

The Emission Spectrum of OsCl_6^{2-} Doped in Various Cubic Host Lattices

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The incorporation of OsCl_6^{2-} ions as impurity into several cubic host crystals of A_2MCl_6 type by simultaneous precipitation from solutions has been investigated. Due to varying solubilities, only for a few compounds could sufficient quantities of the chromophore be doped into the host lattices to obtain well-resolved emission spectra. For this purpose the rate of cooling during precipitation has been found to be of importance. The host lattice effects on the emission spectra become particularly apparent in the zero-phonon transition energies and stretching frequencies involved in the vibronic transitions. The experimental results are explained by ligand field theory and by simple vibrational models.

Introduction

Lattice effects on the luminescence spectrum of ReCl_6^{2-} impurities in a variety of cubic lattices with antiferite-type (Fm3m) structure have been investigated earlier [1]. In all cases the $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ emission spectrum of powder materials at low temperature was sufficiently well resolved to analyze the vibrational fine structure resulting from internal vibrations of the complex molecule. Since corresponding systems doped with osmium(IV) have equally well-resolved narrow line emission spectra [2–6], it would also be worthwhile to investigate OsCl_6^{2-} impurity spectra in these lattice environments. Pursuing this project is however more difficult, mainly for the reason that preparation of doped powder materials suitable for good spectra cannot be obtained so easily as for rhenium. Also, due to the various low energy levels in octahedral d^4 complexes, split by spin-orbit coupling, many more electronic transitions are possible which make spectra from infrared to ultraviolet rather complicated. Nevertheless, the interest in the electronic and vibrational structure of octahedral osmium(IV) has greatly increased lately, as can be seen by the numerous investigations of this problem using such physical methods as optical absorption, Raman and

magnetic circular dichroism [7–11]. Several questions regarding the d–d energy level scheme are still open for discussion, and some problems concerning band assignments remain unsolved.

The present paper emphasizes the effort required to obtain appropriately doped materials from solutions by varying the conditions for precipitation. The emission spectra are also optimized by using different excitation wavelengths, in order to avoid emission from host crystals. The vibrational fine structure of the electronic transitions allows lattice effects on the vibronic transitions to be investigated in different host crystals.

Experimental

Compounds

The inserted K_2OsCl_6 was a product of Ferak, Berlin, and was recrystallized repeatedly from 4 *N* HCl. Starting materials for the host lattices were synthesized by literature methods and were identified by ultraviolet spectroscopy [12–18]. The preparation of the doped materials followed the method for rhenium given by Dorain and Wheeler [19]. An HCl solution of the host compound, nearly saturated at 95 °C, was prepared and small amounts (0.01 to 5 Mol-%) of K_2OsCl_6 solutions added. The acid concentration was chosen to avoid hydrolysis, and in one case this required a concentration of 12 *M* HCl. The solutions were cooled over varying periods of time (see Discussion), using different cooling techniques. Table I compiles the concentrations used for preparing materials from solution appropriate for recording emission spectra. For some systems investigated, however, no emission was obtained, although the K_2OsCl_6 concentration was varied within limits as indicated. The amount of osmium complex impurity in the solid material was determined spectrophotometrically using the charge transfer absorption region of OsCl_6^{2-} . Due to absorption overlap with the host compound a reliable determination of small amounts of osmium could only be made for the compounds listed in Table II.

TABLE I. Quantities of Host and Guest (K_2OsCl_6) Compounds Dissolved in 10 ml HCl Solution at 95 °C to Obtain Doped Materials.

Host	HCl (Molarity)	Host Material (mg)	K_2OsCl_6 (mg)
Cs_2SeCl_6	-	12	150
Rb_2TeCl_6	-	8	350
Cs_2TeCl_6	+ ^a	8	25
Cs_2IrCl_6	-	8	12.5
Rb_2PtCl_6	+	4	28
Cs_2PtCl_6	+	1	14
Cs_2SnCl_6	+	4	75
Rb_2PbCl_6	-	6	250
Cs_2PbCl_6	-	1	75

^a(+) Material for which an emission spectrum is observed.

