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Syntheses, characterization and crystal structures of novel amine adducts of metal saccharinates, orotates and salicylates

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Abstract

Seven novel adducts of ethylenediamine (en), N,N'-dimethylethylenediamine (dmen) and N,N-dimethylethylenediamine (ndmen) with saccharinate, orotate and salicylate as counter-ions were synthesized and characterized with physico-chemical methods (IR and UV/vis spectroscopy, magnetic susceptibility and thermoanalytical measurements) and X-ray diffraction. Reaction of dmen with tetraaquabis(saccharinato-*N*)copper(II) dihydrate yielded diaquabis(dmen)copper(II) saccharinate, whereas with the corresponding nickel derivative it afforded bis(dmen)bis(saccharinato-*O*)nickel(II). In the copper complex the coordinated water and the primary nitrogen end of the donor ligand interact with the saccharinate anion [$\mathrm{O1w}\cdots\mathrm{O3} = 2.833(2)$, $\mathrm{N1}\cdots\mathrm{N2} = 2.992(2)$ Å]. Adjacent molecules are linked by two more hydrogen bonds into a layer structure. In the nickel compound, the dmen ligand also chelates the metal atom, which is bonded to the carbonyl oxygen of the anionic group. The negatively-charged nitrogen atom of the anion is intramolecularly linked to the dmen [$\mathrm{N1}\cdots\mathrm{N2} = 2.968(2)$ Å]; hydrogen bonds link the molecules into layers. Under mildly basic conditions, the reaction of orotic acid with cobalt(II) afforded tetraaqua(2,6-dioxo-1,2,6-trihydropyrimidine-4-carboxylato-*N*,*O*)cobalt(II) hydrate. The complex was oxidatively reacted with en to give a mixed-ligand cobalt(III) adduct which includes both mono- and bisdeprotonated orotate ions. The metal atom in tetraaqua(2,6-dioxo-1,2,6-trihydropyrimidine-4-carboxylato-*N*,*O*)cobalt(II) hydrate is chelated by the orotato dianion through the carboxyl oxygen and 3-pyrimidyl nitrogen atoms, and its octahedral geometry is completed by four water molecules. The 1-pyrimidyl nitrogen atom engages in hydrogen bonding with the lattice water molecule. The cobalt atom is similarly chelated by the orotato dianion in bis(en)(2,6-dioxo-1,2,6-trihydropyrimidine-4-carboxylato-*N*,*O*)cobalt(III) 2,6-dioxo-1,2,3,6-tetrahydropyridimidine-4-carboxylate pentahydrate. The copper atom in the five-coordinate aqua(en)orotatocopper(II) monohydrate is chelated by the en ligand, the deprotonated N1 pyrimidine atom and the orotate carboxylate oxygen; the water molecule completes the square-pyramidal coordination. The nickel and copper atoms in bis(en)bis(salicylato-*O*)nickel(II) and bis(ndmen)bis(salicylato-*O*)copper(II) monomeric octahedral complexes are coordinated by the salicylato monoanion through the carboxylate oxygen in a monodentate fashion and by the en and ndmen molecules through the two amine nitrogen atoms in a bidentate

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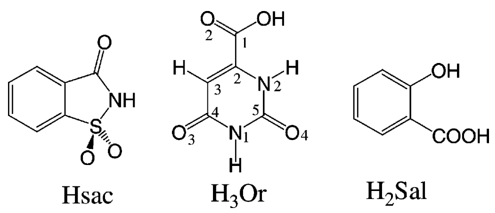
chelating manner. In the copper complex, the carboxylate oxygen atom engages in hydrogen bonding with the lattice water molecule.

Keywords: Amine complexes; Coordination; Orotate; Saccharinate; Salicylate

1. Introduction

The increasing scientific attention in the chemistry of saccharin (*o*-sulfobenzimide, sac; Scheme 1), an artificial sweetener, has been turned recently from model studies of its pathological action to its potentials for inclusion in functional solid materials. Sulfimide proton/cation acceptor sites appoint the *o*-sulfobenzimidate counter-anion as a valuable structural tool for construction of well-habited crystalline solids of desired structure. Several recent reviews deal with the structural preferences of the *o*-sulfobenzimidate moiety in the solid state [1–3]. Saccharinates readily form adducts with *N*-donor aromatic heterocycles, which in turn provide an insight into their coordination preferences in presence of ancillary ligands. Recently, there has been increased interest in the saccharinate adducts with alkyl or hydroxyalkyl amines, studied extensively by Yilmaz et al. [4–15] and others [16], as the conformational flexibility of such readily-coordinating ligands allows for the saccharinate ion to adopt the thermodynamically-preferred coordination mode. As the flexible short aliphatic amine backbones can occasionally result in polymeric triangulo-trimetal clustered complexes that model the active sites of some enzymes [17,18], we were challenged to combine these lower aliphatic diamines with the polyfunctional rigid saccharinate moiety in mixed-ligand saccharinates. In the present paper, the syntheses of three N,N'-dimethylethylenediamine (dmen) disaccharinate adducts and the X-ray crystal structures of the copper(II) and nickel(II) adducts are described.



Scheme 1.

Orotic acid (6-uracilic acid, 1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidine carboxylic acid, vitamin B_{13}, H_3Or; Scheme 1) is a key compound in the biosynthesis of pyrimidine bases of nucleic acids in living organisms [19]. It also exhibits bacteriostatic and cytostatic properties. Besides the biological relevance, the orotic acid and its anions H_2Or^-, HOr^{2-} and Or^{3-} are interesting multidentate ligands as they can coordinate through the two pyrimidine nitrogen atoms, the two carbonyl oxygens and the oxygens from the carboxyl group. The equilibrium composition of the reactant mixture and thus the solution pH are critical factors which determine the mode of coordination. Between pH 3 and 9, orotic acid exists mainly as readily-coordinating monodeprotonated H_2Or^- (the carboxylic group has $pK = 2.07$). The literature lists many reports on the coordinating preferences of the orotate moiety in metal complexes. It was found that in solutions with neutral or slightly acidic pH, Cu(II), Zn(II), Co(II), Mn(II), Fe(III), Cr(III), VO(II), Cd(II), Hg(II) and Ag(I) are coordinated through the carboxylate group, while Ni(II), Co(II) and Cu(II) are coordinated through the carboxylate end and the adjacent N1 [20–24]. Bidentate binding through N1 and the carboxylate group was observed by several crystal structure determinations [25–29]. In the complexes $[Co(HOr)(OH)(H_2O)(NH_3)]_n$ and $[Ni(HOr)(OH)(H_2O)_2(NH_3)]_n$ the orotate anion bridges the metal ions through the carboxylate and the N1 and O2 atoms, forming one-dimensional polymeric chains [30]. A recent reinvestigation of nickel(II) orotate pentahydrate $[Ni(HOr)(H_2O)_4]\cdot H_2O$ by modern diffraction, spectroscopic and theoretical methods revealed novel structural features [31]. In the present study, we have synthesized and characterized the analogous pentahydrate salt of cobalt(II). In order to investigate the difference in the coordination type of the orotate with the same metal in different oxidation states, the metal was oxidized and stabilized in situ by chelation with ethylenediamine (en). The resulting crystalline product included both mono and bisdeprotonated orotate anions in the same structure. Here are also presented the results of the syntheses, characterization and crystal structure determination of the ethylenediamine adduct of copper(II) orotate dihydrate.

Salicylic acid (H_2sal; Scheme 1) and metal salicylates have been used for many years as anti-inflammatory, antipyretic and analgesic drugs in medicine [32–35]. In aqueous solutions, the acid affords hydrogensalicylate (Hsal$^-$) and salicylate (sal^{2-}) ions. The 2-$HOC_6H_4CO_2^-$ (Hsal$^-$) anion can bind to metals as unidentate carboxylate, bidentate chelating (employing one carboxylate oxygen and hydroxyl oxygen atoms) or bidentate bridging carboxylate ligand. The bisdeprotonated anion $[OC_6H_4CO_2]^{2-}$ (sal^{2-}) regularly chelates through the hydroxyl and one of the carboxylate oxygen atoms [36]. The X-ray structures of several mononuclear metal(II) complexes of salicylate derivatives with *N*-donor ligands have been reported [33–37]. It has been found that the increase of acidity of the alkylcarboxylate ligands or of the basicity of the basic ligands promotes formation of monomeric complexes [33]. Crystalline coordination polymers, such as [Mn(Hsal)$_2$(bipyridine)]·H_2O, are also known [38]. The present report describes the synthesis, characterization and crystal structures of two novel metal (copper and nickel) salicylate adducts, with en and *N*,*N*-dimethylethylenediamine (ndmen) as secondary ligands.

