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NOTE

Synthesis of $[CrFe_2O(AcO)_6(CH_3CONH_2)_3]Cl$ as a New Oxo-centered Hetero-trinuclear Carboxylate Complex

REZA TAYEBEE* and MASSOUD RAFIZADEH†
Department of Chemistry, Sabzevar Teacher Training University, Sabzevar, Iran
E-mail: rtayebee@sttu.ac.ir

$[CrFe_2O(AcO)_6(CH_3CONH_2)_3]Cl$ was prepared by the reaction of the $[CrFe_2O(AcO)_6(H_2O)_3]Cl$ with acetamide and replacing the three water molecules under normal reaction conditions. Some structural and physical aspects of this complex are studied.

Key Words: **Synthesis, Iron, Chromium, Oxo-centred complex.**

Triangular oxo-centred complexes with general formula $[M_3O(OOCR)_6L_3]^{n+}$ have been shown as distinctively substantial platforms for delibrately studying metal-metal interactions in clusters[1]. These types of complexes have been characterized with a wide variety of first-row and heavier transition metals incorporating mixed-metal combinations and/or with mixed-valency combinations[2–6]. X-ray diffraction structural analysis of oxo-centered carboxylate-bridged complexes have confirmed that an oxygen atom is positioned at the centre of a triangle surrounded by three metal ions (M_3O). Six carboxylate ligands (OOCR) are also bridged with the metal centres. The sixth coordination site of each metal ion is blocked with a neutral monodentate ligand (L) such as water, pyridine and amines[7] (Fig. 1). The geometry of the central cluster remains relatively constant and is often very close to 3-fold symmetry with a planar OM_3 unit. Among the issues of interest, synthesis and characterization of mixed-metal[7–10] and mixed-valence clusters[3, 11, 12] have provided a special theme for inorganic chemists.

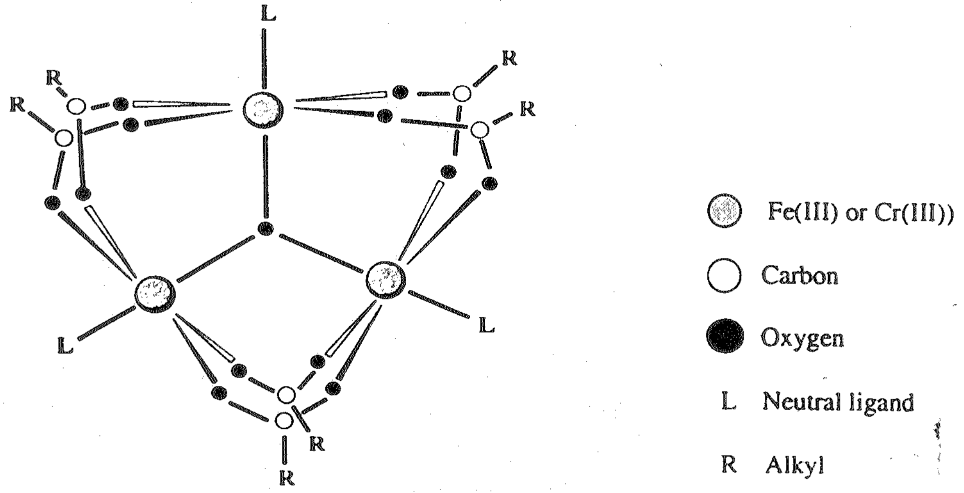

Fig. 1. Molecular structure for complex cations of the salts $[M_3O(OOCR)_6L_3]Cl{\cdot}6H_2O$

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†Department of Chemistry, Tehran Teacher Training University, Tehran, Iran.

Chemical reagents were obtained from commercial suppliers and used after further purification. Solvents were used as received or were distilled prior to use. Synthetic routes for the preparation of precursors are essentially the same as the methods previously reported for the mixed valence iron carboxylate-aqua complexes[13]. Infrared spectra were recorded on a Hitachi 270-50 FTIR spectrophotometer using KBr pellets or nujol mulls. Melting points were determined using Thermal 1A 9100 Certain automated analyzer. The elemental analyses were performed on a GNBH elemental analyzer.

Preparation of $[CrFe_2O(AcO)_6(H_2O)_3]Cl$

54 mmol of $FeCl_3 \cdot 6H_2O$ (14.607 g) and 27 mmol of $CrCl_3 \cdot 6H_2O$ (7.194 g) were dissolved in minimum water. Then 60 mL (2.7 M) of NaOH was slowly added and the resulting mixture was stirred for 2 h. Afterwards, the produced precipitate was filtered, dissolved in 15.6 mL (0.26 mol) of glacial acetic acid and purified further in a soxhlet apparatus at 50–55°C for 2 h. Dark brown crystals were formed after two weeks. These crystals were recrystallized in 30 mL of HCl (0.5 M) to produce brown crystals after 15 d. These crystals were washed with a mixture of isooctane and acetone and dried in a vacuum desiccator for 1 week. Selected IR bands (KBr, cm^{-1}) were 3416 s, 1605 s, 1445 s, 1350 m sh, 1048 m, 955 m, 677 s, 640 s, 620 s, 410 s and 285 w.

