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Synthesis, characterization and crystal structure analysis of a novel oxo-centered mixed-metal complex containing unsaturated bridging carboxylates

Research Article

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Abstract: A novel oxo-centered trinuclear mixed-metal carboxylate complex with unsaturated bridging ligands $[Fe_2Cr(\mu_3-O)(C_3H_3O_2)_6(H_2O)_3] \cdot NO_3 \cdot 4H_2O$ has been synthesized and characterized by means of Elemental analyses, Infrared spectroscopy and Crystal structure analysis. The compound crystallizes isotypically in the monoclinic space group type $P2_1/c$. In the compound, each $M^{(III)}$ cation is coordinated by six O atoms from four unsaturated carboxylate groups as bridging ligands, one water molecule as the terminal ligand, and a μ_3-oxygen atom in the center of an equilateral triangle. The infrared spectra show resolved bands arising from $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ vibration of bridging carboxylate ligands along with those of $\nu_{asym}(M_2M'O)$ vibration in the complex. The difference between symmetrical and asymmetrical (COO) ligands indicate that the acrylate bridge is present in the structure of complex.

Keywords: Trinuclear oxo-centered complex • Bridging carboxylate • Acrylic acid • IR spectra • Crystal structure

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1. Introduction

Oxo-centered trinuclear mixed-metal complexes, $[M_2M'(\mu_3-O)(\mu-RCOO)_6(L)_3]^{z+}$ have played an important role in understanding the nature of metal-metal interaction. In particular, magnetic properties of first-row transition elements have been investigated using these kind of complexes [1]. Complexes with this structure contain a triangular arrangement of metal ions bridged by a central μ_3-oxo atom. Each carboxylate anion spans two metal centers at the periphery of the $[M_3(\mu_3-O)]^{6+}$ core, while the neutral monodentate ligands occupy the remaining coordination sites on each metal centre, and as a result the coordination around the metal centre is approximately octahedral (Fig.1).

These carboxylate complexes are of additional interest when the carboxylate ligand is unsaturated, because there is the potential scope of investigation that could be furthered by polymerization in the solid state *via* cross-linking of substituents [2]. One important application of such polymerization reactions is in the quest for dental materials as substitute for amalgams [3] and to produce materials that are active as selective metallic sieves [4].

In previous studies, we reported mixed-bridged and mixed-metal trinuclear oxo-centered complexes with saturated and unsaturated carboxylate ligands [5-8]. This work describes synthesis, elemental analysis, IR and single-crystal X-ray diffraction studies of a new $[Fe_2Cr(\mu_3-O)(C_3H_3O_2)_6(H_2O)_3] \cdot NO_3 \cdot 4H_2O$ (1) heterotrinuclear complex with an unsaturated bridging ligand.

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2. Experimental Procedure

2.1. Methods and Materials

C, H and N analyses were carried out on a Thermo Finnigan Flash model EA 1112 elemental analyzer, Atomic absorption analyses were carried out on a Shimadzu model AA-670 Atomic Absorption Spectrometry. IR spectra of sample in a KBr disc were recorded on a Buck 500 spectrometer. The melting point was determined using an electrothermal digital melting point apparatus. Reagent metal salts used in this study were purchased from Merck. Acrylic acid was distilled prior to use.

2.2. Preparation of $[Fe_2Cr(\mu_3\text{-}O) (C_3H_3O_2)_6(H_2O)_3] \cdot NO_3 \cdot 4H_2O$ (1)

For preparation of this compound, 2.02 g (5 mmol) $Fe(NO_3)_3 \cdot 9H_2O$ and 1 g (2.5 mmol) $Cr(NO_3)_3$ were dissolved in 15 mL water and a solution containing 1 mL (15 mmol) acrylic acid and 0.795 g (7.5 mmol) sodium carbonate in 30 mL water were gradually added with continuous stirring. After allowing the solution to stand for 1 week at room temperature, small dark brown crystals were formed. The dark brown crystals were then filtered, washed, and dried in a vacuum dedicator.

Yield: 70%, Mp: 165°C, Anal. Calcd. for $C_{18}H_{32}O_{23}NFe_2Cr$: C, 27.22; H, 3.95; N, 1.80; Fe, 14.1; Cr, 6.54. Found: C, 27.72; H, 3.65; N, 1.76; Fe, 14.31; Cr, 6.71.

