Copper(II), Nickel(II), Cobalt(II), and Chromium(III) Complexes Based on 6,6′-Bis{[methyl(oxido)imino]methyl}-2,2′-bipyridine

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The bipyridine-based ligand 6,6′-bis{[methyl(oxido)imino]methyl}-2,2′-bipyridine (L) reacts with copper(II) chloride in methanol to produce a tetrachlorocuprate(II) salt [CuL][$CuCl_4$] (**1**). Reactions of equimolar quantities of $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ with L in methanol produce compounds [$ML(NO_3)_2$] (M = Ni (**2**), M = Co (**3**)). Reaction of $Cr(NO_3)_3 \cdot 6H_2O$ with L affords [$Cr(L)(H_2O)_2$]$(NO_3)_3 \cdot 0.5H_2O$ (**4**). The structures of compounds **1** – **4** were determined by X-ray diffraction. In all four complexes L exhibits the tetradentae chelating mode of coordination.

Key words: Bipyridine-*bis*-nitrone Complexes, Copper(II), Nickel(II), Cobalt(II), Chromium(III)

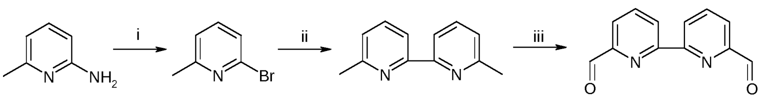
Introduction

Substituted bipyridine derivatives have found numerous applications in design and construction of artificial proteins and in modeling active sites of metalloenzymes. The utility of modified bipyridine ligands can be illustrated, for example, by the syntheses of (*S*)-2-amino-3-(2,2′-bipyridin-4-yl)- and (*S*)-2-amino-3-(2,2′-bipyridin-5-yl)propanoic acids [1] as well as (*S*)-2-amino-3-(2,2’-bipyridine-6-yl)propanoic acid [2, 3] which, when incorporated into the rationally designed peptide sequences, form on addition of metal ions the synthetic metalloproteins. A few unnatural 6,6′-bis(acylamino)-2,2′-bipyridine-based amino acids were synthesized and incorporated in different peptides as metal binding β-turn mimics [4]. Their ability to nucleate the formation of the β-sheet structure by coordination to copper(II) was investigated by spectroscopic methods. In order to predict the geometry around the Cu(II) atom in peptides containing these β-turn mimics three model compounds were prepared, *viz.* 6,6′-bis(phenylacetamide)-2,2′-bipyridine as well as its deprotonated (neutral) and 2+ charged (protonated) Cu(II) complexes, and their structures were established by X-ray crystallography [4].

2,2′-Bipyridine-4,4′-dicarboxylic acid was covalently attached to the N-terminus of a 15-residue amphiphilic peptide, and a three-α-helix bundle protein was synthesized using an iron(II) *tris*-bipyridine complex as a template [5]. Furthermore, the four diastereomeric forms obtained for the Fe(II) complex of three unsymmetrical bidentate ligands are in accordance with the metastable states of this template-assembled protein [6]. The analogous approach was employed in work [7] in which 5-carboxy-2,2′-bipyridine was coupled to the N-terminus of a 15-residue peptide that underwent trimerization in the presence of transition metal cations.

To model the features of active sites of natural phosphodiesterases the copper(II) complexes of the ammonium-substituted ligands 6,6′-($Me_2(H)N^+$-$CH_2C{\equiv}C$)$_2$bipy and 6,6′-(Me_3N^+-$CH_2C{\equiv}C$)$_2$bipy have been prepared and investigated [8].

Ferrocenyl ligands bearing one or two bipy subunits can be used for electrochemical recognition of certain metal cations [9]. As a rule, coordination of the (*mono*)bipy substituted ferrocenes leads to a gradual positive shift in the Fc/Fc^+ redox potential (one-wave-behavior) due to electrostatic repulsion between the bound cation and the positive charge on the oxidized ferrocenyl subunit. Oxidation of the ferrocene center is accompanied by a destabilization of the resultant complex. Bis(bipy)-substituted ferrocenes form much more stable complexes with the stoichiometry 1 : 1 and ex-

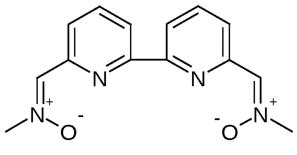


Scheme 1.

hibit *a sandwich effect* that gives rise to a two-wave behavior – the growth of a new redox wave at the expense of the original wave for the free ligand [9].