2. Experimental

2.1. Syntheses

2.1.1. [M(sac)$_2$(H_2O)$_4$]·2H_2O (M = Co, Cu, Ni)

To prepare the starting tetraaquadi(*o*-sulfobenzimidato)copper(II) dihydrate precursor, sodium saccharinate (1.025 g, 5 mmol) in water (50 ml) was added to a warm stirred aqueous (50 ml) solution of the respective metal sulfates (2.5 mmol, Co(II): 0.703 g; Ni(II): 0.657 g; Cu(II): 0.624 g). The pink (Co), light blue (Cu) and green (Ni) crystals of the respective saccharinates [M(sac)$_2$(H_2O)$_4$]·2H_2O (M = Co, Cu, Ni) that appeared upon cooling of the solution were filtered out and washed with cold distilled water (10 ml) and dried in vacuo.

2.1.2. [Co(dmen)$_2$(sac)$_2$], [Ni(dmen)$_2$(sac)$_2$] and [Cu(dmen)$_2$(H_2O)$_2$](sac)$_2$

Solution of *N*,*N′*-dimethylethylenediamine (dmen) (0.176 g, 2 mmol) in water (30 ml) was dropped upon stirring to the solution of the metal saccharinates (1.0 mmol; Co(II): 0.531 g; Ni(II): 0.530 g; Cu(II): 0.535 g) in 50 ml of hot water. The mixtures were heated to 80 °C in a temperature-controlled bath with stirring during 4 h. The crystals that formed upon cooling to room temperature were separated by filtration, washed with 10 ml-portions of cold water/acetone and dried in vacuo. Specimens suitable for the diffraction experiment were selected among the regular large deep blue prisms of the copper adduct and the irregular magenta crystals of the nickel complex; the pink cobalt compound did not furnish crystals of good quality. The elemental analyses, magnetic susceptibility, spectral (UV/Vis and IR) and thermal (TG/DTG/DTA) data of the products detailed elsewhere [39] support the compositions $[Co(C_4H_{12}N_2)_2(C_7H_4NO_3S)_2]$, $[Ni(C_4H_{12}N_2)_2(C_7H_4NO_3S)_2]$ and $[Cu(C_4H_{12}N_2)_2(H_2O)_2](C_7H_4NO_3S)_2$.

2.1.3. [Co(HOr)(H_2O)$_4$]·H_2O and [Cu(HOr)(H_2O)$_4$]·H_2O

Mixture of $CoCl_2·6H_2O$ (1.19 g, 5 mmol) or $CuCl_2·2H_2O$ (0.85 g, 5 mmol) in water (25 ml) and $NaHCO_3$ (0.42 g, 5 mmol) in water (25 ml) was dropped with stirring into an aqueous (25 ml) suspension of orotic acid (0.87 g, 5 mmol) at 80 °C. The suspension was refluxed and stirred for 24 h at 80 °C in a temperature-controlled bath. After degassing from CO_2, the clear solution was cooled to room temperature. The pinkish-orange crystals from the cobalt complex and the blue crystals from the copper complex were filtered off and washed with 10 ml-portions of cold distilled water and acetone and dried in vacuo. Yield, Co complex: 1.40 g (82.8%). Found: C, 20.2; H, 3.9; N, 9.5. Calc. for $Co(C_5H_2N_2O_4)(H_2O)_5$: C, 19.8; H, 4.0; N, 9.2%. Yield, Cu complex: 1.22 g (81.4%).

2.1.4. [Co(HOr)(en)$_2$]·H_2Or·5H_2O

Solution of ethylenediamine (0.24 g, 4 mmol) in water (10 ml) was dropped into a stirred solution of [Co(HOr)(H_2O)$_4$]·H_2O (0.61 g, 2 mmol) in water (50 ml). The solution was heated to 60 °C in a temperature-controlled bath and then refluxed and stirred for 12 h at 60 °C while bubbling air to oxidize the metal. The violet-pink crystals that formed after cooling to room temperature were filtered off and washed with 10 ml-portions of cold distilled water and acetone and dried in vacuo. Yield: 0.92 g (79.3%). Found: C, 29.5; H, 5.3; N, 19.7. Calc. for $Co(C_5H_2N_2O_4)(C_2H_8N_2)_2(C_5H_3N_2O_4)(H_2O)_5$: C, 29.1; H, 5.4; N, 19.4%.

2.1.5. [Cu(HOr)(H_2O)(en)]·H_2O

A solution of en (0.24 g, 4 mmol) in water (10 ml) was dropped into a stirred solution of [Cu(HOr)$(H_2O)_4$]·H_2O (0.60 g, 2 mmol) in water (50 ml). The solution was heated to 60 °C and refluxed with stirring at that temperature for 12 h. The blue crystals that formed upon cooling to room temperature were washed with cold water and acetone and dried in vacuo. Yield: 0.57 g (90.8%). Found: C, 26.99; H, 4.0; N 17.67. Calc for $Cu(C_5H_2N_2O_4)(C_2H_8N_2)(H_2O)_2$: C, 26.77; H, 4.46; N, 17.85%.

2.1.6. [Ni(Hsal)$_2$$(H_2O)_4$]·$2H_2O$

$NiSO_4·6H_2O$ (1.31 g, 5 mmol) in water (25 ml) was dropped into a stirred solution of sodium salicylate (1.60 g, 10 mmol) in water (25 ml) at 50 °C. The mixture was stirred at 50 °C in a temperature-controlled bath during 4 h. The green crystals formed upon cooling to room temperature were filtered off and washed with 10 ml-portions of cold water and acetone, and dried in vacuo. Yield: 0.91 g. (41.4%).

2.1.7. [Ni(Hsal)$_2$(en)$_2$]

Ethylenediamine (0.12 g, 2 mmol) in water (15 ml) was dropped into a stirred solution of [Ni(Hsal)$_2$$(H_2O)_4$]·$2H_2O$ (0.41 g, 1 mmol) in water (25 ml). The mixture was heated to 50 °C and stirred for 2 h in a temperature-controlled bath. The yellow crystals that formed upon cooling to room temperature were filtered off and washed with 10 ml-portions of cold water and acetone, and dried in vacuo. Yield: 0.38 g (82.7%). Found: C, 47.83; H, 6.06; N, 11.94. Calc. for $C_{18}H_{26}N_4NiO_6$: C, 47.66; H, 5.74; N, 12.35%.

2.1.8. [Cu(Hsal)$_2$$(H_2O)_4$]·$2H_2O$

$CuSO_4·5H_2O$ (1.25 g, 5 mmol) in water (25 ml) was dropped into a stirred solution of sodium salicylate (1.60 g, 10 mmol) in water (25 ml) at 50 °C. The mixture was stirred at 50 °C in a temperature-controlled bath for 4 h. The green crystals that formed upon cooling of the clear solution to room temperature were filtered off and washed with 10 ml-portions of cold water and acetone, and dried in vacuo. Yield: 0.95 g. (43.4%).

2.1.9. [Cu(Hsal)$_2$(ndmen)$_2$]·H_2O

N, *N*-dimethylethylenediamine (0.18 g, 2 mmol) in water (15 ml) was dropped into a stirred solution of [Cu(Hsal)$_2$$(H_2O)_4$]·$2H_2O$ (0.45 g, 1 mmol) in water (25 ml). The solution was heated to 50 °C and stirred for 2 h in a temperature-controlled bath and then cooled to room temperature. The blue crystals that formed were filtered off and washed with 10 ml-portions of cold water and acetone, and dried in vacuo. Yield: 0.33 g (43.8%). Found: C, 49.29; H, 6.78; N, 9.92. Calc. for $C_{22}H_{36}CuN_4O_7$: C, 49.64; H, 6.76; N, 10.53%.

2.1.10. Materials and physico-chemical measurements

All chemicals used were analytical regent products. Elemental (C, H, N) analyses were carried out by standard methods (TÜBITAK Marmara Research Center, Turkey). Magnetic susceptibility measurements at room temperatures were performed using a Sherwood Scientific MXI model Gouy magnetic balance. UV/vis spectra were obtained from the aqueous solutions of the complexes with a Unicam UV2 spectrometer in the 900–190 nm range. IR spectra were recorded in the 4000–400 cm^{-1} region with a Mattson 1000 FT IR spectrometer using KBr pellets. A Rigaku TG8110 thermal analyzer was used to record simultaneous TG, DTG and DTA curves in a static air atmosphere (a flow rate of 80 ml min^{-1} dynamic nitrogen atmosphere was employed for Co(II) and Co(III) complexes only) at a heating rate of 10 min^{-1} in the temperature range 20 − 1000 °C using platinum crucibles. Highly sintered α-Al_2O_3 was used as reference and the DTG sensitivity was 0.05 mg s^{-1}. The final decompositions products were identified by IR comparison with the pure oxides.

