ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 2, pp. 125–130. © Pleiades Publishing, Ltd., 2014.

Synthesis, Spectroscopic Characterization, and Crystal Structures of Copper(I) Iodide Clusters of *N*-Methylthiourea and 1,3-Diazinane-2-Thione[1]

T. Ahmad[a], R. Mahmood[b], S. C. Lee[c], and S. Ahmad[a], *

[a] *Department of Chemistry, University of Engineering and Technology, Lahore, 54890 Pakistan*
[b] *Division of Science and Technology, University of Education, Township, Lahore, Pakistan*
[c] *Department of Chemistry, University of Waterloo, Waterloo, Canada*
**e-mail: saeed_a786@hotmail.com*

Received November 19, 2012

Abstract—Two copper(I) iodide complexes, $[Cu_4(Metu)_6I_4]$ (**I**) and $[Cu_8(Diaz)_{12}I_8]$ (**II**) (Metu = *N*-methylthiourea; Diaz = 1,3-diazinane-2-thione), have been prepared and their structures been determined by X-ray crystallography. The crystal structures show that complex **I** is a tetranuclear, while **II** is an octanuclear cluster, both having a Cu : S ratio of 2 : 3, characteristic of metallothioneins. In **I**, each of the four copper atoms is coordinated to three thiourea ligands and one iodide ion in a distorted tetrahedral mode adopting admantane-like structure. In **II**, four types of core arrangements are observed around copper(I), which include, $Cu(\mu\text{-}S_2)I_2$, $Cu(\mu\text{-}S_2)(\mu\text{-}I)I$, $Cu(\mu\text{-}S_3)I$, and $Cu(\mu\text{-}S_3)S$ each having copper(I) tetrahedrally coordinated. The complexes were also characterized by IR and ^1H and ^{13}C NMR spectroscopy.

DOI: 10.1134/S1070328414020018

INTRODUCTION

Copper(I) has a strong tendency to form polynuclear aggregates and polymeric structures [1–8], which have significant importance in biological systems [8, 9] and have potential applications in catalysis [8, 10], in solar energy conversion systems, chemical sensors or display devices [11–14] and also in optical and electronic systems [14–16]. Sulfur or phosphorous containing ligands, halide ions or carbanionic organic molecules are the preferred ligands in such compounds. Among these ligand systems special attention is being given to heterocyclic thiones, which have been known to have wide ranging applications in analytical chemistry [17, 18] and metal treatment [19]. The metal–ligand interaction in such complexes has been found to be highly flexible, resulting in an extraordinary variety of molecular structures [1–3, 20–23]. Such copper(I) complexes may help to mimic bio-relevant metal sulfur interactions for example, in copper-metallothioneins the metals are coordinated by cysteine sulfur atoms only [9, 24].

In the present study, we attempted to prepare mixed ligand copper(I) complexes of thiones and a thiolate ligand, 2-mercaptopropanoic acid, but it is interesting to note that the compounds crystallized as products $[Cu_4(Metu)_6]I_4$ (**I**) and $[Cu_8(Diaz)_{12}I_8]$ (**II**) containing only thione ligands. The complex **I** has the adamantane structure, which is the characteristic of most of the copper(I) thiolates clusters and metallothioniens [7, 8, 24, 25]. The compound **II** is a two dimensional polymer with copper to sulfur ratio of 2 : 3, which is often suggested for copper(I)-metallothionein cluster core types, Cu_6S_9 and Cu_8S_{12} [24, 25].

EXPERIMENTAL

Materials and instrumentation. Copper(I) iodide was obtained from Merck Chemicals Co. Germany. 2-Mercaptopropanoic acid and *N*-methylthioura from Acros Organics, Belgium. Diazinane-2-thione was prepared according to the published procedure [26].

Solid state infrared spectra in the region of 4000–400 cm^{-1} were recorded as KBr pallets on a Nicolet FT-IR 6700 spectrophotometer. The ^1H and ^{13}C NMR spectra of the complexes in DMSO-d_6 were obtained on a Bruker Avance 300 MHz NMR spectrometer operating at frequencies of 300.00 and 75.47 MHz, respectively at 297 K. The spectral conditions were: 32 K data points, 1.822 s acquisition time, 2.00 s pulse delay and 6.00 μs pulse width. The ^{13}C chemical shifts were measured relative to TMS.

