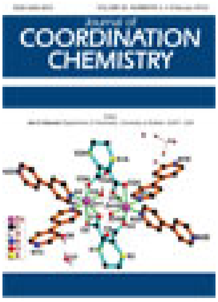

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Copper(II) complex with 6-(3,5-dimethyl-1H-pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidin-4-amine: synthesis, crystal structure, and electronic spectroscopy

Mark B. Bushuev [a] [b] , Yuri V. Gatilov [c] , Viktor P. Krivopalov [c] & Elena B. Nikolaenkova [c]

[a] Nikolaev Institute of Inorganic Chemistry , Siberian Branch of Russian Academy of Sciences , 3, Akad. Lavrentiev Ave., Novosibirsk 630090 , Russia

[b] Department of Natural Sciences , Novosibirsk State University (National Research University) , 2, Pirogova str., Novosibirsk 630090 , Russia

[c] N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences , Novosibirsk , Russia

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Copper(II) complex with 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidin-4-amine: synthesis, crystal structure, and electronic spectroscopy

MARK B. BUSHUEV*†‡, YURI V. GATILOV§,
VIKTOR P. KRIVOPALOV§ and ELENA B. NIKOLAENKOVA§

†Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Akad. Lavrentiev Ave., Novosibirsk 630090, Russia
‡Department of Natural Sciences, Novosibirsk State University (National Research University), 2, Pirogova str., Novosibirsk 630090, Russia
‡N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia

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A copper(II) complex with 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidin-4-amine (L), [$CuLCl_2$], has been synthesized. This compound is formed irrespective of the Cu : L molar ratio (Cu : L = 1 : 1, 2 : 1, and 20 : 1) in the MeOH/H_2O/DMF mixture as a single product. ESI-MS data demonstrate that the additional amount of $CuCl_2$ above the Cu : L = 1 : 1 molar ratio, is effectively solvated, and high-nuclearity species are formed in trace amounts in the solution. The complex adopts a distorted square-pyramidal geometry with two chlorides and three nitrogen atoms from L. The electronic spectrum of the complex contains a broad band with a maximum at 12,820 cm^{-1} within the region characteristic for square-pyramidal chromophores CuA_5 (A = Cl, N). Due to Cu ··· Cl contacts, the molecules of [$CuLCl_2$] form the dinuclear [$CuLCl_2$]$_2$ unit. Surprisingly, the NH_2-group participates in the formation of NH ··· Cl hydrogen bonds instead of the formation of $(NH \cdots N3_{(pyrimidine)})_2$ synthon, which is common for *N*-heteroaromatic compounds containing the NH_2-group in the α-position to aza-atom. These hydrogen bonds together with Cu ··· Cl contacts result in the formation of a 3-D-structure.

Keywords: Copper(II); *N*-ligands; Synthesis; Supramolecular chemistry

1. Introduction

While studying chemistry of complexes with 4(6)-pyrazolylpyrimidines (see [1] and the references therein) we were interested in the modification of the 4(6)-pyrazolylpyrimidine core by introducing an additional nitrogen-containing heteroaromatic group (e.g., pyridin-2-yl) in the C^2 position of pyrimidine. Introducing pyridin-2-yl in the C^2 position of 4(6)-pyrazolylpyrimidine allows the changing of basicity of *N* donor atoms and coordination mode as well. A promising candidate, 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidin-4-amine (L), has previously been reported as an A_{2A}

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*Corresponding author. Email: bushuev@niic.nsc.ru

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receptor antagonist [2] but, to the best of our knowledge, its coordination behavior, coordination behavior of its derivatives, or 6(4)-(pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidines have not been studied (Cambridge Structural Database (Version 5.32; updates November 2010, February 2011, and May 2011) and Chemical Abstracts, SciFinder). 4-Pyrazolylpyrimidines and 2-(pyridin-2-yl)pyrimidines have been separately studied as ligands [3–34]. Since transition metal complexes based on 4-pyrazolylpyrimidines and 2-(pyridin-2-yl)pyrimidines have attracted considerable attention we believe that new hybrid ligands containing three different heterocycle rings within a single-molecule, 6(4)-(pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidines, as well as complexes with these ligands will be of interest. In this context, at the first stage of our research of complexes with 6(4)-(pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidines, we study coordination behavior of L toward copper(II) chloride at various metal-to-ligand molar ratios.

