Surface and Intercalate Chemistry of Layered Silicates. Part I. General Introduction and the Uptake of Benzidine and Related Organic Molecules by Montmorillonite

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Various types of novel reactions (relevant in bio-organic, inorganic, and prebiological contexts) which can be effected within spaces between the layers, or at the surfaces, of sheet-silicate minerals are summarized. The colour reactions displayed by nine selected nitrogen-containing small aromatic molecules when they complex with montmorillonite are also briefly reviewed, together with the results of a quantitative adsorptive study of benzidine on this particular mineral. Concurrent measurement of Na^+-ion release from, and uptake of benzidine by, the mineral, and *X*-ray measurements of interlayer spacings, clearly reveal pre- and post-intercalation stages of the formation of the complex.

THE recent renascence of interest [1-4] in intercalation, where stable inclusion complexes are formed by ordered insertion of various types of species between individual sheets of layered solids such as graphite [5] and transition-metal chalcogenides,[2,3] has prompted us to embark on a series of inter-related studies of selected micaceous silicates, a class of material long known [6-9] to display marked aptitudes towards the uptake of a large range of organic molecules. Adequate reviews, which summarize the contributions of Hofmann, Weiss, Barrer, Bodenheimer, Brindley, and others are already available.[6-9] These describe, *inter alia*, the types of organic molecules which can be more or less readily assimilated by minerals such as muscovites, glauconites, illites, vermiculites, and, more particularly, montmorillonites (Figure 1), which are the parent solids, the surface and intercalate properties of which we shall describe in the earlier parts of this series of papers.

Though much is known about the various intercalates that are formed, a great deal still remains to be discovered even about such fundamental issues as, for example, precisely why the amount of penetration of water and other molecules between the silicate layers varies from essentially zero for zero-charge layers (as in talc or prophyllite) to a maximum with low-charge layers (as in hectorites and montmorillonites) down to a minimum again as the layer charge increases (beidellites < vermiculites < lepidolites < muscovite) culminating in zero uptake for margarite. Nevertheless, there is an impressive phenomenology [9-12] relating to the conditions under which various types of molecules may be intercalated by members of the micaceous silicates; it is evident, particularly from the work of Weiss *et al.*,[6,7] that a versatile range of chemical reactions, including electron transfer, condensation, and polymerization, may be effected within the restricted and often well defined spaces between contiguous charged sheets of chosen aluminosilicates.

There are two main reasons why organic intercalates of layered silicates currently merit further systematic study. First our own [13] and other [14] investigations reveal that several novel and highly specific reactions

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[1] J. A. Wilson and A. D. Yoffe, *Adv. Phys.*, 1969, **18**, 193.

[2] F. R. Gamble, J. H. Osiechi, M. Cais, R. Pisharody, F. J. Di Salvo, and T. H. Geballe, *Science*, 1971, **174**, 493.

[3] B. Bach and J. M. Thomas, *J.C.S. Chem. Comm.*, 1972, 301.

[4] K. Watanobe, T. Kondow, M. Soma, T. Onishi, and K. Tamaru, *Proc. Roy. Soc.*, 1973, **A333**, 51.

[5] A. R. Ubbelohde, G. S. Parry, and D. E. Nixon, *Proc. Roy. Soc.*, 1965, **A291**, 324; A. R. Ubbelohde, *ibid.*, 1968, **A304**, 25.

[6] A. Weiss in ' Organic Geochemistry,' eds. G. Eglington and M. T. J. Murphy, Springer-Verlag, Berlin, 1969.

[7] A. Weiss, *Chem. Ber.*, 1958, **91**, 487.

[8] R. E. Grim, ' Clay Mineralogy,' McGraw–Hill, New York, 1968.

[9] G. W. Brindley in ' *X*-Ray Identification and Crystal Structures of Clay Minerals,' Mineralogical Society, London, 1951, p. 89.

[10] R. M. Barrer in ' Non-stoicheiometric Compounds,' ed. L. Mandelcorn, Academic Press, London, 1964, p. 309.

[11] W. Bodenheimer, L. Heller, B. Kirson, and S. H. Yariv, *Clay Minerals Bull.*, 1969, **5**, 145.

