

Chloro-Bridged Dimeric Cadmium(II)-Isothiocyanate Complex with a Tridentate NNN Type Ligand: Synthesis, X-ray Structure, Thermal Analysis

Çiğdem Hopa · Mahir Alkan · Canan Kazak ·
N. Burcu Arslan · Raif Kurtaran

Received: 20 March 2009 / Accepted: 29 August 2009 / Published online: 16 September 2009
© Springer Science+Business Media, LLC 2009

Abstract The dinuclear cadmium(II) complex with 2,6-bis(3,4,5-trimethyl-*N*-pyrazolyl)pyridine (btmpp) has been synthesized, and characterized by single crystal X-ray diffraction, IR, UV–Vis and TGA–DTA methods. Cd atoms are located in a distorted octahedral environment in the complex. The complex crystallizes in monoclinic space group $C 2/c$, with unit cell dimensions $a = 20.5636(12) \text{ \AA}$, $b = 14.0167(13) \text{ \AA}$, $c = 15.6598(11) \text{ \AA}$, $\beta = 113.425(5)^\circ$, $V = 4141.7(5) \text{ \AA}^3$. There are two intermolecular and a intramolecular hydrogen bonds interactions in crystal.

Keywords Chloro-bridged · Hydrogen bond · Thiocyanate · Dimeric Cd(II) complex

Introduction

One of our research interests has been the synthesis and solid state characterization of NNN type tridentate planar ligands based on the analogues of 2,2':6',2''-terpyridine (terpy) and pseudohalide ions due to their stable coordination configuration that the N-donors chelate various transition metal ions and bridging ligand, respectively [1]. Subsequently, the resultant complexes possess a wide range of chemical and/or physical properties, such as catalytic [2], magnetic [3], photophysical [4], electrochemical properties [5–7]. Particularly cadmium-thiocyanate

coordination complexes have attracted attention due to their topological aspects as well by the potential use as optical materials very effective in blue light emission [8, 9]. A number of one- to three-dimensional chloro-bridged cadmium (II) compounds have been reported [10–15]. However, a few investigations of the photoluminescent spectra properties [16, 17] by halogen-bridged Cd(II) polymers have been carried out. Lee et al. reported a ferromagnetically coupled interaction chloro-bridged quasi-cubane 1-D Cd(II) cluster $[\text{Cd}_4\text{Cl}_8(\text{NTToPy})_4]$ with pyridyl-substituted nitronyl nitroxide (NTToPy=2(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1 H-imidazol-1-oxy 3-*N*-oxide) which showed a weak ferromagnetic coupling between the radicals [18]. As a part of our systematic studies on transition metal/terpy derivative ligand/pseudohalide ion [19, 20], we recently prepared an unusual complex with terminal isothiocyanate ion and chloro-bridging ligand. It is worth mentioning that these kind of di- and poly-nuclear complexes are usually bridged by pseudohalide ions instead of chloride ion. Sometimes pseudohalide ions can coordinate to metal atom as a terminal ligand. In this study, chloride ions bridge two cadmium ions instead of isothiocyanate ion. In this work, we present the synthesis, spectral, thermal studies and X-ray single crystal structural analysis of a di- μ -chloro bridged dicadmium(II) complex with the tridentate ligand (btmpp), $[\text{Cd}(\text{btmpp})(\text{NCS})(\mu\text{-Cl})_2]$ complex shown in Fig. 1.

Ç. Hopa · M. Alkan · R. Kurtaran (✉)
Department of Chemistry, Faculty of Arts and Sciences,
Balıkesir University, Cagis, 10145 Balıkesir, Turkey
e-mail: kurtaran@balikesir.edu.tr

C. Kazak · N. Burcu Arslan
Department of Physics, Faculty of Arts and Sciences, Ondokuz
Mayis University, 55139 Samsun, Turkey

Experimental

Materials and Apparatus

All reagents and solvents were purchased from Merck, Aldrich or Carlo Erba and were used without further

