Available online at www.sciencedirect.com

ScienceDirect

Spectrochimica Acta Part A 69 (2008) 1077–1081

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Synthesis of new oxamide-based ligand and its coordination behavior towards copper(II) ion: Spectral and electrochemical studies

K.R. Krishnapriya, D. Saravanakumar, P. Arunkumar, M. Kandaswamy *

Department of Inorganic Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus, Chennai 600025, India

Received 2 February 2007; accepted 2 June 2007

Abstract

A new ligand *N*,*N*′-bis{3-(2-formyl-4-methyl-phenol)-6-iminopropyl}oxamide (**L**) and its mono- and binuclear copper(II) complexes have been synthesized and characterized. The ligand shows absorption maxima at 249 and 360 with a weak transition at 455 nm. The ligand was found to be fluorescent and shows an emission maximum at 516 nm on excitation at 360 nm. The electronic spectra of the mono- and binuclear Cu(II) complexes exhibited a d–d transition in the region 520–560 nm characteristic of square planar geometry around Cu(II) ion. The ESR spectrum of the mononuclear complex showed four lines with nuclear hyperfine splitting. The binuclear complex showed a broad ESR spectrum with $g = 2.10$ due to antiferromagnetic interaction between the two Cu(II) ions. The room-temperature magnetic moment values (μ_{eff}) for the mono- and binuclear Cu(II) complexes are found to be $1.70\mu_{\mathrm{B}}$ and $1.45\mu_{\mathrm{B}}$, respectively. The electrochemical studies of the mononuclear Cu(II) complex showed a single irreversible one-electron wave at -0.70 V (E_{pc}) and the binuclear Cu(II) complex showed two irreversible one-electron reduction waves at -0.75 V (E^1_{pc}) and -1.27 V (E^2_{pc}) in the cathodic region.

Keywords: Oxamide ligand; Fluorescence; Mono- and binuclear Cu(II) complexes; Magnetic studies; Electrochemical studies

1. Introduction

The current interest for inorganic chemists is to design and synthesize [1] bi- and polydentate ligands and their transition metal complexes because of their applications such as new types of magnetic materials [2,3], catalytic reagents [4,5], models of metalloenzymes [6], sensors [7] and DNA-cleavage agents [8]. Generally two main strategies followed for the synthesis of bi and polymetallic complexes are (i) the use of polynucleating ligands and (ii) the use of 'metal complexes as ligands' [9,10]. In this respect, oxamide-bridged compounds have gained increasing interest [11], since they can form a large number of supramolecules in simple routes by following both the strategies. Oxamide-based ligands such as *N*,*N*′-bis(aminoalkylsubstituted)oxamide [12] have been of great interest due to their ability to form variety of complexes from mono to poly [13]. The monomeric *cis*-oxamidato metal complexes of *N*,*N*′-bis(aminoalkylsubstituted)oxamide easily yields binuclear [14] and polynuclear [15] complexes by changing its conformation from *cis* to *trans* form. Further, Schiff bases have photochromic properties, many of them have non-linear optical property [16], and the complexes with tetradentate Schiff base ligands having the salen-type skeleton are found to generate molecular oxygen [17,18] in the absence of *p*-quinone, and all of these have been given great attention now [19]. With these facts in mind and in continuation of our recent work on oxamide-based compounds [20–23], we have designed and synthesized a ligand and studied its complexation behaviour towards copper(II) ions. This paper reports absorbance and fluorescence spectra of the ligand, and spectral, electrochemical and magnetic studies of the mono- and binuclear copper(II) complexes of the ligand.

2. Experimental

2.1. Physical measurements

Elemental analysis was carried out on a Carlo Erba model 1106 elemental analyzer. ^{1}H NMR spectrum was recorded using a model FX-80-Q Fourier transition NMR spectrometer. IR spectra were recorded on a Hitachi model 270-50 spectrophotometer on KBr disc in the wavenumber range 4000–250 cm^{-1}.

---

* Corresponding author. Tel.: +91 44 22300488; fax: +91 44 22300488.
E-mail address: mkands@yahoo.com (M. Kandaswamy).

