Preparation and reactivity of metal-containing monomers
38.* Investigation of $[Cr_3O(OCOCH=CH_2)_6]OH$ cluster monomer and its polymer by means of IR, XP, and mass spectroscopy

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The monomer $[Cr_3O(OCOCH=CH_2)_6]OH$ was produced by reaction of acrylic acid with fresh chromium hydroxide. This monomer was investigated by a number of physicochemical methods. It was found that acrylate residues are bonded to the metal atoms *via* the carboxy group so that the double bond is not involved in coordination. A comparative study of the dissociative fragmentation of the $[M_3OAcr_6]^+$ clusters, where M is Cr or Fe and Acr is $OCOCH=CH_2$, shows that in the case of Fe the $[M_3OAcr_3]^+$ fragment is the main product of decomposition of $[M_3OAcr_3]^+$ cluster cation, whereas this was not observed in the case of Cr. The $[M_2OAcr_4]^+$ fragments are characteristic of decomposition products of the Cr complex and do not form in the case of Fe. The radical polymerization of Cr-containing monomers results in monodentate coordination of the carboxy groups, which does not appear in the initial monomer.

Key words: chromium(III) acrylate, structure; iron(III) acrylate; metal-containing polymers; XPS, IR and mass spectra.

Previously[1], the synthesis of the $[Fe_3O(OCOCH=CH_2)_6]OH$ cluster monomer and the results of investigations of this monomer and its polymerization products have been reported.

It was found that upon electrospraying an alcohol solution of the monomer at atmospheric pressure, only one molecular cation, the $[Fe_3OAcr_6]^+$, could be detected by mass spectrometry. Dissociative fragmentation of the $[Fe_3OAcr_6]^+$ cation can be observed when the ion moves in an electric field at gas pressure ~5 Torr. The fragmentation starts with elimination of one acrylic ligand. In the IR spectra of the monomer the $\nu^a(COO)$ and $\nu^s(COO)$ vibrations of the acrylic group are split. This is related to the two types of coordination present in the monomer, namely, bridge-type coordination and bidentate coordination. Polymerization of the cluster monomer results in decreased splitting of these vibrations. The symmetry of the Fe^{3+} cations in the solid monomer and in the polymer differ substantially. It was also found that polymerization of $[Fe_3OAcr_6]OH$ proceeds without reduction of the Fe^{3+} cations, unlike polymerization of copper(II) acrylate where such reduction occurs[2].

In this work we report the results of an investigation of the $[Cr_3OAcr_6]OH$ cluster monomer and its polymer studied by X-ray photoelectron spectroscopy (XPS) and IR spectroscopy. The data of comparative studies of the dissociative fragmentation of $[M_3OAcr_6]^+$ ions, where M is Cr or Fe, are discussed.

Experimental

The Cr^{3+} acrylate was produced according to a previously reported technique[3], by the reaction of fresh Cr(III) hydroxide with excess acrylic acid. The product was isolated from the reaction mass by reprecipitation with diethyl ether and then dried *in vacuo*. The acrylate was purified by repeated precipitation from a methanol solution with diethyl ether.

Polymerization was performed at 70 °C in an alcohol solution with 2 % AIBN as the initiator.

Chemical analysis showed the following composition of the product (wt.%): Cr, 24.60 (23.32); C, 32.01 (32.29); H, 3.91 (3.73). Here the figures in parentheses show the theoretical values for the composition of $[Cr_3O(OCOCH=CH_2)_6]OH \cdot 3\ H_2O$.

The XPE spectra were recorded on a VIEE device with a magnesium anode ($h\nu$ = 1253.6 eV). The resolution of the device determined as the half-amplitude width of the $Au4f_{7/2}$ peak of metal gold was 1.60 eV throughout the range of experimental measurements. The pressure in the chamber of the spectrometer did not exceed $2 \cdot 10^{-6}$ Torr. The spectra were calibrated by the C1s peak (285.0 eV) of the vapor of oil that adsorbed onto the sample surface within the chamber of the spectrometer. The procedure for preparation of the samples for XPS was reported previously[1,2].

