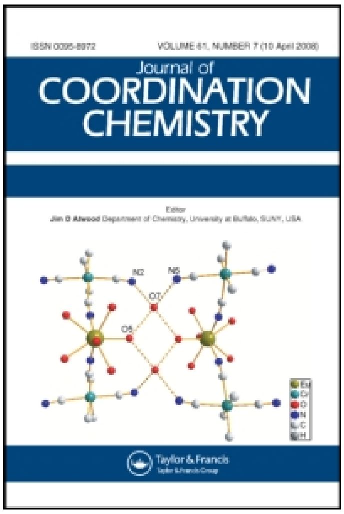

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure, and properties of a new cadmium(II) polymer with mixed Cl^-/SCN^- ligands: [CdCl(SCN)]*_n*

Jian-Jun Zhang[a]
[a] School of Material Science and Engineering, Nanchang Hangkong University, Nanchang 330063, P.R. China

To cite this Article Zhang, Jian-Jun(2010) 'Synthesis, crystal structure, and properties of a new cadmium(II) polymer with mixed Cl^-/SCN^- ligands: [CdCl(SCN)]*_n*', Journal of Coordination Chemistry, 63: 7, 1139 — 1146

To link to this Article: DOI: 10.1080/00958971003725375

URL: http://dx.doi.org/10.1080/00958971003725375

Journal of Coordination Chemistry
Vol. 63, No. 7, 10 April 2010, 1139–1146

Synthesis, crystal structure, and properties of a new cadmium(II) polymer with mixed Cl^-/SCN^- ligands: $[CdCl(SCN)]_n$

JIAN-JUN ZHANG*

School of Material Science and Engineering, Nanchang
Hangkong University, Nanchang 330063, P.R. China

(*Received 9 June 2009; in final form 17 November 2009*)

A 1-D chain complex, cadmium(II) chloride thiocyanate (**1**), $[CdCl(SCN)]_n$ was synthesized by evaporation and characterized by single-crystal X-ray diffraction and FT-IR techniques. The compound crystallizes in the space group *Pnma* of orthorhombic system with cell parameter $a = 9.5967(7)$, $b = 4.2595(3)$, and $c = 10.1789(7)$ Å; $V = 416.08(5)$ Å^3 and $Z = 4$. The cadmium(II) is five-coordinate, surrounded by one pair of (μ-1,1-NCS) bridging NCS^- and three Cl^- as a μ_3-linker coordinating three Cd(II) centers, approximately a severely distorted square-pyramidal configuration. Cd(II), Cl^-, and SCN^- form an infinite 1-D chain with chair-like features, a new example of mixed Cd–NCS–Cl discrete compounds. The photophysical properties of the crystals have been investigated with one emission peak at 473 nm observed for the title complex in the solid state, which exhibits blue luminescence. The mechanical properties of the crystals have been studied using Vickers microhardness tester and the hardness was 78.6 kg mm^{-2}.

Keywords: Cadmium(II) coordination polymer; Crystal structure; Photoluminescence properties; Mechanical properties

1. Introduction

Supramolecular metal complexes formed by self-assembly have attracted a great deal of attention because of their potential applications as catalysts, molecular recognition, molectronics, photonic materials, etc. [1–8]. Coordination polymers can form 1-D, 2-D, or 3-D networks [9–14]; all have been obtained by changing the organic ligand [15, 16].

The pseudohalide NCS^- is a versatile bridging ligand coordinating end-on (μ-1,1-NCS, μ-1,1-SCN) or end-to-end (μ-1,3-NCS). The thiocyanate may link a third metal giving μ-1,1-3 (μ-N,N,S or μ-S,S,N) [17]. Cadmium-thiocyanate coordination solids are of considerable interest owing to their topological aspects [18], potential applications in electrooptics and piezoelectricity [19] and the second harmonic generation (SHG) [20]. In this article, we report the synthesis, structure, and properties of a new and very interesting polymeric complex with mixed Cl^-/SCN^- ligands, $[CdCl(SCN)]_n$.

