

## From molecular to micro structure via nanostructure of a nickel(II) dithiolene complex

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Received 6 May 2011; revised and accepted 1 July 2011

The nanocrystal structure of a hetero-polyatomic metal-ligand complex,  $[\text{PPh}_4][\text{Ni}^{\text{II}}(\text{L}^{2-})(\text{L}^{1-})]$ , (**1**) ( $\text{L} = 1,2$ -dicarbomethoxyethylene dithiolate) has been arrived at from its molecular structure obtained by X-ray crystallography. The complex (**1**) exhibits dimorphism, existing in two crystal habits at the micro level, viz., rectangular prismatic and hexagonal. Rectangular or hexagonal repeating motifs manifest in the lattice packing of the two crystal structures of (**1**) in two different solvents which extend up to nano dimension and result in nano sized rectangular and hexagonal prismatic crystals. This provides major clues to understand the shapes of hetero-poly atomic nanocrystals at the molecular level.

**Keywords:** Coordination chemistry, Dimorphism, Nanocrystals, Crystal structure, Rectangular shape, Hexagonal shape, Nickel

Nanocrystals are of current research interest owing to their unique size and shape dependent chemical, electronic, catalytic, magnetic and optical properties. The size and shape of nanocrystals can be synthetically, thermodynamically or kinetically (or both) controlled<sup>1-7</sup>. Although metallic nanocrystals of different shapes/sizes and their control by synthetic techniques have been well investigated, the atomistic-level understanding of metallic- or the molecular level understanding of metal-ligand complex nanocrystals still remains a challenge<sup>8-13</sup>. In the past, several attempts have been made to visualize the structures of nanocrystals, viz., the structures of nanocrystalline  $\text{K}_{8-x}\text{Nb}_{16-x}\text{W}_{12+x}\text{O}_{80}$  ( $x \sim 1$ )<sup>14</sup>, thiol-capped gold nano cluster<sup>15</sup>, nano-meter sized spin cross over polymer,  $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ <sup>16</sup>, perylene derived dye,  $3,4,9,10$ -[*t*-BuC(O)NH]<sub>4</sub>C<sub>20</sub>H<sub>8</sub><sup>17</sup>, a complex zeolite material<sup>18</sup>, crystal structure of staurolite ( $\text{HFe}_2\text{Al}_2\text{Si}_4\text{O}_{24}$ )<sup>19</sup>, and the structure of a recently reported 12-porphyrin nano-ring with a diameter of 4.7 nm (ref. 20).

Self-assembly, a fundamental process in the formation of nanocrystal/nanoparticles, involves non-covalent molecular bonds such as hydrogen bonding, hydrophobic and  $\pi$ -stacking or it can be an electrostatic process which has been exploited in several ways<sup>21,22</sup>. For example, in the formation of single crystals of single-walled carbon nano tubes (SWCNTs) from nano-patterned precursors, in self-

assembly of short dipeptides, viz., diphenylalanine (FF) in the formation of peptide nano tubes (PNTs)<sup>23</sup> and their nanocrystalline building blocks (viz., quantum dots)<sup>24-27</sup> and in the formation of diamond-like lattice by charged/equally sized gold/silver nano particles<sup>28</sup>.

Our long-standing quest in nano-scientific research has been whether a correlation can be drawn between the structures of metal-ligand complex crystals in nano domain and that in the atomic domain by means of intermolecular interactive forces which might extend to microscopic/macrosopic domain as well. Although the number of X-ray crystal structures of single macroscopic crystal has crossed five millions so far, and reports on nanocrystals have increased numerically, the structural elucidation of these complexes at the nano level is still unclear. This is because the X-ray crystal structures are probed mainly for polyatomic and metalloorganic complexes which are hardly isolated as nanocrystals. Herein we report a metal-ligand complex,  $[\text{PPh}_4][\text{Ni}^{\text{II}}(\text{L}^{2-})(\text{L}^{1-})]$ , (**1**) ( $\text{L}$ , 1,2-dicarbomethoxyethylene dithiolate)<sup>29</sup>, which has been structurally characterized and isolated also as nanocrystals. This complex (**1**) exhibits dimorphism, existing in two crystal habits at the micro level, viz., rectangular prismatic and hexagonal. Rectangular or hexagonal repeating motifs are manifested in lattice packings of both crystal structures which extend up to nano dimension and

result in nano sized rectangular prismatic and hexagonal crystals.

