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FULL PAPER

Co-ordination ability of novel tetradentate amide-and-oxime ligands: differential binding to Cu^{II} and Ni^{II}

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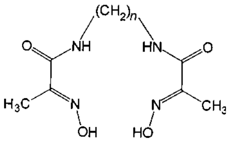
Four cationic and anionic complexes of Ni^{II} and Cu^{II} with new open chain oxime-and-amide ligands, *N*,*N*′-bis(2-hydroxyiminopropionyl)-1,2-diaminoethane (H_2pen) and 1,4-diaminobutane (H_2pab) were isolated and characterised by X-ray crystallography and a variety of spectroscopic techniques. The ligands were found to exhibit two types of co-ordination modes depending on pH: N(oxime),O(amide) bis-bidentate and N_2(oxime),N_2(amide) tetradentate. The first bonding mode leads to bridging of the two ligands thus forming binuclear cationic complexes $[\{Cu(Hpab)(ClO_4)\cdot 2H_2O\}_2]$ **1b** and $Li[Ni(H_{-1}pen)]\cdot 4H_2O$ **2a** which have been determined by single-crystal X-ray analysis. In **1b** the bis-bidentate co-ordination mode leads to the formation of a dimeric complex cation containing a loose 22-membered macrocyclic cavity incorporating two Cu^{II} ions as a part of the ring skeleton. The central atoms in **1b** are distorted square-pyramidal with the water molecule in the apical position. N_4-tetradentate co-ordination observed in **2a** leads to the formation of a square-planar complex anion with a closed pseudo-macrocyclic environment stabilised by a short intramolecular H-bond between the oxime oxygen atoms.

Recently we reported a solution study of complex formation of Cu^{II} and Ni^{II} ions with a new open chain oxime ligand *N*,*N*′-bis(2-hydroxyiminopropionyl)-1,3-diaminopropane (H_2pap, $n = 3$) as well as the synthesis, crystal structures and spectroscopic characterisation of the ligand and its solid state complexes.[1] H_2pap appeared to be a very efficient chelating agent for the above metal ions. The square planar anionic complexes of composition $[M(Hpap)(pap)]^-$ containing a short intramolecular H-bond between *cis*-oximino oxygen atoms may be deprotonated upon increasing pH forming doubly charged species $[M(pap)(pap)]^{2-}$. The latter can be considered as suitable 'building blocks' for obtaining bi- and poly-nuclear complexes, as the proximity of the two oxime oxygen atoms facilitate O,O-chelating co-ordination of the additional metal ion or metal-containing capping agent to the complex anions, thus leading to a macrocyclic[2] or even cage[3] environment of the central atom of the initial complex, the extra metal ions being the part of the macrocyclic moiety. Here, we report copper(II) and nickel(II) complexes with open-chain ligands differing from H_2pap by the number of methylene groups linking two amide-and-oxime moieties: *N*,*N*′-bis(2-hydroxyiminopropionyl)-1,2-diaminoethane (H_2pen, $n = 2$) and *N*,*N*′-bis(2-hydroxyiminopropionyl)-1,4-diaminobutane (H_2pab, $n = 4$). The crystal structure of the Ni^{II} anionic complex with H_2pen reported below reveal several important differences as compared to the analogous structure with H_2pap where the same co-ordination mode of the ligand is realised.[1] These differences may be crucial in chelation reactions with additional metal ions of the anionic complexes, which will be reported elsewhere.



In previous work, we have paid much attention to the role of the short intramolecular H-bonds between oxygen atoms characteristic for *cis*-(bis-oximato) complexes.[1,4] This bond is a key factor determining the *cis*-arrangement of the co-ordination sphere in bis(bidentate oxime) complexes, but plays a less significant role in open chain tetradentate oxime ligands,[1] and is absent in metal complexes with ligands containing strong electron withdrawing groups attached to the oxime carbon atom. For example, this bond is not observed for cyano oximes on chelation, and square planar Cu^{II} and Ni^{II} complexes reveal a *trans*-arrangement of the ligands.[5] Here, we report, in particular, new important features of this short H-bond: the critical impact of its formation on the spontaneous self-assembly of metallamacrocyclic molecules.

