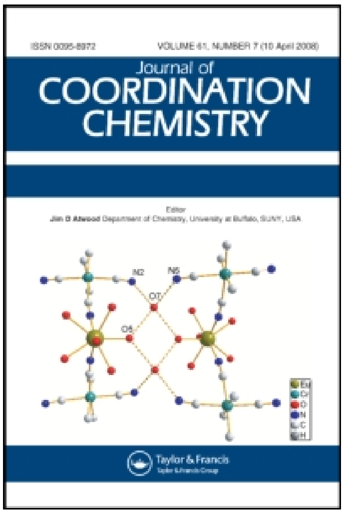


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses and X-ray crystal structures of five- and six-coordinate copper(II) complexes of *N,N,N',N'*-tetraalkylpyridine-2,6-dicarboxamides containing-$OClO_3$ and-OSO_2CF_3 counter ions

Pratibha Kapoor[a]; Ajay Pal Singh Pannu[b]; Mukesh Sharma[a]; Maninder Singh Hundal[b]; Ramesh Kapoor[c]
[a] Department of Chemistry, Panjab University, Chandigarh 160 014, India [b] Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India [c] Indian Institute of Science Education and Research Mohali, Chandigarh 160 019, India

To cite this Article Kapoor, Pratibha , Pal Singh Pannu, Ajay , Sharma, Mukesh , Singh Hundal, Maninder and Kapoor, Ramesh(2010) 'Syntheses and X-ray crystal structures of five- and six-coordinate copper(II) complexes of *N,N,N',N'*-tetraalkylpyridine-2,6-dicarboxamides containing-$OClO_3$ and-OSO_2CF_3 counter ions', Journal of Coordination Chemistry, 63: 20, 3635 — 3647

To link to this Article: DOI: 10.1080/00958972.2010.517267

URL: http://dx.doi.org/10.1080/00958972.2010.517267

Journal of Coordination Chemistry
Vol. 63, No. 20, 20 October 2010, 3635–3647

Taylor & Francis
Taylor & Francis Group

Syntheses and X-ray crystal structures of five- and six-coordinate copper(II) complexes of *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamides containing –$OClO_3$ and –OSO_2CF_3 counter ions

PRATIBHA KAPOOR†, AJAY PAL SINGH PANNU‡, MUKESH SHARMA†, MANINDER SINGH HUNDAL*‡ and RAMESH KAPOOR§

†Department of Chemistry, Panjab University, Chandigarh 160 014, India
‡Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India
§Indian Institute of Science Education and Research Mohali, Chandigarh 160 019, India

(*Received 9 March 2010; in final form 2 July 2010*)

Reactions of anhydrous copper(II) chloride with NaX (1 : 1 or 1 : 2) and AgX (1 : 2) containing appropriate *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamides(O-daap) in CH_3CN yield monosubstituted five-coordinate $[Cu(L_1)Cl(CF_3SO_3)]$ (**1**), $[Cu(L_2)Cl(ClO_4)]$ (**2**), $[Cu(L_3)Cl(ClO_4)]$ (**3**), and six-coordinate $[Cu(L_2)(CF_3SO_3)_2]\cdot H_2O$ (**4**) ($X = -OClO_3$ and $-OSO_2CF_3$; $L_1 =$ *N*,*N*,*N*′,*N*′-tetraethylpyridine-2,6-dicarboxamides; $L_2 =$ *N*,*N*,*N*′,*N*′-tetraisopropylpyridine-2,6-dicarboxamides; $L_3 =$ *N*,*N*,*N*′,*N*′-tetraisobutylpyridine-2,6-dicarboxamides). The structures of these complexes have been determined by X-ray crystallography. The Cu^{2+} in **1**–**3** adopts distorted square-pyramidal geometry, while **4** exhibits octahedral structure. Steric factors in conjunction with lattice effects and the nature of the anions are responsible for the variety in coordination spheres. These compounds undergo extensive intermolecular H-bonding to give to 2-D sheets extending along various planes.

Keywords: Alkyl-substituted pyridine-2,6-dicarboxamides; X-ray crystal structures; Metathetical reactions; Steric and anionic effects

1. Introduction

Coordination behavior of pyridine carboxamides toward transition metal ions has been widely investigated [1–16]. Upon deprotonation of the carboxamide, nitrogens chelate to metal ions and provide complexes with a range of coordination numbers, nuclearities, and geometries. Tridentate ligands containing fully substituted tetraalkyl/aryl pyridine-2,6-dicarboxamide [1, 17–25] use both the carbonyl oxygens and pyridine nitrogen, as hindered C–N bond rotation renders the amide nitrogens

---

*Corresponding author. Email: mshundal.chem@gndu.ac.in

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.517267

almost inactive. A systematic study of steric and electronic effects on the formation of lanthanide complexes with neutral tridentate *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamides(O-daap) (scheme 1) shows a reduced affinity with increasing size of R on the terminal carboxamide side arms [17, 18]. Gracia-Lozano *et al.* [19, 20] and de Preez *et al.* [21, 22] have also reported structural studies on the complexes of these ligands with a number of first-row transition metals.

Our interest in *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamide(O-daap) and *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dithiocarboxamide(S-daap) (scheme 1) [23–26] has been threefold: first, to study the effect of steric crowding brought by employing various alkyl groups at the terminal carboxamide side arms; second, to investigate the effect of change in the donors in the two side arms on coordination geometry [23–26], and third, the role played by counter ions, such as $–OClO_3$, $–OSO_2CF_3$, and $–ONO_2$, in determining the geometry around the metal.

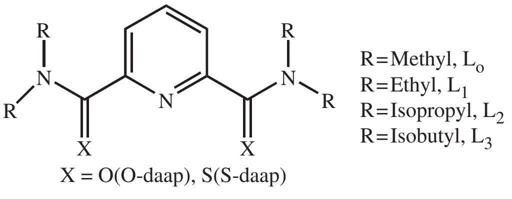
In the present work, we carried out metathetical reactions of anhydrous $CuCl_2$ with NaX (1 : 1 or 1 : 2) and AgX (1 : 2) ($X = –OClO_3$ and $–OSO_2CF_3$) in the presence of planar tridentate *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamides(O-daap) [R = Et, L_1 = *N*,*N*,*N*′,*N*′-tetraethylpyridine-2,6-dicarboxamides; R = *i*-Pr, L_2 = *N*,*N*,*N*′,*N*′-tetraisopropylpyridine-2,6-dicarboxamides; R = *i*-Bu, L_3 = *N*,*N*,*N*′,*N*′-tetraisobutylpyridine-2,6-dicarboxamides]. Variation in the alkyl bulk on carboxamide nitrogens of the ligand has important consequences on geometrical parameters of the complexes formed. Furthermore, substitution of one Cl^- by the counter ion X^- gives five-coordinate CuCl(X)(O-daap), while disubstitution results in the formation of six-coordinate $Cu(X)_2(O\text{-daap})(H_2O)$ complex. We previously reported the formation of a similar five-coordinate copper(II) complex, $[CuCl(L_1)(ClO_4)]$, which was obtained by reaction of L_1 with $CuCl_2$ and sodium perchlorate [23].

