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Structure of the Cobalt Weberite Na_2CoAlF_7

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Abstract. Aluminium cobalt disodium heptafluoride, $AlCoNa_2F_7$, $M_r = 264.88$, monoclinic, $C2/c$, $a = 12.3777$ (4), $b = 7.2100$ (3), $c = 24.0192$ (9) Å, $\beta = 99.670$ (2)°, $V = 2113.1$ (1) Å^3, $Z = 16$, $D_x = 3.33$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 3.645$ mm^{-1}, $F(000) = 2000$, $T = 298$ (2) K, final $R = 0.021$ for 2403 independent reflections with $I > 3\sigma(I)$. The title structure is an intermediate case between the orthorhombic mineral weberite, Na_2MgAlF_7, and the trigonal Na_2MnAlF_7. As with Na_2CuFeF_7, Na_2CoAlF_7 is monoclinic ($C2/c$) and two $[CoF_5]^{3n-}$ chain directions are present (61.7° to each other). In Na_2CoAlF_7 a change of direction occurs for a sequence of two layers $[Co_2AlF_{10}]_n^{3n-}$ and the cell parameter c is therefore doubled.

Introduction. Compounds of the general formula $Na_2M^{II}M^{III}F_7$ have been widely studied and are derived from the mineral weberite, Na_2MgAlF_7, which crystallizes in the orthorhombic system (Bystrom, 1944). Most of these compounds have the same symmetry (Tressaud, Dance, Portier & Hagenmuller, 1974; Giusepetti & Tadini, 1978; Haegele, Verscharen, Babel, Dance & Tressaud, 1978; Knop, Cameron & Jochem, 1982; Laligant, Ferey, Heger & Pannetier, 1987); however some structures containing Mn^{II} are trigonal (Verscharen & Babel, 1978; Courbion, Ferey, Holler & Babel, 1988), probably due to the large divalent-cation size. Recently, structural modifications have been observed for Cu^{II} compounds (Kummer, Massa & Babel, 1988; Renaudin, Leblanc, Ferey, De Kozak & Samouël, 1988; Yakubovich, Urusov, Frenzen, Massa & Babel, 1990; Ruchaud, 1991) and these have been attributed to cationic Jahn–Teller effects. An intermediate monoclinic symmetry was previously assigned to $Na_2CuFe(Ga)F_7$ with space group $C2/c$ and a c cell parameter of around 12.9 Å. We report here the structure of a new weberite, Na_2CoAlF_7, which is directly derived from the Cu^{II} compound. The symmetry of the cell is also monoclinic with space group $C2/c$ but the cell parameter c is doubled.

Experimental. Na_2CoAlF_7 was prepared from a stoichiometric mixture of the dried binary fluorides by prolonged heating at 1020 K in a sealed platinum tube. Na_3AlF_6 and CoF_2 are present as impurities in the polycrystalline main product. Pink single crystals obtained by slow cooling (3 K h^{-1}) from 1100 K. A crystal of pyramidal shape with axis along **b** and with dimensions 0.20 × 0.14 × 0.20 mm was selected for data collection. Monoclinic symmetry was carefully established by film methods (Laue, Weissenberg, precession). During this study an apparent pseudo-threefold axis was checked and rejected by Laue films. Cell reduction trials point to a pseudo-rhombohedral cell ($a_R \simeq 24.04$ Å, $\alpha_R \simeq 17.17°$) which is deduced from the proposed monoclinic C lattice by the transformation

$$(a_R, b_R, c_R) = (a, b, c)\begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & -\frac{1}{2} \\ 1 & 1 & 1 \end{pmatrix}.$$