2. Experimental

2.1. *General*

6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidin-4-amine (L) has been prepared according to the reported procedure [2]. All other reagents and solvents were commercially available and used without additional purification. Elemental analysis (C, H, and N) was performed with a Carlo–Erba analyzer using standard technique. Electronic spectrum (diffuse reflectance) of the complex was recorded on a UV-3101 PC Shimadzu spectrophotometer from 240 to 2000 nm. Mass spectra were recorded on a Bruker MicrOTOF-Q instrument (Bruker Daltronics, Bremen, Germany) using electrospray ionization (ESI) in both positive and negative mode.

2.2. *Synthesis of [$CuLCl_2$]*

Method A: A solution containing L^1 (0.020 mmol, 5.3 mg) and $CuCl_2 \cdot 2H_2O$ (0.020 mmol, 3.4 mg) in MeOH/H_2O/DMF (3 mL/1 mL/0.3 mL) mixture was allowed to stay. In 2–3 days, when the volume of the solution became *ca* 3 mL, bluish-green hexagonal single crystals appeared. They were allowed to stay in contact with the mother liquor for 4–5 days (while the mixture was concentrated to *ca* 1 mL), filtered off, washed with EtOH, and dried in ambient air. Yield: 5.0 mg (62%). Anal. Calcd for $C_{14}H_{14}CuCl_2N_6$ (%): C, 42.0; H, 3.5; N, 21.0. Found: C, 42.2; H, 3.9; N, 20.8.

Method B: The procedure was performed in the same way as that for Method A. The quantities of reagents were: 0.020 mmol (5.3 mg) of L^1 and 0.040 mmol (6.8 mg) of $CuCl_2 \cdot 2H_2O$. Yield: 5.5 mg (74%). Anal. Calcd for $C_{14}H_{14}CuCl_2N_6$ (%): C, 42.0; H, 3.5; N, 21.0. Found: C, 41.7; H, 3.7; N, 21.0.

Method C: The procedure was performed in the same way as that for Method A. The quantities of reagents were: 0.020 mmol (5.3 mg) of L^1 and 0.40 mmol (68.2 mg) of $CuCl_2 \cdot 2H_2O$. Yield: 6.1 mg (76%). Anal. Calcd for $C_{14}H_{14}CuCl_2N_6$ (%): C, 42.0; H, 3.5; N, 21.0. Found: C, 42.1; H, 3.5; N, 20.5.

Table 1. Crystal data and structure refinement for the complex.

Empirical formula	$C_{14}H_{14}Cl_2CuN_6$
Formula weight	400.75
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	10.8056(8)
b	16.0865(12)
c	9.0367(6)
β	100.862(3)
Volume (Å^3), *Z*	1542.66(19), 4
Calculated density (g cm^{-3})	1.726
Absorption coefficient (mm^{-1})	1.769
F(000)	812
Crystal size (mm^3)	$0.39 \times 0.32 \times 0.15$
θ range for data collection (°)	1.92–27.52
Limiting indices	$-14 \le h \le 14$; $-17 \le k \le 20$; $-11 \le l \le 11$
Reflections collected/unique	12,909/3527 [R(int) = 0.0545]
Completeness to $\theta = 25.00$ (%)	99.6
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4915 and 0.3746
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3527/0/211
Reflections [$I > 2\sigma(I)$]	3315
Goodness-of-fit on F^2	1.070
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0328$, $wR_2 = 0.0882$
R indices (all data)	$R_1 = 0.0364$, $wR_2 = 0.1035$
Extinction coefficient	0.0223(17)
Largest difference peak and hole (e Å^{-3})	0.852 and −0.802

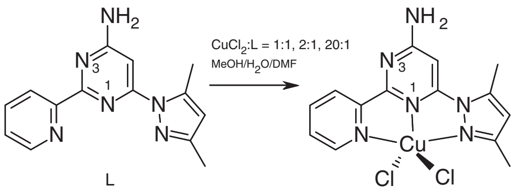
2.3. *X-ray crystallographic analysis*

Data were collected using a Bruker Kappa Apex II CCD equipped with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were initially processed and absorption correction applied using APEX II and SADABS [35]. The structure was solved by direct methods; all non-H atoms were refined in the anisotropic approximation using SHELXTL [36]. Hydrogen atoms were placed in idealized positions and refined using a riding model to the atom to which they are attached. Crystal data are displayed in table 1.

