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Template synthesis of square-planar nickel(II) and copper(III) complexes based on hydrazide ligands

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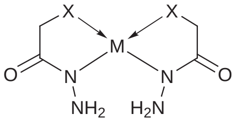
Ring-closure reactions between anionic complexes of nickel(II) and copper(II) with the hydrazide ligands (2-hydroxyiminopropionohydrazide [$CH_3C(=NOH)C(O)NHNH_2$, H_2poh] and oxalodihydrazide [$NH_2NHC(O)$-$C(O)NHNH_2$, H_2oxh] and formaldehyde have been investigated. The isolated compounds were characterised by means of NMR, IR spectroscopy, cyclic voltammetry and single crystal X-ray analysis. In the case of the copper complex with H_2oxh the cyclisation is accompanied by oxidation of the central atom to the +3 state with oxygen in the air. The central atoms in the complexes are square-planar with four nitrogen atoms belonging to the deprotonated hydrazide (Cu) or two hydrazide and two oxime (Ni) groups. The cyclic 1,3,5-oxodiazinane fragment in the complexes adopts a chair conformation which is retained in solution.

Template synthesis has been widely used as a powerful tool for creation of functionalised macrocyclic complexes.[1] In the last few years much synthetic effort has been made to prepare, in particular, pendant arm macrocycles,[2] polytopic molecules containing several spatially separated reactive sites,[3] functionalised cage compounds[4] as well as bi- and poly-nucleating macrocycles[5] using template ring closure procedures. One of the perspective type of functionalised mononuclear complexes based on the macrocyclic and open-chain ligands is that containing additional donor atoms which may serve as exo co-ordination sites.[6] A particular case is when the external donor sites can provide appropriate pathways for exchange interaction between the metal ions, so that the initial mononuclear complexes can be used as building blocks for design of polynuclear compounds exhibiting specific magnetic properties. Macrocyclic and macroacyclic mononuclear complexes containing strong donor atom sets as well as exo co-ordination sites can be regarded as suitable molecules for this strategy. The mononuclear complexes based on chelating (not macrocyclic) ligands in such reactions often undergo reco-ordination processes,[7] or hydrolytic destruction of the initial ligand can occur (*e.g.* in the widely used family of oxamide derivative ligands[8]), so that the structure of the resulting products is different from that initially designed. The modification of such insufficiently stable mononuclear complexes into macrocyclic or non-cyclic products using ring-closure reactions is a very convenient way to obtain suitable precursors for polynuclear compounds. However, this approach still has not received wide application.

Square-planar transition-metal *cis*-bis(hydrazide) complexes (Scheme 1) possess a suitable topology for ring-closure reactions and for the co-ordination of additional metal ions thus producing bi- and poly-nuclear species. Suitable matrices for this purpose can be complexes based on chelating hydrazide ligands containing the neighbouring strong donor groups X (*e.g.* the second hydrazide group, amide, hydroxamic, oxime or amine function). Unlike hydrazone complexes,[9] anionic hydrazide complexes have been rarely used in template synthesis of macrocyclic or open chain co-ordination compounds.[10] Interaction of copper(II) salts with oxalodihydrazide and aldehydes or ketones in the presence of molecular oxygen resulting in the formation of products giving intensely coloured solutions with unusually high extinction in the visible region[11] has been the subject of several studies. On the basis of this observation, several analytical methods for microdetermination of copper(II) have been developed,[12] and as it was suggested that a dioxygen copper(II) complex is formed,[13] this reaction has been widely used as a model for "blue" copper proteins and hemocyanin.[14] Clark *et al.*[10] determined the crystal structure of the condensation products from reaction of copper(II) bis(oxalodihydrazide) with acetaldehyde which revealed unambiguously that no molecular oxygen is present in the co-ordination sphere, and the ligand formed possesses a macrocyclic structure. Finally, Loehr and co-workers[15] demonstrated by a variety of spectroscopic techniques that copper(III) complexes are formed, and that molecular oxygen is necessary as an oxidant. Although many efforts have been made to reveal the nature of this reaction,[10–16] no regular synthetic method for the template synthesis of macrocyclic co-ordination compounds has been developed so far.



Scheme 1

The present paper reports synthetic methods for the complexes containing macrocyclic and open-chain tetraaza ligands based on ring-closure reactions upon interaction between square-planar nickel(II) and copper(II) hydrazide complexes with formaldehyde and their structures, spectral and electrochemical properties. As oxalodihydrazide (like some other aliphatic hydrazides) is known to inhibit protease enzymes in some parasitic species[17] and diamine oxidases,[18] and its activity may be connected with its interaction with carbonyl groups, the reported reactions can serve as appropriate models.

