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Synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes of 4-amino-1,2,4-triazolidine-3,5-dione (urazine)

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Abstract

The complexing capability of urazine as neutral (Hur) or monoanionic (ur) ligand towards divalent cations (Co, Ni, Cu, Zn) was examined. Complexes $CoCl_2(Hur)_2 \cdot 4H_2O$ (**1**), $NiCl_2(Hur)_2 \cdot 4H_2O$ (**2**) and $Zn(SO_4)(Hur) \cdot 2H_2O$ (**3**), in which urazine acts as neutral ligand, were synthesized and characterized. It is worth noting that in the examined crystal the chiral complex **3** shows only the *A* enantiomer due to a spontaneous resolution. Complexes $Co(ur)_2 \cdot 4H_2O$ (**4**), $NiCl(ur) \cdot H_2O$ (**5**), $CuCl(ur) \cdot 2H_2O$ (**6**) and $Zn(ur)_2 \cdot 2H_2O$ (**7**), in which coordinated deprotonated urazine molecules are present, were synthesized in aqueous solution starting from the urazine sodium salt. Other copper(II) complexes $Cu_3(NO_3)_2(ur)_4 \cdot 6H_2O$ (**8**), $Cu(ur)_2 \cdot 4H_2O$ (**9**), $Cu_2(SO_4)(ur)_2 \cdot 2H_2O$ (**10**) were synthesized in aqueous solution starting from the free ligand. The crystal structures of **1**, **3**, **8**, **9**, **10** were determined by X-ray diffraction methods. In the structurally characterized complexes Hur acts only as *N*,*O* chelating agent in **1** and **3**, whereas ur acts as monodentate through the deprotonated triazolidine nitrogen atom in **9**, tridentate in **8** and tetradentate in **8** and **10**. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Copper(II) complexes; Cobalt(II) complexes; Nickel(II) complexes; Zinc(II) complexes; Triazolidine; Crystal structures

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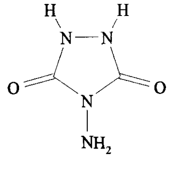
1. Introduction

Cyclic derivatives of carbonohydrazide and in particular the *s*-triazole ones are subject of study in the biological, technological and analytical fields [1]. Urazine (Hur) is a weak monoprotic acid with a $pK_a = 5.49(1)$ (the pH of a saturated solution at 25°C is 3.4) and therefore the neutral molecule can be coordinated only at low pH values [2]. Potential coordination sites of urazine are the oxygen atoms of the two carbonylic groups, and the exocyclic amine nitrogen atom. In addition, an amide nitrogen atom can also function as a coordinating atom when the ligand is deprotonated (Scheme 1).



Scheme 1.

Nitrogen atoms present in the ring show a partial electrophilic character due to the amide resonance, and react with nucleophilic agents like dienes (Diels–Alder reaction) [3]. Structural studies show that urazine presents a wide positive charge delocalization on its five-membered ring. The exocyclic nitrogen atom shows nucleophilic rather than basic character, and functions as one of the coordinating atom in the *N*,*O* chelating system. Complexes of zinc, nickel(II) and cobalt(II) were studied in aqueous solution to determine complexation constants ($\log \beta_1(Zn^{2+}) = 2.17(2)$, $\log \beta_1(Ni^{2+})$

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Table 1
Crystallographic data of **1** and **3** as well as details of the structure solution and refinement procedures

Compound	**1**	**3**
Empirical formula	$C_4H_{16}Cl_2CoN_8O_8$	$C_2H_8N_4O_8SZn$
Formula weight	434.08	313.55
Wavelength (Å)	0.71073	1.54184
Crystal system, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1$
Unit cell dimensions		
a (Å)	5.859(3)	6.230(2)
b (Å)	6.875(3)	7.490(2)
c (Å)	11.132(4)	10.250(3)
α (°)	74.06(2)	90
β (°)	81.96(2)	101.86(2)
γ (°)	65.38(2)	90
Volume (Å^3)	391.8(3)	468.1(2)
Z, Calculated density [Mg m^{-3}]	1, 1.840	2, 2.225
Absorption coefficient (mm^{-1})	1.490	6.225
F(000)	221	316
Crystal size (mm)	$0.15\times0.20\times0.22$	$0.38\times0.25\times0.18$
θ range for data collection (°)	3.36–25.04	4.41–69.98
Index ranges	$-6\leq h\leq 6$, $1\leq k\leq 8$, $-12\leq l\leq 13$	$-7\leq h\leq 7$, $-9\leq k\leq 2$, $-12\leq l\leq 12$
Reflections collected/unique, R_{int}	1378/1378, 0.0000	984/965, 0.0239
Data/restraints/parameters	1378/6/126	965/1/165
Goodness-of-fit on F^2	0.840	1.027
Final R indices [$I>2\sigma(I)$] (R_1, wR_2)[a]	0.0688, 0.1714	0.0321, 0.0885
R indices (all data) (R_1, wR_2)[a]	0.1282, 0.1990	0.0327, 0.0890
Largest difference peak and hole (e Å^{-3})	1.115 and -0.868	0.704 and -0.430

[a] $GOOF=[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$, $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P=[\max(F_o^2,0)+2F_c^2]/3$

$=2.65(1)$, $\log\beta_2(Ni^{2+})=4.80(4)$ and $\log\beta_1(Co^{2+})=2.34(2)$) [2]. The following salts: $NH_4C_2H_3N_4O_2\cdot H_2O$, $N_2H_5C_2H_3N_4O_2$, $NaC_2H_3N_4O_2\cdot H_2O$, $AgC_2H_3N_4O_2$ and $Ba(C_2H_3N_4O_2)_2\cdot 3H_2O$ are described in the literature, and the last two are quite insoluble in water [4]. At the present time the only structurally characterized complex of urazine is the Jahn–Teller distorted octahedral complex $[CuCl_2(Hur)_2]$ [5] in which the two urazine ligands act as *N*,*O* chelating agents with the oxygen atoms in axial positions. The objective of this work is to study the ligand behaviour of urazine as a neutral or anionic molecule towards the divalent metals Co, Ni, Cu and Zn.

2. Experimental

2.1. General

Elemental analyses (C, H, N, S) were performed with a Carlo Erba EA 1108 automated analyzer. FTIR spectra were recorded on a Nicolet 5PC FT spectrometer. NMR spectra were collected in DMSO-d_6 on a Bruker AC-300 spectrometer. Metal salts and solvents were commercially available and used without further purification. The synthesis of urazine was performed according to a published procedure [4].

2.2. Synthesis of $[Co(OH_2)_2(Hur)_2]Cl_2\cdot 2H_2O$ (*1*)

Urazine (100 mg, 0.86 mmol) and HCl (6 M) (0.14 ml, 0.86 mmol) were added to 10 ml of distilled water, stirred vigorously and heated to 80°C. Once complete dissolution was achieved, the solution was added dropwise to 10 ml of an aqueous solution of $CoCl_2\cdot 6H_2O$ (103 mg, 0.43 mmol). The reaction mixture was heated and stirred for an additional hour. Subsequentely, the solution was cooled to r.t., and the solvent was allowed to evaporate over a few days. After this period, pale brown crystals were obtained. Yield 104 mg (56%), dec. > 278°C.

Anal. Calc. for $C_4H_{16}Cl_2CoN_8O_8$ (434.08): C, 11.06; H, 3.68; N, 25.41. Found: C, 11.24; H, 3.69; N, 25.36. IR (KBr pellet, cm^{-1}): ν(OH), 3408(w); $\nu(NH_2)$, 3350(w), 3252(s); ν(NH), 3190(m), 3127(m); Amide I, 1776(s), 1698(m); $\delta(NH_2)$, 1605(s); Amide II, 1501(m); Amide III, 1287(m); $\gamma(NH_2)$, 1176(m); Amide IV, 741(s).

