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Macromolecule Complexes of Unsaturated Polynuclear Metal Oxocarboxylates

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Summary: Transition metal μ_3-oxo-carboxylates on the base of acrylic, maleic, itaconic, and acetylenedicarboxylic acids are first obtained and characterized using the elemental analysis, IR spectroscopy, EXAFS, magnetochemistry, and mass-spectrometry. The metal atoms form a trinuclear cluster core with oxygen atom in the center and bridge carboxylate ligands. For maleate Fe(III), the lengths of Fe – Fe, Fe – O_{bridge}, Fe – O_{ligand} bonds are equal to 3.29, 1.94, and 2.03 Å, respectively. For polymer metal oxo-acrylates molecular-weight characteristics and topology structure are analyzed. They are network amorphous or amorphous-crystal metal-containing polymers.

Introduction

Trinuclear oxo-centered transition metal carboxylates of the general composition of $[M_3O(O_2CR)L_3]^+$ (R = H, CH_3, C_6H_5, etc., L = H_2O, pyridine, etc.) are widely used as catalysts or intermediates of the oxidation of many organic substrates[1,2] as well as models of active centers of metalloproteins.[3,4] Their structure, spectroscopic, magnetic, and electronic properties have been extensively studied[5-8]. However, there is no information about polynuclear carboxylates with unsaturated carboxyl ligands. Though such compounds have an additional interest for synthesis of metal-containing polymers with unusual structure and properties.[9] We have obtained for the first time trinuclear Cr(III), Fe(III), and V(III) acrylates (MAcr), [10, 11] as well as Cr(III) and Fe(III) maleates (MHMal), itaconates (MItac), and acetylenedicarboxylates (MAdc). This paper reports on structure and properties of unsaturated metal μ_3 – oxo – carboxylates and their polymers.

Spectroscopic properties of metal oxo – carboxylates

The general method for the preparation of metal oxo – carboxylates is the reaction

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of metal hydroxides and carbonates with the unsaturated carboxylic acids. These reactions are straight forward and the side-products are easily removed. The analytical and IR spectroscopic data of the compounds obtained are given in Table 1.

As known, carboxyl groups can be mono- and bidentate that determines a great variety of structural functions of unsaturated acids as ligands. IR-spectra of metal oxo-carboxylates exhibit absorption bands at 1530-1590 cm^{-1} and 1366-1400 cm^{-1} associated with the antisymmetric (ν_{as}(COO) and symmetric (ν_s(COO)) stretching vibrations of the carboxyl groups which have bridging coordination. In addition, for FeAcr, CrAcr, and Vacr very intense bands are observed at 1515-1527 cm^{-1} and 1435-1444 cm^{-1} that can be attributed to the antisymmetric and symmetric stretching vibrations of the carboxyl groups possessing bidentate coordination.[12] The stretching vibrations of >C=C< are altered slightly depending both upon the types of ligand and metal atoms.

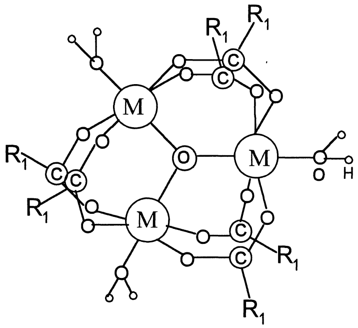
Table 1. Analytical and IR-spectroscopic data of transition metal oxo-carboxylates.

Oxy-carboxylate	found/calcd %			IR spectral characteristic band frequencies, cm^{-1}				
	C	H	M	ν, >C=C<	ν, =CH-C	ν_{as}, COO	ν_s, COO	ν, M-O
FeAcr	31.7/	3.67/	24.6/	1635	1065	1575,	1435,	525
	31.98	3.05	24.06			1515	1370	
CrAcr	32.0/	3.91/	24.6/	1635	1065	1575,	1440,	540
	32.29	3.73	23.32			1525	1370	
VAcr	32.1/	3.43/	21.5/	1635	1065	1590,	1444,	
	32.43	3.75	22.97			1527	1375	
Fe(HMal)	29.7/	3.17/	17.9/	1638	1065	1592	1444,	520
	30.49	2.65	17.74				1366	
Cr(HMal)	31.1/	2.8/	15.7/	1635	1060	1590	1399	530
	29.19	3.16	15.8					
Cr(Itac)	28.5/	2.9/	18.7/	1637	1060	1599	1398	520
	29.19	3.16	15.8					
Fe(Adc)	25.14/	3.6/	27.7/			1597	1387	533
	24.40	1.19	28.36					
Cr(Adc)	30.7/	2.5/	17.1/			1626	1402,	530
	31.29	1.42	16.93				1320	

Table 2. Magnetic properties of transition metal oxy-carboxylates.