1386-1425/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2007.06.006

The EI–mass spectrum of the ligand was recorded on a JEOL DX-303 mass spectrometer. Electronic spectral studies were carried out on a Hitachi model 320 spectrophotometer in the wavelength range of 250–800 nm. Molar conductivity was measured with an Elico model SX 80 conductivity-bridge using a freshly prepared solution of the complex in DMF. The cyclic voltammograms of complexes (10^{-3} M DMF solution) were recorded on CHI600A electrochemical analyzer. The measurements were carried out under oxygen-free conditions by purging nitrogen gas using a three-electrode cell in which glassy carbon electrode was the working electrode, saturated Ag/AgCl electrode was reference electrode and platinum wire was used as the auxiliary electrode. For coulometric studies the platinum foil (1 cm^2) is used as a working electrode instead of glassy carbon electrode. Ferrocene/ferrocenium (1+) couple was used as an internal standard and $E_{1/2}$ of the ferrocene/ferrocenium (Fc/Fc^+) couple, under the experimental condition, is 470 mV in dimethylformamide (DMF) and the ΔE_p value for Fc/Fc^+ is 70 mV. Tetra(*n*-butyl) ammonium perchlorate was used as the supporting electrolyte. Room-temperature magnetic moments for Cu(II) complexes were measured on a PAR Model-155 vibrating sample magnetometer. The apparatus was calibrated using Ni. The effective magnetic moment was calculated using the relation $\mu_{Cu} = 2.83\sqrt{\chi_{Cu}T}$, where χ_{Cu} is the molar magnetic susceptibility per Cu. X-band ESR spectra was recorded on a Varian EPR-E 112 spectrometer using diphenylpicrylhydrazine (DPPH) as the reference. The emission spectrum of the ligand was recorded in HPLC grade chloroform on Perkin-Elmer LS-5B spectrophotometer.

2.2. Materials

2,6-Diformyl-4-methyl-phenol [24] and *N,N′*-bis(3-aminopropyl)oxamide [25] were prepared by following the literature methods. Tetra(*n*-butyl)ammonium perchlorate (TBAP) was used as the supporting electrolyte in electrochemical measurements (*Caution*! TBAP is potentially explosive; hence, care should be taken in the handling of the compound). All the other chemicals and solvents were of analytical grade and used as received.

2.3. Synthesis of the ligand *N,N′*-bis{3-(2-formyl-4-methyl-phenol)-6-iminopropyl} oxamide (**L**)

The ligand **L** was prepared by the dropwise addition of ethanolic solution (30 ml) of *N,N′*-bis(3-aminopropyl)oxamide (0.6 g, 3 mmol) to a stirred solution of 2,6-diformyl-4-methyl-phenol (1 g, 6 mmol) in ethanol (30 ml). After the addition was completed, the stirring was continued for further 1 h. The resulting yellow precipitate was filtered off, and then washed with diethyl ether and air-dried. The crude product was recrystallized from chloroform. Yield: 0.85 g (60%). m.p. 188–190 °C. EI–mass spectrum: $m/z = 496\ (M+1)^+$. Anal. Calc. for $C_{26}H_{30}N_4O_6$: C, 63.15; H, 6.11; N, 11.33. Found: C, 63.15; H, 6.10; N, 11.32. ^{1}H NMR ($CDCl_3$, δ ppm): 1.90–1.96 (m, $NCH_2\mathbf{CH_2}CH_2N$, 4H), 2.0 (t, $\mathbf{CH_2}$NCH, 4H), 2.32 (s, $\mathbf{CH_3}$, 6H), 3.65 (t, $\mathbf{CH_2}$NHCO, 4H), 7.01–7.12 (m, **Ar**–**H**, 4H), 7.33 (s, **CH**=N, 2H), 10.2 (s, **Ar**–**OH**, 2H), 10.5 (s, C**H**O, 2H). Selected IR data (KBr, ν cm^{-1}): 1585, 1635, 1667, 3271, 3340. UV–vis (λ_{max}, nm) (ε, $M^{-1}\ cm^1$) in DMF: 455 (81), 360 (58,000), 249 (208,000).

