

Synthesis of Isomorphous Prototypic [CrFe₂O(AcO)₆(TEP)₃]Cl and [CrFe₂O(AcO)₆(TMP)₃]Cl As Oxo-Centered Hetero Tri-Nuclear Carboxylate Complexes

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[CrFe₂O(AcO)₆(TEP)₃]Cl, (**1**), and [CrFe₂O(AcO)₆(TMP)₃]Cl, (**2**), were prepared by replacing 3 water molecules in the [CrFe₂O(AcO)₆(H₂O)₃]Cl complex with triethyl- and trimethyl-phosphates, respectively. FT-IR spectroscopy confirmed an oxo-centered, carboxylate-bridged, heteronuclear triangular structure for the title compounds. M₃O and MO₄ units adopted D_{3h} and D_{4h} local symmetry, respectively, and are surrounded by 6 bridging acetates with C_{2v} local symmetry.

Key Words: Iron, chromium, infrared, synthesis, band assignment

Introduction

Oxo-centered carboxylate-bridged triangular complexes of the general type [M₃(μ₃-O)(μ-RCO₂)₆L₃]ⁿ⁺ (M = metal; L = pyridine derivative, THF, water, etc. R = CH₃, Ph, CF₃, H) are particularly valuable as frameworks for systematically studying metal-metal interactions in clusters and constitute an important class of compounds in transition metal chemistry. They have been characterized with a wide variety of first-row and heavier transition metals, with mixed-metal¹⁻⁵ and mixed-valency combinations⁶⁻⁸. These complexes are prototypes of the general class of tri-nuclear “basic carboxylates” whose physical properties have been intensively studied for over 50 years.

The oxo-centered carboxylate-bridged complexes involve an oxygen atom located at the center of a triangle generated by 3 metal ions (M₃O), 6 carboxylate circumference ligands bridged with metal atoms, and 3 monodentate neutral L ligands, such as water, pyridine and amines⁹⁻¹¹. For mixed-metal cases, their ligand-substitution properties have been less explored, and remain open to further investigation¹².

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In the present study and in continuation of our previous paper¹³, our aim was to investigate, for the first time, the preparation of 2 new hetero-nuclear complexes, namely $[\text{CrFe}_2\text{O}(\text{AcO})_6(\text{TEP})_3]\text{Cl}$, (**1**), and $[\text{CrFe}_2\text{O}(\text{AcO})_6(\text{TMP})_3]\text{Cl}$, (**2**), through substitution of 3 water molecules in $[\text{CrFe}_2\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]\text{Cl}$ with triethyl- and trimethyl-phosphates, respectively.

Experimental

Materials

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 complexes¹².

Instrumentation and characterization methods

Infrared spectra were recorded on a Hitachi 270-50FT-IR 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 $[\text{CrFe}_2\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]\text{Cl}$

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (7.194 g, 0.027 mol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (14.607 g, 0.054 mol) were dissolved in minimum water and 60 mL of NaOH (2.7 M) was slowly added with stirring. Then the precipitate was filtered, dissolved in 15.6 mL (0.26 mol) of glacial acetic acid and purified in a soxholet apparatus at 50-55 °C for 2 h. After allowing the solution to stand for 2 weeks, small, dark brown crystals were formed. Then crystals were recrystallized in 30 mL of HCl (0.5 M) to produce brown crystals after 15 days. Crystals were washed with a mixture of iso-octane and acetone and dried in a vacuum desiccator for 1 week. Selected IR bands (KBr; ν , 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 $[\text{CrFe}_2\text{O}(\text{AcO})_6(\text{TEP})_3]\text{Cl}$, (**1**), and $[\text{CrFe}_2\text{O}(\text{AcO})_6(\text{TMP})_3]\text{Cl}$, (**2**)

To a solution of $[\text{CrFe}_2\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]\text{Cl}$ (1.247 g, 0.002 mol) in 10 mL of anhydrous ethanol, triethylphosphate (5 mL, 0.029 mol) and/or trimethylphosphate (4 mL, 0.034 mol) were slowly added with continuous stirring. The resulting mixtures were heated (60-65 °C, 8 h, for the synthesis of (**1**) and 55-60 °C, 7 h, for the synthesis of (**2**)) in a soxholet apparatus. The bright brown products (precipitate for (**1**), and liquid for (**2**)) were obtained by concentration of the solution in vacuum.

