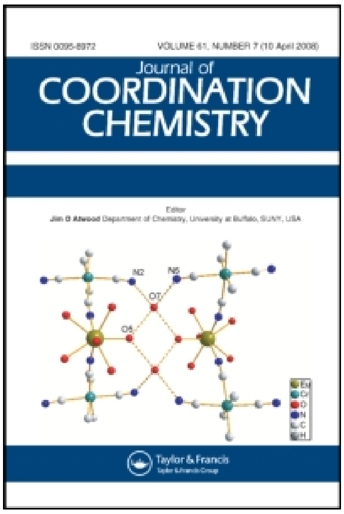


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Copper(II) complexes of tridentate SNO ligands: synthesis, characterization and crystal structure

Sandipan Sarkar[a]; Pulak K. Dhara[a]; M. Nethaji[b]; Pabitra Chattopadhyay[a]
[a] Department of Chemistry, The University of Burdwan, Golapbag, Burdwan-713104, India [b] Department of Inorganic and Physical Chemistry, Bangalore-560012, India

To cite this Article Sarkar, Sandipan , Dhara, Pulak K. , Nethaji, M. and Chattopadhyay, Pabitra(2009) 'Copper(II) complexes of tridentate SNO ligands: synthesis, characterization and crystal structure', Journal of Coordination Chemistry, 62: 5, 817 — 824

To link to this Article: DOI: 10.1080/00958970802314951

URL: http://dx.doi.org/10.1080/00958970802314951

Journal of Coordination Chemistry
Vol. 62, No. 5, 10 March 2009, 817–824

Copper(II) complexes of tridentate SNO ligands: synthesis, characterization and crystal structure

SANDIPAN SARKAR†, PULAK K. DHARA†, M. NETHAJI‡ and
PABITRA CHATTOPADHYAY*†

†Department of Chemistry, The University of Burdwan, Golapbag, Burdwan-713104, India
‡Department of Inorganic and Physical Chemistry, IISc., Bangalore – 560012, India

(*Received 26 January 2008; in final form 14 May 2008*)

A new series of binary copper(II) complexes, $[Cu(L)_2]$ (**2**) [where L is a monobasic tridentate methylthioazophenolate having NSO donor sets], has been synthesized. The reddish brown colored complexes have been characterized by elemental analyses, spectroscopic and other physico-chemical tools. The detailed structure analysis of one of the complexes, $[Cu(1a)_2]$ (**2a**), by single-crystal X-ray crystallography shows that thioether-S donor center participates in coordination with the copper(II) ion with a weak interaction with long Cu–S(thioether) bond distances [2.956(2) Å and 2.925(2) Å]. Electrochemical study of the complexes in methanol using TBAP as supporting electrolyte shows that heterogeneous electron-transfer rate is low at the applied potential.

Keywords: Binary copper(II) complex; SNO ligands; Crystal structure

1. Introduction

Coordination chemistry of copper complexes of chelating ligands is of continuing interest in connection with their structures, spectral, and redox properties in general [1] and from their relevance to copper-containing metalloproteins, in particular [2, 3]. Copper and its compounds have many medical applications [4–6]. Copper(I) prefers tetrahedral geometry, while copper(II) complexes exhibit coordination number dependent structures, four-coordinate prefers square planar, five-coordinate is square pyramidal or trigonal bipyramidal and six-coordinate complexes are distorted octahedral [7–9]. Thioether donors destabilize copper(II) [10–14]. Redox nature of the complexes is important to control nuclease activity [15].

Considering the importance of nitrogen-sulfur donor sets in coordination chemistry of copper complexes [15, 16], herein we report the synthesis, characterization and structure of a series of binary copper(II) complexes of methylthioazophenolate chelators having SNO donor sets.