Incorporation of pyridine-based ligands generally leads to the construction of supramolecular frameworks [27–29] using hydrogen bonds or coordination polymerization, or a combined effort of both. In this work, 1-D and 2-D networks are formed *via* intermolecular H-bonds.

2. Experimental

2.1. *Materials*

All reactions were carried out in anhydrous solvents under dry N_2. Solvents and other reagents were dried using standard techniques as described earlier [30]. Sodium perchlorate (Merck) and silver trifluoromethanesulfonate (Aldrich) were



Scheme 1.

used as received. Anhydrous copper(II) chloride was prepared by refluxing hydrated copper(II) chloride with thionyl chloride. The anhydrous product was filtered, washed with toluene, and dried *in vacuo*. The ligands were prepared as described previously [23].

2.2. *Preparation of complexes*

Complexes **1**–**3** were prepared by reacting anhydrous copper(II) chloride (1.34 g, 10 mmol) with NaX (1 : 1 or 1 : 2) (X = $-OClO_3$ (1.22 g, 10 mmol) and $-OSO_2CF_3$ (1.72 g, 10 mmol)) in 50 mL of CH_3CN. The contents were stirred for 12 h. Sodium chloride was filtered off and the clear solution was stirred with the appropriate ligand [(L_1, 5.54 g, 20 mmol for **1**), (L_2, 6.66 g, 20 mmol for **2**), (L_3, 7.78 g, 20 mmol for **3**)] for another 8 h. The solid compounds were recovered by filtration and dried under vacuum. Irrespective of whether the $CuCl_2$ to NaX ratio is 1 : 1 or 1 : 2 the product is always monosubstituted and only 10 mmol of NaCl is recovered each time.

[Cu(L_1)Cl(CF_3SO_3)] (1): m.p. 210–214°C. Anal. Calcd for $C_{16}H_{23}N_3O_5SClF_3Cu$ (%): C, 36.57; H, 4.38; N, 8.00. Found (%): C, 36.56; H, 4.30; N, 7.90. IR (KBr pellet, cm^{-1}): 1615(ν_{CO}); 1279, 1244, ν_4(E)SO_3 asym; 1029(ν_1(A_1)SO_3 sym; 761 ν(SCF_3). Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$): 132.0 ($CH_3CN$).

[Cu(L_2)Cl(ClO_4)] (2): m.p. 250–253°C. Anal. Calcd for $C_{19}H_{31}N_3O_6Cl_2Cu$ (%): C, 42.90; H, 5.90; N, 7.90. Found (%): C, 42.39; H, 6.11; N, 7.79. IR (KBr pellet, cm^{-1}): 1595(ν_{CO}); 1109{ν_4(E)}; 1050{ν_1(A_1)}; 921{ν_2(A_1)}; 641{ν_5(E)}; 624{ν_3(A_1)}. Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$): 127.0 ($CH_3CN$), 52.0 ($CH_3OH$).

[Cu(L_3)Cl(ClO_4)] (3): m.p. 170–173°C. Anal. Calcd for $C_{23}H_{39}N_3O_6Cl_2Cu$ (%): C, 46.98; H, 6.64; N, 7.15. Found (%): C, 46.66; H, 6.82; N, 7.10. IR (KBr pellet, cm^{-1}): 1594(ν_{CO}); 1097{ν_4(E)}; 1046{ν_1(A_1)}; 930{ν_2(A_1)}; 625{ν_5(E)}; 590{ν_3(A_1)}. Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$): 125.0 ($CH_3CN$), 46.2 ($CH_3OH$).

Reaction of $CuCl_2$ with $AgOSO_2CF_3$: Reaction of anhydrous $CuCl_2$ (1.34 g, 10 mmol) with $AgOSO_2CF_3$ (5.14 g, 20 mmol) was carried out in 60 mL of CH_3CN. The contents were stirred for 4 h. AgCl (2.8 g, 20 mmol) was removed and L_2 (6.66 g, 20 mmol) was added to the solution with stirring. After 8 h of stirring a solid separated, was filtered and dried *in vacuo* (**4**).

[Cu(L_2)(CF_3SO_3)$_2$] · H_2O (4): m.p. 183–185°C. Anal. Calcd for $C_{21}H_{33}N_3O_9S_2F_6Cu$ (%): C, 35.37; H, 4.63; N, 5.89. Found (%): C, 36.06; H, 5.13; N, 6.16. IR (KBr pellet, cm^{-1}): 3530(ν_{OH}); 1605(ν_{CO}); 1280, 1245, ν_4(E)SO_3 asym.; 1026(ν_1(A_1)SO_3 sym.; 740 ν(SCF_3). Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$): 168.0 ($CH_3CN$).

2.3. *Physical methods*

Elemental analyses (C, H, N) were performed on a Perkin-Elmer model 2400 CHN elemental analyzer. Chlorine was estimated as chloride by Volhard's method. IR spectra were recorded as KBr pellets on a Perkin-Elmer RX-1 FTIR spectrophotometer. Molar conductance measurements were made using a digital conductivity bridge model CC601.

2.4. *X-ray crystallography*

Crystallization of **1**–**4** by very slow evaporation of their saturated acetonitrile solution at room temperature yielded good single crystals. The data were collected at 298 K on a Siemens P4 single crystal X-ray diffractometer using the XSCANS package [31]. The data were collected by the θ–2θ scan mode with a variable scan speed up to a maximum of $2\theta = 60^\circ$ using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). To monitor the stability of the crystal, three standard reflections were measured after every 97 reflections. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using SIR97 [32] and refined by full-matrix least-squares on F^2 using SHELXS-97 [33] in the WINGX package [34] of programs. All atoms were refined anisotropically. All hydrogens were attached geometrically riding on their respective carrier atoms with U_{iso} being 1.5, 1.2, and 1.2 times the U_{iso} of their carrier for methyl, methylene, and aromatic carbons, respectively.

