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Syntheses of platinum(II) complexes of cyclo-octenyl group and isolation of a self-assembled oxo-bridged macrocyclic complex [Pt₄(Spy)₄(C₈H₁₂-O-C₈H₁₂)₂]

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ABSTRACT

Reactions of $[Pt_2(\mu-Cl)_2(C_8H_{12}OMe)_2]$ (1) $(C_8H_{12}OMe = 8$ -methoxy-cyclooct-4-ene-1-yl) with various anionic chalcogenolate ligands have been investigated. The reaction of 1 with Pb(Spy)_2 (HSpy = pyridine-2-thiol) yielded a binuclear complex $[Pt_2(Spy)_2(C_8H_{12}OMe)_2]$ (2). A trinuclear complex $[Pt_3(Spy)_4(-C_8H_{12}OMe)_2]$ (3) was isolated by a reaction between 2 and $[Pt(Spy)_2]_n$. The reaction of 1 with HSpy in the presence of NaOMe generated 2 and its demethylated oxo-bridged tetranuclear complex $[Pt_4(Spy)_4(C_8H_{12}-O-C_8H_{12})_2]$ (4). Treatment of 1 with ammonium diisopropyldithiophosphate completely replaced $C_8H_{12}OMe$ resulting in $[Pt(S_2P\{OPr^i\}_2)_2]$ (5), whereas non-rigid 5-membered chelating ligand, Me_2NCH_2. CH_2E⁻, produced mononuclear complexs $[Pt(ECH_2CH_2NMe_2)(C_8H_{12}OMe)]$ (E = S (6), Se (7)). These complexes have been characterized by elemental analyses, NMR (¹H, ¹³C{¹H}) and absorption spectroscopy. Molecular structures of 2, 3, 4, 5 and 7 were established by single crystal X-ray diffraction analyses. Thermolysis of 2, 6 and 7 in HDA gave platinum nanoparticles.

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1. Introduction

The chemistry of cyclometalated palladium and platinum complexes has been extensively explored for about five decades. There are several obvious reasons for this sustained interest as these complexes find numerous applications in many fields such as organic synthesis [1–3], metallomesogens [4–6], solar cells [7,8], opto-electronic devices [9–11] and materials science [12–14], etc. Platinum complexes such as $[Pt_2(\mu-OR)_2(C_8H_{12}OMe)_2]$ (R = Me, Ac) [14] and PtMe₂(COD) (COD = cycloocta-diene) [15,16] have been used to prepare platinum thin films and nanoparticles.

Cyclometalated binuclear palladium and platinum complexes $[M_2(\mu-X)_2(L^{\cap}C)_2]$ (M = Pd or Pt; X = Cl or OAc; L = N, P, etc.), undergo a wide range of reactions. These can broadly be clubbed into (i) bridge cleavage reactions by neutral donor ligands; (ii) reaction at the metal–carbon bond, and (iii) substitution of the bridging Cl/OAc with another ionic ligand. The latter reaction yields a myriad of complexes. Structure of the resulting complex is governed by the nature of L, metal atom and the incoming anionic ligand. Recently we have described reactions of $[Pt_2(\mu-Cl)_2[Bu_2^fPC(Me_2)CH_2]_2]$ [17] and $[Pt_2(\mu-Cl)_2(ppy)_2]$ (ppy = metalated 2-phenylpyridine) [18] with a variety of anionic ligands. The

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nature of L (N or P) and the size of the metalacycle greatly influenced the reactivity as well as the structural features of the resulting complex. In pursuance of our work on cyclometalated platinum complexes and development of platinum group metal chalcogenolates as precursors for the synthesis of platinum group metal chalcogenides [19,20], we have chosen a precursor with a very large metalacycle ring (6-membered) and a weak L ligand (π olefinic group) as in [Pt₂(μ -Cl)₂(C₈H₁₂OMe)₂] and explored its reactions with a variety of chalcogenolate ligands. The results of this work are reported herein.

2. Experimental

2.1. General procedures

Solvents were dried and distilled prior to use by standard methods. All reactions were carried out in Schlenk flasks under a nitrogen atmosphere. The compounds 2-mercaptopyridine (HSpy), Me₂NCH₂CH₂SH+HCl and other reagents were procured from commercial sources. The compounds, (Me₂NCH₂CH₂Se)₂ [21], K₂PtCl₄ [22], PtCl₂(COD) [23] and [Pt₂(μ -Cl)₂(C₈H₁₂OMe)₂] (1) [24] were prepared according to the literature methods. Syntheses and analytical data for [Pb(Spy)₂] and [Pt(Spy)₂] are given in Supplementary information, Fig. S2.

Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were carried out on a Carlo-Erba



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EA-1110 CHN-O instrument. Electronic spectra were recorded on a Chemito Spectrascan UV 2600 spectrophotometer. Mass spectra were recorded on a Waters Q-TOF micro (YA-105) time of flight mass spectrometer. ¹H, ¹³C{¹H}, ³¹P{¹H}, ⁷⁷Se{¹H} and ¹⁹⁵Pt{¹H} NMR spectra were recorded on a Bruker Avance II-300 NMR spectrometer operating at 300, 75.47, 121.5, 57.24 and 64.29 MHz, respectively. Chemical shifts are relative to internal chloroform peak (δ 7.26 ¹H and 77.0 for ¹³C), external Me₂Se for ⁷⁷Se{¹H} (secondary reference Ph₂Se₂ in CDCl₃ δ 463 ppm) and Na₂PtCl₆ in D₂O for ¹⁹⁵Pt{¹H}. TG curves were obtained at a heating rate of 10 °C min⁻¹ under flowing argon on a Setaram Setsys evolution-1750 instrument. Powder XRD patterns were recorded on a Philips PW1820 using Cu-K α radiation.

2.2. Synthesis of $[Pt_2(Spy)_2(C_8H_{12}OMe)_2]$ (2)

(a) To a benzene solution (20 mL) of $[Pt_2(\mu-Cl)_2(C_8H_{12}OMe)_2]$ (0.206 g, 0.278 mmol), solid Pb(Spy)₂ (0.122 g, 0.285 mmol) was added and stirred for 2 h. A yellow solution containing a white precipitate of PbCl₂ was obtained. The reaction mixture was filtered through celite and the filtrate was concentrated to 3 mL and 1 mL of hexane was added and cooled at 10 °C to yield yellow crystals of **2** (0.172 g, 0.193 mmol, 69%). [In some preparations a few red crystals were also formed which were separated manually and characterized as $[Pt_3(Spy)_4(C_8H_{12}OMe)_2]$ (**3**) (see later).]

