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Compounds of chromium(VI) as ligands

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Contents

Abstract

The coordination chemistry of the compounds of chromium(VI) as ligands is mainly the chemistry of anions such as chromates, dichromates, polychromates, chromate–dichromate, halochromates and heteropolychromates in metal complexes. In this review, only the compounds whose structures are known will be considered. Some of these compounds, such as the double alkali metal–rare earth chromates, may present a certain technological interest because of their physical properties. Thermal decomposition products of some of the compounds containing copper(II) are industrially important catalysts. The complexing ability of chromium(VI) anions provides an insight into the mechanistic pathway of chromate or dichromate oxidations of substrates of biological importance. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chromates; Dichromates; Polychromates; Halochromates; Heteropolychromates

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1. Introduction

This review covers the coordination chemistry of the compounds of chromium(VI) as ligands whose structures are known and is based on structural data generally obtained from X-ray diffraction since complexes only characterised by methods such as vibrational spectroscopy have been previously reported [1–3].

The industrial importance of chromium(VI) compounds, together with their toxic and genotoxic character and in relation to environmental pollution problems [4], made the study of the metal complexes containing compounds of chromium(VI) as ligands interesting.

Factors that constrain the role of oxoanions as ligands, in general, have been discussed [1,2]. For the CrO_4^{2-} anion a thermochemical radii is assigned (2.40 Å) [2]. In the case of oxoanions of chromium(VI) to the above factors, the conformation of the oxoanions must be considered.

The optimised geometries of CrO_4^{2-}, $HCrO_4^-$, H_2CrO_4, $Cr_2O_7^{2-}$, $HCr_2O_7^-$ and CrO_3X^- ($X = F$, Cl) have been theoretically determined [5–8] and compared with experimental results obtained from X-ray diffraction. Thus, the CrO_4^{2-} have the T_d symmetry with Cr–O experimental bond distance 1.66 Å [9] (theoretical value 1.591 [5] or 1.604 Å [10]). In the protonated species such as $HCrO_4^-$, the Cr–O bond lengths decrease with respect to non-protonated species with the exception of the Cr–O distance of the oxygen bonded to hydrogen, which increases; consequently, the OH^- groups must become more labile in the substitution reactions. Thus, three Cr–O short bond distances: 1.54(2), 1.55(3) and 1.58(2) Å are found in the crystal structure of $(Ph_4P)[Cr^{VI}O_3(OH)]$ [11] (theoretical value 1.513 Å [5]) and one Cr–O (hydroxy) long bond distance 2.02(3) Å (theoretical value 1.853 Å [5]). In the complexes, especially with transition metals, the increase in Cr–O bond distances in the bridging Cr–O–M (M = metal cation) and the decrease of Cr–O bond distances are less significant than in protonated species, though the oxoanions (mainly chromate and dichromate) generally are more distorted with respect to ideal symmetries (vide infra). The $Cr_2O_7^{2-}$ anion adopts twists of about 7–9° away from an exactly eclipsed conformation [6], values that lie within the range of twists observed in the metal complexes. The Cr–O–Cr observed angle for the same anion is between 122 and 139° [5,12] whereas the theoretical value is 139.2° [6].

In accordance with the electronic structures of CrO_4^{2-} [5] and $Cr_2O_7^{2-}$ [6] anions theoretically studied, the terminal oxo atoms of the CrO_4^{2-} are slightly more negative than the same atoms of the $Cr_2O_7^{2-}$ (atomic charges calculated) and therefore it seems that the CrO_4^{2-} anion could be a better ligand than $Cr_2O_7^{2-}$. In the species distribution diagram of chromate(VI) in aqueous solution [5], at $2 \leq pH \leq 6$, the $Cr_2O_7^{2-}$ is the most abundant species. However, complexes containing CrO_4^{2-} are obtained since other factors sach as total metal concentration and the solubility of the complex are also important. On the other hand, in chromates and dichromates metal complexes, the M–O (M = metal) bond distances are similar (vide infra), indicating a comparable complexing ability of these species.

The $Cr_3O_{10}^{2-}$ can adopt different conformations in the alkali complexes [13]. Löfgren [14] compared the conformation of the $Cr_4O_{13}^{2-}$ anion with those of $Cr_2O_7^{2-}$ anions, the $Cr_3O_{10}^{2-}$ anion and $(CrO_3)_\infty$.

In a report by Pressprich et al. [15], an interesting comparison of Cr–O bond lengths for all types of anions of the form $Cr_nO_{3n+1}^{2-}$ is presented. The species selected for this structural comparison follow the criteria of Löfgren [16]: only structures that have been studied by single-crystal X-ray diffraction with estimated standard deviations in the Cr–O distances of $\sigma < 0.02$ Å were considered. Pressprich et al. [15] have found that terminal bridging bond lengths and inner tetrahedral bridging bond lengths increase smoothly on average in correlation with increasing polymerisation of the chromates. Similarly, nonbridging bond lengths show an equally smooth decrease in Cr–O bond length on average with increasing polymerisation.

Cr–O bond lengths have also be examined in terms of a cluster expansion [15]:

$$\mathrm{L}(\Gamma) = \sum_{j\varepsilon\Gamma} N(\Gamma, \gamma) l(\gamma)$$

where Γ is the graphical symbol for the $Cr_nO_{3n+1}^{2-}$ moiety, γ is a subgraph of Γ representing a cluster within $Cr_nO_{3n+1}^{2-}$. Then L(Γ) is the length of the Cr–O bonds in the structure. The observed values for terminal and bridging Cr–O distance for dichromates of organic bases [12] and trichromate of 2-methylquinolinium [17] are in good agreement with the calculated bond distances, but not in complexes in general where the Cr–O bond distances can change as a consequence of the coordination (vide infra).

The halochromates CrO_3X^- (X = F, Cl) anions present a structure of a more or less distorted tetrahedron [7,8]. For CrO_3F^-, the Cr–O experimental bond distances are 1.638(2)–1.654(11) Å (theoretical value 1.507 Å [7]) and the Cr–F experimental bond distance 1.582(10) Å [7] (theoretical value 1.834 Å [7]). For CrO_3Cl^- the Cr–O experimental bond distances are from 1.588(4) to 1.622(2) Å (theoretical value 1.502 Å [8]) and Cr–Cl experimental distances are from 2.158(1) to 2.189(1) Å [8,18] (theoretical value 2.340 Å [8]). These Cr–O experimental bond distances are slightly shorter than the values reported for the CrO_4^{2-} anion (1.66 Å [9]), and larger than the values for CrO_2F_2 (Cr–O 1.575(2) Å [19]) and CrO_2Cl_2 (Cr–O 1.581(2) Å [19]).

Finally, to our knowledge no theoretical data for heteropolychromates corresponding to general formula $XCr_nO_{3n+4}^{3-}$, X being P or As are available. For the metal complexes formed by these polyanions as ligands, experimental data are given below (see Section 2).

2. Compounds with main group elements

The $KCrO_3F$ and $CsCrO_3F$ have the tetragonal scheelita structure [18], with disposition to random of oxide and fluoride ions. The CrO_3F^- anion is close to a regular tetrahedron. The structure of $KCrO_3Cl$ was determined by Helmholz and Foster [20], the CrO_3Cl^- having a structure of distorted tetrahedron (Cl–Cr–O, 109°46′, O–Cr–O, 103–112°). The Cr–O distance is 1.53(5) Å, which is shorter than the values reported for other CrO_3Cl^- (1.588(4) Å [8], CrO_4^{2-} (1.66 Å [9]) and chromyl chloride (1.581(2) Å [19]). The Cr–Cl distance is 2.16(4). The coordination number of K(I) ion is ten (three chlorine and seven oxygen atoms). The K–O bond distances are from 2.81 to 3.08 Å, whereas the K–Cl bond distances are from 3.29 to 3.48 Å. The K–O and K–Cl experimental bond distances are close to the sum of ionic radii of K(I), oxide and chloride, considering the coordination number for K(I) ion as ten (ionic radii from Ref. [21]).

