Synthesis and Physico-chemical Studies on Hexacoordinate Silicates of 2,3-Dihydroxynaphthalene

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Chapter 1 Introduction

Chapter 2 Experimental Methodology

Chapter 3 Synthesis and characterization of hexacoordinate silicate of 2,3-dihydroxynaphthalene with ammonium counter ion

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Chapter 5 Pyrolytic and hydrolytic stability of bis(ammonium)tris(2,3-dihydroxynaphthalato)silicates: A study with relevance for biosilification

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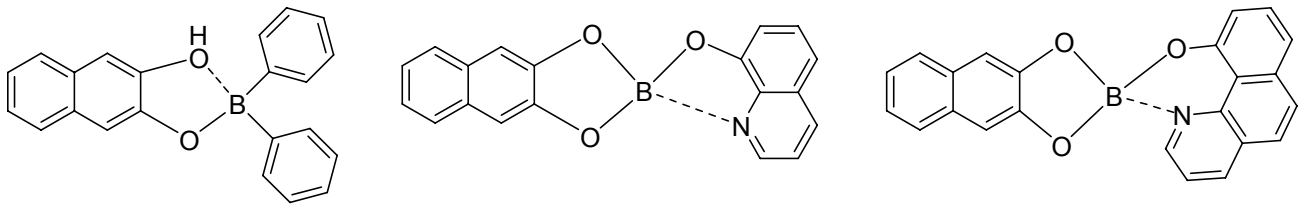
Summary and Conclusions

Importance of 2,3-naphthalenediol

- specific competitive inhibitor of phenolase

A Rescigno, F Sollai, B Pisu, A Rinaldi, E Sanjust *J Enz. Inh. Med. Chem.* **2002**, *17*, 207 - 218

- optical material (its Boron complex)



Lim, HJ, Kim, SM, Lee, SJ, *Opt. Mater.*, **2003**, *21*, 211-215

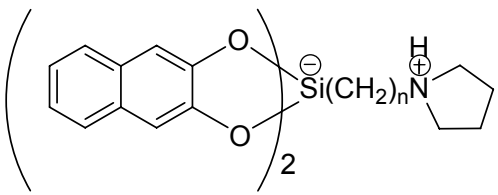
- uranium extraction

J. Rad. Nucl. Chem. **2002** *253*, 135-142

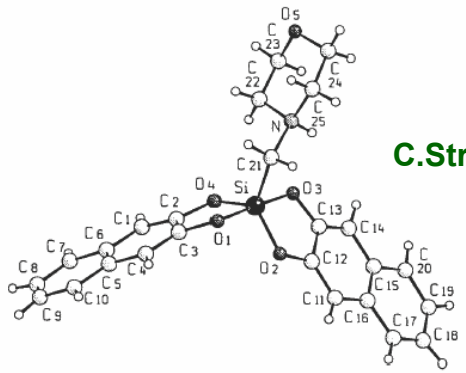
- extraction of Iron in picomolar concentration in sea water K=11.9 (13.9)

Van de Berg CMG *Anal. Chem.* **2006**, *78*, 156-163

Silicon pentacoordinate complexes were well studied structurally



(R=Ph, n-C_6H_{11}, Me, MeO)(n=1, 2)



C.Strohmann, R.Tacke, *J.Orgmet.Chem.* **1991** *403*,63-71

OBJECTIVES OF THE STUDY

- To develop synthetic strategy for hexacoordinate silicates incorporating 2, 3-dihydroxynaphthalene with various counter cations such as alkyl ammonium ion or ethylenediamine complexes of 3d- transition metals.

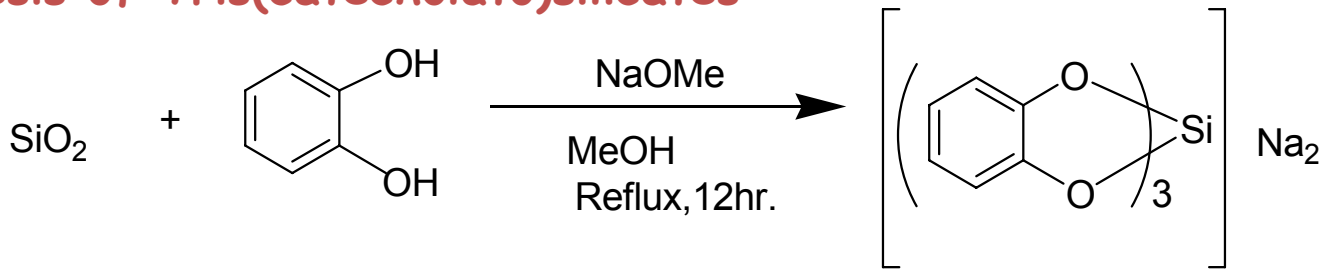
- To investigate their structure and also their stability in presence of different counter ions under thermal and hydrolytic conditions.

- To study the redox behavior of 2,3-dihydroxynaphthalene ligand in hexacoordinate silicon environment.

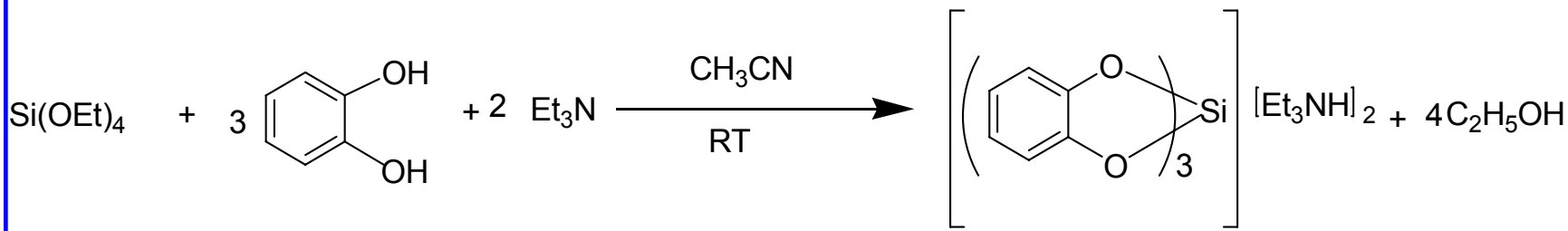
- To utilize these silicates for the synthesis of catalytic materials such as mesoporous silica and metal silicates.

Chapter 3: Synthesis and Characterization of hexacoordinate silicates of 2,3-dihydroxynaphthalene

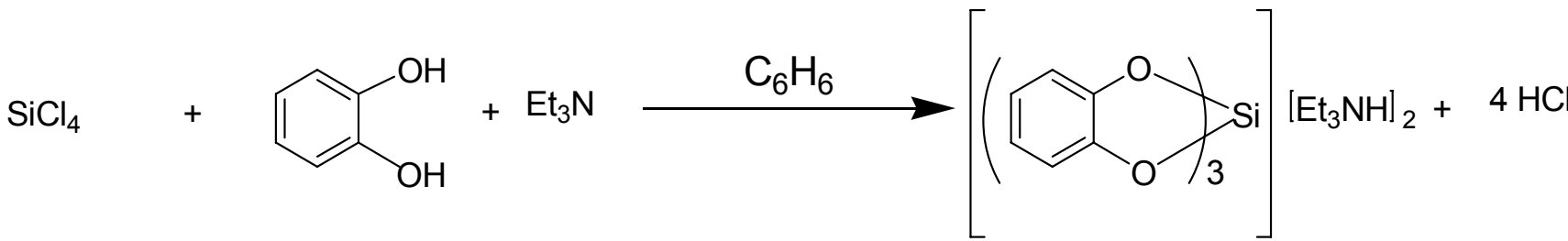
Synthesis of Tris(catecholato)silicates



M.L.Hoppe, R.M.Laine, J . Kampf, M.S. Gordon, L.W *Angew Chem*. **1993** 105,283

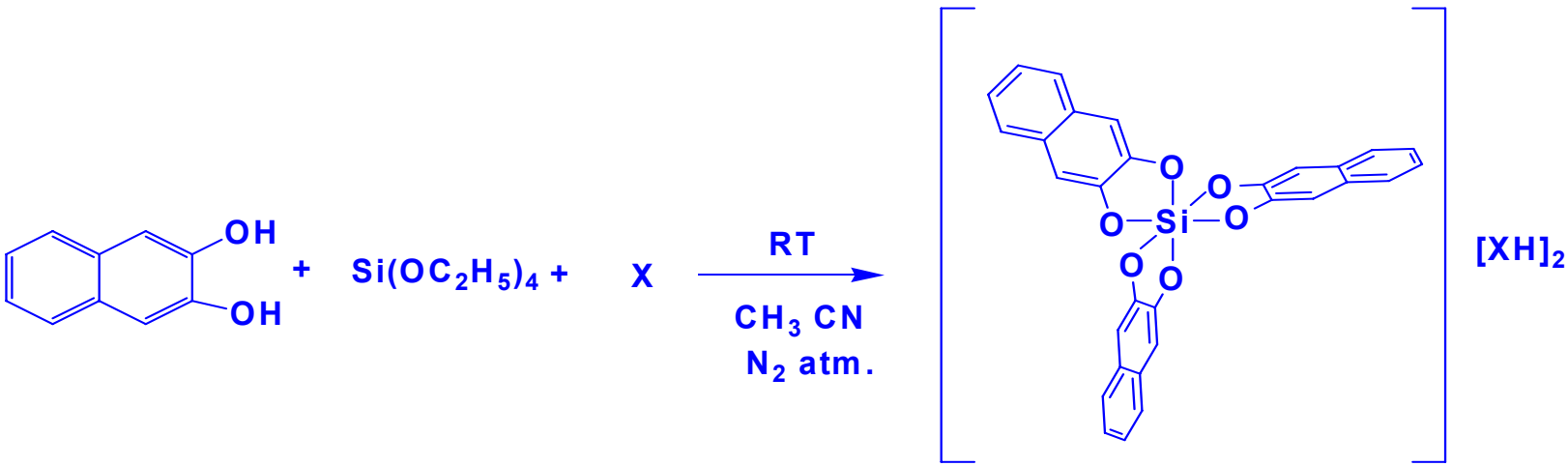


J.V.Kingston, B.Varghese, M.N.S.Rao *Main Group Chem*. **2000**,3,79



A.Rosenheim O.Sorge, *Ber Dtsch. Chem. Ges* **1920**,53,932

Synthesis of Hexacoordinate Silicates of 2,3- DHN

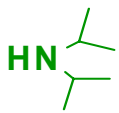
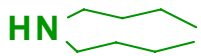


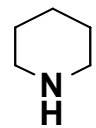
3⁰ Amines

2⁰ Amines

Cyclic Amines

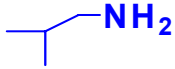
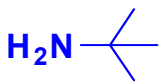
X = (1)  (2) 

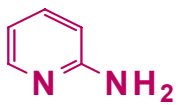
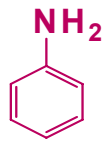
(3)  (4) 

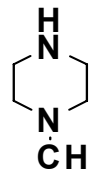
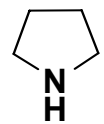
(5)  (6) 

1⁰ Amines

Aromatic Amines

(9)  (10) 

(11)  (12) 

(7)  (8) 

List of compounds and their percentage Yield at RT

Compd no.	Bis(**ammonium**)tris(2,3-dihydroxynaphthalato)silicate	Compound name	pK_a of amines	% Yield
1	**Triethyl**ammonium	TEASINAP	10.75	96
2	**Tri-*n*-butyl**ammonium	TnBASINAP	11.95	92
3	**Di*iso*butyl**ammonium	DIBASINAP	12.78	93
4	**Di*iso*propyl**ammonium	DIPASINAP	11.72	60
5	***Sec*-Butyl**ammonium	secBASINAP	10.56	75
6	***t*-Butyl**ammonium	*t*-BASINAP	10.68	65
7	**Pyrrolidinium**	PydSINAP	12.0	60
8	**Piperidinium**	PidaSINAP	10.70	72
9	**morpholinium**	MopSINAP	8.36	68
10	**N- Methylpiperazinium**	NMPSINAP	4.75	75
11	**2-Aminopyridinium**	2AmSINAP	6.82	70
12	**Anilinium**	AniliniumSINAP	30.6	45

Advantages and Shortcomings

Advantages

- Reaction is feasible even at room temperature in good yield.
- By product of this reaction ethanol (green chemistry)
- This reaction is viable for a variety of amines

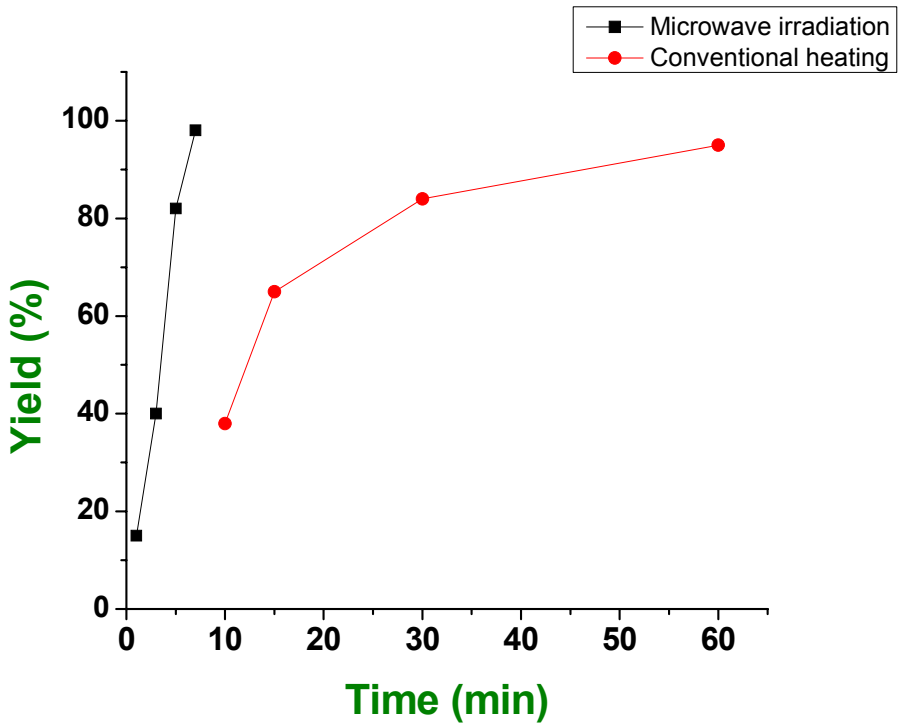
Shortcomings

- Reaction time is longer
- In acetonitrile medium product undergoes cleavage

Effective Synthesis – Microwave Condition

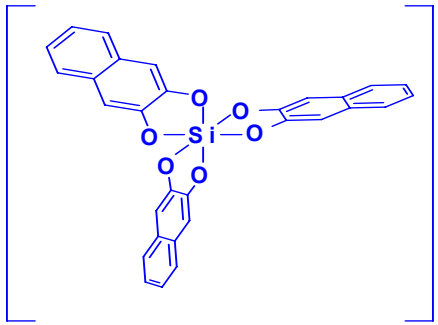
- Kinetic enhancement - decrease of the energy of activation resulting from changes in the entropy of activation term
- The temperature of alumina can differ from probe temperature by 100-200 °C
- The oil bath temperature set at 110 °C for 10, 15, 30, and 60 min.

