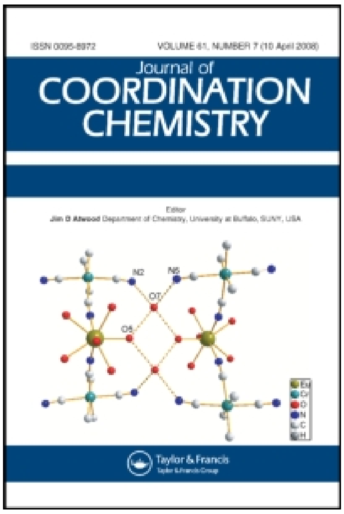

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Crystal structure and solid state IR-LD analysis of a mononuclear Cu(II) complex of 4-aminopyridine

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Crystal structure and solid state IR-LD analysis of a mononuclear Cu(II) complex of 4-aminopyridine

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A new mononuclear Cu(II) complex of 4-aminopyridine (4AP), $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$ (**1**), was obtained and structurally characterized by single-crystal X-ray diffraction methods. The complex is square-planar involving four monodentate 4AP molecules coordinated through the N_{py} atoms. A solid-state linear-dichroic spectroscopic analysis (IR-LD) as a suspension in a nematic liquid crystal was carried out over the 4000–400 cm^{-1} range and determined stereochemical parameters compared crystallographic data. Detailed IR characteristics are reported.

Keywords: 4-Aminopyridine; Mononuclear Cu(II) complex; Crystal structure; IR-LD analysis

1. Introduction

Interest in amino–imino tautomerism of 4-aminopyridine (4AP) and its salts is due to its biological activity mainly as an Ca^{2+} and K^+ channel inhibitor [1,2]. IR investigations of the tautomerizm in solid state and solution using isotropic and mesomorphic media have been reported previously [3,4]. The coordination mode of 4AP is also of interest in that the basicity of the N_{py} nitrogen atom leads to monodentate behaviour [5]. Only a Ni(II) complex showing bidentatey coordination through N_{py} and the NH_2 group is known [6].

A saccharinato salt of an octahedral Cu(II) complex with 4AP, structurally similar to (**1**), is known [7]. The metal ion is six-coordinate, through four 4AP ligandsand two *trans* H_2O molecules, with the saccharinato anion lying outside the coordination sphere. Supramolecular structural organization and amino-imino tautomerism of 4AP as a result of coordination in a new mononuclear, square-planar Cu(II) complex is presented here. Solid-state IR-LD spectral analysis in a nematic liquid crystal suspension and

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Table 1. Crystal data, data collection and refinement details for $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$.

Empirical formula	$C_{22}H_{32}N_8O_2Cl_2Cu$
M	575.00
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 10.717(7)$ Å $\beta = 107.532(19)°$ $b = 14.201(12)$ Å $c = 9.774(6)$ Å
V	1418.4(17) $Å^3$
Z, Calculated density	2, 1.346 $mg\,m^{-3}$
Absorption coefficient	0.991 mm^{-1}
$F(000)$	598
Crystal size	$0.47 \times 0.65 \times 0.53$ mm
θ Range for data collection	1.99–25.00°
Limiting indices	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $0 \leq l \leq 11$
Reflections collected/unique	4913/2379 [R(int) = 0.0495]
Completeness to $\theta = 25.00$	95.7%
Absorption correction	Empirical
Max. and min. transmission	0.200 and 0.124
Data/restraints/parameters	2429/0/162
Goodness-of-fit on F^2	1.325
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0651$, $wR2 = 0.1773$
R indices (all data)	$R1 = 0.0798$, $wR2 = 0.1864$
Largest diff. peak and hole	0.820 and −0.643 e $Å^{-3}$

a single-crystal X-ray diffraction study are reported. In addition, a detailed IR analysis has been performed.

2. Experimental

2.1. *Materials and methods*

4-Aminopyridine and $CuCl_2 \cdot 2H_2O$ were purchased from Sigma. X-ray diffraction intensities were measured on a Siemens diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods [8] and refined on F^2 [9]. Hydrogen atoms were positioned on geometrical grounds. Relevant crystallographic data and refinement details are presented in table 1. Selected bond distances and angles are listed in table 2.

