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Cobalt(II), nickel(II), and copper(II) complexes of 14-membered hexaazamacrocycles: synthesis and characterization

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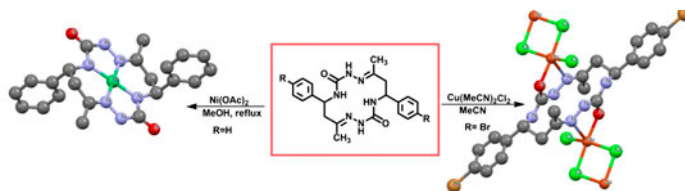# Cobalt(II), nickel(II), and copper(II) complexes of 14-membered hexaazamacrocycles: synthesis and characterization

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VLADIMIR V. CHERNYSHEV†‡, ELENA V. SAVINKINA§, VADIM F. CHUVAEV†,
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Cobalt(II), nickel(II), and copper(II) complexes containing 5,12-di(4-bromophenyl)-7,14-dimethyl-1,2,4,8,9,11-hexaazacyclotetradeca-7,14-diene-3,10-dione (H_2L^1) and 5,12-diphenyl-7,14-dimethyl-1,2,4,8,9,11-hexaazacyclotetradeca-7,14-diene-3,10-dione (H_2L^2) have been synthesized. All complexes were characterized by elemental analysis, MALDI TOF-MS spectrometry, and electronic absorption spectroscopy. The crystal structures of two compounds, $[Cu_2(H_2L^1)Cl_4]_n$ and $[NiL^2]$, were determined by X-ray powder diffraction. In the polymeric $[Cu_2(H_2L^1)Cl_4]_n$, the Cu_2Cl_4 units and H_2L^1 molecules are situated on inversion centers. Each Cu(II) has a distorted trigonal-bipyramidal coordination environment formed by N and O from H_2L^1 [Cu–N 2.340(14) Å, Cu–O 1.952(11) Å], two bridging chlorides [Cu–Cl 2.332(5), 2.279(5) Å] and one terminal chloride [Cu–Cl 2.320(6) Å]. In the $[NiL^2]$ complex, the Ni(II) situated on inversion center has a distorted square-planar coordination environment formed by four nitrogens from L^2 [Ni–N 1.860(11), 1.900(11) Å].

Keywords: Co(II), Ni(II), and Cu(II) complexes; Nitrogen-containing heterocycles; Hexaazamacrocycles; Semicarbazide

Introduction

Coordination chemistry of macrocyclic ligands is a booming area of modern inorganic chemistry [1–3]. Macrocyclic compounds and their complexes with transition metals and

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lanthanides show a wide range of biological activities (antimicrobial, anticancer, antiviral, etc.) [4–11]; they can be used as potential MRI contrast agents [12] and fluorescent sensors [13, 14]. Semicarbazide is able to coordinate metal ions [15–24] and the biological activities of these complexes are associated with the formation of chelates with various metal ions, bonding through N or O donors. Semicarbazides and their metal complexes attract considerable attention because they have applications in medicine as lathyrogenic and teratogenic agents [25]. Jevtovic *et al.* have demonstrated that copper(II) complexes with pyridoxal semicarbazone exhibit cytotoxic activity on cancer cell lines [26].

Thus, finding of new macroheterocyclic ligands containing semicarbazide fragments and investigation of their complex formation is useful. Recently, we have developed the approach to find new macroheterocycles, containing semicarbazide fragments [27].

In this paper, we report synthesis of copper(II), cobalt(II), and nickel(II) complexes with semicarbazide-based macrocycles, 7,14-dimethyl-5,12–di(4-bromophenyl)-1,2,4,8,9, 11-hexaazacyclotetradeca-7,14-diene-3,10-dione (H_2L^1) and 7,14-dimethyl-5,12-diphenyl-1,2,4,8,9,11-hexaazacyclotetradeca-7,14-diene-3,10-dione (H_2L^2), and their spectral and structural characterization.

Experimental

Materials and methods

Copper(II) acetate monohydrate, copper(II) chloride dihydrate, nickel(II) acetate tetrahydrate, and cobalt(II) acetate tetrahydrate were purchased from Sigma-Aldrich and used without purification. Reagent grade solvents were dried by refluxing over calcium hydride (acetonitrile) or magnesium turnings (methanol). Bis(acetonitrile)dichlorocopper(II) was prepared by reported procedure in literature via interaction of copper(II) chloride and excess acetonitrile with 97% yield.

MALDI TOF mass spectra were obtained with a Bruker Daltonics Ultraflex II spectrometer without use of a matrix. Electronic spectra from 190 to 900 nm were recorded on a Hitachi U-2900 UV–vis spectrophotometer. Reactions were monitored by thin-layer chromatography carried out on Merck silica gel 60 F254 coated plates.

Synthesis of μ-Cl₂-7,14-dimethyl-5,12-di(4-bromophenyl)-1,2,4,8,9,11–hexaazatetradeca-7,14–diene-3,10-dionecopper(II) $[Cu_2(H_2L^1)Cl_4]_n$. To a suspension of 7,14-dimethyl-5,12-di(4-bromophenyl)-1,2,4,8,9,11-hexaazatetradeca-7,14-diene-3,10-dione (0.065 g, 0.115 mM) in 10 mL dry acetonitrile was added a solution of Cu(MeCN)₂Cl₂ (0.049 g, 0.23 mM) in 10 mL dry acetonitrile and stirred for 4 h at room temperature. The resulting reaction mixture was evaporated in vacuo. The residue was washed with dry acetonitrile (2 × 2 mL) and resulting precipitate was collected, washed with hexane (1 × 5 mL), and dried under vacuum yielding the desired complex as yellow powder. Yield 85%. MS (MALDI): *m/z* 833.185 (calculated for [M + H]⁺ 833.200). UV–vis (DMSO) λ_{max} nm (lgε): 278 (89), 287(77).