Bis(triethylammonium) tris(2,3-dihydroxynaphthalato)silicate



A. Suvitha, Babu Varghese, M.N.S. Rao, G.Sundararajan and B.Viswanathan *Indian Journal of Chemistry A* (2006) ***45A***, *2193-2198.*

Comparison of Reaction Yield Under Different Conditions



$[XH]_2$

X = (1) $N(C_2H_5)_3$ (2) $N(n\text{-}C_4H_9)_3$

(3) $HN(i\text{-}C_3H_7)_2$ (4) $HN(C_4H_9)_2$

(5) $O(CH_2)_2NH$ (6) $t\text{-}C_4H_9NH_2$

Complexes	Reaction Conditions and yield					
	RT		Microwave		Conventional	
	Time (hr)	Yield (%)	Time (min)	Yield (%)	Time (hr)	Yield (%)
TEASINAP(1)	4	96	7	95	1	92
TnBASINAP(2)	5	92	6	98	1	90
DIPASINAP(3)	4	60	7	88	1	75
DnBASINAP(4)	6	93	5	94	1	90
MOPSINAP(5)	4	60	7	90	1	88
t-BASINAP(6)	4	65	5	90	1	87

RT - Room temperature in acetonitrile solvent
MW - Microwave condition, neat reaction with excess amine
CH - conventional oil bath heating with excess amine without solvent

Analytical Data of Bis(ammonium)tris(2,3-dihydroxynaphthalato)silicate

	AmSINAP	IR (cm^{-1})	Elemental analysis			MALDI MS Negative mode
			C (%)	H (%)	N (%)	
1	TEASINAP	3020,**1586,1478,1266,1166,871, 846,742,692,640,583,484,420**	71.09 (71.39)	6.96 (7.08)	4.10 (3.97)	503.1(100%)
2	TnBASINAP	3039,2960,2872,**1586,1477,1381 ,1247,1166,871,850,738,688, 639,589,485,420**	73.83 (74.14)	8.55 (8.47)	3.19 (3.20)	503.3(100%)
3	DIBASINAP	3030,2986,**1587,1477,1260,1167 ,871,846,744,686,744,689,640, 591,485,420**	70.71 (71.39)	7.03 (7.08)	4.33 (3.97)	503.2(100%)
4	DIPASINAP	2962,2931, 2868, **1587, 1472,1261, 1167,1108,871, 739, 693, 638, 586, 485**	72.4) (73.94)	7.71 (7.61)	3.33 (3.67)	503.5(100%)
5	MOPSINAP	3030,2937,2857,**1586,1474,1274 ,1166,868,839,743,696,585,484 ,419**	74.93 (74.83)	7.73 (7.62)	3.28 (3.23)	503.2(100%)
6	NMPSINAP	3020,**1586,1478,1260,1166,871 ,846,742,692,640,583,484,420**	67.89 (68.04)	4.61 (4.51)	4.07 (4.17)	503.5(100%)

	AmSINAP	IR (cm^{-1})	Elemental analysis			MALDI MS Negative mode
			C(%)	H(%)	N(%)	
7	PidASINAP	3050,2986,**1587,1477,1265,1167,871,846,744,686,744,689,640,591,485,420**	68.28 (68.14) (7.95)	6.58 (6.29)	7.75	503.9 (100%)
8	PYDASINAP	3030,2986,**1587,1477,1263,1167,871,846,744,686,744,689,640,591,485,420**	70.66 (70.56) (4.33)	5.87 (5.92)	4.55	503.6 (100%)
9	SecBASINAP	3020,**1586,1478,1247,1166,871,846,742,692,640,583,484,420**	70.20) (70.12)	6.4 (6.52)	4.42 (4.31)	503.5 (100%)
10	t-BASINAP	3026,2958,**1587,1473,1257,1166,868,845,748,698,638,595,487,421**	70.30) (70.12)	6.8 (6.52)	4.32 (4.31)	503.2 (100%)
11	AniliniumSINAP	3035,2958,**1587,1473,1259,1166,868,845,748,698,638,595,487,421**	72.3) (72.48)	4.87 (4.56)	4.12 (4.22)	503.5 (100%)
12	2AmpySINAP	3041,**1586,1478,1266,1166,871,846,742,692,640,583,484,420**	73.18 (73.07)	4.20 (4.09)	7.39 (7.19)	503.7 (100%)

NMR Data Table of Bis(ammonium)tris(2,3-dihydroxynaphthalato)silicate

	AmSINAP	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)	^{29}Si NMR (δ, ppm)
1	TEASINAP	**7.40(m,6H),7.01(m,6H),6.68(s,6H),** 3.07(q,12H), 1.18(t,18H)	**153.4, 130.2, 125.1, 122.1, 103.4**, 46.1, 7.6	-139.0
2	TnBASINAP	**7.43(m,6H),7.08(m,6H),6.69(s,6H)**,3.27(m,6H),1.71(m,6H),1.25(m,6H),0.74(t,9H)	**152.30, 129.65, 125.24, 121.11,104.18,52**.88,25.20 .11,13.45	-141.35
3	DIPASINAP	**7.48(m,6H),7.11(m,6H),6.76(s,6H)** 3.50(sep,24H),.40(d,4H)	**153.81,130.59,126.20, 122.07,104.44**,49.23, 19.44	-140.98
4	DIBASINAP	**6.75(s,6H),7.05(m,6H), 7.44(m,6H)** 0.90(d,18H),2.13(sep,3H), 2.98(d,18H),	20.3,26.1,56.2, **104.7,122.3,126.3, 130.6,153.5**	-143.9
5	MOPSINAP	**7.46(m,6H),7.06 (m,6H), , 6.79 (s,6H)**,3.91 (m, 8H); 3.35 (b,4H), 3.32 (m,8H)	**153.53,131.00,126.66,122.6,105.22**,65.17,45	-142.8
6	NMPSINAP	**7.46(m,6H),7.06 (m,6H), 6.79 (s,6H),** 2.30(s,6H),3.00(t,8H),3.3(t,8H)	**153.53,131.00,126.66,122.6,105.22**,46,57.4,43.1	-142.10

7	PidaSINAP	**7.45(m,6H), 7.05(m,6H), 6.68(s,6H),**3.27 (m,6H),1.71(m,6H),1.25(m,6H),0.74(t,9H)	**152.30, 129.65, 125.24,121.11,104.18,**48.3, 28.1, 25.6	-140.92
8	PYDASINAP	**7.33(m,6H), 7.18(m,6H), 6.70(s,6H)**,3.27 (m,6H),1.71(m,8H),1.25(m,8H)	**153.53,131.00,126.66,122.6,105.22**,48.7, 28.1	-141.20
9	*Sec*BASINAP	**7.43(m,6H), 7.08(m,6H), 6.77(s,6H)**,3.27 (m,4H),1.71(m,12H),1.25(m,2H)	**152.30, 129.65, 125.24,121.11,104.**50.5,31.4, 20.3	-142.89
10	*t*-BASINAP	**7.45(m,6H), 7.14(m,6H), 6.93(s,6H),** 1.04(*s*,18H)	**153.46, 130.59, 126.29,122.23,104.79**,28.26,	-140.60
11	AniliniumSINAP	**7.43(m,6H), 7.08(m,6H), 6.69(s,6H),** 6.27(m,6H),7.01(m,4H),	**153.53,131.00,126.66,122.6,105.22**,148,122,130	-142.91
12	2-AmPySINAP	**7.43(m,6H),7.08(m,6H),6.69(s,6H),** .6.7(m,4H),7.48(m,4H),8.11(m,2H)	**153.81,130.59,126.20, 122.07,104.44,**148,159,109,113,138	-143.26

Chapter 4 Single Crystal X-ray Structures of $[(n\text{-}C_4H_9)_3NH]_2[Si(C_{10}H_6O_2)_3]$ & $[(i\text{-}C_4H_9)_2NH_2]_2[Si(C_{10}H_6O_2)_3].3CH_3CN$

- Bis(ammonium)tris(catecholato)silicates Si-O bond length (Å) details

$[(OH)(CH_2)_2N(Me)_2H^+]$

Si-O1 - 1.773
Si-O2 - 1.791
Si-O3 - 1.798

1

$(C_3H_7)_2NH_2^+$

Si-O1 - 1.791
Si-O2 - 1.808
Si-O3 - 1.766

2

Li^+

Si-O1 - 1.772
Si-O2 - 1.784
Si-O3 - 1.793

3

$[HP(tBuNCH_2CH_2)_3N]$

Si-O(1) - 1.7819
Si-O(2) - 1.7882
Si-O(3) - 1.7848

- H-bonding in the first 1-3 there is extended network has formed whereas in the case 4 there is no hydrogen bonding interaction is seen

Kingston J V and Verkade J G., *Inorg. Chem. Com.* ***2005,*** *8, 643-646*

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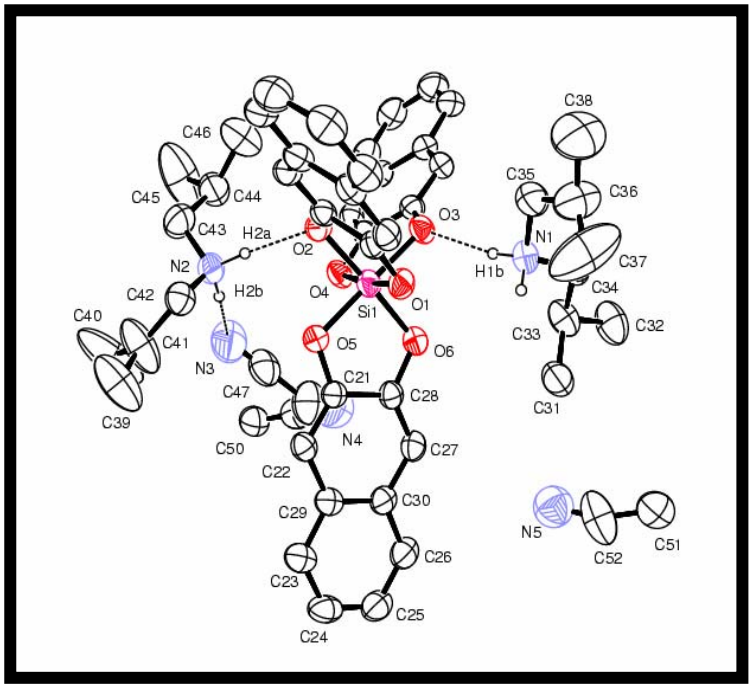
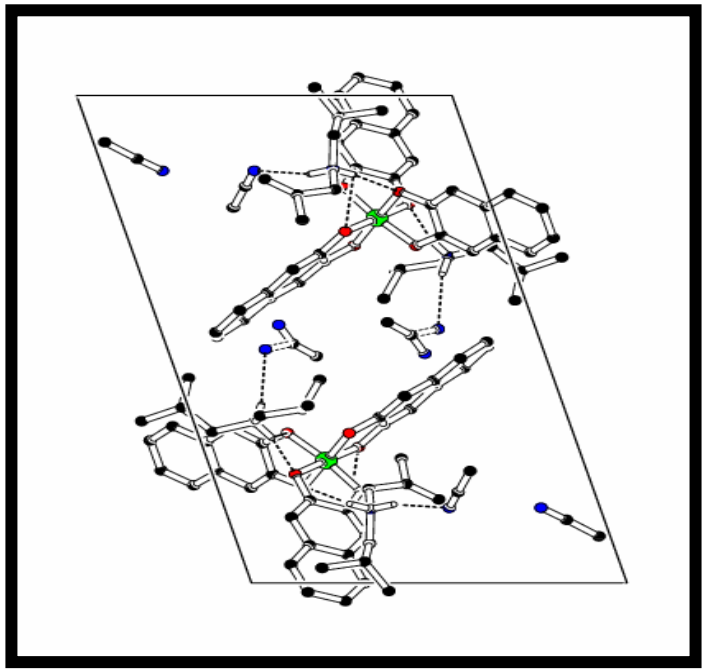
Bis(diisobutylammonium)tris(2,3-dihydroxynaphthalato)silicate