2.1.11. X-ray diffraction

The diffraction measurements for all crystals were carried out at −90 °C with a Siemens CCD area-detector diffractometer. The intensities were corrected for absorption effects [40]. The structures were solved by direct methods and refined on F^2 [41]; the crystallographic details are listed in Table 1. The structures are illustrated as ORTEP [42] plots in the figures.

3. Results and discussion

3.1. Saccharinate complexes

3.1.1. General discussion

The reaction of the corresponding tetraaquadisaccharinatemetal(II) dihydrate with dmen results in partial substitution of the ligands by the bidentate amine chelator, yielding compounds characterized by physicochemical methods as $[Co(dmen)_2(sac)_2]$, $[Ni(dmen)_2(sac)_2]$ and $[Cu(dmen)_2(H_2O)_2](sac)_2$. While the amine replaces all aqua molecules in the tetraaquadisaccharinato pro-complexes of cobalt(II) and nickel(II), under virtually identical reaction conditions the strongly bonded pair of water molecules in the Jahn–Teller distorted copper reagent is retained, the *o*-sulfobenzimidate ligands being displaced to the outer sphere instead. The *o*-sulfobenzimidate exchange is feasible due to the intermediate covalency of the metal-N(sac) bonds in the parent saccharinates [43]. It becomes apparent that the *o*-sulfobenzimidate counter-ion has only a secondary role in the determination of the coordination type; its eventual participation in the coordination sphere is primarily directed by the available sites at the metal center and the chelation requirements of the amine.

3.1.2. X-ray structures and spectral data

The metal atom in diaquabis(dmen)copper(II) di(*o*-sulfobenzimidate) (Fig. 1) is placed at a center of symmetry, being octahedrally coordinated by a pair of equatorial bidentate dmen ligands and contacted by two apical trans-aqua molecules. The coordination results in a single electronic band at $\lambda_{max} = 563$ nm which is assigned to a $^2E_g \rightarrow {}^2T_{2\,g}$ transition [39]. The equatorial angles around the metal sum up to 360°. The *o*-sulfobenzimidate ions contact the metal indirectly, via hydrogen bonds with the coordinated water $O1w\cdots O = 2.833(2)$. The negative nitrogen end simultaneously binds to the amine hydrogen [$N\cdots N = 2.992(2)$ Å], the carboximide acceptor thus bridging the two ligands. *Trans*-octahedral $N_4(O\,w)_2$-coordinated copper centers with both *o*-sulfobenzimidate counter-ions in the lattice were also observed in the *p*-aminopyridine [44] and *N*-allylimidazole [45] adducts; in all cases, the saccharinate contacts the metal indirectly through the carbonyl group. Analysis of large number of saccharinates shows that electronic effects favor the carboximide side of the heterocycle for coordination over the sulfimide part [2]. In the tetrakis(isoquinoline) adduct [44], two *o*-sulfobenzimidate carbonyl oxygens contact the metal; only occasionally, the sulfonyl oxygen can play the role as in the case of the tetrakis(*p*-methylpyridine) compound. The molecular parameters of the dmen ligand are normal if compared with its average Cambridge Structural Database (CSD) structure (CH_3–$N = 1.480$, N–$CH_2 = 1.477$, C–$C = 1.497$ Å) [46][1]. The amine chelates the copper atom at larger angle (85.3(1)°) than that of the ethanolamine, 80.97(6)° [5], but close to the average CSD value of 84.5°. The adjacent molecules are linked by two more hydrogen bonds between the sulfobenzimide oxygen atoms and the water/amine donors [$N3$–$H\cdots O3 = 3.062(2)$; $O1w$–$H\cdots O2 = 2.844(2)$ Å] into a layer structure (Fig. 2). The carbonyl stretching mode of the copper complex at 1623 m^{-1}, is red-shifted by the hydrogen bonding from the typically 'ionic' saccharinate value in copper (II) saccharinates (1638 cm^{-1}) closer to the *O*-coordinated (ca. 1625 cm^{-1}).

In the structure of the neutral solvent-free adduct bis(dmen)bis(sac-*O*)nickel(II) (Fig. 3), the nickel atom is octahedrally surrounded by a pair of equidistant bidentate dmen ligands. The analytical data [39] suggested possible isostructurality with the cobalt(II) analogue. The internal angle of the amine chelation ring at the metal amounts 83.9(1)°, the bond distances being normal. The four N–Ni–N angles add to 360°. The saccharinato ligands bind to the metal at slightly longer distance. The elongated carbonyl group at 1.248(2) Å and shortened C7–N1 bond at 1.343(2) Å reveal dominance of the 1,2-benzisothiazolyl-3-olato 1,1-dioxide resonant form in the imidate structure. Strong red-shift of the saccharin carbonyl

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[1] October 2001 version of the CSD. Only unsubstituted dmen ligands (12 residues in 9 hits) chelated to a single transition metal were included in the analysis.

Table 1
Crystal data

Compound	$[Cu(dmen)_2(H_2O)_2](sac)_2$	$[Ni(dmen)_2(sac)_2]$
Colour	Deep blue	Lilac
Empirical formula	$C_{22}H_{36}CuN_6O_8S_2$	$C_{22}H_{32}N_6NiO_6S_2$
Formula weight	640.23	599.37
Space group	$P2_1/n$	$P2_1/c$
Cell dimensions		
a (Å)	11.8408(5)	8.7752(4)
b (Å)	7.8447(3)	11.7297(5)
c (Å)	5.6141(7)	12.9264(6)
β (°)	110.802(1)	94.919(1)
Volume (Å^3)	1355.8(1)	1325.6(1)
Z	2	2
θ_{max} (° for data collection)	29.4	29.4
Reflections collected	9473	9322
Independent reflections	3448 ($R_{int} = 0.090$)	3357 ($R_{int} = 0.098$)
Reflections with $I > 2\sigma(I)$	2964	2854
No. parameters refined	187	170
$R[I > 2\sigma(I), R$ (all reflections)	0.048/0.057	0.045/0.056
$wR[I > 2\sigma(I)], R$ (all reflections)	0.120/0.125	0.110/0.114
w	$[\sigma^2 + (0.0549P)^2]^{-1}$	$[\sigma^2 + (0.0472P)^2]^{-1}$
Goodness-of-fit on F^2	1.05	1.00
Diff. hole and peak (eÅ^{-3})	−0.83 to 0.72	−0.86 to 0.72
CCDC deposition no.	179764	179765

Compound	$[Co(HOr)(H_2O)_4]\cdot H_2O$	$[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$
Color	Orange	Orange
Empirical formula	$C_5H_{12}CoN_2O_9$	$C_{14}H_{31}CoN_8O_{13}$
Formula weight	303.10	578.40
Space group	$P-1$	$P-1$
Cell dimensions		
a (Å)	7.2609(5)	8.3124(4)
b (Å)	8.3340(6)	10.5308(6)
c (Å)	10.0864(7)	13.7098(8)
α (°)	70.458(1)	102.199(1)
β (°)	80.528(1)	93.028(1)
γ (°)	64.666(1)	96.387(1)
Volume (Å^3)	519.71(6)	1162.1(1)
Z	2	2
θ_{max} (° for data collection)	29.4	29.3
Reflections collected	3818	8281
Independent reflections	2521 ($R_{\rm int} = 0.056$)	5497 ($R_{\rm int} = 0.084$)
Reflections with $I > 2\sigma(I)$	2315	3237
No. parameters refined	194	325
$R[I > 2\sigma(I)], R$ (all reflections)	0.061/0.066	0.084/0.123
$wR[I > 2\sigma(I)], R$ (all reflections)	0.159/0.162	0.201/0.215
w	$[\sigma^2 + (0.1101P)^2]^{-1}$	$[\sigma^2 + (0.0831P)^2]^{-1}$
Goodness-of-fit on F^2	1.02	0.97
Diff. hole and peak (eÅ^{-3})	−1.15 to 1.13	−1.60 to 2.32
CCDC deposition no.	179906	179907

Table 1 (*continued*)

Compound	$[Co(HOr)(H_2O)(en)]\cdot H_2O$
Color	Blue
Empirical formula	$C_7H_{14}CuN_4O_6$
Formula weight	313.76
Space group	$P-1$
Cell dimensions	
a (Å)	7.3609(5)
b (Å)	9.0149(6)
c (Å)	9.4968(6)
α (°)	67.100(1)
β (°)	72.923(1)
γ (°)	82.687(1)
Volume (Å^3)	554.9(1)
Z	2
θ_{max} (° for data collection)	29.3
Reflections collected	4069
Independent reflections	2695 ($R_{int} = 0.079$)
Reflections with $I > 2\sigma(I)$	2539
No. parameters refined	176
$R[I > 2\sigma(I)], R$ (all reflections)	0.078/0.083
$wR[I > 2\sigma(I)], R$ (all reflections)	0.185/0.188
w	$[\sigma^2 + (0.1000P)^2]^{-1}$
Goodness-of-fit on F^2	1.12
Diff. hole and peak (eÅ^{-3})	-2.39 to 1.84
CCDC deposition no.	179908