General route for preparing Ni(II), Co(II), and Cu(II) complexes of 1,2,4,8,9,11-hexaazacyclotetradeca-3,10-diones. To a suspension of the corresponding macrocycle (1 equiv.) in 10 mL methanol was added a solution of metal acetate (metal = Ni(II), Co(II), Cu(II)) (2 equiv.) in 2 mL dry methanol under vigorous stirring. The resulting reaction mixture

was refluxed for 4 h and then evaporated in vacuo. The residue was washed with methanol (2×2 mL) and resulting precipitate was collected, washed with hexane (1×5 mL), and dried in vacuo yielding the desired complex as powder.

7,14-Dimethyl-5,12-di(4-bromophenyl)-1,2,4,8,9,11–hexaazatetradeca-7,14–diene-3,10-dionenickel(II) [Ni(L^1)]. Yield 85%. Anal. Calcd for $C_{22}H_{22}Br_2N_6NiO_2$: C, 42.55; H, 3.57; N, 13.53. Found: C, 42.68; H, 3.64; N, 13.63. MS (MALDI): *m/z* 623.531 (calculated for $[M + H]^+$ 623.232). UV–vis (DMSO) λ_{max} nm (lgε) 234.5 (87), 275 (89), 309 (77).

7,14-Dimethyl-5,12-diphenyl-1,2,4,8,9,11–hexaazatetradeca-7,14–diene-3,10-dionenickel (II) [Ni(L^2)]. Yield 82%. Anal. Calcd for $C_{22}H_{24}N_6NiO_2$: C, 57.05; H, 5.22; N 18.15. Found: C, 57.31; H, 5.42; N, 18.48. MS (MALDI): *m/z* 464.136 (calculated for $[M + H]^+$ 464.235). UV–vis (DMSO) λ_{max} nm (lgε) 235 (86), 275 (88), 308 (76).

7,14-Dimethyl-5,12-di(4-bromophenyl)-1,2,4,8,9,11–hexaazatetradeca-7,14–diene-3,10-dionecobalt(II) [Co(L^1)]. Yield 77%. Anal. Calcd for $C_{22}H_{22}Br_2N_6CoO_2$: C, 42.54; H, 3.57; N, 13.53. Found: C, 42.71; H, 3.65; N, 13.62. MS (MALDI): *m/z* 622.282 (calculated for $[M + H]^+$ 622.334). UV–vis (DMSO) λ_{max} nm (lgε): 233 (90), 274 (87), 309 (78).

7,14-Dimethyl-5,12-diphenyl-1,2,4,8,9,11–hexaazatetradeca-7,14–diene-3,10-dionecobalt (II) [Co(L^2)]. Yield 79%. Anal. Calcd for $C_{22}H_{24}N_6CoO_2$: C, 57.02; H, 5.22; N, 18.14. Found: C, 57.25; H, 5.38; N, 18.36. MS (MALDI): *m/z* 463.204 (calculated for $[M + H]^+$ 463.230). UV–vis (DMSO) λ_{max} nm (lgε): 233 (86), 274 (88), 307 (76).

7,14-Dimethyl-5,12-bis(*p*-bromophenyl)-1,2,4,8,9,11–hexaazatetradeca-7,14–diene-3,10-dionecopper(II) [Cu(L^1)]. Yield 81%. Anal. Calcd for $C_{22}H_{22}Br_2N_6CuO_2$: C, 42.22; H, 3.54; N, 13.43. Found: C, 42.54; H, 3.68; N, 13.81. MS (MALDI): *m/z* 625.981 (calculated for $[M + H]^+$ 624.945). UV–vis (DMSO) λ_{max} nm (lgε): 234 (98), 276 (87), 308 (77).

7,14-Dimethyl-5,12-diphenyl-1,2,4,8,9,11–hexaazatetradeca-7,14–diene-3,10-dionecopper(II) [Cu(L^2)]. Yield 75%. Anal. Calcd for $C_{22}H_{24}N_6CuO_2$: C, 49.64; H, 4.17; N, 15.79. Found: C, 56.46; H, 5.17; N, 17.96. MS (MALDI): *m/z* 467.152 (calculated for $[M + H]^+$ 467.135). UV–vis (DMSO) λ_{max} nm (lgε): 235 (89), 276 (89.3), 308 (78).

Structure determination

The synthesized compounds did not produce single-crystals suitable for X-ray diffraction. Moreover, only two of them, $[Cu_2(H_2L^1)Cl_4]_n$ and $[Ni(L^2)]$, respectively, provided X-ray powder patterns with sufficient number of well-resolved diffraction peaks that their crystal structures could be determined from powder diffraction data with the use of direct space search methods [28–36].

The X-ray powder diffraction data for $[Cu_2(H_2L^1)Cl_4]_n$ and $[Ni(L^2)]$ were collected on a Panalytical EMPYREAN instrument with a linear X'celerator detector using

non-monochromated Cu Kα radiation. The powder was sprinkled onto oriented silicon plate which, to improve the powder averaging, was rotated during measurements at a rate of 120 rpm.

