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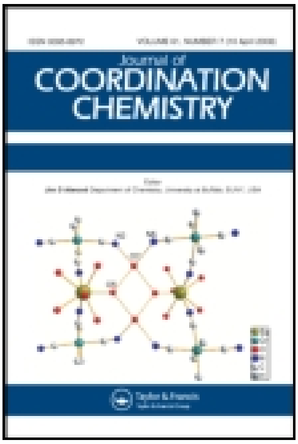

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Isothiocyanate and selenocyanate complexes of Cu(II), Ni(II), and Co(II) with a pyridylpyrazole-based ligand: synthesis, characterization, and structure

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Mononuclear NCS^- containing complexes, $[M(NCS)_2L]$ (L = *N,N-bis*(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine), $[Cu(NCS)_2L']$ (L′ = N-(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine), and $NCSe^-$ containing complexes $[ML(NCSe)(H_2O)]ClO_4$ ($M = Ni^{+2}$, Co^{+2}) have been synthesized and characterized by elemental analysis, spectroscopic, and physico-chemical methods. Structural studies of $[Cu(NCS)_2L']$ show copper is five coordinate with distorted trigonal bipyramidal geometry with two *cis* NCS^-. $[M(NCS)_2L]$ and $[ML(NCSe)(H_2O)]ClO_4$ ($M = Ni^{+2}$ and Co^{+2}) are expected to be octahedral.

Keywords: Cu(II), Ni(II), and Co(II) complexes; Tetradentate ligand; Tridentate ligand; NCS^- and $NCSe^-$ ions; Mononuclear complex; Crystal structure

1. Introduction

Pseudohalide-containing transition metal complexes can form mono-, di-, and polynuclear complexes using different blocking ligands and they have potential applications as magnetic materials. Pseudohalides can bind to metal ions end-to-end or end-on, generally forming polyatomic molecules. Among the psuedohalides, azido-bridged complexes are most studied; thiocyanate-bridged complexes are fewer and they are not widely used as magnetic materials [1–4].

Metal complexes of nitrogen-containing heterocyclic ligands have biological activity. Metal complexes of pyrazole-based ligands have been used as models for the active sites of metalloenzymes [5–8]. As our interest was in the synthesis of new transition metal complexes with biologically active pyrazole-based ligands, we were interested to study complexing properties of N_4-coordinated *N,N-bis*(3,5-dimethylpyrazol-1-ylmethyl) aminomethylpyridine. Recently, we reported synthesis, structure, and magnetic properties of azido-bridged binuclear complexes of Ni(II) and Cu(II) with the ligand [9].

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There are some reports on tridentate pyrazole and pseudohalide-containing complexes of Cu(II), Ni(II), and Co(II) [10–14], but tetradentate N_4-containing pseudohalide complexes are limited [15]. In continuation of our research on pseudohalide-containing polynuclear complexes with L, we report here the syntheses, spectroscopic characterization, and crystal structure of mononuclear complexes $[M(NCS)_2L]$, $[M(NCSe)(H_2O)]ClO_4$, and $[Cu(NCS)_2L']$, where L = *N,N-bis*(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine, L′ = N-(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine, M = Ni^{+2} and Co^{+2}. The ligand L′ is transformed from L during reaction. The crystal structure of $[Cu(NCS)_2L']$ is reported.

2. Experimental

2.1. *Materials and methods*

Chemicals and solvents were of analytical grade. 2-(Aminomethyl)pyridine (Aldrich), hydrazine hydrate (GR, Loba, India), acetylacetone (GR, Loba, India), paraformaldehyde (GR, Loba, India), copper carbonate and nickel carbonate (Loba, India), potassium thiocyanate (Qualigens, India), and potassium selenocyanate (99%) (Aldrich) were used as received. *N*-(hydroxymethyl)-3,5-dimethylpyrazole [16] and *N,N-bis*(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine (L) [9] were synthesized by published procedures. Solvents were purified following the standard procedures.

2.2. *Instruments*

Infrared spectra were recorded on a Perkin Elmer FT-IR spectrometer RX1 using KBr pellets. The elemental analysis was carried out using a Perkin Elmer IA 2400 series elemental analyzer. UV-Vis spectra (900–190 nm) were recorded on a Perkin Elmer spectrophotometer model Lambda 35 in acetonitrile. Room temperature magnetic susceptibilities of powder samples were measured using a Faraday magnetic balance equipped with a Mettler UMX 5 balance, OMEGA temperature controller with a field strength of 0.8 Tesla using $Hg[Co(SCN)_4]$ as the reference. $M(ClO_4)_2{\cdot}6H_2O$ (M = Cu^{+2}, Ni^{+2}, and Co^{+2}) were prepared on the treatment of metal carbonate with dilute $HClO_4$ acid and followed by slow evaporation of the solution.

