Excited-State Properties of a Diplatinum(II) Complex under High Pressure[1]

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Abstract: The pressure effects on the relaxation process of excited $K_4[Pt_2(H_2P_2O_5)_4]\cdot 2H_2O$ (Pt_2) crystal have been studied at room temperature. The emission properties such as maximum energy and peak intensity are discussed on the basis of X-ray diffraction study and infrared spectroscopy. Lower energy shifts of the emission energy were observed (−170 and −190 cm^{-1}/GPa for fluorescence and phosphorescence, respectively), which was interpreted as due to reduction of the intramolecular Pt–Pt distance. The pressure-induced excimer fluorescence appearing at the lower energy side of the normal fluorescence also exhibited a lower energy shift with increasing pressure (−1000 cm^{-1}/GPa). This phenomenon was observed only for well-grown Pt_2 crystals.

Photophysical studies of the relaxation processes of excited metal complexes are of current interest. Recent advancement in time-resolved emission spectroscopy has provided us with fertile information of molecular environmental effects on both the excited molecule itself[2] and the relaxation dynamics.[3] In solution, the surrounding solvent relaxation from the Franck–Condon excited state immediately after excitation to the solvent-equilibrated excited state plays an important role for determining the emission energy and lifetime, which is a function of solvent viscosity.[4] Although the solvent properties can be tuned by appropriate choice of solvent, temperature, and/or pressure, the pressure variation seems to be the best method to tune the viscosity without altering much of the rest of the solvent properties. In a previous paper we showed that temperature- and pressure-controlled experiments provided complementary results on the solvent-assisted relaxation dynamics of Ru(II) complexes.[4]

In solid state, on the other hand, the reorganization of molecular environment is unlikely since the motion of the surrounding molecules is prevented. Therefore, both *intramolecular factors* (overlaps of atomic orbitals, distortion of bond angles, change in interatomic distance, and so forth) and *intermolecular factors* (morphology, crystal structure, intermolecular distance and orientation, and so forth) are major parameters to decide the excited properties. High-pressure studies at the gigapascal level is a promising approach to bringing about a perturbation on the solid structure and therefore on the spectroscopic properties. This approach proposed by Drickamer[5] as *pressure tuning spectroscopy* expanded its usefulness when the method was elaborated as pressure- and temperature-controlled time-resolved emission spectroscopy.[6] High-pressure study is more useful in the solid state than in solution since the tuning of the solid structure by an external factor is possible only by applying pressure.

In choosing a sample for high-pressure measurement, it is preferable to identify the particular site susceptible to pressure. A group of candidates are face-to-face square-planar binuclear complexes containing a metal–metal interaction. Such intermetal interaction is weak and expected to be affected by applying pressure. The d_{z^2} orbitals of mutually facing metal ions will be most strongly affected. Pressure effects on absorption and raman spectra of $Re_2Cl_8^{2-}$ were recently studied in the solid state, and the results were interpreted as due to reduced spacing between facing $ReCl_4^-$ units.[7,8] However, the pressure dependence of the electronic spectrum of $[Rh(CNPh)_4]_2^{2+}$ (CNPh = phenyl isocyanide) was attributed to the fully staggered conformer rather than the reduction of the metal–metal distance. Thus, the pressure effects on the square-planar binuclear complexes have not been understood well.

In this report, the pressure effects on both the emission properties and the structure of $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ (Pt_2) crystal are presented. Pt_2 is an excellent material for emission spectroscopy since it exhibits both strong phosphorescence with a long lifetime and fluorescence with a much shorter lifetime.[9] Recently, Fetterolf et al.[10] reported the pressure effect on the absorption spectrum of Pt_2 solution, which was interpreted by changes in the solvent properties. In the solid, on the other hand, the pressure effect should be attributed exclusively to the changes in both intra- and intermolecular structure as described above. While this article was being prepared, Stroud et al.[11] reported the pressure dependence of absorption spectrum on $(n\text{-}Bu_4N)_4[Pt_2(P_2O_5H_2)_4]$ and attributed the nonlinear dependence of the pressure-induced shift of electronic transitions to a strong coupling between d_{z^2} and p_z orbitals, and a nonlinear compression of the intra Pt–Pt distance. Since emission properties are much more sensitive to the molecular environment than is the absorption spectrum, emission spectroscopy under high pressure will provide more versatile information including pressure modulation of both inter- and intramolecular interactions in the excited state.