### Materials and Methods

All solvents and chemicals were purchased from commercial sources. Dimethyl acetylenedicarboxylate was purchased from Sigma-Aldrich (USA). The complex,  $[\text{PPh}_4][\text{Ni}^{\text{II}}(\text{L}^{2-})(\text{L}^{1-\bullet})]$ , (**1**) (L, 1,2-dicarbo-methoxyethylene dithiolate), was prepared as reported previously by us<sup>29,30</sup>.

The single crystals suitable for X-ray diffraction were obtained by recrystallization from EtOH (rectangular prisms) or from MeCN-Et<sub>2</sub>O (hexagonal prisms). The intensity data were collected on a Bruker AXS Smart Apex CCD diffractometer with graphite monochromated Mo-K<sub>α</sub> radiation (0.71073 Å). Data reduction and absorption corrections were done using SAINTPLUS program package. The structures was solved by direct and conventional Fourier methods and refined on  $F^2$  by full-matrix least-squares technique using SHELXTL program package<sup>13</sup>. All non-hydrogen atoms were refined anisotropically, with H atoms at idealized positions in riding mode. Selected crystallographic data of complex (**1**) recrystallized from EtOH are given in Table 1. The crystal data for the complex (**1**) recrystallized from MeCN-Et<sub>2</sub>O is reported earlier<sup>29</sup>.

Samples for SEM measurements were prepared by taking a few single crystals from each case and redissolved in either EtOH or MeCN-Et<sub>2</sub>O, sonicated for 5 min. and 5 μL of each sample was deposited onto brass stubs. The samples were dried for 3 h under a table lamp and mounted onto a SUPRA 40VP field emission scanning electron microscope (CARL ZEISS NTS GmbH, Oberkochen, (Germany) equipped with energy dispersive X-ray (EDX) facility. The samples for TEM measurements were prepared in a similar fashion as for SEM, but the samples were deposited on carbon film coated copper grids (400 square mesh), dried for 3 h under table lamp and then mounted on to a FEI Technai 20 U Twin transmission electron microscope equipped with EDS detector.

### Results and Discussion

The complex  $[\text{PPh}_4][\text{Ni}^{\text{II}}(\text{L}^{2-})(\text{L}^{1-\bullet})]$  (**1**) (L= 1,2-dicarbo-methoxyethylene dithiolate) was prepared by the reported synthetic procedure and single crystals suitable for X-ray diffraction were obtained either from ethanol (EtOH, rectangular prisms) or acetonitrile-diethylether (MeCN-Et<sub>2</sub>O, hexagonal

Table 1—Crystal data for  $[\text{PPh}_4][\text{Ni}^{\text{II}}(\text{L}^{2-})(\text{L}^{1-\bullet})]$  (**1**) recrystallized from EtOH

Empirical formula	C <sub>36</sub> H <sub>32</sub> NiO <sub>8</sub> PS <sub>4</sub>
Formula weight	810.54
Temp. (K)	100(2)
Wavelength Mo-K <sub>α</sub> (Å)	0.71069
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (Å), (°)	$a = 10.816(5)$ ; $\alpha = 86.355(5)$ $b = 11.097(5)$ ; $\beta = 82.974(5)$ $c = 15.453(5)$ ; $\gamma = 81.917(5)$
Volume (Å <sup>3</sup> )	1820.5(13)
Z	2
Density (mg/m <sup>3</sup> )	1.479
Abs. coeff. (mm <sup>-1</sup> )	0.857
F(000)	838
Crystal size (mm)	0.123 × 0.084 × 0.032
θ range for data collection (°)	1.9 to 26.00
Unique reflections	6997
Observed reflections	5796
Completeness to θ = 26.00°	97.6 %
Abs. corr.	Empirical
Refinement method	Full matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	6997/0/454
Goodness of fit on F <sup>2</sup>	0.835
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0635$ , $wR_2 = 0.1821$
R indices (all data)	$R_1 = 0.0763$ , $wR_2 = 0.2104$

