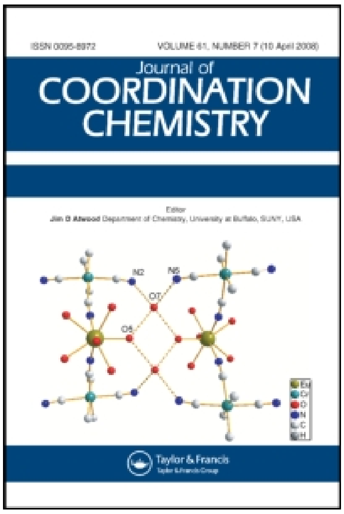

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Sadegh Salehzadeh[a]; Reza Golbedaghi[a]; Allan G. Blackman[b]
[a] Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran [b] Department of Chemistry, University of Otago, Dunedin, New Zealand

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Synthesis, characterization, and X-ray crystal structure analysis of Cd(II) and Cu(II) complexes of an acyclic pentadentate Schiff base

SADEGH SALEHZADEH*†, REZA GOLBEDAGHI† and
ALLAN G. BLACKMAN‡

†Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran
‡Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand

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Cd(II) and Cu(II) complexes of an acyclic pentadentate Schiff base were prepared by template condensation of two equivalents of 2-acetylpyridine with one equivalent of bis(3-aminopropyl)-amine in methanol. The resulting complexes $[CdL(NO_3)]ClO_4$ (**1**) and $[CuL](ClO_4)_2 \cdot CH_3CN$ (**2**) were characterized by X-ray crystallography, elemental analysis, IR and mass spectrometry in both cases and by NMR in the case of **1**. The X-ray crystallographic structure determination of these complexes revealed six-coordinate distorted octahedral geometry for **1**, with the sixth coordination by nitrate and five-coordinate for **2** with trigonal-bipyramidal Cu(II).

Keywords: Schiff-base complexes; Pentadentate ligand; Copper(II) and cadmium(II) ions; X-ray crystal structure

1. Introduction

Schiff bases have been employed in understanding molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport, and separation phenomena, hydrometallurgy, etc. [1–4]. Many variously shaped polydentate chelating ligands have been prepared and successfully used in selective coordination of metal ions. Recently, the synthesis and characterization of a large number of new Schiff-base metal complexes for antibacterial [5–10], catalytic [11], magnetic properties [12], etc., have been reported. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of unusual configuration, structural lability, and sensitivity to molecular environments. We have been interested in the synthesis and characterization of a number of macrocyclic [13, 14] and macroacyclic [15–17] pentadentate (N_5) Schiff-base complexes derived from [1 + 1] template condensation of tripodal tetraamines and 2,6-diacetylpyridine and 2-acetylpyridine, respectively. We showed that Cu(II) and Ni(II) complexes of the latter macroacyclic pentadentate (N_5) Schiff-base ligands have trigonal bipyramidal (TBP) and distorted

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*Corresponding author. Email: saleh@basu.ac.ir

