ELSEVIER

Thermochimica Acta 390 (2002) 187–193

thermochimica
acta

www.elsevier.com/locate/tca

Tetra chlorocopper(II) chemistry: delineation of optical, thermal properties

Arup Purkayashtha, Jubaraj B. Baruah*

Department of Chemistry, Indian Institute of Technology, Guwahati 781 039, India

Received 27 February 2002; accepted 28 February 2002

Abstract

The thermal decomposition paths of pyridinium tetra chlorocopper(II) (**A**) differs from the anilinium tetra chlorocopper(II) (**B**). In the case of pyridinium tetra chlorocopper(II) it loses two molecules of pyridinium hydrochloride and $CuCl_2$ is formed in the temperature range of 140–350 °C. Whereas the anilinium tetra chlorocopper(II) (**B**) loses one mole of anilinum hydrochoride along with one molecule of aniline. The compound **B** has a well define structural change taking place in the region of 70–110 °C which is reflected in DSC as well as resistance measurements. The *p*-methoxy anilinium tetra chlorocopper(II) monohydrate (**C**) shows solvatochromicity. The absorption maximum of *p*-methoxy anilinium tetra chlorocopper(II)monohydrate in acetonitrile (460 nm) changes to 570 nm on addition of methanol. The absorption at 570 nm can be switched back to 460 nm by suppression of ligand exchange with addition of hydrochloric acid. Thus, chemically driven optical switching properties can be observed.

Keywords: Tetra chlorocopper(II) complexes; Thermoelectric switching; Chemically driven optical switch

1. Introduction

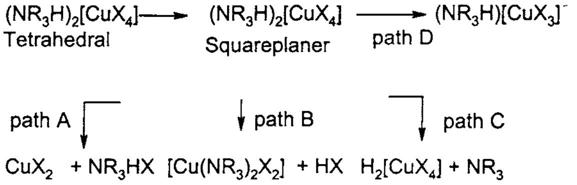
The geometrical changes taking place around a transition metal centers have been of interest to understand electronic properties and also to make new devices [1–4]. The dynamic properties of the co-ordination changes are used in design of molecular motors [5,6], chemical sensor [7,8] etc. One of the basic conditions for such design is the presence of a reversible interaction between two substrates that accompanies some physical changes. Such process can occur in systems having ability to change co-ordination geometry around a metal center through recognition of a guest or binding to a ligand [9–15]. There are numerous examples in which the co-ordination causes change in colour [16,17]. Among these the tetra halocobalt(II) is a commonly referred example [18,19]. The tetra cholorocopper(II) complexes having bipyridinium cations with different metal ions show varieties of geometry around the central atom and are influenced by supramolecular interactions [20]. The fluorescence property on co-ordination change in square planar nickel complexes are used for temperature sensor [21]. The tetra halocopper(II) complexes are found to be thermo chromic and shows different colors due to interconversion between different structures [17,22,23] The counter ions derived from ammonia derivatives are usually studied for this purpose. However, due to the polymerising and oxidising properties of anilinic compounds, the

---

* Corresponding author. Fax.: +91-361-690762.
E-mail address: juba@iitg.ernet.in (J.B. Baruah).

0040-6031/02/$ – see front matter
PII: S0040-6031(02)00129-6

use of anilinium cations for such studies have attracted less attention [24]. There is another aspect that needs clear attention, is the ability of these complexes to release acid and exchange the co-ordination position of the halogens. Some of the possibilities are as follows:



Scheme 1.

This article describes how the different equilibriums shown in Scheme 1 can be utilized for obtaining thermoelectric switching and for obtaining chemically driven optical switching properties.