Experimental

Preparations

All chemicals were commercial products of reagent grade used without further purification. Elemental analyses (C, H, N) were conducted by the Microanalytical Service of the University of Wrocław. Oxalodihydrazide was synthesized from diethyl oxalate and hydrazine hydrate according to the literature method.[19] ^{1}H NMR: δ 4.493 (s, 4 H, NH_2) and 9.955 (s, 2 H, NH).

2-Hydroxyiminopropionohydrazide (H_2poh). To a solution of the ethyl ester (1.31 g, 10 mmol) of 2-hydroxyiminopropanoic acid (synthesized according to ref. 20) in methanol (20 cm^3) was added hydrazine hydrate (0.5 cm^3) at room temperature. After 1 h the white precipitate which had formed was filtered off, washed with methanol and acetone, and air-dried. Recrystallisation was carried out from water. Yield 1.04 g (88.9%). The oxime is fairly soluble upon heating in water, methanol and ethanol (Found: C, 30.8; H, 6.0; N, 35.8. Calc. for $C_3H_7N_3O_2$: C, 30.51; H, 6.20; N, 35.55%). ^{1}H NMR: δ 1.872 (s, 3 H, CH_3), 4.314 (s, 2 H, NH_2), 9.106 (s, 1 H, NH) and 11.580 (s, 1 H, OH). ^{13}C NMR: δ 9.836 (CH_3), 149.819 (C=N) and 163.323 (C=O). IR (cm^{-1}): 1022 [ν(N–O)], 1536 (Amide II), 1615 [ν(C=O), Amide I], 1678 [ν(C=N)], 3268 (br) [ν(O–H)] and 3310 [ν(N–H)].

LiK[CuL^1]$_2$·10H$_2$O 1. An aqueous solution (3 cm^3) of KOH (2 M) was added to $Cu(NO_3)_2\cdot 3H_2O$ (0.483 g, 2 mmol) dissolved in water (10 cm^3) with stirring. The copper(II) hydroxide obtained was filtered off and washed with water until the resulting filtrate was neutral. It was then suspended in an aqueous solution of oxalodihydrazide (0.472 g, 4 mmol) at 90 °C. The resulting mixture was heated with continuous stirring for 10 min in the air. To the resultant dark blue solution were added $LiOH\cdot H_2O$ (0.084 g, 2 mmol), KOH (0.056 g, 1 mmol) and paraformaldehyde (0.360 g, 12 mmol, depolymerised in 10 cm^3 of water). The resulting mixture was then heated for 15 min and set aside in a Petri dish for evaporation at room temperature. Black prismatic crystals were obtained after 48 h. They were stable in the air, fairly soluble in water but poorly soluble in methanol. Yield 0.510 g (49.3%) (Found: C, 23.2; H, 4.3; Cu, 12.5; K, 3.5; Li, 0.8; N, 21.9. Calc. for $C_{10}H_{12}CuK_{0.5}Li_{0.5}N_8O_6\cdot 5H_2O$: C, 23.24; H, 4.29; Cu, 12.29; K, 3.78; Li, 0.67; N, 21.68%). ^{1}H NMR: δ 3.446 (dt, 2 H, $^2J_{H5b,H5a} = {}^2J_{H8b,H8a} = 13.6$, $^4J_{H5b,H6,7b} = {}^4J_{H8b,H9,10b} = 2.1$, H5,8b), 4.412 (dd, 4 H, $^2J_{H6b,H6a} = {}^2J_{H7b,H7a} = {}^2J_{H9b,H9a} = {}^2J_{H10b,H10a} = 10.6$ Hz, H6,7,9,10b), 4.802 (d, 4 H, H6,7,9,10a) and 5.442 (d, 2 H, H5,8a). ^{13}C NMR: δ 75.47 (OCH_2N), 81.40 (NCH_2N) and 161.29 (C=O). IR (cm^{-1}): 1640 (br) [ν(C=O), Amide I], 2871, 2918, 2955 [ν(C–H)], 3430 (br) [ν(O–H)]. Absorption spectrum (pH 6.7), λ/nm (ε/M^{-1} cm^{-1}): 228 (15550), 257 (sh) (10000), 291 (9750), 334 (sh) (6950), 395 (4890), 534 (14960) and 643 (5780).