The cited papers are only a small selection from many others that demonstrate the importance of further development of bipyridine-like ligands.

The coordination chemistry of nitrones attracts a growing interest. Nitrone complexes are shown to be intermediates in metal catalyzed nucleophilic additions and cycloadditions with electron-rich alkenes. As part of our continuing study on coordinative properties of heterocyclic nitrones [10 – 12], we describe here the synthesis of a 2,2′-bipyridine ligand containing two nitrone groups in 6,6′-positions, adjacent to the ring N atoms.



L

The preparation and crystal structures of its complexes $[Cu(L)][CuCl_4]$ (**1**), $[Ni(L)(NO_3)_2]$ (**2**), $[Co(L)(NO_3)_2]$ (**3**), and $[Cr(L)(H_2O)_2](NO_3)_3 \cdot 0.5H_2O$ (**4**) are also reported in this paper.

Results and Discussion

The ligand L was obtained by condensation of 2,2′-dipyridyl-6,6′-dicarbaldehyde with *N*-methylhydroxylamine (see Experimental Section). The starting dicarbaldehyde was synthesized from 2-amino-6-methylpyridine in three steps, which include formation of 2-bromo-6-methylpyridine, subsequent bis-aryl coupling on a Pd/C catalyst and finally oxidation of the methyl groups to aldehydes. The sequence of reactions is shown in Scheme 1.

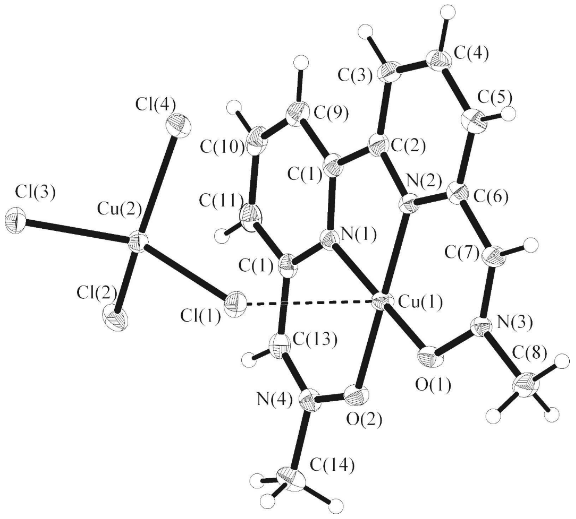


Fig. 1a. Molecular unit of $[CuL][CuCl_4]$ (**1**). Selected bond lengths and angles: Cu(1)–O(2) 1.920(2), Cu(1)–O(1) 1.932(2), Cu(1)–N(1) 1.941(3), Cu(1)–N(2) 1.953(3) Å; N(1)–Cu(1)–N(2) 82.5(3), O(1)–Cu(1)–N(2) 94.0(3), O(2)–Cu(1)–N(1) 95.3(3), O(2)–Cu(1)–O(1) 88.4(3)°.

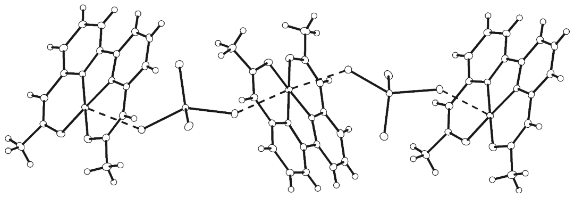


Fig. 1b. Fragment of the one-dimensional chain of cations and anions in $[CuL][CuCl_4]$ (**1**).

The coordination ability of ligand L was tested on Cu(II), Ni(II), Co(II) and Cr(III) ions. Reaction of L with copper(II) chloride in methanol in both 1 : 1 and 1 : 2 molar ratio leads to a rapid precipitation of the tetrachlorocuprate(II) salt $[Cu(L)][CuCl_4]$ (**1**). Green crystals of **1** suitable for X-ray analysis were grown by slow diffusion of a dichloromethane solution of L and a methanol solution of copper(II) chloride through an "empty" CH_3OH/CH_2Cl_2 layer. The complexes **2** (brown), **3** (deep red) and **4** (red) were produced from methanol solutions containing equimolar amounts of L and of the corresponding nitrate. The method employed for obtaining crystals of **1** has enabled us also to grow crystals of compounds **2**, **3** and **4** in the solvent system CH_3OH/CH_2Cl_2.