Data of 2. m.p. 182 °C (darkens above 165 °C). Anal. Calcd. for C₂₈H₃₈N₂O₂Pt₂S₂: C, 37.8; H, 4.3; N, 3.1; S, 7.2. Found: C, 37.9; H, 4.3; N, 3.0; S, 7.3%. ¹H NMR (300 MHz, C_6D_6): $\delta = 8.26$ (m), 8.03, 7.88 (br, s) (2H, H-6), 7.45 (m, 2H, H-4), 6.56 (m, 2H, H-5), 6.13, 6.02 (br s, 2H, H-3), 5.58 (br s, ${}^{2}I_{HPt} = 73.2$ Hz), 5.48 (br s, ${}^{2}I_{HPt} = 67.8$ Hz), 4.84 (br s, ${}^{3}I_{\text{HPt}} = 53.1 \text{ Hz}$, 3.99 (br s) (4H, CH=CH), 4.49, 4.12 (br s, 2H, MeOCH), 3.70, 3.64, 3.61 (each s, 6H, OMe), 2.85-1.80 (m, 8H, CH₂); ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 171.5, 170.3 (br s, Δ 1/2 = 40 Hz, C-2), 150.6, 150.1, 149.8 (s, C-6), 134.9, 134.8 (s, C-4), 131.0, 130.6, 130.0 (s, C-3), 120.3, 119.9, 119.5 (s, C-5), 88.9, 87.6, 86.6, 86.3, 85.0, 84.7, 83.9, 83.6, 81.0, 80.6 (C=C, COMe) (The platinum satellites could not be assigned), 56.4, 56.2 (s, COMe), 36.2 (s, ${}^{3}J_{CPt} = 38.1 \text{ Hz}$; CH₂COMe), 34.8 (s, CH₂CH₂COMe), 31.0, 30.6 (s, CH₂CH₂CHPt), 29.4 (m, CH₂CHPt), 25.4, 24.1, 23.2 (each s, ¹*J*_{CPt} = 628, 620, 632 Hz respectively; Pt–C); 195 Pt{¹H} NMR (64 MHz, C₆D₆): -3508 ($\Delta 1/$ 2 = 272 Hz); -3541 ($\Delta 1/2 = 679$ Hz) ppm (2:1) ratio; UV/Vis (CH₂Cl₂) λ_{max} (ε): 277 (18,000), 324 (8000), 371 nm (sh, 3000 $M^{-1} cm^{-1}$); ESI-MS, m/z (%): 778 ([M - (Spy)]⁺, 100%), 748 ([Pt₂(Spy)₂(C₈H₁₂OMe) – H]⁺, 20%), 638 ([Pt₂(Spy)(C8H12OMe) – H]+, 13%), 413 ([Pt(Spy)₂ – 2H]⁺, 49%) (Supplementary information, Fig. S1).

(b) To a methanolic solution (15 mL) of NaSpy (freshly prepared by reaction between HSpy (0.062 g, 0.563 mmol) and NaOMe in methanol (1.1 mL, 0.53 N, 0.572 mmol)), a dichloromethane solution (10 mL) of $[Pt_2(\mu-Cl)_2(C_8H_{12}OMe)_2]$ (0.209 g, 0.282 mmol) was added and stirred for 3 h. The solvents were evaporated under reduced pressure and the residual solid was chromatographed on a silica gel column (3 × 40 cm), 30:70 v/v ethylacetate/hexane to elute $[Pt_4(Spy)_4(C_8H_{12}-O-C_8H_{12})_2]$ (4) and 10:90 v/v methanol/ chloroform to elute **2**. The solvent was removed from the product containing fractions by rotary evaporation and oil pump vacuum to give yellow crystalline solid of **2** (0.160 g, 0.180 mmol, 64%), m.p. 184 °C. The volume of fraction containing **4** was made up to 5 mL, few drops of diethylether added to yield pale yellow crystals of **4**·OEt₂ (0.037 g, 0.021 mmol, 15%).

2.3. Synthesis of $[Pt_3(Spy)_4(C_8H_{12}OMe)_2]$ (3)

To a benzene solution (15 mL) of $PtCl_2(COD)$ (0.027 g, 0.072 mmol), solid $Pb(Spy)_2$ (0.030 g, 0.070 mmol) was added and

stirred. After 30 min, benzene solution (10 mL) of [Pt₂(Spy)₂(- $C_8H_{12}OMe_{2}$] (0.060 g, 0.067 mmol), was added and the contents were further stirred for 3 h. The reaction mixture was dried by evaporating the solvents under vacuum, washed with ether $(2 \times 2 \text{ mL})$ and hexane $(2 \times 2 \text{ mL})$, and extracted from dichloromethane. The latter on volume reduction to 3 mL followed by refrigeration gave reddish solid of **3** (0.043 g. 0.032 mmol. 48%), m.p. 145 °C. Anal. Calcd. for C₃₈H₄₆N₄O₂Pt₃S₄: C, 35.0; H, 3.5; N, 4.3; S, 9.8. Found: C, 34.8; H, 3.5; N, 4.3; S, 9.2%; UV/Vis (CH₂Cl₂) λ_{max} (ε): 275 (21,000), 297 nm (16,000 $M^{-1} cm^{-1}$); ¹H NMR (300 MHz, CDCl₃): $\delta = 8.46, 8.35$ (br m, 4H, H-6), 7.63 (br s, 4H, H-4), 7.15 (m, 4H, H-5), $6.95, 6.57 (m, 4H, H-3), 5.61 (s, {}^{2}J_{HPt} = 66.9 Hz, 4H, CH=CH), 3.71 (br,$ 2H, MeOCH), 3.50, 3.48, 3,36 (s, 6H, OMe), 2.92-2.40 (m, 8H, CH₂), 2.27 (d, ${}^{3}J_{HH} = 9$ Hz, PtCH), 2.05–1.55 (m, 8H, CH₂); 195 Pt{ 1 H} NMR (64 MHz, CDCl₃): $\delta = -3470 (\Delta 1/2 = 458 \text{ Hz}), -3333$, other minor broad peaks at -3447, -3454 and -3481 ppm; ESI-MS, m/z (%): 859 $[M - Pt(Spy)(C_8H_{12}OMe)]$ (5%), 415 $[{Pt(Spy)_2}]^+$ (100%)(Supplementary information, Fig. S2).