3. Results and discussion

3.1. *Synthetic aspects (Part 1)*

L has been synthesized according to the literature procedure [2]. Taking into account its potential tridentate chelation as well as potential formation of mono- and polynuclear complexes, $CuLCl_2$ and Cu_nLCl_{2n}, the syntheses have been performed in various metal-to-ligand molar ratios. The reaction performed in a 1 : 1 metal-to-ligand molar ratio produced the complex having the same stoichiometry, $CuLCl_2$. To obtain the single-crystal product, the H_2O/MeOH/DMF mixture has to be used since the crystallization



Scheme 1. Synthesis of the complex.

from MeOH, EtOH, or EtOH/$CHCl_3$ produces only light blue powder. This certainly is due to the presence of the NH_2-group at the C^4 position of the pyrimidine ring. It seems to be reasonable that the presence of this group decreases the solubility of the complex in MeOH, EtOH, and EtOH/$CHCl_3$ with respect to more polar mixture of the solvents, H_2O/MeOH/DMF, and leads in the former case to the formation of powder product instead of single-crystals.

X-ray diffraction data (see below) reveal that $CuLCl_2$ has molecular mononuclear structure with distorted square-pyramidal CuN_3Cl_2 coordination core. X-ray powder diffraction confirmed the bulk composition. Since chlorides can act as bridging ligands, we endeavored to obtain di- or polynuclear complexes with L. To obtain these complexes, $Cu : L = 2 : 1$ and $20 : 1$ molar ratios were used for syntheses in the same H_2O/MeOH/DMF mixture. Surprisingly, neither produced a complex other than $CuLCl_2$. The complex was obtained with good yield and is stable in air. Thus, the following transformation was carried out (scheme 1).

3.2. *Structural aspects*

The complex has a mononuclear structure (figure 1). The heteroaromatic system of ligand is nearly planar, the root-mean-square deviation from the common least-squares plane is 0.070 Å. The molecule of L is coordinated to copper(II) ions through pyrazolyl N5, pyrimidine N2, and pyridinyl N1 adopting tridentate coordination and forming two practically planar five-membered chelate rings (CuN_3C and CuN_2C_2). The coordination polyhedron of copper in the structure is a distorted square pyramid formed by two chlorides and three nitrogen atoms from the ligand (figure 1; table 2). This is confirmed by the value of an angular structural parameter, τ (0.13), proposed as a characteristic of the geometry around the central atom in five-coordinated compounds ($\tau = (\beta - \alpha)/60$, where β and α are the two largest angles in the coordination core, $\beta > \alpha$; the τ value for the square-pyramidal and trigonal-bipyramidal geometries is 0 and 1, respectively) [37]. The base of the pyramid is formed by three nitrogen atoms and a chloride (Cl2). Another chloride (Cl1) occupies a vertex of the pyramid; the corresponding Cu–Cl1 bond has more ionic character with respect to Cu–Cl2 since Cu–Cl1 distance is noticeably longer than Cu–Cl2. It also seems reasonable that Cl1 has a higher effective negative charge. We confirmed this hypothesis by calculations using Amsterdam Density Functional (ADF2010.01) program suite [38]. The VWN-BP functional and the all-electron basis set of the TZP type were applied for the calculations [39–42]. The geometry of the mononuclear [$CuLCl_2$] molecule has not been optimized and the atom coordinates have been extracted directly from X-ray data. Mulliken charges for Cl1 and Cl2 are −0.5657 and −0.4342, respectively.