Oxy-carboxylate	μ_{ef}, M.B		μ_s, M.B	Valence state of the metal	Configuration	Antiferro-magnetic exchange
	292 K	77K				
FeAcr	3.36	2.31	5.92	Fe^{3+}	$3d^5$	exchange
CrAcr	3.48	2.84	3.87	Cr^{3+}	$3d^3$	exchange
VAcr	2.87	2.60	2.83	V^{3+}	$3d^2$	exchange
Fe(HMal)	2.53	2.42	5.92	Fe^{3+}	$3d^5$	exchange
Fe (Itac)	2.47	2.03	5.92	Fe^{3+}	$3d^5$	exchange

All compounds synthesized are crystal hydrates ($\nu_{OH}(H_2O)$ = 2990 ÷3570. The data of magnetochemistry are also indicate trinuclear structure of the complexes. The value of effective magnetic moment at room temperature is lower than the spin value and decreased at low temperature (Tab. 2). This attests to antiferromagnetic exchange interactions between the paramagnetic centers. Thus, the spectroscopic data allow to propose the trinuclear structure of oxo – carboxylates as follows:



Extended X-ray absorption-edge fine structure spectroscopy has been used to obtain information about the individual metal co-ordination environments. Thus, for Fe(III) – maleate, the M – M (3.29 Å), M – O_{bridge} (1.94 Å), M – O_{ligand} (2.03 Å) distance agree with the values already published, for example, for $[Fe_3O(OCOCME)_6(py)_3](py)$.[13]

The mass-spectrometry

In view of the fact that the cluster of the proposed structure is charged it can be identified by time-of slight mass spectrometry with the extraction of dissolved ions. The main peak in the mass spectrum (m/z = 598) coincides with the theoretical peak for the $[Cr_3OAcr_6)]^+$ cation (Figure 1). The presence of additional peaks corresponding to m/z = 596, 599, 600, and 601 is due to isotopic substitution of chromium, carbon, and oxygen. Compounds containing metal-oxo-carboxylate fragments exhibit a wide range of structural features and can be considered as precursors for larger assemblies. Thus, in mass spectra of Cr(III)-itaconate along with peaks of one charge ions there are peaks corresponded to double- and triple charge ions ($[(Cr_3O)_2(OCOCH_2C(COOH)=CH_2)_{10}\cdot(OCOCH_2C(COO)=CH_2)]^{2+}$ (m/z = 880.90), $[(Cr_3O)_2(OCOCH_2C(COOH)=CH_2)_8\cdot(OCOCH_2C(COO)=CH_2)_2]^{2+}$ (m/z = 815,85), $[(Cr_3O)_3(OCOCH_2C(COOH)=CH_2)_8\cdot(OCOCH_2C(COO)=CH_2)_5]^{3+}$ (m/z = 729,48)).

The triangle cations are bounded with each other through bridges of tetradentate itaconate ligands resulting in the formation of infinite chains of the coordination polymer.

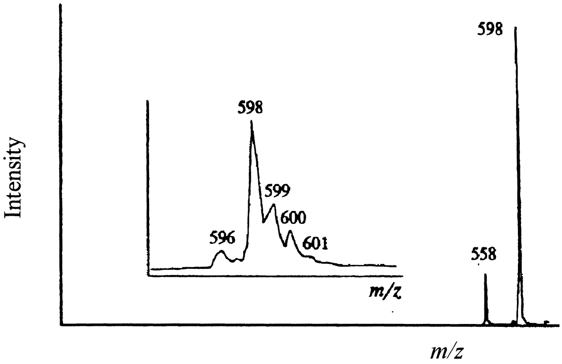


Figure 1. Mass-spectra of the positive ions extracted from an aqueous alcoholic solution of cluster-type Cr(III) acrylate recorded at U = 200 V