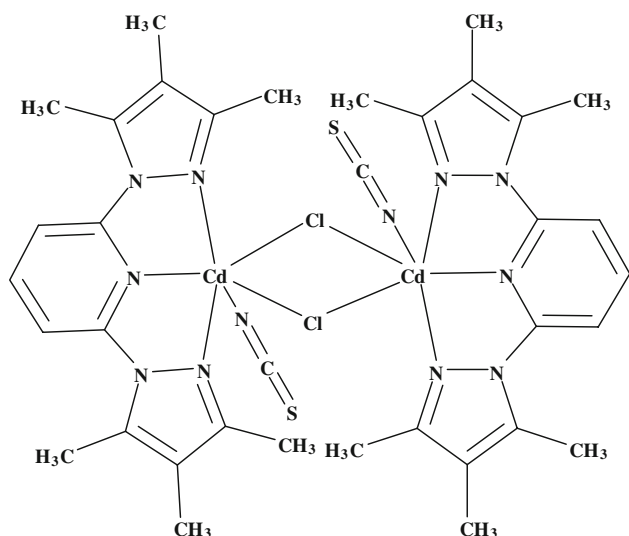


Fig. 1 Chemical structure of the title compound

purification. C, H and N data were obtained using Eurovector 3018 CHNS analyzer. Melting points were measured using STUART Melting Point SMP3. Infrared spectra were measured as KBr pellets using Perkin–Elmer 1600 Series FTIR spectrophotometer. The electronic spectra were obtained using a Cary 1E UV–Visible spectrophotometer (Varian). The thermogravimetry/differential thermal analysis (TG/DTA) measurements were run on a Perkin Elmer Diamond DTA/TG thermal analyzer. In this study, thermogravimetric curves were obtained with a flow rate of the carrier gas of 200 mL/min and a heating rate of 20 °C/min in nitrogen (3 bar) with ceramic crucibles.

Synthesis of btmpp

Synthesis of 2,6-bis(3,4,5-trimethyl-*N*-pyrazolyl)pyridine (btmpp) was achieved by 2,6-dichloropyridine and the potassium salt of 3,4,5-trimethyl-*N*-pyrazol by refluxing in diglyme as described previously [21].

Synthesis of [Cd(btmpp)(NCS)(μ-Cl)₂]₂

To a solution of btmpp (0.590 g, 2 mmol) in 20 mL hot ethanol, a 20 mL hot ethanolic solution of CdCl₂·9H₂O (0.688 g, 2 mmol) was added. After mixing well, a solution of KSCN (0.190 g, 2 mmol) in 5 mL hot water was added the former mixture while stirring. The mixture was filtered off while the solution was hot. The resulting mixture was set aside for 2 days and colourless crystals of the complex formed. The crystals were filtered off and dried in the open air. Yield: 65%, mp: 258 °C, ¹H NMR (500 MHz, 298 K, (CD₃)₂SO) 1.98 (s, 6H), 2.11 (s, 6H), 2.50 (s, 6H), 7.64 (bs, 2H), 8.07 (bs, 1H); ¹³C NMR (125 MHz, 298 K, (CD₃)₂SO) 8.15, 12.61, 13.80, 113.21, 115.67, 132.30,

142.06, 149.72, 150.93. Anal. Calc. For C₃₆ H₄₂ Cd₂ Cl₂ N₁₂ S₂: C, 43.09; H, 4.19; N, 16.76. Found: C, 42.78; H, 4.13; N, 16.57.

X-ray Crystallography

One of the fine colourless single crystal of [Cd(btmpp)(NCS)(μ-Cl)₂] was mounted on a glass fiber and the intensity data of the cadmium (II) complexes were collected using a STOE IPDS 2 diffractometer (Mo–Kα radiation, λ = 0.71073 Å) at 293 K. The structure (Fig. 2) was solved by direct methods using SHELXS-97 [22] and refined by a full-matrix least-squares procedure (SHELXL-97) [22] in the Wingx package [23]. All nonhydrogen atoms were easily found from the difference Fourier map and refined anisotropically. All hydrogen atoms of the title compound were refined freely. The molecular plots were prepared by using ORTEPIII [24]. The details of data collection, refinement and crystallographic data are summarized in Table 1.

