ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2018, *63*(10), 897-902

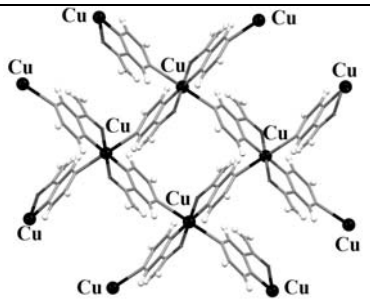
SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE DETERMINATION OF A PYRAZINE-2-CARBOXAMIDE-BRIDGED TWO-DIMENSIONAL POLYMERIC COPPER(II) COMPLEX

AMIN EBADI*

Department of Chemistry, Kazerun Branch, Islamic Azad University, Kazerun, Iran

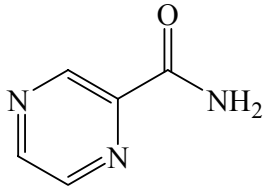
Received June 22, 2017

The new complex of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ (1) was synthesized from the reaction of $Cu(NO_3)_2\cdot 3H_2O$ with pyrazine-2-carboxamide (PYZ-AM) in methanolic solution. Suitable crystals of **1** for X-ray single crystal diffraction analysis were obtained by slow evaporation from methanol. Resulted complex was characterized by IR, UV-Vis, elemental analysis, thermal analysis and single crystal X-ray diffraction. The polymeric title compound, $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ crystallizes with one copper ion, two pyrazine-2-amide ligand, two nitrate anions and two methanol molecules in the asymmetric unit in *C*2/*c* monoclinic space group. The coordination geometry of copper ion is an elongated octahedral type. This compound has an equatorial-axial-type pyrazineamide bridge in the two-dimensional grid polymer.



INTRODUCTION

The construction of coordination polymers based on copper(II) ions and pyrazine has received considerably interest.[1-5] In this regard, the multifunctionality of the pyrazine-2-carboxamide (PYZ-AM) ligand offers interesting possibilities in crystal structure assemblies, owing to its chelating properties, in addition to its potential as a linker molecule between metal centers. Pyrazine-2-carboxamide (PYZ-AM) is known as an antitubercular agent.[6-7] Various coordination compounds involving PYZ-AM are known,[8-10] where the role of a bridging ligand between Cu ions is highlighted.[11-12] The two-dimensional grid polymer $[Cu(PYZ\text{-}AM)_2](ClO_4)_2$ has been known since 1973,[13] and it has a repeating $Cu_{(equatorial)}$–PYZ-AM–$Cu_{(axial)}$ coordination mode. It is notable that the constructing of the copper complexes having a Cu(equatorial)–PYZ-AM–Cu(axial) motif is a target of novel high spin species. Herein, we report the synthesis, characterization and crystal structure of a new copper(II) complex of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ (**1**) containing pyrazine-2-carboxamide (PYZ-AM), Scheme 1, as an example of an equatorial-axial-type pyrazineamide bridge in the two-dimensional grid polymer.



Scheme 1 – Molecular structure of pyrazine-2-carboxamide, PYZ-AM.

EXPERIMENTAL

Materials and physical methods

$Cu(NO_3)_2\cdot 3H_2O$ and pyrazine-2-carboxamide and other materials were obtained from Merck and used as received and

* Corresponding author: ebadiamin58@gmail.com, Fax: +98 7142230508

without further purification. Infrared spectrum (4000-250 cm^{-1}) of solid sample was taken as 1% dispersion in CsI pellets using a Shimadzu-470 spectrometer. UV–Vis spectra were recorded on a Shimadzu 2100 spectrometer, using a 1 cm path length cell, in the range of 250-600 nm. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. Melting point was obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus. Thermogravimetric analyses (TGA/DTA) were performed on a Bahr STA-503 thermal analyzer apparatus, in air, in the temperature range 35-400 °C, with a heating rate of 10 °C/min^{-1}.