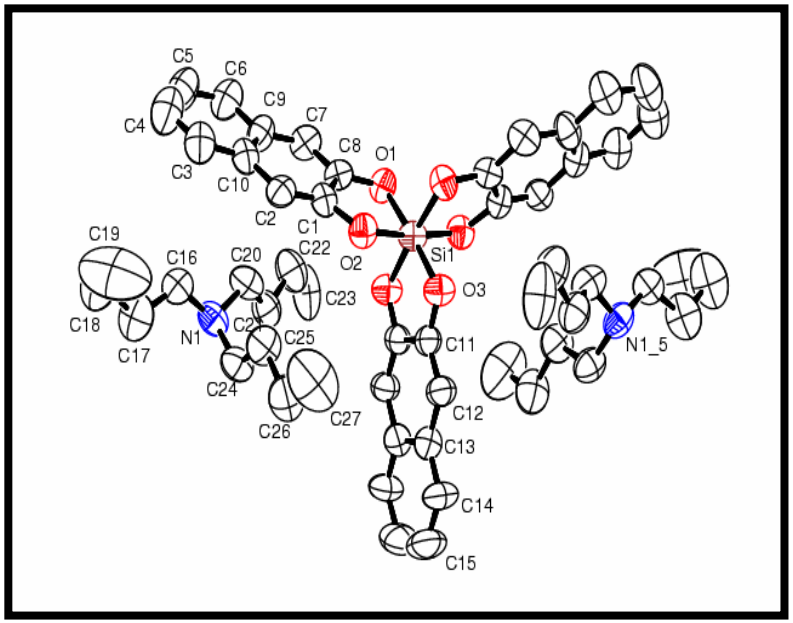


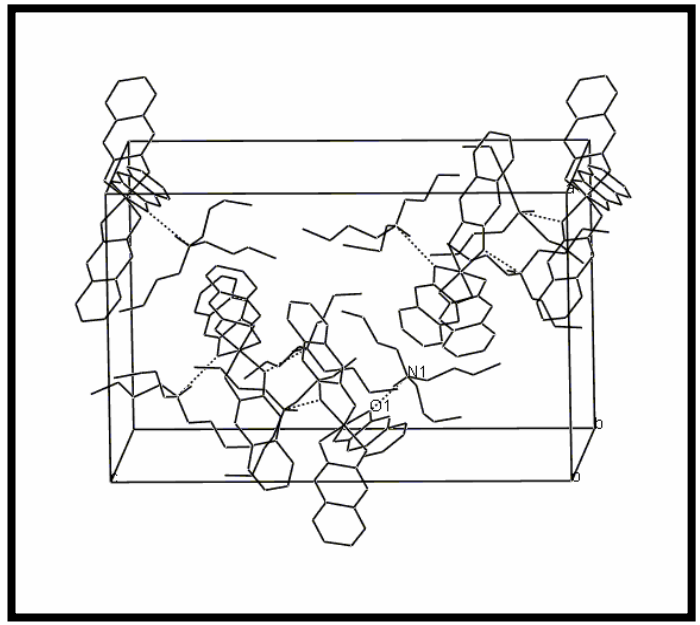


Crystal system - Triclinic
Space group - P-1
Hydrogen bonding
O…H-N
N…H-N

A.Suvitha, Babu Varghese & M.N.Sudheendra rao *Acta Cryst.* 2006, *E62*, o344-o346

Bis(tri-*n*-butylammonium)tris(2,3-dihydroxynaphthalato)silicate





Crystal system - Tetragonal
Space group - P41 21 2
Hydrogen bonding O….H-N

A. Suvitha, Babu Varghese, M.N.S. Rao, G.Sundararajan and B.Viswanathan *Indian Journal of Chemistry A, (2006)* ***45A****, 2193-2198.*

Chapter 5 Pyrolytic and hydrolytic stability of bis(ammonium) tris(2,3-dihydroxynaphthalato)silicates: A study with relevance for biosilification

- 2,3-DHN and ammonium surfactant – template for tube silicate synthesis

  Isayama, M, Nomiyama, K, Yamaguchi *Chem. Lett.* 2005 *34* 462-463

- Silica in diatoms are with Particle size = 50-100nm with Pore size ranging from micro to nanoporous

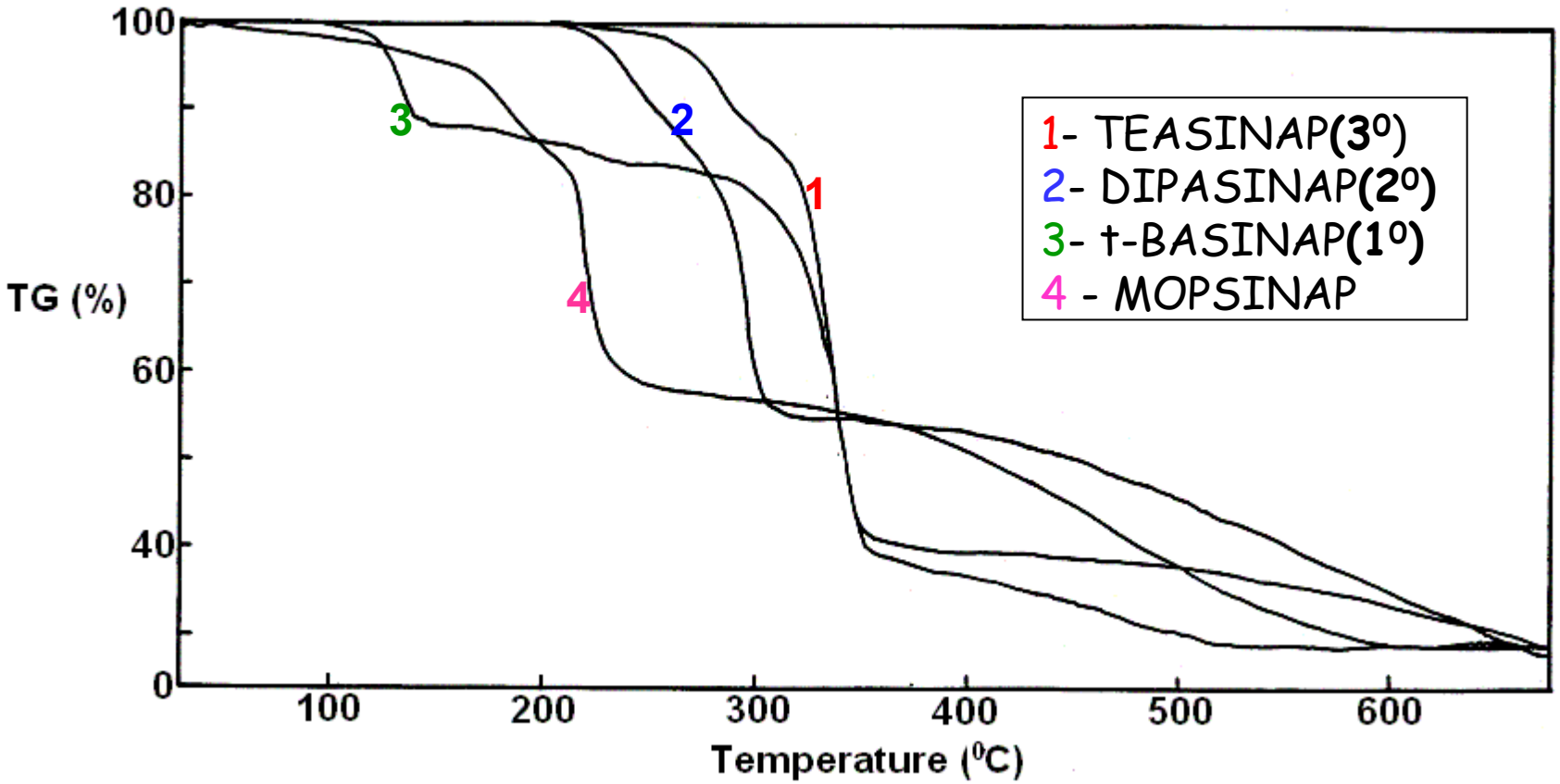
  Coradin et al curr. Sci 2005, 1(1), 73-82

- Ion conducting polymer by heating Ba [tris(ethylenedioxy)silicate(2-)] in presence of ethylene glycol at 120 degree

  Chew, K. W.; Dunn, B.; Faltens, T.; *Polymer Preprints*, 1993, *34*, 254-5.

Counter ion effect on thermal stability

TGA of Bis(ammonium)tris(2,3-dihydroxynaphthalato)silicate



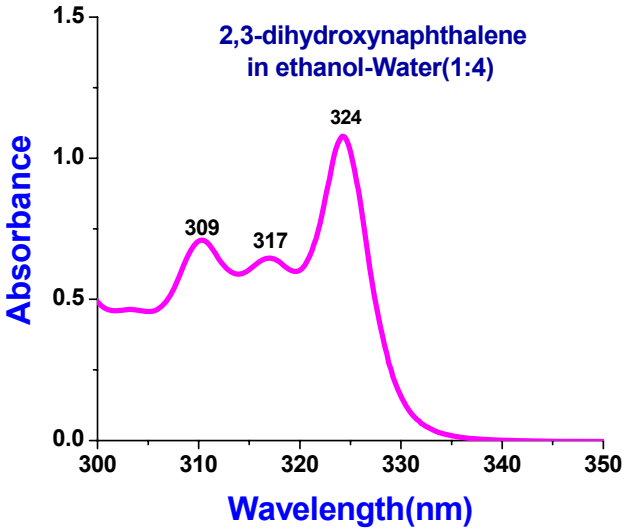
- Thermal stability of these derivatives lies in the following order 3° >2° >1
- Spirosilane formation is not observed unlike in tris(catecholato)silicate

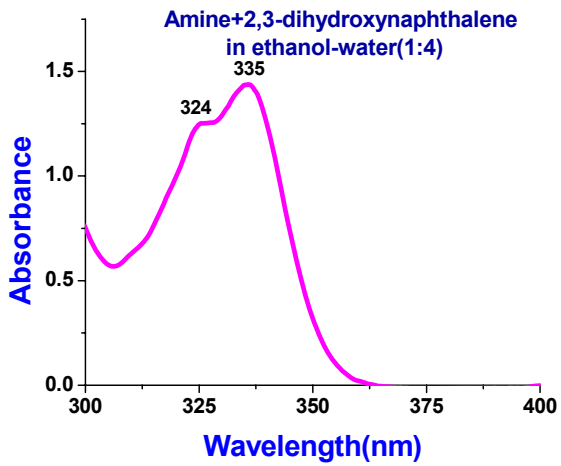
TGA –DTA data table of Bis(ammonium)tris(2,3-dihydroxynaphthalato)silicates

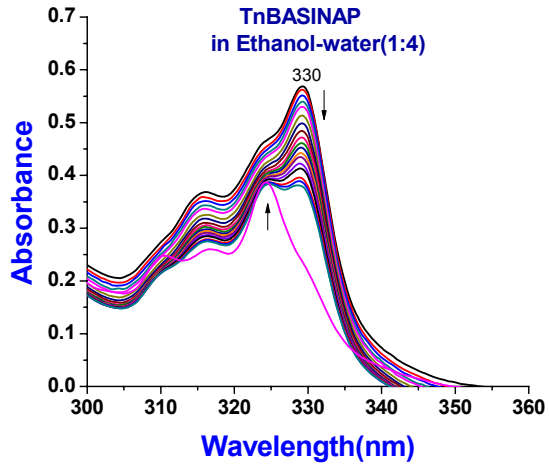
Compd.	Decomposition I*			Decomposition II @			Decomposition III#		
	Temp. range (°C)	Wt.loss (%)	DTA (°C)	Temp. range (°C)	Wt.loss (%)	DTA (°C)	Temp range (°C)	Wt.loss (%)	DTA (°C)
TnBASINAP	50-290	13.9	227	225-375	49.55	347.0	375-800	27.43	610.9
TEASINAP	50-280	11.9	150	280-425	52.8	282.0	425-800	23.9	-
DIPASINAP	210-300	11.9	-	300-390	65.62	-	390-800	12.47	-
DIBASINAP	50-270	23.5	-	270-800	68.7	-	-	-	-
MopSINAP	50-290	11.16	255.1	290-390	38.28	316.4	390-900	38.47	688.2
NMPSINAP	50-250	2.65	-	150-350	14.59	-	305-800	75.60	-
PIDASINAP	50-325	30.1	-	325-800	61.1	-	-	-	--
PyDASINAP	50-100	2.60	-	100-550	54.8	-	550-800	32.00	--
Sec-BASINAP	50-145	3.38		145-294	30.9	-	294-800	48.10	--
t-BASINAP	50-220	18.7	212.6	220-480	65.6	382.1	480-800	23.00	660.0
2AmPySINAP	50-280	26.8	-	280-800	52.2	- --	---	----	-----

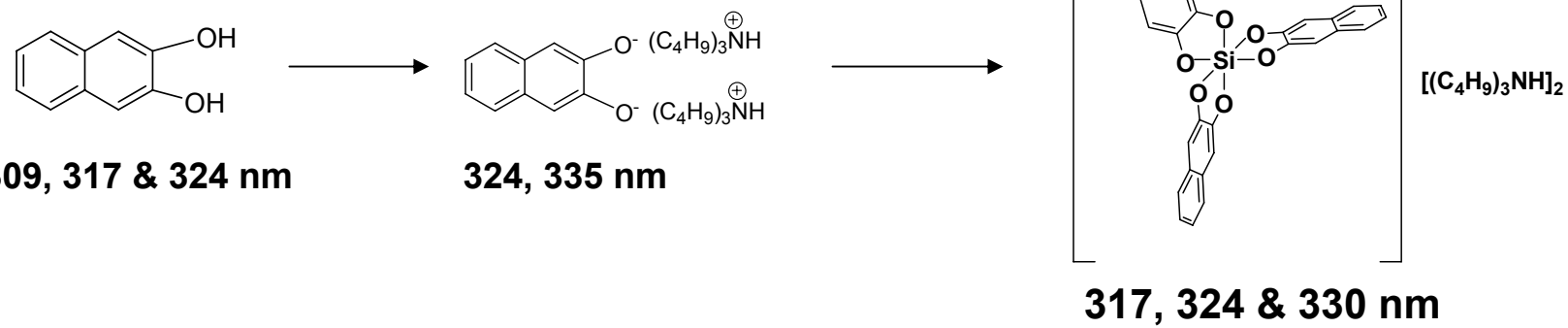
*Loss of solvent/water
@ loss of ammonium naphthalate/2,3-dihydroxynaphthalene
# loss of 2,3-dihydroxynaphthalene(no.)

