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Review

Coordination geometry of Cr(VI) species: Structural and spectroscopic characteristics

Maria Cieślak-Golonka*, Marek Daszkiewicz

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław University of Technology,
ul. Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland

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Dedicated to Professor Adam Bartecki on the occasion of his 85th birthday.

Contents

Abstract

In this review, the speciation of chromium(VI) entities, the key to understanding the further redox processes related to this ion, is presented and discussed. Two possible modes of Cr(VI) binding, i.e. as a centre of coordination and as a ligand, have been characterized. In contrast to the gas and solid-state phases, where coordination number four is generally preserved, the Cr(VI) coordination sphere may be more flexible and chromium(VI) forms can even be seven-coordinate in solution. In the solid state, the pseudotetrahedral stereochemistry of the $[CrO_4]^{2-}$ species does not exclude versatility of its coordination modes, e.g. monodentate, polymeric bridging, bidentate, chelate, etc. The difficulties and various problems associated with structural aspects of Cr(VI) forms, mainly in relation to their spectroscopic properties, are shown.

Keywords: Chromium(VI); Coordination geometry; Intermediates; Structure; Spectroscopy

1. Introduction

Chromium(VI) is an industrially very important form of this element [1]. It is used, e.g. in stainless steel welding,

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* Corresponding author. Tel.: +48 71 320 22 80; fax: +48 71 328 43 30.
E-mail address: maria.golonka@pwr.wroc.pl (M. Cieślak-Golonka).

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chrome plating and the production of dyes [2,2a]. However, the anthropogenic emission and contamination of soil and ground water (up to 11,000 t/year [3]) with Cr(VI) compounds used in the production of metallic chromium and its compounds cause a serious environmental pollution [3a]. Moreover, chromium(VI) compounds are strong toxins and human carcinogens [2,4,5a]. Being a labile species, in the presence of various environmental reductants, e.g. Fe(II) and organic substances [5b–d], it is usually converted Cr(III), the dominant form of chromium in nature. However, Cr(VI), the dangerous pollutant can also be resistant to reduction [6].

Cr(III) is regarded by most nutritionists as an essential micronutrient for humans, although this opinion has been disputed [7,8].

Both in the environment, and as found recently, in living organisms, chromium-based redox processes can be reversible [7,9,10]. Moreover, on the basis of recent observations, it seems clear, that the paradigm: “carcinogenic” Cr(VI) and “beneficial” Cr(III) is no longer valid [7,11] as Cr(VI) is not genotoxic per se [12] and Cr(III) can also be mutagenic [8,13,14].

As most reductants are only one- or two-electron donors, the Cr(VI) → Cr(III) redox processes (which require the transfer of three electrons) proceed through several stages. In the redox processes [Cr(VI)-organic substrate], the two most important pathways are known [15a]:

(1) Watanabe and Westheimer
  (a) $Cr(VI) + S \leftrightarrow [Cr(VI){-}S]$;
  (b) $[Cr(VI){-}S] \rightarrow Cr(IV) + P$;
  (c) $Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$;
  (d) $Cr(V) + S \rightarrow Cr(III) + P$;
(2) Roček
  (a) $Cr(VI) + S \leftrightarrow [Cr(VI){-}S]$;
  (b) $[Cr(VI){-}S] \rightarrow Cr(IV) + P$;
  (c) $Cr(IV) + S \rightarrow Cr(III) + R^{\bullet}$;
  (d) $Cr(VI) + R^{\bullet} \rightarrow Cr(V) + P$;
  (e) $Cr(V) + S \rightarrow Cr(III) + P$;

where S, P are substrates and products, respectively.

Both proposals assume the presence of Cr(VI) intermediate species (stage (a)).

Generally, mechanisms of Cr(VI) ↔ Cr(III) reactions are very complicated with the following factors contributing predominantly:

(i) kinetic lability of both the Cr(VI) species and the transient Cr(V)/Cr(IV)/Cr(II) intermediates [16,17];
(ii) dependence of the reaction mechanisms on the experimental conditions, such as the pH value, concentration of the reactants, the Cr/ligand ratios [15] or nature of the solvent [18];
(iii) solvent-dependent changes in the coordination numbers of some Cr(VI) complexes [18];
(iv) nature of the reductants (the presence of Cr(VI/V)-binding functional groups like thiols or *cis*-diols) [16], charge of the nucleophiles [19];
(v) additional factors including the presence or absence of catalysts, such as γ-Al_2O_3 [20], Zn^{2+} [21], imidazole, picolinic acid, bpy, phen [22], nature of the buffer, such as acetate, citrate, phosphate [21,23,24], or TRIS [19], and the presence or absence of oxygen [25].

Thus, systematic studies on the speciation in the frame of one oxidation state seem to be a very important although weakly explored field of research in Cr chemistry [26,27].

This review describes the structural aspects of Cr(VI) complexes, in most cases, the starting point, but sometimes also the intermediate one in various important redox reactions [28]. We have attempted to collect, characterise and discuss mostly biologically relevant Cr(VI) species, which act as precursors and intermediates in the process of chromium-induced carcinogenesis. Other aspects of chromium in biological systems, of interest to coordination, biological and environmental chemists, were covered in several recent reviews [15a,16,29–32].

2. Uptake–reduction model 25 years later

Wetterhahn and co-worker were the first to propose the mechanistic *uptake–reduction* model explaining the problem of Cr(VI) carcinogenicity [33]. She assumed that the carcinogenic effect is related to chromate, $[CrO_4]^{2-}$, the predominant Cr(VI) oxo complex at physiological pH values (∼7.4), which, by taking advantage of its similar size and symmetry to the sulfate and phosphate anions, exhibits the ability to cross the cellular membrane via non-specific anionic transport channels. In the cytoplasm, in contact with the cellular reductants, such as ascorbate, glutathione, cysteine or NADH, the $[CrO_4]^{2-}$ anions undergo a series of redox processes with the formation of both Cr(V/IV) complexes and various organic radicals, all of which are potentially DNA-damaging agents. Generally, the assumptions of the *uptake–reduction* model are still valid. However, after almost a quarter of a century, several new facts have been added to this model, as described below.

(1) Developments in the instrumental techniques, including X-ray absorption spectroscopic methods (XANES and XAFS) [7], electrospray mass spectrometry (ESMS) [7,34] and global kinetic analysis [16,18] lead to a significant increase of knowledge on the chemistry of unstable Cr(VI/V/IV) complexes [7,26,35–37]. Some of the most important observations are: (i) the unusual stability of Cr(V) bound to carbohydrate ligands [16,38,39] and (ii) strong DNA-cleaving ability of some Cr(V) and Cr(IV) complexes [7,12,40,41]. In addition, decomposition of Cr(V/IV) complexes formed in biological media can lead to the formation of reactive Cr(III) complexes capable of binding to DNA [42].
(2) The potential importance of extracellular reactions including various transformations within one oxidation state (e.g. Cr(VI) pre-redox complexation) in the whole

process of chromium metabolism has been proposed [32,43].

(3) Phagocytosis has been postulated as a likely way of transportation of insoluble Cr(VI) particles (e.g. $PbCrO_4$) to the cell [12,16,44].

(4) The reversibility of the Cr(VI) conversion to Cr(III) under biologically relevant conditions has been established experimentally [7,10,16]. The oxidation of Cr(III) may take place both in extra- and in intracellular ways and its mechanism is dependent on the nature of Cr(III) species [10]. Extracellular oxidation of Cr(III) to Cr(VI) is likely to lead to the enhanced cellular uptake of Cr [10]. Moreover, this re-oxidation of Cr(III) may be responsible for anti-diabetic activities previously ascribed to Cr(III) itself [10,17].

(5) The versatility of Cr(VI) ↔ Cr(III) pathways [15a,16,35,45,46] especially in the interaction of chromium metabolic species Cr(V)/Cr(IV)/Cr(III) with DNA [7,16,17,42,47–49].

3. Chromium(VI) ion as a centre of coordination

3.1. Simple oxo ligands

Chromium(VI) exists predominantly in the form of rigid oxo complexes in the solid state, in solutions or in the gas phase [29,34,50,51]. The crystal and electronic structures of Cr(VI) oxo species have been for years the subject of thorough theoretical and experimental studies [16,52,53]. Recently, the structure of $[CrO_4]^{2-}$ ion has been recalculated using density functional theory (DFT) methods [52]. The analysis has supported the earlier observations that the chemical bonds are composed of d orbitals of the Cr atoms and p orbitals of the O atoms. Good agreement was obtained between the theoretical (1.67 Å) and experimental (1.634 Å) values of the Cr–O bond length [52].

The Cr(VI) ion, being relatively small (0.40 Å radius) [54] is able to coordinate predominantly four oxygen ligands forming tetrahedrally oriented $[CrO_4]^{2-}$ species with the radius of 2.40 Å [50]. The π orbitals in the four Cr–O bonds (consisting of O 2p Cr 3d orbitals) play a more significant role than in heavier Cr analogues (Mo and W) [52].

Consequently, in Cr(VI), the reaction leading to increase of coordination number from four to six is less likely as it will weaken the π-bonding system due to the increase of the average Cr–O bond distance.

There are two particularly important stable Cr(VI) forms in the solid state: monomeric $[CrO_4]^{2-}$ and dimeric $[Cr_2O_7]^{2-}$; the latter is composed of two tetrahedra linked by oxygen atom [52], with a Cr–O–Cr bond angle of 122.9° [55]. Other Cr(VI) anions, e.g. the less abundant $[Cr_3O_{10}]^{2-}$ and $[Cr_4O_{13}]^{2-}$ isolated from solutions of high acidity [56] can be regarded as polynuclear species of Cr(VI)-containing $[CrO_4]^{2-}$ tetrahedra sharing an oxygen atom. However, under ESMS condition (rapid evaporation of the solvent in an applied electric field) significant polymerization of up to 12 Cr atoms can take place, including the formation of such exotic ions as $[H_3Cr_3O_5]^-$, $[HCr_3O_{10}]^-$ and $[HCr_4O_{13}]^-$ [34].

