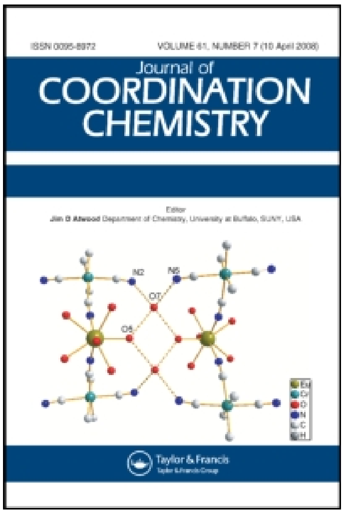


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization, crystal structure and thermal analysis of a copper(II) mononuclear compound with 2,6-<i>bis</i>(3,5-dimethyl-<i>N</i>-pyrazolyl)pyridine (bdmpp) and selenocyanate as ligands

Raif Kurtaran[a]; Hilmi Namli[a]; Canan Kazak[b]; Onur Turhan[a]; Orhan Atakol[c]
[a] Faculty of Arts and Sciences, Department of Chemistry, Balıkesir University, Balıkesir 10100, Turkey
[b] Faculty of Arts and Sciences, Department of Physics, Ondokuz Mayıs University, Samsun [c] Faculty of Sciences, Department of Chemistry, University of Ankara, Tandoğan 06100, Ankara, Turkey

To cite this Article Kurtaran, Raif , Namli, Hilmi , Kazak, Canan , Turhan, Onur and Atakol, Orhan(2007) 'Synthesis, characterization, crystal structure and thermal analysis of a copper(II) mononuclear compound with 2,6-**<i>bis</i>**(3,5-dimethyl-**<i>N</i>**-pyrazolyl)pyridine (bdmpp) and selenocyanate as ligands', Journal of Coordination Chemistry, 60: 20, 2133 — 2138

To link to this Article: DOI: 10.1080/00958970701340511

URL: http://dx.doi.org/10.1080/00958970701340511

Journal of Coordination Chemistry
Vol. 60, No. 20, 15 October 2007, 2133–2138

Synthesis, characterization, crystal structure and thermal analysis of a copper(II) mononuclear compound with 2,6-*bis*(3,5-dimethyl-*N*-pyrazolyl)pyridine (bdmpp) and selenocyanate as ligands

RAIF KURTARAN*†, HILMI NAMLI†, CANAN KAZAK‡,
ONUR TURHAN† and ORHAN ATAKOL§

†Faculty of Arts and Sciences, Department of Chemistry,
Balıkesir University, Balıkesir 10100, Turkey
‡Faculty of Arts and Sciences, Department of Physics,
Ondokuz Mayıs University, Samsun
§Faculty of Sciences, Department of Chemistry, University of Ankara,
Tandoğan 06100, Ankara, Turkey

(*Received 13 April 2006; revised 12 June 2006; in final form 13 June 2006*)

A single crystal of the copper(II) compound, [Cu(bdmpp)$(SeCN)_2$], **2**, was obtained and its crystal structure was determined by X-ray diffraction methods. The complex was characterized by elemental, thermal and FTIR analysis. The FTIR analysis of the complex clearly shows the SeCN peaks at 2096 and 2061 cm^{-1} which did not exist in the free organic ligand (bdmpp). X-ray analysis showed that **2** crystallized in the monoclinic space group $P2_1/c$. Cu(II) has a distorted trigonal bipyramidal coordination involving three N atoms from the ligand and two N atoms from the selenocyanate group.

Keywords: Pyrazolyl complexes; Selenocyanate; Trigonal-bipyramidal Cu(II) complexes; Thermal analysis

1. Introduction

Transition metal complexes with azide, thiocyanate and cyanate anions have been attracted much interest due to their structures and magnetic properties [1–4]. Recently, this laboratory reported [5, 6a] a number of interesting azido, thiocyanato and cyanato bridged mononuclear, dinuclear and polynuclear complexes of transition metals with Schiff bases and terpyridine derivative ligands [6b]. However, complexes containing selenocyanate anion have been rarely studied. The selenocyanate ligand is a versatile ligand acts as a monodentate [7] as well as a bridging group adopting the end-on $\mu(1,1)$ and end-to-end $\mu(1,3)$ [8] bridging modes. Both possibilities have been structurally characterized for transition metal complexes [8]. In this study, as a part of our ongoing research on the synthesis and structural characterization of complexes with

---

*Corresponding author. Email: kurtaran@balikesir.edu.tr

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701340511

pseudohalide ligands, the synthesis, IR spectral, thermal and X-ray single crystal structural analysis of a mononuclear [Cu(bdmpp)$(SeCN)_2$] complex are presented.

