sium hydrogen di-*p*-hydroxybenzoate hydrate (Blinc, Hadži & Novak, 1960) is consistent with the above view. And so is the agreement of the O(2)···O(2^{i}) bond length with the value of about 2·45 Å, tentatively suggested by Coulson (1957, 1959) to be the upper limit for the length of a truly symmetrical OHO bond.

The environment of the O(2)···O(2^{i}) bond is symmetrical and also closely packed; the non-bonded distances H(2)···O(3) of 2·42 Å and H(2)···C(1) of 2·08 Å are shorter than the sum of van der Waals radii. It might be that the resulting strain is sufficient to establish symmetry within the bond itself.

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The Crystal Structure of $(CH_3)_4NNiCl_3$*

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The crystal structure of $(CH_3)_4NNiCl_3$ has been determined from three-dimensional Mo $K\alpha$ X-ray data collected by counter methods. The structure has been refined by the full-matrix least-squares technique. The material crystallizes in the space group $P6_3/m$ (C_{6h}^2) or $P6_3$ (C_6^6) of the hexagonal system, with two molecules in a unit cell of dimensions $a=b=9{\cdot}019$, $c=6{\cdot}109$ Å. The structure consists of linear one-dimensional chains of nickel atoms with three bridging chlorine atoms between the nickel atoms.

Introduction

Furlani & Morpurgo (1961) first reported the syntheses of two colored complexes, one red and one blue, from solutions of tetramethylammonium bromide and nickel bromide in nitromethane. Magnetic susceptibility measurements gave $\mu_{\text{eff}}=3{\cdot}8$ B.M. (370°K) for the blue crystals and 3·23 B.M. (299°K) for the red crystals. The elementary analyses were reported to give the same stoichiometry, namely $[(CH_3)_4N]_2NiBr_4$. Both complexes dissolved in nitromethane to give blue solutions, and the red crystals could be converted to the blue crystals upon heating. It was proposed that the red and blue forms were isomers similar to the α and β forms of $CoCl_2.2C_5H_5N$ (Dunitz, 1957). We have repeated Furlani & Morpurgo's synthesis and readily obtained the two forms of the crystals; however, the red modification proved to be $(CH_3)_4NNiBr_3$ with Ni^{2+} ions in a trigonally distorted octahedral ligand field. The electronic absorption spectra of this complex matched that given by Furlani & Morpurgo (1961) and agreed with the structural results (Stucky, D'Agostino & McPherson, 1966).

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Solutions of the corresponding chlorides also give two crystalline compounds, yellow-brown needles of $(CH_3)_4NNiCl_3$ and blue prisms of $[(CH_3)_4N]_2NiCl_4$. In connection with some electron spin resonance and optical spectroscopic studies of the first row transition metal complexes, we wished to verify that $(CH_3)_4NNiCl_3$ was indeed isostructural with $(CH_3)_4NNiBr_3$ and to obtain interatomic distances and angles for the former complex. The results of the structural analysis of $(CH_3)_4NNiCl_3$ are reported here.

Experimental

$(CH_3)_4NNiCl_3$ was prepared by slow evaporation of a solution of nitromethane with stoichiometric amounts of $(CH_3)_4NCl$ and anhydrous $NiCl_2$. Transmission absorption spectra were measured with a Cary model 14m recording spectrometer using a Nujol mull on filter paper. The results agreed well with those reported by Goodgame, Goodgame & Weeks (1964). The crystals were stable to 100°C and were examined on a hot plate with a polarizing microscope at this temperature in order to prevent decomposition due to reaction with water in the atmosphere. The crystals grew in the form of rods along [0001] with triangular or hexagonal cross sections. Unlike crystals of $(CH_3)_4NNiBr_3$, which can be grown very easily and to almost any size desired by the method above, crystals of $(CH_3)_4NNiCl_3$ were always small and frequently grew with large numbers of striations along the length of the rod. A needle crystal with a hexagonal cross section which showed good optical properties was measured and sealed into a 0·2 mm soft glass capillary for data collection. The crystal was approximated as a cylinder with a radius of 0·055 mm and a length of 0·50 mm. From Weissenberg and precession photographs the compound was found to possess Laue symmetry $6/m$ with systematic absences of $000l$ for l odd. Lattice parameters and their standard deviations were obtained from a least-squares refinement of the setting angles of twenty high-order reflections from a crystal which had been carefully centered on a Picker four-circle X-ray diffractometer. The results were:

$$a=b=9{\cdot}019\pm0{\cdot}001,\ c=6{\cdot}109\pm0{\cdot}001\ \text{Å},\ \alpha=\beta=90°,$$
$$\gamma=120°\ (t=28°\text{C},\ \lambda\ (\text{Mo}\ K\alpha_1)=0{\cdot}70926\ \text{Å}).$$

The observed density was found by the flotation method to be 1·78 ± 0·01 $g.cm^{-3}$; the calculated density for two formula weights per unit cell is 1·817 $g.cm^{-3}$. The linear absorption coefficient with Mo $K\alpha$ radiation is 30·32 cm^{-1}, giving a μR value of 0·167.

The procedures used in data collection and processing were the same as those described elsewhere (Stucky, Folkers & Kistenmacher, 1967). Data were collected manually by the θ–2θ scan technique on a Picker diffractometer with zirconium filtered Mo$K\alpha$ radiation. A takeoff angle of 0·7° was used. Standard reflections were measured every twelve hours and indicated no decomposition or change in intensity with time. Backgrounds were measured by a stationary-crystal, stationary-counter technique for 20 seconds at the beginning and end of each scan. One form of data was collected to a 2θ value of 60°. 460 unique reflections were measured, of which 176 were called unobserved. At the 99·7% confidence level, an observation is statistically significant if $I_{\text{obs}} > 3\sigma(I)$. This criterion was used to determine whether a reflection was observed or unobserved. The intensity assigned to all reflections for which $I_{\text{obs}} < 3\sigma(I)$ was $I_{\text{obs}} = \sigma(I)$. The large number of unobserved data is undoubtedly partly due to the small size of the crystal used. All data were included in the full-matrix least-squares refinement; however, during the refinement unobserved reflections were given a weight of zero if $F_{\text{obs}} > F_{\text{calc}}$. Absorption corrections were made for the cylindrical crystal described above and led to transmission factors ranging from 0·70 to 0·76. The secondary extinction correction of Zachariasen (1963) was included and a version of the least-squares program ORFLS (Busing, Martin & Levy, 1962) was modified to allow refinement of the secondary extinction parameter, C. Corrections were made to F_{calc} according to the relation