The 4000–400 cm^{-1} solid-state IR spectra were recorded on a Bomem Michelson 100 FTIR spectrophotometer (resolution ±2 cm^{-1}, 150 background scans) equipped with a Perkin Elmer wire-grad polarizer. N non-polarized solid-state IR spectra were recorded using KBr pellets. Oriented solid samples as a nematic liquid crystal suspension were studied using a 4′-cyano-4′-alkylbicyclohexyl mixture (ZLI 1695, Merck). The orientation technique has been described in detail [6,10,11], as has the so-called step-wise reduction procedure for interpretation of the polarized IR spectra [11–13].

FAB mass spectra were recorded on a Fisons VG Autospect instrument employing 3-nitrobenzylalcohol as matrix. Elemental analyses were obtained using standard procedures for C and H (as CO_2 and H_2O) and for N by the Dumas method. Cu was determined by titration with EDTA (Murexid indicator, pH 8, ammonium buffer) of an HNO_3 solution of a sample of the complex.

Table 2. Selected bond lengths [Å] and angles [°] for $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$.

Cu(1)–N(11)	2.006(3)
Cu(1)–N(1)	2.045(4)
N(1)–C(6)	1.341(6)
N(1)–C(2)	1.339(6)
N(11)–C(16)	1.353(5)
N(11)–C(12)	1.354(6)
C(4)–N(10)	1.353(6)
C(14)–N(110)	1.343(5)
O(100)–C(100)	1.404(7)
N(11)–Cu(1)–N(11)#1	180.0
N(11)–Cu(1)–N(1)	88.13(14)
N(11)#1–Cu(1)–N(1)	91.87(14)
C(6)–N(1)–Cu(1)	118.8(3)
C(2)–N(1)–Cu(1)	126.1(3)
C(16)–N(11)–Cu(1)	122.3(3)
C(12)–N(11)–Cu(1)	122.1(3)
N(110)–C(14)–C(13)	122.4(4)
N(110)–C(14)–C(15)	121.8(4)
N(11)–C(16)–C(15)	123.4(4)
C–C bonds are within 1.405(6)–1.350(7)	
C–C–C angles are within 115.8(4)–120.7(4)	

Symmetry transformation used is #1: $-x+2, -y+2, -z$.

2.2 *Synthesis*

$[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$ (**1**) was obtained as follows. A methanol solution (4 cm^3) of $CuCl_2 \cdot 2H_2O$ (0.0682 g) was added to 4-aminopyridine (0.1506 g) dissolved in 16 cm^3 of CH_3OH and the mixture set aside. Blue crystals that formed after 1 month were filtered off, washed with CH_3OH and dried at 298 K in air (yield 33%). *Anal.* Calc. for $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$ (%): C, 45.96; H, 5.61; N, 19.49; Cu, 11.05%. Found: C, 45.93; H, 5.59; N, 19.44; Cu, 11.06. The most intense signal in mass spectra of (**1**) is at m/z 439.10, corresponding to $[Cu(4AP)_4^{2+}]$ with molecular weight of 440.01. Peaks at m/z 136.0 and 154.0 arise from the 3-nitrobenzyl-alcohol matrix used.

3. Results and discussion

3.1. *Crystal structure of $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$*

In contrast to the known octahedral complex $[Cu(4AP)_4(H_2O)_2(sac)_2]$, (sac = saccharitano) [7], in (**1**) the cooper atom is square-planar, coordinated through pyridine nitrogen atoms from four 4AP molecules (figure 1). Two solvent methanol molecules and two chloride ions lie outside the coordination sphere. The structural orientation of (**1**) shows a coplanar orientation of opposed 4AP molecules (Scheme 1), while in $[Cu(4AP)_4(H_2O)_2(sac)_2]$ the corresponding ligand planes make an angle of 56.62(3)° [7]. Bond lengths and angles for CuN_4 fragments in both complexes are similar, except for the differences in torsion angles between 4AP planes (see table 2 and [7]). An asymmetric (H)NH···Cl intermolecular hydrogen bond in (**1**) with a bond length at 2.234 Å is also established.

