Polyhedron 47 (2012) 79–86

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, characterization and X-ray crystal structures of thiolate sulfur-bridged dimeric copper(II) complexes of the 2-aminoacetophenone Schiff base of S-methyldithiocarbazate

Mohammad Akbar Ali [a,*], Aminul Huq Mirza [a], Malai Haniti S.A. Hamid [a], Nuzuhath Aminath [a], Paul V. Bernhardt [b]

[a] Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, BE 1410, Brunei Darussalam
[b] School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, QLD 4072, Australia

ARTICLE INFO

Article history:
Received 22 June 2012
Accepted 8 August 2012
Available online 17 August 2012

Keywords:
2-Aminoacetophenone Schiff base of S-methyldithiocarbazate
Thiolate sulfur-bridged dimeric copper(II) complexes
Copper(II) complexes of 2-aminoacetophenone Schiff base of S-methyldithiocarbazate

ABSTRACT

Copper(II) complexes of general empirical formula, Cu(apsme)X (apsme = monodeprotonated form of the 2-aminoacetophenone Schiff base of S-methyldithiocarbazate (Hapsme); X = Cl^-, Br^-, NCS^-) have been prepared and characterised by a variety of physico-chemical techniques. The crystal and molecular structures of the Schiff base, Hapsme (**1**), [Cu(apsme)Br] (**2**), [Cu(apsme)(NCS)] (**3**) and [Cu(apsme)Cl] (**4**) have been determined by X-ray diffraction. In the solid state the copper(II) complexes **2**, **3** and **4** are dimers in which the anionic Schiff base, ($apsme^-$) coordinates with a copper(II) ion as a tridentate NNS chelating agent *via* the amino nitrogen atom, the azomethine nitrogen atom and the thiolate sulfur atom. The fourth and fifth coordination positions of a copper atom are occupied by a co-ligand and bridging thiolate sulfur atoms, respectively.

1. Introduction

Metal complexes of dithiocarbazic acid and its derivatives have received considerable attention because of their interesting physico-chemical properties [1], varied structural features [2] and potentially useful chemotherapeutic properties [3,4]. However, most work on this class of compounds involved tridentate NNS Schiff bases formed by condensation of heterocyclic aldehydes and ketones with S-methyl- and S-benzyldithiocarbazates [5–9]. Schiff bases formed by condensation of 2-aminobenzaldehyde or 2-aminoacetophenone with S-alkyl/aryl dithiocarbazates did not receive much attention. The presence of an amino nitrogen atom in the NNS set of donor atoms in a tridentate dithiocarbazate ligand offers additional possibilities of intermolecular hydrogen bond formation which may lead to metal complexes with three dimensional network structures exhibiting interesting physical and chemical properties. Also, transition metal complexes of this type of ligands may exhibit useful chemotherapeutic properties. In fact, several copper(II) complexes of the 2-aminobenzaldehyde Schiff base of S-methyldithiocarbazate have already been found to exhibit very high inhibitory activities against the pathogenic fungi, *Alternaria alternata* and *Curvularia geniculata* [3].

In view of the paucity of X-ray structural data on copper(II) complexes of this type of ligands and as part of our continued interest on metal complexes of dithiocarbazates, we report here the preparation, spectroscopic characterization and X-ray crystal structures of three dimeric copper(II) complexes of Hapsme, together with the structure of the free ligand, **1**.

2. Experimental

2.1. Reagents

Chemicals and solvents used were of analytical reagent grades and used without any further purification. 2-Aminoacetophenone and the copper salts were purchased from the Aldrich Chemical Company and S-methyldithiocarbazate was prepared according to the published procedure [10].

2.2. Physical measurements

Microanalyses for C, H and N were performed by the Elemental Analysis Laboratory, National University of Singapore, Singapore. Molar conductances of ca. 10^{-3} M solutions of the complexes in

---

* Corresponding author. Present address: Apt. #101A, Plot #11/A, Road #71, Gulshan-2, Dhaka 1212, Bangladesh. Tel.: +880 2 8822665.
E-mail address: palonkuri@yahoo.com (M. Akbar Ali).

0277-5387/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2012.08.024

Table 1
Crystal and refinement data.

	Hapsme (**1**)	[Cu(apsme)Br] (**2**)	[Cu(apsme)(NCS)] (**3**)	[Cu(apsme)Cl] (**4**)
Formula	$C_{10}H_{13}N_3S_2$	$C_{10}H_{12}BrCuN_3S_2$	$C_{11}H_{12}CuN_4S_3$	$C_{10}H_{12}ClCuN_3S_2$
Formula weight	239.35	381.80	359.97	337.34
T (K)	293	293	293	293
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/a$	$P2_1/n$
a (Å)	5.7972(5)	7.5409(6)	7.926(7)	7.5124(9)
b (Å)	11.688(2)	11.426(2)	16.201(5)	11.326(2)
c (Å)	17.040(3)	15.235(2)	12.183(6)	15.066(2)
α (°)	102.171(1)			
β (°)	93.736(9)	95.110(10)	108.33(6)	94.99(2)
γ (°)	99.151(9)			
V (Å^3)	1108.4(2)	1307.5(3)	1485(2)	1277.0(3)
Z	4	4	4	4
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ (g cm^{-3})	1.434	1.940	1.610	1.755
μ (mm^{-1})	0.450	5.025	1.882	2.225
$\theta_{min,max}$ (°)	3.37–25.00	2.23–24.97	1.76–24.99	2.25–24.99
$F(000)$	504	756	732	684
Measured reflections	7235	2482	2819	2413
Independent reflections	3874	2482	2615	2231
R_{int}	0.0369	0.0605	0.0473	0.029
Observed reflections	2574	1326	1332	1379
R_1 (observed data)	0.0565	0.0659	0.0772	0.0410
wR_2 (all data)	0.1321	0.1723	0.2352	0.1032
GOF	1.029	0.979	0.997	0.993
CCDC No.	885661	885662	885663	885664

DMSO were measured by means of a CMD400 conductivity meter. Magnetic susceptibilities were measured at 300 K using a Sherwood Scientific balance. $Hg[Co(NCS)_4]$ was used as a standard. The IR spectra in KBr discs and the electronic spectra either as Nujol mulls or in solution were recorded on a Perkin-Elmer 1600 FT IR spectrometer and a Shimadzu UV-3100 spectrophotometer respectively. The ^1H NMR spectra were recorded on a Bruker Avance 300 MHz FT-NMR DPX 300 K spectrometer using either DMSO-d_6 or $CDCl_3$ as solvents and TMS as an internal standard.