Experimental

All chemicals were commercial products of reagent grade and used without further purification. Elemental analyses (C,H,N) were conducted by the Microanalytical Service of the University of Wrocław. Absorption spectra were recorded on a Beckman DU 650 spectrophotometer. UV–VIS diffuse-reflectance spectra measurements were performed on a Beckman UV 5240 spectrometer. The EPR spectra were recorded on a Bruker ESP 300E spectrometer at X-band (9.3 GHz) at 120 K, in ethane-1,2-diol–water (1 : 2) or methanol solution. Infrared spectra (KBr pellets) were recorded on a Perkin-Elmer 180 spectrometer in the range 400–4000 cm^{-1}. ^1H and ^{13}C NMR spectra were obtained on Bruker (300 MHz) and JEOL EX (270 MHz) spectrometers in $(CD_3)_2SO$ using $SiMe_4$ as an internal standard. The spectroscopic data for the compounds studied are given in Table 1.

Magnetic susceptibility measurements were carried out on polycrystalline samples in the temperature range 1.73–300 K with a Quantum Design SQUID magnetometer operating at 0.5 T. Diamagnetic corrections of the constituent atoms were

Table 1 Absorption and EPR spectra of the synthesised compounds

Compound	UV–VIS absorption bands, λ/nm^a (ε/M^{-1} cm^{-1})	Reflectance bands/nm	EPR parameters
1a [{Cu(Hpen)(ClO_4)·H_2O}$_2$]	688 (74)^b	351^c 620	$g_{\parallel} = 2.210$ $g_{\perp} = 2.080$
1b [{Cu(Hpab)(ClO_4)·2H_2O}$_2$]	330 (sh)^c (1651) (pH 4.16) 628 (105)	360^c 644	$g_{\parallel} = 2.160$ $g_{\perp} = 2.070$ solution $A_{\parallel} = 182$ G $g_{\parallel} = 2.240$ $g_{\perp} = 2.060$
2a Li[Ni(H_{-1}pen)]·4H_2O	354^c (5856) 380 (sh)^c (4484) 400 (sh) (3836)	405 (sh)	
2b Li[Ni(H_{-1}pab)]·1.5H_2O	367^c (5056)	408 (sh)	

^{a} d–d transition except where indicated otherwise. ^{b} In dmso–water (4 : 1) solution. ^{c} Charge transfer.

estimated from Pascal's constants.[6] Experimental susceptibilities were also corrected for temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1} per Cu^{II}) and the magnetisation of the sample holder.

Preparations

The synthesis and characterisation of the ligands H_2pen and H_2pab † will be reported elsewhere.[7]

[{Cu(Hpen)(ClO_4)·H_2O}$_2$] 1a and [{Cu(Hpab)(ClO_4)·2H_2O}$_2$] 1b. CAUTION: perchlorate salts are potentially explosive and should be handled with great care and in small quantities. The compound Cu(ClO_4)$_2$·6H_2O (0.371 g, 1 mmol) dissolved in water (10 ml) was added to H_2pen (0.115 g, 0.5 mmol) or H_2pab (0.129 g, 0.5 mmol) dissolved in water (10 ml), for **1a** and **1b**, respectively. The obtained clear green solutions were heated for 10 min on a water bath and then set aside. The dark green crystalline products formed in 24 h were separated by filtration, washed with water and dried in the air. Complex **1a** is insoluble in water and soluble in dmso, **1b** is soluble in water.

1a: Calc. for $CuC_8H_{15}N_4O_9Cl$ (M = 410.23): C, 23.42; H, 3.69; N, 13.66; Cu, 15.49; Cl, 8.64. Found: C, 23.59; H, 3.72; N, 13.69; Cu, 15.35; Cl, 8.93%. IR (cm^{-1}): 1086 (νN–O), 1118 (νCl–O ClO_4^-), 1536 (Amide II), 1622 br (νC=O, Amide I), 3220 (sh) (νN–H), 3400 br (νO–H).