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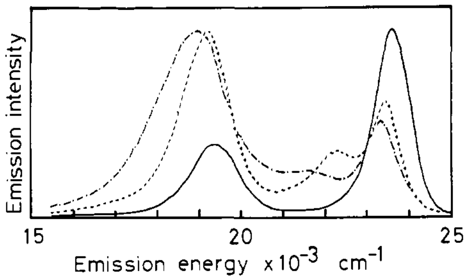

Figure 1. Emission spectra of Pt_2 crystal as a function of pressure at 1 atm (—), 1.1 GPa (---), and 2.0 GPa (-·-). Intensities are normalized to the highest intensity.

Experimental Section

Materials.[12-14] K_2PtCl_4 (Kanto Chemical Co., Ltd.) and H_3PO_3 were refluxed in water for 3 h. After reprecipitation from the aqueous solution by adding methanol, pale yellow and fluorescent microcrystals of Pt_2 were obtained as the potassium salt, which was stored in a vacuum cell. Elemental analysis (calculated value as $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2CH_3OH$): C, 2.14% (2.02%); H, 1.49% (1.34%).

The microcrystals were placed in one arm of a Y-shaped Pyrex glass cell, another arm of the cell being filled with enough purified water to dissolve the sample. The cell was sealed under vacuum after degassing by repeated freeze–pump–thaw cycles. After the sample solution was made up by mixing in the sealed cell, the well-grown Pt_2 crystals were obtained by slow evaporation over a period of several days. This crystallization process was repeated more than three times to remove completely the remaining methanol. Elemental analysis confirmed the absence of organic carbons. Since the crystals are also sensitive to oxygen and decompose by losing the crystal water, it must be stored in a cell under a saturated vapor pressure of water.

Measurements.[6] The crystals were finely powdered and set into a diamond anvil cell (DAC). Silicone oil was used as a pressure-transmitting medium.[15] The sample setting in the DAC was carried out quickly under aerated condition.

Emission properties were measured by the combination of a pulsed Nd:YAG laser (DCR-1, Quanta Ray) with a spectrometric multichannel analyzer (SMA, Tokyo Instrument Inc./Princeton Instrument Inc., gate width = 20 ns). The emission signal from the DAC set in a microscope was introduced via quartz fiber optics to the detector.

The X-ray diffraction under high pressure was measured by the Debye–Scherrer method at the Institute for Solid State Physics.[16] The Mo Kα radiation from a rotating anode type X-ray source (55 kV, 160 mA) was collimated to a thin beam (0.1-mm diameter), and the diffraction pattern was recorded on a film. Typical exposure time was 22 h.

Infrared spectroscopy was conducted with a FT-IR spectrometer (IR-3510, JEOL; resolution = 2 cm^{-1}) with a beam condenser (beam diameter = 3.2 mm).[6] The fine Pt_2 crystals suspended in degassed Nujol (pressure-transmitting medium) with a concentration of 4–5% (v/v) were set in a DAC. It required more than 10^4 accumulations to get one spectrum since the signals were extremely weak. Peak assignments at atmospheric pressure were taken from the literature.[17]

Results

Emission spectra of Pt_2 crystals at various pressure are shown in Figure 1. These pressure effects on the spectral shape were reversible and reproducible upon applying and releasing pressure. Both the maxima of fluorescence (ν_F) and phosphorescence (ν_P) from Pt_2 crystals shifted to lower energies almost linearly with increasing pressure (Figure 2). The amounts of shift were −170 and −190 cm^{-1}/GPa for ν_F and ν_P, respectively, which are comparable to those for Pt_2 microcrystals. The most striking feature