In the structure of triclinic $K_2Cr_2O_7$ [22], the $Cr_2O_7^{2-}$ anion is almost in the eclipsed conformation and two crystallographically distinct $Cr_2O_7^{2-}$ ions are present in the structure. When viewed along the Cr–Cr directions, the ions show twists of about 5 and 10° away from an exactly eclipsed conformation, reducing the ideal symmetry from C_{2v} to C_2. The Cr–O–Cr bridging angles in two ions are significantly different with values of 124.0 and 127.6°. In both $Cr_2O_7^{2-}$ anions the two bridging Cr–O distances are equal within experimental error (mean 1.79 (1) Å) as are the terminal Cr–O distances (mean 1.63 (1) Å). The K–O bond distances reported are in the range 2.70–3.90 Å. Considering the sum of ionic radii of K(I) ion (coordination number ten) and oxide as 2.97 Å (ionic radii taken from [21]), some values reported by Brandon and Brown [22] for the K–O bond distance seem too high. Taking the value 2.89 Å as the sum of the ionic radii of K(I) (coordination number eight) and oxide anion, eight could be considered to be the coordination number of K(I) in the triclinic $K_2Cr_2O_7$.

For the α-K_2CrO_4 [23], the CrO_4^{2-} ion is close to regular tetrahedron. The average Cr–O bond length is 1.646(1) Å and O–Cr–O bond angle 109.54(7)°. Oxygen atoms are surrounded by five K(I) ions in an approximately square pyramid and the K–O interatomic distances are in the range 2.681(2)–3.660(3) Å. The potassium–oxygen coordination is complex with little or no directional character and with the same considerations as above, eight could be considered to be the coordination of K(I) ion by oxygen atoms.

Raman scattering and energy-dispersive X-ray diffraction in a diamond-anvil cell were used to study the compounds $NaKCrO_4$ and $K_3Na(CrO_4)_2$ to pressures of 22.5 GPa [24]. These measurements reveal that the CrO_4 tetrahedra in the monopotassium compound become disordered, while the tripotassium compounds remain ordered. The disordering occurs without a significant change in the structural arrangement of the cations. Bernardin III and Hammack [24] suggest that the disordering results from an impeded ferroelastic phase transition, which causes the zone boundaries, and therefore the CrO_4 tetrahedra to be distorted. The structures of both compounds differ by one symmetry element, which leaves the neighbouring tetrahedra inequivalent.

The structure of $HgCrO_4$ (**1**) was determined [25] (Fig. 1). Each Hg(II) ion is coordinated to two oxygen atoms in an almost linear way with Hg–O 2.097(10), 2.121(9) Å, O–Hg–O 163.3(4)°. As in $HgCrO_4 \cdot 0.5H_2O$ [26], the structure consists of infinite chains $(HgCrO_4)_n$. In $HgCrO_4$ the chains are connected to form a 3-D network with five Hg–O contacts of 2.48–2.79 Å, all shorter than 2.90 Å, the sum of the Van der Waals radii of the Hg and oxygen atoms. In both $HgCrO_4$ and $HgCrO_4 \cdot 0.5H_2O$ the polyhedron around Hg is a distorted pentagonal bipyramid. The CrO_4^{2-} anion acts as a monodentate ligand, with two large Cr–O bond

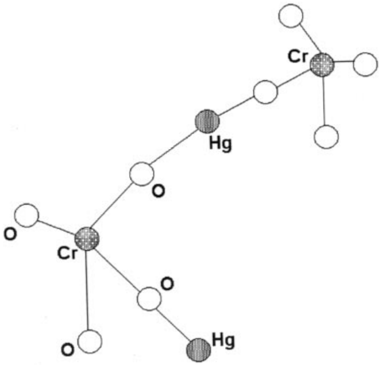

Fig. 1. Structural diagram of $HgCrO_4$. Adapted from Ref. [25].

distance large (1.698(9) and 1.712(10) Å) corresponding to oxygen atoms bonded to Hg(II) ion and two short ones (1.604(11) and 1.617(9) Å).

In the compound $Hg^{I}_4Hg^{II}Cr^{VI}O_6$ [27], three distinct Hg sites are found in the structure. A Hg–Hg (2.526 Å) bond exists between the Hg(I) centres. One of the Hg(I) centres is four-coordinate and the other is five-coordinate. The Hg(II) ion possesses an octahedral coordination geometry composed of oxide ions.

The structure of $(NH_4)_2[Zn(CrO_4)_2(NH_3)_2]$ is presented below together with the analogous copper complex (Fig. 3).

The crystal structure of bis(triphenylsilyl)chromate $[(C_6H_5)_3Si]_2CrO_4$ has been determined [28]. The crystals are built up of molecules, each of which is formed by a CrO_4 tetrahedron which is linked to the silicon atoms by oxygen bridges. In addition to the oxygen contact each silicon atom is also in contact with three aromatic rings which project from it like propeller blades. Two Cr–O bond distances for oxygen bridges of the Cr–O–Si groups (1.782(10) and 1.706(10) Å) are much longer than the remaining two in the CrO_4 tetrahedron (1.568(12) and 1.514(13) Å). The O–Cr–O bond angles are in the 107.4(6)–112.0(6)° range. The Si–O bond distances are 1.601(11) and 1.605(11) Å.

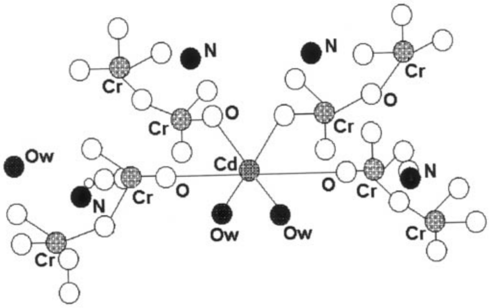

Fig. 2. Structural diagram of $Cd(NH_4)_2(Cr_2O_7)_2 \cdot 2H_2O$. Adapted from Ref. [34].

Löfgren [16,29] has determined the structure of the monoclinic phase $Rb_2Cr_2O_7$ (space group $P2_1/n$). The $Cr_2O_7^{2-}$ anion is in a nearly eclipsed conformation. The Cr–O terminal distances are in the range 1.580(18)–1.617(18) Å.

The two Cr–O bridging distances are 1.795(14) and 1.796(14) Å. The O–Cr–O terminal bond angles within the chromate tetrahedra range from 108.3(9) to 110.2(9)°. The Cr–O (bridge)–Cr angle is 122.9(9)°. The coordination polyhedron around the Rb(I) ions is irregular. Eight oxygen atoms are coordinated to both Rb(I) ions. The Rb(1)–O distances range from 2.897(19) to 3.173(19) Å including oxygen of five different $Cr_2O_7^{2-}$ anions. Rb(2) has six $Cr_2O_7^{2-}$ neighbours and the contact distances range from 2.857(20) to 3.084(20) Å. Eleven Rb(I) ions surround each $Cr_2O_7^{2-}$ anion.

Comparison of the structures of the monoclinic $Rb_2Cr_2O_7$ ($P2_1/n$) and the monoclinic $Rb_2Cr_2O_7$ ($C2/c$) [16,30] reveals a very close relationship between the two structures with regard to the dimensions of the $Cr_2O_7^{2-}$ anions and also to the Rb–O bonding scheme between sheets. The Rb(I) ions also present the same coordination. The eight oxygen atoms of the coordination polyhedra RbO_8 in the $C2/c$ type and $Rb(2)O_8$ in the $P2_1/n$ type belong to six different $Cr_2O_7^{2-}$ groups. The $Rb(1)O_8$ polyhedron of the latter structure is formed by oxygen atoms from five different $Cr_2O_7^{2-}$ anions. This difference is due to the different roles of the bridging oxygen atoms of the $Cr_2O_7^{2-}$ anions in the two structures. A bridging oxygen atom is in contact with the Rb(1) ion in the $P2_1/n$ structure but not in the $C2/c$ structure. Twelve Rb(I) ions surround each $Cr_2O_7^{2-}$ anion in the $C2/c$ phase.

The structures of $MCr_2O_7 \cdot 2[(CH_2)_6N_4] \cdot nH_2O$ ($M = Mg(II)$, Ca(II), $n = 7$, 8) have been reported [31,32]. In both compounds the cation is hydrated $[Mg(H_2O)_6]^{2+}$ or $[Ca(H_2O)_7]^{2+}$ and does not coordinate with the dichromate oxygen ions. A hydrogen-bonding system between the hydrated cation, the organic molecule and the $Cr_2O_7^{2-}$ anion support the crystal structure.