2.4. Synthesis of complexes

2.4.1. Synthesis of mononuclear copper(II) complex [CuL]

A solution of $Cu(CH_3COO)_2\cdot H_2O$ (0.40 g, 2 mmol) dissolved in methanol (60 ml) was added in dropwise to a stirred solution of the ligand (1.0 g, 2 mmol) in MeOH (60 ml). After the addition, the stirring was continued for one more hour. A green colour compound precipitated, that was filtered off and washed with diethyl ether. The resultant complex was recrystallized from acetonitrile. Yield: 1.12 g (75%). Anal. Calc. for $C_{26}H_{28}N_4O_6Cu$: C, 56.16; H, 5.08; N, 10.08; Cu, 11.43. Found: C, 56.14; H, 5.08; N, 10.06; Cu, 11.42%. Selected IR data (KBr, ν cm^{-1}): 1627, 1668, 3410. Conductance in DMF was given as $\Lambda_m = 14\ \Omega^{-1}\ mol^{-1}\ cm^2$. UV–vis ($\lambda_{max}$, nm) (ε, $M^{-1}\ cm^1$) in DMF: 520 (235), 372 (21,400), 267 (35,300). $\mu_{eff} = 1.70\mu_B$, $g_\perp$ at 2.11, $g_\parallel = 2.34$ and $A_\parallel = 133$.

2.4.2. Synthesis of binuclear copper(II) complex [Cu_2L]

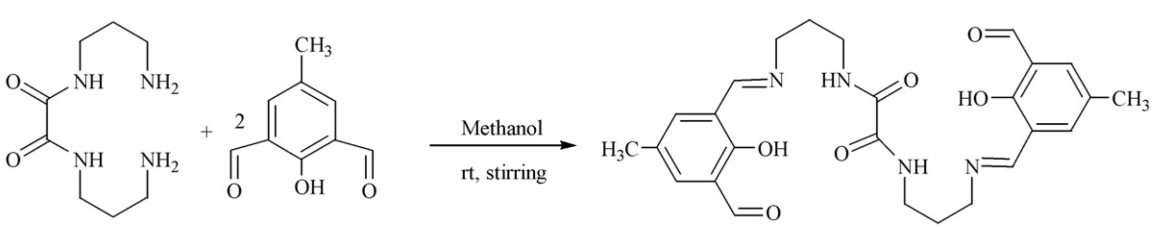
A methanolic solution (60 ml) of $Cu_2(CH_3COO)_2\cdot H_2O$ (1.0 g, 5 mmol) was added dropwise to the stirred solution containing the ligand (1.26 g, 2.5 mmol) dissolved in MeOH (60 ml) and stirring was continued for further one more hour. The resultant pale green precipitate was filtered off and washed with diethyl ether. The crude complex was then recrystallized from acetonitrile. Yield: 1.64 g (80%). Anal. Calc. $C_{26}H_{26}N_4O_6Cu_2$: C, 50.56; H, 4.24; N, 9.07; Cu, 20.58. Found: C, 50.54; H, 4.24; N, 9.06; Cu, 20.57%. Selected IR data (KBr, ν cm^{-1}): 1624, 1669, 2930. Conductance in DMF (Λ_m) = 13 $\Omega^{-1}\ mol^{-1}\ cm^2$. UV–vis ($\lambda_{max}$, nm) (ε, $M^{-1}\ cm^{-1}$) in DMF: 560 (470), 365 (27,200), 266 (38,400). $\mu_{eff} = 1.45\mu_B$, $g = 2.10$.

3. Results and discussion

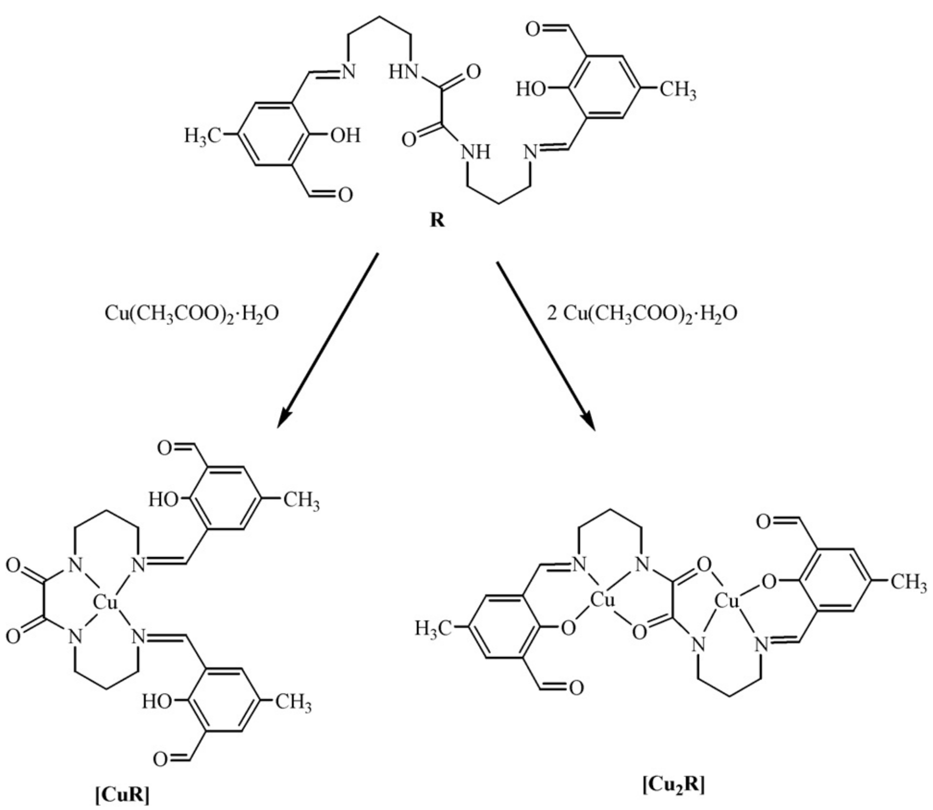
A new oxamide-based ligand (**L**) was synthesized by Schiff's base condensation between 2,6-diformyl-4-methyl-phenol and *N,N′*-bis(3-amino propyl)oxamide as shown in Scheme 1. The mono- and binuclear Cu(II) complexes of this ligand were prepared by using the ligand and copper(II) acetate monohydrate in 1:1 and 1:2 mole ratios, respectively as shown in Scheme 2.