---

*Corresponding author. Email: pabitracc@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802314951

2. Experimental

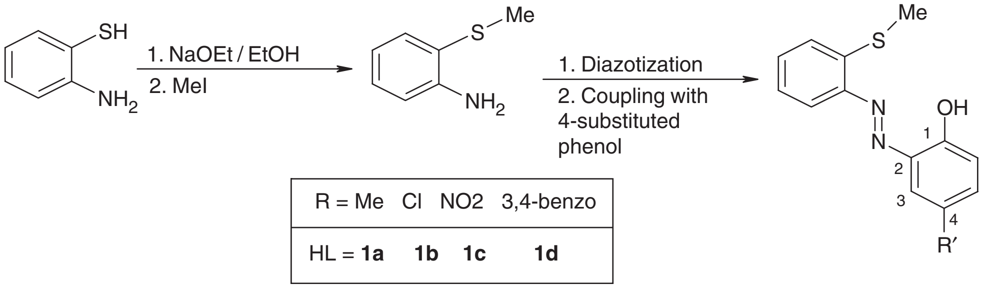
2.1. *Materials and physical measurements*

All reagents were obtained from commercial sources and used without further purification. Tetra-*n*-butylammoniumperchlorate was prepared by the addition of sodium perchlorate to a hot solution of tetra-*n*-butylammonium-bromide (Aldrich). The product was recrystallized from aqueous ethanol and tested for the absence of bromide. Solvents were distilled from an appropriate drying agent [17].

Microanalyses were performed with a Perkin-Elmer 2400 CHN elemental analyzer and copper analyses were carried out by iodometric titration [18]. IR spectra by JASCO FT-IR model 460 plus using KBr disks and UV–Vis by JASCO UV–Vis/NIR model V-570 spectrometer were obtained. The ^{1}H-NMR spectra were obtained on a Bruker AC300 spectrometer with chemical shifts reported in δ relative to the residual solvent resonance of $CDCl_3$. Molar conductances (Λ_M) were measured in a Systronics conductivity meter 304 model using $\sim 10^{-3}$ M solutions in MeOH. Magnetic moments (μ, B.M.) were obtained from a vibrating sample magnetometer PAR 155 model. Electrochemical measurements were made with a computer controlled EG & G PAR model 270 VERSTAT electrochemical instrument using Ag/AgCl electrodes. All measurements were made at 298 K in dry MeOH with $[Bu_4N]ClO_4$ as supporting electrolyte in deoxygenated environment maintained by bubbling research grade nitrogen. The reported potentials are uncorrected junction potentials.

2.2. *Synthesis of the ligands (HL, 1)*

The syntheses of the ligands were carried out by coupling different *para*-substituted phenols with the diazotized 2-(methylthio)aniline (scheme 1). At the first step 2-aminothiophenol was converted to 2-(methylthio)aniline by methyliodide (1.0 mmol) addition to 2-aminothiophenol (1.0 mmol) in dry ethanol containing sodium ethoxide (1.0 mmol) at low temperature. Then this mixture was allowed to stir at room temperature for 0.5 h and then refluxed for 1 h. The mixture was cooled to room temperature, water was added and finally the ethanol was removed by rotary evaporator. The product was extracted into ether and dried using $NaHSO_3$. The product 2-(methylthio)aniline as yellow oil was obtained by removing the ether by rotary evaporator.



Scheme 1. Synthetic procedure of the ligands.