Synthesis of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ (1)

$Cu(NO_3)_2.3H_2O$ (2.0 gr, 8.3 mmol) and pyrazine-2-carboxamide (2.0 gr, 16.6 mmol) were dissolved in methanol (40 mL). Resulted solution was stirred 2h at room temperature. Suitable crystals for X-ray diffraction measurement were obtained by slow evaporation from the resulted solution over three weeks (yield 2.45 g, 69.0%, m.p. 282 °C-decomposed). IR (CsI, cm^{-1}): 3501m, 3409w, 3275m, 3245m, 1698s, 1520s, 1482s, 1415m, 1386m, 1068m, 850m, 730w, 489w and 412w. Anal. Calcd. C, 28.95; H, 3.64; N, 22.51. Found: C, 28.98; H, 3.69; N, 22.54%.

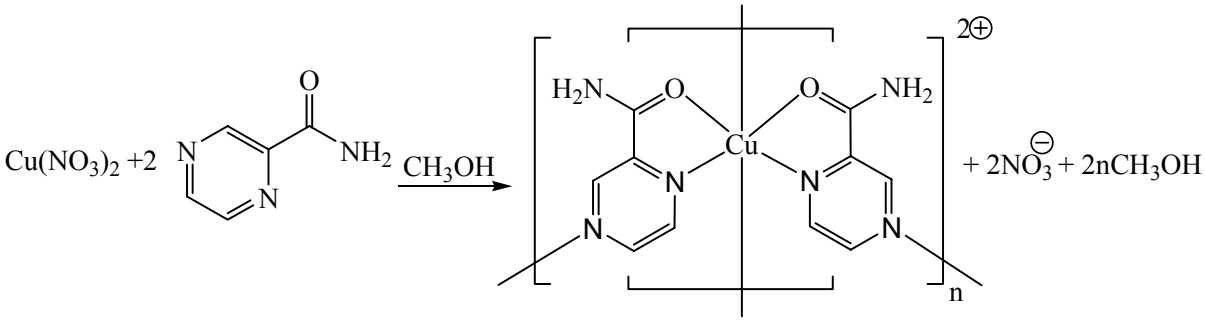
Crystallographic Data Collection and Structure Determination

The X-ray diffraction measurement was made on a Bruker APEX II CCD (Karlsruhe, Germany) area detector diffractometer at 298 K and with Mo-Kα radiation, graphite monochromator, λ = 0.71073Å. The structure of **1** was solved by SHELX-97 and absorption correction was done using the SADABS programs.[14] Data collection, cell refinement, and data reduction was done by APEX II, SAINT, SHELXTL, PLATON, and MERCURY software.[14-17] CCDC reference number is 1543495.

RESULTS AND DISCUSSION

Synthesis and characterization of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ (1)

Complex **1** was prepared by the reaction of copper(II) nitrate and pyrazine-2-carboxamide in 1:2 molar ratio in methanol at room temperature during 2 hours, as shown in the following scheme 2:



Scheme 2.

Suitable blue block crystals for X-ray diffraction analysis of **1** were obtained by slow evaporation from methanol solution after three weeks.

Spectroscopic characterization of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ (1)

IR absorptions of **1** have been listed in the experimental section. The infrared spectrum for this complex shows several bands in the region of 3275-3245 cm^{-1}, which are assigned to the C-H stretching vibrations of the pyrazine ring. The stretching of C=C and C=N in the pyridine moiety appears at 1520 and 1482 cm^{-1}. IR spectrum of mentioned complex contains asymmetric OCN and symmetric OCN stretching bands.[18] The asymmetric and symmetric stretching of OCN were observed in the 1698 and 1415 cm^{-1}, respectively. The N–H stretching bands were found in the region 3501-3409 cm^{-1}. Far infrared spectrum of complex **1** was recorded between 500 and 300 cm^{-1}. Vibrations that apear at 489 and 412 cm^{-1} can correspond to Cu-N and Cu-O stretchings vibrations.[19] Also vibrations that apear at 1386, 1068, 850 and 730 cm^{-1} can correspond to nitrate stretching and bending vibrations.[19]

The UV-Vis spectrum of free ligand in methanol solution, Figure 1, features two absorption bands at λ_{max} = 273 and 324 nm, corresponding to the aromatic rings. The spectrum of the complex, Figure 1, besides these two expected bands, shifted to lower wavelength and appearing at 270 and 318 nm, also displays a band at 388 nm. This band can be related to a charge-transfer between copper and ligand.

