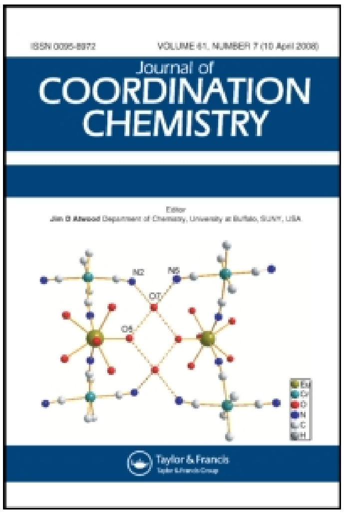

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Copper(II) complexes of thiazolylazo dye with triphenylphosphine and or NCS⁻ as coligands: synthesis, spectral characterization, electrochemistry and luminescence properties

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Copper(II) complexes of thiazolylazo dye with triphenylphosphine and N_3^- or NCS^- as coligands: synthesis, spectral characterization, electrochemistry and luminescence properties

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A series of copper(II) complexes $[Cu(L_1 \text{ or } L_2 \text{ or } L_3)(PPh_3)_2(N_3)_2]$ (**1a**–**3a**) and $[Cu(L_1 \text{ or } L_2 \text{ or } L_3)(PPh_3)_2(NCS)_2]$ (**1b**–**3b**) (where $L_1 = $ 4-(4′-phenyl,2′-thiazolylazo)chlorobenzene, $L_2 = $ 4-(4′-phenyl,2′-thiazolylazo)bromobenzene, and $L_3 = $ 4-(4′-phenyl,2′-thiazolylazo)iodobenzene) have been prepared and characterized on the basis of microanalytical data, molar conductances, magnetic moments, UV-Vis, infrared, and ESR spectra. On the basis of electronic spectra and magnetic susceptibility octahedral geometry has been proposed for the complexes. The ESR spectral data provide information about their structures on the basis of Hamiltonian parameters and degree of covalancy. The electrochemical behavior of the complexes showed that the redox responses of Cu(II) complexes shifted to more negative potential with decrease in electron-withdrawing substituents on the azo ligands. Complexes exhibit blue-green emission with high-quantum yield.

Keywords: Azo complexes; Spectral studies; Luminescence spectra; Cyclic voltammetry

1. Introduction

Copper(II) complexes have been widely explored for versatility of coordination, exquisite colors, technical applications, spectroscopic properties, and biochemical significance. Octahedral copper(II) complexes of mixed electron donor ligands have been studied due to applications as molecular materials [1–4]. Considerable research has focused on synthesis and properties of copper(II) complexes of hybrid ligands as new materials with properties such as magnetic exchange [5, 6], electrical conductivity [7], photoluminescence [8], non-linear optical response [9], and antimicrobial activity [10]. Azo-containing ligands have received much attention as these compounds possess properties including aggregation, optical data storage and tautomerization defining a distinct class of dyestuffs [11, 12]. Thiazolylazo compounds and their metal complexes [13–17] have been examined.

In the present article, we report the synthesis, properties and molecular structure of copper(II) complexes of thiazolylazo ligands with triphenylphosphine and N_3^- (**1a**–**3a**)

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or NCS^- (**1b**–**3b**) as coligands. The complexes were characterized on the basis of elemental analyses, infrared (IR), molar conductances, magnetic moments, and ESR studies. Photoluminescence and electrochemical behavior of the complexes were also been reported.

2. Experimental

2.1. *Materials*

All chemicals were of analytical grade. 4-phenyl-2-aminothiazole was synthesized by the reported method [18]. Solvents were purified and dried according to the standard procedure. $Cu(NO_3)_2 \cdot 4H_2O$ (E-Merk India), NaN_3 (Aldrich, USA), NH_4NCS (Aldrich, USA), and triphenylphosphine (Alfa Aesar) were purchased and used as received.