2.3. Synthesis of $NiCl_2(Hur)_2\cdot 4H_2O$ (*2*)

2 was prepared similarly to **1**, starting from $NiCl_2\cdot 6H_2O$ (0.43 mmol). The solvent was allowed to evaporate over a few days, and pale green microcrystals were obtained. Yield 102 mg (55%), dec. > 138°C.

Anal. Calc. for $C_4H_{16}Cl_2N_8NiO_8$ (433.89): C, 11.07; H, 3.72; N, 25.83. Found: C, 11.44; H, 3.97; N, 25.34. IR (KBr pellet, cm^{-1}): ν(OH), 3425(w); $\nu(NH_2)$, 3197(m); ν(NH), 3080(m), 3020(m); Amide I, 1741(s), 1686(m); $\delta(NH_2)$, 1610(s); Amide II, 1497(s); Amide III, 1293(s); $\gamma(NH_2)$, 1186(s); Amide IV, 742(s).

2.4. Synthesis of $[Zn(SO_4)(OH_2)_2(Hur)]_n$ (*3*)

3 was prepared similarly to **1**, starting from $ZnSO_4\cdot 7H_2O$ (248 mg, 0.86 mmol). The solvent was allowed to evaporate over a few days, and colourless crystals were obtained. Yield 180 mg (67%), dec. > 121°C.

Anal. Calc. for $C_2H_8N_4O_8SZn$ (313.55): C, 7.65; H, 2.57; N, 17.86; S, 10.23. Found: C, 7.89; H, 2.99; N,

Table 2
Crystallographic data of **8**, **9** and **10** as well as details of the structure solution and refinement procedures

Compound	**8**	**9**	**10**
Empirical formula	$C_8H_{24}Cu_3N_{18}O_{20}$	$C_4H_{14}CuN_8O_8$	$C_4H_{10}Cu_2N_8O_{10}S$
Formula weight	883.07	365.77	489.34
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system, space group	monoclinic, $P2_1/a$	triclinic, $P\bar{1}$	orthorhombic, $Fdd2$
Unit cell dimensions			
a (Å)	20.666(9)	6.069(3)	18.267(5)
b (Å)	9.905(5)	6.897(3)	22.482(7)
c (Å)	6.685(4)	8.436(3)	6.392(3)
α (°)	90	111.27(2)	90
β (°)	91.91(2)	100.36(2)	90
γ (°)	90	109.61(2)	90
Volume ($Å^3$)	1367.6(12)	291.1(2)	2625.1(16)
Z, Calculated density [Mg m^{-3}]	2, 2.144	1, 2.086	8, 2.476
Absorption coefficient (mm^{-1})	3.852	3.317	6.308
$F(000)$	890	187	1952
Crystal size (mm)	0.15 × 0.35 × 0.43	0.14 × 0.18 × 0.40	0.25 × 0.31 × 0.48
θ range for data collection (°)	4.28–59.98	5.99–69.98	7.60–69.98
Index ranges	$-23 \leq h \leq 23$, $-1 \leq k \leq 11$, $-7 \leq l \leq 7$	$-1 \leq h \leq 7$, $-8 \leq k \leq 7$, $-10 \leq l \leq 10$	$-21 \leq h \leq 22$, $-27 \leq k \leq 27$, $-7 \leq l \leq 0$
Reflections collected/unique, R_{int}	2215/2031, 0.0485	1098/1098, 0.0000	1298/681, 0.0642
Data/restraints/parameters	2031/9/253	1098/9/122	681/4/122
Goodness-of-fit on F^2	1.105	1.119	1.071
Final R indices [$I > 2\sigma(I)$] (R_1, wR_2)[a]	0.0559, 0.1525	0.0546, 0.1547	0.0450, 0.1179
R indices (all data) (R_1, wR_2)[a]	0.0703, 0.1671	0.0587, 0.1616	0.0457, 0.1190
Extinction coefficient			0.00030(10)
Largest difference peak and hole (e $Å^{-3}$)	0.952 and −0.772	1.067 and −0.905	0.582 and −0.868

[a] GOOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$

18.13; S, 9.91. ^1H NMR (δ): 9.89 [s, 2H, NH], 4.91 [s, 2H, NH_2], 3.64 [s, 4H, H_2O]. ^{13}C NMR (δ): 154.82 [s, 2C, CO]. IR (KBr pellet, cm^{-1}): ν(OH), 3450(w); $\nu(NH_2)$, 3331(m), 3250(w); ν(NH), 3140(vw); Amide I, 1747(m), 1700(m); $\delta(NH_2)$, 1620(m); Amide II, 1477(m); Amide III, 1250(m); $\nu(SO_4)$, 1100(m); $\gamma(NH_2)$, 1152(m); Amide IV, 757(s); Def. (O=S=O), 631 (s), 619 (s).

2.5. Synthesis of $Co(ur)_2 \cdot 4H_2O$ (4), $NiCl(ur) \cdot H_2O$ (5), $CuCl(ur) \cdot 2H_2O$ (6) and $Zn(ur)_2 \cdot 2H_2O$ (7)

Compounds **4**, **5**, **6** and **7** were synthesized in aqueous solution from the urazine sodium salt (2 mmol) and from $M(II)Cl_2$ (1 mmol). Precipitates were observed in all cases immediately after mixing the reagents, and they resulted to be highly insoluble in any solvent. The sodium salt of urazine was prepared adding a stoichiometric amount of 1 M NaOH to the free ligand. Yields and m.p.: 322 mg (89%), dec. > 70°C; 194 mg (85%), dec. > 270°C; 199 mg (80%), dec. > 280°C; 284 mg (86%), dec. > 170 °C for **4**, **5**, **6** and **7**, respectively.

Anal. Calc. for $C_4H_{14}CoN_8O_8$ (361.18) (**4**): C, 13.30; H, 3.91; N, 31.03. Found: C, 12.91; H, 4.05; N, 30.91. IR (KBr pellet, cm^{-1}): ν(OH), $\nu(NH_2)$, 3380(w); ν(NH), 3160(m), 3088(m); Amide I, 1703(m); $\delta(NH_2)$, 1649(m); Amide II, 1488(m); Amide III, 1265(m).

Anal. Calc. for $C_2H_5ClN_4NiO_3$ (227.23) (**5**): C, 10.57; H, 2.22; N, 24.66. Found: C, 10.57; H, 2.54; N, 24.34. IR (KBr pellet, cm^{-1}): ν(OH), $\nu(NH_2)$, 3406(w); ν(NH), 3240(m); Amide I, 1718(m); $\delta(NH_2)$, 1640(m); Amide II, 1479(m); Amide III, 1292(m).