The rejection is confirmed by the inconsistency of the induced equivalent intensities ($R_{\rm int} = 0.21$ in the $\bar{3}$ Laue group). Cell parameters refined by the Pawley (1981) method: Philips PW1050 diffractometer, graphite-monochromated Cu $K\alpha$ radiation; 2θ range and step 18–70°, 0.02°; 1239 reflections; pseudo-Voigt profile function; background correction with a polynomial function [degree 5 in (2θ)]; 24 parameters refined; $R_p = 0.10$, $R_{wp} = 0.15$, $R_B = 0.05$. Data collection with an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; ω–2θ scan; 12 059 reflections measured, 2992 being unobserved; $(\sin\theta)/\lambda < 0.704$ Å^{-1}, $-16 \leq h \leq +16$, $-10 \leq k \leq +10$, $-30 \leq l \leq +30$; scan width $(0.80 + 0.35\tan\theta)$°; counter slit width $(3.00 + 1.50\tan\theta)$ mm; max. scan time 120 s; two standard reflections every 6 h with no systematic variation observed and a maximum relative deviation of 1%. Variance on each integrated intensity I assigned with the formula $\sigma^2(I) = \sigma^2_{\rm cs}(I) + (0.04I)^2$, where $\sigma_{\rm cs}$ is based on counting statistics. Corrections for Lorentz–polarization effects and for absorption based on azimuthal scans of eight reflections spanning the θ range [$(\Delta T/T)_{\rm max} = 4\%$]. Equivalent reflections for which $I/\sigma(I) > 3$ were averaged to give 2403 unique reflections ($R_{\rm int} =$

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Table 1. *Atomic fractional coordinates and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Wyckoff position	Site symmetry	*x*	*y*	*z*	B_{eq}
Na(1)	4(*a*)	$\bar{1}$	0	0	0	2.52 (6)
Na(2)	4(*b*)	$\bar{1}$	0	0.5	0	3.00 (7)
Na(3)	4(*c*)	$\bar{1}$	0.25	0.25	0	4.13 (9)
Na(4)	4(*e*)	2	0	0.2853 (2)	0.25	2.87 (6)
Na(5)	8(*f*)	1	0.2469 (1)	0.0456 (2)	0.24761 (4)	1.96 (4)
Na(6)	8(*f*)	1	0.3732 (1)	0.0089 (2)	0.12145 (5)	2.49 (4)
Co(1)	8(*f*)	1	0.12240 (3)	0.01138 (4)	0.37239 (1)	0.672 (8)
Co(2)	8(*f*)	1	0.37334 (3)	0.26382 (4)	0.37400 (2)	0.646 (8)
Al(1)	4(*d*)	$\bar{1}$	0.25	0.25	0.5	0.66 (3)
Al(2)	4(*e*)	2	0.5	0.2522 (1)	0.25	0.65 (3)
Al(3)	8(*f*)	1	0.1264 (1)	0.2651 (1)	0.12584 (4)	0.62 (2)
F(11)	8(*f*)	1	0.1680 (1)	0.0930 (2)	0.4530 (1)	1.53 (5)
F(12)	8(*f*)	1	0.3503 (1)	0.2767 (2)	0.4546 (1)	1.46 (5)
F(13)	8(*f*)	1	0.1723 (1)	0.4493 (2)	0.4687 (1)	1.46 (5)
F(21)	8(*f*)	1	0.4225 (1)	0.0751 (2)	0.2093 (1)	1.32 (5)
F(22)	8(*f*)	1	0.3949 (1)	0.2580 (2)	0.2933 (1)	1.36 (5)
F(23)	8(*f*)	1	0.4242 (1)	0.4372 (2)	0.2092 (1)	1.42 (5)
F(31)	8(*f*)	1	0.2618 (1)	0.3155 (2)	0.1126 (1)	1.42 (5)
F(32)	8(*f*)	1	0.0083 (1)	0.2118 (2)	0.3599 (1)	1.43 (5)
F(33)	8(*f*)	1	0.1738 (1)	0.0305 (2)	0.1401 (1)	1.29 (5)
F(34)	8(*f*)	1	0.0877 (1)	0.2210 (2)	0.0511 (1)	1.45 (5)
F(35)	8(*f*)	1	0.0783 (1)	0.4985 (2)	0.1115 (1)	1.30 (4)
F(36)	8(*f*)	1	0.1652 (1)	0.3109 (2)	0.2008 (1)	1.28 (5)
F(4)	8(*f*)	1	0.4704 (1)	0.3255 (2)	0.0948 (1)	1.27 (5)
F(5)	8(*f*)	1	0.2173 (1)	0.1996 (2)	0.3418 (1)	1.26 (5)