Then, the preparation of 2-(methylthio)phenylazo-(4-methyl)phenolate was carried out. The details are given for (**1a**). To an alkaline solution of *p*-cresol (1.0 g, 9.3 mmol) at 5°C was added diazotized solution of 2-(methylthio)aniline (2.0 g, 9.3 mmol) dropwise with continuous stirring. The temperature was controlled at 0°C. The resulting solution was acidified and the pH controlled between 6.0–7.0. The red compound so precipitated was filtered and washed with water. Finally, the pure recrystallized compound was obtained from ethanol–water in 70% yield. The yield of the other ligands varied from 57–68% following similar method. **1a**: $C_{14}H_{14}N_2OS$: Anal. Calcd: C, 65.09; H, 5.47; N, 10.85. Found: C, 65.35; H, 5.41; N, 10.95. **1b**: $C_{13}H_{11}N_2ClOS$: Calcd: C, 56.00; H, 3.98; N, 10.05. Found: C, 56.15; H, 3.88; N, 10.09. **1c**: $C_{13}H_{11}N_3O_3S$: Calcd: C, 53.96; H, 3.81; N, 14.53. Found: C, 54.33; H, 3.74; N, 14.79. **1d**: $C_{17}H_{14}N_2OS$: Calcd: C, 69.36; H, 4.80; N, 9.58. Found: C, 69.52; H, 4.69; N, 9.61. m.p. (°C): **1a**: 94 ± 1, **1c**: 77 ± 1, **1d**: 88 ± 1. IR (cm^{-1}): **1a**: $\nu_{N=N}$, 1505; $\nu_{C–S}$, 781. **1b**: $\nu_{N=N}$, 1500; $\nu_{C–S}$, 779. **1c**: $\nu_{N=N}$, 1503; $\nu_{C–S}$, 778. **1d**: $\nu_{N=N}$, 1498; $\nu_{C–S}$, 780. ^1H-NMR δ(ppm) (in $CDCl_3$): **1a**: 12.52(s, 1H), 7.84(m, 1H), 7.76(s, 1H), 7.42–7.38(m, 2H), 7.22–7.18(m, 2H), 6.97(d, 1H), 2.51(s, 3H) 2.38(s, 3H); **1b**: 12.38(s, 1H), 7.97(s, 1H), 7.85(m, 1H), 7.39–7.31(m, 3H), 7.22(m, 1H), 7.04(d, 1H), 2.49(s, 3H); **1c**: 12.59(s, 1H), 8.74(d, 1H), 8.22(m, 1H), 7.85(m, 1H), 7.41–7.38(m, 2H), 7.24(m, 1H), 7.20(d, 1H), 2.52(s, 3H); **1d**: 12.61(s, 1H), 7.86–7.81(m, 2H), 7.70–7.59(m, 2H), 7.42–7.33(m, 3H), 7.21–7.27(m, 3H), 2.52(s, 3H).

2.3. *Synthesis of Cu(II) complexes of HL*

The preparation of the complexes was carried out following a common procedure as follows. To the mixture of the corresponding **1** (2.0 mmol) and triethylamine (0.20 g) in methanol (20 mL), methanolic solution of $CuCl_2 \cdot 2H_2O$ (0.17 g) was added dropwise with stirring. The reddish-brown solution was stirred for 2–3 h at 298 K, filtered, and the filtrate was left undisturbed for a week. Dark brown crystalline compounds separated. The crystals were filtered, washed with water, cold methanol and dried *in vacuo*. The pure reddish-violet crystallized product was obtained from dichloromethane. Yield: 82–87%.

[Cu(**1a**)$_2$] (**2a**): $C_{28}H_{26}N_4O_2S_2Cu$: Anal. Calcd: C, 58.16; H, 4.54; N, 9.69; Cu, 10.99. Found: C, 58.45; H, 4.61; N, 9.62; Cu, 10.89. IR (cm^{-1}): $\nu_{N=N}$, 1486; $\nu_{C\text{-}S}$, 758. Magnetic moment (μ, B.M.): 1.86. Conductivity (Λo, $Ohm^{-1} cm^2 mol^{-1}$) in methanol: 18.

[Cu(**1b**)$_2$] (**2b**): $C_{26}H_{20}N_4Cl_2O_2S_2Cu$: Anal. Calcd: C, 50.43; H, 3.26; N, 9.05; Cu, 10.26. Found: C, 50.61; H, 3.16; N, 9.11; Cu, 10.12. IR (cm^{-1}): $\nu_{N=N}$, 1482; $\nu_{C–S}$, 762. Magnetic moment (μ, B.M.): 1.91. Conductivity (Λo, $Ohm^{-1} cm^2 mol^{-1}$) in methanol: 15.

[Cu(**1c**)$_2$] (**2c**): $C_{26}H_{20}N_6O_6S_2Cu$: Anal. Calcd: C, 48.78; H, 3.13; N, 13.13; Cu, 9.93. Found: C, 48.99; H, 3.05; N, 13.90; Cu, 9.79. IR (cm^{-1}): $\nu_{N=N}$, 1485; $\nu_{C–S}$, 763. Magnetic moment (μ, B.M.): 1.82. Conductivity (Λo, $Ohm^{-1} cm^2 mol^{-1}$) in methanol: 20.