Of the dichromates with two different cations, the following have been described: $CdK_2(Cr_2O_7)_2 \cdot 2H_2O$ [33] and $Cd(NH_4)_2(Cr_2O_7)_2 \cdot 2H_2O$ (**2**) [34] (Fig. 2). In both compounds the Cr–O–Cr bond angles are 120.4 and 121.1°, respectively. These values are lower than those found in the other dichromates. Also in both compounds the Cd(II) ions present an octahedral coordination, four oxygen atoms of the $Cr_2O_7^{2-}$ groups and two water molecules. The K(I) ions have a coordination formed by seven oxygen atoms of the $Cr_2O_7^{2-}$ groups and one water molecule. It is interesting to note that the oxygen bridge of the Cr–O–Cr group participates in this bond. The NH_4^+ group in the second compound also has the same coordination as the K(I).

The structure of $Rb_2Cr_3O_{10}$ is described by Löfgren [13,16]. It consists of Rb(I) and $Cr_3O_{10}^{2-}$ anions. The $Cr_3O_{10}^{2-}$ is composed of three CrO_4^{2-} tetrahedra joined by shared corners. The distortion of the CrO_4^{2-} tetrahedra (O–Cr–O angles 105.1–112.8) is larger than in the mono- and dichromates. Thus, the deformation of the chromium tetrahedra increases as the number of tetrahedra forming the chain increases. The coordination of the oxygen atoms to Rb(I) is complex with no directional character. Rb(1) is surrounded by eleven oxygen atoms in the range 2.91–3.35 Å. Rb(2) has ten oxygen neighbours between 2.98 and 3.39 Å and two

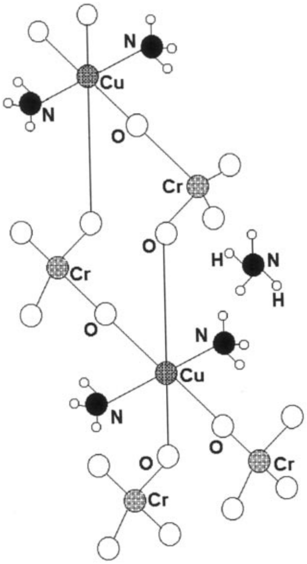

Fig. 3. Structural diagram of $(NH_4)_2[Cu(CrO_4)_2(NH_3)_2]$. Adapted from Ref. [43].

more located 3.61 and 3.78 Å from the Rb(I) ion. The two Rb(I) ions are each surrounded by oxygen atoms belonging to six different trichromate ions.

Different conformations of the $Cr_3O_{10}^{2-}$ anions have been found. Thus, in the β-$Cs_2Cr_3O_{10}$ [35], the $Cr_3O_{10}^{2-}$ anion presents an arrangement of the tetrahedra similar to the chain found in $(CrO_3)_\infty$ and is distinct from the $Rb_2Cr_3O_{10}$. In the compound β-$Cs_2Cr_3O_{10}$, the Cs(I) ion in special position is surrounded by nine oxygen atoms at 3.20–3.30 Å whereas the Cs(I) ion in general position is surrounded by ten oxygen atoms at 3.11–3.43 Å.

The structure of $Rb_2Cr_4O_{13}$ is reported by Löfgren [14,16]. The structure consists of Rb(I) and $Cr_4O_{13}^{2-}$ anions. The latter is composed of four CrO_4 tetrahedra joined by shared corners. From the range of O–O distances of CrO_4 tetrahedra also indicate that the distortion of these tetrahedra increases with the number of polyhedra forming the chain. It is interesting to note that on the whole (di-, tri-, and tetrachromates) the Cr–O–Cr bridging angles seem to increase with the number of tetrahedra sharing corners. Thus in the dichromates the majority of the bridge angles are in the range 122–139° [12]; in $Rb_2Cr_3O_{10}$ they are 140 and 136° [13,16], in $Rb_2Cr_4O_{13}$ the angles are remarkably variable: 147.2, 139.3 and 120.5° and finally in the $(CrO_3)_\infty$ 143° [14,16]. However, in $Rb_2Cr_2O_7$ (space group $P\bar{1}$) there is a large difference between the bridge angles 123 and 138° of the two crystallographically independent anions. The coordination of the Rb(I) ions in $Rb_2Cr_4O_{13}$ is complex with no directional bond character. The Rb(I) ions are each surrounded by eleven oxygen atoms. The Rb(1)–O distances range from 2.883 to 3.474 Å and the eleven oxygen atoms belong to six different tetrachromate ions. The Rb(2)–O distances from five tetrachromate anions range from 2.887 to 3.348

Å. The Rb–O coordination in $Rb_2Cr_4O_{13}$ can be compared with the ten- and eleven-coordination in $Rb_2Cr_3O_{10}$ and eight-coordination in the rubidium dichromates. The relatively high coordination number of the Rb(I) ions in the $Rb_2Cr_4O_{13}$ seems to be correlated with the oxygen–rubidium ratio.

Structural studies have provided evidence for the existence of a series of heteropolychromates corresponding to the general formula: $XCr_nO_{3n+4}^{3-}$, X being P or As [36]. Thus, for $n = 1$, the $PCrO_7^{3-}$ anion has been described in $CuK_2H_2(PCrO_7)$. For $n = 2$, $PCr_2O_{10}^{3-}$ or $AsCr_2O_{10}^{3-}$ anions have been studied in several compounds: $K_2HAsCr_2O_{10}$, $BaHPCr_2O_{10} \cdot H_2O$ and $BaHPCr_2O_{10} \cdot 3H_2O$. In $K_2HAsCr_2O_{10}$ [37], two independent K(I) ions have different coordination. K(1) is surround by eight oxygen atoms in the range 2.72(2)–3.10(2) Å, while K(2) has nine oxygen atoms neighbours between 2.76(2)–3.11(2) Å. The Cr–O terminal distances are in the range of 1.62(2)–1.65(2) Å, whereas the Cr–O bridging distances (Cr–O–As) are 1.84(1) and 1.83(1) Å. The Cr–O–As bridging angles are 127.9(8) and 129.4(8)°. In $BaHPCr_2O_{10} \cdot H_2O$ [38], the Ba(II) cations are surround by nine oxygen atoms at 2.706(8)–2.984(6) Å, one of them belong to the water molecule. The Ba(II) cations are joined by two oxygen atoms forming a infinite chain. The Cr–O terminal distances are in the range of 1.585(7)–1.630(8) Å. The Cr–O bridging distances (Cr–O–P) are 1.826(7) and 1.828(8) Å. The Cr–O–P bridging angles are 131.2(5) and 138.0(5)°. In $BaHPCr_2O_{10} \cdot 3H_2O$ [38], the Ba(II) cations are ten-coordinated by oxygen atoms at 2.674(6)–2.972(8) Å, two of them belong to two water molecules. For $n = 3$, $AsCr_3O_{13}^{3-}$ and $PCr_3O_{13}^{3-}$ anion configurations have been described in $Na_3PCr_3O_{13} \cdot 3H_2O$ and $(NH_4)_2HAs\,Cr_3O_{13}$ [36].

In $K_3AsCr_4O_{16}$ and $(NH_4)_3AsCr_4O_{16}$ (where $n = 4$), a central AsO_4 tetrahedron shares its four corners with CrO_4 tetrahedra forming a finite anion [36]. For these compounds more structural data are necessary.

3. Compounds with transition elements

The structure of $CuCrO_4$ is described by Seferiadis and Oswald [39]. The structure is built up by chains of edge-linked tetragonally distorted CuO_6 octahedra, which are connected by slightly distorted CrO_4^{2-} tetrahedra sharing their oxygen atoms with the octahedra.

The CrO_4 tetrahedra present two Cr–O(1) short bond distances 1.599(3) Å and other two Cr–O(2) large bond distances 1.731(2) Å. The Cu(II) cation shows the usual tetragonally distorted octahedral coordination with four shorter equatorial Cu–O(2) 1.965(2) Å and two longer axial Cu–O(1) 2.400(3) Å bonds. It is interesting to note that the longer axial Cu–O bonds correspond to the shorter Cr–O bond distance (oxygen atom common) and viceversa.

Structures of isomorphous chromates with cobalt and nickel have been determined by neutron diffraction [40].