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

Co(1)F$_6$ octahedra		Co(2)F$_6$ octahedra	
Co(1)—F(31^{i})	2.001 (1)	Co(2)—F(22)	2.001 (2)
Co(1)—F(32)	2.008 (1)	Co(2)—F(4^{v})	2.003 (1)
Co(1)—F(4^{i})	2.010 (2)	Co(2)—F(12)	2.006 (2)
Co(1)—F(11)	2.012 (2)	Co(2)—F(5)	2.010 (1)
Co(1)—F(5)	2.013 (2)	Co(2)—F(35^{i})	2.017 (2)
Co(1)—F(23^{i})	2.020 (2)	Co(2)—F(33^{ii})	2.021 (2)
⟨Co(1)—F⟩	2.011	⟨Co(2)—F⟩	2.010
Co—F—Co angles			
Co(1^{ii})—F(4)—Co(2^{v})	125.5 (1)		
Co(1)—F(5)—Co(2)	126.6 (1)		
Al(1)F$_6$ octahedra		Al(2)F$_6$ octahedra	
Al(1)—F(11)(×2)	1.789 (2)	Al(2)—F(21)(×2)	1.786 (2)
Al(1)—F(12)(×2)	1.795 (2)	Al(2)—F(22)(×2)	1.797 (2)
Al(1)—F(13)(×2)	1.820 (2)	Al(2)—F(23)(×2)	1.820 (2)
⟨Al(1)—F⟩	1.801	⟨Al(2)—F⟩	1.801
Al(3)F$_6$ octahedra		Co—F—Al angles	
Al(3)—F(31)	1.795 (2)	Co(1)—F(11)—Al(1)	146.1 (1)
Al(3)—F(32^{iii})	1.798 (2)	Co(1^{ii})—F(23)—Al(2)	138.9 (1)
Al(3)—F(35)	1.799 (2)	Co(1^{ii})—F(31)—Al(3)	140.6 (1)
Al(3)—F(33)	1.804 (2)	Co(1)—F(32)—Al(3^{iii})	141.0 (1)
Al(3)—F(34)	1.807 (3)	Co(2)—F(12)—Al(1)	143.7 (1)
Al(3)—F(36)	1.814 (3)	Co(2)—F(22)—Al(2)	142.0 (1)
⟨Al(3)—F⟩	1.803	Co(2^{i})—F(33)—Al(3)	141.7 (1)
		Co(2^{ii})—F(35)—Al(3)	140.8 (1)
Na(1)F$_8$ polyhedra		Na(2)F$_8$ polyhedra	
Na(1)—F(34)(×2)	2.185 (2)	Na(2)—F(13^{iii})(×2)	2.405 (2)
Na(1)—F(12^{i})(×2)	2.556 (1)	Na(2)—F(34)(×2)	2.507 (2)
Na(1)—F(11^{iii})(×2)	2.615 (2)	Na(2)—F(35)(×2)	2.691 (2)
Na(1)—F(4^{vi})(×2)	2.680 (2)	Na(2)—F(12^{ii})(×2)	2.815 (1)
Na(3)F$_8$ polyhedra		Na(4)F$_8$ polyhedra	
Na(3)—F(13^{i})(×2)	2.439 (2)	Na(4)—F(21^{ii})(×2)	2.434 (2)
Na(3)—F(34)(×2)	2.533 (2)	Na(4)—F(36)(×2)	2.534 (2)
Na(3)—F(31)(×2)	2.725 (2)	Na(4)—F(32)(×2)	2.677 (2)
Na(3)—F(11^{ii})(×2)	2.835 (2)	Na(4)—F(23^{i})(×2)	2.798 (2)
Na(5)F$_8$ polyhedra		Na(6)F$_8$ polyhedra	
Na(5)—F(36^{i})	2.265 (2)	Na(6)—F(21)	2.149 (3)
Na(5)—F(36)	2.359 (2)	Na(6)—F(13^{i})	2.186 (3)
Na(5)—F(22)	2.496 (2)	Na(6)—F(33)	2.586 (2)
Na(5)—F(21)	2.508 (2)	Na(6)—F(35^{iv})	2.591 (2)
Na(5)—F(33)	2.591 (2)	Na(6)—F(32^{i})	2.593 (2)
Na(5)—F(5)	2.601 (2)	Na(6)—F(31)	2.595 (2)
Na(5)—F(23^{i})	2.629 (2)	Na(6)—F(4)	2.707 (2)
Na(5)—F(22^{i})	2.787 (2)	Na(6)—F(5^{i})	2.709 (2)