3. Results and Discussion

3.1. IR Spectra

Selected bands of the infrared spectrum and assignments related to stretching and bending modes of fucntional groups for this compound, according to [9-16], are given in Table 1. The infrared spectrum of the complex is dominated by the asymmetric, v_{asym}, and symmetric, v_{sym}, stretching vibrations of the carboxylate groups. The IR spectrum of this complex is shown in Fig. 2 and indicates the presence of unsaturated carboxylates, H_2O, NO_3^-, and {Fe_2MO} groups. The band corresponding to $v_{asym}(COO)$ is located at 1574 cm^{-1}, whereas the $v_{sym}(COO)$ is located at 1441 cm^{-1}: and the difference $\Delta v = v_{asym}(COO) - v_{asym}(COO)$ is 133 cm^{-1}, suggesting a bridging bidentate binding of the carboxylate group to the central metal ion [9,10]. A medium intensity band at 1642 cm^{-1} evidences the double bond (C=C) character present for acrylic acid ligands. For the identification of M_3O fragment metal-oxygen bonds, IR spectra in the

range of 400-800 cm^{-1} were analyzed and the band for the asymmetric vibration associated with the $v_{as}(M_3O)$ unit splits into two components, A_1 and B_2 [11,12]. These spectra showing the characteristic bands for the valence oscillations $v_{as}(Fe_2CrO)$ in the region 680 cm^{-1} (A_1) and 630 cm^{-1} (B_2) were identified. The presence of ionic NO_3^- follows from the spectrum of this compound through the appearance of the $u_3(\acute{E})$ [$u_d(NO)$] mode of the D_3h ionic nitrate at 1375 cm^{-1} [13]. The IR spectra of the complex exhibits a medium to strong band at 3390 cm^{-1}, assignable to the $v(OH)$ vibration of the solvate/coordinated water molecules. The broadness and relatively low frequency of this band are both indicative of strong hydrogen bonding [14].

3.2. Crystallographic study and structural description

Crystallographic data and refinement parameters for this complex are presented in Table 2. A dark brown crystal of dimensions 0.26×0.22×0.17 mm was attached to a thin glass fiber and mounted on a Siemens SMART 1000 CCD platform diffractometer. Data for the title compound were collected at 193(2) K with Mo Kα radiation (λ = 0.71073 Å). The final unit cell was determined from 9,904 reflections in the range of 1.27° < θ < 26.45°. The structure was solved by direct methods and refined via full-matrix least-squares on F^2 using the Bruker AXS SHELXTL Vers. 6.12 software [17]. The largest peak and hole on the final difference Fourier-map were 0.852 and –1.046 eÅ^{-3}.
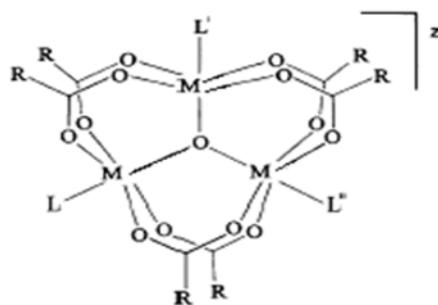

Figure 1. The general Structure of the cluster unit $[M_3O (RCOO)_6(L)_3]^z$.
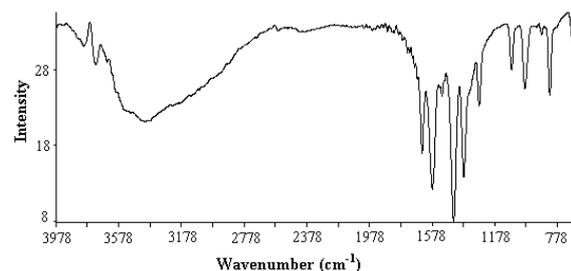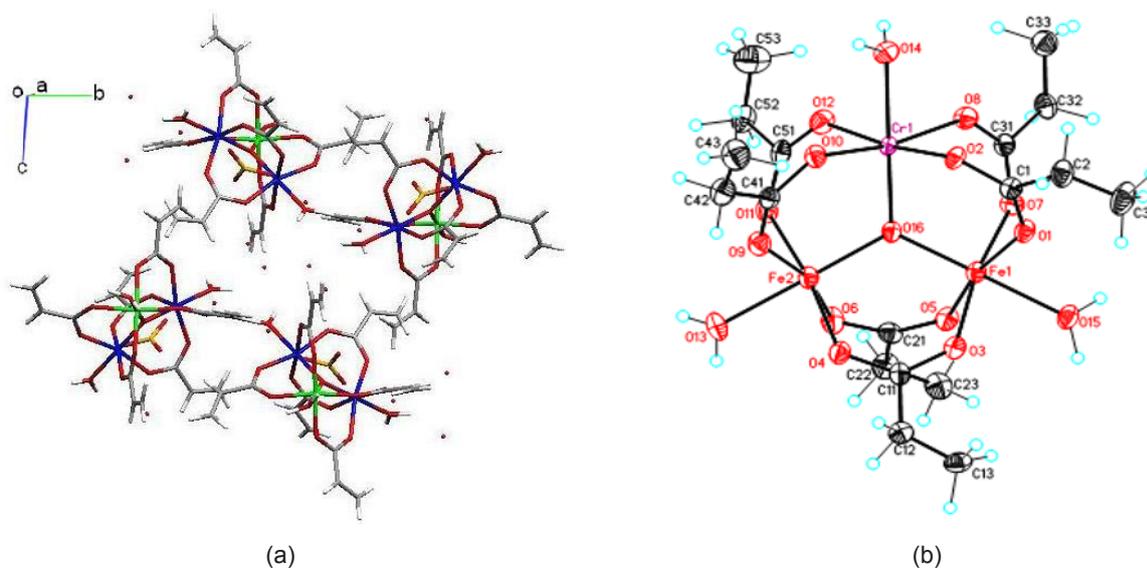