The emission spectra of crystalline powders were measured at 10 K using the apparatus described previously [20]. Excitation was provided by the intensive lines of a Spectra Physics model 165 argon ion laser. For longer wavelength excitation a dye laser, Spectra Physics model 375 (Rhodamine 6 G) was used, which allowed tuning in the region between 570 and 630 nm. The frequency was monitored by a Jarrel Ash monochromator, model 82 410 (slit width 0.05 mm).

The absorption spectra for analytical purposes were taken on a Beckman model 25 spectrophotometer.

Results and Discussion

Doped Materials

The preparation of materials containing osmium impurities using precipitation from solution is complicated by the unfavorable solubility relations: the osmium complex is much more soluble than all compounds used as host crystals (the solubility of K_2OsCl_6 in 5 M HCl at 100 °C is 32.8 g/l). Although the solubility of OsCl_6^{2-} chloride complexes decreases at higher HCl concentration, the insertion of osmium is still small, since the osmium concentration in solution must be kept low in order to avoid concentration discontinuities and osmium accumulations in the

TABLE III. Mol-% OsCl_6^{2-} Incorporated into Solid Cs_2PtCl_6 Obtained by Precipitation from a Solution (Relative Concentrations 0.8 Mol-%) Cooled from 95 °C to 0 °C over Different Periods of Time.

Cooling Time [min]	Doped OsCl_6^{2-} [Mol-%]
10	- ^a
60	3 ± 1
180	7 ± 1

^aBelow detection limit.

crystal. Thus the amount of osmium in solution must be a compromise between the small concentration needed to achieve homogeneity and the larger concentrations necessary, because of high solubility, to insert the requisite amounts in the crystal.

In addition, the data in Table I reveal that other effects must also be important in controlling the growth of an evenly distributed material with a sufficiently high impurity concentration. Since rhenium(IV) is easily doped into these host materials [1], although the solubility is almost equal to that of the osmium(IV) complex (29.9 g/l in 5 M HCl at 100 °C), the kinetic conditions must be more favorable for rhenium than for osmium.

It was found that when precipitating the material from solution, the rate of cooling from 95 °C to 0 °C was important for the incorporation of osmium. Table III shows for a platinum host that different amounts of osmium can be doped, depending on the rate of temperature decrease. Substantial improvement by varying the rate of cooling was obtained in particular for the $\text{Cs}_2[(\text{Pt}, \text{Os})\text{Cl}_6]$ system. For other host compounds only minor improvements (if any) were noted while searching for the most suitable materials for well-resolved spectra.

Emission Spectra

Failure to detect emission was primarily due to the low concentration of doped osmium in certain systems. An osmium content as low as 0.1 Mol-% (cf. Table II) was obviously not sufficient to obtain a spectrum, even though the sensitivity of the detection system used was relatively high. Apart from this, other reasons for the absence of an emission must be

TABLE II. Molar Relations of OsCl_6^{2-} in Powder Materials Obtained from Precipitation of Solutions Specified in Table I.

Hosts	Cs_2SeCl_6	Cs_2PtCl_6	Rb_2PtCl_6	Cs_2SnCl_6
Mol-% Os	~0.1	7 ± 1	1 ± 0.2	1 ± 0.2