2.3. *Syntheses of compounds*

2.3.1. $[Cu(NCS)_2L']$ (1). A solution of L (0.324 g, 1 mmol) in methanol (10 mL) was added to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.242 g, 1 mmol) in methanol (10 mL). The color changed to deep blue immediately. To this solution, potassium thiocyanate (0.192 g, 2 mmol) in methanol was added dropwise with stirring. After 3 h, the mixture was filtered off and the solution was left for slow evaporation. Blue crystals were obtained after five days. Found (%): C, 42.50; H, 4.05; and N, 21.28. Anal. Calcd for $C_{14}H_{16}CuN_6S_2$(%): C, 42.43; H, 4.04; and N, 21.21; Yield, 0.158 g (40%). IR (KBr pellet) cm^{-1}; ν(>NH), 3129; $\nu(NCS^{-1})$, 2091 vs; ν(C=C) + ν(C=N)/pyrazole ring, 1607 s, 1559 vs. UV-Vis spectra: λ_{max} (nm) (ε_{max}(mol^{-1} cm^{-1})): 700(65), 390(6213), 382(6534), 370(14,880). Λ_M (Ω^{-1} cm^2 mol^{-1}); 10. $\mu_{eff} = 1.80$ BM.

2.3.2. [Ni(NCS)$_2$L] (2). A methanol solution (10 mL) in L (0.324 g, 1 mmol) was added dropwise to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.290 g, 1 mmol) in methanol (10 mL). To this solution, potassium thiocyanate (0.192 g, 2 mmol) in methanol (10 mL) was added dropwise. After 2 h, sky blue compound was filtered off, washed with methanol, and dried in vacuum. Yield: 0.250 g (50%). Found(%): C, 48.46; H, 4.87; and N, 22.64; Anal. Calcd for $C_{20}H_{24}NiN_8S_2$(%): C, 48.10; H, 4.81; and N, 22.45; MS (EI): *m*/*z* 440 (100%) $(C_{19}H_{24}N_7SNi)^+$. IR (KBr pellet) cm^{-1}; ν(NCS$^-$), 2091, ν(C=C) + ν(C=N)/pyrazole ring, 1607 s, 1550 vs. UV-Vis spectra: λ_{max}(nm) (ε_{max}(mol^{-1} cm^{-1})): 535(sh, 15), 350(sh), 270(24,560). Λ_M (CH_3CN) (Ω^{-1} cm^2 mol^{-1}); 10. $\mu_{eff} = 2.88$ BM.

2.3.3. [Co(NCS)$_2$L] (3). A solution of L (0.324 g, 1 mmol) in methanol (10 mL) was added to a solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1 mmol) in methanol (10 mL). The color changed to bluish violet immediately. To this solution, potassium thiocyanate (0.192 g, 2 mmol) in methanol was added dropwise with stirring. After 2 h, the mixture was filtered and the solution was left for slow evaporation. Light purple powder was obtained after slow evaporation. Found(%): C, 48.15; H, 4.85; and N, 22.28. Anal. Calcd for $C_{20}H_{24}CoN_8S_2$(%): C, 48.10; H, 4.81; and N, 22.44; Yield: 0.300 g (60%). MS (EI): *m*/*z* 441(100%) $[C_{19}H_{24}N_7SCo]^+$. IR (KBr pellet) cm^{-1}; ν(NCS$^-$), 2081 vs, ν(C=C) + ν(C=N)/pyrazole ring, 1603 s, 1555 vs. UV-Vis spectra: λ_{max}(nm) (ε_{max}(mol^{-1} cm^{-1})) 750(sh), 580(285), 490(123), 325(17,425), 285 (29,710). Λ_M (CH_3CN) (Ω^{-1} cm^2 mol^{-1}); 8. $\mu_{eff} = 3.89$ BM.