2. Experimental

The thermogravimetry were carried out by a Metler Toledo TGA/STDA 821^e under nitrogen atmosphere, while the DSC were carried out by Metler Toledo DSC 821^e instrument under nitrogen. The UV–Visible spectra were recorded on a Hitachi UV–Visible spectrometer model U2001. The resistance of film of the compounds was measured with a two probe method as reported earlier [11–14] The tetra cholorocopper(II) complexes investigated in this study were prepared by the reaction as shown in Eq. (1).

$$p\text{-OMeC}_6\text{H}_4\text{NH}_2 + \text{CuCl}_2 + \text{HCl} \xrightarrow{\text{MeOH}} \underset{\textbf{C}}{[p\text{-OMeC}_6\text{H}_4\text{NH}_3]_2[\text{CuCl}_4](\text{H}_2\text{O})} \qquad (1)$$

2.1. Typical procedure for synthesis of quaternary ammonium salt of tetra chlorocopper(II)

To a solution of copper(II) chloride dihydrate (600 mg, 3.5 mmol in 5 ml methanol) hydrochloric acid (11.6 N, 0.3 ml) was added. A dark brown colored solution was obtained. To this solution the amine (10 mmol) was added drop wise. The reaction mixture was stirred at room temperature for hours. Addition of diethyl ether (40 ml) to the resultant reaction mixture led to precipitation of the desired complex.

2.1.1. The analytical data for the complexes

*2.1.1.1. Pyridinium tetra chlorocopper(II) (**A**).* Isolated yield: 32%; IR (KBr) 3071 (bs), 1599 (s), 1524 (s), 1482 (s), 1444 (s), 1327 (s), 1183 (m), 1044 (m), 905 (w), 745 (s), 676 (s) cm^{-1}. Elemental analysis calculated for $C_{10}H_{12}N_2CuCl_4$: C, 32.83, H, 3.28, N, 7.66; found C, 32.86, H, 3.26, N, 7.58, magnetic moment 1.78 BM.

*2.1.1.2. Anilinium tetra chlorocopper(II) (**B**).* Isolated yield: 40%; IR (KBr) 3012 (bs), 1553 (s), 1493 (s), 1306 (w), 1095 (m), 744 (s), 684 (s), 472 (s) cm^{-1}. Elemental analysis calculated for $C_{12}H_{16}N_2CuCl_4$: C, 36.78, H, 4.06, N, 7.15; found C, 36.59, H, 4.09, N, 7.07; magnetic moment: 1.78 BM.

*2.1.1.3. p-Methoxy anilinium tetra chlorocopper (II) monohydrate(**C**).* Isolated yield: 23%; IR (KBr) 3456 (bm), 3054 (bm), 1619 (m), 1519 (s), 1493 (s), 1307 (w), 1267 (s), 1220 (m), 1122 (w), 823 (s), 511 (s) cm^{-1}. Elemental analysis calculated for $C_{14}H_{22}N_2O_3CuCl_4$: C, 35.63, H, 4.35, N, 5.93; found C, 35.81, H, 4.66, N, 5.96; magnetic moment: 1.79 BM.

*2.1.1.4. p-Methyl anilinium tetra chlorocopper(II) trihydrate (**D**).* Isolated yield: 12%; IR (KBr) 3087 (s), 2574 (s), 1599 (s), 1506 (s), 1201 (s), 1102 (s), 823 (s), 578 (w), 489 (w) cm^{-1}. Elemental analysis calculated for $C_{14}H_{26}N_2O_3CuC_{14}$: C, 35.33, H, 5.04, N, 5.88; found C, 35.48, H, 5.49, N, 5.91; magnetic moment: 2.08 BM.

3. Results and discussions

3.1. Thermo chemical study

The thermogram of pyridinium tetra chlorocopper(II) and anilinium tetra chloro copper(II) has distinct difference that not only occur from the obvious molecular weight difference but from the thermal reactivity point of view (Figs. 1 and 2). The thermal analysis ensures the differences between the thermo chemical reactions leading to cleavage of bond or