2.3. Preparation of the ligand

2.3.1. Preparation of **1**

A solution of 2′-aminoacetophenone (2.0 g; 0.0148 mol) in abs. ethanol (15 mL) was mixed with a boiling solution of S-methyldithiocarbazate (1.81 g; 0.0148 mol) in the same solvent (50 mL). Two drops of conc. HCl were added and then the mixture was refluxed for ca. 3.5 h and cooled. The resulting crystals of the Schiff base were filtered off, washed. Yield, 1.80 g (50%). M.p. 183 °C. *Anal.* Calc. for $C_{10}H_{13}N_3S_2$: C, 48.36; H, 5.68; N, 16.92. Found: C, 47.92; H, 5.91; N, 16.48%, ^1H NMR [DMSO-d_6] δ_H: 2.54 (s, 3H, SCH_3), 2.39 (s,3H, C–CH_3), 6.90 (s, 2H, NH_2), 6.55 (t, 1H, ArH), 6.54 (d, 1H, ArH), 7.47 (d, 1H, ArH), 7.90 (t, 1H, ArH), 12.43H (s, NH); ^{13}C NMR [DMSO-d_6]: 16.66 (–CH_3), 17.58 (SCH_3), 115.50, 116.73, 117.10, 130.44, 130.97, 148.21 [Ar C], 197.56 (CS), 157.21 (C=N).

2.4. Preparation of the complexes

2.4.1. General method of preparation of **2** and **4**

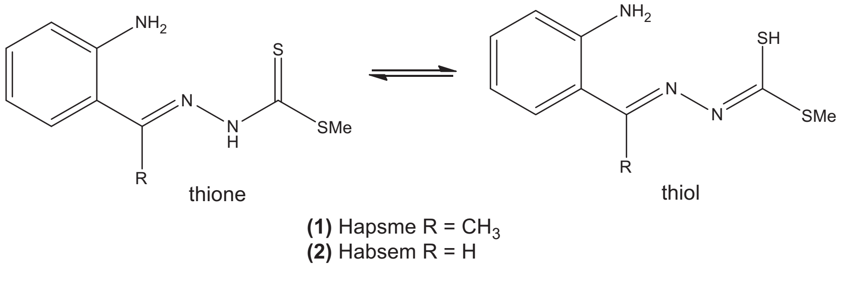
The appropriate hydrated copper(II) salt (2 mmol) dissolved in hot acetonitrile (20 mL) was mixed with a boiling solution of the Schiff base (2.2 mmol) in the same solvent (50 mL) and the mixture heated on a water bath for about 5 min and filtered. The filtrate on being left to stand overnight, yielded shining dark green crystals of the complexes which were filtered off, washed with ethanol and dried in a desiccator over anhydrous silica gel. Recrystallization of the crude product from a 1:1 mixture of DMF and methanol afforded diffraction quality crystals.

2: Yield, 0.382 g (50%). Λ (Ω^{-1} cm^2 mol^{-1}): 27.0; μ_{eff} (BM): 1.73. *Anal.* Calc. for $C_{10}H_{12}CuBrN_3S_2$: C, 29.39; H, 2.74; N, 11.43. Found: C, 29.50; H, 2.80; N, 11.20%. UV–Vis: λ_{max}/nm, (logε (dm^3 cm^{-1} mol^{-1}): 628 (1.60), 445 (4.71), 326 (5.03), 306 (5.05); IR/cm^{-1}: 3234 m (νNH), 1598s (νCN), 1072s (νNN), 730s (νCS).

4: Yield, 0.40 g (60%). Λ (Ω^{-1} cm^2 mol^{-1}): 18.3; μ_{eff} (BM): 1.73. *Anal.* Calc. for $C_{10}H_{12}CuClN_3S_2$: C, 35.61; H, 3.68; N, 12.46. Found: C, 35.59; H, 3.58; N, 12.35%. UV–Vis: λ_{max}/nm, (logε (dm^3 cm^{-1} mol^{-1}): ca. 580 sh, 450 (4.40), 330 (4.87), ca. 320 sh; IR/cm^{-1}: 3300 br (νNH), 1572 s (νCN), 1096 w (νNN), 720 s (νCS).

2.4.2. Preparation of **3**

A solution of copper(II) nitrate tetrahydrate (0.41 g; 2.2 mmol) in ethanol (25 mL) was added to a solution of the Schiff base



(1) Hapsme R = CH_3
(2) Habsem R = H

Fig. 1. The thione and thiol tautomers of Hapsme (R = CH_3).

(0.30 g; 2.2 mmol) in the same solvent (50 mL) and the mixture was heated on a water bath for ca. 5 min and filtered while hot. A solution of anhydrous lithium thiocyanate (0.285 g; 4.4 mmol) in boiling abs. ethanol (20 mL) was added to the filtrate and the resulting dark green solution was heated for about 5 min and then left to stand for 7 days whereupon the dark green crystals that had formed were filtered off and recrystallized from acetonitrile. Yield, 0.50 (63%). Λ (Ω^{-1} cm^2 mol^{-1}): 35.2; μ_{eff} (BM): 1.73. *Anal.* Calc. for $C_{11}H_{12}CuN_4S_3$: C, 34.45; H, 3.36; N, 15.61. Found: C, 36.70; H, 3.06; N, 15.57%. UV–Vis: $\lambda_{\max}$/nm, (log ε (dm^3 cm^{-1} mol^{-1}): 639 (2.59), 445 (4.87), 326 (5.19), ca. 340 sh, 306 (5.36); IR/cm^{-1}: 3300 br (νNH), 1584 s (νCN), 1065 s (νNN), 720 s (νCS).

2.5. Crystallography

For compound **1** data were collected on an Oxford Diffraction Gemini S Ultra CCD diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å) and data reduction and absorption correction (multi-scan) was performed with the CRYSALISPRO software (vers. 171.35.31). Cell constants for compounds **2**, **3** and **4** were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured on an Enraf–Nonius CAD4 four-circle diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å) and operating in the ω–2θ mode within the range $2° < 2\theta < 50°$. An empirical absorption correction (ψ scans) and data reduction [11] were performed within the WINGX [12] suite programmes. The structures were solved by direct methods with SHELX86 and refined by full-matrix least-squares analysis with SHELXL97 [13]. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were included at estimated positions. Drawings of all molecules were produced with ORTEP3 [14] and PLATON [15]. A summary of the crystal data, structure solution and refinement parameters are given in Table 1.

3. Results and discussion

Compounds containing the thioamide (–NH–C=S) moiety can display thione–thiol tautomerism. However, an X-ray crystallographic structure determination of Hapsme (*vide infra*) shows that, in the solid state, it exists solely as the thione form. However, in solution, **1** may exist either as the thione (–NH–C=S) or the thiol (–N=C–SH) tautomeric forms or as a mixture of these two forms (Fig. 1).