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The electron spectra were recorded with a Specord M-40 spectrophotometer. The samples were prepared in the form of a thin layer of a mixture of the substance studied with Vaseline oil spread between two quartz plates. The absorption IR spectra were recorded on a Specord 75-IR spectrophotometer on samples prepared either in the form of pellets with KBr or as Vaseline emulsions.

The mass-spectrometric studies of acrylates were performed on a time-of-flight mass-reflectron type mass spectrometer that has been described previously[4,5]. The dissolved ions were extracted at atmospheric pressure. A water—alcohol or acetonitrile solution of the substance studied was supplied to the ion source *via* a metal capillary with an inner diameter of 0.1 mm at a feed rate of 2 μL min^{-1}. Upon application of 2 kV potential, fine atomization of the solution occurred. The final stage of this atomization was the field evaporation of the ions contained in the liquid; a fraction of these ions was directed to the mass analyzer *via* a vacuum interface with differential evacuation.

The magnetic susceptibility was measured using the Faraday method.

Results and Discussion

Our previous studies showed that the synthesis of metal-containing monomers based on acrylates of certain transition metals is accompanied by an increase in the nuclearity of the complexes. For example, in the case of Cu^{II} acrylate, according to X-ray diffraction[3], the formation of the $[Cu_2(OCOCH{=}CH_2)_4 \cdot C_2H_5OH]C_2H_5OH$ binuclear complex with a Cu—Cu distance of 2.609 Å occurs. This increased nuclearity of complexes can result in the formation of clusters where one of the ligands is a group incorporating a double bond.

Trinuclear μ_3-oxocomplexes of transition metals where the $[M_3O(OCOCR)_6]^+$ complex is the basic structural unit (R = H, CH_3, C_6H_5, *etc.*) are well known[6—8]. In all of the compounds of this class whose structure has been studied, the oxygen atom is located in the same plane as the three metal atoms surrounding it, forming a virtually rectilineal triangle, and the carboxy groups form bridges between the metal atoms. In the literature, however, there is no data concerning the structure of multinuclear transition metal complexes with unsaturated carboxylates as ligands. To our knowledge, we are the first to report the synthesis and structure of trinuclear Fe^{III} acrylate.

Since spectral methods of analysis do not provide unambiguous information on the multinuclear structure of complexes, the cluster-type structure of the complexes of metal-containing monomers had to be obtained by X-ray diffraction, as was performed for acetate complexes of Cr^{III} (Refs. 6, 8). Unfortunately, all attempts to produce monocrystals of iron and chromium acrylates failed. Mass-spectrometric analysis on a time-of-flight spectrometer with ions extracted from the solvent might also provide direct evidence on the structure and composition of these compounds. Figure 1, *a* presents the mass spectrum of positive ions isolated from a water—alcohol solution of the compound studied. The insertion (Fig. 1, *b*) presents a part of this mass spectrum with higher resolution in mass. The main peak in the mass spectrum (m/z = 598) coincides with the theoretical peak for the $[Cr_3OAcr_6]^+$ cation. The presence of additional peaks corresponding to m/z = 596, 599, 600, and 601 is due to isotopic substitution of chromium, carbon, and oxygen.

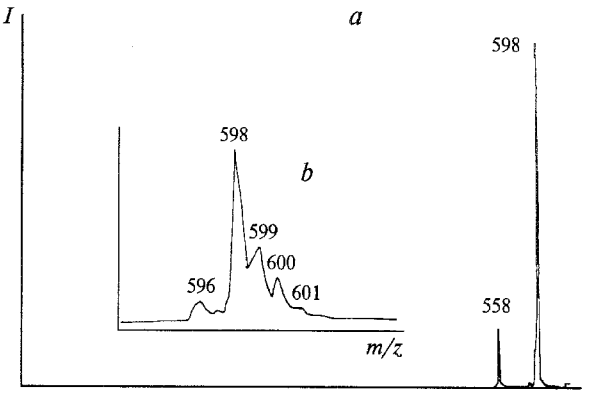


Fig. 1. (*a*) The mass-spectrum of positive ions extracted from a water—alcohol solution of the chromium(III) cluster acrylate recorded at U = 200 V; (*b*) the expanded spectrum near the mass of the $[Cr_3O(OCOCH{=}CH_2)_6]^+$ molecular ion.