The thermal decomposition of $CuCrO_4$ proceeds according to the equation:

$$2CuCrO_4 \rightarrow CuO + CuCr_2O_4 + 1.5O_2$$

The $CuO + CuCr_2O_4$ system is active in several oxidation–hydrogenation, dehydrogenation, alkylations, etc. reactions [41].

The crystal structure of Ag_2CrO_4 [42] consists of chromate groups linked together by Ag(I) ions to form a 3-D network through the crystal. The two crystallographically independent Ag(I) ions have different coordination polyhedra. The coordination of Ag(1) can be best described as a tetragonal bipyramid with approximate D_{4h} symmetry. The coordination of Ag(2) forms a badly distorted tetrahedron with an average O–Ag–O angle of 107°, ranging from 84 to 139°. The chromate group is slightly distorted with an average Cr–O distance of 1.66 Å and angles ranging from 106.1 to 111.6(8)°. Ag–O distances range from 2.34(1) to 2.62(1) Å compared with K–O distances 2.681(2)–3.225(2) Å in α-K_2CrO_4 [23].

The structure of $(NH_4)_2[Cu(CrO_4)_2(NH_3)_2]$ [43] consists of infinite anion chains, parallel to the *c*-axis, in which octahedral copper(II) ions are linked by two bridging CrO_4^{2-} tetrahedra (**3**). The Cu(II) ion is coordinated by four oxygen atoms and two nitrogen atoms. The two pairs of oxygen atoms are from chromate groups and have widely differing Cu–O distances: Cu–O(1) 2.425(1) and Cu–O(2) 2.022(2) Å, compared with the analogous $(NH_4)_2[Zn(CrO_4)_2(NH_3)_2]$ [44], Zn–O 2.23(2) Å. The Cu–N (ammonia) distance is 1.972(2) Å [Zn–N 2.00(3) Å] and is similar to that of Cu–O(2), thus indicating a Jahn–Teller distortion of the octahedron. The CrO_4^{2-} tetrahedron presents only slight distortion (average Cr–O bond distance 1.65(2) Å). For the zinc compound, this bond distance is 1.66(3) Å.

The bridging ligands between paramagnetic metal ions usually mediate antiferromagnetic interactions due to the magnetic orbital overlap through the bridge. In order to study magnetic interactions mediated through tetraoxo anions as CrO_4^{2-}, Oshio et al. [45] have prepared and characterised the complex: $[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)] \cdot 4CH_3OH \cdot 4H_2O$, where acpa = *N*-(1-acetyl-2 propyridine)(2-pyridylmethyl)amine. In this compound, the CrO_4^{2-} presents a pseudotetrahedral structure where the Cr–O bond lengths are in the range 1.606(6)–1.679(4) Å with O–Cr–O bond angles of 108.6(2)–110.7(2)°. The coordination geometry about the Cu(II) ions is square planar with a N_2O chelate group from acpa and an oxygen atom from CrO_4^{2-}. The Cu(II) ion is 0.03(1) Å above the mean plane N_2O_2. The bond distances between the Cu(II) and coordinated atoms are 1.903(4)–1.984(5) Å, which implies that the magnetic orbital of the Cu(II) is $d_{x^2-y^2}$. The bond length of Cr with the oxygen atom coordinated to the Cu(II) is the longest (1.679(4) Å) of the Cr–O bonds and the bond angle Cr–O–Cu about the oxygen atom is 141.3(2). The magnetic behaviour of this compound suggests that a ferromagnetic interaction between the Cu(II) ions is predominant at intermediate temperature and then a weaker antiferromagnetic coupling is involved at lower temperature. The magnetic susceptibility data were analysed by the Bleaney–Bowers equation. The best fit parameters were $2J = +14.6(1)$ cm^{-1}, $g = 2.12(1)$ and $\theta = -0.8(1)$ K. An EPR measurement showed no signal at 77 K, which might be due to a rapid spin relaxation. The CrO_4^{2-} anion bridges Cu(II) ions along the equatorial directions, two of the t_2 type molecular orbitals of the CrO_4^{2-} anion form two sets of σ-type bonding and antibonding orbitals with $d_{x^2-y^2}$ orbitals of the Cu(II) ions and the remainder of the t_2 type orbitals remain nonbonding. The ferromagnetic interaction is due to accidental degeneracy of the σ-type frontier orbitals.

The crystal structure and magnetic properties of catena-(ν-CrO_4-O,O′)[Ni(cyclam)] · $2H_2O$ have been determined [46]. In this compound, Ni(II) ions are bridged by the chromate anion to form a 1-D chain. Magnetic susceptibility measurements revealed that ferromagnetic interactions between Ni(II) cations are propagated through the CrO_4^{2-} bridges and the coupling constant was evaluated to be 0.6(1) cm^{-1} ($H = -2JS_1S_2$). The ferromagnetic interactions were explained by the orbital topology of frontier orbitals.

One of the hydrometallurgical processes that produce waste waters with high toxicity is that corresponding to chromium plating, owing to the high toxicity of Cr(VI). In these kinds of waste waters some transition metals like Fe(III), Ni(II) and Cu(II) are present. Information on the equilibra in the Ni(II)–Cr(VI)–H_2O system is given [47]. A mixed precipitate $NiCrO_4 \cdot 3Ni(OH)_2$ has been found and its thermodynamic solubility constant was determined but its structural characterisation in solid phase was not carried out.

The kinetics of the complexation reaction between $[M(NH_3)_5(OH_2)]^{3+}$ (M = Co, Cr) [48] and $HCrO_4^-$ have been determined by stopped-flow measurements in acidic aqueous solution ($\mu = 0.50$ M). Also these complex equilibria have been studied spectrophotometrically in aqueous acid solution [49]. The chromate complex exists in both $[M(NH_3)_5(HCrO_4)]^{2+}$ and $[M(NH_3)_5(CrO_4)]^+$. The acidity constants for the protonated chromate species at 25°C are $(4.43 \pm 0.05) \times 10^{-3}$ M (Co) and $(3.37 \pm 0.63) \times 10^{-2}$ M (Cr). The temperature dependence of the Cr(III) complexation with $HCrO_4^-$ is described and the resultant thermodynamic parameters discussed in relation to other chromate reactions [49].

In the structure of $K[Fe(CrO_4)_2H_2O]$ [50], the chains of $[Fe_2(CrO_4)_42H_2O]^{2-}$ are formed by CrO_4 tetrahedra and $FeO_5 \cdot H_2O$ distorted octahedra. The Cr–O bond distances, where the oxygen atoms are bound to Fe(III) are large (from 1.658(15) to 1.674(18) Å) and correspond to Fe–O bond distances from 1.975(18) to 2.007(15) Å. The remaining Cr–O bond distances are short (from 1.575(18) to 1.604(18) Å). The tetrahedra CrO_4 are distorted with O–Cr–O angles between 107.7 (8) and 111.2(8)°. The K(I) is ten-coordinated, the K–O bond distances of the KO_{10} are in the range 2.714(19)–3.190(18) Å. Each K(I) is joined to three chains of $[Fe_2(CrO_4)_4 \cdot 2H_2O]^{2-}$.

