Synthesis and reactivity of metal-containing monomers
49.* Synthesis and structure of low-valence transition metal acrylates and their polymers**

G. I. Dzhardimalieva, I. N. Ivleva, Yu. M. Shul'ga, E. N. Frolov, and A. D. Pomogailo*

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: dzhardim@icp.ac.ru

The methods for synthesis of Cu^{1+}, Fe^{2+}, Cr^{2+}, and V^{3+} acrylates were elaborated. The compounds obtained were characterized by elemental analyses, data of IR, X-ray photoelectron, and Mössbauer spectroscopy, magnetochemistry, and mass spectrometry. Polymeric products were obtained by liquid-phase radical polymerization of metal acrylates. Changes in the electronic state of the ions and their nearest ligand environment during polymerization were observed.

Key words: metal acrylates, metal in lowest oxidation state; metal polyacrylates, synthesis, structure.

Compounds of transition metals in the lowest oxidation states are usually unstable. In recent years, these compounds have evoked great interest, and different routes of their stabilization are considered, for example, complex formation of the transition metal ion, its incorporation in the cavity of the macrocyclic ligand, *etc.*[2] It can be suggested that the transformation of the low-molecular-weight compound of the metallomonomer into the polymer increases the stability of these complexes, since the (co)polymeric chain has a stabilizing effect.[3,4] Low-valence metal acrylates, except vanadium(III) acrylate,[5] have not been described in the literature. The development of convenient methods for syntheses of these compounds is also of interest. This work is devoted to syntheses of monomeric and polymeric Cu^{1+} (**1**), Cr^{2+} (**2**), Fe^{2+} (**3**), and V^{3+} acrylates (**4**) and to studying their properties. The corresponding metals were chosen, first of all, due to their potential catalytic properties in different reactions.

Results and Discussion

Syntheses and properties of low-valence metal acrylates. The following methods were developed for preparing these acrylates: Cu^{1+} acrylate was synthesized by the reduction of Cu^{2+} acrylate, Cr^{2+} and V^{3+} acrylates were obtained by ligand exchange reactions, and Fe^{2+} acrylate was prepared by dissolution of the metal in acrylic acid.

Thus, Cu^{1+} acrylate was obtained in acetonitrile at room temperature in an inert atmosphere with vigorous stirring of finely-dispersed copper with its diacrylate.

$$Cu + Cu(OCOCH{=}CH_2)_2 \xrightarrow{Cu\ (excess)} 2\ CuOCOCH{=}CH_2$$

The exchange reaction in water at room temperature

$$CrCl_2 + 2\ CH_2{=}CHCOONa \longrightarrow Cr(OCOCH{=}CH_2)_2\downarrow + 2\ NaCl$$

resulted in the formation of Cr^{2+} acrylate as a red-brown precipitate.

Fe^{2+} acrylate was obtained at 40 °C either in the absence of a solvent or in a water-alcohol medium.

$$Fe + 2\ CH_2{=}CHCOOH \longrightarrow Fe(OCOCH{=}CH_2)_2 + H_2$$

V^{3+} acrylate was synthesized according to the modified procedure[5] by the exchange reaction of VCl_3 with acrylic acid.

$$3\ VCl_3 + 7\ CH_2{=}CHCOOH + H_2O \longrightarrow [V_3O(CH_2{=}CHCOO)_6](CH_2{=}CHCOO) + 9\ HCl$$

The parameters of the compounds obtained are presented in Table 1.

Structures of low-valence metal acrylates. The specific features of the compounds synthesized were studied by comparing them to the previously studied acrylates of the corresponding metals in stable oxidation states.[6–8]

Cu^{1+} and Cu^{2+} acrylates. It is known that Cu^{1+} monoalkene compounds are often π-complexes.[9] In addition, there are several compounds in which a metal

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** Dedicated to the memory of Academician M. E. Vol'pin timed to his 75th birthday.

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Table 1. Parameters of low-valence transition metal acrylates and their polymers[a]

Acrylates	Yield (%)	Found/Calculated (%) C	H	M	μ_{eff}/μ_B 293 K	97 K
1	98	26.00 26.67	2.10 2.22	48.40 48.10	[b]	[b]
Polyacrylate 1	60	—	—	47.20 48.10	[b]	[b]
2	95	31.90 31.31	4.10 4.38	18.10 22.58	1.45	1.22
Polyacrylate 2	20	—	—	24.50 26.79	4.02	—
3	61	28.90 30.77	4.01 4.31	24.00 23.91	4.92	4.35
Polyacrylate 3	54	—	—	27.20 28.21	5.03	4.00
4	30	36.60 36.85	4.11 3.39	19.00 22.35	2.87	2.60
Polyacrylate 4	25	—	—	18.50 23.30	1.86	1.67

[a] For polymeric products, only the metal content was determined.