The X-ray diffraction study of **1** reveals the structure shown in Fig. 1a. The unit cell consists of $[Cu(L)]^{2+}$ cations and tetrachlorocuprate(II) anions. In the $CuCl_4^{2-}$ anion the copper atom adopts a coordination geometry intermediate between tetrahedral and square-planar: the sum of the four *cis* angles is 389.7° compared to the ideal sums of 438° for tetrahedral and 360° for planar geometry. The *trans* angles are 135.4(3) and 140.1(4)°, and the Cu–Cl distances are in the range from 2.223(3) to 2.284(3) Å. The ligand L coordinates to the copper(II) ion tetradentately *via* the two nitrogen atoms of the pyridine rings and the two oxygen atoms of the nitrone groups. The coordination polyhedron of copper is square-planar despite of a deviation of the N(3)–O(1) nitrone group from the plane of the pyridine ring (torsion angle N(2)–C(6)–C(7)–N(3) −8.2(5)°). The nitrone fragments O(1)–N(3)–C(8)–C(7) and O(2)–N(4)–C(14)–C(13) are planar within 0.005 and 0.009 Å, respectively. The coordination sphere of the copper atom is completed by long axial bonds Cu(1)–Cl(1) 2.284(1) Å and Cu(1)–Cl(3′) 2.275(1) Å. These interactions link the $[Cu(L)]^{2+}$ cations and the $CuCl_4^{2-}$ anions into infinite chains running parallel to the (0 1 0) crystallographic axis (Fig. 1b). The chlorine atoms Cl(1) and Cl(3′) occupy the two semicoordinate sites in the coordination environment of Cu(1). Therefore the coordination around the Cu(1) atoms can be considered as $4+2$, and the $CuCl_4^{2-}$ ions can be assumed as bridging ligands. The bridging angles Cu(1)–Cl(1)–Cu(2) and Cu(1)–Cl(3′)–Cu(2′) are 119.4° and 134.7°, respectively. The majority of the known tetrachlorocuprate(II) compounds are salts of organic cations, usually protonated N-heterocycles and alkylamines [13–22]. Together with a number of complexes where the $CuCl_4^{2-}$ anions are involved in coordination to other copper(II) ions [13, 23, 24], there is also one example of a Cu(I) complex, whose charge is compensated by a $CuCl_4^{2-}$ anion [25].

Neighboring chains in the crystal of complex **1** are bound together by sets of C–H ··· Cl and stacking interactions. It should be noted that each chlorine atom forms three contacts. Based on the geometrical parameters some of them may be considered as weak hydrogen bonds, namely Cl(3) ··· H–C(5′) 2.63 Å (angle Cl ··· H–C 148°) and Cl(4) ··· H–C(11′) 2.66 Å (Cl ··· H–C 168°). Other interactions correspond to strong electrostatic attraction: Cl(1) ··· H–C(14′) 2.93 Å, Cl(1) ··· H–C(13′) 2.81 Å, Cl(1) ··· H–C(10′) 2.74 Å, Cl(3) ··· H–C(4′) 2.76 Å, Cl(3) ··· H–C(7′) 2.80 Å, Cl(4) ··· H–C(14′) 2.80 Å, Cl(4) ··· H–C(8) 2.73 Å (sum of van der Waals radii [26] 2.96 Å). A significantly different environment is observed in the case of the Cl(2) atom which is involved in one weak hydrogen bond [Cl(2) ··· H–C(3′) 2.62 Å (Cl ··· H–C is 172°)], one electrostatic attraction [Cl(2) ··· H–C(9′) 2.95 Å] and an interaction with one of the pyridine rings [Cl(2) ··· C(7′) 3.394 Å (sum of van der Waals radii 3.51 Å)]. Taking into account the value of the Cu(1)–Cl(2) ··· C(7′) angle (104.3°) this interaction should rather be described as a repulsive interaction [27].