In addition to the thione and thiol forms, the Schiff base may also exist as *E* or *Z* conformational isomers or a mixture of both isomers in solution. Thiosemicarbazones having structural backbones similar to the present Schiff bases have been found to exist in solution as a mixture of *E* and *Z* forms [16] and NMR spectroscopy has been successfully used to distinguish between these two isomers in solution [17]. The ^{1}H NMR spectrum of **1** in DMSO-d_6 exhibits the sec-NH resonance at 12.34 ppm, indicating that in solution, it exists only as the *Z* isomer [17].

The IR spectrum of **1** lacks a ν(S–H) band at ca. 2600 cm^{-1} (Table 3) indicating that, in the solid state, it exists only as the thione tautomer. A single crystal X-ray crystal structure determination (*vide infra*; Fig. 2) of **1** unequivocally proves that, in the solid it remains in the *E* configuration about the azomethine C7a–N2a bond. The ^{1}H NMR spectrum (in DMSO) of **1** lacks any signal at ca. 4 ppm attributable to the –SH proton indicating that it remains solely in its thione tautomeric form even in a polar solvent like DMSO. However, in solution and in the presence of copper(II) salts, it readily converts to the thiol form, deprotonates and coordinates to the copper(II) ion in its thiolate form. Thiosemicarbazones having structural backbones similar to the present Schiff bases, however, have been found to coordinate with metal ions in both their protonated thione [18] and deprotonated thiolate [19] forms. There are even examples of metal–thiosemicarbazone complexes in which both the protonated thione and deprotonated thiolate forms of a ligand are present in the same complex [20]. However, Schiff bases derived from S-alkyl/aryl dithiocarbazates have invariably been found to coordinate with nickel(II) and copper(II) ions in their deprotonated forms [5–9] which reflects significant differences in the electronic effects of the terminal (–SR as opposed to –NHR) substituents.

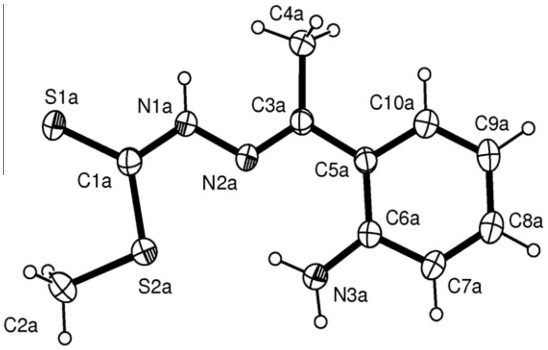


Fig. 2. Crystal structure of **1** (30% probability ellipsoids) with the general atom numbering scheme used in this paper.

Reaction of hydrated copper(II) salts with the Schiff base, Hapsme in a boiling mixture of methanol and acetonitrile yield copper(II) complexes of empirical formula, [Cu(apsme)X] (X = Cl, Br, NCS). The copper complexes are stable at room temperature and show no sign of decomposition on standing in desiccators for a long period of time. Their room-temperature magnetic moments (1.73–1.75 BM) are consistent with the $3d^9$ electronic configuration of copper(II) in a magnetically dilute coordination environment. Their molar conductivities in DMF show that, although some dissociation of the complexes occur in this solvent, the conductance values are still much lower than that observed for 1:1 electrolytes in this solvent indicating that the anions are coordinated to the copper(II) ion. Coordination of the anions to the copper(II) ion is also supported by the IR spectrum of the [Cu(apsme)(NCS)] complex which exhibits a strong band at 2100 cm^{-1} characteristic of an N-bonded thiocyanate group [21].

The mode of coordination of the ligand to the copper(II) ion in the present copper complexes can be ascertained by examining their IR spectra. The absence of the N–H stretching band of the *sec* N–H group of the uncomplexed ligands in the IR spectra of the complexes supports their deprotonation upon coordination.

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

	1[a]	**2**	**3**	**4**
Cu–S_{eq}		2.245(3)	2.260(3)	2.254(2)
Cu–S_{ax}		2.871(3)	2.747(4)	2.895(2)
Cu–X		2.4325(17)	1.942(9)	2.282(2)
Cu–$N_{azomethine}$		1.995(8)	1.977(8)	2.010(4)
Cu–N_{amine}		2.007(9)	2.030(8)	1.994(5)
C1–S1	1.631(3)	1.75(1)	1.751(10)	1.745(3)
C1–N1	1.321(4)	1.30(1)	1.295(12)	1.281(6)
N1–N2	1.355(4)	1.38(1)	1.394(9)	1.391(5)
N2–C3	1.276(4)	1.31(1)	1.324(11)	1.280(6)
C6–N3	1.337(4)	1.44(1)	1.45(1)	1.427(6)
N_{amine}–Cu–N_{azo}		87.9(4)	88.5(3)	87.12(17)
N_{amine}–Cu–S_{eq}		166.0(3)	164.9(2)	166.05(14)
N_{amine}–Cu–X_{eq}		89.7(3)	91.4(4)	89.89(12)
N_{azo}–Cu–S_{eq}		86.3(3)	85.9(2)	86.48(13)
N_{azo}–Cu–Xeq		169.6(2)	168.3(3)	170.19(13)
S_{eq}–Cu–X_{eq}		93.74(9)	91.3(3)	94.35(6)
S_{axial}–Cu–S_{eq}		96.4(1)	97.1(1)	96.47(5)

[a] Data for molecule A only shown (bond lengths for molecule B not significantly different).

Table 3
Comparison of Cu-donor atom distances in some copper(II) complexes of tridentate NNS dithiocarbazate and thiosemicarbazone ligands.