2. Experimental

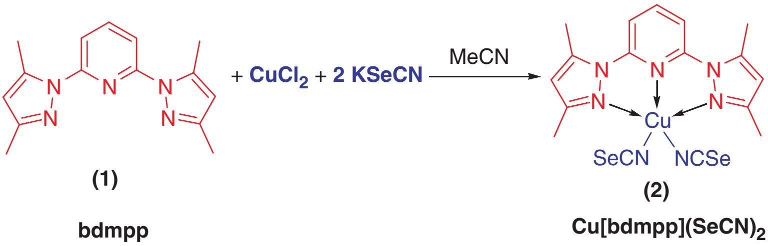
2.1. *Materials and measurements*

All reagents and solvents were purchased from Merck, Aldrich or Carlo Erba and used without further purification. Elemental analyses for the ligands and complexes were carried out on a Eurovector 3018 CHNS analyzer. Melting points were measured using a Gallenkamp melting point apparatus. A Hitachi 8200 atomic absorption spectrometer was used for copper analyses. IR spectra were obtained by using IR grade KBr disks on a Perkin-Elmer 1600 Series FTIR spectrophotometer in the range 4000–250 cm^{-1}. Electronic spectra were obtained using a Cary 1E UV-Visible Spectrophotometer (Varian). Thermogravimetry/differential thermal analysis (TG/DTA) measurements were run on a Shimadzu DTG-60H. Thermogravimetric curves were obtained with a flow rate of carrier gas of 100 mL min^{-1} and a heating rate of 10°C min^{-1} in nitrogen (3 bar) with an alumina pan. Experiments were carried out in the range 35–750°C and clean up range 750–800°C under oxygen. With the help of the software, TA-60 WS Version 2.01, the data recorded was analyzed.

2.2. *Synthesis*

Synthesis of 2,6-*bis*(3,5-dimethyl-*N*-pyrazolyl)pyridine (bdmpp) **1** was accomplished by 2,6-dichloropyridine and the potassium salt of 3,5-dimethyl-*N*-pyrazol by refluxing in diglyme as described previously [9]. All spectral data agreed with the literature.

2.2.1. Synthesis of [Cu(bdmpp)(SeCN)$_2$] (2). A 20 mL solution of bdmpp (0.266 g, 1 mmol) in hot acetonitrile was added to a 20 mL hot methanolic solution of $CuCl_2 \cdot 2H_2O$ (0,171 g, 1 mmol). After mixing well, a 5 mL aqueous solution of KSeCN (0.288 g, 2 mmol) was added to the former mixture and was filtered off while the solution was hot. The resulting mixture was aside for two days and the dark brown fine crystals formed. The crystals were filtered off and dried in open air [10]. Yield: 78%, m.p.: 199–202°C. Anal. Calcd for $C_{17}H_{17}Cu\ N_7Se_2$: Cu, 11.74; C, 37.75; H, 3.14; N, 18.12. Found: Cu, 11.69; C, 37.71; H, 3.09; N, 18.08. Suitable crystals were selected for XRD study (scheme 1).



Scheme 1. Synthetic pathway for [Cu(bdmpp)$(SeCN)_2$].