1b: Calc. for $CuC_{10}H_{21}N_4O_{10}Cl$ (M = 456.30): C, 26.32; H, 4.64; N, 12.28; Cu, 13.93; Cl, 7.77. Found: C, 26.05; H, 4.83; N, 11.98; Cu, 13.72; Cl, 8.09%. IR (cm^{-1}): 1086 (νN–O), 1120 (νCl–O ClO_4^-), 1536 (Amide II), 1620 br (νC=O, Amide I), 3236 (sh) (νN–H), 3440 br (νO–H).

Li[Ni(H_{-1}pen)]·4H_2O 2a. To a suspension of complex Ni(pen)·H_2O (synthesised according to ref. 8) (0.305 g, 1 mmol) was added an excess of an aqueous solution (1.6 ml) of LiOH (2 M). The mixture was stirred while heating at 70 °C until complete dissolution of the solid (*ca.* 20 min). The clear yellow solution obtained was filtered off and set aside for crystallisation at room temperature in a Petri dish. Needle shaped amber yellow single crystals suitable for X-ray analysis were obtained in 24 h. As they lose part of their crystallisation water upon exposure to the air, the crystal chosen for X-ray analysis was removed from the mother liquor and sealed in a capillary. Calc. for $LiNiC_8H_{11}N_4O_4$·4H_2O (M = 364.94): C, 26.33; H, 5.26; N, 15.36; Ni, 16.08. Found: C, 26.22; H, 4.91; N, 15.07; Ni, 15.90%. ^{1}H NMR [$(CD_3)_2SO$, 300 MHz], δ 1.636 (s, 6H, CH_3), 3.870 (br s, 4H, CH_2), 18.866 (s, H, NOH · · · ON). IR (cm^{-1}): 1113 (νN–O), 1598 br (νC=O, Amide I), 1632 (νC=N), 3220 br (νO–H).

Li[Ni(H_{-1}pab)]·1.5H_2O 2b. The compound was synthesised analogously to **2a** using Ni(pab)·3H_2O (synthesised according to ref. 8) (0.369 g, 1 mmol) as the starting material. After complete drying of the reaction solution, the solid residue was treated with methanol (20 ml) and filtered; the solvent then was removed on a rotary evaporator, the resulting solid suspended in acetone, filtered, washed with diethyl ether and dried in the air. Calc. for $LiNiC_{10}H_{15}N_4O_4$·1.5H_2O (M = 347.91): C, 34.52; H, 5.21; N, 16.10; Ni, 16.87. Found: C, 34.55; H, 4.85; N, 15.83; Ni, 16.99%. ^{1}H NMR [$(CD_3)_2SO$, 300 MHz], δ 1.461 (m, 4H, β-CH_2), 1.699 (s, 6H, CH_3), 2.891 (m, 4H, α-CH_2), 18.842 (s, H, NOH · · · ON). IR (cm^{-1}): 1150 (νN–O), 1592 br (νC=O, Amide I), 3435 br (νO–H).

Complexes **2a** and **2b** are fairly soluble in water and methanol and insoluble in acetone and diethyl ether.

Crystallography

Details of the crystal data and refinement for the compounds studied are given in Table 2. Atomic coordinates have been deposited with the other supplementary data. Accurate unit cell parameters and orientation matrices were calculated using least-square techniques. Intensities were collected using a KUMA KM4 diffractometer in the ω–2θ scan mode at 293(2) K. The intensities of three standard reflections, monitored after every 100 intensity scans showed no evidence of crystal decay. Corrections for Lorentz-polarisation effects but not for absorption were applied. The structures were solved by direct methods using SHELXS 86[9] and refined by full-matrix least squares on all F_o^2 using SHELXL 93.[10] Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 11; real and imaginary components of anomalous dispersion were included for all non-H atoms. Non-hydrogen atoms were refined anisotropically. The O–H and N–H hydrogen atoms were found on the Fourier-difference map but were not included in the refinement while the C–H atoms of methyl and methylene groups were set in calculated positions and allowed to ride on the atoms to which they were linked.

CCDC reference number 186/1159.