[b] Cu^{1+} acrylate and polyacrylate are diamagnetic.

atom does not interact with the multiple bond. For example, in Cu^{1+} bimaleate monohydrate, both the C=C bond and the O atoms of the carboxyl group participate in coordination with the metal atom, which results in the formation of more stable chelate complexes.[10,11] In the similar Ag^{1+} complex, only O atoms of the carboxyl groups coordinate to the metal atom, and no π-complex is formed.[10] Cu^{1+} carboxylates based on monocarboxylic acids, such as acetate, trifluoro- and trimethylacetates, vinylacetates, and others, have dimeric or polymeric structures[12,13] of the type of binuclear carboxylates with sufficiently short metal—metal distances. It is noteworthy that the syntheses of several unsaturated carboxylates, including Cu^{1+} acrylate, are described;[13] however, no studies of the structure and properties were performed. The Cu^{2+} acrylate studied previously[5] belongs to the family of transition metal structures with quaternary carboxylate complexes. Crystals obtained from an ethanol solution have the $[Cu_2(OCOCH{=}CH_2)_4 \cdot (EtOH)_2]$ composition. An interesting structural feature is the formation of a binuclear cluster in which the Cu—Cu distance is equal to 2.609 Å.

It can be assumed that its low-valence analog, the Cu^{1+} acrylate under study (**1**), has a close structure. For example, according to IR spectroscopy, no shifts of the frequency of the stretching vibration of the C=C band (1639 cm^{-1}) occur, *i.e.*, the Cu atom does not interact with the double bond, and the carboxylate function plays the role of the bidentate bridging ligand. This is evident from the value of the difference between the frequencies ($\Delta\nu(OCO) = \nu_{as}(OCO) - \nu_s(OCO)$) of asymmetrical, $\nu_{as}(OCO)$, and symmetrical, $\nu_s(OCO)$, stretching vibrations of the carboxylate group[14] (Table 2). The data of magnetic measurements and X-ray photoelectron spectroscopy (XPS) confirm the univalent state of copper (see Fig. 1, Tables 1 and 3). In the case of copper, the standard determination of the chemical state from the position of the main peak in the photoelectron spectrum is ambiguous. The position of the Auger peak (CuL_3VV), Wagner's Auger parameter (α), and the relative intensity of the satellite accompanying the photoelectron $Cu2p_{3/2}$ peak (I_{sat}/I_{main}, where I_{sat} and I_{main} are the intensities of the satellite and main peaks, respectively) give additional information on the chemical state of copper.[15] According to the data in Table 3, we can confirm that copper in molecule **1** is univalent. This is confirmed by the fact that the modified Wagner's parameter α′ ($\alpha' = \alpha + h\nu$) for compound **1** is lower than 1850 eV, while for the Cu^{2+} and Cu^0 compounds, $\alpha' > 1850$ eV.

Based on the aforesaid and taking into account the relative stability of the compound obtained and its re-

Table 2. Characteristic frequencies in IR spectra of transition metal acrylates

Metal	$\nu(C{=}C)$	$\nu_s(COO)$	$\nu_{as}(COO)$	$\Delta\nu(COO)$	$\nu OH(H_2O)$	Coordination
			cm^{-1}			
Cu^I	1639	1433	1569	136	—	Bridging
Cu^{II}	1640	1440	1575	135	—	The same
Fe^{II}	1637	1450	1545	95	3045	Bidentate
Fe^{III}	1635	1370, 1435	1575, 1515	205, 80	3460	Bridging Bidentate
Cr^{II}	1640	1420	1591	171	3310	Bridging
Cr^{III}	1635	1370, 1440	1575, 1525	205, 85	3500	The same Bidentate
V^{III}	1651	1444, 1375	1527, 1590	83, 215	3053	The same Bridging

