International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JENSEN, L. & SUNDARALINGAM, M. (1964). *Science*, **145**, 1185–1187.
KOIZUMI, M. (1953). *Mineral. J.* **1**, 36–47.
KUCHITSU, K. (1971). *Bull. Chem. Soc. Jpn*, **44**, 96–99.
KVICK, A. & SMITH, J. V. (1983). *J. Chem. Phys.* **79**, 2356–2362.
KVICK, A., STAHL, K. & SMITH, J. V. (1985). *Z. Kristallogr.* **171**, 141–154.
LUNDGREN, J. O. (1983). *Crystallographic Computer Programs.* Report No. UUIC-B13-4-05, Univ. of Uppsala, Sweden.
PECHAR, F. (1982). *Acta Montana*, **59**, 143–152.
PENG, C. J. (1955). *Am. Mineral.* **40**, 834–856.
PLUTH, J. J., SMITH, J. V. & KVICK, A. (1985). *Zeolites*, **5**, 74–80.
SMITH, J. V. (1983). *Z. Kristallogr.* **165**, 191–198.
TAYLOR, W. H., MEEK, C. A. & JACKSON, W. W. (1933). *Z. Kristallogr.* **84**, 373–398.
TOMIIE, Y. (1958). *J. Phys. Soc. Jpn*, **13**, 1030–1037.
VAN REEUWIJK, L. P. (1972). *Am. Mineral.* **57**, 499–510.

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Structure of Tetraamminecopper(II) Dipermanganate

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Abstract. $[Cu(NH_3)_4(MnO_4)_2]$, $M_r = 369·53$, monoclinic, $P2_1/m$, $a = 5·413\ (1)$, $b = 9·093\ (1)$, $c = 10·749\ (1)$ Å, $\beta = 96·18\ (1)°$, $V = 526·0\ (2)$ Å^3, $Z = 2$, D_m(flotation) = 2·39, $D_x = 2·33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 43·1$ cm^{-1}, $F(000) = 366$, $T = 293$ K. $R = 0·024$ with 1123 unique observed reflections. The structure contains isolated units of $[Cu(NH_3)_4(MnO_4)_2]$. The Cu atoms show the usual (4+2) distorted octahedral coordination with four N atoms in the equatorial positions [Cu—N = 2·013 (2), 2·016 (3) Å] and two O atoms from the tetrahedral permanganate groups occupying the axial sites [Cu—O = 2·456 (3), 2·512 (3) Å]. Thermoanalytical results are discussed.

Introduction. Solid-state precursors with cations mixed at the atomic level can serve for the synthesis at moderate temperature of catalytically active mixed metal oxides. As a part of our study of the thermal decomposition of different copper manganese coordination compounds, we prepared crystals of the title compound, a possible precursor for hopcalite-type catalysts.

This complex was first described by Klobb (1890). An unindexed powder diffraction diagram and IR data have been reported by Müller, Böschen, Baran & Aymonino (1973). Since an understanding of the mechanism of structural changes during decomposition requires a knowledge of the crystal structure, it was decided to investigate this phase.

Experimental. A solution of 10 g $CuSO_4.5H_2O$ in 40 ml H_2O, cooled in an ice bath, was first treated with an excess of concentrated ammonia. Adding a cold saturated solution of potassium permanganate yielded a dark-violet precipitation of $[Cu(NH_3)_4(MnO_4)_2]$. Prismatic, twinned crystals could be grown by slow evaporation of a saturated aqueous solution of the above product over concentrated H_2SO_4 at ~278 K. After washing with cold water, ethanol and ether, the crystals were dried in air. They decompose slowly in air at temperatures above 283 K.

For structure determination it was possible to separate a 0·25 × 0·08 × 0·12 mm single crystal, which was mounted in a glass capillary.