The monoclinic cell dimensions were determined using three indexing programs: TREOR90 [37], ITO [38], and AUTOX [39, 40]. The powder pattern of $[Ni(L^2)]$ contains some very weak peaks (d spacings = 11.511, 9.756, 8.237, 7.673, 6.874, 5.991, 5.745, 5.485 Å, and some others) from an unknown impurity. Based on systematic extinctions, the space groups for $[Cu_2(H_2L^1)Cl_4]_n$ and $[Ni(L^2)]$ were determined as $P2_1/n$ and $P2_1/c$, respectively. The unit-cell parameters and space groups were further tested using a Pawley fit [41] and confirmed by crystal structure solution. Each crystal structure has been solved with the use of simulated annealing technique [42] following the methodology described in our recent publication [27]. The solutions found were fitted with the program MRIA [43] using a split-type pseudo-Voigt peak profile function [44]. In the bond-restrained Rietveld refinement, restraints were applied to the intramolecular bond lengths and contacts (<2.6 Å), the strength of the restraints was a function of interatomic separation and, for intramolecular bond lengths, corresponded to rms deviation of 0.02 Å. Additional restraints were applied to the planarity of the benzene ring with the attached non-H atoms, with the maximal allowed deviation from the mean plane 0.03 Å. In $[Cu_2(H_2L^1)Cl_4]_n$, all non-H atoms were isotropically refined, while in $[Ni(L^2)]$ one common isotropic displacement parameter U_{iso} was refined to 0.145(9) Å for all non-H atoms. Hydrogens were positioned geometrically (N–H 0.86 Å; C–H 0.93–0.98 Å) and not refined. The crystal data, data collection, and refinement parameters for $[Cu_2(H_2L^1)Cl_4]_n$ and $[Ni(L^2)]$ are given in table 1.

The molecular structure of $[Cu_2(H_2L^1)Cl_4]_n$ is shown in figure 1, the molecular structure of $[Ni(L^2)]$ is shown in figure 2. The diffraction profiles after the final bond-restrained Rietveld refinements are shown in figure 3.

Table 1. Crystallographic data for $[Cu_2(H_2L^1)Cl_4]_n$ and $[Ni(L^2)]$.

	$[Cu_2(H_2L^1)Cl_4]_n$	$[Ni(L^2)]$
Empirical formula	$C_{22}H_{24}Br_2Cl_4Cu_2N_6O_2$	$C_{22}H_{24}N_6NiO_2$
Formula weight	833.18	463.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	11.7706(15)	12.6259(19)
b (Å)	13.4030(17)	8.9029(16)
c (Å)	8.8830(13)	10.1508(16)
β (°)	96.366(18)	112.376(17)
V (Å³)	1392.8(3)	1055.1(3)
M_{20}[a]	43	29
F_{30}[b]	75 (0.007, 39)	53 (0.008, 49)
Z	2	2
Wavelength (Å)	1.5418	1.5418
ρ_{Calcd} (g/cm³)	1.987	1.458
μ (mm⁻¹)	9.067	1.592
$2\theta_{min}$–$2\theta_{max}$, increment (°)	5.00–80.00, 0.017	5.00–70.00, 0.008
Number of parameters/restraints	111/51	82/62
$R_p/R_{wp}/R_{exp}$[c]	0.020/0.024/0.021	0.018/0.025/0.015
Goodness-of-fit	1.145	1.626

[a]M_{20} is defined according to [45].
[b]F_{30} is defined according to [46].
[c]R_p, R_{wp}, and R_{exp} are defined according to [47].
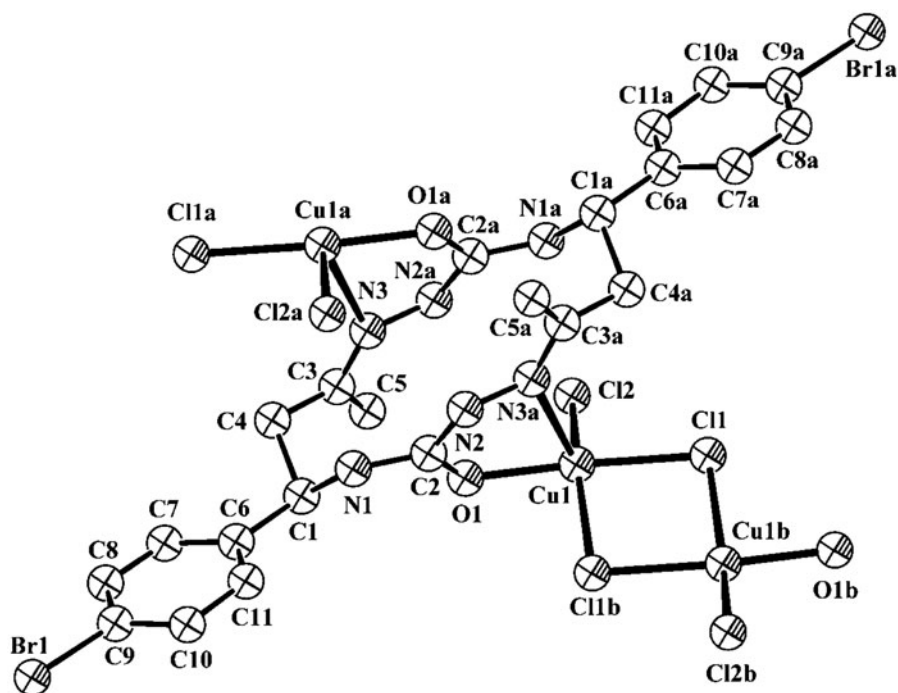
Figure 1.   A portion of the crystal structure of $[Cu_2(H_2L^1)Cl_4]_n$ showing the atom numbering and 50% probability displacement spheres.
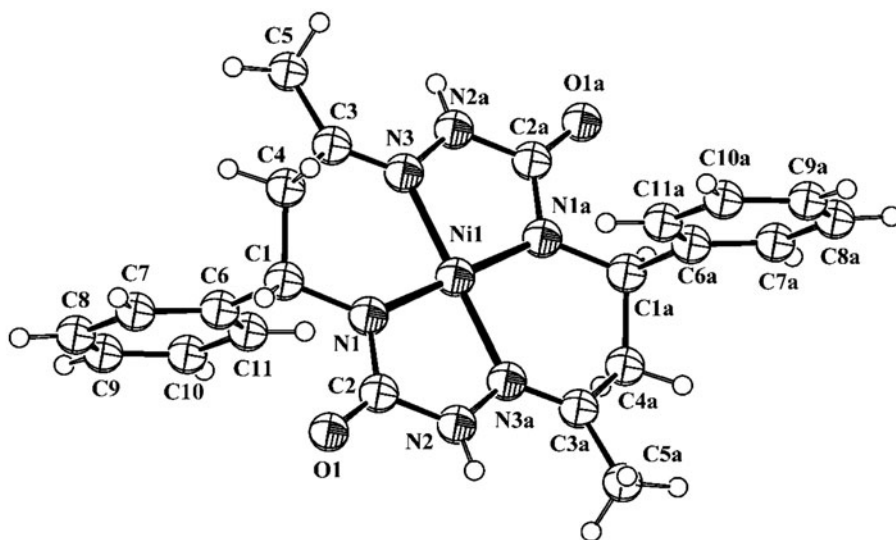Notes: Symmetry codes: (a) $2 - x$, $-y$, $2 - z$; (b) $2 - x$, $-y$, $3 - z$. Hydrogens are omitted for clarity.