K[NiL^2]·1.5H$_2$O 2. To H_2poh (0.234 g, 2 mmol) dissolved in water (15 cm^3) were added sequentially $NiCl_2\cdot 6H_2O$ (0.237 g, 1 mmol) dissolved in water (10 cm^3) and then KOH (0.168 g, 3 mmol) in water (3 cm^3). To the resultant dark red mixture, paraformaldehyde (0.120 g, 4 mmol, depolymerised in 5 cm^3 of water) was added. The mixture was heated for 10 min under reflux with stirring, and then the solvent was removed on a rotary evaporator. The solid residue was treated with acetone (30 cm^3), the insoluble material filtered off, and the filtrate placed in a vacuum desiccator over $CaCl_2$ for evaporation at room temperature. Amber-yellow single crystals were obtained after 24 h. The product is soluble in water, methanol and acetone. Yield 0.230 g (56.1%) (Found: C, 26.5; H, 3.8; N, 20.3; Ni, 14.5. Calc. for $C_9H_{13}KN_6NiO_5\cdot 1.5H_2O$: C, 26.36; H, 3.93; N, 20.50; Ni, 14.31%). ^{1}H NMR: δ 1.726 (s, 6 H, CH_3), 3.285 (dt, 1 H, $^2J_{H5b,H5a} = 13.5$, $^4J_{H5b,H6,7b} = 1.9$, H5b), 4.201 (dd, 2 H, $^2J_{H6b,H6a} = {}^2J_{H7b,H7a} = 10.8$ Hz, H6,7b), 4.510 (d, 1 H, H5a), 4.599 (d, 2 H, H6,7a) and 18.747 (s, 1 H, H1). ^{13}C NMR: δ 10.349 (CH_3), 73.804 (OCH_2N), 82.465 (NCH_2N), 146.798 (C=N) and 166.088 (C=O). IR (cm^{-1}): 1150 [ν(N–O)], 1610 [ν(C=O), Amide I], 1678 (sh) [ν(C=N)], 2860, 2910, 2981 [ν(C–H)] and 3410 [ν(O–H)]. Absorption spectrum (pH 6.7), λ/nm (ε/M^{-1} cm^{-1}): 225 (25150), 253 (sh) (11000), 283 (sh) (5590), 369 (5820) and 406 (2760).

Crystallography

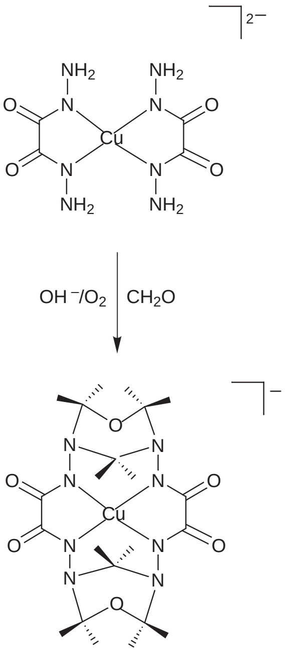
Crystal data and experimental details are presented in Table 1. Accurate unit cell parameters and the orientation matrices were calculated using the least-squares technique. Intensities were collected using a KUMA KM4 diffractometer (for compound **1**) or an Enraf-Nonius FAST TV area detector diffractometer (for **2**) in the ω–2θ scan mode at 293(2) K. The intensities of three standard reflections, monitored every 100 intensity scans, showed no evidence for crystal decay. Corrections for Lorentz-polarisation effects but not for absorption were applied. The structure **1** was solved by direct methods using SHELXS 86[21] and refined by full-matrix, least squares on all F_o^2 using SHELXL 93.[22] The structure **2** was solved by direct methods in the $P1$ space group which made it possible to localise the positions of nickel and potassium atoms and some non-hydrogen atoms. Then the remaining non-hydrogen atoms were located in a subsequent Fourier synthesis and refined isotropically in the named space groups. All attempts to solve the structure in the $P\bar{1}$ group both by direct and heavy atom methods did not give any reasonable solution. In the course of the refinement in the $P1$ space group it became evident that the structure possessed an inversion centre, and further refinement was continued in the $P\bar{1}$ space group by full-matrix least-squares techniques using SHELXL 93. Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 23; real and imaginary components of anomalous dispersion were included for all non-H atoms. The non-hydrogen atoms were refined anisotropically. For complex **1** both the potassium and lithium atoms had occupancy factors of 0.5 which is in agreement with stoichiometry. The former occupied a partial position (being on the two-fold axis) while the latter was observed in a common position and had a disordered distribution. For complex **2** a water molecule of solvation was found to be disordered over two positions with occupancy factors of 0.5 and the other water molecule had an occupancy factor of 0.5. The hydroxyimino hydrogen atom in **2** was observed in the Fourier-difference map, and its positional and isotropic thermal parameters were included in the further stages of refinement. All the protons of the water molecules in **1**, and three out of six protons of the disordered water molecules in **2**, were localised from the Fourier-difference map as well, and their parameters included without further refinement. The C–H atoms of methyl and methylene groups were placed in calculated positions and allowed to ride on the atoms to which they were linked.

CCDC reference number 186/1090.

See http://www.rsc.org/suppdata/dt/1998/3269/ for crystallographic files in .cif format.

Physical techniques

Absorption spectra were recorded on a Beckman DU 650 spectrophotometer, ^{1}H and ^{13}C NMR spectra on a Bruker (300 MHz) spectrometer in $(CD_3)_2SO$ using $SiMe_4$ as an internal standard. Chemical shifts δ are given in ppm downfield from the reference. As in the spectra of the complexes the signals of the methylene protons were overlapped with the signal of HOD, a drop of D_2O was added in order to shift the latter downfield.