The O5, O6, and F6 in **1**, **3**, and **4**, respectively, show disorder which could be resolved by splitting each of these atoms into two parts with total site occupancy factor (sof) one. Their sofs and U_{iso} values were refined as free variables. A summary of crystal data, experimental details, and refinement details is given in table 1.

3. Results

3.1. *Syntheses*

Metathetical reactions between anhydrous $CuCl_2$ and NaX or AgX (X = $-OClO_3$ and $-OSO_2CF_3$) in 1 : 1 and 1 : 2 mole ratios, in the presence of appropriate ligand (L_1–L_3), yielded **1**–**4**. The complexes are blue to bluish-green hygroscopic solids, characterized through elemental analyses, IR data, conductivity measurements, and X-ray crystallography. The compounds easily dissolve in polar solvents and their millimolar solutions in CH_3CN and CH_3OH show significant dissociation into ions. For **1**–**3**, the molar conductance values are in agreement with those expected for 1 : 1 electrolytes, while **4** exhibits values which are lower than expected for bi-univalent electrolytes [35].

IR spectra of **1**–**4** [Supplementary material (S1, complex **1**), (S2, complex **2**), (S3, **3** and S4, **4**)] show ν_{CO} peaks in the range 1590–1615 cm^{-1} as compared to 1625 cm^{-1} in the free ligand, showing a shift to a lower wavenumber due to the coordination to copper(II) [23, 25]. Six fundamental modes of vibrations, all IR active, are observed for $SO_3CF_3^-$ of C_{3v} symmetry. The ν_4(E)SO_3 asymmetric stretch of non-coordinated triflate falling at 1271 cm^{-1} splits into 1279 and 1244 cm^{-1} for **1** and into 1280 and 1245 cm^{-1} for **4**. The $SO_3CF_3^-$ is easily recognizable from the number and position of sulfur–oxygen stretching frequencies [36]. The number of bands in the IR spectra of **1** and **4** indicate lowering of the local site symmetry of $-CSO_3$ from C_{3v} to C_s. The unidentate mode of coordination was unambiguously established by their X-ray crystal structures. IR spectra of **2** and **3** indicate coordinated perchlorates since bands at 1109, 1050, 921, and 624 cm^{-1} (for **2**) and 1097, 1046, 930, and 625 cm^{-1} (for **3**) indicate monodentate (O–ClO_3) coordination [23]. The T_d symmetry of ClO_4^- is lowered to C_{3v} in these complexes [37, 38].

Table 1. Crystallographic data for **1**–**4**.

Empirical formula	$C_{16}H_{23}ClCuF_3N_3O_5S$	$C_{19}H_{31}Cl_2CuN_3O_6$	$C_{23}H_{39}Cl_2CuN_3O_6$	$C_{21}H_{35}CuF_6N_3O_{10}S_2$
Formula weight	525.42	531.91	588.01	731.18
Crystal size (mm^3)	$0.10 \times 0.15 \times 0.20$	$0.20 \times 0.20 \times 0.18$	$0.18 \times 0.18 \times 0.16$	$0.20 \times 0.10 \times 0.10$
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\ 2_1/n$	$P\ 2_1/c$	$P\ 2_1/n$
Unit cell dimensions (Å, °)				
a	8.118(5)	8.292(2)	12.248(2)	7.794(2)
b	10.416(5)	25.983(1)	15.011(4)	22.746(4)
c	13.345(4)	11.450(3)	15.595(1)	9.002(4)
α	88.453(4)	90.0	90.0	90.0
β	87.691(5)	101.118(5)	94.570(5)	98.410(5)
γ	78.996(3)	90.0	90.0	90.0
Volume (Å^3), Z	1106.6(9), 2	2420.6(19), 4	2858.1(18), 4	1578.7(14), 2
ρ_{Calcd} ($mg\,m^{-3}$)	1.577	1.460	1.367	1.538
$F(000)$	538	1108	1236	774
$\mu(mm^{-1})$	1.259	1.161	0.991	0.912
Θ (°)	1.53–25.50	1.57–25.50	1.67–25.51	1.79–25.52
No. of reflections	4444	4521	5580	3262
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0485$, $wR_2 = 0.1221$	$R_1 = 0.0649$, $wR_2 = 0.1024$	$R_1 = 0.0522$, $wR_2 = 0.1177$	$R_1 = 0.0564$, $wR_2 = 0.1310$
CCDC No.	746896	747639	746897	746898

Table 2. Comparison of selected bond distances (Å) for **1**–**4**.

N1–Cu	1.948(3)	1.956(5)	1.937(4)	1.900(6)
O1–Cu	2.026(3)	1.986(4)	1.987(3)	1.966(6)
O2–Cu	2.026(3)	2.007(4)	1.982(3)	1.952(7)
Cu–O3	2.212(3)	2.350(5)	2.539(4)	2.584(2)
Cu–Cl1	2.188(1)	2.175(2)	2.173(2)	2.172(2)[a]

[a] Cu–O1W.

3.2. *X-ray crystal structures*

Table 2 compares important bond lengths for **1**–**4**.

3.3. *Molecular and crystal structure of 1*

The Cu(II) in **1** (figure 1) occupies a distorted square-pyramidal geometry with the ligand tridentate using the carbonyl oxygens and pyridine nitrogen with the other two sites occupied by Cl and a coordinated triflate. O3 of the triflate occupies the apical position and pyridine N1, carbonyl oxygens O1 and O2, and Cl1 complete the base of a distorted square pyramid. In this structure the conformation of the terminal alkyl carbons is such that on one carboxamide side arm a methyl, C15, is above the basal plane while the other terminal C13 is below. For the other carboxamide side arm, C9 is below the plane while terminal C11 is almost in the plane.