Figure 2. IR spectrum of complex 1, KBr discs, T = 298 K, vertical scale, transmission (%).

Table 1. Selected bands for the infrared spectra of compound.

Assignments								
v (O-H)	v (C=C)	v_{asy} (COO)[a]	v_{sy} (COO)[a]	v (NO$_3$)[b]	v (C-CO$_2$)[c]	δ (OCO)[d]	γ(COO)[d]	v_{asy} (Fe$_2$CrO)[d]
3393	1642	1574	1441	1375	825	673	612	680(A$_1$),630(B$_2$)

[a][10], [b][13], [c][15], [d][16]

(a)   (b)

Figure 3. Molecular structure and atomic labeling of the mixed metal trinuclear complex [Fe$_2$Cr(μ_3-O) (C$_3$H$_3$O$_2$)$_6$(H$_2$O)$_3$] •NO$_3$•4H$_2$O (**1**) (a) and the Packing diagram (unit cell) viewed along the a-axis (b). The thermal ellipsoids are drawn at the 50% probability level.

Treatment of hydrogen atoms conducted by riding model on idealized geometries with the 1.2 isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom. Water hydrogen atom positions of O(13-15) taken from a Fourier-map and also refined as riding group with the 1.5 fold isotropic displacement parameters of the equivalent Uij of the corresponding oxygen atom. Oxygen atom O(24) is disordered over two sites with SOF 0.5, and Heavy atom types (Fe,Cr) are assigned by refinement of the SOF.

Fig. 3 shows an ORTEP projection (a) and unit cell (b) of the complex molecule [Fe$_2$CrO(C$_3$H$_3$O$_2$)$_6$(H$_2$O)$_3$] •NO$_3$•4H$_2$O that crystallize isotopically in the monoclinic space group type P2$_1$/c. The charge on the complex is a (Fe$_2$Cr)^{III} description. Selected bond lengths and bond angles are given in Table 3. From Fig. 2 and Table 3, we found that the Fe(1)Fe(2)Cr(1) triangle is also very close to an equilateral triangle, with Fe(1)–Fe(2), Cr(1)–Fe(1) and Cr(1)–Fe(2) distances of 3.28(3), 3.30(2) and 3.29(5)Å, respectively. The Cr(1)–Fe(1)–Fe(2), Cr(1)–Fe(2)–Fe(1) and Fe(1)–Cr(1)–Fe(2) angles are 60.03, 60.27 and 59.70˚, respectively. The central oxygen O(16) atom lies slightly below the Fe(1)Fe(2)Fe(3) plane 0.003Å. The Fe(1), Fe(2) and Cr(1) coordination geometry can be described as slightly distorted

Table 2. Crystal data and structure refinement for **1**.

Parameter	Data
Empirical formula	C$_{18}$H$_{24}$CrFe$_2$NO$_{19}$•4H$_2$O
Formula weight	794.08 Da
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Crystal description	prism
Space group	P2$_1$/c
	a =12.547(6) Å α = 90
Unit cell dimensions	b =15.602(7) Å β = 90.345
	c =16.052(7) Å γ = 90
Volume	3142(2) Å^3
Z	4
Crystal size	0.26×0.22×0.17 mm
Crystal colour	Brown
Density (calculated)	1.662 g cm^{-3}
F(000)	1596
Theta range for data collection	1.27° to 26.45°
Index ranges	-15≤h≤15, -19≤k≤19, -20≤l≤20
Absorption coefficient	1.343 mm^{-1}
Max. / min. transmission	0.96 / 0.87
Refinement method	Full-matrix least-squares on F^2
Reflections collected	79470
Independent reflections	6353 [R(int) = 0.0750]
Data / restraints / parameters	5595 / 0 / 417
Goodness-of-fit on F²	0.959
Final R indices [I>2σ(I)]	R1 = 0.0568, wR2 = 0.1520
R indices (all data)	R1 = 0.0634, wR2 = 0.1587
Largest diff. peak and hole	0.852 and -1.046 eÅ^{-3}

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Table 3. Selected Bond lengths [Å] and angles [] for title compound.