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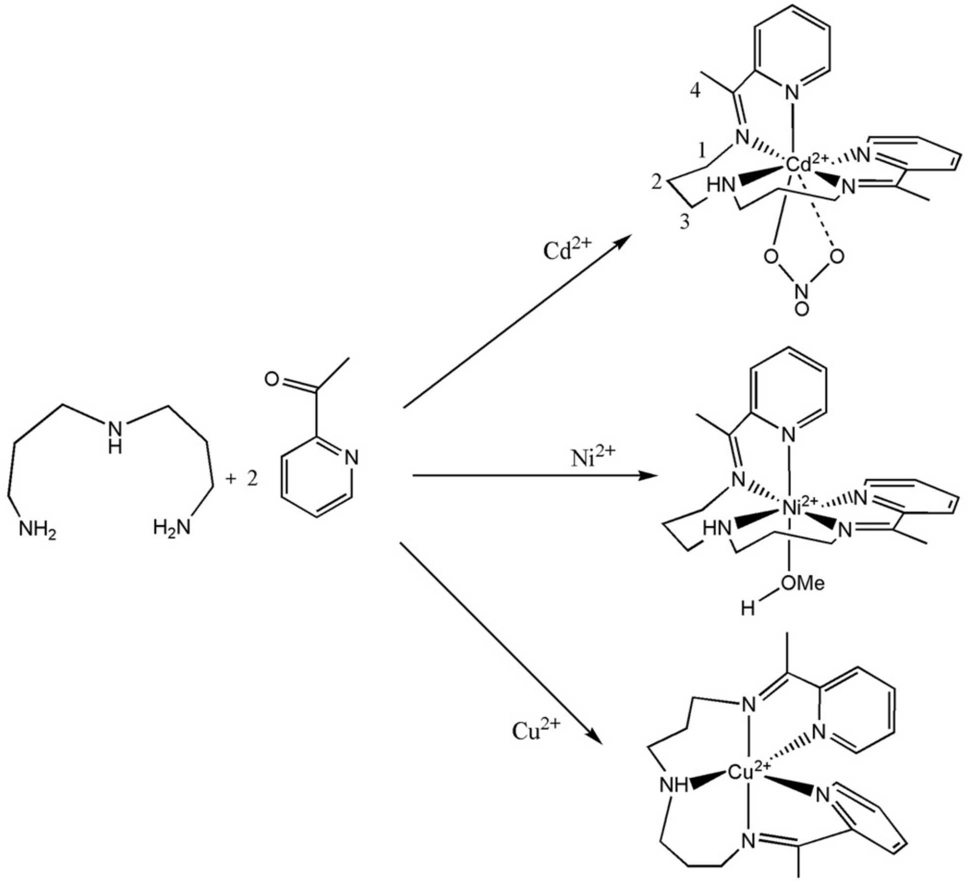
octahedral geometry, respectively. Very recently we reported the synthesis and characterization of a Ni(II) complex of a macroacyclic pentadentate (N_5) Schiff base derived from [1 + 2] template condensation of a triamine, bis(3-aminopropyl)amine, and 2-acetylpyridine [18]. We showed that the latter complex has also a distorted octahedral geometry in which the sixth coordination is achieved by methanol (scheme 1). In this work we report the molecular structure and full characterization of Cu(II) and Cd(II) complexes of the latter ligand [19] and make a comparison with the corresponding Ni(II) complex.

2. Experimental

2.1. *General information*

Bis(3-aminopropyl)amine, 2-acetylpyridine, and hydrated metal salts were obtained from Aldrich and used without purification. IR spectra were measured on a Perkin-Elmer FT-IRGX spectrophotometer. Mass spectra were measured on a Bruker micro TOFQ. NMR spectra were measured on a Bruker DPX 300 spectrometer.



Scheme 1. Template condensation of bis(3-aminopropyl)amine and 2-acetylpyridine in the presence of Cd(II) and Cu(II) (this article) and Ni(II) [10] in dry methanol solution.

2.2. *X-ray crystallography*

Suitable crystals of **1** and **2** were obtained by slow diffusion of diethyl ether vapor into a methanol solution. Crystal data and the major experimental parameters for the crystal structures of **1** and **2** are reported in table 1. A white crystal of 0.2 × 0.1 × 0.05 mm^3 for **1** and a blue crystal of 0.21 × 0.20 × 0.15 mm^3 for **2** were mounted on a glass fiber and used for data collection. X-ray data were collected at temperatures between 85 and 90 K on a Bruker Kappa APEX-II system using graphite-monochromated Mo-Kα radiation with exposures over 0.5°, and were corrected for Lorentz and polarization effects using SAINT [20]. Both structures were solved using SIR-97 [21] running within the WinGX package [22] and weighted full-matrix refinement on F^2 was carried out using SHELXL-97 [23]. Hydrogens attached to carbon and nitrogen were included in calculated positions and refined as riding atoms with individual (or group, where appropriate) isotropic displacement parameters. Only water hydrogens, which could be found in the difference map, were included in the final cycles of refinement.

Table 1. Crystal data and refinement details of **1** and **2**.