Increasing the voltage at the first stage of differential evacuation, when the gas pressure is 5 Torr, makes possible a the controlled fragmentation of ions by their dissociation upon impact. The mass spectrum presented in Fig. 1, *a* was recorded at U = 200 V, when the cluster bonds are still intact. In order to obtain structural information, the voltage was increased to U = 370 V. The corresponding mass spectra are presented in Fig. 1, *b*. Some ions in the spectra are easy to identify, if one invokes the presumed structure of the compound studied. The ions having m/z = 527 and 456 (see Fig. 2, *a*) apparently correspond to elimination of one or two acrylate residues, and the ion with m/z = 404 corresponds to elimination of a $CrAcr_2$ molecule from the $[Cr_3OAcr_6]^+$ molecular ion. This agrees well with the data of magnetochemistry; the value of 3.48 mB for the apparent magnetic susceptibility μ_e per one chromium atom at room temperature is lower than the spin value (3.87 mB, for Cr^{III}); at 80 K this susceptibility is 2.84 mB. This attests to antiferromagnetic type exchange interactions occurring between the paramagnetic centers of the μ_3-complex studied.

Comparative study of the dissociative fragmentation of $[M_3OAcr_6]^+$ ions with different metals is a matter of special interest. For this purpose one should obtain solutions of these ions with the same concentration in the same solvent. It turned out that water—alcohol solvents are inconvenient for this purpose, because chromium acrylate dissolves well only in methanol, whereas iron acrylate dissolves in ethanol. Solutions with equal concentrations were obtained in acetonitrile.