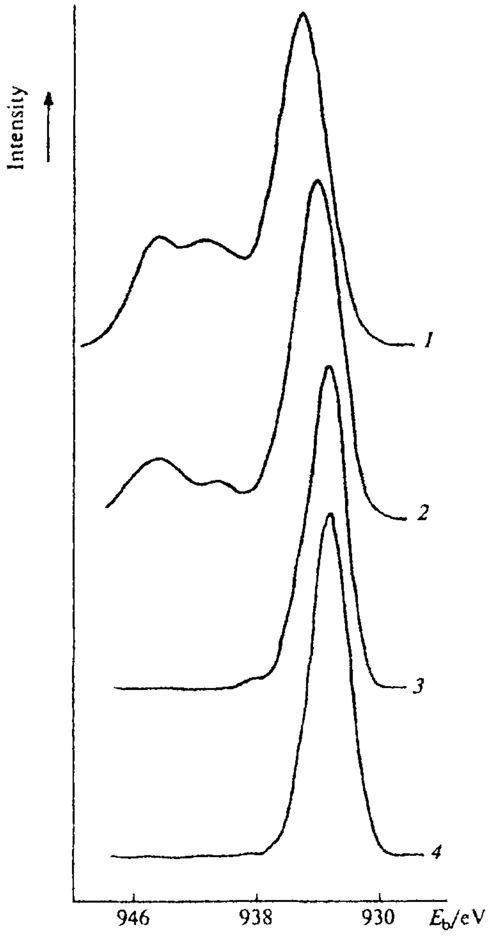
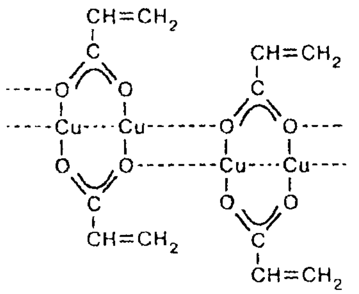


Fig. 1. X-ray photoelectron $Cu2p_{3/2}$ spectra of Cu^{2+} polyacrylate (*1*), Cu^{2+} acrylate (*2*), Cu^{1+} polyacrylate (*3*), and Cu^{1+} acrylate (*4*).

stricted solubility, we can suggest that Cu^{1+} acrylate has a polymeric structure.



Similar structures of several univalent copper carboxylates, including Cu^{1+} acrylate, contain dimeric fragments in the vapor phase, which has been shown previously[13] by mass spectral analysis.

Table 3. XPS data for Cu^{1+} and Cu^{2+} acrylates, their polymers, and reference compounds

Compound	$Cu2p_{3/2}$ /eV	I_{sat}/I_{main}	$Cu(L_3VV)$	α'	State of copper
			eV		
Cu (metal)	932.7	0	335.2	1851.1	Cu^0
Cu_2O	932.6	0	337.0	1848.2	Cu^{1+}
CuO	933.7	0.42	336.3	1851.0	Cu^{2+}
$CuOCOCH=CH_2$	933.2	0	339.4	1847.4	Cu^{1+}
Cu^{1+} polyacrylate	933.1	0	338.2	1848.5	Cu^{1+}
$Cu(OCOCH=CH_2)_2$	934.8	0.34	—	—	Cu^{2+}
Cu^{2+} polyacrylate	933.8	0.19	—	—	Cu^{2+} + Cu^{1+}

Cr^{2+} and Cr^{3+} acrylates. Cr^{3+} acrylate is related to the known type of trinuclear complexes in which metal atoms form a regular triangle with the oxygen atom in the center, and the carboxylate groups are bridges between the metal atoms.[8] Therefore, it was of interest to reveal a change in the nuclearity of the complex on going to its low-valence analog. All known Cr^{2+} carboxylates based on saturated carboxylic acids are binuclear.[16] They are characterized by anomalously low values of the effective magnetic moment (μ_{eff}), which can be explained by the strong exchange interaction in these structures. The Cr^{2+} acrylate under study also has a low effective magnetic moment μ_{eff} = 1.45 μ_B (293 K), whose value depends on the temperature (see Table 1). The decrease in the $\Delta\nu(COO)$ value to 171 cm^{-1} (see Table 2) (for Cr^{3+} acrylate, $\Delta\nu(COO)$ = 205 cm^{-1}) is most likely associated with the fact that the O—C—O angle decreases due to the strong Cr—Cr interaction, as observed previously.[17] Thus, we synthesized for the first time Cr^{2+} acrylate with the $Cr_2(OCOCH=CH_2)_4 \cdot 4H_2O$ composition (**2**) confirmed by elemental analysis, IR spectroscopy, and magnetic measurements.