Double chromates of stoichiometric $M^ICr^{III}(Cr^{VI}O_4)_2$ (M = Na, K, Rb) [51] are very interesting not only due to the complexity of their structural arrangement, but also because of the simultaneous presence of chromium in two different oxidation states and in two different oxygen coordination polyhedra. The compounds $NaCr(CrO_4)_2$, $KCr(CrO_4)_2$ and $RbCr(CrO_4)_2$ are isostructural. The structure can be described as being formed by $Cr^{III}O_6$ octahedra and $Cr^{VI}O_4^{2-}$ tetrahedra arranged in layers by sharing corners. The generated layers are held together by the alkaline cations. Four Cr^{III}–O bond distances are in the range 2.002(1)–2.030(1) Å and two in the range 1.924(1)–1.959(1) Å, for the three compounds. The Cr(VI) ions are coordinated to one oxygen atom with one bond distance at 1.626(1)–1.635(1) Å (oxygen atom shared by Cr(VI) and Cr(III)), one oxygen atom at 1.651(1)–1.698(1) Å, and two oxygen atoms at 1.651(1)–1.698(1) Å (oxygen atoms shared by Cr(VI) and Cr(III)), for these compounds. In the vibrational spectra, it is highly probable that mixing occurs to some extent between these lower internal vibrations of the $Cr^{VI}O_4^{2-}$ moieties and motions of the $Cr^{III}O_6$ octahedra. The overall thermal decomposition occurs according to:

$$M^{I}Cr^{III}(Cr^{VI}O_4)_2 \rightarrow 1/2M^{I}_2Cr^{VI}O_4 + 5/4Cr^{III}_2O_3 + 9/8O_2.$$

The reaction of $(NH_4)_2CrO_4$ with $LFeCl_3$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) in water leads to the formation of the tris(μ-chromato)diiron(III) complex [LFe(μ-CrO_4)$_3$FeL] [52] (Fig. 4). Compounds of bridged dinuclear iron are important because of their biological relevance; they are believed, and in some cases known, to comprise the active centre of various metalloproteins. In complex (**4**), the Fe(III) coordinate geometry is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate amine and three oxygen atoms from three bridging chromate groups. The Fe–O (average 1.89(8) Å) and Fe–N (average 2.224(9) Å) bond lengths are consistent with a d^5 high-spin electron configuration of the Fe(III) centres. The tetrahedral geometry of the CrO_4^{2-} anion is distorted. Thus, Cr–O bond lengths with the oxygen atoms coordinated to Fe(III) are from 1.663(7) to 1.694(7) Å, whereas the bond length of Cr–O bond length with oxygen atoms non-coordinated to Fe(III) are from 1.549(9) to 1.593(8) Å. This compound shows a magnetic behaviour as an antiferromagnetically coupled binuclear compound. The μ_{eff}/Fe values over the temperature range vary from 0.43 μ_B at 4.2 K to 5.30 μ_B at 289.5 K and $J = -15$ cm^{-1}. The observed $\langle g \rangle$ values are very close to the free-electron spin value of 2.00, showing that the iron atoms are in a $^6A_1$ ground state with practically no contribution from orbital angular momentum. The Fe···Fe separation of 4.552(5) Å in [LFe(μ-CrO_4)$_3$FeL] is so large that the origin of the exchange integral cannot lie in direct Fe···Fe interaction. Thus the observed spin coupling is likely to arise through a superexchange mechanism operating via Fe–O–Cr–O–Fe linkages, although the antiferromagnetic interaction in the Fe(III) complexes might be accounted for by an extra π-orbital overlap between $[CrO_4]^{2-}$ and Fe(III) ions leading to nondegenerate frontier orbitals of the [Fe_2^{III}(μ-CrO_3)$_3$] chromophore [45].

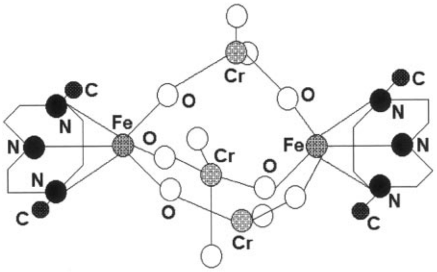

Fig. 4. Structural diagram of [LFe(μ-CrO_4)$_3$FeL], where L = 1,4,7-trimethyl-1,4.7-triazacyclononane. Adapted from Ref. [52].

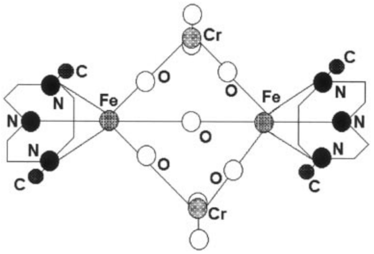

Fig. 5. Structural diagram of $[L_2Fe_2(\mu\text{-}O)(\mu\text{-}CrO_4)_2] \cdot 4H_2O$, where L = 1,4,7-trimethyl-1,4,7-triazacyclononane. Adapted from Ref. [53].

Another multinuclear complex with CrO_4^{2-} as the bridging ligand has been structurally and magnetically characterised $[L_2Fe_2(\mu\text{-}O)(\mu\text{-}CrO_4)_2] \cdot 4H_2O$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) [53] (Fig. 5). The structure of this compound differs from $[L_2Fe_2(\mu\text{-}CrO_4)_3] \cdot H_2O$ [50]. The latter contains three bidentate chromato bridges and no μ-oxo bridge and the Fe···Fe distance is 4.552(5), whereas in $[L_2Fe_2(\mu\text{-}O)(\mu\text{-}CrO_4)_2] \cdot 4H_2O$ is 3.285(4) Å (**5**). The Cr(VI) ions in the latter compound are a distorted tetrahedral environment of four oxygen atoms. There are three significantly different Cr–O distances at 1.560(6), 1.615(6) and 1.664(3) Å. The two long distances of Cr–O correspond to oxygen atoms bonded to Fe(III) ions. Each Fe(III) ion has a distorted octahedral coordination sphere comprised of two bridging bidentate chromates, a bridging μ-oxo group and a tridentate facially coordinating amine ligand. $[L_2Fe_2(\mu\text{-}O)(\mu\text{-}CrO_4)_2] \cdot 4H_2O$ presents an antiferromagnetic behaviour with $J = -124(2)\ \text{cm}^{-1}$, which indicates strong intramolecular antiferromagnetic coupling.

Another multinuclear complex with CrO_4^{2-} as bridging ligand has been structurally characterised: $[Cu_3(CrO_4)_3(OH)_2(py)_2]$ [54]. This compound was prepared by slow crystallisation from a hot aqueous solution of copper(II) dichromate and pyridine. In the structure, two Cu(II) distorted octahedra are linked by a common edge. This arrangement leads to complex chains of edge-sharing octahedra forming a 2-D infinite network. The pyridine rings extend into the space between these layers. The CrO_4^{2-} anion bridges the Cu(II) cations. The Cr–O bond distance (1.600(4) Å) with oxygen atoms non-coordinated to Cu(II) is shorter than the other Cr–O bond distances with oxygen atoms coordinated to Cu(II) (1.621(4), 1.689(4) and 1.694(4) Å). The thermal decomposition in a nitrogen atmosphere can be summarised by the following sequence of steps:

$$Cu_3(CrO_4)_2(OH)_2(py)_2 \underset{-\,H_2O,\ -\,2(py)}{\overset{220\text{-}320°C}{\rightarrow}} Cu_3O(CrO_4)_2 \underset{-\,1.5O_2}{\overset{320\text{-}550°C}{\rightarrow}} 2CuO + CuCr_2O_4$$

Copper chromites are industrially important catalysts [54].

$[Cu(Cr_2O_7)(en)_2]$ has been prepared and structurally characterised by Jameson et al. [55] (Fig. 6). The Cu(II) ion is octahedrally coordinated, with Jahn–Teller distortion, forming the square plane with the ethylenediamine [Cu–N, 2.015(4), 2.008(4) Å] and $Cr_2O_7^{2-}$ anions occupying the axial sites [Cu–O, 2.525(3) Å], giving rise to infinite –Cu–O–Cr–O–Cr–O–Cu chains parallel to the *c*-axis (**6**). In this complex, the CrO_4 group forms nearly regular tetrahedra. The crystal structure is similar to that of $[Cu(Cr_2O_7)(1{,}2\text{-propanediamine})]$ [56]. Magnetic susceptibility data of $[Cu(Cr_2O_7)(en)]$ in the range 1.7–80 K are well fit by the Curie–Weiss expression $\chi_m = 0.4122/(T + 0.198)$, indicating little coupling of electron spins. On heating, the compound loses ethylenediamine and oxygen in three well-defined steps to yield polycrystalline $CuCr_2O_4$ and Cr_2O_3. The intermediates, empirical formulae $CuCr_2O_7(en)$ and $CuCr_2O_5$ are X-ray amorphous. The thermal decomposition is consistent with the following sequence:

$$[Cu(Cr_2O_7)(en)_2] \xrightarrow[-\,en]{483\ K} [Cu(Cr_2O_7)(en)] \xrightarrow[-\,(en+O_2)]{588\ K} CuCr_2O_5 \xrightarrow[-\,1/2O_2]{728\ K} CuCr_2O_4$$

In $AgCr_2O_7$ [57], the AgO_6 octahedra are distorted with Ag–O bond distances ranging from 2.374(2) to 2.676(3) Å. The $Cr_2O_7^{2-}$ anion in this compound is characterised by a low value of the Cr–O–Cr bond angle, 121.6°.