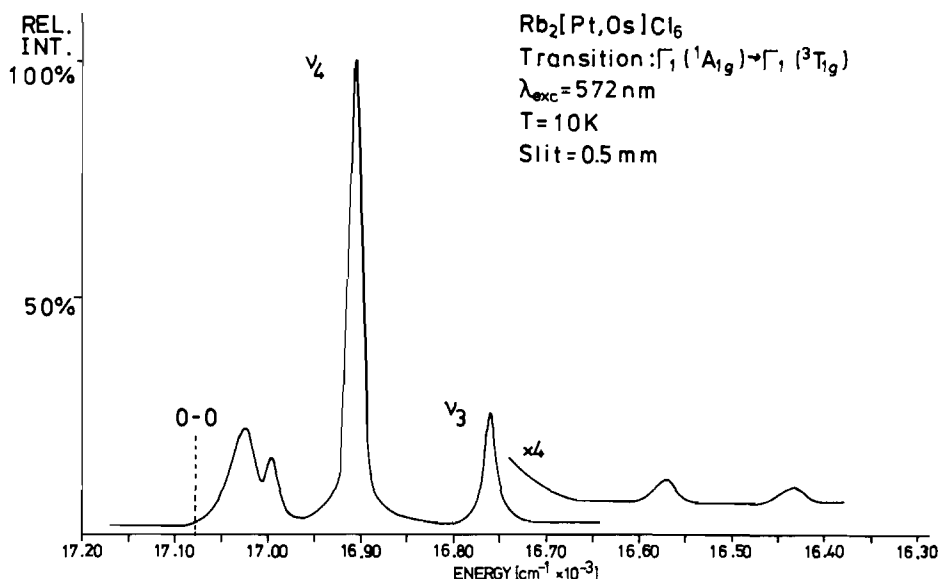


Fig. 1. Emission spectrum of OsCl_6^{2-} (1 ± 0.2 Mol-%) doped in Rb_2PtCl_6 in the $\Gamma_1(1A_{1g}) \rightarrow \Gamma_1(3T_{1g})$ transition region.

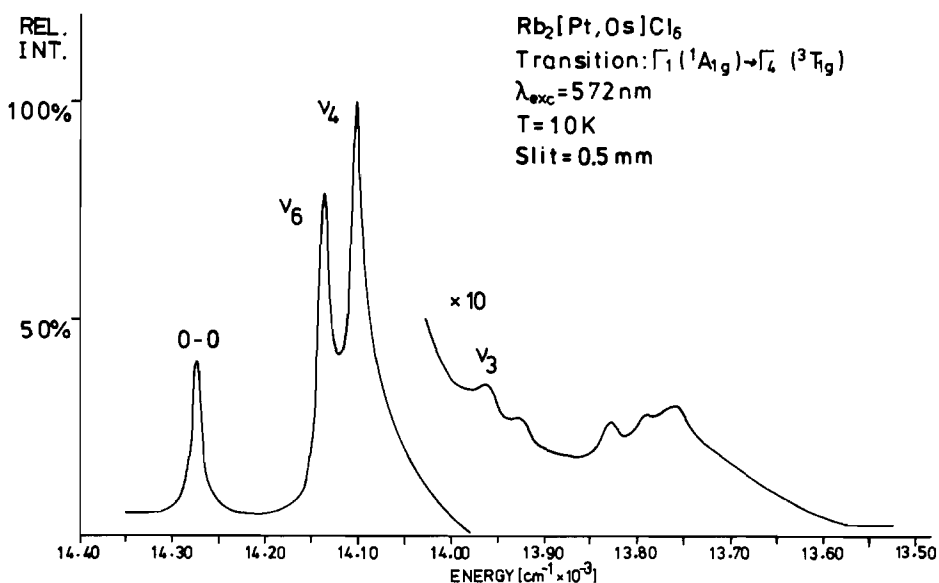


Fig. 2. Emission spectrum as in Fig. 1 belonging to the $\Gamma_1(1A_{1g}) \rightarrow \Gamma_4(3T_{1g})$ transition.

present. Quenching processes, due to energy transfer from the chromophore to the host lattice, are possible. For example in IrX_6^{2-} hosts, radiation-free transitions to low-lying electronic levels arising from spin-orbit splitting of the $2T_{2g}$ ground state will depopulate excited osmium states, from which emission can occur. Also the self-emission of host crystals, e.g. Cs_2TeCl_6 , Rb_2PtCl_6 , Cs_2PtCl_6 , when excited in the ultraviolet causes difficulties since it may overlap with the osmium spectrum. This can be avoided by choosing excitation wavelengths longer than the first absorption band of the host molecules,

which improves the relation of the guest to host luminescence intensity. Optimal excitation for obtaining narrow line osmium emission has been obtained for the Cs_2TeCl_6 host ($1A_{1g} \rightarrow 3T_{1u}$ absorption peak at 24500 cm^{-1}) [21] by the 454.5 nm line of an argon ion laser, and for the platinum hosts ($1A_{1g} \rightarrow 3T_{1g}$ absorption peak at 22500 cm^{-1}) [22] by 572 nm excitation line with a dye laser. In the case of the hexachlorostannate host an excitation wavelength of 363.8 nm (argon ion laser) was used.