Hydrolysis of Complex in presence of water









309, 317 & 324 nm

324, 335 nm

317, 324 & 330 nm

- **Silicon complexes decomposes to 2,3-dihdyroxynaphthalene, Alkyl ammonium hydroxide and silicic acid**

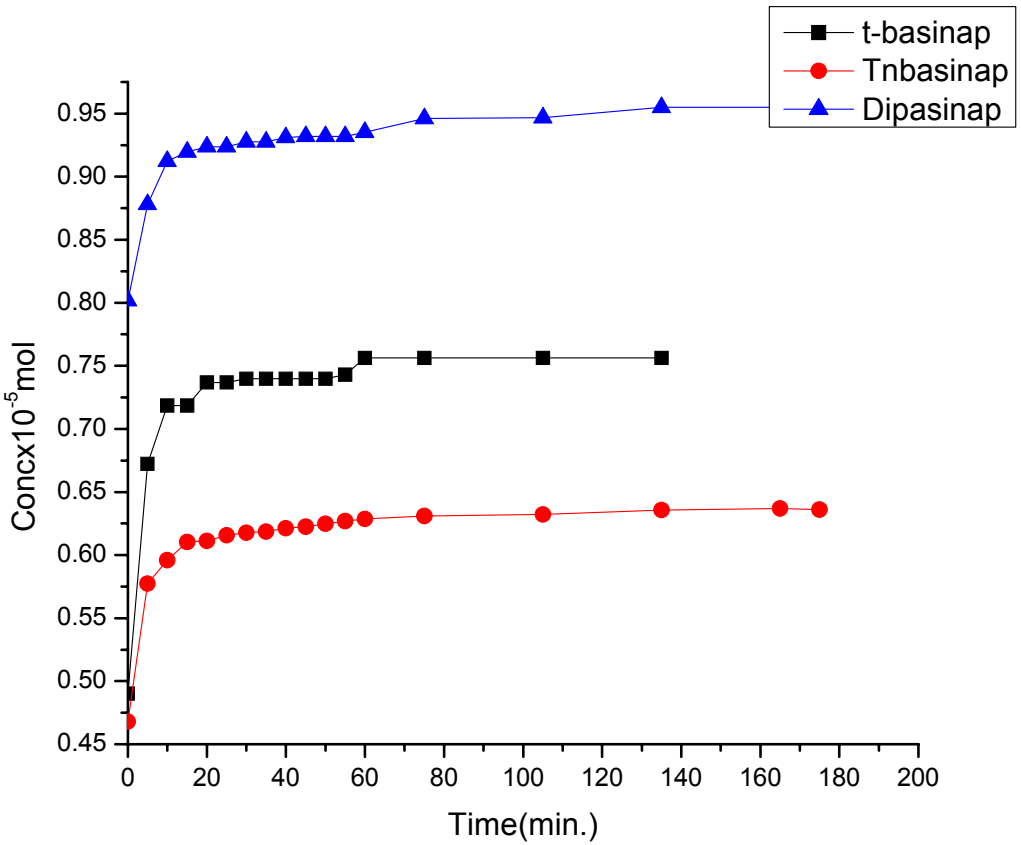
Molybdate Blue Test

$AmSINAP + H_2O \rightarrow$ "$Si(OH)_4$" + C10H8O2 + AmOH

"$Si(OH)_4$" $\xrightarrow{AmOH}$ $(Si\text{-}O\text{-}Si\text{-})_n$

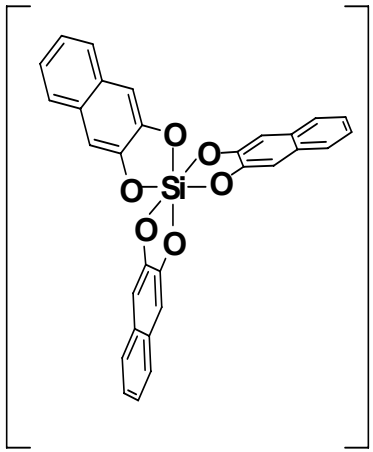
$(Si\text{-}O\text{-}Si\text{-})_n \rightarrow Si(OH)_4$

$Si(OH)_4 \xrightarrow{NH_4MoO_4} H_2SiO_3\ MoO_4^{2-}$



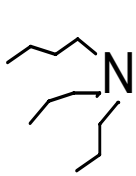
Silica - Hydrolytic and Pyrolytic Conditions

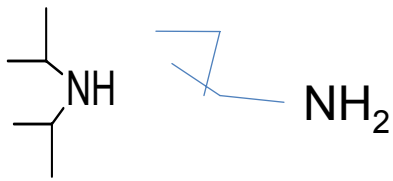
Bulk pyrolysis - Silicates as precursor - porous silica



$[XH]_2$ $\xrightarrow[\text{at 700 °C for 3 hrs}]{\text{Heat}}$ SiO_2

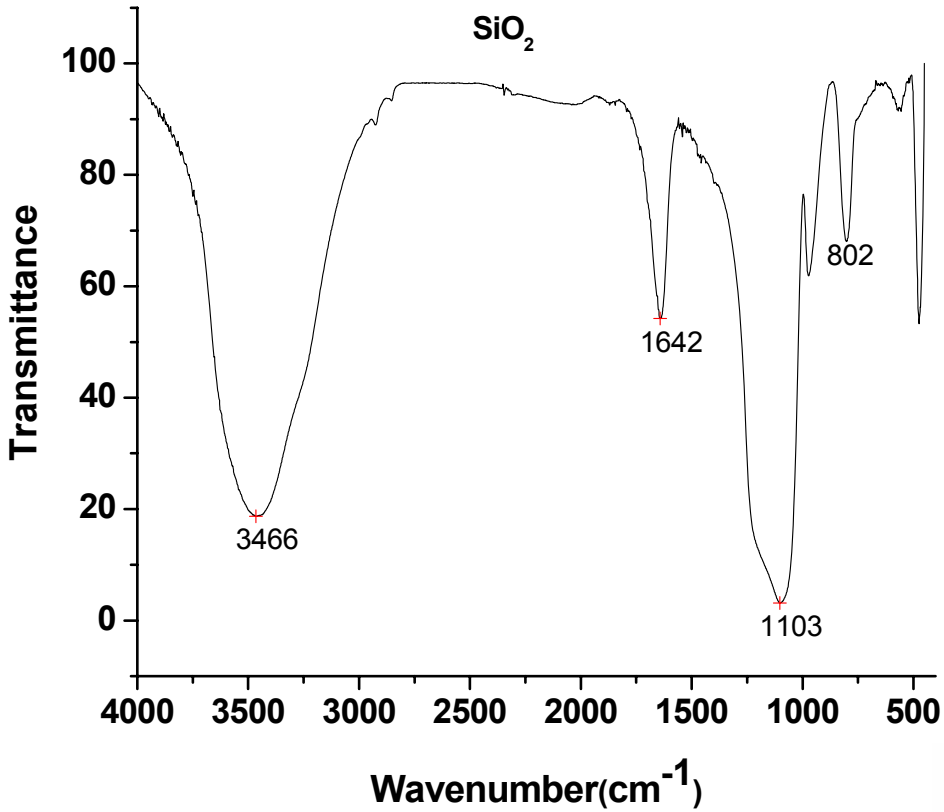
X=

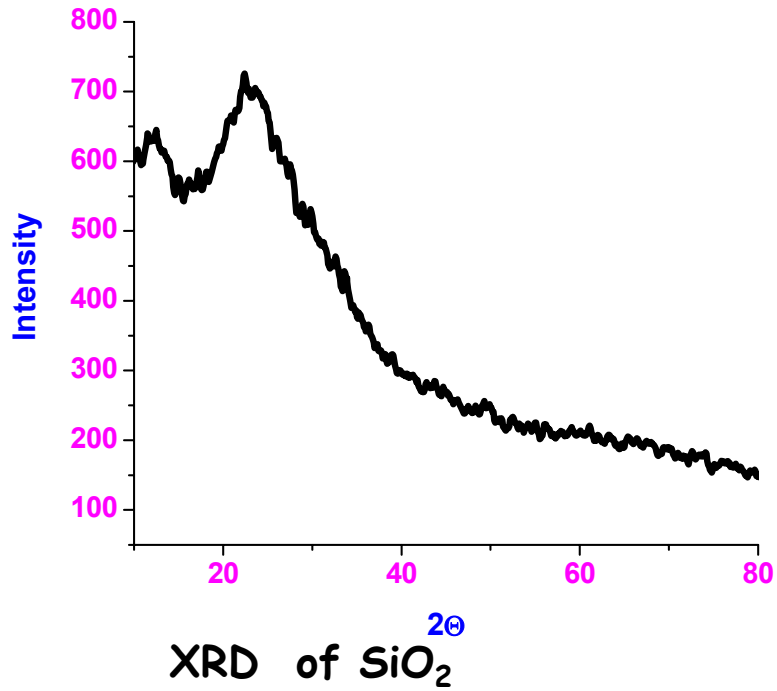




- **Silica obtained by pyrolysis is amorphous**

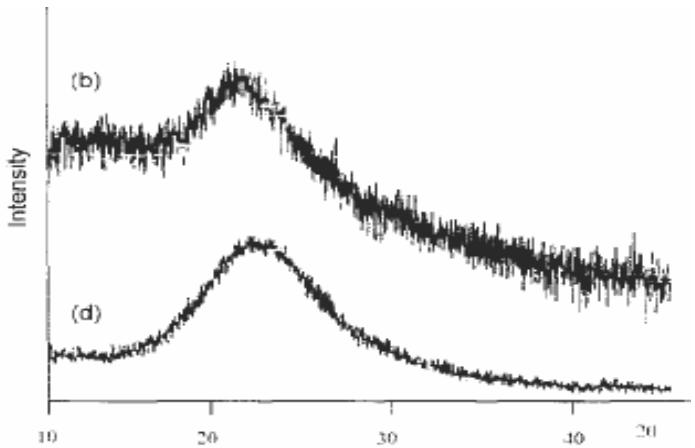
IR and XRD of Silica





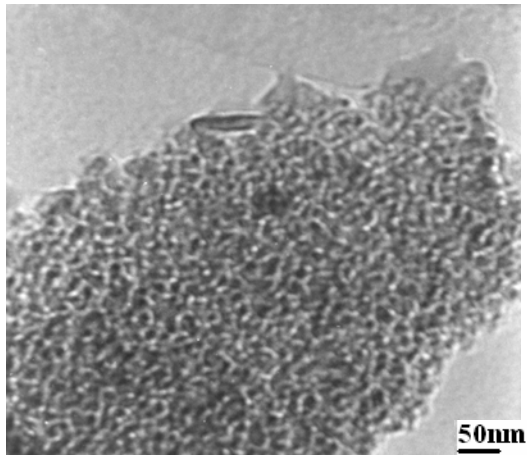
XRD of SiO_2

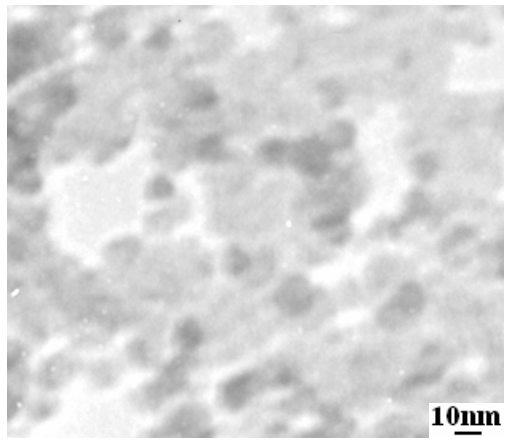
- Silica has been characterised
- XRD- amorphous
- IR - Si-O stretch at 1103cm^{-1}