Fe^{2+} and Fe^{3+} acrylates. Fe^{3+} acrylate with the $[Fe_3O(CH_2=CHOCO)_6 \cdot 3H_2O]OH$ composition, as Cr^{3+} acrylate, belongs to the family of trinuclear complexes and has the identical composition and structure,[7] unlike their low-valence analogs. As a rule, adducts of bivalent transition metal (Mn, Fe, Co, and Ni) carboxylates have the $ML_2(RCOO)_2$ or $ML_4(RCOO)_2$ compositions, being monomeric complexes.[18] In the case of the Fe^{2+} acrylate (**3**) under study, this is confirmed by magnetic and spectral data. According to magnetic measurements, compound **3** is a high-spin octahedral complex, whose μ_{eff} changes slightly with temperature (see Table 1), which agrees with the data of γ-resonance spectroscopy. The parameters of the γ-resonance spectrum of Fe^{2+} acrylate (δ = 1.14 mm s^{-1}, Δ = 1.96 mm s^{-1}) are close to the corresponding values typical of compounds of bivalent high-spin iron ions (Table 4).

The IR spectrum of complex **3** contains absorption bands at 1545 and 1450 cm^{-1}, which are assigned to stretching $\nu_{as}(COO)$ and $\nu_s(COO)$ vibrations of the carboxylate groups with the bidentate type of coordination (see Table 2). It is noteworthy that similar absorption bands in the IR spectrum of Fe^{3+} acrylate are somewhat

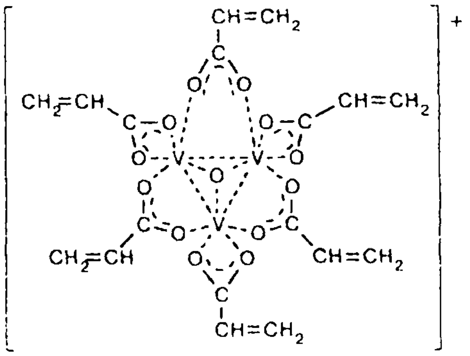
Table 4. Parameters of Mössbauer spectra of Fe^{2+} and Fe^{3+} acrylates

Compound	T/K	δ	Δ
		mm s^{-1}	
Fe^{2+} acrylate	295	1.14	1.96
Fe^{3+} acrylate	295	0.64	0.65

Note: δ is isomeric shift, and Δ is quadrupole splitting.

shifted to the low-frequency region. According to the elemental analysis data, compound **3** has the $Fe(OOCCH=CH_2)_2 \cdot 2H_2O$ composition and it is isostructural to the previously studied[6] Co^{2+} and Ni^{2+} acrylates.

V^{3+} acrylate. The composition and degree of oxidation of vanadium in carboxylate complexes are known to depend substantially on the nature of R in RCOOH and on synthetic conditions. For example, the oxo cluster containing only V^{3+} was obtained[19] by the reactions of VCl_3 or VBr_3 with RCOOH, while the oxidation of the V^{2+} complexes by RCOOH resulted in the formation of mixed-valence vanadium oxo complexes.[20] As mentioned above, we used VCl_3 and, unlike the procedure described previously,[5] the reaction was carried out in an alcohol medium to avoid undesirable side processes of polymerization of acrylic acid. The IR spectrum of the complex obtained (**4**) contains bands of stretching vibrations of the bridging and bidentate carboxylate groups (see Table 2). The μ_{eff} value at 293 K is 2.87 μ_B, which corresponds to the purely spin value for V^{III}. The elemental analysis data (see Table 1) correspond to the $[V_3O(CH_2=CHCOO)_6 \cdot H_2O] \cdot (CH_2=CHCOO)$ composition, which suggests the structure of a binuclear oxo cluster similar to those of Fe^{3+} and Cr^{3+} acrylates.



The data of mass spectrometry with extraction of ions from the solvent confirm this structure. The mass spectrum (U = 300 V) of the positive ions isolated from a water-alcohol solution of the complex studied contains peaks with m/z 595 (with the maximum intensity), 631 (much less intense), and 666 (with the lowest intensity). The main peak in the mass spectrum (m/z = 595) coincides in mass with the value calculated for the dehydrated $[V_3O(CH_2=CHCOO)_6]^+$ cation.

Polyacrylates of metals in the lowest oxidation states. To obtain polymeric products, the complexes under study were subjected to radical polymerization in the presence of an initiator. The yields of the polymeric products were not high (20—60%). The polymers formed are insoluble in organic solvents, which impedes the estimation of their molecular weights. The electronic states of the ions and symmetry in the structure of their nearest environment change during polymerization and are related to the nature of the metal. For example, during polymerization of complex **2** the binuclear structure is most likely monomerized, because μ_{eff} for Cr^{2+} polyacrylate is 4.05 μ_B (293 K), which is characteristic of the high-spin state of the Cr^{2+} ion and its monomeric adducts.[21] It is noteworthy that, unlike the low-molecular-weight complex **2**, which is very unstable and, being freshly prepared, is simultaneously ignited in air (!), Cr^{2+} polyacrylate is relatively stable to oxygen and atmospheric moisture.

