Int. J. Chem. Sci.: 11(2), 2013, 1064-1074
ISSN 0972-768X
www.sadgurupublications.com

SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND CRYSTAL STRUCTURE OF (N,N,N',N'-TETRAMETHYLETHYLENEDIAMINE) DI (P-HYDROXYBENZOATO) COPPER (II)

SANTHA LAKSHMI SUNDARAMURTHY*, S. MANORANJITHAM[a] and GEETHA KANNAPPAN[a]

D. K. M. College for Women (Autonomous), VELLORE – 632001 (T.N.) INDIA
[a]Muthurangam Govt. Arts College (Autonomous),VELLORE (T.N.) INDIA

ABSTRACT

In the present study, a monomeric copper (II) complex has been prepared and characterized by elemental analysis, molar conductance, UV-Vis., IR and ESR spectra. The paramagnetic nature of the complex was confirmed by ESR study. The structure was unambiguously confirmed by the single crystal X-ray diffraction studies. The complex crystallizes in orthorhombic system, space group with Pbca with the values a = 17.9939 (15), b = 12.9246 (11), c = 22.2342 (13) Å and $\alpha = 90.0^\circ$, $\beta = 90.0^\circ$ and $\gamma = 90.0^\circ$, V = 5170.87 Å^3, Z = 8. In the X-ray structure packing is predictably influenced by strong O (5)-H (5)… O (3) and O (6)-H (6A)…O (4) hydrogen bonds.

Key words: Copper (II) complex, Paramagnetic, Single crystal X-ray diffraction, Hydrogen bonding.

INTRODUCTION

Recently the study of coordination compounds has emerged as one of the major center of attraction for the inorganic chemist. In fact, the rapidly developing field of bioinorganic chemistry is centered on the presence of metal complexes in the biological systems. The transition metal complexes have been shown to exhibit biological and medicinal applications like radio pharmaceuticals, antibacterial, antifungal, antimalarial, anti-inflammatory, anti tuberculosis, antihelmintic and anticancer agents[1-8]. They have also been used as model systems for biological macromolecules[9].

The coordination compounds play an important role in catalysis, photography, analytical chemistry, dyes, superconductors and in metallurgy for extraction of metals[10-12].

---

*Author for correspondence; E-mail: santhalakshmi_s@yahoo.com, senthil_geetha@reddifmail.com

Among the transition metals copper has been found to be an essential trace element in living systems, which is present in the parts per million concentration range. It is a key co-factor in a diverse array of biological oxidation-reduction reactions primarily in the reduction of oxygen to water[13]. This metal is used in the electrical industry due to high conductivity and it is also used for water pipes because of its inertness. Due to the presence of unpaired electron, the copper (II) complexes exhibit paramagnetic nature.

The development of carboxylate chemistry is a central theme in transition metal chemistry, for catalysis, bioinorganic and materials chemistry. In general copper (II) carboxylates exhibit the dinuclear *paddlewheel* cage structure. Carboxylate anions are versatile ligands, because each carboxylate oxygen atom carries two lone pairs. Various coordination modes are thus possible. In most structures only one of the lone pairs of each oxygen atom is involved in coordination, like in the dinuclear paddle-wheel structure. However, if the second lone pair is donated to a metal ion of another paddlewheel unit, the stepped polymeric structure results[14].

Many binuclear Cu (II) carboxylato complexes are an attractive target of chemical research, owing to their magnetism and electrochemical behavior. The $[Cu_2(\mu\text{-}O_2CR)_4L_2]$ complexes [L= H_2O, DMF (dimethylformamide), DMSO (dimethyl sulfoxide), Py (pyridine)] are susceptible to core conversion on reaction with chelating bidentate ligands like 2,2'-bipyridine, 1,10-phenanthroline, ethylenediamine, tmen etc., and the products are often dinuclear copper (II) complexes with a reduced number of carboxylate bridging ligands[15-25]. In general, binuclear copper (II) carboxylates exhibit a paddle-wheel cage structure, but due to the various coordination modes of the carboxylato ligand, additional interesting structures have been confirmed by X-ray crystallography. N,N,N',N'-tetramethylethylenediamine (tmen) is widely employed as a chelating ligand for metal ions. It forms stable complexes with many metal halides, e.g. zinc chloride and copper (I) iodide, giving complexes that are soluble in organic solvents. In such complexes, tmen serves as a bidentate ligand. In the present work we report, $[Cu_2(\mu\text{-}O_2CC_6H_4\text{-}p\text{-}OH)_4(H_2O)_2]$ undergoes cleavage to give mononuclear copper (II) complex $[Cu(O_2CC_6H_5\text{-}p\text{-}OH)_2(tmen)]$ C_2H_5OH by the reaction with chelating diamine tmen.