---

*Email: zhangjianjun71@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958971003725375

2. Experimental

All chemicals and solvents obtained from commercial sources were of A.R. grade and used without purification. The IR spectrum of **1** was recorded from 400 to 4000 cm^{-1} employing a Nicolet 5700 spectrometer (Nicolet Corporation, USA) by KBr pellets. Elemental analyses were performed on a Perkin-Elmer 240 instrument (Perkin Elmer Instruments Corporation, USA). The chemical composition of **1** was determined by the carbon, hydrogen, nitrogen, and sulfur test. Single-crystal X-ray diffraction (XRD) analysis was carried out using a Bruker Smart Apex CCD diffractometer (Brucker Corporation, Germany) with Mo-Kα ($\lambda = 0.710703$ Å) radiation to identify the structure and to estimate the lattice parameters. Luminescence (excitation and emission) spectra for the solid samples were determined using a Perkin-Elmer LS-55 spectrophotometer (Perkin Elmer Instruments Corporation, USA).

2.1. *Synthesis of 1*

Compound **1** was synthesized according to the following reaction:

$$CdCl_2 + NH_4SCN \rightarrow CdCl(SCN) + NH_4Cl \qquad (1)$$

In the reaction, 22.8 g $CdCl_2 \cdot 2.5H_2O$ and 7.6 g NH_4SCN were added into 100 mL doubly distilled water and stirred for 5 h to obtain a homogeneous mixture. Then the mixture was filtered. The filtrate stood at room temperature for 3 weeks, and colorless crystals suitable for XRD study were obtained. Yield 70%. Anal. Calcd (%) for CClNSCd: C, 5.83; N, 6.80; S, 15.57. Found (%): C, 5.79; N, 6.62; S, 15.36.

2.2. *X-ray crystallography*

The crystal structures of the title compounds were determined from single-crystal XRD data. Intensity data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 153 K. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 employing the SHELX 97 program package [21, 22]. Crystallographic data and experimental details for the structure analysis of **1** are listed in table 1.

3. Results and discussion

3.1. *Description of the crystal structure*

Cadmium(II) chloride thiocyanate $[CdCl(SCN)]_n$ crystal and crystal data are first reported. Atomic coordinates and equivalent isotropic displacement parameters are given in "Supplementary material". Bond lengths and angles are listed in table 2. The ORTEP of **1** is shown in figure 1.

Single-crystal XRD analysis indicates that **1** crystallizes in the space group *Pnma* (No. 62) of orthorhombic system. Cadmium is coordinated to three chlorides and two nitrogens from two thiocyanates. N(1), N(#3), Cd(1), and Cl(1) are almost on a trigonal plane and two chlorine atoms (Cl(#1) and Cl(#2)) lie on the same side of

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

Chemical formula	CdCl(SCN)
Formula weight	205.93
Temperature (K)	153(2)
Wavelength (Å)	0.71073
Space group	*Pnma*
Crystal system	Orthorhombic
Crystal size (mm^3)	$0.26 \times 0.12 \times 0.05$
Unit cell dimensions (Å, °)	
a	9.5967(7)
b	4.2595(3)
c	10.1789(7)
α	90
β	90
γ	90
Volume (Å^3), Z	416.08(5), 4
Calculated density ($mg\,m^{-3}$)	3.287
θ range for data collection (°)	2.92–25.45
Limiting indices	$-11 \le h \le 11$; $-4 \le k \le 5$; $-12 \le l \le 12$
$F(000)$	376
Absorption coefficient (mm^{-1})	6.173
Reflections collected/unique	2357/429 [$R(\text{int}) = 0.0540$]
Completeness to $\theta = 25.45\%$	97.3
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	429/0/32
Goodness-of-fit on F^2	0.926
Final R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.0573$, $wR_2 = 0.1713$
R indices (all data)	$R_1 = 0.0583$, $wR_2 = 0.1724$
Largest difference peak and hole (e Å^{-3})	1.438 and −2.155

[a] $\sum \|F_o| - |F_c\| / \sum |F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