In Figs. 1–3 the 10 K spectra of the system $\text{Rb}_2[(\text{Pt}, \text{Os})\text{Cl}_6]$, recorded in three spectral regions,

TABLE IV. Vibrational Intervals (cm^{-1}) of the $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_5(^3T_{1g})$ Transition in OsCl_6^{2-} in Various Host Crystals.

$\text{Rb}_2\text{SnCl}_6^a$ 12 322	Cs_2SnCl_6 12 174	Cs_2TeCl_6 12 142	Rb_2PtCl_6 12 170	Cs_2PtCl_6 12 068	Host Zero Phonon Line ^b
35	33	36		35	lattice (w)
52	47			52	
	59	56	56	65	
70	71	71	83	73	
136m	142s ^c	140m	139m 154 w	143m	ν_6 $\nu_4(\text{LO})$
170s	174s	173s	172s	176s	$\nu_4(\text{TO})$
314m	310m	318m	319m	313m	ν_3
331w	338w	333w	334w	341w	$\nu_4 + \nu_5$
480w			489w	490w	$\nu_6 + \nu_1, \nu_3 + \nu_5$
510w	507w	509w	516w	510w	$\nu_4 + \nu_1$

^aFrom ref. [23]. ^bExtrapolated as described in the text. ^cRelative intensities: s strong, m medium, w weak.

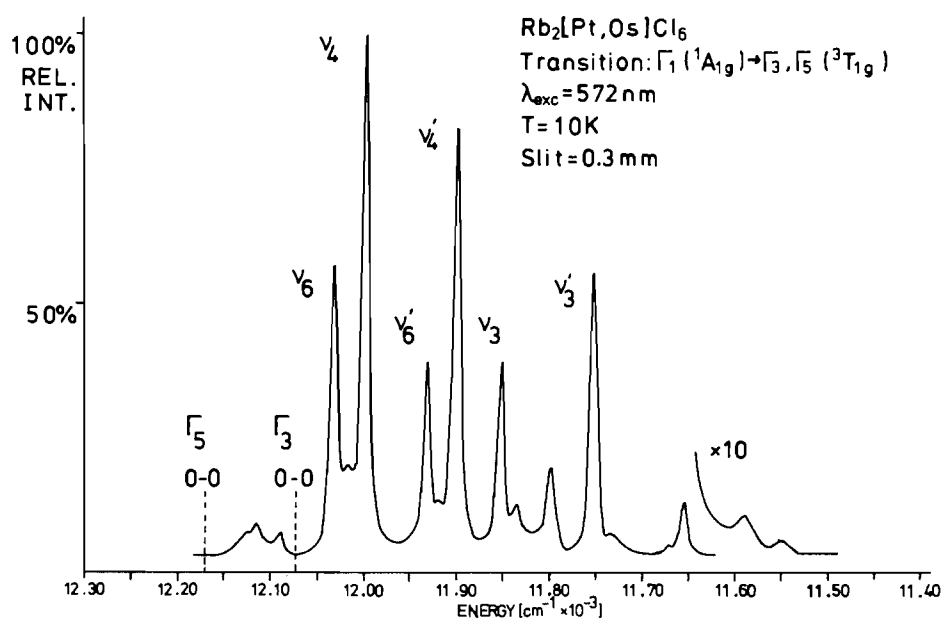


Fig. 3. Emission spectrum as in Fig. 1 in the region of three d-d transitions.

are shown. Some of the assignments indicated are still being discussed in the literature and are only tentative [6, 11, 23]; e.g., the $\Gamma_3(^1E_g) \rightarrow \Gamma_1(^3T_{1g})$ spectrum (cf. Fig. 3), as assigned by Flint *et al.* [6], should according to Keiderling *et al.* [11] be due instead to a Jahn-Teller active mode combined with the three odd vibrations inducing the electronic transition by vibronic coupling. Also the sequence of the spin-orbit levels Γ_3 and Γ_5 (resulting from $^3T_{1g}$) which are closely similar in energy does not seem to be certain. Intensity relations of band splitting observed in low-symmetry environments would suggest a reversed order for these levels [23].