Results and Discussion

Description of Crystal Structure

Crystal data collection and refinement of the title compound is summarized in Table 1. The ORTEP and molecular packing diagrams are displayed in Figs. 2 and 3. The geometry around the cadmium atom is best described as a distorted octahedron with a CdN₄Cl₂ chromophore. The two nitrogen atoms (N1 and N5) of btmpp, a bridging

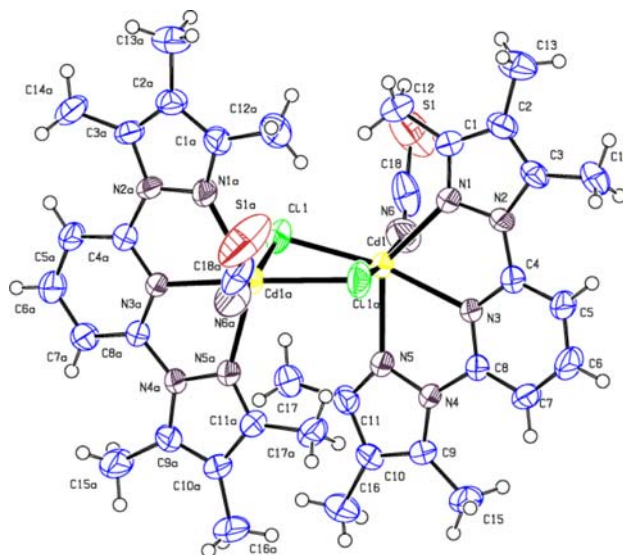
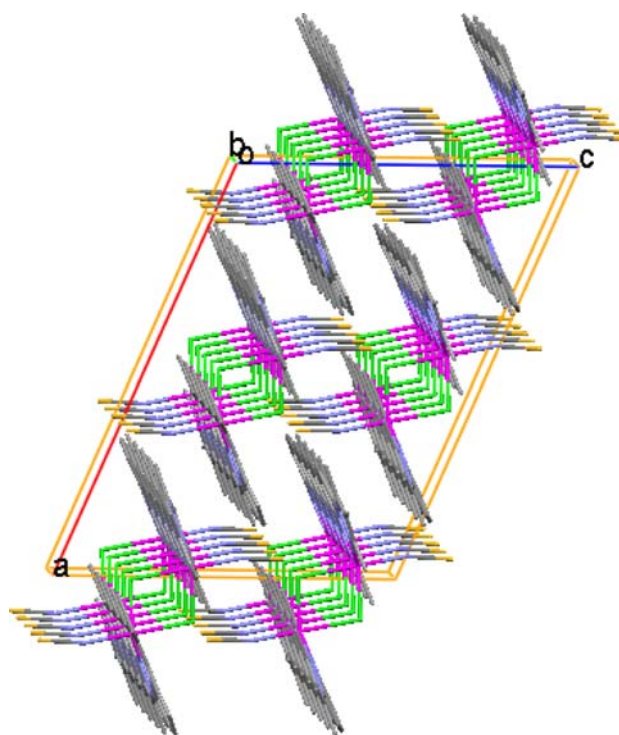


Fig. 2 The Ortep drawing of the [Cd(btmpp)(NCS)(μ-Cl)₂]₂ with the atom-numbering scheme (displacement ellipsoids are drawn at the 50% probability level)

Table 1 Crystal data and structure refinement for the title compound

CCDC no.	693634
Chemical formula	C ₃₆ H ₄₂ Cd ₂ Cl ₂ N ₁₂ S ₂
Formula weight	1002.64
Crystal system	Monoclinic
Space group	C 2/c
<i>a</i> (Å)	20.5636(12)
<i>b</i> (Å)	14.0167(13)
<i>c</i> (Å)	15.6598(11)
β (°)	113.425(5)
Unit cell volume <i>V</i> (Å ³)	4141.7(5)
<i>Z</i>	4
Calculated density <i>D_x</i> (Mg m ⁻³)	1.608
Electron number (<i>F</i> ₀₀₀)	2016
Linear absorption coefficient μ (mm ⁻¹)	1.299
Crystal colour, shape	Colourless, prism
Crystal dimensions (mm)	0.35 × 0.23 × 0.15
X-ray and wavelength	MoK α , 0.71073
Data collection temperature, <i>T</i> (K)	293(2)
<i>R</i> _{int}	0.095
<i>h</i> , <i>k</i> , <i>l</i> intervals (°)	–24/25, –17/17, –18/19
θ _{max} (°)	26
Data collection device	STOE IPDS II
Data collection method	ω Scan
Reflections with (<i>I</i> > 2 σ (<i>I</i>))	2409
Measured reflections	18400
Independent reflections	4072
Used programs	Wingx, SHELXS–97, SHELXL–97
Structure refinement	For full matrix (<i>F</i> ²)
Weight function	1/[$\sigma^2(F_o^2) + (0.0173P)^2$], $P = (F_o^2 + 2F_c^2)/3$
Parameter number	250
<i>R</i> , <i>R</i> _w (<i>I</i> > σ (<i>I</i>))	0.033, 0.061
<i>S</i>	0.80
$\Delta\rho$ _{min} , $\Delta\rho$ _{max} (e/Å ³)	–0.37, 0.52