The precipitate of (**1**) was washed with iso-octane, and then dried in a desiccator under vacuum. Needle-like, bright brown crystals (1.41g, 74.07%) of (**1**) formed after 1 week. The product was soluble in polar solvents and melted at 240 °C. Anal. Calcd for $\text{C}_{30}\text{H}_{63}\text{CrFe}_2\text{O}_{25}\text{P}_3\text{Cl}$ (%): Cr, 4.098; Fe, 9.89; C, 32.128; H, 5.51; P, 8.268 and Cl, 3.05, which supports the formation of (**1**). Selected IR bands (KBr; ν , cm^{-1}): 2995 m, 2970 w, 1620 s, 1440 s, 1365 w, 1240 s, 1165 w, 1100 sh, 1040 s, 980 sh, 840 w, 820 w, 680 s, 520 m, 423 w, 410 w, and 380 m.

The liquor of (2) was dissolved in chloroform. Finally, a dark brown precipitate was obtained after addition of iso-octane to the above solution. The resulting product dried in a desiccator under vacuum to create bright brown crystals (1.32 g, 76.06%) of (2) after 1 week. The crystals were soluble in polar solvents and melted at 235 °C. Anal. Calcd for $C_{21}H_{45}CrFe_2O_{25}P_3Cl$ (%): Cr, 5.1668; Fe, 11.188; C, 25.38; H, 4.33; P, 9.29 and Cl, 3.68, which proved the formation of $[CrFe_2O(AcO)_6(TMP)_3]Cl$. Selected IR bands (KBr; ν , cm^{-1}): 3395 w, 2965 w, 2860 w, 1621 s, 1453 s, 1353 w, 1223 s, 1047 s, 869 s, 620 m, 507 w, 481 w, 420 w sh, and 395 m.

Figure describes the general structure of $[CrFe_2O(AcO)_6(L)_3]^+$, L=TEP,TMP.