Synthesis of complexes. A solution of 1 mmol of copper(I) iodide in 10 mL acetonitrile was treated with

---

[1] The article is published in the original.

Table 1. Crystallographic data and details of the structure refinement for compounds **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	654.35	2917.93
Crystal system	Tetragonal	Monoclinic
Space group	$P\bar{4}n2$	$P2_1/c$
a, Å	14.1096(6)	18.8262(8)
b, Å	14.1096(6)	20.4911(9)
c, Å	9.6522(9)	23.5768(10)
β, deg	90	100.8340(10)
V, Å^3	3912.4(3)	8933.1(7)
Z	8	22
ρ_{calcd}, g cm^{-1}	2.222	2.169
Crystal size, mm	55 × 18 × 38	40 × 32 × 23
F(000)	2488	5600
μ, mm^{-1}	5.647	4.959
Temperature, K	296(2)	293(2)
$\lambda(\mathrm{Mo}K_\alpha)$, Å	0.71073	0.71073
θ Range, deg	2.89–30.04	2.97–30.03
Limiting indices h, k, l	$-19 \le h \le 19$, $-19 \le k \le 19$, $-27 \le l \le 27$	$-26 \le h \le 26$, $-28 \le k \le 28$, $-33 \le l \le 33$
Reflections collected/unique	57773/5730	136015/26095
R_{int}	0.0172	0.0270
Observed data ($I > 2\sigma(I)$)	5226	13886
T_{min}, T_{max}	0.559, 0.746	0.614, 0.746
Data, restraints, parameters	5730, 0, 203	26095, 36, 939
R_1, wR_2, $S(I > 2\sigma(I))$	0.0330, 0.0769, 1.706	0.0342, 0.0755, 1.001
Largest diff. peak, hole, e Å^{-3}	1.006, −1.213	0.958, −1.399

1 mmol of 2-mercaptopropionic acid in 5 mL acetonitrile. A clear colorless solution was obtained that was stirred for 15 min. To this solution was added 2 equivalents of *N*-methylthiourea or diazinane-2-thione slowly. The resulting colorless solution was stirred for 30 min at room temperature. The clear solution was filtered and left for crystallization at room temperature. White crystals were obtained after 48 h, which were washed with acetonitrile and dried in air at room temperature. The yield was 40% for **I** (m.p. 143–144°C) and 25% for **II** (m.p. 168–169°C).

For $C_{12}H_{36}N_{12}S_6I_4Cu_4$ (**I**)

anal. calcd., %:	C, 11.06;	H, 2.79;	N, 12.90.
Found, %:	C, 11.67;	H, 2.82;	N, 13.41.

For $C_{48}H_{96}N_{24}S_{12}I_8Cu_8$ (**II**)

anal. calcd., %:	C, 19.76;	H, 3.32;	N, 11.52.
Found, %:	C, 21.50;	H, 3.59;	N, 12.75.

X-ray crystallography. Single crystal X-ray diffraction analyses of compound **I** and **II** was carried out on a Bruker SMART APEX diffractometer processed with the Bruker APEX2 software package [27]. The structure was solved by direct methods with SHELXS-97 [28] and refined by full-matrix least squares procedures on F^2 with all measured reflections using SHELXL-97 [28]. The details of the crystallographic data and refinement parameters are provided in Table 1. Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 907221 and 907222, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Reactions of CuI with Metu and Diaz in a 1 : 2 molar ratio in the presence of 2-mercaptopropionic acid resulted in the formation of products of empirical composition $[Cu(L)_{1.5}I]$. The selected IR bands of the

Table 2. Selected IR frequencies (cm^{-1}) and NMR (^{1}H and ^{13}C) chemical shifts (in DMSO) of free ligands and their copper(I) complexes