Scheme 2

The UV/VIS absorption spectra of aqueous solutions were recorded on a Beckman UV 5240 spectrometer, infrared spectra (KBr pellets) on a Perkin-Elmer 180 spectrometer in the range 400–4000 cm^{-1}.

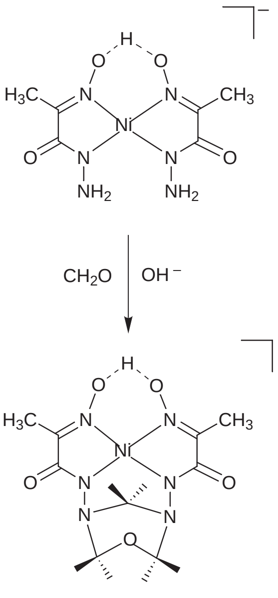
Polarographic measurements by cyclic sweep voltammetry (CSV) were performed on a PA 4 polarograph. For complex **1** a hanging mercury drop electrode (HMDE) was used as a working electrode; the saturated calomel electrode (SCE) and a platinum wire were used as a reference electrode and counter electrode, respectively. A scan rate range from 20 to 200 mV s^{-1} and potential range from +0.150 to −0.700 V were applied. For **2** a three-electrode system was employed with a platinum ultramicroelectrode as working electrode, Ag–AgCl (0.1 M KCl in water) as a reference electrode (separated from the test solution by a salt bridge containing the solvent/supporting electrolyte) and platinum as auxiliary electrode. Ferrocene was added as an internal potential standard. Aqueous solutions of **1** (5×10^{-3} M) and acetonitrile solutions of **2** (1×10^{-3} M) were purged with argon to remove oxygen. A constant ionic strength 0.2 M was maintained by means of Na_2SO_4 (0.2 M, **1**) or NEt_4BF_4 (0.1 M, **2**). The measurements were carried out at 25 °C.

Results and discussion

The structures of the complexes **1** and **2** were established by elemental analysis and multinuclear NMR spectroscopy and then confirmed by single crystal X-ray analyses. As a result of the ring-closure reaction featuring co-ordinated *cis*-hydrazide groups in both **1** and **2**, bicyclic fragments containing N,N-substituted residues of 1,3,5-oxodiazinane are formed. In case of oxalodihydrazide (H_2oxh), bicyclisation occurs from the both sides of the co-ordination sphere, and the resulting complex **1** possesses a macrocyclic structure (Scheme 2). It is noteworthy that the reaction is accompanied by oxidation of the central atom to the +3 oxidation state by oxygen in air.

In the system containing H_2poh, interaction with formaldehyde affected only co-ordinated *cis*-hydrazide groups whereas *cis*-oximino groups did not react. Therefore, the resulting ligand exhibits an open-chain structure (Scheme 3).

It is evident that the course of the reactions is determined by the spatial proximity of the co-ordinated *cis*-hydrazide groups, high stability of the anionic nickel(II) and copper(II) complexes with deprotonated amide ligands, and, in the case of complex **2**, the stabilising effect of the short intramolecular hydrogen bond between the oxygen atoms of *cis*-oximino groups.[24] It should be noted that, in the cases of both **1** and **2**, interaction with formaldehyde leads to formation of a substituted residue of 1,3,5-oxodiazinane. At the same time, use of acetaldehyde as a locking agent in the reaction with H_2oxh and copper(II) salts gave rise to the isolation of two different macrocyclic products. One of them is formed as a result of ring closure between two NH_2 groups upon condensation with one molecule of the aldehyde and contains the $-NHCH(CH_3)NH-$ fragment. The structure of the second product is similar to that of **1**: it contains bicyclic fragments with a six-membered 1,3,5-oxodiazinane ring. Presumably, in the present case the formation of complexes **1** and **2**, corresponding to the complete substitution of the NH_2 groups, is due to the higher reactivity of formaldehyde in the condensation reactions with amino groups.



Scheme 3

Infrared spectra of complexes **1** and **2** reveal several weak absorption bands in the region 2800–3000 cm^{-1} characteristic of ν(C–H) stretching mode vibrations of the methylene groups. These bands are absent in the spectra of the initial ligands H_2oxh and H_2poh. Disappearance of the bands corresponding to ν(N–H) stretching mode vibrations of the primary and secondary amino groups suggests the substitution of their protons with metal ions and methylene bridges. The high frequency shift of the ν(N–O) band in the spectrum of **2** is due to co-ordination of the oximino group *via* nitrogen.[25] Its position in the region 1140–1150 cm^{-1} is very specific for square-planar nickel(II) bis(oximato) complexes with the short intramolecular hydrogen bond between *cis*-oximino groups.[24]