[12] A. Weiss, *Clays and Clay Minerals*, 1963, **10**, 191.

[13] See, for example, D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and S. H. Graham, *J.C.S. Chem. Comm.*, 1974, 124.

[14] M. Hasegawa, *J. Phys. Chem.*, 1962, **66**, 834.

may be effected within expanded sheets of the appropriate aluminosilicates. The limited coupling of benzene or toluene,[15] the formation of polypeptides,[6] the polymerization of styrene or of unusually bonded metal–aromatic complexes,[16-19] or of aniline (in high yield) from *trans*-4,4′-diaminostilbene[13] are but a few of the transformations which emphasize the considerable synthetic potential of such reactions in both bio-organic and inorganic systems. The relevance of such reactions to the fundamentals of the science of soil conditioning and the technology of paper making requires no further elaboration. Secondly, a number of powerful new spectroscopic and diffraction techniques have recently become available which promise to shed much light on the electronic and structural properties of these complexes.

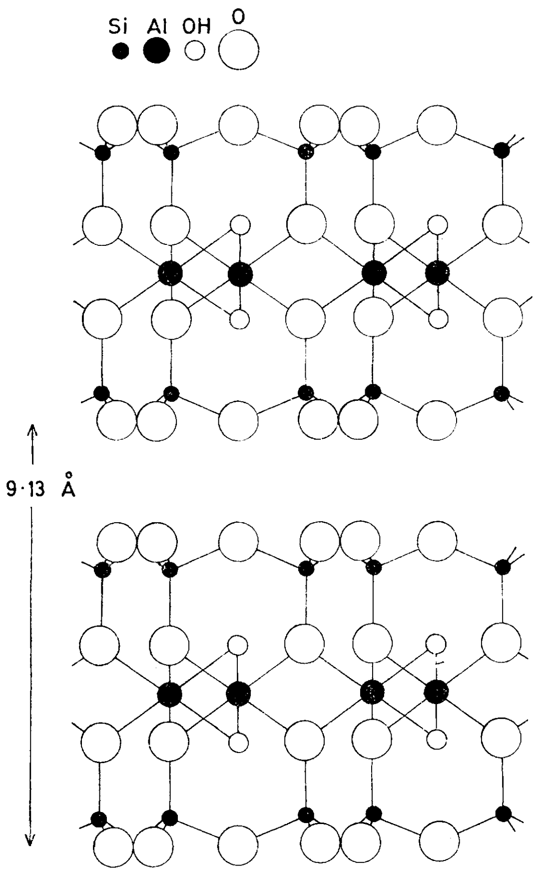

FIGURE 1 Elevation drawing of an idealized t.o.t. layer in a sheet silicate of general composition $Al_4Si_8O_{20}(OH)_4$. In montmorillonite substitution of Al or Si by other cations (*e.g.* Mg^{2+} or Fe^{2+} for Al and Al^{3+} for Si) takes place

We concentrated our early studies on the clay mineral montmorillonite, principally because it exhibits the greatest propensity for uptake of a range of molecular species. Here we summarize the results of a survey of the colour reactions displayed by a number of nitrogen-containing small aromatic molecules when they complex with montmorillonite suspended in aqueous solution; we also deal with quantitative aspects of the uptake of benzidine by the clay mineral. This paper is intended to serve as a foundation for later ones, which will describe Mössbauer-spectroscopic studies of electron transfer to and from the sheet-silicate layers, *X*-ray diffraction studies, and mass-spectrometric analyses of novel reactions undergone by some of the organic montmorillonite intercalates.