Preliminary precession and Weissenberg photographs established symmetry and systematic absences consistent with the monoclinic space groups $P2_1/m$ or $P2_1$. Data collection: Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation; unit-cell parameters and crystal orientation from least-squares refinement of 18 automatically centered reflections in range $25 < 2\theta < 43°$; ω–2θ scan; total number of reflections measured 4361 (including standards), max. $\sin\theta/\lambda = 0·8063$ Å^{-1}, h −2 to 8, k −2 to 14, l −17 to 17. Intensities and setting angles of six standard reflections monitored at regular intervals; total loss of intensity 3·9% within 82·5 h of exposure time. Intensities reduced to F_o by applying corrections: Lorentz, polarization, linear decay (correction factors 1·00–1·02) and absorption (empirical correction using ψ scans with nine reflections, transmission factors 0·84–1·00).

After averaging of equivalent reflections ($R = 0·017$ on F_{obs}) 2423 unique data remained. 1123 reflections with $I > 2\sigma(I)$ were used for structure determination. Unless otherwise stated, all calculations carried out on a PDP 11/34 computer using Enraf–Nonius CAD-4 *SDP*

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programs (Frenz, 1982). Structure solved using *MULTAN*11/82 in space group $P2_1/m$. All H atoms could be located on difference Fourier maps. In last cycles of refinement they were included with a fixed temperature factor B of 4 Å^2. A parameter for secondary extinction was refined [final value $1{\cdot}7\,(1)\times 10^{-6}$]. Full-matrix refinement [98 variables, weighting scheme $1/\sigma^2(F_o)$, ignorance factor $p = 0{\cdot}04$] converged to $R = 0{\cdot}024$ and $wR = 0{\cdot}029$ including all observed reflections. Maximum shift/e.s.d. 0·02, e.s.d. of an observation of unit weight $S = 0{\cdot}999$. Final difference maps showed max. peaks of $|0{\cdot}67|$ e Å^{-3}. Error analysis showed no systematic errors as function of $\sin\theta/\lambda$ or F_o. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final positional parameters are given in Table 1.* The structure contains isolated units of $[Cu(NH_3)_4(MnO_4)_2]$. A similar structure type of a Cu^{II} compound has also been found in perchlorates, as for example $[Cu(1,2\text{-propanediamine})_2(ClO_4)_2]$ (Pajunen & Lehtonen, 1972). The coordination geometry of each Cu^{II} ion is that of a tetragonally elongated octahedron as illustrated in Fig. 1. The basal plane of the four N atoms is a nearly perfect square with a mean Cu—N distance of 2·015 (3) Å, which compares well with corresponding values in other $Cu(NH_3)_4^{2+}$ complexes (Hathaway & Tomlinson, 1970): 2·013 (5) Å in $Cu(NH_3)_4I_4$ (Dubler & Linowsky, 1975), 2·005 (9) Å in $Cu(NH_3)_4SeO_4$ and 2·032 (6) Å in $Cu(NH_3)_4SO_4.H_2O$ (Morosin, 1969). The axial sites of the Cu coordination octahedron are occupied by two O atoms with Cu—O distances of 2·456 (3) and 2·512 (3) Å, signalizing weak bonding to the two permanganate ions. The Cu^{II} stereochemistry in $[Cu(NH_3)_4(MnO_4)_2]$ follows the general features recently reviewed by Hathaway (1984). The MnO_4^- groups have nearly tetrahedral symmetry with a mean bond length Mn—O = 1·607 (3) Å. This distance coincides with the corresponding value of 1·605 (14) Å found, for example, in $Sr(MnO_4)_2.3H_2O$ (Ferrari, Braibanti, Bigliardi & Manotti Lanfredi, 1966). After libration correction (Sheldrick, 1983) taking the MnO_4 groups as rigid bodies our mean Mn—O distance extends to 1·625 Å, which is only slightly shorter than the corrected mean distance of 1·633 Å in $AgMnO_4$ (Chang & Jansen, 1984). The shortest N···O contact [N(1)···O(12)] distance is 3·085 (4) Å. According to Lautié, Fromen & Novak (1976) this fact indicates the absence of strong or even medium-strong N—H···O bridges in $[Cu(NH_3)_4(MnO_4)_2]$.