Compound	Cu–S$_{equatorial}$	Cu–S$_{axial}$	Cu–N$_{azomethine}$	Cu–N$_{py/pyrazine/quinoline}$	Cu–X$_{equatorial}$	Cu–X$_{axial}$	Ref.
$[Cu(apsme)Br]_2$	2.245(3)	–	1.995(8)	2.007(9)	2.4325(17) X = Br^-	–	this work
$[Cuapsme)NCS]_2$	2.260(3)	2.746(3)	1.977(8)	2.030(7)	1.942(9) X = NCS^-	–	this work
$[Cu(apsme)Cl]_2$	2.2544(6)	–	1.994(4)	2.010(4)	2.2826(5) X = Cl^-	–	this work
$[Cu(acpyrsme)NCS]_2$	2.265(1) 2.263(2)	3.003(2) 3.126(2)	1.950(4) 1.964(4)	2.030(4) 2.032(4)	1.901(4) 1.912(4) X = NCS^-	–	[8]
$[Cu(acpyrsme)Cl]_2$	2.270(1)	2.924(1)	1.965(3)	2.029(3)	2.212(1) X = Cl^-	–	[8]
$[Cu(acpyrsbz)NO_3]_\infty$	2.260(4)	–	1.96(1)	2.03(1)	1.92(2) X = NO_3^-	2.39(1) N-pyrazine	[8]
$[Cu(quinolsme)NCS]_2$	2.314(2)	2.783(2)	1.945(6)	2.139(5)	1.897(6) X = NCS^-	–	[6]
$[Cu(pytsc)Cl]_2$	2.278(1)	2.760(2)	1.975(3)	2.034(4)	2.240(2) X = Cl^-	–	[24]
$[Cu(pytsc)Br]_{2=}$	2.275(2)	2.743(2)	1.987(3)	2.023(4)	2.405(1) X = Br^-	–	[24]
$[Cu(4Nphpytsc)Cl]_2$	2.248(6)	–	1.9784(14)	2.0325(14)	2.2587(7) X = Cl^-	2.7245(12)	[37]
$[Cu(4Nphbenzpytsc)Cl]_2{\cdot}H_2O$	2.2318(8)	–	1.963(2)	2.014(2)	2.2459(7) X = Cl^-		[38]
[Cu(4Nphbenzpytsc)NCS]	2.2600(6)		1.9524(15)	2.0063(15)	1.9240(19) X = NCS^-		[38]
$[Cu(6mepy2aldsme)NO_3]_2{\cdot}0.5CH_3COCH_3$	2.2974(14)	2.7987 (15)	1.940(4)	2.102(4)	1.972(3) X = NO_3^-		[7]
$[Cu(6mepy2aldsme)(NCS)]_\infty$	2.2969(15)	2.7445(14) S of NCS	1.945(4)	2.108(4)	1.926(4) X = NCS^-		[7]
[Cu(6mepy2aldtsc)Cl]	2.282(2)	–	1.978(5)	2.088(6)	2.234(2) X = Cl^-		[34]
[Cu(Lhexim)Br]	2.236(3)		1.963(5)	2.016(6)	2.359(2) X = Br^-		[36]
Cu(Lpip)Br]	2.2544(16)	–	1.989(1)	2.001	2.344(3) X = Br^-		[32]
$[Cu(6mepy2aldsme)(CH_3COO)]$	2.295(4)	–	1.95(1)	2.08(1)	1.98(1) X = CH_3COO^-		[35]
$[Cu(Bpsme)NO_3]$	2.244(9)	–	1.957(2)	2.010(2)	1.943(2) X = NO_3^-		[33]
$[Cu(Apsbz)(NO_3)]$	2.2420(3)	–	1.938(3)	2.010(3)	1.982(3) X = NO_3^-		[39]

acpyrsme = anionic form of the 2-acetylpyrazine Schiff base of S-methyldithiocarbazate; acpyrsbz = anionic form of the 2-aqcetylpyrazine Schiff base of S-benzyldithiocarbazate; quinolsme = anionic form of the 2-quinoline carboxaldehyde Schiff base of S-methyldithiocarbazate; py2aldsme = anionic form of the 2-pyridinecarboxaldehyde Schiff base of S-methyldithiocarbazate; 6mepy2aldtsc = anionic form of the 6-methyl-2-pyridinecarboxaldehyde thiosemicarbazone; 6mepy2aldsme = anionic form of the 6-methylpyrine-2-aldehyde Schiff base of S-methyldithiocarbazate; Lpip = anionic form of 2-acetylpyridine piperidinyl thiosemicarbazone; Lhexim = anionic form of 2-acetylpyridine hexamethyleneiminyl thiosemicarbazone; Bpsme = anionic form of the 2-benzoylpyridine Schiff base of S-methyldithiocarbazate; Apsbz = anionic form of the 2-acetylpyridine Schiff base of S-benzyldithiocarbazate; 4Nphbenzpytsc = anionic form of 4-N-phenyl-2-benzoyldpyridine thiosemicarbazone; 4Nphpytsc = anionic form of 4-N-phenyl pyridine-2-aldehyde thiosemicarbazone.

The azomethine ν(C=N) bands in the IR spectra of the free ligand appears at 1602 cm^{-1} which shifts to lower frequencies supporting coordination of the azomethine nitrogen atom to the copper(II) ion [6–8]. This is further corroborated by the shift of the hydrazinic ν(N–N) band of the free ligand at 1060 cm^{-1} to higher wave numbers 1065–1096 cm^{-1} in the spectra of the complexes as noted previously [22]. The splitting of the ν(SCS) band of the free ligands at ~961–965 cm^{-1} in the spectra of the complexes also reflects coordination of one of the sulfur atoms [23].

The electronic spectrum of **2**, **3** and **4** exhibit *d*–*d* maxima in the range 580–640 nm. A strong S → Cu^{II} charge transfer band is also observed at about 450 nm in each spectrum supporting coordination of the sulfur to the copper(II) ion. Similar ligand-to-metal charge transfer bands have also been observed in complexes of other NNS thiosemicarbazones [24–27] and dithiocarbazates [6–8]. The related five-coordinate dimeric copper(II) complex, $[Cu(pytsc)Br]_2$ (pytsc = anionic form of the 2-pyridinecarboxaldehyde thiosemicarbazone), whose structure has been determined by X-ray diffraction, also displays a single *d*–*d* band at 640 nm in its electronic spectrum [24].

3.1. Description of the crystal structures

3.1.1. The structure of 1

Fig. 2 depicts the molecular geometry, thermal ellipsoids and numbering system of **1** and selected bond lengths and bond angles are given in Table 2.

The structure comprises two molecules in the asymmetric unit which exhibit identical geometries and conformations. Both molecules are essentially planar with all non-H atoms lying within 0.1 Å of each least squares plane of the ligand. The bond distances in the dithiocarbazate chain [$NNCSSCCH_3$] are close to those observed in the thiosemicarbazone analogue [28] and in other Schiff bases derived from S-alkyl/aryldithiocarbazates [6–9]. The C9a–S1a distance [1.631(3) Å] is by far the shortest value observed in this class of compounds, but the value is still intermediate between a C–S single bond [1.82 Å] and a C=S double bond [1.56 Å] [29]. The C9a–N3a and C37a–N2a bond distances are 1.321(4) Å and 1.276(4) Å, respectively indicating that the bond order of the former is greater than one while the latter is a true double bond. A comparison of the N2a–N3a distance [1.355(4) Å] with that in

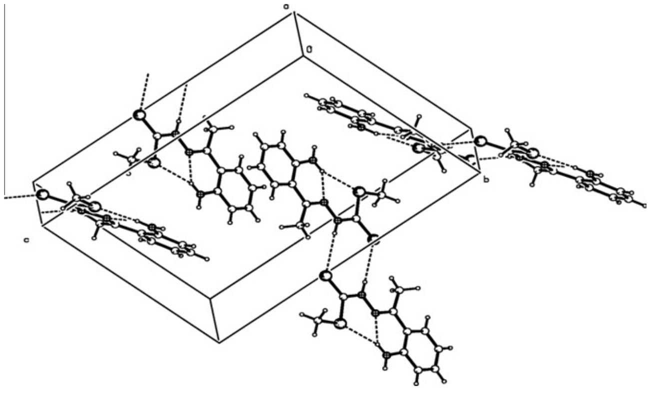


Fig. 3. Intra- and intermolecular hydrogen bonding in **1**.