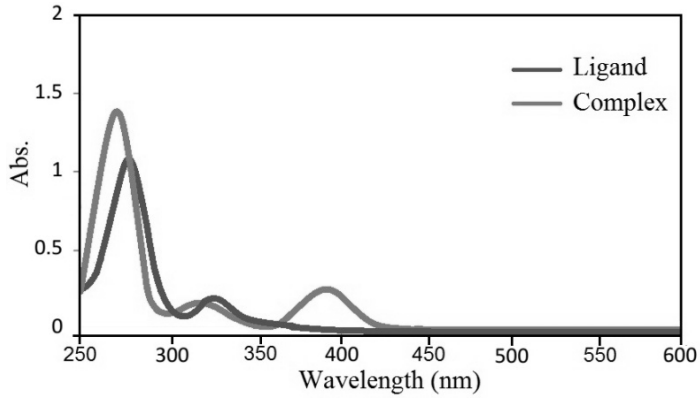


Fig. 1 – The UV-Vis spectra of free ligand and complex **1**, $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ **(1),** in CH_3OH solution.

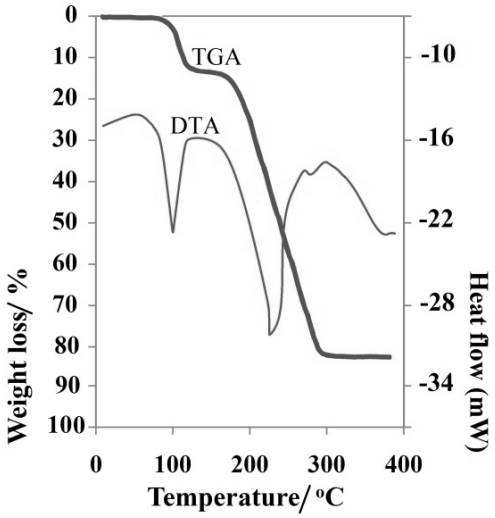


Fig. 2 – Thermogravimetric analysis of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ **(1)**.

Thermal studies of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ (1)

The thermal stability of **1** has been determined on single-crystalline samples between 35-400 °C in air atmosphere with a heating rate of 10 °C min^{-1} by thermogravimetric analysis (TGA)/differential thermal analysis (DTA), Figure 2. The TGA curve shows that compound **1** decomposed in two steps. In the first one, chemical decomposition starts at about 98 °C and ends around 105 °C with the weight loss of ~14% which corresponds to the removing of methanol solvents (calcd. 12.9%). Second one starts at about 198 °C and ends around 285 °C with the weight loss of ~72% corresponding to the decomposition of pyrazine-2-carboxamide ligands and nitrate anions (calcd. 70.6%). These desolvation and decomposition processes show up on DTA curve as two endotherms. The remaining weight of ~17% is corresponded to the CuO (calcd. 16.0 %).

Single crystal X-ray diffraction study of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ (1)

The crystal structure of **1** was determined by the X-ray diffraction study, Table 1. The asymmetric unit and the atom numbering scheme for complex **1** is shown in Figure 3. Selected bond distances and bond angles of interest are listed in Table 2. This compound crystallizes in the monoclinic *C*2/*c* space group. The coordination geometry of Cu ion is an elongated octahedral type. The Cu1–N2 and Cu1–$N3^i$ bond lengths are 1.983(4) and 2.467(4) Å, respectively, Table 2. The equatorial positions are occupied by two oxygen atoms, which are situated trans to each other. The equatorial Cu1–O1 distance of 1.264(6) Å is somewhat shorter than equatorial Cu1–N2 one. Consequently, this compound has an equatorial-axial-type pyrazine bridge in the two-dimensional grid polymer. The Cu ion has a distorted O_h structure. The bond angle of N2–Cu1–$N3^i$ in **1** is 91.77(14)° around the ideal angle of