Compound	$[Cu(Hsal)_2(ndmen)_2]\cdot H_2O$	$[Ni(Hsal)_2(en)_2]$
Color	Blue	Yellow
Empirical formula	$C_{22}H_{36}CuN_4O_7$	$C_{18}H_{26}N_4NiO_6$
Formula weight	532.09	453.14
Space group	$C2/c$	$P2_1/c$
Cell dimensions		
a (Å)	17.0630(8)	10.4537(4)
b (Å)	9.4689(4)	9.3767(4)
c (Å)	15.5823(7)	20.3746(9)
β (°)	99.475(1)	94.447(1)
Volume (Å^3)	2483.3(2)	1991.1(1)
Z	4	4
θ_{max}, for data collection (°)	29.6	29.5
Reflections collected	8788	13617
Independent reflections	3143 ($R_{int} = 0.100$)	5003 ($R_{int} = 0.096$)
Reflections with $I > 2\sigma(I)$	2547	3260
No. parameters refined	161	267
$R[I > 2\sigma(I)]$, R (all reflections)	0.049/0.065	0.046/0.074
$wR[I > 2\sigma(I)], R$ (all reflections)	0.117/0.122	0.105/0.113
w	$[\sigma^2 + (0.0635P)^2]^{-1}$	$[\sigma^2 + (0.0327P)^2]^{-1}$
Goodness-of-fit on F^2	0.95	0.88
Diff. hole and peak (eÅ^{-3})	-1.45 to 0.65	-1.49 to 0.58
CCDC deposition no.	181779	181780

stretching mode in the IR spectrum of the nickel complex (1618 cm^{-1}), below the region of ionic saccharinates, reveals the pronounced depletion of electron density along the C–O group due to the coordination of the ligand. This is considered [1] a firm spectroscopic evidence of the ionic character of the metal-saccharinate bonds. The negatively charged nitrogen atom participates in an intramolecular

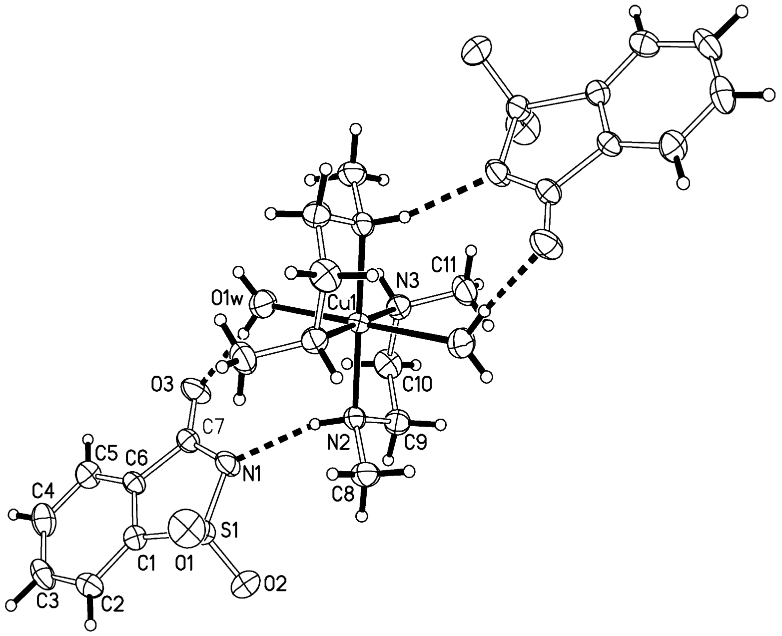

Fig. 1. ORTEP plot of bis(N,N'-dimethylethylenediamine)diaquacopper(II) di(o-sulfobenzimidate) at the 75% probability level illustrating the octahedral geometry of the copper atom. Selected bond distances and angles: Cu1–N2 = 2.040(2), Cu1–N3 = 2.052(2) Cu1–O1w = 2.522(2) Å; N2–Cu1–N2^i = 180.0, N2–Cu1–N3 = 85.3(1), N2–Cu1–N3^i = 94.7(1), N2–Cu1–O1w = 87.6(1), N2–Cu1–O1w^i = 92.4(1), N3–Cu1–N3^i = 180, N3–Cu1–O1w = 81.0(1), N3–Cu1–O1w^i = 99.0(1) O1w–Cu1–O1w^i = 180°. Symmetry transformation: i = $1/2 - x, 1/2 - y, 1/2 - z$.

hydrogen bond with the amino group of the amine ligand [N2–H···N1 = 2.968(2) Å]. An additional intermolecular hydrogen bond between the amine donor and the saccharinate sulfonyl group [N3–H···O2 = 3.094(2) Å] links the molecules into layers (Fig. 4). The bands at λ_{max} of 366, 600 and 900 nm in the electronic spectrum, assigned to the ν_3 : $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, ν_2 : $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ν_1 : $^3A_{2g} \rightarrow {}^3T_{2g}$ d–d transitions [39] correspond with the octahedral coordination.

3.2. Orotate complexes

3.2.1. General discussion

Weakly basic aqueous mixture of orotic acid afforded with cobalt(II) a pentahydrate salt $[Co(HOr)(H_2O)_4]\cdot H_2O$. The compound, when oxidized with air in presence of en, gave a high yield of crystalline bis(en) pentahydrate adduct, for which the analytical data indicated the formula $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$. The molar conductance values of the complexes (Λ_M = 81 and 113 Ω^{-1} cm^2 mol^{-1} for $[Co(HOr)(H_2O)_4]\cdot H_2O$ and $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$, respectively) confirmed that $[Co(HOr)(H_2O)_4]\cdot H_2O$ is a non-electrolyte and $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$ is a 1:1 electrolyte in aqueous solutions. $[Co(HOr)(H_2O)_4]\cdot H_2O$ exhibits magnetic moment value of 4.31 BM which corresponds to three unpaired electrons, consistent with a high-spin weak-field octahedral geometry. The complex $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$ proved to be diamagnetic and a strong-field octahedral complex.

The molar conductance value of the copper complex (Λ_M = 61 Ω^{-1} cm^2 mol^{-1}) indicated that $[Cu(HOr)(H_2O)(en)]\cdot H_2O$ is an non-electrolyte and exhibits an experimental magnetic moment value of 1.61 BM, corresponding to one unpaired electron.

3.2.2. UV–vis spectra

The d–d transition spectra of the complexes in H_2O are compatible with distorted octahedral configurations. The λ_{max} values in the absorption spectrum of $[Co(HOr)(H_2O)_4]\cdot H_2O$ amount 524 and 582 nm, the corresponding e values are 18.1 and 15.4 cm^{-1} M^{-1}. These bands are assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and

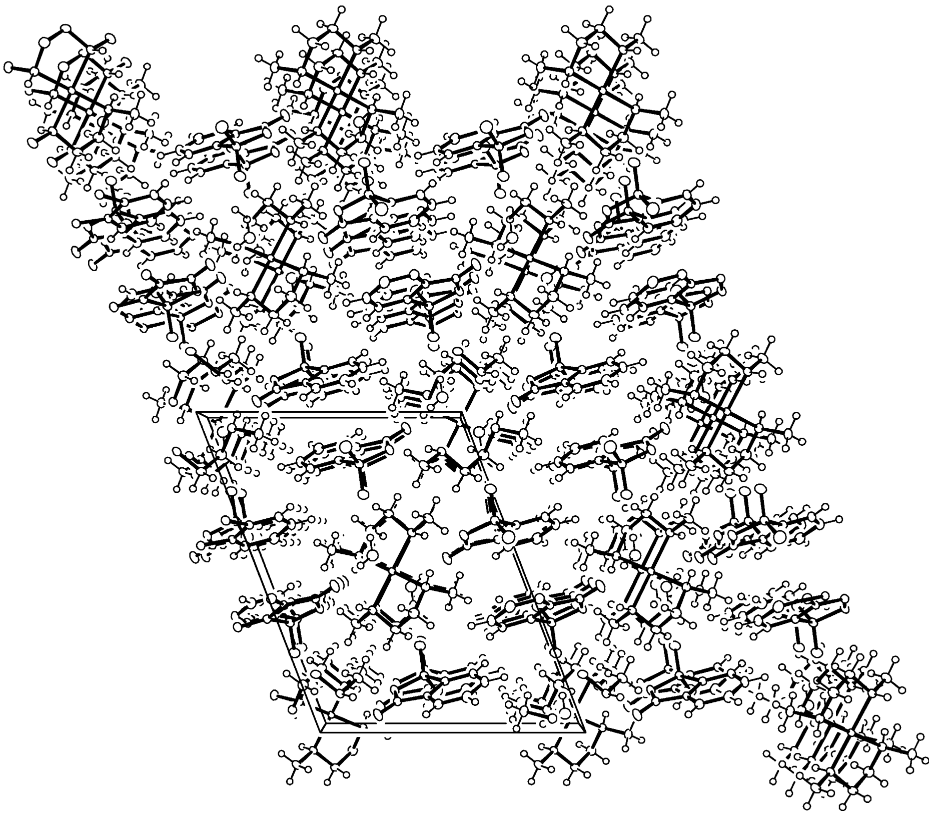

Fig. 2. The molecular packing in the structure of bis(N,N'-dimethylethylenediamine)diaquacopper(II) di(o-sulfobenzimidate) viewed along the b-axis (the hydrogen bonds are not shown).