S-methyldithiocarbazate [30] shows that the bond is shorter than a single bond indicating significant π-charge delocalization along the C(S)NNC moiety. Conjugation with the phenyl ring is probably responsible for shortening of the N1–N2 distance. The aromatic primary amino group is trigonal planar as a result of the N3 lone pair being conjugated with the phenyl ring. Consequently the C6–N3 bonds (∼1.33 Å) have partial double bond character.

The structure of **1** also shows that the azomethine nitrogen atom, N2a and the thione sulfur atom, S1a are in *anti* conformation with respect to the azomethine C7a–N2a bond. The amino nitrogen atom N1a and the azomethine nitrogen atom, N2a are, however in the *syn* conformation. In this *anti–syn* conformation, the Schiff base is unable to act as an *NNS* tridentate chelating agent. However, in solution rotation about the C9–N2 bond can place all the three donor atoms on one side and thereby enable it to act as a tridentate NNS chelating agent.

There are both intra- and intermolecular hydrogen bonds (Fig. 3). One of the NH_2hydrogen atoms in the Schiff base is involved in bifurcated hydrogen bonding between the azomethine nitrogen atom N2a and the thioether sulfur atom, S2a. In addition to the intramolecular hydrogen bond, the hydrogen atom on N3a of one molecule forms a H-bond with the thione sulfur atom, S1a of another molecule leading to dimers (Fig. 3).

3.1.2. Crystal structures of the dimeric copper(II) complexes

3.1.2.1. The structure of [Cu(apsme)Br]. The asymmetric (monomeric) unit comprises the Cu ions coordinated to the tridentate deprotonated Schiff base plus a monodentate bromido ligand (Fig. 4A). The S-donor forms an additional coordinate bond to the axial site of an adjacent Cu ion resulting in a centrosymmetric dimer (Fig. 4B). Selected bond lengths and bond angles are given in Table 2. The coordination environment around each copper(II) ion is square pyramidal comprising a N_2S_2Br set of donor atoms.

Each ligand coordinates with a copper(II) ion as a tridentate NNS chelating agent *via* the amino nitrogen atom, the azomethine nitrogen atom and the thiolate sulfur atom. The fourth and fifth coordination positions of a copper atom are occupied by a bromide and bridging thiolate sulfur atoms, respectively.

There are several structurally characterised dimeric copper(II) complexes of tridentate NNS thiosemicarbazones [24–27] and dithiocarbazates [6–8] bearing a similar four-membered metallocyclic thiolate bridging motif. The Cu–S1, Cu–N2, Cu–N3 and Cu–Br1 bond distances 2.245(3) Å, 1.995(8) Å, 2.007(9) Å and 2.4325(17) Å, respectively, compare well with that of the related dimeric copper(II) complexes of related NNS ligands [6–8,24–26].

The copper atom sits 0.22 Å above the basal plane displaced toward the axially coordinated thiolate S-donor. The Cu–S–Cu bridging angle 83.6° and the Cu–Cu separation 3.44 Å, respectively, are close to that in the related dimeric copper(II) complex, $[Cy(pytsc)Br]_2$ [(87.1(1)°) and [3.474(1) Å] [24].

The bridging arrangement observed in this complex is very similar to those of other dimeric copper(II) complexes of analogous NNS dithiocarbazates [5–7]. The $Cu–S_{equatorial}$ [2.245(3) Å], Cu(1)–N(2a) [1.995(8) ÅÅ], Cu(1)–N(3a) [2.007(9) ÅÅ], $Cu–S_{axial}$ [2.746(3) ÅÅ] and Cu–Br [2.4325(17) ÅÅ] bond distances compare well with those observed in the dimeric copper(II) complexes of [6–8,24–27]. The coordination geometry around each copper atom can be considered as approximately square-pyramidal on the basis of the parameter, $\tau = 0.051$ [31] where $\tau = (\beta - \alpha)/60°$; α and β being the two largest coordinate angles N(2)–Cu(1)–Br(1) [169.6(2)°] and N(3)–Cu(1)–S(1) [166.0(3)°]. For ideally square pyramidal geometry $\tau = 0$ while for trigonal bipyramidal $\tau = 1$.

One striking feature of this structure is the distinctly buckled conformation of the tridentate coordinated apsme ligand. The coordinated primary amine N-atom (N3) clearly adopts a tetrahedral geometry (on the basis of the H-atoms that were identified during the structure refinement) compared with the trigonal geometry seen in the free ligand. This leads to a contraction of the preferred Cu–N3–C6 angle (i.e. from 120° to ∼109.5°) for the now sp^3 hybridised atom. The observed Cu–N3–C6 angle [117.5(7)°] indicates considerable strain in the chelate ring which is also revealed in a twisting of the phenyl ring well out of the basal coordination plane. Moreover, the lone pair on N3, formerly conjugated with the phenyl ring, now contributes to the Cu–N3 coordinate bond and so C6–N3 lengthens to be consistent with a typical C–N single bond.

An examination of bond angle data in Table 2 indicates that the complex does not have a perfect square-pyramidal geometry. Be-

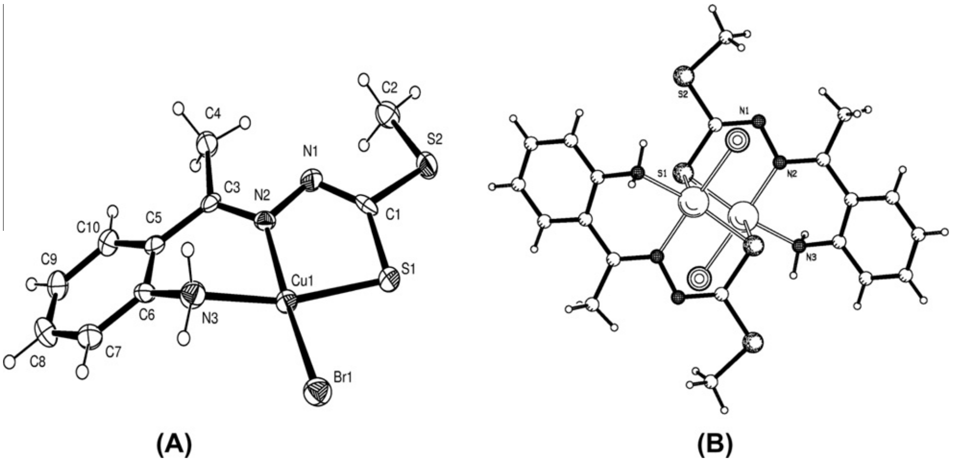


Fig. 4. (A) ORTEP view (30% probability ellipsoids) of the asymmetric monomeric unit of **2** and (B) PLATON view of the centrosymmetric dimer.