Anal. Calc. for $C_2H_7ClCuN_4O_4$ (250.10) (**6**): C, 9.60; H, 2.82; N, 22.41. Found: C, 9.49; H, 2.63; N, 22.54. IR

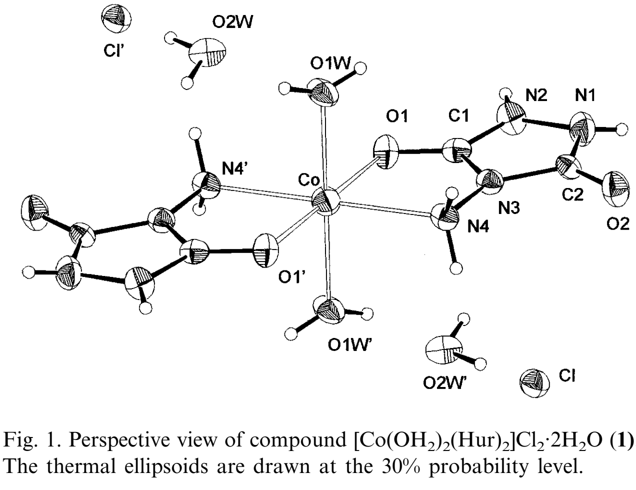

Fig. 1. Perspective view of compound $[Co(OH_2)_2(Hur)_2]Cl_2 \cdot 2H_2O$ (**1**). The thermal ellipsoids are drawn at the 30% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for **1**, **3**, **8**, **9** and **10**

Complex **1**			
Co–O(1W)	2.060(6)	N(1)–N(2)	1.426(11)
Co–O(1)	2.077(5)	N(2)–C(1)	1.307(10)
Co–N(4)	2.185(6)	N(3)–C(1)	1.345(10)
O(1)–C(1)	1.249(9)	N(3)–C(2)	1.380(9)
O(2)–C(2)	1.241(9)	N(3)–N(4)	1.375(9)
N(1)–C(2)	1.300(10)		
O(1W)–Co–O(1)	90.2(2)	C(2)–N(3)–N(4)	129.7(6)
O(1W)–Co–N(4)	89.7(2)	O(1)–C(1)–N(2)	127.8(8)
O(1)–Co–N(4)	79.9(2)	O(1)–C(1)–N(3)	123.6(7)
C(2)–N(1)–N(2)	109.4(6)	N(2)–C(1)–N(3)	108.6(7)
C(1)–N(2)–N(1)	106.4(7)	O(2)–C(2)–N(1)	128.0(7)
C(1)–N(3)–C(2)	109.6(7)	O(2)–C(2)–N(3)	125.9(7)
C(1)–N(3)–N(4)	120.5(7)	N(1)–C(2)–N(3)	106.0(7)
Complex **3**			
Zn–O(3)	2.040(4)	O(2)–C(2)	1.228(8)
Zn–O(2W)	2.056(5)	N(1)–C(2)	1.342(8)
Zn–O(4)′	2.090(5)	N(1)–N(2)	1.393(8)
Zn–O(1)	2.131(4)	N(2)–C(1)	1.334(8)
Zn–N(4)	2.160(5)	N(3)–C(1)	1.377(8)
Zn–O(1W)	2.224(5)	N(3)–C(2)	1.384(8)
O(1)–C(1)	1.224(8)	N(3)–N(4)	1.408(6)
O(3)–Zn–O(2W)	87.0(2)	C(2)–N(1)–N(2)	108.6(5)
O(3)–Zn–O(4)′	85.5(2)	C(1)–N(2)–N(1)	110.4(5)
O(2W)–Zn–O(4)′	94.7(2)	C(1)–N(3)–C(2)	112.0(5)
O(2W)–Zn–O(1)	90.5(2)	C(1)–N(3)–N(4)	120.5(5)
O(4)’–Zn–O(1)	92.7(2)	C(2)–N(3)–N(4)	127.4(5)
O(3)–Zn–N(4)	101.5(2)	O(1)–C(1)–N(2)	131.4(6)
O(4)’–Zn–N(4)	93.1(2)	O(1)–C(1)–N(3)	124.6(5)
O(1)–Zn–N(4)	81.3(2)	N(2)–C(1)–N(3)	104.0(5)
O(3)–Zn–O(1W)	94.4(2)	O(2)–C(2)–N(1)	129.1(6)
O(2W)–Zn–O(1W)	87.2(2)	O(2)–C(2)–N(3)	126.3(6)
O(1)–Zn–O(1W)	87.4(2)	N(1)–C(2)–N(3)	104.6(5)
N(4)–Zn–O(1W)	85.1(2)		
Symmetry transformation used to generate equivalent atoms: $'-x,\ y+1/2,\ -z+1$			
Complex **8**			
Cu(1)–O(11)	1.967(4)	C(11)–N(21)	1.323(7)
Cu(1)–N(41)	2.052(5)	C(21)–N(11)	1.343(8)
Cu(1)–O(3)	2.415(5)	N(11)–N(21)	1.400(7)
Cu(2)–O(12)	1.985(4)	N(31)–N(41)	1.411(6)
Cu(2)–N(42)	2.060(5)	C(12)–O(12)	1.254(7)
Cu(2)–N(22)″	1.971(4)	C(22)–O(22)	1.228(7)
Cu(2)–O(21)‴	2.362(4)	C(22)–N(32)	1.382(8)
Cu(2)–N(21)	1.967(4)	C(12)–N(32)	1.381(7)
C(11)–O(11)	1.266(7)	C(12)–N(22)	1.331(7)
C(21)–O(21)	1.237(7)	C(22)–N(12)	1.334(8)
C(21)–N(31)	1.385(7)	N(12)–N(22)	1.407(6)
C(11)–N(31)	1.369(7)	N(32)–N(42)	1.406(7)
N(41)–Cu(1)–O(11)	85.7(2)	O(11)–C(11)–N(31)	122.5(5)
O(11)–Cu(1)–O(3)	94.2(2)	N(21)–C(11)–N(31)	108.9(5)
N(41)–Cu(1)–O(3)	92.1(2)	O(21)–C(21)–N(11)	130.6(5)
N(21)–Cu(2)–N(42)	90.9(2)	O(21)–C(21)–N(31)	127.3(5)
N(22)″–Cu(2)–N(21)	97.2(2)	N(11)–C(21)–N(31)	102.1(5)
N(22)″–Cu(2)–O(12)	88.8(2)	C(22)–N(12)–N(22)	113.7(5)
N(42)–Cu(2)–O(12)	83.8(2)	C(12)–N(22)–N(12)	104.7(4)
N(21)–Cu(2)–O(21)‴	89.9(2)	C(12)–N(32)–C(22)	111.3(5)
N(22)″–Cu(2)–O(21)‴	96.4(2)	C(12)–N(32)–N(42)	118.8(4)
O(12)–Cu(2)–O(21)‴	87.9(2)	C(22)–N(32)–N(42)	129.9(4)
N(42)–Cu(2)–O(21)‴	100.7(2)	O(12)–C(12)–N(22)	131.3(5)
C(21)–N(11)–N(21)	113.4(4)	O(12)–C(12)–N(32)	120.6(5)
C(11)–N(21)–N(11)	104.6(4)	N(22)–C(12)–N(32)	108.0(5)
C(11)–N(31)–C(21)	110.9(4)	O(22)–C(22)–N(12)	130.4(6)

Table 3 (*Continued*)

C(11)–N(31)–N(41)	118.8(4)	O(22)–C(22)–N(32)	127.3(5)
C(21)–N(31)–N(41)	130.2(5)	N(12)–C(22)–N(32)	102.3(4)
O(11)–C(11)–N(21)	128.6(5)		

Symmetry transformation used to generate equivalent atoms: $'-x, y, -z$; $''-x+1/2, y-1/2, -z+1$; $'''-x+1/2, y+1/2, -z$