In aqueous solution, depending upon acidity and concentration, various equilibria have been found with the participation of the $[CrO_4]^{2-}$, $[HCrO_4]^-$, $[H_2CrO_4]$, $[Cr_2O_7]^{2-}$ and $[Cr_3O_{10}]^{2-}$ species [19,51]. For example, using the isotopic ^{17}O NMR exchange studies [19a], the equilibria and the rate constants of the dimerization reaction (and the opposite hydrolysis), were measured and found to be dependent of the buffer, H^+ and OH^- concentration [19a].

Generally, the most important reactions can be schematically written [19b]:

$$[H_2CrO_4] \Leftrightarrow [HCrO_4]^- + H^+,$$
$$K_1 = 0.18\,(I = 0.16; 25\,^\circ C) \quad (1)$$

$$[HCrO_4]^- \Leftrightarrow [CrO_4]^{2-} + H^+,$$
$$K_2 = 1.58 \times 10^{-6}\,(I = 0.5; 25\,^\circ C) \quad (2)$$

$$2[HCrO_4]^- \Leftrightarrow [Cr_2O_7]^{2-} + H_2O,$$
$$K_3 = 74 \pm 3\,(I = 0.5; 25\,^\circ C) \quad (3)$$

$$[HCr_2O_7]^- \Leftrightarrow [Cr_2O_7]^{2-} + H^+ \quad (4)$$

$$2[H_2CrO_4] \Leftrightarrow [HCr_2O_7]^- + H_3O^+ \quad (5)$$

Recently, it was found that under biological and environmental conditions, the dimeric forms of Cr(VI) are not expected to be present at significant concentrations, as the dimerization reactions occur only at Cr(VI) concentration over 2 M [19a]. However, the concentration of the reagents can be changed when, e.g. less soluble products (e.g. dichromates) are formed, even at very low concentration [57]. As a result, the dichromates can be isolated (pH ~8) in spite of the chromates used as substrates. $[Ni(phen)_3][Cr_2O_7]\cdot 3H_2O$ was obtained from the $[Ni(II)–phen–CrO_4]$ system [57,58].

The $[HCrO_4]^-$ ($[CrO_3(OH)]^-$) ion is a product of electrophilic proton attack on $[CrO_4]^{2-}$. The former anion is an important species under biological conditions, as the reactive form of Cr(VI) in the redox processes. Its existence, once questioned [59–61], is now supported both theoretically [62] and experimentally [19,34,58,63,64] (Fig. 1).

A protonated form of chromic acid, $[H_3CrO_4]^+$, was also postulated to exist in solution, particularly under micellar conditions [15a,65,66]. However, as the protonation constant of $[H_2CrO_4]$ is very low, the existence of this species is disputable and has not been proven even for strongly acid solutions [15a].

For the $[Cr_2O_7]^{2-}$ ion in aqueous solution, cleavages of the terminal and bridging Cr–O bonds with transient five coordination were found to be equally probable (Fig. 2) [19]. However, a four-coordinate corner-shared tetrahedron was found to be the most abundant structural unit also under the “extremal” ESMS conditions [34].

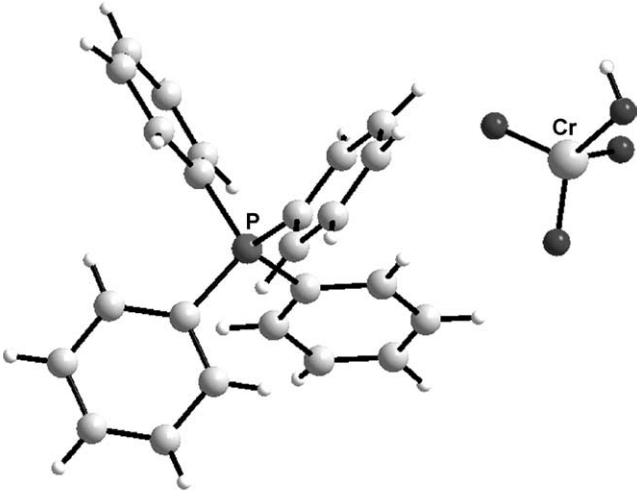


Fig. 1. Crystal structure of $[Ph_4P][Cr^{VI}O_3(OH)]$ [63]. The hydrogen atom was added to the original data; four-fold distortion of chromate was omitted for clarity.

Generally, for mono- and polychromates for non-bridging oxygen atoms, the mean distance is 1.56–1.72 Å, while for bridging ones, it is 1.75–1.86 Å (Table 1).

In the $[CrO_4]^{2-}$ ion (Cr(VI) $3d^0$ configuration) of tetrahedral symmetry, $1t_1$ (HOMO) and 2e (LUMO) orbitals are taking part in the electronic transitions observed in the spectral range of 22,000–30,000 cm^{-1}: the former primarily exhibits oxygen character, whereas 2e possesses large Cr character [53]. The $1t_1 \rightarrow 2e$ excitations yields $^{1,3}T_2$ $^{1,3}T_1$ excited states of the order $^1T_2 > {}^1T_1 > {}^3T_1 > {}^3T_2$ [52–54,110]. The transition to these states can be seen in the electronic spectra of the chromates (Table 2). The most prominent among long-wavelength transition are the $^1A_1 \rightarrow {}^1T_2$ band at ca. 370 nm (27,000 cm^{-1}) of $\varepsilon \sim 4800\,dm^3\,mol^{-1}\,cm^{-1}$ and a much weaker and often overlooked $^1A_1 \rightarrow {}^1T_1$ band at ca. 420 nm ($\varepsilon \sim 120\,dm^3\,mol^{-1}\,cm^{-1}$) (Table 2). The spin- and orbitally forbidden $^1A_1 \rightarrow {}^3T_{1,2}$ transitions ($\varepsilon \sim 0.1$–$0.8\,dm^3\,mol^{-1}\,cm^{-1}$) are sometimes observed in the 13,000–18,000 cm^{-1} absorption region [76,111].

The characteristic feature of the chromate, dichromate and monosubstituted chromate anions is vibrational fine structure usually observed on the 370 nm (27,000 cm^{-1}) absorption band. This structure is attributed to the $\nu_1(A_1)$ Cr–O vibration coupled to the electronic $^1A_1 \rightarrow {}^1T_2$ transition. The degree of the structure resolution was found to be temperature, solvent, counter-ion, X-atom (CrO_3X^-) and technical advances-dependent [51].

Substitution of one O^{2-} ion in the $[CrO_4]^{2-}$ entity for OH^- or other anionic group or simply the formation of the $[CrO_3O']$ entity as in the dichromate ion provides symmetry-lowering $T_d \rightarrow C_{3v}$ and the trigonal splitting of the electronic transitions [51].

3.2. Chromate ion and mineral acids: $[CrO_3X]$ entities

Mineral acids play an important role in biological milieu, e.g. in the gastric system. Moreover, it was found that they interfere in the reaction mechanisms not only through determination of the respective acidity but also through bonding of its anionic part to the Lewis acid, e.g. Cr(VI) ion.

$$[HCrO_4]^- + H^+ + HX \Leftrightarrow [HOCr(O_2)X] + H_2O \tag{6}$$

$X = ClO_4{}^-, HSO_4{}^-, Hal^-$(halogenanion)

Depending upon concentration, this reaction can be accompanied by the reduction of Cr(VI) to Cr(III) [126].

The electronic structure of monosubstituted chromates can be derived from that of $[CrO_4]^{2-}$. In a trigonally deformed tetrahedron, the $t_1 \rightarrow a_2 + e$ correlation takes place with the highest filled orbitals of trigonal C_{3v} symmetry. For example, in the halogeno-substituted chromates, the highest occupied a_2 (and predominantly e orbital) retains an oxygen character [53]. The LUMO orbital in $[CrO_3Hal]^-$ has predominantly chromium character, similarly to that in $[CrO_4]^{2-}$. However, this may not be valid in the CrO_3S chromophore due to lower electronegativity of the S atom (2.58 for S versus 3.16 for Cl) [54].

Thus, in halogenochromates, the states derived from T_d symmetry are trigonally split. In the C_{3v} symmetry, neglecting forbidden splitting of e–e excitation, the $a_2 \rightarrow e$ transitions are present. The $^1T_2$ and $^1T_1$ states in T_d symmetry are trigonally split into $^1E^a$ and $^1A_1 + {}^1E^b$ and $^1E^c$ components. In halogenochromates, the O → Cr CT transitions from the $^1A_1$ to the respective states have the following band positions (and intensity): band I ∼22,000 (170) $dm^3\,mol^{-1}\,cm^{-1}$, band II 27,000 (1200) $dm^3\,mol^{-1}\,cm^{-1}$, and band III 35,000 (1700) $dm^3\,mol^{-1}\,cm^{-1}$. Generally, the first two bands can be easily seen in the electronic spectra of pseudotetrahedral $[CrO_3X]^-$ (X = OH, O′, OR) (Table 2).

3.3. Cr(VI) oxo compounds and small inorganic species

Simple inorganic molecules: O_2, NO, H_2O_2 play an important role in biological systems (see, for example [127–130]).

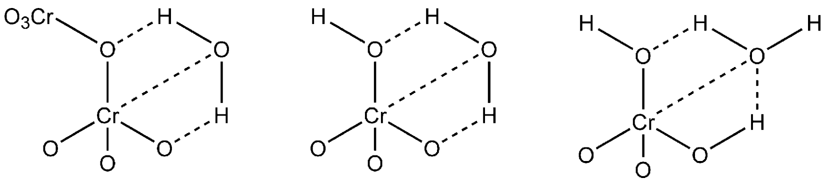


Fig. 2. Role of solvent in cleaving the dichromate anion NMR studies. On the basis of [19].