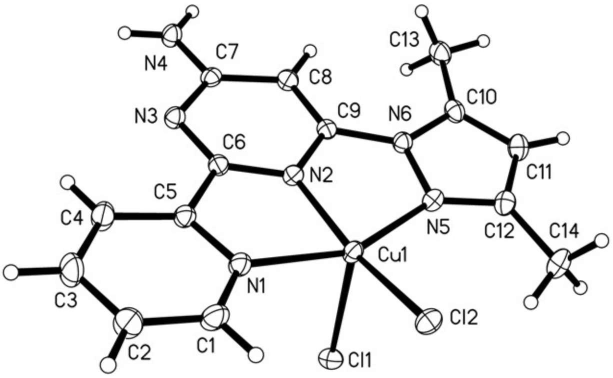


Figure 1. The molecular structure of [$CuLCl_2$].

Table 2. Bond lengths (Å) and angles (°) for the coordination sphere of copper.

Cu(1)–N(2)	1.9406(16)	Cu(1)–N(5)	2.0537(17)
Cu(1)–N(1)	2.0839(17)	Cu(1)–Cl(2)	2.2286(5)
Cu(1)–Cl(1)	2.6207(5)	N(2)–Cu(1)–N(5)	77.91(7)
N(2)–Cu(1)–N(1)	78.61(7)	N(5)–Cu(1)–N(1)	155.85(7)
N(2)–Cu(1)–Cl(2)	163.81(5)	N(5)–Cu(1)–Cl(2)	103.75(5)
N(1)–Cu(1)–Cl(2)	97.28(5)	N(2)–Cu(1)–Cl(1)	96.16(5)
N(5)–Cu(1)–Cl(1)	92.84(5)	N(1)–Cu(1)–Cl(1)	95.18(5)
Cl(2)–Cu(1)–Cl(1)	99.822(18)		

Hirshfeld charges, −0.5201 for Cl1 and −0.3364 for Cl2, although somewhat different from the abovementioned values, are of the same order. The deviations of Cl from Cu1N1N2N5 mean plane (RMS 0.0464) are 2.6786(11) Å (for Cl1) and −0.4894(27) Å (for Cl2). Due to the formation of an additional $Cu \cdots Cl2(1-x, 2-y, 1-z)$ (3.2184(6) Å) "bond," the coordination geometry around copper atom can be regarded as highly distorted octahedral. As a result, dinuclear [$CuLCl_2$]$_2$ units are formed (figure 2). The NH_2-group participates in the formation of two $NH \cdots Cl$ hydrogen bonds with chloride occupying a vertex of a CuN_3Cl_2 pyramid, N4–H4A $\cdots$ Cl1 (H $\cdots$ Cl 2.45 Å, N–H $\cdots$ Cl 166°) and N4–H4B $\cdots$ Cl1 (H $\cdots$ Cl 2.43 Å, N–H $\cdots$ Cl 157°) (figure 2). In addition, weak C–H $\cdots$ Cl hydrogen bonds are also formed. These hydrogen bonds (table 3) together with Cu $\cdots$ Cl contacts contribute to the formation of a 3-D-architecture. Surprisingly, N3 of [$CuLCl_2$] is not involved in the formation of a hydrogen bond. Usually *N*-heteroaromatic compounds containing the NH_2-group in the α-position to aza-atom form homomeric $(NH \cdots N_{(azine)})_2$ synthon, due to the formation of "head-to-tail" type hydrogen bonds [43]. The formation of $NH \cdots Cl$ hydrogen bonds instead of $(NH \cdots N3_{(pyrimidine)})_2$ can be favored by the fact that Cl1 has substantial effective negative charge.

3.3. *Spectroscopic aspects*

To gain insight into the electronic structure of the complex, an electronic diffuse reflectance spectrum was recorded (figure 3). The spectrum contains an intense

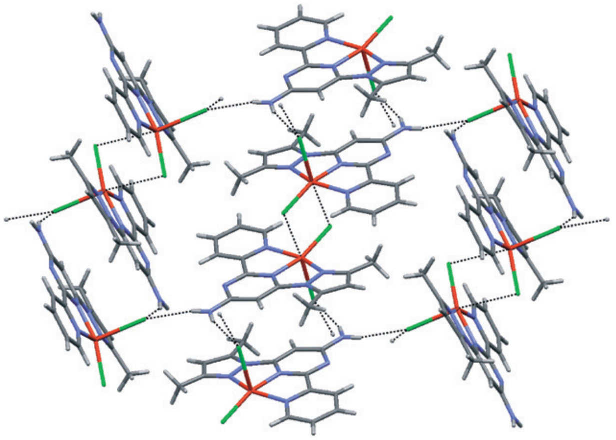


Figure 2. The Cu ··· Cl contacts and NH ··· Cl hydrogen bonds in the structure of the complex.