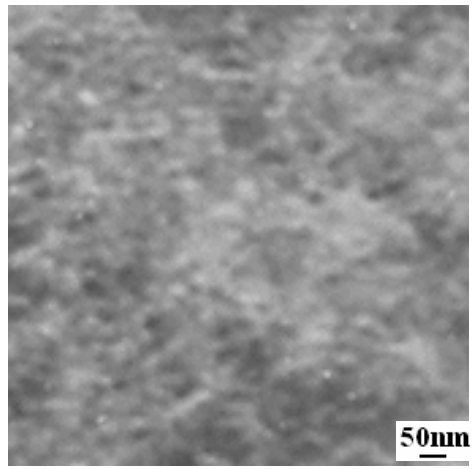


H.Hamdan et.al *J. Non Cry. Solid* **1997**,211,126-131

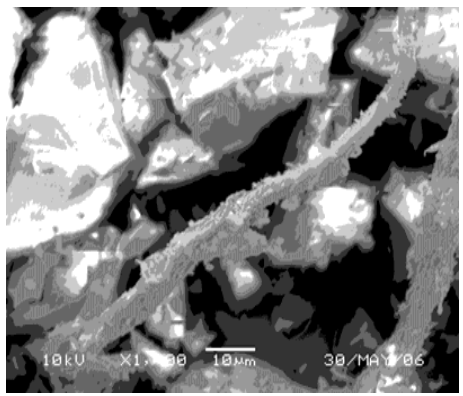
TEM pictures of Silica



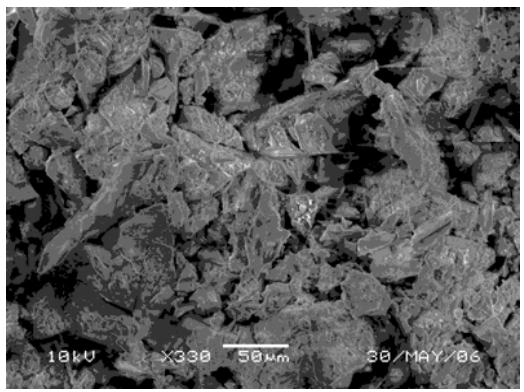




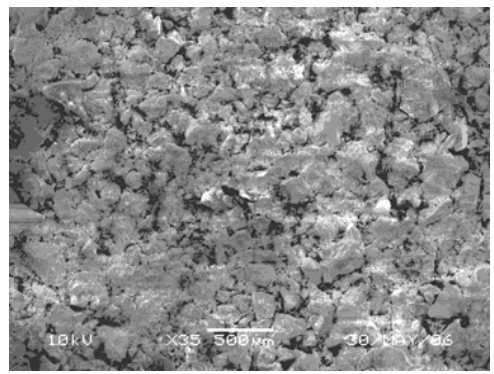
SEM pictures of silica



TnBASINAP



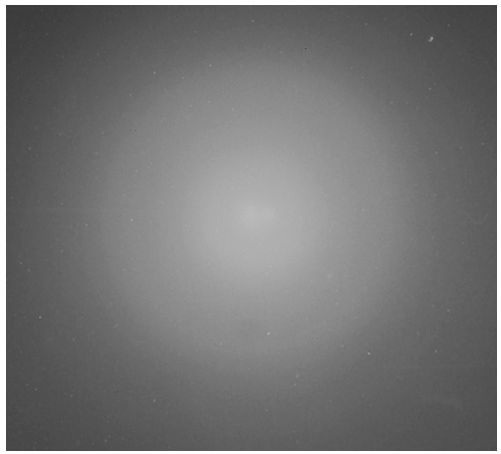
^{t}BASINAP

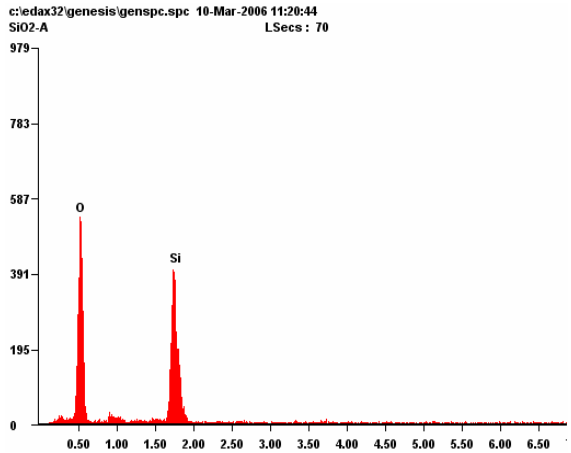


DIPASINAP

Particle size range - 2-8 nm

EDAX and Selective area diffraction



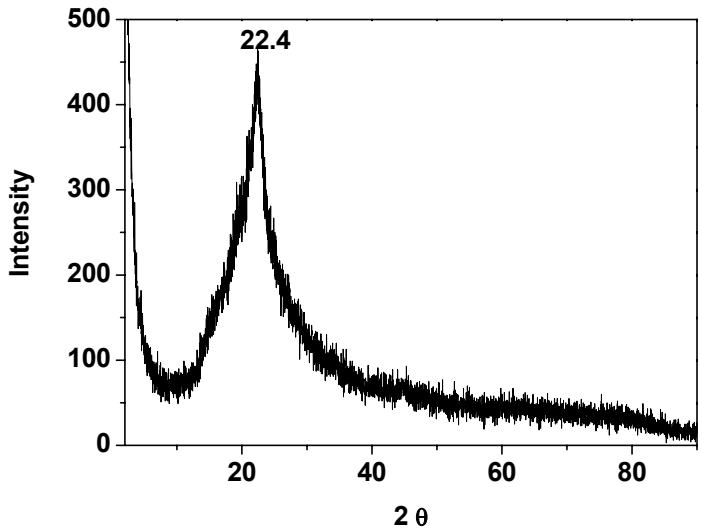


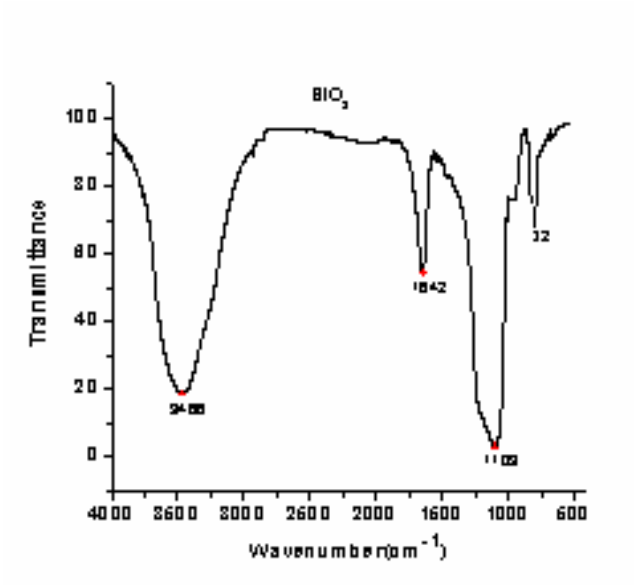
- Silica obtained is amorphous –Diffraction pattern
- Qualitative composition of silica material - EDAX

Surface area and pore volume of silica obtained by pyrolysis

Compound name	Surface area/m^2g^{-1}	Pore volume/cm^3g^{-1}
t-BASINAP	426.4	0.46
DIPASINAP	378.3	0.81
T*n*BASINAP	226.9	0.19

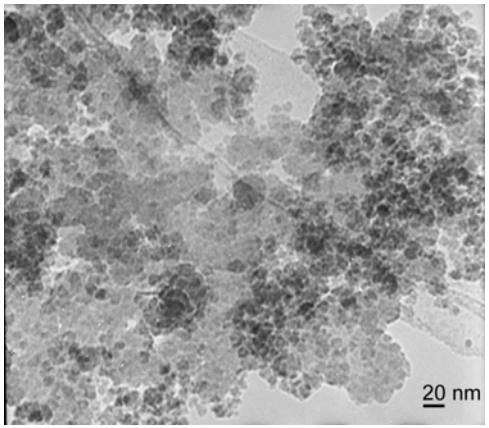
Silica - Hydrolytic route

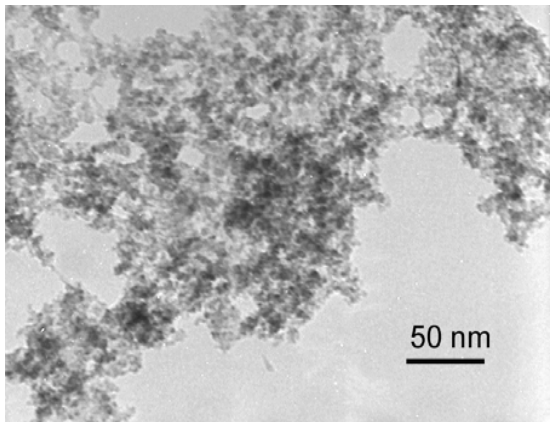


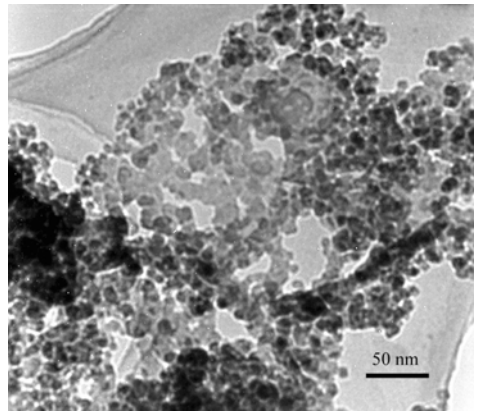


- XRD pattern shows the amorphous nature of silica
- IR gives Si-O characteristic peak at 1103 cm^{-1}

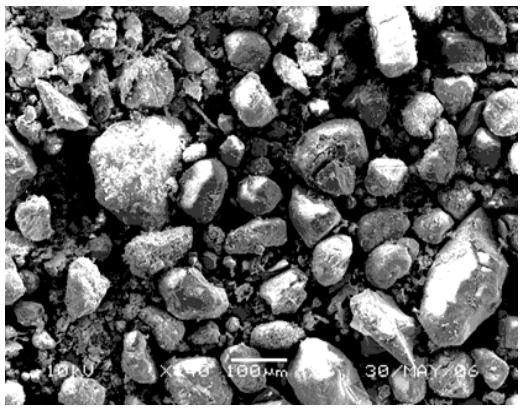
TEM Picture of Silica-hydrolytic condition



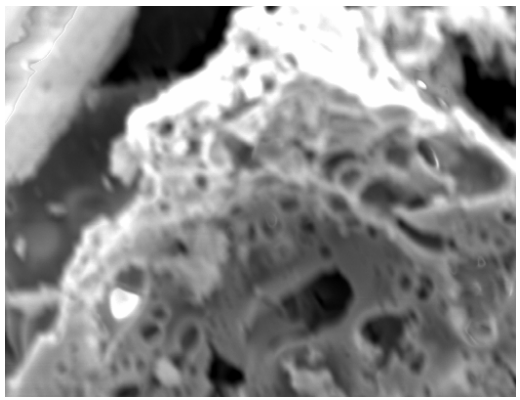




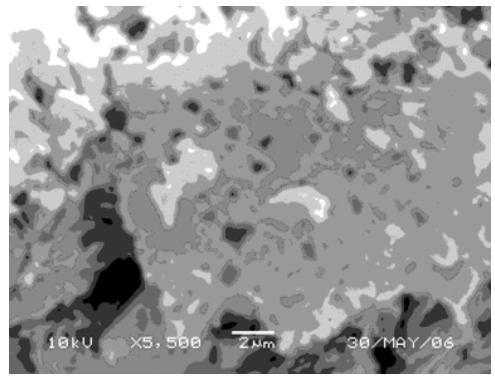
SEM pictures of silica



TnBASINAP



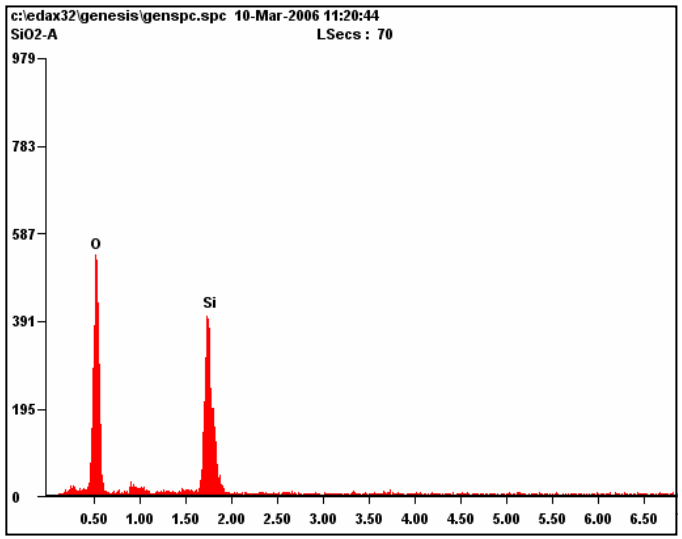
^{t}BASINAP

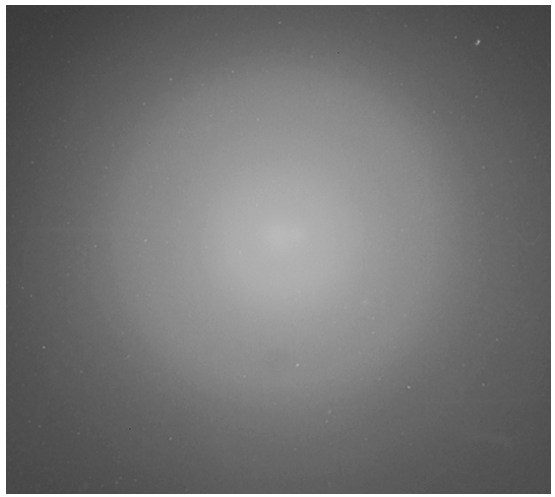


DIPASINAP

Partiicle size range – 6-15nm

EDAX and Selective area diffraction





- Silica obtained is amorphous –Diffraction pattern
- Qualitative composition of silica material - EDAX

Surface area and pore volume of silica obtained by hydrolysis

Compound	Surface area/m^2g^{-1}	Pore volume/cm^3g^{-1}
t-BASINAP	336.4	0.76
DIPASINAP	298.3	0.81
TnBASINAP	196.9	0.19

Chapter -6 Cyclic Voltammetric studies of bis(ammonium) tris(2, 3-dihydroxynaphthalato)silicate

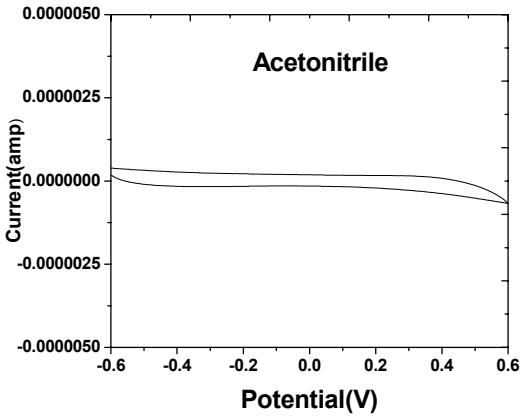
- Higher coordinate silicate with porphyrine and phthalocyanine were studied under electrochemical condition.