Table 1
Bond lengths (Å) in Cr(VI)-containing species

	Cr–OM	Cr–O$_{\mathrm{free}}$	Ref.
Uncoordinated (anionic)			
$[PPh_4][HCrO_4]$		1.540; 1.547; 1.581; 2.021	[63]
$[C(NH_2)_3][CrO_4]$		1.629; 1.641; 1.652; 1.659	[67]
$[N(CH_3)_4][CrO_4]$		all 1.646	[68]
$L^1[CrO_4]\cdot 3H_2O$		1.620; 1.632; 1.636; 1.639	[69]
$[C_3H_6(NH_3)_2][CrO_4]$		1.620; 1.662; 1.662; 1.667	[70]
$L^2[CrO_4][ClO_4]_4\cdot 7H_2O$		1.560; 1.646; 1.646; 1.649	[71]
$[t\text{-}BuNH_3][CrO_4]$		1.620; 1.631; 1.631; 1.633	[72]
$[(TMSO)_2][CrO_4]$		1.624; 1.624; 1.628; 1.640	[73]
$[(CH_3)_2C(CH_2NH_3)_2][CrO_4]$		1.616; 1.639; 1.666; 1.687	[74]
$[Cu(HL^3)L^3]_2[CrO_4]$		1.589; 1.618; 1.628; 1.708	[75]
$[Zn(bpy)_3][CrO_4]\cdot 7.5H_2O$		1.583; 1.600; 1.615; 1.626	[76]
$[Ni(bpy)_3][CrO_4]\cdot 7.5H_2O$		1.602; 1.608; 1.626; 1.671	[77]
$[Zn(bpy)_3][CrO_4]_{0.5}[NO_3]\cdot 6.5H_2O$		1.613; 1.613; 1.656; 1.656	[78]
Monodentate coordinated			
$[Cr(\eta\text{-}Ar)_2][MeOCrO_3]$	1.795	1.609; 1.597; 1.592	[79]
$[NicOCrO_3]$	1.881	1.588; 1.589; 1.603	[80]
$[Os(N)(L^4)(OCrO_3)]$	1.705	1.628; 1.631; 1.634	[81]
$[CuL^5(H_2O)_2][CuL^5(H_2O)OCrO_3]\cdot H_2O$	1.687	1.607; 1.607; 1.672	[82]
$[Ni(bpy)_2(H_2O)OCrO_3]\cdot 5H_2O$	1.677	1.603; 1.630; 1.642	[77]
$[Ni(phen)(H_2O)_3OCrO_3]\cdot H_2O$	1.623	1.606; 1.621; 1.649	[57]
$Li(H_2O)_5[Co(en)_2(OCrO_3)_2]$	1.680	1.633; 1.636; 1.652	[83]
	1.697	1.627; 1.638; 1.641	
$K[Co(en)_2(OCrO_3)_2]$	1.707	1.624; 1.635; 1.645	[83]
Bidentate coordinated			
$N(Bu)_4[Ru(TMS)O_2CrO_2]$	1.722; 1.728	1.603; 1.604	[84]
$[PPh_4][Os(N)(CH_3)(TMS)O_2CrO_2]\cdot CH_2Cl_2$	1.746; 1.755	1.586; 1.603	[84]
$[EuL^6O_2CrO_2]_2[O_2CrO_2]\cdot 10H_2O$	1.662; 1.676	1.614; 1.619	[85]
$[EuL^6(H_2O)O_2CrO_2]_2[Cr_2O_7]\cdot 2H_2O$	1.665; 1.679	1.604; 1.633	[85]
$[SmL^6(H_2O)O_2CrO_2]_2[Cr_2O_7]\cdot 2H_2O$	1.659; 1.662	1.612; 1.616	[85]
$[TbL^6(H_2O)O_2CrO_2]_2[Cr_2O_7]\cdot 2H_2O$	1.642; 1.676	1.606; 1.631	[86]
Bridging coordinated			
$[L^7O_2CrO_2OL^7]$	1.742; 1.786	1.572; 1.598	[87]
$[(CPh_3)O_2CrO_2O(CPh_3)]$	1.736; 1.736	1.577; 1.577	[88]
$[Si_8O_{10}(C_6H_{11})_7(C_3H_9)CrO_4]\cdot C_6H_{14}$	1.730; 1.730	1.556; 1.576	[89]
$[[(SiPh_2)_2O]_2O_2CrO_2]$	1.724; 1.724	1.568; 1.579	[90]
$[(SiPh_3)_2][O_2CrO_2]$	1.706; 1.782	1.515; 1.568	[91]
$[NiL^2O_2CrO_2]_2\cdot 10H_2O$	1.594; 1.632	1.631; 1.654	[92]
$[CuL^2O_2CrO_2]_2\cdot 10H_2O$	1.626; 1.633	1.623; 1.661	[92]
$[ZnL^2O_2CrO_2]_2\cdot 10H_2O$	1.635; 1.661	1.629; 1.644	[93]
$[Fe_2(L^8)_2(O_2CrO_2)_3]\cdot H_2O$	1.663; 1.685	1.584; 1.591	[94]
	1.676; 1.695	1.549; 1.585	
	1.672; 1.677	1.564; 1.569	
$[ZnL^2O_2CrO_2]_2\cdot 6H_2O$	1.640; 1.655	1.628; 1.649	[95]
$[NiL^2O_2CrO_2]\cdot 5H_2O$	1.648; 1.651	1.633; 1.666	[96]
$[Fe_2(L^8)_2O(O_2CrO_2)_2]\cdot 4H_2O$	1.664; 1.664	1.561; 1.615	[97]
$[NiL^2O_2CrO_2]_2\cdot 6H_2O$	1.640; 1.648	1.630; 1.648	[98]
$[NiL^2O_2CrO_2]\cdot 2H_2O$	1.646; 1.655	1.642; 1.656	[99]
$[Cu_2(L^9)_2O_2CrO_2]\cdot 4CH_3OH\cdot 4H_2O$	1.679; 1.679	1.606; 1.613	[100]
$[Co_2en_2(O_2CrO_2)_2]Br_2$	1.696; 1.701	1.610; 1.630	[83]
$\{Co_2[N(C_2H_4NH_2)_3]_2[O_2CrO_2]_2\}[ClO_4]$	1.684; 1.685	1.616; 1.635	[83]
Other (containing groups V–IX – see Scheme 2):			
$[U_2(DMU)_4O_4(O_2CrO_2)]$	1.681; 1.723	1.590; 1.594	[101]
$[U_2(DEAc)_4O_4(O_2CrO_2)]$	1.678; 1.726	1.580; 1.581	[102]
$[U_2(DEAc)_2O_4(O_3CrO)_2]$	1.636; 1.673; 1.721	1.561	[103]
$[U_2(CH_3CONH_2)_4O_4(O_3CrO)_2]$	1.635; 1.666; 1.686	1.594	[104]
$[UL^{10}O_3H_2O(O_3CrO)_2]$	1.650; 1.659; 1.663	1.599	[105]
$\{[Np\cdot[CO(NH_2)_2]_2O_2[O_3CrO]\}$	1.668; 1.669; 1.680	1.586	[106]
$[Cu_3(bpy)_6(O_3CrO)][ClO_4]_4\cdot H_2O$	1.647; 1.648; 1.670	1.605	[107]
$[Cu_3(py)_2(OH)_2(O_3CrO)]$	1.621; 1.689; 1.694	1.600	[108]
$\{[(CH_3)_3Sn]_3(OH)(O_4Cr]\}$	1.561; 1.615; 1.699; 1.778		[109]

Ph, phenyl; L^1, 4-ammonio-2,2,6,6-tetramethylpiperidine; L^2, cyclam; Bu, butyl; TMSO, trimethyloxosulfonium; L^3, 2-amino-2-hydroxymethyl-1,3-propanediolato; bpy, 2,2′-bipyridine; Ar, benzene; Nic, nicotinate; L^4, 1,2-bis(diphenylphosphino)ethane-bis(trimethylsilylmethyl); L^5, bis(2-pyridylcarbonyl)amido; phen, 1,10-phenanthroline; en, 1,2-ethylenediamine; TMS, trimethylsilylmethyl; L^6, bis(pyridine-2,6-bis(ethylimino))bis(*N*,*N*′-ethane-1,2-diamine); L^7, cedryl; L^8, 1,4,7-trimethyl-1,4,7-triazacyclononane-*N*,*N*′,*N*″; L^9, *N*-(1-acetyl-2-propyl)(2-pyridylmethyl)amine; DMU, *N*,*N*-dimethylureamide; DEAc, *N*,*N*-diethylacetamide; L^{10}, *N*-methyl-*N*′-acetylcarbamide.