3.1. Spectral studies of ligand

The EI–mass spectrum of the ligand **L** is shown in Fig. 1. The ligand **R** showed the molecular ion peak at $m/z = 495$, which is assignable to the $(M+1)^+$ fragment. The IR spectrum of the ligand showed a ν(C=O) of aldehyde peak at 1695 cm^{-1} and at 1667 cm^{-1} for ν(C=O) of oxamide carbonyl group. The peak appeared at 1644 cm^{-1} is due to ν(C=N). A band responsible for OH group $\nu_{(OH)}$ was observed at 3270 cm^{-1}. The bands at 3271 and 1585 cm^{-1} appeared due to –NH stretching and –NH bending, respectively in the IR spectrum of the ligand, and these



Scheme 1. Synthesis of the ligand **R**.



Scheme 2. Synthesis of [CuH_2L] and [Cu_2L] complexes.

bands disappeared on complexation supporting the coordination with the metal ion in complexes as in Scheme 2.

The ligand was found to be exhibiting fluorescence and the electronic absorption and emission spectra of the ligand were recorded in $CHCl_3$. The absorption and emission spectra of the ligand are shown in Figs. 2 and 3, respectively. The absorption spectrum (5×10^{-5} M) showed bands at 249 and 360 nm with a weak band at about 455 nm. The first band (249 nm) could

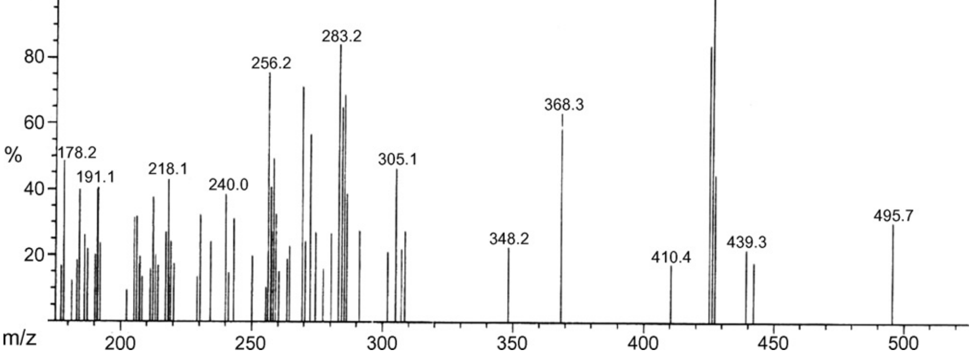


Fig. 1. EI–mass spectrum of the ligand **L**.

