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Copper(II) complexes based on a new chelating 4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-(piperidin-1-yl)pyrimidine ligand: Synthesis and crystal structures. Lone pair- π , C-H... π , π - π and C-H...A (A = N, Cl) non-covalent interactions

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ABSTRACT

A new bidentate chelating pyrazolylpyrimidine ligand bearing a strong electron-donating substituent, i.e. 4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-(piperidin-1-yl)pyrimidine (L) (Scheme 1), has been synthesized and used to obtain the copper(II) complexes by reaction with CuCl₂. The molar ratio Cu:L = 1:2 leads to isolation of a complex having CuL₂Cl₂ empirical formula, while the molar ratio Cu:L = 1:1 gives a complex with CuLCl₂ empirical formula. The crystal structure of L as well as the structures of both complexes were studied by single crystal X-ray diffraction. The crystal structure of CuL₂Cl₂ compound is formed by *trans*-[CuL₂Cl₂] mononuclear molecules. Surprisingly, in contrast to the previous compound having molecular structure, the crystal structure of CuLCl₂ complex can be represented as [CuL₂Cl₂]Cu₂Cl₆]. In both complexes molecules of L adopt bidentate chelating coordination mode through N² atom of pyrazole and N³ atom of pyrimidine rings forming five-membered CuN₃C metallocycles. Owing to C-H…N interactions and π -π-stacking L molecules form 2D network. In the structure of *trans*-[CuL₂Cl₂] there exist double lone pair(N(piperidine))- π (pyrimidine) interactions and C-H…Cl, C-H… π and double lone pair (Cl([CuL₂Cl⁺ complex cation)- π (pyrimidine) interactions.

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1. Introduction

Pyrazolylpyrimidines are frequently reported in literature as compounds manifesting various kinds of biological activity [1–11]. Due to the presence of donor nitrogen atoms they can act as ligands for synthesis of complex compounds [12,13]. Design of pyrazolylpyrimidine moiety allows to obtain transition metal coordination compounds manifesting desirable magnetic or catalytic properties [14–17].

A search for metal complexes based on 4-pyrazolylpyrimidine or 4,6-bis(pyrazolyl)pyrimidine ligands in the Cambridge Structural Database (Version 5.30; updates November 2008 and February 2009) gave only two palladium complexes [12] and seven copper complexes [18–20]. Due to the presence of planar aromatic and heteroaromatic fragments favoring π - π -stacking interactions, copper(II) complex, obtained in Ref. [18], exist in three differently colored polymorphic modifications.

Recently we reported data on cobalt(II), copper(II) and copper(I) halide complexes with 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methyl-2-phenylpyrimidine [18,21]. In solution, copper(II) bromide complex reduces producing binuclear copper(I) complex. The complexes of M^{2+} (M = Co, Cu) show weak antiferromagnetic interactions between the M^{2+} ions.

Copper(II) chloride and bromide coordination compounds with ditopic ligands, 4,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)pyrimidine and 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-(3,5-diphenyl-1*H*-pyrazol-1-yl)pyrimidine, have dinuclear structure according to the spectroscopic and magnetic data [22]. They manifest catalytic activity in ethylene polymerization [22]. Rhodium(I) complex with 4,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)pyrimidine also has dinuclear structure [23].

In this paper we report synthesis and crystal structure studies of a new pyrazolylpyrimidine ligand, i.e. 4-(3,5-diphenyl-1*H*-pyrazol-

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Scheme 1. 4-(3,5-Diphenyl-1H-pyrazol-1-yl)-6-(piperidin-1-yl)pyrimidine (L).

1-yl)-6-(piperidin-1-yl)pyrimidine (L) (Scheme 1) as well as copper(II) chloride complexes with this ligand. Formally, this ligand, L, can be regarded as a product of substitution of 3,5-dimetylpyrazolyl group by piperidino one in 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-(3,5-diphenyl-1*H*-pyrazol-1-yl)pyrimidine.

This compound, L, bears a strongly electron-donating piperidino-group in ortho-position to N¹ and in para-position to N³ atoms of the pyrimidine ring, increasing thus their effective negative charge particularly due to manifestation of direct conjugation of +M substituent in combination with an electron-withdrawing effect of nitrogen heteroatoms. Taking into account potential chelating coordination of L by means of N³ atom of pyrimidine and N² atom of pyrazole moieties to metal centers we were endeavored to study how introduction of electron-donating substituent in pyrazolylpyrimidine unit will affect composition and structure of copper(II) chloride complexes based on L. Taking into account previously reported data [18,20] we also kept in mind a possibility of formation of supramolecular self-assemblies due to non-covalent interactions. It is well known, that non-covalent interactions (anion… π , lone pair(lp)– π , C–H… π , cation… π , π – π , "conventional" and "non-conventional" H-bonds) have attracted considerable attention [24-30] since they play a pivotal role in various biological and chemical systems. In this context it ought to underline, that L molecule incorporate pyrimidine cycle that can favor anion... π and $lp-\pi$ interactions due to its electron-deficiency [26b]. Nitrogen atoms of piperidino- and pyrazolyl groups can be regarded as donors of electron lone pair participating in $lp-\pi$ interactions [26b]. Finally, both phenyl groups and heteroaromatic moieties can produce π - π -stacking.

Complexes reported here are examples of copper halide compounds. The latters are of fundamental and practical importance since they demonstrate not only wide structural diversity but also catalystic and photophysic properties, magnetic, redox activity, etc. [31]. As we have previously mentioned, there are only a few examples of copper halide complexes with 4-pyrazolylpyrimidines [18–23], and there are no data on the synthesis of complexes based on pyrazolylpyrimidines bearing electron-donating substituents.