EXPERIMENTAL

Materials and physical measurements

All the reagents and chemicals were procured from commercial sources and were used without purification. $CuSO_4.5H_2O$ and p-hydroxybenzoic acid were purchased from S.D. fine Chemicals, Mumbai (India) and tmen was purchased from Central Drug House (P) Ltd, Mumbai (India).

Molar conductance of the complex was measured in DMF (10^{-3} M) solution using a Guna digital conductivity meter. Infrared spectra of solid complex was recorded using KBr pellet in the region of 4000-400 cm^{-1} on Schimadzu FT-IR spectrophotometer. Electronic absorption spectra of the complex was recorded in the region 200-800 nm using a Systronics double beam UV-Vis spectrophotometer-2202 in DMF. The band EPR spectra of the complex in solid state was recorded using Bruker EMX-10/2.7 EPR spectrometer at 77 K using DPPH the g marker. The magnetic susceptibility measurement of the complex was determined using Lake Shore Cryotronics magnetometer at 300 K.

Synthesis

The precursor complex was synthesized as follows: NaOH (2 mmol) was added to 10 mL of a methanol solution containing p-hydroxybenzoic acid (2 mmol). The mixture was stirred for 30 min at room temperature. Then, 5 mL of an aqueous solution containing $CuSO_4 \cdot 5H_2O$ (1 mmol) was added to the mixture, and stirred for another 30 min at room temperature. The product was filtered and dried. A suspension of the precursor complex (1 mmol) in ethanol (25 mL) was treated with tmen (2 mmol) under stirring for 30 min at room temperature. The resulting solution was filtered and kept in a refrigerator. On slow evaporation blue coloured crystals were obtained which was collected and dried. Yield: 79%. M.P.:170° C. Anal. Calc. for $C_{20}H_{26}CuN_2O_6.0.5C_2H_5OH$ (F.wt.457.30) : C 52.93, H 6.03, N 5.88, Found: C 53.01, H 6.11, N 5.91. μ_{eff} = 1.95 BM.

RESULTS AND DISCUSSION

The copper (II) complex was found to be stable at room temperature and soluble in DMF and DMSO. The molar conductivity measurement of the complex showed a lower molar conductivity value of 18 $\Omega^{-1}cm^2mol^{-1}$ in DMF, indicated a non-electrolytic nature of the complex[26-27].

The band appeared in UV-Vis spectra of the copper(II) complex (Fig. 1) at 235 nm is associated with $\pi \rightarrow \pi^*$ transition of benzene ring and a broad peak appeared at 680 nm corresponds to d-d transition of Cu (II) ion.

The IR spectra of the copper (II) complex (Fig. 2) showed a band at 3425 cm^{-1}, which may be due to hydrogen bonded OH group present in p-hydroxybenzoic acid. The bands appeared in the region of 511 and 462 cm^{-1} corresponds to Cu-N and Cu-O linkages. The group of bands appeared at 2980 cm^{-1} are due to the υ_s vibration of methyl groups present on nitrogen atoms of tmen[28]. The peaks observed at 1602 cm^{-1} and 1388 cm^{-1}, corresponds to $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$, respectively. The large difference of $\Delta\upsilon$ ($\Delta\upsilon = \Delta\upsilon_{as}-\Delta\upsilon_s$) confirmed a monodentate coordination nature of the carboxylate group present in the complex[29].

