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Preparation, Characterization, and Solid State Thermal Studies of Nickel(II) Squarate Complexes of 1,2-Ethanediamine and Its Derivatives

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$[NiL_3]C_4O_4$ [L=1,2-ethanediamine (en) and 1,2-*N*,*N*′-dimethylethanediamine (*N*,*N*′-dmen)], $[NiL_3]C_4O_4\cdot nH_2O$ [for L=1,2-*N*-methylethanediamine (meen) and 2-methyl-1,2-propanediamine (ibn); $n=1$, and for L = 1,2-propanediamine (pn); $n=2$], and $[NiL_2C_4O_4]\cdot 2H_2O$ [L = 1,2-*N*-ethylethanediamine (eten), 1,2-*N*-propylethanediamine (pren), 1,2-*N*,*N*-dimethylethanediamine (*N*,*N*-dmen) and 1,2-*N*,*N*′-diethylethanediamine (*N*,*N*′-deten)] have been synthesized by the addition of the respective diamines to finely powdered nickel(II)squarate dihydrate, $NiC_4O_4\cdot 2H_2O$. All of the tris-species, except for $[Ni(N,N'\text{-dmen})_3]C_4O_4$ were also prepared by adding diamines to $NiC_4O_4\cdot 2H_2O$ dissolved in aqueous ammonia (25%). When the latter method was followed, the bis-species $[NiL_2C_4O_4]$ [L = eten, pren, 1,2-*N*-isopropylethanediamine (ipren), *N*,*N*-dmen, *N*,*N*′-dmen, and *N*,*N*′-deten] were also obtained. $[NiL_2C_4O_4]$ (L = en, meen, *N*,*N*′-dmen, pn, and ibn) were also prepared from their corresponding tris(diamine) species upon heating in the solid state. $[Ni(ibn)_3]C_4O_4\cdot nH_2O$ after dehydration underwent an irreversible endothermic (145—160 °C; $\Delta H = 6.5$ kJ mol^{-1}) phase transition without showing any visual color change. $[Ni(ipren)_2C_4O_4]$ exhibited a reversible phase transition (78—107 °C; $\Delta H = 1.4$ kJ mol^{-1} for heating and 105—72°C; $\Delta H = -1.3$ kJ mol^{-1} for cooling). The phase transitions are considered to have been due to conformational changes of the diamine chelate rings. All of the tris as well as bis(diamine) complexes possess an octahedral geometry, except for $[Ni(ibn)_2]C_4O_4$, which is square-planar. The bis-species $[NiL_2C_4O_4]$ (L = eten, pren, *N*,*N*-dmen, and *N*,*N*′-deten) exists in two isomeric forms.

Solid state thermally induced phase transition as well as decompositions of 5-membered diamine chelates of nickel(II) with various counter anions are well documented in the literature.[1—10] Our study has revealed that a phase transition and/or decomposition depends on the substitution on diamine as well as on the nature of the counter anions. The versatility of the squarate anion ($C_4O_4{}^{2-}$) as a ligand has been amply demonstrated,[11,17] which suggests that it may act as a monodentate, bidentate or bridging ligand. Solid state thermal studies of several metal squarate, including the nickel(II) squarate, have been reported, indicating a high thermal stability of the squarate moiety. Since, the squarate anion has a very good ligating property, and at the same time has a high thermal stability, our previous experiences suggest that it should be an appropriate choice for exhibiting interesting thermally induced phase transitions and/or decomposition phenomena in its 5-membered diamine chelates in the solid phase. To our knowledge, reports on the syntheses, characterization, and solid state thermal investigation of nickel(II) squarate complexes of 5-membered diamine have not been documented. The insolubility of the nickel(II) squarate in common solvents perhaps restricts the preparation of its complexes with the aforesaid ligands. However, we tackled this problem efficiently, and here report on the preparation, characterization and a solid state thermal investigation of nickel(II) squarate complexes with ten 5-membered diamines e.g. : (i) 1,2-ethanediamine (en), (ii) 1,2-*N*-methylethanediamine (meen), (iii) 1,2-*N*-ethylethanediamine (eten), (iv) 1,2-*N*-propylethanediamine (pren), (v) 1,2-*N*-isopropylethanediamine (ipren), (vi) 1,2-*N*,*N*-dimethylethanediamine (*N*,*N*-dmen), (vii) 1,2-*N*,*N*′-dimethylethanediamine (*N*,*N*′-dmen), (viii) 1,2-*N*,*N*′-diethylethanediamine (*N*,*N*′-deten), (ix) 1,2-propanediamine (pn), and (x) 2-methyl-1,2-propanediamine (ibn).

Experimental

Reagents. High-purity squaric acid, en, meen, eten, pren, ipren, *N*,*N*-dmen, *N*,*N*′-dmen, *N*,*N*′-deten, pn, and ibn were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals used were of analytial reagent grade.

Preparation of Nickel(II) Squarate dihydrate. Nickel(II) squarate dihydrate, $NiC_4O_4\cdot 2H_2O$, was prepared by adding one gram (0.09 mol) of dipotassium squarate dissolved in 10 cm^3 of water to 2.2 gram (0.09 mol) of nickel(II) chloride hexahydrate dissolved in 10 cm^3 of water at room temperature. An immediately precepitated green-colored $NiC_4O_4\cdot 2H_2O$ was filtered, washed with hot water, acetone and ether, and dried at ambient temperature,as described by R. West and H. Y. Niu.[16]

Preparation of the Complex. The diamine complex of nickel(II) squarate was prepared by adopting the following two techniques:

Technique 1. After diamine (3—4 mmol) was added to finely powdered nickel(II) squarate (1 mmol) the resulting mixture was kept in a stoppered conical flask. After a few days the mixture was treated with water and filtered. Upon keeping the