The crystal packing diagram shows that the molecules are stacked in a parallel fashion. Two such stacked molecules are held together by C11–H11B$\cdots$O1^{i} [3.606(7) Å, $^{i} = -x, -y+1, -z$] and C2–H2$\cdots$Cl1^{i} [3.636(5) Å, $^{i} = -x, -y+1, -z$] H-bonding contacts, thereby behaving as a dimeric unit. Such dimers are propagated in the form of 1-D chain by C12–H12A$\cdots$Cl1^{ii} [3.619(5) Å and $^{ii} = -x, -y+1, -z+1$]

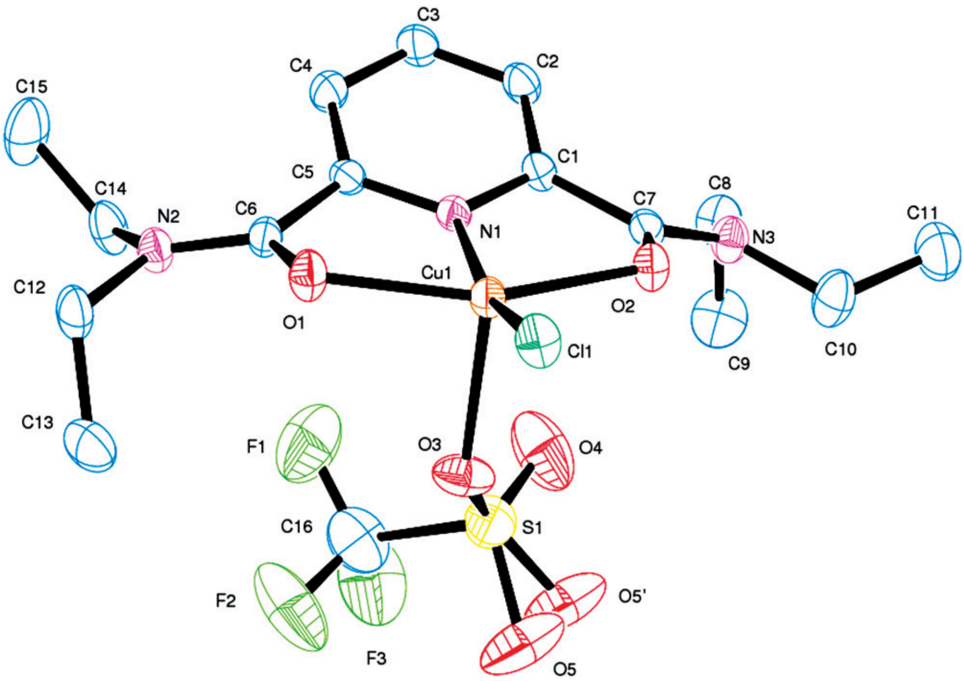


Figure 1. ORTEP diagram (30% probability) and labeling scheme for **1**. The triflate ion shows a slight disorder.

H-bonding along the *b*-axis. A 2-D sheet running parallel to the *ab* plane is formed when these parallel chains are further held together by C14–H14A $\cdots$ F2^{iii} [3.504(7) Å, $^{iii} = -x, -y, -z + 1$] H-bonding contacts (figure 2).

3.4. *Molecular and crystal structure of 2*

In **2** (figure 3), the copper is square pyramidal with O3 of perchlorate occupying the apical position while O1, O2, pyridine N1, and Cl1 form the base of the pyramid. In this structure the steric bulk on the carboxamide side arms is more than in **1**. The terminal carbons C19, C16, C13, and C10 are below the carboxamide plane, while C9, C12, C15, and C18 have oriented themselves above this plane to minimize steric strain and maximize stability.

The perchlorate O6 develops H-bonding contacts of the type C17–H17 $\cdots$ O6^{i} [3.219(9) Å, $^{i} = x - 1/2, -y + 1/2, +z - 1/2$] leading to the formation of a zig-zag chain. O3 which is involved in coordination to copper is also an acceptor to phenylene C3 *via* C3–H3 $\cdots$ O3^{ii} [3.343(9) Å, $^{ii} = x - 1, +y, +z$] hydrogen bond, thereby linking these zig-zag chains forming a 2-D corrugated sheet (Supplementary material, figure S5).

3.5. *Molecular and crystal structure of 3*

The apical position in the distorted square pyramid in **3** (figure 4) is occupied by O3 of perchlorate with amide O1 and O2, pyridine N1, and Cl1 forming the base of

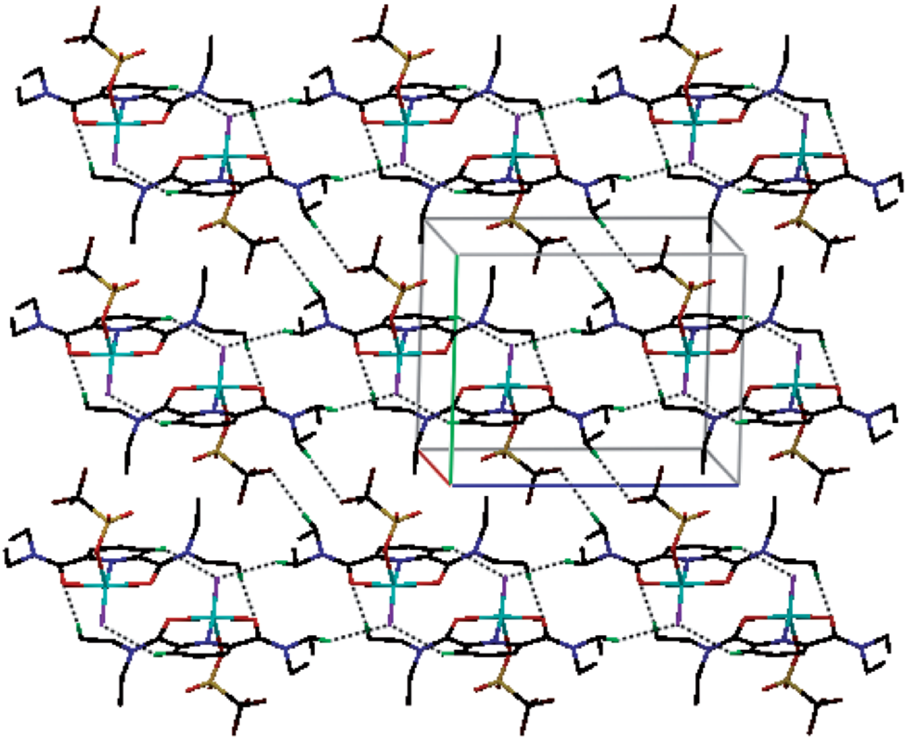


Figure 2. 2-D sheet formation in **1** down the *c*-axis due to intermolecular H-bonds. Hydrogens other than those involved in these interactions have been removed for clarity.