prisms) mixture. The magnetic susceptibility measurements of these two forms of (**1**) showed identical magnetic moment values, ( $\mu_{\text{eff}} = 1.74 \mu_{\text{B}}$ ), consistent with one unpaired electron. The localization of this unpaired electron on the ligand in complex (**1**) has been reported earlier, based on its electronic structure by us<sup>30</sup>. Rectangular prismatic or hexagonal shaped nanocrystals were obtained on recrystallization of the complex (**1**) from EtOH or MeCN-Et<sub>2</sub>O mixture respectively at  $\sim 10^{-3}$  M concentration. In a typical preparation, macroscopic and single crystals of the complex (**1**) were powdered finely in a pestle-mortar, sonicated in EtOH or MeCN-Et<sub>2</sub>O solvents for 5 min. and a drop of the suspension was deposited on a brass stub, dried for 3 h under a table lamp and then subjected to scanning electron microscopic (SEM) measurements. The results at low and high magnification levels are shown in Fig. 1.

The low magnification SEM images (Fig. 1A and 1E) show the array of rectangular and hexagonal shaped crystals in EtOH and MeCN-Et<sub>2</sub>O solvents. Both types of crystals are of comparable nano dimensions as indicated in the Fig. 1B and 1F. The

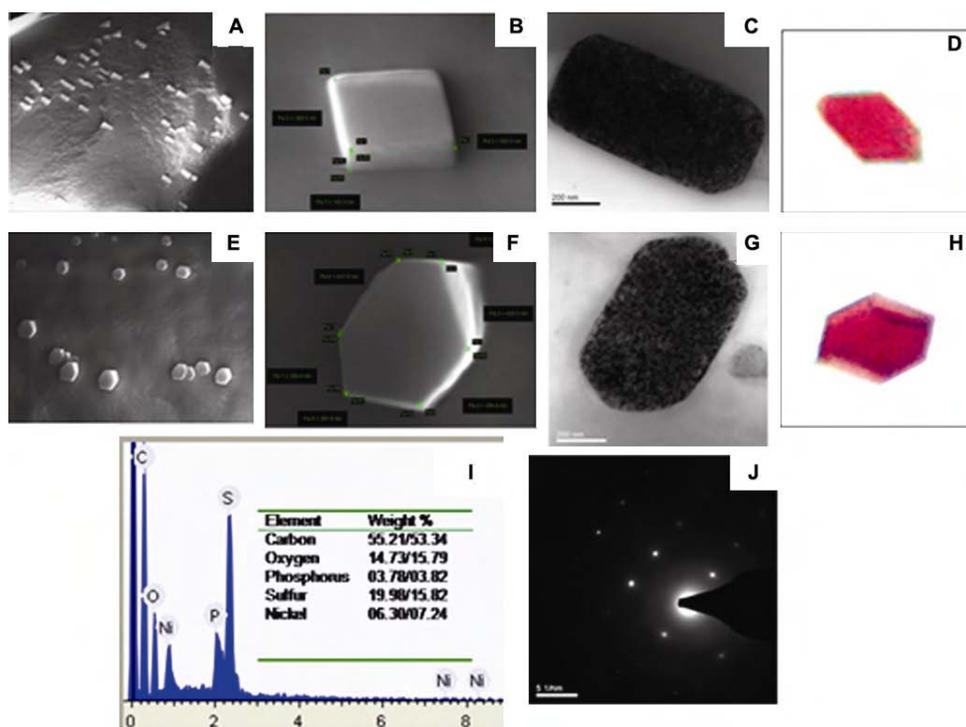


Fig. 1—(A) – (D): SEM images of nanocrystals of complex (1) recrystallized from EtOH, and, (E) – (H): recrystallized from MeCN-Et<sub>2</sub>O. (A) & (E): Low magnification SEM images of rectangular prisms (15.00 KX) and hexagons (25.00 KX) respectively of complex (1); (B) & (F): High magnification SEM images of a rectangular prismatic shaped nanocrystal (200.00 KX) and of a hexagon (200.00 KX) of (1) respectively; (C) & (G): TEM images of rectangular prismatic and hexagonal crystals respectively; (D) & (H): optical microscopic images