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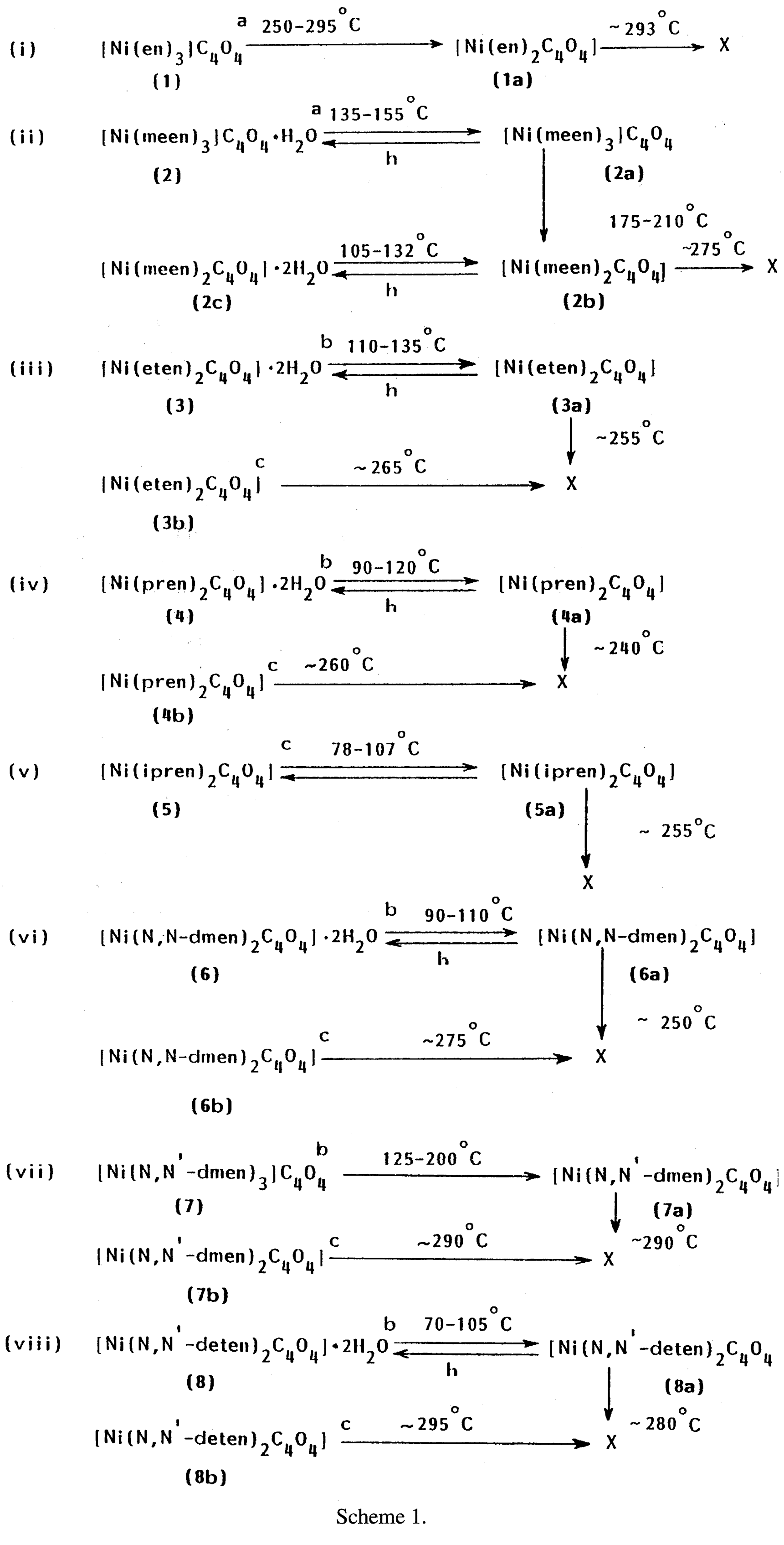
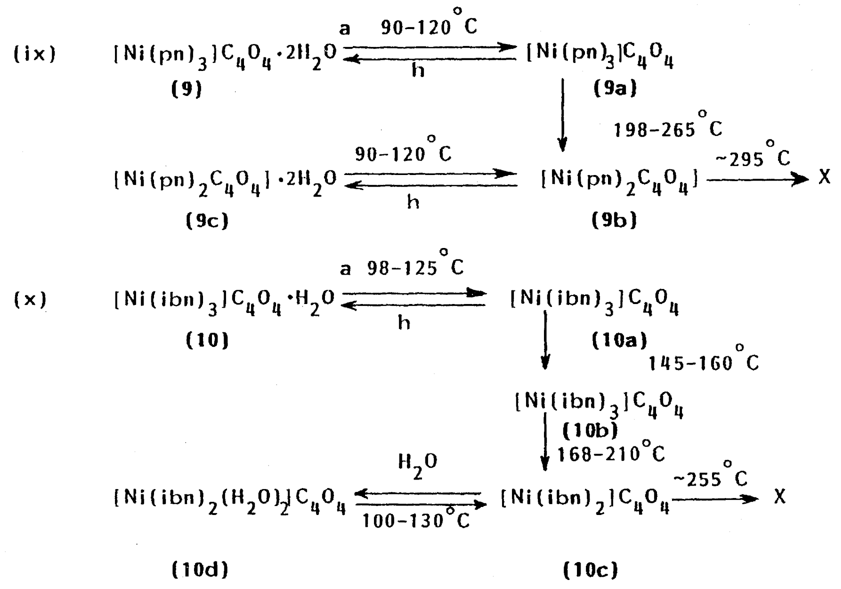

(i)
[Ni(en)3]C4O4
(1)
a 250-295 °C
[Ni(en)2C4O4]
(1a)
~293 °C
X
(ii)
[Ni(meen)3]C4O4·H2O
(2)
a 135-155 °C
h
[Ni(meen)3]C4O4
(2a)
175-210 °C
[Ni(meen)2C4O4]·2H2O
(2c)
105-132 °C
h
[Ni(meen)2C4O4]
(2b)
~275 °C
X
(iii)
[Ni(eten)2C4O4]·2H2O
(3)
b 110-135 °C
h
[Ni(eten)2C4O4]
(3a)
~255 °C
[Ni(eten)2C4O4]
(3b)
c ~265 °C
X
(iv)
[Ni(pren)2C4O4]·2H2O
(4)
b 90-120 °C
h
[Ni(pren)2C4O4]
(4a)
~240 °C
[Ni(pren)2C4O4]
(4b)
c ~260 °C
X
(v)
[Ni(ipren)2C4O4]
(5)
c 78-107 °C
[Ni(ipren)2C4O4]
(5a)
~ 255°C
X
(vi)
[Ni(N,N-dmen)2C4O4]·2H2O
(6)
b 90-110 °C
h
[Ni(N,N-dmen)2C4O4]
(6a)
~ 250 °C
[Ni(N,N-dmen)2C4O4]
(6b)
c ~275 °C
X
(vii)
[Ni(N,N'-dmen)3]C4O4
(7)
b 125-200 °C
[Ni(N,N'-dmen)2C4O4]
(7a)
~290 °C
[Ni(N,N'-dmen)2C4O4]
(7b)
c ~290 °C
X
(viii)
[Ni(N,N'-deten)2C4O4]·2H2O
(8)
b 70-105 °C
h
[Ni(N,N'-deten)2C4O4
(8a)
~280 °C
[Ni(N,N'-deten)2C4O4]
(8b)
c ~295 °C
X

Scheme 1.