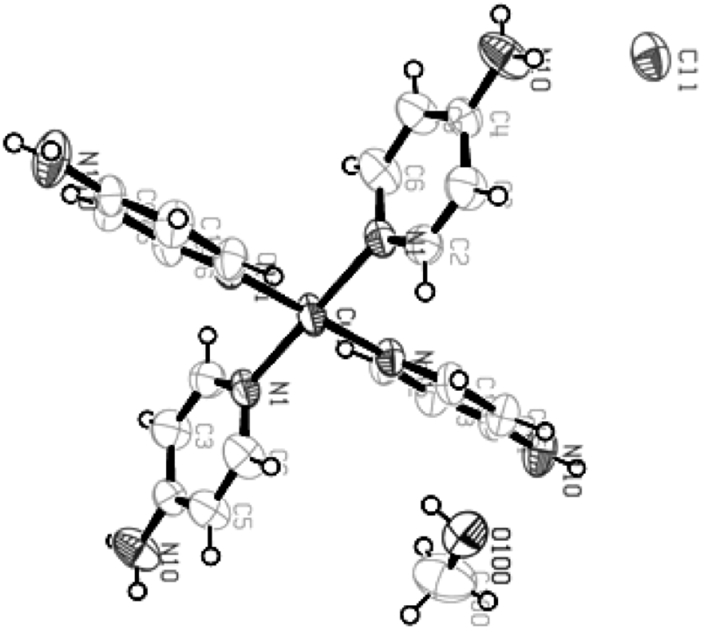
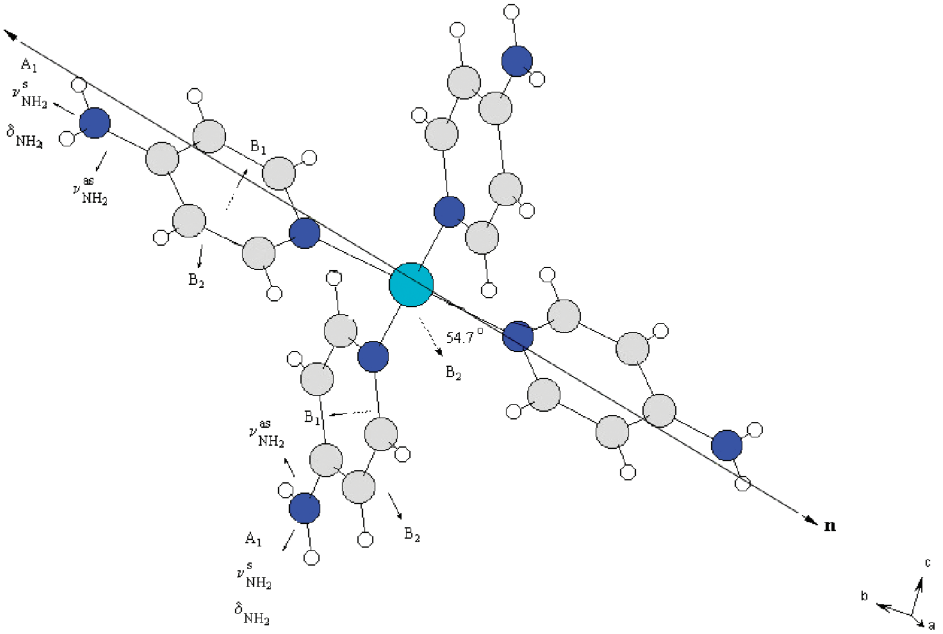


Figure 1. ORTEP plot of $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$ with 50% thermal ellipsoids, showing the atom numbering scheme. Hydrogen atoms are shown as spheres of arbitrary radius.

3.2. *Linear dichroic infrared spectroscopic analysis*

The solid-state IR spectrum of (**1**), shown in figure 2, is characterized by a 3478 cm^{-1} $\nu_{as}(NH_2)$ band and a doublet ($\nu_s(NH_2)$ Fermi-resonance) at 3318 and 3195 cm^{-1} in line with an asymmetrical, intermolecularly bonded NH_2 group [3,4]. These results correlate well with crystallographic data for (**1**) in terms of (H)NH$\cdots$Cl hydrogen bond formation (see above). In the 1700–1450 cm^{-1} region an intense 1633 cm^{-1} peak, $\delta(NH_2)$, and a series of aromatic pyridine modes at 1617 (8a), 1559 (8b), 1517 (19a), 1465 (19b), 1022 (18a), 851 (4) and 827 cm^{-1} (11-γ_{CH} op) is also observed [3,4]. The spectrum (figures 2 and 4) display low intensity peaks at 3380, 3287 and 1656 cm^{-1}, typical of protonated 4AP salts [14,17], indicating negligible charge redistribution in 4AP molecule as a result of coordination.