$$F_{\text{obs}} = K'F_{\text{calc}}[1 + B(2\theta)CJ_{\text{obs}}]^{-1}$$

where K' is a scale factor and the remaining terms are the same as those given by Zachariasen (1963). The overall temperature factor option was dropped from the program and the corresponding derivatives replaced by the appropriate derivatives which arise from the above expression. The reflection 1000 was not included in the refinement because a large streak component and the close proximity of an incompletely attenuated $K\beta$ peak made an accurate estimation of the background difficult. Weights were determined from the relation

$$\sigma(F) = 0{\cdot}5K(F/I)[\text{Tc} + \text{Bg} + (kI)^2]^{\frac{1}{2}}$$

where K = scale factor
F = observed structure factor
I = observed intensity
Tc = total integrated counts
Bg = background counts
$k = 0{\cdot}03$.

Anomalous dispersion corrections for Cl and Ni and form factors for Cl^0, Ni^0, C^0 and N^0 were taken from Tables 3.3.3C and 3.3.1A of *International Tables for X-ray Crystallography* (1962).

Solution and refinement of the structure

A three-dimensional Patterson function gave initial Cl, Ni and N coordinates. The following four models were refined by the full-matrix least-squares method:

(I) No disorder, space group $P6_3$
(II) No disorder, inverted, space group $P6_3$
(III) Disordered methyl groups, space group $P6_3/m$
(IV) Twinned crystal with equal contributions of (I) and (II) .

Table 1. *Positional and thermal parameters* for* $(CH_3)_4NNiCl_3$

	Model	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	(I)	0·0903 (2)	0·2362 (2)	0·7596 (17)	0·0129 (3)	0·0082 (3)	0·0112 (4)	0·0053 (3)	0·0015 (18)	0·0012 (16)
	(II)	0·0903 (3)	0·2362 (2)	0·7550 (17)	0·0129 (3)	0·0082 (3)	0·0113 (4)	0·0053 (3)	0·0017 (17)	0·0013 (15)
	(III)	0·0903 (2)	0·2361 (2)	$\frac{3}{4}$	0·0130 (3)	0·0083 (3)	0·0112 (4)	0·0053 (2)	0	0
	(IV)	0·0902 (2)	0·2360 (2)	0·7567 (17)	0·0126 (3)	0·0081 (3)	0·0111 (4)	0·0051 (2)	0·0012 (19)	0·0010 (16)
Ni	(I)	0	0	0	0·0069 (2)	0·0069	0·0084 (4)	0·0035	0	0
	(II)	0	0	0	0·0069 (2)	0·0069	0·0084 (4)	0·0035	0	0
	(III)	0	0	0	0·0070 (2)	0·0060	0·0086 (4)	0·0035	0	0
	(IV)	0	0	0	0·0068 (2)	0·0068	0·0082 (3)	0·0034	0	0
C(2)	(I)	0·161 (2)	0·538 (2)	0·318 (5)	0·014 (2)	0·028 (3)	0·072 (13)	0·007 (2)	0·013 (4)	0·019 (6)
	(II)	0·161 (2)	0·539 (2)	0·311 (5)	0·013 (2)	0·028 (3)	0·074 (14)	0·006 (2)	0·014 (5)	0·019 (6)
	(III)	0·160 (2)	0·539 (2)	0·312 (3)	0·014 (2)	0·028 (3)	0·050 (10)	0·006 (2)	0·009 (4)	0·015 (4)
	(IV)	0·162 (2)	0·538 (2)	0·313 (5)	0·014 (2)	0·028 (3)	0·079 (14)	0·005 (2)	0·011 (4)	0·016 (5)
C(1)	(I)	$\frac{1}{3}$	$\frac{2}{3}$	0·023 (4)	0·059 (7)	0·059	0·003 (5)	0·029	0	0
	(II)	$\frac{1}{3}$	$\frac{2}{3}$	0·017 (4)	0·059 (7)	00·59	0·004 (5)	0·029	0	0
	(III)	$\frac{1}{3}$	$\frac{2}{3}$	0·010 (5)	0·057 (7)	0·057	0·011 (6)	0·028	0	0
	(IV)	$\frac{1}{3}$	$\frac{2}{3}$	0·019 (4)	0·063 (7)	0·063	0·006 (6)	0·031	0	0
N	(I)	$\frac{1}{3}$	$\frac{2}{3}$	0·270 (10)	0·008 (1)	0·008	0·016 (7)	0·004	0	0
	(II)	$\frac{1}{3}$	$\frac{2}{3}$	0·268 (10)	0·008 (1)	0·008	0·014 (7)	0·004	0	0
	(III)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0·008 (1)	0·008	0·019 (3)	0·004	0	0
	(IV)	$\frac{1}{3}$	$\frac{2}{3}$	0·262 (10)	0·009 (1)	0·009	0·018 (6)	0·004	0	0

* The form of the anisotropic ellipsoid is $\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right]$. For Cl, $B_{13}=B_{23}=0$ and for Ni, C(1) and N, $B_{11}=B_{22}=2B_{12}$; $B_{13}=B_{23}=0$.

The refinements of the four models are compared in Table 1. Difference Fourier calculations did not reveal the positions of the hydrogen atoms and they are not included. Extinction proved to be negligible in this compound, the refined value of C being less than 10^{-6} in all cases. The maximum value of J_{obs} was 12547·4. The values of $B(2\theta)$ were between 1·00 and 1·46, so that the upper limit of the quantity $[1+B(2\theta)CJ_{\text{obs}}]$ was 1·02.

(I): Carbon atom positions were calculated from the known geometry of the tetramethylammonium ion and packing considerations. Isotropic least-squares refinement quickly led to a value of $R_1=\Sigma\,||F_o|-|F_c||/\Sigma F_o=$ 6·9% for observed data. Subsequent anisotropic refinement gave values of $R_1=4\cdot8$ for observed data and $R_2=[\Sigma w(F_o-F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}=5\cdot0\%$ for all data.