2. Experimental

2.1. General

Starting reagents for the synthesis of L, 4-chloro-6-(3,5-diphenyl-1*H*-pyrazol-1-yl)pyrimidine and 4-hydrazino-6-(piperidin-1yl)pyrimidine, were synthesized according to reported procedures [22,32,33]. All other reagents and solvents were commercially available and were used without additional purification. The copper content was determined by complexometric titration, the samples were mineralized in a 1:1 mixture of concentrated H₂SO₄ and HClO₄. Elemental analysis was performed with a Carlo–Erba analyzer using standard technique. The electronic reflection spectra were recorded on a Unicam 700A spectrophotometer at 340– 2300 nm. IR absorption spectra were recorded on a Scimitar FTS 2000 spectrophotometer at 375–4000 cm⁻¹ and on a BOMEM MB-102 spectrophotometer at 200–400 cm⁻¹; a high-resolution mass spectrum was taken on a Finnigan MAT-8200 spectrometer, electron impact, 70 eV. Magnetic susceptibilities (χ) of complexes were measured at 295 K using Faraday balances. The diamagnetism of the atoms was considered according to the Pascal additive scheme. The effective magnetic moment was calculated by the formula $\mu_{\text{eff}} \approx (8\chi T)^{1/2}$.

2.2. Synthesis of 4-(3,5-diphenyl-1H-pyrazol-1-yl)-6-(piperidin-1-yl)pyrimidine (L, (1))

2.2.1. Method 1

The title compound L was synthesized by the reaction of 4-hydrazino-6-(piperidin-1-yl)pyrimidine (1.93 g, 10 mmol) and dibenzoylmethane (2.24 g, 10 mmol) at boiling for 8 h in 50 ml of EtOH. The solvent was then removed under reduced pressure and residue was purified by silica gel column chromatography (eluent chloroform) to provide L. Yield: 2.74 g (69%), m.p. 124–126 °C. *Anal.* Calc. for $C_{24}H_{23}N_5$: C, 75.6; H, 6.1; N, 18.4. Found: C, 75.6; H, 6.3; N, 18.5%. ¹H NMR (CDCl₃): 1.53–1.75 (m, 6H, piperidine), 3.53–3.61 (m, 4H, piperidine), 6.75 (d, *J* = 0.9 Hz, 1H, 5-H_{pyrimidine}), 6.79 (s, 1H, 4-H_{pyrazole}), 7.30–7.47 (m, 8H, Ph), 7.89–7.96 (m, 2H, Ph), 8.31 (d, *J* = 0.9 Hz, 1H, 2-H_{pyrimidine}). Single crystals suitable for X-ray analysis were obtained by slow crystallization of L from ethanolic solution.

2.2.2. Method 2

A solution of 4-chloro-6-(3,5-diphenyl-1*H*-pyrazol-1-yl)pyrimidine (1.0 g, 3 mmol) and piperidine (0.56 g, 6.6 mmol) in 20 ml of EtOH was heated at reflux for 1 h. The solvent was removed *in vacuo* and the concentrate was washed with water and dried. Recrystallization from hexane afforded ligand L. Yield: 0.71 g (62%), m.p. 124–126 °C.

2.3. Synthesis of CuL_2Cl_2 (2)

A hot solution of L (0.60 mmol, 229 mg) in EtOH (5 ml) was added dropwise to a stirred hot solution of $CuCl_2 \cdot 2H_2O$ (0.30 mmol, 51 mg) in EtOH (2 ml). Resulting solution became dark green. Brown-green precipitate, which began to form, was dissolved when all amount of L was added. Salade-green precipitate was formed in *ca*. 5 min. After stirring with heating for 1 h the precipitate was filtered off, washed with EtOH and dried in ambient air. Yield: 210 mg (78%). m.p. 209 °C (dec.). *Anal.* Calc. for C₄₈H₄₆N₁₀Cl₂Cu: C, 64.2; H, 5.2; N, 15.6; Cu, 7.1. Found: C, 63.8; H, 5.2; N, 15.4; Cu, 7.1%. Single crystals suitable for X-ray analysis were obtained by slow crystallization of CuL₂Cl₂ from mixture CH₂Cl₂:CH₃CN (1:1).

2.4. Synthesis of $CuLCl_2$ (3)

A hot solution of L (0.50 mmol, 191 mg) in EtOH (5 ml) was added dropwise to a stirred hot solution of $CuCl_2 \cdot 2H_2O$ (0.50 mmol, 85 mg) in EtOH (2 ml). Resulting solution became dark green. Brown-green precipitate was formed in *ca.* 2 min. After stirring with heating for 1 h the precipitate was filtered off, washed with EtOH and dried in ambient air. Yield: 170 mg (66%). m.p. 225 °C (dec.). *Anal.* Calc. for $C_{24}H_{23}N_5Cl_2Cu$: C, 55.9; H, 4.5; N, 13.6; Cu, 12.3. Found: C, 55.2; H, 4.6; N, 13.2; Cu, 12.4%. Single crystals suitable for X-ray analysis were obtained by slow evaporation of mother liquor.

2.5. X-ray crystallographic study

Single crystal data for L, CuL₂Cl₂ and CuLCl₂ were collected at ambient temperature with Mo K α radiation (λ = 0.71073 Å) using a Bruker Nonius X8Apex CCD diffractometer equipped with graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software [34]. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software [35]. All the non-H atoms were refined in the anisotropic approximation. The crystallographic parameters of the compounds studied are given in Table 1.

3. Results

3.1. Synthesis of the compounds

Synthesis of L was carried out *via* the routes shown in Scheme 2. In Method 1, 4-hydrazino-6-(piperidin-1-yl)pyrimidine [32,33] was subjected to the construction of a pyrazole ring with dibenzoylmethane to provide 4-(3,5-diphenyl-1H-pyrazol-1-yl)-6-(piperidin-1-yl)pyrimidine (L, (1)). In the frame of the alternative route (Method 2) L was prepared by reaction of 4-chloro-6-(3,5-diphenyl-1H-pyrazol-1-yl)pyrimidine [22] with piperidine. Since both 4-hydrazino-6-(piperidin-1-yl)pyrimidine and 4-chloro-6-(3,5-diphenyl-1H-pyrazol-1-yl)pyrimidine can be obtained from the same starting reagent, 4-chloro-6-hydrazinopyrimidine [22,32,33], by reaction of the latter with piperidine either dibenzoylmethane, respectively, both methods of the ligand's preparation differ only by the order of introducing or construction of corresponding heterocyclic rings on pyrimidine moiety. Both methods provide L with relatively high yield.