Figure 2.   The molecular structure of $[Ni(L^2)]$ showing the atom numbering and 50% probability displacement spheres.
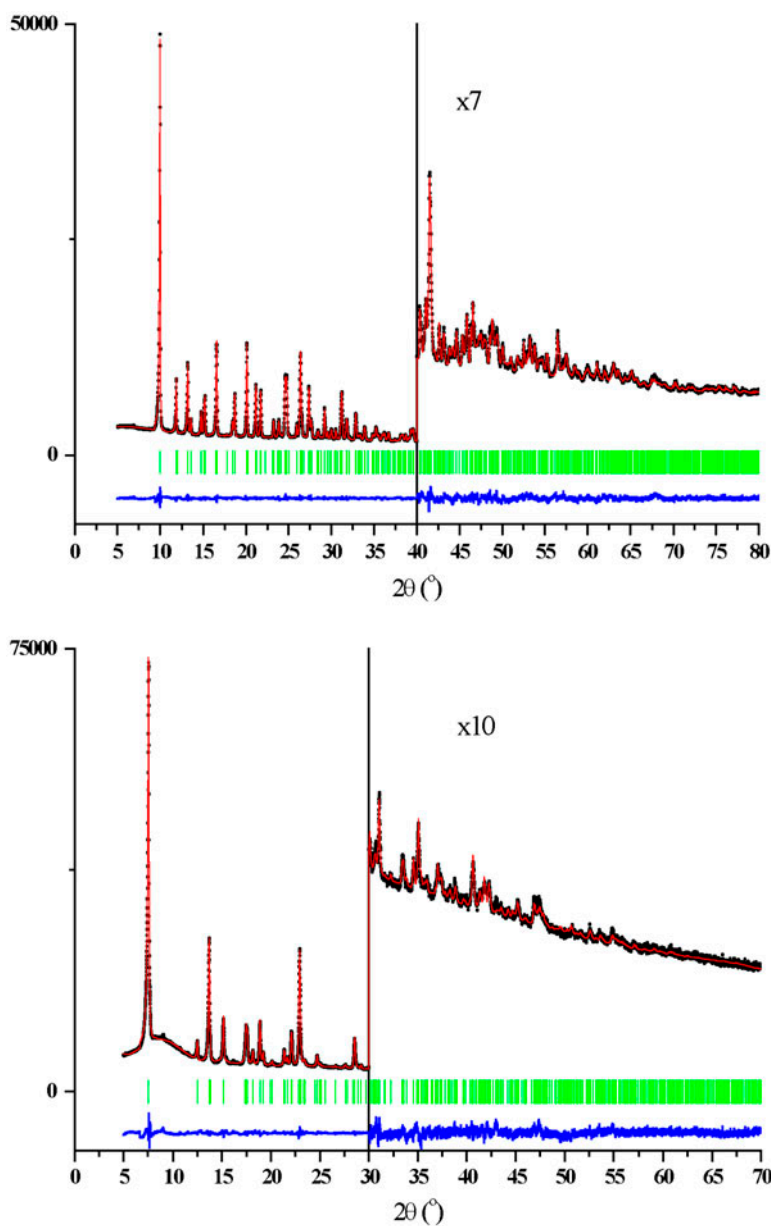Note: Symmetry code: (a) $1 - x$, $1 - y$, $1 - z$.

Figure 3. The Rietveld plots for $[Cu_2(H_2L^1)Cl_4]_n$ (top) and $[Ni(L^2)]$ (bottom) showing the experimental (black dots), calculated (red), and difference (blue) curves. The vertical bars denote calculated positions of the diffraction peaks (see http://dx.doi.org/10.1080/00958972.2014.961442 for color version).