X = Product not identified

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a = Obtained by Technique 1 and Technique 2.
b = Obtained by Technique 1 only.
c = Obtained by Technique 2 only.
h = Humid atmosphere (60% or above).

Scheme 1. (Continued).

filtrate in a $CaCl_2$-desiccator the desired complex was separated out, and then filtered, washed with isopropanol and dried over a $CaCl_2$-desiccator. The following complexes were synthesized by this technique (Scheme 1): $[Ni(en)_3]C_4O_4$ (**1**), $Ni(meen)_3]$-$C_4O_4\cdot H_2O$ (**2**), $[Ni(eten)_2C_4O_4]\cdot 2H_2O$ (**3**), $[Ni(pren)_2C_4O_4]\cdot 2H_2O$ (**4**), $[Ni(N,N\text{-dmen})_2C_4O_4]\cdot 2H_2O$ (**6**), $[Ni(N,N'\text{-dmen})_3]C_4O_4$ (**7**), $[Ni(N,N'\text{-deten})_2C_4O_4]\cdot 2H_2O$ (**8**), $[Ni(pn)_3]C_4O_4\cdot 2H_2O$ (**9**), and $[Ni(ibn)_3]C_4O_4\cdot H_2O$ (**10**).

Technique 2. Nickel(II) squarate (1 mmol) was dissolved in minimum amount of aqueous ammonia (25%), (5 cm^3), to which diamine (3—4 mmol) was added. The resulting mixture was heated on a water bath in order to remove any ammonia, and then isopropanol (10 cm^3) was added. The complex which separated out was filtered, washed with isopropanol and dried over a $CaCl_2$-desiccator. The complexes prepared by this technique were (Scheme 1): $[Ni(en)_3]C_4O_4$ (**1**), $[Ni(meen)_3]C_4O_4\cdot H_2O$ (**2**), $[Ni(eten)_2C_4O_4]$ (**3b**), $[Ni(pren)_2C_4O_4]$ (**4b**), $[Ni(ipren)_2C_4O_4]$ (**5**), $[Ni(N,N\text{-dmen})_2C_4O_4$ (**6b**), $[Ni(N,N'\text{-dmen})_2C_4O_4]$ (**7b**), $[Ni(N,N'\text{-deten})_2C_4O_4]$ (**8b**), $[Ni(pn)_3]C_4O\cdot 2H_2O$ (**9**), and $[Ni(ibn)_3]C_4O_4\cdot H_2O$ (**10**).

Measurements. Thermal analyses (TG-DTA) were carried out using a Shimadzu DT-30 thermal analyses under a flow of nitrogen (flow rate: 30 $cm^3\,min^{-1}$). The sample (particle size of 150—200 mesh) was heated in a platinum crucible at a rate of 10 °C min^{-1} with inert alumina as a reference. The enthalpy changes of the phase transitions were calculated by a Perkin–Elmer DSC-7 differential scanning calorimeter using indium metal as a calibrant (rate of heating/cooling, 10 °C min^{-1}). Elemental analyses were preformed using a Perkin–Elmer 240C elemental analyser. IR-spectra (4000—400 cm^{-1}) were taken at 27 °C using a Perkin–Elmer IR 783 and a Nicolet FT-IR 755, where KBr/Nujol® was used as medium/reference material. UV-visible absorption spectra (900—190 nm) were obtained at 27 °C using a Shimadzu UV 2100, where Nujol® was used as a medium as well as a reference; X-ray powder diffraction patterns were performed at 25°C using a Seifert XRD-3000P, where the source of X-rays was Cu radiation (30 kV/30 mA); the prim slits were 3 mm/soller/2 mm and the secondary slits were soller/0.2 mm. The magnetic susceptibility was measured at 27 °C using an EG and G PAR 155 vibrating sample magnetometer, where $[HgCo(SCN)_4]$ was used as a reference material[18] and diamagnetic corrections were made using Pascal's constants.[19]

Results and Discussion

Characterization of the Complexes. The complexes were recrystallized several times and the purity assured from their reproducible elemental analyses, magnetic susceptibility, electronic and IR spectra, thermal (TG-DTA) and X-ray powder diffraction data. The elemental analyses (Table 1) revealed that among the ten diamines only five diamines yielded tris-species, $[NiL_3]C_4O_4\cdot nH_2O$ (for L = en and N,N'-dmen, $n = 0$; for L = meen and ibn, $n = 1$, and for L = pn, $n = 2$); another four diamines produced bis-species, $[NiL_2C_4O_4]\cdot 2H_2O$ (L = eten, pren, N,N-dmen, and N,N'-deten) and the remaining one ipren did not react when Technique 1 was followed. On the other hand, when Technique 2 was adopted, only four diamines (en, meen, pn, and ibn) produced tris-species having the same

Table 1. Data of the Elemental Analyses, Magnetic Moments, and Some Selective Bands of Electronic Spectra of Diamine Complexes of Nickel(II) Squarate