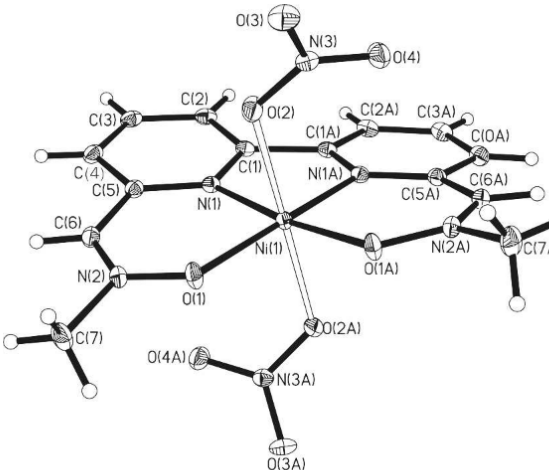


Fig. 2a. Molecular unit of $[NiL(NO_3)_2]$ (**2**). Selected bond lengths and angles: Ni(1)–N(1) 1.995(3), Ni(1)–O(1) 2.000(3), Ni(1)–O(2) 2.126(3) Å; N(1A)–Ni(1)–N(1) 81.8(5), N(1)–Ni(1)–O(1) 92.8(4), O(1)–Ni(1)–O(1A) 92.9(4), O(1)–Ni(1)–O(2) 86.8(3)°.

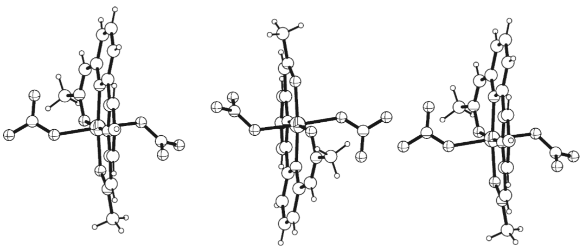


Fig. 2b. Fragment of one-dimensional chain of $[NiL(NO_3)_2]$ (**2**) formed by interactions of the nitrate anions.

Additional attraction between neighboring chains is provided by the stacking of pyridine rings. The distance of 3.301 Å between the parallel planes indicates the presence of strong stacking interactions between the π systems of the aromatic rings.

The crystal structure of **2** is shown in Figs. 2a, 2b. The nickel(II) atom occupies a special position at a crystallographic center of symmetry and has a distorted octahedral environment. The ligand L is disposed in the equatorial plane of the octahedron and coordinates to the nickel atom *via* the nitrogen atoms of the two pyridine rings (Ni(1)–N(1) 1.995(3) Å) and the oxygen atoms of the two nitrone groups (Ni(1)–O(1) 2.000(3) Å). The axial positions of the octahedron are occupied by oxygen atoms of two nitrate anions

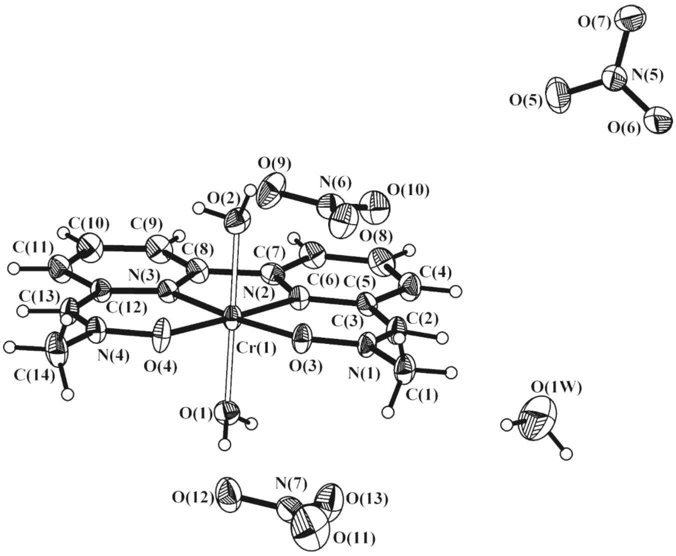


Fig. 3. Molecular unit of $[Cr(L)(H_2O)_2](NO_3)_3 \cdot 0.5H_2O$ (**4**): Cr(1)–O(4) 1.945(2), Cr(1)–O(3) 1.958(2), Cr(1)–O(1) 1.997(3), Cr(1)–O(2) 2.006(1), Cr(1)–N(3) 2.010(3), Cr(1)–N(2) 2.030(4) Å; O(3)–Cr(1)–N(2) 92.9(1), O(4)–Cr(1)–N(3) 93.3(1), N(3)–Cr(1)–N(2) 81.3(2)°.