A summary of bond distances and angles in $[Cu(NH_3)_4(MnO_4)_2]$ is given in Table 2. The atomic arrangement in the unit cell is shown in Fig. 2.

The only other M^{II}-tetrammine dipermanganate complexes of which we are aware are those of Zn and Cd. According to Müller *et al.* (1973) they are isostructural to the analogous diperrhenate complexes and crystallize in the cubic space group $F\bar{4}3m$. $Cd(NH_3)_4(ReO_4)_2$ (Pitzer, 1935) with $a_0 = 10{\cdot}53$ Å and $Z = 4$ bears similarities to the structure of $[Cu(NH_3)_4(MnO_4)_2]$ described here, but the atomic arrangement is based on isolated tetrahedral $[Cd(NH_3)_4]^{2+}$ and ReO_4^- groups. $Zn(NH_3)_4(MnO_4)_2$ in contrast is believed to exhibit a superstructure with $a = 20{\cdot}65$ (3) Å and $Z = 32$ (Müller *et al.*, 1973).

Table 1. *Positional and isotropic thermal parameters for* $[Cu(NH_3)_4(MnO_4)_2]$

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $U_{eq} = B_{eq}/8\pi^2$, $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{eq}\times 10^4$(Å^2)
Cu	0·30013 (9)	$\frac{1}{4}$	0·24751 (4)	208 (1)
Mn(1)	0·0706 (1)	$\frac{1}{4}$	0·56189 (5)	241 (1)
Mn(2)	0·5314 (1)	$\frac{1}{4}$	0·93229 (5)	239 (1)
O(11)	0·9572 (4)	0·3948 (3)	0·6196 (2)	479 (6)
O(12)	−0·0018 (6)	$\frac{3}{4}$	0·5889 (2)	342 (6)
O(13)	0·6337 (6)	$\frac{3}{4}$	0·4085 (3)	438 (9)
O(21)	0·6228 (5)	0·6050 (3)	0·1119 (2)	477 (5)
O(22)	0·5843 (5)	$\frac{1}{4}$	0·0841 (2)	343 (6)
O(23)	0·7924 (6)	$\frac{1}{4}$	0·8772 (3)	529 (9)
N(1)	0·4981 (4)	0·9083 (3)	0·6583 (2)	328 (5)
N(2)	0·0985 (4)	0·0932 (3)	0·1506 (2)	305 (5)
H(11)	0·364 (6)	0·616 (4)	0·608 (3)	507
H(12)	0·421 (6)	0·035 (4)	0·386 (3)	507
H(13)	0·547 (6)	0·465 (4)	0·304 (3)	507
H(21)	0·050 (5)	0·622 (4)	0·883 (3)	507
H(22)	0·094 (6)	0·021 (4)	0·185 (3)	507
H(23)	0·830 (5)	0·574 (4)	0·908 (3)	507