In $[Cu(H_2O)_2(Cr_2O_7)]$ [58], the coordination about the Cu(II) atom is a distorted octahedral, formed by two water molecules and four oxygen atoms which belong to four different $Cr_2O_7^{2-}$ anions. The CuO_6 presents the Jahn–Teller distortion, four short distances (average 1.962 Å) and two large ones (average 2.371 Å). Two Cr–O bond distances, where the oxygen atoms are bound to Cu(II) are relatively large (1.669(2) Å) and correspond to short distances Cu–O (1.955(1) and 1.956(1) Å) and vice versa (Cr–O, 1.609(2), 1.616(2), Cu–O, 2.355(2), 2.387(2) Å). The $Cr_2O_7^{2-}$ anion adopts an almost eclipsed conformation. The CuO_6 octahedra are bound by hydrogen bonds from water molecules, forming infinite bidimensional chains.

A new copper(II) complex of formula $[Cu(bipym)(Cr_2O_7)]$ (bipym = 2,2′-bipyrimidine) [59] has been synthesised in aqueous solution by a slow-diffusion method using a H-double-tube glass vessel. The starting solutions were aqueous solutions of $[Cu(bipym)](NO_3)_2$ in one arm and K_2CrO_4 in the other. The occurrence of the equilibrium between dichromate and chromate in the aqueous solution of K_2CrO_4, the minority species being dichromate in neutral or basic medium, accounts for the formation of single crystals of $[Cu(bipym)(Cr_2O_7)]$, possibly formed due to the lesser solubility of the dichromate complex. In this complex, the Cu(II) exhibits a distorted, elongated-octahedral coordination. Two differing bis-(chelating) bipym groups alternate regularly within the chains. These chains are joined by means of bis(monodentate)–dichromate groups to form a 2-D polymer. The four nitrogen atoms of one of them build the equatorial positions of two

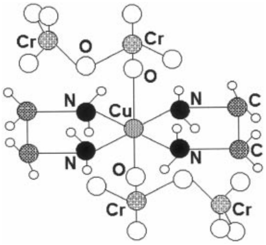

Fig. 6. Structural diagram of $[Cu(Cr_2O_7)(en)_2]$. Adapted from Ref. [55].

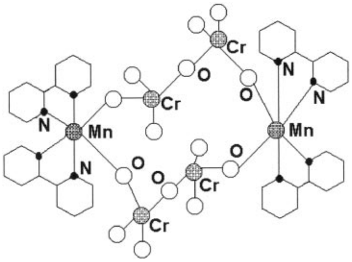

Fig. 7. Structural diagram of $[Mn_2(Cr_2O_7)_2(bpy)_4]$, where bpy = 2,2′-bipyridine. Adapted from Ref. [60].

neighbouring octahedra and the two remaining equatorial sites around each metal atom are filled by an oxygen atom of the $Cr_2O_7^{2-}$ group and a nitrogen atom of the second bipym. The two *trans* axial positions are occupied by another nitrogen atom of the second bipym and an oxygen atom of the $Cr_2O_7^{2-}$ anion. The three equatorial Cu–N (bipym) bond lengths average 2.038(2) Å, a value which is somewhat longer than the equatorial Cu–O bond ($Cr_2O_7^{2-}$) 1.933(2) Å. Both values are significantly shorter than the axial Cu–N (2.339(2) Å and Cu–O ($Cr_2O_7^2$) 2.405(2) Å bond lengths. Each chromium atom in this compound presents a distorted tetrahedral geometry. Within the terminal Cr–O bonds, a significant lengthening is observed for the values of Cr–O, where the oxygen atoms are coordinated to Cu(II). Thus, Cr–O 1.675(2) Å is the bond distance for the oxygen atom in equatorial position and Cr–O 1.623(2) Å is that for the oxygen atom in axial position. The Cr–O for oxygen atoms non-coordinated to Cu(II) are in the 1.596(2)–1.603(2) Å range. The two CrO_4 groups are joined by a shared oxygen atom (Cr–O–Cr 125.1(1)°) forming a dichromate anion in an almost eclipsed conformation. The plot of the magnetic susceptibility per mol of Cu(II) versus T is characteristic of an antiferromagnetic interaction (susceptibility maximum at 135 K). In accordance with structural features, a significant spin density of Cu(II) will be delocalised on the equatorial oxygen atom of $Cr_2O_7^{2-}$ but practically no spin density will be present on the axial oxygen atom of $Cr_2O_7^{2-}$. The lack of significant spin overlapping through the bridging dichromate would lead to a very weak magnetic coupling between the Cu(II) ions involved. Consequently, the magnetic coupling observed in this complex should be mainly mediated by the bridging bipym. The interpretation of the coupling through the bipym bridge was performed by using the model of interaction of localised nonorthogonal magnetic orbitals by Kahn and Briat.

In $[Mn_2(Cr_2O_7)_2(bpy)_4]$ [60] (bpy = 2,2′-bipyridine, see Fig. 7), the coordination about Mn(II) is distorted octahedral, with bond angles ranging from 71.8(4) to 104.3(3)° and Mn–O bonds averaging 2.090 Å. The structure contains a centre of inversion with two μ-dichromate bridges between the two Mn(II) ions, forming a 12-membered 'polymetalloether' ring with a Mn···Mn separation of 7.880 Å and two terminal bpy ligands on each Mn(II) ion completing the coordination (**7**). In this compound an interesting feature is the formation of an oxo bridge between two different metals with highly disparate oxidation states Mn(II) and Cr(VI). The resulting ‘mixed-valences’ heterobimetallic Mn(II)–O–Cr(VI) system represents a substantial stabilisation relative to an intermetal electron-transfer excited state, most probably due to a large amount of reorganisation energy required to break the d^5 and d^0 stable configurations on Mn(II) and Cr(VI), respectively. These energetic constraints may be responsible for the fact that Mn(II) is not oxidised under the conditions in which the compound is formed. In this case, the Cr–O bond distances in the $Cr_2O_7^{2-}$ anion do not seem to change as a consequence of the coordination.

4. Compounds with lanthanide elements

In $KLa(CrO_4)_2$ [61] (Fig. 8), the La(III) ions are coordinated to nine oxygen atoms. The polyhedron around La(III) ion is not regular but can be considered to be an irregular pentagon with two additional oxygen atoms above and another two below the plane of the pentagon (**8**). The crystal consists of parallel layers of composition $[La(CrO_4)]^{n-}$ perpendicular to the a axis. Each layer is formed by double rows of the independent CrO_4^{2-} tetrahedra linked to the La(III) ion through the oxygen atoms. The K(I) ions are located between these layers. Each is surrounded by nine oxygen atoms at distances 2.722(5)–3.076(5) Å, which are less or more than the sum of the ionic radii. The CrO_4^{2-} anions are distorted tetrahedra. Thus, the Cr–O bond distances are in the range 1.648(5)–1.684(5) Å for oxygen atoms also bound to La(III) and 1.607 Å for the oxygen atom non-coordinated to La(III). The Cr–O–Cr bond angles are between 101.0(2) –112.3(3)°. $KLa(CrO_4)_2$ remains stable up to 720°C and decomposes in one step, between 720 and 760°C, in accordance with the reaction:

$$KLa(CrO_4)_2 \rightarrow LaCrO_3 + KCrO_2 + 3/2O_2$$

Studies of the potassium rare earth chromates have produced several compounds with the general formula $KLn(CrO_4)_2$ where Ln = La–Lu, Y and Sc [62]. Their structures were characterised by the infinite layers or tunnels formed by $\{Ln(CrO_4)_2\}_\infty$ groups with K(I) inside. These solids may present a certain techno-

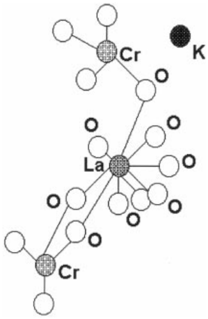

Fig. 8. Structural diagram of $KLa(CrO_4)_2$. Adapted from Ref. [61].

logical interest due to the possibility of substituting the alkaline cations by other positive ions. In this way new materials were devised having the necessary electrophysical properties for thermistors [62].