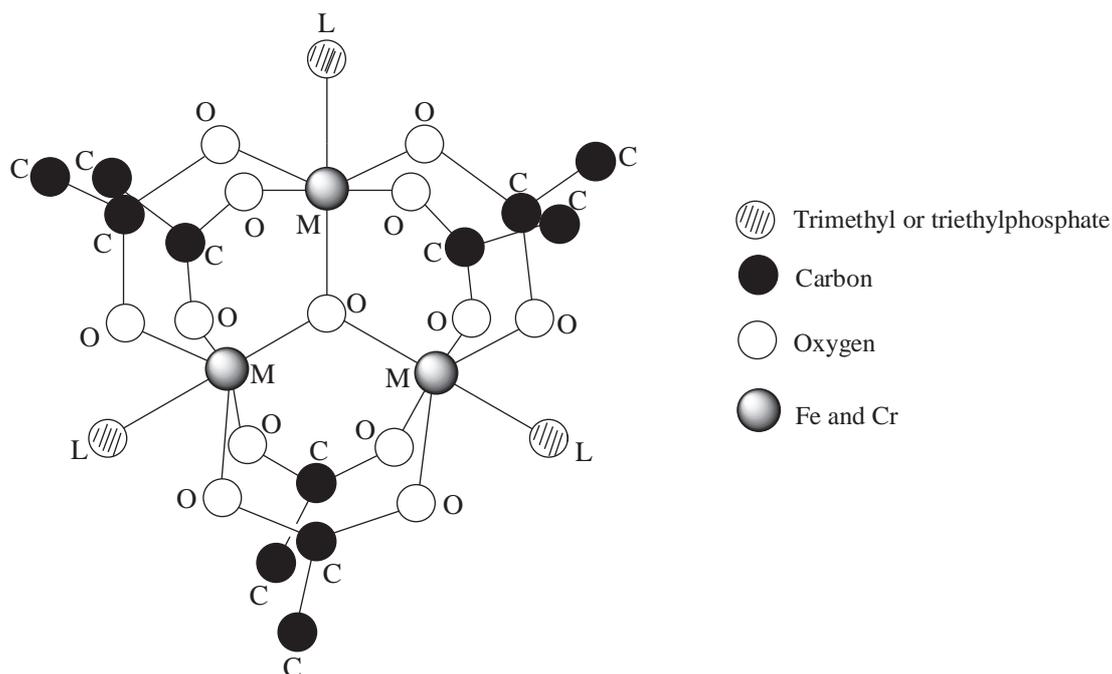


Figure. General structure of hetero-tri-nuclear $[CrFe_2O(AcO)_6(L)_3]^+$, L=TEP,TMP.

Results and Discussion

Cannon and White¹⁴ intensively studied the physical properties of $[Fe_3O(AcO)_6(H_2O)_3]^+$ and $[Cr_3O(AcO)_6(H_2O)_3]^+$, and of some mixed-valence homonuclear analogues of these complexes. Structural analysis demonstrated the general structure involving an oxo-centered moiety incorporating a planar triangle, ending in 6 bridging acetate ligands (Figure). Hetero-tri-nuclear complexes of carboxylates with the general formula $[M_2M'O(O_2CR)_6L_3]^{n=+1,0}$, M, M' = Cr, Fe, Zn, Ru, Rh, Mn and L= H₂O, Py, were also prepared and their structures characterized¹⁵.

Clearly, all 3 homo- and heteronuclear oxo-centered carboxylates represent similar structures, and their IR spectra have been generally discussed considering the vibrational properties of particular M₃O, MO₄ and M-L units in the molecule. Infrared and Raman spectral findings of the M₃O unit have provided 4 A₁' (Raman active), A₂' (IR active) and 2E' (IR and Raman active) principal vibrations (Table).

The existence of δ_{asy} , ν_{asy} , δ_{sy} for M₃O demonstrates planarity of the oxo-centered species with D_{3h} symmetry. Notably, deviation of the $(\mu_3-O)M_3(L)_3$ central triangle from planarity depends on the L

ligands coordinated to the metal atom^{16–19}. Each metal ion in these complexes is surrounded by 4 oxygen atoms of acetates, resulting in 3 MO₄ square planar arrays with D_{4h} local symmetry. Vibrational spectra of these complexes are generally derived from the interaction of central M₃O units with their surrounding MO₄ units. Each MO₄ square planar fragment produces 7 vibrational modes of A_{1g}(R), B_{1g}(R), A_{2u}(IR), B_{2g}(R), B_{2u}(inactive) and 2E_u(IR), whose interactions with the vibrational pattern of M₃O lead to the observation of 14 vibrations. Two bands at 408 and 439 cm⁻¹ with a weak shoulder at 360 cm⁻¹ are also characterized for CrO₄. For Cr₂FeO, these broad bands are detected in the region of 380-430 cm⁻¹ with a weak shoulder at 420 cm⁻¹.

Table. Band assignment of M₃O and M₂M' O units in [M₂M' O(O₂CR)₆L₃]ⁿ⁺.

| Unit | Band assignment | $\nu(\text{cm}^{-1})$ |
|-------------------------------|---------------------------|-----------------------|
| Cr ₃ O | ν_{asy} | 660 |
| | δ_{asy} | 100 |
| | δ_{sy} | 290 |
| Fe ₃ O ν_{asy} | 530-560 | |
| | δ_{sy} | 350 |
| M ₂ M' O | δ_{sy} | 285 |
| | δ_{asy}, ν_{asy} | 625-665 |