RESULTS AND DISCUSSION

Colour Reactions of Montmorillonite.—(a) *Structural aspects*. The idealized formula (Figures 1 and 2) for montmorillonite, $Si_8Al_4O_{20}(OH)_4$, implies that the so-called dioctahedral structure,* with its two bridging hydroxo-groups attached to each of the octahedrally co-ordinated Al^{3+} ions, has no net charge on the individual tetrahedral–octahedral–tetrahedral (t.o.t.) layers. In reality, substitution either of Si^{4+} by Al^{3+} (or Fe^{3+}) at the tetrahedral sites or, more commonly, of Al^{3+} by Mg^{2+} (or Fe^{2+}) at the octahedral sites confers a residual negative charge on each t.o.t. layer, the entire structure being rendered neutral by incorporation of interlayer cations, *e.g.* Na^+ or Ca^{2+} (which are exchangeable), so that a typical composition would be $M_{x+y}{}^{+}$-$(Si_{8-y}Al_y)(Al_{4-x}Mg_x)O_{20}(OH)_4$. The cation-exchange capacity[8,9] (c.e.c.) of the clay is usually expressed in milliequivalents per 100 g. For a c.e.c. of 98 milliequivalents per 100 g, a typical[8] value for montmorillonites, there is a net value of 0·33 electronic charges per layer $(Si,Al)_4O_{10}$ unit of each t.o.t. layer, or, expressed differently, 70 Å^2 per unit charge in each layer. The extent of penetration of water, and other neutral species such as pyridine[20] is governed both by the magnitude of this charge density and the nature of the interlayer cation (see refs. 6 and 21 for further details).

In practice, cation-exchange sites will arise both at planar surfaces and at exposed sites on the prismatic or pyramidal faces, which constitute crystallite edges, the ratio of such sites being a function of particle size. Owing to solvation and other factors, many molecules especially water can penetrate between the layers with consequential swelling and *c*-axis expansion. Large expansions may be brought about by uptake of massive organic cations exemplified by octadecylammonium[22] which results in a *c* spacing for the resulting intercalate of *ca.* 33 Å.

(b) *Colour reactions*. Many organic molecules notably amines (see Theng)[23] when brought into contact with

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* Two thirds of the potentially octahedral vacancies between the $[Si_4O_{10}]^{4-}$ units are occupied.

[15] D. T. B. Tennakoon, J. M. Thomas, and M. J. Tricker, unpublished work.

[16] D. H. Solomon, *Clays and Clay Minerals*, 1968, **16**, 31.

[17] M. M. Mortland and T. J. Pinnavavaia, *Nature Phys. Sci.*, 1971, **229**, 75.

[18] D. M. Clementz and M. M. Mortland, *Clays and Clay Minerals*, 1972, **20**, 181.

[19] H. E. Doner and M. M. Mortland, *Science*, 1969, **166**, 1406.

[20] R. Green-Kelly, *Trans. Faraday Soc.*, 1955, **51**, 412.

[21] A. Weiss, *Angew. Chem.*, 1963, **75**, 113.

[22] E. Suito and T. Yoshide, *Nature Phys. Sci.*, 1971, **229**, 22.

[23] B. K. G. Theng, *Clays and Clay Minerals*, 1971, **19**, 383.

montmorillonite yield intensely coloured complexes, a fact which is of some analytical value (both chemical and geological). These reactions may be utilized for probing Brønsted and Lewis-acid sites, expected to be of importance in catalytic behaviour of the clay, and also form the basis of the production of non-carbon copying paper. We made a qualitative survey of the colour reactions of various organic molecules when brought into contact with aqueous suspensions of Na^+-exchanged Wyoming montmorillonite characterized by the analytical information given in the Experimental section. The results are summarized in the Table. One of these systems, benzidine–montmorillonite, has been much studied previously,[24-26] but many ambiguities still remain.