chlorine atom (Cl1) and nitrogen (N6) of the thiocyanate ligand define the equatorial plane around the cadmium atom. The apical positions of the octahedron are occupied by the other bridging chlorine atom and nitrogen atom (N3) of the btmpp. Selected bond lengths and angles in the complex are listed in Table 2. The angle of Cd1–Cl1–Cd1a is 97.10(3)° which is slightly bigger with the reported di-chloro-bridging compounds [15, 16, 28, 29]. Also this gives rise to a Cd⋯Cd distance of 4,002 Å than those reported for doubly chlorine-bridged compounds. The Cd–N bond lengths are in the range 2.319(3)–2.386(3) Å for the btmpp but the Cd–N6 bond distance (2.290(4)) is slightly shorter than the other Cd–N lengths while the apical Cd–Cl1a bond distance (2.8454(12) Å) is slightly longer than the axial Cd–Cl1 bond

**Fig. 3** Crystal packing of the title compound along *b* axis**Table 2** Selected bond lengths (Å) and bond angles (°)

N1 Cd1	2.319(3)	Cd1 N6	2.290(4)
N3 Cd1	2.386(3)	Cd1 Cl1	2.485(9)
N5 Cd1	2.327(3)	Cd1 Cl1a	2.845(12)
N6 Cd1 N1	89.97(13)	N3 Cd1 Cl1	161.26(7)
N6 Cd1 N5	96.05(14)	N6 Cd1 Cl1	169.06(12)
N1 Cd1 N5	135.56(10)	N1 Cd1 Cl1	81.19(8)
N6 Cd1 N3	100.23(12)	N5 Cd1 Cl1	94.79(8)
N1 Cd1 N3	67.74(10)	N3 Cd1 Cl1	82.45(7)
N5 Cd1 N3	67.86(10)	Cl1 Cd1 Cl1	80.85(3)
N6 Cd1 Cl1	97.76(10)	Cd1 Cl1 Cd1	97.10(3)
N1 Cd1 Cl1	117.62(8)	N6 C18 S1	178.4(6)
N5 Cd1 Cl1	105.13(7)		

distance [2.4848(9) Å] (Table 2). Angles of the trans axial angle [N5–Cd–N1 = 135.57] show much more deviation from ideal 180° whereas the equatorial plane [Cl1–Cd–N6 169.04, N3–Cd–Cl1a 161.26(6)] is close to the ideal 180°. The thiocyanate ions is almost linear with N6 C18 S1 bond angle of 178.4(6)°. All the bond lengths and angles are comparable with the similar structures [20, 30, 31]. Cadmium(II) ion is known as soft metal in inorganic literature. According to Pearson when the metal ion hardness values are compared, the value for Cd(II) is 10.29 whereas this value 10,88 for Zn(II) within the hard-soft boundary. According to the hardness values Cd(II) is a harder metal

Fig. 4 Hydrogen bonding geometry of [Cd(btpp)(NCS)(μ -Cl)]₂ compound along a axis

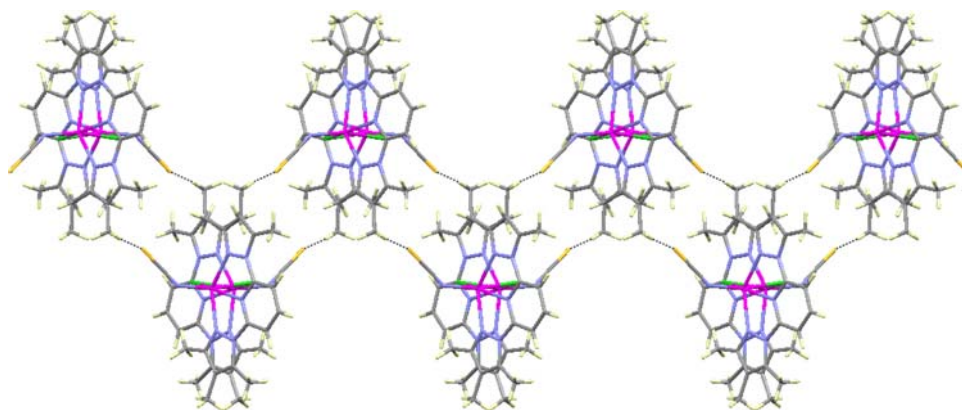


Table 3 Hydrogen-bonding geometry (Å, °)