Table 3. Hydrogen bonds (Å, °).

D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A
N(4)–H(4A) ··· Cl(1)^{a}	0.88	2.45	3.3108(17)	166
N(4)–H(4B) ··· Cl(1)^{b}	0.88	2.43	3.2579(17)	157
C(8)–H(8) ··· Cl(1)^{b}	0.95	2.73	3.494(2)	137
C(13)–H(13A) ··· Cl(1)^{c}	0.98	2.65	3.618(2)	168
C(14)–H(14B) ··· Cl(1)^{d}	0.98	2.79	3.689(2)	153

^{a} $-x, -1/2+y, 1/2-z$; ^{b} $-x, 2-y, 1-z$; ^{c} $x, y, 1+z$; ^{d} $x, 5/2-y, 1/2+z$.

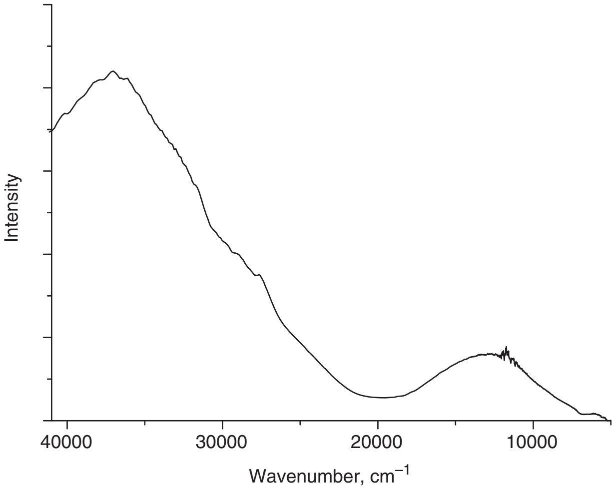


Figure 3. The diffuse reflectance spectrum of the complex.

high-energy band with $\nu_{max} = 37{,}040\,cm^{-1}$ and, within the range 20,000–7000 cm^{-1}, an unsymmetrical broad band with a maximum at 12,820 cm^{-1}. Although the assignment of these bands without detailed quantum chemical calculations seems not to be unambiguous, it is natural to assume that the high-energy band (at 37,040 cm^{-1}) can be assigned to the charge transfer (this is confirmed by the data of Lever that the charge transfer bands for copper(II) complexes are observed above 20,000 cm^{-1} [44]), while the low-energy one (at 12,820 cm^{-1}) seems to be due to d–d transitions. Although the position and form of the latter band itself can hardly be indicative of the symmetry of the chromophore of the copper(II) complex, nevertheless we can state that its position is out of the region characteristic for pseudooctahedral (4 + 2) copper(II) complexes [44] and its position and form does not contradict with square-pyramidal coordination geometry, CuN_3Cl_2, determined by X-ray diffraction. The latter moment is in accord with the data of Lever on copper(II) complexes having this coordination geometry [44]. Indeed, for square-pyramidal chromophores CuA_5 (A = Cl, Br, and N) these transitions are observed usually within the range 11,050 (for $CuCl_4Cl$ chromophore)–15,300 cm^{-1} (for CuN_5 chromophore) [44].

3.4. *Synthetic aspects (Part 2)*

After describing the observations made during crystallization experiments, a question arises: why despite numerous experiments on crystallization made at various metal-to-ligand molar ratios have we not observed the formation of any di- or polynuclear complex Cu_nLCl_{2n} ($n \geq 2$) and why does only a compound with a 1 : 1 stoichiometry form? The possible explanation can be as follows: taking into account these observations, it is natural to assume that using polar mixed solvent can contribute to effective solvation of Cu^{2+} in the case of metal-enriched metal-to-ligand molar ratios within the solution, obstructing thus the formation of polynuclear species Cu_nLCl_{2n} ($n \geq 2$) and leading to precipitation of $[CuLCl_2]$ as a single product independent of metal-to-ligand molar ratio.