Table 2
Collected data on the electronic transitions [nm] in simple and mixed-ligand Cr(VI) chromophores

Species	Coordination number	Chromophore	Band positions (ε)	Solvent	Ref.
$[CrO_4]^{2-}$	4	$[CrO_4]$	372 (3950)	DMF	[112]
			~373 (~4900)	H_2O	[113]
			372 (4810)		[114]
			384 (4780)	H_2O	[110]
			370	H_2O	[115]
			374 (4570)	H_2O (pH 9.98)	[19]
$[CrO_3(OH)]^-$	4	$[CrO_3O']$	350 (~1600)	(pH 3.05)	[116]
			355 (1620)	DMF	[112]
			351 (1395)	H_2O	[117]
			348 (1490)	H_2O (pH, 3.05)	[19]
$[H_2CrO_4]$	4	$[CrO_2O_2']$	363 (1380)	DMF	[117]
$[Cr_2O_7]^{2-}$	4	$[CrO_3O']$	374 (2250)	DMF	[112]
			374 (2160)	DMF	[118]
			371 (2300)	DMF	[117]
			350 (1580)	H_2O	[117]
			350	0.75 M $HClO_4$	[119]
			350	0.5 M $HClO_4$	[120]
			420	0.5 M $HClO_4$	[120]
Cr(VI) + D-lactobionic acid	6	$[CrO_2(OR)OO']$	374		[121]
Cr(VI) + disaccharides	6	$[CrO_3O_2'O]$	350	1 M $NaClO_4/HClO_4$	[122]
			420–500		
$[(AcO)CrO_3H]/[(AcO)CrO_3]^-$	4	$[CrO_3O']$	350	50% acetic acid	[123]
$[HSerCrO_2(OH)(OH_2)]$	6	$[CrO_2O'O''O''']$	350	H_2O	[124]
			420–500		
$[(HSer)_2CrO_2]^+$	6	$[CrO_4O_2']$	350	H_2O	[124]
			420–500		
$[HNicCrO_3]$	4	$[CrO_3O']$	360	Reflectance sp.	[80]
			450 (a weak band)		
$[CrO_3(GSH)]^-$	4	$[CrO_3(SR)]$	Asym. 420–450 (2000)	DMF/ether	[18]
$[(n\text{-BuS})CrO_3]^-$	4	$[CrO_3(SR)]$	416 (1890)	DMF	[112]
$[Ph_4As][p\text{-BrC}_6H_4SCrO_3]$	4	$[CrO_3(SR)]$	414 (2440)	DMF	[125]
$[CrO_3(GSH)OH]^{2-}$	5	$[CrO_3O'(SR)]$	~435	H_2O/CH_3OH	[18]
$[CrO_3(GSH)OH_2]$	5	$[CrO_3O'(SR)]$	~435	H_2O/CH_3OH	[18]
$[CrO_3Cl]^-$	4	$[CrO_3(Hal)]^-$	~360, 450	CH_3CN	[51]

DMF, dimethylformamide; Ac, acetate; Ser, serine; Nic, nicotinate; GSH, glutathione; *n*-BuS, *n*-buthylthiolate; Ph, phenyl.

In negatively charged anions, one may expect slight interactions with H_2O_2 and NO (preferably NO^+). In the presence of the cellular reductants, Cr(VI) interacts with O_2 indirectly: reactions of Cr(VI/V/IV) complexes with cellular reductants produce organic radicals which then react with O_2 [131].

The reaction of Cr(VI) with H_2O_2 was extensively studied and still provides a fascinating field of research [132]. The main feature is its strong dependence upon acidity of the medium [132]. Vander Griend et al. have investigated kinetically the Cr(VI) + H_2O_2 reaction in basic solutions [132]. They found gradual exchange of two oxo groups by peroxo ligands leading to the following pre-redox intermediates: $[Cr^{VI}(O)_3(O_2)]^{2-}$ and $[Cr^{VI}(O)_2(O_2)_2]^{2-}$. Hexacoordinate Cr(VI) species have also been theoretically studied showed transformations of the $[CrO_4]^{2-}$ anion in reaction with H_2O_2 in both acidic and basic environment [133]. The Cr(VI) geometry changes from tetrahedral and pseudotetrahedral ($[CrO_4]^{2-}$ and $[Cr(O)_3(OH)]^-$) to pseudooctahedral ($[Cr^{VI}(O)(O_2)_2(OH)]^-$ and $[Cr^{VI}(O)(O_2)_2(OH_2)]$) but no pentacoordinated intermediates were detected [133]. Subsequent transformations involve a one-electron reduction to $[Cr^V(O)(O_2)_2(OH_2)]$, followed by the formation of hepta- and octacoordinated species $[Cr^V(O_2)_3(OH)]^{2-}$ and $[Cr^V(O_2)_4]^{3-}$ [133,134]. Stopped-flow XAFS studies [135] confirmed the existence of the oxodiperoxochromate(VI) species, which can additionally interact with water (vide supra). However, it excluded the following forms: $[Cr^{VI}(O)(O)_4(H_2O)_x]$, $[Cr^{VI}(OH)_2(O)_4(H_2O)_x]$ and $[Cr^{VI}(O)(O\text{–}O)_2(H_2O)_x]^{2-}$, where O–O is a monodentate ligand. It was also found that the exchange of the water molecule in $[Cr^{VI}(O)(O_2)_2(OH_2)]$ or hydroxyl group in $[Cr^{VI}(O)(O_2)_2(OH)]^-$ with the organic ligand (py, bpy, phen) can stabilize six or higher coordination number for

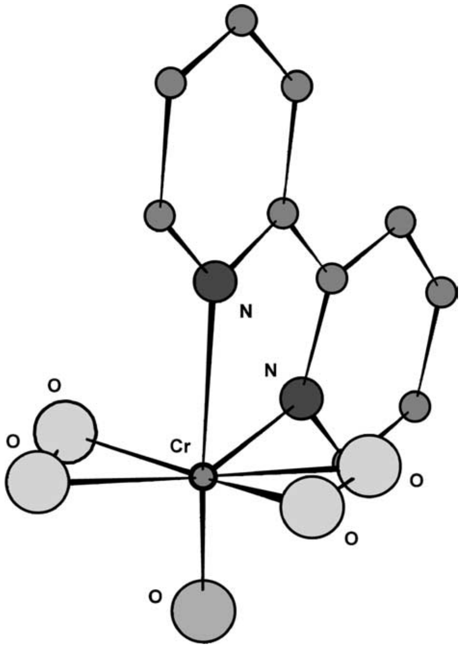


Fig. 3. The crystal structure of the [CrO(O_2)$_2$bpy] molecule. Adapted from [136].

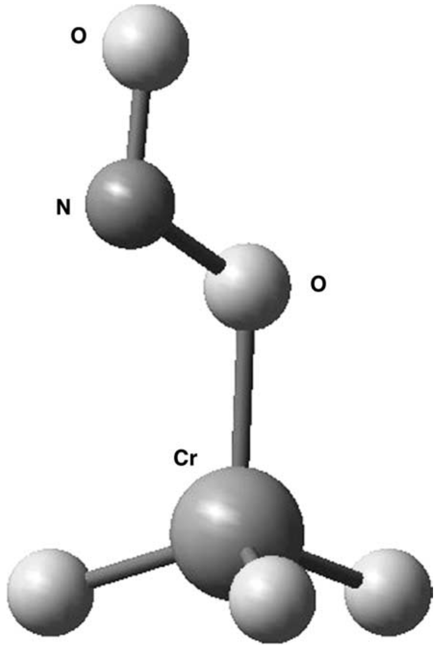


Fig. 4. Proposed structure of the $[CrO_4NO]^-$ anion based on the DFT studies.

Cr(VI) [133,136]. Fig. 3 presents the crystal structure for the [$Cr^{VI}O(O_2)_2$bpy], which is known almost for 40 years [136].

In summary, on the basis of recent studies [132–135], one can conclude that in the presence of hydrogen peroxide, the coordination number of Cr(VI) ion increases to six or seven, when an organic ligand (py, bpy, phen) is present (Fig. 3) [133,136]. Chromium(VI) peroxo complexes can be used as catalysts for the oxidation of organic compounds, as reviewed by Muzart [137].

Although it does not take into account solid-state effects, the DFT method very often reproduces the experimental data on the crystal and molecular structure of Cr(VI) species [52]. Recently, theoretical studies have been performed on the interaction between $[CrO_4]^{2-}$ and small inorganic molecules, such as NO, NO^+, O_2, $O_2{}^+$ and hydroxyl radical [138,139].

Out of the two possible cases, i.e. (i) direct Cr–ligand coordination [$CrLO_4$] and (ii) outer-sphere coordination [CrO_4L], the calculation pointed to the latter. The interactions (except for O_2, which does not react) result in a *trans*-staggered conformation (Fig. 4) and, in the case of hydroxyl radical, additionally, in hydrogen bond formation (Fig. 5a and b), with the following ΔG^0 sequence: $O_2{}^+ > NO^+ > {}^{\bullet}OH > NO$. A comparison with the results of the calculation for an analogous $[SO_4]^{2-}$ anion shows that the latter is more weakly bound to the small inorganic species studied here and that, contrary to $[CrO_4]^{2-}$, it does not react with ${}^{\bullet}OH$ [138,139]. In the light of the experimental observations that this radical does not play any important role in the chromium-induced carcinogenesis [7] these results are very interesting suggesting that both toxins (i.e. chromate and hydroxyl radical) might neutralize each other. However, the hydroxyl radical is unlikely to exist in the free form in aqueous media [7]; only in very specific conditions can they be produced. Such a synergistic effect was recently found in the photodegradation of two environmental toxins Cr(VI) and phenols [6]. However, this has to be verified experimentally, and one should remember that the DFT calculation results are limited to the gas phase.

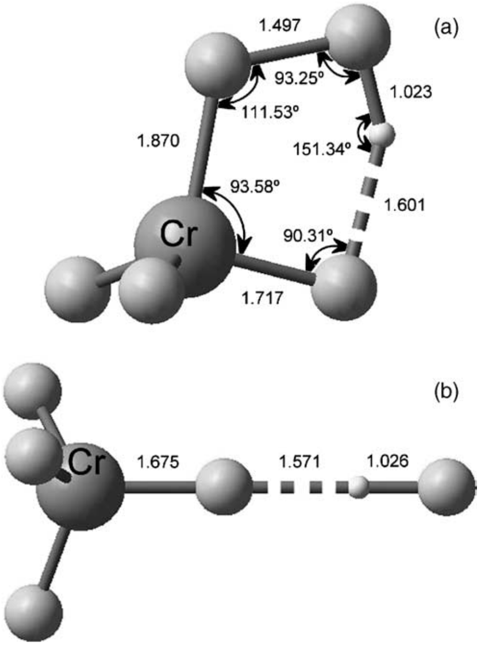


Fig. 5. The DFT studies on the interaction of $[CrO_4]^{2-}$ with small molecules. The [$CrO_4{}^{2-}$–OH] proposed structures: local (a) and global (b) minima.