2.2. *Physical measurement*

Microanalyses (C, H, N) were performed using a Thermo Finnegan FLASH EA 1112 CHNS elemental analyser. Electronic spectra from 200 to 1100 nm were obtained in CH_2Cl_2 on a Shimadzu UV-Vis NIR spectrometer. IR spectra were recorded in KBr pellets with a Perkin–Elmer FT-IR spectrometer from 4000 to 400 cm^{-1}. Magnetic measurements were carried out at room temperature by the Gouy balance method using $Hg[Co(SCN)_4]$ for calibration. Molar conductances (Λ_m) were measured on the ELICO (CM-185) conductivity bridge using *ca* 10^{-3} M solution in CH_2Cl_2. ESR spectra of all the complexes were recorded by X-band ESR at room temperature on a Varian E-112 spectrometer using TCNE as the standard. Luminescence properties were measured using a JASCO F.P.750 fluorescence spectrophotometer equipped with quartz cuvette of 1 cm^3 path length at room temperature. Cyclic voltammetry measurements were performed with a CH-400A electrochemical analyzer. A standard three electrode system, consisting of Platinum disk working electrode, Platinum wire counter electrode, and Ag/AgCl reference electrode containing aqueous 3 M KCl was used. All potentials were converted to SCE scale. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte and all measurements were carried out in CH_2Cl_2 solution at room temperature with scan rate 50 mV s^{-1}.

2.3. *Synthesis of thiazolylazo ligands*

The thiazolylazo ligands 4-(4′-phenyl,2′-thiazolylazo)chlorobenzene (L_1), 4-(4′-phenyl, 2′-thiazolylazo)bromobenzene (L_2), and 4-(4′-phenyl,2′-thiazolylazo)iodobenzene (L_3) were prepared by diazotization of 4-phenyl-2-aminothiazole by procedure reported earlier [15] and characterized by elemental analysis, IR, and UV-Vis spectra.

2.4. *Preparation of copper(II) complexes*

Copper(II) complexes **1a**–**3a** were prepared from copper(II) nitrate using the molar ratio (1 : 1 : 2 : 2) of metal, $L_1/L_2/L_3$, PPh_3, and azide. Complexes **1b**–**3b** were prepared similarly using thiocyanate. Typical synthesis is described later.

2.4.1. Copper(II) azido complexes 1a–3a. A methanolic solution (5 mL) of azo dye (1 mmol, 0.299 g, L_1; 1 mmol, 0.344 g, L_2; 1 mmol, 0.391 g, L_3) was added dropwise to a solution (5 mL) of $Cu(NO_3)_2 \cdot 4H_2O$ (1 mmol, 0.241 g) in the same solvent followed by PPh_3 (2 mmol, 0.524 g) and NaN_3 (2 mmol, 0.130 g) in warm methanol. The resultant mixture was stirred for 2 h, solid complexes precipitated, were collected by filtration, washed several times with 1 : 1 ethanol: water mixture and dried under vacuum over $CaCl_2$.

Compound 1a: Yield 61%; m.p. 140°C; Anal. Calcd for $C_{51}H_{40}N_9P_2SClCu$: C, 63.02; H, 4.14; N, 12.97; found: C, 62.69; H, 4.08; N, 13.10; IR (KBr, cm^{-1}) ν(C=N) 1585; ν(N=N) 1437; $\nu(PPh_3)$ 1483, 752, 694; $\nu(N_3)$ 2172; Λ_m (DCM, $\Omega^{-1}\,cm^2\,mol^{-1}$): 31.8; UV-Vis (DCM, λ_{max} nm): 601, 425, 348; Magnetic moment: μ, 1.89 B.M.

Compound 2a: Yield 61%; m.p. 120°C; Anal. Calcd for $C_{51}H_{40}N_9P_2SBrCu$: C, 60.27; H, 3.96; N, 12.40; found: C, 60.17; H, 4.02; N, 12.28; IR (KBr, cm^{-1}) ν(C=N) 1589; ν(N=N) 1435; $\nu(PPh_3)$ 1478, 748, 695; $\nu(N_3)$ 2172; Λ_m (DCM, $\Omega^{-1}cm^2mol^{-1}$): 27.8; UV-Vis (DCM, λ_{max} nm): 560, 420, 347; Magnetic moment: μ, 1.81 B.M.