To check this hypothesis, ESI-MS measurements were carried out on the MeOH/H_2O/DMF (0.5 mL/0.5 mL/0.05 mL) solutions containing $CuCl_2$ and L in a 1 : 1 and in a 20 : 1 metal-to-ligand molar ratios ($C_L = 3 \times 10^{-3}\,mmol\,mL^{-1}$). The spectrum of a 1 : 1 mixture in the positive mode shows an intense peak of $[CuLCl]^+$ cation (m/z 364.03). The intensity of the other peaks is substantially lower. The peaks at lower m/z correspond to $[CuL]^{2+}$ (m/z 164.53), to $[CuL(H_2O)]^{2+}$ (m/z 173.53), to $[CuL(DMF)]^{2+}$ (m/z 201.05), and to $[CuL_2]^{2+}$ (m/z 297.59). The spectrum of a 1 : 1 mixture in the negative mode shows an intense peak of $[CuCl_3]^-$ (m/z 169.83). The peak corresponding to $[CuCl_2]^-$ (m/z 134.87) has low intensity. The spectrum of a 20 : 1 mixture in the positive mode shows two intense peaks of $[Cu(DMF)_2]^+$ (m/z 209.03) and $[CuCl(DMF)_2]^+$ (m/z 244.00). Two less intense peaks correspond to $[Cu(DMF)]^+$ (m/z 135.98) and to $[CuCl(DMF)]^+$ (m/z 170.95). The peak at m/z 364.03 indicates the presence of $[CuLCl]^+$ cation (middle intensity). The spectrum of a 20 : 1 mixture in the negative mode shows an intense peak of $[CuCl_2]^-$ (m/z 134.87) and a somewhat less intense peak of $[CuCl_3]^-$ (m/z 169.83). Several species of higher nuclearity were observed only as traces: $[Cu_2Cl_5]^-$ (m/z 304.70), $[Cu_3Cl_7]^-$ (m/z 437.57).

The spectrum of a 1 : 1 mixture (positive mode) detected the formation of a series of species having 1 : 1 and 1 : 2 metal-to-ligand stoichiometries. An increase of copper(II) concentration up to 20 : 1 resulted in the formation of a series of mononuclear copper-DMF species and, at the same time, to the disappearance of the Cu : L = 1 : 2 species. The only peak corresponding to the Cu : L species in a 20 : 1 mixture is that of $[CuLCl]^+$. Thus, the latter is detected irrespective of the metal-to-ligand molar ratio. The spectra of mixtures, 1 : 1 and 20 : 1 (negative mode), detected the formation of mononuclear halocuprate species; the species of higher nuclearity were observed only as traces. The detection of Cu(I) species in the spectra of both systems, 1 : 1 and 20 : 1, is due to reducing of Cu(II) under ESI-MS conditions.

These results are in accord with our hypothesis. Thus, the additional amount of $CuCl_2$ regarding the Cu : L = 1 : 1 molar ratio is effectively solvated and the high-nuclearity species are formed in the solution only in trace amounts. This accounts for the fact that $[CuLCl_2]$ has been obtained as a single product irrespective of the metal-to-ligand ratio.

4. Conclusion

A copper(II) chloride complex with 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidin-4-amine (L), $[CuLCl_2]$, is formed irrespective of the Cu : L molar ratio in $MeOH/H_2O/DMF$ mixture. This is due to the effective solvation of Cu^{2+} cations for metal-enriched metal-to-ligand molar ratios, obstructing thus the formation of polynuclear species. This compound is the first example of a metal complex with 6(4)-(pyrazol-1-yl)-2-(pyridin-2-yl)pyrimidines. The dinuclear $[CuLCl_2]_2$ units are formed in the structure owing to Cu ··· Cl contacts arising between mononuclear $[CuLCl_2]$ molecules. Interestingly, the NH_2-group participates in the formation of NH ··· Cl1 hydrogen bonds instead of $(NH \cdots N3_{(pyrimidine)})_2$ synthon, due to a substantial effective negative charge sitting on Cl1 occupying a vertex of a CuN_3Cl_2 pyramid.

Supplementary material

CCDC 833218 contains the supplementary crystallographic data for the complex. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44)1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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