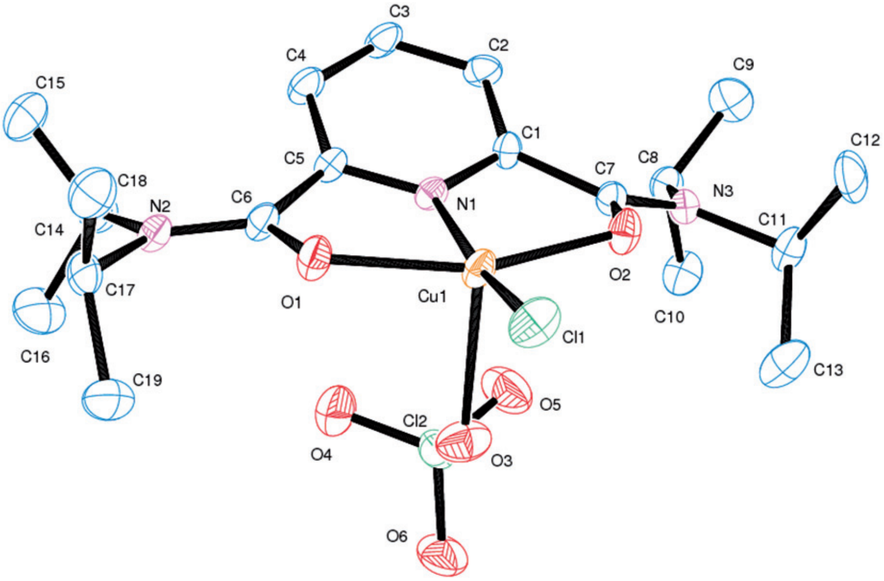


Figure 3. ORTEP representation (30% probability) of **2** and numbering scheme used in structure analysis.

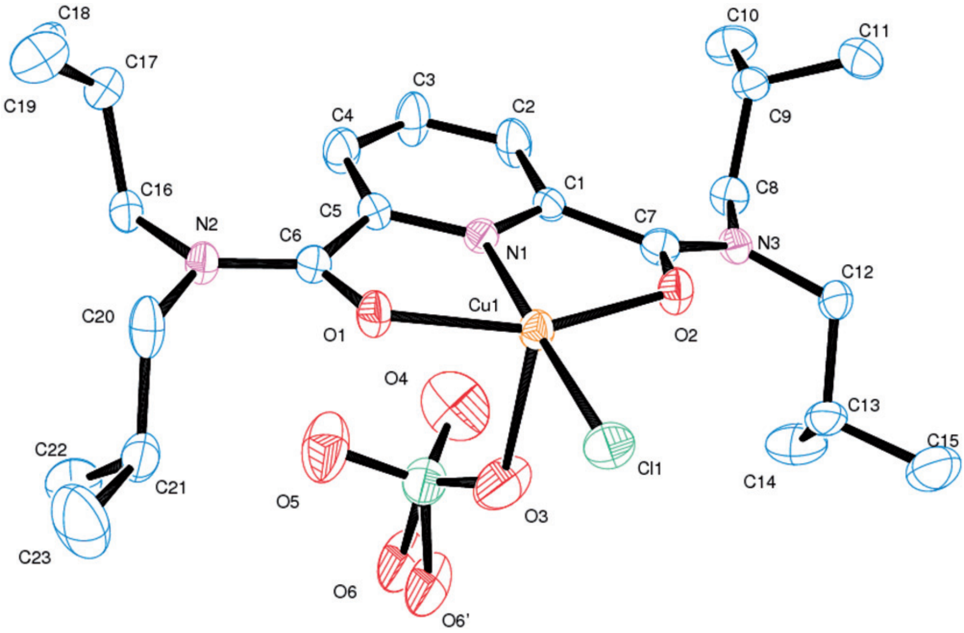


Figure 4. ORTEP view (30% probability) of **3** with atom numbering scheme used along with disorder in the perchlorate.

this pyramid. The copper is 0.08 Å above the plane containing these four atoms. The alkyl carbons attached to amide N2 [C16 and C20] and N3 [C8 and C12] are approximately in their respective amide planes as indicated by torsion angle values of $-179.9(1)^\circ$ [O1–C6–N2–C16], $-3.0(2)^\circ$ [O1–C6–N2–C20], $-176.1(5)^\circ$ [O2–C7–N3–C8], and $3.0(2)^\circ$ [O2–C7–N2–C12]. The other carbons of the bulky alkyl chains are oriented above [C13, C14, C15, C21, C22, and C23] and below [C9, C10, C11, C17, C18, and C19] the corresponding amide planes to reduce steric strain.

The crystal packing diagram (Supplementary material, figure S6) shows that two molecules are stacked over each other and held together by C4–H4$\cdots$O4^{i} [3.331(9) Å], C3–H3$\cdots$O5^{i} [3.319(8) Å], and C18–H18A$\cdots$O4^{i} [3.422(10) Å], where $^{i} = -x, -y, -z+1$, H-bonding contacts. Every such pair behaves as a dimer. The C16–H16A$\cdots$O6^{ii} [3.46(2) Å, $^{ii} = -x, +y-1/2, -z+1/2$] hydrogen bonds link such dimeric pairs which are almost perpendicular to each other. This arrangement leads to the formation of a pleated ribbon-like 1-D chain, running diagonally in the *bc* plane.

3.6. *Molecular and crystal structure of 4*

The copper in **4** is in a distorted octahedral environment. The ligand is tridentate using two oxygens O1, O2, and pyridine N1; these atoms along with a water O1W complete the square planar arrangement around the metal ion. The octahedron around copper is completed by O3 and O7 from two triflates occupying *trans* positions with Cu1–O3 distance being 2.584(2) Å and Cu1–O7 being 2.760(3) Å (figure 5). Carbons directly attached to the carboxamide nitrogens N2 [C14 and C17] and N3 [C8 and C11] are almost in the carboxamide plane. The orientation of the terminal alkyl carbon is such that