(II): Following the notation of Patterson (1963), we have for (I)

$$F_+(\text{I})=A+\sum_r\delta_{1r}A_r-\sum_r\delta_{2r}B_r \qquad\qquad$$
$$\qquad\qquad +i(B+\sum_r\delta_{1r}B_r+\sum_r\delta_{2r}A_r)\,, \quad (1)$$

where A_r, B_r, δ_{1r}, and δ_{2r} are the structure factor components and dispersion constants for the rth dispersive element, and A and B are the non-dispersive structure factor components for the whole structure. F_+ is the structure factor for positive Miller indices. (II) can be obtained by operating with the symmetry operation $\bar{1}$ on (I). Thus, for (II),

$$F_+(\text{II})=A+\sum_r\delta_{1r}A_r+\sum_r\delta_{2r}B_r \qquad\qquad$$
$$\qquad\qquad -i(B+\sum_r\delta_{1r}B_r-\sum_r\delta_{2r}A_r)\,. \quad (2)$$

This is the same expression which one obtains if the positional parameters are left as in (I) and the signs of the Miller indices changed [in Patterson's (1963) notation $F_-(\text{I})$]. The original indices were accordingly changed in sign and the data refined to $R_1=4\cdot7\%$ for observed data and $R_2=5\cdot0\%$ for all data.

(III): The methyl groups are reflected through a mirror plane at $z=\frac{1}{4}$ and $\frac{3}{4}$. The nitrogen and chlorine atoms are assumed to be fixed at $z=\frac{1}{4}$ and $z=\frac{3}{4}$. The structure factor is of the form

$$F_+(\text{III})=F_-(\text{III})=2A+2\sum_r\delta_{1r}A_r+2i\sum\delta_{2r}A_r\,. \quad (3)$$

The final R values were $R_1=4\cdot8\%$ for observed data and $R_2=5\cdot0\%$ for all data. We were unable to distinguish between this model and a model in which the chlorine and nitrogen atoms were slightly displaced from $z=\frac{1}{4}$ and $z=\frac{3}{4}$.

Table 2. *Selected distances and angles for model* (III)

For atom numbering, see Figs. 1 and 2. The values have not been corrected for the possible effects of thermal motion.

Bonded distances		Angles	
Ni–Cl(1)	2·408 (1) Å	Cl(1)–Ni–Cl(2)	84·05 (4)°
N –C(1)	1·46 (3)	Cl(1)–Ni–Cl(3)	95·95 (4)
N –C(2)	1·45 (1)	C(1) –N –C(2)	104·99 (74)
		C(2) –N– C(3)	113·56 (60)

Near neighbor distances within an ion		Near neighbor distances between ions*	
C(1) –C(2)	2·31 (3) Å		
C(2) –C(3)	2·43 (3)	Cl —C(2)	3·60 (1) Å
Cl(1)–Cl(4)	3·224 (3)	Cl —C(1)	3·73 (1)
Cl(1)–Cl(3)	3·577 (1)	C(1)–C(2)	4·06 (2)

* The shortest distance of the type specified is given.

Table 3. *Observed and calculated structure factors*

Unobserved reflections are indicated by an asterisk.