Compound	IR frequencies			NMR shifts		
	ν(C=S)	ν(N–H)	ν(C–N)	δ(N–H)	δ(C=S)	δ(N–C)
Metu	634	3163, 3245	1488	6.95, 7.45, 7.65	181.10, 184.10	29.93, 31.10
[$Cu_4(Metu)_6I_4$]	610	3170, 3218, 3340	1440	7.22, 7.68, 7.97	176.532, 180.773	30.08, 31.06
Diaz	510	3200	1450	7.81	175.62	39.76 (19.19)*
[$Cu_8(Diaz)_{12}I_8$]	520	3215	1440	8.16	170.88	39.96 (18.65)*

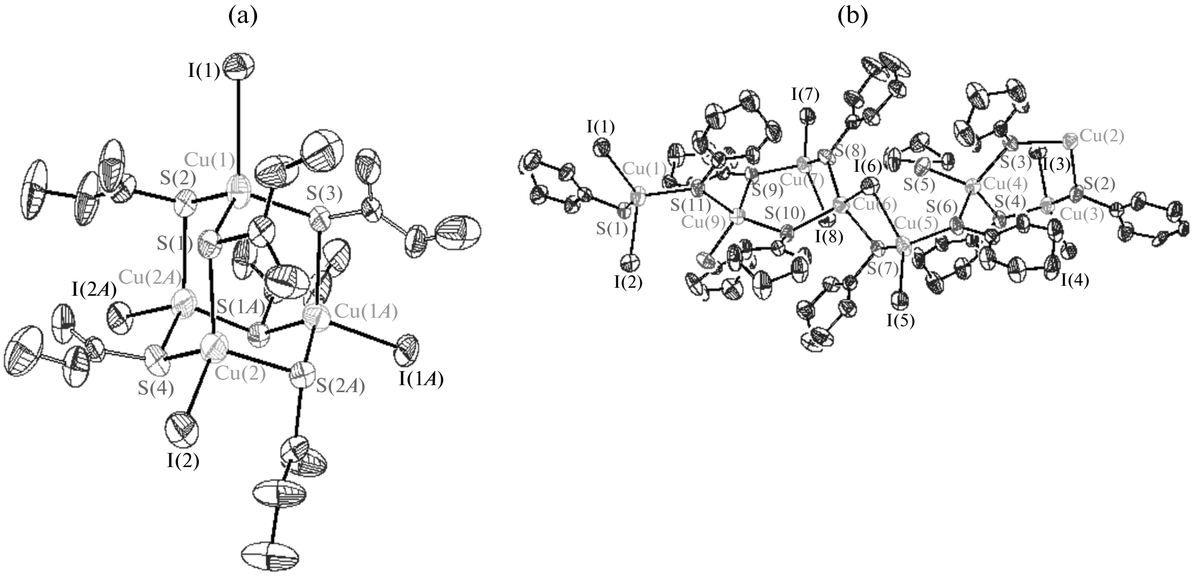
* Signals due to C(5) carbons.

ligands and their copper(I) complexes are given in Table 2. In IR spectrum of thiones, the characteristic bands are expected in three frequency regions; ν(C=S) appears around 600 or 500 cm^{-1}, ν(C–N) bands at about 1500 cm^{-1} and ν(N–H) is observed near 3200 cm^{-1}. The N–H bending vibration appears around 1600 cm^{-1}. The N–H bending vibrations in **I** appeared at 1540 and 1596 cm^{-1}, while in **II** at 1522 cm^{-1}. As shown in Table 2, the shifts in the ν(C=S), ν(N–H), and ν(C–N) bands in IR spectra of the complexes are indicative of coordination of the ligands to the metal center in the solid state.

The ^{1}H and ^{13}C chemical shifts of the complexes in DMSO-d_6 are summarized in Table 2. In ^{1}H NMR spectra of the complexes, the N–H signal of thioureas became less intense upon coordination and shifted down field from their positions in free forms. The appearance of N–H signal shows that the ligands are coordinated to copper(I) via the thione group. Table 2 shows that N–H protons of Metu are non-equivalent (NH_2 appears as a doublet) [29].