		Analyses/%[a]				μ_{eff}	λ_{max}
Complex	Color	Ni	C	H	N	B.M.	nm
$[Ni(en)_3]C_4O_4$ (**1**)	Blue-Violet	16.7 (16.7)	34.3 (34.2)	6.8 (6.8)	23.9 (24.0)	3.1	525, 345
$[Ni(en)_2C_4O_4]$ (**1a**)	Pink	20.1 (20.2)	32.8 (33.0)	5.5 (5.5)	19.1 (19.3)	3.2	550, 365
$[Ni(meen)_3]C_4O_4 \cdot H_2O$ (**2**)	Blue-Violet	14.2 (14.3)	37.9 (38.0)	7.8 (7.8)	20.3 (20.5)	3.1	548, 355
$[Ni(meen)_3]C_4O_4$ (**2a**)	Blue-Violet	14.9 (14.9)	39.6 (39.7)	7.4 (7.6)	21.3 (21.4)	3.1	550, 355
$[Ni(meen)_2C_4O_4]$ (**2b**)	Pink	18.4 (18.4)	37.8 (37.6)	6.2 (6.3)	17.5 (17.6)	3.2	555, 375
$[Ni(meen)_2C_4O_4] \cdot 2H_2O$ (**2c**)	Pink	16.5 (16.5)	33.8 (33.8)	6.7 (6.7)	16.4 (15.8)	3.1	556, 380
$[Ni(eten)_2C_4O_4] \cdot 2H_2O$ (**3**)	Pink	15.3 (15.3)	37.6 (37.6)	7.4 (7.4)	14.6 (14.6)	3.1	550, 365
$[Ni(eten)_2C_4O_4]$ (**3a/3b**)	Pink	16.8 (16.9)	41.5 (41.5)	6.8 (6.9)	16.0 (16.1)	3.2	560, 355
$[Ni(pren)_2C_4O_4] \cdot 2H_2O$ (**4**)	Bluish-Pink	14.2 (14.3)	40.8 (40.9)	7.7 (7.9)	13.6 (13.6)	3.2	555, 370
$[Ni(pren)_2C_4O_4]$ (**4a/4b**)	Pink	15.6 (15.6)	44.7 (44.8)	7.4 (7.5)	14.9 (14.9)	3.2	560, 375
$[Ni(ipren)_2C_4O_4]$ (**5/5a**)	Bluish-Pink	15.6 (15.6)	44.8 (44.8)	7.5 (7.5)	14.8 (14.9)	3.2	550, 380
$[Ni(N,N\text{-dmen})_2C_4O_4] \cdot 2H_2O$ (**6**)	Pink	15.3 (15.3)	37.5 (37.6)	7.2 (7.3)	14.4 (14.6)	3.1	545, 360
$[Ni(N,N\text{-dmen})_2C_4O_4]$ (**6a/6b**)	Pink	16.8 (16.9)	41.3 (41.5)	6.8 (6.9)	16.0 (16.1)	3.2	550, 370
$[Ni(N,N'\text{-dmen})_3]C_4O_4$ (**7**)	Blue-Violet	13.5 (13.5)	44.1 (44.2)	8.1 (8.3)	19.2 (19.3)	3.2	545, 340
$[Ni(N,N'\text{-dmen})_2C_4O_4]$ (**7a/7b**)	Pink	16.9 (16.9)	41.4 (41.5)	6.7 (6.9)	16.0 (16.2)	3.2	560, 365
$[Ni(N,N'\text{-deten})_2C_4O_4] \cdot 2H_2O$ (**8**)	Pink	13.3 (13.4)	43.7 (43.8)	8.2 (8.2)	12.8 (12.8)	3.1	555, 380
$[Ni(N,N'\text{-deten})_2C_4O_4]$ (**8a/8b**)	Pink	14.5 (14.6)	47.6 (47.7)	7.7 (7.9)	13.9 (13.9)	3.2	565, 355
$[Ni(pn)_3]C_4O_4 \cdot 2H_2O$ (**9**)	Pink	13.6 (13.7)	36.4 (36.4)	7.9 (7.9)	19.6 (19.6)	3.1	540, 370
$[Ni(pn)_3]C_4O_4$ (**9a**)	Pink	14.9 (14.9)	39.7 (39.7)	7.5 (7.6)	21.3 (21.4)	3.1	545, 375
$[Ni(pn)_2C_4O_4]$ (**9b**)	Pink	18.4 (18.4)	37.5 (37.6)	6.2 (6.3)	17.4 (17.6)	3.2	550, 385
$[Ni(pn)_2C_4O_4] \cdot 2H_2O$ (**9c**)	Pink	16.5 (16.5)	33.8 (33.8)	6.6 (6.8)	15.6 (15.8)	3.1	555, 385
$[Ni(ibn)_3]C_4O_4 \cdot 2H_2O$ (**10**)	Blue-Violet	12.9 (13.0)	42.3 (42.4)	8.5 (8.5)	18.6 (18.5)	3.1	550, 365
$[Ni(ibn)_3]C_4O_4$ (**10a/10b**)	Blue-Violet	13.5 (13.5)	44.1 (44.1)	8.3 (8.3)	19.3 (19.3)	3.1	560, 375
$[Ni(ibn)_2]C_4O_4$ (**10c**)	Yellow	16.9 (16.9)	41.5 (41.5)	6.9 (6.9)	16.1 (16.1)	D	445
$[Ni(ibn)_2(H_2O)_2]C_4O_4$ (**10d**)	Pink	15.3 (15.3)	37.6 (37.6)	7.3 (7.3)	14.4 (14.6)	3.2	565, 380

a) Theoretically calculated values are in parentheses. D = Diamagnetic.