Data of [*Pt*₄(*Spy*)₄(*C*₈*H*₁₂-O-*C*₈*H*₁₂)₂] (**4**). M.p. 198 °C (dec.). Anal. Calcd. for C₅₆H₇₄N₄O₃Pt₄S₄ (**4**•OEt₂): C, 38.2; H, 4.2; N, 3.2; S, 7.3. Found: C, 38.3; H, 4.0; N, 3.1; S, 7.7%. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.10$ (m, 4H, 6-H), 7.46 (m, 4H, H-4), 7.07 (m, 4H, H-5), 6.54 (m, 4H, H-3), 5.58 (br s, 8H, CH=CH), 3.68 (br s, 4H, OCH), 2.85–1.45 (m, 36H, CH₂ + PtCH). The peaks at δ 4.12 (q), 1.26 (t) are due to the solvated Et₂O in the crystals of **4**; ¹³C{¹H} NMR (75 MHz, CDCl₃): $\delta = 170.1$ (br s, C-2), 150.3 (s), 149.5, 149.0 (br s, C-6), 134.62 (s), 134.60 (br s, C-4), 129.8, 128.8 (br s, C-3), 119.6, 119.5 (br s, C-5), 87.3 (s, MeOCH), 80.6, 79.7 (s, C=C), 35.8, 30.0, 29.7, 28.3, 26.8 (s, CH₂), 25.05, 24.9 (br s, PtC); ¹⁹⁵Pt{¹H} NMR (64 MHz, CDCl₃): $\delta = -3495$ (major, $\Delta 1/2 = 312$ Hz), other minor broad peaks at -3523, -3554, -3607 (each approx. of $\Delta 1/2 = 624$ Hz) ppm.

2.4. Synthesis of $[Pt(S_2P\{OPr^i\}_2)_2]$ (5)

To a dichloromethane (10 mL) solution of $[Pt_2(\mu-Cl)_2(C_8H_{12} OMe)_2]$ (0.104 g, 0.140 mmol), methanolic (5 mL) NH₄S₂P(OPr¹)₂ (0.065 g, 0.280 mmol) was added. The color of the solution turned yellow and the whole reaction mixture was stirred for 2 h. The solvents were evaporated under reduced pressure and the residue was extracted with dichloromethane (2 × 5 mL) and passed through a Florisil column. The filtrate was concentrated to 3 mL and 1 mL of hexane was added to yield yellow crystals of **5** (0.125 g, 0.201 mmol, 71%), m.p. 123 °C (dec.). Anal. Calcd. for C₁₂H₂₈O₄P₂PtS₄: C, 23.2; H, 4.5; S, 20.6. Found: C, 23.2; H, 4.4; S, 20.0%; ¹H NMR (300 MHz, CDCl₃): δ = 4.98 (hep, ³*J*_{HH} = 6 Hz, 4H, CHMe₂), 1.41 (d, ³*J*_{HH} = 6 Hz, 24H, CHMe₂); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 74.2 (s, CHMe₂), 23.8 (s, CHMe₂); ¹³P{¹H} NMR (121 MHz, CDCl₃): δ = 97.4 (t, ⁴*J*_{PP} = 10.2 Hz, ²*J*_{PPt} = 441 Hz); ¹⁹⁵Pt{¹H} NMR (64 MHz, CDCl₃): δ = -3981 (²*J*_{PPt} = 441 Hz) ppm.

2.5. Synthesis of $[Pt(SCH_2CH_2NMe_2)(C_8H_{12}OMe)]$ (6)

To a methanolic solution of Me₂NCH₂CH₂SH·HCl (0.072 g, 0.508 mmol), NaOMe in methanol (1.95 mL, 0.52 N) was added and stirred for 15 min. To this reaction mixture [Pt₂(μ -Cl)₂(C₈H₁₂OMe)₂] (0.187 g, 0.248 mmol) was added and the whole was further stirred for 2 h. The solvent was evaporated to dryness and the residual solid was extracted with dichloromethane (3 × 6 mL) to yield **6** as a colorless solid (0.184 g, 0.419 mmol, 83%), m.p. 178 °C (dec.). Anal. calcd for C₁₃H₂₅NOPtS: C 35.6, H 5.7, N 3.2, S 7.3; found: C 35.6, H 5.7, N 3.0, S 6.3%; UV/Vis (CH₂Cl₂) λ_{max} (ε): 275 (sh) (4400), 293 nm (5400 M⁻¹ cm⁻¹); ¹H NMR (300 MHz, CDCl₃): δ = 4.23 (t, ³J_{HH} = 8.7 Hz, ²J_{HPt} = 70 Hz, 1H, CH₂CH=CH), 3.90–3.87 (m, ²J_{HPt} = 62 Hz, 1H, CH₂CH=CH), 3.50 (m, 1H, MeOCH), 3.24 (s, 3H, OMe), 2.92 (m, 2H, NCH₂), 2.84 (t, ³J_{HH} = 5.4 Hz, 2H, SCH₂),

2.65–2.79 (m, 4H, CH₂); 2.48, 2.42 (each s, ${}^{3}J_{HPt}$ = 13.4 Hz, 6H, NMe₂), 2.15 (q, ${}^{3}J_{HH}$ = 8.4 Hz, 1H, PtCH), 1.72–1.80 (m, 4H, CH₂); 13 C {¹H} NMR (75 MHz, CDCl₃): δ = 86.6 (s, ${}^{1}J_{CPt}$ = 159 Hz, CH₂CH=CH), 83.5 (s, MeOCH), 81.9 (s, ${}^{1}J_{CPt}$ = 170 Hz, CH₂CH=CH), 71.1 (s, ${}^{2}J_{CPt}$ = 53 Hz, NCH₂), 55.8 (s, OMe), 49.2, 46.5 (each s, NMe₂), 33.7 (s, ${}^{3}J_{CPt}$ = 15 Hz, CH₂CHOMe), 29.4 (s, ${}^{2}J_{CPt}$ = 14 Hz, CH₂CH₂COMe), 28.9 (s, ${}^{2}J_{CPt}$ = 16 Hz, CH₂CH₂CHPt), 27.8 (s, ${}^{2}J_{CPt}$ = 18 Hz, CH₂CHPt); 26.9 (s, ${}^{2}J_{CPt}$ = 29 Hz, SCH₂), 17.9 (s, ${}^{1}J_{CPt}$ = 647 Hz; PtC); 195 Pt{¹H} NMR (64 MHz, CDCl₃): δ = –3722 (s) ppm.