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

Cd(1)–Cl(1)	2.751(7)	Cl(1)–Cd(1)–N(1)	128.8(5)
Cd(1)–Cl(1)#1	2.983(1)	Cl(#1)–Cd(1)–N(1)	71.0(5)
Cd(1)–N(1)	2.762(19)	N(#3)–Cd(1)–N(1)	101.3(1)
S(1)–C(1)	1.56(3)	Cl(#1)–Cd(1)–Cl(1)	76.1(1)
N(1)–C(1)	1.16(4)	Cl(#2)–Cd(1)–Cl(1)	76.1(1)
		C(1)–N(1)–Cd(1)	127.3(6)
		N(1)–C(1)–S(1)	177(3)

Symmetry transformations used to generate equivalent atoms: #1: $[2-x, y-1/2, 1-z]$; #2: $[2-x, y+1/2, 1-z]$; #3: $[x, 1+y, z]$.

the trigonal plane. Addison *et al.* [23] have used an angular structural parameter τ (index of trigonality) for distinguishing between a trigonal-bipyramidal and a square-pyramidal geometry in five-coordinate metal complexes. The angular structural parameter τ was calculated using the expression:

$$\tau = \beta - \alpha / 60^\circ \tag{2}$$

where α and β are the two largest angles, $\tau = 0$ for an ideal square-pyramid ($\alpha = \beta = 180^\circ$), and $\tau = 1$ for an ideal trigonal-bipyramid ($\alpha = 120^\circ$ and $\beta = 180^\circ$). The τ value is 0.46 for **1**, indicating that each Cd(II) in the 1-D infinite chain (figure 2a) has a severely distorted square-pyramidal geometry. One chloride (Cl(1)) and two nitrogens (N(1) and N(#3)) from the thiocyanate form an almost trigonal planar arrangement

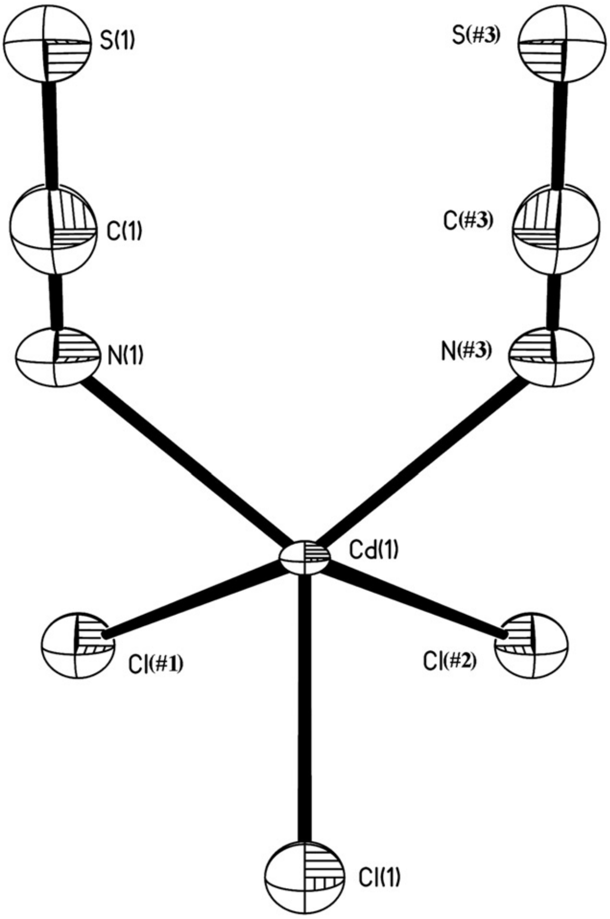

Figure 1. An ORTEP of the structure of **1**. Symmetry transformations used to generate equivalent atoms: #1: $[2-x, y-1/2, 1-z]$; #2: $[2-x, y+1/2, 1-z]$; #3: $[x, 1+y, z]$.