Preparation of $[CrFe_2O(AcO)_6(CH_3CONH_2)_3]Cl$

To a solution of 2 mmol (1.247 g) $[CrFe_2O(AcO)_6(H_2O)_3]Cl$ in 10 mL anhydrous ethanol, 0.8 mmol of acetamide salt dissolved in 5 mL of anhydrous ethanol was slowly added by continues stirring. The resulting mixture was heated (70–75°C) in a soxhlet apparatus for 8 h. Dark-brown precipitate was obtained after one week. Then, the precipitate was washed with acetone-isooctane mixture and the purified crystals were dried in a desiccator under vacuum for one week. Obtained crystals (1.3 g, 87.70%) were soluble in polar solvents and were decomposed at 210°C. Anal. Calcd. (%) for $C_{18}H_{33}CrFe_2O_{16}N_3Cl$: C, 6.721; Fe, 14.675; C, 28.698; H, 4.368; N, 5.584 and Cl, 4.54 which confirmed the formation of $[CrFe_2O(AcO)_6(CH_3CONH_2)_3]Cl$. Selected IR bands (KBr, cm^{-1}) were 3434 s, 3351 w, 1756 s, 1683 s, 1578 sh, 1538 s, 1416 w, 1196 w, 1110 w, 941 w, 694 s, 645 w and 390 s.

Chromium(III) and iron(III) complexes of $[M_3O(AcO)_6(H_2O)_3]^+$ and some mixed-valence homonuclear analogues of these complexes are studied thoroughly and their physical properties are fully characterized. Hetero-trinuclear complexes of simple carboxylates with the general formula $[M_2MO(O_2CR)_6L_3]^{n=+1,0}$, M, M = first row transition metals and lanthanides and L = neutral Lewis base, were also prepared and their structures are characterized[14]. These homo- and hetero-nuclear oxo-centered complexes have similar structure and their infrared spectra are generally discussed considering vibrational frequencies of particular M_3O, MC_4 and M-L units in the molecule. As previously described, infrared band assignments of $CrFe_2O$ unit in $[CrFe_2O(AcO)_6(CH_3CONH_2)_3]Cl$ demonstrated planarity of the oxo-centred species with D_3h symmetry[15]. Each metal ion in this complex is surrounded by four oxygen atoms, forming an MO_4 square-planar with D_4h local symmetry. Vibrational spectra of this complex would be described considering interaction of central M_3O unit with their surrounding four MO_4 units. These units have revealed seven vibrational modes of A_{1g}(R), B_{1g}(R), A_{2u}(IR), B_{2g}(R), B_{2u}(in) and $2E_u$(IR) whose interactions with the vibrations of M_3O resulted in 14 vibrations. These bands are observed at 390 cm^{-1} with a small shoulder at 420 cm^{-1} for $CrFe_2O$. Bridging acetates with C_{2v} local symmetry have shown six Raman and IR active vibrational modes of A_1: $\nu_{sym}(OCO)$, B_1: $\nu_{asym}(OCO)$, B_2: $\pi(OCO)$, and A_1: $\delta_{sym}(OCO)$. These vibrations are detected at 1414, 1578, 615 and 646 cm^{-1}, respectively[16].

Symmetric and asymmetric stretchings of bridging acetates[17] appeared at 1600–1400 cm^{-1} for $[CrFe_2O(AcO)_6(CH_3CONH_2)_3]Cl$. Strong and distinct vibrations in 1000–1900 cm^{-1} have proved the existence of organophosphorus moiety in the inner coordination sphere of the metal atom. These bands are given to the synchronous C—O and P—O vibrations. Frequency and intensity of these vibrations are dependent to the electronic and steric properties of neighbouring groups attached to the phosphoryl portion[18, 19].

Appearance of distinct and sharp bands at 440 cm^{-1} is ascribed to strong M—N bond in $[CrFe_2O(AcO)_6(CH_3CONH_2)_3]Cl$. Bands at 3200 and 3425 cm^{-1}, respectively, correspond to symmetric and asymmetric stretching vibrations of N—H. Stretching vibration of carbonyl appears at 1665 cm^{-1}, whereas bands at 1445 and 1610 cm^{-1} are devoted to symmetric and asymmetric stretching vibrations of bridging acetates. Bending N—H vibrations, $\delta(OCO)$, and $\pi(OCO)$, are detected at 1120, 655 and 605 cm^{-1}, respectively.

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