Complex **9**			
Cu–N(2)	1.992(3)	C(1)–N(3)	1.399(4)
Cu–O(1W)	2.042(3)	C(1)–N(2)	1.320(5)
Cu–O(2W)	2.318(3)	C(2)–N(1)	1.343(5)
C(1)–O(1)	1.241(4)	N(1)–N(2)	1.403(4)
C(2)–O(2)	1.241(4)	N(3)–N(4)	1.403(4)
C(2)–N(3)	1.368(5)		
N(2)–Cu–O(1W)	90.7(1)	N(1)–C(2)–N(3)	103.8(3)
N(2)–Cu–O(2W)	89.4(1)	O(2)–C(2)–N(3)	128.2(3)
O(1W)–Cu–O(2W)	88.1(1)	C(2)–N(1)–N(2)	112.0(3)
N(2)–C(1)–N(3)	107.6(3)	C(1)–N(2)–N(1)	106.2(3)
O(1)–C(1)–N(2)	129.1(3)	C(1)–N(3)–C(2)	110.4(3)
O(1)–C(1)–N(3)	123.4(3)	C(1)–N(3)–N(4)	125.9(3)
O(2)–C(2)–N(1)	128.0(3)	C(2)–N(3)–N(4)	123.7(3)
Complex **10**			
Cu–O(1)″	1.922(5)	C(2)–N(3)	1.377(8)
Cu–N(4)″	2.130(5)	C(1)–N(3)	1.374(8)
Cu–O(3)	1.983(4)	C(1)–N(2)	1.309(8)
Cu–N(2)	1.959(6)	C(2)–N(1)	1.348(9)
Cu–O(2)‴	2.336(6)	N(1)–N(2)	1.406(7)
C(1)–O(1)	1.266(7)	N(3)–N(4)	1.411(7)
C(2)–O(2)	1.236(8)		
O(1)″–Cu–O(3)	87.5(2)	C(1)–N(3)–C(2)	110.0(5)
N(2)–Cu–O(3)	91.1(2)	C(1)–N(3)–N(4)	118.6(5)
O(1)″–Cu–N(4)″	84.3(2)	C(2)–N(3)–N(4)	131.0(5)
N(2)–Cu–N(4)″	96.8(2)	O(1)–C(1)–N(2)	128.6(6)
O(3)–Cu–O(2)‴	98.7(2)	O(1)–C(1)–N(3)	121.9(6)
O(1)″–Cu–O(2)‴	93.3(2)	N(2)–C(1)–N(3)	109.5(5)
N(4)″–Cu–O(2)‴	93.6(2)	O(2)–C(2)–N(1)	129.2(6)
N(2)–Cu–O(2)‴	88.2(2)	O(2)–C(2)–N(3)	127.7(7)
C(2)–N(1)–N(2)	112.0(5)	N(1)–C(2)–N(3)	103.0(6)
C(1)–N(2)–N(1)	105.0(5)		

Symmetry transformation used to generate equivalent atoms: $'-x+1, -y, z$; $''x+1/4, -y+1/4, z+1/4$; $'''-x+1/2, -y, z+1/2$

(KBr pellet, cm^{-1}): ν(OH), ν(NH$_2$), 3399(w); ν(NH), 3212(m); Amide I, 1717(s); δ(NH$_2$), 1653(m); Amide II, 1472(m); Amide III, 1288(m).

Anal. Calc. for $C_4H_{10}N_8O_6Zn$ (331.59) (**7**): C, 14.49; H, 3.04; N, 33.80. Found: C, 14.54; H, 3.12; N, 33.49. IR (KBr pellet, cm^{-1}): ν(NH), 3260(m); ν(NH$_2$), 3152(m), 3071(w); Amide I, 1703(m); δ(NH$_2$), 1639(m); Amide II, 1479(m); Amide III, 1292(m).

2.6. Synthesis of [$Cu_3(NO_3)_2(ur)_4]_n\cdot 6nH_2O$ (**8**) and [$Cu(ur)_2(OH_2)_4$] (**9**)

Urazine (100 mg, 0.86 mmol) was added to 10 ml of distilled water, stirred vigorously and heated to 80°C. The solution was then added dropwise to 10 ml of an aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (104 mg, 0.43 mmol). The reaction mixture was heated and stirred for an additional hour. Subsequently, the solution was cooled to r.t., and the solvent was allowed to evaporate over a few days. After this period, green crystals of two different kinds were obtained. Compound **8** was isolated as deep green colored crystals, and **9** as pale green ones. No yield was determined at this stage. Dec. > 180°C and dec. > 220°C for **8** and **9**, respectively.

Anal. Calc. for $C_8H_{24}Cu_3N_{18}O_{20}$ (883.07) (**8**): C, 10.88; H, 2.73; N, 28.56. Found: C, 10.11; H, 2.35; N, 27.73. IR (KBr pellet, cm^{-1}): ν(OH), 3590(s), 3433(w); ν(NH$_2$), 3380(m); ν(NH), 3185(m), 3100(m); Amide I, 1714(s), 1652(m); δ(NH$_2$), 1614(s); Amide II, 1489(m); ν(NO$_3$), 1385(s).

Anal. Calc. for $C_4H_{14}CuN_8O_8$ (365.78) (**9**): C, 13.13; H, 3.85; N, 30.64. Found: C, 13.23; H, 3.81; N, 30.30. IR (KBr pellet, cm^{-1}): ν(OH), 3551(s), 3441(w); ν(NH$_2$), 3288(m); ν(NH), 3190(m); Amide I, 1709(s), 1653(s); δ(NH$_2$), 1607(s); Amide II, 1488(m).

2.7. Synthesis of [$Cu_2(SO_4)(ur)_2]_n\cdot 2nH_2O$ (**10**)

Green crystals of **10** were prepared similarly to **8**, starting from $CuSO_45H_2O$ (0.43 mmol). Yield 61 mg (29%), dec. > 210°C.

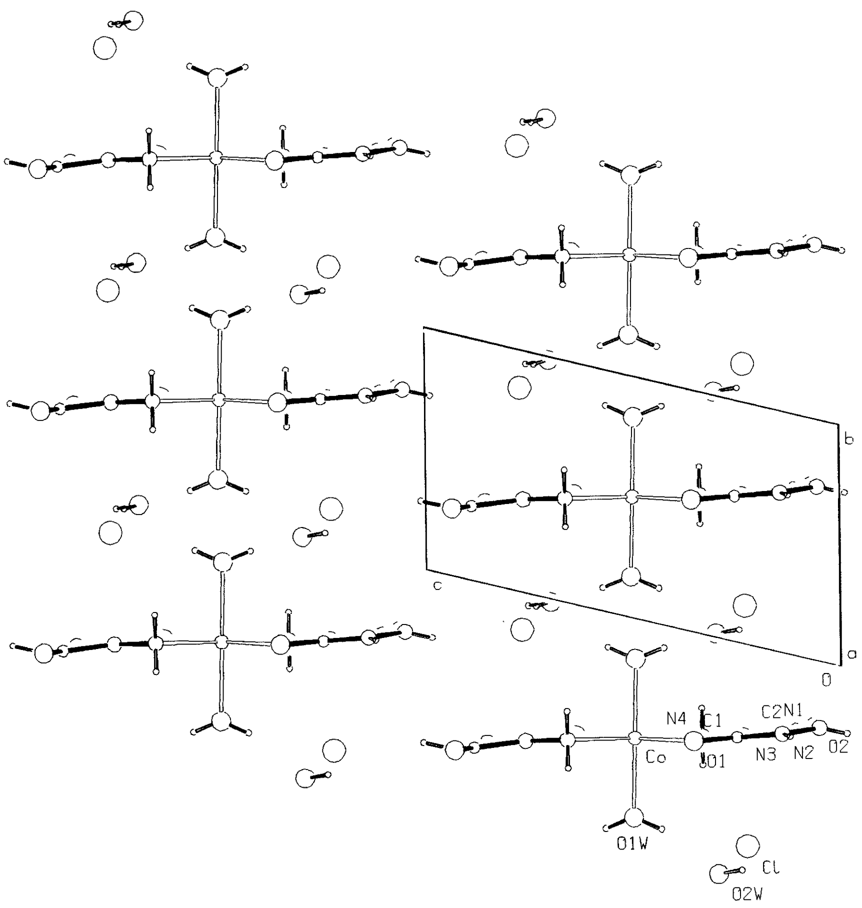

Fig. 2. Packing of $[Co(OH_2)_2(Hur)_2]Cl_2{\cdot}2H_2O$ (**1**) projected along **a**.