2.3.4. [Ni(NCSe)L(H$_2$O)]ClO$_4$ (4). A solution of L (0.324 g, 1 mmol) in methanol (10 mL) was added to a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.365 g, 1 mmol) in methanol (10 mL) in the dark. After 10 min, potassium selenocyanate (0.192 g, 2 mmol) in methanol was added dropwise with stirring. After 1 h, the light blue precipitate was filtered off, washed with methanol, and dried. Yield: 0.330 g (55%). Found (%): C, 38.02; H, 4.19; and N, 16.45. Anal. Calcd. for $NiC_{19}H_{26}N_7SeClO_5$(%): C, 37.66; H, 4.29; N, 16.19. MS (EI): *m*/*z* 488 $(C_{19}H_{24}N_7SeNi)^+$. IR (KBr pellet), cm^{-1}: ν(OH$^-$), 3437 s, br; ν(NCSe^{-1}), 2091 vs; ν(C=C) + ν(C=N)/pyrazole ring, 1608 s, 1559 vs; ν_{asmy}(Cl–O), 1086 vs; δ(O–Cl–O), 627 s. UV-Vis spectra λ_{max}(nm) (ε_{max}(mol^{-1} cm^{-1})) 600(sh), 535(15), 270(21,350). Λ_M (CH_3CN) (Ω^{-1} cm^2 mol^{-1}); 118. $\mu_{eff} = 2.89$ BM.

2.3.5. [Co(NCSe)L(H$_2$O)]ClO$_4$ (5). A solution of L (0.324 g, 1 mmol) in methanol (10 mL) was added to a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.365 g, 1 mmol) in methanol (10 mL) in the dark. After 10 min, potassium selenocyanate (0.288 g, 2 mmol) in methanol (15 mL) was added dropwise with constant stirring. After 1 h, the mixture was filtered and the solution was left for slow evaporation. Brownish compound was obtained after a few days. Yield: 0.360 g (60%). Found (%): C, 37.98; H, 4.25; and N, 16.50. Anal. Calcd for $CoC_{19}H_{26}N_7SeClO_5$(%): C, 37.66; H, 4.29; and N, 16.19. MS (EI): *m*/*z* (100%) 489 $(C_{19}H_{24}N_7SeCo)^+$. IR (KBr pellet), cm^{-1}: ν(OH$^-$), 3427 s, br; ν(NCSe^{-1}), 2107 vs; ν(C=C) + ν(C=N)/pyrazole ring, 1604 s, 1556 vs; ν_{asmy}(Cl–O), 1102 vs; δ(O–Cl–O), 628 s. UV-Vis spectra: λ_{max}(nm) (ε_{max}(mol^{-1} cm^{-1})) 700(sh), 576(281), 484(183), 346(20,426), 287(30,244). Λ_M (CH_3CN) ($\Omega^{-1}cm^2mol^{-1}$); 116. $\mu_{eff} = 3.90$ BM.

2.4. *X-ray crystallography*

2.4.1. X-ray crystal data and refinement. Crystallographic data and details of data collection for **1** are given in table 1. Single crystals of suitable size of **1** were obtained by slow evaporation of methanol. A deep blue crystal was mounted on glass fiber with epoxy resin. Data were collected with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K on a Bruker SMART APEX diffractometer equipped with a CCD area detector. Of the 17,510 reflections, 3420 with $I > 2\sigma(I)$ were used for structure solutions. The data were processed with SAINT [17] and empirical absorption correction was applied with SADABS [18] programs. The structure was solved by direct methods using SHELXTL [19] and the refinement was based on $|F|^2$ by full-matrix least-squares using SHELXL-97 [20]. All non-hydrogen atoms were refined with anisotropic displacement parameter. Hydrogen positions were calculated from the difference Fourier map.

2.4.2. Description of crystal structure of 1. The molecular structure of the complex and the atom-labeling scheme are shown in figure 1. Selected bond lengths and angles

Table 1. Crystal data and structure refinement for **1**.

Formula	$C_{14}H_{16}CuN_6S_2$
Formula weight	395.99
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions (Å, °)	
a	16.375(3)
b	14.173(3)
c	14.954(3)
α	90
β	90
γ	90
Volume (Å^3), *Z*	3470.6(12), 8
Density calculated (Mg m^{-3})	1.516
Absorption coefficient (mm^{-1})	1.506
F(000)	1624
Crystal size (mm^3)	0.58 × 0.37 × 0.33
θ range for data collection (°)	2.34–26.00
Index ranges	$-18 \leq h \leq 20$; $-17 \leq k \leq 14$; $-18 \leq l \leq 18$
Reflections collected	17,510
Independent reflections	3420 [R(int) = 0.0352]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6364 and 0.4754
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3420/0/206
Goodness-of-fit on F^2	1.174
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0885$, $wR_2 = 0.2441$
R indices (all data)	$R_1 = 0.1201$, $wR_2 = 0.2635$
Largest difference peak and hole (e Å^{-3})	0.932 and −0.354