Discussion

We have used reaction of $CuCl_2$ and 5,12-di(4-bromophenyl)-7,14-dimethyl-1,2,4,8,9, 11-hexaazacyclotetradeca-7,14-diene-3,10-dione (H_2L^1) in refluxing acetonitrile for prepara- tion of $[Cu_2(H_2L^1)Cl_4]_n$ (scheme 1). We used bis(acetonitrile)dichlorocopper(II) complex
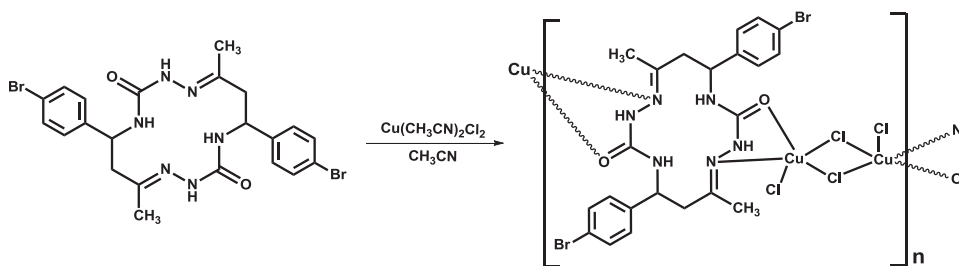
Scheme 1. The synthesis of bridged μ-Cl$_2$ copper complex [Cu$_2$(H$_2$L^1)Cl$_4$]$_n$.

for preparing copper complex with H$_2$L^1 because of the existence of weak bonds Cu–N in acetonitrile complex and, thereby, rapid substitution by other chelating groups as shown earlier in the metallation of porphyrins and other heteroazamacrocycles [48]. Bis(acetonitrile)-dichlorocopper(II) was prepared by known literature procedure via interaction of copper(II) chloride with excess acetonitrile with 97 yield% [49]. The significant advantages of this reaction are short reaction time, high yields, and easy work up.

The UV/Vis spectrum of H$_2$L^1 (figure 4) shows two peaks at 265 and 268 nm, which are assigned to C=N imine group transitions [50] and two peaks at 310 and 318 nm correspond to π–π* transitions of benzene rings. In [Cu$_2$(H$_2$L^1)Cl$_4$]$_n$, two peaks of H$_2$L^1 become broader and red-shifted to 278 and 287 nm, respectively, as a result of coordination. In this spectrum we did not observe d–d transitions of copper(II), since they should be observed at $\lambda > 450$ nm [51, 52].

MALDI TOF mass spectra of dinuclear copper(II) complex [Cu$_2$(H$_2$L^1)Cl$_4$]$_n$ were studied in positive mode without matrix. The MALDI TOF-MS data show the parent ion peak indicating the stability of the structure in solid and gas phases. The experimental results prove that the compound [Cu$_2$(H$_2$L^1)Cl$_4$]$_n$ has no impurities; its spectrum demonstrates only one cluster of molecular ion.

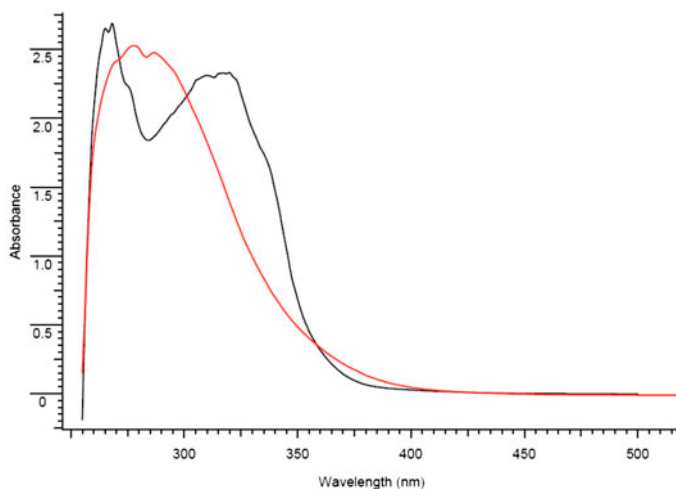Figure 4. UV–vis spectrum of [Cu$_2$(H$_2$L^1)Cl$_4$]$_n$ (red line) and H$_2$L^1 (black line) (see http://dx.doi.org/10.1080/00958972.2014.961442 for color version).

The crystal structure of $[Cu_2(H_2L^1)Cl_4]_n$ was investigated by X-ray powder diffraction. There are many examples in literature [53–56] for copper and other transition metals forming complexes with semicarbazide and amide ligands via N,O binding.

In $[Cu_2(H_2L^1)Cl_4]_n$, the Cu_2Cl_4 units and macroheterocyclic molecules are situated on inversion centers. Each Cu(II) is five-coordinate by N and O from the macroheterocyclic ligand [Cu–N 2.340(14) Å, Cu–O 1.952(11) Å], two bridging chlorides, and one terminal chloride (figure 1); its coordination geometry is distorted square-base pyramidal ($\tau = 0.29$). The parameter τ is defined as $(\beta-\alpha)/60$ [in our case β (Cl1–Cu1–O1) = 173.2(3)° and α (Cl2–Cu1–Cl1 $(2 - x, -y, 3 - z)$) = 156.1(2)°] and its value varies from 0 (regular square-base pyramidal) to 1 (regular trigonal bipyramidal) [57]. In the Cu_2Cl_4 unit, the coordinating Cu–Cl bond lengths are 2.279(5)–2.332(6) Å and Cu···Cu distance is 3.394(4) Å.

The most striking feature of $[Cu_2(H_2L^1)Cl_4]_n$ is unusual conformation of macroheterocycle, where O1 and C5a (figure 1) are in *trans*-positions to the N2–N3a bond situated between them, while in all other compounds investigated [27], these atoms were in *cis*-positions. Significant deformation of the ligand along the line between the two spiro atoms exist – the C1···C1a distance in $[Cu_2(H_2L^1)Cl_4]_n$ is 7.15(3) Å, while in free ligand (H_2L^1) the C1···C1a distance was 5.75(3) Å in the monoclinic polymorph and 6.13(3) Å in the triclinic polymorph [27]. The macroheterocyclic ligands in $[Cu_2(H_2L^1)Cl_4]_n$ serve as tetradentate linkers which bridge the Cu_2Cl_4 units into polymeric chains propagated in [0 0 1] (figure 5; prepared with Mercury [58]). N–H···Cl hydrogen bonds (table 2) are observed within the polymeric chain.