2.6. Synthesis of $[Pt(SeCH_2CH_2NMe_2)(C_8H_{12}OMe)]$ (7)

To a freshly prepared methanolic solution (5 mL) of NaSeCH₂CH₂NMe₂ (prepared from (SeCH₂CH₂NMe₂)₂ (0.147 g, 0.486 mmol) and solid NaBH₄ (0.040 g, 1.057 mmol)) was added $[Pt_2(\mu-Cl)_2(C_8H_{12}OMe)_2]$ (0.357 g, 0.482 mmol). The reaction mixture was stirred for 2 h. The solvent was evaporated to dryness and the residual solid was extracted with dichloromethane $(3 \times 10 \text{ mL})$ to yield a pale yellow solid **7** (0.385 g, 0.793 mmol, 82%), m.p. 187 °C (dec.). Anal. Calcd. for C13H25NOPtSe: C, 32.2; H, 5.2; N, 2.9. Found: C, 32.1; H, 5.1; N, 2.3%; UV-vis (CH₂Cl₂) λ_{max} (ε): 274 (4400); 302 nm (7700 M⁻¹ cm⁻¹); ¹H NMR (300 MHz, CDCl₃): $\delta = 4.27 (t, {}^{3}J_{HH} = 7.4 \text{ Hz}, {}^{2}J_{HPt} = 69.9 \text{ Hz}, 1\text{H}, \text{CH}_{2}\text{CH}=\text{CH}), 4.01-3.90$ $(m, {}^{2}J_{HPt} = 61.2 \text{ Hz}, 1\text{H}, CH_{2}CH = CH), 3.51 - 3.45 (m, 1\text{H}, MeOCH), 3.24$ (s, 3H, OMe); 3.01-3.53 (m, 2H, NCH₂), 2.90-2.65 (m, 4H, CH₂), 2.48, 2.39 (each s, ${}^{3}J_{HPt} = 13.5$ Hz; NMe₂, the peak due to SeCH₂ merged in the base), 2.13 (q, ³J_{HH} = 8.7 Hz, 1H, PtCH), 1.90–1.55 (m, 4H, CH₂); ¹³C{¹H} NMR (75 MHz, CDCl₃): $\delta = 87.3$ (s, ¹*J*_{CPt} = 157 Hz, CH₂CH= CH), 83.6 (s, MeOCH), 82.2 (s, ${}^{1}J_{CPt} = 170$ Hz, CH₂CH=CH), 71.9 (s, NMR (64 MHz, CDCl₃): $\delta = -3720$ ppm.

2.7. Crytallography experiments

Single crystal X-ray diffraction measurements were made on Rigaku AFC 7S diffractometer at room temperature $(298 \pm 2 \text{ K})$ using graphite monochromated Mo-K α ($\lambda = 0.71069 \text{ Å}$) radiation. The structures were solved by direct methods [25] and refinement was on F^2 [26] using data corrected for Lorentz and polarization effects with an empirical procedure [27,28]. The non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were fitted in their calculated positions and refined in isotropic approximation using riding model. Neutral atom scattering factors were taken from Cromer and Waber [29]. All calculations were performed using crystal structure crystallographic software package [30,31]. Molecular structures were drawn using ORTEP [32].

3. Results and discussion

3.1. Synthesis and spectroscopy

Reactions of **1** with various anionic chalcogenolate ligands differing in mode of coordination to metal atom and the ligand bite have been investigated (Scheme 1). Treatment of **1** with freshly prepared $Pb(Spy)_2$ afforded a binuclear Spy-bridged complex $[Pt_2(Spy)_2(C_8H_{12}OMe)_2]$ (**2**) as a yellow crystalline solid. The **2**, unlike **1** which converts in $PtCl_2(COD)$ in halogenated solvents [33], was quite stable both in polar and non-polar solvents like benzene, CH_2Cl_2 , $CHCl_3$ at least for a week without any decomposition or disproportionation (by NMR). It is worth

noting that a similar reaction between $[Pt_2(\mu-Cl)_2(ppy)_2]$ (ppy = metalated 2-phenylpyridine) with Pb(Spy)_2 readily yields a platinum(III) complex $[Pt_2Cl_2(Spy)_2(ppy)_2]$ [18]. The NMR spectra (¹H, ¹³C{¹H}, ¹⁹⁵Pt{¹H}) of **2** revealed the existence of more than one isomeric species in solution (Supplementary information, Figs. S3–S5). The ¹H NMR spectrum showed three peaks due to OMe protons. Similarly the ¹³C{¹H} NMR spectrum displayed three sets of resonances for the pyridyl group and σ -bonded carbon atom (with ¹⁹⁵Pt couplings). The ¹⁹⁵Pt{¹H} NMR spectrum exhibited two resonances in 1:2 ratio.