Compound 3a: Yield 70%; m.p. 141°C; Anal. Calcd for $C_{51}H_{40}N_9P_2SICu$: C, 57.60; H, 3.79; N, 11.85; found: C, 57.48; H, 3.42; N, 11.84; IR (KBr, cm^{-1}) ν(C=N) 1601; ν(N=N) 1435; $\nu(PPh_3)$ 1478, 748, 694; $\nu(N_3)$ 2173; Λ_m (DCM, $\Omega^{-1}cm^2mol^{-1}$): 23.9; UV-Vis (DCM, λ_{max} nm): 584, 422, 352; Magnetic moment: μ, 1.81 B.M.

2.4.2. Copper(II) thiocyanato complexes 1b–3b. A methanolic solution (5 mL) of azo dye (1 mmol, 0.299 g, L_1; 1 mmol, 0.344 g, L_2; 1 mmol, 0.391 g, L_3) was added dropwise to a solution (5 mL) of $Cu(NO_3)_2 \cdot 4H_2O$ (1 mmol, 0.241 g) in the same solvent followed by PPh_3 (2 mmol, 0.524 g) and NH_4NCS (2 mmol, 0.152 g) in warm methanol. The resultant mixture was stirred for 2 h, the solid precipitated, was collected by filtration, washed several times with 1 : 1 ethanol : water mixture and dried under vacuum over $CaCl_2$.

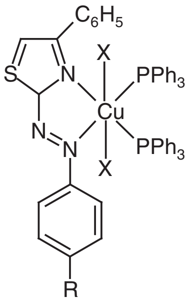
Complex 1b: Yield 64%; m.p. 280°C; Anal. Calcd for $C_{53}H_{40}N_5P_2S_3ClCu$: C, 63.39; H, 4.01; N, 6.98; found: C, 63.66; H, 3.97; N, 7.08; IR (KBr, cm^{-1}) ν(C=N) 1590; ν(N=N) 1437; $\nu(PPh_3)$ 1480, 744, 694; ν(NCS) 2096; Λ_m (DCM, $\Omega^{-1}cm^2mol^{-1}$): 25.4; UV-Vis (DCM, λ_{max} nm): 588, 432, 345; Magnetic moment: μ, 1.76 B.M.

Compound 2b: Yield 61%; m.p. 225°C; Anal. Calcd for $C_{53}H_{40}N_5P_2S_3BrCu$: C, 60.71; H, 3.84; N, 6.68; found: C, 60.62; H, 3.77; N, 6.78; IR (KBr, cm^{-1}): ν(C=N), 1590; ν(N=N), 1437; $\nu(PPh_3)$ 1478, 748, 694; ν(NCS), 2096; Λ_m (DCM, $\Omega^{-1}\,cm^2\,mol^{-1}$): 23.10; UV-Vis (DCM, λ_{max} nm): 578, 438, 350; Magnetic moment: μ, 1.88 B.M.

Compound 3b: Yield 67%; m.p. 280°C; Anal. Calcd for $C_{53}H_{40}N_5P_2S_3ICu$: C, 58.10; H, 3.68; N, 6.39; found: C, 58.02; H, 3.41; N, 6.36; IR (KBr, cm^{-1}) ν(C=N), 1596; ν(N=N) 1434; $\nu(PPh_3)$ 1478, 744, 693; ν(NCS), 2095; Λ_m (DCM, $\Omega^{-1}\,cm^2\,mol^{-1}$): 31.10; UV-Vis (DCM, λ_{max} nm): 572, 434, 348; Magnetic moment: μ, 1.80 B.M.