Table 1

Crystal data and structure refinement for compound 1-3.

The complex compounds **2** and **3** were synthesized by the reaction of copper(II) chloride with L in ethanol solutions on heating. Taking into account possible bidentate chelating function of L as well as potential formation of molecular bis- and mono-chelate copper(II) chloride compounds, $[CuL_2Cl_2]$ and $[CuLCl_2]$, the Cu:L = 1:2 and 1:1 molar ratios were applied for the synthesis of complexes. As follows from the chemical analysis data, the compounds having CuL_2Cl_2 and $CuLCl_2$ stoichiometry were obtained suggesting thus at the first glance the molecular mononuclear structure of the both complexes. X-ray diffraction data (see below) revealed that CuL_2Cl_2 has molecular structure (*trans*-[CuL_2Cl_2]), but $CuLCl_2$ surprisingly appeared to be an ionic [CuL_2Cl_2[Cu_2Cl_6] compound instead of [CuLCl_2] expected one.

In ethanolic solutions compound **2** can be converted to **3** when it reacts with 1 equiv. of $CuCl_2 \cdot 2H_2O$, inverted transformation of **3** into **2** takes place in the presence of 1 equiv. of L. Identity of such reaction products was confirmed by microanalytical and m.p. data.

Thus, the following transformations were performed (Scheme 2).

Complexes are stable in air. They are soluble in organic solvents, i.e. ethanol, MeCN, isopropyl alcohol, toluene, CH₂Cl₂, CHCl₃, and their mixtures; they are insoluble in water.

3.2. Description of the structures of compounds

3.2.1. General remarks

The molecular and crystal structures of 1, 2 and 3 are shown in Figs. 1–6. (Hetero)aromatic rings are nearly planar in all reported compounds, piperidino-group adopts conformation of chair. Bond distances as well as valence angles in L molecules coordinated by copper atoms in 2 and 3 are very close to those of free L molecules in 1. They are in a good agreement with the data [36]. On the other hand the relative orientations of phenyl and heterocyclic groups of L molecules are different in 1-3. The most noticeable change

Compound	1	2	3
Empirical formula	C ₂₄ H ₂₃ N ₅	$C_{48}H_{46}Cl_2CuN_{10}$	$C_{96}H_{92}C_{18}Cu_4N_{20}$
Formula weight	381.47	897.39	2063.66
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	ΡĪ	ΡĪ
a (Å)	8.6360(3)	10.2938(2)	10.094(1)
b (Å)	23.3341(8)	10.7113(3)	14.316(2)
c (Å)	9.9594(3)	11.4176(3	16.640(2)
α (°)		88.803(1)	83.973(3)
β (°)	104.906(1)	67.068(1)	78.031(4)
γ (°)		66.924(1)	83.536(5)
$V(Å^3)$	1939.4(1)	1053.65(5)	2329.1(5)
Ζ	4	1	1
T (K)	150(2)	90(2)	296(2)
D_{calc} (g cm ⁻³)	1.306	1.414	1.471
$\mu (\mathrm{mm}^{-1})$	0.080	0.694	1.189
Crystal size (mm ³)	$0.31\times0.25\times0.15$	$0.16 \times 0.16 \times 0.05$	$0.26 \times 0.21 \times 0.14$
θ Range for data collection (°)	1.75-25.68	1.96-25.68	1.83-25.68
Index ranges	$-8\leqslant h\leqslant 10$, $-28\leqslant k\leqslant 28$,	$-9 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$,	$-12\leqslant h\leqslant 10$, $-17\leqslant k\leqslant 17$,
	$-11 \leq l \leq 12$	$-13 \leqslant l \leqslant 13$	$-20 \leqslant l \leqslant 20$
Reflections collected	13068	10688	15866
Independent reflections (R_{int})	3683(0.0234)	3945(0.0209)	8370(0.0806)
Completeness to θ	99.9% (25.00°)	99.0% (25.00°)	95.0% (25.00°)
Absorption correction	SADABS	SADABS	SADABS
Maximum and minimum transmission	0.9881 and 0.9756	0.9635 and 0.8947	0.8484 and 0.7442
Refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on F ²
Data/restraints/parameters	3683/0/262	3945/0/329	8370/0/577
Goodness-of-fit (GOF) on F ²	1.087	1.063	0.817
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0392, wR_2 = 0.0990$	$R_1 = 0.0292, wR_2 = 0.0706$	$R_1 = 0.0588, wR_2 = 0.0836$
R indices (all data)	$R_1 = 0.0525, wR_2 = 0.1039$	$R_1 = 0.0383, wR_2 = 0.0732$	$R_1 = 0.1822, wR_2 = 0.0999$
Largest difference in peak and hole	0.223 and -0.192	0.311 and -0.350	0.383 and -0.379
(e A ⁻³)			



Scheme 2. Synthesis of L ligand and trans-[CuL₂Cl₂], [CuL₂Cl₂]₂[Cu₂Cl₆] complexes.



Fig. 1. 2D network in the structure of 1.

accompanying the ligand's coordination is the turn of pyrimidine ring respectively to pyrazole one when L molecules coordinate to copper atoms in **2** and **3** through N^2 (pyrazole) and N^3 (pyrimidine) atoms adopting thus bidentate chelating coordination mode. As a result of the ligand coordination, the CuCN₃ chelate cycles are closed.