See http://www.rsc.org/suppdata/dt/1998/3629/ for crystallographic files in .cif format.

Results and discussion

Synthesis and characterisation of complexes

The noticeable high frequency shifts of νN–O and νC=N

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† H_2pen: Calc. for $C_8H_{14}N_4O_4$ (M = 230.26): C, 41.73; H, 6.14; N, 24.34. Found: C, 41.61; H, 6.20; N, 24.12%. ^{1}H NMR [$(CD_3)_2SO$, 270 MHz], δ 1.859 (s, 6H, CH_3), 3.253 (br t, 4H, ^3J = 2.6 Hz, CH_2), 7.956 (s, 2H, NH), 11.646 (s, 2H, OH). IR (cm^{-1}): 1022 (νN–O), 1624 (νC=O, Amide I), 1667 (νC=N), 3416 (νN–H). H_2pab: Calc. for $C_{10}H_{18}N_4O_4$ (M = 258.32): C, 46.49; H, 7.04; N, 21.69. Found: C, 46.27; H, 6.99; N, 21.95%. ^{1}H NMR [$(CD_3)_2SO$, 270 MHz], δ 1.402 (m, 4H, ^3J = 2.8 Hz, β-CH_2), 1.857 (s, 6H, CH_3), 3.115 (q, 4H, ^3J = 6.1 Hz, α-CH_2), 7.857 (t, 2H, ^3J = 5.8 Hz, NH), 11.563 (br s, 2H, OH). IR (cm^{-1}): 1019 (νN–O), 1628 (νC=O, Amide I), 1668 (νC=N), 3378 (νN–H).

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

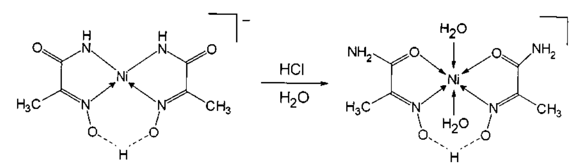
	$[\{Cu(Hpab)ClO_4{\cdot}2H_2O\}_2]$ **1b**	$Li[Ni(H_{-1}pen)]{\cdot}4H_2O$ **2a**
Empirical formula	$C_{10}H_{21}ClCuN_4O_{10}$	$C_8H_{19}LiN_4NiO_8$
M	456.30	364.92
Wavelength λ/Å	0.71079	1.54180
a/Å	8.734(2)	6.8340(10)
b/Å	9.479(2)	8.924(2)
c/Å	11.988(2)	12.525(3)
α/°	103.20(3)	100.62(3)
β/°	90.87(3)	96.37(3)
γ/°	107.56(3)	97.05(3)
U/Å^3	919.2(3)	738.1(3)
D_c/Mg m^{-3}	1.649	1.642
μ/cm^{-1}	13.90	23.36
$F(000)$	470	380
Crystal size/mm	0.25 × 0.25 × 0.25	0.18 × 0.15 × 0.15
θ range/°	4.6–60.2	3.62–81.05
Range hkl	−11 to 11, −13 to 12, 0–16	−8 to 8, −11 to 11, 0–16
Data/parameters	3162/238	3140/202
Goodness-of-fit on F^2	1.068	1.052
Final R indices $[I > 2\sigma(I)]$ $R1$[c]	0.0436	0.0347
$wR2$[d]	0.1294	0.0988
Final R indices (all data) $R1$[c]	0.0586	0.0432
$wR2$[d]	0.1393	0.1014
Extinction coefficient	0.014(3)	0.0103(7)
Max., min. electron density/e Å^{-3}	0.726, −0.634	0.477, −0.518

[a] Details in common: triclinic space group $P\bar{1}$, $Z = 2$. [b] Weighting schemes applied: for **1b**: $w = 1/\sigma^2(F_o^2) + (0.0938P)^2 + 0.1834P$; for **2a**: $w = 1/\sigma^2(F_o^2) + (0.0601P)^2 + 0.35P$ $[P = (F_o^2 + 2F_c^2)/3]$. [c] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

stretching mode vibrations in the IR spectra of all the reported complexes as compared to the spectra of the free ligands are indicative of co-ordination of the oxime groups *via* the nitrogen atoms.[12] Bands characteristic of N–H vibrations of the secondary amide group (νN–H and 'Amide II') are found in the spectra of the ligands and cationic complexes **1a**, **1b** but are absent in the spectra of the anionic complexes **2a** and **2b** which suggests that the latter contain only deprotonated amide groups co-ordinated to the metal ion.