90°, while those of O1–Cu1–N2 and O1–Cu1–N3^{i} deviate from the right angle, Table 2. Further, the basal Cu1–N2–C2–C5 plane is appreciably pyramidalized, similarly to that of the 2-substitued-pyrazine bridged copper(II) complexes.[20] The crystallographic analysis of **1** reveals the presence of a linear chain containing the copper(II) ion. The PYZ-AM ligand exhibits a tridentate coordination mode bridging two copper(II) ions, thus leading to an infinite 2D sheets with an intra-chain Cu…Cu separation of 7.162 Å. The 2-D grid structures of **1** is shown in Figure 4(a). The infinite two-dimensional polymer is located parallel to the crystallographic *bc*-plane. Side-view of the layered structure for **1** is shown in Figure 4(b). There are two nitrate anions in the unit cell of crystal packing of this compound, each one of these nitrate anions is disordered. Disordered nitrate anions are located in the 2D windows while the second ones, are located in the two-dimensional sheets of [{Cu(PYZ-AM)$_2$}$^{2+}$] cations parallel to the *bc*-plane, that is, the alternating cation and anion layers are stacked along the *a*-axis. As shown in Figure 4(b), stacking of these cations and anion layers cooperate by N-H…O hydrogen bonding between solvent methanol molecules and amidic NH_2-moiety from one side and O-H…O hydrogen bondings between methanol molecules and disordered nitrate anions from the other side, Table 3.

CONCLUSION

A new two-dimensional polymeric complex of copper (II) ion and pyrazine-2-carboxamide ligand, $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$, has been synthesized and characterized by spectroscopic methods in addition to establishing its single-crystal structure. The coordination geometry of copper ion is an elongated octahedral type. The crystallographic analysis of this compound reveals the presence of a linear chain containing the copper(II) ion. The pyrazineamide ligand exhibits a tridentate coordination mode bridging two copper(II) ions, thus leading to an infinite 2-D sheet. This compound has an equatorial-axial-type pyrazineamide bridge in the two-dimensional grid polymer.

Acknowledgments. We would like to thank the Graduate Study Councils of Islamic Azad University, Kazerun branch, for financial support.

Table 1

Crystallographic and structure refinement data for $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ **(1)**

Formula	$C_{12}H_{18}CuN_8O_{10}$
Formula weight *(g mol^{-1})*	497.89
Temperature /K	298
Wavelength λ/Å	0.71073
Crystal system	Monoclinic
Space Group	*C2/c*
a/Å	18.3883(10)
b/Å	9.5919(6)
c/Å	10.6392(5)
α/°	90
β/°	93.525(4)
γ/°	90
Volume/Å^3	1872.98(18)
Z	4
Density (calc.) /g cm^{-3}	1.766
θ ranges for data collection	2.40 -27.00
F(000)	1020
Absorption coefficient mm^{-1}	1.241
Index ranges	$-23 \le h \le 22$ $-12 \le k \le 12$ $-13 \le l \le 13$
Data collected	6108
Unique data (R_{int})	2049, 0.0458
Completeness to theta	99.9
Parameters, restrains	1363, 0
Final R_1, wR_2 (Obs. data)	0.0610, 0.1536
Final R_1, wR_2 (All data)	0.0736, 0.1601
Goodness of fit on F^2 (S)	1.061
Largest diff peak and hole/e.Å^{-3}	1.071, -1.100
CCDC	1543495