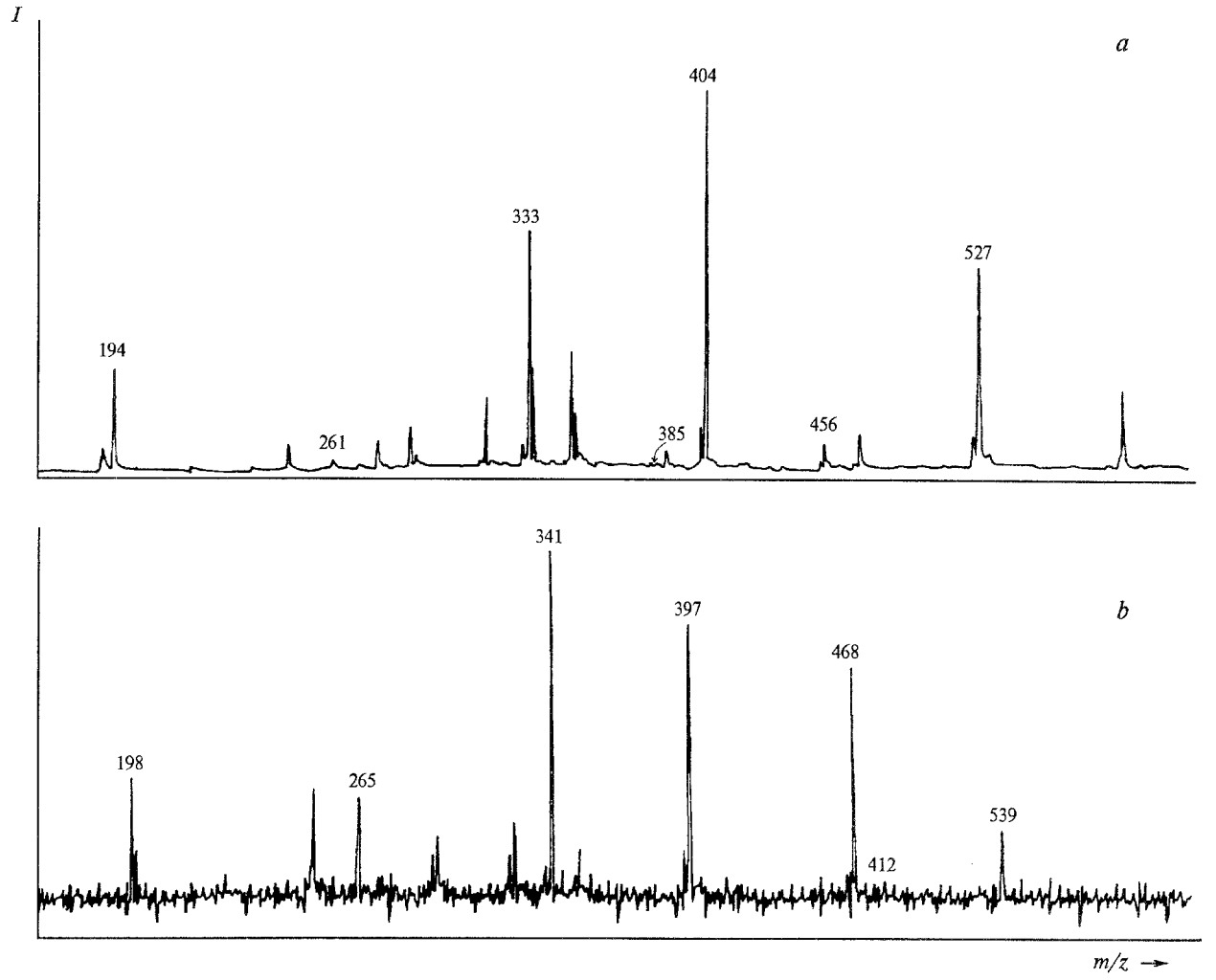


Fig. 2. The mass-spectra of positive ions extracted from solutions in acetonitrile of cluster acrylate of (*a*) iron and (*b*) chromium; the spectra are recorded at U = 370 V.

The mass spectra of positively charged fragments of $[M_3OAcr_6]^+$ ions (M = Cr or Fe) measured under identical conditions are presented in Fig. 2. The results of analysis of the positions of the most intense peaks in the mass spectra are shown in Table 1. One can see that the cluster ions of iron and chromium acrylates decompose in different ways. For iron acrylate, the typical reaction is elimination of three acrylic groups, whereas for chromium acrylate no fragment that would indicate the occurence of this reaction was observed. Isolation of

Table 1. The data of mass-spectroscopy for dissociative fragmentation of $[M_3OAcr_6]^+$ ions in the gas phase; U = 370 V

Dissociation path	M = Fe		M = Cr	
	Ion mass /amu	Intensity (%)	Ion mass /amu	Intensity (%)
$[M_3O(AAcr)_5]^+ + AAcr$	539	5	527	20
$[M_3O(AAcr)_4]^+ + 2\ AAcr$	468	14	456	1
$[M_3O(AAcr)_3]^+ + 3\ AAcr$	397	17	385	0
$[M_2O(AAcr)_4]^+ + M(AAcr)_2$	412	0	404	17
$[M_2O(AAcr)_3]^+ + M(AAcr)_3$	341	17	333	10
$[M(AAcr)_3]^+ + [M_2O(AAcr)_3]$	265	6	261	0
$[M(AAcr)_2]^+ + [M_2O(AAcr)_4]$	198	6	194	3

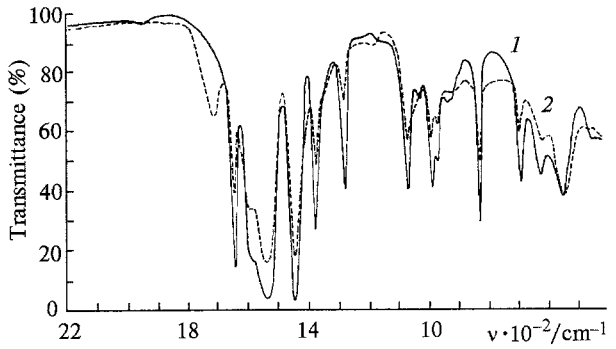
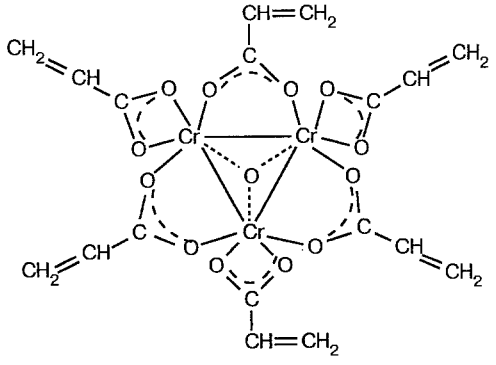