The ^{13}C NMR spectra of complexes **1** and **2** in comparison with those of the initial ligands showed the presence of new signals in the region δ 70–85 characteristic of methylene groups. The ^1H NMR spectra of both complexes in $(CD_3)_2SO$ lacked signals corresponding to labile NH protons, which indicates their substitution. At the same time a series of new resonances for the methylene groups appeared in the region δ 3.2–5.5. It is notable that the spectra of **1** and **2** in this region are very similar, and differ in the more upfield position of the signals in the spectrum of **1** due to the inductive effect of the methyl groups. The methylene resonances appear as two AB patterns with relative intensities of 2 : 1 on account of the coupling between the equatorial (labelled b in Figs. 2, 3) and axial protons of two types of CH_2 groups (NCH_2N and NCH_2O) in the rigid ring system of 1,3,5-oxodiazinane in a chair conformation. The NCH_2O groups, due to the symmetry of the complex anions **1** and **2**, are magnetically equivalent [$^2J(NCH_2N) = 13.6$, 13.5,

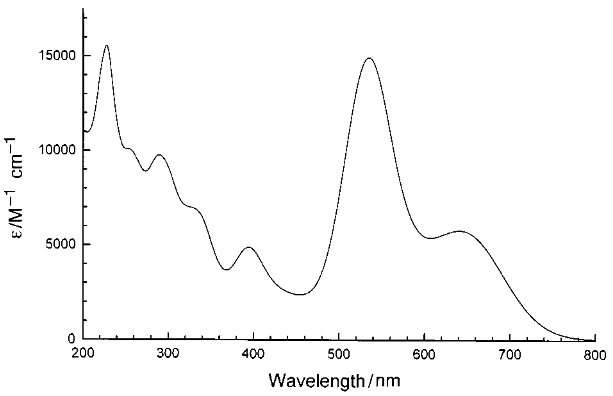


Fig. 1 Absorption spectrum of complex **1** in aqueous solution.

$^2J(NCH_2O) = 10.6, 10.8$ Hz, for compounds **1** and **2**, respectively]. The resonances of the equatorial protons are additionally coupled due to the interaction with the equatorial protons of the neighbouring methylene groups arranged in a W conformation, and appear as a doublet of doublets or a doublet of triplets ($^4J = 2.1$ and 1.9 Hz for **1** and **2**, respectively). The chemical shifts and their couplings are similar to those reported for N,N-substituted derivatives of 1,3,5-oxodiazinane.[26] The ^{1}H NMR spectrum of **2** indicates a singlet for the methyl groups and very low field resonance for the hydroxyimino proton, which is typical of *cis*-bis(oximato) complexes containing a short intramolecular hydrogen bond.[27]

A remarkable feature of the absorption spectrum of complex **1** (Fig. 1) is the presence of three very intense bands in the visible region. The two bands at shorter wavelengths (at 395 and 534 nm) can reasonably be assigned as $Cu^{3+}\leftarrow N$ charge-transfer bands. The band at 534 nm with an unusually high absorption coefficient is likely to have the same origin as that in the spectrum of the complex with the acetaldehyde-derived ligand.[10] In the UV region **1** exhibits a series of absorption bands due to intraligand transitions (Fig. 1). The absorption spectrum of **2** exhibits bands typical of a square-planar nickel(II) complex with a tetraaza bis(amidato)bis(oximato) co-ordination environment,[24] the d–d absorption band (ν_1) appearing as a shoulder at 406 nm ($\varepsilon = 2760$ M^{-1} cm^{-1}) overlapped with a more intense charge-transfer band (ν_2) at 369 nm ($\varepsilon = 5820$ M^{-1} cm^{-1}) attributable to N (oxime)$\leftarrow Ni^{2+}$ electron transfer.

Complex **1** undergoes one-electron reduction in aqueous solution with $E_{\frac{1}{2}} = -0.133$ V *vs.* SCE, a value which is much lower than typical values reported for tetraazamacrocyclic complexes with amide donors (+0.4 to +0.6 V *vs.* SCE)[2,3] and indicative of very high stabilisation of the +3 oxidation state of the complex. This is ascribed to very strong σ-donor effects from the four deprotonated amide nitrogen donor atoms, and to a significant increase in the ligand field due to the four chelate rings and a macrocyclic effect. However, the observed value of the electrode potential is noticeably higher than those reported by Collins and co-workers[28a] for CuN_2(amide)-O_2(alkoxo) systems (−0.44 to −0.60 V) which appear to be the lowest values for the Cu^{III}–Cu^{II} redox couple reported to date.