The difference IR-LD spectrum of (**1**) in nematic liquid crystal suspension (figure 3.2) contains reduced B_2 peaks at 1565 (8b), 1465 (19b) and 530 cm^{-1} (18b), thus indicating an orientation of the guest molecule towards the direction (n) as is shown in Scheme 1. The B_2 and $\nu_{as}(NH_2)$ transition moments, however, are not co-linear, and for this reason the observed negative maximum at 3474 cm^{-1} for $\nu_{as}(NH_2)$ is expected. In-plane (ip) A_1 (1616 cm^{-1}) and out-of-plane (op) B_1 (851 and 827 cm^{-1}) transition moments are oriented in pairs, and this fact explains the presence in the difference spectrum of simultaneously positive and negative maxima for the corresponding modes. Pairs of bands corresponding to $\nu_s(NH_2)$ and $\delta(NH_2)$ and A_1 modes are obtained by curve-fitting in non-polarized spectra (figure 4). The presence of a pair for $\nu_{as}(NH_2)$ at 3496 and 3477 cm^{-1}, a Fermi-resonance $\nu_s(NH_2)$ doublet at 3317 and 3335 cm^{-1}, and 3189 and 3210 cm^{-1}, and A_1 peaks at 1617 and 1613 cm^{-1}) is explained by Cu–N bond



Scheme 1.

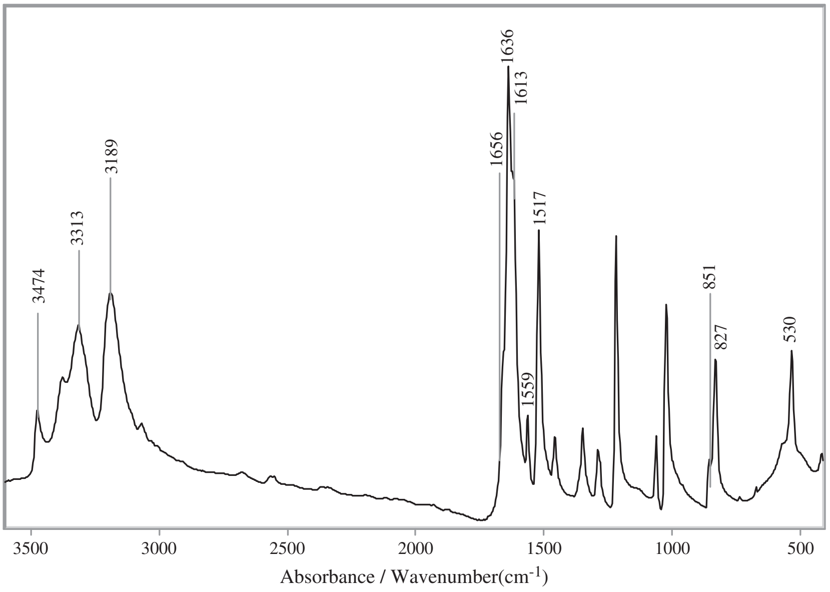


Figure 2. Solid state IR spectrum of $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$ (KBr disk).

length differences, as determined in the X-ray structure (table 2 and figure 1). Detailed vibrational assignment is result of application of the step-wise reduction procedure to the 19a peak at $1517\,cm^{-1}$. Its elimination (figure 5.2) leads to the disappearance of the $\delta(NH_2)$ maximum at $1637\,cm^{-1}$, the simultaneous elimination of A_1 and B_1

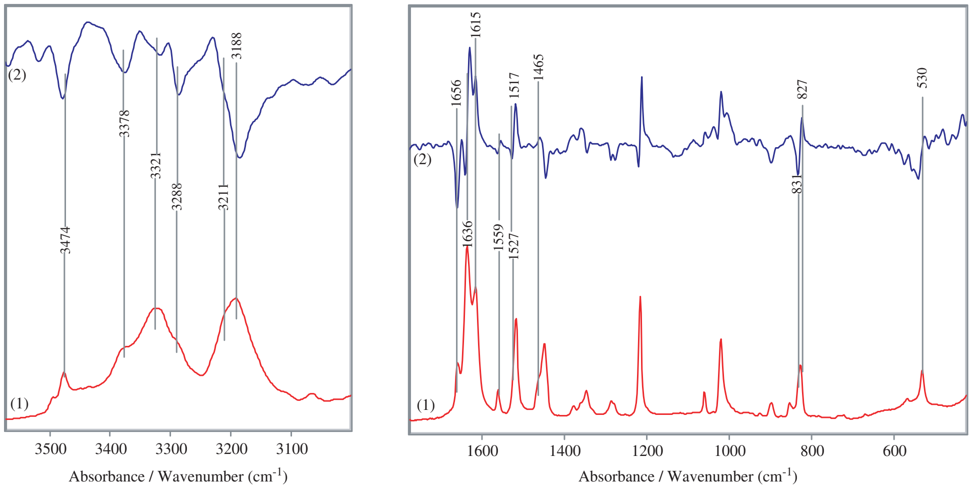


Figure 3. Non-polarized (lower) and difference (upper) IR-LD spectra of $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$ in ZLI 1695 suspension.