Anal. Calc. for $C_4H_{10}Cu_2N_8O_{10}S$ (489.34): C, 9.81; H, 2.06; N, 22.90; S, 6.55. Found: C, 9.60; H, 2.46; N, 23.17; S, 6.29. IR (KBr pellet, cm^{-1}): ν(OH), 3444(w); $\nu(NH_2)$, 3238(m); ν(NH), 3100(m); Amide I, 1734(s), 1666(s); $\delta(NH_2)$, 1635(s); Amide II, 1493(m); $\nu(SO_4)$, 1180(m), 1089(m); Def. (O=S=O), 648 (s), 601 (s).

2.8. Crystal structure analysis

Diffraction data for all compounds were recorded at 293(2) K with the $\theta/2\theta$ technique on a Siemens AED diffractometer. The individual profiles have been analyzed following the method of Lehmann and Larsen [6]. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods [SIR-92] [7] and refined by least-squares methods based on F^2 using the SHELXL-93 and SHELXL-97 [8] programs. All the non-hydrogen atoms in every compound were refined anisotropically. The hydrogen atoms for **1** and **3**, except the amine ones riding on their nitrogen atoms, were refined freely. For all the other complexes they were placed in calculated positions and refined with a riding model except those of the water molecules and of the uncoordinated amine nitrogen atoms, which were taken from difference Fourier maps and freely refined. Empirical absorption corrections were applied for all compounds (max. and min. absorption coefficient 1.000, 0.730 (**1**), 1.000, 0.847 (**3**), 1.000, 0.694 (**8**), 1.000, 0.823 (**9**) and 1.000, 0.593 (**10**)) [9]. The absolute structure parameters are 0.00(5) and 0.15(8) for **3** and **10**, respectively. Crystal data and some details of the structure determination are listed in Tables 1 and 2. All calculations were carried out on the DIGITAL AlphaStation 255 of the 'Centro di Studio per la Strutturistica Diffrattometrica' del CNR, Parma. The programs PARST [10], ORTEP [11] and PLUTON [12] were also used.

3. Results and discussion

3.1. NMR and IR spectra

^1H NMR spectra of Hur presents two peaks, one at $\delta = 9.86$ ppm assigned to the amide protons and one at $\delta = 4.75$ ppm assigned to the amine protons. ^1H NMR of **3** presents the amine protons peak shifted downfield (4.91 ppm) due to the coordination of the nitrogen atom, whereas the chemical shift of the amide protons are practically unchanged (9.89 ppm). A peak at $\delta = 3.64$ ppm is assigned to the protons of the coordinated

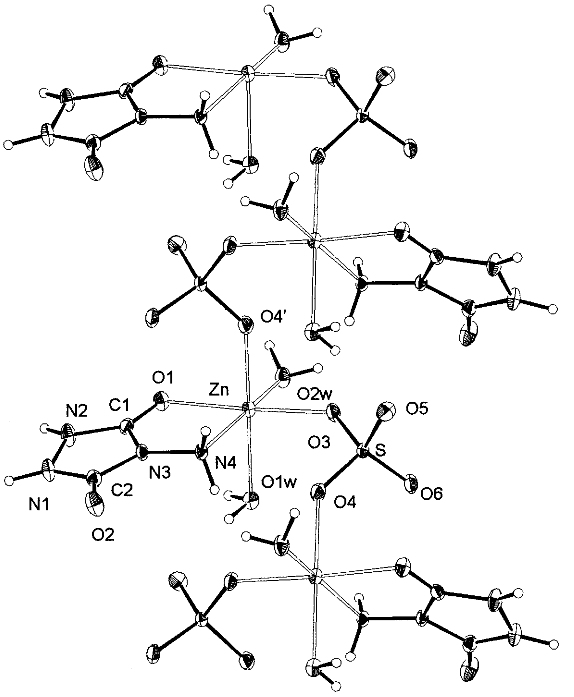

Fig. 3. Perspective view of compound $[Zn(SO_4)(OH_2)_2(Hur)]_n$ (**3**). The thermal ellipsoids are drawn at the 30% probability level.

water molecules [13]. The ^{13}C NMR spectrum of Hur presents one peak at 155.02 ppm. The ^{13}C NMR spectrum of **3** shows one peak at 154.82 ppm.

IR spectroscopy is used to determine the presence of Hur or ur in a given complex. Free urazine presents three characteristic bands at 1743, 1701 and 1629 cm^{-1} corresponding to the Amide I and the NH_2 bending (δNH_2). Spectra of Hur complexes show that these three characteristic bands are slightly shifted, whereas ur complexes have these bands shifted of about 30 cm^{-1} towards a lower frequency.

3.2. Crystal structures

3.2.1. $[Co(OH_2)_2(Hur)_2]Cl_2 \cdot 2H_2O$ (1)

The structure of **1** consists of centrosymmetric cationic octahedral complexes, chloride anions and water molecules. Two molecules of urazine are coordinated in the equatorial positions by forming two five-membered chelate rings via the N and O atoms, two water molecules in the axial positions complete the pseudo octahedral coordination sites around the central Co(II) atom (Fig. 1). Coordination bond distances are as usual. The urazine skeleton is nearly planar (max. dev. 0.028(6) Å for N(3)) and the cobalt atom is 0.1702(3) Å out of the mean plane. Bond distances and angles are listed in Table 3. The complex presents a pseudo C_{2h} symmetry with σ_h plane almost parallel to **a** (Fig. 2). The NH_2 and one NH group together with the water molecules participate in hydrogen bonds of the type $N–H\cdots O_w$, $N–H\cdots Cl$, $N–H\cdots O$, $O_w–H\cdots Cl$ and $O_w–H\cdots O_w$ resulting in layers of complexes parallel to (001). The second NH group interacts with a Cl anion and links the layers together.

3.2.2. $[Zn(SO_4)(OH_2)_2(Hur)]_n$ (3)

The crystal structure of **3** consists of polymeric chains of octahedral (*OC*-6-32-*A*) chiral complexes of Zn. The metal atom is surrounded by a *N,O* chelating Hur, two water molecules in *cis* positions and two oxygen atoms from two sulfate groups. These groups link the complexes in chains with Δ helicity (Fig. 3). It is worth noting that in the crystal examined only the *A* enantiomer of the complex and the Δ configuration of the helix are present, due to a spontaneous resolution. Selected bond distances and angles are listed in Table 3. The five Zn–O bond distances are not easily compara-

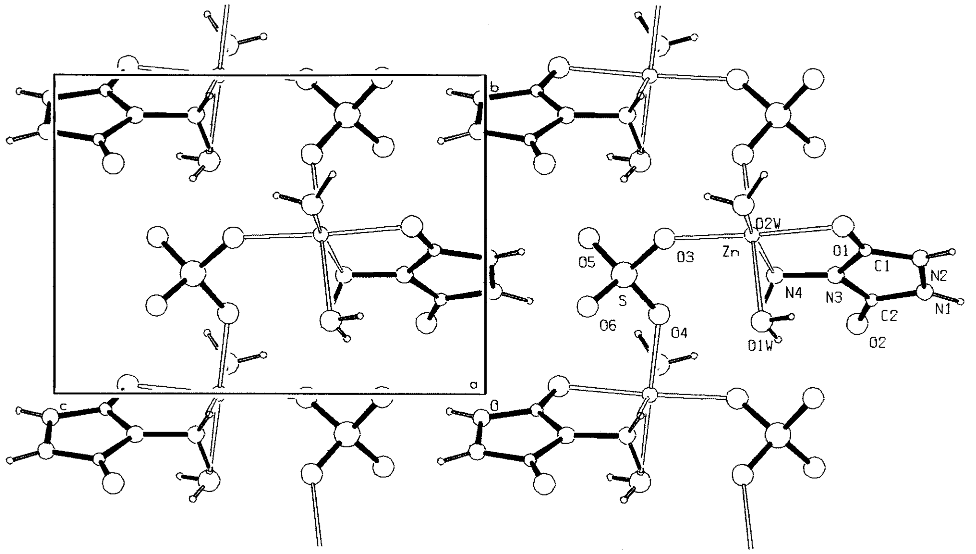

Fig. 4. Packing of $[Zn(SO_4)(OH_2)_2(Hur)]_n$ (**3**) projected along **a**.