related to the metal coordination sphere for the structure are given in table 2. The structure shows that two *cis* NCS$^-$ ions are bonded to copper through nitrogen. N-(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine (L′) is tridentate through pyridine nitrogen (N1), secondary amine nitrogen (N2), and a pyrazole nitrogen (N4). Copper is five coordinate with distorted trigonal bipyramidal CuN_5 from L′ and N5 and N6 from two NCS$^-$. The Cu–N2, Cu–N1 and Cu–N4 bond distances are 1.992, 1.999, and 1.981 Å, respectively, while Cu–N5 (2.096 Å) and Cu–N6 (2.012 Å) from two NCS$^-$ are approximately equal to each other. N6–C14–S2 of 177.9° is linear compared to N5–C13–S1 of 162.4°.

3. Results and discussion

3.1. *General characterization*

The tetradentate *N,N-bis*(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine (L) was synthesized and characterized as per published procedure [9]. Mononuclear complexes

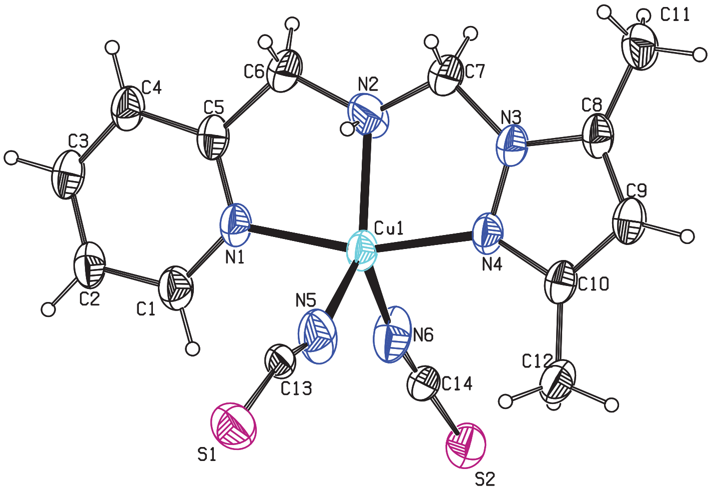
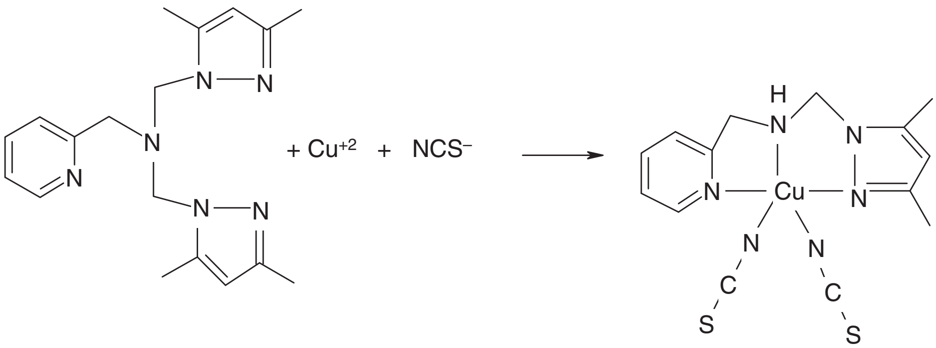


Figure 1. ORTEP diagram of **1** with atom numbering scheme.

Table 2. Bond lengths (Å) and angles (°) of **1**.

Bond lengths		Bond angles	
Cu(1)–N(4)	1.981(6)	N(4)–Cu(1)–N(2)	80.5(3)
Cu(1)–N(2)	1.992(10)	N(4)–Cu(1)–N(1)	161.8(3)
Cu(1)–N(1)	1.999(6)	N(2)–Cu(1)–N(1)	81.3(3)
Cu(1)–N(6)	2.012(10)	N(4)–Cu(1)–N(6)	97.0(3)
Cu(1)–N(5)	2.096(10)	N(2)–Cu(1)–N(6)	126.4(5)
		N(1)–Cu(1)–N(6)	95.2(3)
		N(4)–Cu(1)–N(5)	97.3(3)
		N(6)–Cu(1)–N(5)	104.5(5)



Scheme 1. Synthesis of $Cu(NCS)_2L$.