composition as that obtained by following Technique 1; the rest of the diamines formed bis-species having no water of crystallization (Scheme 1). In Technique 1 the complexes were formed by a direct interaction of diamine to nickel(II) squarate, whereas, in Technique 2 they were formed by a replacement of the ammonia molecules from the coordination sphere. The chelate effect favoured this replacement reaction. However, the formation of tris-diamine complexes may have been hindered sterically if the alkyl group was present in the N of diamine; this may have offset the chelate effect. These ideas are evident from the results that ipren, having a bulky substituent in N, did not react in Technique 1 but easily formed bis-complexes in Technique 2. On the other hand, *N,N*-dmen yielded a tris complex in Technique 1, but resulted in only bis-complexes in Technique 2. Thus, Technique 2 is more efficient in the formation of bis-complexes, whereas, for the formation of tris-complexes Technique 1 is superior. The bis-species synthesized pyrolytically in the solid state from their respective tris-species are of two types. One type, $[NiL_2C_4O_4]$ (L = meen and pn), is hygroscopic and transforms to $[NiL_2C_4O_4]\cdot 2H_2O$ upon exposure to a humid atmosphere (60% or above). However, the other type, $[NiL_2C_4O_4]$ (L = en, *N,N′*-dmen, and ibn), is not hygroscopic at all. All of the complexes exhibit IR-bands due to $\nu(NH_2)$ and $\nu(CH_2)$, which are comparable to those of similar diamine systems, where the chelate character of the diamines have been established by X-ray single-crystal analyses.[8] As a result, the tris-species should possess N_6-chromophore around nickel(II) and their magnetic and electronic spectral (Nujol® mull) data (Table 1) are compatible with an octahedral geometry. The IR-bands of the squarate ligand in the tris-species were observed in the region from ca. 1525 to ca. 1540 cm^{-1}, which is very strong and broad, and was assigned to a mixture of C–C and C–O stretching vibrations of a squarate ligand (Fig. 1, Table 2).[16] In addition, only one sharp band at ca. 1710 cm^{-1}, assigned to C=O (Fig. 1), was observed in all tris-species. Among the bis-species, only $[Ni(ibn)_2]C_4O_4$ (**10c**) is yellow in color, diamagnetic and exhibits a strong electronic absorption band at ca. 445 nm, which suggests that it possesses a square-planar geometry around nickel (II).[3,7] However, all other bis-species show effective magnetic moments of 3.1 B.M., and their electronic spectra (Nujol® mull) [assigned to $^3A_{2g}\rightarrow{}^3T_{1g}$ (F)[20] and $^3A_{2g}\rightarrow{}^3T_{1g}$(P)[20]] (Table 1) are typical of octahedral nickel(II). In Fig. 1 the IR bands assigned to C–C and C–O stretching vibration of the squarate ligand shift towards a lower wave-number region (ca. 1475 cm^{-1}). The high-energy band (ca. 1710 cm^{-1}) obtained in the case of the tris-species becomes weakend and two additional bands appear at ca. 1620 and ca. 1750 cm^{-1} (Fig. 1), indicating that all four oxygen atoms are not in the same environment.[17] From the above discussion, it

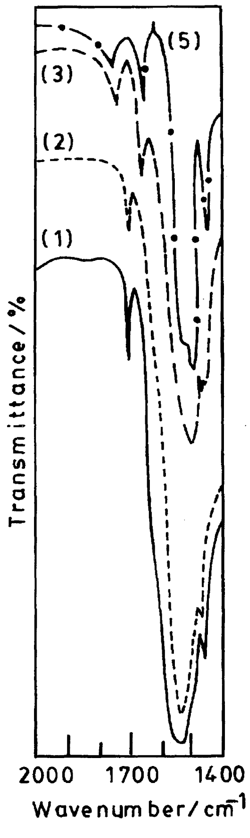

Fig. 1. IR-spectra (KBr) of $[Ni(en)_3]C_4O_4$ (**1**) (——), $[Ni(meen)_3]C_4O_4\cdot H_2O$ (**2**) (- - -), $[Ni(eten)_2C_4O_4]\cdot 2H_2O$ (**3**) (—–—), and $[Ni(ipren)_2C_4O_4]$ (**5**) (—•—).

Table 2. IR-Bands of the Complexes Attributable to the Squarate Ligand in the 1850—1400 (cm^{-1}) Region

Compound	ν(C=O)	ν(C=C)	ν[(C–C)+(C–O)]
1	1712 s	a	1540 vs, br 1457 w
2	1711 s	a	1532 vs, br 1455 w
3	1749 s	1623 m	1495 vs, br 1460 w 1444 vw
4	1747 s	1622 m	1492 vs, br 1455 w
5	1755 w	1624 s	1487 vs, br 1440 s
6	1752 s	1628 m	1489 vs, br 1445 w
7	1715 s	a	1538 vs, br 1458 w
8	1745 s	1623 m	1490 vs, br 1448 w
9	1710 s	a	1535 vs, br 1465 w
10	1712 s	a	1539 vs, br 1455 w

s = strong, vs = very strong, w = weak, m = medium, br = broad.
a) Here $C_4O_4^{2-}$ anion does not take part in coordination. As a result, C=C becomes too weak to exhibit IR band at ca. 1600 cm^{-1}.

can be considered that in all the bis-species squarate ion is coordinated. Species (**3a**), (**4a**), (**6a**), and (**8a**) (Scheme 1) have the same composition as (**3a**), (**4b**), (**6b**), and (**8b**), respectively. However, although the former are soluble in water, the latters are not. The IR-spectra of the pairs (**3a**, **3b**), (**4a**, **4b**), (**6a**, **6b**), and (**8a**, **8b**) show some differences in the regions of 3320—3100, 3000—2820, 1400—1350, 1330—1000, and 1000—430 cm^{-1}, where the vibrations of $\nu(\mathrm{NH_2})$, $\nu(\mathrm{CH_2})$, $\rho_\omega(\mathrm{CH_2})$, $\tau(\mathrm{NH_2})+\rho_\omega(\mathrm{NH_2})+\tau(\mathrm{CH_2})$, and $\rho_\gamma(\mathrm{NH_2})+\nu(\mathrm{M{-}N})$ (Table 3) appear. However, they exhibit the same effective magnetic moments and electronic spectra, which nullify the possibility of configurational changes in the pairs. It has been documented that the five-membered chelate ring formed by 1,2-ethanediamine and its derivatives is not planar; thus, it exists in either of two conformations, delta (δ) or lamda (λ), in a chelate complex, thus causing the existance of different conformational isomers.[21)] As an example, in a *trans*-bis (en) complex the (en) rings can form three conformational isomers ($\delta\lambda$, $\delta\delta$, and $\lambda\lambda$; of which the latter two are mirror image to each other and identical in energy). In previous studies it was observed that the conformational isomers exhibit differences in their IR-bands at the regions described above.[4,8)] Therefore, it may be assumed that the members of the respective pairs [(**3a**, **3b**), (**4a**, **4b**), (**6a**, **6b**), and (**8a**, **8b**)] are conformational isomers to each other. It is quite reasonable that the conformational changes in the diamine chelate rings would require changes in the crystal packing; as a result, two conformational isomers should exhibit non-identical d-lines.[2,4,21,22)] The slight changes observed in the spacing and intensities of the X-ray