(Ni(1)–O(2) 2.126(3) Å). The N(1)–Ni(1)–N(1A) bite angle shows a significant deviation from the ideal octahedron (81.8(5)°) because of the geometric constraints imposed by the bipyridine moiety. The bite angle in the six-membered N,O-chelate ring, N(1)–Ni(1)–O(1), is 92.8(4)°. Both chelating units show some deviation from planarity. So, the torsion angle between the two pyridine rings is −10.6(1)°. The nitrone fragment O(1)–N(2)–C(7)–C(6) is planar within 0.002 Å, and the torsion angle with the adjacent pyridine ring N(1)–C(5)–C(6)–N(2) is equal to 6.8(2)°. The angle between the O ··· O and N ··· N lines is 6.3°.

The crystal packing of compound **2** is very similar to that of **1**, but no coordination polymers are present. The molecules of **2** form infinite chains with contacts between nitrate anions (Fig. 2b). The two nitrate anions form parallel planes in such way that the N–O bonds are placed in a head-to-tail manner providing electrostatic attraction between the negatively charged oxygen and positively charged nitrogen atoms. The N ··· O distance of 3.059 Å is longer than the sum of the corresponding van der Waals radii (2.79 Å). Neighboring chains of **2** are bound together in a way similar to that of **1**. There are sets of C–H ··· O interactions with participation of the oxygen atoms of nitrate anions and stacking interactions between bipyridyl ligands (the distance between the average planes is 3.283 Å). The O(3) atom forms one weak hydrogen bond O(3) ··· H–C(3) [2.39 Å, O ··· H–C 121°] and has three additional attractive contacts: O(3) ··· H–C(4) 2.60 Å, O(3) ··· H(7A)–C(7) 2.51 Å, and O(3) ··· H(7B)–C(7) 2.47 Å. Other oxygen atoms are also involved in attractive interactions: O(2) ··· H–C(4) 2.71 Å, O(2) ··· H–C(6) 2.69 Å, and O(4) ··· H–C(2) 2.57 Å. It should be noted that the oxygen atom of the nitrone group also has such an interaction (O(1) ··· H–C(7) 2.56 Å).

In the X-ray diffraction study of **3** it has been demonstrated that this compound is isostructural with **2**. This concerns both the molecular structure and the crystal packing.

The X-ray diffraction study of **4** has shown that the presence of water drastically changes the structure of the complex (Fig. 3). The asymmetric part of the unit cell contains a $[Cr(L)]^{3+}$ cation, three $[NO_3]^-$ anions and 2.5 water molecules. The ligand L coordinates to the chromium(III) ion in the same way as to the other metal cations in compounds **1**–**3**. The chromium atom adopts an octahedral coordination. The nitrone ligand is situated in the equatorial plane and the two water molecules occupy the axial positions. The coordinative bonds are within the range 1.945–2.030 Å. It should be noted that all Cr–O bonds (1.945–2.006 Å) are slightly shorter than the Cr–N bonds (2.010–2.030 Å). The nitrone fragments O(3)–N(1)–C(2)–C(1) and O(4)–N(4)–C(14)–C(13) are planar within 0.005 and 0.003 Å, respectively, and slightly twisted with respect to the pyridine rings (the torsion angles N(1)–C(2)–C(3)–N(2) and N(3)–C(12)–C(13)–N(4) are −7.5(7) and 2.9(7)°, respectively). The central bipyridine part is also not planar. The torsion angle N(2)–C(3)–C(2)–N(1) is −8.9(2)°. Despite of the slight non-planarity of the ligand the coordination of the chromium atom in the equatorial plane is planar. The angle between the O ··· O and N ··· N lines is only 1.8°.