Fig. 3. IR absorption spectra of (*1*) $[Cr_3O(OCOCH{=}CH_2)_6]OH$ and (*2*) its polymer.

a non-charged $MAcr_2$ molecule from the $[M_3OAcr_6]^+$ molecular ion is a typical reaction for chromium acrylate, whereas it does not occur in the case of iron acrylate.

The fact that at U = 370 V the peak corresponding to the $[Fe_3OAcr_6]^+$ molecular ion was not observed attests to the fact that, other conditions being similar, iron acrylate is less stable with respect to thermal fragmentation in gas than chromium acrylate of the same structure.

In the IR spectrum of the chromium acrylate cluster (Fig. 3), as in that of iron acrylate[1], one can distinguish the absorption bands of the asymmetrical and symmetrical valent vibrations of the carboxy group (ν^a(COO) and ν^s(COO)) at 1575 and 1370 cm^{-1}, respectively. According to the literature[9], these frequencies correspond to the bridge coordination of carboxyl. Apart from this, one can see deep absorption bands at 1525 and 1440 cm^{-1}. We identified these bands as the ν^a(COO) and ν^s(COO) vibrations of the carboxy group with bidentate coordination, but with one metal atom[9]. Of the other absorption bands, note the 1635 cm^{-1} ν(C=C) vibration (Ref. 10), ν(C—C) at 1065 cm^{-1}, and the weak band of ν^e(Cr—O) at 540 cm^{-1}.[9] Taking into account the approximately equal intensities of the absorption bands corresponding to the two types of carboxyl coordination, the structure of the chromium acrylate complex can be drawn as follows:



Let us consider now the main features that distinguish the cluster monomer from its polymer. A comparison of the IR spectra (Fig. 3) shows that as a result of polymerization, the number of C=C bonds decreases (intensity of the 1635 cm^{-1} band decreases). Polymerization also results in the appearance of a new absorption band at ~ 1700 cm^{-1}. Apparently, this indicates that there are acrylic groups with monodentate coordination in the polymer. The monodentate groups apparently form due to cleavage of the bridge bonds. The convergence of the frequencies corresponding to the bridge and non-bridge bidentate carboxy groups, which was observed in the polymerization of cluster iron acrylate[1], was not observed for chromium acrylate. The polymer of chromium acrylate also has an adsorption band at 1040 cm^{-1} that apparently is related to vibrations of the —C—C—C— fragment in the polymer chain.

The XPE C1s spectra of both the polymer and the monomer have at least two peaks. The peak at 285.0 eV is due to carbon atoms that neighbor either another carbon or a hydrogen atom, and the peak at 288.5 eV corresponds to the carbons of the carboxy groups.

The half-width of the main peak in the C1s spectrum is 2.9 eV for the monomer and 3.1 eV for polymer. Apparently, the increase in the peak width is related to a change in the effective charge on carbon atoms that occurs in the course of polymerization and/or to changes in the energetics of the relaxation processes pertaining to photoionization of the C1s level. The position of the $Cr2p_{3/2}$ peak (577.6 eV) in the XPE spectrum, unlike