In the earlier reported polymeric complexes with similar ligands, $[CuLN_3]_n[ClO_4 \cdot 3/2H_2O]_n$ (L = 3,10-bisbenzyl-1,3,5,8,10,12-hexaazacyclotetradecane or 3,10-bisbenzyl-6,13-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane), Cu(II) ions are bridged by single azide in the μ-1,3 (end-to-end) bridging mode in a *trans*-position with respect to the azide, and each heterocyclic ligand forms bonds with one copper [59].

Our attempts to obtain the same polymeric complexes with nickel(II) and cobalt(II) varying reaction conditions and metal sources failed. Most probably, this failure was caused by
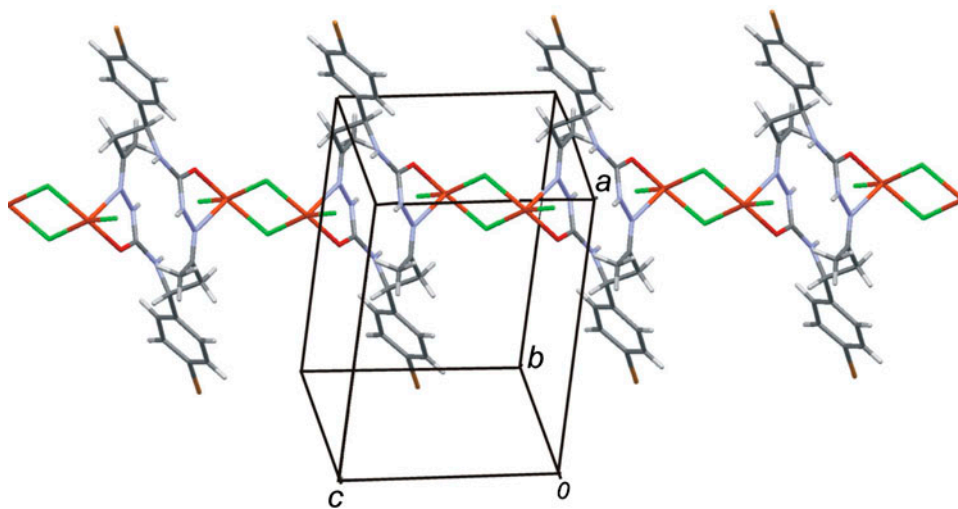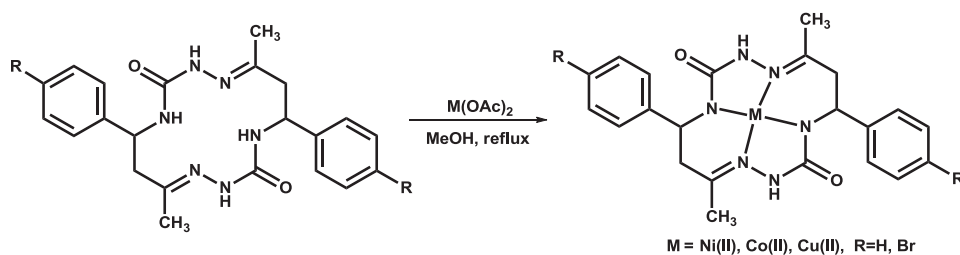

Figure 5.   A polymeric chain in the crystal structure of $[Cu(H_2L^1)Br_2Cl_4]_n$.

Table 2. Hydrogen-bonding geometry (Å, °) in $[Cu_2(H_2L^1)Cl_4]_n$ and $[Ni(L^2)]$.

	D–H···A	D–H	H···A	D···A	D–H···A
$[Cu_2(H_2L^1)Cl_4]_n$	N2–H2···Cl2i	0.86	2.60	3.128(14)	121
	N1–H1···Cl2i	0.86	2.82	3.333(14)	120
$[Ni(L^2)]$	N2–H2···O1ii	0.86	1.92	2.764(15)	165

Note: Symmetry codes: (i) $2 - x, -y, 2 - z$; (ii) $1 - x, -y, 1 - z$.

Scheme 2. The synthesis of complexes (ML^1 and ML^2) via reaction of ligands (H_2L^1 and H_2L^2) with metal acetates.
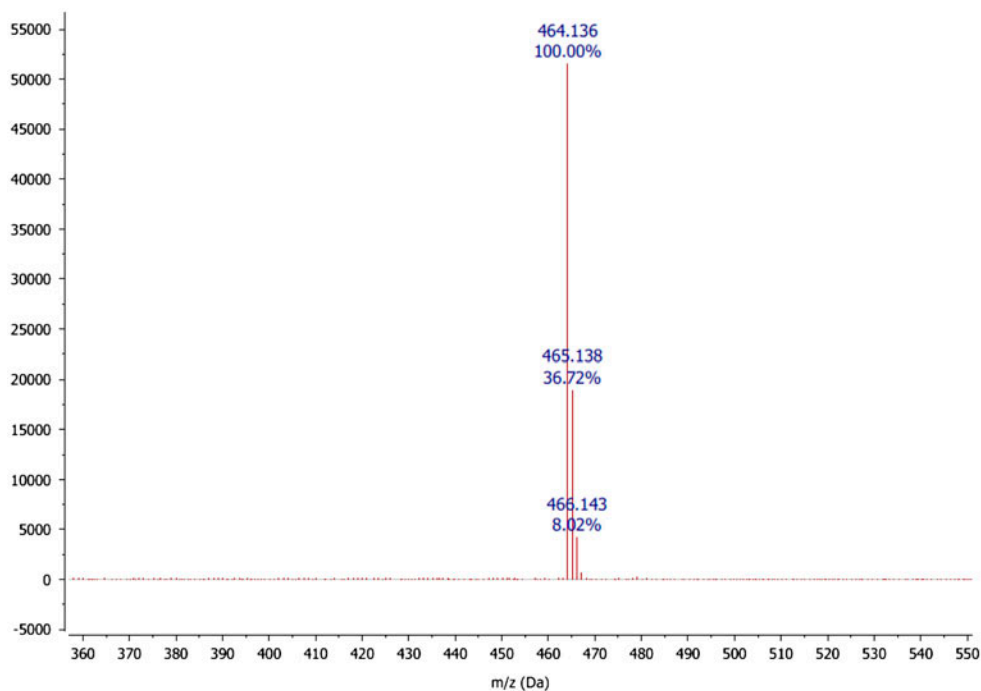

