathrm{CH_3COO^-} \rightarrow \mathrm{Cr(CH_3COO)(H_2O)_5}^{2+} + \mathrm{H_2O} \qquad -\,476.21\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [8]$$

$$\mathrm{Cr(H_2O)_6}^{3+} + \mathrm{HCOO^-} \rightarrow \mathrm{Cr(HCOO)(H_2O)_4}^{2+} + \mathrm{2H_2O} \qquad -\,406.92\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [9]$$

$$\mathrm{Cr(H_2O)_6}^{3+} + \mathrm{HCOO^-} \rightarrow \mathrm{Cr(HCOO)(H_2O)_5}^{2+} + \mathrm{H_2O} \qquad -\,429.43\Delta H_\mathrm{R}(\mathrm{kcal\,mol^{-1}}) \qquad [10]$$

$$\Delta \mathrm{H_R}(\mathrm{kcal\ mol^{-1}})$$

$$\mathrm{Cr(OH)(H_2O)_5}^{2+} + \mathrm{Cr(H_2O)_6}^{3+} \rightarrow [\mathrm{(H_2O)_5Cr{-}{-}(OH){-}{-}Cr(H_2O)_5}]^{5+} + \mathrm{H_2O} \qquad 330.1 \qquad [11]$$

$$\mathrm{Cr(OH)_2(H_2O)_4}^{+} + \mathrm{Cr(H_2O)_6}^{3+} \rightarrow [\mathrm{(H_2O)_4(OH)Cr{-}{-}(OH){-}{-}Cr(H_2O)_5}]^{4+} + \mathrm{H_2O} \qquad 149.9 \qquad [12]$$

$$\mathrm{Cr(OH)_2(H_2O)_4}^{+} + \mathrm{Cr(OH)(H_2O)_5}^{2+} \rightarrow [\mathrm{(H_2O)_4(OH)Cr{-}{-}(OH){-}{-}Cr(OH)(H_2O)_4}]^{3+} + \mathrm{H_2O} \qquad 162.7 \qquad [13]$$

$$2[\mathrm{Cr(OH)(H_2O)_5}]^{2+} \rightarrow [\mathrm{(H_2O)_4Cr} < \mathrm{(OH)_2} > \mathrm{Cr)(H_2O_4}]^{4+} + \mathrm{2H_2O} \qquad 418.7 \qquad [14]$$

$$\mathrm{Cr(OH)(H_2O)_5}^{2+} + \mathrm{Cr(OH)_2(H_2O)_4}^{+} \rightarrow [\mathrm{(H_2O)_4Cr} < \mathrm{(OH)_2} > \mathrm{Cr(OH)(H_2O)_3}]^{3+} + \mathrm{2H_2O} \qquad 234.8 \qquad [15]$$

$$2[\mathrm{Cr(OH)_2(H_2O)_4}]^{+} \rightarrow [\mathrm{(H_2O)_3(OH)Cr} < \mathrm{(OH)_2} > \mathrm{Cr(OH)(H_2O)_3}]^{2+} + \mathrm{2H_2O} \qquad 20.1 \qquad [16]$$

The most stable of the binuclear complexes $Cr_2(OH)_2(SO_4)_2(H_2O)_6$ has the two chromium ions linked through two ol bridges and two sulfate bridges, but it resists binding of an acetate exothermically. The least stable one is that in which the two chromium ions are bridged with two ol bridges and the sulfates are on separate chromium ions, not involved in bridging. Between the two with intermediate stability, is the complex with one sulfate bridge and two ol bridges, in this complex an acetate anion can easily replace a water exothermically after olation. Schemes 2 and 3 seem to be plausible sequences of reactions for the formation of the polynuclear complexes.

To conclude, in this study the structures that may lead to polynuclear chromium complexes to cross-link the collagen fibrils in chromium tanning are modeled. Pathways have been suggested to the olation reaction. The role of sulfate as a facilitator has been shown. Further work toward the understanding of the process in leather making at the molecular level is under way.

Acknowledgements We thank Kerem Kurumlu for initiation of the project and providing information. This work has been supported by Bogazici University Research Funds Project No. 00B502.

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