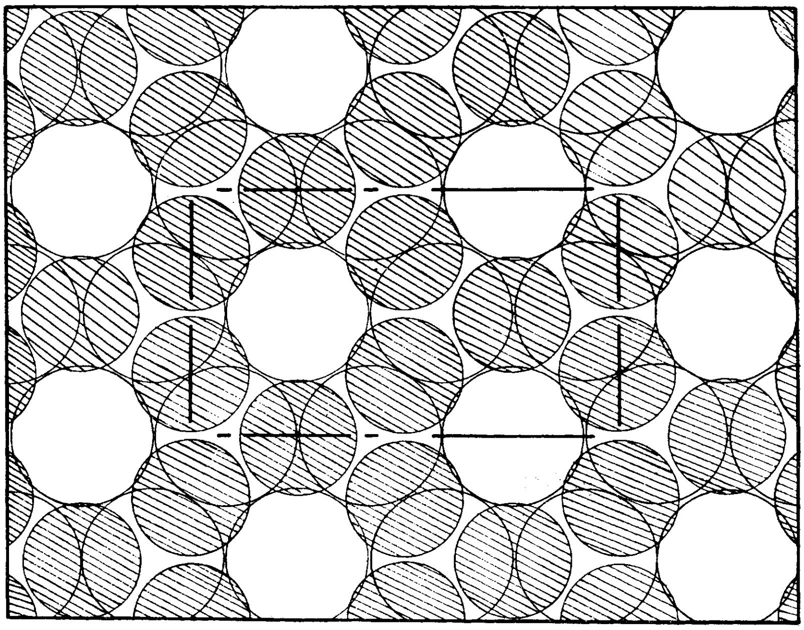

FIGURE 2 Schematic illustration of the arrangement of the silica layer (made of SiO_4 tetrahedra) on top of the octahedral layer. The hatched oxygen atoms belong only to the other sheet of the tetrahedral layers, the others bridging the tetrahedral and octahedral layers (after Brindley [9])

Summary of colours and properties exhibited by various montmorillonite–organic complexes

	Colour			
Reagent	Wet	Dry	Aged	Comments
Benzidine	Blue	Yellow	Yellow form stable	Yellow form easily produced by dehydration, easily reversed
NNN′N′-Tetramethylbenzidine	Green	Brown	Green form stable	Brown form only produced at 80 °C and 10^{-3} Torr
Triphenylamine	Green	Purple	Purple form stable	Not easily reversed; density of colour dependent on nature of montmorillonite
p-Phenylenediamine	Brown	Purple	Purple form stable	Easily reversed
N,*N*′-Dimethyl-*p*-phenylenediamine	Green	Purple	Purple form stable	Easily reversed
NNN′N′-Tetramethyl-*p*-phenylenediamine	Purple	Purple	Faded to pale blue after 1 month	Not easily reversed
trans-4,4′-Diaminostilbene dihydrochloride	Green	Brown	Brown form stable	
7,7,8,8-Tetracyanoquinodimethane	Brown	Brown	Stable	
Tetracyanoethylene	No change	No change		Solution turns green

A deep blue colouration results on reaction of benzidine and montmorillonite in the presence of water, the colour changing through green to yellow on drying.[24] Although it is generally agreed that [23] the blue colouration is due to formation of the positively charged radical cation of benzidine, there are conflicting theories concerning the origin of the yellow colour.[24,27] Convincing direct spectroscopic evidence of the nature and location of the Lewis-acid sites responsible for the colour formation was not, prior to this work, available. Moreover, few quantitative studies of the uptake of benzidine by montmorillonite have been carried out. This system has therefore been selected for detailed study using the unique probe of ^{57}Fe Mössbauer spectroscopy: we demonstrated unequivocally that structurally

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[24] C. G. Dodd and S. Ray, *Clays and Clay Minerals*, 1960, **8**, 237.

[25] M. Weil-Maherle and J. Weiss, *J. Chem. Soc.*, 1948, 2164.

[26] D. H. Solomon, B. C. Loft, and J. D. Swift, *Clays and Clay Minerals*, 1968, **7**, 389.

[27] Y. Matsunaga, *Bull. Chem. Soc. Japan*, 1972, **45**, 770.

incorporated Fe^{3+} ions function as electron-acceptor sites and are involved in the production of benzidine blue at the surfaces of montmorillonite. We also studied the shape of the sorption isotherm of this system at room temperature, and recorded the relation between the release of Na^+ ions from the exchanged silicate and the uptake of benzidine.

Sorption Isotherm of Benzidine–Na^+*-exchanged Montmorillonite.*—The results of the variation of amount sorbed as a function of equilibrium concentration of benzidine in aqueous solution at *ca.* 290 K, together with the Na^+-release curve, are presented in Figure 3. Up to point (A) our results are in line with the kind of data presented previously.[28] Beyond (A), however, flocculation of the clay occurred, and further there was a sharp increase * in the uptake of benzidine and concomitant dramatic release of Na^+ ions from the interlayer regions. Clearly, from (A) onwards we are witnessing genuine intercalation of cationic benzidine. Up to point (A) it is likely that benzidine species are retained only at exterior surfaces of the particles of the clay mineral. As flocculation occurs at this point, the quantity of benzidine sorbed can be taken to correspond to monolayer coverage.[29] Working on the assumption that each species lies flat, thereby occupying an area of *ca.* 56 Å^2, the surface area of the dispersed clay was estimated [on the assumption that point (A) signifies completion of a monolayer of the external surface] to be 228 m^2 g^{-1}, a figure not unrealistic in the light of previous results.*