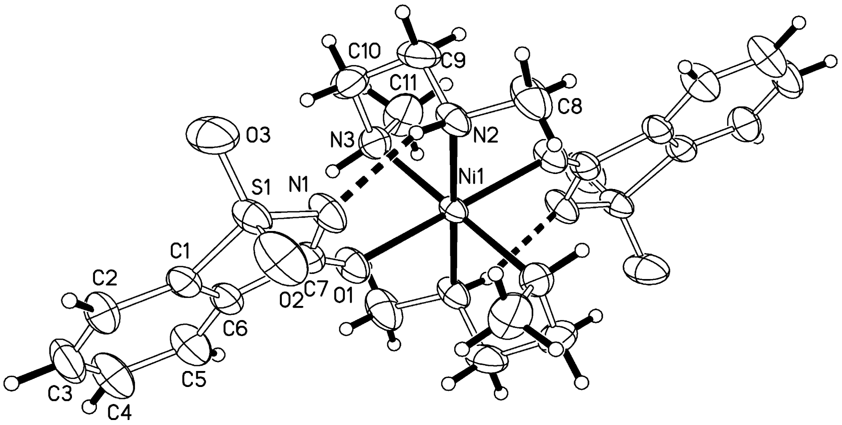

Fig. 3. ORTEP plot of bis(N,N'-dimethylethylenediamine)bis(o-sulfobenzimidato-O)nickel(II) at the 75% probability level illustrating the octahedral geometry of the nickel atom. Selected bond distances and angles: Ni1–N2 = 2.105(1), Ni1–N3 = 2.102(2), Ni1–O1 = 2.133(1) Å; N2–Ni1–N2^{i} = 180.0, N2–Ni1–N3 = 83.9(1), N2–Ni1–N3^{i} = 96.1(1), N2–Ni1–O1 = 94.0(1), N2–Ni1–O1^{i} = 86.0(1), N3–Ni1–N3^{i} = 180.0, N3–Ni1–O1 = 85.7(1), N3–Ni1–O1^{ii} = 94.3(1), O1-Ni1-O1^{ii} = 180.0°. Symmetry transformation: i = $1/2 - x, 1/2 - y, 1/2 - z$; ii = $-x, -y, -z$.

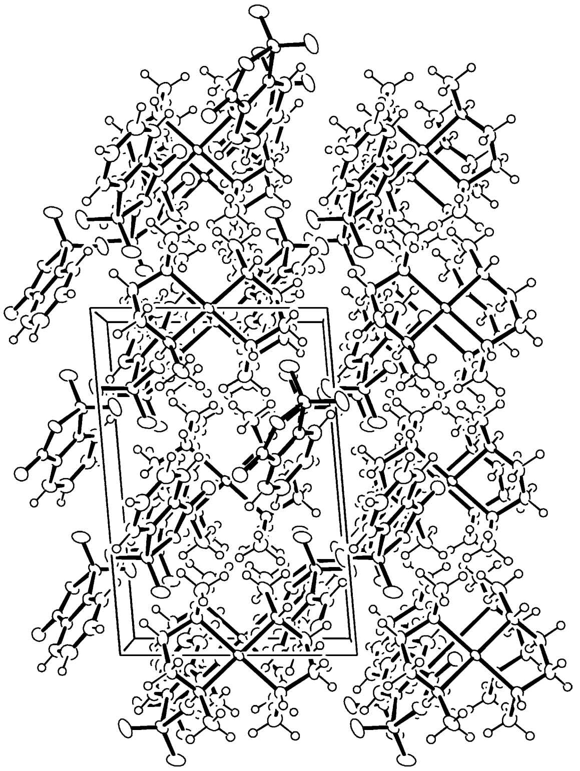

Fig. 4. The molecular packing in the structure of bis(*N*,*N*′-dimethylethylenediamine)bis(*o*-sulfobenzimidato-*O*)nickel(II) viewed along the *b*-axis (the hydrogen bonds are not shown).

$^4T_1g \rightarrow {}^4A_{2\ g}$ d–d transitions. The MLCT band is centered at 310 nm. The complex $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$ has a band around 488 nm ($\varepsilon = 160\ cm^{-1}\ M^{-1}$) which is assignable to the $^1A_{1g} \rightarrow {}^1T_{1\ g}$ transition and suggests a distorted octahedral stereochemistry. The MLCT band appears around 294 nm. The absorption spectra indicate that the cobalt(III) complex forms a stronger crystal field than the cobalt(II) compound.

The d–d transition spectrum of $[Cu(HOr)(H_2O)(en)]\cdot H_2O$ is compatible with distorted square-pyramidal configuration. The maximal absorption is at 601 nm and the respective ε value is $68.0\ cm^{-1}\ M^{-1}$. This band is assigned to the $a_1 \rightarrow b_1$ d–d transition. The band observed at around 307 nm ($\varepsilon = 1829\ cm^{-1}\ M^{-1}$) is attributed to MLCT.

3.2.3. IR spectra

In the spectrum of $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$, the N1/N3–H stretching bands at 3154/3137 cm^{-1} of orotic acid [47] were clearly observable as strong doublet at 3220/3130 cm^{-1} accompanied by two bands probably resulted by Fermi resonance (2983, 2812 cm^{-1}). In the spectrum of $[Co(HOr)(H_2O)_4]\cdot H_2O$, the expected N3–H band was heavily overlapped with the OH stretchings and could not be discerned with confidence among the peaks at 3326, 3212 and 3126 cm^{-1} on the broad absorption in the 3650–2600 cm^{-1} region. Deformation of the N3–H group (contribution of ca. 60% to the respective mode) in the latter complex gives rise to a band at 1392 cm^{-1}, close to the 1388 cm^{-1} band in the spectrum of $[Ni(HOr)(H_2O)_4]\cdot H_2O$ [13]. A doublet of $\delta_{N1/N3-H}$ bands at 1425 and 1381 cm^{-1} appears in the spectrum of $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$, consistent with the presence of H_2Or^- ligands. In $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$, the water stretching gives bands at 3482 and 3433 cm^{-1}. The spectral data suggest notably stronger hydrogen bonding in the structure of cobalt(II) orotate than in the amine adduct.

Stretchings of the carbonyl groups of polycrystalline H_3Or give rise to three strong and overlapped bands, at 1729 ($66\%\nu_{C=O(carboxylic)} + 17\%\nu_{C5=O4,in\text{-}phase}$), 1719 ($56\%\nu_{C5=O4} + 19\%\nu_{C=O(carboxylic),\ out\text{-}of\text{-}phase}$) and 1700 cm^{-1} ($73\%\nu_{C4=O3} + 11\%\nu_{ring}$) [47]. In the infrared spectrum of nickel orotate [31], a complex band at 1612 cm^{-1} appears. Three carbonyl bands were observed in the Raman spectrum, at 1661 ($88\%\nu_{C=O(carboxylic)}$), 1618 ($58\%\nu_{C4=O3} + 10\%\nu_{ring,in\text{-}phase}$) and 1572 cm^{-1} ($58\%\nu_{ring} + 11\%\nu_{C4=O3,out\text{-}of\text{-}phase}$) and assigned from the theoretical calculations. The bisdeprotonation of the acid therefore leads to red-shift of all three bands; the two orotic acid bands which were mainly C5=O4 stretchings become mainly coupled C4=O3 stretchings in the spectrum of the orotate ion. In the IR spectrum of $[Co(HOr)(H_2O)_4]\cdot H_2O$, the carbonyl stretchings are overlapped with the water bending and give a broadened very strong absorption at 1632 cm^{-1}. Additional sharp and much weaker band at 1727 cm^{-1} in the carbonyl stretching region might be due to the stretching of the carboxylate group or a second-order vibration; its definite assignment remains unclear at the present. Two more shoulders (1650, 1638 cm^{-1}) in the spectrum of nickel orotate were assigned as water bendings [31] and also appear on the carbonyl stretching band of cobalt(II) orotate. In the spectrum of $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$, two equally strong $\nu_{C=O}$ bands at 1697 and 1628 cm^{-1} correspond to the stretching of the carbonyl groups in the mono- and bisdeprotonated orotate ligands. The frequency order of the stretchings of the endo-carbonyl groups is $H_3Or > H_2Or^- > HOr^{2-}$. From the IR spectra, it can be assumed that in both complexes the orotate residues HOr^{2-} are coordinated as bidentate ligands to the metal through the carboxylic oxygen and N1 from the pyrimidine ring.

