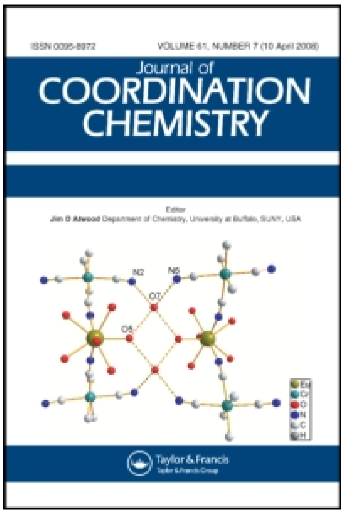

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Self-assembly of copper(II) complexes with substituted aroylhydrazones and monodentate N-heterocycles: synthesis, structure and properties

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Self-assembly of copper(II) complexes with substituted aroylhydrazones and monodentate N-heterocycles: synthesis, structure and properties

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Two ternary copper(II) complexes [Cu(L^1)(py)] (**1**) and [Cu(L^2)(Himdz]·CH$_3$OH (**2**) with substituted aroylhydrazones, 5-bromo-salicylaldehyde-3,5-dimethoxy-benzoylhydrazone (H$_2$L^1) and 5-bromo-salicylaldehyde-p-methyl-benzoylhydrazone (H$_2$L^2), pyridine (py) and imidazole (Himdz), have been synthesized. Their crystal structures and spectroscopic properties have been studied. In each complex, the metal is in a square-planar N$_2$O$_2$ coordination formed by the phenolate-O, the imine-N and the deprotonated amide-O atoms of L^{2-}, and the sp^2 N atom of the neutral heterocycle. In the solid state, **1** exists as a centrosymmetric dimer due to very weak apical coordination of the metal bound phenolate-O. Complex **2** has no such apical coordination and exists as a monomer. Self-assembly *via* C–H···O, N–H···O and O–H···N interaction leads to a one-dimensional chain arrangement; other non-covalent interactions such as C–H···π and $\pi\cdots\pi$ are not involved.

Keywords: Copper(II) complexes; Crystal structure; Self-assembly; Substituted aroylhydrazone

1. Introduction

Supramolecular species involving metal ions are of considerable interest due to their possible applications as molecule-based metals and magnets, optical and thermal switches and as probes for DNA structures [1–6]. Self-assembly of transition metal complexes into desired supramolecular entities has been achieved by utilizing the metal ion's preference for different coordination geometries, designing suitable ligands and using weak intermolecular interactions such as hydrogen bonding and π–π interactions [1–9]. Recently, Das *et al.* reported a ternary square-planar copper(II) complex, [Cu(bhac)(Hdmpz)], with a deprotonated O,N,O-donor Schiff base, acetylacetone benzoylhydrazone (H$_2$bhac), and 3,5-dimethylpyrazole (Hdmpz) [10]. In the solid state, the plate-like molecules of [Cu(bhac)(Hdmpz)] form a one dimensional assembly with alternate short (3.5952(8) Å) and long (5.5960(12) Å) Cu···Cu distances due to intermolecular π–π interactions involving the chelate rings and the Hdmpz moieties.

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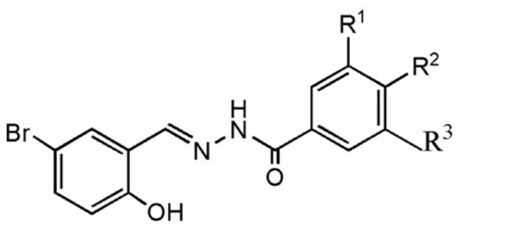
Self-assembly patterns of analogous complexes [Cu(bhac)(hc)] with other monodentate N-donor heterocycles (hc = pyrazole, imidazole, and pyridine) are very different [11]. In each of these three complexes, variations in the relative orientations of both the phenyl ring plane of $bhac^{2-}$ and the heterocycle ring plane with respect to the plane constituted by rest of the molecule result in non-planarity of the whole molecule. As a result, the nature and directionality of the weak intermolecular interactions and the ensuing supramolecular structures differ drastically in these apparently very similar complexes [11].