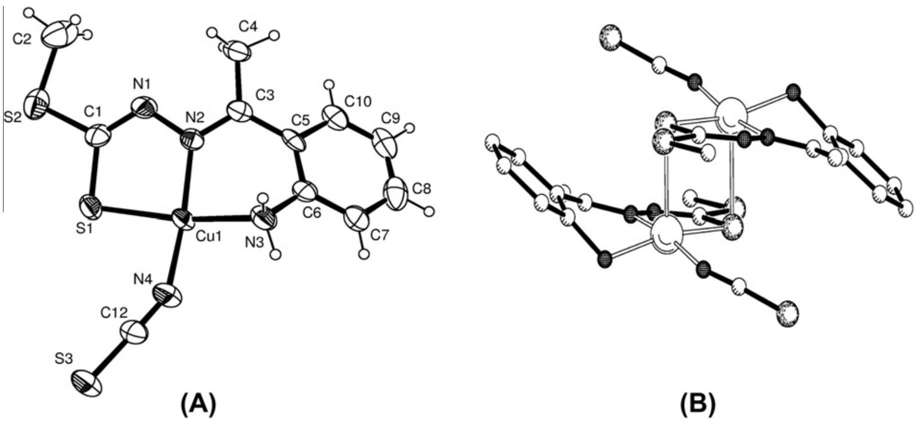


Fig. 5. (A) ORTEP view of the asymmetric unit of **3** and (B) PLATON view of the centrosymmetric dimer.

cause of the restricted bite angles imposed by five-membered chelate rings, the coordinate angles deviate significantly from 90° or 180°: N(3)–Cu–S1 [166.0(3)° versus 180°], N2–Cu–Br1: [169.6(2)° versus 180°], N2–Cu–N3 [87.9(4)° versus 90°] and N2–Cu–S1 [86.3(3)° versus 90°].

*3.1.2.2. The crystal structure of **3**.*

The structure of the asymmetric monomeric unit of **3** is depicted in Fig. 5A and that of the centrosymmetric dimer is shown in Fig. 5B.

In this complex, the Schiff base is also coordinated to the copper(II) ion in its iminothiolate form *via* the amino nitrogen atom, the azomethine nitrogen atom and the thiolate sulfur atom. While coordinating in this form the negative charge generated on the thiolate sulfur atom of the Schiff base is delocalized over the N1–C1–S1 chain as indicated by the intermediate C1–S1 [1.73(1) Å] and C1–N1 [1.28(1) Å] bond distances.

The thiocyanate ion in this complex is coordinated with the copper(II) ion as a monodentate ligand *via* the nitrogen atom N4. The Cu1–N4 distance [1.942(9) Å] is close to that observed in the related thiolate sulfur-bridged dimeric $[Cu(quinolsme)(NCS)]_2$ complex (quinolsme = anionic form of the 2-quinolinecarboxaldehyde Schiff base of S-methyldithiocarbazate) [6], which also has a structure similar to that of **3**.

The overall geometry adopted by each copper atom in the dimer may be considered as approximately square-pyramidal since the geometric factor, τ has a value of 0.027. The basal plane of the square-pyramid contains the amino nitrogen atom N3, the azomethione nitrogen atom N2, the nitrogen atom N4 of the thiocyanate ligand and the thiolate sulfur atom S1. The apical site of the five-coordinate copper atom is occupied by the bridging thiolate sulfur atom of the other monomeric unit in the dimer. The Cu–S–Cu bridging angle [82.88(9)°] and the Cu–Cu distance [3.33 Å] is close to that observed in **2**. The bond angle data in Table 2 show that the complex does not have a perfect square-pyramidal geometry since both the *trans* angles, S1–Cu1–N3 and N2–Cu1–N4 deviate substantially from that required for an ideal square-pyramidal geometry.

*3.1.2.3. The crystal structure of **4**.*

The structure of **4**, together with the atom numbering scheme adopted, is shown in Fig. 6 and selected bond lengths and bond angles are given in Table 2.

The structure shows that, like **2** and **3**, **4** is also dimeric in the solid state. In this case a chlorido ligand occupies the coordination site *trans* to N2. The Schiff base, Hapsme is coordinated to the copper(II) ion in its iminothiolate form as an NNS tridentate chelating agent *via* the amino nitrogen atom, the azomethine nitrogen atom and the thiolate sulfur atom. The complex has a long N1–N2 bond, a short C1–N1 bond and a long C1–S1 bond. This is indicative of the dithiocarbazate's greater conjugation and therefore, more delocalized electron density. The Cu1–S1, Cu1–N2 and Cu1–Cl1 bond distances, 2.254(2) Å, 2.010(4) Å and 2.283(2) Å, respectively. A comparison of these bond distances with those observed in other copper(II) complexes of NNS ligands whose structures have been determined by X-ray diffraction (Table 3) shows that the Cu-donor atom distances in the present dimeric copper(II) complexes

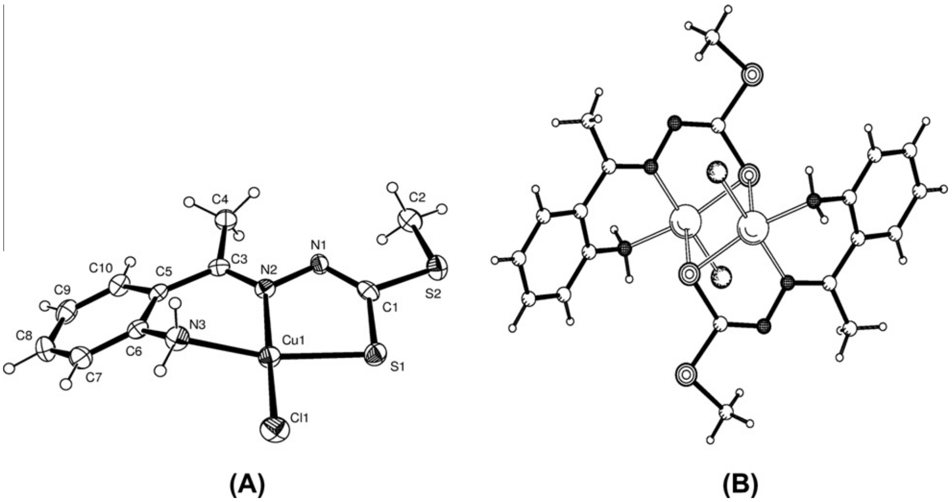


Fig. 6. (A) The crystal structure of the asymmetric unit of **4** (30% probability ellipsoids) with the atom numbering scheme and (B) PLATON view of the centrosymmetric dimer.

are close to those observed in other related copper(II) complexes of NNS thiosemicarbazones and dithiocarbazates. The bond distance data in Table 3 also shows that despite the different stereochemistries adopted by the copper(II) complexes of NNS thiosemicarbazone and dithiocarbazate ligands, there is not much variation in the Cu-donor atom distances in these complexes. The strength of the Cu–N_{amine} bond is also very similar to that of a Cu–$N_{pyridine/pyrazine/quinoline}$ bond.