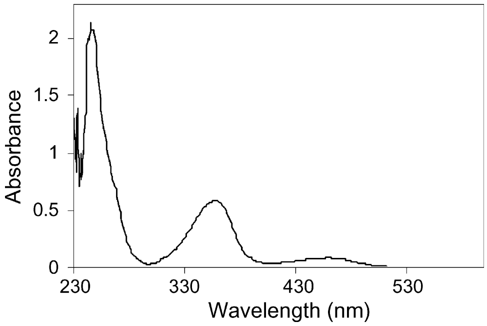


Fig. 2. Absorption spectrum of the ligand **L**.

be assigned to the excitation of the π electrons of the aromatic system. The second band (around 360 nm) is due to transition between the π orbital localized on the band of azomethine group (C=N). The third band in the region (320–400 nm) which can be effect of an intramolecular charge-transfer transitions within the whole of the Schiff base molecule [26]. The ligand displayed an emission maximum at 516 nm on excitation at 360 nm.

3.2. Spectral studies of complexes

The IR spectra of the mono- and binuclear Cu(II) complexes showed ν(C=N) bands at 1627 and 1624 cm^{-1}, respectively. A band due to ν(OH) appeared at 3340 and 3410 cm^{-1} for the free ligand and the mononuclear Cu(II) complex, respectively. The absence of this band in the binuclear complex is an indication of deprotonation of phenolic-OH group.

The electronic spectra of the mono- and binuclear Cu(II) complexes showed three main transitions. The mononuclear complex CuL exhibited a d–d transition ($T_{2g} \rightarrow E_g$) at 520 nm consistent with the tetracoordinated Cu in CuN_4 in a nearly square planar geometry [27,28]. Binuclear complex displayed a d–d band at 560 nm. The λ_{max} value of the binuclear complexes is higher than that of the mononuclear species; such a red shift implies that the conformation of ligand is altered from *cis* to *trans* so as to change the environment of Cu(II) ions from N_4 to N_2O_2. This is consistent with a previously reported observation [29]. Besides d–d transition, a moderate intensive band observed in the region 360–370 nm due to ligand to metal charge-transfer transition, and the strong band observed around 260–270 nm due to intraligand charge-transfer transition [28] for these complexes.

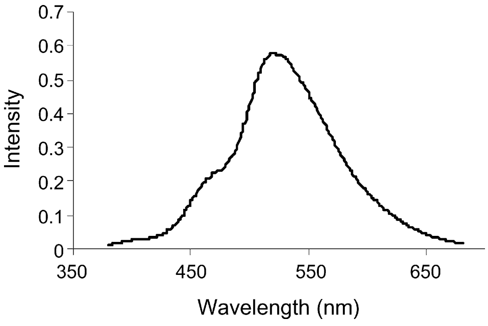


Fig. 3. Emission spectrum of the ligand **L**.

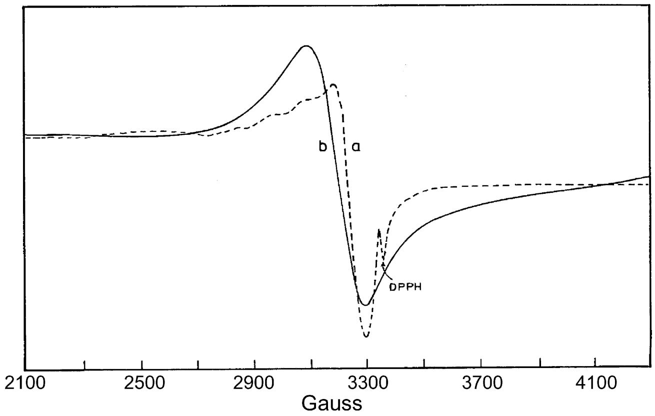


Fig. 4. ESR spectra of the copper(II) complexes (a) [CuH_2L] and (b) [Cu_2L].

3.3. Magnetic studies

The room-temperature (25 °C) solid-state X-band ESR spectra of the mono- and binuclear copper (II) complex are shown in Fig. 4. The mononuclear complex showed four lines [30] due to nuclear hyperfine splitting (spin 3/2) with the $g_{\parallel}$ value of 2.11, $g_{\perp} = 2.34$ and $A_{\parallel} = 133$. The ESR spectrum of the binuclear copper(II) complex showed a broad band centered at $g = 2.10$ and this broad ESR spectrum indicated the presence of antiferromagnetic interaction [31] between two copper(II) ions in the complex.

The room-temperature magnetic studies of mononuclear Cu(II) complex resulted in magnetic moment value of 1.70μ_B, which is nearer to the spin-only value of 1.73μ_B. This indicates the presence of one Cu(II) ion with a single unpaired electron sited in the $d_{x^2-y^2}$ orbital [32]. The observed room-temperature magnetic moment value for binuclear Cu(II) complex is found to be 1.45μ_B per metal ion. This also suggested the presence of strong antiferromagnetic exchange interaction between the two Cu(II) paramagnetic centers in the same environment through the orbital overlap of the bridging atoms to an adjacent metal ion [22,33]. The orbitals are located in same plane and hence, they overlap on each side of the bridge, favouring strong antiferromagnetic coupling the oxamide bridge.