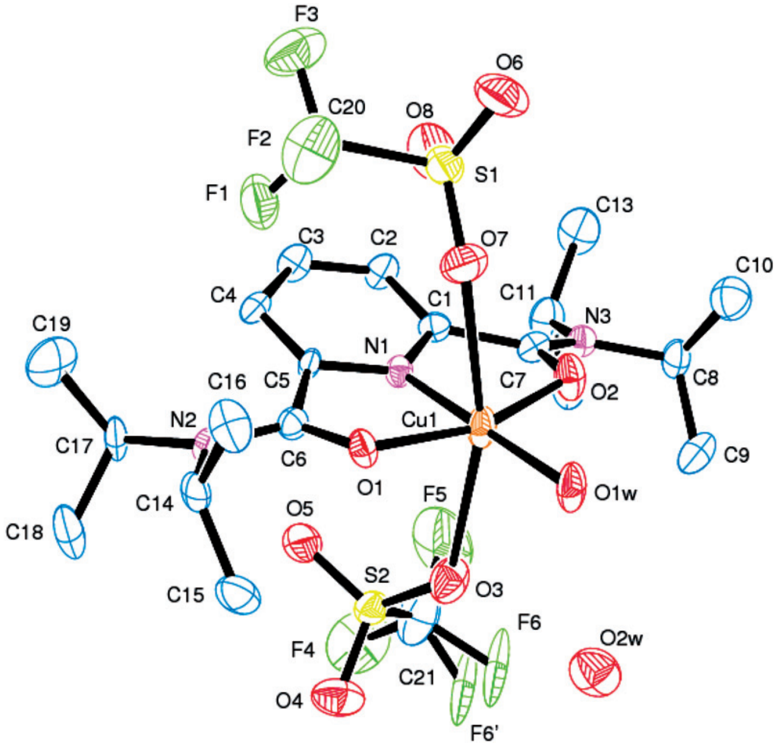


Figure 5. ORTEP representation (30% probability) and the numbering scheme used in **4**. Hydrogens omitted for clarity. One of the triflates shows disorder.

carbons C9, C12, C13, and C10 are above the carboxamide plane, while C15, C16, C18, and C19 are below to minimize steric strain in the structure. The torsion angles between the pyridine ring plane and the amide planes are −19.4(12)° [N1–C1–C7–O2] and 16.4(12)° [N1–C5–C6–O1]. The coordinating water Cu1–O1W distance is 1.897(6) Å.

Due to lattice water along with coordinated water, the molecule exhibits extensive hydrogen-bonding in the crystal lattice. O2W of the lattice water is acceptor to amide oxygen O1–H11W···O2W$^{\rm i}$ [2.653(3) Å, $^{\rm i} = x, +y, +z+1$], O1W–H12W···O2W$^{\rm i}$ [2.70 Å, $^{\rm i} = x, +y, +z+1$], and C13–H13A···O2W$^{\rm ii}$ [3.52(2) Å, $^{\rm ii} = x, y, z$] H-bonding contacts (figure 6). Also the lattice water develops H-bonding contacts of the type O2W–H21W···O4$^{\rm iii}$ [2.747(2) Å, $^{\rm iii} = x+1, +y, +z+1$] and O2W–H22W···O6$^{\rm ii}$ [2.922(2) Å, $^{\rm ii} = x, y, z$] to the anions. The coordinated triflate anion is also involved in C4–H4···O6$^{\rm iv}$ [3.266(10) Å, $^{\rm iv} = x-1, +y, +z$] and C19–H19A···F2$^{\rm iv}$ [3.536(1) Å, $^{\rm iv} = x-1, +y, +z$] H-bonding contacts. These intermolecular H-contacts collectively form a 2-D sheet running diagonally along the *ac* plane.

4. Discussion

Most five-coordinate complexes have neither an ideal trigonal bipyramidal (*tbp*) nor square pyramidal (*sp*) environment, but their geometry falls between depending upon a

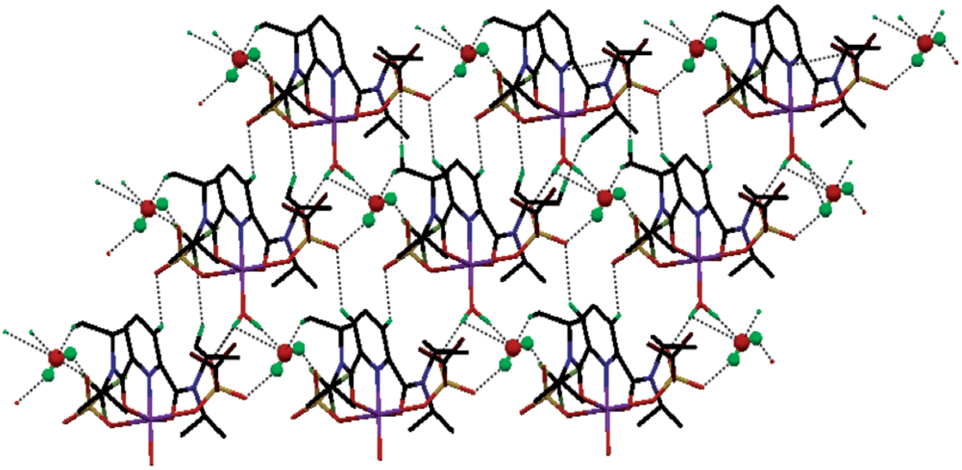


Figure 6. The 2-D lattice running diagonally along the *ac* plane in **4**. Lattice waters are shown in ball and stick representation. The hydrogens other than those involved in H-bonds are omitted for clarity.

parameter τ suggested by Addison *et al.* [39]. The parameter τ is determined by the relation $\tau = (\beta - \alpha)/60$ (where α and β are the larger basal angles with $\beta > \alpha$) and its value may vary from 0, representing ideal *sp* geometry to 1, denoting ideal *tbp* geometry. Geometries of **1**, **2**, and **3** may be defined as moving from regular square pyramidal to increasingly distorted square pyramidal with τ values equal to 0.057, 0.134, and 0.344, respectively, where angle β is N1–Cu1–Cl1 and angle α is O1–Cu1–O2. In all these complexes the ligand coordinates tridentate to copper using pyridine nitrogen and the two carbonyl oxygens, characteristic of pyridine-2,6-dicarboxylate and related ligands $[Cu(\mu\text{-dpc})(\mu\text{-4-hymp})]_n$, $[Ni(dpc)(\mu\text{-hymp})(H_2O)_2]$ [40], and $[Zn(pydc)tatp)]_n$ [41]. In $[Cu(\mu\text{-dpc})(\mu\text{-4-hymp})]_n$ and $[Zn(pydc)tatp)]_n$ the dpc/pydc ligand, besides showing its usual tridentate coordination, also connects metal centers to form coordination networks [40, 41]. Among the amide derivatives a comparison of these complexes can be made with similar five-coordinate Cu(II) complexes $CuCl_2(L_1)$ and $CuCl(ClO_4)(L_1)$ [23]. The tridentate ligand (L_1) occupies three equatorial sites while a chloride Cl(2) lies at the fourth coordination site in $CuCl_2(L_1)$. Another chlorine Cl(1) occupies the apical position of the square pyramid. The only difference in $CuCl(ClO_4)(L_1)$ is that a ClO_4 occupies the apical position instead of Cl. The torsion angles N1–C1–C7–O2 and N1–C5–C6–O1 are −27.2(5)° and 25.1(5)° for **1**, −29.4(8)° and 20.9(8)° for **2** along with −9.9(6)° and 5.5(6)° for **3**, while in the X-ray crystal structure of the only known analogous free ligand having methyl- and pyridine-substituted amide nitrogen [42], these torsion angles are 132.6(2)° and 128.2(2)°. This suggests that in the presence of metal, coordinating carbonyl groups are "flipped in" or orient themselves in "*syn*" conformation with respect to pyridine nitrogen so as to facilitate tridentate coordination.