In the spectrum of the copper complex, the crystal and coordinated water stretchings appear at 3588 and 3338 cm^{-1}, respectively. The IR spectrum shows weak absorption bands at 3287 and 3258 cm^{-1}. These bands represent the asymmetrical and symmetrical NH stretching modes, respectively. The bands are shifted to longer wavelengths as compared with the typical values of primary amines (3500 and 3400 cm^{-1}). The very broad and strong band at 1655 cm^{-1} is prescribed to overlapped C=O and CC stretchings, and bending water and amine modes. The medium-intense band at 1481 cm^{-1} is assigned to the C–N stretching of the uracilate ring. The red-shift of the band from the typical C–N stretching frequencies indicates increase of the bond order upon deprotonation.

3.2.4. Thermal analyses

Thermal decomposition of $[Co(HOr)(H_2O)_4]\cdot H_2O$ and $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$ proceeds in two stages. The first stage is related to dehydration. The thermal dehydration stage of the complex occurs in three steps in the temperature range 44–154 °C, accompanied by endothermic effects (DTG_{max}: 96, 116 and 133 °C). In the second stage, the anhydrous cobalt(II) complex decomposes in several consecutive steps in the temperature range 272–645 °C to give metallic cobalt. The three-step dehydration of the cobalt(III) complex occurs in the temperature range 33–123 °C (DTG_{max}: 42, 61 and 88 °C). The anhydrous residue is stable up to 250 °C and subsequently decomposes to metallic cobalt at 700 °C. The cobalt(II) complex contains both crystallization and coordination water, while the cobalt(III) complex includes only uncoordinated water. The weak bonding of the lattice water molecules is confirmed by the low temperature of thermal dehydration.

The decomposition of the copper complex takes place in three stages in the interval 20–1000 °C. The thermal dehydration occurs in two successive steps by giving endothermic peaks at 105 and 150 °C. The weight loss (exp. 10.98%, theor. 10.42%) in the range 60–160 °C correspond to loss of one lattice water and one coordinated water molecule. The anhydrous complex is stable up to 275 °C. The following steps are related to decomposition of the en and orotato ligands. The decomposition starts at 275 °C and continues up to 900 °C, when CuO is formed. The overall weight loss (78.88%, theor. 81.61%) agrees with the proposed structure. The final decomposition product was identified with IR spectroscopy.

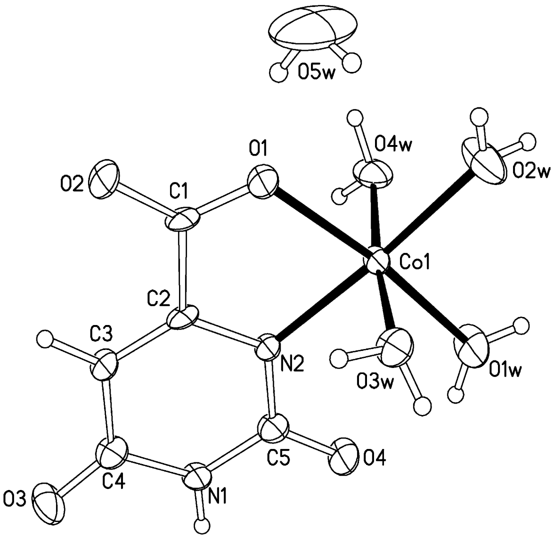

Fig. 5. ORTEP plot of $[(H_2O)_4\cdot Co(C_5H_2N_2O_4)]\cdot H_2O$ at the 90% probability level; hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: Co1–O1 = 2.057(2), Co1–O1w = 2.048(2), Co1–O2w = 2.111(2), Co1–O4w = 2.148(2), Co1–O3w = 2.151(2), Co1–N2 = 2.094(2) Å; O1–Co1–O1w = 172.7(1), O1–Co1–O2w = 96.0(1), O1–Co1–O3w = 91.0(1), O1–Co1–O4w = 89.8(1), O1–Co1–N2 = 78.9(1), O1w–Co1–O2w = 91.3(1), O1w–Co1–O3w = 89.2(1), O1w–Co1–O4w = 90.8(1), O1w–Co1–N2 = 93.9(1), O2w–Co1–O3w = 87.4(1), O2w–Co1–O4w = 85.8(1), O2w–Co1–N1 = 174.7(1), O3w–Co1–N2 = 91.2(1), O3w–Co1–O4w = 173.3(1), O4w–Co1–N2 = 95.5(1)°.

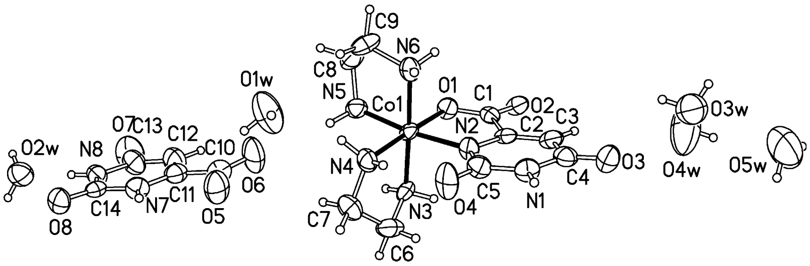

Fig. 6. ORTEP plot of $[(C_2H_8N_2)_2Co(C_5H_2N_2O_4)][C_5H_2N_2O_4]\cdot 5H_2O$ at the 90% probability level; hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: Co1–O1 = 1.914(4), Co1–N2 = 1.974(4), Co1–N3 = 1.954(4), Co1–N4 = 1.944(4), Co1–N5 = 1.954(4), Co1–N6 = 1.961(4) Å; O1–Co1–N2 = 83.6(2), O1–Co1–N3 = 90.3(2), O1–Co1–N4 = 176.1(2), O1–Co1–N5 = 88.8(2), O1–Co1–N6 = 90.1(2), N2–Co1–N3 = 92.0(2), N2–Co1–N4 = 97.0(2), N2–Co1–N5 = 171.6(2), N2–Co1–N6 = 90.1(2), N3–Co1–N4 = 85.9(2), N3–Co1–N5 = 91.6(2), N3–Co1–N6 = 177.9(2), N4–Co1–N5 = 90.8(2), N4–Co1–N6 = 93.7(2), N5–Co1–N6 = 86.3(2)°.

3.2.5. X-ray crystal structures

The crystal structures of the complexes are presented in Figs. 5–7. The bisdeprotonated orotic acid ligand in the crystal of tetraaquaorotatocobalt(II) monohydrate, $[Co(HOr)(H_2O)_4]\cdot H_2O$ (Fig. 5) acts as a bidentate *N*,*O*-chelator. Three water molecules and the deprotonated orotate nitrogen make up the equatorial plane of the cobalt coordination octahedron. An additional aqua molecule and the carboxyl oxygen from the orotate bind to the metal axially at shorter distances. The orotate intraligand bond lengths are comparable with those in the similar nickel complex [31]. Deprotonation brings to electron accumulation and strong shortening of C2–C3, N2–C5 and N2–C2 (1.351(4), 1.359(3) and 1.362(3) Å); the C3–C4 (1.435(3) Å) is lengthened more than in the nickel compound (1.419(2) Å). The endo carbonyl groups C5–O4 and C4–O3 are similar in length (1.243(3) and 1.252(3) Å) and also with the nickel compound (1.254(2) and 1.246(2) Å). The carboxylate group is asymmetric due to the coordination and participation in the hydrogen bonding (C1–O2 = 1.245(3), C1–O1 = 1.256(3) Å).