2.3. *Crystal structure determination*

One of the fine dark-brown single crystals was mounted on a glass fiber and the intensity data of the copper(II) complex collected using a STOE IPDS 2 diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å) at 293 K. The structure (figure 1) was solved by direct methods using SHELXS-97 [11] and refined by a full-matrix least-squares procedure (SHELXL-97) [11]. All nonhydrogen atoms were easily found from the difference Fourier map and refined anisotropically. All H atoms attached to C atoms were refined using a riding model, with C–H (aromatic CH) = 0.93 %A, C–H (CH_2) = 0.97\%A and C–H (CH_3) = 0.96\%A. The U~iso~ values were calculated as 1.5 U~eq~(methyl group). However, the R_{int} value is a little higher due to the poor quality of the crystal. Molecular plots were prepared by using ORTEPIII [12]. The details of data collection, refinement and crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *Spectral properties*

3.1.1. FTIR spectra. To study the binding of bdmpp to copper in the complex, the IR spectrum of the free ligand was compared with the spectrum of [Cu(bdmpp)(SeCN)$_2$] in KBr pellets. Interest in the IR spectrum of the title complex lies mainly in the bands due to the SeCN$^-$ groups around 2100 cm^{-1}. The FTIR spectrum of the free ligand shows weak peaks at 2977, 2921 cm^{-1} and 3134, 3106 cm^{-1} assignable to CH_3 and aromatic

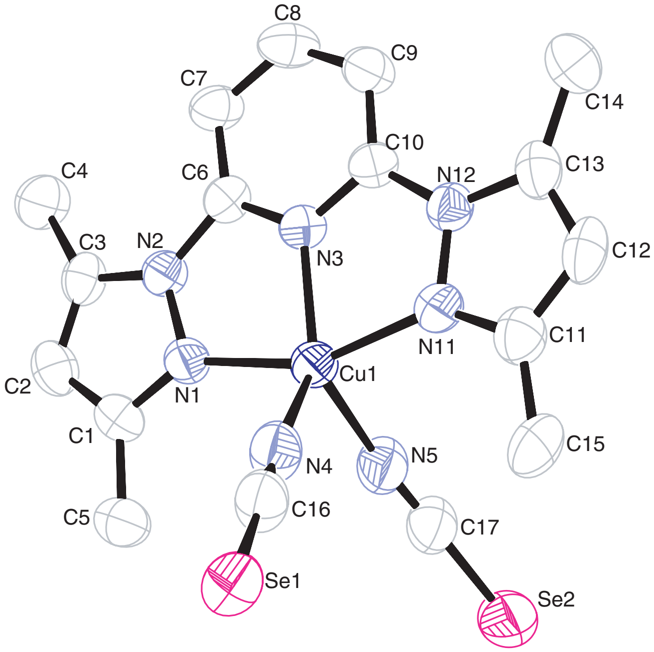


Figure 1. The ORTEP drawing of the title compound with the atomic numbering scheme. (Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity).

Table 1. Crystal data and experimental details of the [Cu(bdmpp)(SeCN)$_2$].

Empirical formula	[Cu(bdmpp)(SeCN)$_2$]
Formula weight	540.84
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal size (cm^3)	$0.09 \times 0.23 \times 0.50$
Crystal dimensions (Å, °)	
a	7.712(6)
b	15.403(11)
c	17.2680(15)
α	90.00
β	94.757(7)
γ	90.00
Volume (Å^3)	2044.2(3)
Z	4
ρ (min, max)	−1.214, 0.879
D_{Calcd} (Mg m^{-3})	1.757
Absolute coefficient (mm^{-1})	4.646
$F(000)$	1060
Theta range (°)	2.37–27.83
Absorption correction	Psi-scan ($T_{\text{min}} = 0.242$, $T_{\text{max}} = 0.626$)
h, k, l ranges	−10–8, −20–20, −22–22
Refinement on F^2	$w = 1/[\sigma^2 F_o^2 + (0.0580P)^2]$, $P = (F_o^2 + 2F_c^2)/3$
Reflections collected	12,770 [$R_{\text{int}} = 0.0463$]
Unique data	4673
Observed [$I > 2\sigma(I)$]	2720
Data/restrains/parameters	2720/1/236
Goodness of fit on F^2	1.073
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0710$, $wR_2 = 0.1308$
R indices [all data]	$R_1 = 0.0891$, $wR_2 = 0.1444$
Largest ΔF peak and hole (e Å^{-3})	1.79 and −2.17

hydrogen bonds. There is no band in the neighborhood of 2100 cm^{-1} in the free ligand spectra, where it is the main peak in the spectrum of the complex; this fact, together with the shifts of γ(CH) and δ(ring) in the spectrums may indicate interaction between the Cu atom and the pyridine ring. Beside of the strong C=N bands of selenocyanate at the 2061 and 2096 cm^{-1} the main pyridine ring stretching at 1590, 1438 and 1353 cm^{-1} shift to 1615, 1563, and 1480 cm^{-1} respectively due to the strong binding to the copper atom through electron donation from nitrogen.