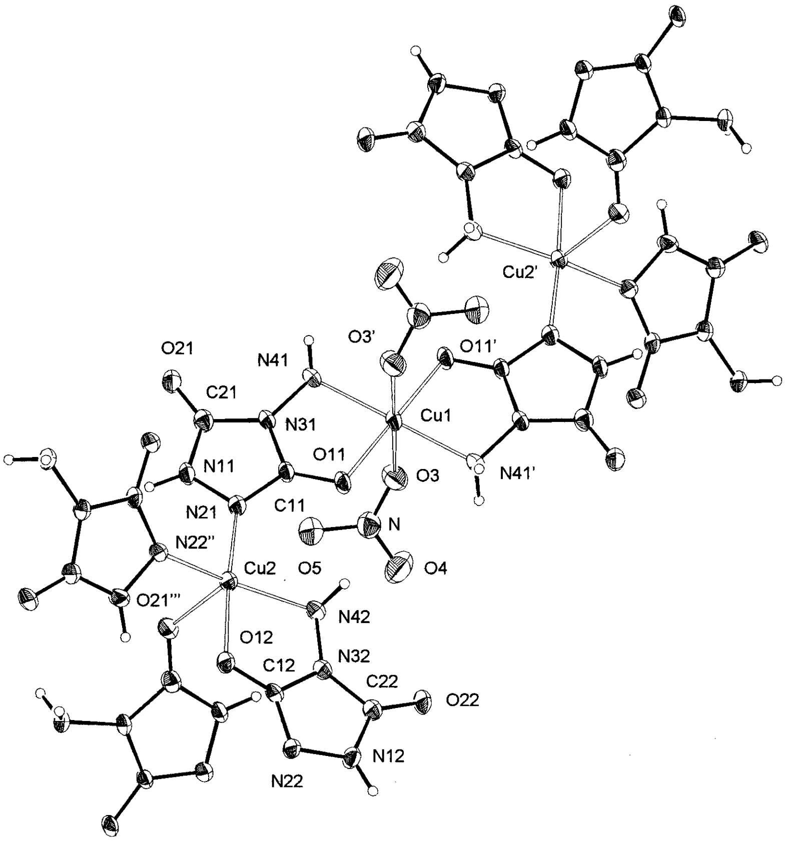

Fig. 5. Perspective view of compound $[Cu_3(NO_3)_2(ur)_4]_n \cdot 6nH_2O$ (**8**). The thermal ellipsoids are drawn at the 30% probability level.

ble, because two of them are relatively much longer (Zn–O(1) = 2.131(4), Zn–O(1w) = 2.224(5) Å) than the other three (Zn–O(3) = 2.040(4), Zn–O(4)′ = 2.090(5), Zn–O(2w) = 2.056(5) Å), and this is due to a remarkable *trans* influence of the coordinated sulfate oxygen atoms O(3) and O(4)′. The non-hydrogen atoms of the coordinated urazine molecule are coplanar and the Zn atom is out of the mean plane by 0.1483(8) Å. Bond distances and angles of Hur in **3** fit the values found in $[CuCl_2(Hur)_2]$ [5] and with respect to the free ligand [5] an enlargement of the exocyclic N(2)–C(1)–O(1) bond angle (131.4(6) vs. 126.5(1)°) is envisaged, due to the coordination of O(1). The water molecules and the NH_2 groups form hydrogen bonds of the type N–H···O_w, N–H···O, O_w–H···O and O_w–H···O_w and link the chains in layers parallel to (001). The NH groups interact with the sulfate oxygen atoms not involved in the coordination of adjacent layers, linking them along **c** (Fig. 4).

3.2.3. $[Cu_3(NO_3)_2(ur)_4]_n \cdot 6nH_2O$ (8)

Complex **8** presents two independent copper atoms with different coordination. One (Cu(1)) lies on a centre of symmetry and shows a distorted Jahn–Teller octahedral environment with two chelating *N*,*O* ur anions, and two apical monodentate nitrate ions. The other (Cu(2)) shows a square pyramidal coordination with a chelating *N*,*O* ur anion, two deprotonated amide nitrogen atoms of two ur from adjacent complexes, and a carbonyl oxygen atom from another adjacent complex in an apical position (Fig. 5). The complexes are joined in a polymeric 3D structure with an ur ion being tridentate, and another ur ion being tetradentate. The two independent ur anions are practically planar as the maximum deviation from the mean plane is 0.030(5) Å for N(31) in the first, and 0.023(4) Å for O(22) in the second. One ur chelates the Cu(1) atom through N(41) and O(11), bridges the Cu(2) atom through N(21), and another Cu(2) atom ($-x+1/2$, $y-1/2$, $-z$) through the carbonyl O(21). The metals are out of the mean plane of the anion by 0.2356(3), 0.1507(9) and 1.4737(9) Å, respectively. The other independent ur anion chelates the Cu(2) atom and bridges another Cu(2) atom ($-x+1/2$, $y+1/2$, $-z+1$) through N(22), but in this case the metals lie practically in the plane of the ligand being out of the mean plane by 0.0122(9) and 0.0900(9) Å, respectively. Selected bond distances and angles are summarized in Table 3. The coordination bond distances from Cu(1) to the chelating ur anions (Cu(1)–O(11) = 1.967(4), Cu(1)–N(41) = 2.052(5) Å) are slightly shorter than those from Cu(2) (Cu(2)–O(12) = 1.985(4), Cu(2)–N(42) = 2.060(5) Å) and the bite angles are 85.7(2)° for Cu(1) and 83.8(2)° for Cu(2). The bond distances Cu(2)–N(21) = 1.967(5) and Cu(2)–N(22)″ = 1.971(4) Å are shorter than the Cu(1)–N(41) and