$[M(NCS)_2L]$ ($M = Ni^{+2}$ and Co^{+2}) and $[Cu(NCS)_2L']$ were obtained in good yield (~50%) through one-pot reaction of metal salt (nitrate/perchlorate/acetate), L and sodium thiocyanate in 1 : 1 : 2 mole ratio in methanol. Complexes containing NCS^- were mononuclear even on changing starting metal salts during the preparation of complexes. Similar NCS^- containing mononuclear complexes are reported [10–15]. The tetradentate N_4–L is transformed into tridentate N_3-coordinated L′ with Cu^{+2}, NCS^- and L under reaction condition for the formation of five-coordinate copper (scheme 1). Isolation of 3,5-dimethylpyrazole from reaction leading to **1** suggests that Cu^{+2} promotes the cleavage of C–N single bond of L in the presence of methanol. Such change of ligand and consequent change of geometries during complexation are already reported [21–23]. When complexation with Cu(II) is carried out in solvents other than alcohol, we obtained product with unknown composition. For Ni(II) and Co(II) complexes, L is expected to utilize all four potential N_4-donor sites plus two nitrogen donor sites from NCS^- to form octahedral complexes. Diffraction quality crystals for structural studies were obtained only for copper complex by slow evaporation of the solution; we were unsuccessful with nickel and cobalt complexes. All complexes (**1–3**) are moderately soluble in acetonitrile, alcohol, and DMF but insoluble in dichloromethane, acetone, etc. Conductance measurements show that all the complexes are nonelectrolytes indicating both NCS^- are coordinated. The complexes gave satisfactory microanalytical data. The crystal structure of $[Cu(NCS)_2L']$ shows two *cis* NCS^- attached to copper. Due to the unavailability of X-ray quality single crystals, the structures of **2** and **3** could not be solved. However, based on spectroscopic and other physicochemical data, we expect that both Ni(II) and Co(II) complexes are octahedral two *cis* NCS^- ions.

The mononuclear selenocyanate complexes were synthesized in good yield (>50%) through one-pot reaction of metal perchlorate, L, and sodium selenocyanate in 1 : 1 : 2 mole ratio in methanol. For copper, we obtained gummy product with unknown composition. Complexes **4** and **5** gave satisfactory microanalyses confirming their composition. The ESI–MS spectral measurement showed an intense peak (100%) at *m*/*z* 489 indicating the integrity of the complexes in solution. The complexes are moderately soluble in acetonitrile but insoluble in dichloromethane, acetone, etc. Conductivity in CH_3CN shows that **4** and **5** are 1 : 1 electrolytes indicating the presence of ClO_4^- as counter anion. Due to unavailability of diffraction quality crystals, crystal structures of **4** and **5** could not be solved. On the basis of spectral, magnetic, and microanalytical data, we expect that the complexes are octahedral.

3.2. *IR spectra*

The IR spectrum of the free ligand and **1–5** show two strong bands at 1604–1556 cm^{-1} due to pyrazole $\nu(\mathrm{C{=}N}) + \nu(\mathrm{C{=}C})$ vibrations indicating coordination of pyrazole to the metal. One strong band at *ca* 2085 cm^{-1} for NCS^- containing complexes **1–3** and at 2077 cm^{-1} for NCSe^- containing complexes **4** and **5** indicate bonding of NCS^- and NCSe^-. Position and nature of NCS^- spectral bands for **1–3** are the same type indicating *cis* NCS^- for cobalt and nickel complexes like the Cu(II) complex. For **1**, one band at 3129 cm^{-1} due to $\nu(>\mathrm{NH})$ is absent in other complexes indicating the transformation of ligand of **1**. Two strong bands at 1102 and 628 cm^{-1} indicate the presence of ClO_4^- as counter anion and one broad brand at ~3437 cm^{-1} is due to $\nu(\mathrm{OH}^-)$ from water present in **4** and **5** [24]. All other bands of the ligand are also present in the complexes.

3.3. *Electronic spectral analysis and magnetic susceptibility*

The electronic spectra of the complexes were measured in $\mathrm{CH_3CN}$. Very similar bands appear in both NCS^- and NCSe^- complexes. Electronic spectral bands at higher wavelength (800–400 nm) are attributed to d–d transitions or metal-to-ligand charge transfer and spectral bands below 400 nm are due to intraligand charge transfer. Room temperature magnetic susceptibilities show one electron paramagnetism for **1** [μ_{eff} ~1.80 BM], two electron paramagnetism for **2** and **4** [μ_{eff} ~ 2.88 BM], and three electron paramagnetism for **3** and **5** [μ_{eff} ~ 3.90 BM]. This indicates that **2** and **4** and **3** and **5** have the same geometries.