H	L	OBS	CAL
******K= 0*******			
0	2	46.8	46.3
0	4	87.6	84.0
0	6	11.7	9.1
0	8	33.3	32.0
1	1	18.8	16.4
1	2	12.4	13.1
1	3	3.8	.9*
1	4	50.6	49.5
1	5	4.6	1.5*
1	6	4.8	4.0*
1	7	5.1	2.2*
1	8	20.7	20.0
2	0	22.3	19.5
2	1	52.7	55.6
2	2	56.0	58.5
2	3	35.0	33.4
2	4	15.4	14.5
2	5	20.8	21.7
2	6	27.3	26.4
2	7	12.4	13.2
2	8	5.6	5.4*
3	0	19.9	18.9
3	1	43.4	42.4
3	2	60.4	60.9
3	3	34.5	34.3
3	4	15.4	15.2
3	5	24.5	25.1
3	6	27.8	27.6
3	7	16.8	16.5
3	8	5.5	5.1*
4	0	22.8	18.8
4	1	10.5	10.3
4	2	41.8	43.5
4	3	4.4	5.2*
4	4	16.3	16.0
4	5	4.8	2.7*
4	6	20.2	19.9
4	7	5.3	2.6*
4	8	5.7	6.7*
5	0	23.5	21.2
5	1	16.5	16.4
5	2	35.8	35.9
5	3	14.6	15.0
5	4	12.1	12.5
5	5	13.0	11.9
5	6	18.8	18.8
5	7	8.7	8.5
6	0	24.7	18.9
6	1	16.5	15.7
6	2	29.9	30.1
6	3	13.3	13.5
6	4	11.9	10.9
6	5	9.9	10.5
6	6	17.8	17.9
6	7	6.0	7.2*
7	0	22.7	17.2
7	1	4.8	.4*
7	2	21.1	21.6
7	3	4.9	.9*
7	4	10.9	11.8
7	5	5.1	1.3*
7	6	14.0	12.4
8	0	21.3	23.9
8	1	7.7	6.5
8	2	7.6	7.4
8	3	7.6	6.0
8	4	18.4	18.7
8	5	5.4	4.7*
9	0	20.4	18.3
9	1	5.2	4.7*
9	2	8.4	6.8
9	3	8.5	4.1
9	4	13.8	14.6
9	5	5.4	2.9*
10	0	6.6	4.0*
10	1	8.4	5.7
10	2	14.2	15.3
10	3	5.4	5.4*
11	0	6.4	4.1*
11	1	5.5	1.6*
******K= 1*******			
1	0	69.6	68.0
1	1	12.5	10.9
1	2	43.4	43.1
1	3	8.8	8.6
1	4	31.8	32.3
1	5	5.8	6.3*
1	6	21.4	21.2
1	7	6.3	4.2*
1	8	11.1	11.6
2	0	4.3	1.8*
2	1	49.5	49.6
2	2	68.5	68.7
2	3	30.8	32.2
2	4	7.9	7.2
2	5	20.2	20.3
2	6	29.3	29.4
2	7	14.1	14.2
2	8	5.7	2.7*
3	0	29.1	29.4
3	1	36.7	35.2
3	2	44.8	44.1
3	3	25.2	25.7
3	4	11.6	11.9
3	5	17.0	18.1
3	6	24.5	25.0
3	7	10.2	11.3
3	8	5.7	4.5*
4	0	26.1	23.6
4	1	21.5	21.2
4	2	37.4	39.1
4	3	12.2	13.6
4	4	15.5	16.8
4	5	9.5	8.7
4	6	19.6	19.7
4	7	5.3	6.0*
5	0	6.1	6.0*
5	1	32.9	34.7
5	2	41.1	42.7
5	3	28.9	29.4
5	4	4.8	4.6*
5	5	20.4	21.8
5	6	22.3	22.7
5	7	14.3	14.1
6	0	13.9	11.8
6	1	14.0	12.5
6	2	28.2	29.2
6	3	11.5	10.7
6	4	9.0	9.7
6	5	8.1	8.0
6	6	15.2	15.1
7	0	35.5	34.3
7	1	4.8	1.7*
7	2	4.9	1.4*
7	3	4.9	.3*
7	4	25.2	25.9
7	5	5.1	.3*
7	6	5.2	.4*
8	0	33.6	32.6
8	1	5.0	1.0*
8	2	4.9	3.3*
8	3	5.1	1.0*
8	4	22.2	23.9
8	5	5.3	1.0*
9	0	18.3	15.7
9	1	5.1	1.1*
9	2	5.2	6.8*
9	3	5.3	1.1*
9	4	12.8	11.5
10	0	6.3	5.0*
10	1	5.6	4.6*
10	2	11.6	12.2
******K= 2*******			
1	0	20.9	19.2
1	1	5.3	4.3
1	2	56.0	55.6
1	3	4.0	3.2*
1	4	13.6	12.7
1	5	4.6	1.7*
1	6	27.1	26.6
1	7	5.2	2.1*
1	8	5.7	4.5*
2	0	48.6	48.4
2	1	7.9	8.0
2	2	29.7	30.4
2	3	10.2	9.7
2	4	33.4	33.0
2	5	8.9	8.5
2	6	14.2	13.2
2	7	6.4	5.8*
2	8	14.5	13.1
3	0	40.9	41.2
3	1	4.1	.3*
3	2	19.2	20.8
3	3	4.6	2.3*
3	4	30.5	31.0
3	5	4.8	2.9*
3	6	9.5	8.0
3	7	5.3	1.3*
4	0	26.4	25.4
4	1	15.1	13.8
4	2	28.3	29.3
4	3	13.9	12.4
4	4	15.9	15.7
4	5	9.7	9.5
4	7	5.5	6.6*
5	0	13.1	14.8
5	1	4.6	7.6*
5	2	30.3	30.8
5	3	4.9	7.2*
5	4	10.7	9.8
5	5	5.0	6.1*
5	6	15.7	17.2
5	7	5.7	4.3*
6	0	24.3	23.8
6	1	4.9	.2*
6	2	13.3	14.4
6	3	4.9	.7*
6	4	15.1	15.4
6	5	5.2	.8*
7	0	30.4	30.8
7	1	4.8	1.5*
7	2	5.0	.2*
7	3	5.0	2.3*
7	4	23.0	23.9
7	5	5.3	2.2*
8	0	25.1	23.2
8	1	5.0	2.5*
8	2	5.1	1.2*
8	3	5.2	2.2*
8	4	19.1	18.4
9	0	8.7	5.6
9	1	5.3	2.5*
9	2	13.8	13.1
9	3	5.5	2.0*
******K= 3*******			
1	0	46.9	46.2
1	1	15.9	16.2
1	2	26.3	26.5
1	3	14.1	13.2
1	4	27.6	28.1
1	5	10.5	10.1
1	6	13.9	12.8
1	7	5.2	6.0*
1	8	13.3	12.0
2	0	74.2	75.6
2	1	6.3	5.7
2	2	9.0	6.5
2	3	6.9	4.0
2	4	46.8	48.4
2	5	4.8	2.5*
2	6	5.0	3.7*
2	7	5.3	1.0*