The complex 2 may exist in different geometrical and optical configurations. In case of geometrical configurations cis and trans isomers are possible [34] (Supplementary information, Fig. S6). For trans isomer only one set of olefinic, OMe and pyridyl ring proton/ carbon resonances are expected whereas *cis* isomer, in which the relative disposition of the ligands around Pt centers is different, would display two sets of olefinic, OMe and pyridyl ring proton/ carbon resonances in the NMR spectra. Also the OMe groups can be endo or exo or at the same or different side with respect to the plane passing by the mid points of the two olefinic bonds and the PtC-C(OMe) bonds which would generate different isomeric forms. In addition to above geometrical isomers, the presence of two chiral centers in octenyl group, the complex 2 is capable to generate various diastereomers having different chemical shifts in NMR spectra. All the above isomeric forms may not give at different chemical shifts as for example the broadness of one of the ${}^{195}Pt{}^{1}H$ NMR resonance $(-3541 \text{ ppm}, \Delta 1/2 = 679 \text{ Hz})$ indicates the presence of mixtures of similar but different species.

In some reactions between **1**, when slightly contaminated with PtCl₂(COD), and Pb(Spy)₂, a red crystalline trinuclear complex $[Pt_3(Spy)_4(C_8H_{12}OMe)_2]$ (**3**) (by X-ray analysis) was also formed in poor yield together with **2** as a major product. The structure of **3** can be compared with an allyl complex $[Pd_3(SMes)_4(C_4H_7)_2]$ [35]. The latter could be isolated by refluxing $[Pd(SMes)_2]_n$ with $[Pd_2(SMes)_2(C_4H_7)_2]$ in dichloromethane. Thus the reaction between **2** and freshly prepared $[Pt(Spy)_2]$ (as the sample showed poor solubility on aging) in refluxing benzene afforded **3**, structure of which was again ascertained by X-ray crystallography. The ¹H NMR spectrum of **3** showed different resonances for OMe group and the ¹⁹⁵Pt{¹H} NMR spectrum displayed two major peaks at δ –3470 ppm (terminal Pt) and –3333 ppm (central Pt) together with other small peaks indicative of the existence of other isomeric forms in solution (Supplementary information, Fig. S7).

In an attempt to prepare **2** by an alternative route, reaction of **1** with 2-mercaptopyridine in the presence of sodium methoxide was carried out. The reaction gave a mixture of products as revealed by ¹⁹⁵Pt{¹H} NMR spectroscopy. From this mixture at least two complexes, viz. 2 (64% yield) and a self-assembled tetranuclear complex $[Pt_4(Spy)_4(C_8H_{12}-O-C_8H_{12})_2]$ (4) (15% yield) could be separated by column chromatography on silica gel. The **4** appears to be formed by demethylation of 2 during the reaction in the presence of 2-mercaptopyridine and NaOMe in CH₂Cl₂-MeOH mixture. Demethylation of aliphatic as well as aromatic methylethers is well documented in literature [36-38]. Demethylation of ether involving metal complex, to our knowledge, is the first example. Other probable route, i.e. first demethylation of **1** to form $[Pt_4(\mu-Cl)_4(C_8H_{12}-O_{12}+C_8H_{12}-O_{12}+C_8H_{12}+O_{12}+C_$ C_8H_{12} , followed by substitution of chloro-bridge by pyS⁻, is ruled out in the presence of strong nucleophilic pyS⁻. The reaction at higher temperature was not attempted to improve the yield of 4 due to decomposition of thermodynamically unstable metalated octenyl groups which is discussed in thermal studies. The decomposition of 2 begins at 80 °C. The ¹⁹⁵Pt{¹H} NMR spectrum of **4** showed a relatively sharp resonance at δ –3495 ppm and three small broad peaks at δ -3523, -3554 and -3607 ppm due to the existence of other possible isomeric forms with different coordination environment





around platinum in solution (Supplementary information, Fig. S8). The resonance due to OMe group, as expected, was absent in the 1 H and 13 C{ 1 H} NMR spectra of **4**.

The reaction of **1** with a large bite thiolate ligand, diisopropyldithiophosphate, gave $[Pt\{S_2P(OPr^i)_2\}_2]$ (**5**), formed by extrusion of metalated octenyl ligand. Extrusion of metalated dienylmethoxy moiety in platinum complexes by neutral and anionic ligands is not uncommon [39–41].

The reaction of **1** with non-rigid 5-membered chelating ligands, Me₂NCH₂CH₂E⁻ afforded mononuclear platinum complexes [Pt(ECH₂CH₂NMe₂)(C₈H₁₂OMe)] (E = S (**6**), Se (**7**)) in ~82% yield as colorless (**6**)/pale-yellow (**7**) crystalline solids. These complexes showed expected resonances in the ¹H and ¹³C{¹H} NMR spectra. The ¹⁹⁵Pt{¹H} NMR spectra of **6** and **7** displayed a sharp singlet at ~-3720 ppm.

3.2. Crystal structures

Crystal and molecular structures of **2**, **3**, **4**, **5** and **7** have been established unambiguously by single crystal X-ray diffraction

analyses. The ORTEP drawings with crystallographic numbering scheme are shown in Figs. 1–5, and the selected interatomic parameters are given in Table 1. The complexes **3** and **4** were crystallized each with a molecule of dichloromethane and dieth-ylether, respectively.

The metalated $C_8H_{12}OMe$ group in **2**, **3**, **4** and **7** has a distorted boat conformation and is bonded to platinum atom through a σ and olefinic bond. The olefinic bond and the platinum coordination plane are at an angle varying between 73.76 and 83.66°. The methoxy group of cyclooctene adopts an *exo* configuration with respect to the platinum. The Pt– C_{σ} and Pt– $C_{(olefin)}$ distances are similar to those observed in [PtCl(py)($C_8H_{12}OMe$)] [42] and [Pt₂(OMe)₂($C_8H_{12}OMe$)₂] [43,44]. The Pt– $C_{(olefin)}$ bond in the case of **7** is, however, significantly shorter (~2.05 Å) than those observed for **2**, **3**, **4** and also [PtCl(py)($C_8H_{12}OMe$)] [42].