4. Conclusion

Three mononuclear complexes $[\mathrm{M(NCS)_2L}]$ ($\mathrm{M} = \mathrm{Ni}^{+2}$, Co^{+2}) (L = *N,N-bis*(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine), $[\mathrm{Cu(NCS)_2L'}]$ (L′ = *N*-(3, 5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine), and two NCSe^- containing complexes, $[\mathrm{ML(NCSe)(H_2O)}](\mathrm{ClO_4})$ are reported. Compared to azido complexes, all NCS^- coordinated complexes are mononuclear. Crystal structure of $[\mathrm{Cu(NCS)_2L'}]$ shows that it has distorted trigonal bipyramidal geometry.

Supplementary material

Crystallographic data for the structural analysis have been deposited with CCDC no. 784906 for **1**. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk). Mass spectra of Ni(II) and Co(II) complexes are available as a supplementary material in the online version of this article.

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References

[1] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama, R. Rozo. *Coord. Chem. Rev.*, **193–195**, 1027 (1999).
[2] O. Khan. *Molecular Magnetism*, VCH, New York (1993).
[3] C.G. Pierpont, D.N. Hendrickson, D.M. Duggan, F. Wagner, E.K. Barefield. *Inorg. Chem.*, **14**, 604 (1975).
[4] P. Chaudhuri, R. Wagner, S. Khanra, T. Weyhermuller. *J. Chem. Soc., Dalton Trans.*, 4962 (2006).
[5] K.D. Karlin, Z. Tyeklar, *Bioinorganic Chemistry of Copper*, Chapman & Hall, New York (1993).
[6] Z. Tyeklár, R.R. Jacobson, N. Wei, N.N. Murthy, J. Zubieta, K.D. Karlin. *J. Am. Chem. Soc.*, **106**, 2677 (1984).
[7] W.G. Haanstra, W.A.J.W. van der Donk, W.L. Driessen, J. Reedijk, J.S. Wood, M.G.B. Draw. *J. Chem. Soc., Dalton Trans.*, 3123 (1990).
[8] N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa, Y. Morooka. *J. Am. Chem. Soc.*, **113**, 5664 (1991).
[9] Z. Mahendrasinh, S.B. Kumar, E. Suresh, J. Ribas. *Transition Met. Chem.*, **35**, 757 (2010).
[10] R. Gupta, T.K. Lal, R. Mukherjee. *Polyhedron*, **21**, 1245 (2002).
[11] J.G. Haasnoot, W.L. Drissen, J. Reedijk. *Inorg. Chem.*, **23**, 2803 (1984).
[12] T.L. Lal, R. Gupta, S. Mahapatra, R. Mukherjee. *Polyhedron*, **18**, 1743 (1999).
[13] R. Gupta, R. Mukherjee. *Polyhedron*, **20**, 2545 (2001).
[14] S.-C. Sheu, M.-J. Tien, M.-C. Cheng, T.-I. Ho, S.-M. Peng, Y.-C. Lin. *J. Chem Soc., Dalton Trans.*, 3503 (1995).
[15] U. Mukhopadhyay, I. Bernal, S.S. Massoud, F.A. Mautner. *Inorg. Chim. Acta.*, **357**, 3673 (2004).
[16] W.L. Driessen. *Recl. Trav. Chim. Pays-Bas*, **101**, 441 (1982).
[17] G.M. Sheldrick. *SAINT*, 5.1 ed. Siemens Industrial Automation Inc., Madison, WI (1995).
[18] G.M. Sheldrick. *SADABS, Empirical Absorption Correction Program*, University of Göttingen, Göttingen, Germany (1997).
[19] G.M. Sheldrick. *SHELXTL Reference Manual (Version 5.1)*, Bruker AXS, Madison, WI (1997).
[20] G.M. Sheldrick. *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen, Göttingen (1997).
[21] S. Bhattacharyya, T.J.R. Weakley, M. Chaudhury. *Inorg. Chem.*, **38**, 633 (1999).
[22] S. Bhattacharyya, T.J.R. Weakley, M. Chaudhury. *Inorg. Chem.*, **38**, 5453 (1999).
[23] B. Barszcz, T. Glowiak, J. Jezierska, A. Tomkiewicz. *Polyhedron*, **23**, 1309 (2004).
[24] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B, Application in Coordination, Organometallic, and Bioinorganic Chemistry*, John Wiley & Sons Inc., New York (1997).