3.4. *Chromium(VI) oxo compounds and organic ligands: esters and thioesters*

Simple oxo complexes of Cr(VI) form, in the pre-redox stage, various covalently bound compounds: esters and thioesters of the formulae $[CrO_3(OR)]^-$ and $[CrO_3(SR)]^-$, respectively. Thus, oxidation of the organic compounds begins with the substitution of the (OH) group in $[CrO_3(OH)]^-$ with the respective organic fragment, followed by electron donation to Cr(VI). The Cr–O distance in Cr–OH group in the $[CrO_3(OH)]^-$ moiety was found to be 1.794 Å and is longer than the mean Cr–O distance in CrO_3 (1.537 Å) (theoretical calculations [80,140,141]). However, a dramatic discrepancy between the theoretical (1.794 Å) and crystallographic (2.02 Å) data for the Cr–OH bond length is observed [63,142]. As the crystal structure for the $[PPh_4][HCrO_4]$ is the only example of the compound containing $[HCrO_4]^-$ anion in the solid state, more examples are required to explain this discrepancy (∼0.2 Å).

Upon interaction of $[(HO)CrO_3]^-$ with organic ligands, the relatively long Cr–O(H) bond can be easily broken. In these processes, the tetrahedral geometry of Cr(VI) oxo complexes is generally preserved; in the solid state and in the gas-phase Cr(VI) always retains its tetracoordinated state, whereas in aqueous solutions, the coordination number may be more flexible and may sometimes increase to five or (perhaps) more [18]. Esters and thioesters are generally very unstable species, rapidly transforming via intramolecular electron transfer to the subsequent intermediates with lower oxidation states of Cr [16].

Several Cr(VI) oxo complexes, e.g. CrO_2OCPh_3X (X = Cl or $OCPh_3$), which have been crystallographically characterized, were discussed in a recent review [29].

Since the concentration of $[HCrO_4]^-$ at physiological pH is very low, the possibility of the $[CrO_4]^{2-}$ ion interaction with the organic ligands cannot be excluded. The suggestion by Wetterhahn and co-worker [18c] on the formation of five-coordinate $[CrO_4L]$ transition sates is worth further examination. However, even very low concentration of $[HCrO_4]^-$ at pH 7.4 is important as the addition of organic substrates results in consuming the $[HCrO_4]^-$ ions with a decrease of the concentration of the $[CrO_4]^{2-}$ according to the equilibrium: $[HCrO_4]^- \Leftrightarrow [CrO_4]^{2-} + H^+$.

3.4.1. *Cr(VI) and O-donor ligands*

3.4.1.1. Alcohols. Oxidations of alcohols, glycols and dicarboxylic acids with Cr(VI) proceed through the formation of Cr(VI) esters [143]. For alcohols, the reaction has the following stoichiometry:

$$2[H_2CrO_4] + 3RCH_2OH + 6H^+ \rightarrow 2Cr^{3+} + 3RCHO + 8H_2O, \qquad (7)$$

and its first fast stage is [15,143,144]:

$$ROH + [H_2CrO_4] \rightarrow H[(RO)Cr^{VI}O_3] + H_2O. \qquad (8)$$

Various factors that affect the reaction mechanisms are listed in Section 1. For example, oxidations of methanol or ethanol by Cr(VI) in concentrated aqueous $HClO_4$ involve the formation of chromate–perchlorate complexes, including $H[CrO_3(OClO_3)]$ and $[CrO_2(OClO_3)_2]$, prior to the redox process [145].

3.4.1.2. Saccharides. This system is a very important one because of the significance of sugar ligands in the biological and environmental sciences. However, their ability towards Cr(VI) reduction is much lower than, e.g. ascorbic acid and GSH. It was found that naturally occurring saccharides stabilize the labile intermediate Cr(V) oxidation state. For example, the redox process in the Cr(VI)–disaccharides is not finished even after 1 year [122]. Various types of Cr(VI) interaction with neutral and acid sugars, e.g.: 2-acetamido-2-deoxy-D-glucose [119], D-ribono-1,4-lactone [120], disaccharides [122] D-galacturonic acid [146] and D-lactobionic acid [121] were kinetically studied by Sala and co-workers. Similarly to other types of organic O-donor ligands, saccharides reduce Cr(VI) through the formation of Cr(VI) esters. For example, the first step in the reaction between Cr(VI) and D-lactobionic acid (lba) is the formation of Cr(VI)–lba monochelate with a tridentate form of the ligand, with the coordination number of Cr(VI) being six (Fig. 6), followed by electron transfer reactions leading to Cr(IV) complexes.

Recently, two different intermediate species were observed while studying the system Cr(VI)–D-galacturonic acid [146]. However, while enlarging of the coordination sphere by changing the coordination number from four to six ($MO_4 \rightarrow MO_6$), a bathochromic shift (shift to lower frequency) of the spectroscopic bands due to weakening of the Cr–O bonds (lower covalency, larger Cr(VI) radius) should be observed [147]. On the other hand, the band position observed in the electronic spectra of the Cr(VI)–sugar system (the absorption at 350–370 nm and the shoulder at ca. 420 nm) (Table 2) are typical for the pseudotetraheral configuration of the $[CrO_3X]$ chromophore (e.g. $X = OH^-$, Cl^-). Evidently, the MO_4 and MO_6 should exhibit different spectroscopic properties. Thus, the electronic spectra of Cr(VI)–sugar species deserve further studies.

3.4.1.3. L-Ascorbic and nicotinic acids. L-Ascorbic acid (H_2A), a widely known reductant, is employed, e.g. as “antichrom” agent for protection against Cr(VI) toxicity [3]. It reduces the Cr(VI) and scavenges various radicals (superoxide, hydrogen peroxide, hydroxide). Various data suggest that the ascorbate molecule containing a *cis*-diol group, similarly to SH group of thiols, belongs to the main cellular reductants [148] and accounts for about 80% of the Cr(VI) reduction of rat liver and kidney [148].

The two-electron donation of H_2A involves formation between reactive $[CrO_3(OH)]^-$ and HA^- a four-coordinate Cr(VI)–ester intermediate (Fig. 7) [115,149,150]. This reaction is followed by formation of intermediate Cr(V) and

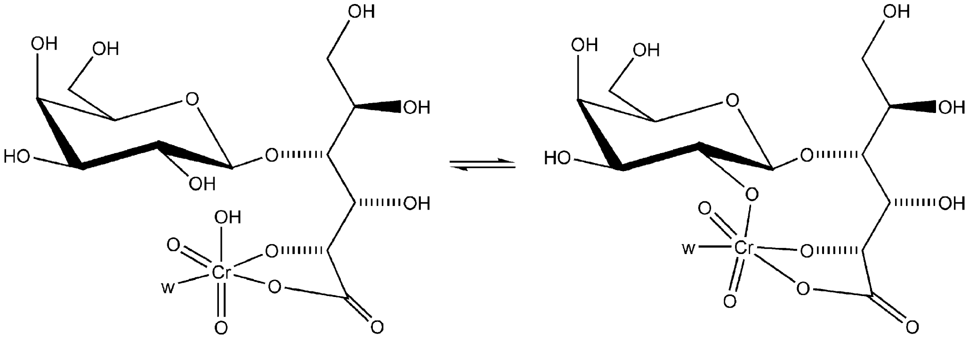


Fig. 6. Proposed structure of Cr(VI) complexes with D-lactobionic acid: kinetic studies. On the basis of [121].

Cr(IV) complexes [12,151]. The final products are various Cr(III) complexes with L-ascorbic acid [115,152–157].

The reaction of Cr(VI) with L-ascorbic acid and other cellular reductants in the presence of O_2 was studied by Lay and Levina [131] and O'Brien and Woodbridge [150]. Oxygen reacts in these systems indirectly with the earlier formed organic radicals [131,150].

The intermediate usually exhibits a coordination number of four as was shown in the case of nicotinatochromate whose crystal structure was solved and refined (Fig. 8) [80].

$[HNicCrO_3]$ was formed in water solution and CrO_3 as substrate according to the reaction:

$$C_5H_6NCO_2H + [HCrO_4]^- \Leftrightarrow [(HNicO–)Cr^{VI}O_3] + OH^- \quad (9)$$

with $[HCrO_4]^-$ being the key intermediate.

The Cr(VI) ion in $[(HNicO–)Cr^{VI}O_3]$ exhibits a distorted tetrahedral coordination with the $Cr–O_T$ bond lengths lying between 1.588 (6) and 1.603 (6) Å, whereas $Cr–O'$ bridging is 1.881 Å, just as expected. However, in anhydrous conditions under nitrogen the chromic anhydride, CrO_3 reacts with pyridine forming the air sensitive $[(py)_2CrO_3]$ complex of trigonal bipyramid structure with two Cr–N bonds at 2.147 and 2.152 Å and three Cr–O at 1.617, 1.630 and 1.631 Å [158]. Thus, stable forms exhibiting other than T_d structures are possible in the solid state but less probable in water solutions and air atmosphere. However, unstable (transition) forms of five-coordinate geometry cannot be excluded in solution [17,18a].

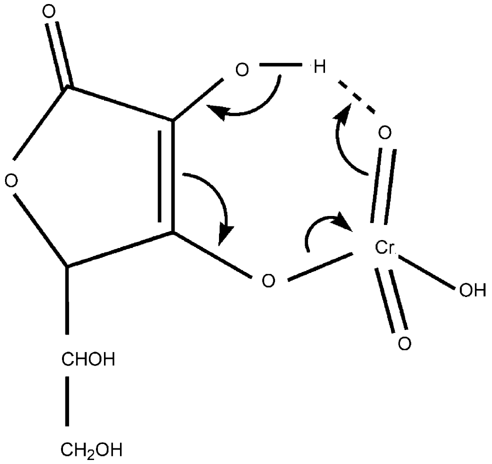


Fig. 7. Cr(VI) complex with L-ascorbic acid proposed on the basis of kinetic studies [115].