The pyridine-2-thiolate ion (pyS⁻) in **2**, **3** and **4** acts as a bridging ligand and binds two platinum atoms through S^{\cap}N coordination. The thiolate sulfur in these complexes occupies a position *trans* to olefinic bond while the nitrogen atom is *trans* to the Pt–C_{σ} bond. Such a trend – a strong *trans* influencing ligand (e.g. PPh₃)



Fig. 1. Molecular structure of [Pt₂(Spy)₂(C₈H₁₂OMe)₂] (2), ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

occupying a position *trans* to olefinic bond, has been reported in bridge splitting reactions of $[Pt_2(\mu-Cl)_2(C_8H_{12}OMe)_2]$ with neutral donor ligands [45]. The Pt–S distances (2.277(5)–2.323(4) Å) are well within the range reported in platinum(II) thiolate complexes, e.g., $[Pt_3(Stol)_4(dppm)_2][SO_3CF_3]_2$ [46], $[Pt\{(OPPh_2)N(PPh_2S)\}(C_8H_{12}OMe)]$ [47], $[Pt\{(SPPh_2)N(PPh_2S)\}(C_8H_{12}OMe)]$ [48] and $[PtMe_2(Spy)_2]$ [49]. The Pt–N distances (2.160(15)–2.239(17) Å) reflects

the large *trans* influence of the σ -bonded carbon atom and are slightly longer than those reported in [PtCl(SCH₂CH(Me)NMe₂)(P-Me₂Ph)] (2.130(9) Å) [50] and [Pt₂(ppy)₂(Spy)₂] (2.142(7) Å) [51].

The complex **2** is a Spy-bridged binuclear platinum(II) complex with a *trans* or *anti* configuration. The molecule adopts a head-to-tail configuration similar to the other cyclometalated binuclear platinum complexes containing bridging Spy ligands,



Fig. 2. Molecular structure of [Pt₃(Spy)₄(C₈H₁₂OMe)₂] (3), ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.



Fig. 3. Molecular structure of $[Pt_4(Spy)_4(C_8H_{12}-O-C_8H_{12})_2]$ (4), ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

e.g. $[Pt_2(Spy)_2(ppy)_2]$ [51], $[Pt_2(Spy)_2(bipy)_2]^{2+}$ [52], $[Pt_2(Spy)_2(dtby)_2]^{2+}$ (dtby = 4,4'-di-tert-butyl-2,2'-bipyridine) [53]. The Pt…Pt separation in **2** is much larger (3.448 Å) than those reported in Spy-bridged binuclear platinum complexes, e.g. $[Pt_2(Spy)_2(ppy)_2]$ (2.849(4) Å) [51].

The **3** is a trinuclear complex in which three platinum atoms are held together by double-edge bridges of Spy ligand. The trinuclear complex has a two-fold axis on the central Pt square plane passing between S–Pt–S and N–Pt–N angles. The coordination environment around the central platinum atom is defined by *trans* disposed S and N donor atoms.

In the tetranuclear complex **4**, the two " $Pt_2(Spy)_2$ " units are held together by bridging dicyclooctene-yl groups. The molecular



Fig. 4. Molecular structure of [Pt(S₂P{OPrⁱ}₂)] (**5**), ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

structure can be compared with the structure of chloro(allyl) platinum(II) [54] and tetranuclear palladium complexes [Pd₄(OAc)₄($C^{\cap}N$)₂] formed by double metalation of organic ligands by palladium acetate [20]. The Pd···Pd separation in the latter is ~ 2.9 Å while in **4** the two platinum atoms in 'Pt₂(Spy)₂' units are 3.804 Å apart possibly to relieve crowding of the two bulkier ether ligands. The molecule has a two-fold axis perpendicular to the Pt···Pt axis containing two platinum atoms of the same binuclear unit. The angle between the two Pt square planes (four atom least square plane [55]) decreases as Pt···Pt separation decreases in complexes **4**, **2** and **3**, which agrees well with the literature [56].

The two dithiophosphate ligands in **5** are coordinated to platinum atom in a chelating bidentate fashion. The platinum coordination plane and the two four-membered chelate rings all lie in a plane. The Pt–S distances are as expected [57].

The complex **7** is a discrete monomer having distorted square planar platinum atom. The chalcogenolate ligand is coordinated to the metal atom in a bidentate mode. The Pt–Se distance is unusually short (2.266(11) Å). The Pt–Se distances in [PtCl(SeCH₂CH(Me)NMe₂)(PMe₂Ph)] [50] and [Pt₂Cl₂(μ -Cl)(μ -SeCH₂CH₂COOMe)(PPr₃)₂] [58] are ~2.38 Å. This may be due to very weak *trans* influence of olefin. The five-membered "PtSCCN" ring is puckered.

3.3. Thermal studies

Recently we have employed binuclear platinum complexes $[Pt_2(OR)_2(C_8H_{12}OMe)_2]$ (R = Me, Ac) for the preparation of platinum nanoparticles (~10 nm) by thermolysis in HDA (1-hexadecylamine) [14]. The complexes with chalcogenolate ligands may yield platinum chalcogenides on pyrolysis as several palladium chalcogenolate complexes have been used as single source molecular precursors for the synthesis of palladium chalcogenides [35,19,59,60]. The complexes described here may serve as precursors for the preparation of platinum chalcogenides as the presence of comparatively stronger Pt–E bond in these complexes than the Pt–O bond in the earlier complexes [14]. The complex



Fig. 5. Molecular structure of [Pt(SeCH₂CH₂NMe₂)(C₈H₁₂OMe)] (7), ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

as revealed by TG curve (Supplementary information, Fig. S9). The weight loss in the first step corresponds to the loss of methoxy groups at 80 °C (wt. loss found 6.9%, calcd. 7.0%). The second step of decomposition (at 180 °C) can be attributed to the loss of cyclooctenyl group (wt. loss found 23%, calcd. 24.3%). The final step of decomposition corresponds to the loss of pyS- ligand (wt. loss found 23%, calcd. 24.5%) leading to the formation of platinum metal. The TG curve of 6 (Supplementary information, Fig. S10) showed a two-step decomposition wherein the first step corresponds to the loss of $(C_8H_{12}OMe)$ and the second step corresponds to the loss of SCH₂CH₂NMe₂ group. The TG curve of **7** showed a single step of decomposition corresponding to the loss of (C₈H₁₂OMe) group. When **2**, **6** and **7** are thermolysed in HDA in the temperature range 210-250 °C platinum nanoparticles, rather than platinum chalcogenides, were formed. The observed lattice planes in the XRD pattern indicate the formation of fcc phase of platinum particles [61]. The average size estimated from XRD pattern (Supplementary

Table 1

Selected interatomic distances [Å] and angles [°].