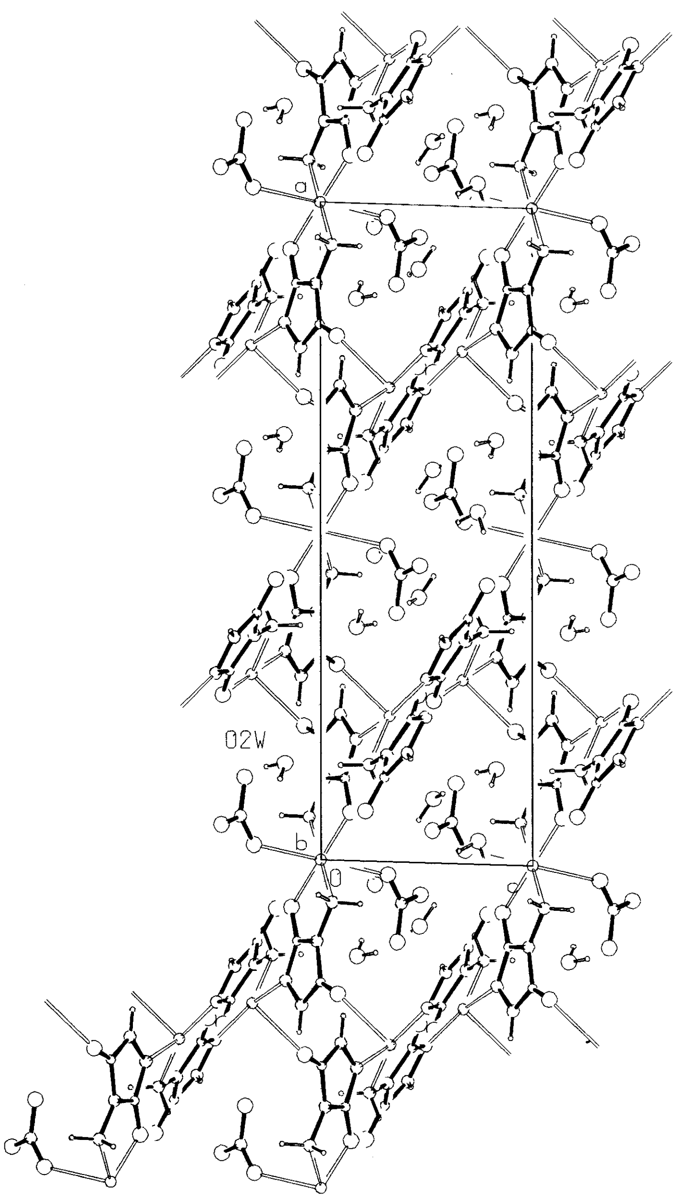

Fig. 6. Packing of $[Cu_3(NO_3)_2(ur)_4]_n \cdot 6nH_2O$ (**8**) projected along **b**.

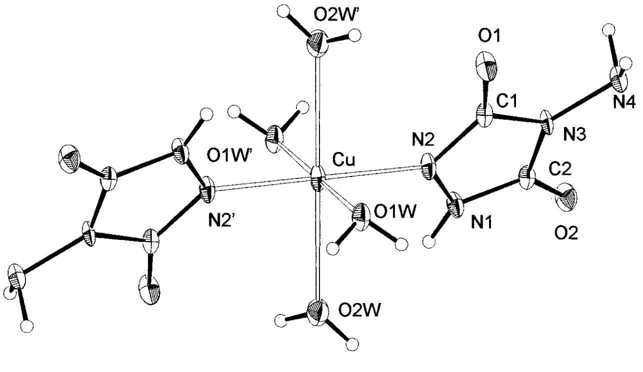

Fig. 7. Perspective view of compound $[Cu(ur)_2(OH_2)_4]$ (**9**). The thermal ellipsoids are drawn at the 30% probability level.

Cu(2)–N(42) due to the sp^2 character of N(21) and N(22). The copper atoms are disposed in layers parallel to $(10\bar{2})$ with the ur anions chelating and bridging in the same plane. The O(21) carbonyl oxygen atom, from parallel layers, completes the coordination of Cu(2). Cavities are filled by six water molecules and by the coordinated nitrate groups (Fig. 6). A complicated network of hydrogen bonds of the type $N–H\cdots O_w$, $N–H\cdots O$, $O_w–H\cdots O$ and $O_w–H\cdots O_w$ contributes to the packing.

3.2.4. *$[Cu(ur)_2(OH_2)_4]$ (9)*

The molecular structure of **9** (Fig. 7) shows discrete units of neutral centrosymmetric copper complexes with a tetragonally distorted octahedral coordination. Two deprotonated triazolidine nitrogen atoms from two ur anions (Cu–N(2) = 1.992(3) Å) and two oxygen atoms from water molecules (Cu–O(1w) = 2.042(3) Å), lie in the equatorial plane, two other water molecules occupy the axial positions (Cu–O(2W) = 2.318(3) Å). Important bond lengths and angles are summarised in Table 3. The ur anions are essentially planar (max. dev. from the mean plane 0.038(4) Å for O(1)), and form a dihedral angle with the equatorial plane of 60.65(9)°; the Cu atom is out of the ur mean plane by 0.2507(3) Å. The coordinated ur anions are oriented parallel to [100] and the Cu–N(2) bond is roughly perpendicular to (100) (Fig. 8). The packing is determined by hydrogen bonds between ur anions translated along **a** (N–H···O and HN–H···O) and between centrosymmetrically related ur anions along **b** (HN–H···O). The water molecules determine a 3D network of hydrogen bonds. Moreover a partial stacking between the ur anions is envisaged (N(3)···C(1) = 3.274(5) Å).

3.2.5. *$[Cu_2(SO_4)(ur)_2]_n \cdot 2nH_2O$ (10)*

The crystal structure of **10** consists of copper complexes linked by ur and SO_4^{2-} anions which result in a polymeric 3D packing. Each copper atom is surrounded by a chelating *N,O* ur anion, Cu–O(1)″ = 1.922(5), Cu–N(4)″ = 2.130(5) Å, an amide N atom, Cu–N(2) = 1.959(6) Å, a carbonyl oxygen atom, Cu–O(2)‴ = 2.336(6) Å, and an oxygen atom, Cu–O(3) = 1.983(4) Å, from a sulfate anion (Figs. 9 and 10). The coordination polyhedron can be described as a distorted square pyramid with O(2)‴ in axial position and a sixth extra position occupied by a water molecule with a semicoordinative interaction, Cu–O(1W) = 2.787(8) Å $(-x+3/4, y+1/4, z-1/4)$. The S atom of the sulfate anion lies on a crystallographic twofold axis bridging two copper atoms through O(3) and O(3)′ and as for **1** a remarkable *trans* influence of SO_4^{2-} is noted (Cu–N(4) = 2.130(5) Å). The ur anion is practically planar with a maximum deviation from the mean plane of 0.046(6) Å for N(3). It acts as tetradentate ligand, linking three symmetry related copper atoms and deter-

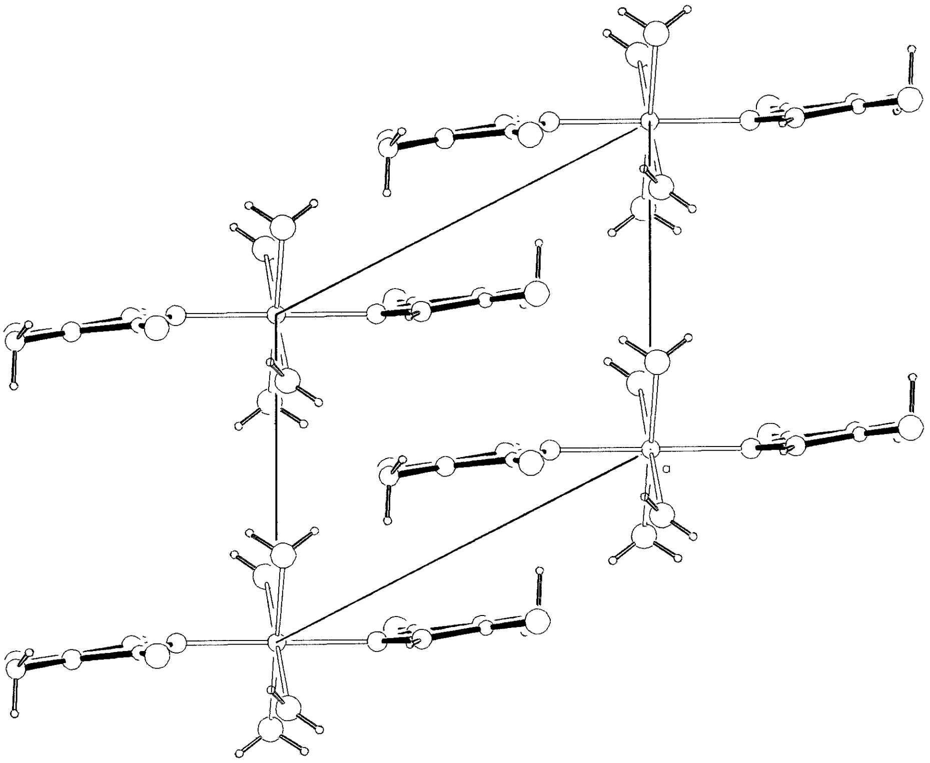

Fig. 8. Packing of $[Cu(ur)_2(OH_2)_4]$ (**9**) projected along **a**.