	1	**2**
Empirical formula	$C_{20}H_{27}CdClN_6O_7$	$C_{22}H_{30}Cl_2CuN_6O_8$
Formula weight	611.33	640.96
Temperature (K)	89(2)	89(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Orthorhombic
Space group	*P2(1)/n*	*Pbca*
Unit cell dimensions (Å, °)		
a	15.235(5)	15.652(5)
b	8.536(5)	14.424(5)
c	18.923(5)	24.032(5)
α	90.000(5)	90.000
β	104.637(5)	90.000
γ	90.000(5)	90.000
Volume (Å^3), *Z*	2381.0(17), 4	5426(3), 4
Calculated density (mg m^{-3})	1.705	1.569
Absorption coefficient (mm^{-1})	1.084	1.059
F(000)	1240	2648
Crystal size (mm^3)	0.2 × 0.1 × 0.05	0.21 × 0.20 × 0.15
θ range for data collection (°)	1.54–25.50	2.10–24.24
Limiting indices	$-15 \le h \le 17$; $-10 \le k \le 9$; $-20 \le l \le 20$	$-18 \le h \le 14$; $-16 \le k \le 15$; $-23 \le l \le 27$
Reflections collected	17637	22653
Independent reflection	3833 [*R*(int) = 0.0538]	4324 [*R*(int) = 0.0602]
Completeness to $\theta = 25.00$ (%)	99.9	99.7
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.829251	1.000000 and 0.699961
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3833/0/318	4324/0/365
Goodness-of-fit on F^2	1.052	1.067
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0360$; $wR_2 = 0.1095$	$R_1 = 0.0788$; $wR_2 = 0.1976$
R indices (all data)	$R_1 = 0.0488$; $wR_2 = 0.1171$	$R_1 = 0.1190$; $wR_2 = 0.2227$
Largest difference peak and hole (e Å^{-3})	1.304 and −1.004	0.980 and −0.805

2.3. *Synthesis*

2.3.1. Preparation of [CdL(NO$_3$)]ClO$_4$ (1). 2-Acetylpyridine (0.484 g, 4 mM) and Cd(NO$_3$)$_2\cdot$6H$_2$O (0.616 g, 2 mM) dissolved in MeOH (5 mL) was added to a solution of bis(3-aminopropyl)amine (0.262 g, 2 mM) in absolute MeOH (50 mL). The resulting solution was refluxed and stirred for 36 h and then NaClO$_4$ (0.49 g, 4 mM) was added; a white precipitate was formed, washed with ethanol and dried in vacuum, then dissolved in acetonitrile. Crystalline compound was obtained by slow diffusion of Et$_2$O vapor into this solution. Yield: 1 g (83%) of **1**. Anal. Calcd for $C_{20}H_{27}CdClN_6O_7$ (%): C, 39.25; H, 4.42; N, 13.74. Found (%): C, 38.63; H, 4.67; N, 13.77. IR (Nujol, cm^{-1}): 1575, 1598, and 1631 (νC=N and νC=C), 3251 (νN–H), 1095(νClO_4^-). ^{1}H-NMR (CD$_3$CN, ppm, 300 MHz): δ 1.88 (m, 2H, 2-H$_\alpha$), 1.96 (m, 2H, 2-H$_\beta$), 2.14 (s, 6H, 4-H), 2.12 (s, 2H, N–H), 3.02 (t, 4H, 1-H), 3.96 (t, 4H, 3-H), 7.53 (m, 3H), 8.09 (m, 5H). ^{1}H COSY (DMSO, 300 MHz) δ 1.88./1.96 (2-H$_\alpha$/2-H$_\beta$), 1.88/3.02 (2-H$_\alpha$/1-H), 1.88/3.96 (2-H$_\alpha$/3-H), 1.96/3.02 (2-H$_\beta$/1-H), 1.96/3.96 (2-H$_\beta$/3-H). ^{13}C NMR (CD$_3$CN, ppm, 75 MHz): δ 15.75 (C-2), 29.69 (C-4), 51.76 (C-1), 53.59 (C-3), 125.78, 128.52, 141.68, 149.85, and 163.48 (from C-5 to C-9). Accurate mass spectrometry (FAB-MS): $m/z = 513.1182$ [Cd(L)NO$_3$]$^+$, $CdC_{20}H_{27}N_6O_3$, requires 513.1178.

2.3.2. Preparation of [CuL](ClO$_4$)$_2$ (2). Complex **2** was prepared in an analogous manner. Yield: 1.1 g (86%) of **2**. Anal. Calcd for $C_{22}H_{30}Cl_2CuN_6O_8$ (%): C, 41.12; H, 4.68; N, 13.10. Found (%): C, 41.10; H, 4.73; N, 12.75. IR (Nujol, cm^{-1}): 1572, 1595, and 1633 (νC=N and νC=C), 3252 (νN–H), 1085 (νClO_4^-). Accurate mass spectrometry (FAB-MS): $m/z = 499.1042$ [Cu(L)](ClO$_4$)$^+$, $CuC_{20}H_{27}ClN_5O_4$, requires 499.1147.