In a recent reinvestigation of nickel orotate, Wysokinski et al. [31] reported that the lattice water is bonded to the proton of the coordinated water molecule, O5w···H–O2w = 2.643(2) Å, in addition of the hydrogen bond between the uncoordinated water molecule O5w and the pyrimidine proton N1H of the neighbor unit. In our study of the cobalt complex, the lattice water showed some disorder with smeared thermal ellipsoids (Fig. 5). Under the constraints used to locate the hydrogen atoms (O–H = 0.85 ± 0.01 Å, equal Co···H distances for the coordinated water), we were able to observe hydrogen bonding of O5w with both the pyrimidine hydrogen N1–H (2.763(3) Å) and the coordinated oxygen atom (2.702(3) Å). The uncoordinated water is also bonded to the coordinated water O2w from

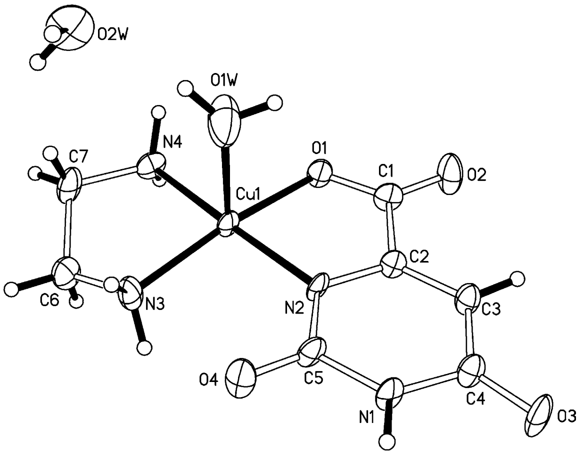

Fig. 7. ORTEP plot of $[Cu(H_2O)(C_2H_8N_2)(C_5H_2N_2O_4)]\cdot H_2O$ at the 90% probability level: hydrogen atoms are drawn as spheres of arbitrary radii: Selected bond distances and angles: Cu1–O1 = 1.990(2), Cu1–N2 = 1.986(3), Cu1–N3 = 2.009(3), Cu1–N4 = 2.012(3), Cu1–O1W = 2.367(3) Å; O1–Cu1–N2 = 81.9(1), O1–Cu1–N3 = 166.8(1), O1–Cu1–N4 = 93.3(1), O1–Cu1–O1W = 93.3(1), N2–Cu1–N3 = 99.5(1), N2–Cu1–N4 = 173.7(1), N2–Cu1–O1W = 90.4(1), N3–Cu1–N4 = 84.3(1), N3–Cu1–O1W = 99.8(1), N4–Cu1–O1W = 93.9(1)°.

the neighbor unit (O5w–H5w1···O2w = 3.052(4) Å). The difference probably results from the different metal-O2w distances, 2.111(2) Å in the cobalt and 2.066(1) Å in the nickel complex. Each of the three coordinated water molecules uses its protons to form a pair of hydrogen bonds: O1w, O3w and O4w bond to carbonyl oxygen atoms and O2w bonds to coordinated water molecules. A strong intramolecular hydrogen bond (2.660(3) Å) connects O1w and O4.

In the structure of the ethylenediamine adduct of cobalt(III) orotate (Fig. 6), $[Co(HOr)(en)_2]\cdot H_2Or\cdot 5H_2O$, two amine ligands and the bisdeprotonated orotate act as bidentate ligands, sufficing the metal coordination sphere. The metal-ligand bonds ranging 1.914(4)–1.974(4) Å are all shorter than those in the cobalt(II) complex. The refinement confirmed the other analytical results that a second orotate was re-protonated during the oxidation and included as a counter anion. The bite angle of the orotate to the metal is similar with those of the amine ligands. Ethylenediamine chelators are twisted, with N3–C6–C7–N4 = 51.2° and N5–C8–C9–N6 = 46.8°, with normal intraligand distances. Orotate moieties are planar, with slightly more rotated carboxylate group in the coordinated one (ca. 7° compared with 4°). The carboxylate functionality of the ionic orotate is symmetric (C–O = 1.250(7) and 1.251(7) Å), while that of the ligated orotate is distorted by the coordination (C–O = 1.278(6) and 1.223(6) Å). Both endocyclic carbonyl groups in the ionic orotate are shortened from the respective values in the ligand (C13–O7 = 1.218(7), C14–O8 = 1.235(6), C4–O3 = C5–O4 = 1.243(6) Å). The differences in the ring bonds were precluded by the large e.s.d values. Five molecules of water in the lattice participate in the hydrogen bonding network.

Similarly to the previously discussed ethylenediamine adduct of Co(III) orotate, the ethylenediamine as well as the dideprotonated orotic acid ligand in the structure of monoaquaethylenediamineorotoatocopper(II) monohydrate, $[Cu(HOr)(H_2O)(en)]\cdot H_2O$, act as a bidentate ligands. In addition to the two en nitrogens and to the orotate nitrogen and oxygen atom which form the square plane, the distorted square pyramidal coordination of copper atom is completed by the water oxygen atom. An additional uncoordinated water molecule is present in the structure. The C–O distances in the endo carbonyl groups C4–O3 and C5–O4 are close to each other (1.242(4) and 1.233(4) Å, respectively). Larger discrepancy between the carboxylate C1–O1 (1.270(4) Å) and C1–O2 (1.240(4) Å) distances is influenced by the coordination as well as participation in hydrogen bonding. Both (coordinated and uncoordinated) water molecules participate in hydrogen bonding of OW···O, OW···OW and OW···N type (ranging from 2.751 to 2.943 Å), whereas the en NH_2 groups are included in the hydrogen bonds of N···O type (ranging from 2.819 to 3.176 Å).

3.3. Salicylate complexes

3.3.1. General discussion

The molar conductance values of the complexes ($\Lambda_M = 81$ and $71\ \Omega^{-1}\ cm^2\ mol^{-1}$ for $[Ni(Hsal)_2(en)_2]$ and $[Cu(Hsal)_2(ndmen)_2]\cdot H_2O$, respectively) indicate that the complexes are not electrolytes in water. The nickel and copper complexes exhibit a experimental magnetic moment value of 2.81 and 1.53 BM corresponding to three and one unpaired electron, respectively, consistent with a weak field octahedral geometry.

3.3.2. UV/vis spectra

For the yellow complex $[Ni(Hsal)_2(en)_2]$ no d–d bands were resolved in ethanol, suggesting an octahedral structure. The band at 561 nm is assigned to ligand-to-metal charge transfer. The electronic spectrum of $[Cu(Hsal)_2(ndmen)_2]\cdot H_2O$ in water exhibits a very broad d–d absorption transition centered at 577 nm ($e = 123\ cm^{-1}M^{-1}$). This band is assigned to the $^2E_g \rightarrow {}^2T_{2\,g}$ d–d transition. The spectrum also exhibits a band at 400 nm ($\varepsilon = 139\ cm^{-1}M^{-1}$) assigned to ligand-to-metal charge transfer. A similar band between 400 and 450 nm previously reported for the mononuclear copper(II) salicylate compounds was ascribed to a ligand-to-metal charge transfer transition [34].

3.3.3. IR Spectra

The bands due to the antisymmetric and symmetric carbonyl stretches ν(COO) of the solid salicylic acid are positioned at 1637 and 1448 cm^{-1}, respectively. The bands are shifted to lower frequencies, 1590 and 1399 cm^{-1} in the spectrum of $[Ni(Hsal)_2(en)_2]$ and to 1594 and

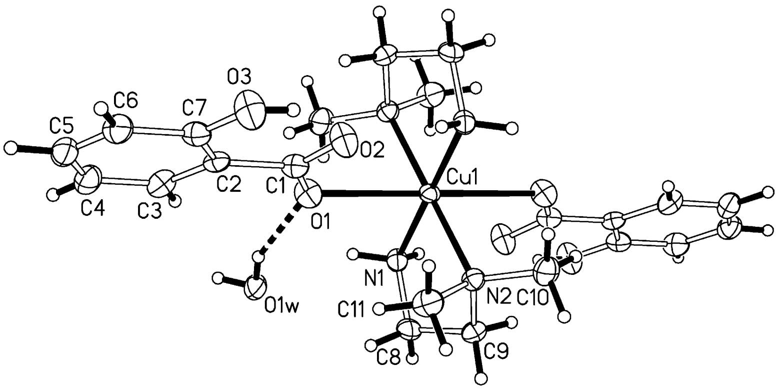

Fig. 8. ORTEP plot of bis(*N,N*-dimethylethylenediamine)bis(salicylato-O)copper(II) hydrate at the 75% probability level; hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: Cu1–O1 = 2.639(1), Cu1–N1 = 1.990(2), Cu1–N2 = 2.114(2) Å; O1–Cu1–O1^i = 180.0, O1–Cu1–N1 = 91.4(1), O1–Cu1–N1^i = 88.6(1), O1–Cu1–N2 = 96.7(1), O1–Cu1–N2^i = 83.3(1), N1–Cu1–N1^i = 180.0, N1–Cu1–N2 = 85.0(1), N1–Cu1–N2^i = 95.0(1), N2–Cu1–N2^i = 180.0°. Symmetry transformation: i = $1 - x, 1 - y, 1 - z$.

1389 cm^{-1} in that of [Cu(Hsal)$_2$(ndmen)$_2$]·H$_2$O. The band positions and their separations indicate that carboxylate groups are monodentate [34]. The ν(OH) bands of the Ni(II) and Cu(II) complexes were observed at 3365 and 3324 cm^{-1}, respectively. The phenolic δ(OH) peak at 1305 cm^{-1} of the salicylic acid remained at nearly the same position in both complexes, suggesting that the phenol group retains the proton. The ν(NiN) and ν(CuN) vibrations can be tentatively assigned as bands at 459 and 449 cm^{-1}, respectively.