In ^{13}C NMR, the >C=S resonance of the ligands in the complexes is shifted upfield by about 4–5 ppm as compared to their positions in uncomplexed form in accordance with the data observed for other complexes of d^{10} metals with thiones [29, 30]. An upfield shift of this magnitude is a diagnostic test for thione sulfur donation. A small deshielding effect is observed in N–C carbon atoms, which is due to an increase in π character of the C–N bond. Metu gives two signals for both >C=S and N–CH_3 carbons showing that the compound exists in two isomeric forms [29].

The molecular structures of [$Cu_4(Metu)_6I_4$] (**I**) and [$Cu_8(Diaz)_{12}I_8$] (**II**) with the atomic numbering schemes are depicted in figure. Selected bond distances (Å) and bond angles (deg) for **I** and **II** are given in Table 3. In complex **I**, four copper(I) iodide and six Metu ligands are combined through μ-bridging sulfur atoms to form a tetranuclear core $Cu_4S_6I_4$. In



The molecular structure of **I** (a) and **II** (b) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 3. Selected bond distances (Å) and bond angles (deg) for compounds **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
I			
Cu(1)–S(1)	2.3382(13)	Cu(2)–S(2)	2.3613(14)
Cu(1)–S(2)	2.2924(13)	Cu(2)–I(2)	2.8127(9)
Cu(1)–S(3)	2.2917(11)	C(10)–S(1)	1.731(5)
Cu(1)–I(1)	2.7767(8)	C(10)–N(10)	1.302(7)
Cu(2)–S(4)	2.2825(12)	C(10)–N(11)	1.294(7)
Cu(2)–S(1)	2.2887(13)	C(11)–N(11)	1.460(8)
II			
Cu(1)–S(1)	2.3094(12)	Cu(5)–I(6)	2.8196(8)
Cu(1)–I(1)	2.6204(7)	Cu(6)–S(7)	2.4026(14)
Cu(1)–I(2)	2.8247(8)	Cu(6)–S(8)	2.3010(14)
Cu(1)–S(11)	2.3311(14)	Cu(6)–S(10)	2.3883(12)
Cu(1)–Cu(2)	3.0157(9)	Cu(6)–I(6)	2.6927(6)
Cu(2)–S(1)	2.4072(14)	Cu(7)–S(8)	2.3316(13)
Cu(2)–S(2)	2.2983(14)	Cu(7)–S(9)	2.3558(14)
Cu(2)–S(3)	2.3828(12)	Cu(7)–I(7)	2.6435(7)
Cu(2)–I(2)	2.6944(6)	Cu(7)–I(8)	2.6493(7)
Cu(3)–S(2)	2.3304(12)	Cu(8)–S(9)	2.3033(13)