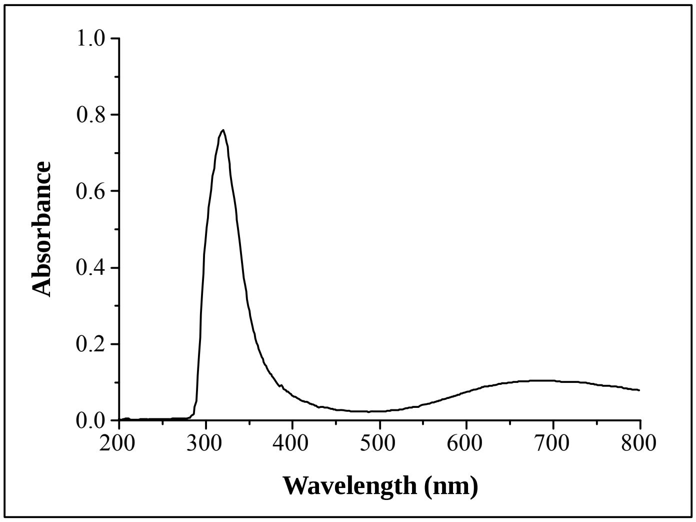

Fig. 1: UV-Vis spectra of copper (II) complex

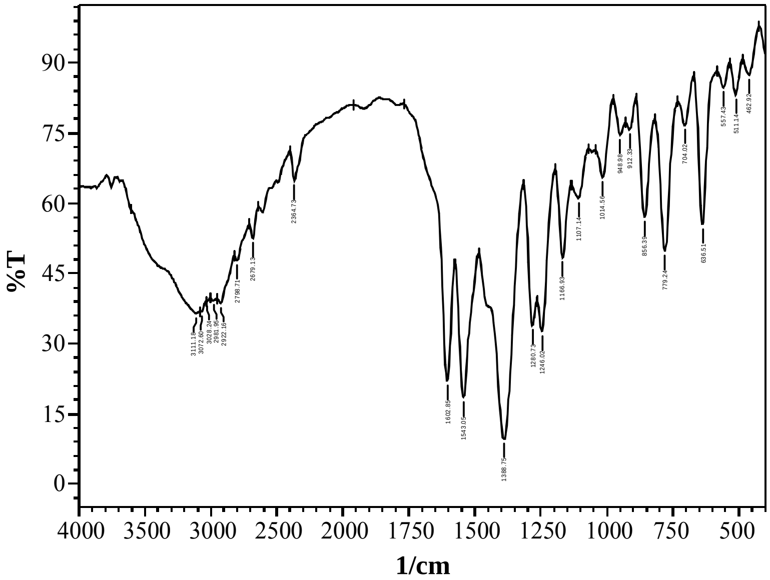

Fig. 2: FTIR spectra of copper (II) complex

The solid state X-band EPR spectra (Fig. 3) of polycrystalline copper (II) complex was recorded at 77 K in LNT. The EPR spectra show an isotropic spectrum with a broad signal indicating that the copper ion displayed a distorted square planar geometry[30] with g_{iso} value of 1.9905.

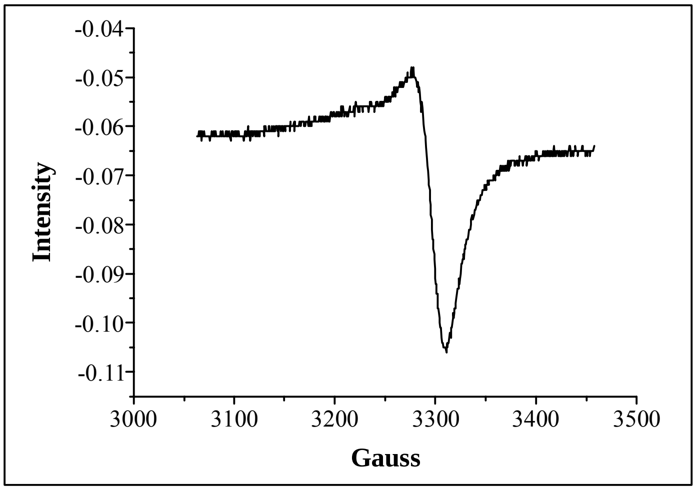

Fig. 3: ESR spectra of copper (II) complex

X-ray crystallography

Single crystals suitable for X-ray diffraction study for the complex were grown from slow evaporation of the mother liquor at low temperature. A blue coloured crystal of the copper (II) complex having the size 0.45 x 0.38 x 0.25 mm was mounted on a glass fiber and used for data collection. Crystal data were collected using graphite monochromatised Mo-Kα radiation (λ = 0.71073 Å) at 298(2) K.