Complex **2** exhibits two reversible anodic waves in acetonitrile solution with $E_{\frac{1}{2}} = 0.62$ and 1.14 V *vs.* Ag–AgCl electrode, corresponding to one-electron oxidation steps Ni^{2+}–Ni^{3+} and Ni^{3+}–Ni^{4+}, respectively. The observed value of the Ni^{3+}–Ni^{2+} electrode potential is close to those reported for nickel(II) tetraazamacrocyclic complexes with mixed N(amide)N(amine) environments[2c,3,6c] and indicates remarkable stabilisation of the trivalent oxidation state of nickel by the open-chain ligand.

Table 1 Crystal data and structure refinement for complexes **1** and **2**[a]

	1	**2**
Empirical formula	$C_{10}H_{22}CuK_{0.5}Li_{0.5}N_8O_{11}$	$C_9H_{16}KN_6NiO_{6.5}$
M	516.92	410.05
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a/Å	22.808(5)	8.089(1)
b/Å	13.909(3)	10.376(4)
c/Å	13.034(3)	10.640(1)
α/°		99.51(4)
β/°	112.33(3)	111.95(2)
γ/°		106.86(2)
U/Å^3	3824.8(15)	754.2(3)
Z	8	2
D_c/Mg m^{-3}	1.795	1.806
μ(Mo-Kα)/mm^{-1}	1.328	1.61
Reflections collected	3929	3049
Independent reflections	2689	1556
Final *R*1, *wR*2		
[$I > 2\sigma(I)$][b]	0.0327, 0.0796	0.0425, 0.0977
(all data)	0.0656, 0.0876	0.0532, 0.1066

[a] Weighting schemes applied: for **1**, $w = 1/\sigma^2(F_o^2) + (0.0461P)^2$; for **2**, $w = 1/\sigma^2(F_o^2) + (0.0531P)^2$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

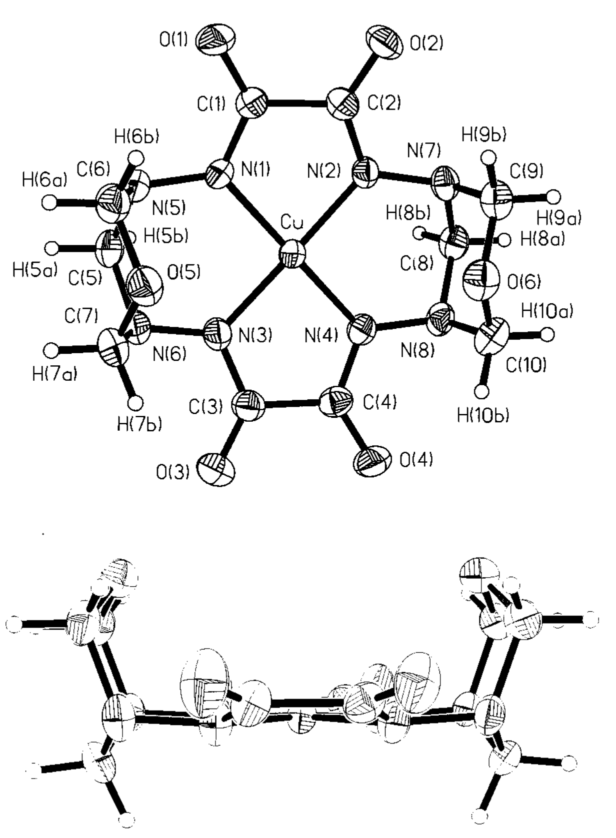


Fig. 2 Crystal structure of the anion of complex **1** (top, viewed from above, with the atom-numbering scheme; bottom, side view). Thermal ellipsoids are at the 50% probability level.

Structural studies

Views of the complex anions in compounds **1** and **2**, and the numbering schemes, are shown in Figs. 2 and 3 (top), and selected bond lengths and angles are shown in Tables 2 and 3, respectively. Both **1** and **2** are ionic, and consist of the complex anions ([CuL^1]$^-$ or [NiL^2]$^-$, respectively), counter ions (K$^+$ and Li$^+$ in **1** and K$^+$ in **2**) and the solvating water molecules. All the elements of the structures are linked to each other by multi-branched systems of hydrogen bonds.

The anion of complex **1** comprises a square-planar copper(III) ion co-ordinated to four nitrogen atoms belonging to the deprotonated amide groups of the 14-membered octaazamacrocyclic ligand 8,17-dioxa-1,2,5,6,10,11,14,15-octaazatricyclo[13.3.1]eicosane-3,4,12,13-tetrone. The co-ordination geometry is different from that of the related copper(III) complex containing an acetaldehyde-derived ligand,[10] where the