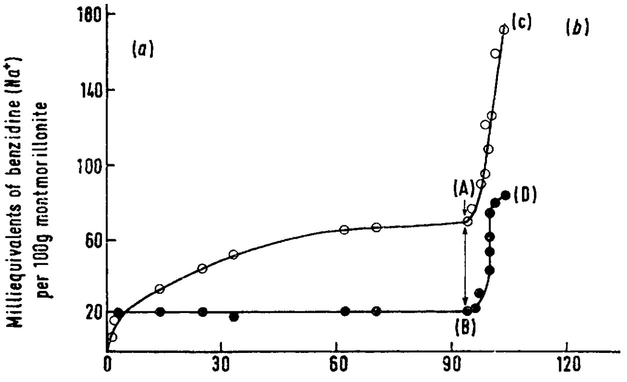

FIGURE 3 Sorption isotherm (○) showing uptake of benzidine from aqueous solution on, and in, to sodium-exchanged montmorillonite. The Na^+-ion ' release ' curve (●) is also shown. (*a*), Pre-intercalation [*c* spacings: 18·01, 15·24, and 12·27 (wet); 12·27 Å (dry)]; (*b*), post-intercalation (dry *c* spacings: 20·14, 15·50, and 10·92 Å)

There was no 1 : 1 correspondence between the release of Na^+ ions (and the necessary concomitant appearance of hydroxide ions in solution †) and the quantity of benzidine taken up in the pre- and post-intercalation regimes. U.v.- and visible-transmission [27,30] and reflectance studies indicated that the majority, if not all, of the benzidine species are present as the blue monopositive radical cation of benzidine. We therefore conclude, from the shape of the Na^+-release curve, that benzidine is first oxidized at Lewis-acid sites (which themselves involve cation-exchange sites) at the exterior surfaces and thereafter at sites which increase the net negative charge on the clay which is neutralized by the positively charged benzidine radicals. The extent of extra negative charge endowed to the layer after the initial oxidation process is given directly by the height (AB) in Figure 3, *i.e.* 47 milliequivalents per 100 g. A similar sequence occurs on intercalation, and the extra negative charge is now given approximately by (CA) — (DB), *i.e.* 39 milliequivalents per 100 g. [Point (D) does not correspond to saturation, so this is a lower estimate. Moreover there is rather a large error (±5 milliequivalents per 100 g) involved in the estimation of the c.e.c. from point (D).] The ratio of Na^+ ions released up to point (A) to the total finally released was *ca.* one third, which reflects the ratio of cation-exchange sites at external surfaces to the total available sites.

The hypothesis that from point (A) onwards we are witnessing genuine intercalation of benzidine species by montmorillonite was borne out by *X*-ray powder-diffraction measurements of *c* spacings of montmorillonite–benzidine complexes isolated from the sorption system. *c* Spacings, and the variation of the *X*-ray diffraction patterns as a function of moisture content for the benzidine–clay complexes in the pre-intercalation regime, were the same as those of the original wet clay: the three spacings clearly correspond to montmorillonite containing different stoicheiometric amounts of water. The fact that we observed two strong peaks corresponding to expanded *c* dimensions (15·5 and 20·1 Å) ‡ itself strongly indicates the reality of the intercalation, and suggests that either two distinct orientations of the included species or, alternatively, two distinct stoicheiometries (varying, for example, in water content) are possible.

Quantatative Considerations.—The c.e.c. of the montmorillonite used in this work was 68 ± 2 milliequivalents per 100 g, and the theoretical total (internal + external) surface area of montmorillonite, from its lattice dimensions, 752 m^2 g^{-1}. Assuming a uniform distribution

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* Drs. J. B. Donnet and B. Sieffert, CNRS Mulhams, have drawn our attention to the fact that acetamide–montmorillonite yields a sorption isotherm similar to that shown in Figure 3. Polyacetamides, however, do not intercalate and sorption is confined to exterior surfaces.