3.4. Electrochemical studies

Conductivity measurements [34] of both mono- and binuclear Cu(II) complexes in DMF resulted in Λ_m values in the range of 10–15 Ω^{-1} mol^{-1} cm^2 indicated that the complexes are neutral. The electrochemical properties of both the complexes reported in the present work were studied by cyclic voltammetry in DMF containing 10^{-1} M TBAP as supporting electrolyte. Cyclic voltammograms for the complexes were recorded in the potential range −0.2 to −1.5 V. The cyclic voltammograms of the complexes are shown in Fig. 5.

The mononuclear Cu(II)complex showed reduction potential at −0.70 V (E_{pc}) and the reduction process is found to be irreversible [35] in nature. Coulometric studies performed for this complex at 100 mV more negative relative to the reduction wave consumed approximately one electron ($n = 0.93$), which indi-

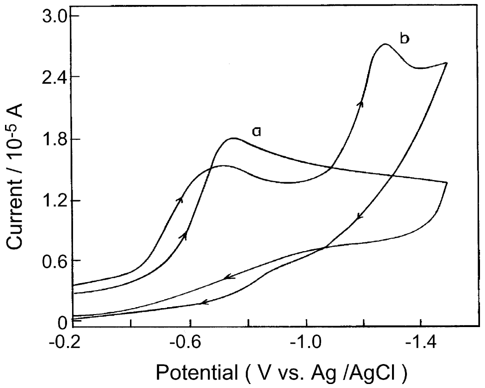


Fig. 5. Cyclic voltammograms of the copper(II) complexes (a) [CuH_2L] and (b) [Cu_2L].

cated that the mononuclear complex undergoes single-electron reduction.

The binuclear Cu(II) complex showed two reduction waves at cathodic region and the reduction potentials are found to be −0.75 V (E^1_{pc}) and −1.27 V (E^2_{pc}). Coulometric studies performed at 100 mV more negative relative to the first reduction wave consumed approximately one electron ($n = 0.90$) and at 100 mV more negative to the second reduction wave consumed two electrons ($n = 1.85$) per molecule, which indicated the involvement of two single-electron transfers in the reduction process and which can be assigned as follows:

$$Cu^{II}Cu^{II} \rightarrow Cu^{II}Cu^{I} \rightarrow Cu^{I}Cu^{I}$$

The above two reduction processes are found to be irreversible in nature.

4. Conclusion

A new oxamide-based ligand **L** has been designed and synthesized in a simple route. The ligand shows fluorescence at 516 nm. Depending upon the metal ion concentration, the ligand forms either mononuclear or binuclear complexes. In mononuclear complex, four nitrogens were coordinated to the metal ion in *cis* manner and, two nitrogens and two oxygen atoms of the polydentate ligand were coordinated to the metal ions, and the binuclear complex is existed in the trans configuration. This fluorescent compound can be useful as a fluorescent probe for cations and anions. We are currently studying the recognition behaviour of this receptor towards various halide anions and transition metal cations to find the sensitivity and selectivity of this receptor.

Acknowledgement

The authors acknowledge Department of Science and Technology, Government of India and Science City (Government of Tamil Nadu), Chennai for financial assistance.