around Cd; the other chlorides (Cl(#1) and Cl(#2)) form very long contacts to generate a five-coordinate Cd. However, these contacts lie on the same side of the trigonal plane giving irregular five-coordination. Each thiocyanate bridges two Cd(II)'s with the angle of 102.4(3)° and Cd–N bond distance of 2.762(19) Å, much longer than those reported in the literature [24, 25]. Each Cl^- is a μ_3-linker coordinating three Cd(II) centers with bond distances between Cd and Cl from 2.751(7) to 2.983(1) Å (table 2), much longer than those reported in [25, 26]. Arrangement of these Cd(II), Cl^-, and SCN^- results in the formation of a 1-D unique, chair-like polymer chain (figure 2a). Furthermore, the chair-like unit consists of four-membered rings, Cd–Cl–Cd–Cl. The intramolecular $Cd \cdots Cd$ distance in **1** is about 4.3062(5) Å, shorter than $Cd \cdots Cd$ separation [5.6423(3) Å] through bi-bridged thiocyanates [25].

Figure 2(b) shows very clearly that the infinite chain propagates along crystallographic *b*-axis and the adjacent chains are antiparallel. The weak $Cd \cdots S$ contacts of 3.184 Å are observed between chains (figure 2c), within the sum of the van der Waals radii of Cd and S (3.4 Å) [27], and the $Cl \cdots S$ contacts of 3.446 Å are observed between

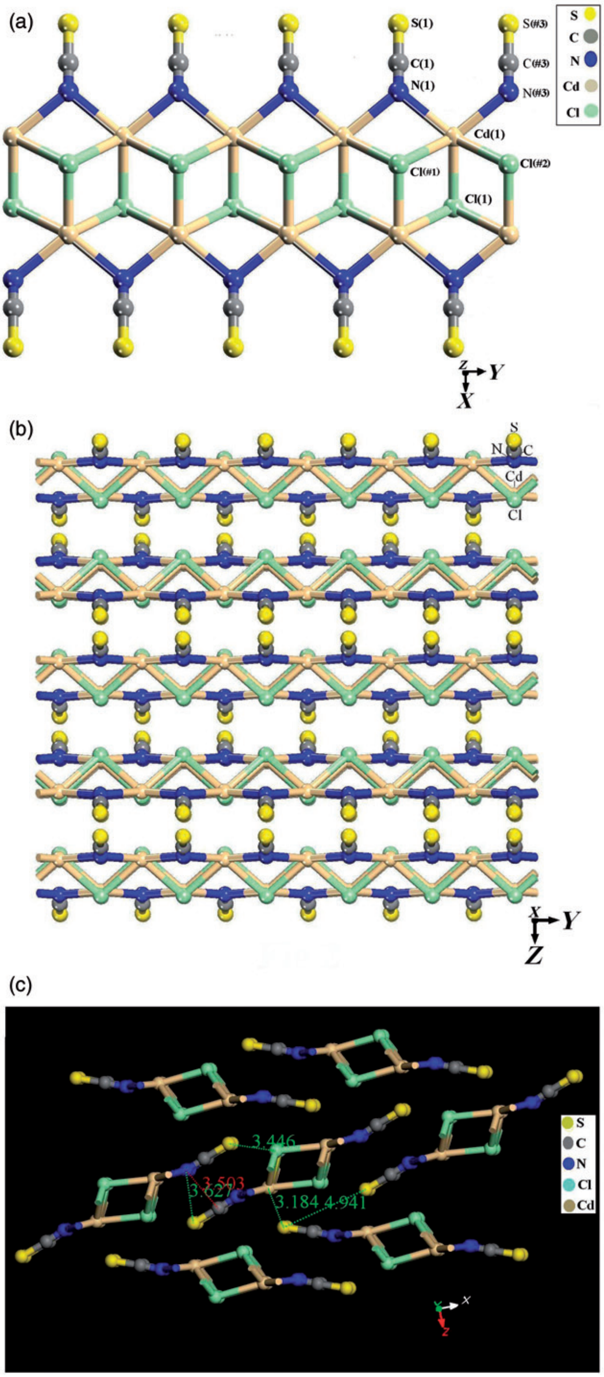

Figure 2. (a) View of the infinite chain with the chair-like features in **1**. (b) View of the infinite $[CdCl(SCN)]_n$ polymeric chains. Note that $[CdCl(SCN)]_n$ chains are "antiparallel" to one another in a single chain. (c) The packing diagram of **1** showing weak $Cd\cdots S$ and $Cl\cdots S$ interactions between the nearest chains. Symmetry transformations used to generate equivalent atoms: #1: $[2-x, y-1/2, 1-z]$; #2: $[2-x, y+1/2, 1-z]$; #3: $[x, 1+y, z]$.