In **1**, **2**, and **3**, N1, Cl1, O1, and O2 form the basal plane and copper shows deviation from this mean plane. Such deviations are energetically favorable and this phenomenon is observed in related five-coordinate square-pyramidal complexes like $CuCl_2(L_1)$, $CuCl(ClO_4)(L_1)$, and $NiBr_2(dpda)$ (where dpda ligand has a methyl and a phenyl group on each of its carboxamide nitrogens) [20, 23, 43, 44]. This has a considerable significance since the four basal atoms effectively restrict the approach of a ligand to the sixth coordination site, thereby fixing the coordination to five [20]. The small O1–Cu1–N1 and O2–Cu1–N1 angles (table 2) indicate the restrictions which the rigid nature of ligand places on the donors. This makes the coordination of a carbonyl oxygen from the apical position unlikely, as found in other tridentate complexes [45]. Thus, we see that even if trigonal-bipyramidal symmetry is more stable in theoretical terms [46], as compared to square-pyramidal geometry, such a coordination approach is not possible due to steric factors.

Complex **4** has octahedral copper with apical Cu1–O distances significantly longer than basal Cu1–O distances [45] pointing to tetragonally distorted octahedral geometry [20]. These distortions can be attributed to the Jahn–Teller effects and the presence of bulky isopropyl groups near the carbonyl oxygen donors. In similar copper complexes a more regular octahedral geometry is observed when the ligand L has both methyl groups on amide nitrogens as compared to a tetragonally distorted geometry when the ligand contains a more bulky phenyl along with the methyl on each of the amide nitrogens [47]. This observation is consistent with similar nickel-containing complexes containing less bulky methyl or ethyl groups on the amide nitrogen and having more regular octahedral geometry [12].

The Cu–O3 (anion) bond distances show a very interesting trend with increase in the size of alkyl groups on the carboxamide nitrogens. In **2** this distance is 2.350(5) Å, less than the range of 2.55–2.82 Å [48, 49], reported for copper(II) complexes containing coordinated perchlorate. As the steric bulk on carboxamide nitrogens increases from isopropyl (**2**) to isobutyl (**3**), the Cu1–O3 distance stretches from 2.350(5) to 2.539(4) Å. Similarly, in **1** and **4** both containing triflate, the Cu1–O3 distance increases from 2.212(3) to 2.584(2) Å as the alkyl groups change from ethyl (**1**) to isopropyl (**4**). The other *trans* bond in this octahedral complex is even longer, with Cu1–O7 distance stretching to 2.760(3) Å. This can be attributed to the Jahn–Teller distortions leading to a further increase in Cu1–O7 *trans* bond.

The torsion angles between the pyridine ring plane and the two carboxamide planes also follow a similar path. In **2** and **3** the N1–C1–C7–O2 torsion angle increases from −29.4(8) to −9.9(6)°, whereas the N1–C5–C6–O7 torsion angle decreases from 20.9° to 5.5° as the alkyl bulk on carboxamide nitrogens increases from isopropyl to isobutyl. Similarly, the N1–C1–C7–O2 torsion angle increases from −27.2(5) to −19.9° and N1–C5–C6–O7 torsion angle decreases from 25.1 to 16.1° as the alkyl group changes from ethyl to isopropyl for **1** and **4**, respectively. Thus, increasing the steric bulk from isopropyl to isobutyl (in **2** and **3**) or from ethyl to isopropyl (in **1** and **4**) twists the N–C–C–O torsion angles to make the pyridine N and carboxamide oxygens more coplanar.

5. Conclusions

Metathetical reactions between anhydrous $CuCl_2$ and NaX or AgX ($X = -OClO_3^-$ and $-OSO_2CF_3^-$) in 1 : 1 and 1 : 2 mole ratios in the presence of L_1–L_3 yielded **1**–**4**. The X-ray crystal structures show that the alkyl groups on the carboxamide nitrogen and the counter ions have remarkable effects on the geometrical parameters of the complexes. Increasing alkyl bulk on the carboxamide nitrogens pushes the coordinated counter ion further from the metal center. The particular geometry adopted by the metal ion depends on the counter ion used while synthesizing the complex. In complexes where one mole of counter ion is consumed, monosubstituted square pyramidal $[CuCl(X)(L_2)]$ are formed, while two moles of counter ion result in octahedral $[CuX_2(L_2)(H_2O)]$. Intra- and intermolecular H-bonds give interesting 1-D and 2-D crystal structures as expected from complexes containing pyridine-based amide ligands.

Acknowledgments

Ajay Pal Singh Pannu thanks UGC-SAP New Delhi for research fellowship. Dr Pratibha Kapoor thanks Council of Scientific and Industrial Research New Delhi for the financial support.

