



E-ISSN: 2664-8784
P-ISSN: 2664-8776
Impact Factor: RJIF 8.26
IJRE 2026; SP-8(1): 67-69
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www.engineeringpaper.net

Received: 14-02-2026

Accepted: 16-03-2026

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Recent Advancement in Multidisciplinary innovation and research RAMIR-25

Coordination chemistry of chromium (III) complexes

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DOI: <https://www.doi.org/10.33545/26648776.2026.v8.i1a.183>

Abstract

Coordination complexes of Chromium(III) are receiving attention again owing to their remarkable and well-known photophysical and photochemical characteristics. The chemistry of anions including chromates, polychromates, heteropolychromate and chromate-dichromate halochromates in metal complexes is primarily responsible for the coordination chemistry of the compounds containing chromium as ligands chromium(III) complexes are known with a variety of amide urea coordinated. Intramolecular hydrogen bonds between neighboring urea ligands within the complex helps to stabilize chromium (III). In addition to this, the structures of several compounds have also demonstrated supramolecular characteristics and intermolecular hydrogen bonding between coordinated urea and electronegative atoms of outer-sphere anions. This review focuses on the synthesis of chromium complexes with various monoanions, dianions, trianions, or hypervalent anions, as well as their examination using different spectroscopic methods and X-ray diffraction analysis.

Keywords: Coordination chemistry; spectroscopic analysis; X-ray diffraction; supramolecular

1. Introduction

Coordination compounds are involved in everything from modern technology to our everyday lives. These compounds can be found in a variety of forms, including pigments^[1], dyes^[2], hemoglobin^[3], vitamin B12^[4], and chlorophyll^[5]. These substances are essential to the development of catalysts^[6, 7], electroplating^[8, 9], photochemical processes^[10], molecular devices^[11-13], and drug delivery systems^[14-16] in terms of chemistry and technology. Additionally, they are used for both quantitative and qualitative metal ion estimation^[17-21]. Coordination complexes of Chromium are among the most significant in terms of stability and applicability. The anionic, cationic, and neutral forms of chromium (III) compounds are well recognized. Elemental chromium can be dissolved in mineral acids to create chromium (III) complexes. Numerous chromium (III) complexes including chromate, sulphonates, phenolates and nitrophenolates etc. with a spectrum of ligands are known. Several industrial goods, including agrochemicals, petrochemicals, medicines, ammunition, textiles, and leather, include phenolates and nitrophenolates^[22]. Additionally, they contribute to the degradation of harmful and carcinogenic insecticides including nitrofen^[23] and parathion^[24]. Alkanesulfonates are recognized as particular anionic surfactants^[25-26] due to their superior water solubility, high chemical stability, high compatibility with electrolytes, and superior biodegradability. They are extensively utilized in cleaning products, liquid emulsifiers, additives for paints and plastics, etc. Various researchers have reported their papers on the application of chromium complexes such as the mechanism of Cr toxicity, carcinogenicity, and allergenicity, chromium removal from water, chromium interference with biological systems in yeasts and fungi, chromium speciation in solid matrices and regulation, the role of chromium in the immune system, research trends in chromium remediation, chromium toxicities and detoxification, chromium pollution: a threat to the environment, the role of Cr(III) in the organism and its potential use in the treatment of diabetes and obesity^[27-30]. This review primarily focuses on the synthesis of hexaureachromium(III) complexes with a homologue series of alkanesulfonates, phenolates and nitrophenolates with different monoanions, dianions, trianions, or hypervalent anions and their characterization by different spectroscopic techniques and X-ray diffraction analysis.

2. Synthesis of hexaureachromium (III) complexes

Hexaureachromium (III) complexes can be prepared with different monoanions, dianions, trianions, or hypervalent anions. $[\text{Cr}(\text{OC}(\text{NH}_2)_2)_6]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ has been synthesized by reacting $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and urea in a 1:6 molar ratio in the acidic medium which results in light green, needle-shaped crystals^[31]. These crystals are capable to react with salts of mono-, di-, tri- or hypervalent anions to give respective new hexaureachromium (III) complexes.