3	0	64.2	63.6
3	1	5.3	3.2*
3	2	4.5	2.6*
3	3	5.9	1.6*
3	4	42.9	43.1
3	5	6.1	.8*
3	6	5.5	1.7*
3	7	6.6	.7*
4	0	20.0	20.9
4	1	4.6	1.6*
4	2	25.1	25.2
4	3	4.8	2.4*
4	4	14.6	14.7
4	5	5.1	2.4*
4	6	12.7	13.8
4	7	5.5	1.9*
5	0	4.9	5.8*
5	1	17.8	16.8
5	2	30.5	31.0
5	3	16.3	14.9
5	4	4.9	5.5*
5	5	12.9	11.8
5	6	16.3	16.6
6	0	19.1	17.4
6	1	11.3	11.2
6	2	14.2	14.3
6	3	8.6	8.7
6	4	14.6	13.6
6	5	5.2	6.2*
6	6	8.8	7.9
7	0	15.8	16.0
7	1	5.2	5.3*
7	2	10.5	10.1
7	3	5.3	4.9*
7	4	11.6	11.6
7	5	5.5	3.9*
8	0	5.3	7.0*
8	1	5.4	4.2*
8	2	14.5	13.5
8	3	5.4	3.7*
9	0	6.6	5.6*
9	1	5.4	2.0*
******K= 4*******			
1	0	63.3	65.4
1	1	4.1	4.3*
1	2	4.2	2.9*
1	3	4.4	2.5*
1	4	41.9	43.5
1	5	4.8	1.6*
1	6	5.0	1.3*
1	7	5.2	1.2*
2	0	57.0	57.8
2	1	4.5	6.5*
2	2	4.4	1.8*
2	3	4.6	3.9*
2	4	41.4	41.9
2	5	5.0	2.0*
2	6	5.0	3.2*
2	7	5.4	.8*
3	0	28.2	28.6
3	1	8.7	8.8
3	2	16.5	17.5
3	3	4.6	5.9*
3	4	20.8	22.0
3	5	4.9	3.7*
3	6	5.2	8.0*
3	7	5.5	2.4*
4	0	12.5	12.8
4	1	21.2	20.3
4	2	27.1	27.5
4	3	16.1	16.7
4	4	7.9	7.3
4	5	14.4	12.1
4	6	17.7	16.3
5	0	5.0	7.4*
5	1	16.1	16.2
5	2	25.1	25.0
5	3	14.3	14.7
5	4	5.0	4.2*
5	5	13.7	11.3
5	6	15.0	15.1
6	0	10.2	9.4
6	1	5.0	1.1*
6	2	18.4	16.9
6	3	5.1	1.4*
6	4	8.6	7.1
6	5	5.3	1.3*
7	0	7.6	6.9
7	1	14.2	12.1
7	2	15.1	14.2
7	3	11.6	10.4
7	4	5.4	5.6*
8	0	6.4	2.0*
8	1	9.3	8.1
8	2	15.3	14.5
******K= 5*******			
1	0	28.3	29.2
1	1	12.2	11.3
1	2	19.8	21.3
1	3	8.3	8.0
1	4	21.2	22.2
1	5	4.9	4.9*
1	6	9.2	9.8
1	7	5.5	2.7*
2	0	32.1	33.4
2	1	10.7	9.7
2	2	15.0	15.2
2	3	5.0	8.4*
2	4	19.0	20.2
2	5	5.0	6.4*
2	6	11.7	10.3
2	7	5.5	4.3*
3	0	7.6	8.0
3	1	7.4	6.1
3	2	28.3	29.3
3	4	4.9	6.3*
3	5	5.3	1.7*
3	6	16.6	16.3
4	0	9.7	8.0
4	1	13.1	12.2
4	2	23.0	23.4
4	3	8.4	10.3
4	4	5.0	6.7*
4	5	5.5	7.8*
4	6	13.1	13.2
5	0	16.9	16.3
5	1	6.1	4.1*
5	2	11.8	10.9
5	4	12.3	12.6
6	0	8.4	9.2
6	1	5.7	8.6*
6	2	13.7	12.6
6	3	5.3	7.9*
6	4	5.6	7.4*
7	0	5.3	3.7*
7	1	5.6	6.6*
7	2	14.1	14.0
******K= 6*******			
1	0	4.9	8.0*
1	1	18.5	17.4
1	2	32.9	32.5
1	3	13.6	13.3
1	4	4.9	7.2*
1	5	5.0	9.3*
1	6	15.9	16.9
2	0	4.8	3.9*
2	1	16.1	16.2
2	2	30.0	31.5
2	3	16.4	15.7
2	4	5.0	3.4*
2	5	13.6	12.7
2	6	16.6	17.4
3	0	15.0	14.2
3	1	5.4	7.2*
3	2	17.5	18.2
3	3	5.0	6.3*
3	4	10.3	9.3
3	5	5.2	4.9*
3	6	12.0	11.0
4	0	20.8	21.6
4	1	4.9	.6*
4	2	5.1	5.4*
4	3	5.1	.5*
4	4	16.6	16.6
4	5	5.4	.2*
5	0	22.9	22.5
5	1	5.2	.8*
5	2	5.1	.6*
5	3	5.4	.6*
5	4	16.9	16.6
6	0	12.0	11.6
6	1	6.3	3.8*
6	2	6.5	6.5*
******K= 7*******			
0	2	21.0	21.6
1	0	12.4	13.6
1	1	18.3	18.4
1	2	21.1	21.5
1	3	15.2	15.4
1	4	8.9	8.5
1	5	9.6	11.6
1	6	13.2	13.1
2	0	9.2	7.5
2	1	12.5	13.6
2	2	25.7	21.7
2	3	12.6	11.5
2	4	5.1	6.0*
2	5	5.2	8.8*
3	0	19.3	19.8
3	1	5.0	.0*
3	2	5.0	6.2*
3	3	5.1	.0*
3	4	14.5	14.9
3	5	5.4	.1*
4	0	26.3	26.4
4	1	5.1	.2*
4	2	5.3	4.1*
4	3	5.4	.1*
4	4	20.0	20.8
5	0	15.2	15.5
5	1	5.4	.8*
5	2	5.3	2.6*
******K= 8*******			
1	0	10.9	10.8
1	1	4.9	1.4*
1	2	16.2	16.8
1	3	5.0	1.3*
1	4	5.4	7.9*
1	5	5.4	.8*
2	0	11.9	11.0
2	1	5.2	5.4*
2	2	13.1	12.8
2	3	5.2	4.6*
2	4	5.3	8.9*
3	0	15.7	16.0
3	1	5.3	4.1*
3	2	5.4	5.0*
3	3	5.3	3.2*
4	0	13.7	14.0
4	1	5.3	.0*
4	2	5.5	3.7*
******K= 9*******			
1	0	8.2	6.1
1	1	9.9	9.8
1	2	16.1	15.9
1	3	9.7	8.5
1	4	5.3	4.0*
2	0	8.3	5.1
2	1	11.3	10.0
2	2	12.8	13.7
2	3	9.9	9.2
3	0	5.6	8.0*
3	1	5.4	.4*
******K=10*******			
1	0	5.4	4.1*
1	1	11.1	8.6
1	2	13.8	12.8