3.4.2. Cr(VI) + S-donor ligands

In the reaction between Cr(VI) and S-containing organic ligands the formation of thioesters, very important pre-redox intermediates, was firmly established [21,125,112].

$$[HCrO_4]^- + RSH \Leftrightarrow [RSCrO_3]^- + H_2O \quad (10)$$

The substitution of a hydroxyl group in $[CrO_3(OH)]^-$ for RS^- with the formation of Cr–S bond produces the thiolatochromates(VI) [118]. Replacement of one oxygen atom on Cr(VI) by thiolate ligand was clearly seen in the O^{17} NMR spectra [118].

The stability of Cr(VI)–thiolato complexes increases according to the length of the side chain: cysteine < *N*-acetylcysteine < γ-glutamylcysteine [118]. It is unusual that when one offers various donor sides in the thiolate ligand, e.g. glutathione (O, N, S), binding is exclusively through sulfur, the soft Lewis base, yet bound to Cr(VI) – a hard Lewis acid [118]. However, the presence of oxygen- and nitrogen-donor groups directly influences the stability of the Cr–S bond [118].

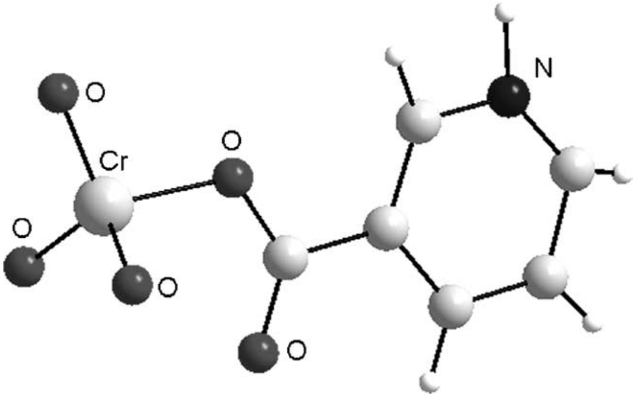


Fig. 8. The crystal structure of the $[(HNicO–)Cr^{VI}O_3]$ [80].

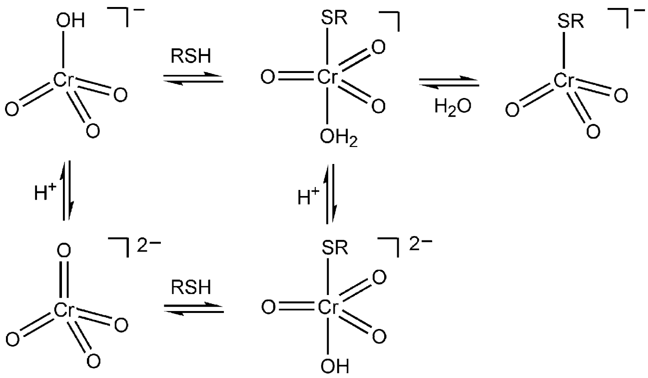


Fig. 9. The structure of the chromate–GSH equilibria. On the basis of XANES studies [17,18a].

The mechanism for the interactions of biological thiols with Cr(VI) is dependent upon the solvent [112,118] and the nature of buffer (for aqueous solutions) [21].

Glutathione (GSH) belongs to the group of main cellular reductants, which interact with Cr(VI) not as rapidly as L-ascorbic acid, but forming stable Cr(V) and Cr(IV) intermediates [159,160], which together with organic radicals, are capable of damaging DNA [47]. Chromium(II) was also postulated as an intermediate in the reduction of Cr(VI) with biological thiols [161].

Recently, the interaction of Cr(VI) with GSH and other thiols was studied by Levina and Lay [18] applying X-ray absorption fine structure (XAFS), X-ray absorption near-edge structure (XANES) and ESMS methods. The modelling of the spectra showed that thiolatochromates in DMF retained a four-coordinate structure, $[CrO_3(SR)]^-$, while in aqueous solution they become five-coordinate $[CrO_3(SR)(H_2O)]^-$ [18]. The Cr–O ligand bond lengths were found to be 1.61–1.62 Å for Cr–O and 2.26 Å for Cr–S (Fig. 9) [18] very close to the values found earlier [125] for thioester *p*-bromothiophenol chromate. This bipyramidal assembly can be easily bound via covalent and hydrogen bonding network to Cys residues in the enzymes [10,17].

The crystal structure in the solid state of tetraphenylarsonium salt of ((*p*-bromophenyl)-thiolato)chromate(VI) was obtained by Mazurek et al. [125] (Fig. 10). The Cr–O bond lengths are in the range typical for anionic chromate, e.g. $[Ni(bpy)_3][CrO_4]\cdot 7.5H_2O$ [77] (Table 1).

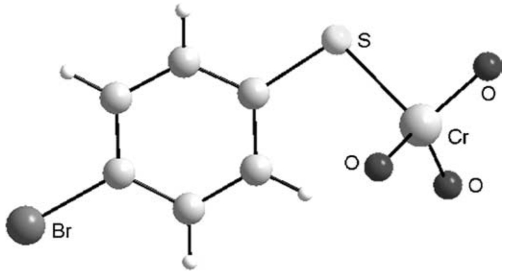


Fig. 10. The crystal structure of the $[p\text{-}BrC_6H_4SCr^{VI}O_3]^-$ anion [125].

Although the formation and the composition of the $[CrO_3(SH)]^-$ entity was firmly established, there is no clear picture of the spectral characteristics of this pseudotetrahedral assembly. Generally, it is established that the evidence of the thioester formation is a strong band at ca. 450 nm ($\varepsilon \sim 2000\ dm^3\ mol^{-1}\ cm^{-1}$) assigned to the S → Cr charge-transfer transition (Table 2) [21,112]. Fig. 11 presents the time-dependent electronic spectra of the reaction showing the formation and decay of a Cr(VI) thiolato complex [162]. As $[CrO_3S]$ core has C_{3v} symmetry, similarly to the halogenochromates, the characteristic CT transitions should be expected in the spectrum. However, the difference between the electronegativity of oxygen and sulfur (3.44 and 2.58, respectively, on Pauling scale) [54] points out that the MO description can be different and the respective molecular levels (HOMO) may have a different mixture of the oxygen and sulfur atomic orbitals. Thus, the $[CrO_3O']$, $[CrO_3X]$ and $[CrO_3S]$ chromophores should be compared with caution.

In the sulfur-substituted chromates, the highest occupied a_2 (and predominantly e orbital) should retain oxygen character and the LUMO orbital in $[CrO_3S]^-$ should have predominantly Cr character. $^1T_2$ and $^1T_1$ states in T_d symmetry are trigonally split into $^1E^a$ and $^1A_1 + {}^1E^b$ and $^1E^c$. The most prominent band (at 450 nm) in the spectra (Fig. 11), is broad and asymmetric suggesting the complexity of its origin. Thus, the tentative description of the electronic spectra should be as follows:

The most prominent band (I) in $[CrO_3S]^-$ chromophore at ca. 450 nm and intensity ca. 2000 can be: (a) a superposition of the $e \rightarrow e^*$ (π S → Cr) CT transition and first spin allowed $^1A_1 \rightarrow {}^1E^a$ (O → Cr) CT transition. Alternatively (b), it may be the shifted “main” 27,000 cm^{-1} $^1A_1 + {}^1E^b$ (O → Cr) CT transition due to heavy mixing of the oxygen

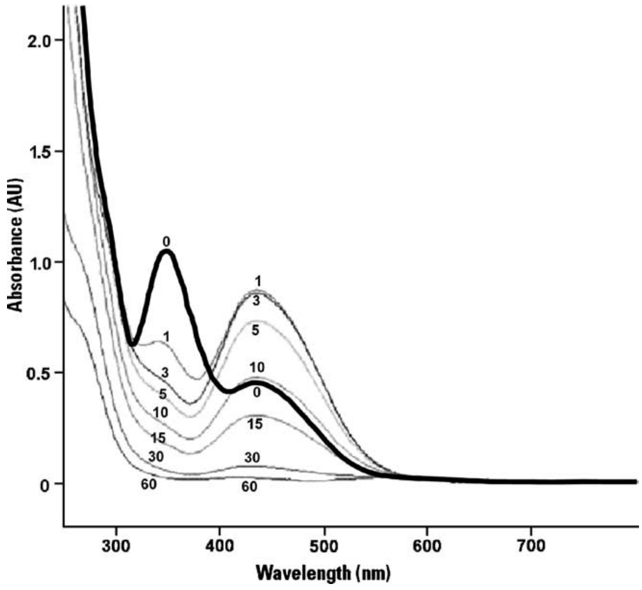


Fig. 11. Time-dependent UV–vis spectra (*t* [min]) of the Na_2CrO_4 solution upon treating with GSH at pH 7.4 and $T = 300$ K. Adapted from [162].

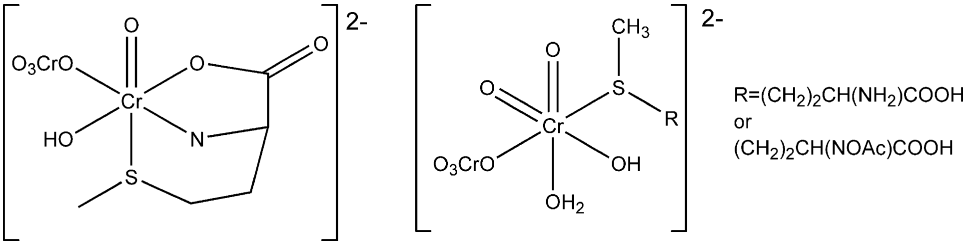


Fig. 12. The proposed structure of Cr(VI) with the L-methionine and its *N*-acetyl derivative: kinetic studies. On the basis of [163].

and sulfur orbitals (the pure (πS → Cr) CT should then lie at a shorter wavelength). Studies of the resonance Raman effects and deconvolution of the spectra will help to confirm the spectral assignment and indicate the origin(s) of this most characteristic band usually described in the literature as a S → Cr CT transition.