3. Results and discussion

The reaction of thiazolylazo ligands with Cu(II) salts in presence of PPh_3 and NaN_3 or NH_4NCS in 1 : 1 : 2 : 2 molar ratio yields mononuclear six-coordinate



R = Cl, Br, I; X = N_3^- (**1a**–**3a**), NCS^- (**1b**–**3b**)

Figure 1. Proposed structure of copper(II) complexes.

complexes (figure 1). The azo ligands are bidentate to copper *via* N, N′ donor sites. The air stable, moisture insensitive complexes are soluble in dichloromethane, acetonitrile, and chloroform producing intense violet solutions. The paramagnetic nature of all the complexes is consistent with +2 oxidation state. The conductivity data of the complexes in dichloromethane (10^{-3} M) indicates non-electrolytes.

3.1. *IR spectra*

Comparison of IR spectra of the azo dye with isolated metal complexes indicates the bonding. A strong band observed at 1618–1630 cm^{-1} in the spectra of L_1, L_2, and L_3 is due to $\nu(C{=}N)$ of the thiazole nitrogen. This band shifts to lower frequencies in the complexes indicating thiazole nitrogen coordinates [19]. The band at 744 cm^{-1} in the ligands remains unaltered in the spectra of complexes, indicating non-involvement of the thiazole sulfur. The $\nu(N{=}N)$ frequency of L_1, L_2, and L_3 at 1459–1468 cm^{-1} shifts to lower frequency (20–30 cm^{-1}) in the complexes, indicating participation of one nitrogen of the azo in complex formation [20, 21]. This was also supported by appearance of a new band at ~438 cm^{-1} due to the $\nu(M–N)$. The azido complexes **1a**, **2a**, and **3a** exhibit a strong sharp stretch corresponding to $\nu(N_3)$ at ~2172 cm^{-1}; similarly, the thiocyanato complexes **1b**, **2b**, and **3b** exhibit $\nu(NCS)$ at ~2095 cm^{-1}, typical for N-bonded thiocyanate [22]. The spectra of all Cu(II) complexes show triphenylphosphine bands at 1480, 744, and 694 cm^{-1} as expected.

3.2. *Electronic spectra and magnetic susceptibility*

Electronic spectra of all copper(II) complexes show a broad band centered at 580 nm assigned to $^2E_g \rightarrow {}^2T_2g$ transition in an octahedral environment [23]. The d–d absorption of thiocyanato complexes **1b**–**3b** are blue shifted by 10–20 nm compared to azido complexes **1a**–**3a**. The transition below 400 nm in complexes may be attributed to usual n–π^* and π–π^* transitions occurring within ligand orbitals. Room temperature magnetic susceptibilities of the complexes in the polycrystalline state fall in the 1.76–1.89 B.M. range, close to the spin only value of 1.73 B.M. for d^9.

Table 1. Spin Hamiltonian parameters and bonding coefficient for copper(II) complexes.

Complex	$g_{\|\|}$	$g_{\perp}$	G	g_{ave}	$A_{\|\|} \times 10^{-4}$	$A_{\perp} \times 10^{-4}$	α^2	β^2
1a	2.295	2.093	3.17	2.16	158	47	0.78	0.93
2a	2.295	2.107	2.75	2.16	140	46	0.84	0.93
3a	2.287	2.086	3.30	2.15	158	56	0.77	0.94
1b	2.186	2.040	4.65	2.08	187	56	0.65	0.72
2b	2.193	2.047	4.10	2.09	177	65	0.66	0.75
3b	2.189	2.040	4.72	2.09	177	47	0.65	0.74

3.3. *ESR spectra*

ESR spectra of the complexes in polycrystalline state at 298 K were recorded in the X band using 9.5 GHz field modulation with g factor quoted relative to the standard marker TCNE ($g = 2.00277$). ESR spectral assignments of the Cu(II) complexes along with the spin-Hamiltonian parameters are given in table 1. The ESR spectra of all compounds show typical axial behavior with slightly different $g_{||}$ and $g_{\perp}$ values. The geometric parameter G, a measure of the exchange interaction between the copper centers in the polycrystalline compounds, is calculated using the equation $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ for axial spectra. According to Hathaway [24, 25], if the value of G is greater than 4, exchange interaction is negligible, while a value of G less than 4 indicates a considerable exchange interaction. In all the copper(II) complexes $g_{\parallel} > g_{\perp} > 2.0023$ agrees with the ground state configuration of $d_{x^2-y^2}$. The axial symmetry parameter G is within the range 2.75–4.72, supporting axially elongated octahedral geometry [26].