Cu(3)–S(4)	2.3590(13)	Cu(8)–S(10)	2.3494(11)
Cu(3)–I(3)	2.6576(7)	Cu(8)–S(11)	2.3921(13)
Cu(3)–I(4)	2.6404(7)	Cu(8)–S(12)	2.2861(12)
Cu(4)–S(3)	2.3470(11)	S(1)–C(11)	1.735(5)
Cu(4)–S(4)	2.3012(12)	S(2)–C(21)	1.719(5)
Cu(4)–S(5)	2.2885(12)	N(16)–C(11)	1.311(5)
Cu(4)–S(6)	2.3947(12)	N(12)–C(11)	1.323(6)
Cu(5)–S(6)	2.3249(13)	N(12)–C(13)	1.456(6)
Cu(5)–S(7)	2.3098(12)	N(16)–C(15)	1.463(6)
Cu(5)–I(5)	2.6213(7)		
Angle	ω, deg	Angle	ω, deg
I			
S(2)Cu(1)S(1)	113.47(5)	S(1)Cu(1)I(1)	104.04(4)
S(3)Cu(1)S(1)	112.79(4)	S(2)Cu(1)I(1)	108.65(4)
S(3)Cu(1)S(2)	107.87(4)	S(1)Cu(2)I(2)	107.74(4)
S(3)Cu(1)I(1)	109.89(4)	S(2)Cu(2)I(2)	107.02(4)
S(4)Cu(2)S(1)	109.09(4)	Cu(2)S(1)Cu(1)	104.79(5)
S(1)Cu(2)S(2)	111.12(5)	Cu(1)S(2)Cu(2)	104.62(5)
S(4)Cu(2)S(2)	112.79(4)	Cu(1)S(3)Cu(1)	107.39(7)
S(4)Cu(2)I(2)	108.93(4)	Cu(2)S(4)Cu(2)	108.53(8)
II			
S(1)Cu(2)S(11)	97.57(5)	S(6)Cu(5)I(5)	119.60(4)
S(1)Cu(1)I(1)	122.59(4)	S(6)Cu(5)I(6)	106.63(4)
S(1)Cu(1)I(2)	105.94(4)	S(7)Cu(5)I(5)	123.08(4)
S(11)Cu(1)I(1)	120.01(4)	I(6)Cu(5)I(7)	103.93(2)
S(11)Cu(1)I(2)	106.83(4)	S(7)Cu(6)S(8)	119.83(6)
I(1)Cu(1)I(2)	102.62(2)	S(7)Cu(6)S(10)	104.95(5)
S(2)Cu(2)S(1)	116.40(5)	S(8)Cu(6)S(10)	99.68(5)
S(2)Cu(2)S(3)	100.02(5)	S(7)Cu(6)I(6)	104.92(3)
S(3)Cu(2)S(1)	104.83(4)	S(8)Cu(6)I(6)	112.71(4)
S(2)Cu(2)I(2)	113.40(4)	S(10)Cu(6)I(6)	114.88(3)
S(3)Cu(2)I(2)	114.79(3)	S(8)Cu(7)S(9)	91.93(5)
S(2)Cu(2)I(2)	107.22(3)	S(8)Cu(7)I(7)	119.97(4)
S(2)Cu(3)S(4)	91.64(5)	S(8)Cu(7)I(8)	109.63(4)
S(2)Cu(3)I(4)	119.49(4)	S(9)Cu(7)I(7)	115.09(4)
S(4)Cu(3)I(4)	115.28(4)	S(9)Cu(7)I(8)	109.80(4)
I(4)Cu(3)I(3)	107.61(2)	I(7)Cu(7)I(8)	109.24(2)
S(5)Cu(4)S(4)	115.40(4)	S(9)Cu(8)S(10)	108.49(4)
S(5)Cu(4)S(3)	115.29(5)	S(9)Cu(8)S(11)	106.31(6)
S(4)Cu(4)S(3)	108.26(4)	S(9)Cu(8)S(12)	115.32(4)
S(3)Cu(4)S(6)	109.75(4)	S(10)Cu(8)S(11)	110.05(4)
S(4)Cu(4)S(6)	106.55(6)	S(10)Cu(8)S(12)	115.19(5)
S(6)Cu(5)S(7)	98.21(5)	S(11)Cu(8)S(12)	100.81(5)