of the micrometer sized (7-8 μm) rectangular prismatic and hexagonal crystals respectively; (I): EDX spot analysis (SEM) of the nanocrystals of (1) (inset, % weight of the constituents); (J): Electron diffraction pattern of the hexagonal shaped nanocrystal of (1) shown in (G).

EDS analysis of these nanocrystals gave the percentages of nickel, carbon, oxygen, sulfur and phosphorous, which matched with the expected values of the complex (1) (Fig. 1I).

The transmission electron microscopic (TEM) analysis of the sonicated samples in EtOH or MeCN-Et<sub>2</sub>O followed by deposition on carbon film coated copper grids also indicate the formation of rectangular (Fig. 1C) and hexagonal (Fig. 1G) crystals and the discrete and bright spots in electron diffraction image shown in Fig. 1J prove the single crystal nature of the sample. The nanocrystal growth was observed in EtOH or in MeCN-Et<sub>2</sub>O media whereas in other solvents like, methanol, dichloromethane and pure acetonitrile, the nanocrystals did not form under comparable conditions. We propose that the solvents, EtOH or MeCN-Et<sub>2</sub>O, assist and direct the growth of nanocrystals and its termination are reminiscent of the function of capping agents in the formation of metallic nanocrystals. To rationalize the function of solvent media in the formation of nanocrystals of (1), we compared the single crystal X-ray structures of the complex (1) recrystallized from EtOH or MeCN-Et<sub>2</sub>O (Fig. 2A and Fig. 2B).

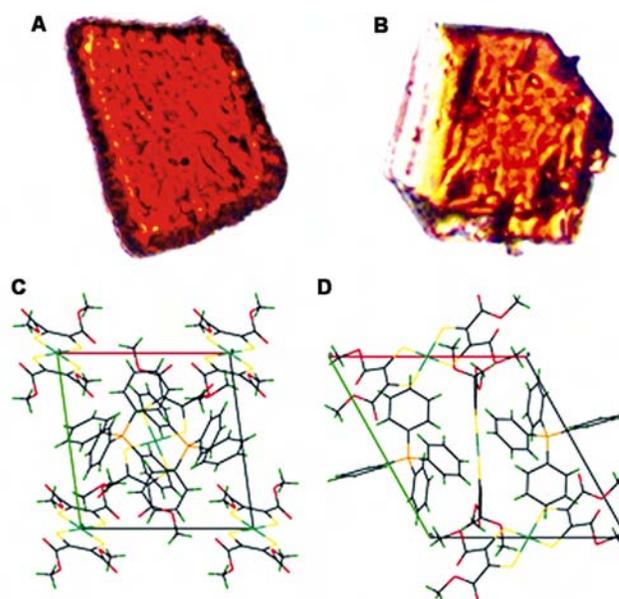


Fig. 2—Microscopic images of the single crystals of (1) from (A) EtOH (25 × 40 μm) and (B) MeCN-Et<sub>2</sub>O (10 μm) of (1) mounted on the X-ray diffractometer. (C) and (D): unit cell contents in the crystal structure of (1) obtained from EtOH and MeCN-Et<sub>2</sub>O respectively.