Symmetry code: (i) $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; (ii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (iii) $-x$, y, $\frac{1}{2}-z$; (iv) $\frac{1}{2}+x$, $y-\frac{1}{2}$, z; (v) $1-x$, y, $\frac{1}{2}-z$; (vi) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$.

0.015). Systematic absences $h+k=2n+1$ for *hkl* and $l=2n+1$ for *h*0*l* consistent with two possible space groups: *C*2/*c* and *Cc*. Atomic scattering factors for Na$^+$, Co^{2+}, Al^{3+}, F$^-$ and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Structure solved in the *C*2/*c* group by heavy-atom methods using *SHELX*76 (Sheldrick, 1976) on an IBM 3090-400 computer at the Computing Center of Montpellier. Sites of Co atoms found by Patterson-function deconvolution and Al, Na and F atoms located with several difference Fourier syntheses. Calculations (on *F*) with individual isotropic thermal parameters, a weighting scheme $w = 1/\sigma^2(F_o)$ and an empirical isotropic extinction parameter x $[F_c = F(1 - 10^{-4}xF^2/\sin\theta)]$ converged to $R = 0.058$ and $wR = 0.055$. The structure refined to $R = 0.021$ and $wR = 0.022$ with anisotropic thermal factors for all atoms; 207 parameters refined; $x = 38\ (1) \times 10^{-5}$; max. shift/e.s.d. in last cycle <0.06; $S = 2.68$; residual electron density range +0.51 [near Na(6)], -0.43 e Å^{-3}. The final atomic parameters are given in Table 1* and selected bond lengths and angles are listed in Table 2.

Discussion. Fig. 1(*a*) shows a polyhedral representation of the Na_2CoAlF_7 structure. As in the orthorhombic weberite, the structure contains $[M_2^{II}M^{III}F_{10}]_n^{3n-}$ layers of octahedra parallel to the (001) plane in which the M^{II} ions form chains of corner-sharing octahedra. The Co^{II}—F distances range from 2.001 to 2.021 Å which is in good agreement with the sum of the Shannon radii, 2.03 Å (Shannon, 1976). Two Co(1)—F—Co(2) angles exist along the direction of the chain (125.5 and 126.6°). Relationships have been found between the different weberite types based on relative orientation of $[M^{II}F_5]_n^{3n-}$ chains in successive $[M_2^{II}M^{III}F_{10}]_n^{3n-}$ layers (Babel & Tressaud, 1985; Yakubovich *et al*, 1990). These are: (*a*) in orthorhombic weberites all the chains are parallel to