The bond angles in **4** (Table 2) indicates that it has a distorted square-pyramidal geometry. Thus, the two *trans* angles, *viz.* N1–Cu1–S1 [166.05(14)°] and N2–Cu1–Cl1 [170.19(13)°] deviate by about 10–14° from the ideal value of 180°, but the *cis* angles (Table 2) are close to that required for an ideal square-pyramidal geometry.

As in the two other Cu complexes reported here, the Cu–S–Cu angle (83.53(5)°) and Cu…Cu separation 3.46 Å are similar.

4. Conclusion

The 2-aminoacetophenone Schiff base of S-methyldithiocarbazate (Hapsme), upon reacting with copper(II) salts, does not lead to the formation form any monomeric four-coordinate copper(II) complexes but self-assemble to yield thiolato sulfur-bridged dimeric copper(II) complexes in which each copper atom adopts an approximately square-pyramidal geometry with the N_2S_2X (X = Cl, NCS, Br) donor environment. While the related NNS thiosemicarbazones have been shown to yield both thiolato sulfur-bridged as well as anion-bridged dimeric copper(II) complexes, the NNS dithiocarbazates have been found to yield only thiolato sulfur-bridged complexes, which reflects significant differences in the electronic effects of the terminal (–SR as opposed to –NHR) substituents.

Acknowledgements

M. Akbar Ali, A.H. Mirza and Malai Haniti S.A. Hamid thank the University of Brunei Darussalam for supporting this work. Support from the Australian Research Council is also gratefully acknowledged.

Appendix A. Supplementary data

CCDC 885661, 885662, 885663 and 885664 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] (a) Y. Tian, C. Duan, C. Zhao, X. You, T.C.W. Mak, Z.Y. Zhang, Inorg. Chem. 36 (1997) 1247;
(b) Z.A. Abu-Raqabah, G. Davies, M.A. El-Sayed, A. El-Toukhy, S.N. Shaikh, J. Zubieta, Inorg. Chim. Acta 193 (1992) 43;
(c) Z.H. Liu, C.Y. Duan, J. Hu, Inorg. Chem. 38 (1999) 1719;
(d) C.Y. Duan, X.Z. You, Chem. Lett. Jpn. 10 (1999) 1063;
(e) Y. Tian, C.Y. Duan, X. You, T.C.W. Mak, Q. Luo, J. Zhou, Transition Met. Chem. 23 (1998).

[2] (a) M. Akbar Ali, A.H. Mirza, Hjh Junaidah Hj Abu Bakar, P.V. Bernhardt, Polyhedron 30 (2011) 556;
(b) M. Akbar Ali, A.H. Mirza, R.J. Butcher, P.V. Bernhardt, M.R. Karim, Polyhedron 30 (2011) 1478;
(c) M. Akbar Ali, A.H. Mirza, M.H.S.A. Hamid, I.C. Siew, L.P. Sia, P.V. Bernhardt, Inorg. Chem. Commun. 13 (2010) 1445;
(d) M. Akbar Ali, A.H. Mirza, R.J. Butcher, M.T.H. Tarafder, M.A. Ali, Inorg. Chim. Acta 320 (2001) 1;
(e) M. Yazdanbakhsh, R. Takjooa, Struct. Chem. 19 (2008) 895.

[3] M. Rahman, M. Akbar Ali, Transition Met. Chem. 19 (1994) 237.

[4] (a) M.T. Basha, J.D. Chartres, N. Pantara, M. Akbar Ali, A.H. Mirza, D.S. Kalinowski, D.R. Richardson, P.V. Bernhardt, Dalton Trans. 41 (2012) 6536;
(b) T.B.S.A. Ravoof, K.A. Crouse, M.I.M. Thahir, A.R. Cowley, M. Akbar Ali, Polyhedron 23 (2004) 2491.;
(c) M. Akbar Ali, A.H. Mirza, R.J. Butcher, M.T.H. Tarafder, T.B. Keat, A.M. Ali, J. Inorg. Biochem. 92 (2002) 141;
(d) M. Das, S.E. Livingstone, Br. J. Cancer 37 (1978) 101;
(e) A. Saxena, J.K. Koacher, J.P. Tandon, Antibact. Antifung. Agents 9 (1981) 435;
(f) A. Saxena, J.K. Koacher, J.P. Tandon, J. Toxicol. Environ. Health 15 (1985) 503.

[5] (a) R. Takjooa, R. Centoreb, M. Hakimic, S.A. Beyramabadid, A. Morsalid, Inorg. Chim. Acta 371 (2011) 36;
(b) M. Akbar Ali, D.J. Phillips, S.E. Livingstone, Inorg. Chim. Acta 6 (1972) 39;
(c) M. Akbar Ali, S.E. Livingstone, Coord. Chem. Rev. 13 (1974) 101;
(d) M. Akbar Ali, M.T.H. Tarafder, J. Inorg. Nucl. Chem. 39 (1977) 1785;
(e) M. Akbar Ali, A.H. Mirza, R.J. Butcher, K.A. Crouse, Transition Met. Chem. 31 (2006) 79;
(f) M.E. Hossain, M.N. Alam, J. Begum, M. Akbar Ali, M. Nazimuddin, Transition Met. Chem. 18 (1993) 497.

[6] M. Akbar Ali, A.H. Mirza, F. Hj Bujang, M.H.S.A. Hamid, P.V. Bernhardt, Polyhedron 25 (2006) 3245.

[7] M. Akbar Ali, A.H. Mirza, R.J. Fereday, R.J. Butcher, J.M. Fuller, S. Drew, L.R. Gahan, G.R. Hanson, B. Moubaraki, K.S. Murray, Inorg. Chim. Acta 358 (2005) 3937.

[8] M.H.S.A. Hamid, M. Akbar Ali, A.H. Mirza, P.V. Bernhardt, B. Moubaraki, K.S. Murray, Inorg. Chim. Acta 363 (2009) 3648.

[9] M. Akbar Ali, A.H. Mirza, M.H.S.A. Hamid, P.V. Bernhardt, Polyhedron 24 (2005) 383.