The spectra show vibrational structures of different abundances. In Table IV the vibrational intervals for the $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_5(^3T_{1g})$ transition of osmium in different host lattices are listed. The zero phonon transitions were not detected. They were extrapolated using mean values of frequencies ν_3 , ν_4 and ν_6 obtained from the $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_4(^3T_{1g})$ transition (cf. Fig. 2). The most intense bands are satellite absorptions due to ν_3 , $\nu_4(t_{1u})$ and $\nu_6(t_{2u})$ vibrations which induce the parity-forbidden electronic transition through vibrational coupling. The relative intensities of these vibronic fundamentals are, however, different for each of the electronic transitions. Only

TABLE V. Zero Phonon Lines (cm^{-1}) of OsCl_6^{2-} Observed for $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_1(^3T_{1g})$ Transitions and Totally Symmetric Vibrational Modes in Various Host Lattices.

Host		Γ_1	Γ_4	Γ_5	Γ_3	$\bar{\nu}_1 (a_{1g})$	Lattice Constant ^b [Å]
Cs_2ZrCl_6	[5]	17 077	14 293	12 185	12 086		10.407
Cs_2HfCl_6	[2]	17 088					—
K_2SnCl_6	[23] ^a	17 230	{ 14 503 14 533	{ 12 362 12 380	{ 12 261 12 273	351	10.002
Rb_2SnCl_6	[23]	17 245	14 432	12 322	12 227	343	10.118
Cs_2SnCl_6		17 053	14 271	12 174	12 076	335	10.381
Cs_2TeCl_6		17 020	14 239	12 142	12 044	335	10.447
K_2PtCl_6	[4]	17 091	14 282	12 176	12 078	353	9.775
Rb_2PtCl_6		17 079	14 273	12 170	12 069	342	9.90
Cs_2PtCl_6		16 938	14 158	12 068	11 967	337	10.215

^aLevel splittings are due to phase transition to lower symmetry. ^bSee ref. [24].

the transitions from Γ_1 to Γ_3 and Γ_5 show all three transitions strongly. For the transition into Γ_1 no ν_6 frequency can be detected, as expected from vibronic selection rules. Why the ν_3 frequency is rather weak in the $\Gamma_1 \rightarrow \Gamma_4$ spectrum with an intensity comparable to combination bands, cannot be explained by symmetry arguments. Since this is found for all host lattices investigated, the result must be due to transition probabilities which are governed primarily by intramolecular properties not much influenced by the host molecules of the outer sphere.

Apart from the vibrational fundamentals, some weaker bands were observed due to combinations of odd vibrations with ν_1 and ν_5 vibrational modes, which is to be expected from a small, totally symmetric expansion of the molecular complex in the excited state compared to the ground state, and from Jahn-Teller distortions in the degenerate states. The resolution of spectra from single crystals is, however, significantly greater [5, 6], which would allow a more definite assignment of combinations than is possible on the basis of the present results. In addition, lattice modes were detected close to the electronic origins. The only zero phonon transition which was observed in all host lattices is due to the magnetic dipole allowed $\Gamma_1 \rightarrow \Gamma_4$ transition; all others are forbidden and were calculated using the odd vibronic fundamentals taking a mean value from the peaks of the strongest absorptions.

Host Lattice Interactions

Zero Phonon Transitions

The largest effect on the OsCl_6^{2-} emission spectrum due to interaction with the lattice is observ-

ed for the zero phonon transitions. In Table V these frequencies are listed for all host lattices being investigated. Obviously all spectra due to transition from Γ_1 to any of the $\Gamma_1(^3T_{1g})$ levels change in a similar fashion. Host lattices with larger cations move the zero-zero transitions to lower frequencies. As in corresponding rhenium(IV) compounds [1], the positions of the zero phonon bands are (except for the Pt-hosts) primarily determined by the cation, with less dependence on the host central metal. For example, all cesium host lattices show closely similar zero phonon lines, which are different from rubidium or potassium compounds.