The nitrate anions do not form coordinative bonds to the chromium atom. However, they play an important role in the organization of the crystal structure. The components form layers parallel to the (101) crystallographic plane. Within one layer the units are linked by H bonds between water molecules and nitrate anions: O(7) ··· H–O(2) 2.01 Å (O ··· H–O 139°), O(9) ··· H–O(2) 1.71 Å (O ··· H–O 144°), O(8) ··· H–O(1) 1.96 Å (O ··· H–O 153°), O(9) ··· H–O(1) 2.38 Å (O ··· H–O 148°), O(8) ··· H–O(1) 1.96 Å (O ··· H–O 153°), and O(13) ··· H–O(1) 2.53 Å (O ··· H–O 121°). The neighboring layers are bound by attractive C–H ··· O interactions between the complex cations and nitrate anions: C(5)–H ··· O(10) 2.52 Å, C(11)–H ··· O(8) 2.48 Å, C(11)–H ··· O(13) 2.61 Å, C(13)–H ··· O(14) 2.36 Å, and C(14)–H ··· O(11) 2.55 Å. One of the nitrate anions is oriented almost parallel to the plane of the N(2)–C(3)–C(7) pyridine ring. This orientation, together with the distance between the planes (3.13 Å), indicates the presence of stacking interactions between the π systems of the anion and the heterocycle.

Experimental Section

Commercially available reagents *N*-methylhydroxylamine hydrochloride and 2-amino-6-methyl-pyridine were used without further purification. The ligand L was prepared by reaction of *N*-methylhydroxylamine with 2,2′-dipyridyl-6,6′-dicarbaldehyde in a molar ratio 2 : 1. 6,6′-Dimethyl-2,2′-bipyridine [28] and 2,2′-dipyridyl-6,6′-dicarbaldehyde [29] were synthesized according to literature procedures. The yield of 6,6′-dimethyl-2,2′-bipyridine can be increased when applying ethylene glycol as solvent under conditions described in [28]. The ^{1}H and ^{13}C NMR spectra were recorded on a "Mercury 400" Varian (400 MHz) spectrometer.

Synthesis of bis-C-(2,2′-bipyridine-6,6′-diyl)-N-methylnitrone (L)

N-Methylhydroxylamine hydrochloride (2.35 g, 28.1 mmol) and 2,2′-dipyridyl-6,6′-dicarbaldehyde (2.6 g, 12.3 mmol) were added to a well stirred suspension of sodium carbonate (7.8 g, 73.6 mmol) in 100 mL of dichloromethane. The mixture was refluxed for 3 h, then filtered, and the precipitate washed twice with hot CH_2Cl_2. The combined filtrates were evaporated under reduced pressure to dryness. Yield of crude product 2.18 g (73.4 %), after recrystallization from dichloromethane 1.64 g (55.2 %). – ^{1}H NMR (400.45 MHz, [D$_6$]DMSO): δ = 3.90 (s, 3 H), 8.06 (t, $^{3}J_{4-3}$ = $^{3}J_{4-5}$ = 7.2 Hz, 1 H), 8.09 (s, 1 H), 8.32 (d, $^{3}J_{3-4}$ = 7.2 Hz, 1 H), 9.05 (d, $^{3}J_{5-4}$ = 7.2 Hz, 1 H). – ^{13}C{^{1}H} NMR (100.70 MHz, [D$_6$]DMSO): δ = 55.0, 121.1, 122.9, 135.4, 138.3, 149.8, 155.3. – $C_{14}H_{14}N_4O_2$ (270.3): calcd. C 62.21, H 5.22, N 20.73; found C 62.16, H 5.28, N 20.68.

*Synthesis of [Cu(L)][CuCl$_4$] (**1**)*

To a hot solution of L (0.07 g, 0.29 mmol) in methanol (10 mL) was added $CuCl_2 \cdot 2H_2O$ (0.1 g, 0.59 mmol) dissolved in methanol (10 mL). An immediate color change to deep green was observed followed by precipitation of a microcrystalline solid. The product was filtered off and washed several times with the solvent mixture CH_3OH/CH_2Cl_2 [1 : 1]. Yield 0.114 g (76.1 %). – $C_{14}H_{14}Cl_4Cu_2N_4O_2$ (539.2): calcd. C 31.19, H 2.62, N 10.39; found C 31.06, H 2.69, N 10.27.