References

[1] S.L. Jain, P. Bhattacharyya, H.L. Milton, A.M.Z. Slawin, J.A. Crayston, J.D. Woolins. *Dalton Trans.*, 862 (2004).
[2] F.A. Chavez, M.M. Olmstead, P.K. Mascharak. *Inorg. Chem.*, **35**, 1410 (1996).
[3] F.A. Chavez, M.M. Olmstead, P.K. Mascharak. *Inorg. Chem.*, **36**, 6323 (1997).
[4] D.S. Marlin, M.M. Olmstead, P.K. Mascharak. *Inorg. Chem.*, **38**, 3258 (1999).
[5] D.S. Marlin, M.M. Olmstead, P.K. Mascharak. *Inorg. Chim. Acta*, **297**, 106 (2000).
[6] D.S. Marlin, M.M. Olmstead, P.K. Mascharak. *J. Mol. Struct.*, **554**, 211 (2000).
[7] D.S. Marlin, M.M. Olmstead, P.K. Mascharak. *Inorg. Chem.*, **40**, 7003 (2001).
[8] J.C. Noveron, M.M. Olmstead, P.K. Mascharak. *J. Am. Chem. Soc.*, **121**, 3553 (1999).
[9] J.C. Noveron, M.M. Olmstead, P.K. Mascharak. *J. Am. Chem. Soc.*, **123**, 3247 (2001).
[10] A.K. Singh, V. Balamurugan, R. Mukherjee. *Inorg. Chem.*, **42**, 6497 (2003).
[11] M. Ray, D. Ghosh, Z. Shirin, R. Mukherjee. *Inorg. Chem.*, **36**, 3568 (1997).
[12] A.K. Patra, R. Mukherjee. *Inorg. Chem.*, **38**, 1388 (1999).
[13] D.S. Marlin, P.K. Mascharak. *Chem. Soc. Rev.*, **29**, 69 (2000).
[14] S.M. Redmore, C.E.F. Rickard, S.J. Webb, L.J. Wright. *Inorg. Chem.*, **36**, 4743 (1997).
[15] T. Yano, R. Tanaka, T. Nishioka, L. Kinoshita, K. Isobe, L.J. Wright, T. Collins. *Chem. Commun.*, 1396 (2002).
[16] T. Kawamoto, B.S. Hammes, R. Ostrander, A.L. Rheingold, A.S. Borovik. *Inorg. Chem.*, **37**, 3424 (1998).
[17] F. Renaud, C. Piguet, G. Bernardinelli, J.C.G. Bunzli, G. Hopfgartner. *Chem. Eur. J.*, **3**, 1646 (1997).
[18] T.Le. Borgne, J.M. Benech, S. Floquet, G. Bernardinelli, C. Aliprandini, P. Bettens, C. Piguet. *J. Chem. Soc., Dalton Trans.*, 3856 (2003).
[19] J. Gracia-Lozano, M.A. Martinez-Lorento, E. Escriva, R. Ballesteros. *Synth. React. Inorg. Met. Org. Chem.*, **24**, 365 (1994).
[20] J. Gracia-Lozano, L. Soto, J.V. Folgado, E. Escriva. *Polyhedron*, **15**, 4003 (1996).
[21] J.G.H. de Preez, B. van Brecht, J.F. de Wet, J. Koorts. *Inorg. Nucl. Chem. Lett.*, **10**, 935 (1974).
[22] J.G.H. de Preez, B.J.A.M. van Brecht. *Inorg. Chim. Acta*, **162**, 49 (1989).
[23] P. Kapoor, A. Kumar, J. Nistandra, P. Venugopalan. *Transition Met. Chem.*, **25**, 465 (2000).
[24] P. Kapoor, A. Kataria, P. Venugopalan, R. Kapoor, M. Corbella, M. Rodriguez, M. Romero, A. Llobet. *Inorg. Chem.*, **43**, 6699 (2004).
[25] P. Kapoor, A. Pathak, R. Kapoor, P. Venugopalan, M. Corbella, M. Rodriguez, J. Robles, A. Llobet. *Inorg. Chem.*, **41**, 6153 (2002).
[26] R. Kapoor, A. Kataria, P. Kapoor, P. Venugopalan. *Transition Met. Chem.*, **29**, 425 (2004).
[27] S. Youngme, A. Cheansirisomboon, C. Danvirutai, N. Chaichit, C. Pakawatchai, G.A. Albada, J. Reedijk. *Inorg. Chem. Commun.*, **9**, 973 (2006).
[28] C. Adhikary, D. Mal, R. Sen, A. Bhattacharjee, P. Gutlich, S. Chaudhuri, S. Koner. *Polyhedron*, **26**, 1658 (2007).
[29] W. Huang, D. Hu, S. Gou, H. Qian, H.-K. Fun, S.S.S. Raj, Q. Meng. *J. Mol. Struct.*, **649**, 269 (2003).
[30] W.L.F. Armarego, D.D. Perrin. *Purification of Laboratory Chemicals*, 4th Edn, Butterworth-Heinemann, London (1999).

[31] *XSCANS*, *X-ray Single Crystal System* (*Version 2.1*), Siemens Analytical Instruments Inc., Madison, WI, USA (1994).

[32] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Cryst.*, **32**, 115 (1999).

[33] G.M. Sheldrick. *SHELXS-97*, *Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).

[34] L.J. Farrugia. *J. Appl. Cryst.*, **32**, 837 (1999).

[35] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).

[36] M.S. Gill, A.K. Sethi, R.D. Verma. *Can. J. Chem.*, **65**, 409 (1987).

[37] M.R. Rosenthal. *J. Chem. Educ.*, **50**, 331 (1973).

[38] F.A. Cotton, D.L. Weaver. *J. Am. Chem. Soc.*, **87**, 4189 (1965).

[39] A.W. Addison, T.N. Rao, J. Reedijk, J.V. Rijn, G.C. Verrschoor. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).

[40] I. Ucar, I. Bulut, A. Bulut, A. Karadag. *Struct. Chem.*, **20**, 825 (2009).

[41] Y. Ma, Z.B. Han, G.X. Han. *Russ. J. Coord. Chem.*, **34**, 891 (2008).

[42] I. Okamoto, M. Nabeta, T. Minami, A. Nakashima, N. Morita, T. Takeya, H. Masu, I. Azumaya, O. Tamura. *Tetrahedron Lett.*, **48**, 573 (2007).

[43] L. Ackerman, J.G.H. Du Preez, M.L. Gibson. *Inorg. Chim. Acta*, **5**, 539 (1971).

[44] J.G.H. du Preez, B.J.A.M. van Brecht, I. Warden. *Inorg. Chim. Acta*, **131**, 259 (1987).

[45] J. Coetzer. *Acta Crystallogr., Sect. B*, **26**, 1414 (1970).

[46] J. Zeeman. *Z. Anorg. Allg. Chem.*, **241**, 324 (1963).

[47] B.J.A.M. van Brecht. Low symmetry complexes of divalent 3rd transition metals with N-donor ligands, MSc thesis, University of Port Elizabeth (1975).

[48] P.J. Burke, K. Henrick, D.R. McMillin. *Inorg. Chem.*, **21**, 1881 (1982).

[49] P.A. Taskar, L. Sklar. *J. Cryst. Mol. Struct.*, **5**, 329 (1975).