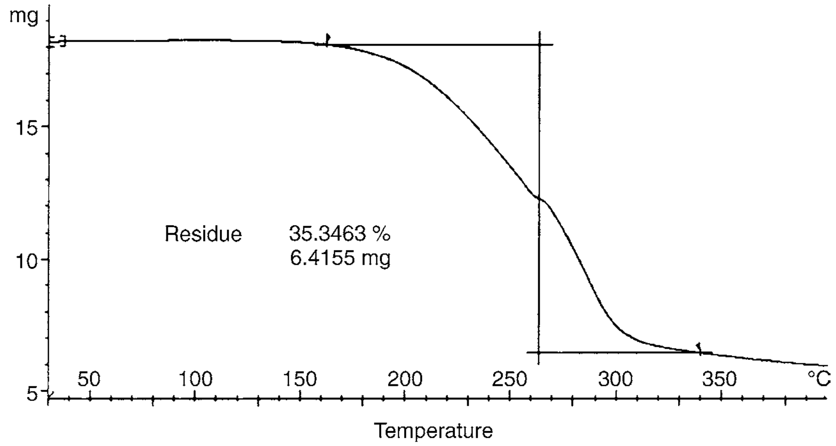


Fig. 1. The thermogram of pyridinium tetra chlorocopper(II).

rearrangement of the ligand. Based on the percentage of the weight loss the following equations explains the weight loss:

$(PyH)_2[CuCl_4]$	$(AnH)_2[CuCl_4]$
↓2 PyHCl	↓An + AnHCl
↓loss = 63.00% (theory)	↓loss = 56.83% (theory)
↓loss = 64.65% (found)	↓loss = 55.24% (found)
$CuCl_2$	$H[CuCl_3]$ or 0.5 $H_2[Cu_2Cl_6]$

Py: pyridine; An: aniline.

In the case of the aniline one may argue that the aniline being a reducing agent a part of $CuCl_2$ is converted to CuCl on heating but this indeed is not the case as the product of thermal reaction did not show any significant amount of dimeric or oligomeric aniline in absence of oxygen. Furthermore, there are well known $[CuCl_3]^-$ species and these types of species prefer to remain in dimeric form if the cation are small [25]. The above results are indicative of the fact that the pyridinium system behaves in different manner on thermal decomposition than the corresponding anilinium analogue. The compound **C** and **D** has a loss of weight in the region of 63.73% (64.00%), 65.64 (theory 64.30%) that corresponds to loss of one neutral molecule of parent aniline and the parent anilinium hydrochloride and the water of crystallization. The thermal properties of **A** described in the literature [26] suggests loss of HCl molecules at 90 °C but we did not observe any loss of weight in this region in thermogravimetry

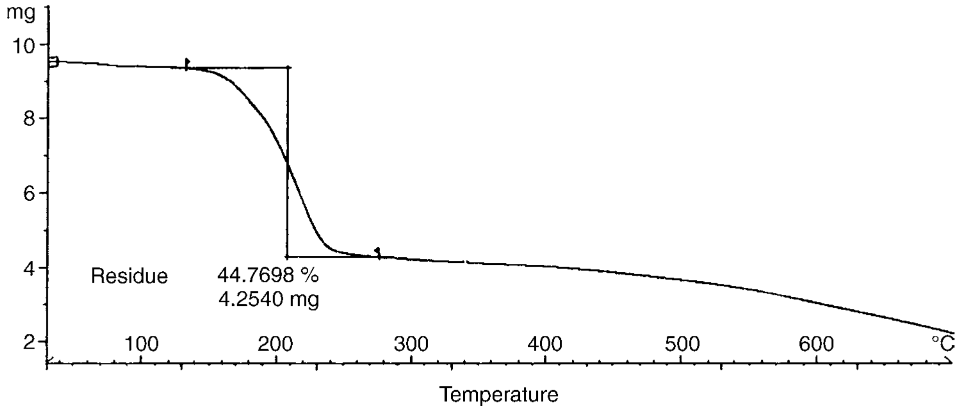


Fig. 2. The thermogram of anilinium tetra chlorocopper(II).

but we have observed an endothermic process in DSC.