*Synthesis of [Ni(L)(NO$_3$)$_2$] (**2**)*

To a hot solution of L (0.068 g, 0.28 mmol) was added a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.083 g, 0.29 mmol) in methanol (10 mL). The resulting brown solution was allowed to boil for a while and left to stand in a beaker for 4 d. After evaporation of methanol the brown precipitate was filtered off and washed with several portions of the solvent mixture CH_3OH/CH_2Cl_2 [1 : 1]. Yield 0.096 g (79.3 %). – $C_{14}H_{14}N_6NiO_8$ (453.0): calcd. C 37.12, H 3.12, N 18.55; found C 37.05, H 3.18, N 18.47.

*Synthesis of [Co(L)(NO$_3$)$_2$] (**3**)*

The procedure used to prepare **2** was followed except that $Co(NO_3)_2 \cdot 6H_2O$ was used as the metal salt. Compound **3** was obtained as a deep red solid in 76.4 % yield. – $C_{14}H_{14}CoN_6O_8$ (453.2): calcd. C 37.10, H 3.11, N 18.54; found C 37.02, H 3.24, N 18.45.

*Synthesis of [Cr(L)(H$_2$O)$_2$](NO$_3$)$_3$ · 0.5H$_2$O (**4**)*

The same procedure as described for **2** and **3** was followed except that $Cr(NO_3)_3 \cdot 6H_2O$ was employed as the metal salt. Compound **4** was obtained as a red solid in 70 % yield. – $C_{28}H_{38}Cr_2N_{14}O_{27}$ (1106.7): calcd. C 30.39, H 3.46, N 17.72; found C 30.19, H 3.52, N 17.63.

Crystal structure determination

For determination of the structures of compounds **1** – **4**, X-ray diffraction studies were performed. Intensities of reflections were measured on an automatic Xcalibur 3 diffractometer (graphite-monochromated MoK_α radiation, CCD

	1	**2**	**3**	**4**
Formula	$C_{14}H_{14}Cl_4Cu_2N_4O_2$	$C_{14}H_{14}N_6NiO_8$	$C_{14}H_{14}CoN_6O_8$	$C_{28}H_{38}Cr_2N_{14}O_{27}$
M_r	539.19	453.02	453.24	1106.72
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$
a, Å	7.199(2)	4.279(3),	14.570(2)	8.125(2)
b, Å	8.114(2)	13.426(3),	13.503(2)	9.587(3)
c, Å	14.2591(3)	8.839(3),	8.7663(3)	8.7663(3)
α, deg	90	90	90	99.46(3)
β, deg	91.34(3)	103.57(3)	104.14(3)	102.52(3)
γ, deg	90	90	90	98.04(2)
V, Å^3	1858.5(3)	1647.2(8)	1672.4(4)	1126.7(6)
Z	4	4	4	1
D_{calc}, g cm^{-3}	1.927	1.827	1.800	1.631
μ(MoK_α), mm^{-1}	2.881	1.243	1.090	0.591
F(000), e	1072	928	924	568
$2\theta_{max}$, deg.	60	60	60	50
Refls. measured	10972	7798	5709	10825
Refls. unique	3669	2282	1942	2308
R_{int}	0.047	0.017	0.044	0.059
Param. refined	235	133	133	291
$R1$ $[F \geq 4\sigma(F)]$	0.039	0.021	0.038	0.059
$wR2$	0.081	0.055	0.088	0.111
GoF (F^2)	0.855	1.084	1.002	0.995
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.49/−0.46	0.45/−0.39	0.49/−0.63	0.39/−0.40

Table 1. Crystal structure data for [CuL][CuCl$_4$] (**1**), [ML(NO$_3$)$_2$] (M = Ni (**2**), M = Co (**3**)), [Cr(L)(H$_2$O)$_2$](NO$_3$)$_3$ · H$_2$O (**4**).

detector ω scans). The essential experimental conditions and crystal data are given in Table 1. All structures were solved by Direct Methods using the SHELX97 package [30, 31]. Positions of the hydrogen atoms were located from electron density difference maps and refined by a "riding" model with $U_{iso} = nU_{eq}$ of the carrier non-hydrogen atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms). Full-matrix least-squares refinement was carried out against F^2in anisotropic approximation.

CCDC 660705 (**1**), 660707 (**2**), 660706 (**3**), and 660708 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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