| | 2 | $3 \cdot CH_2Cl_2$ | $4 \cdot OEt_2$ | 7 |
|---------------------------|----------|--------------------|-----------------|------------|
| Pt(1)-C(10) | 2.15(2) | 2.046(19) | 2.033(15) | 2.039(9) |
| Pt(1)-C(6) | 2.15(2) | 2.151(19) | 2.124(19) | 2.061(9) |
| Pt(1)-C(13) | 2.11(2) | 2.18(2) | 2.10(2) | 2.045(8) |
| Pt(1)-S(1)/Se(1) | 2.282(5) | 2.323(4) | 2.308(5) | 2.2660(11) |
| Pt(2)-C(19) | 2.15(2) | - | 2.145(17) | _ |
| Pt(2)-C(23) | 2.02(2) | - | 2.009(15) | _ |
| Pt(2)-C(26) | 2.13(2) | - | 2.113(19) | _ |
| Pt(2)-S(2) | 2.277(5) | 2.295(5) | 2.297(5) | _ |
| C(6)-C(13) | 1.332 | 1.411 | 1.350 | 1.411(14) |
| C(13)–Pt(1)–C(6) | 36.4(8) | 38.1(7) | 37.4(8) | 40.2(4) |
| C(13)-Pt(1)-C(10) | 81.8(10) | 80.2(7) | 81.2(8) | 82.2(4) |
| C(13) - Pt(1) - S(1) | 153.4(9) | 168.7(7) | 153.8(6) | 158.8(3) |
| C(23)-Pt(2)-C(26) | 82.1(9) | - | 82.2(7) | - |
| C(26)-Pt(2)-C(19) | 38.2(9) | _ | 38.9(7) | _ |
| C(26)-Pt(2)-S(2) | 165.8(9) | _ | 154.0(5) | _ |
| Pt…Pt | 3.448 | 3.136 | 3.832 (Pt1) | _ |
| | | | 3.775 (Pt2) | |
| Pt sq. plane ^a | 52.75 | 33.37 | 69.44 (Pt1) | _ |
| | | | 63.41 (Pt2) | |

^a The angle between two platinum square planes. As the metal planes are distorted square planar, so four atom least square plane and their angle has been calculated [55]. information, Figs. S11–S13) as prepared samples corresponds to 20 (from **2**); 4 (from **6**); 7 (from **7**) nm.

4. Conclusions

Mono-, bi- and trinuclear complexes **7**, **2** and **3**, respectively with weakly coordinated octenyl group and strongly bonded chalcogenolate ligand have been synthesized and structurally characterized. A new oxo-bridged tetranuclear macrocyclic complex **4** has been isolated and structurally characterized. Thermolysis of mono- or binuclear complexes of platinum containing strong Pt–E bond in HDA yields fcc phase of platinum nanoparticles.

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Appendix. Supplementary information

Details of synthesis of $[Pb(Spy)_2]$, $[Pt(Spy)_2]$, crystallographic and structure refinement data tables of all complexes, mass spectra of 2 and 3; ¹H ¹³C{¹H} and ¹⁹⁵Pt{¹H}NMR spectra of 2; ¹⁹⁵Pt{¹H} NMR spectra of 3 and 4; TG curves of 2 and 6 and powder XRD pattern of platinum nanoparticles, single crystal X-ray diffraction studies (cif file) of 2, 3, 4, 5 and 7 are provided in supplementary information. CCDC 801696, 801697, 801698, 801695 and 801694 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via HYPERLINK "http://www.ccdc. cam.ac.uk/data_request/cif." www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found in the on-line version at doi:10.1016/j.jorganchem.2011.07.025.

References

- [1] N. Selander, K.J. Szabo, Dalton Trans. (2009) 6267-6279.
- [2] R.B. Bedford, Chem. Commun. (2003) 1787–1796.
- [3] M. Pfeffer, Pure Appl. Chem. 64 (1992) 335–342.

- [4] A.S. Mocanu, M. Ilis, F. Dumitrascu, M. Ilie, V. Circu, Inorg. Chim. Acta 363 (2010) 729–736.
- [5] A.P. Polishchuk, T.V. Timofeeva, Russ. Chem. Rev. 62 (1993) 291–321.
- [6] M. Ghedini, D. Pucci, A. Crispini, G. Barberio, Organometallics 18 (1999) 2116–2124.
- [7] E.A.M. Geary, L.J. Yellowlees, L.A. Jack, I.D.H. Oswald, S. Parsons, N. Hirata, I.R. Durrant, N. Robertson, Inorg. Chem. 44 (2005) 242–250.
- [8] M. Hissler, J.E. McGarrah, W.B. Connick, D.K. Geiger, S.D. Cummings, R. Eisenberg, Coord. Chem. Rev. 208 (2000) 115–137.
- [9] Y. Chi, P.-T. Chou, Chem. Soc. Rev. 39 (2010) 638–655.
- [10] J.A.G. Williams, Chem. Soc. Rev. 38 (2009) 1783-1801.
- [11] R.C. Evans, P. Douglas, C.J. Winscom, Coord. Chem. Rev. 250 (2006) 2093–2126.
- [12] M. Albrecht, Chem. Rev. 110 (2010) 576-623.
- [13] Y. Unger, D. Meyer, O. Molt, C. Schildknecht, I. Münster, G. Wagenblast, T. Strassner, Angew. Chem. Int. Ed. 49 (2010) 10214–10216.
- [14] N. Ghavale, S. Dey, V.K. Jain, R. Tewari, Bull. Mater. Sci. 32 (2009) 15-18.
- [15] C. Thurier, P. Doppelt, Coord. Chem. Rev. 252 (2008) 155–169.
- [16] J.C. Hierso, R. Feurer, P. Kalck, Coord. Chem. Rev. 178–180 (1998) 1811–1834.
- [17] N. Ghavale, S. Dey, A. Wadawale, V.K. Jain, J. Organomet. Chem. 695 (2010) 2296–2304
- [18] N. Ghavale, A. Wadawale, S. Dey, V.K. Jain, J. Organomet. Chem. 695 (2010) 1237–1245.
- [19] S. Dey, V.K. Jain, Platinum Met. Rev. 48 (2004) 16–29.
- [20] V.K. Jain, L. Jain, Coord. Chem. Rev. 254 (2010) 2848-2903.
- [21] S. Dey, V.K. Jain, S. Chaudhary, A. Knoedler, F. Lisner, W. Kaim, J. Chem. Soc. Dalton Trans. (2001) 723-728.
- [22] R.N. Keller, T. Moeller, J.V. Quagliano, Inorg. Synth. 2 (1963) 247-250.
- [23] D. Drew, J.R. Doyle, A.G. Shaver, Inorg. Synth. 13 (1972) 47–55.
- [24] J. Chatt, L.M. Vallarino, L.M. Venanzi, J. Chem. Soc. (1957) 2496-2505.
- [25] SIR-92, A. Altomare, G. Cascarano, C. Gracovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343–350.
- [26] G.M. Sheldrick, Programs SHELXS97 (Crystal Structure Solution) and SHELXL97 (Crystal Structure Refinement). University of Göttigen, Germany, 1997.
- [27] T. Higashi, ABSCOR Empirical Absorption Correction based on Fourier Series Approximation. Rigaku Corporation, 3-9-12 Matsubara, Akishima, Japan, 1995.
- [28] PSISCANS, A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. A 24 (1968) 351–359.
- [29] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol. IV, The Kynoch Press, Birmingham, England, 1974, Table 2.2 A.
- [30] Crystal Structure 3.7.0: Crystal Structure Analysis Package, Rigaku and Rigaku MSC 2000–2005, 9009 New Trials Dr. The Woodlands, TX 77381, USA.
- [31] D.J. Watkins, C.K. Prout, J.R. Carruthers, P.W. Betteridge, Chemical Laboratory, Oxford (U.K.), 1996.
- [32] C.K. Johnson, ORTEP-II, Report ORNL-5136. Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