Magnetic susceptibility measurements of the series $KLn(CrO_4)_2$ (Ln = Y, Dy–Lu) [63] were made in the temperature range 4.2–300K. The susceptibility obeys a Curie or Curie–Weiss law for all the compounds. Raman and IR spectra were recorded and studied for these compounds using factor group analysis [63].

Synthesis and crystallographic data for a family of compounds of general formula $RbLn(CrO_4)_2$ where Ln = Y, Sc and La–Lu have been reported [62]. The compounds are closely related to the $KLn(CrO_4)_2$ but have a slightly different distribution of structural types. The results of indexing the X-ray powder data for the compounds of La, Sm, Lu and Sc were given. The thermal stability of Rb compounds is much less than the analogous one of K. The thermal decomposition starts at over 450°C and, according to X-ray patterns, leads to the formation of rare earth chromites which are always found as final products. Single crystals of Cr_2O_3 are also formed [62].

Lanthanum–lithium–sodium double chromates $Li_{1-x}Na_xLa(CrO_4)_2$ were prepared and analysed by means of admittance spectroscopy [64]. Their electrical conductivity parameters were correlated with structural data of high and low temperature forms of pure lanthanum–lithium–sodium double chromates. Lithium compounds show the lowest conductivity values and the highest activation energy for ion motion, while the sample $Li_{0.5}Na_{0.5}La(CrO_4)$ exhibits the highest conductivity 10^{-5} S cm^{-1} and the lowest activation energy 0.58 eV.

The structure of $Sm_2(CrO_4)_3 \cdot 7H_2O$ has been reported [65]. The Sm(III) ions are located in two types of sites and both are nine-coordinated. Sm(1) is coordinated with one water molecule and eight oxygen atoms of CrO_4^{2-} groups whereas Sm(2) is bound with four water molecules and five oxygen atoms of CrO_4^{2-} groups.

Cristensen et al. [66] investigated the system CrO_3–La_2O_3–H_2O at room temperature, as well as under hydrothermal conditions, and single crystals of the following two compounds were found: $La_2(CrO_4)_3 \cdot 7H_2O$ and $La_3(OH)(CrO_4)_4 \cdot 3.5H_2O$. The crystal structures of these compounds were solved. The structure of $La_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ [66] contains LaO_9 polyhedra forming alternating double and single layers of polyhedra parallel to the bc plane. The oxygen atoms in the LaO_9 polyhedra belong, for La(1) and La(2), to CrO_4^{2-} ions, water molecules and the OH^- ion. For the LaO_9 polyhedron of La(3), the oxygen atoms belong to CrO_4^{2-} anions and to a water molecule. The Cr–O distances in the CrO_4^{2-} ions are in the range 1.57(3)–1.71(2) Å. These interatomic distances do not deviate significantly from the interatomic distances found in the structure of $La(OH)CrO_4$ [67]. In the latter, the La(III) ions are coordinated to nine oxygen atoms in a very irregular manner. Six of these oxygen atoms belong to six different CrO_4^{2-} groups, and the remaining three are hydroxyl oxygens which are common to another two La(III) ions. There is no significant difference between the La–O and La–OH distances which average 2.578 and 2.567 Å, respectively. The CrO_4^{2-} tetrahedra are almost regular, with Cr–O bond distances ranging from 1.613(7) to 1.696(5) Å.

The structure of $La_2(CrO_4)_3 \cdot 7H_2O$ [66] contains two independent LaO_9 coordination polyhedra, each forming a layer that is separated by the CrO_4^{2-} ions. The layers are parallel to the *ac*-plane. The two coordination polyhedra are of the same kind as those found in $La(OH)_3$. The oxygen atoms in the LaO_9 polyhedra belonging to La(1) come from one water molecule and the remaining oxygen atoms come from CrO_4^{2-} ions. The LaO_9 polyhedron of La(2) has four oxygen atoms belonging to the water molecules and the remaining five oxygen atoms come from CrO_4^{2-} ions. The Cr–O bond distances range from 1.61(2) to 1.69(2) Å.

The thermal decomposition, vibrational study and magnetic properties of the compounds $Ln_2(CrO_4)_3 \cdot 7H_2O$ (Ln = La–Eu) were studied in [68]. The thermal decomposition can be explained for the entire series by the following equations:

$$Ln_2(CrO_4)_3 \cdot 7H_2O \rightarrow Ln_2(CrO_4)_3 + 7H_2O$$

$$Ln_2(CrO_4)_3 \rightarrow 2LnCrO_4 + 1/2CrO_3 + 5/4O_2$$

$$2LnCrO_4 + 1/2CrO_3 \rightarrow 2LnCrO_3 + 1/2Cr_2O_3 + O_2$$

For $Pr_2(CrO_3)_3 \cdot 7H_2O$ and $Nd_2(CrO_3)_3 \cdot 7H_2O$, the reciprocal molar magnetic susceptibility versus T obeys a Curie–Weiss Law [68]. For $Sm_2(CrO_3)_3 \cdot 7H_2O$, the magnetic susceptibility can be fitted as a first approximation to the Van Vleck and Frank equation [68].

Lindgren [69] has isolated the compound $Ce^{IV}(CrO_4)_2(H_2O)_2$ dissolving freshly precipitated ceric hydroxide in concentrated chromic acid. In the structure, the chromate groups are approximately layered whereas the Ce(IV) ions and water molecules lie in the mirror planes between these layers. The oxygen coordination of cerium is 8-fold, six of the oxygen atoms belong to six different chromate groups and the other two belong to water molecules. The Ce–O bond distances are in the range 2.23(2)–2.57(2) Å. The CrO_4^{2-} group presents distortion. Thus, the Cr–O bond distances range from 1.58(1) to 1.68(1) Å and O–Cr–O bond angles 108.8(8)–111.1(7)°. The chromate group is bonded to three different Ce(IV) ions with the fourth chromate oxygen probably involved in hydrogen bonding to a water molecule. This is also reflected in the bond lengths within the chromate group, since the distances from the Cr(VI) ion to the three cerium-bonded oxygen atoms (mean 1.66(1) Å) are significantly longer than the fourth Cr–O distance 1.58(1) Å.

Three isomorphous series of compounds of the general formula $Ln(OH)CrO_4$ (Ln = La–Lu), have been found [70]. These series comprise Ln = La–Nd, Ln = Eu–Tb and Ln = Dy–Lu depending on the ionic radii of lanthanide. The structure of $Er(OH)CrO_4$ has been determined [70]. In this structure each Er(III) ion is bonded to eight oxygen atoms. The coordination polyhedron can be considered to be a distorted quadrangular antiprism in which five of the oxygen atoms belong to five different CrO_4 groups, and the remaining three, which are hydroxyl oxygen atoms, bridge Er(III) ions. Comparing the structure with those corresponding to $La(OH)CrO_4$ [67] resulted in the following differences: in $La(OH)CrO_4$ the La(III) ion is coordinated to nine oxygen atoms in a very irregular manner, whereas in $Er(OH)CrO_4$ the Er(III) occur in almost quadrangular antiprism exhibiting a lower coordination, as expected on the basis of the differences in the ionic radii between

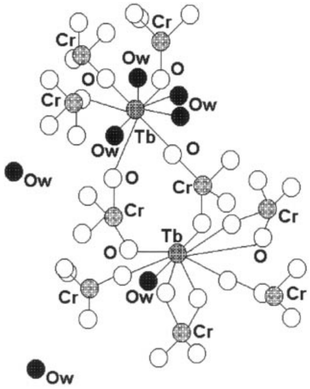

Fig. 9. Structural diagram of $[Tb_2(CrO_4)_3(H_2O)_5] \cdot 2H_2O$. Adapted from Ref. [72].

La(III) and Er(III). The coordination distances in ErO_8 are shorter (average 2.379 Å) than LaO_9 (average 2.578 Å).