3.2.2. Crystal structure of L

The crystal structure of **1** is molecular (Figs. 1 and 2). Possibly, the repulsion of lone pairs of N(11) and N(13) donor atoms produces *anti*-disposition of these atoms in the molecule of L, the corresponding dihedral angle N(11)–N(12)–C(14)–N(13) is 141.3°. In the crystal packing it should outline the presence of intermolecular





Fig. 3. Molecular structure of trans-[CuL₂Cl₂]. Short intramolecular contacts are shown as dashed lines.

contacts C–H···N (N(11)···H(17)' = 2.788 Å, N(13)···H(16A)' = 2.323 Å, N(13)···H(15)' = 2.608 Å) as well as weak π – π -stacking interactions between phenyl groups of neighboring L molecules (centroid–centroid distance is 3.763 Å, distance between corresponding adjacent planes is 3.448 Å). These interactions result in the layers formed by L molecules (Fig. 1). Additional

non-covalent C–H··· π interactions exist between pyrimidine and phenyl rings (2.895–3.444 Å) (Fig. 2).

3.2.3. Crystal structure of complex **2**

The crystal structure of complex **2** is molecular mononuclear (Figs. 3 and 4), the geometry around each copper atom is distorted



Fig. 4. 1D chains in the structure of 2.



Fig. 5. Structure of [CuL₂Cl]⁺ cation. Short intracationic contacts are shown as dashed lines.

trans-octahedral (4+2): two chlorine atoms and two nitrogen (pyrimidine) atoms form slightly distorted square plane, remaining positions of distorted octahedron are occupied by two nitrogen atoms (pyrazole) (Table 2). Pyrazole and pyrimidine rings of coordinated L molecules are not coplanar, N(11)–N(12)–C(14)–N(13) dihedral angle is 29.5°. This produces non-planar geometry of CuCN₃ chelate ring. Copper atom deviates from mean chelate plane by 0.1905 Å, its deviation of from N(11)–N(12)–C(14)–N(13) plane is more noticeable (1.045 Å). Lengths of the Cu–N(pyrimidine) bonds are in agreement with those for copper complexes with pyrazolylpyrimidines [18,21,37]. At the same time Cu–N(pyrazole) bond length is markedly longer, then it was previously observed [18,21,37]. This makes the chelate rings highly unsymmetrical regarding to Cu–N distances.

Within the CuL₂Cl₂ molecule there present close intramolecular contacts between two coordinated L molecules (H(116)…H(17)' = 2.758 Å, H(115)…H(16H)' = 2.667 Å and H(135)…H(16C) = 2.944 Å) (Fig. 3).

Copper atoms are placed in the structure according to face-centred cubic packing (ABC...). It should outline the formation of double lp(N(piperidine))– π (pyrimidine) interaction between pyrimidine rings and nitrogen atoms of piperidino-group of neighboring molecules of **2**. The distance between the centroid of pyrimidine ring and N(15) atom is 3.211 Å, the angle between the N(piperidine), the ring centroid and the aromatic plane is 85.7°. These double lp– π interactions in combination with C–H…Cl hydrogen bond (Cl(1)…H(16B)' = 2.745 Å) result in the formation of 1D chains (Fig. 4).

3.2.4. Crystal structure of complex 3

Compound **3** is ionic one with a $[CuL_2Cl]_2[Cu_2Cl_6]$ formula (Figs. 5 and 6). The highly distorted coordination polyhedron of copper atom (Cu(1)) in $[CuL_2Cl]^+$ cation is intermediate between square pyramid and trigonal bipyramid. This is confirmed by the value of an angular structural parameter, τ (0.40), proposed as a characteristics of the geometry around the central atom in fivecoordinated compounds $(\tau = (\beta - \alpha)/60$, where β and α are the two largest angles in the coordination core, $\beta > \alpha$; the τ value for square pyramidal and trigonal bipyramidal geometries is 0 and 1, respectively) [38]. The coordination polyhedron is formed by four nitrogen atoms bearing from two L molecules and a chlorine atom (Table 2). Similar to the structure of 2, values of N(11)-N(12)-C(14)-N(13) and N(21)-N(22)-C(24)-N(23) dihedral angles are far from zero, they are 24.4° and 18.7° for both coordinated L molecules, respectively. Contrary to complex 2, chelate cycles CuCN3 are less distorted, deviations of copper atom from mean planes of the cycles are 0.1284 and 0.1509 Å; corresponding deviations from N(11)-N(12)-C(14)-N(13) and N(21)-N(22)-C(24)-N(23) planes are 0.7120 and 0.5960 Å, respectively. Dissymmetry of the chelate cycles with respect to Cu-N distances was found to be also noticeably less, than in 2.

Within the $[CuL_2Cl]^+$ ion, a number of short intramolecular contacts have been found $(H(116)\cdots H(27) = 2.898 \text{ Å}, H(236)\cdots H(112) = 2.736 \text{ Å}, H(212)\cdots H(136) = 2.621 \text{ Å}, H(214)\cdots H(16C) = 2.865 \text{ Å}, H(214)\cdots H(16H) = 2.896 \text{ Å}, H(115)\cdots H(26H) = 2.604 \text{ Å}, H(114)\cdots H(26H) = 2.869 \text{ Å})$ (Fig. 5).



Fig. 6. 2D layers of $[CuL_2Cl]^+$ cations interposed by $[Cu_2Cl_6]^-$ anions.

Table 2			
Selected bond lengths (Å) and angles	[°]	[] for compounds 2 and 3 .	