[Cu(**1d**)$_2$] (**2d**): $C_{34}H_{26}N_4O_2S_2Cu$: Anal. Calcd: C, 62.80; H, 4.03; N, 8.62; Cu, 9.77. Found: C, 62.99; H, 3.94; N, 8.77; Cu, 9.64. IR(cm^{-1}): $\nu_{N=N}$, 1482; $\nu_{C–S}$, 760. Magnetic moment (μ, B.M.): 1.84. Conductivity (Λo, $Ohm^{-1} cm^2 mol^{-1}$) in methanol: 14.

2.4. *X-ray crystal structure analysis*

A suitable single crystal of **2a** was mounted on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The intensity data were corrected for Lorentz and polarization effects. A total 5507 reflections were measured and 3993 reflections were observed applying the condition $I > 2\sigma(I)$. The structure was solved by Patterson syntheses, followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. The refinement converged to residual indices $R_1 = 0.0474$, $wR_2 = 0.0988$ with $I > 2\sigma(I)$. Complex neutral atom scattering factors [19a] were used throughout. All calculations were carried out using SHELXS-93 [19b], SHELXL-97 [19c], PLATON 99 [19d] and ORTEP3 [19e] programs.

3. Results and discussion

3.1. *Syntheses and characterization*

The ligands in this study have been synthesized by coupling diazotized 2-(methylthio)aniline with different *para*-substituted phenols in alkaline medium. The red compounds are soluble in common organic solvents and stable to air and moisture in the solid state. The molecular formulation has been established by microanalytical data and spectral characterization; the organic moieties behave as tridentate monobasic ligands.

The copper(II) complexes of the type $[Cu(L)_2]$ were obtained from the reaction of $CuCl_2 \cdot 2H_2O$ with the ligands in the ratio of 1 : 2 in methanol containing triethylamine. All the complexes are soluble in common organic solvents. Microanalytical data and copper analyses have been used to establish composition of the complexes as $[Cu(L)_2]$. Conductivity of the complexes in methanolic solution lies in the range 14–20 $\Lambda o\,mol^{-1}\,cm^{-1}$, suggesting non-electrolytes in solution. Magnetic susceptibility data reveal spin-only values for the copper complexes as the values are close to 1.75 B.M. (in the range 1.74–1.91 B.M.).

3.2. *X-ray structure of 2a*

The ORTEP view of **2a** is in figure 1 with the atom numbering scheme. Selected bond distances and angles are listed in tables 1 and 2. The crystal is monoclinic with space group $P2_{1/c}$ having crystallographic data: $a = 9.604(7)$ Å, $b = 26.561(19)$ Å, $c = 10.812(8)$ Å and $\alpha = 90.0°$, $\beta = 104.9(1)°$, $\gamma = 90.00°$ and $Z = 4$ with cell volume of 2665(3) Å^3. The copper is bonded to two tridentate monobasic SNO donor thioazophenolate (**1a**) ligands.

The coordination geometry is elongated octahedral where the two thioether-S donors have axial contacts at 2.956(2) and 2.925(2) Å. The thioether-S is weakly coordinated with copper and the bond distance is longer than axial Cu-S bond distances in other complexes [20–22]. The donors of one ligand coordinated with copper are at less distance in comparison to the corresponding bond distances for donor atoms of another ligand, while the reverse is observed for thioether-S coordination. The Cu1–N(2) bond