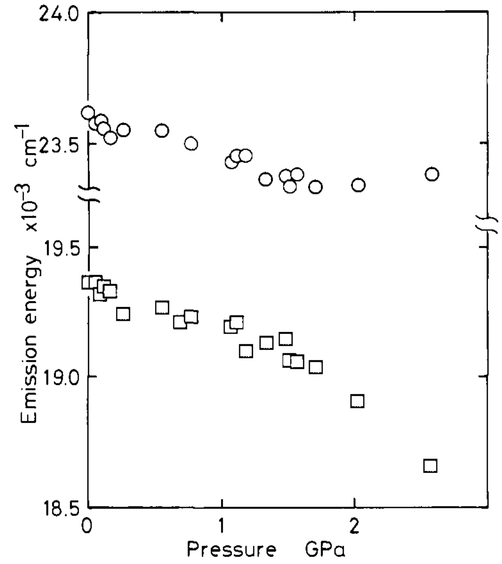

Figure 2. Maximum energies of fluorescence (○) and phosphorescence (□) of the Pt_2 crystals as a function of pressure.

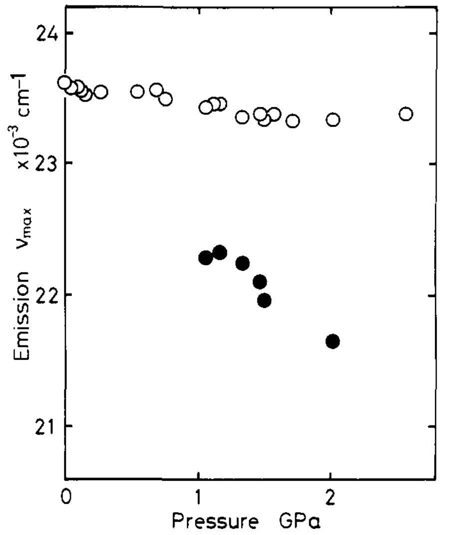

Figure 3. Maximum energies of fluorescence (○) and new emission (●) of the Pt_2 crystals as a function of pressure. Since it is difficult to separate the new emission from the fluorescence in lower pressure region, the ν_{Ex} at atmospheric pressure was estimated by extrapolation from the values in higher pressure region.

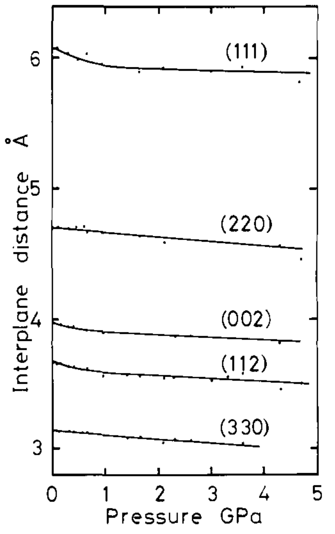

Figure 4. Pressure dependence of distances in the Pt_2 crystal planes for each direction by use of X-ray diffraction (Debye–Scherrer method).

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(15) Silicone oil (KF-96, 30 c/s; Shin-etsu Silicone Co., LTD.) is a good pressure-transmitting medium for photophysical measurements because it exhibits neither absorption nor emission in UV–vis region and no chemical interaction with the sample. The limit of applied hydrostatic pressure is around 8 GPa.[6]

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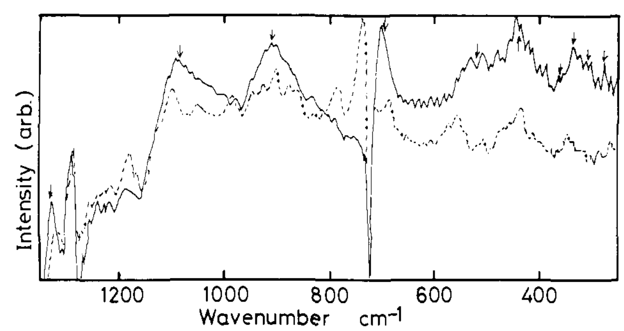

Figure 5. Pressure dependence of the IR absorption spectrum of the Pt_2 crystals at 1 atm (—) and 2.0 GPa (---). The band assignments (cm^{-1}) are as follows: POH bending (1329), PO_{term} stretching (1085), PO_{term} stretching (910), POP stretching (695), PO_2 bending (520), PO_2 bending (442), ring bending (360), Pt–P stretching (335), and ring bending (278).

of the Pt_2 crystals is the emergence of a new emission at the lower energy side of the fluorescence, while Pt_2 microcrystals did not develop this new emission.[18] The peak position of this new emission (ν_{ex}) shifted also to lower energy with increasing pressure (Figure 3, −1000 cm^{-1}/GPa).