The compound **A** shows endothermic process at 87 °C as and 104 °C in the differential scanning calorimetry. There are two endothermic process for **A** and no weight loss in TGA was observed. These two transitions are referred to structural changes namely, at 87 °C **A** changes its structure from tetrahedral to square planar and at 104 °C it exchanges halide ligands making the *N*, *N* co-ordination [17]. The compound **B** shows an endothermic process at 102 °C (Fig. 3) due to change in the tetrahedral structure to square planar.

The electrical properties of the copper(II) complexes also has reflection of this endothermic process. The plot of normalized resistance versus temperature in the region of 40–140 °C shows a sudden decrease in resistance in the region where the endothermic process takes place (Fig. 4). Based on the crystallographic evidences presented on the structural changes of related compounds from tetrahedral to square planar geometry, the decrease in resistance is attributed to the parallel stacking of the copper centers on transforming from tetrahedral to square planar geometry. In a square planar geometry the interaction between the d_z^2 orbital gets maximized and thereby causes enhancement of electron flow in one direction.

The tetra chlorocopper (II) complex **C** has a molecule of water of crystallization in the interstices of the crystals. It has a structural change at 70–108 °C (from DSC). The complex **C** has also a labile water molecule/s present in the system which is lost at around 120–140 °C. The compound has a resistance versus temperature profile having an exponential shape in the region 80–104 °C (Fig. 5). The fitting of the plot to a simulated exponential plot is shown by dotted line in the Fig. 5. This observation is important in biological systems such as DNA nano-particles it is observed that the resistance versus temperature profile are greatly influenced by presence of water molecules [27,28]. The low temperature resistance data on such system has a transition near the freezing point of water [28]. The change in structure at this region causes lowering of the resistance in the temperature range of 80–104 °C. It is already mentioned that the tetra halocopper(II) complexes are thermochromic and their thermochromicity is generally associated with a structural change around the copper(II) centers [22,23]. We had also shown that the structural changes around copper(II) can affect the resistance profile of a system and we have demonstrated the thermoelectric switching property from such possibilities [11–14] also.

The *p*-methoxyanilinium tetra chlorocopper(II) monohydrate has two IR absorptions at 3456 and 3045 cm^{-1} due to the O–H and N–H frequency, respectively (Fig. 6a). The sample on heating to 100 °C results in considerable loss of absorption at 3456 cm^{-1}. This

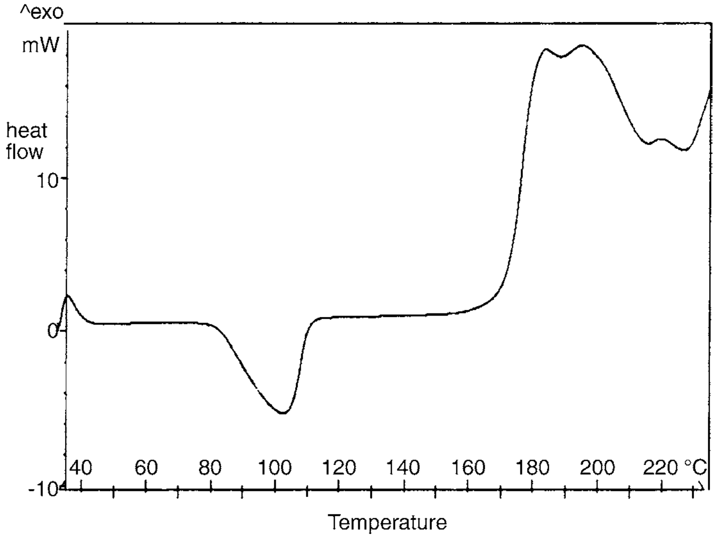


Fig. 3. The DSC of anilinium tetra cholorocopper(II).