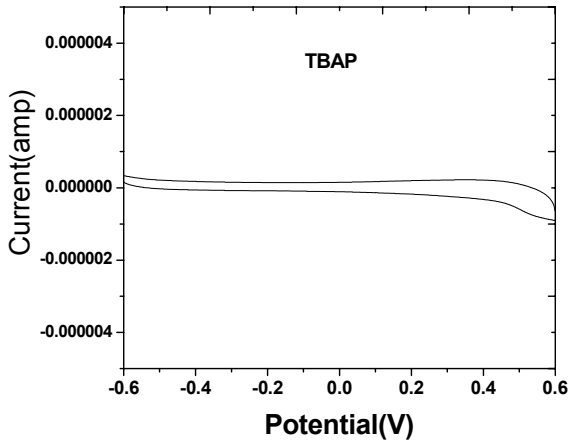
- 2,3 –dihydroxynaphthalene shows its redox potential at 700mV in acetone

- Boron complexes of 2,3-dihydroxynaphthalene reported to have oxidation potential at 0.94V

H.J.Lim, *Opt. Mat.* **2003** ,21, 1-3, 211-215

Cyclic Voltammetric studies of AmSINAP





Working electrode : Glassy carbon
Reference electrode : Ag/AgCl
Counter electrode : Pt

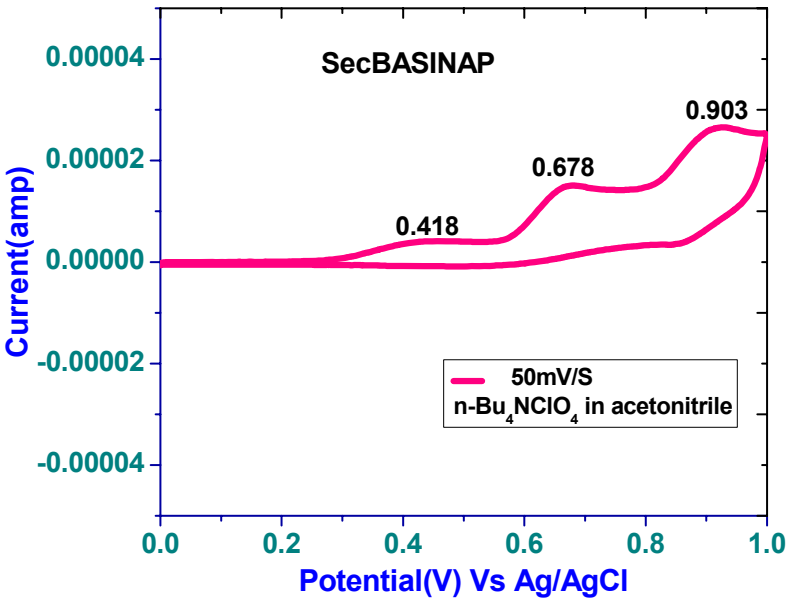
Supporting electrolyte: Tetrabutylammonium perchlorate in acetonitrile

Compounds considered for the study are

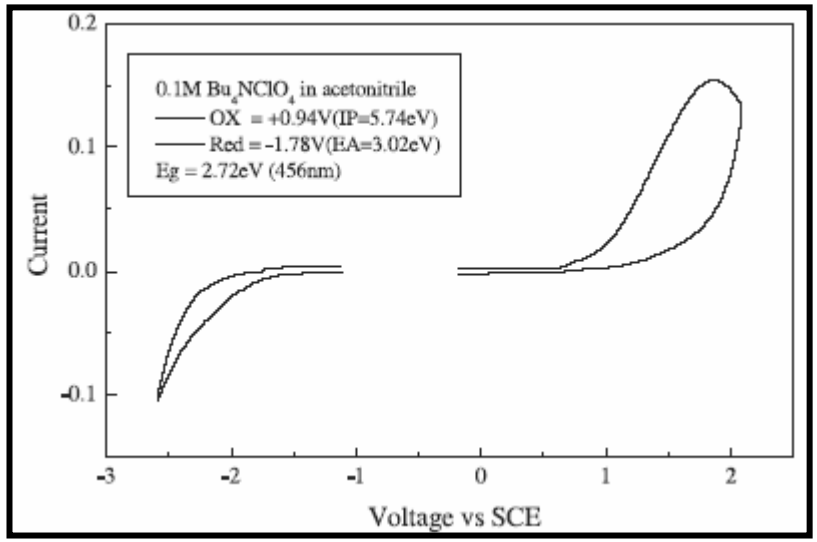
Ammonium containing silicates with variety

1° ammonium ions	-	*sec*- $C_4H_9NH_3^+$, *t*-$C_4H_9NH_3^+$
2° ammonium ions	-	$(i\text{-}C_3H_7)_2NH_2^+$, $(i\text{-}C_4H_9)_2NH_2$
3° ammonium ions	-	$(C_2H_5)_3NH^+$, $(n\text{-}C_4H_9)_3NH^+$
Cyclic ammonium ions	-	$O(CH_2)_4NH2^+$, $CH_3N(CH_2)_4NH_2+$,
Aromatic ammonium ions	-	$C_6H_5NH_3^+$, C6H4N$(NH_3)^+$

Voltammogram of silicon complexes



Voltammagram of boron complexes(Lit.)



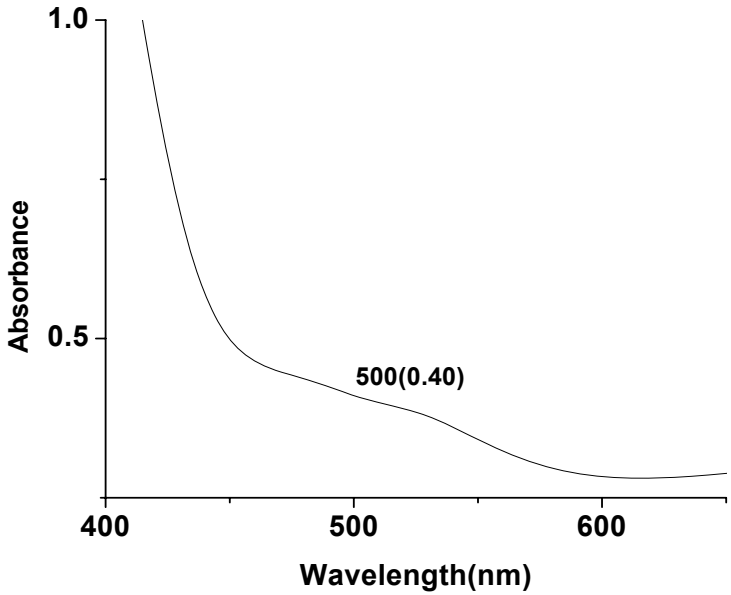
Lim, HJ, Kim, SM, Lee, SJ *Opt. Mat.* **2002**, *21*, 211-215

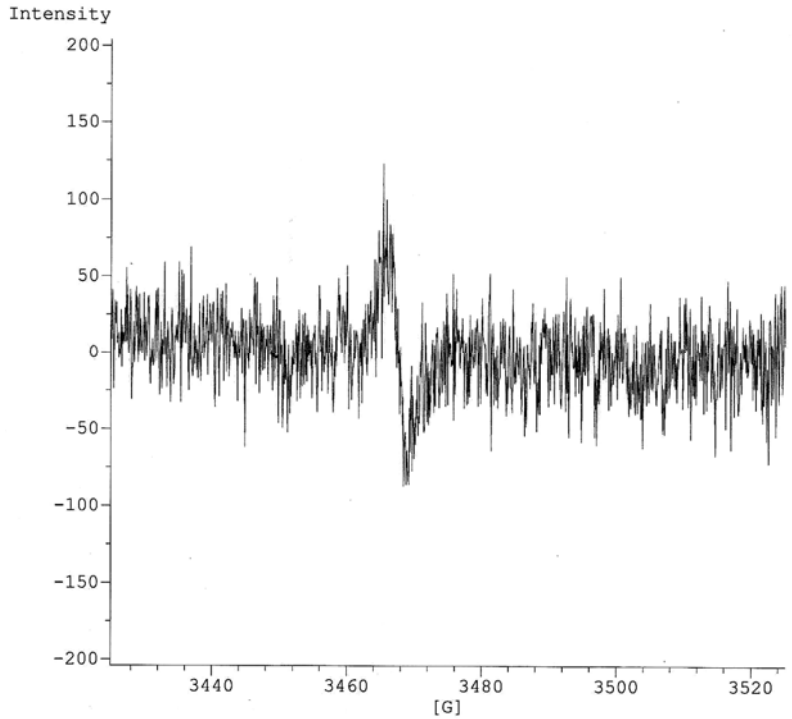
- 1st oxidation potential varies from 0.339 - 0.487V
- 2nd and 3rd oxidation potential not much varied with respect to counter ion.

Cyclic Voltammetric data of Bis(ammonium)tris(2,3-dihydroxynaphthalato)silicate

	Oxidation potential (Voltage)		
AmSINAP	1st	2nd	3rd
TEA	0.372	0.604	0.987
TnBA	0.473	0.683	0.966
DIPA	0.409	0.670	0.968
DIBA	0.240	0.601	0.953
Mop	0.339	0.695	0.973
Pida	0.355	0.621	0.955
Pyda	0.355	0.592	0.968
NMP	0.428	0.634	0.961
t-BA	0.420	0.668	0.968
SecBA	0.435	0.652	0.943
2-AmPy	0.487	0.693	0.966
Aniline	0.408	0.574	0.917

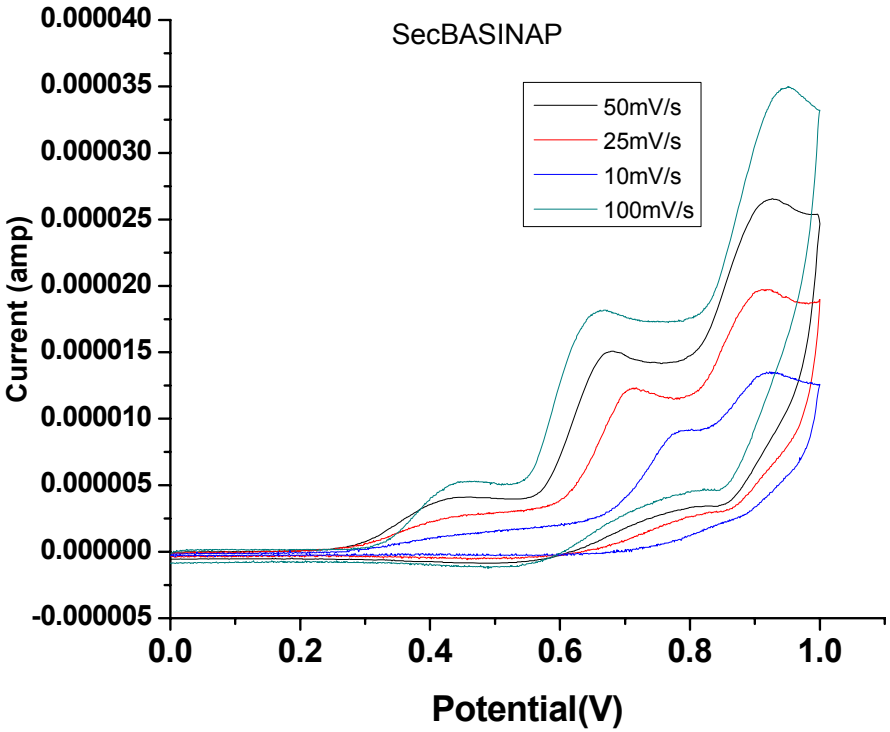
Chemical oxidation of tris(2,3-dihydroxynaphthalato)silicate