3.1.2. Absorption spectra. Absorption spectra of the ligand (bdmpp) and complex [Cu(bdmpp)(SeCN)$_2$] were recorded in dimethylformamide; the complex has good solubility only in DMF. The UV spectra for ligand and complex have two strong absorptions between 250 and 310 nm. For the complex, a band occurs near 265 nm (18,500 M^{-1} cm^{-1}) with a shoulder at 328 nm. The spectra of the free ligand exhibit intense peaks at 258 (12,800 M^{-1} cm^{-1}) and 300 nm, indicating ligand-centered bands 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 reported by Willison *et al.* [13]. For comparison, coordination of

2,2′-bipyridine to an acidic metal center is known to result in intense and structured π–π^* absorptions in the vicinity of 290–310 nm, very different from the spectrum of the free ligand [14]. The corresponding transition in the bdmpp complex may occur at longer wavelength, possibly associated with the feature near 328 nm. The absorption shifts to longer wavelengths at 258 nm and gains intensity and the absorption at 300 nm has less intensity. In DMF solution, a distinct shoulder near 328 nm is evident, suggesting transition energy of the bdmpp complex.

3.2. *Thermal analysis*

The TGA and DTA analysis of [Cu(bdmpp)(SeCN)$_2$] was investigated both under inert and open-air atmospheres. Thermal analysis shows weight loss under nitrogen till 500°C is about 44–45% which the rest may be assumed as CuSe$_2$. The calculated weight loss of the complex is 41.07%. This 3–4% difference may be due to pyrolysis of the ligand.

Under open air loss was observed to about 347°C and the difference was the instability of the copperselenate over 315–400°C. We suggest that under open air, some of the selenate in CuSe$_2$ oxidizes to SeO$_2$ and over 450°C the selenoxide sublimes with weight loss about 75.88% (77.77 in theoretical).

3.3. *Description of the crystal structure*

The structure of **2** consists of a neutral [Cu(bdpp)(SeCN)$_2$] monomer which has a monoclinic unit cell. Previously, we published a mononuclear copper(II) complex with a similar coordination sphere [11]. In this case, azide replaced selenocyanate. As can be seen in figure 1, the copper has a distorted trigonal

Table 2. Selected bond lengths and bond angles (Å, °).

C16–N4	1.148(7)	N3–Cu1	1.972(4)
C16–Se1	1.780(6)	N4–Cu1	1.995(5)
C17–N5	1.126(7)	N5–Cu1	2.113(5)
C17–Se2	1.781(6)	N11–N12	1.384(6)
N1–N2	1.374(5)	N11–Cu1	1.998(4)
N1–Cu1	2.021(4)		
N4–C16–Se1	177.7(5)	N12–N11–Cu1	114.2(3)
N5–C17–Se2	178.6(6)	C13–N12–N11	110.5(4)
C1–N1–N2	106.5(4)	C13–N12–C10	133.7(4)
C1–N1–Cu1	139.8(3)	N11–N12–C10	115.7(4)
N2–N1–Cu1	113.8(3)	N3–Cu1–N4	136.25(18)
C3–N2–N1	110.2(4)	N3–Cu1–N11	78.56(17)
C3–N2–C6	133.3(4)	N4–Cu1–N11	96.16(19)
N1–N2–C6	116.5(4)	N3–Cu1–N1	77.89(16)
C6–N3–C10	121.3(4)	N4–Cu1–N1	98.91(18)
C6–N3–Cu1	120.1(3)	N11–Cu1–N1	156.30(17)
C10–N3–Cu1	118.6(3)	N3–Cu1–N5	123.32(18)
C16–N4–Cu1	171.9(5)	N4–Cu1–N5	100.4(2)
C17–N5–Cu1	153.2(5)	N11–Cu1–N5	96.22(19)
C11–N11–N12	106.0(4)	N1–Cu1–N5	98.92(18)
C11–N11–Cu1	139.6(4)		

Symmetry code: $1-x$, $1-y$, $1-z$.

bipyramidal geometry with the equatorial plane consisting of N3, N4, N5 from the pyridine and two selenocyanate and N1, N11 from the pyrazole groups in the axial positions.