The structure was solved with SHELXS-97[31] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97[32]. The perspective views of the complexes were obtained using ORTEP[33]. All e non-hydrogen atoms were refined anisotropically. A summary of pertinent crystal data along with further details of structure determination and refinement are given in Table 1. Selected bond lengths and bond angles are given in Table 2.

Table 1: Crystal data and structure refinement for the complex

Empirical formula	$C_{20}H_{26}CuN_2O_6$, 0.5 (C_2H_5O)
Formula weight	457.30
Temperature (K)	298 (2) K
Wavelength (A)	0.71073
Crystal system, space group	Orthorhombic, Pbca

Cont…

Unit cell dimensions	
a (Å)	17.9939 (15)
b (Å)	12.9246 (11)
c (Å)	22.2342 (13)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	5170.9 (7)
Z, Calculated density (mg/m^3)	8, 1.154
Absorption coefficient (mm^{-1})	0.695
F (000)	1880
Crystal size (mm)	0.45 x 0.38 x 0.25
θ range for data collection (°)	1.83 – 28.31
Limiting indices	-23 < = h < = 18, -17 < = k < = 15, -23 < = l < = 26
Reflections collected / unique	22318 / 5943
R (int)	0.0460
Completeness to theta = 25.00 (%)	96.2
Absorption correction None < 41	Multi-scan
Max. and min. transmission	0.8455 and 0.7451
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5943 / 2 / 274
Goodness-of-fit on F^2	1.102
Final R indices [I > 2 sigma (I)]	R1 = 0.0847, wR2 = 0.2648
R indices (all data)	R1 = 0.1417, wR2 = 0.3214
Largest diff. peak and hole (e.Å^{-3})	1.809 and -0.440

Table 2: Bond lengths [Å] and angles [deg] for the complex

Cu (1)-O (1)	1.948 (3)
Cu (1)-O (2)	1.948 (3)
Cu (1)-N (2)	2.028 (5)
Cu (1)-N (1)	2.005 (6)
O (1)-Cu (1)-O (2)	94.6 (1)
O (1)-Cu (1)-N (2)	160.6 (2)
N (2)-Cu (1)-O (2)	93.3 (2)
N (1)-Cu (1)-N (2)	86.3 (2)

Crystal structure

The copper (II) complex crystallizes with the solvent ethanol in the orthorhombic system, space group Pbca with the values a = 10.7016 (2), b = 13.2710 (3), c = 15.1759 (3) Å and α = 90.0º, β = 90.0º and γ = 90.0º, V = 2155.30 (8) Å^3, Z = 4. An ORTEP view of complex along with the atom numbering scheme is shown in Fig. 4.

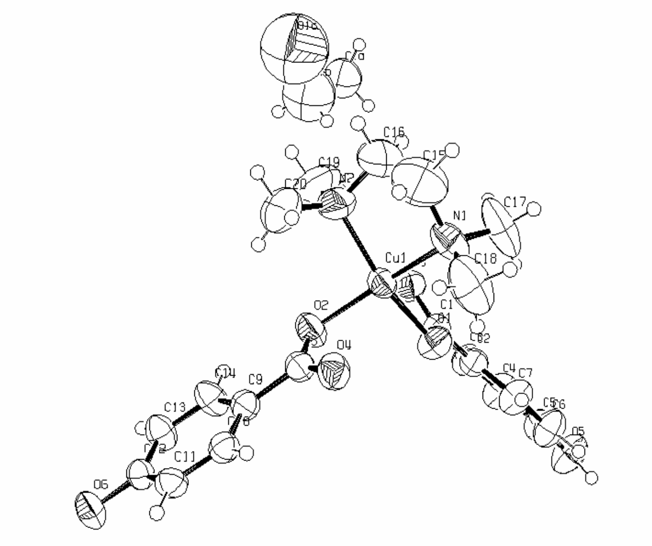

Fig. 4: ORTEP view of the copper (II) complex

The synthesized complex is mononuclear and the copper atom is linked symmetrically by nitrogen atoms of tmen and by oxygen atoms [O(2) and O(1)] of carboxylate present in the p-hydroxybenzoate. The other oxygen atoms [O(3) and (O4)] of the carboxylate group remains uncoordinated. The copper (II) ion is coordinated to two nitrogen atoms of tmen and two oxygen atoms of different carboxylates forming square planar with N_2O_2 geometry. Here p-hydrobenzoate acts as a monodentate ligand.