The unit cell contents of both of these structures are identical as shown in Fig. 2C and Fig. 2D and they do not contain any solvent molecule in the crystal lattices. Although the crystal system and space groups are identical in both cases, they differ in their cell parameters and their crystallographic packing features are strikingly different as shown in Fig. 3B – 3D and Fig. 4B – 4D respectively. Both crystal structures consist of the anion shown in Fig. 2E along with tetraphenylphosphonium  $[PPh_4]^+$  cation.

The van der Waals type short contacts present at the molecular level (2.583 Å – 3.116 Å) between the sulfur, oxygen and carbon atoms of the anion and the hydrogens or carbons of the tetraphenylphosphonium cations are highlighted in red color and shown in Fig. 3A and Fig. 4A. By expanding all of the red colored short contacts possible at the molecular level and viewing the resulting structure along the *c*-axis, a rectangular motif is obtained as shown in Fig. 3B. Further expansion of the short contacts possible in a rectangular motif leads to the generation of four adjacent rectangular motifs (Fig. 3C) and then to nine

motifs (Fig. 3D). In the structure of the crystals obtained from  $CH_3CN-Et_2O$ , the expansion of the van der Waals type contacts (red) results in repeating hexagonal motifs as shown in Fig. 4A – 4D. The analysis of the short contacts existing in this crystal structure indicates that seven van der Waals contacts are present whereas in the case of the structure of crystal obtained from EtOH, only five van der Waals type contacts are present. In the former (from  $CH_3CN-Et_2O$ ), the expansion of all of the seven contacts possible at the molecular level leads to a hexagonal motif which increases in number on further expansion of the contacts present in a single hexagonal motif. We propose that the formation of rectangular shaped nanocrystals from EtOH or the hexagonal nanoprisms from  $CH_3CN-Et_2O$  must have resulted from the repetition followed by layer by layer stacking of the building blocks as shown in Fig. 3D and Fig. 4D and the growth is controlled by the EtOH or  $CH_3CN-Et_2O$  solvent molecules. The solvent molecules are reminiscent of the function of capping agents in the formation of metallic