Selected bond lengths and angles are listed in table 2. The bond distances and angles within the bdmpp ligand and selenocyanate anions have expected values. The five nearest neighbors around the Cu atom are the three N atoms [Cu–N1 2.021(4), Cu–N3 1.972(4), Cu–N11 1.998(4) Å] from the bdmpp ligand and two N atoms [Cu–N4 1.995(5), Cu–N5 2.113(5) Å] from the selenocyanate group occupying the basal plane and axial position. The selenocyanate ions are almost linear with N4–C16–Se1 and N5–C17–Se2 bond angles of 177.7(5)° and 178.6(6)°, respectively.

Supplementary data

Crystallographic data for the structure **2** reported in this article have been deposited with the Cambridge Crystallographic Data Centre (The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Email: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk; Fax: +44-(0)1223-336033) and are available free of charge on request, quoting the deposition number CCDC 603092.

Acknowledgements

The financial support of the Scientific and Technical Research Council of Turkey (TÜBİTAK-TBAG-2452 (104T064), and Balıkesir University is gratefully acknowledged.

References

[1] C. Diaz, J. Ribas, N. Sanz, X. Solans, M.C. Bardia. *Inorg. Chim. Acta*, **286**, 169 (1999).
[2] A. Escuer, R. Vicente, F.A. Mautner, M.A.S. Goher. *Inorg. Chem.*, **36**, 1233 (1997).
[3] M. Julve, M. Verdaugher, G. De Munno, J.A. Real, G. Bruno. *Inorg. Chem.*, **32**, 795 (1993).
[4] C.C. Wang, W.C. Lo, C.C. Chou, G.H. Lee, J.M. Chen, S.M. Peng. *Inorg. Chem.*, **37**, 4059 (1998).
[5] R. Kurtaran, K.C. Emregul, C. Arici, F. Ercan, V.J. Catalano, O. Atakol. *Synth. React. Inorg. Met. Org. Chem.*, **33**, 281 (2003).
[6] (a) F. Ercan, C. Arici, D. Ülkü, R. Kurtaran, M. Aksu, O. Atakol. *Z. Kristallogr.*, **219**, 295 (2004); (b) M.A. Halcrow. *Coord. Chem. Rev.*, **249**, 2880 (2005).
[7] T.K. Maji, G. Mostafa, P.S. Mukherjee, A. Mondal, A.J. Welch, K. Okamoto, N.R. Chaudhuri. *Polyhedron*, **19**, 1903 (2000).
[8] C.R. Choudhury, S.K. Dey, N. Mondal, S. Mitra, V. Gramlich. *Inorganica Chimica Acta*, **353**, 217 (2003).
[9] L. Jameson, K.A. Goldsby. *J. Org. Chem.*, **55**, 4992 (1990).
[10] R. Kurtaran, C. Arici, S. Durmus, D. Ulku, O. Atakol. *Anal. Sci.*, **19**, 335 (2003).
[11] G.M. Sheldrick. *SHELXS97 and SHELXL97. Program for Crystal Structure Solution and Refinement*, University of Gottingen, Germany (1997).
[12] L.J. Farrugia. ORTEP-3. *J. Appl. Cryst.*, **30**, 565 (1997).
[13] S.A. Willison, H. Jude, R.M. Antonelli, J.M. Rennekamp, N.A. Eckert, A. Jeanette, Krause Bauer, W.B. Connick. *Inorg. Chem.*, **43**(8), 2548 (2004).
[14] (a) R.G. Bray, J. Ferguson, C. Hawkins. *J. Aust. J. Chem.*, **22**, 2091 (1969); (b) T. Ohno, S. Kato. *Bull. Chem. Soc., Jpn*, **47**, 2953 (1974).