Polymer metal oxo-carboxylates

Using of radical polymerization (azobisisobutironitrile initiation, in ethanol) metal-containing polymers on the base of oxo-carboxylates are obtained. It was established that a trinuclear structure of metal oxo-acrylates remains during polymerization. Thus, the electron absorption of the monomer and polymer Cr(III) – oxo-acrylate are compared. The spectrum of the monomer has two weak bands at 24000 and 17500 cm^{-1} that correspond to the spin-forbidden d – d transitions in electron shell of Cr^{3+}. Both these bands are also observable in the spectrum of polymer, with a somewhat different ratio of the intensities.

Molecular topology structure of metal-containing polymers obtained was studied using the thermomechanical spectroscopy.[14] Thus, polymer Cr(III)-oxo-acrylate has a monoblock network structure. In the region below glass temperature (T_g) the polymer is expanded with the coefficient of linear expansion (α_1, curve AB) (Figure 2).

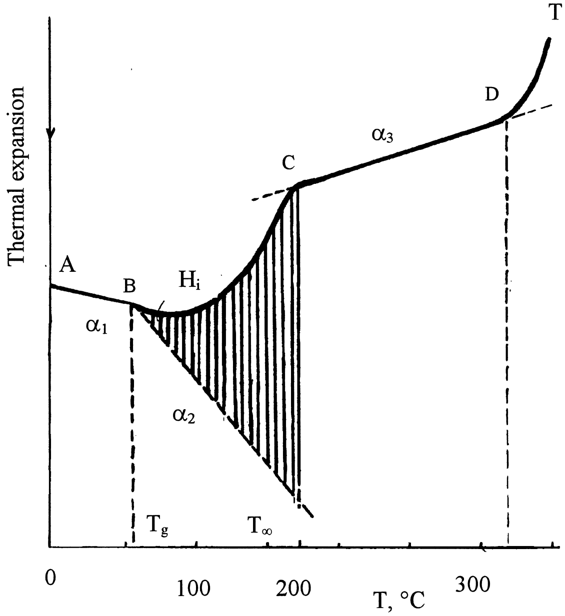


Figure 2. Thermomechanical curve of polymer Cr(III) -oxy-acrylate

At the T_g a segmental mobility is observed and thermomechanical deformation (H_i) occurs. An envelope of all deformations jumps is the pseudointegrated function of the molecular-weight distribution. At temperature T_f the thermal degradation of the polymer proceeds. The ratio of coefficients α_l and α_2 (high elastic expansion) is less than 4 that is typical for amorphous polymers. Molecular-weight characteristics are given in Table 3. The topology structure of polymer Fe(III)-oxo-acrylate is amorphous-crystal. There are two low- and high-melting crystal modifications. The glass state of amorphous block is below – 50 °C. This block has a flexible chain structure.

Table 3. Molecular-topology characteristics of polymer metal-oxo-acrylates.

	Polymer–oxo-acrylate			
	Cr	Fe		
	amorphous		crystal	
			low-melting	high-melting
T_g (T_{cr}),°C	60	-50	-7	242
$\alpha_l(\alpha_{cr})\cdot 10^{-5}$ degree^{-1}	10,42	8,16	363,6	428,6
$\alpha_2 . 10^{-5}$ degree^{-1}	31,25	24,41		
$\alpha_3\cdot 10^{-5}$ degree^{-1}	-28,6			
$M_n\cdot 10^{-3}$	446,4	1.58	7,03	98,3
$M_w\cdot 10^{-3}$	660,0	2.17	50,13	138,1
K	1,48	1.37	7,142	1,41
φ	1,0	0.12	0,43	0,45
T_f,°C	318		42	285

Conclusion

Transition metal μ_3-oxo-carboxylates have trinuclear structure with oxygen atom in the center and bridging carboxyl groups. For Fe(III) – oxo - maleate, the lengths of Fe – Fe, Fe – O_{bridge}, Fe – O_{ligand} bonds are equal to 3.29, 1.94, and 2.03 Å, respectively. The topology structure and molecular-weight characteristics of polymer metal-oxo-carboxylates are analyzed. They are network amorphous and amorphous-crystal metal-containing polymers.

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