The copper ion is coordinated by two N atoms of tmen and two oxygen [O(1), O(2)] atoms from the carboxylate ions with slightly distorted square-planar coordination geometry. The Cu(1)-O(2), Cu(1)-O(1), Cu(1)-N(1) and Cu(1)-N(2) distances are 1.947(3) Å, 1.948(3) Å, 2.005(5) Å and 2.028(6) Å, respectively. The N(1)-Cu(1)-N(2), N(2)-Cu(1)-O(2), O(2)-Cu(1)-O(1) and N(1)-Cu(1)-O(1) angles are 86.4(2)°, 93.3(2)°, 94.7(1)° and 160.6(2)°, respectively. The sum of the bond angles around Cu (I) is 366.6° which confirms the deviation of copper (II) ion from the basal plane.

Crystal packing

It is well know that the stabilization energy of a hydrogen bond is much greater than that of typical van der Walls interactions[34]. Hence, intermolecular hydrogen bonds are favoured during the process of crystallization. In the crystal structure, packing is predictably influenced by strong intermolecular hydrogen bonds (Table 3), O(5)-H(5)…O(3), which combine with O(6)-H(6A)…O(4) contacts. These O-H…O type intermolecular interactions stabilise the molecules in the crystal (Fig. 5).

Table 3: Hydrogen bond lengths (Å) and bond angles (°)

D–H···A	d (D–H)	d (H···A)	d (D···A)	∠DHA
O(5)–H(5)···O(3)[a]	0.95	1.753	2.686	165.15
O(6)– H(6A)···O(4)[b]	0.94	1.799	2.685	156.37

Symmetry codes: (a) x,y,z (b) 1.5x,1-y,-1/2+z D→ Donor A→Acceptor

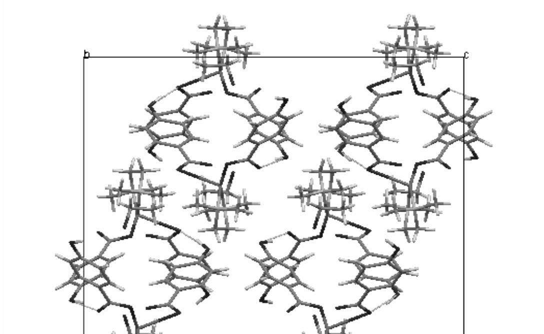

Fig. 5: Packing diagram of the copper (II) complex viewed along the b axis. Hydrogen bond are shown in dotted lines

In conclusion, the synthesis and crystal structure of the copper (II) complex have been reported herein. In the crystal structure, the copper (II) ion is four coordinated with two nitrogen atoms of tmen and the remaining coordination takes place through two oxygen atom of carboxylate group of p-hydroxy benzoic acid groups. The crystal packing involves some intermolecular hydrogen bonding.

ACKNOWLEDGEMENT

Authors thank Department of Chemistry, IITM, Chennai for single crystal XRD data collection and structure refinement.