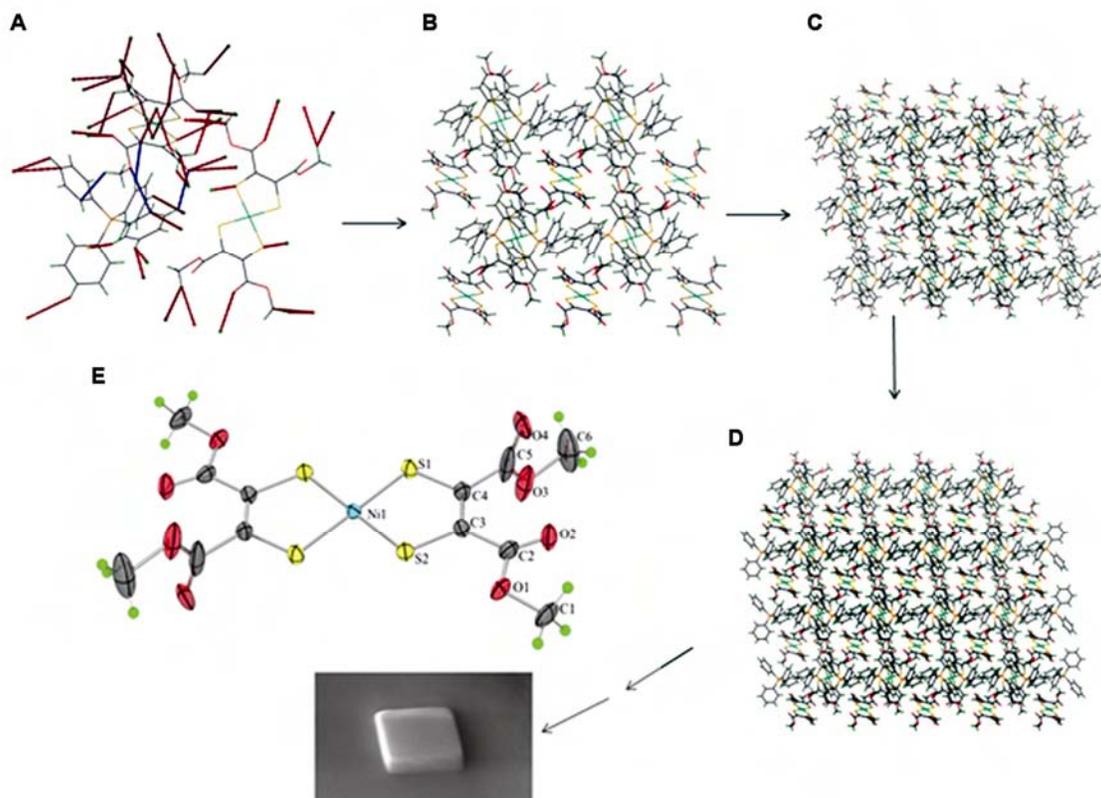


Fig. 3—(A) – (D): The stepwise generation of rectangular shaped motifs leading to the formation of rectangular prismatic nanocrystals of (1) in EtOH. (A): Extended- and hanging contacts are shown in blue and red colors respectively. (E): Perspective view of the anion,  $[Ni^{II}(L^{2-})(L^{1*})]^-$  present in the single crystal X-ray structure of (1) obtained from EtOH.

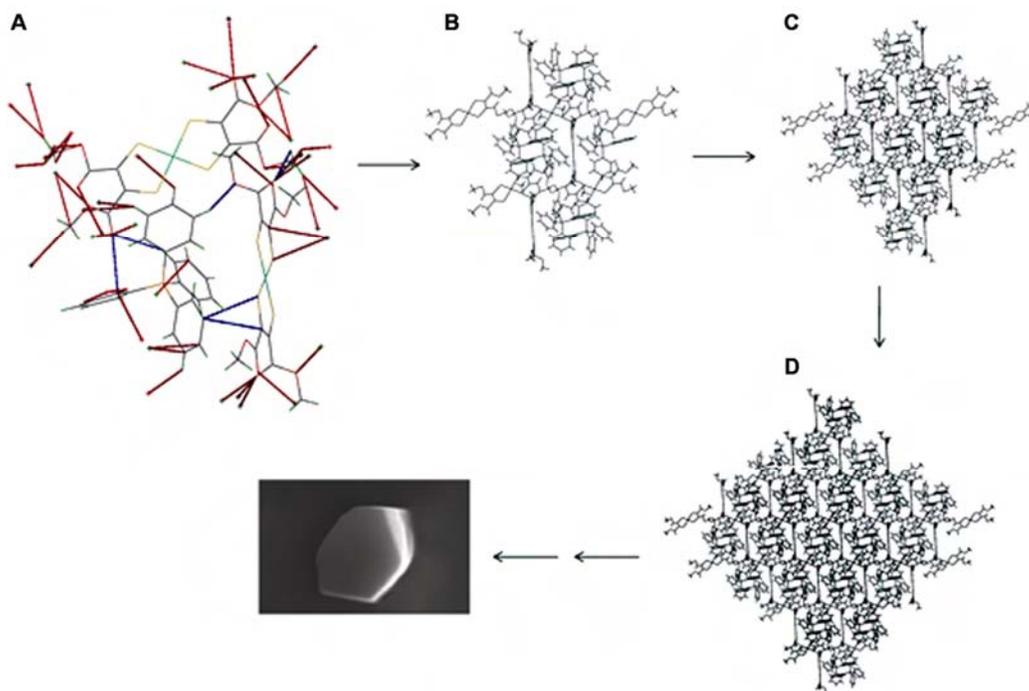


Fig. 4—(A) – (D): The stepwise generation of hexagonal shaped motifs leading to the formation of hexagonal shaped nanocrystals of (1) in MeCN-Et<sub>2</sub>O. (A): Extended and hanging contacts are shown in blue and red colors respectively.

nanocrystals and terminate the lattice expansion and leave the lattice once it is formed.