The shifts of the pure electronic transitions of OsCl_6^{2-} can be rationalized from ligand field theory. If it is assumed that lattice effects on the spin-orbit coupling are small (which is supported by the observed similar shifts of spin-orbit split levels), the ligand field and electronic repulsion part of this transition is given approximately by [22]

$$\Delta E = E(^1A_{1g}) - E(^3T_{1g}) = 15B + 5C - \frac{372B^2}{Dq} \quad (1)$$

The variation of electronic repulsion (Rachah-) parameters from one host lattice to another is difficult to predict. A decrease of zero phonon frequencies ΔE would indicate a higher nephelauxetic (covalent bonding) effect in the OsCl_6^{2-} octahedron. Since covalent bonding effects are, however, short range interactions, they should be less influenced by outer sphere ions. Therefore (coulombic) crystal field effects become dominant for long range interactions which, therefore, would primarily influence the transition energy ΔE of eqn. (1) through the parameter Dq . The net cubic ligand field parameter due

to the (negative) potentials arising from the octahedrally coordinated chloride ligands and the (positive) alkali ions arranged as a cube in the second sphere is

$$Dq = Dq_{\text{oct}}^{\text{Cl}^-} - Dq_{\text{cube}}^{\text{A}^+}$$

with

$$Dq_{\text{cube}}^{\text{A}^+} = -\frac{8}{9} Dq_{\text{oct}}^{\text{A}^+} \quad (2)$$

Since the ligand field parameter Dq increases with effective charge on the ions surrounding the chromophore, and decreases with the interatomic distances, the experimental findings are well explained by the variation of Dq : for decreasing (positive) effective nuclear charge in the series K^+ , Rb^+ , Cs^+ , and at the same time increasing cation-anion distances (comparing lattice constants of host crystals), the parameter Dq and, by eqn. (1), the transition energy ΔE , both shift to lower energy. This is reflected by the data of Table V. The variation of zero phonon energies with the complex anions of the host, which except for the platinum compounds is very small, cannot be explained so easily. The sequence of electronegativities of host central ions and internuclear distances follow different orders, which cannot be put into a relation with the zero phonon energy shifts. The platinum hosts do not fit into this category, presumably because d-orbital levels intermix into the valence or conduction energy bands of the crystals, shifting the transitions by some 100 cm^{-1} to lower energy. These results have also been obtained for corresponding rhenium(IV) systems [1].

Vibrational Intervals

The vibrational intervals for each of the vibronic transitions do not vary very much in different host crystals. Nevertheless, distinct dependences can be detected for the $\Gamma_1 \rightarrow \Gamma_5$ transition (cf. Table IV), with corresponding frequency shifts in the other spectra. In each case the frequencies belonging to angular vibrations (e.g. ν_6 , and at the most part, ν_4) increase for crystals with larger lattice constants, while frequencies belonging to stretching modes (ν_3 , and even more, ν_1) decrease with increasing lattice parameters. Apparently, the potential energy curves of the OsCl_6^{2-} framework are either squeezed or flattened depending on how much space the lattice is able to supply when incorporating an impurity anion into the host crystal. The largest effect demonstrating the repulsive forces on potential curves of the molecules should be expected for the totally symmetric mode which performs a breathing vibration of the complex molecule. Since the $\nu_1(\text{a}_{1g})$ vibration cannot be detected directly, it must be extrapolated from the progressions superimposed on the false origins, which have their peak maxima

at $\nu_{\text{O-O}} + \nu_u + n\nu_1$. A mean value for ν_1 is calculated from the combinations with the three false origins belonging to ν_3 , ν_4 and ν_6 (as far as they can be detected).

$$\bar{\nu}_1 = \frac{1}{3} \sum_i [\nu_{\text{comb}}(\nu_1 + \nu_{\text{ui}}) - \nu_{\text{ui}}] \quad i = 3, 4, 6 \quad (3)$$

If these $\bar{\nu}_1$ are calculated for each of the four electronic transitions $\Gamma_1 \rightarrow \Gamma_i$, another mean value $\bar{\nu}_1$ can be calculated, which is presented in Table V. The data show a distinct decrease in frequency for host crystals with larger cubic lattice constants. This result holds particularly well for homologous compounds but host crystals in different parts of the periodic table (e.g. Sn, Te) also follow this rule quite well. In platinum hosts, deviations due to a_{1g} -resonance vibrations are expected, since guest and host molecules have equal fundamental frequencies [25].

For a closer analysis of lattice effects more data from other host crystals are necessary. A discussion should also take into account thermal changes of lattice constants, and possible electronic effects connected with them. These and other implications have not been considered here.

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