- [33] J.K. Stille, R.A. Morgan, J. Am. Chem. Soc. 88 (1966) 5135–5141.
- [34] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, J. Organomet. Chem. 468 (1994)
- 285–290. [35] N. Ghavale, S. Dey, A. Wadawale, V.K. Jain, Organometallics 27 (2008) 3297–3302.
- [36] L.F. Frey, K.M. Marcantonio, C.-Y. Chen, D.J. Wallace, J.A. Murry, L. Tan, W. Chen, U.H. Dolling, E.J.J. Grabowski, Tetrahedron 59 (2003) 6363–6373.
- [37] M. Node, K. Nishide, K. Fuji, E. Fujita, J. Org. Chem. 45 (1980) 4275–4277.
- [38] S. Berényi, C. Csutorás, S. Gyulai, G. Rusznyák, Synth. Commun. 31 (2001) 1987–1992.
- [39] G. Carturan, L. Busetto, A. Palazzi, U. Belluco, J. Chem. Soc. A (1971) 219–222.
 [40] R. Pietropaolo, F. Cusmano, E. Rotondo, A. Spadaro, J. Organomet. Chem. 155 (1978) 117–122.
- [41] H.C. Clark, A.B. Goel, S. Goel, J. Organomet. Chem. 216 (1981) C25-C28.
- [42] G. Bombieri, E. Forsellini, R. Graziani, J. Chem. Soc. Dalton Trans. (1972) 525–527.
- [43] A.B. Goel, S. Goel, D.G. Vanderveer, Inorg. Chim. Acta 54 (1981) L169–L170.
- [44] F. Giordano, A. Vitagliano, Inorg. Chem. 20 (1981) 633–635.
- [45] J. Soulie, J.-C. Chottard, D. Mansuy, J. Organomet. Chem. 171 (1979) 113–120.
 [46] A. Singhal, V.K. Jain, A. Klein, M. Niemeyer, W. Kaim, Inorg. Chim. Acta 357
- (2004) 2134–2142. [47] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996)
- [47] A.M.Z. Stawin, M.B. Smith, J.D. Woonins, J. Chen, Soc. Daton Trans. (1996) 3659–3665.
 [48] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, J. Chem. Soc. Dalton Trans. (1998)
- 2467–2476.
- [49] K.J. Bonnington, M.C. Jennings, R.J. Puddephatt, Organometallics 27 (2008) 6521-6530.
- [50] S. Dey, L.B. Kumbhare, V.K. Jain, T. Schurr, W. Kaim, A. Klein, F. Belaj, Eur. J. Inorg. Chem. (2004) 4510–4520.
- [51] T. Koshiyama, A. Omura, M. Kato, Chem. Lett. 33 (2004) 1386-1387.
- [52] M. Kato, A. Omura, A. Toshikawa, S. Kishi, Y. Sugimoto, Angew. Chem. Int. Ed. 41 (2002) 3183–3185.
- [53] B.-C. Tzeng, W.-F. Fu, C.-M. Che, H.-Y. Chao, K.-K. Cheung, S.-M. Peng, J. Chem. Soc. Dalton Trans. (1999) 1017–1024.
- [54] G. Raper, W.S. McDonald, J. Chem. Soc. Dalton Trans. (1972) 265-269.
- [55] W. Mohr, J. Stahl, F. Hampel, J.A. Gladysz, Chem. Eur. J. 9 (2003) 3324–3340.
 [56] B. Ma, J. Li, P.I. Djurovich, M. Yousufuddin, R. Bau, M.E. Thompson, J. Am.
- Chem. Soc. 127 (2005) 28–29. [57] V.K. Jain, S. Chaudhury, A. Vyas, R. Bohra, J. Chem. Soc. Dalton Trans. (1994) 1207–1211.
- [58] L.B. Kumbhare, V.K. Jain, P.P. Phadnis, M. Nethaji, J. Organomet. Chem. 692 (2007) 1546–1556.
- [59] B. Radha, G.U. Kulkarni, Adv. Funct. Mater. 20 (2010) 879–884 and references therein.
- [60] S. Dey, V.K. Jain, J. Singh, V. Trehan, K.K. Bhasin, B. Varghese, Eur. J. Inorg. Chem. (2003) 744–750.
- [61] Powder Diffraction File No. 04-0802, Compiled by JCPDS. International Centre for Diffraction Data, USA, 1997.