the tetranuclear core, each copper is tetrahedrally coordinated to three sulfur atoms of Metu and with one iodide in the terminal position. The angles around Cu vary over a range of 107.02°–113.47(5)° representing a nearly regular tetrahedral geometry. The Cu–S (2.2825(12) to 2.3613(14) Å) and Cu–I ((2.2825(12) to 2.3613(14) Å) bond distances are unequal. However, they are within the range of the Cu–S and Cu–I bond distances found in other complexes [1, 2, 31–37]. The arrangement of four copper centers leads to a tetrahedral array inscribed inside a distorted octahedron formed by six μ-Metu bridging ligands. The copper–sulfur interaction gives rise to a tetracyclic system involving four six-membered rings consisting of Cu_3S_3 moieties. The six-membered rings adopt a half-chair conformation and are interconnected in an arrangement characteristic of adamantane. This cluster type is very common for copper(I) thiolates [7, 25] and copper(I) thiourea systems [31, 32]. The Cu : S ratio of 2 : 3 of core unit is the characteristic of metallothioniens and synthetic polynuclear copper(I) complexes with thiolates [24, 38].

Complex **II** exists in the form of an octanulcear cluster consisting of two equivalent segments of the type $Cu_4S_6I_4$, which are oriented face to face and are connected together through μ_2 bridging sulfur atoms of Diaz and iodide ions. Four types of cores (coordination environments) are observed around copper atoms. Cu(1) and Cu(5) are coordinated to two sulfur atoms of Diaz, one bridging and one terminal I^- ion $(Cu(\mu\text{-}S_2)(\mu\text{-}I)I)$. Cu(2) and Cu(6) are bound to three $\mu\text{-}S_2$ sulfur atoms of Diaz and one $\mu\text{-}I^-$ $(Cu(\mu\text{-}S_3)I)$ The coordination spheres of Cu(3) and Cu(7) are completed by two doubly bridging Diaz and two terminal iodido ligands $(Cu(\mu\text{-}S_2)I_2)$. Cu(4) and Cu(8) are attached only to Diaz ligands; three μ- bridging and one terminal $(Cu(\mu\text{-}S_3)S$ (Fig. 2)). The terminal Cu–S distance (Cu(4)–S(5) 2.2885(12) Å) is reasonably shorter than the bridging distances ranging from 2.3012(12) to 2.3947(12) Å. All of the copper atoms in the cluster show tetrahedral geometry with distortions indicated by the bond angles ranging from 91.64(5)°–122.59(4)° (Table 3). Copper atoms, bridging sulfur and iodide ion the cluster are arranged in the form of four- and six-membered rings. This different type of ligation around different Cu centers in the same cluster has also been found previously [5]. The Cu–S and Cu–I bond distances fall within the range of the Cu–S and Cu–I bond distances found in other complexes [1, 31–37]. The SCN_2 moieties in both complexes are essentially planar with bond lengths corresponding to values intermediate between single and double bonds. This is attributed to the delocalization of electrons in the SCN_2 fragment and the significant sp^2 character of the two nitrogen atoms. Formation of polynuclear clusters with copper iodide have also been demonstrated in other studies [1, 2, 32, 36].

The octanuclear units are associated to each other through S(1) and I(1) of Diaz to form a polymeric structure. The polymer structure is supported by significant Cu–Cu interactions. The Cu(1)–Cu(2) distance of 3.0157 Å is close to similar distances observed in other complexes [1, 36, 37], for example, $[Cu_2(Py_2TH)_4I_2]$ with a separation Cu---Cu of 3.139 Å (Py_2TH = 1H-pyridine-2-thione) [37].

This paper reports the crystal structures of two novel complexes of copper(I) iodide with thiourea ligands, which exist in the form of tetra or octa nuclear clusters. In both, the copper atoms have distorted tetrahedral geometries and the thiourea ligands coordinate through the sulfur atom in a bridging or terminal mode. The Cu : S ratio of 2 : 3 of core units in both complexes is the characteristic of metallothioniens. The study also demonstartes the role of thiones and metal-bound halides in the construction of copper(I) clusters and novel polymers.