$\begin{array}{c c} Compound 2 \\ Cu(1)-N(11) & 2.591(1)\times 2 \\ Cu(1)-N(13) & 1.989(1)\times 2 \\ Cu(1)-Cl(1) & 2.3177(1)\times 2 \\ N(13)-Cu(1)-Cl(1)\#1 \\ S.78(4) \\ Cu(1)-Cl(1) & 2.3177(1)\times 2 \\ N(13)\#1-Cu(1)-Cl(1)\#1 \\ N(13)\#1-Cu(1)-Cl(1) \\ N(13)\#1-Cu(1)-Cl(1) \\ S.78(5) \\ Cl(1)\#1-Cu(1)-Cl(1) \\ S.78(5) \\ Cl(1)\#1-Cu(1)-Cl(1) \\ S.78(5) \\ Cl(1)\#1-Cu(1)-Cl(1) \\ S.78(5) \\ Cl(1)\#1-Cu(1)-Cl(1) \\ S.78(5) \\ Cl(1)+N(13) \\ 1.966(4) \\ N(23)-Cu(1)-N(21) \\ Cu(1)-N(21) \\ 2.230(4) \\ N(13)-Cu(1)-N(21) \\ Cu(1)-N(23) \\ 1.964(4) \\ N(23)-Cu(1)-N(11) \\ S.72(1) \\ Cu(2)-Cl(2) \\ 2.194(2) \\ N(23)-Cu(1)-N(11) \\ S.7(1) \\ Cu(2)-Cl(3) \\ 2.304(2) \\ N(23)-Cu(1)-Cl(1) \\ S.7(1) \\ Cu(2)-Cl(3) \\ 2.304(2) \\ N(23)-Cu(1)-Cl(1) \\ S.7(1) \\ Cu(2)-Cl(3) \\ 2.304(2) \\ N(23)-Cu(1)-Cl(1) \\ S.7(1) \\ Cu(2)-Cl(3) \\ 2.313(1) \\ N(13)-Cu(1)-Cl(1) \\ S.7(1) \\ Cl(4)-Cu(2)-Cl(3) \\ S.7(1) \\ Cl(4)-Cu(2)-Cl(3) \\ S.7(1) \\ Cl(4)-Cu(2)-Cl(3) \\ S.7(1) \\ Cl(2)-Cu(2)-Cl(3) \\ S.7(1) \\ Cl(3)-Cu(2)-Cl(3) \\ S.7(1) \\ Cl(3)-Cu(2$	Bond	d (Å)	Angle	ω (°)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Compound 2			
$\begin{array}{cccc} Cu(1)-N(13) & 1.989(1)\times 2 \\ Cu(1)-Cl(1) & 2.3177(1)\times 2 \\ N(13)\#1-Cu(1)-Cl(1)\#1 & 91.22(5) \\ N(13)-Cu(1)-Cl(1) & 91.22(4) \\ N(13)\#1-Cu(1)-Cl(1) & 91.22(4) \\ N(13)\#1-Cu(1)-Cl(1) & 88.78(5) \\ Cl(1)\#1-Cu(1)-Cl(1) & 180.00(1) \\ \end{array}$	Cu(1)-N(11)	$2.591(1) \times 2$	N(13)-Cu(1)-N(13)#1	180.00(8)
$\begin{array}{cccc} {\rm Cu}(1)-{\rm Cl}(1) & 2.3177(1)\times 2 & {\rm N}(13)\#1-{\rm Cu}(1)-{\rm Cl}(1)\#1 & {\rm 91.22(5)} \\ {\rm N}(13)-{\rm Cu}(1)-{\rm Cl}(1) & {\rm 91.22(4)} \\ {\rm N}(13)\#1-{\rm Cu}(1)-{\rm Cl}(1) & {\rm 91.22(4)} \\ {\rm N}(13)\#1-{\rm Cu}(1)-{\rm Cl}(1) & {\rm 91.22(4)} \\ {\rm N}(13)\#1-{\rm Cu}(1)-{\rm Cl}(1) & {\rm 88.78(5)} \\ {\rm Cl}(1)\#1-{\rm Cu}(1)-{\rm Cl}(1) & {\rm 88.78(5)} \\ {\rm Cl}(1)\#1-{\rm Cu}(1)-{\rm Cl}(1) & {\rm 180.00(1)} \end{array} \\ \end{array}$	Cu(1)-N(13)	$1.989(1) \times 2$	N(13)-Cu(1)-Cl(1)#1	88.78(4)
$\begin{array}{c ccc} N(13)-Cu(1)-Cl(1) & 91.22(4) \\ N(13)\#1-Cu(1)-Cl(1) & 88.78(5) \\ Cl(1)\#1-Cu(1)-Cl(1) & 180.00(1) \end{array}$	Cu(1)-Cl(1)	$2.3177(1) \times 2$	N(13)#1-Cu(1)-Cl(1)#1	91.22(5)
$\begin{array}{c ccc} N(13)\#1-Cu(1)-Cl(1) & 88.78(5) \\ Cl(1)\#1-Cu(1)-Cl(1) & 180.00(1) \\ \hline \\ \hline \\ \hline \\ Compound \ 3 \\ \hline \\ Cu(1)-N(11) & 2.233(3) & N(23)-Cu(1)-N(13) & 171.5(1) \\ Cu(1)-N(13) & 1.966(4) & N(23)-Cu(1)-N(21) & 76.3(2) \\ Cu(1)-N(21) & 2.230(4) & N(13)-Cu(1)-N(21) & 100.2(1) \\ Cu(1)-N(23) & 1.964(4) & N(23)-Cu(1)-N(11) & 94.9(1) \\ Cu(1)-Cl(1) & 2.248(1) & N(13)-Cu(1)-N(11) & 77.2(1) \\ Cu(2)-Cl(2) & 2.194(2) & N(21)-Cu(1)-N(11) & 89.0(1) \\ Cu(2)-Cl(3) & 2.304(2) & N(23)-Cu(1)-Cl(1) & 93.6(1) \\ Cu(2)-Cl(3)\#2 & 2.313(1) & N(13)-Cu(1)-Cl(1) & 94.7(1) \\ Cu(2)-Cl(4) & 2.192(1) & N(21)-Cu(1)-Cl(1) & 123.5(1) \\ N(11)-Cu(1)-Cl(1) & 147.5(1) \\ Cl(4)-Cu(2)-Cl(3) & 145.5(1) \\ Cl(2)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(2)-Cu(2)-Cl(3)\#2 & 145.2(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \\ \hline \end{array}$			N(13)-Cu(1)-Cl(1)	91.22(4)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			N(13)#1-Cu(1)-Cl(1)	88.78(5)