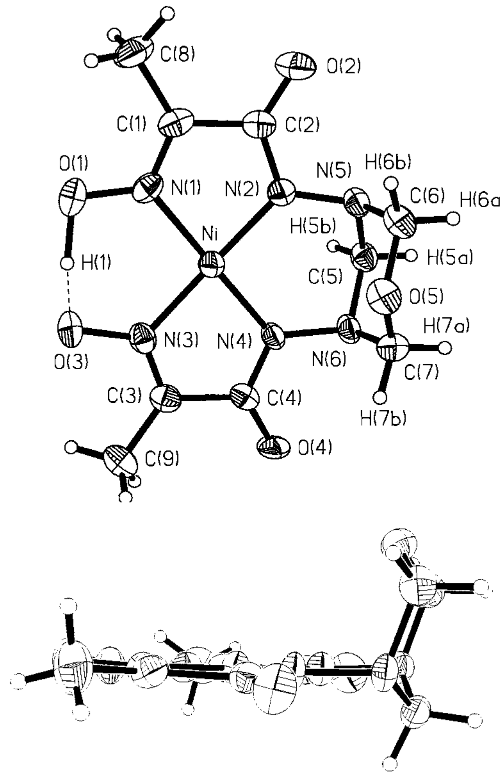


Fig. 3 Crystal structure of the anion of complex **2**. Details as in Fig. 2.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Cu–N(2)	1.868(2)	N(2)–Cu–N(1)	84.30(9)
Cu–N(1)	1.875(2)	N(2)–Cu–N(3)	176.83(10)
Cu–N(3)	1.880(2)	N(1)–Cu–N(3)	95.48(10)
Cu–N(4)	1.884(2)	N(2)–Cu–N(4)	95.49(9)
		N(1)–Cu–N(4)	177.21(10)
		N(3)–Cu–N(4)	84.57(10)
O(1)–C(1)	1.237(3)	C(1)–N(1)–N(5)	118.3(2)
O(2)–C(2)	1.234(3)	C(2)–N(2)–N(7)	118.2(2)
O(3)–C(3)	1.226(3)	C(3)–N(3)–N(6)	118.6(2)
O(4)–C(4)	1.224(3)	C(4)–N(4)–N(8)	117.8(2)
O(5)–C(7)	1.414(3)	N(1)–N(5)–C(5)	110.2(2)
O(5)–C(6)	1.426(3)	N(1)–N(5)–C(6)	113.4(2)
O(6)–C(10)	1.418(3)	N(3)–N(6)–C(7)	113.6(2)
O(6)–C(9)	1.432(3)	N(3)–N(6)–C(5)	110.4(2)
N(1)–C(1)	1.325(3)	N(2)–N(7)–C(8)	110.9(2)
N(1)–N(5)	1.404(3)	N(2)–N(7)–C(9)	113.2(2)
N(2)–C(2)	1.318(3)	N(4)–N(8)–C(10)	113.1(2)
N(2)–N(7)	1.396(3)	N(4)–N(8)–C(8)	110.2(2)
N(3)–C(3)	1.341(4)	O(1)–C(1)–N(1)	127.1(2)
N(3)–N(6)	1.394(3)	N(1)–C(1)–C(2)	111.4(2)
N(4)–C(4)	1.329(3)	O(2)–C(2)–N(2)	127.6(3)
N(4)–N(8)	1.397(3)	N(2)–C(2)–C(1)	112.3(2)
N(5)–C(6)	1.455(4)	O(3)–C(3)–N(3)	128.3(3)
N(6)–C(7)	1.450(4)	N(3)–C(3)–C(4)	112.0(2)
N(7)–C(9)	1.453(4)	O(4)–C(4)–N(4)	127.9(3)
N(8)–C(10)	1.456(4)	N(4)–C(4)–C(3)	112.4(2)

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Ni–N(2)	1.843(4)	N(2)–Ni–N(4)	96.7(2)
Ni–N(4)	1.851(4)	N(2)–Ni–N(1)	83.0(2)
Ni–N(1)	1.861(4)	N(4)–Ni–N(1)	178.2(2)
Ni–N(3)	1.878(4)	N(2)–Ni–N(3)	178.8(2)
		N(4)–Ni–N(3)	82.1(2)
		N(1)–Ni–N(3)	98.2(2)
O(1)–N(1)	1.352(5)	C(7)–O(5)–C(6)	110.6(4)
O(2)–C(2)	1.249(7)	C(1)–N(1)–O(1)	119.9(5)
O(3)–N(3)	1.347(5)	C(2)–N(2)–N(5)	117.4(4)
O(4)–C(4)	1.245(7)	C(3)–N(3)–O(3)	120.3(4)
O(5)–C(7)	1.407(7)	C(4)–N(4)–N(6)	116.6(4)
O(5)–C(6)	1.442(8)	N(2)–N(5)–C(6)	111.3(4)
N(1)–C(1)	1.285(7)	N(2)–N(5)–C(5)	110.1(4)
N(2)–C(2)	1.323(8)	C(6)–N(5)–C(5)	109.6(4)
N(2)–N(5)	1.420(5)	N(4)–N(6)–C(7)	110.1(4)
N(3)–C(3)	1.267(7)	N(4)–N(6)–C(5)	109.3(4)
N(4)–C(4)	1.308(7)	C(7)–N(6)–C(5)	108.5(4)
N(4)–N(6)	1.450(5)	N(1)–C(1)–C(2)	111.9(5)
N(5)–C(6)	1.429(7)	O(2)–C(2)–N(2)	128.9(5)
N(5)–C(5)	1.455(7)	N(3)–C(3)–C(4)	111.9(5)
N(6)–C(7)	1.465(7)	O(4)–C(4)–N(4)	128.2(4)
N(6)–C(5)	1.474(7)		