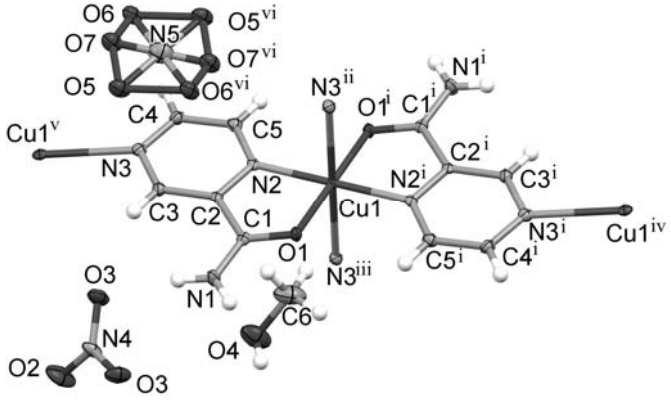
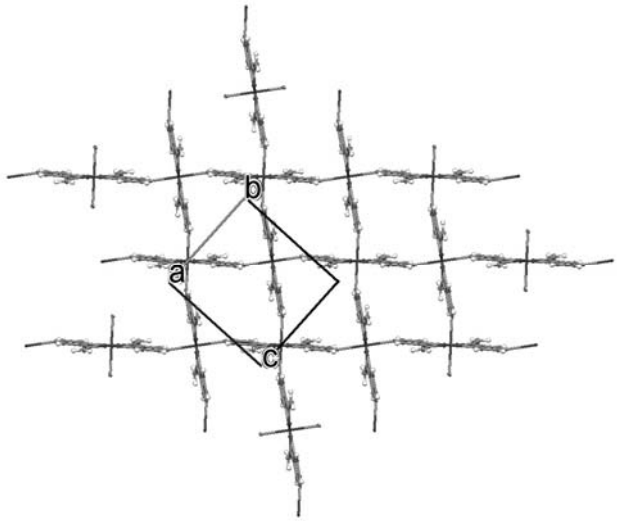
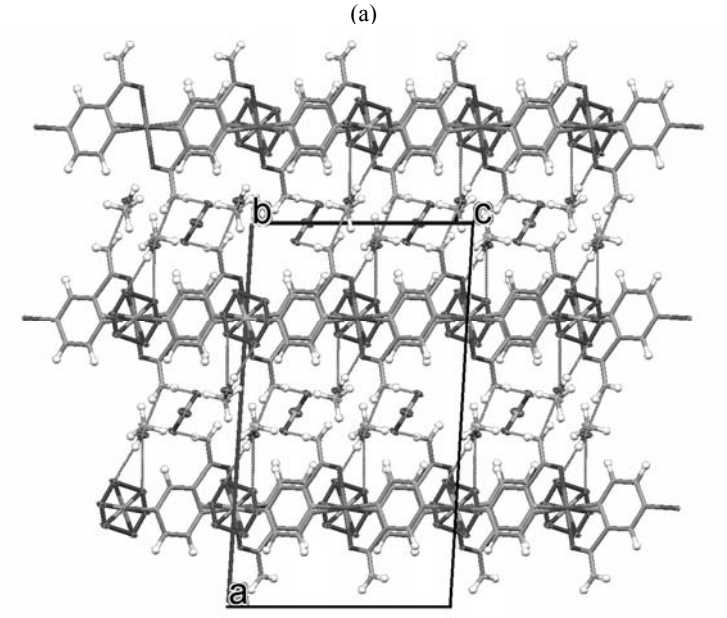


Fig. 3 – The labeled diagram of $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_2{\cdot}2CH_3OH$ **(1).** Thermal ellipsoids are at 50% probability level. One of the nitrate anions is disordered. Symmetry codes: (i) 1/2-x,1/2-y, 1/2-z, (ii) 1/2-x, 1/2+y,-1/2-z, (iii) x, -y, 1/2+z, (iv) 1/2-x,1/2+y, 1/2-z, (v) 1/2-x, -1/2+y,-1/2-z, (vi) 1/2-x, 1/2-y,-1-z.



(a)



(b)

Fig. 4 – Crystal packing diagram for $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_2{\cdot}2CH_3OH$ **(1)**. (a) formation of 2-D sheets parallel to *bc*-plane (anions and sovent molecules are omitted for better clarity) and (b) stacking of these layers in a-direction, by cooperation of N-H…O hydrogen bonding between solvent methanol molecules and amidic NH_2-moiety from one side and O-H…O hydrogen bondings between methanol molecules and disordered nitrate anions from the other side. Intermolecular interactions are shown as dashed lines.