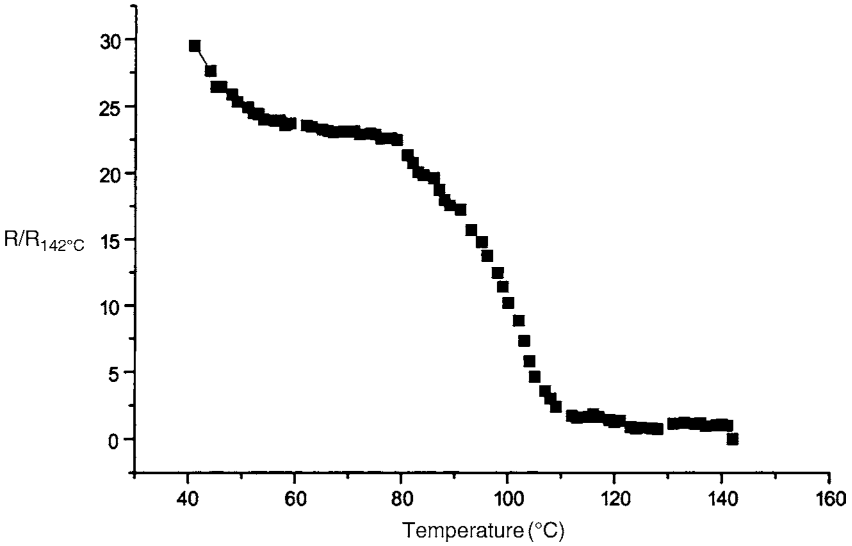


Fig. 4. The plot of resistance normalized to resistance at 142 °C vs temperature of a thin film of **B**.

shows that the loss of weakly bound water molecule as well as the change in the co-ordination geometry around the copper(II) center effects the resistance. Further proof to this result is observed from the thermal study. The DSC of the sample has an endothermic process at 60–104 °C without loss of weight followed by another endothermic process at 115–140 °C for loss of the water molecule.

3.2. Solvatochromicity and design of chemically driven optical switch

The *p*-methoxyanilinium tetra chlorocopper(II) monohydrate has an absorption maximum at 460 nm ($\varepsilon = 1726\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) in acetonitrile whereas in methanol it has an absorption at 570 nm. The change in the visible spectrum of a solution in acetonitrile

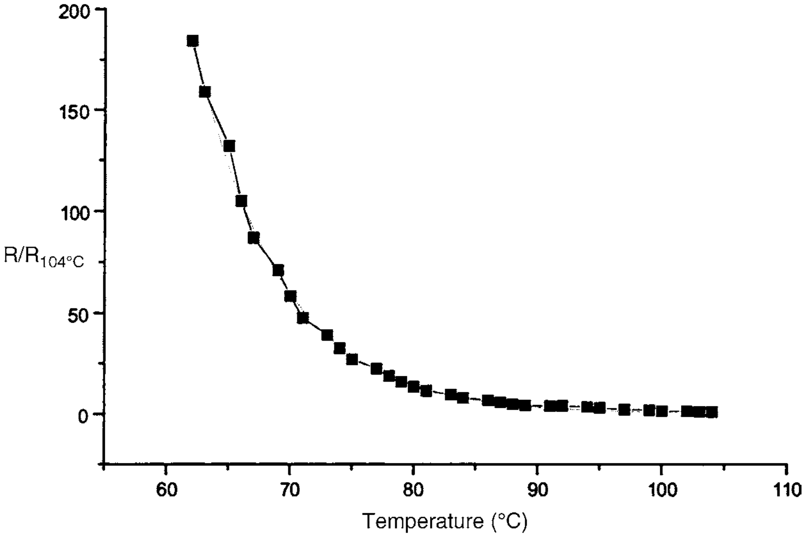


Fig. 5. The plot of resistance normalized to resistance at 104 °C vs temperature of pallet of **C**.

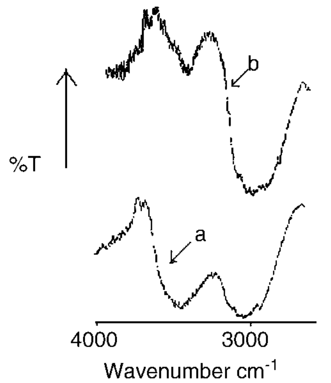


Fig. 6. IR (KBr) of **C** (a) without heating (b) heated to 100 °C in the region 3000–4000 cm^{-1}.