Bond lengths		Bond angels	
Fe1-O16	1.893(3)	O16-Fe1-O1	94.95(14)
Fe1-O3	1.997(4)	O16-Fe1-O5	96.48(15)
Fe1-O1	2.001(3)	O1-Fe1-O5	168.27(14)
Fe1-O5	2.008(3)	O3-Fe1-O7	170.35(15)
Fe1-O7	2.015(4)	O16-Fe1-O15	179.30(15)
Fe1-O15	2.062(3)	O16-Fe2-O6	97.60(15)
Fe2-O16	1.906(3)	O16-Fe2-O9	97.59(15)
Fe2-O6	1.982(4)	O6-Fe2-O9	164.58(16)
Fe2-O9	1.982(4)	O4-Fe2-O11	171.50(16)
Fe2-O4	2.015(4)	O16-Fe2-O13	179.18(17)
Fe2-O11	2.036(4)	O16-Cr1-O2	94.41(14)
Fe2-O13	2.082(4)	O16-Cr1-O12	93.31(16)
Cr1-O16	1.905(4)	O2-Cr1-O12	172.27(16)
Cr1-O12	1.995(4)	O8-Cr1-O10	167.48(16)
Cr1-O8	2.003(4)	O16-Cr1-O14	179.01(14)
Cr1-O10	2.004(4)	Fe1-O16-Cr1	120.75(17)
Cr1-O2	2.039(3)	Fe1-O16-Fe2	119.61(18)
Cr1-O14	2.059(4)	Cr1-O16-Fe2	119.64(17)
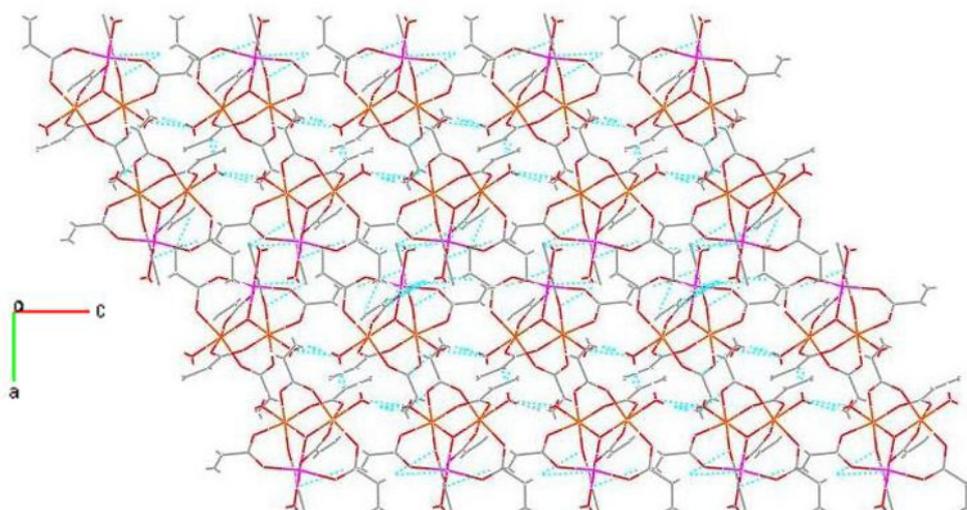
Figure 4. Extended structure of the $[Fe_2Cr(\mu_3\text{-}O)(C_3H_3O_2)_6(H_2O)_3]^+$ moieties, projected along b-axis, dashed lines represent intermolecular contacts.

octahedron with four oxygen atoms from the bridging carboxylate groups, one terminal water oxygen atom and an oxygen atom in the center of the triangle completing the coordination to each metal atom. Also, we found that the Fe(1,2)–O(16) and Cr(1)–O(16) distances are almost the same (1.891, 1.905, 1.909 Å), moreover the three M–O$_{(H2O)}$ bonds in **1** are approximately equal (2.06, 2.08, 2.06 for Fe$_1$-O, Fe$_2$-O and Cr$_1$-O), respectively. It is clear in these systems that the M–OH$_2$ distances are all greater than those found in the analogous mononuclear complexes [M(OH$_2$)$_6$]$^{3+}$ [17]. This confirms that M–OH$_2$ bonds in the oxo-centered trimer complexes are weakened, as suggested previously on the basis of vibrational spectroscopy [19] and reaction kinetics [20].