central atom is square-pyramidal having an apically co-ordinated hydroxyl group, and being noticeably displaced from the basal plane towards the apical ligand. The Cu–N distances [1.868(2)–1.884(2) Å] are close to the values reported for the acetaldehyde-derived macrocyclic complex[10] as well as other copper(III) complexes with deprotonated amide ligands[28,29] and noticeably shorter than typical for Cu^{II}–N (amide) bonds (1.91–1.96 Å).[30] The co-ordination sphere consists of two five- and two six-membered alternating chelate rings. The central atom is 0.049(1) Å out the plane defined by the donor atoms and is situated towards the side of the ether oxygen atoms (Fig. 2, bottom). The carbon and oxygen atoms of the amide carbonyls are also displaced from this plane in the same direction [0.217(3)–0.311(4) Å for carbons, 0.388(4)–0.588(4) Å for oxygen atoms] so that the five-membered chelate rings CuN(1)C(1)C(2)N(2) and CuN(3)C(3)C(4)N(4) are folded along the N(1)–N(2) and N(3)–N(4) lines and exhibit an envelope conformation [the corresponding dihedral angles are 12.8(2) and 16.5(2)°, respectively]. The two six-membered 1,3,5-oxodiazinane rings are in *cis* positions with respect to the plane of the macrocycle (similar to the previous structural studies of the macrocyclic complexes derived from oxalodihydrazide and butane-2,3-dione dihydrazone, such that the intrinsic symmetry of the complex anion approaches C_{2v}).

The central ion in the anion of complex **2** is square-planar with four nitrogen donors from the deprotonated amide and oximino groups. The central and the donor atoms defining the mean plane deviate by no more than 0.016(2) Å (Fig. 3, bottom). The open-chain ligand 3,5-bis(2-hydroxyimino-propanoylamino)-1,3,5-oxadiazinane is triply deprotonated and forms three condensed chelate rings (five-, six- and five-membered) and is fused into a closed pseudo-macrocyclic conformation by means of the short intramolecular hydrogen bond between the oxime oxygen atoms. The Ni–N distances [Ni–N (amide) = 1.843(4) and 1.851(4), Ni–N (oxime) 1.861(4) and 1.878(4) Å] and the angular parameters of the co-ordination sphere are normal when compared to those of related square-planar nickel(II) complexes of 2-hydroxyiminopropanamide derivatives.[24,30b] Both five-membered chelate rings are nearly planar, and the deviations of the atoms from the corresponding mean planes do not exceed 0.026(3) Å. The short intramolecular hydrogen bond between the *cis*-oximino oxygen atoms exhibits parameters typical of square-planar *cis*-bis(oximato)nickel(II) complexes: O(1)–H 1.19; H · · · O(3) 1.26; O(1) · · · O(3) 2.436(6) Å; O(1)–H · · · O(3) 169°.

The six-membered chelate rings in both complexes **1** and **2** have envelope conformations with dihedral angles of 62.0(2) (for **1**) and 61.5(4)° (**2**) along the N(5)–N(6) line, and 61.0(3)° (for **1**) along the N(7)–N(8) line. The cyclic 1,3,5-oxodiazinane fragments in both complexes adopt clear chair conformations; the values of the corresponding dihedral angles along N(5)–N(6), C(6)–C(7) (in **1** and **2**) and N(7)–N(8), C(9)–C(10) (in **1**) lie in the range 48.2(3)–52.0(2)°.

The bond lengths and angles of the ligands in complexes **1** and **2** are typical of N-co-ordinated amide and oxime groups. The C=O (amide) distances are in the range of 1.224(3)–1.237(3) Å for **1** and 1.249(7), 1.245(7) Å for **2**, the C–N (amide) 1.319(3)–1.329(3) Å for **1** and 1.323(8), 1.308(7) Å for **2** are normal for amide bonds, and the N–N hydrazide bond lengths

1.394(3)–1.404(3) Å for **1** and 1.420(5), 1.450(5) Å for **2** are consistent with single bonds. The N–O and C=N bond lengths in the oxime groups [1.352(5), 1.347(5) and 1.285(7), 1.276(7) Å, respectively] suggest the isonitroso form and are close to values reported for *cis*-bis(oximato) complexes of nickel(II).[24,30*b*]

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