The ESR parameters $g_{||}$, $g_{\perp}$, g_{ave}, $A_{||}$, and $A_{\perp}$ and the d–d transitions were used to evaluate the bonding parameters α^2 (a measure of covalancy of the in-plane σ-bonding between a copper 3d orbital and the ligand orbitals) and β^2 (covalancy of the in-plane π-bonding). Values of α^2 and β^2 were estimated from the following expression [27, 28], where $\alpha^2 = 1.0$ indicates complete ionic character and $\alpha^2 = 0.5$, 100% covalent bonding (assuming negligible small values of the overlap integral):

$$\alpha^2 = -(A_{\parallel}/0.036) + (g_{\parallel}/2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

$$\beta^2 = (g_{\parallel} - 2.0023)E/ - 8\lambda\alpha^2$$

where $\lambda = -828\,\text{cm}^{-1}$ for free copper ion and E is the electronic transition energy. The lower value of α^2 compared to β^2 indicates that the in-plane σ-bonding is more covalent than in-plane π-bonding. These data are in accord with reported values.

3.4. *Cyclic voltammetry*

Redox of the azo ligands and their copper(II) complexes were investigated in CH_2Cl_2 by cyclic voltammetry in the potential range +1.5 to −1.5 V with scan rate of $50\,\text{mVs}^{-1}$. The ligands displayed a quasireversible redox process ($\Delta E_{\text{p}} > 59\,\text{mV}$) for oxidation of the azo nitrogen at +0.41 to +0.44 V, and reduction at +0.19 to +0.28 V. For all the copper(II) complexes the reduction wave (E_{pc}, 0.30–0.51 V *vs.* saturated calomel

Table 2. Electrochemical data for copper(II) complexes.

	Oxidation potentials (V)			
Compound	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)
1a	0.39	0.50	110	0.445
2a	0.37	0.49	120	0.430
3a	0.25	0.38	130	0.315
1b	0.27	0.51	240	0.390
2b	0.24	0.37	130	0.305
3b	0.22	0.30	80	0.260

Supporting electrolyte: n-Bu_4NClO_4 (0.05 M); complex: 0.001 M; solvent: CH_2Cl_2; $\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively; $E_{1/2} = ½(E_{pa} + E_{pc})$; scan rate: 50 mVs^{-1}.

electrode, SCE) corresponds to Cu(II)/Cu(I). During the reverse scan the oxidation of Cu(I)/Cu(II) occurs in the potential range E_{pa}, 0.22–0.39 V. Peak to peak separations (ΔE_p) from 80 to 240 mV indicate that the process is quasireversible. Comparison of the electrochemical data of the complexes (table 2) reveals that the respective redox responses of Cu(II) complexes shifted to more negative potential with decrease in electron-withdrawing substituents on the azo ligands [29]; redox potential is less positive for **1b**–**3b** compared to **1a**–**3a**.

3.5. *Photoluminescence properties*

The photoluminescence properties of L_1, L_2, L_3, and their Cu(II) complexes were studied at room temperature in $CHCl_3$. The excitation spectra of L_1, L_2, and L_3 show a maximum at 340–345 nm. The emission spectra of ligands excited at 340–345 nm show an emission peak at 410–415 nm. The Cu(II) complexes show strong fluorescence with high-quantum yield (table 3); excitation at 345–350 nm gives an emission at 409–425 nm, assigned to π–π^* intraligand fluorescence, red shifted by > 80 nm. Emission intensity of the Cu(II) complexes is higher than that of free ligands. The enhanced fluorescence efficiency of the complexes is attributed to coordination increasing the rigidity, thereby reducing energy loss by thermal vibrational decay [30, 31]. Introduction of the substituent on the azo ligand has an interesting effect on the intensity of emission spectra (figure 2).