D–H...A	D–H	H...A	D–A	D–H...A
C(5)–H(5)...Cl(1) ^(a)	0.93	2.68	3.438(4)	139
C(13)–H(13A)...S(1) ^(b)	0.96	2.83	3.758(6)	164
C(17)–H(17C)...Cl(1)	0.96	2.81	3.699(4)	155

Symmetry codes: (a) $-1/2+x, 1/2-y, -1/2+z$, (b) $x, 1-y, -1/2+z$

than Ni(II) and Cu(II). The most recent by Pearson [32], suggest that S in SCN⁻ is soft and will prefer to coordinate with soft acids whereas N in SCN⁻ is hard and coordinates with hard acids. So cadmium ions are coordinated with the hardest part of the SCN ion. There are two intermolecular and a intramolecular hydrogen bonding interactions in the crystal. Details of the hydrogen bonding geometry are shown Fig. 4 and Table 3.

FTIR Spectra

In order to study the binding mode of the btpp to the cadmium metal in the complex, the IR spectrum of the free ligand was compared with the spectra of [Cd(btpp)(NCS)(μ -Cl)]₂ in KBr pellets. The interest of the IR spectrum of the title complex lies mainly in the bands due to the NCS⁻ groups. The thiocyanate CN stretching vibration appears a very strong absorption bands at 2047 cm⁻¹. This lower observed CN stretching band frequency indicates generally in N-bonded complexes (near and below 2050 m-1) than in S-bonded complexes (near 2100 cm-1) [25, 26]. The lower absorption peak assigned to C=N vibration mode to complex appears at lower frequencies, while that assigned to C=S vibration mode appears at higher frequencies comparing with KSCN due to the coordination between Cd and N of SCN. In addition, this assignment is combined with the two weak bands at 796 and 755 cm⁻¹ that account for the stretching frequency of ν (CS) and indicates the monodentate N-coordination of the NCS⁻ ion to the Cd(II) ion.

Absorption Spectra

The absorption spectra of btpp ligand and [Cd(btpp)(NCS)(μ -Cl)]₂ were recorded in dimethylformamide, while the complex are good soluble only in DMF. The UV spectra for ligand and complex have shown two strong absorptions bands between 265 and 303 nm. For the btpp cadmium complex, a band occurs near 269 nm (27500 M⁻¹ cm⁻¹) and 305 nm (36400 M⁻¹ cm⁻¹). The spectra of the free ligand exhibit intense peaks at 265 nm (12600 M⁻¹ cm⁻¹) and 303 nm (17500 M⁻¹ cm⁻¹). Indicating ligand-centered bands occur in this region, though other charge-transfer transitions also may contribute significant intensity. The relative intensity of this band was lower than the free ligand. Similar observation was mention by Willison et al. [27].

Thermal Analysis

The titled compound were studied by thermogravimetric analysis from ambient temperature to 1000 °C in nitrogen atmosphere. DTA/TG curves are shown in Fig. 4. Thermal studies of [Cd(btpp)(NCS)(μ -Cl)]₂ show that the complex is fairly stable up to the 230 °C and shows no weight loss before this temperature. Two endothermic peaks are noted clearly at 253 and 369 °C. The first endothermic peak at 253 °C corresponds to the melting point of complex. This is agree with the measured using STUART Melting Point apparatus (m.p. 258 °C). The decomposition of complex starts at the same time with the melting of complex. The second endothermic peak is due to the decomposition of ligand. Decomposition occurs between 253–520 °C with an 55.15% mass loss (58.93% in theoretical).

Conclusions

In conclusion, a new chloro bridged Cd(II) complex with btpp ligand have been prepared and structurally

characterized by single crystal X-ray diffraction, elemental analyses, thermal analysis, IR and electronic spectra. Although the pseudohalide ions are attractive as co-ligands due to their bridging metal ions to each other, and neutralize the charges of the complexes, in this complex chloro ion bridged the cadmium ions and thiocyanate ions are bonded as a terminal ligand. Studies along these lines are currently in progress in our laboratory.

Supplementary Material

Crystallographic data for the title complex have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 693634. Copies of available material can be obtained, free charge, on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>; fax: +44-(0)1223-336033).