Herein, we reported the self-assembly patterns of two ternary copper(II) complexes, $[Cu(L^1)(py)]$ (**1**) and $[Cu(L^2)(Himdz] \cdot CH_3OH$ (**2**) with substituted aroylhydrazones, 5-bromo-salicylaldehyde-3,5-dimethoxy-benzoylhydrazone (H_2L^1) and 5-bromo-salicylaldehyde-*p*-methyl-benzoylhydrazone (H_2L^2), and pyridine and imidazole; crystal structure and spectroscopic properties are reported.



$R^1 = R^3 = CH_3O$, $R^2 = H$ H_2L^1
$R^1 = R^3 = H$, $R^2 = CH_3$ H_2L^2

2. Experimental

2.1. *Materials and instrumentation*

C, N and H elemental analyses were carried out with a Varian EL elemental analyzer. IR spectra were recorded on a Bruker Tensor27 FT-IR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Shimadzu 240 spectrophotometer. Cyclic voltammetry measurements were performed on a LK98 Microcomputer-based electrochemical analyzer with glassy carbon as a working electrode, a platinum wire as a counter electrode and Ag–AgCl ($1\,mol \cdot dm^{-3}$ KCl) as a reference electrode. Two substituted aroylhydrazone ligands, H_2L^1 and H_2L^2 were prepared by condensation of substituted benzoylhydrazine with 5-bromo-salicylaldehyde in methanol. All other chemicals and solvents used were of analytical grade.

2.2. *Synthesis*

$[Cu(L^1)(py)]$ (1). To a mixed solution of methanol ($40\,cm^3$) and DMF ($10\,cm^3$) of H_2L^1 (0.35 g, 1 mmol) and pyridine (0.4 g, 5 mmol), a methanol solution ($20\,cm^3$) of $Cu(O_2CCH_3)_2 \cdot H_2O$ (0.19 g, 1 mmol) was added gradually with stirring. The resulting green solution was further stirred for 2 h. The volume of the reaction mixture was then reduced to 25 mL on a steam bath, cooled to room temperature and filtered. Greenish brown crystals separated after about 4 days and were collected. Yield: 75%.

m.p. >300°C. Anal. Calcd for **1** (%): C, 48.52; N, 8.09; H, 3.50; Found: C, 48.46; N, 7.98; H, 3.42.

[Cu(L^2)(Himdz]·CH_3OH (2). This complex was prepared by the same method as for **1**, but with H_2L^2 and imidazole instead of H_2L^1 and pyridine, respectively. Yield: 82%. m.p. >300°C. Anal. Calcd for **2** (%): C, 46.12; N, 11.33; H, 3.88; Found: C, 46.32; N, 11.21; H, 3.68.

2.3. *Crystal structure determination*

Intensity data for single crystals of **1** and **2** were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. All the hydrogen atoms were located geometrically and refined isotropically. The data collection and refinement details are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure*

The molecular structures of **1** and **2** are illustrated in figures 1 and 2 with the atom numbering scheme. The bond parameters associated with the metal ion are listed in table 2. In each complex, the metal is in square-planar N_2O_2 coordination formed by the phenolate-O, the imine-N and the deprotonated amide-O atoms of L^{2-}, and the sp^2 N atom of the neutral heterocycle.