chains also, much shorter than the sum of the van der Waals radii of Cl and S (3.7 Å) [28]. Neighboring 1-D chair-like polymer chains are further connected by the weak Cd $\cdots$ S and Cl $\cdots$ S interactions to generate a 3-D network.

Compared with the cadmium coordination polymers reported in [26, 29, 30], the most interesting aspect of **1** is the chair-like building unit cadmium being five-coordinate and each Cl^- a μ_3-linker coordinating three Cd(II) centers. Commonly, cadmium is six-coordinate [24–26, 29, 30] and it is rare for cadmium to be five coordinate.

3.2. *IR spectra*

The IR spectrum of **1** is provided in "Supplementary material". In general, the $\nu_{(CN)}$ of a bridging thiocyanate is found at $2100\,cm^{-1}$ [31–33], whereas terminally N-bonded NCS^- occurs at $2050\,cm^{-1}$ [33, 34]. For M–SCN–M the CN stretching frequency is above $2100\,cm^{-1}$ [35]. The stretching CN frequencies at $2079.6\,cm^{-1}$ for **1** clearly indicate that thiocyanate is coordinated to cadmium through nitrogen. The frequency is significantly higher than the corresponding one found in KSCN ($2063\,cm^{-1}$ [36]). The reason may be that SCN is a good electron supplier and electron transfer from SCN^- to Cd^{2+} ions causes an increase in CN stretching frequency. This value is consistent with the metal–nitrogen bonding found for thiocyanate bridged polymers in the N-bonded thiocyanate complex ($2073\,cm^{-1}$) [37]. The C–S stretching frequencies in the region $860–690\,cm^{-1}$ is usually employed for differentiating S- from N-bonded terminal thiocyanates; $\nu_{(CS)}$ lies in the range $860–780\,cm^{-1}$ (N-bonding) or $720–690\,cm^{-1}$ (S-bonding) and δ_{SCN} lies near $480\,cm^{-1}$ (N-bonding) or $420\,cm^{-1}$ (S-bonding) [38]. However, $\nu_{(CS)}$ in the IR spectrum of **1** appears at 789.8 and $727.6\,cm^{-1}$ and the deformation frequency δ_{SCN} is at $458.1\,cm^{-1}$, confirming the metal–nitrogen coordination.

3.3. *Photoluminescent properties*

The excitation and emission spectra of the complex in the solid state at room temperature with photon excitations at 387 nm are provided in "Supplementary material". The emission of the complex has one broad peak centered at 473 nm (a characteristic blue emission), corresponding to the energy of 2.62 eV. The emission band at 473 nm might be attributed to ligand-to-metal charge transfer (LMCT), which has been observed in other polynuclear d_{10} metal polymers [39, 40], suggesting that the complex may be a good candidate of blue-light emitting diode devices, as the material is thermally stable and insoluble in common solvents.

3.4. *Microhardness studies*

Hardness of a material is the resistance offered by a material to localized deformations caused by scratching or indentations. Microhardness studies have been carried out on **1** single crystals using micro Vickers hardness tester fitted with a Vickers diamond pyramidal indenter (Suzhou Instruments Corporation, China) attached to an incident light microscope. The Vickers microhardness number (Hv) was calculated using the expression [41]:

$$\mathrm{Hv} = 1.8544P/d^2 \tag{3}$$

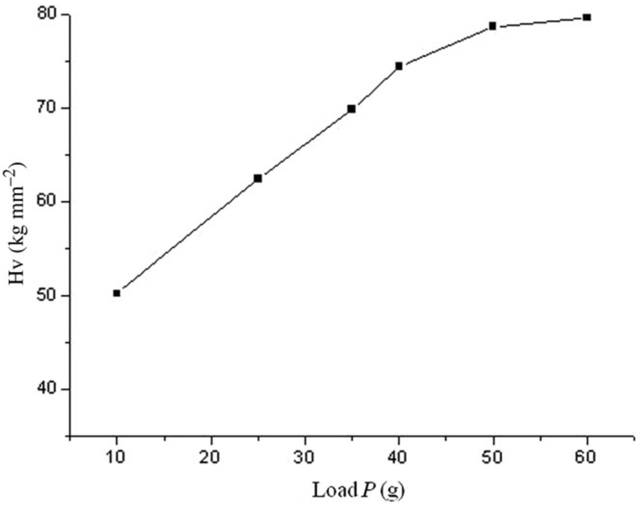

Figure 3. Variation of Hv with load.

where Hv is the Vickers hardness number in kg mm^{-2}, P is the applied load in kg, and d is the mean diagonal length of the indenter impression in mm. The relation between hardness number (Hv) and load (P) for **1** is shown in figure 3. It is clear that Hv increases gradually with the increase of load at lower loads and the microhardness shows a tendency to saturate at higher loads. Beyond 50 g, cracks develop on the smooth surface of the crystal due to the release of internal stresses generated locally by indentation. The Vicker hardness of **1** single crystal was measured to be 78.6 kg mm^{-2}.

4. Conclusion

In the present work, using Cl^- and SCN^-, we synthesized a 1-D coordination polymer, $[CdCl(SCN)]_n$, as a centrosymmetric 1-D framework containing CdN_2Cl_3 severe distorted square-pyramidal structural unit. Its particular arrangement of Cd(II), Cl^-, and SCN^- forming an infinite 1-D chain with the chair-like features is a new example of mixed Cd–NCS–Cl discrete compounds. The fluorescence excitation and emission spectral studies reveal that **1** exhibits blue emission in the solid-state at 473 nm with photon excitation at 387 nm and the complex is a good candidate of blue-light emitting diode materials. Vickers microhardness was 78.6 kg mm^{-2} in order to understand the mechanical stability of the compound crystals.

Acknowledgments

This work was supported by the Fund for the Doctoral Program of Nanchang Hangkong University (No. EA200601189).