Figure 6. MALDI TOF mass spectrum for $[NiL^2]$.

the poor stability of dinuclear Ni(II) and Co(II) complexes with five-coordinate metal centers bridged through two chlorides – only a few examples of such complexes with additional stabilization by phenolate ligands were found in the literature [60].

ML^1 and ML^2 (M = Cu, Co, Ni) were synthesized by the reaction of corresponding metal acetates (M(OAc)$_2$, M = Cu, Co, Ni) with 5,12–diphenyl-7,14-dimethyl-1,2,4,8,9,11-hexaazacyclotetradeca-7,14-diene-3,10-dione (H$_2$L^2) and 5,12-di(4-bromophenyl)-7,14-dimethyl-1,2,4,8,9,11-hexaazacyclotetradeca-7,14-diene-3,10-dione (H$_2$L^1) in refluxing methanol (scheme 2).

Metal acetates are weak acids causing deprotonation of amide in macrocyclic ligands (H$_2$L^1, H$_2$L^2) and producing complexes via coordination of metal ion by four nitrogens.

The MALDI TOF mass spectra of metal complexes were carried out in positive and negative modes without the use of a matrix. The MALDI TOF data show the complex ion peak, indicating stability of the structure both in solid and gaseous phases. The MALDI TOF mass spectral data of the complexes confirm the proposed formulas of the complexes. MALDI TOF-MS spectra of [NiL^2] and [CoL^2] are presented in figures 6 and 7, showing molecular ion peaks 464.136 and 463.204, respectively.

The UV/Vis spectra for the complexes were obtained in DMSO solution (table 3). The spectra display intense absorbance at 230–310 nm due to intramolecular (π–π^*) electron transitions. The UV spectra of metal complexes display intense absorbance at 260–290 nm due to intraligand charge transfer and are assigned to π–π^* transitions of benzene rings and C=N. We did not observe peaks from 450 to 800 nm to assign to d–d transitions of four-coordinated metal. It may be lost in the low energy tail of the charge transfer transition. Coordination compounds exhibit strong charge-transfer absorptions, typically in the ultraviolet and/or visible portion of the spectrum, much more intense than d–d transitions. Many ligands give highly colored complexes that have a series of overlapping absorption bands in
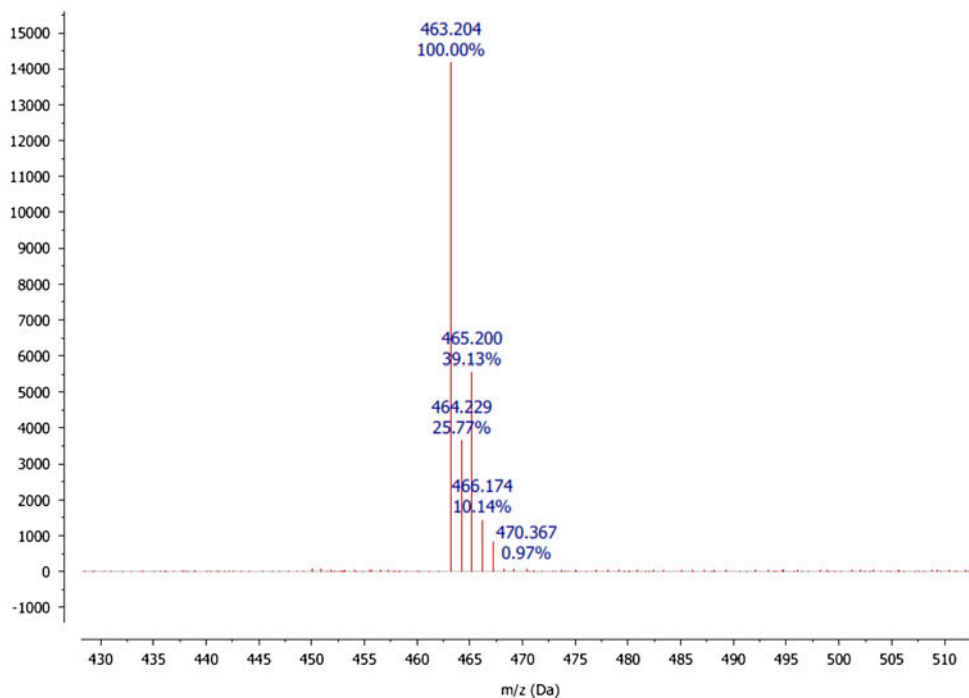

Figure 7.   MALDI TOF mass spectrum for [CoL^2].

the ultraviolet part of the spectrum as well as the visible. In such cases, the d–d transitions may be completely overwhelmed and essentially impossible to observe.

Absorption peaks in the spectra of the complexes are all red-shifted and broadened as compared to the peaks in the spectra of the ligands due to formation of the M(II)–N (M = Ni, Co, Cu) bonds which affect the π–π conjugative system. As shown in figure 8, formation of CuL^2 with four-coordinate copper results in the red shift by 18 nm as compared to the spectra of free H_2L^2.