Table 1. Crystal data and structure refinements for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{21}H_{18}BrCuN_3O_4$	$C_{19}H_{19}BrCuN_4O_3$
Formula weight	519.83	494.83
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.812(2)	11.774(3)
b (Å)	9.990(3)	12.235(3)
c (Å)	11.551(3)	16.074(4)
α (°)	109.048(3)	70.533(4)
β (°)	101.604(4)	69.261(3)
γ (°)	93.316(4)	89.902(4)
V (Å^3)	1039.0(4)	2023.8(8)
Z	1	4
D_{Calcd} (Mg m^{-3})	1.662	1.624
μ (mm^{-1})	3.007	3.081
Reflection collected	5500	10653
Independent reflection	3610 ($R_{(\text{int})} = 0.0192$)	7035 ($R_{(\text{int})} = 0.0408$)
Reflections with [$I > 2\sigma(I)$]	2749	3442
Goodness-of-fit on F^2	1.018	0.996
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0363$, $wR_2 = 0.0817$	$R_1 = 0.0556$, $wR_2 = 0.1127$
R indices (all data)	$R_1 = 0.0548$, $wR_2 = 0.0922$	$R_1 = 0.1377$, $wR_2 = 0.1444$
Largest diff. peak and hole (e Å^{-3})	0.751 and −0.516	0.841 and −0.692

The C8–O2 (1.292(4), 1.311(7) Å) and C8–N2 (1.317(4), 1.302(8) Å) distances are consistent with the enolate form of the amide functionality [10–14]. The Cu(II)–O(amide) distance (1.942(2), 1.911(4) Å) is shorter than the distances (1.976(2)–2.063(2) Å) found in copper(II) complexes in which the O-coordinating

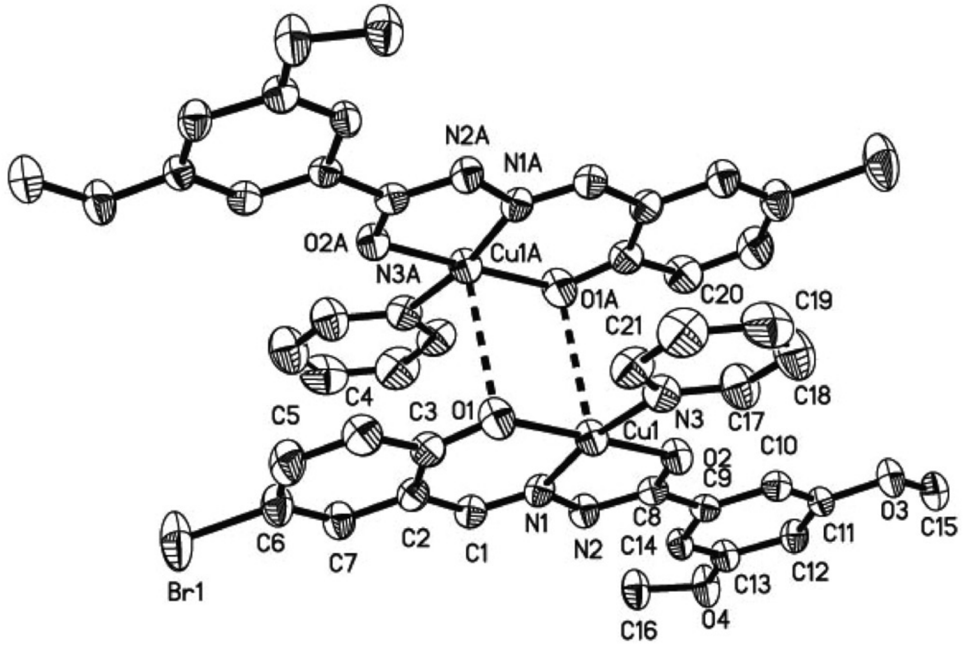


Figure 1. Dimeric structure of $[Cu(L^1)(py)]$ (**1**) with the atom labeling scheme.