Table 3. IR-Spectral Data (cm^{-1}) of Some Diamine Complexes of Nickel(II) Squarate

Complex	$\nu(\mathrm{NH_2})$	$\nu(\mathrm{CH_2})$	$\rho_\mathrm{w}(\mathrm{CH_2})$	$\tau(\mathrm{NH_2})$ + $\rho_\mathrm{w}(\mathrm{NH_2})$ + $\tau(\mathrm{CH_2})$	$\rho_\mathrm{r}(\mathrm{CH_2})+\nu(\mathrm{M-N})$	
$[\mathrm{Ni(eten)_2}]\mathrm{C_4O_4}$ (**3a**)	3319 s 3277 s 3208 s	2952 s 2890 w	1384 s 1354 w	1330 w 1079 vs 1037 vw 1008 vs	984 w 913 s	647 vs 553 s
$[\mathrm{Ni(eten)_2}]\mathrm{C_4O_4}$ (**3b**)	3259 vs 3182 s	2972 vw 2948 vw 2879 s	1390 vw 1353 s	1290 w 1090 vs 1030 s 1010 vs	895 w 828 vs 792 vw	640 w 550 vw
$[\mathrm{Ni(pren)_2}]\mathrm{C_4O_4}$ (**4a**)	3276 s 3246 vs 3166 s	2962 s 2932 s 2875 s	1382 vw	1282 s 1145 w 1095 vw 1088 vs	973 s 813 s	630 vw 535 vw
$[\mathrm{Ni(pren)_2}]\mathrm{C_4O_4}$ (**4b**)	3269 vs 3164 s	2959 vs 2932 w 2872 vs	1386 vw 1354 w	1324 s 1078 vs 1037 s	992 vw 963 vs	651 vs 545 s
$[\mathrm{Ni}(N,N\text{-dmen})_2]\mathrm{C_4O_4}$ (**6a**)	3265 s 3243 vs 3175 s 3132 w	2976 w 2881 w 2846 vw	1392 vw	1294 vs 1254 s 1162 vs 1117 vs 1065 vs	935 vs 891 s 827 vs 788 s	632 w 487 s
$[\mathrm{Ni}(N,N\text{-dmen})_2]\mathrm{C_4O_4}$ (**6b**)	3258 w 3232 s 3145 s	2965 s 2881 w 2820 vw	1388 w	1275 s 1150 s 1075 vs 1008 s	945 s 875 vs 809 s	595 s 475 w
$[\mathrm{Ni}(N,N'\text{-deten})_2]\mathrm{C_4O_4}$ (**8a**)	3260 s 3245 vs 3165 s 3129 s	2965 w 2875 vw 2833 s	1385 vw	1298 vs 1245 s 1155 vs 1055 vs	923 vs 875 s 823 s	640 w 508 s
$[\mathrm{Ni}(N,N'\text{-deten})_2]\mathrm{C_4O_4}$ (**8b**)	3255 vs 3220 s 3145 s	2965 vw 2881 w 2820 s	1375 w	1278 s 1240 s 1152 vs 1100 s 1040 s	915 vs 845 s	625 w 508 s 435 s

key: s = strong; w = weak, vs = very strong; vw = very weak.

powder diffraction patterns of each pair are thus compatible with conformational isomerism (Fig. 5).

Thermal Decomposition and Phase Transitions. Simultaneous TG- DTA analyses showed that [NiL$_3$]-C$_4$O$_4$·nH$_2$O (when L = meen; n = 1 and L = pn; n = 2) start to dehydrate at 134 and 95 °C, respectively (Fig. 2, Scheme 1), without showing any visual color changes. [NiL$_3$]C$_4$O$_4$ becomes rehydrated upon exposure to an open atmosphere. [Ni(meen)$_3$]C$_4$O$_4$ and [Ni(pn)$_3$]C$_4$O$_4$ undergo deamination followed by a squarate anion coordination reaction in the temperature range 175—210 and 198—265 °C to produce their corresponding bis-species, [NiL$_2$C$_4$O$_4$], which transforms to [NiL$_2$C$_4$O$_4$]·2H$_2$O (Scheme 1) upon being kept in an open atmosphere. Similarly, [Ni(en)$_3$]C$_4$O$_4$ and [Ni-(N,N'-dmen)$_3$]C$_4$O$_4$ form their corresponding bis-species, [NiL$_2$C$_4$O$_4$], in the temperature ranges 250—295 and 125—200 °C, respectively. However, these bis-species do not become hydrated in a humid atmosphere (Scheme 1). However, in all cases a tris- to bis-transformation is accompanied by a shifting of the electronic spectral band positions to a longer wavelength region (Table 1), thus corroborating a chromophoric change, N$_6$ to N$_4$O$_2$, around nickel(II), though a color change due to deamination followed by a squarate anion coordination reaction is not very visible. It is noted that the above shiftings are in accordance of spectrochemical series of the ligands (Fig. 4).

The complex [Ni(ibn)$_3$] C$_4$O$_4$·H$_2$O (**10**) starts to undergo dehydration upon heating at 98 °C, and transforms to [Ni-(ibn)$_3$]C$_4$O$_4$ (Fig. 2) at 125 °C. The dehydrated species becomes rehydrated upon keeping it in a humid atmosphere (Scheme 1). [Ni(ibn)$_3$]C$_4$O$_4$ upon heating exhibits an irreversible endothermic phase transition (145—160 °C; ΔH = 6.5 kJ mol^{-1}) (Figs. 2 and 3), without showing any color change. Although the IR-spectra of the low- and high-temperature phase species do not differ considerably, their X-ray powder diffraction patterns show some differences (Fig. 6).