(IV): Again, following Patterson (1963), one has

$$F_{\pm}^2 = A^2+B^2+2\sum_r \delta_{1r}(AA_r+BB_r) - 2\sigma\sum_r \delta_{2r}(AB_r-BA_r)+\sum_{r,}\sum_{s}(\delta_{1r}\delta_{1s}+\delta_{2r}\delta_{2s})(A_rA_s + B_rB_s)-\sigma\sum_{r,}\sum_{s}(\delta_{1r}\delta_{2s}-\delta_{1s}\delta_{2r})(A_rB_s-A_sB_r)\,. \quad (4)$$

The intensity given by model (IV) is

$$I(\mathrm{IV})\propto|F_+(\mathrm{I})|^2+|F_+(\mathrm{II})|^2 \quad (5)$$

$$\propto|F_+(\mathrm{I})|^2+|F_-(\mathrm{I})|^2\,, \quad (6)$$

so that

$$I(\mathrm{IV})/2\propto A^2+B^2+2\sum_r \delta_{1r}(AA_r+BB_r) + \sum_{r,}\sum_{s}(\delta_{1r}\delta_{1s}+\delta_{2r}\delta_{2s})(A_rA_s+B_rB_s)\,. \quad (7)$$

This problem is easily treated as suggested by Patterson (1963). We define

$$|F|_o^2=S_o-2\sum_r \delta_{1r}(AA_r+BB_r) - \sum_{r,}\sum_{s}(\delta_{1r}\delta_{1s}+\delta_{2r}\delta_{2s})(A_rA_s+B_rB_s)\,, \quad (8)$$

where

$$S_o=\tfrac{1}{2}\{|F_+(\mathrm{I})|_o^2+|F_-(\mathrm{I})|_o^2\}\propto\tfrac{1}{2}I_{\mathrm{obs}}(\mathrm{IV})\,. \quad (9)$$

$|F|_o$ is then used to construct the difference vector in the least-squares analysis. The least-squares program of Busing, Martin & Levy (1962) was modified to calculate a new set of values of $|F|_o$ between successive stages of refinement according to the above equation. The final values of R were $R_1=4{\cdot}7\%$ for observed data and $R_2=4{\cdot}8\%$ for all data.

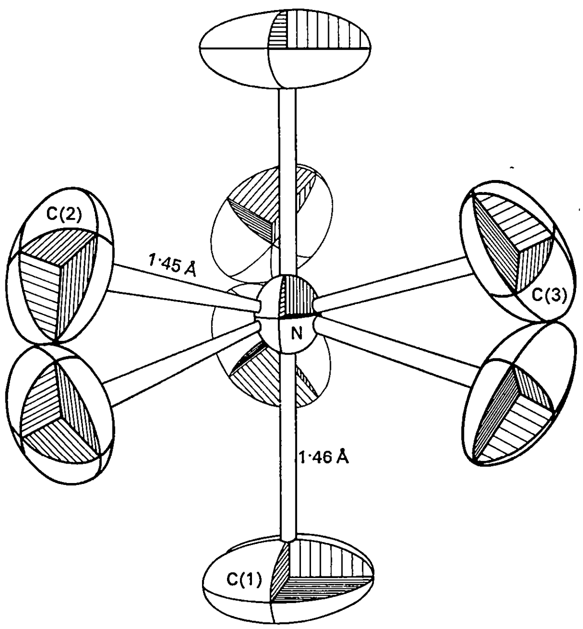

Fig. 1. Bond distances and thermal ellipsoids obtained for the disordered model of the tetramethylammonium cation assuming the space group $P6_3/m$ [model (III)].

Discussion

There are very few differences among the four models which were tried. The thermal parameters for model (III) were slightly less along [0001] for the C(2) atoms. In addition, the nitrogen–carbon bond lengths were more consistent with each other and with the commonly accepted value of 1·47 Å. Model (IV), however, is favored (see below) by Hamilton's (1965) R-factor test. Our main interest in the structure is the anion. The maximum variation in the nickel–chlorine bond length is 0·03 Å among the four models. This is also the same magnitude of the difference in length when the Ni–Cl bond length was calculated assuming a model in which the chlorine was riding on the nickel and a model in which the two atoms were assumed to move independently of each other. The accuracy of the structural determination is limited by the room temperature data and by our inability to locate the hydrogen atoms.

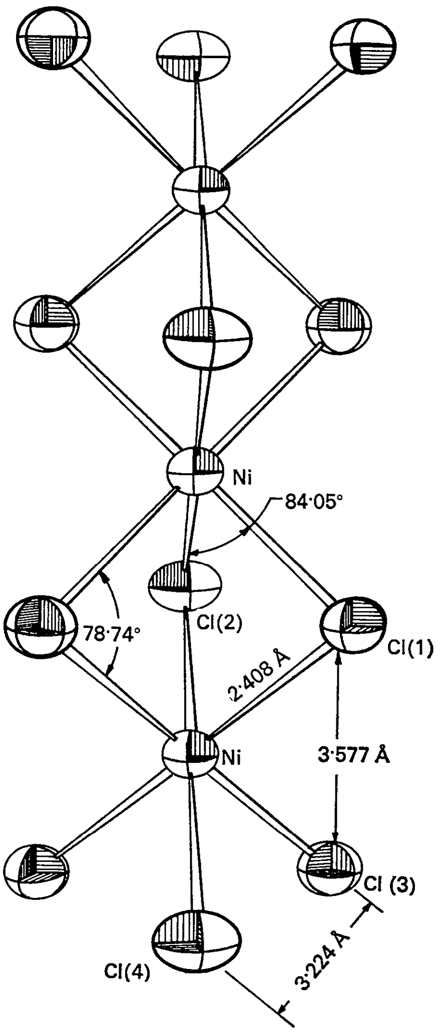

Fig. 2. Distances and angles found for the anion in $(CH_3)_4NNiCl_3$ [model (III)].

Table 4. *Positional and thermal parameters for* $(CH_3)_4NNiBr_3$

	Model	x	y	z	B
Br	(I)	0·1466 (3)	0·2461 (4)	0·7794 (29)	4·97 (11)
	(II)	0·1466 (4)	0·2460 (4)	0·7837 (29)	4·98 (11)
	(III)	0·1459 (3)	0·2452 (3)	$\frac{3}{4}$	5·12 (11)
	(IV)	0·1463 (3)	0·2459 (3)	0·7748 (31)	5·03 (10)
	(V)	0·1459 (3)	0·2454 (3)	0·7769 (57)	5·05 (11)
Ni	(I)	0	0	0	2·49 (14)
	(II)	0	0	0	2·49 (15)
	(III)	0	0	0	3·87 (14)
	(IV)	0	0	0	3·69 (14)
	(V)	0	0	0	4·05 (16)
C(2)	(I)	0·168 (4)	0·638 (4)	0·328 (7)	5·36 (75)
	(II)	0·169 (4)	0·638 (4)	0·324 (7)	5·15 (76)
	(III)	0·165 (4)	0·640 (4)	0·315 (6)	5·36 (82)
	(IV)	0·163 (3)	0·639 (3)	0·324 (6)	4·25 (55)
	(V)	0·165 (4)	0·638 (4)	0·320 (5)	5·31 (81)
C(1)	(I)	$\frac{1}{3}$	$\frac{2}{3}$	0·015 (8)	5·84 (95)
	(II)	$\frac{1}{3}$	$\frac{2}{3}$	0·016 (13)	6·05 (96)
	(III)	$\frac{1}{3}$	$\frac{2}{3}$	0·032 (12)	7·74 (1·53)
	(IV)	$\frac{1}{3}$	$\frac{2}{3}$	0·004 (13)	6·84 (1·01)
	(V)	$\frac{1}{3}$	$\frac{2}{3}$	0·031 (11)	7·36 (1·21)
N	(I)	$\frac{1}{3}$	$\frac{2}{3}$	0·256 (9)	2·31 (46)
	(II)	$\frac{1}{3}$	$\frac{2}{3}$	0·255 (9)	2·43 (47)
	(III)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	2·29 (42)
	(IV)	$\frac{1}{3}$	$\frac{2}{3}$	0·232 (9)	1·75 (42)
	(V)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	2·40 (43)