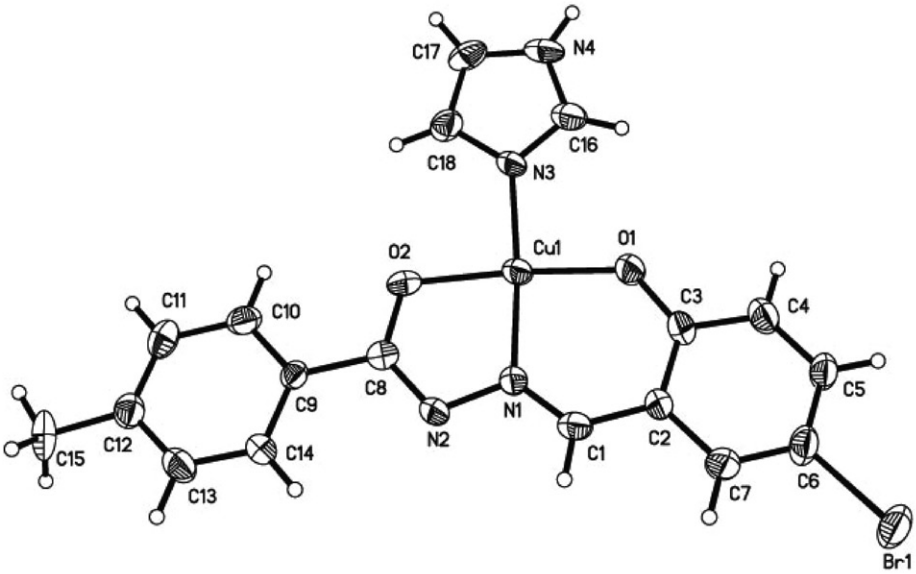


Figure 2. Structure of $[Cu(L^2)(Himdz)] \cdot CH_3OH$ (**2**) with the atom labeling scheme.

Table 2. Selected bond distances (Å) and angles (°) for 1 and **2**.

	1	**2**
Cu(1)–O(1)	1.909(2)	1.890(5)
Cu(1)–N(1)	1.918(3)	1.920(5)
Cu(1)–O(2)	1.942(2)	1.911(4)
Cu(1)–N(3)	2.009(3)	1.951(5)
O(1)–Cu(1)–N(1)	93.1(2)	93.7(2)
O(1)–Cu(1)–O(2)	173.5(2)	175.2(2)
N(1)–Cu(1)–O(2)	81.2(2)	81.9(2)
O(1)–Cu(1)–N(3)	92.8 (2)	91.3(2)
N(1)–Cu(1)–N(3)	171.1(2)	174.5(2)
O(2)–Cu(1)–N(3)	93.2 (2)	93.2(2)

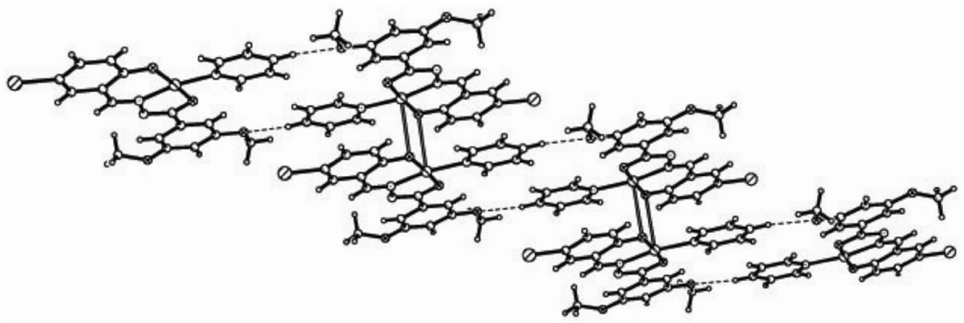


Figure 3. One-dimensional zigzag chain arrangement of [Cu(L^1)(py)] (**1**).

amide functionality is protonated [15,16] and comparable with the distances (1.914(4)–1.989(5) Å) observed for complexes in which copper(II) is coordinated to deprotonated amide-O [10, 11, 14, 17]. The Cu–O(phenolate) (1.909(2), 1.890(5) Å) and Cu–N(imine) (1.918(3), 1.920(5) Å) bond lengths (table 2) are comparable to the bond lengths observed in copper(II) complexes having the same coordinating atoms [12, 13, 18]. The Cu–N(heterocycle) bond lengths are unexceptional [10–13].