The results of the X-ray diffraction measurement indicate that Pt_2 crystals were deformed without changing the symmetry much and the intermolecular distance was reduced by about 5% at 1 GPa. The pressure dependence of the interplanar distance can be discussed by dividing into two groups (Figure 4). The interplanar distance for group I (e.g., crystal planes (220) and (330), which are parallel to the Pt–Pt axis) decreased monotonously with increasing pressure. In the lower pressure region up to about 1 GPa, however, those for group II (e.g., the crystal planes (111), (002), and (112), which are nonparallel to the Pt–Pt axis) decreased rapidly with increasing pressure. Group II is sensitive to deformation of the Pt–Pt direction, whereas group I is not. Thus, these results manifest that the crystals are more compressive along the Pt–Pt axis. This interpretation is in agreement with the very recent spectroscopic results by Stroud et al.[11]

Intramolecular structure under high pressure was studied by IR spectroscopy. Under high pressure, almost all vibrational modes shifted to higher energies, whereas the PO_2 bending mode showed a lower energy shift (Figure 5).[17] It was difficult to measure the Pt–Pt distance directly under high pressure, since the Pt–Pt stretching mode was infrared inactive (Raman active). It was however not successful in measuring the Raman scattering from the present Pt_2 crystals owing to their strong emission.

The pressure effect on the IR spectrum suggests shrinking of the inter Pt–Pt distance. While the vibrations perpendicular to the Pt–Pt direction such as Pt–P stretching and P–O–H bending are subject to a gradual and monotonous increase with increasing pressure (Figure 6), a rapid increase in the P–O–P stretching along the Pt–Pt direction is observed up to 1 GPa. This finding suggests that the pressure-induced deformation occurs mostly along the Pt–Pt axis.

Both results of X-ray diffraction measurement and IR spectroscopy indicate that applying pressure to the Pt_2 crystals brings about no phase change and reduction in both intra and inter Pt–Pt distance.

Discussion

Emission Profile of Pt_2 Crystals. For the face-to-face binuclear complex, approximate molecular orbitals (MO) can be constructed by the combination of orbitals for two square-planar complexes constituting the binuclear complex.[9] For example, the MO of a Rh_2 complex is derived from the a_{1g} and a_{2u} orbitals of the relevant monomeric square-planar complex. The a_{1g} splits into $1a_{1g}$ and $1a_{2u}$, and the a_{2u} into $2a_{1g}$ and $2a_{2u}$. The energy difference between $1a_{1g}$ and $1a_{2u}$ (or between $2a_{1g}$ and $2a_{2u}$) is decided by the strength of the metal–metal interaction (i.e., the metal–metal distance). The pressure-induced lower energy shift is interpreted as the result of stronger destabilization of the HOMO ($1a_{2u}$) than that of the LUMO ($2a_{1g}$) which is brought about by the compression of the Pt–Pt distance.

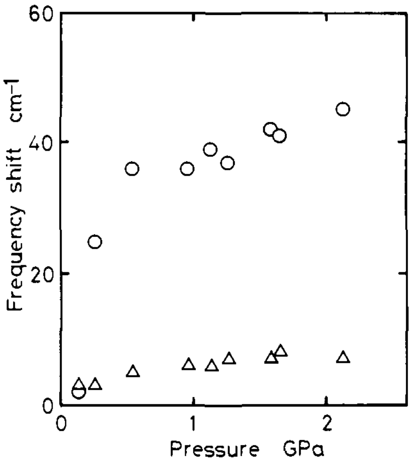

Figure 6. Pressure dependence of vibrational frequency shifts for P–O–P stretching (○) and Pt–P stretching (△) in the Pt_2 crystals.