Figs. 1, 2, and 3 illustrate the structure obtained for model (III). One-dimensional linear chains of Ni atoms parallel to [0001] are bridged by chlorine atoms which are in approximately octahedral sites about the Ni atoms. The carbon atoms of the tetramethylammonium cations are disordered by reflection through a mirror plane passing through the nitrogen atom and normal to [0001]. The nitrogen atom is thus on a crystallographic D_{3h} symmetry site. The distortions observed in $CH_3NH_3NiCl_3$ (Willett, 1966) can be attributed to hydrogen bonding (N–H···Cl) and are not expected to be observed in the $(CH_3)_4N^+$ structures.

Using the film data reported previously, we have reexamined the structural results obtained for $(CH_3)_4NNiBr_3$ (Stucky, D'Agostino & McPherson, 1966) in view of the results found for $(CH_3)_4NNiCl_3$. It was possible to refine Model (III) with the bromine atoms disordered ($z \neq \frac{3}{4}$) as well as ordered ($z = \frac{3}{4}$). In keeping with the notation used above, Model (III) in the subsequent discussion refers to a centrosymmetric structure ($P6_3/m$) with ordered bromine atoms while Model (V) refers to a centrosymmetric structure ($P6_3/m$) with disordered bromine atoms. The results are given in Table 4. All refinements were carried out with isotropic thermal parameters and a scale factor for each of the four layers of film data. The discrepancy factors for these models are given in Table 5.

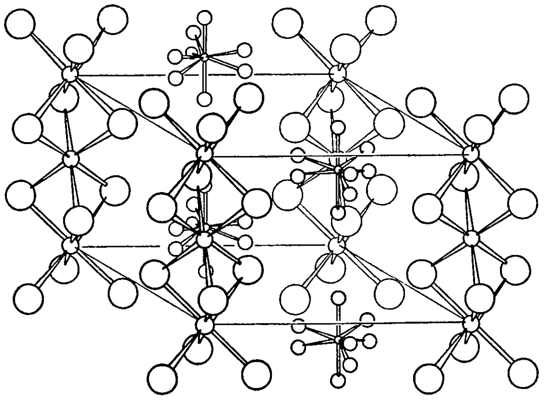

Fig. 3. Perspective view of the unit cell of $(CH_3)_4NNiCl_3$ [model (III)].

Table 5. *R values for* $(CH_3)_4NNiBr_3$

	R_1*	R_1†	R_2*	R_2†
(I)	10·3	11·1	13·9	13·9
(II)	10·3	11·1	13·9	13·9
(III)	9·3	10·0	13·9	13·9
(IV)	9·5	10·3	12·4	12·4
(V)	9·4	10·2	13·8	13·8

* Unobserved reflections not included.
† Unobserved reflections included.

The weighted R factor required for Hamilton's (1965) test for Model (IV) is 12·4% and for Model (III) is 13·9%, so that the R factor ratio is 1·121. There are seventeen parameters in question and 207 observations. This gives $\mathscr{R}_{17,190,0\cdot005} = 1\cdot094$ for the hypothesis that Model (III) is correct. According to this test then, Model (III) can be rejected at the 0·5% level of significance. The same conclusion is reached for Models (I), (II), and (V). Both the weighting and the data are more reliable for $(CH_3)NNiCl_3$, and we now consider the preceeding analysis for this compound. $R_2=4\cdot8\%$ for Model (IV) and $5\cdot0\%$ for Model (III), giving an R factor ratio of $5\cdot0/4\cdot8=1\cdot041$. There are 460 observations and 33 parameters which were assigned different values in the two models. $\mathcal{R}_{33,427,0\cdot25}=1\cdot042$ and $\mathcal{R}_{33,427,0\cdot50}=1\cdot035$, implying that the odds are approximately 3 to 1 that Model (IV) is correct.

The above statistical test requires that no systematic errors be present in the data. $(CH_3)_4NNiBr_3$ has a larger linear absorption coefficient than does $(CH_3)_4NNiCl_3$ ($\mu=185\cdot5$ and $30\cdot32$ cm^{-1} respectively for the two crystals used to collect data) and it seems likely that the isotropically refined film data for $(CH_3)_4NNiBr_3$ could be seriously affected by systematic errors. Model (IV) does, however, appear to be favored over the other models for both compounds.

In both compounds, the nitrogen atom is within three standard deviations of being at $z=\frac{1}{4}$. The Ni–Br distances in $(CH_3)_4NNiBr_3$ are 2·55 (1) Å [Model (III)] and 2·66 (1), 2·46 (1) Å [Model (II)]. The difficulty in ascertaining the correct bond length is evident even though the differences in bond lengths lie well outside the estimated standard deviations.