REFERENCES

1. O. H. S. Al-Obaidi, Int. J. Chem. Res., **3(2)**, 1-5 (2012).
2. S. Santha Lakshmi, S. Syed Tajudeen and Kannappan Geetha, J. Pharm. Res., **4(5)**, 1531-1532 (2011).
3. R. Suganthi, S. S. Lakshmi, K. Geetha and A. A. Rahuman, J. Pharm. Res., **4(12)**, 4574-4576 (2011).
4. B. Rizwana and S. S. Lakshmi, Int. J. Chem. Tech. Res., **4(1)**, 464-473 (2012).
5. R. Prabu, A. Vijayaraj, R. Suresh, L. Jagadish, V. Kaviyarasan and V. Narayanan Bull. Korean Chem. Soc., **32(5)**, 1669-1678 (2011).
6. S. Zhang, Y. Zhu, C. Tu, H. Wei, Z. Yang, L. Lin, J. Ding, J. Zhang and Z. Guo, J. Inorg. Biochem., **98**, 2099-2106 (2004).
7. B. Jing, L. Li, J. Dong, Ji. Li and T. Xu, Transition Met Chem., **36**, 565-571(2011).
8. J. Ziegler, T. Schuerle, L. Pasierb, C. Kelly, A. Elamin, K. A. Cole and D. W. Wright, Inorg. Chem., 7, **39(16)**, 3731-3733 (2000).
9. O. P. Anderson, A. L. Cour, M. Findeisen, L. Hennig, O. Simonsen, L. Taylor and H. Toftlund, J. Chem. Soc., Dalton Trans., **1**, 111-120 (1997).
10. J.-S. Bae and H. S. Freeman, Dyes and Pigments, **73**, 126-132 (2007).
11. J. García-Álvarez, J. Díez and J. Gimeno, Green Chem., **12**, 2127-2130 (2010).
12. J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura and S. Uchida, Nature, **375**, 561-563 (1995).

13. E. I. Solomon, U. M. Sundaram and T. E. Machonkin Chem. Rev., **96**, 2563-2605 (1996).

14. F. P. W. Agterberg, H. A. J. Provo´ Kluit, W. L. Driessen, H. Oevering, W. Buijs, M. T. Lakin, A. L. Spek and J. Reedijk, Inorg. Chem., **36**, 4321-4328 (1997).

15. A. Zeloxka and M. C. Baird, Inorg Chem., **11(1)**, 134-137 (1972).

16. S. P. Perlepes, J. C. Huffman and G. Christou, Polyhedron, **14(8)**, 1073-1081 (1995).

17. K. S. Burger, P. Chaudhur and K. Wieghardt, J. Chem. Soc., Dalton Trans., **2**, 247-248 (1996).

18. G. Christou, S. P. Perlepes, E. Libby, K. Folting, J. C. Huffman, R. J. Webb and D. N. Hendrickson, Inorg. Chem., **29**, 3657-3666 (1990).

19. D. Gatteschi and C. Mealli, Cryst. Struct. Comm., **8**, 305 (1979).

20. K. Geetha, M. Nethaji, A. R. Chakravarty and N. Y. Vasanthacharya, Inorg. Chem., **35**, 7666-7670 (1996).

21. K. Geetha, M. Nethaji, Y. Vasanthacharya and A. R. Chakravarty, J. Coord. Chem., **47**, 77-89 (1999).

22. S. Meenakumari and A. R. Chakravarty, Polyhedron, **12**, 347-349 (1993).

23. P. de Meester, S. R. Fletcher and A. C. Skapski, J. Chem. Soc., Dalton Trans., 2575-2578 (1973).

24. S. P. Perlepes, J. C. Huffman, K. H. Scheller and P. Baltzer, Polyhedron, **11**, 1471-1479 (1992).

25. E. Tokii, E. N. Watanabe, M. Nakashima, Y. Muto, M. Morooka, S. Ohba, S. and Y. Saito, Bull. Chem. Soc. Jpn, **63**, 364-369 (1990).

26. W. J. Geary, Coord. Chem. Rev., **7**, 81-122 (1971).

27. K. Robert, David Boggess and A. Zatko, J. Chem. Edn., **52(10)**, 649-651 (1975).

28. J. Costa Pessoa, I. Cavaco, I. Correia, M. T. Duarte, R. D. Gillard, R. T. Henriques, F. J. Higes, C. Madeira and I. Tomaz, Inorganica Chimica Acta, **293**, 1-11 (1999).

29. M. X. Li, M. Shao, H. Dai, B. L. An, W. C. Lu, Y. Zhu and C. X. Du, Chinese Chemical Letters, **16(10)**, 1405-1408 (2005).

30. C. L. Leese and H. N. Rydon, J. Chem. Soc., 303-309 (1955)

31. G. M. Sheldrick, SHELXS-97 Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany (1997).

32. G. M. Sheldrick, SHELXL-97, Program for the Crystal Structure Refinement; University of Göttingen, Göttingen, Germany (1997).

33. C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN (1976).

34. C. P. Brock and J. D. Dunitz, Chem. Mater. **6,** 1118-1127 (1994).

Revised : 22.04.2013 *Accepted : 25.04.2013*