The characteristics of the new emission are the large pressure-induced low-energy shift (−1000 cm^{-1}/GPa) and the immeasurably short lifetime. In the Pt_2 crystals the electronic state of the singlet is not expected to split any more by perturbation even if spin–orbit coupling is considered.[19] The excited states in the crystal are relaxed via both intramolecular and intermolecular processes, the former being observed as fluorescence, phosphorescence, and nonradiative pathway, and the latter as exciton. The exciton in the molecular crystal exists in a band close to the excitation level resulting from the condensed state of molecules.[20] The excited state is transferred through the band and recombines with a ground-state molecule at some trap site in crystal, which is observed as excimer emission, for example.

The Pt_2 crystal obtained as the potassium salt has the intermolecular distance of 5.1 Å along the Pt–Pt axis, which is roughly equivalent to the size of the $5d_{z^2}$ and/or $6p_z$ atomic orbitals. While the applied pressure reduces the intermolecular distance (about 5% at 1 GPa), the interaction between Pt_2 molecules becomes stronger than at atmospheric pressure.

The present results may be compared with the case of pyrene crystals in which excimer emission owing to exciton migration and subsequent trapping in excimer-forming sites is observed at atmospheric pressure. Under high pressure, the excimer emission shifts to lower energy with increasing pressure. Reduction of intermolecular distances increases the binding energy in the excited state and augments the repulsive potential in the Franck–Condon ground state. Excimer formation in the Pt_2 complex is unprecedented, and it is difficult to obtain direct evidence from kinetic analysis of its emission rise and decay profile. However, the finding that the new emission is observed clearly under high pressure when the inter Pt_2 distance is comparable to or somewhat longer than the excimer-forming distance in organic systems is in support of the present assignment. If $5d_{z^2}$ and/or $6p_z$ orbitals participate in excimer formation, excimer formation at a larger separation than in the case of organic excimers is reasonable. The new emission is characteristic of the well-grown crystals but not of the microcrystals in which the molecular arrangement is thought to be irregular. Random molecular arrangement in the solid is certainly unfavorable for excimer formation. Not only for excimer formation, energy migration is suppressed in microcrystals as

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(18) ν_F and ν_P for microcrystalline Pt_2 were 24.57 × 10^3 and 19.65 × 10^3 cm^{-1}, respectively, which were comparable to the values for the Pt_2 crystals. However, (1) the microcrystals do not show the new emission, and (2) the phosphorescence decay profile is single exponential with the lifetime = 3.7 μs, while the decay profile for the Pt_2 crystals is nonexponential containing much shorter lifetime components. These findings clearly suggest that inter Pt_2 interactions exist in the Pt_2 crystals.[21,22]

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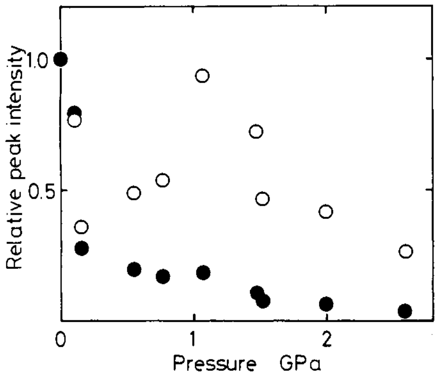

Figure 7. Pressure dependence of the relative peak intensities of fluorescence (●) and phosphorescence (○) of the Pt_2 crystals. The intensities are normalized to the values at atmospheric pressure.

manifested by the absence of T–T annihilation.[21,22]

Emission Intensity of the Pt_2 Crystal. Since it is difficult to separate these three emissions from each other, the peak intensities of each emission is taken to represent the relative quantum efficiency. As the full width at half-maximum is also dependent on pressure, this is not an ideal procedure and should be considered as a qualitative index. The relative value of the intensity at ambient pressure to that at atmospheric pressure was chosen for the following analysis.

The pressure dependence of the relative emission intensity is shown in Figure 7 for fluorescence (I_F) and phosphorescence (I_P). I_F decreased very much with pressure up to 0.2 GPa, whereas it is almost constant over 0.2 GPa. I_P decreases rapidly up to 0.2 GPa, increases (0.2–1.0 GPa), and decrease again at high pressure.