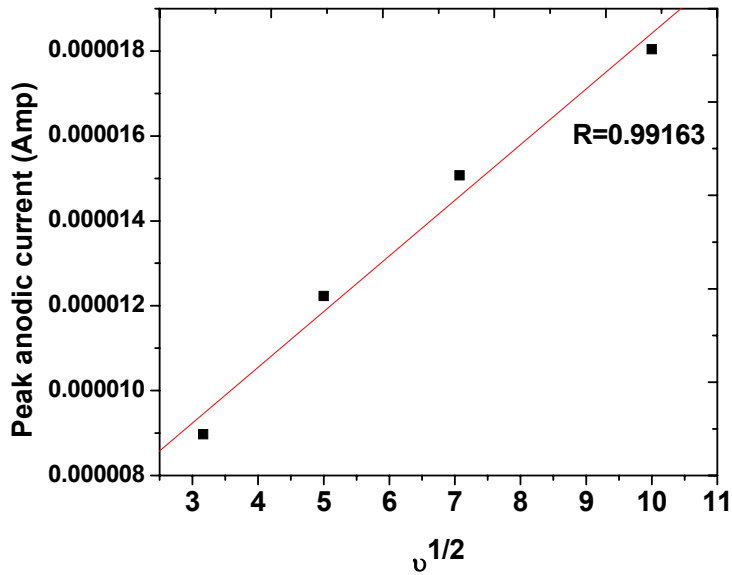




- Oxidised species of 2,3-dihydroxynaphthalene – 2,3 -naphthoquinone
- Aqueous KIO3 – oxidising agent

Cyclic Voltammogram at different scan rates





Randles-Sevick equation

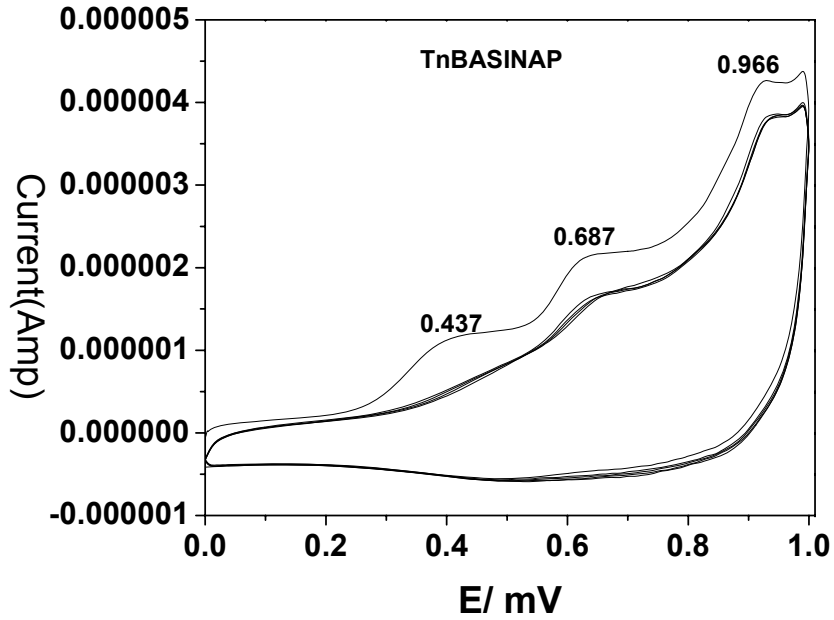
$$Ip = 0.4463nFA(nF/RT)^{1/2}D^{1/2}v^{1/2}c_{analyte}$$

Ip=Peak current
C_{analy}= bulk conc.
A=electrode area
n = no. of electron
D=diffusion coefficient
v = scan rate

- **As scan rate increases current increase – diffusion controlled process**

Tetrahedron Letters, Vo1.22, No.3'7, pp 3577 - 3578, 1981

Electrochemical stability



Multiple cycle voltammogram of tri-*n*-butylammonium containing tris(2,3-dihydroxynaphthalato)silicate recorded at sweep rate of 50 mV/s

After three cycle the aniodic current remains constant – stability

Chapter -7 Synthesis and thermal studies on tris(2,3-dihydroxynaphthalato) silicate with transition metal complexes as counter ions

- Higher coordinate silicates exist as ion pairs –

  Metal ion recovery from wastes and photographic hypo solution

- Tris(catecholato)silicates as Precursor -

  metal silicate at lower temperature

P. Bindu, J V Kingston, M.N.Sudheendra Rao *Polyhedron,* 2004, 23, 679-686

Synthesis

Metal ethylenediamine complex

$$MX.nH_2O + C_2H_8N_2 \xrightarrow{MeOH} [M(C_2H_8N)_n]X + n\,H_2O$$

M= Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

n = 2,3, X= SO_4^{2-}, Cl^-,Br^-

Transition metal silicates

$$(AmH)_2[Si(C_{10}H_6O_2)_3] + [M(en)_n]X \xrightarrow[RT,\ 2hr.]{MeOH - ACN} [M(en)_n][(Si(C_{10}H_6O_2)_3] + AmHX$$

M= Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

n = 2,3, X= SO_4^{2-}, Cl^-,Br^-

- All ion-exchanged ion pair are insoluble in most of the organic solvents

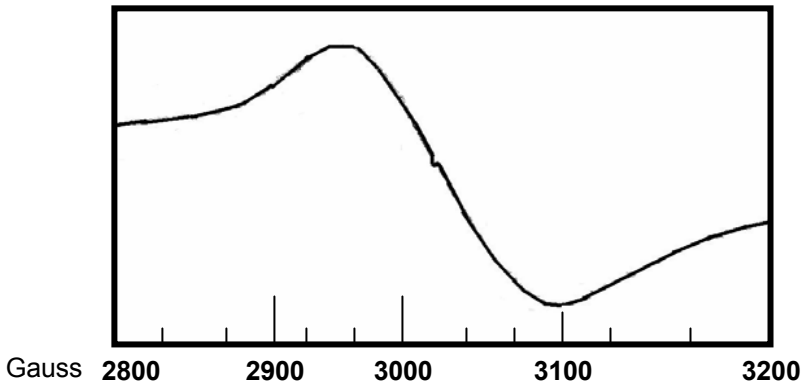
Spectral Data of tris(2,3-dihydroxynaphthalato)silicate with transition metal complexes

S.No	Compd.	UV-Vis. (λ_{max}, nm)	IR(cm^{-1})	% Yield
1.	CrSINAP	457	3226, 3092, 2956, **1556, 1472,1262 1168,1112, 870, 752, 585,456**	42
2.	MnSINAP	617	3331, 3270, 2930, **1585, 1473,1263 1167,1111, 870, 755, 585,485**	81
3.	FeSINAP	570	3322, 3254, 2934, **1586, 1474,1264 1167,1111, 871, 755, 690, 585, 485**	94
4.	CoSINAP	488	3330, 3274, 2936, **1585, 1475,1264 1168,1110, 871, 755, 690, 583, 485**	78
5.	NiSINAP	550	3300, 3221, 3021, **1586, 1473,1263 1167,1111, 871, 756, 690, 588,485**	81
6.	CuSINAP	545	3312, 3219, 2924, **1584, 1473,1264 1166,1112, 871, 756,686, 588,485**	67
7.	ZnSINAP	--	3336, 3276, 2937, **1585, 1473,1264 1167,1111, 870, 755,688, 585,486**	89

Analytical Data of tris(2,3-dihydroxynaphthalato)silicate with transition metal complexes

Comp no	MALDI-MS		Elemental Analysis (%)			
	Positive	Negative	C	H	N	M
CrSINAP	234	502.9	56.14 (56.32)	5.45 (5.64)	10.91 (10.67)	6.68 (6.75)
MnSINAP	61.8	503.3	57.96 (58.62)	5.41 (5.69)	10.98 (11.39)	7.38 (7.45)
FeSINAP	235	503.3	55.86 (55.93)	5.43 (5.62)	10.86 (11.02)	7.28 (7.56)
CoSINAP	61.8	503.5	55.61 (55.36)	5.41 (5.46)	10.81 (10.67)	7.32 (7.58)
NiSINAP	239	-	58.32 (58.63)	5.63 (5.69)	11.3 (11.54)	8.12 (7.92)
CuSINAP	61.8 184	503.0	57.98 (57.92)	5.67 (5.46)	11.26 (11.34)	8.33 (8.52)
ZnSINAP	184	503.0	58.14 (57.80)	4.89 (5.62)	11.05 (11.24)	8.48 (8.75)

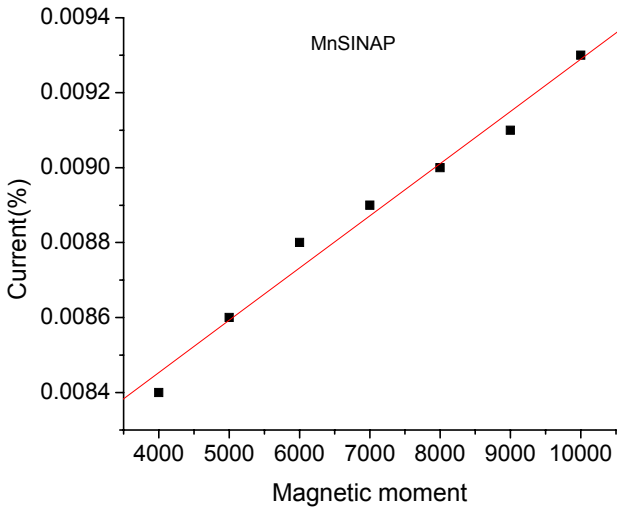
EPR of CuSINAP

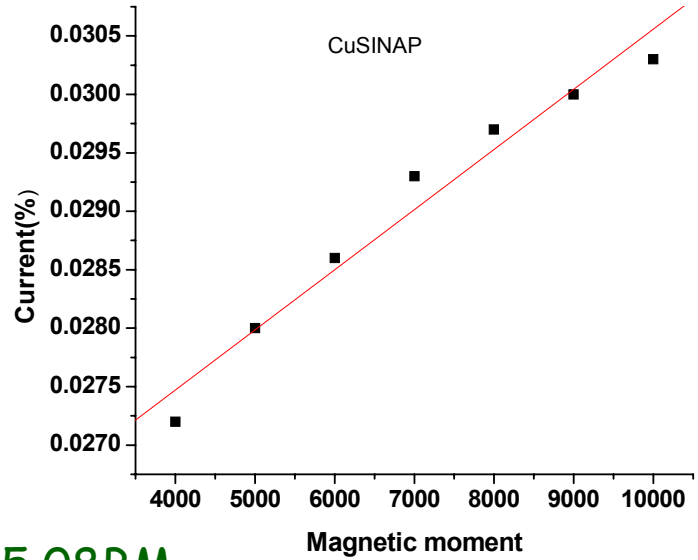


- CuSINAP in EPR $g = 2.085$

EPR - CuSICAT $g = 2.056$

Magnetic Measurement





MnSINAP = 5.08BM
CuSINAP = 1.98BM
CoSINAP = diamagnetic

MnSICAT - 5.08BM
CuSICAT - 1.65BM

P. Bindu, J V Kingston, M.N.Sudheendra Rao *Polyhedron*, 2004, 23, 679-686

Thermal studies – TGA-DTA

Compd.	Decomposition I@			Decomposition II*			Decomposition III#		
	Temp. range (°C)	Wt.loss (%)	DTA (°C)	Temp. range (°C)	Wt.loss (%)	DTA (°C)	Temp range (°C)	Wt.loss (%)	DTA (°C)
CrSINAP	50-185 -	16.39 (15.95)		185-275	6.89	-	275-800	39.77	-
MnSINAP	50-125	5.75	106	125-40	23.41	-596	400-789	23.12	666
FeSINAP	50-175	5.63	106	175-475	38.7	310	475-790	17.6	-
CoSINAP	50-150	10.58	130	150-270	9.11	233	270-780	41.09	-
NiSINAP	50-280	10.37	146.7	280-420	12.56	349.1	420-700	36.93	840
CuSINAP	50-275	3.48	-	275-450	49.28	336	400-700	14.99	-
ZnSINAP[1]	50-275	12.96	135.9	275-400	24.32	358.3	400-700	34.57	590

@- elimination ethylenediamine
* - loss of ethylenediamine/ethylenediammoniumNaphthalato
# - 2,3-dihydroxynaphthalene
Incomplete decomposition

Pyrolysis of $[M(en)_n][(Si(C_{10}H_6O_2)_3]$

- **Transition metal complexes containing silicates - Pyrolysed at 800ºC for 3 hrs in muffle furnace**

$[M(en)_n][(Si(C_{10}H_6O_2)_3]$

M= Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

n = 2,3, X= SO_4^{2-}, Cl^-,Br^-

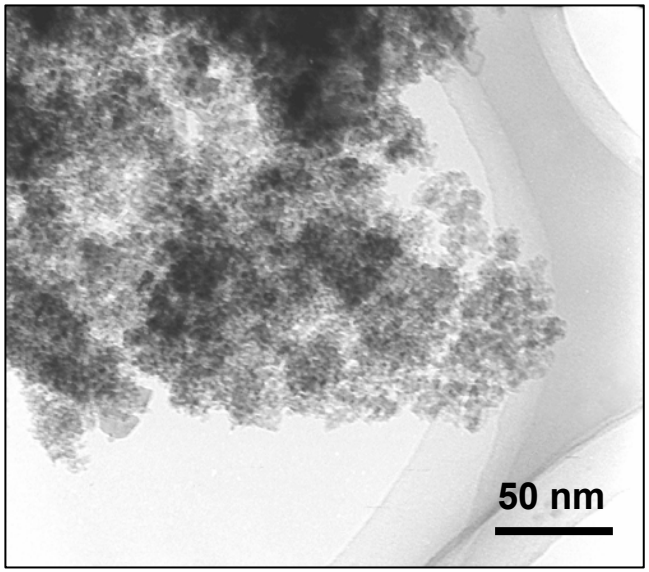
- **Products obtained are characterized to be mixture of silica-metal oxide**