The fluorescence quantum yield of complexes was determined using quinine sulfate as reference with known Φ_R of 0.52. The area of emission spectrum was integrated using the software available in the instrument and quantum yield was calculated according to the following equation:

$$\Phi_S = A_S/A_R \times (Abs)_R/(Abs)_S \times \Phi_R$$

where Φ_S and Φ_R are the fluorescence quantum yield of the sample and reference, respectively, A_S and A_R are the area under the fluorescence spectra of the sample and reference, respectively, and $(Abs)_S$ and $(Abs)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation. The quantum yields are 0.01–0.09.

Table 3. Photoluminescence data of Cu(II) complexes.

Complex	Excitation wavelength (nm)	Emission maxima (nm)	Quantum yield, Φ
1a	348	416	0.011
2a	345	425	0.032
3a	345	420	0.030
1b	347	409	0.029
2b	350	416	0.099
3b	350	416	0.044

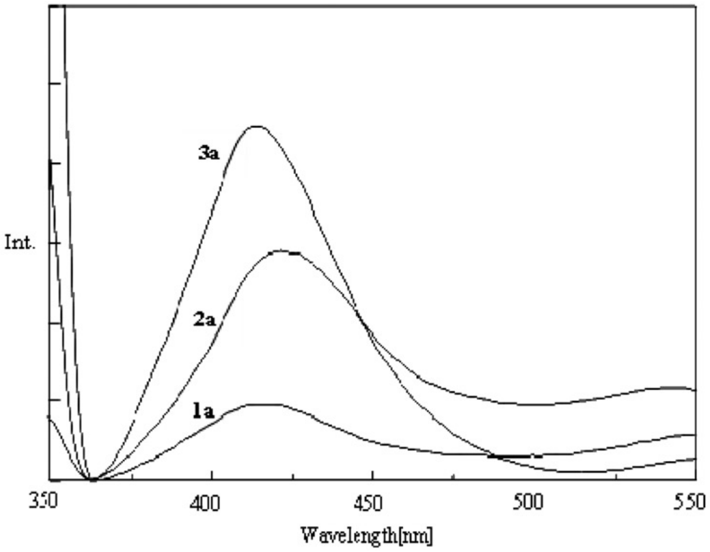


Figure 2. Emission spectra of **1a**, **2a**, and **3a** at room temperature.

4. Conclusions

In the present study, the synthesis and spectroscopic characterization of Cu(II) complexes of thiazolylazo dye with PPh_3 and N_3^- or NCS^- as coligands have been carried out by elemental analyses, IR, UV-Vis, and ESR spectral studies. Electronic spectral data and magnetic susceptibility measurements support octahedral geometry of the complexes. Cyclic voltammetry indicates that the redox responses of Cu(II) complexes shift to more negative potential with decrease in electron-withdrawing substituents on the azo ligand. In chloroform solution, the complexes show blue-green emission with high-quantum yield.

References

[1] G.G. Mohamed, Z.H. Abd El-Waheb. *Spectrochim. Acta, Part A*, **61**, 1059 (2001).
[2] P.K. Panchal, M.N. Patel. *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 1277 (2004).

[3] M.M. Mashaly, A.T. Ramadan, B.A. El-Shetary, A.K. Dawoud. *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 1319 (2005).

[4] M.S. Masoud, M.F. Amira, A.M. Ramadan, G.M. El-Ashry. *Spectrochim. Acta, Part A*, **69**, 230 (2008).

[5] R.C. Maurya, P. Sharma, D. Sutradhar. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 669 (2003).

[6] Y.T. Li, C.W. Yan, C.Y. Zhu, H.S. Guan. *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 1165 (2004).