Acknowledgments The financial support of the Scientific and Technical Research Council of Turkey (TUBITAK-TBAG (108T622), and Balikesir University is gratefully acknowledged.

References

1. Halcrow MA (2005) *Coord Chem Rev* 249:2880
2. Çetinkaya B, Çetinkaya E, Brookhart M, White PS (1999) *J Mol Catal A-Chem* 142:101
3. Manikandan P, Muthukumaran R, Thomas KRJ, Varghese B, Chandramouli GVR, Manoharan PT (2001) *Inorg Chem* 40:2378
4. Willison SA, Jude H, Antonelli RM, Rennekamp JM, Eckert NA, Jeanette A, Krause B, Connick WB (2004) *Inorg Chem* 43:2548
5. Kurtaran R, Arici C, Emregül KC, Ülkü D, Atakol O, Taştekin M, Anorg Z (2003) *Allg Chem* 629:1617
6. Constable EC (1986) *Adv Inorg Chem Radiochem* 30:69
7. Agrifoglio G, Karam AR, Catari EL, Gonzalez T, Atencio R (2005) *Acta Cryst Sec.E* 61:2613
8. Bose D, Banerjee J, Rahaman SHJ, Mostafa G, Fun HK, Walsh RDB, Zaworotko MJ, Ghosh BK (2004) *Polyhedron* 23:2045
9. Zhu H, Ströbele M, Yu Z, Wang Z, Meyer HJ, You X (2001) *Inorg Chem Commun* 4:577
10. Ahmadi R, Khalighi A, Kalateh K, Amani V, Khavasi HR (2008) *Acta Crystallogr E* 64:1233
11. Soka I, Fischer A, Kloo L (2008) *Struct Chem* 19:51
12. Karmakar R, Choudhury CR, Hughes DL, Mitra S (2007) *Inorg Chim Acta* 360:2631
13. Cheng M-L, Li H-X, Zang Y, Lang J-P (2006) *Acta Crystallogr C* 62:74
14. Evans IR, Szecsenyi KM, Leovac VM (2005) *Acta Crystallogr E* 61:641
15. Choi K-Y, Jeon Y-M (2003) *Inorg Chem Commun* 6:1294
16. Chattopadhyay T, Banerjee A, Banu KS, Suresh E, Netahji M, Birarda G, Zangrando E, Das D (2008) *Polyhedron* 27:2452
17. Zhang R-F, Shi W, Wang H-S, Cheng P (2008) *J Coord Chem* 61:1606
18. Lee C-J, Wei H-H, G-H Lee, Wang Y (2000) *Inorg Chem Commun* 3:690
19. Tastekin M, Arici C, Svoboda I, Emregül KC, Kurtaran R, Atakol O, Fuess H (2007) *Z Kristallogr* 222:255
20. Kurtaran R, Odabasioglu S, Azizoglu A, Kara H, Atakol O (2007) *Polyhedron* 26:5069
21. Hopa Ç, Alkan M, Kazak C, Arslan NB, Kurtaran R (2009) *Transition Metal Chem* 34:4
22. Sheldrick GM (1997) SHELXS-97 and SHELXL-97. Programs for crystal structure analysis, University of Göttingen, Germany
23. Farrugia LJ (1999) WinGX program for crystallography package. *J Appl Cryst* 32:837–838
24. Farrugia LJ (1997) *J Appl Crystallogr* 30:565
25. Nakamoto K (1978) *Infrared spectra of inorganic and coordination compounds*. Wiley, New York
26. Guha S, Mukherjee AK, Maji TK, Ray Chaudhuri N (2006) *Cryst Res Technol* 41(2):198–203
27. Willison SA, Jude H, Antonelli RM, Rennekamp JM, Eckert NA, Krause Bauer JA, Connick WB (2004) *Inorg Chem* 43:8
28. Karmakar R, Choudhury CR, Hughes DL, Mitra S (2007) *Inorg Chim Acta* 360:2631
29. Ahmadi R, Khalighi A, Kalateh K, Amani V, Khavasi HR (2008) *Acta Crystallogr E* 64:1233
30. Odabaşioğlu S, Kurtaran R, Azizoglu A, Kara H, Öz S, Atakol O (2008) *Cent Eur J Chem CEJC-D-08-00144*
31. Kurtaran R, Namli H, Kazak C, Turhan O, Atakol O (2007) *J Coord Chem* 60:2133
32. Pearson RG (1988) *Inorg Chem* 27:734