There is no significant displacement (0.004–0.028 Å) of the metal centre from the N_2O_2 square plane. The two complex molecules are essentially planar, barring a small variation in the orientation of the phenyl ring plane of the benzoyl fragment in L^{2-} and that of the heterocycle plane with respect to the plane containing the rest of the molecule. The dihedral angles between the phenyl ring plane and the plane constituted by O1, O2, N1, N2, C1–C8 atoms (mean deviations are in the range 0.001–0.0973 Å) are 2.83(17)° and 6.99(30)° for **1** and **2**, respectively. The dihedral angles between the heterocycle plane and the plane containing O1, O2, N1, N2, C1–C8 atoms are 9.46(21)° and 8.67(37)° for **1** and **2**, respectively.

3.2. *Self-assembly of 1 and 2*

Square-planar copper(II) complexes are known to form dimeric species containing equatorial–apical bridges due to weak interactions of the metal ion with another atom of a neighboring molecule at the apical position [14]. Complex **1** forms a

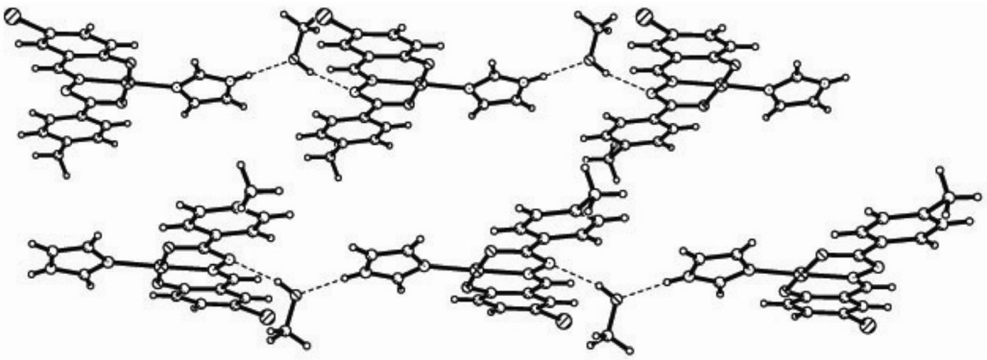


Figure 4. One-dimensional arrangement of $[Cu(L^2)(Himdz)] \cdot CH_3OH$ (**2**).

centrosymmetric dimer due to very weak apical coordination of the phenolate-O in a reciprocal fashion (figure 1). The Cu1–O1A distance is 2.8377(5) Å. In the Cu_2O_2 core, the Cu1–O1–Cu1A bridge angle and the Cu1 ··· Cu1A distance are 99.55(11)° and 3.6731(9) Å. In the crystal lattice, each dimer of **1** participates in four hydrogen bonds and a zigzag chain arrangement is formed (figure 3). The pyridine *para* C–H group is hydrogen bonded with methoxy of a neighbouring dimer. The C ··· O distance and C–H ··· O angle are 3.327 Å and 169.02°. Therefore, each molecule in this zigzag chain is connected to the two adjacent molecules in two ways. On one side there are two reciprocal Cu–O ··· Cu equatorial-apical interactions and on the other side there are two reciprocal C–H ··· O interactions.

Compound **2** does not form dimeric units *via* weak apical interaction, but exists in a one dimensional arrangement. Each methanol molecule participates in two hydrogen bonds and a chain-like arrangement is formed (figure 4). On one side, the O–H group of methanol acts as a donor to the uncoordinated and deprotonated amide-N atom of L^{2-}. The O ··· N distance and O–H ··· N angle are 2.736 Å and 172.04°. On the other side, it acts as an acceptor to the N–H group of the imidazole moiety of an adjacent molecule (figure 4). The N ··· O distance and N–H ··· O angle are 2.745 Å and 167.59°.