3. Results and discussion

3.1. *Synthesis and characterization*

Compounds **1** and **2** were prepared through full condensation of bis(3-aminopropyl)-amine with 2-acetylpyridine in the presence of Cd(II) and Cu(II), respectively. The resulting compounds were characterized by IR, elemental analysis and X-ray diffraction, and NMR for **1**. The condensation of both primary amino groups is confirmed by the lack of N–H stretching split band at 3150–3450 cm^{-1} and the presence of strong C=N (Schiff-base) stretching band at 1630–1640 cm^{-1}. The sharp band at 3250–3260 cm^{-1} can be assigned to secondary N–H. Broad intense bands at *ca* 1080–1100 cm^{-1} due to ClO_4^- show no splitting, indicating the absence of coordination of ClO_4^-. The mass spectra of both complexes are consistent with their structure and formulation. The clear intense peaks associated to [CuL](ClO$_4$)$^+$ and [CdL(NO$_3$)]$^+$ species are observable in the mass spectra of copper and cadmium complexes, respectively. The isotopic pattern of latter peaks is the same to the calculated isotopic patterns (figure 1). Compound **1** was studied with ^{1}H-NMR, ^{13}C-NMR, DEPT, COSY, and H-MQC spectroscopy and NMR spectra are completely consistent with its formulation. While the ^{13}C-NMR and DEPT 135° spectra show that there are, as we expect, three distinct methylene carbons, its ^{1}H-NMR, COSY, and H-MQC spectra show four kinds of protons. Indeed, two peaks from the four observed peaks are related

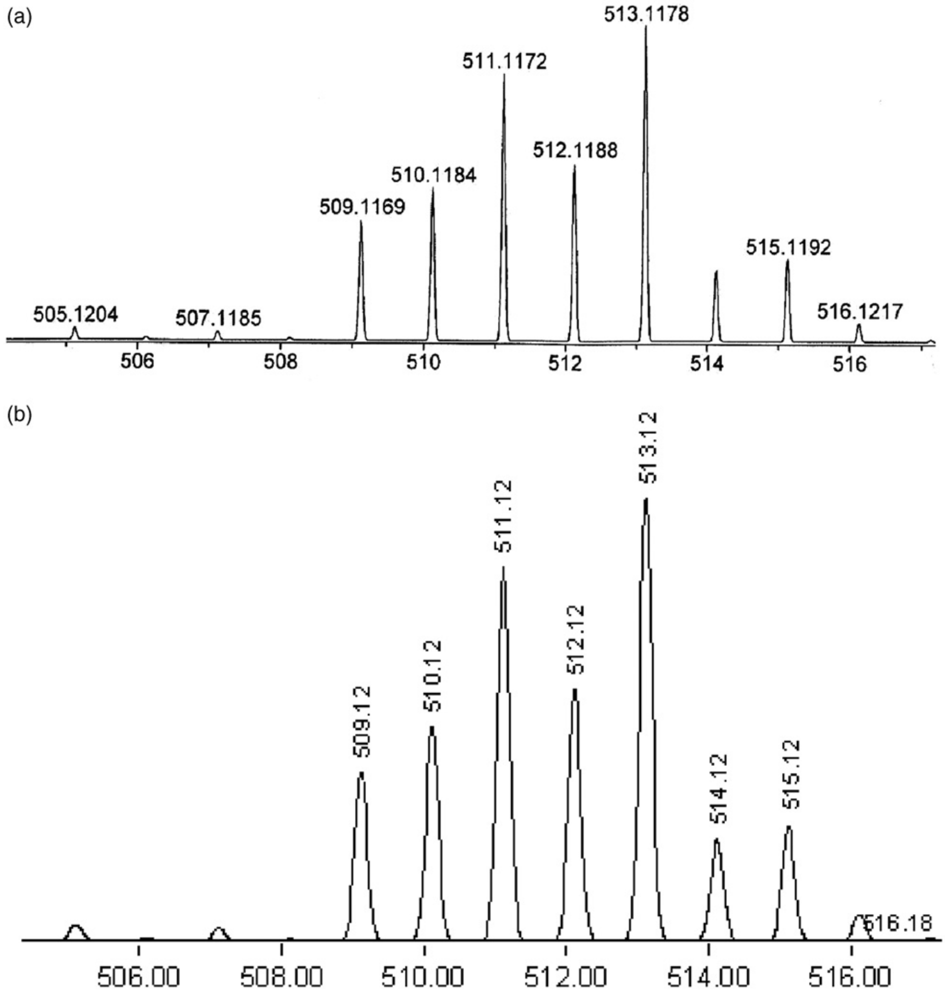


Figure 1. A comparison of observed isotopic pattern (a) and calculated isotopic pattern (b) for **1**.