The type of interaction between the molecular units in the crystal is essential for the crystal packing [21]. The crystal structure of 1 is characterized by short intermolecular contacts and consists of the mutually interpenetrated two-dimensional layers. The structure of these layers is given in Fig. 4.

4. Conclusion

A nw oxo-centered acrylate complex with formula $[Fe_2Cr(\mu_3\text{-}O)(C_3H_3O_2)_6(H_2O)_3]\cdot NO_3\cdot 4H_2O$ has been prepared and its crystal structure has been determined using single-crystal X-ray diffractometry and characterized further by typical spectroscopic methods. For the first time, in this work, we demonstrate the possibility to obtain trinuclear complex with six acrylate groups. Since there is a small amount of dimer in acrylic acid, it is necessary to purify it before use when synthesizing this compound by incorporation of acrylic acid.

5. Supplementary material

Tables with atomic coordinates, bond lengths, bond angles and thermal parameters for all atoms, including hydrogen atoms, may be obtained from the authors on request. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-803873. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: (int.) +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

References

[1] J.K. McCusker, H.G. Jang, S. Wang, G. Christou, D.N. Hendrickson, Inorg. Chem. 31, 1874 (1992)

[2] W. Kuchen, J. Schram, Angew. Chem. 100, 1757 (1988)

[3] F. Broad, Chem. Br. 192 (1986)

[4] A.A. Efeniev, V.A. Kabanov, Appl. Chem. 54, 2077 (1982)

[5] M. Yazdanbakhsh, M.H. Alizadeh, H. Zare Khorramdel, W. Frank, Z. Anorg. Allg. Chem. 633, 1193 (2007)

[6] M. Yazdanbakhsh, H. Tavakkoli, M. Taherzadeh, R. Boese, J. Mol. Struct. 982, 176 (2010)

[7] M. Yazdanbakhsh, H. Tavakkoli, Polish J. Chem. 82, 1519 (2008)

[8] M. Yazdanbakhsh, N. Lotfian, H. Tavakkoli, Bull. Chem. Soc. Ethiop. 23, 463 (2009)

[9] S.T. Warzeska, F. Micciche, M.C. Mimmi, E. Bouwman, H. Kooijman, A.L. Spek, J. Reedijk, J. Chem. Soc. Dalton Trans. 3507 (2001)

[10] M.C. Mimmi, F. Micciche, H. Kooijman, A.L. Spek, S.T. Warzeska, E. Bouwman, Inorg. Chim. Acta 340, 197 (2002)

[11] C. Turta, S. Shova, D. Prodius, V. Mereacre, M. Gdaniec, Y. Simonov, J. Lipkowski, Inorg. Chim. Acta 357, 4396 (2004)

[12] D. Prodius, C. Turta, V. Mereacre, S. Shova, M. Gdaniec, Y. Simonov, J. Lipkowski, V. Kuncser, G. Filoti, A. Caneschi, Polyhedron 25, 2175 (2006)

[13] U. Casellato, P.A. Vigato, M. Vidali, Coord. Chem. Rev. 36, 183 (1981)

[14] I. Chadjistamatis, A. Terzis, C.P. Raptopoulou, S.P. Perlepes, Inorg. Chem. Commun. 6, 1365 (2003)

[15] R. Wu, U.A. Jayasooriya, R.D. Cannon, Spectrochim. Acta A 56, 575 (2000)

[16] L. Meesuk, U.A. Jayasooriya, R.D. Cannon, Spectrochim. Acta A 43, 687 (1987)

[17] G.M. Sheldrick, SHELXTL v. 6.12, Structure Determination Software Suit (Bruker AXS, Madison, 1998)

[18] R.S. Armstrong, J.K. Beattie, S.P. Best, G.P. Braithwaite, P. Del Favero, B.W. Skelton, A.H. White, Aust. J. Chem. 43, 393 (1990)

[19] C.E. Anson, N. Chai-Saard, J.P. Bourke, R.D. Cannon, U.A. Jayasooriya, A.K. Powell, Inorg. Chem. 32, 1502 (1993)

[20] J.P. Bourke, E. Karu, R.D. Cannon, Inorg. Chem. 35, 1577 (1996)

[21] G.R. Desiraju, Acc. Chem. Res. 29, 441 (1996)