The initial decrease in I_F and I_P up to about 0.2 GPa is possibly ascribed to an increase of nonradiative decay from the S_1 state to the S_0 state. Application of pressure increases both intra- and intermolecular interaction so that the nonradiative pathway is facilitated. Ultimately, the pressure effect appears as the S_1 state excimer formation, which is reminiscent of strong inter Pt–Pt interaction, as discussed above. I_P increases between 0.2 and 1 GPa, reaching a maximum value comparable to the value at atmospheric pressure, while I_F stays nearly constant or decrease slightly in this pressure region. If an increase in the intersystem crossing efficiency were the origin of the increase in I_P, I_F should have decreased more drastically to compensate for the increase in I_P. The observed decrease in I_F is much smaller than expected. The reason is consequently attributed to an enhanced phosphorescence rate constant (k_P). Since T–T annihilation participates in the crystals, the estimation of k_P requires complex mathematical analysis.[21,22] The change in k_P is however very likely as judged by pressure-induced change in absorption spectrum. The absorption energy maximum and the molar extinction coefficient (ϵ) of Pt_2 in aqueous solution are 452 nm (110 M^{-1} cm^{-1}; $^1A_{1g} \rightarrow {}^3A_{2u}$) and 367 nm (33 200 M^{-1} cm^{-1}; $^1A_{1g} \rightarrow {}^1A_{2u}$). In the crystal at atmospheric pressure, the absorption at 367 nm is mainly observed, since $\epsilon(452)$ is very small. Under high pressure, the metal–metal interaction become stronger, so that the S–T mixing and hence $\epsilon(452)$ are expected to be enhanced.[23] This enhanced S–T mixing brings about an increase in k_P and thus I_P. Further increase in applied pressure (above 1 GPa) causes stronger intermolecular interaction, and the intermolecular processes such as T–T annihilation and other bimolecular nonradiative decay paths become dominant. As a consequence, the drop of I_P is observed above 1 GPa.

The lower energy shifts of both fluorescence and phosphorescence with increasing pressure are the manifestations that an increasing in the d–d splitting is caused by reduction of the intra Pt–Pt distance. The pressure-dependent new emission is most likely to be excimer emission, which is observable only in the crystal. Application of high pressure changes both intermolecular and intramolecular interaction and thus influences emission properties as well as their dynamic photophysical process.[22]

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(23) Considerable S–T mixing is expected for complexes of heavy metals since spin–orbit coupling is large, which is further enhanced under high pressure. In fact, our preliminary absorption spectroscopy by using the DAC indicated that $\epsilon(452)$ of $K_4[Pt_2(P_2O_5H_2)_4]$ crystals increased under high pressure.[1b] However, a recent report by Stroud et al. did not mention the enhancement of S–T mixing for $(n\text{-}Bu_4N)_4[Pt_2(P_2O_5H_2)_4]$ crystals.[11] The difference in the countercation is an important factor affecting the density of crystals mainly owing to the difference in size.[22] This discrepancy between Stroud's and our result may therefore be attributed to the difference in the countercation.

Pressure Effects on the Absorption and Emission of Tetracyanoplatinates(II) in Solution

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Abstract: Absorption and emission spectra of solutions of different tetracyanoplatinate(II) compounds as functions of concentration, solvent, temperature (278 K $\lesssim T \lesssim$ 333 K), and applied pressure (1 bar $\leq p \leq$ 17 kbar) are reported. The spectra of aqueous solutions with $c_0 \gtrsim 0.1$ M at room temperature and p = 1 bar exhibit features that can be assigned to the formation of oligomers $[Pt(CN)_4]_n^{2n-}$ with $n \geq 3$. Increasing the pressure lowers the minimum concentration at which oligomers are formed, shifts the equilibrium to oligomers of larger size, and reduces the intercomplex distance in the oligomers.

The optical properties of tetracyanoplatinates(II) (≡CP) are changed considerably, if the compounds are transferred from their dilute aqueous solutions to the crystalline state. The reason for this is a strong coupling between neighboring complex ions in the single crystals, which contain mutually parallel columns of closely stacked $[Pt(CN)_4]^{2-}$ ions.[1] This structural feature of the crystals

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