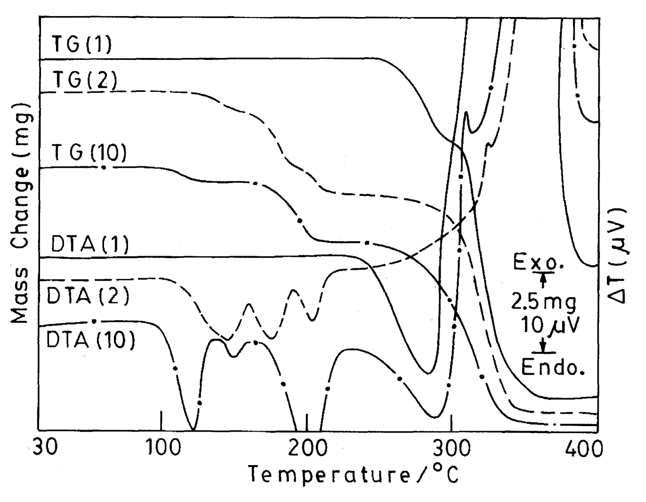

Fig. 2. TG-DTA curves for [Ni(en)$_3$]C$_4$O$_4$ (**1**) (wt taken = 13.65 mg) (—), [Ni(meen)$_3$] C$_4$O$_4$·H$_2$O (**2**) (wt taken = 13.40 mg) (- - -), and [Ni(ibn)$_3$]C$_4$O$_4$·H$_2$O (wt taken = 10.80 mg) (**10**) (– • –).

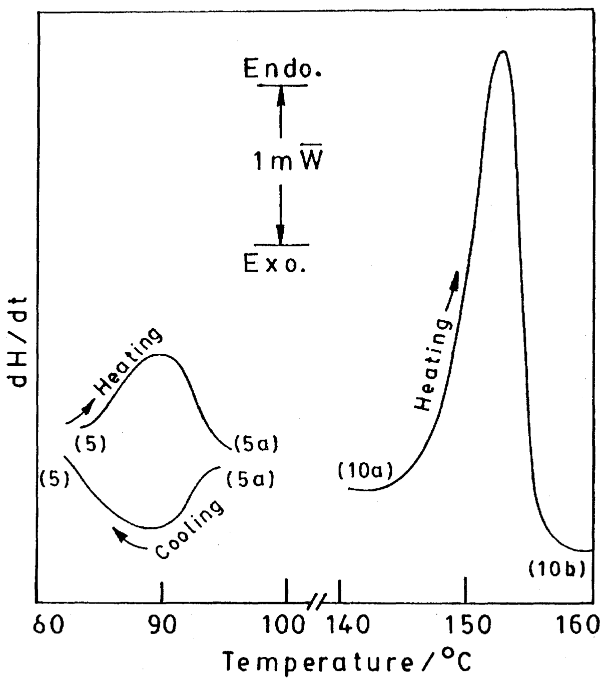

Fig. 3. DSC curves for [Ni(ipren)$_2$C$_4$O$_4$] (**5**) (wt taken = 8.05 mg) and [Ni(ibn)$_3$]C$_4$O$_4$ (**7a**) (wt taken = 7.55 mg).

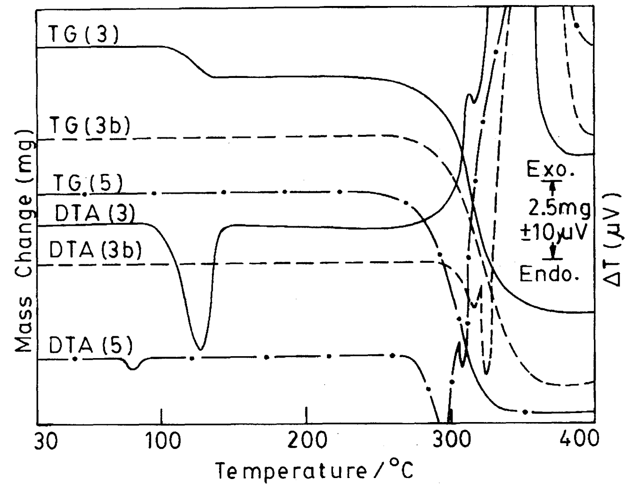

Fig. 4. TG-DTA curves for [Ni(eten)$_2$C$_4$O$_4$]·2H$_2$O (**3**) (wt taken = 10.70 mg) (—)[Ni(eten)$_2$C$_4$O$_4$] (**3b**) (wt taken = 11.80 mg) (- - -), and [Ni(pren)$_2$C$_4$O$_4$] (**5**) (wt taken = 11.00 mg) (– • –).

The magnetic and electronic spectral data (Nujol® mull) (Table 1) are typical of octahedral nickel(II). Thus, upon heating [Ni(ibn)$_3$]C$_4$O$_4$ (**10b**) undergoes an octahedral- to -octahedral phase transition, which may be due to conformational changes of the diamine chelate rings (see above). Upon further heating it undergoes deamination at 168 °C and transforms to square-planar [Ni(ibn)$_2$]C$_4$O$_4$.

Amongst the bis-species, only [Ni(ipren)$_2$C$_4$O$_4$] (**5**) exhibits a reversible endothermic phase transition (78—107 °C; ΔH = 1.4 kJ mol^{-1} for heating and 105—72 °C; ΔH = −1.3 kJ mol^{-1} for cooling; Fig. 3). The IR-spectra and X-ray powder diffraction of the high temperature phase species cannot