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55414 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0332]

the *a* axis; (*b*) in the monoclinic $C2/c$ type found for Na_2CuFeF_7, there are two different successive directions (61.2° to each other) along [$\bar{1}$10] and [110]; and (*c*) in the trigonal Na_2MnFeF_7 type there are three different chain directions, changing from layer to layer by a 60° rotation. In Na_2CoAlF_7 there are also two $[CoF_5]^{3n-}$ chain directions (61.7° to each other) along [$\bar{1}$10] and [110] but the change occurs within a two-layer sequence. Fig. 1(*b*) shows such a sequence at the level $z = \frac{1}{2}$ with chains running along [110]. Therefore, the *c* parameter of the monoclinic lattice of Na_2CoAlF_7 has to be multiplied by a factor of two. This new model was first proposed for Na_2CuFeF_7 with space group $A2/n$ (Kummer *et al.*, 1988) but there were difficulties with structure refinement ($R = 0.12$) which were attributed to possible twinning. The conversion to the $C2/c$ cell is carried out using the transformation

$$(V') = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \\ V \\ \\ \end{pmatrix} + (-\tfrac{1}{4}, \tfrac{1}{4}, 0).$$

In $[Al(3)F_{4/2}F_2]$ octahedra, which make an interchain connection within the $[M_2^{II}M^{III}F_{10}]$ layer, and also in $[Al(1)F_{4/2}F_2]$ octahedra, which make an interlayer connection in a 'double layer', the terminal F atoms are in the *trans* position. Bond lengths for these terminal ligands [F(13) for the Al(1) atoms, F(34) and F(36) for the Al(3) atoms] are longer than the bridging ligands (Fig. 2*a*). $[Al(2)F_{4/2}F_2]$ octahedra connect together two consecutive 'double layers'. The terminal F(21) atoms are in the *cis* position here and form shorter bond lengths than the bridging F atoms (Fig. 2*b*). The Na atoms exhibit similar eightfold coordination, as seen in the orthorhombic and trigonal weberites. Na(1) and Na(6) are included in flattened hexagonal bipyramids with two short Na—F distances (~2.18 Å) and six longer Na—F distances in the equatorial hexagon (~2.66 Å). Na(2), Na(3) and Na(4) are included in distorted cubes with four Na—F distances of about