[7] Y. Aydogdu, F. Yakuphanoglu, A. Aydogdu, E. Tas, A. Cukurovali. *Mater. Lett.*, **57**, 3755 (2003).

[8] S.H. Ramadan, H.K. Fun, B.K. Ghosh. *Polyhedron*, **24**, 3074 (2005).

[9] H.Y. Bie, J.H. Yu, J.Q. Xu, J. Lu, Y. Li, X.B. Cui, X. Zhang, Y.H. Sun, L.Y. Pan. *J. Mol. Struct.*, **660**, 107 (2003).

[10] X.-Y. Xu, T.-T. Xu, J. Gao, M.-Y. Wang, S.-R. Niu, S.-S. Ni, G.-X. Xu. *Synth. React. Inorg. Met.-Org. Chem.*, **36**, 681 (2004).

[11] W.M. Fabian, L. Antonov, D. Nedeltcheva, F.S. Kamounad, P.J. Taylor. *J. Phys. Chem.*, **108**, 7603 (1997).

[12] X. Chen, J. Zhang, H. Zhang, Z. Jiang, G. Shi, Y. Li, Y. Song. *Dyes and Pigments*, **77**, 223 (2008).

[13] S. Wu, W. Qian, Z. Xia, Y. Zou, S. Wang, S. Shen, H. Xu. *Chem. Phys. Lett.*, **330**, 535 (2000).

[14] Z.M. Zaki. *Spectrochim. Acta A*, **56**, 1917 (2000).

[15] P.P. Hankare, S.S. Chavan. *Indian J. Chem., Sect. A*, **42**, 540 (2003).

[16] P.P. Hankare, S.S. Chavan. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 423 (2003).

[17] M.M. Omar, G.G. Mohamed. *Spectrochim. Acta, Part A*, **61**, 929 (2005).

[18] B. Dash, M.K. Rout. *J. Ind. Chem. Soc.*, **32**, 663 (1955).

[19] G.G. Mohamed, N.E.A. El-Gamel, F. Teixidor. *Polyhedron*, **20**, 2689 (2001).

[20] T. Mathur, U.S. Ray, J.-C. Liou, J.-S. Wu, T.-H. Lu, C. Sinha. *Polyhedron*, **24**, 739 (2005).

[21] U. Ray, D. Banerjee, S. Chantrapromma, H.-K. Fun, J.-N. Lin, T.-H. Lu, C. Sinha. *Polyhedron*, **24**, 1071 (2005).

[22] B. Chand, U.S. Ray, G. Mostafa, T.H. Lu, C. Sinha. *Polyhedron*, **23**, 1969 (2004).

[23] N. Kabey, E. Erdem, R. Kilincarslan, E.Y. Sari. *Transit. Met. Chem.*, **32**, 1068 (2007).

[24] B.J. Hathaway, D.E. Billing. *Coord. Chem. Rev.*, **5**, 143 (1970).

[25] B.J. Hathaway. *Struct. Bond.*, **57**, 55 (1984).

[26] U. Ray, D. Banerjee, G. Mostafa, T.-H. Lu, C. Sinha. *New J. Chem.*, **28**, 1437 (2004).

[27] R.K. Ray, G.R. Kauffman. *Inorg. Chim. Acta*, **173**, 207 (1990).

[28] V.S.X. Anthonisamy, R. Murugesan. *Chem. Phys. Lett.*, **287**, 353 (1998).

[29] S. Baitalik, B. Adhikary. *Polyhedron*, **16**, 4073 (1997).

[30] S.H. Ramadan, R. Ghosh, T.H. Lu, B.K. Ghosh. *Polyhedron*, **24**, 1525 (2005).

[31] T. Yu, K. Zhang, Y. Zhao, C. Yang, H. Zhang, L. Qian, D. Fan, W. Dong, L. Chen, Y. Qiu. *Inorg. Chim. Acta*, **361**, 233 (2008).