One of the prerequisites for a π-stacked assembly is planarity of the whole molecule [10, 11, 19–21]. Although **1** and **2** are more planar than [Cu(bhac)(hc)] (hc = pyrazole, imidazole, and pyridine) [11], non-covalent interactions such as C–H ··· π and $\pi \cdots \pi$ observed in these complexes are not involved in **1** and **2**. Steric constraints imposed by methoxyl and methyl substituents may prevent π-stacked assembly of **1** and **2**.

3.3. *IR spectra and electronic spectra*

IR spectra of **1** and **2** do not display the C=O stretch of the amide functionality observed for free H_2L, consistent with deprotonation and the enolate form of the amide functionality in complexes [11, 12]. Strong bands at 1607 and 1594 cm^{-1} are attributed to the conjugated C=N–N=C fragment [10–14].

The electronic spectra of **1** and **2** in DMF show a weak band at ca 570 nm which is assigned to d–d transition. Several intense bands in the range 310–390 nm are likely to be due to ligand-to-metal charge transfer and intraligand transitions [22, 23].

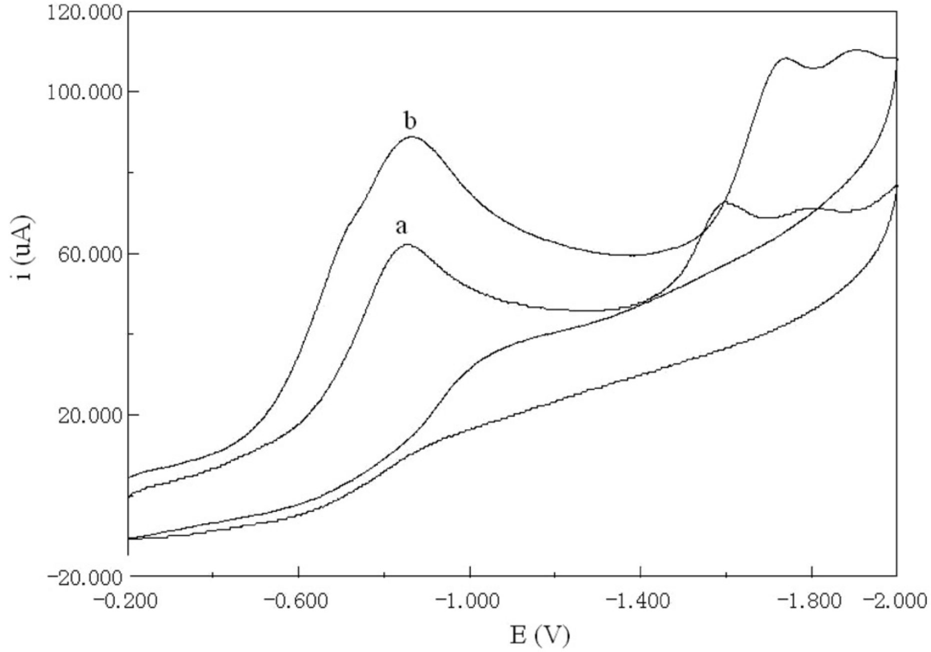


Figure 5. Cyclic voltammogram ($100\,\mathrm{mV\,s^{-1}}$) of the copper(II) complexes: (a) $[Cu(L^1)(py)]$ (**1**); (b) $[Cu(L^2)(Himdz)] \cdot CH_3OH$ (**2**).

3.4. *Cyclic voltammetry*

Cyclic voltammograms of **1** and **2**, shown in figure 5, were measured in DMF with $0.1\,\mathrm{mol \cdot dm^{-3}}$ $(n\text{-}Bu)_4NClO_4$ (TBAP) as a supporting electrolyte in the potential range −0.2 to −2.0 V. The complexes exhibited an irreversible reduction wave at −0.855 and −0.861 V (*versus* Ag–AgCl) for **1** and **2**, respectively. On the anodic side no anodic wave occurs. Similar results have previously been reported for copper(II) complexes with Schiff-base ligands [24–26]. The reduction observed for **1** and **2** may be assigned to Cu(II) to Cu(I) reduction.