References

[1] P. Guerriero, S. Tamburini, P.A. Vigato, Coord. Chem. Rev. 139 (1995) 17.
[2] M. Zhao, C. Stern, A.G.M. Barrett, B.M. Hoffman, Angew. Chem. Int. Ed. 42 (2003) 462.
[3] M.D. Santana, G. Garcia, M. Julve, F. Lloret, J. Perez, M. Liu, F. Sanz, J. Cano, G. Lopez, Inorg. Chem. 43 (2004) 2132.
[4] I.O. Fritsky, R. Ott, H. Pritzkow, K. Kramer, Chem. Eur. J. 7 (2001) 1221.
[5] G.X. Zheng, Q.F. Wang, S.L. Yan, Polish J. Chem. 78 (2004) 19.
[6] S. Torelli, C. Belle, L. Gautier-Luneau, J.L. Pierre, Inorg. Chem. 39 (2000) 3526.
[7] M. Shamsipur, M. Yousefi, M. Hosseini, M.R. Ganjali, H. Sharghi, H. Naeimi, Anal. Chem. 73 (2001) 2869.
[8] F. Mancin, P. Scrimin, P. Tecilla, U. Tonellato, Chem. Commun. (2005) 2540.
[9] N. Fukita, M. Ohba, T. Shiga, H. Okawa, Y. Ajiro, J. Chem. Soc., Dalton Trans. (2001) 64.
[10] L. Cronin, A.R. Mount, S. Parsons, N. Robertson, J. Chem. Soc., Dalton Trans. (1999) 1925.
[11] L. Cronin, P.A. McGregor, S. Parsons, S. Teat, R.O. Gould, V.A. White, N.J. Long, N. Robertson, Inorg. Chem. 43 (2004) 8023.
[12] R. Ruiz, J. Faus, F. Lloret, M. Julve, Y. Journaux, Coord. Chem. Rev. 193 (1999) 1069.
[13] F. Lloret, Y. Journaux, M. Julve, Inorg. Chem. 29 (1990) 3967.
[14] F. Lloret, M. Julve, J.A. Real, J. Faus, R. Ruiz, M. Mollar, I. Castro, C. Bois, Inorg. Chem. 31 (1992) 2627.
[15] V. Mckee, Adv. Inorg. Chem. 40 (1993) 323.
[16] S. Mitra, N. Tamai, Chem. Phys. Lett. 282 (1998) 391.
[17] N. Aurangzeb, C.E. Hulme, C.A. McAuliffe, R.G. Pritchard, M. Watkinson, M.R. Bermejo, A. Garcia-Deibe, M. Rey, J. Sanmartin, A. Sousa, J. Chem. Soc., Chem. Commun. (1994) 1153.
[18] M. Watkinson, A. Whiting, C.A. McAuliffe, J. Chem. Soc., Chem. Commun. (1994) 2141.
[19] N.E. Borisova, M.D. Reshetova, Y.A. Ustynyuk, Chem. Rev. 107 (2007) 46.
[20] D. Saravanakumar, N. Sengottuvelan, M. Kandaswamy, P.G. Aravindan, D. Velmurugan, Tetrahedron Lett. 46 (2005) 7255.
[21] D. Saravanakumar, N. Sengottuvelan, M. Kandaswamy, Inorg. Chem. Commun. 8 (2005) 386.
[22] D. Saravanakumar, N. Sengottuvelan, V. Narayanan, M. Kandaswamy, K. Chinnakali, G. Senthilkumar, H.K. Fun, Eur. J. Inorg. Chem. (2004) 872.
[23] N. Sengottuvelan, D. Saravanakumar, S. Sridevi, V. Narayanan, M. Kandaswamy, Supramol. Chem. 16 (2004) 129.
[24] C.N. Verani, E. Rentschler, T. Weyhermuller, E. Bill, P. Chaudhuri, J. Chem. Soc., Dalton Trans. (2000) 251.
[25] J. Chang, O. Vogl, J. Polym. Sci. 15 (1977) 311.
[26] H.H. Hammud, A. Ghannoum, M.S. Masoud, Spectrochim. Acta A 63 (2006) 255.
[27] J.C. Kim, J.C. Fettinger, Y.I. Kim, Inorg. Chim. Acta 286 (1999) 67.
[28] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, Amsterdam, 1984.
[29] J.P. Costes, F. Dahan, J.P. Laurent, M. Drillon, Inorg. Chim. Acta 294 (1999) 8.
[30] S. Zhu, F. Kon, H. Lin, C. Lin, M. Lin, Y. Chen, Inorg. Chem. 35 (1997) 3851.
[31] J.P. Costes, F. Dahan, J.P. Laurent, Inorg. Chim. Acta 230 (1995) 199.
[32] A. Bottcher, H. Elias, E. Jager, H. Lanffelderova, M. Mazur, L. Mullor, H. Paulus, P. Pelikan, M. Rudolph, M. Valko, Inorg. Chem. 32 (1993) 4131.
[33] H. Okawa, N. Matsumoto, M. Koikawa, K. Takeda, S. Kida, J. Chem. Soc., Dalton Trans. (1990) 1383.
[34] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
[35] R.C. Agarwal, N.K. Singh, R.P. Singh, Inorg. Chem. 20 (1981) 2794.