to diastereotopic protons of C2. The COSY spectrum confirms the geminal coupling. Furthermore, it shows that both protons of C2 have coupling to protons of C1 and C3. However, from protons of C1 and C3, the protons with higher chemical shifts couple with each other and there is also similar coupling between protons with smaller chemical shifts. Although the X-ray crystal structure of **1** (see the following section) shows that two pyridyl arms are in unequivalent environments in the crystalline state (*cis* and *trans* positions to the nitrato ligand), the corresponding NMR signals (both the ^{1}H- and ^{13}C-NMR) are observed as averaged signals. Thus, it seems that in the solution there is a fast geometrical interconversion.

3.2. *X-ray crystal structure analysis*

The molecular structures of both **1** and **2** were determined in the solid state. X-ray crystallographic data are given in tables 1 and 2 and the structures of **1** and **2** with the

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

1		**2**	
Cd(1)–N(1)	2.330(3)	Cu(1)–N(1)	2.075(6)
Cd(1)–N(2)	2.383(4)	Cu(1)–N(2)	1.958(8)
Cd(1)–N(3)	2.353(3)	Cu(1)–N(3)	1.958(8)
Cd(1)–N(4)	2.360(4)	Cu(1)–N(4)	1.983(6)
Cd(1)–N(5)	2.311(4)	Cu(1)–N(5)	2.103(6)
Cd(1)–O(1)	2.440(3)		
N(5)–Cd(1)–N(1)	80.7(13)	N(3)–Cu–N(2)	90.4(4)
N(5)–Cd(1)–N(3)	119.6(12)	N(3)–Cu–N(4)	91.0(3)
N(1)–Cd(1)–N(3)	159.4(13)	N(2)–Cu–N(4)	178.5(3)
N(5) Cd(1)–N(4)	69.9(12)	N(3)–Cu–N(1)	127.9(4)
N(1)–Cd(1)–N(4)	107.1(13)	N(2)–Cu–N(1)	79.6(4)
N(3)–Cd(1)–N(4)	84.5(13)	N(4)–Cu–N(1)	99.2(2)
N(5)–Cd(1)–N(2)	162.3(14)	N(3)–Cu–N(5)	129.2(4)
N(1)–Cd(1)–N(2)	91.3(13)	N(2)–Cu–N(5)	100.9(3)
N(3)–Cd(1)–N(2)	70.0(12)	N(4)–Cu–N(5)	78.6(2)
N(4)–Cd(1)–N(2)	97.8(12)	N(1)–Cu–N(5)	102.8(2)
N(5)–Cd(1)–O(1)	107.7(12)		
N(1)–Cd(1)–O(1)	83.2(12)		
N(3)–Cd(1)–O(1)	87.3(11)		
N(4)–Cd(1)–O(1)	168.6(12)		
N(2)–Cd(1)–O(1)	86.7(12)		