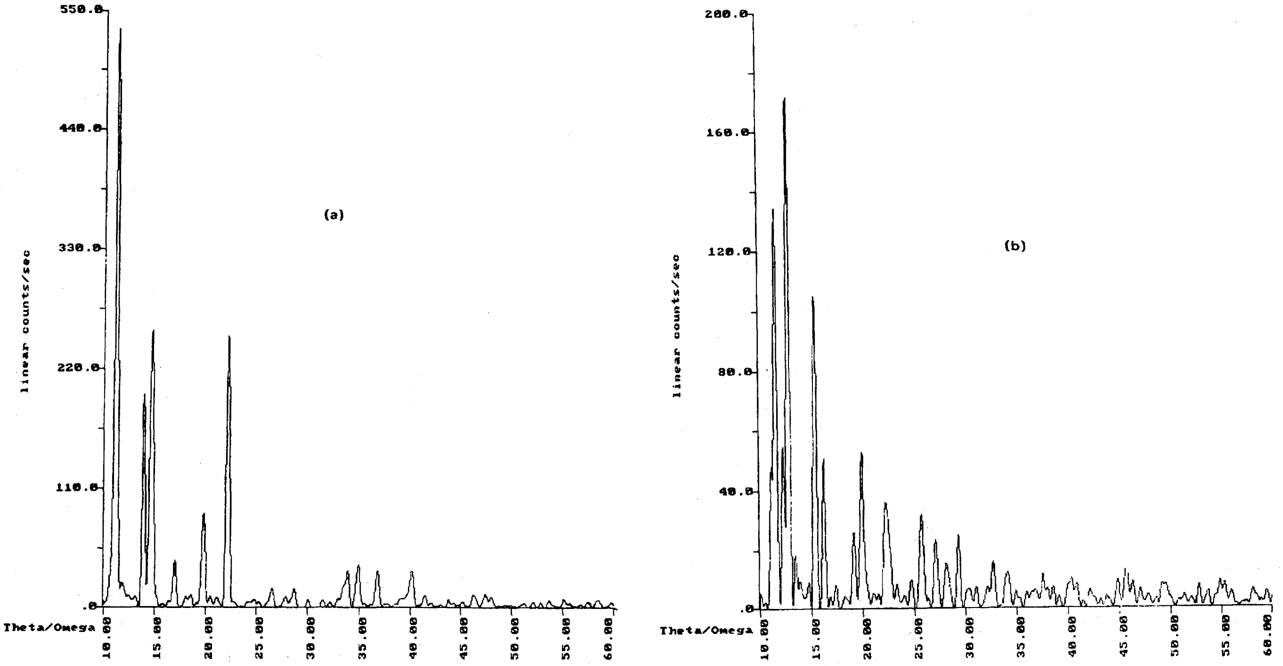

Fig. 5. (a) XRD-patterns of [Ni(eten)$_2$C$_4$O$_4$] (**3a**) [values of 2θ and d for major lines: 11.154, 7.9261; 13.921, 6.3564; 14.680, 6.0294, 19.788, 4.4830; 22.164, 4.0075]. (b) XRD-patterns of [Ni(eten)$_2$C$_4$O$_4$] (**3b**) [values of 2θ and d for major lines: 11.609, 7.6167; 12.284, 7.1998; 12.830, 6.8942; 15.411, 5.7449; 16.248, 5.4508; 19.947, 4.4477; 22.255, 3.9913].

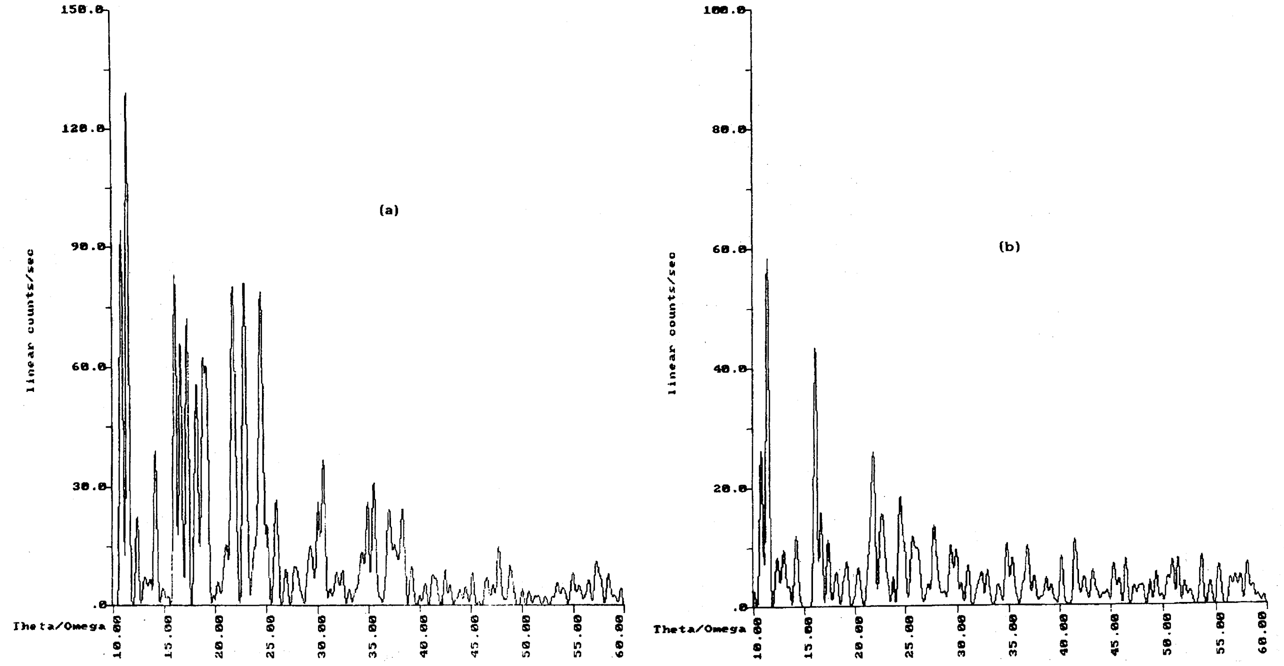

Fig. 6. (a) XRD-patterns of [Ni(ibn)$_3$]C$_4$O$_4$ (**10a**) [values of 2θ and d for major lines: 10.858, 8.1419; 11.479, 7.7027; 16.098, 5.5014; 16.669, 5.3141; 17.300, 5.1218; 18.220, 4.8651; 18.900, 4.6916; 21.808, 4.0722; 22.923, 3.8764; 24.511, 3.6289.]. (b) XRD-patterns of [Ni(ibn)$_3$]C$_4$O$_4$ (**10b**) [values of 2θ and d for major lines: 10.787, 8.1949; 11.419, 7.7430; 16.108, 5.4981; 21.823, 4.0694; 24.482, 3.6330.].

be measured because of a lack of instrumental facilities; thus, the cause behind the reversible phase transition remains unexplored. The bis (diamine) dihydrate complexes [(**3**), (**4**), (**6**), and (**8**)] obtained by Technique 1 upon heating lose two molecules of water, but revert upon keeping them in an open atmosphere (Scheme 1). The bis-species [(**3b**), (**4b**), (**6b**), and (**8b**)] obtained by Technique 2 do not become hydrated upon keeping them in an open atmosphere, and undergo decomposition at a slightly higher temperature (Scheme 1) than the corresponding bis-species derived form Technique 1.

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