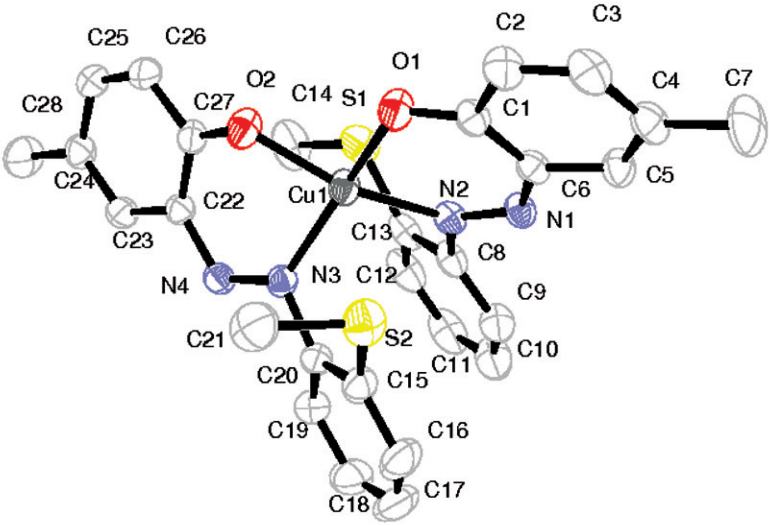


Figure 1. An ORTEP view of **2a** with thermal ellipsoids at 50% probability level and the atom numbering scheme [axial Cu–S bonds have not been shown].

Table 1. Summarized crystallography data for **2a**.

Empirical formula	$C_{28}H_{26}CuN_4O_2S_2$
Formula weight	577.7
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P21/c$
Unit cell dimensions (Å, °)	
a	9.604(7)
b	26.561(19)
c	10.812 (8)
α	90.00
β	104.91(11)
γ	90.00
V (Å^3)	2665(3)
Z, D_{Calcd} (mg m^{-3})	4, 1.4410
Absorption coefficient (μ)	1.009
F(000)	1196
θ range for data collection	1.53–27.29°
Reflections collected/unique	5507/3993
Completeness to θ	1.53–26.50°
Goodness-of-fit on F^2	1.085
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0474$, $wR_2 = 0.0988$

distance [1.992(3) Å] is slightly smaller than Cu1–N(3) [1.998(2) Å] and Cu1-O1 bond distance [1.903(2) Å] is slightly smaller than the bond Cu1–O(2) [1.912(2) Å], though their geometrical positions are in the basal plane.

3.3. *Spectral properties*

The bands around ~3320 cm^{-1} (O–H of H bonded phenol) [23] exhibited by the ligands (**1**) are absent in IR spectra of the complexes, indicating coordination of oxygen to the

Table 2. Selected bond distances (Å) and angles (°) of **2a**.

Cu1–O1	1.903(2)	Cu1–O2	1.912(2)
Cu1–N2	1.992(3)	Cu1–N3	1.998(2)
Cu1–S1	2.956(2)	Cu1–S2	2.925(2)
N1–N2	1.270(3)	N4–N3	1.274(3)
S1–C13	1.763(4)	S1–C14	1.793(4)
S2–C21	1.791(5)	S2–C15	1.781(4)
O1–Cu1–O2	89.90(10)	O2–Cu1–N2	157.86(10)
O1–Cu1–N2	90.44(10)	O1–Cu1–N3	160.66(9)
O2–Cu1–N3	88.48(10)	N2–Cu1–N3	98.23(10)
C13–S1–C14	104.1(3)	C15–S2–C21	101.8(2)
C27–O2–Cu1	120.06(18)	C1–O1–Cu1	123.27(19)

Table 3. UV–Vis spectral and electrochemical data.

Compound	λnm ($\log\varepsilon$) (ε, dm^3 mol^{-1} cm^{-1})	Electrochemical data* $E^{\circ\prime}$, mV(ΔE_p, mV) [E_{pa} mV E_{pc} mV]
2a	230(4.390), 282(4.153), 354(4.153), 384(3.762), 540(3.770), 714(2.483)	−31 (286)
2b	232(4.377), 272(4.132), 354(4.147), 384(3.721), 540(3.710), 712(3.476)	51 (214)
2c	236(4.360), 275(4.147), 356(4.145), 390(3.740), 536(3.763), 711(2.501)	80 (204)
2d	234(4.368), 278(4.223), 359(4.127), 394(3.776), 541(3.827), 716(2.510)	21.5 (233)

*Scan rate of 50 mVs^{-1}.

copper [24]. The characteristic band (1498–1505 cm^{-1}) for $\nu_{N=N}$ of the free ligand is shifted to lower wavenumbers ($\Delta \sim 15$–20 cm^{-1}) in the complexes, suggesting coordination of copper to azo [25]. The observed $\nu_{N=N}$ band for all the complexes is around 1482–1486 cm^{-1}. In addition, $\nu_{C–S}$ at 780 cm^{-1} for the ligands shifts to 760 cm^{-1} for the complexes.