$\begin{array}{c c} Compound \ \textbf{3} \\ \hline Cu(1)-N(11) & 2.233(3) & N(23)-Cu(1)-N(13) & 171.5(1) \\ Cu(1)-N(13) & 1.966(4) & N(23)-Cu(1)-N(21) & 76.3(2) \\ Cu(1)-N(21) & 2.230(4) & N(13)-Cu(1)-N(21) & 100.2(1) \\ Cu(1)-N(23) & 1.964(4) & N(23)-Cu(1)-N(11) & 94.9(1) \\ Cu(1)-Cl(1) & 2.248(1) & N(13)-Cu(1)-N(11) & 77.2(1) \\ Cu(2)-Cl(2) & 2.194(2) & N(21)-Cu(1)-N(11) & 89.0(1) \\ Cu(2)-Cl(3) & 2.304(2) & N(23)-Cu(1)-Cl(1) & 93.6(1) \\ Cu(2)-Cl(3) & 2.304(2) & N(23)-Cu(1)-Cl(1) & 93.6(1) \\ Cu(2)-Cl(3) & 2.313(1) & N(13)-Cu(1)-Cl(1) & 94.7(1) \\ Cu(2)-Cl(4) & 2.192(1) & N(21)-Cu(1)-Cl(1) & 123.5(1) \\ & N(11)-Cu(1)-Cl(1) & 147.5(1) \\ Cl(4)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(4)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(2)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(2)-Cu(2)-Cl(3) & 297.4(1) \\ Cl(3)-Cu(2)-Cl(3) & 28.56(1) \\ \end{array}$			Cl(1)#1-Cu(1)-Cl(1)	180.00(1)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Compound 3			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu(1) - N(11)	2.233(3)	N(23)-Cu(1)-N(13)	171.5(1)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu(1)-N(13)	1.966(4)	N(23)-Cu(1)-N(21)	76.3(2)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu(1)-N(21)	2.230(4)	N(13)-Cu(1)-N(21)	100.2(1)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu(1)-N(23)	1.964(4)	N(23)-Cu(1)-N(11)	94.9(1)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu(1)-Cl(1)	2.248(1)	N(13)-Cu(1)-N(11)	77.2(1)
$\begin{array}{c ccccc} Cu(2)-Cl(3) & 2.304(2) & N(23)-Cu(1)-Cl(1) & 93.6(1) \\ Cu(2)-Cl(3)\#2 & 2.313(1) & N(13)-Cu(1)-Cl(1) & 94.7(1) \\ Cu(2)-Cl(4) & 2.192(1) & N(21)-Cu(1)-Cl(1) & 123.5(1) \\ N(11)-Cu(1)-Cl(1) & 147.5(1) \\ Cl(4)-Cu(2)-Cl(2) & 99.4(1) \\ Cl(4)-Cu(2)-Cl(3) & 145.5(1) \\ Cl(2)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(4)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \\ \end{array}$	Cu(2)-Cl(2)	2.194(2)	N(21)-Cu(1)-N(11)	89.0(1)
$\begin{array}{cccc} Cu(2)-Cl(3)\#2 & 2.313(1) & N(13)-Cu(1)-Cl(1) & 94.7(1) \\ Cu(2)-Cl(4) & 2.192(1) & N(21)-Cu(1)-Cl(1) & 123.5(1) \\ N(11)-Cu(1)-Cl(1) & 147.5(1) \\ Cl(4)-Cu(2)-Cl(2) & 99.4(1) \\ Cl(4)-Cu(2)-Cl(3) & 145.5(1) \\ Cl(2)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(4)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \end{array}$	Cu(2)-Cl(3)	2.304(2)	N(23)-Cu(1)-Cl(1)	93.6(1)
$\begin{array}{c cccc} Cu(2)-Cl(4) & 2.192(1) & N(21)-Cu(1)-Cl(1) & 123.5(1) \\ N(11)-Cu(1)-Cl(1) & 147.5(1) \\ Cl(4)-Cu(2)-Cl(2) & 99.4(1) \\ Cl(4)-Cu(2)-Cl(3) & 145.5(1) \\ Cl(2)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(2)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \end{array}$	Cu(2)-Cl(3)#2	2.313(1)	N(13)-Cu(1)-Cl(1)	94.7(1)
$\begin{array}{lll} N(11)-Cu(1)-Cl(1) & 147.5(1) \\ Cl(4)-Cu(2)-Cl(2) & 99.4(1) \\ Cl(4)-Cu(2)-Cl(3) & 145.5(1) \\ Cl(2)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(4)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(2)-Cu(2)-Cl(3)\#2 & 145.2(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \\ \end{array}$	Cu(2)-Cl(4)	2.192(1)	N(21)-Cu(1)-Cl(1)	123.5(1)
$\begin{array}{rl} Cl(4)-Cu(2)-Cl(2) & 99.4(1) \\ Cl(4)-Cu(2)-Cl(3) & 145.5(1) \\ Cl(2)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(4)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(2)-Cu(2)-Cl(3)\#2 & 145.2(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \\ \end{array}$			N(11)-Cu(1)-Cl(1)	147.5(1)
$\begin{array}{ccc} Cl(4)-Cu(2)-Cl(3) & 145.5(1) \\ Cl(2)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(4)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(2)-Cu(2)-Cl(3)\#2 & 145.2(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \\ \end{array}$			Cl(4)-Cu(2)-Cl(2)	99.4(1)
$\begin{array}{ccc} Cl(2)-Cu(2)-Cl(3) & 97.0(1) \\ Cl(4)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(2)-Cu(2)-Cl(3)\#2 & 145.2(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \end{array}$			Cl(4)-Cu(2)-Cl(3)	145.5(1)
$\begin{array}{ccc} Cl(4)-Cu(2)-Cl(3)\#2 & 97.4(1) \\ Cl(2)-Cu(2)-Cl(3)\#2 & 145.2(1) \\ Cl(3)-Cu(2)-Cl(3)\#2 & 85.6(1) \end{array}$			Cl(2)-Cu(2)-Cl(3)	97.0(1)
Cl(2)-Cu(2)-Cl(3)#2 145.2(1) Cl(3)-Cu(2)-Cl(3)#2 85.6(1)			Cl(4)-Cu(2)-Cl(3)#2	97.4(1)
Cl(3)-Cu(2)-Cl(3)#2 85.6(1)			Cl(2)-Cu(2)-Cl(3)#2	145.2(1)
			Cl(3)-Cu(2)-Cl(3)#2	85.6(1)