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References

[1] Proceedings of the Inorganic Crystal Engineering (Dalton Discussion No. 3) *J. Chem. Soc., Dalton Trans.*, 3705 (2000).
[2] O.R. Evans, W. Lin. *Acc. Chem. Res.*, **35**, 511 (2002).

[3] B. Schoentjes, J.M. Lehn. *Helv. Chim. Acta*, **78**, 1 (1995).
[4] O. Kahn, C.J. Martinez. *Science*, **279**, 44 (1998).
[5] T. Mallah, S. Thiébault, M. Verdaguer, P. Veillet. *Science*, **262**, 1554 (1993).
[6] T.J. Marks. *Angew. Chem., Int. Ed. Engl.*, **29**, 857 (1990).
[7] D. Braga, F. Grepioni, G.R. Desiraju. *Chem. Rev.*, **98**, 1375 (1998).
[8] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000).
[9] P.N.W. Baxter, J.M. Lehn, B.O. Kneisel, D. Fenske. *Angew. Chem., Int. Ed. Engl.*, **36**, 1978 (1997).
[10] S. Das, G.P. Muthukumaragopal, S.N. Pal, S. Pal. *New J. Chem.*, **27**, 1102 (2003).
[11] S. Das, S. Pal. *J. Mol. Struct.*, **741**, 183 (2005).
[12] M.F. Iskander, T.E. Khalil, R. Werner, W. Haase, I. Svoboda, H. Fuess. *Polyhedron*, **19**, 1181 (2000).
[13] M.F. Iskander, T.E. Khalil, W. Haase, R. Werner, I. Svoboda, H. Fuess. *Polyhedron*, **20**, 2787 (2001).
[14] N.R. Sangeetha, S. Pal. *Polyhedron*, **19**, 1593 (2000).
[15] N.R. Sangeetha, S.N. Pal, C.E. Anson, A.K. Powell, S. Pal. *Inorg. Chem. Commun.*, **3**, 415 (2000).
[16] N.R. Sangeetha, S. Pal. *J. Chem. Crystallogr.*, **29**, 287 (1999).
[17] N.R. Sangeetha, K. Baradi, R. Gupta, C.K. Pal, V. Manivannan, S. Pal. *Polyhedron*, **18**, 1425 (1999).
[18] N.R. Sangeetha, S.N. Pal, C.E. Anson, A.K. Powell, S. Pal. *Inorg. Chem. Commun.*, **3**, 415 (2000).
[19] C. Janiak. *J. Chem. Soc., Dalton Trans.*, **7**, 3885 (2000).
[20] C.A. Hunter, J.K.M. Saunders. *J. Am. Chem. Soc.*, **112**, 5525 (1990).
[21] A. Mukhopadhyay, G. Padmaja, S.N. Pal. *Inorg. Chem. Commun.*, **6**, 381 (2003).
[22] N.M.H. Salen, L.E. Sayed, W. Haase, M.F. Iskander. *J. Coor. Chem.*, **58**, 1327 (2005).
[23] H.Y. Liu, H.Y. Wang, H. Wu, D.Z. Niu. *J. Coor. Chem.*, **58**, 1345 (2005).
[24] J. Gao, X.Y. Xu, M.Y. Wang, Q.L. Liu, H.B. Song. *J. Coor. Chem.*, **58**, 1351 (2005).
[25] S. Zolezzi, E. Spodine, A. Decinti. *Polyhedron*, **21**, 55 (2002).
[26] K.S. Bharathi, A.K. Rahiman, K. Rajesh, S. Sreedaran, P.G. Aravindan, D. Velmurugan, V. Narayanan. *Polyhedron*, **25**, 2859 (2006).