The electronic absorption spectra of the azo ligands and its complexes were recorded at room temperature, table 3, using MeOH as the solvent. Intraligand charge transfer $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ appear at 354–359 and 230–282 nm, respectively. All the complexes exhibit a band for thioether-S(σ) $\rightarrow$ Cu(II) charge transfer (LMCT) in the range 384–394 nm [15a, 16, 26]. The copper(II) complexes exhibit the characteristic broad d-d absorption around 715 nm in solution and an intense band at 538 nm demonstrates square planar geometry around the copper ion in the solution state [16].

3.4. *Electrochemistry*

Electrochemical activities of the complexes are examined by cyclic voltammetry using a Pt-disk working electrode and a Pt-wire auxiliary electrode in dry MeOH and in presence of [n-Bu$_4$N]ClO$_4$ as supporting electrolyte. In solution, all compounds displayed a quasi-reversible voltammogram having $i_{pc}/i_{pa} \approx 1$ in the range −31 mV to 80 mV with $\Delta E = 204$–286 mV, ascribed to Cu(I)/Cu(II). The peak-to-peak separation is dependent on the scan rates (10 mVs^{-1} to 600 mVs^{-1}), but at the range of low scan rates (10–50 mV s^{-1}), ΔE_P remains almost constant (also the ΔE_{Pa} and the ΔE_{Pc} values), suggesting that the heterogeneous electron-transfer rate constant is low at the applied potential. Bond reorganization energy may be reasonably high due to fast change in

Cu–S bond length which will be longer in Cu(II) than Cu(I) [11]. The potentials for the quasi-reversible voltammogram due to Cu(I)/Cu(II) couple with reference to Ag/AgCl electrodes are tabulated in table 3. Besides this quasi-reversible couple, an irreversible reduction around −0.9 V was observed, considered as either [–N = N–]/[–N–N–]$^-$ or Cu(I)/Cu(0) or combination of both. The influence of substituents in the *para*-position of a phenolic group in the ligands is apparent from the data.

Supplementary material

The file CCDC-669437 contains the crystallographic data for **2a**. Copies of these data can be obtained free of charge at www: http://www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Rd, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

The financial assistance from the Council of Scientific and Industrial Research (CSIR), New Delhi, is gratefully acknowledged. We are indebted to Prof. A.R. Chakravarty, Department of Inorganic and Physical Chemistry, IISc, Bangalore, for his valuable suggestion.

References

[1] M.C. Linder. *Biochemistry of Copper*, Plenum Press, New York (1991).

[2] I.A. Koval, K. van der Schilden, A.M. Schuitema, P. Gamez, C. Belle, J.-L. Pierre, M. Lüken, B. Krebs, O. Roubeau, J. Reedijk. *Inorg. Chem.*, **44**, 4372 (2005).

[3] T. Wang, Z. Guo. *Curr. Med. Chem.*, **13**, 525 (2006).

[4] T. Fujimori, S. Yamada, H. Yasui, H. Sakurai, Y. In, T. Ishida. *J. Biol. Inorg. Chem.*, **10**, 831 (2005).

[5] Y. Zheng, Y. Yi, Y. Wang, W. Zhang, M. Du. *Bioorg. Med. Chem. Lett.*, **16**, 4127 (2006).

[6] I. Garcia-Mora, L. Ruiz-Ramirez, C. Gomez-Ruiz, M. Tinco-Mendez, A. Marquez-Quinones, L.R. deLira, A. Marin-Hernandez, L. Macias-Rosales, M.E. Bravo-Gomez. *Metal-Based Drugs*, **8**, 19 (2001).