Bridging acetates with C_{2v} local symmetry produce 6 Raman and IR active vibrational modes of A₁: $\nu_{sy}(\text{OCO})$, B₁: $\nu_{asy}(\text{OCO})$, B₂: $\pi(\text{OCO})$, and A₁: $\delta_{sy}(\text{OCO})$. These vibrations have been identified at 1414, 1578, 615, and 646 cm⁻¹, respectively. It is found that in bridging acetates, symmetric and asymmetric vibrations of CO₂ shift to higher frequencies than in free ions. These shifts seem to be 250-523 cm⁻¹ for monodentate acetates, 155-185 cm⁻¹ for bridging acetates, and 65-94 cm⁻¹ for chelating acetates²⁰.

For Cr(III) acetate, $\nu_{sy}(\text{CO}_2)$ and $\nu_{asy}(\text{CO}_2)$ are observed, respectively, at 1610 and 1450 cm⁻¹, which confirm the bridging mode of acetate ligands. In iron complexes, $\nu_{sy}(\text{CO}_2)$ and $\nu_{asy}(\text{CO}_2)$ are detected, respectively, at 1590 and 1440 cm⁻¹. For CrFe₂O species, $\nu_{sy}(\text{CO}_2)$ and $\nu_{asy}(\text{CO}_2)$ appear at 1440 and 1575 cm⁻¹, respectively. Development of new bands at 425 and 481 cm⁻¹ for trimethylphosphate and 424 and 486 cm⁻¹ for triethylphosphate confirms the formation of M-O-P bonds with D_{3h} local symmetry²¹.

According to previous findings, the coordination of phosphate esters to the transition metals as mono- and/or bi-dentate ligands reduces the vibrational frequency and intensity of the P=O bond²². Strong P=O vibrations at 1080-1880 cm⁻¹ prove the existence of organophosphorus in the inner coordination sphere of the metal atom. The frequency and intensity of these vibrations are dependent on the inductive effects of neighboring groups attached to the phosphoryl species, rotational isomerism of the P-L bond, and bond angles of L-P-L^{23,24}. Coordination of trimethylphosphate and triethylphosphate to the metal center reduces π -back bonding of oxygen to the phosphorous atom, and thus a 35 cm⁻¹ decrease is observed in the region of P=O vibrations in (1) and (2). Organophosphates, organophosphites and organothiophosphates represent strong and distinct infrared spectral bands, due to synchronous C-O and P-O vibrations^{20,25}. IR spectra of (1) and (2) show that C-O and P-O vibrations are identified at 1040-1060 cm⁻¹ and 810-870 cm⁻¹, respectively. However, bands due to C-O and P-O vibrations have been determined at 1037 and 848 cm⁻¹,

respectively, for free trimethylphosphate. C-O and P-O vibrations are also observed at 1032 and 823 cm^{-1} , respectively, for free triethylphosphate. Finally, symmetric and asymmetric C-H vibrations appear at 2860 and 2965 cm^{-1} , respectively, for trimethylphosphate. These bands are detected at 2930 and 2995 cm^{-1} , respectively, for triethylphosphate. C-H bending vibrations are identified at 1353 cm^{-1} and 1350–1375 cm^{-1} for trimethylphosphate and triethylphosphate, respectively.

Conclusion

Two important new oxo-centered hetero-tri-nuclear carboxylate complexes of trimethyl- and triethyl-phosphates, as organic phosphates, were prepared and their characteristic vibrational bands studied. These findings showed that simple monodentate organic phosphates, $(\text{RO})_3\text{PO}$, bearing linear alkyl chains are able to substitute 3 water molecules in $[\text{CrFe}_2\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]\text{Cl}$. Although (**1**) is less stable than (**2**), both have long-term stability at ambient temperatures. Complexation of other organic phosphates, the study of crystal structures and magnetic properties of organophosphates, and investigations into the relevance of these types of synthetic complexes to some biological transformations are under consideration.

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