The Cr(VI) complexes with methionine and *N*-acetylmethionine have been studied kinetically [163], and the authors proposed a hexacoordinate Cr(VI) environment (Fig. 12). Coordination spheres containing not only O and S atoms, but also an N atom, from ammine group of the amino acid, have been proposed [163,164].

In summary, the thiolatochromates are found to be predominantly four-coordinated pseudotetrahedral $[CrO_3(SR)]^-$ species in the solid state and in solutions of aprotic solvents (e.g. DMF) [16–18]. However, in aqueous or methanol solutions of Cr(VI) thiolato complexes one molecule of solvent can be reversibly attached to the Cr(VI) ion with the formation of a five-coordinate species (Fig. 9) [18]. This mixed-ligand anion $[CrO_3(SR)(H_2O)]^-$ of trigonal bipyramidal structure was found to be unstable in neutral aqueous solutions, forming a deprotonated complex $[CrO_3(SR)(OH)]^{2-}$, which then decomposes into $[CrO_4]^{2-}$ and RSH (Fig. 9).

3.5. *Catalytic transformation of Cr(VI) species*

Chromium(VI) compounds are widely used for oxidation of organic substances [165,166]. The reaction pathways depend upon various factors including the presence and nature of a catalyst [15a].

Recently, the problem of catalysis in Cr(VI) oxidation of various organic compounds has been studied with renewed interest [15,137,167,168]. The effects of micelles on the catalytic reduction of Cr(VI) have been discussed in a recent review [15a]. In the Cr(VI) + alcohol (RCH_2OH; R = H, Me, Et, nPr, iPr, nBu, nP) redox system, N-containing heterocyclic compounds (such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen)) accelerate the reduction of Cr(VI) [167]. This catalytic action has been explained through the changes in the redox potential of Cr(VI) species, the complexation effect and the stabilization of the end products. On the molecular level, the catalytic action of heterocycles has been explained as the facilitation of the electron transfer through the π electrons of the phen aromatic rings [15a,167]. Formation of four-coordinate Cr(VI) intermediates $[(phen)Cr^{VI}O_2]$, has been proposed by analogy to the Cr(VI)–anisole complex reported earlier [169]. These intermediates form an “association” complex with alcohol $[phen–Cr(VI)–alc]^+$ which probably facilitate the hydride transfer and CO formation [15a,167]. The catalytic effect by phen in the oxidation of cinnamic acid and substituted *trans*-cinnamic acids to the corresponding benzaldehydes with $[HCrO_4]^-$ was also observed [168]. The proposed geometries and the charge of the intermediate complex of Cr(VI) with the catalyst (Fig. 13) implies very unusual, probably square planar environment around the Cr(VI) ion. Obviously, more evidence is required to describe the nature of Cr(VI)–phen complexes.

Lactic acid was also oxidized by Cr(VI) in the presence of bpy, EDTA and Mn(II) as catalysts [22]. In this case, the formation of a five-coordinate Cr(VI) ester ($[CrO(N_2O_2)]$ chromophore) has been proposed.

The other interesting catalyst for oxidation with Cr(VI) is picolinic acid [170–172]. However, as it is lost through complexation to the final Cr(III), it cannot be regarded as a catalyst sensu stricto [173].

Das et al. [24] oxidized DMSO by Cr(VI) in the presence of picolinic acid and proposed two possible intermediates $[Me_2S^+–Cr(Pic)O_2]$ and $[Me_2S^+–OCr(Pic)O_2]$, containing five-coordinated Cr atoms with $[CrO_2NO'S]$ and $[CrO_2NO'O'']$ chromophores, respectively.

The interaction of Cr(VI) with S-donor ligands can be very complicated. For example, in the Cr(VI)–penicillamine system, the buffers (acetate and phosphate) show catalytic

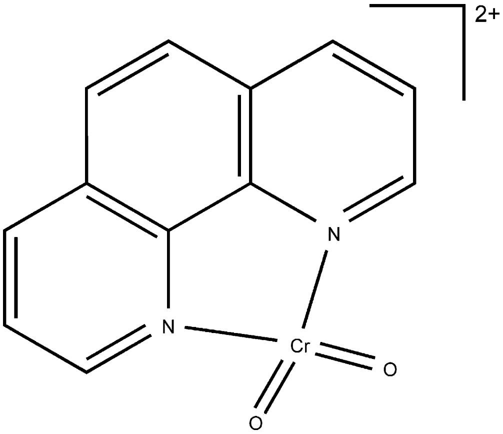
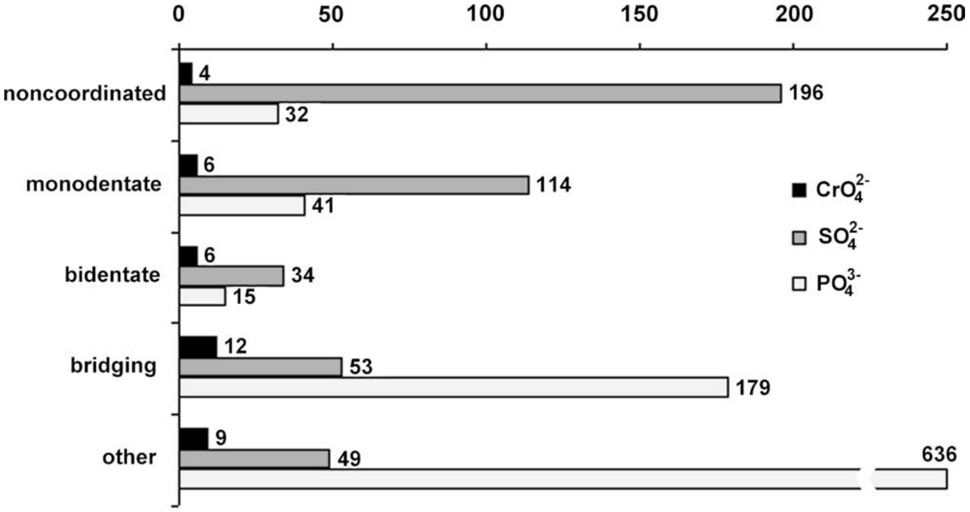


Fig. 13. Proposed structure of $[(phen)Cr^{VI}O_2]$ adapted (and modified) from [169].



Scheme 1. The number of $[CrO_4]^{2-}$, $[SO_4]^{2-}$ and $[PO_4]^{3-}$ structures deposited in CSD.

effects, possibly through the formation of intermediates, such as $[HO_3P–O–CrO_3]^{2-}$ [21]. In addition, Zn(II) may play a catalytic role in the oxidation of penicillamine by Cr(VI) in acetate buffers at pH 5–6, possibly through the formation of Cr(VI)–Zn(II)–acetate intermediates [21]. A slight catalytic effect of Mn(II) in this reaction was also observed but this ion (as well as Mg(II)) can also inhibit the redox reaction at low reductant/oxidant ratios, possibly through the formation of the $[Mn(HCrO_4)(RSH)]^+$ complex, which then slowly decomposes into $[CrO_3(SR)]^-$ and Mn(II) [21]. As the reductant/oxidant ratio increases, a Mn(II)–penicyllamine is preferentially formed.

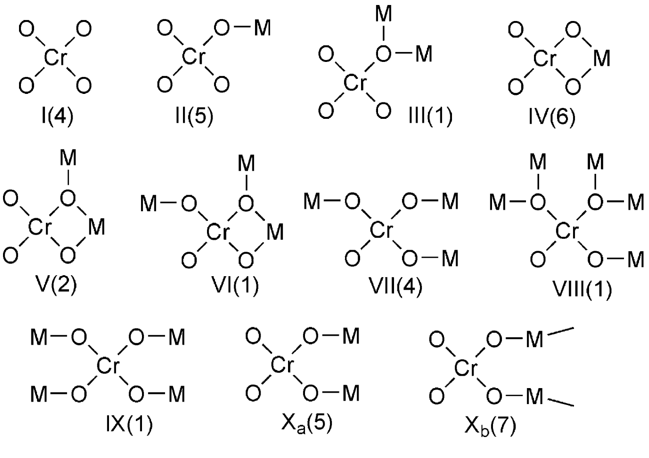
In summary, addition of catalysts to Cr(VI)-containing redox systems can lead to the formation of new Cr(VI) complexes, but these complexes are poorly characterized due to their transient nature.

4. Chromate(VI) ion as a ligand

The coordination ability of Cr(VI) has been studied mostly in the solid state although the coordination to the metal ions in solution has also been observed [174,175]. The solid complexes can be valuable models for solution chemistry. However, it must be kept in mind that solid-state studies cannot be completely compatible with the solution studies for the following reasons:

(1) The crystallized product presents the least soluble form of all species in equilibrium and may not reflect the real situation in the solution (see, for example [57]).
(2) The differences between the concentration level of the reactants in both phases, i.e. the crystals precipitate from the systems generally of larger concentration than those found in the biological systems. It is especially important for Cr(VI) as the equilibria between the particular forms are highly concentration-dependent [51].
(3) The difficulties in growing single crystals from the systems: Cr(VI)-biological ligands, which necessitate the use of easier crystallizing reactants, as for example, exogenic bpy and phen.