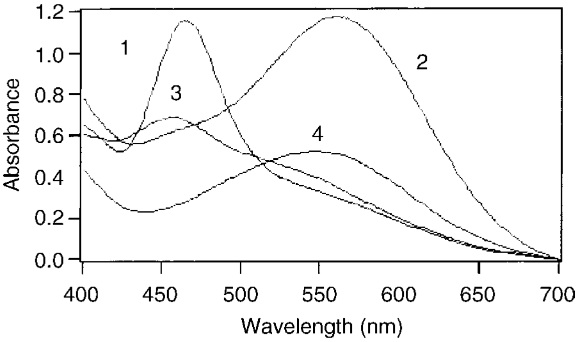


Fig. 8. The visible spectrum of: (1) **C** (0.25 mmol) in acetonitrile (2 ml); (2) on addition of methanol (0.2 ml, 5.3 mmol); (3) on addition of HCl (0.32 mmol); (4) on addition of methanol (0.8 ml, 21.2 mmol).

on addition of methanol in the region of 400–700 nm is shown in Fig. 7. This observation depicts the conversion of one species namely a distorted tetrahedral species to a tri co-ordinated species as depicted in Scheme 1. The IR spectra of the sample before dissolving in methanol and after dissolving in methanol are different. In the case of the freshly prepared sample has strong broad IR absorption at 3045 and at 3456 cm^{-1} whereas the sample on dissolving in methanol the absorption peak of the sample appears as single absorptions at 2900 cm^{-1}. In addition to this there is a clear difference in the absorption at 823 cm^{-1}, this absorption gives rise to two absorptions at 810 and 830 cm^{-1} after treatment with methanol. The clear change in color and its interconversion to another species makes it a potential candidate for recognizing alcoholic solutions. Various alcohols such as methanol, ethanol and isopropanol can be recognized by the system. However, the relative rate of interconversion varies with the alcohols and are in the sequence methanol > ethanol > isopropanol. Bulky hydroxy compounds such as calix arenes are not recognised by the system due to the steric reasons.

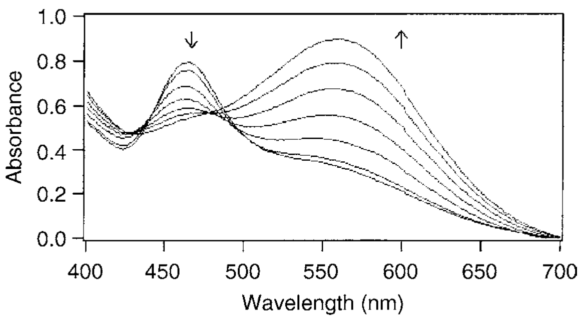


Fig. 7. The change in the visible spectra of **C** (0.2 mmol) in acetonitrile (2 ml) on addition of aliquots of methanol (25 μl, 0.64 mmol).

In order to correlate such phenomenon to optical switch the color changes should be reversible. However, once the optical absorption of the compound changes from 460 to 570 nm on addition of methanol to acetonitrile solution of *p*-methoxyanilinum tetra chlorocopper(II), it could not be brought back to the original state by adding methanol. But it could be possible to bring back to the original state (having absorption at 460 nm) by adding dilute hydrochloric acid. However, due to dilution effect the intensity of absorption goes down (Fig. 8 cycle 3). This solution on addition of methanol once again makes the solution to regain the absorption maximum at 570 nm (Fig. 8 cycle 4). Thus, the solvatochromic shift can be understood with the Scheme 1 (Path D) in which a dissociative equilibrium that can be pushed back and forth by adding appropriate reagent.

In conclusion this study demonstrates the scope for obtaining thermoelectric switching properties as well as designing of chemically driven optical switch from tetra chlorocopper(II) complexes.

Acknowledgements

The authors are thankful to Department of Science and Technology, New Delhi, for financial assistance.

One of the author (AP) is thankful to Council of Scientific and Industrial Research, New Delhi for a senior research fellowship.