atom numbering scheme are shown in figures 2 and 3, respectively. In both cases all imine, pyridine, and secondary nitrogen donors are coordinated to the central metal ion. In **1**, in addition to nitrogen donors, a nitrate is also coordinated to Cd(II). The Cd–N bond lengths are in the normal range (from 2.311(4) to 2.383(4)); the longest bond length in **1** is one of the $\mathrm{Cd{-}N_{imine}}$ (2.383 Å) bond lengths and the shortest one is the second $\mathrm{Cd{-}N_{imine}}$ (2.311 Å) bond length. The structure of $[\mathrm{CdL(NO_3)}]^+$ in **1**, similar to the corresponding Ni(II) complex, $[\mathrm{NiL_{33}(CH_3OH)}]^{2+}$ (scheme 1) [18], is distorted octahedral. In both cations the pyridine groups occupy *cis* positions while the imine groups are *trans*. In the Ni(II) complex, one of the pyridine rings is *trans* to methanol and in **1** this is *trans* to nitrate. For $[\mathrm{NiL_{33}(MeOH)}]^{2+}$ and $[\mathrm{CdL(NO_3)}]^+$ we can consider four geometrical isomers [18]. In two isomers the imine nitrogens occupy *trans* positions, but in the remaining isomers they are *cis*. By DFT and Hartree–Fock calculations, we showed that $[\mathrm{NiL_{33}(MeOH)}]^{2+}$ has adopted the most stable structure in the solid state. Here, we note that the Cd(II) complex synthesized has similar structure with the Ni(II) complex. Thus, it seems that the structures observed in this work for $[\mathrm{CdL(NO_3)}]^+$ and in our previous work for $[\mathrm{NiL_{33}(MeOH)}]^{2+}$ are probably the most stable for $[\mathrm{ML_{33}(X)}]^{2+}$ complexes (where M is metal ion and X a coordinating anion and/or solvent molecule).

In **2**, the Cu(II) is five coordinate, best described as distorted TBP (scheme 1 and figure 3), in which the imine nitrogens are located at axial positions. The Cu−N bond lengths are in the expected range from 1.958(8) to 2.103(6) Å. The longest bond length in **2** is one equatorial $\mathrm{Cu{-}N_{pyridine}}$ (2.103 Å) bond length. Indeed, both $\mathrm{Cu{-}N_{imine}}$ bond lengths located at axial positions are shorter than the mean of Cu–N bond lengths, 2.04 Å, in equatorial positions. Comparing the structure of **2** with $[\mathrm{Cu(ppepy)}]^{2+}$ of a pentadentate (N5) Schiff-base ligand derived from condensation of 2-acetylpyridine

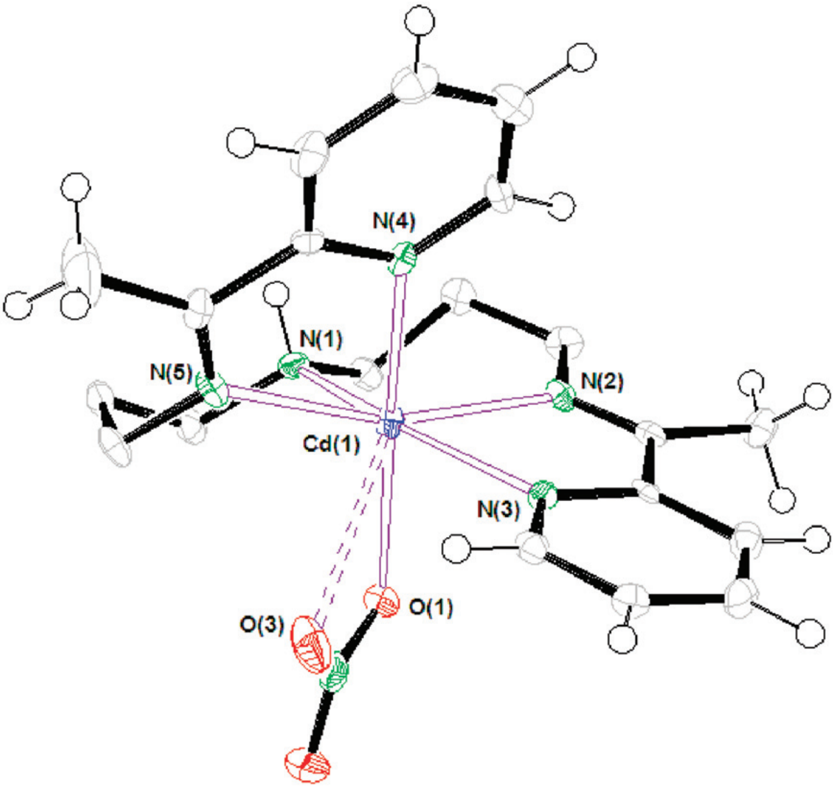


Figure 2. ORTEP view of X-ray crystal structure of **1**. Hydrogens of methylene and perchlorate anion are omitted for clarity.