References

[1] B. Chand, U. Ray, G. Mostafa, T.H. Lu, C.R. Sinha. *Polyhedron*, **23**, 1669 (2004).
[2] O.R. Evans, W.B. Lin. *Chem. Mater.*, **13**, 2705 (2001).
[3] O. Castillo, A. Luque, J. Sertucha, P. Román, F. Lloret. *Inorg. Chem.*, **39**, 6142 (2000).
[4] S.R. Batten, R.J. Robson. *Angew. Chem. Int. Ed.*, **38**, 2639 (1999).
[5] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R.V. Belosludov, T.C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita. *Nature*, **436**, 238 (2005).
[6] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T.C. Kobayashi, S. Horike, M. Takata. *J. Am. Chem. Soc.*, **126**, 14063 (2004).
[7] S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
[8] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003).
[9] M.L. Tong, X.M. Chen, X.L. Yu, T.C.W. Mak. *J. Chem. Soc., Dalton Trans.*, 5 (1998).
[10] P. Lightfoot, A. Snedden. *J. Chem. Soc., Dalton Trans.*, 3549 (1999).
[11] M.L. Tong, H.K. Lee, X.M. Chen, R.B. Huang, T.C.W. Mak. *J. Chem. Soc., Dalton Trans.*, 3657 (1999).
[12] B.D. Wagner, G.J. McManus, B. Moulton, M.J. Zaworotko. *Chem. Commun.*, 2176 (2002).
[13] S.L. Li, T.C.W. Mak. *J. Chem. Soc., Dalton Trans.*, 1519 (1995).
[14] A.Q. Wu, Y. Li, F.K. Zheng. *Cryst. Growth Des.*, **6**, 444 (2006).
[15] S.R. Battern, A.R. Harris, P. Jensen, K.S. Murray, A. Ziebell. *J. Chem. Soc., Dalton Trans.*, **21**, 3829 (2000).
[16] O.R. Evans, W. Lin. *J. Chem. Soc., Dalton Trans.*, **21**, 3949 (2000).
[17] M.A.S. Goher, Q.C. Yang, T.C.W. Mak. *Polyhedron*, **19**, 615 (2000).
[18] D. Bose, J. Banerjee, S.H. Rahaman, G. Mostafa, H.K. Fun, R.D.B. Walsh, M.J. Zaworotko, B.K. Ghosh. *Polyhedron*, **23**, 2045 (2004).
[19] H. Zhu, M. Ströbele, Z. Yu, Z. Wang, H.J. Meyer, X. You. *Inorg. Chem. Commun.*, **4**, 577 (2001).
[20] P.B. da Silva, R.C.G. Frem, A.V.G. Netto, A.E. Mauro, J.G. Ferreira, R.H.A. Santos. *Inorg. Chem. Commun.*, **9**, 235 (2006).
[21] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Solution*, Göttingen University, Göttingen, Germany (1997).
[22] *SMART and SAINT (software packages)*, Siemens Analytical X-ray Instruments Inc., Madison, WI (1996).
[23] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).
[24] D.L. Reger, T.D. Wright, M.D. Smith, A.L. Rheingold, S. Kassel, T. Concolino, B. Rhagitan. *Polyhedron*, **21**, 1795 (2002).
[25] P.B. da Silva, R.C.G. Frem, A.V.G. Netto, A.E. Mauro, J.G. Ferreira, R.H.A. Santos. *Inorg. Chem. Commun.*, **9**, 235 (2006).
[26] G.B. Che, J. Wang, B. Liu, X.Y. Li, C.B. Liu. *J. Coord. Chem.*, **62**, 302 (2009).
[27] Y.X. Sun, H.H. Zhang, L. Wang, Y.N. Cao, S. Zhang, Y.P. Chen. *Chinese J. Sruct. Chem.*, **27**, 100 (2008).
[28] H.J. Lee, H.J. Nam, D.Y. Noh. *Bull. Korean Chem. Soc.*, **20**, 1368 (1999).
[29] J. Lu, N. Wang, H.T. Liu. *J. Coord. Chem.*, **62**, 1980 (2009).
[30] C.M. Jin, Z.F. Chen, C.Y. Chen, J.H. Dong. *J. Coord. Chem.*, **62**, 390 (2009).
[31] S. Banerjee, M.G.B. Drew, A. Ghosh. *Polyhedron*, **22**, 2933 (2003).
[32] J. Luo, M. Hong, R. Wang, R. Cao, Q. Shi, J.B. Weng. *Eur. J. Inorg. Chem.*, 1778 (2003).
[33] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, pp. 231–235, Wiley, New York (1986).
[34] M.C. Suen, T.C. Keng, J.C. Wang. *Polyhedron*, **21**, 2705 (2002).
[35] R. Bala, R.P. Sarma, R. Sarma, B.M. Kariuki. *Inorg. Chem. Commun.*, **9**, 852 (2006).
[36] P.O. Kinell, B. Strandberc. *Acta Chem. Scand.*, **13**, 1607 (1959).
[37] N.Y. Jiang, S.L. Li. *Chin. J. Inorg. Chem.*, **22**, 1861 (2006).
[38] R. Kapoor, A. Kataria, A. Pathak, P. Venugopalan, G. Hundal, P. Kapoor. *Polyhedron*, **24**, 1221 (2005).
[39] S. Dalai, P.S. Mukherjee, E. Zangrando, F. Lloret, N.R. Chaudhuri. *J. Chem. Soc., Dalton Trans.*, 822 (2002).
[40] S. Dalai, P.S. Mukherjee, G. Rogez, T. Mallah, M.G.B. Drew, N.R. Chaudhuri. *Eur. J. Inorg. Chem.*, 3292 (2002).
[41] B.W. Mott. *Microindentation Hardness Testing*, Vol. 206, Butterworths, London (1956).