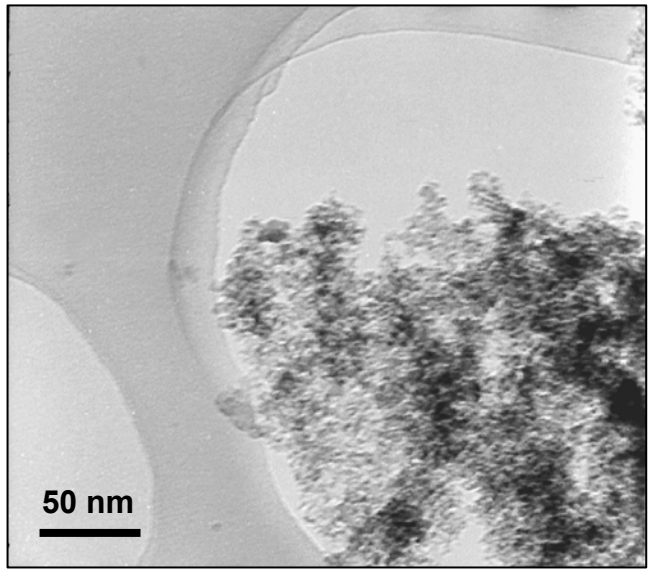
Physico chemical properties of metal oxide silica obtained from metal containing precursors

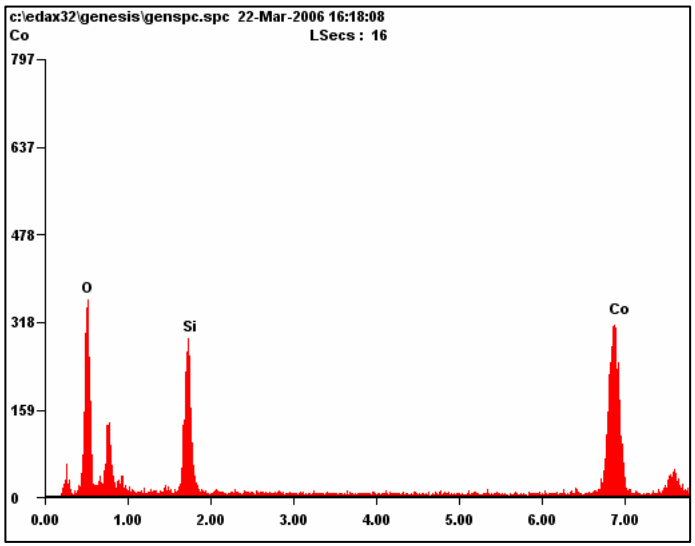
Compd	Surface Area(m^2/g)	Specific pore volume (cm^3/g)	d_{hkl}(Å)#	
			Observed	lit for MO
$Cr_2O_3+SiO_2$	94.4	0.18	2.664, 2.476,3.629	2.668,2.476,3.628
$MnO+SiO_2$	9.8	0.02	2.561, 2.309, 2.298,	2.565, 2.319, 2.161
$Fe_2O_3+SiO_2$	3.7	0.03	3685, 2.705, 2.520	3.684,2.704,2.523
$Co_2O_3+SiO_2$	205	0.36	2.870, 2.300, 1.780	2.868,2.302,1.780
$CuO+SiO_2$	200	0.47	2.450, 2.122, 1.50	2.454,2.128,1.505
$NiO+SiO_2$	113	0.19	2.411, 2.088	2.414, 2.100
$ZnO+SiO_2$	55.8	0.28	2.478, 2.607, 2.817	2.479,2.608,2.820

#-Silica is amorphous and 100,80,60% peaks alone considered

TEM of silica and cobalt (III) Oxide



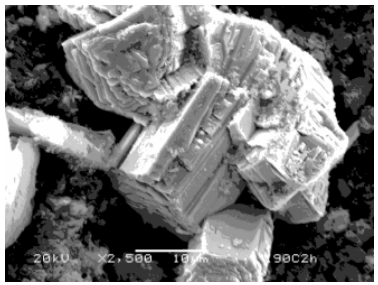




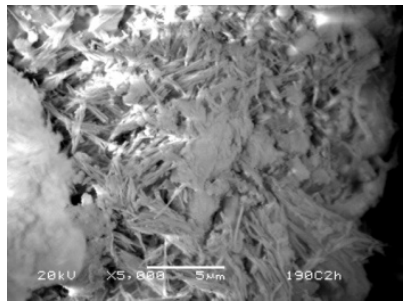
EDAX of $CoO+SiO_2$

Particle size in 8-10 nm

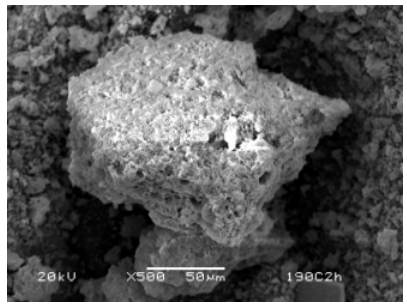
SEM Picture of Silica-metal oxide



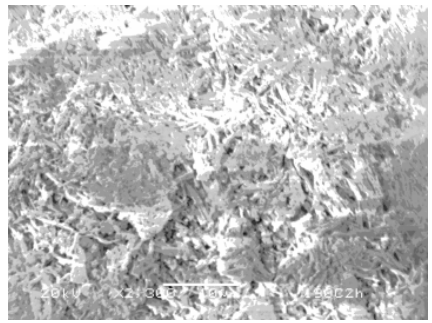
(a)



(b)



(c)



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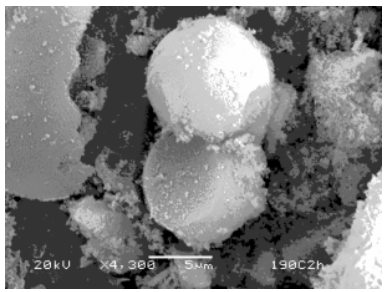
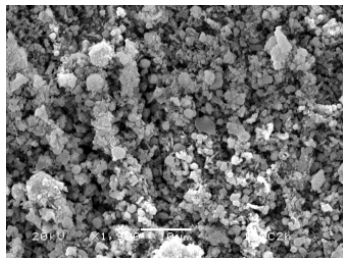
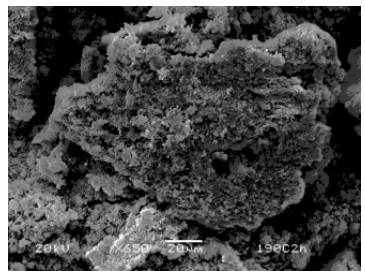


(e)



(f)



(g)

(a) $CuO+SiO_2$ (b) $NiO+SiO_2$ (c) $Fe_2O_3+SiO_2$ (d)$Co_2O_3+SiO_2$ (e)$Cr_2O_3+SiO_2$ (f) $ZnO+SiO_2$ and (g) MnO+SiO2

Particle size ranges from 2-15μm

Summary and Conclusions

- ✓ Microwave method is an effective and eco-friendly method for the synthesis of hexacoordinate silicates of 2,3-dihydroxynaphthalene.
- ✓ Single X-ray structure studies reveal that the number of hydrogen bonding increases from 3º to 2º ammonium ion; however there is no extended H-bonding network or π-stacking.
- ✓ The thermal stability varies with counter ion in the order of 3º > 2º > 1º.
- ✓ The tris(2,3-dihydroxynaphthalato)silicates under pyrolytic and hydrolytic conditions yielded mesoporus silica with high surface area.
- ✓ These silicates undergo decomposition in ethanol water mixture, leads to ammonium naphthalate and silicic acid formation.
- ✓ The rate of silicic acid formation from the breakdown of polymerized silica varies with the counter ion.
- ✓ Under electrochemical conditions, the naphthalato of silicate gives three anoidic peak potential First oxidation peak is sensitive to variation in the counter ion.
- ✓ Transition metal containing silicates are synthesized by ion exchange reaction, which on pyrolysis lead to a mixture of metal oxide and silica with lower surface area compared pure silica.

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Mr.Mohan for NMR measurement
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All non teaching staffs
All friends and research scholars
Last but not least My Almighty God

THANK YOU

Answers for the Examiners questions

1. In the report line 5 : If lack of space around the oxygen is given as the reason for rarity of hexacoordination at silicon what about SiF6 which is a huge industrial waste?

In nature, the rarity of isolated hexacoordinate silicates with oxygen is due to their readiness to form the extended network, under normal pressure of oxygen. $SiF6^{2-}$ is the major byproduct, in the fertilizer industry. If we compare the electronegativity of oxygen and Fluorine we can see that Fluorine has higher electronegative which is the key for stabilization and driving force for the formation of the highercoordinate silicon compounds.

2. P.1, line 5: Silicon doped with germanium? Please check

Silicon can be doped with other elements to adjust its electrical response by controlling the number and charge of current carriers

3. P.2 line 15: What about silylenes that are also low-coordinate?

Yes. They are very reactive species that can be stabilized with bulky substituent on it. They can be trapped using methanol.

4. P.48 line 15 What is the pink colour of the solution due to?

Due to solvent interaction we observe such a colour .

5. Table 4.1: The important parameters R and wR are missing. They must be given. Also GOOF as reported for compound IV is too low
(Checkcif would have helped to find out the problems if any).
Although this can be changed by suitably altering the other parameters,
it would be nice to check it carefully.

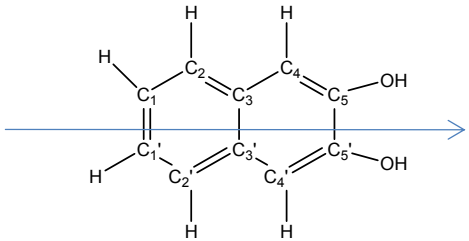
GOOF = $[\Sigma(W(Fo)^2 - (Fc)^2)^2 \setminus (n-p)]^{1\setminus 2}$
Fo^2 – intensity observed n- no. of reflection W- statistical weigh
Fc^2 – intensity calculated p – no of parameters

6.P 77: What does the candidate mean by
'symmetry was not been observed in the unit cell?

When we see the packing diagram in Fig 4.3 we can see the C2 axis of symmetry along the diagonal. However, no such symmetry was observed in packing diagram that is shown in Fig 4.6.

7. P 54 and Table in p 61. Where is the assignments of ^{13}C chemical shifts why there was 5 peaks for dihydroxynaphthalene ligand

Due to C2 symmetry present in the naphthalene ring there are only 5 peaks for the ten carbon atoms that are present.



8. What is the error associated with ^{29} Si chemical shifts the accuracy varies from one to two decimal places for the compounds

Due to solubility problem, some of the spectra are recorded in solid state and few others in solution.

9. What is the idealized point group symmetry for $[Si(naph)_3]^{2-}$ ion

Idealized 2-fold symmetry is present and approximate 3-fold symmetry is present

10. If the compound IV crystallized in p41212(p.66) what does it mean

0 0 l reflections – l , not a multiple if 4 is systematically absent showing 4_1 screw Parallel to C axis. 2_1 along a axis h, 0 0(multiples of 2 is present) and 2 screw is Present in the face diagonal of ab plane on analysing our data for compound IV

11. Have you made any attempt to use optically active ammonium cation to resolve $[Si(naph)_3]^{2-}$ ion

NO. Since the optical purity of the tris(2,3-dihydroxynaphthalato)silicate was not studied no attempt has been made to resolve it with chiral amine.

12.If the crystal structure reflects highest symmetry present in $[Si(naph)_3]$ ion. What Crystal system the compound is expected to crystallize in

Cubic –crystal system with P 2 3 space group

13. p. 86 If 2,3-dihydroxynaphthalene ligands are eliminated as shown in scheme 5.1 it does not account for the formation of SiO2. where does Si get two oxygen atoms

Two oxygen atom is from the solvent moiety adsorbed in silicate molecule.

14. Why the X-ray powder diffraction pattern in Fig 5.3 show a peak at 2Θ~ 23˚ and yet the sample is amorphous

No sharp peak is observed at 2Θ~ 23˚ but only ill defined broad peak is observed due to\ Amorphous nature of silica

15. The discussion on SEM (fig 5.6 in page 90) is very scanty. How is it correlated to TEM results in Fig 5.4 How can fig 5.6 be understood along with fig 5.5a how can You explain the surface area and pore volumes in the light of SEM and TEM It is the Same problem in p 95 and 96. Explain the correlation between Fig 5.11 and Table 5.3

From the SEM and TEM we could arrive at the morphology and size distribution of the particles A detail explanation will be included. Amorphous nature of silica was confirmed from the SAD shown in Figure5.5a, their particle shapes were observed using SEM that are shown in Fig 5.6. Since the SEM and TEM images are not so clear to calculate pore volume, we used BJH for arriving at the pore volume and BET method for measurement of surface area. From the SEM picture we can observe the shape of silica which helps us to understand the surface area variation. Two of the derivatives that are having the spherical shape, hence a higher surface area compare to the tubular shape silica.

16. Explain Fig 5.9 in p 93. what does peak at 22.4 refer to

Due to 101 plane in tetragonal system of cristobalite(89-3606)

17. What is reprography Explain

Reprography - **Reprography** is a general term for the reproduction of documents or images especially those that are virtually indistinguishable from the original. Reprography can be by mechanical, electronic, or photographic means such as photocopying or xerography, scanning, digital printing, nd photography.(These silicates plays a role of toners and charge controlling agents in reprographic materials)