Generally, it can be concluded from database search that the coordination chemistry of Cr(VI) is not a much exploited field of research [29,58], in comparison with the coordination chemistry of structurally similar sulfate and phosphate anions [176]. Scheme 1 shows the abundance of structures deposited in Cambridge Structural Database [142] for $[CrO_4]^{2-}$, $[SO_4]^{2-}$ and $[PO_4]^{3-}$. For the three isostructural anions the following structures has been found: 37, 446 and 903, respectively. The results show that $[CrO_4]^{2-}$ (and not $[HCrO_4]^-$ ion, a very important species in solution with only one known solid-state structure [63]) seems to be a medium strength ligand. Chromate(VI) rarely acts as a simple counterion for complex cations (Scheme 2, four structures) [75–78]. Some simple chromate salts, e.g. $[Ce(CrO_4)]$ with structure



Scheme 2. The chromate anion and its coordination modes found in CSD, numbers of the crystal structures in parentheses.

known since 1977 [177], may also crystallize in a dinuclear form, $[Ce_2(CrO_4)_4]$, containing two chromate bridges [178].

Generally, the large size (240 pm) of $[CrO_4]^{2-}$, its rather rigid geometry and weak donor properties in comparison to N-donors or water [50] determine its rather poor ability to act as a ligand. The results in Scheme 2 point to a preference for the bridging (five structures) and polymeric bridging (seven structures) modes for Cr(VI) oxo species (Table 1) [83,87–100].

An example of unusual (compared with the normal *trans*-bridging mode) *cis*-bridging $[CrO_4]^{2-}$ ions forming two independent (left- and right- handed) helixes, bound together with intra- and interhelical hydrogen bonds, is a Ni(II)–imidazole–chromate catena(μ-CrO_4–O,O′)$[Ni(HIm)_3H_2O]$ (Fig. 14) [179].

Generally, structural analysis of transition metal complexes with $[CrO_4]^{2-}$ as a ligand shows that upon coordination to the metal ions the chromate tetrahedron is slightly distorted in terms of both Cr–O bond lengths and bond angles; most affected are the Cr–OM (M = metal ion) bond lengths (Table 1). However, the Cr^{VI}–OM bonds in such complexes (1.75–1.86 Å, Table 1) are much shorter than the Cr^{VI}–OH in $[Ph_4P][Cr^{VI}O_3(OH)]$ (2.02(3) Å) [58,63] and the Cr^{VI}–S bonds (2.26 Å) [18,125] (Table 1). Moreover, in the structure of $K[Fe(CrO_4)_2H_2O]$, the Cr–OFe bond length is equal to that of uncoordinated $[CrO_4]^{2-}$ (1.658–1.674 Å), and the remaining Cr–O bonds are even shorter (1.575–1.604 Å) [180]. In the case of a dinuclear complex [LFe(μ-CrO_4)$_3$FeL] [94], there is a significant difference between the lengths of the Cr–OM bonds (1.663–1.694 Å) and the terminal Cr–O bonds (1.549–1.593 Å). In most cases, the tetrahedron of $[CrO_4]^{2-}$ is not much deformed upon coordination (Table 1).

The preference of the bridging mode over chelating and monodentate modes of coordination observed in the $[CrO_4]^{2-}$ complexes can be related mainly to the magnitude of the anion (2.40 Å) and to the radii of the metals. For example, for large cations (UO_2^{2+}, Tb^{3+}, Eu^{3+}) the coordination is of the chelating type (Scheme 2, Table 1). However, the chelating structure implies a large distortion in the tetrahedron (with the O–Cr–O angles being 60–80° instead of 109° in T_d) [85,86,101–105].

The coordination of $[Cr_2O_7]^{2-}$ is even weaker than that of $[CrO_4]^{2-}$, possibly due to slightly lower electronegativities of oxo groups in the former anion [58].

5. Cr(VI) transport through anionic channels

Transport of $[CrO_4]^{2-}$ through the cellular membrane with preservation of the Cr(VI) oxidation state can be regarded as a part of pre-redox equilibria involving Cr(VI) species.

As was postulated by Wetterhahn and co-worker [33], the structural similarity of chromate, sulfate and phosphate anions is an important factor in biological transport of Cr(VI). As was mentioned in Section 1, assimilation of free anions takes place though the ionic channels. However, a search in Protein Data Bank [181] shows no data on the crystal structure of sulfate and phosphate transporters [181]. Moreover, in eucariotic organisms, the amino acid sequences for such transporters were only deduced [182–184]. The studies of many transporters exhibit highly conserved amino acid sequence during evolution, and many positively charged amino acid residues (e.g. Arg) are present in the structures [183]. In the Cambridge Structural Database [142], the structure of the guanidinium chromate is deposited, which contains an expanded hydrogen bond network (Fig. 15) [67,142]. This supports the suggestion that Arg plays a significant role in $[CrO_4]^{2-}$ binding by anion transporters through the formation of a network of hydrogen bonds. The function of Arg can also be considered in changes of coordination number

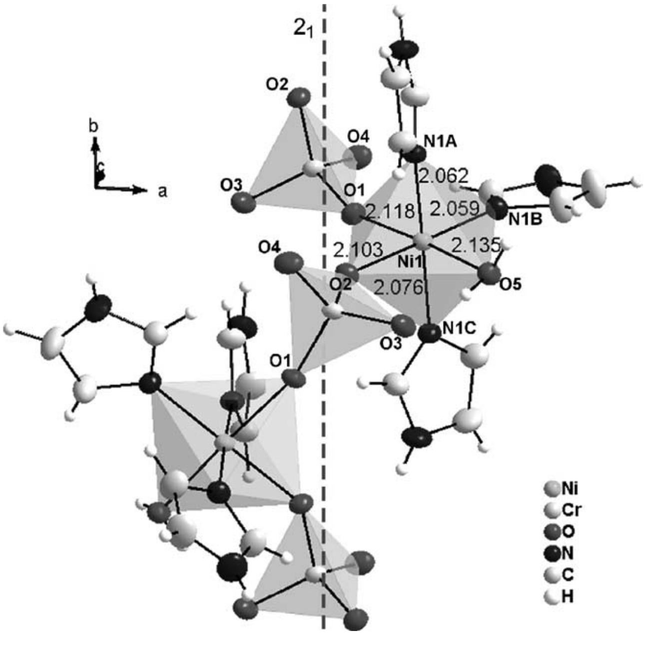


Fig. 14. Crystal structure of the right-handed helix in the catena (μ-CrO_4–O,O′)$[Ni(HIm)_3H_2O]$ [179].

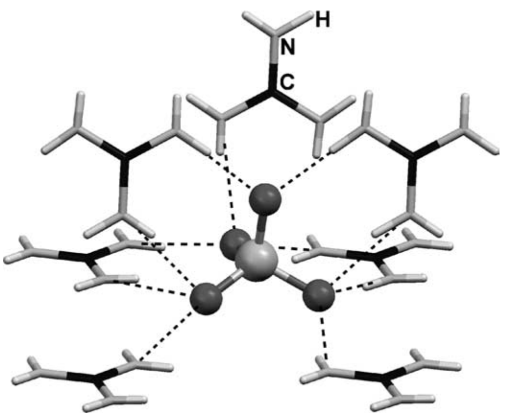


Fig. 15. The HB network in the $[C(NH_2)_3]_2[CrO_4]$ crystal [67].

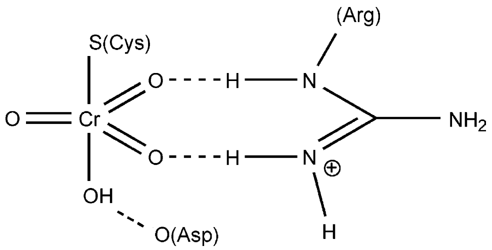


Fig. 16. One of the possible modes of the interaction of Cr(VI) transient complex with protein aminoacids. On the basis of [17].

of chromium on its redox pathway as the stabilizing factor of Cr(VI) complexes by hydrogen bonding. Five-coordinated Cr(VI) species can also be formed and can interact with the channel components in a way depicted in Fig. 16.

Studies on anion channel proteins have shown that they function as H^+/sulfate or Na^+/sulfate co-transporters, and act in a narrow pH range of 5.0–5.5 [183]. Therefore, the Cr(VI)–Arg interactions are likely to involve comparable amounts of $[CrO_4]^{2-}$ and $[HCrO_4]^-$ (the pK_a value for $[HCrO_4]^-$ at 25 °C and $I = 0.5$ M is 5.80) [19]. Thus, the anion–cation interaction and coordination abilities of tetrahedral anions may play a key role in transport in biological systems and may shed a new light on pre-redox equilibria of Cr(VI) species.

6. Summary and general remarks

The formation of one or more transient pre-redox Cr(VI) intermediates seems to be a firmly established phenomenon in the Cr(VI)-induced carcinogenesis. Although very unstable, the Cr(VI) intermediates play a significant role in the subsequent redox pathways. The data summarized in this review indicate that for inorganic species containing Cr(VI), with the exception of hydrogen peroxide and thiolato complexes [18,132], in aqueous solutions, a pseudotetrahedral arrangement was preserved. This is completely valid for solid-state complexes containing chromate as a ligand and for the gas phase. For organic molecules bound to Cr(VI) in solution, the problem is more complicated and an increased coordination number can be found more often. The rigid pseudotetrahedral arrangement of the Cr(VI) oxo centre does not exclude various modes of its binding, e.g. to the metal ion, as seen in the solid state (Section 4).

However, it seems that the speciation of Cr(VI) is still a poorly understood field, and we are at the beginning of the process of uncovering its significance. For example, despite a quarter of a century of investigations in the chemistry of biological chromium redox processes, great effort is still required to observe Cr(VI) species (apart from the simple oxo complexes) and analyse their electronic and structural behavior, especially in solution. For these goals, new physicochemical methods will probably be required in the future.

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