Solvent directed lattice packing leading to the formation of definite crystal shapes, which is a well known phenomenon in chemical as well as biological systems, can also be regarded as one of the synthetic controls for the formation of specific nanocrystalline shapes. Since the concentration of the samples have been maintained at  $10^{-3}$  M in both cases, the formation of two different shapes, viz., rectangular and hexagonal prismatic, is due to the two different solvents which differ in their polarity. Generally the shape of particles grown by deposition of monomeric species is spherical because of isotropic growth. If such a process of growth uses a metastable steady form, a slight change in the growth environment allows the deviation from the steady state resulting in polyhedral shape. Thus, under kinetic growth mode the shape of a crystal may experience anisotropic effect by the shape controller influencing its development in polyhedral form. The decisive forces in the formation of polyhedral forms like the rectangular prismatic or hexagonal shaped nanocrystals are the weaker sub-chemical bonds of van der Waals type (environment controlled) which safeguards the system to retain the shape which is referred to as the MEMORY for the building up of the

nanocrystals of specific shapes. Although the nature of lattice packing is manifested at the macro domain (*cf.* Bravais-Friedel-Donnay-Harker, BFDH morphological calculations) as well, the correlation of the nature of lattice packing at the molecular level to the shapes of the resulting nanocrystals (rectangular prismatic shaped and hexagonal shaped) of a larger poly-atomic metal-ligand complex has not been reported so far. The unit cell volume (1820.55 Å<sup>3</sup>, *cf.* X-ray crystallography) of the crystal of the complex (1) obtained from EtOH with  $Z = 2$  indicates that two molecules of the complex (1) are present in an unit cell. The extrapolation suggests that a rectangular prismatic nanocrystal with dimensions of 102.3 nm, 349.8 nm, 500.5 nm and volume,  $1.79 \times 10^7$  nm<sup>3</sup> should contain  $1.96 \times 10^5$  molecules.

### Conclusions

In summary, we have obtained nanocrystals of a poly-atomic metal ligand complex (1), which shows dimorphism in two different solvents, viz., EtOH (rectangular prismatic) and MeCN-Et<sub>2</sub>O (hexagonal prism). Our results indicate that the different shapes of the nanocrystals of (1) result from the different types of infinitely arranged repeating motifs visualized in the lattice packing at the molecular level and that the rectangular prismatic and hexagonal

prismatic shapes can be retained at all the three, micro-, nano- and molecular, domains. In other words, the shapes of the nanocrystals of a polyatomic metal-ligand complex are governed by the repeating atomic arrangements visualized in the lattice packing at the molecular level which is also solvent dependent. The extension of the theorem of relationship between the repeating motifs visualized in lattice packing and the shape of the nanocrystals of further new metal-ligand complexes are in progress in our laboratory.

### Supplementary Data

The crystallographic information files (CIF) for the crystals of (**1**) obtained from EtOH (CCDC 805926) and MeCN-Et<sub>2</sub>O<sup>30</sup> have been deposited at the Cambridge crystallographic data center. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/data\_request/cif.

### Acknowledgement

AB thanks the Department of Science and Technology (DST), New Delhi, India for the award of fast track scheme for young scientists. MS and SKS thank Council of Scientific and Industrial Research (CSIR), New Delhi, India and IIT Kanpur, Kanpur, India, for doctoral, fellowships. SS thanks his mentor the Late Prof P B Sarkar, University of Calcutta, Kolkata, India in receiving the art of science that was carried by him from his mentor, Acharya P C Ray .

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