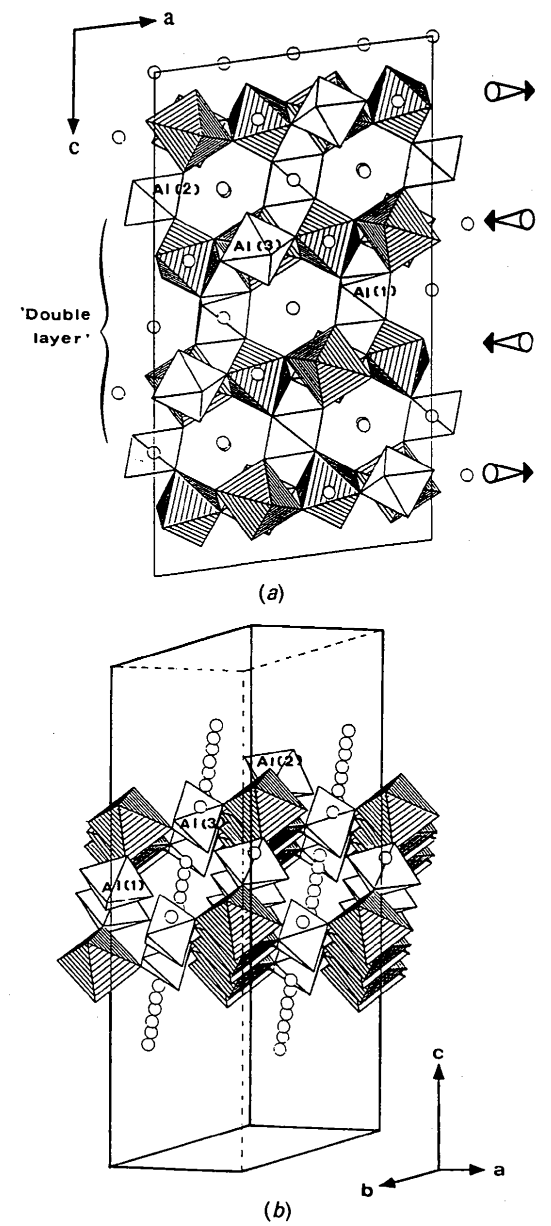

Fig. 1. Polyhedral representation of the Na_2CoAlF_7 structure (*STRUPLO*84; Fischer, 1985) showing its (*a*) projection on the (010) plane, with representation of a 'double layer' and (*b*) sequence of a 'double layer' at the $z = \frac{1}{2}$ level. [Hatched octahedra: $(CoF_6)^{4-}$; blank octahedra: $(AlF_6)^{3-}$; circles: Na^+].

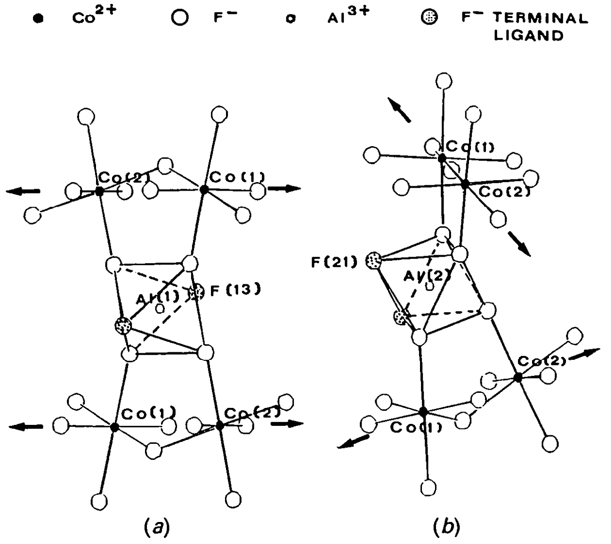

Fig. 2. Representation (*SCHAKAL*88; Keller, 1989) of the $(AlF_{4/2}F_2)^-$ connection between (*a*) $(CoF_5)_n^{3n-}$ parallel chains and (*b*) $(CoF_5)_n^{3n-}$ ~120° rotated Co^{2+} chains.

2.47 Å and four longer ones of about 2.76 Å. Na(5) atoms are included in more distorted polyhedra with Na—F distances ranging from 2.265 to 2.787 Å. Other compounds (Na_2CoFeF_7 and a second modification of Na_2CuFeF_7) exhibiting similar structural features have been investigated by Welsch & Babel (1992). Their results are in good agreement with ours.

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Structure of Methanol(nitrato)(2,2′:6′,2″-terpyridyl)copper(II) Perchlorate

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Abstract. $[Cu(NO_3)(C_{15}H_{11}N_3)(CH_3OH)]ClO_4$, $M_r = 490.3$, triclinic, $P\bar{1}$, $a = 9.105$ (2), $b = 9.588$ (2), $c = 11.753$ (3) Å, $\alpha = 78.21$ (2), $\beta = 80.45$ (2), $\gamma = 69.72$ (1)°, $V = 937.1$ (6) Å^3, $Z = 2$, $D_x = 1.737$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.36$ mm^{-1}, $F(000) = 498$, room temperature, $R = 0.054$ for 3051 independent reflections. The compound consists of discrete mononuclear $[Cu(terpy)(CH_3OH)(NO_3)]^+$ cationic units and non-coordinated perchlorate groups. The Cu atom is hexacoordinated and its configuration corresponds to a tetragonally distorted octahedron. A structural comparison is made with other terpyridyl-containing Cu^{II} complexes and the influence of the counterion in this series of complexes is anlayzed.

Introduction. Six- and five-coordinate complexes of formula $Cu(terpy)X_2.nH_2O$ (X = counterion and terpy = 2,2′:6′,2″-terpyridine) are interesting examples for investigating various aspects of vibronic coupling and the Jahn–Teller effect (Reinen & Friebel, 1979). These mono(terpyridine) complexes

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