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y + 1, -z + 1; #2 -x, -y + 2, -z + 1.

Table 3 The main vibration frequencies in IR spectra (\mbox{cm}^{-1}) of L, CuLCl_2 and CuL_2Cl_2.

Compound	$(v + \delta)_{ring}$	v(Cu–N)	v(Cu–Cl)
L CuL ₂ Cl ₂ CuLCl ₂	1591, 1552, 1531 1620, 1561, 1546 1626, 1572, 1540	276 252	303 327, 305

Coordination polyhedron of each copper atoms in dinuclear $[Cu_2Cl_6]^{2-}$ anions is distorted tetrahedron, $Cu(2)\cdots Cu(2)$ distance is 3.387(1) Å.

In the structure of the complex there exist a network of C–H…Cl and C–H… π hydrogen bonds (Cl(1)…H(12)' = 2.786 Å, Cl(4)…H (235)' = 2.771 Å, Cl(4)…H(212)' = 2.844 Å, Cl(4)…H(22)' = 2.878 Å; H(26B)'…Ph_{centroid} = 2.714 Å). Another interesting feature of the structure is double lp(Cl([CuL₂Cl]⁺)– π (pyrimidine) interactions between Cl(1) atoms and centroids of pyrimidine rings of neighboring complex cations [CuL₂Cl]⁺ (Cl(1)–centroid distance is 3.358 Å, the angle between the Cl, the ring centroid and the aromatic plane is 85.9°). As a result, layers of [CuL₂Cl]⁺ cations interposed by [Cu₂Cl₆]^{2–} anions are formed (Fig. 6). Contrary to the structure of **2**, lone pair of N(piperidine) atom does not participate in lp– π interactions.

3.3. IR- and electronic spectra. Magnetic data

The IR- and electronic spectra of the complexes, as well as their effective magnetic moments are consistent with the structural data.

Table 3 contains IR spectroscopic data for L, **2** and **3**. The positions of the stretching–deformation vibrations of heterocyclic rings including vibrations of the phenyl group in IR spectra of complexes are dramatically changed as compared to the spectrum of L and shifted towards high-frequency region. The far-IR spectra of the complexes exhibit the bands due to the stretching vibrations of the Cu–N bonds. In accordance with X-ray diffraction data this suggests coordination of the heterocyclic rings of L molecule. The low-frequency regions of the spectra of the complexes under discussion contain bands due to the stretching vibrations of the bonds Cu–Cl indicating the coordination of chlorine atoms.

The electronic diffuse reflectance spectrum of **2** contains a band with $v_{max} = 16400 \text{ cm}^{-1}$. The latter can be assigned to $E_g \rightarrow T_{2g} \text{ d} - \text{d}$ -transition for distorted octahedral coordination core. The spectrum of **3** contains in a visible region one very broad band (in the region of ~15000-5000 cm⁻¹) with $v_{max} = 10900 \text{ cm}^{-1}$. Probably, the broadness of the band can be due to the different types of chromophores, as it was observed by X-ray diffraction in **3**.

The effective magnetic moments calculated for CuL_2Cl_2 and $CuLCl_2$ compositions of **2** and **3**, respectively are 1.80 B.M. for both complexes. These values correspond to d⁹ electronic configuration of Cu^{2+} ions.

4. Discussion

Earlier we have reported copper(II) chloride and bromide complexes with similar chelating pyrazolylpyrimidine ligands (PzPym):2-(3,5-diphenyl-1*H*-pyrazol-1-yl)-4,6-diphenylpyrimidine [37], 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methyl-2-phenylpyrimidyne [18,21]. Molar ratio Cu:PzPym = 1:1 leads to the isolation of [Cu(PzPym)Hal₂] complexes having molecular mononuclear structure. Coordination core of copper atom in these complexes represents distorted tetrahedron CuN₂Hal₂.

In contrast to these previously reported copper(II) compounds, the X-ray analysis data for complex with CuLCl₂ empirical formula. which also have been obtained in a Cu:L = 1:1 molar ratio. revealed a rather unexpected result. Indeed, the compound have ionic structure which can be represented as [CuL₂Cl]₂[Cu₂Cl₆] instead of expected molecular one consisting of mononuclear [CuLCl₂] molecules. Coordination polyhedron of copper atom in [CuL₂Cl]⁺ cationic complex represents distorted trigonal bipyramid of CuN₄Cl composition. The isolation of [CuL₂Cl]⁺ cations in the structure of [CuL₂Cl]₂[Cu₂Cl₆] compound could hardly be explained on the basis of pure electronic effects. It seems to be clear that, in comparison with [Cu(PzPym)Hal₂] complexes, electron-donating +M effect of piperidino-group should increase effective negative charge on N³ pyrimidinic atom and, consequently, electronic density on copper atom when one L molecule coordinates obstructing thus coordination of the second L molecule. We propose that steric effects are the principal cause in formation of [CuL₂Cl]⁺ complex instead of $[CuLCl_2]$ molecules. Absence of a substituent at the C² positions of pyrimidine cycle (i.e. in *ortho*-position to N^3 atom (Scheme 1) participating in coordination), in contrast to the complexes reported in Refs. [18,21,37], can favor formation of complex species having Cu:L = 1:2 stoichiometry in the solution and isolation of the latters in solid phase. Additional copper amount in the solution, regarding to Cu:L = 1:2 stoichiometry of the complex species, leads to formation of bulky [Cu₂Cl₆]²⁻ counteranions precipitating together with [CuL₂Cl]⁺ cations forming thus ionic [CuL₂Cl]₂[Cu₂Cl₆] structure. At the same time, molar ratio Cu:L = 1:2 (i.e. without excess of copper regarding to the Cu:L = 1:2 stoichiometry of complex species) allows to isolate molecular trans-[CuL₂Cl₂] mononuclear complex with CuN₄Cl₂ distorted octahedral coordination core. Formation of molecular [CuL₂Cl₂] complex instead of hypothetic ionic [CuL₂Cl]Cl one (an analog for $[CuL_2Cl]_2[Cu_2Cl_6]$) could be explained by inability of relatively small chloride anion to cause precipitation of bulky $[CuL_2Cl]^+$ cation, as well as by high symmetry of *trans*- $[CuL_2Cl_2]$ complex.