The valence state and coordination of the Fe atom of compound **3** remain unchanged during polymerization. The μ_{eff} value of the polymeric product at 293 K is 5.03 μ_B, which corresponds to the high-spin octahedral iron complex (see Table 1).

When complex **4** is polymerized, it is most likely partially oxidized. This is indicated by the data of magnetic measurements. Probably, the oxidation changes the charge value of the cluster cation and leads to the formation of an oxo cluster of vanadium with oxidation degrees II, III, and IV in the trinuclear cycle of the type of trimeric vanadium carboxylates.[20] Presently, this mechanism is under more detailed study.

The polymerization of complex **1** occurs without difficulty and results in the formation of univalent copper acrylate that is stable in air. The stability of the polymeric complex is most likely related to the stabilizing effect of the polymer chain rather than to the structure of the monomeric unit. This is also observed in the case of Cu^{2+} acrylate, whose polymerization is accompanied by a partial reduction of the copper ions (see Table 3). As shown previously,[22] the content of the reduced copper forms in the polymer obtained is sufficiently high and reaches 50%, and the units of the polymer chain are dimers of uni- and bivalent copper with the bridged structure of the ligands. Linkages between the adjacent chains and between the ligands of the adjacent dimers favor the stability of these complexes.

Experimental

X-ray photoelectron spectra were recorded on a VIEE-15 instrument with a magnesium anode ($h\nu$ = 1253.6 eV). The spectra were calibrated by the C1s line (285.0 eV). IR spectra (pellets with KBr or suspensions in Nujol) were recorded on a Perkin—Elmer-325 instrument. Mössbauer spectra were obtained on an electrodynamic γ-resonance spectrometer in the permanent acceleration mode with the ^{57}Co source in the Cr matrix at ~20 °C. The isomeric shifts are presented relative to sodium nitroprusside. The magnetic susceptibility was measured on a Faraday's balance. The magnetic moment was calculated from the formula $\mu_{eff} = 2.84\ \sqrt{\chi}_{at} \cdot T$, where χ_{at} is the paramagnetic susceptibility referred to 1 g-at. metal. Mass spectra were obtained on a time-of-flight mass spectrometer of the mass-reflectron type with extraction of dissolved ions.

All procedures of syntheses of unstable compounds **1—4** were carried out in an inert atmosphere. Solvents were dehydrated and distilled in an Ar flow. Acrylic acid (pure grade) was distilled *in vacuo* at 24—25 °C (2 Torr), n_D^{20} 1.4220. Cu^{2+} acrylate was obtained according to the previously described procedure.[6]

Cu^{1+} acrylate (1) was synthesized by the reduction of Cu^{2+} acrylate with metallic copper in acetonitrile. The reaction was carried out at ~20 °C and with continuous stirring for 5 h. The product that formed was separated by filtration, washed, and dried *in vacuo*. Complex **1** is a light-yellow powder, weakly soluble in acetonitrile and DMF and sensitive to atmospheric oxygen.

Cr^{2+} acrylate (2) was synthesized from freshly prepared $CrCl_2$ and $CH_2{=}CHCOONa$. The exchange reaction was carried out in an aqueous solution at room temperature. The desired product was obtained as a red-brown precipitate, which was separated by filtration, washed, and dried *in vacuo*. Complex **2** is soluble in methanol and very sensitive to atmospheric oxygen: in the freshly prepared state after drying, it is spontaneously ignited in air.

Fe^{2+} acrylate (3) was prepared by dissolution of metallic iron (pure grade) in acrylic acid in a water-alcohol medium with heating to 40 °C. The lemon-yellow mother liquor was filtered off and concentrated *in vacuo*. Complex **3** is a light-yellow powder, which is soluble in methanol, ethanol, DMF, and water and rapidly oxidized in air.

V^{3+} acrylate (4) was prepared by dissolution of VCl_3 in an alcohol solution of acrylic acid. A precipitate was formed in the solution ~24 h after. It was separated by filtration and dried *in vacuo*. Complex **4** is a dark-green powder, which is soluble in methanol and poorly stable in air.

Metal-containing monomers were polymerized in the presence of azobisisobutyronitrile (2%) as the initiator at 60 °C in methanol or DMF.

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