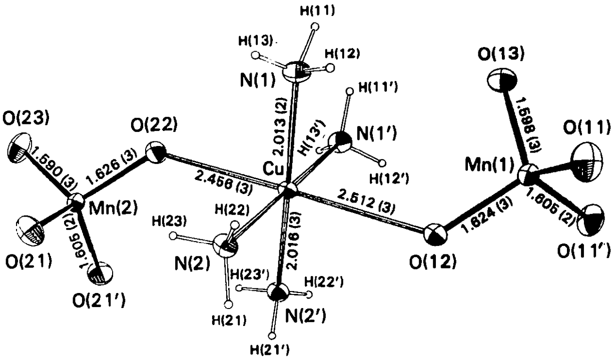

Fig. 1. The $[Cu(NH_3)_4(MnO_4)_2]$ unit in tetraamminecopper(II) dipermanganate. H atoms are drawn artificially small. Thermal ellipsoids are scaled to enclose 20% probability.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42853 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Cu–N(1) 2×	2·013 (2)	N(1)–Cu–N(1′)	91·3 (2)
Cu–N(2) 2×	2·016 (3)	N(1)–Cu–N(2)	89·3 (1)
Cu–O(12)	2·512 (3)	N(1)–Cu–N(2′)	179·1 (1)
Cu–O(22)	2·456 (3)	N(2)–Cu–N(2′)	90·0 (2)
		O(12)–Cu–O(22)	178·8 (1)
		O(12)–Cu–N(1)	90·2 (1)
		O(12)–Cu–N(2)	90·5 (1)
Mn(1)–O(11) 2×	1·605 (2)/1·623*	O(11)–Mn(1)–O(11′)	110·2 (2)
Mn(1)–O(12)	1·624 (3)/1·639	O(11)–Mn(1)–O(12)	109·2 (1)
Mn(1)–O(13)	1·598 (3)/1·617	O(11)–Mn(1)–O(13)	109·9 (1)
		O(12)–Mn(1)–O(13)	108·4 (2)
Mn(2)–O(21) 2×	1·605 (2)/1·623*	O(21)–Mn(2)–O(21′)	110·5 (2)
Mn(2)–O(22)	1·626 (3)/1·643	O(21)–Mn(2)–O(22)	109·1 (1)
Mn(2)–O(23)	1·590 (3)/1·610	O(21)–Mn(2)–O(23)	110·2 (1)
		O(22)–Mn(2)–O(23)	107·8 (1)
N(1)–H(11)	0·88 (4)	H(11)–N(1)–H(12)	104 (3)
N(1)–H(12)	0·86 (4)	H(11)–N(1)–H(13)	103 (4)
N(1)–H(13)	0·72 (4)	H(12)–N(1)–H(13)	96 (4)
		Cu–N(1)–H(11)	120 (3)
		Cu–N(1)–H(12)	116 (3)
		Cu–N(1)–H(13)	115 (3)
N(2)–H(21)	0·88 (4)	H(21)–N(2)–H(22)	112 (4)
N(2)–H(22)	0·76 (4)	H(21)–N(2)–H(23)	104 (3)
N(2)–H(23)	0·80 (4)	H(22)–N(2)–H(23)	104 (4)
		Cu–N(2)–H(21)	115 (3)
		Cu–N(2)–H(22)	114 (3)
		Cu–N(2)–H(23)	107 (3)

* Libration-corrected distances.

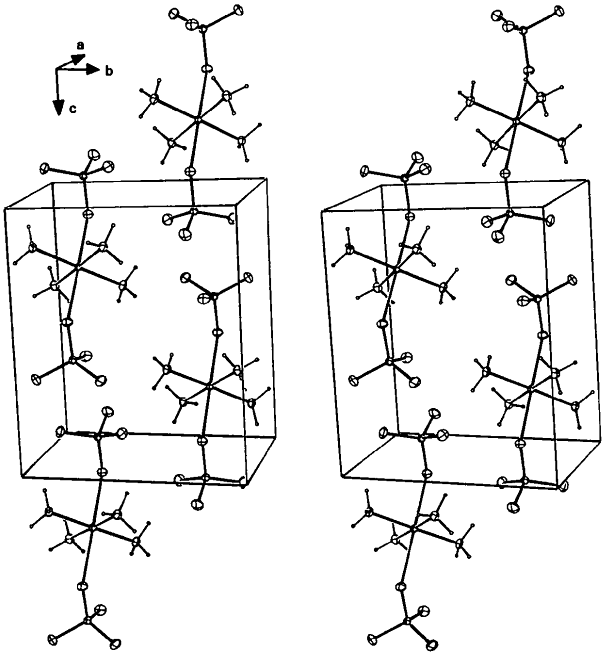

Fig. 2. Stereoview of the unit-cell packing for [$Cu(NH_3)_4(MnO_4)_2$].