Table 2

Selected bond distances (Å) and angles (°) for $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ **(1)**

Cu1-N2	1.983(4)
Cu1-N3^{i}	2.467(4)
Cu1-O1	1.962(3)
C1-O1	1.264(6)
C1-N1	1.300(6)
C2-N2	1.343(6)
C5-N2	1.330(6)
O1-Cu1-N2	82.60(15)
O1-Cu1-N3^{i}	89.27(14)
N2-Cu1-N3^{i}	91.77(14)
O1-Cu1-O1^{ii}	180.0
N2-Cu1-N2^{ii}	180.0
N3^{ii}-Cu1-N3^{iii}	180.0
C1-O1-Cu1-O1^{ii}	-38(3)
C1-O1-Cu1-N2	9.5(3)
C5-N2-Cu1-O1	174.4(4)
C2-N2-Cu1-O1	-4.6(3)

Symmetry codes: (i) x,-y,z+1/2, (ii) -x+1/2,-y+1/2,-z, (iii) -x+1/2,y+1/2,-z-1/2.

Table 3

Hydrogen-bond geometry for $[Cu(PYZ\text{-}AM)_2]_n(NO_3)_{2n}\cdot 2nCH_3OH$ **(1)** in the crystal packing (Å,°)

D-H…A	d(D…H)	d(H…A)	d(D…A)	<(DHA)	Symmetry Code
N1-H1B…O3	0.86	2.026	2.874(6)	169	-
N1-H1A…O4	0.86	2.054	2.864(7)	157	-
O4-H4B…O5	0.70(9)	1.94(9)	2.64(1)	176(10)	-1/2+x,1/2-y,1/2+z
O4-H4B…O6	0.70(9)	2.27(9)	2.83(1)	138(9)	-1/2+x,1/2-y,1/2+z

REFERENCES

1. J. L. Manson, J. G. Lecher, J. Y. Gu, U. Geiser, J. A. Schlueter, R. Henning, X. P. Wang, A. J. Schultz, H. J. Koo and M. H. Whangbo, *Dalton Trans.,* **2003**, 2905.
2. M. Mikuriya, H. Azuma and M. Handa, *Mol. Cryst. Liquid Cryst*., **2000**, *342*, 205.
3. K. Adachi, Y. Sugiyama, H. Kumagai, K. Inoue, S. Kitagawa and S. Kawata, *Mol. Cryst. Liquid Cryst.,* **2002,** *376*, 71.
4. S. A. Barnett, A. J. Blake, N. R. Champness and C. Wilson, *Chem. Commun*., **2002,** 1640.
5. H. W. Park, S. M. Sung, K. S. Min, H. Bang and M. P. Suh, *Eur. J. Inorg. Chem.*, **2001**, 2857.
6. P. K. Fyfe, V. A. Rao, A. Zemla, S. Cameron and W. N. Hunter, *Angew. Chem., Int. Ed.,* **2009,** *48*, 9176.
7. X. Du, W. Wang, R. Kim, H. Yakota, H. Nguyen and S.-H. Kim, *Biochemistry,* **2001,** *40*, 14166.
8. M. Sekizaki and K. Yamasaki, *Rev. Chim. Miner*., **1969,** *6*, 255.
9. M. A. S. Goher and F. A. Mautner, *Polyhedron,* **2000,** *19*, 601.
10. M. A. M. Abu Youssef, A. Escur and V. Langer, *Eur. J. Inorg. Chem.,* **2006,** 3177.
11. M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, K. Moriwaki and S. Kitagawa, *Inorg. Chem.,* **1997,** *36*, 5416.
12. M. A. S. Goher and F. A. Mautner, *J. Chem. Soc., Dalton Trans.*, **1999**, 1535.
13. M. Sekizaki, *Acta Crystallogr., Sect.,* **1973,** *B29*, 327.
14. G. M. Sheldrick, SADABS, Bruker AXS, Madison, WI, USA, **1998**.
15. Bruker SMART and SAINT. Bruker AXS Inc., Madison, WI, USA, **1998**.
16. G. M. Sheldrick, *Acta Crystallogr*, **2008**, *A64*, 112.
17. Mercury 1.4.1, Copyright Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, **2001**.
18. M. Sekizaki and K. Yamasaki, *Rev. Chim. Miner.,* **1969,** *6* , 255.
19. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compound Part B: Application in Coordination, Organometallic and Bioinorganic Chemistry", Wiley, New York, 2009.
20. T. Kogane, K. Kobayashi, M. Ishii, R. Hirota and M. Nakahara, *J. Chem. Soc., Dalton Trans.,* **1994,** *2*, 13.