mining a 3D packing. The *N*,*O* chelated copper atom and the copper atom linked to N(2) are out of the ur mean plane, on opposite sides, by 0.393(1) and 0.331(1) Å, respectively. Selected bond distances and angles are listed in Table 3. The NH_2 and the triazolidine NH group form hydrogen bonds with two sulfate oxygen atoms and with the water molecule, respectively. Only one of the hydrogen atoms of the water molecule interacts with an oxygen atom of the sulfate. The ur anions are involved in partial stacking interactions [$N(1)\cdots N(1)^{iv} = 3.25(1)$, $N(1)\cdots N(3)''' = 3.25(1)$, $N(1)\cdots C(2)''' = 3.04(1)$, $N(2)\cdots C(2)''' = 3.15(1)$ Å; $'''$ $-x+1/2$, $-y$, $z+1/2$; ^{iv} $-x+1/2$, $-y$, $z-1/2$]. The compact network of complexes and the stacking are reflected in the high value of the density (2.476 Mg m^{-3}).

4. Concluding remarks

For Hur and its complexes $[CuCl_2(Hur)_2]$, $[Zn(SO_4)(OH_2)_2(Hur)]_n$ and $[Co(OH_2)_2(Hur)_2]Cl_2{\cdot}2H_2O$ the non-hydrogen atoms of the ligand are essentially coplanar. C–N bonds show a partial double bond character due to the resonance with the C=O bonds, but the endocyclic N–N bond distance is scarcely affected by this resonance being similar to the exocyclic one. The C=O bond lengths are very similar for Hur and the Cu and Zn complexes (range 1.224(2)–1.228(8) Å), but in the Co complex they are slightly longer (1.241(9) and 1.249(9) Å) probably as a consequence of the cationic nature of the complex. Of particular interest is the Zn compound that in the solid state, the examined crystal, presents a spontaneous resolution of the chiral complexes with configuration *OC*-6–32-*A* that are linked

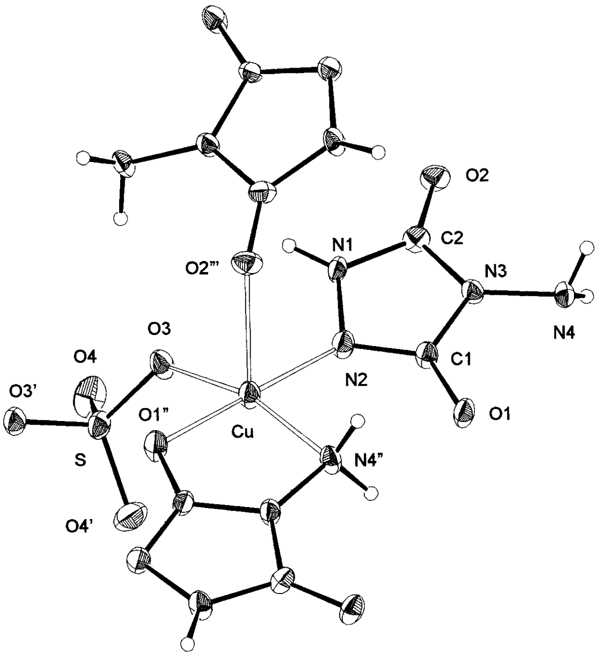

Fig. 9. Perspective view of compound $[Cu_2(SO_4)(ur)_2]_n{\cdot}2nH_2O$ (**10**). The thermal ellipsoids are drawn at the 30% probability level.

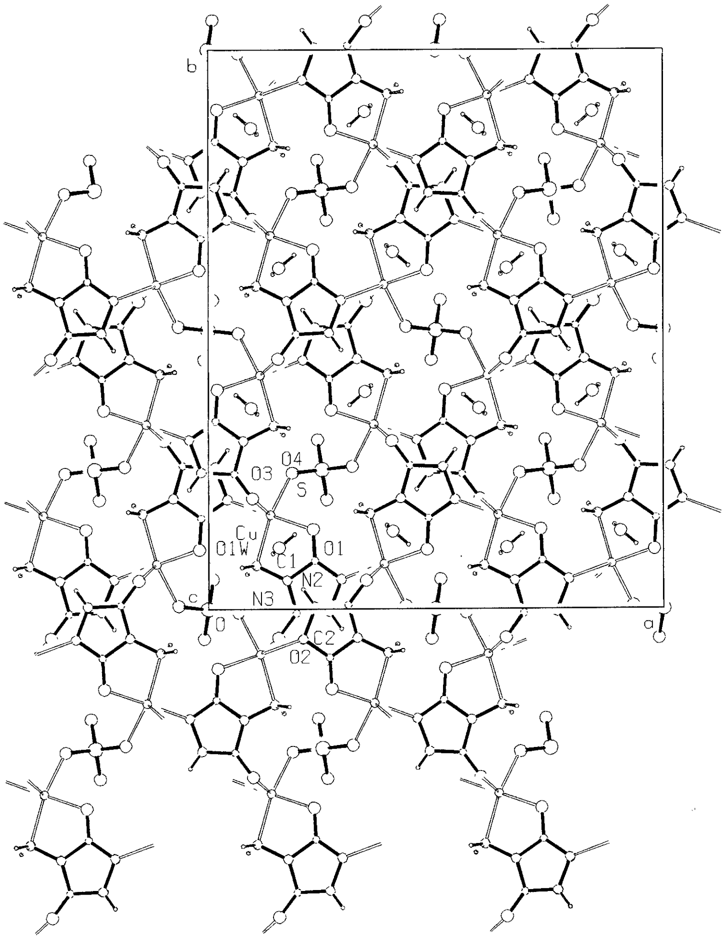

Fig. 10. Packing of $[Cu_2(SO_4)(ur)_2]_n \cdot 2nH_2O$ (**10**) projected along **c**.

together in a helicoidal arrangement with a Δ configuration.

In the Cu complexes **8**, **9** and **10** the non-hydrogen atoms of ur are coplanar and the endocyclic and exocyclic N–N bond lengths are very similar (1.400(7)–1.411(6) for **8**, 1.403(4), 1.403(4) for **9** and 1.406(7), 1.411(7) Å for **10**), the C–N bond distances show a remarkable double bond character enhanced for the C(1)–N(2) bonds involving the deprotonated N atom (1.323(7), 1.331(7) for **8**, 1.320(5) for **9** and 1.309(8) Å for **10**). The C=O bond lengths are in the range 1.228(7)–1.266(7) Å and the longest ones are well related to the strength of the Cu–O bonds. In all these complexes the deprotonated N(2) atoms bind the Cu atoms, the *N*,*O* chelation is observed in **8** and **10**, and the interaction of the second carbonyl oxygen atom with the metal is observed in **10**, and only for one of the two independent ur anionic ligands in **8**. Crystals of **9** were isolated together with crystals of **8** and for both complexes the nitrate anion was replaced totally or partially by an ur anion; this means that urazinate complexes can be obtained also at very low pH values. For both sulfate derivatives **3** and **10** the anion is coordinated and bridges the metal atoms showing a remarkable *trans* influence.

Hur and ur act as very versatile ligands forming complexes in the ratio M:L 1:1 or 1:2 and forming neutral or cationic, monomeric or polymeric 1D and 3D complexes.

5. Supplementary material

A full list of crystal data and refinement has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 146597–146601 for compounds **1**, **3**, **8**, **9** and **10**, respectively. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccd.cam.ac.uk).

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