[10] (a) G. Bahr, G. Schleitzer, Z. Anorg. Allg. Chem. 280 (1955) 176;
(b) M. Das, S.E. Livingstone, Inorg. Chim. Acta 19 (1974) 5.

[11] K. Harms, S. Wocadlo, XCAD-4, Program for Processing CAD-4 Diffractometer Data, University of Marburg, Germany, 1995.

[12] L. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[13] G.M. Sheldrick, SHELX, Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1997.

[14] L. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.

[15] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 1998.

[16] (a) D.X. West, J.P. Scovill, J. Silverton, A. Bavoso, Transition Met. Chem. 11 (1986) 123;
(b) G.F. de Sousa, D.X. West, C.A. Brown, J.K. Swearingen, J. Valdés-Martínez, R.A. Toscano, S. Hernández-Ortega, M. Hörner, A.J. Bortuluzzi, Polyhedron 19 (2000) 841;
(c) E. Bermejo, A. Carballo, A. Castíñeiras, R.R. Domíniguez, C. Maichle-Mössmer, J. Strähle, D.X. West, Polyhedron 18 (1999) 3695;
(d) D.X. West, M.A. Lockwood, A.E. Liberta, X. Chen, R.D. Willet, Transition Met. Chem. 18 (1993) 221;
(e) D.X. West, C.S. Carlson, C.P. Galloway, A.E. Liberta, C.R. Daniel, Transition Met. Chem. 15 (1990) 91.

[17] (a) K.R. Koch, J. Coord. Chem. 22 (1991) 2;
(b) D.X. West, C.S. Carlson, K.J. Bouck, A.E. Liberta, Transition Met. Chem. 16 (1991) 271;
(c) D.X. West, B.L. Mokijewski, H. Gebremedhin, T.J. Romack, Transition Met. Chem. 17 (1992) 384;
(d) C.R. Kowol, R. Trondl, V.B. Arion, M.A. Jakupec, I. Lichtscheidl, B.K. Keppler, J. Chem. Soc., Dalton Trans. 39 (2010) 704.

[18] (a) R. Gronback-Hazel, Acta Chem. Scand. 26 (1992) 1653;
(b) M. Mohan, A. Agarawal, N.K. Jha, J. Inorg. Biochem. 34 (1988) 41;
(c) A. Bino, N. Cohen, Inorg. Chim. Acta 210 (1993) 11;
(d) P. Sengupta, R. Dinda, S. Ghosh, W.S. Sheldrick, Polyhedron 22 (2003) 447;
(e) S.K. Chottopadhya, D. Chattopadhyay, T. Banerjee, R. Kuroda, S. Ghosh, Polyhedron 16 (1997) 1925.

[19] (a) P. Pelagatti, A. Venturini, A. Leporati, M. Carcelli, M. Costa, A. Bacchi, G. Pelizzi, C. Pelizzi, J. Chem. Soc., Dalton Trans. (1998) 2715;
(b) M.D. Timken, S.R. Wilson, D. Hendrickson, Inorg. Chem. 24 (1985) 3450;
(c) D.K. Sau, R.J. Butcher, N. Chaudhuri, N. Saha, Polyhedron 23 (2004) 5;
(d) E. Labisbal, K.D. Haslow, A. Sousa-Pedrares, J. Valdes-Martinez, S. Hernandez-Ortega, D.X. West, Polyhedron 22 (2003) 2831;
(e) D. Kovala-Demertzis, J.R. Miller, C.S. Frampton, J.P. Jasinski, D.X. West, J. Inorg. Biochem. 92 (2002) 137;
(f) D.X. West, J.S. Ives, J. Krejci, M.M. Salberg, T.L. Zumbahlen, G.A. Bain, A.E. Liberta, J. Valdes-Martinez, S. Hernandez-Ortega, R.A. Toscano, Polyhedron 14 (1995) 2189.

[20] (a) P. Souza, A.I. Matesanz, V. Fernandez, J. Chem. Soc., Dalton Trans. (1996) 3011;
(b) D.S. Timken, S.R. Wilson, D.N. Hendrickson, Inorg. Chim. Acta 24 (1985) 3450.

[21] R.A. Bailey, S.L. Kojak, T.W. Michelson, W.N. Mills, Coord. Chem. Rev. 6 (1971) 407.

[22] A. Monaci, F. Trali, Dalton Trans. (1977) 417.

[23] R. Ugo, J Organomet. Chem. 4 (1967) 395.

[24] J. Garcia-Tojal, M.K. Urtiaga, R. Cortes, L. Lezama, M.I. Arriortua, T. Rojo, J. Chem. Soc., Dalton Trans. (1994) 2233.

[25] J. Garcia-Tojal, L. Lezama, J.L. Pizarro, M. Insausti, M.I. Arriortua, Polyhedron 18 (1999) 3703.

[26] E.W. Ainscough, A.M. Brodie, J.D. Ranford, J.M. Waters, K.S. Murray, Inorg. Chim. Acta 197 (1992) 107.

[27] V.P. Philip, V. Sani, M.R.P. Kurup, M. Nethaji, Polyhedron 25 (2008) 1381.

[28] A.A. Nassar, S. Hernandes-Ortega, J. Valdez-Martinez, D.X. West, J. Mexican Chem. Soc. 46 (2002) 251.

[29] F.H. Allen, O. Kennard, D.G. Watson, L. Bremmer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. II (1987) S1.

[30] R. Mattes, H. Weber, J. Chem. Soc., Dalton Trans. (1980) 423.

[31] A.W. Addison, T.N. Rao, J. Reedijk, J. Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.

[32] R.J. Bucther, D.X. West, Transition Met. Chem. 18 (1993) 449.

[33] M.E. Hossain, M.N. Alam, J. Begum, M. Akbar Ali, M. Nazimuddin, F.E. Smith, R.C. Hynes, Inorg. Chim. Acta 249 (1996) 207.

[34] M. Akbar Ali, K.K. Dey, M. Nazimuddin, F.E. Smith, R.J. Butcher, J.P. Jasinski, J.M. Jasinski, Polyhedron 15 (1996) 3331.

[35] M. Akbar Ali, R.J. Butcher, J.C. Bryan, Inorg. Chim. Acta 287 (1999) 8.

[36] D.X. West, H. Gebremedhin, R.J. Butcher, J.P. Jasinski, A.E. Liberta, Polyhedron 12 (1993) 2489.

[37] P.F. Rapheal, E. Manoj, M.R.P. Kurup, Polyhedron 26 (2007) 818.

[38] M. Joseph, M. Kuriakose, M.R.P. Kurup, E. Suresh, A. Kishore, S.G. Bhat, Polyhedron 25 (2006) 61.

[39] M.E. Hossain, M.N. Alam, M. Akbar Ali, M. Nazimuddin, F.E. Smith, R.C. Hynes, Polyhedron 15 (1996) 973.