References

[1] R. Hoss, F. Vogtle, Angew Chemie. Int. Ed. Engl. 33 (1994) 375.

[2] M.V. Alfimov, Yu.V. Fedoroy, O.A. Gromov, R.E. Hester, I.K. Lednev, J.N. Moore, V.P. Oleshko, A.I. Vedernikov, J. Chem. Soc., Perkin Trans. 2 (1996) 1441.

[3] J.M. Rowland, M.L. Thornton, M.M. Olmstead, P.K. Mascharak, Inorg. Chem. 40 (2001) 1069.

[4] Q. Li, H. Ma, Z. Wang, M. Su, H. Xiao, S. Liang, Chem. Lett. (2001) 100.

[5] V. Mendola, L. Fabbrizzi, C. Mangano, P. Pullavicini, Acc. Chem. Res. 34 (2001) 488.

[6] J.-P. Collin, C. Dietrich-Buchecker, P. Gavina, M.C. Jimenezu Molero, J-P. Sauvage, Acc. Chem. Res. 34 (2001) 477.

[7] D.T. McQuade, A.E. Pullen, T.M. Swager, Chem. Rev. 100 (2000) 2537.

[8] H. Morrison (Ed.), Biological Application of Photochemical Switches, Wiley, New York, 1993.

[9] J.C. Lockhart, in: G.W. Gokel (Ed.), Comprehensive Supramolecular Chemistry, Vol. 1, Pergamon Press, Oxford, 1996, pp. 605–634.

[10] H.-J. Schneider, A. Yatismirsky, Principles and Methods in Supramolecular Chemistry, Wiley, Chichester, 2000.

[11] A. Purkayshtha, J.B. Baruah, New J. Chem. 23 (1999) 1141.

[12] A. Puzari, A. Srinivasan, J.B. Baruah, React. Funct. Polym. 44 (2000) 201.

[13] A. Puzari, J.B. Baruah, J. Org. Chem. 65 (2000) 2344.

[14] J.G. Handique, J.B. Baruah, J. Mol. Catal. 166 (2001) 225.

[15] A.G. Kaifer, S. Medoza, in: G.W. Gokel (Ed.), Comprehensive Supramolecular Chemistry, Vol. 1, Pergamon Press, Oxford, 1996, pp. 701–732.

[16] R.B. King (Ed.), Encyclopedia in Inorganic Chemistry, Vol. 2, Wiley, Chichester, 1994, pp. 833–835.

[17] R.L. Harlow, W.J. Wells, G.W. Watt, S.H. Simonsen, Inorg. Chem. 13 (1974) 2106.

[18] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 3rd Edition, Wiley Eastern, New Delhi, 1988.

[19] T.J. Swift, Inorg. Chem. 3 (1964) 526.

[20] B. Dolling, A.L. Gillon, A.G. Orpen, J. Starback, X-M Wang, J. Chem. Soc. Chem. Commun. (2001) 567.

[21] M. Ciampolini, L. Fabbrizzi, M. Licchelli, F. Pezzini, A. Poggi, Inorg. Chem. 25 (1986) 4131.

[22] R.D. Willett, O.L. Lilles Jr., C. Michelson, Inorg. Chem. 6 (1967) 1885.

[23] W.E. Hatfield, T.J. Piper, Inorg. Chem. 3 (1964) 841.

[24] S.-B. Kim, K. Harada, T. Yamamoto, Macromolecules 31 (1998) 988.

[25] M. Textor, E. Dubler, H.R. Oswald, Inorg. Chem. 13 (1974) 1361.

[26] L. Wolf, H. Hennig, Anorg. Allgem. Chem. 329 (1964) 301.

[27] C.A. Mirkin, T.A. Taton, Nature 405 (2000) 626.

[28] S.-J. Park, A.A. Lazardes, C.A. Mirkin, P.W. Brazis, C.R. Kannewurf, R.L. Letsinger, Angew Chemie. Int. Ed. Engl. 39 (2000) 3845.