REFERENCES

1. Li, D., Shi, W.-J., and Hou, L., *Inorg. Chem.*, 2005, vol. 44, p. 3907.
2. Ahmad, S., Mufakkar, M., Khan, I.U., et al., *Acta Crystallogr., E*, 2012, vol. 68, p. m1405.
3. Noreen, F., Ruffer, T., Lang, H., et al., *J. Chem. Crystallogr.*, 2008, vol. 38, p. 765.
4. Jin, S., Wang, D., Li, W., et al., *J. Inorg. Organomet. Polym. Mater.*, 2010, vol. 20, p. 83.
5. York, J.T., Bar-Nahum, I., and Tolman, W.B., *Inorg. Chem.*, 2007, vol. 46, p. 8105.
6. Dubler, E. and Baumgartner, M., *Solid State Ionics*, 1990, vol. 43, p. 193.
7. Baumgartner, M., Schmalle, H., and Dubler, E., *Polyhedron*, 1990, vol. 9, p. 1155.
8. York, J.T., Bar-Nahum, I., and Tolman, W.B., *Inorg. Chim. Acta*, 2008, vol. 361, p. 88.
9. Kaim, W. and Schwederski, B., *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, New York: Wiley, 1994, p. 367.
10. Wang, X.-S., Zhao, H., Li, Y.-H., et al., *Top. Catal.*, 2005, vol. 35, p. 43.
11. Scaltrito, D.V., Thompson, D.W., O'Callaghan, J.A., and Meyer, G.J., *Coord. Chem. Rev.*, 2000, vol. 208, p. 243.
12. McMillin, D.R. and McNett, K.M., *Chem. Rev.*, 1998, vol. 98, p. 1201.
13. Armaroli, N., *Chem. Soc. Rev.*, 2001, vol. 30, p. 113.
14. Cuttell, D.G., Kuang, S.-M., Fanwick, P.E., et al., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 6.
15. Yam, V.W.W., Lee, W.K., and Lai, T.F., *Chem. Commun.*, 1993, p. 1571.
16. Aslanidis, P., Chrissafis, K., and Lalia-Kantouri, M., *J. Therm. Anal. Calorim.*, 2011, vol. 103, p. 797.
17. Stiff, M.J., *Analyst*, 1972, vol. 97, p. 146.
18. Khalifa, M.E., Akl, M.A., and Ghazy, S.E., *Chem. Pharm. Bull.*, 2001, vol. 49, p. 664.
19. Donnelly, B., Downie, T.C., Grzeskowiak, R., et al., *Corros. Sci.*, 1978, vol. 18, p. 109.

20. Raper, E.S., *Coord. Chem. Rev.*, 1985, vol. 61, p. 115.
21. Raper, E.S., *Coord. Chem. Rev.*, 1996, vol. 153, p. 199.
22. Raper, E.S., *Coord. Chem. Rev.*, 2001, vol. 213, p. 181.
23. Lobana, T.S., Khanna, S., Butcher, R.J., et al., *Polyhedron*, 2006, vol. 25, p. 2755.
24. *Metallothionein*, Stillman, M.J., Shaw C.F. III, and Suzuki, K.T., Eds., New York: VCH Publishers Inc., 1992.
25. Baumgartner, M., Schmalle, H., and Dubler, E., *Inorg. Chim. Acta*, 1993, vol. 208, p. 135.
26. Ahmad, S., Isab, A.A., and Perzanowski, H.P., *Can. J. Chem.*, 2002, vol. 80, p. 1279.
27. *SMART and SAINT*, Madison (WI, USA): Bruker AXS Inc., 2008.
28. Sheldrick, G.M., *Acta Crystallogr. A*, 2008, vol. 64, p. 112.
29. Ahmad, S., Isab, A.A., and Arab, M., *Polyhedron*, 2002, vol. 21, p. 1267.
30. Malik, M.R., Vasylyeva, V., Merz, K., et al., *Inorg. Chim. Acta*, 2011, vol. 376, p. 207.
31. Griffith, E.H., Hunt, G.W., and Amma, E.L., *Chem. Commun.*, 1976, p. 432.
32. Pakawatchai, C., Thanyasirikul, Y., Saepae, T., et al., *Acta Crystallogr.*, *C*, 1998, vol. 54, p. 1750.
33. Akrivos, P.D., Karagiannidis, P., Herrema, J., et al., *J. Coord. Chem.*, 1995, vol. 36, p. 259.
34. Mufakkar, M., Isab, A.A., and Ruffer, T., *Transition Met. Chem.*, 2011, vol. 36, p. 505.
35. Mufakkar, M., Ahmad, S., Khan, I.U., et al., *Acta Crystallogr.*, *E*, 2007, vol. 63, p. m2384.
36. Lobana, T.S., Sharma, R., Sharma, R., et al., *Inorg. Chem.*, 2005, vol. 44, p. 1914.
37. Mentzafos, D., Terzis, A., Karagiannidis, P., and Aslanidis, P., *Acta Crystallogr.*, *C*, 1989, vol. 45, p. 54.
38. Byrd, J., Berger, R.M., and McMillin, D.R., *J. Biol. Chem.*, 1988, vol. 263, p. 6688.