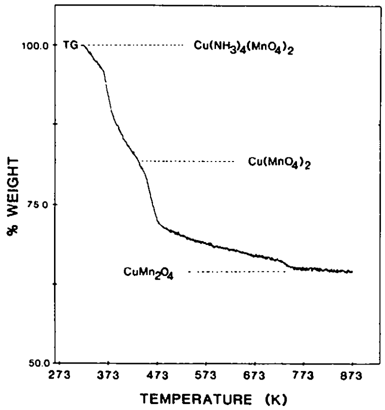

Fig. 3. Thermal decomposition of $Cu(NH_3)_4(MnO_4)_2$: Perkin–Elmer TGS2, sample weight 1·205 mg, scan rate 2 K min^{-1}, N_2 atmosphere (25 ml min^{-1}).

In view of the importance of compounds such as $Cu(NH_3)_4(MnO_4)_2$ for the preparation of mixed oxides at moderate temperatures, preliminary investigations of its thermal behavior were made. The compound explodes at about 363 K when heated, giving a mixture of different Cu and Mn oxides. In thermogravimetric measurements with small samples (about 1 mg) in a nitrogen atmosphere the compound decomposes in at least two steps (Fig. 3). According to the evaluation of the weight losses, the decomposition mechanism may be summarized as follows:

$$Cu(NH_3)_4(MnO_4)_2 \xrightarrow[-4NH_3]{313\text{–}423\ K} \text{‘}Cu(MnO_4)_2\text{’} \xrightarrow[-2O_2]{423\text{–}773\ K} CuMn_2O_4$$

Continuous X-ray powder diffractometry in a Guinier–Lenné heating camera (N_2 atmosphere) shows that the intermediate phase $Cu(MnO_4)_2$ is amorphous whereas the final product is crystalline. Its diagram coincides with the data given for the cubic $CuMn_2O_4$ phase by Beley, Padel & Bernier (1978).

Investigations of the reactivity of the decomposition products in comparison to Cu–Mn mixed oxides prepared by conventional solid-state reactions at high temperatures (~ 1173 K) are in progress.

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References

Beley, M., Padel, L. & Bernier, J. C. (1978). *Ann. Chim. (Paris)*, **3**, 429–452.

Chang, F. M. & Jansen, M. (1984). *Z. Kristallogr.* **169**, 295–298.

Dubler, E. & Linowsky, L. (1975). *Helv. Chim. Acta*, **58**, 2604–2609.

Ferrari, A., Braibanti, A., Bigliardi, G. & Manotti Lanfredi, A. M. (1966). *Acta Cryst.* **21**, 681–685.

Frenz, B. A. (1982). *Structure Determination Package*. Enraf–Nonius, Delft, Holland.

HATHAWAY, B. J. (1984). *Struct. Bonding (Berlin)*, **57**, 55–118.
HATHAWAY, B. J. & TOMLINSON, A. A. G. (1970). *Coord. Chem. Rev.* **5**, 1–43.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KLOBB, M. T. (1890). *Bull. Soc. Chim. Fr.* **3**, 508–510.
LAUTIÉ, A., FROMEN, F. & NOVAK, A. (1976). *Spectrosc. Lett.* **9**, 289–299.
MOROSIN, B. (1969). *Acta Cryst.* B**25**, 19–30.
MÜLLER, A., BÖSCHEN, I., BARAN, E. J. & AYMONINO, P. J. (1973). *Monatsh. Chem.* **104**, 836–847.
PAJUNEN, A. & LEHTONEN, M. (1972). *Suom. Kemistil. B*, **45**, 43–46.
PITZER, K. S. (1935). *Z. Kristallogr. A*, **92**, 131–135.
SHELDRICK, G. M. (1983). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Version 4.1. Univ. of Göttingen.