The structure of Ni(II) complex with 7,14-dimethyl-5,12-diphenyl-1,2,4,8,9,11-hexaaza-tetradeca-7,14-diene-3,10-dione (H_2L^2) was studied by X-ray powder diffraction. In NiL^2, Ni(II), situated on an inversion center, has a distorted square-planar coordination formed by four nitrogens from the macroheterocyclic ligand [Ni–N 1.860(11), 1.900(11) Å] as shown in figure 2. In the crystal, intermolecular N–H···O hydrogen bonds (table 2) link the molecules related by translation along the axis b into chains as shown in figure 9 (prepared with the program Mercury [58]).

The bond lengths and angles in all compounds are standard and correspond well to those found in the Cambridge Structural Database [61] for the structures containing similar molecular fragments.

Table 3. Electronic spectral data of ligands and complexes in DMSO.

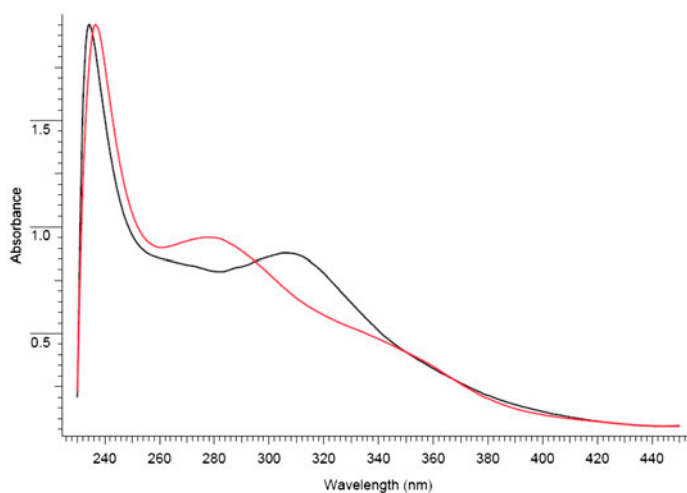| Compound	λ_{max} (nm) (ε M^{-1} cm^{-1})
H_2L^1	265 (90), 268 (87), 310 (76)
H_2L^2	266 (91), 268.5 (88), 305 (74)
$[NiL^1]$	234.5 (87), 275 (89), 309 (77)
$[NiL^2]$	235 (86), 275 (88), 308 (76)
$[CoL^1]$	233 (90), 274 (87), 309 (78)
$[CoL^2]$	233 (86), 274 (88), 307 (76)
$[CuL^1]$	234 (98), 276 (87), 308 (77)
$[CuL^2]$	234 (98), 276 (87), 308 (77)

Figure 8. UV/Vis spectra of $[CuL^2]$ (black line) and H_2L^2 (red line) (see http://dx.doi.org/10.1080/00958972.2014.961442 for color version).
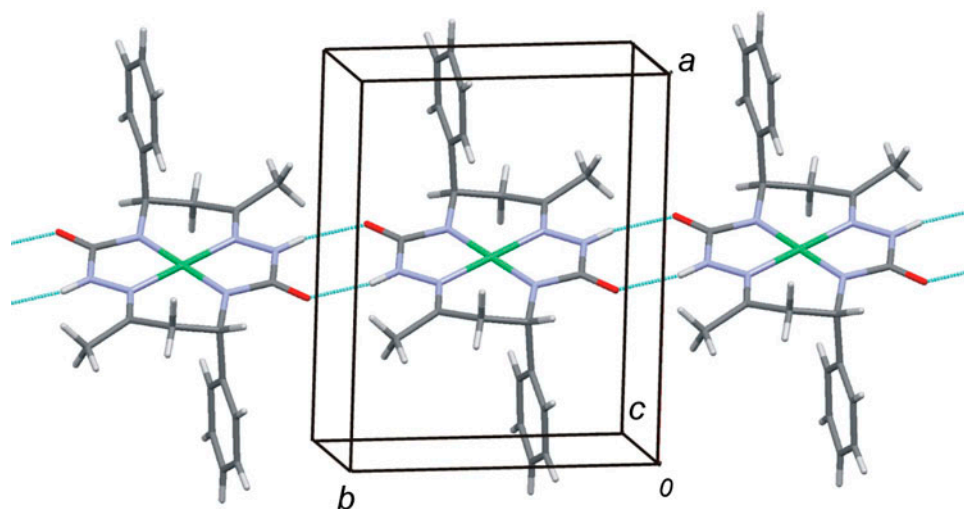
Figure 9. Hydrogen-bonded chain of the molecules in the crystal structure of NiL^2. N–H···O hydrogen bonds are shown by thin green lines (see http://dx.doi.org/10.1080/00958972.2014.961442 for color version).

In contrast to the earlier reported copper(II) complex with a similar ligand, $[CuL(N_3)_2]$ (L = 3,10-bisbenzyl-1,3,5,8,10,12-hexaazacyclotetradecane) [59], which consists of one $[CuL]^{2+}$ and two azide counterions and each copper has axially distorted octahedral geometry, our complexes are formed by deprotonated heterocyclic ligands.

Conclusion

We have synthesized and characterized seven complexes of Ni(II), Co(II), and Cu(II) with hexaazamacrocyclic ligands (H_2L^1, H_2L^2) by various physical methods including UV–vis electronic absorption spectra, MALDI TOF-MS. Crystal structures of two compounds, $[Cu_2(H_2L^1)Cl_4]_n$ and $[NiL^2]$, were determined from X-ray powder diffraction data.

Supplementary material

Crystallographic data for $[Cu(H_2L^1)Cl_4]_n$ and $[NiL^2]$ have been deposited – CCDC Nos. 959883 and 959884, respectively – with the Cambridge Crystallographic Data Center [CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1233 336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)].

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