A comparison with the structure of $(CH_3)_4NMnCl_3$ (Morosin & Graeber, 1967) reveals several interesting similarities, for example, the C(1)–N–C(2) angle of 105·0° and the C(2)–N–C(3) angle of 113·6° compared with 106·3° and 112·5° in $(CH_3)_4NMnCl_3$. Of more interest are the parameters found for the anions. The Mn–Cl distance of 2·560 Å is considerably longer than the Ni–Cl distance of 2·408 Å. The Cl–Ni–Cl angles of 84·05° and 95·95° are, however, almost identical with the Cl–Mn–Cl angles of 84·09° and 95·91°. The shorter distances in the nickel complex are consistent with the difference in the crystal field stabilization energies for octahedral Ni(II) *versus* Mn(II). The same effect can be observed in the complexes $CsMCl_3$, $M=Ni^{2+}, Co^{2+}, Fe^{2+}, Cr^{2+}, V^{2+}$. These compounds are isostructural with $CsNiCl_3$ (Siefert, 1961; Ehrlich & Seifert, 1959; Klatyk & Seifert, 1964; Klatyk & Seifert, 1966; Tishchenko, 1955) so that the metal–metal distances (Fig. 4) show a definite correlation with the octahedral crystal field stabilization energies of the divalent transition metal cations with the higher stabilization energies corresponding to the shorter distances. The structure of $CsMnCl_3$ has not been reported; however, a comparison of the lattice parameters of $(CH_3)_4NNiCl_3$ and $CsNiCl_3$ (Tishchenko, 1955) suggests that a value of 3·15 Å for the Mn–Mn distance in $CsMnCl_3$ would not be unrealistic. The variations in the unit-cell dimension a follow a trend similar to those shown for c, so that the distances illustrated in Fig. 4 can be expected qualitatively to be a good indication of the trends in the metal–halogen interatomic distances.

There is some dispute concerning the structure of $CsCrCl_3$ quoted above. Iberson, Gut & Gruen (1962) first reported this complex to be isostructural with $CsCuCl_3$ (Wells, 1947; Schlueter, Jacobson & Rundle, 1966) as one would expect from electronic considerations. Klatyk & Seifert (1964) later examined $CsCrCl_3$ with zero level Weissenberg and powder photographs and reported it to be isostructural with $CsNiCl_3$. The low temperature magnetic and spectroscopic properties of $CsCrCl_3$ are of some interest to us and we are currently carrying out a three-dimensional structural study of this compound.

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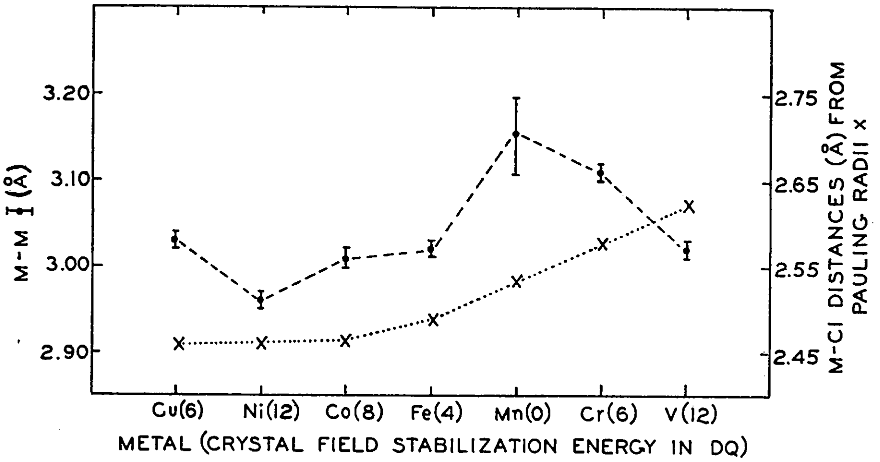

Fig. 4. Metal–metal distances in $CsMCl_3$ complexes. Also shown is the predicted variation of the M–Cl distance as determined by the sum of the Pauling radii.

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The Crystal Structure of Protopine, $C_{20}H_{19}O_5N$

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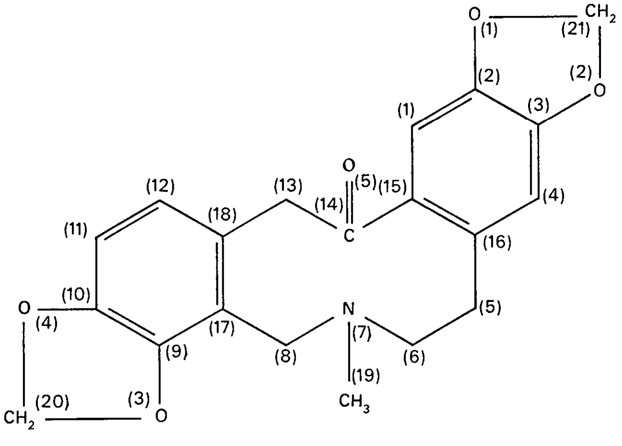
The crystal structure of protopine, $C_{20}H_{19}O_5N$, has been determined by the symbolic addition procedure, and has been refined by least squares to an R index of 0·043, with use of counter data for 2904 observed reflexions. The space group is $P2_1/n$ and the cell constants are $a=13{\cdot}610$, $b=17{\cdot}445$, $c=7{\cdot}102$ Å, $\beta=96{\cdot}75°$. The ten-membered ring in the molecule is severely buckled and contains a short distance across the ring of only 2·555 Å between the C atom of the carbonyl group and the tertiary nitrogen atom. Each of the two benzene rings has a very slight boat form, and the normals to their mean planes are at an angle of 27·8° from each other. The carbonyl group is about 37·4° out of the mean plane of its nearest benzene ring. The carbonyl oxygen atom and the methyl group are on the same side of the ten-membered ring.

Introduction

A natural group of alkaloids in opium is presented by the two members: protopine, $C_{20}H_{19}O_5N$, and cryptopine, $C_{21}H_{23}O_5N$. Protopine is almost the typical alkaloid of the poppy order (Papavaraceae) since it has been found in most species of this order. Molecules in this group are characterized by the presence of a ten-membered *N*-hetero-ring containing one carbonyl group (Manske & Holmes, 1954). The carbonyl group and the tertiary amino function are held very closely together across this medium-sized ring, and it is of interest to define the degree of interaction between them. The two functional groups have been found to interact when a proton is added to the carbonyl oxygen, as for example in protopine hydriodide, with the net result of transforming the ten-membered ring into two six-membered rings. This interaction was studied by Mottus, Schwarz & Marion (1953), and by Anet & Marion (1954) from the ultraviolet and infrared spectra. The molecular structure for the protopine base is shown in (I); the numbering of the atoms is based on that given by Henry (1949), p. 300.



(I) Protopine

X-ray analysis of protopine and cryptopine has been undertaken in order to determine their structures and

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