2.1 Synthesis of hexaureachromium(III) complexes with phenolates

Nitrophenolates can synthesize crystalline complexes with a range of organic molecules, using ionic and non-covalent interactions (π - π and H-bonding) creating a supramolecular architect to create novel complexes. As a result, binding of such commercially and physiologically significant mono, di, and tri-substituted nitro-phenolate ions with possible anion receptors or binders is crucial. Numerous inorganic-based anion receptors have been discovered, including organic-inorganic hybrid materials, transition metal complex cations, and organometallic compounds (metallocene porphyrin, metallocene crown ether, metallocene calixarene, etc.). The reactions between hexaureachromium(III) chloride trihydrate and nitro-substituted phenolates have been studied in aqueous medium. Three new complexes, $[\text{Cr}(\text{CO}(\text{NH}_2)_2)_6](\text{PNP})_3$, $[\text{Cr}(\text{CO}(\text{NH}_2)_2)_6](\text{DNP})_3$, $[\text{Cr}(\text{CO}(\text{NH}_2)_2)_6](\text{TNP})_3 \cdot 3\text{DMSO}$ (where PNP: 4-nitrophenolate, DNP: 2,4-dinitrophenolate, TNP: 2,4,6-trinitrophenolate) have been synthesized by reacting $[\text{Cr}(\text{CO}(\text{NH}_2)_2)_6] \cdot 3\text{H}_2\text{O}$ with sodium salts of nitro substituted-phenolates (in 1:3 molar ratio) in aqueous medium^[22].

2.2 Synthesis of hexaureachromium(III) complexes with sulphonates

Alkanesulfonates are considered specific anionic surfactants due to their advanced water solubility, high chemical stability, high compatibility with electrolytes, and better biodegradability. They are extensively utilized in cleaning products, liquid emulsifiers, additives for paints and plastics, etc. These anionic surfactants are particularly advantageous due to their reduced critical micelle concentration, excellent capacity to reduce water surface tension, strong detergent effect, and effectiveness in eliminating particle soils^[32]. The ionic reactions between hexaureachromium (III) and a homologue series of alkanesulfonates i.e., $[\text{CH}_3(\text{CH}_2)_n\text{O}_2\text{SO}^-]$ (where $n = 2-8$) have been studied and synthesized in aqueous medium and characterized by several spectroscopic techniques^[33].

2.3 Synthesis of hexaureachromium(III) complexes with carbonates

The ionic reactions between anion receptor $[\text{Cr}(\text{CO}(\text{NH}_2)_2)_6]^{3+}$ and carbonated anions (HCO_3^- and CO_3^{2-}) in aqueous solution has been investigated. Spectroscopic (IR and UV-visible) methods have been used to study and describe the ionic interactions between anion receptor $[\text{Cr}(\text{CO}(\text{NH}_2)_2)_6]^{3+}$ and carbonated anions (HCO_3^- and CO_3^{2-}) in aqueous solution^[34]. Using a conventional UV-visible spectrophotometer and the titration method, the binding characteristics of this cation with carbonated anions in an aqueous medium were ascertained. The binding ability of the cation $[\text{Cr}(\text{CO}(\text{NH}_2)_2)_6]^{3+}$ towards carbonated anions is

in the order $\text{CO}_3^{2-} > \text{HCO}_3^-$. Thus the selectivity of receptors for particular anion can be selected. The study revealed that the octahedral geometry of $[\text{Cr}(\text{CO}(\text{NH}_2)_2)_6]^{3+}$ is capable enough to target both the carbonated anions.

3. Conclusion

Hexaureachromium (III) complexes have been synthesized by replacing chloride ions of $[\text{Cr}(\text{OC}(\text{NH}_2)_2)_6]\text{Cl}_3$ with different inorganic monoanions, dianions, trianions and hypervalent anions under suitable conditions. The cation present in the complexes acted as probable anion receptors for oxoanions (due to their high positive charge, a large number of hydrogen donor NH_2 groups and symmetrical arrangement). Moreover, a few complexes have also shown supramolecular features.

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