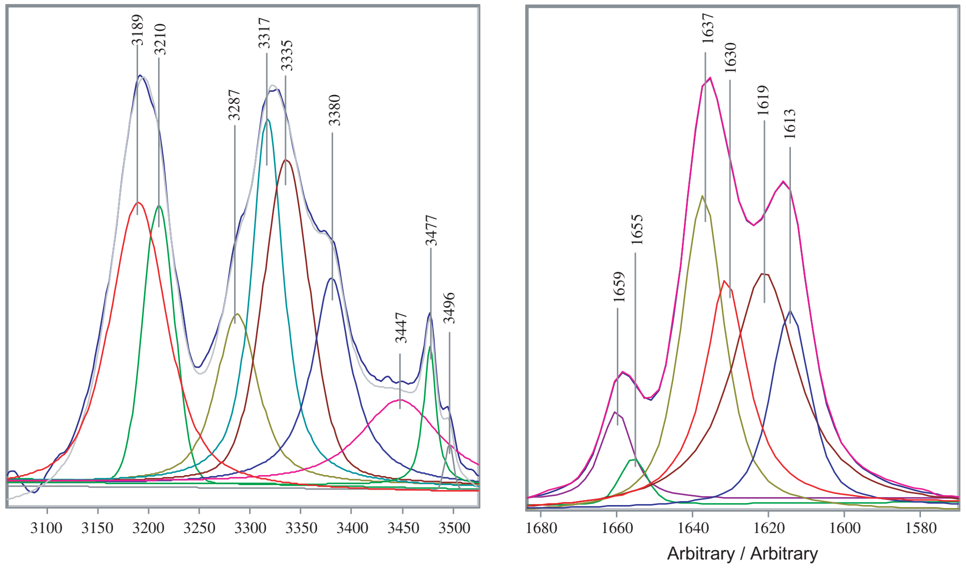


Figure 4. Deconvoluted IR spectra of $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$ in the 3500–3000 and 1680–1580 cm^{-1} regions.

peaks at 1616, 1018, 851 and 827 cm^{-1}, and strong reduction of Fermi-resonance doublet for $\nu_s(NH_2)$ at 3317 and 3190 cm^{-1}. These results are correlated with the solid state structure of (**1**) insofar as in the frame of one molecule it is impossible to obtain the simultaneous elimination of A_1 and B_1 peaks. Additionally, the results indicate the correct assignment of vibrational modes observed for complex (**1**) in the solid state.

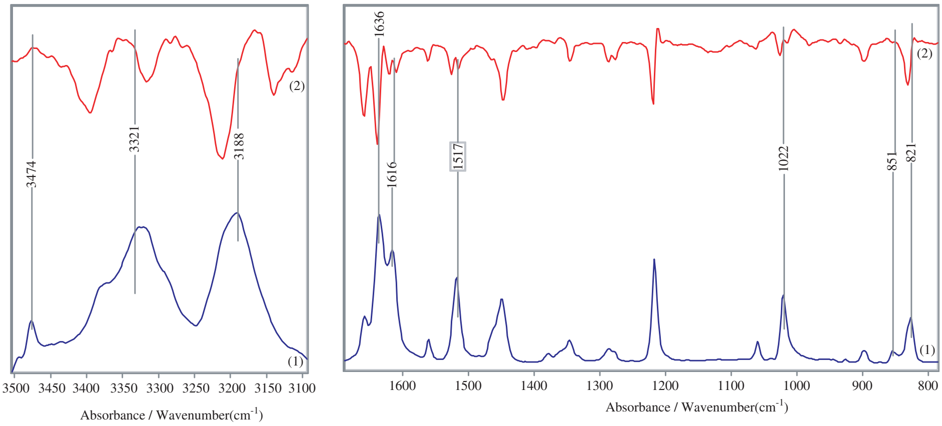


Figure 5. Non-polarized (lower) and reduced (upper) IR-LD spectra of $[Cu(4AP)_4]Cl_2 \cdot 2CH_3OH$ after elimination of the 1517 cm^{-1} peak.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 221529. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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