In contrast to copper complexes reported in Refs. [18,21,37], in both complexes reported now, *trans*-[CuL₂Cl₂] and [CuL₂Cl]₂ [Cu₂Cl₆], chelate CuCN₃ cycles are not planar, copper atom noticeably deviates from N(11)–N(12)–C(14)–N(13) (or N(21)–N(22)– C(24)–N(23)) mean plane. Pyrimidine and pyrazole rings are also non-coplanar. These observations result certainly from steric factors. Indeed, coordination of two bulky L molecules to copper atoms in [CuL₂Cl]⁺ cation and *trans*-[CuL₂Cl₂] complex cause close intramolecular contacts between different moieties of coordinated L molecules (Figs. 3 and 5) obstructing thus formation of planar geometry of pyrazolylpyrimidine units and chelate rings.

It should be also outlined that in both discussed complexes Cu-N³(pyrimidine) bond lengths are the shortest ones in the coordination spheres of copper atoms. This shortening can be due to both (a) absence of a substituent at C^2 position of pyrimidine cycle and (b) electron-donating effect of piperidino-group. Due to unusual elongation of Cu-N²(pyrazole) bond length being much longer then these in [Cu(PzPym)Hal₂] complexes [18,21,37], CuCN₃ chelate cycles become unsymmetrical (with respect to Cu-N distances) in both complexes. The factors causing such a dissymmetry can be both steric and electronic in their nature. It seems to be reasonable that, in principle, the dissymmetry of chelate cycle results from highly unsymmetrical structure of pyrazolylpyrimidine ligand L used in the present study (Scheme 1). The ligand bears bulky phenyl group (on C³(pyrazole) atom) which is in ortho-position to N²(pyrazole) atom participating in coordination. With the absence of any substituent at C²(pyrimidine) position this contributes to unsymmetrical coordination of L. In addition to this, close contacts (intramolecular in 2, intracationic in **3**) arising due to coordination of two L molecules to copper atoms in trans-[CuL₂Cl₂] and [CuL₂Cl]⁺ (Figs. 3 and 5) make the formation of symmetrical CuCN₃ chelate rings failing. At the same time, another reason for elongation of Cu–N²(pyrazole) bond lengths in trans-octahedral [CuL₂Cl₂] complex, respectively to these ones in [CuL₂Cl]⁺ cation is Jahn-Teller effect as usual for six-coordinated copper(II) complexes.

Noticeable feature of structures **2** and **3** is double lone pair– π interaction. In the structure of **2** we observed moderate (according to criteria, reported in Ref. [26b]) lp(N(piperidine))– π (pyrimidine) interactions (3.211 Å) that is unusual for lp(R(R')N–R")– π (pyrimidine) interactions, most of which are week (longer than 3.25 Å) [26b]. Lp(Cl([CuL₂Cl]⁺)– π (pyrimidine) interactions (3.358 Å) in the structure of **3** also can be regarded as moderate ones [26b]; it is noteworthy, that these interactions arise between cations ([CuL₂Cl]⁺), not the molecules. Thus, combination of lone pair do-nor and lone pair acceptor within a single molecule or cation (for **2** and **3**, respectively) afforded compounds with remarkable double lp– π interactions.

5. Conclusions

In summary, we have synthesized two copper(II) chloride complexes based on a new chelating L ligand, bearing a strong electron-donating piperidino-group. Surprisingly, electron-donating +M effect of piperidino-group does not prevent coordination of the second L molecule to copper atom when we use Cu:L = 1:1 molar ratio and allows to isolate $[CuL_2CI]^+$ complex cation in the crystal structure of **3**. It seems to be reasonable that it is the absence of a substituent in 2 position of pyrimidine ring of L (in *ortho*-position to pyrimidinic N³ atom participating in coordination) that favor formation of complex species having

Cu:L = 1:2 stoichiometry – $[CuL_2Cl_2]$ and $[CuL_2Cl]^+$. Crystal structures of L, 2 and 3 show a remarkable number of non-covalent interactions that contribute to the generation of supramolecular 2D and 1D self-assemblies. Owing to C-H...N interactions and π - π -stacking L molecules form 2D network. In the structure of *trans*-[CuL₂Cl₂] there exist double lp(N(piperidine))- π (pyrimidine) interactions and C-H…Cl contacts resulting in the formation of 1D network. 2D structure of [CuL₂Cl]₂[Cu₂Cl₆] results from C-H…Cl, C–H… π and double lp(Cl([CuL₂Cl]⁺)– π (pyrimidine) interactions. This indicates that pyrazolylpyrimidines and their metal complexes are appealing objects for study of non-covalent interactions and for creation of supramolecular self-assemblies. Further research of the other complexes with L is now in progress.

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Appendix A. Supplementary material

CCDC 748747, 748748 and 748749 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.01.013.

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