The thermal decomposition process for $La(OH)CrO_4$ [71], can be explained by the equations:

$$La(OH)CrO_4 \rightarrow 0.5La_2Cr_2O_9 + 0.5H_2O$$

$$0.5La_2Cr_2O_9 \rightarrow LaCrO_4 + 0.25O_2$$

$$LaCrO_4 \rightarrow LaCrO_3 + 0.5O_2$$

A similar process takes place for $Pr(OH)CrO_4$ [71]. For $Nd(OH)CrO_4$ the thermal decomposition occurs in only two steps [71]:

$$Nd(OH)CrO_4 \rightarrow 0.5Nd_2Cr_2O_9 + 0.5H_2O$$

$$0.5Nd_2Cr_2O_9 \rightarrow NdCrO_3 + 0.75O_2$$

The structures of $Nd_2(OH)_2CrO_4$ and $[Tb_2(CrO_4)_3(H_2O)_5] \cdot 2H_2O$ have been reported [72] (Fig. 9). Two kinds of Nd(III) ions with different environments are present in the structure of $Nd_2(OH)_2CrO_4$. The coordination polyhedron of the eight oxygen atoms around the Nd(III) is a square antiprism. The mean Nd–O distance is 2.468(9) Å. There is not much difference between this average value and the average Nd–O distance of 2.49(2) Å for $Nd_2(CrO_4)_3 \cdot 7H_2O$ [73]. Two hydroxyl oxygen atoms, each form a bridge between three Nd(III) ions. These three Nd(III) ions are in one side of a pyramid formed by hydroxyl oxygen atoms with an hydrogen atom at the apex of the pyramid. The CrO_4^{2-} anions are only slightly distorted tetrahedra. The Cr–O bond distances are in the range from 1.63(1) to 1.686(7) Å.

In $[Tb_2(CrO_4)_3(H_2O)_5] \cdot 2H_2O$ (Fig. 9), the Tb(III) ions are nine-coordinated and are located in two types of sites. The coordination polyhedra consist of both a tricapped trigonal prism and a monocapped square antiprism (**9**). The average Tb–O distance is 2.433(7) Å. Environments and coordination polyhedra of Tb(1) and Tb(2) ions are as found for $Ln_2(CrO_4)_3 \cdot 7H_2O$ (Ln = Nd, Eu) [73]. Two chelating CrO_4^{2-} groups are connected to lanthanoid polyhedra in all dimensions. The CrO_4^{2-} tetrahedra are little distorted and the Cr–O bond distances are in the range 1.617(8)–1.678(6) Å.

Chromate and chromate–dichromate complexes of Eu and Sm containing macrocycles have been reported. Complexes with the formula $EuL(CrO_4)(Cr_2O_7)_{0.5} \cdot 2H_2O$, $SmL(CrO_4)(Cr_2O_7)_{0.5} \cdot 2H_2O$ and $Eu_2L_2(CrO_4)_3 \cdot 10H_2O$ are described by Benetollo et al. [74], where L ($C_{22}H_{26}N_6$) is a six-nitrogen donor macrocyclic ligand.

In $Eu_2L_2(CrO_4)_3 \cdot 10H_2O$ (**10**), the molecular structure consists of two $\{EuL\}^{3+}$ moieties joined through a bridging chromate group, which is linked to each Eu(III) via a single oxygen atom (Fig. 10). The $\{EuL\}^{3+}$ moities have a somewhat folded configuration, with the concave sides of the macrocycles facing each other across the bridging chromate. A bidentate chelating chromate completes the coordination sphere of each nine-coordinate Eu(III) ion. The bridging chromate is somewhat asymmetric, with the Cr–O bond lengths of the two coordinated oxygen atoms differing from each other Cr–O 1.696(5), Cr–O 1.796(4) Å and differing also from those of the non-coordinated oxygen atoms Cr–O 1.647(9) and 1.635(9) Å, respectively. The IR spectrum of this compound shows two intense and well-resolved absorptions in the Cr–O stretching region. These absorptions, centred at ca. 900 and 820 cm^{-1}, show appreciable splitting, suggesting the presence of non-equivalent CrO_4^{2-} species.

$SmL(CrO_4)(Cr_2O_7)_{0.5} \cdot 2H_2O$ and $EuL(CrO_4)(Cr_2O_7)_{0.5} \cdot 2H_2O$ are isostructural and have the coordination formula $[ML(CrO_4)(H_2O)L]_2(Cr_2O_7) \cdot 2H_2O$. In the complex cation, the metal centre is bonded to the six nitrogen-donor atoms of the macrocyclic ligand, which has the usual folded configuration. A bidentate chelating chromate on the convex side of the macrocycle and a water molecule on the opposite side complete the coordination sphere. A dichromate anion (one for every two complex cations) provides the ionic charge balance.

A comparison between the Eu(III) complexes $EuL(CrO_4)(Cr_2O_7)_{0.5} \cdot 2H_2O$ and $Eu_2L_2(CrO_4)_3 \cdot 10H_2O$ [74], reveals marked structural similarities. Thus, in both species, the Eu(III) is nine-coordinated and the $\{EuL\}^{3+}$ moities have the folded 'butterfly' configuration common to other lanthanide complexes of this ligand.

In $[TbL(CrO_4)(H_2O)]_2(Cr_2O_7) \cdot H_2O$ [75], the nine-coordinate Tb(III) ion is bound to the six nitrogen atoms of the L ($C_{22}H_{26}N_6$) macrocyclic ligand, with bond

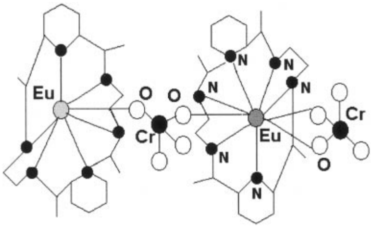

Fig. 10. Structural diagram of $Eu_2L_2(CrO_4)_3 \cdot 10H_2O$, where L = $C_{22}H_{26}N_6$. Adapted from Ref. [74].

distances varying from 2.53(1) to 2.66(1) Å; a water molecule in an axial position on one side of the macrocycle and a bidentate chelating chromate on the opposite side complete the coordination sphere. The (+1) charge of the complex cation is balanced by an ionic dichromate. The Tb-macrocycle moiety has a 'butterfly' shape similar to that found in other lanthanide complexes of this ligand [74].

5. Compounds with actinide elements

The crystal structure of uranyl chromate $UO_2CrO_4 \cdot 5H_2O$ [76] contains CrO_4 tetrahedra and $UO_2(H_2O)_2O_3$ pentagonal bipyramids in endless bands. The remaining water molecules are distributed between these bands. Also the crystal structures of uranyl chromate $UO_2CrO_4 \cdot 2CH_3CONH_2$ [77] and magnesium uranyl hydroxy chromate dodecahydrate $[MgUO_2(OH)CrO_4]_2 \cdot 12H_2O$ have been described [78].

The crystal structure of $[UO_2CrO_4 \cdot 2CH_3CON(C_2H_5)_2]$ [79] has been determined. The U(VI) ion has pentagonal bipyramidal coordination, with oxygen atoms of uranyl on the major axis, two oxygen atoms of the diethylacetamide (deaa) and three oxygen atoms of two chromate groups in the equatorial plane. The crystal structure consists of dimers $[UO_2CrO_4 \cdot 2deaa]$.

6. Conclusions and future prospects

From the results presented in this review, it can be inferred that the compounds of chromium(VI) can act as ligands with elements of all the groups of the Periodic Table and a variety of coordination polyhedra is found. Although much work has been done, a lot of scope for further research remains. Thus, the synthesis and study of new complexes and detailed reinvestigation of presently incompletely characterised compounds can be carried out in the future.

On the other hand, the redox reactions that occur in the cell promote the toxic and genotoxic activity of chromium(VI). The removal of this effect can be achieved by inhibiting the redox process of the chromium(VI) through its complexation or extra-cellular reduction. In this context, a coordination model has been proposed to account for the decreasing mutagenic properties in some chromate complexes containing organic ligands in comparison to simple chromates [3]. This model is based on the study of copper chromate complexes with polypyridines. The in vivo reduction of dichromate with glutathione is slow [60] and trace concentrations of divalent transition metals present in vivo can form species similar to complexes described here such as $[Mn_2(Cr_2O_7)_2(bpy)_4]$ [60] (where bpy = 2,2′-bipyridine). These complexes may be envisioned as *N*-donor residues from nucleotide fragments. The complexing ability of $Cr_2O_7^{2-}$ also provides an insight into the mechanistic pathway of dichromate oxidation of various substrates, which might consist in an initial step involving its coordination of the electrophillic sites on the substrate via the terminal oxo atoms, followed by an oxo atom transfer step. The detoxification of chromium(VI) compounds by complex formation is an area for future research.

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