with one of propylene arms of a tripodal tetraamine ligand, $N\{(CH_2)_3NH_2\}_2\{CH_2)_2NH_2\}$ [17], both complexes have a slightly distorted TBP structure. However, the Cu–N bond lengths of **2** are slightly different with those found in $[Cu(ppepy)]^{2+}$. For example, while in **2**, both the $Cu-N_{pyridine}$ bonds (2.075(6) and 1.983(6) Å) are longer than other bonds; in $[Cu(ppepy)]^{2+}$ this bond is the shortest (2.011(7) Å). We note that both the pyridine nitrogens in **2** are equatorial, while in $[Cu(ppepy)]^{2+}$ the unique pyridine nitrogen is axial. In addition, in **2**, both the $Cu–N_{imine}$ bond lengths are shorter than single $Cu–N_{imine}$ bond length (2.055(9) Å) in $[Cu(ppepy)]^{2+}$. Once again we note that $Cu–N_{imine}$ in $[Cu(ppepy)]^{2+}$ is equatorial but in **2** both the $Cu–N_{imine}$ bonds are axial. Thus, in Cu(II) complexes of pentdentate(N_5) ligands with TBP structures, the value of metal–ligand bond lengths depends on the location of corresponding donor.

Bond angles within the pyridine Schiff-base Cu(II) compound synthesized here are similar to those found in a previously synthesized pyridine Schiff-base Cu(II) complex [17]. For example, the bite angles, N(1)–Cu–N(2) of 79.6(4) and N(4)–CuN(5) of 78.6(2), are typical of pyridyl-α-imine complexes. The latter angle in the corresponding $[Cu(ppepy)]^{2+}$ complex [17] is 79.5(4). Since many five-coordinate structures with geometries intermediate between regular SP and TBP stereochemistries lie on the Berry pathway, methods have been developed which attempt to quantify the degree of distortion and, thus, provide a more precise description of the structure [24, 25].

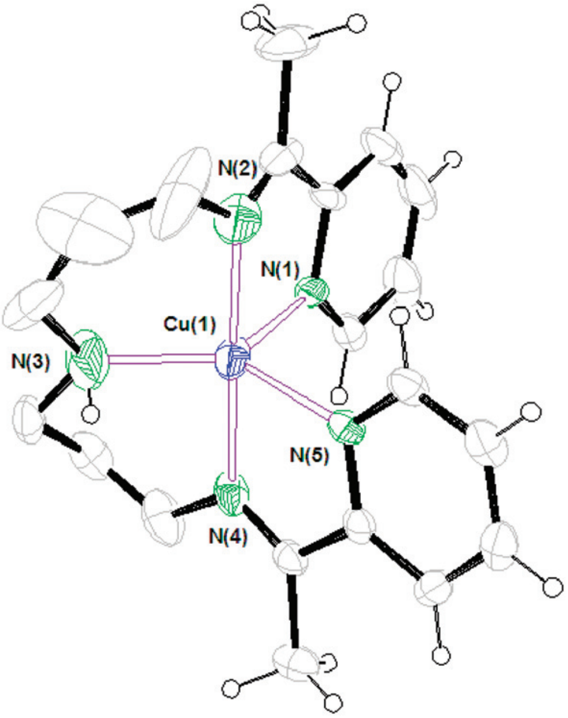


Figure 3. ORTEP view of X-ray crystal structure of **2**. Hydrogens of methylene, CH_3CN molecule and perchlorate anions are omitted for clarity.

The simplest method, applicable to complexes in which one bond is longer than the others and can be identified as the apical bond, utilizes the angles between donor atoms that would form the basal plane in an SP structure. The ratio of the two basal angles, τ, defined [24] as $\tau = [(\theta - \varphi)/60] \times 100$, represents the percentage trigonal distortion from square-pyramidal geometry. For an ideal square pyramid, τ is 0 while for an ideal TBP τ is 100. Employing this method, the relevant angles in **2**, $\theta = 178.57$ and $\varphi = 127.9$, yield a τ value of 84% which indicates a distorted TBP stereochemistry.

4. Conclusions

We synthesized Cd(II) and Cu(II) complexes of a pentadentate Schiff base in absolute methanol. The synthesized complexes were characterized by X-ray diffraction in both cases. X-ray crystal structure revealed six-coordinate cadmium for **1** with a distorted octahedral geometry and a five-coordinate copper for **2** with a distorted TBP structure.

Supplementary material

CCDCs 741739, 741738 contain the supplementary crystallographic data for **1** and **2**, 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 Email: deposit@ccdc.cam.ac.uk.

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