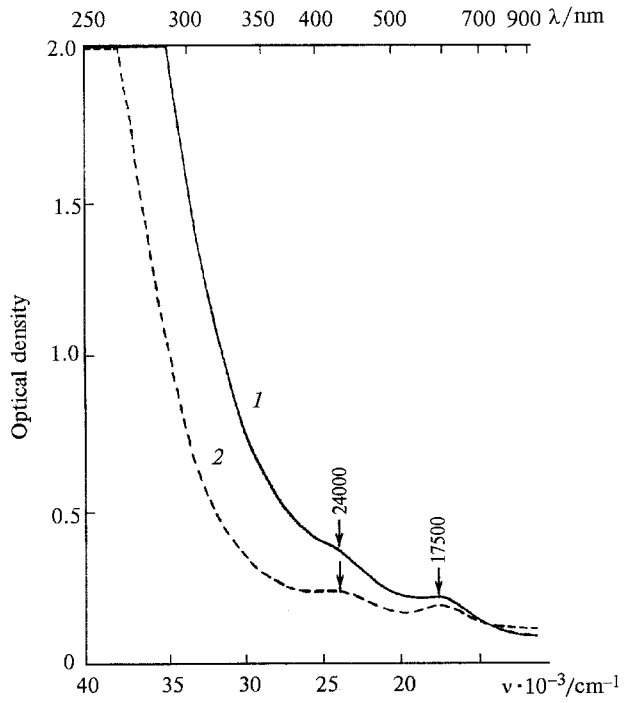


Fig. 4. The electron absorption spectra of (*1*) cluster chromium(III) acrylate and (*2*) its polymer.

that of copper acrylate[2], is virtually the same for the monomer and the polymer. The half-width of the $Cr2p_{3/2}$ peak increases from 3.7 to 4.0 eV, due to polymerization. Nevertheless, we observed no additional peaks that would indicate the appearance of reduced forms of chromium in the polymeric samples.

The electron absorption spectra of the monomer and polymer are compared in Fig. 4. 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 the electron shell of Cr^{3+}. Both these bands are also observable in the spectrum of the polymer, with a somewhat different ratio of the intensities. One might expect that in the course of polymerization the close environment of the Cr^{3+} ions would remain unchanged. In that respect chromium polyacrylate differs from the iron polyacrylate that was studied previously[1].

Thus, in the reaction of fresh chromium hydroxide with acrylic acid we produced the $[Cr_3O(OCOCH{=}CH_2)_6]OH$ monomer in which acrylate residues are bonded to metal ions *via* carboxy groups. Comparative studies of the dissociative fragmentation of $[M_3OAcr_6]^+$ clusters showed that $[M_3OAcr_3]^+$ is the predominant decomposition product of the $[M_3OAcr_6]^+$ cluster cation in the case of Fe acrylate and is not formed in the case of Cr. $[M_2OAcr_4]^+$ fragments form in the case of Cr, but do not form in the case of Fe. Radical polymerization of the chromium acrylate monomer results in the formation of carboxy groups with monodentate coordination, which is not observed in the initial monomer.

References

1. Yu. M. Shul'ga, O. S. Roshchupkina, G. I. Dzhardimalieva, I. V. Chernushevich, A. F. Dodonov, Yu. V. Baldokhin, P. Ya. Kolotyrkin, A. S. Rozenberg, and A. D. Pomogailo, *Izv. Akad. Nauk, Ser. Khim.,* 1993, 1739 [*Russ. Chem. Bull.*, 1993, **42**, 1661 (Engl. Transl.)].
2. Yu. M. Shul'ga, O. S. Roshchupkina, G. I. Dzhardimalieva, and A. D. Pomogailo, *Izv. Akad. Nauk, Ser. Khim.,* 1993, 1565 [*Russ. Chem. Bull.*, 1993, **42**, 1498 (Engl. Transl.)].
3. G. I. Dzhardimalieva, A. D. Pomogailo, V. I. Ponomarev, L. O. Atovmyan, Yu. M. Shul'ga, and A. G. Starikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1525 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1346 (Engl. Transl.)].
4. USSR Inventor's Certificate No. 1681340, *Byul. Izobr,* 1991, No. 36 (in Russian).
5. I. V. Chernushevich, Ph. D. Phys. Thesis, Chernogolovka, 1991 (in Russian).
6. B. N. Figgis and G. B. Robertson, *Nature*, 1965, **205**, 649.
7. G. J. Long, W. T. Robinson, W. P. Tappmeyer, and D. L. Bridges, *J. Chem. Soc., Dalton Trans.*, 1973, 573.
8. S. C. Chang and G. A. Jeffrey, *Acta Crystallogr.*, 1970, **26B**, 673.
9. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* Wiley and Sons, New York, 1962.
10. K. Nakanishi, *Infrared Absorption Spectroscopy: Practical,* Holden—Day, San Francisco, 1962.

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