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$Lu_5Co_4Si_{14}$, a New Monoclinic Structure Type* Related to $Sc_5Co_4Si_{10}$ and $La_3Co_2Sn_7$

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Abstract. $Lu_5Co_4Si_{14}$, $M_r = 1503·8$, monoclinic, $mP46$, $P2_1/c$, $a = 12·245$ (10), $b = 7·756$ (3), $c = 7·684$ (4) Å, $\beta = 98·87$ (3)°, $V = 721·04$ (8) Å^3, $Z = 2$, $D_x = 6·927$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 413$ cm^{-1}, $F(000) = 1318$, $T = 293$ K, $R = 0·048$ for 2108 contributing independent reflections. The structure can be considered as an intergrowth of three different types of slabs. One slab is built up of close-packed Si-centered trigonal rare-earth prisms arranged as in the AlB_2 type. The second slab corresponds to a segment of a ternary $BaAl_4$-derivative structure, constructed of Lu_4Si_4 square antiprisms, but with only one of every two of the available prism centers occupied by Co atoms. The third slab is made up of rare-earth-centered Si cuboctahedra, connected by vertices, and with extra Co atoms positioned in between the polyhedra.

Introduction. In his thesis Yarovets (1978) reported on the new orthorhombic crystal structure of $Ho_3Co_2Si_7$ and 11 isotypic rare-earth–iron(cobalt)–silicon ($R_3T_2Si_7$) compounds. Our attention was retained by the proposed structure model which contains unexpected coordination polyhedra, in the form of very deformed Si cuboctahedra, around part of the rare-earth atoms. Such deformed polyhedra are unexpected and doubtful if one refers to the rare-earth coordination polyhedra observed in closely related structures, such as $La_3Co_2Sn_7$ (Dörrscheidt & Schäfer, 1980). Since the structure was refined to the very poor reliability R-factor value of 0·212, the proposed structure model is not necessarily fully correct.

In view of these unsatisfactory aspects of the original structure determination it appeared of interest to us to study anew this crystal structure. In connection with another study on non-stoichiometric $CeNiSi_2$-type phases in the Lu–Co–Si system (Chabot, Steinmetz & Parthé, 1986) we decided to investigate the crystal structure of '$Lu_3Co_2Si_7$', for which Yarovets reported an orthorhombic A-centered unit cell with $a = 3·826$, $b = 24·315$ and $c = 3·872$ Å. Our experiments demonstrate the existence of a new phase related to Yarovets' results but yet different.

Experimental. Sample of nominal composition $Lu_3Co_2Si_7$ was prepared by arc melting under argon from Lu and Co (99·99%) and Si (99·999%). The sample was then remelted and allowed to cool slowly using a levitation technique. Single crystal of irregular shape with 48 µm mean diameter was obtained from crushed ingots. Automatic four-circle diffractometer (Philips PW 1100), Laue symmetry $2/m$, lattice parameters given in *Abstract* from averaged θ values of 32 reflections and antireflections ($21 < 2\theta < 32°$, Mo $K\alpha$, $\lambda = 0·71069$ Å). Data collection: $\sin\theta/\lambda < 0·71$ Å^{-1}, spherical absorption correction $3·8 <$ s.a.c. $< 4·11$, 2108 unique reflections measured, $-17 \le h \le 17$, $0 \le k \le 10$, $-10 \le l \le 10$; 2 standard reflections (241, $\bar{2}\bar{4}\bar{1}$), ±2·7% variation; ω–2θ scan, ω-scan angle $(1·2 + 0·1\tan\theta)°$; 2108 observed reflections, 1617 with $|F| > 3\sigma(F)$; systematic absences $h0l$: $l \ne 2n$, $0k0$: $k \ne 2n$ leading to unique space group $P2_1/c$. The structure, however, was initially partially solved in space group $A2/m$ (using Patterson functions) because the weakness of the hkl reflections when $k+l \ne 2n$ led us to assume, erroneously, that the unit cell is A-centered

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* In memoriam of Professor Herbert Schäfer, Technische Hochschule Darmstadt, Federal Republic of Germany.

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