3.3.4. Thermal analysis

Thermal decomposition of [Ni(Hsal)$_2$(en)$_2$] and [Cu(Hsal)$_2$(ndmen)$_2$]·H$_2$O proceed in two and three stages, respectively. In the first decomposition stage of [Ni(Hsal)$_2$(en)$_2$], two moles of ethylenediamine and two moles of CO$_2$ are released (exp. weight loss is 46.10%, close to calculated 45.92%) in the temperature range 244–307 °C, giving endothermic effect (DTG$_{max}$: 268 °C). In the second stage, a strong exothermic peak on the DTA curve (DTG$_{max}$: 386 °C) is associated with burning of the organic residue, leading to NiO. The first decomposition stage of [Cu(Hsal)$_2$(ndmen)$_2$]·H$_2$O is related to dehydration in the range 56–102 °C and accompanied by endothermic effect (DTG$_{max}$: 84 °C). The anhydrous Cu(II) complex is thermally stable up to 155 °C and starts to decompose with melting at 172 °C (DTA curve). In the endothermic second and the exothermic third stages (DTG$_{max}$ = 215 and 441 °C, respectively), two moles of ndmen and two moles of Hsal ligands are decomposed, resulting in CuO.

3.3.5. X-ray crystal structures

The metal atom in [Cu(Hsal)$_2$(ndmen)$_2$]·H$_2$O is *trans*-octahedrally coordinated by a pair of bidentate ndmen ligands and two monodentate salicylate ions (Fig. 8). The heavy Jahn–Teller distortion results in two

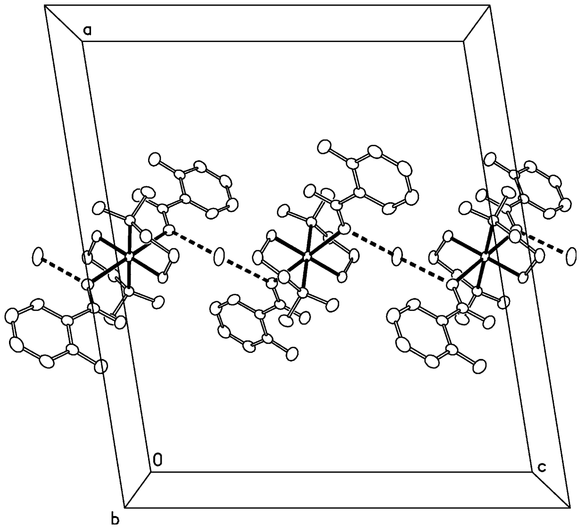

Fig. 9. ORTEP plot of bis(*N,N*-dimethylethylenediamine)bis(salicylato-O)copper(II) hydrate illustrating the hydrogen-bonded chain propagating along the *c*-axis; O···O = 2.788(2) Å.

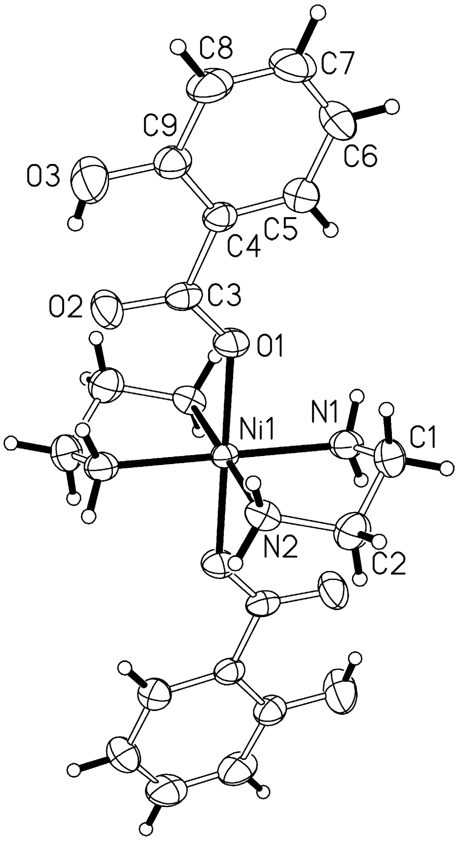

Fig. 10. ORTEP plot of one of the two symmetry independent molecules of $(C_2H_8N_2)_2Ni(C_7H_5O_3)_2$ at the 75% probability level; hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles for molecule a: Ni1*a*–O1*a* = 2.088(2), Ni1*a*–N1*a* = 2.092(2), Ni1*a*–N2*a* = 2.111(2) Å; O1*a*–Ni1*a*–O1*a* = 180.0, O1*a*–Ni1*a*–N1*a* = 86.4(1), O1*a*–Ni1*a*–N1*a*^{i} = 93.6(1), O1*a*–Ni1*a*–N2*a* = 90.6(1), O1*a*–Ni1*a*–N2*a*^{i} = 89.4(1), N1*a*–Ni1*a*–N1*a*^{i} = 180.0, N1*a*–Ni1*a*–N2*a* = 82.8(1), N1*a*–Ni1*a*–N2*a*^{i} = 97.3(1), N2*a*–Ni1*a*–N2*a*^{i} = 180.0°. Selected bond distances and angles for molecule *b*: Ni1*b*–O1*b* = 2.078(1), Ni1*b*–N1*b* = 2.076(2), Ni1*b*–N2*b* = 2.107(2) Å; O1*b*–Ni1*b*–O1*b*^{ii} = 180.0, O1*b*–Ni1*b*–N1*b* = 88.2(1), O1*b*–Ni1*b*–N1*b*^{ii} = 91.8(1), O1*b*–Ni1*b*–N2*b* = 91.2(1), O1*b*–Ni1*b*–N2*b*^{ii} = 88.8(1), N1*b*–Ni1*b*–N1*b*^{ii} = 180.0, N1*b*–Ni1*b*–N2*b* = 96.6(1), N1*b*–Ni1*b*–N2*b*^{ii} = 83.5(1), N2*b*–Ni1*b*–N2*b*^{ii} = 180.0°.

elongated bonds with the disubstituted amine nitrogen N2 and two very long Cu–O1 contacts of ca. 2.6 Å with the carboxylate oxygen atom of the salicylate. The C–C bonds in the amine ligands are stretched by the chelation to 1.500(3) Å and the C–N bonds are nearly equal (C9–N2 = 1.481(2), C8–N1 = 1.484(3) Å). The smaller bond angles at C8 and C9 amount 108.7(2) and 109.9(2)°, respectively; the amine bites the metal at an angle of 85.0(1)°. The ndmen ligands are twisted, with N1–C8–C9–N2 = 52.9(2)°. The salicylate ligands are nearly orthogonal to the equatorial coordination plane of the amine. The carboxylate groups are only slightly distorted (C1–O1 = 1.262(2), C1–O2 = 1.268(2) Å, O1–C1–O2 = 123.9(2)°). A strong intramolecular bond of 2.519 Å connects the hydroxyl proton with the carboxylate oxygen O2. The uncoordinated water molecule joins the adjacent neutral bisaminebissalicylatocopper(II) units through hydrogen bond with the coordinated oxygen O1 into infinite hydrogen-bonded chains that propagate along the c axis (O1w–H···O1 = 2.788(2) Å, Fig. 9). The amine protons are involved in hydrogen bonding with the water (N1–H1a···Ow = 2.972(2) Å) and the carboxyl oxygen O2 (N1–H1b···O2 = 2.901(2) Å).

The en adduct of nickel(II) salicylate salt, $[Ni(Hsal)_2(en)_2]$, has a trans-octahedrally coordinated metal atom (Fig. 10). The amine ligands are non-planar with dihedral angle N1–C1–C2–N2 = 56.5(3) and 53.7(3)° in the two crystallographically independent units a and b. The respective angles at C1 and C2 are 108.3(2) and 108.8(2)° in a, and 109.8(2) and 198.7(2)° in b; the ligand chelates the metal at an angles of 82.8(1) and 83.5(1)°. The intraligand distances (*a*/*b* : C1–N1 = 1.472(3)/1.468(3), C2–N2 = 1.478(3)/1.479(3), C1–C2 = 1.504(3)/1.512(4) Å) are typical for the en adducts and similar with those of the ndmen ligand in the copper(II) complex. The carboxylate groups are nearly symmetric (*a*/*b* : C3–O1 = 1.252(3)/1.257(3), C3–O2 = 1.269(3)/1.261(3) Å). The phenyl protons are strongly hydrogen bonded (O3a–H···O2a = 2.552 Å, O3b–H···O2b = 2.533 Å) to the uncoordinated carboxylate oxygen atoms in both salicylate ligands. The neutral bis(sal)bis(en)nickel(II) entities are held together by weak van der Waals forces.

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