† The pH of the media was found to increase as benzidine was sorbed, but it was not monitored quantitatively.

‡ The cause of the weak peak corresponding to a diminished *c* spacing (10·9 Å) is not at present clear. It may arise from a collapsed structure, the formation of which may be facilitated during the course of reaction, or subsequent vacuum dehydration of the blue complex. Alternatively this spacing may correspond to the 002 reflection of the complex which has a *c* spacing of 20·14 Å. If the latter were indeed so the irrational *l* index would imply the presence of some disorder along the *c* axis.

[28] N. Lahav and S. Raziel, *Israel J. Chem.*, 1971, **9**, 683.

[29] G. W. Brindley and T. D. Thompson, *Israel J. Chem.*, 1970, **8**, 409.

[30] D. T. B. Tennakoon, J. M. Thomas, and M. J. Tricker, unpublished work.

of exchangeable cationic sites, we estimate that the equivalent area per charge is 184 Å^2 which, in turn, corresponds to a (negative) layer charge of 0·25 per $(Si,Al)_4O_{10}$ unit. From the Na^+-release curve it can be seen that the c.e.c. of the external surfaces (of area 228 m^2 g^{-1}) is 22 milliequivalents per 100 g. The remaining c.e.c. of 46 milliequivalents per 100 g is distributed over the internal surfaces which have an area of 514 m^2 g^{-1}. Thus we arrive at the equivalent area per charge of 172 Å^2 per charge and 189 Å^2 per charge for the external and internal surfaces respectively. These values are in good agreement with that of 184 Å^2 per charge calculated by the normal procedure which makes no distinction between internal and external surfaces and would therefore imply that the c.e.c. of the clay arises almost entirely from substitution within the aluminosilicate layers.

EXPERIMENTAL

The montmorillonite used throughout this work was a standard natural sample from Upton, Wyoming (code no. 48W 1250), obtained from Ward's Natural Science Establishment, New York. The clay was crushed, dispersed in distilled water, and allowed to sediment so as to remove dense components such as quartz. The top colloidal fraction, containing particles of $<0{\cdot}02$ μm equivalent spherical diameter, was removed and the clay precipitated by centrifugation and then dried in a vacuum desiccator over calcium chloride. The clay was equilibrated in air prior to carrying out the reactions described above.

The cation-exchange capacity (c.e.c.) was determined by treating an aqueous suspension of the clay with ammonium acetate (1N) for 1 day, centrifuging, and repeated washing with distilled water until all excess of ammonium acetate had been removed. The ammonium-exchanged clay (*ca.* 50 mg) was then transferred to a microdistillation apparatus, the ammonia displaced by boiling with excess of NaOH (3N) and absorbed in a known volume of standard hydrochloric acid. The HCl solution was back titrated with standard borax solution. Sodium-exchanged clays were prepared by treatment of dispersions of clay with NaCl (1N) solutions for 24 h, followed by separation and continual washing with deionised water till no further chloride ion was detected by $AgNO_3$. The clay was then dialysed using a Polythene membrane.

A series of standard solutions were prepared by dissolving benzidine in water and a u.v. spectrophotometric calibration plot was constructed using the benzidine absorption having $\lambda_{max.} = 280$ nm. Subsequent benzidine determinations were made using this calibration plot. The extent of benzidine uptake was determined by adding benzidine solutions of various known concentrations to known weights of sodium-exchanged clay and dispersing the clay ultrasonically. The clay was separated after 12 h using a Serval RC-B ultracentrifuge, and the benzidine concentration of the supernatant solution determined. Sodium-ion concentrations were assayed by atomic-emission spectroscopy. A series of blank determinations of Na^+ in the presence of colloidal suspensions of the clay were also made, so that the necessary small corrections could be made to values determined after benzidine treatment. Semi-quantitative pH measurements were made using an E.I.L. direct-reading pH meter.

c Spacings ($\pm 0{\cdot}02$ Å) were determined using a Phillips *X*-ray powder diffractometer employing Cu-*K* radiation. The benzidine (AnalaR) used was obtained from Koch-Light Laboratories Ltd.

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