[7] (a) F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry*, 3rd Edn, Wiley Eastern Ltd, New Delhi (1978); (b) G. Wilkinson. *Comprehensive Coordination Chemistry*, Vol. 5, p. 775 (1987).

[8] J.E. Hukeey. *Inorganic Chemistry*, 3rd Edn, Harper International SI Edn, London (1983).

[9] E.I. Solomon. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*, K.D. Karlin, J. Zubieta (Eds), pp. 1–22, Adenine, Guilderland, NY (1983).

[10] S. Torelli, C. Belle, C. Philouze, J.-L. Pierre, W. Rammal, E. Saint-Aman. *Eur. J. Inorg. Chem.*, 2452 (2003).

[11] M. Albrecht, K. Hubler, S. Zalis, W. Kaim. *Inorg. Chem.*, **39**, 4731 (2000).

[12] S. Chen, J.F. Richardson, R.M. Buchanan. *Inorg. Chem.*, **33**, 2376 (1994).

[13] U. Sivagnanam, M. Palaniandavar. *J. Chem. Soc., Dalton Trans.*, 2277 (1994).

[14] B. Adhikari, C.R. Lucas. *Inorg. Chem.*, **33**, 1376 (1994).

[15] (a) S. Dhar, D. Senapati, P.K. Das, P. Chattopadhyay, M. Nethaji, A.R. Chakravarty. *J. Am. Chem. Soc.*, **125**, 12118 (2003); (b) S. Dhar, P.A.N. Reddy, M. Nethaji, S. Mahadevan, M.K. Saha, A.R. Chakravarty. *Inorg. Chem.*, **41**, 3469 (2002); (c) D.S. Sigman, T.W. Bruice, A. Mazumder, C.L. Sutton. *Acc. Chem. Res.*, **26**, 98 (1993).

[16] P.K. Dhara, S. Pramanik, T.-H. Lu, M.G.B. Drew, P. Chattopadhyay. *Polyhedron*, **24**, 2357 (2004).

[17] D.D. Perrin, W.L.F. Armarego, D.R. Perrin. *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, U.K (1981).

[18] A.I. Vogel. *A Text Book of Quantitative Inorganic Analysis*, ELBS & Longmans, London (1962).

[19] (a) A.J.C. Wilson. *International Tables for X-Ray Crystallography*, Vol C, Tables 4.2.6.8 and 6.1.1.4. Kluwer, Dordrecht (1992); (b) G.M. Sheldrick. *SHELXS-97*, *Program for the Solution of Crystal Structure*, University of Gottingen, Germany (1997); (c) G.M. Sheldrick. *SHELXL-97*, *Program for the Solution of Crystal Structure*, University of Gottingen, Germany (1997); (d) A.L. Spek. PLATON. *Molecular Geometry Program*, University of Utrecht, The Netherlands (1999); (e) L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).

[20] B.K. Santra, P.A.N. Reddy, M. Nethaji, A.R. Chakravarty. *Inorg. Chem.*, **41**, 1328 (2002).

[21] B.K. Santra, P.A.N. Reddy, M. Nethaji, A.R. Chakravarty. *J. Chem. Soc., Dalton Trans.*, 3553 (2001).

[22] M. Vaidyanathan, R. Balamurugan, U. Sivagnanam, M. Palaniandavar. *J. Chem. Soc., Dalton Trans.*, 3498 (2001).

[23] M.S. Masoud, A.M. Hindway, A.A. Soayed. *Transition Met. Chem.*, **16**, 372 (1991).

[24] P. Chattopadhyay, C. Sinha. *Indian J. Chem., Sect. A*, **34A**, 76 (1995).

[25] H.H. Freedman. *J. Am. Chem. Soc.*, **63**, 2900 (1961).

[26] S. Chattopadhyay, C. Sinha, S.B. Chowdhury, A. Chakravorty. *J. Organomet. Chem.*, **427**, 111 (1992).

[27] M. Kodera, T. Kita, I. Miura, N. Nakayama, T. Kawata, K. Kano, S. Hirota. *J. Am. Chem. Soc.*, **123**, 7715 (2001).