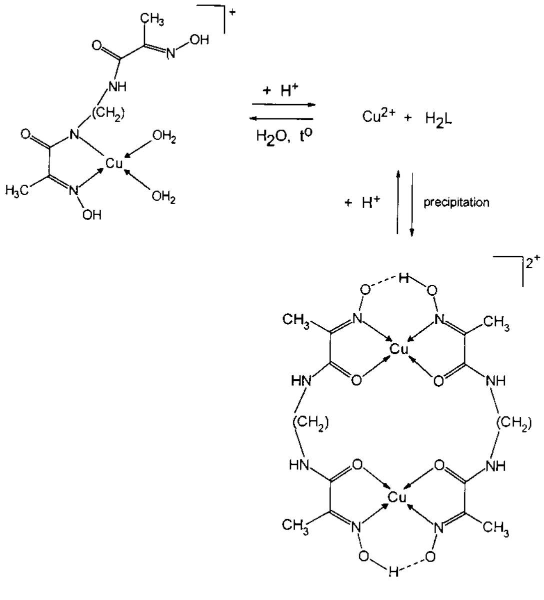
The positions of maxima in the reflectance spectra of **1a** and **1b** are consistent with CuN_2O_2 environment of the central atoms. Thus, one can propose N(oxime),O(amide) chelate coordination in complexes **1a** and **1b** in which one of the oxime groups must be deprotonated with 1+ cations being formed. The N_2O_2 co-ordination is also indicated by the frozen-solution EPR spectrum for **1b** with $g_{\parallel} = 2.240$ and $A_{\parallel} = 182$ G being typical for two nitrogen binding. The EPR spectra of **1a** and **1b** differ in symmetry (Table 1) and clearly indicate the impact of the bridging $-(CH_2)_n-$ chain on the geometry around the metal ion. The shorter $-(CH_2)_2-$ chain induces strong steric effects between the two complex centres reducing the geometry around each metal ion.

Derivatives of 2-(hydroxyimino)propanamide (Hpox) show ionisation of the oxime group in solution at higher pH (5–7) while the amide group starts to deprotonate at pH 3–5.[1,13] By contrast, the solid complexes **1a** and **1b** crystallised from aqueous solution at pH = 3–4 (concentration *ca.* 1 M), contain the ligand with protonated amide and partly deprotonated oxime groups which is consistent with IR spectral data and was confirmed by a single crystal X-ray study of **1b**. Such an inversion of the order of ionisation in solution and in the crystal phase is understandable in terms of the important stabilising role of short intramolecular H-bonds in oximato complexes as observed previously. For example, addition of HCl to an aqueous solution of the square planar complex $Li[Ni(pox)(H_{-1}pox)]{\cdot}5H_2O$ to pH 4 leads to the crystallisation of octahedral $[Ni(Hpox)(pox)(H_2O)_2]Cl$[14] with retention of the short H-bond between *cis*-oximato groups and rearrangement of the amide group [eqn. (1)] (both initial and resulting complexes have been structurally characterised).



(1)

Dissolution of **1a** and **1b** in water leads to the rearrangement of the co-ordination sphere $\{CuN_2(oxime)O_2(amide)\} \longrightarrow \{CuN_2(amide)(H_2O)_2\}$ so that the surrounding atoms around copper remain the same: CuN_2O_2. This is consistent with only small shifts of d–d transition maxima in the reflectance and absorption spectra (Table 1) and with the relatively similar ligand field produced by deprotonated oxime and amide nitrogen donor atoms. Since at pH 3–4 there is a high abundance of free ligand and metal ions (*ca.* 30–70%), the dissolution and crystallisation processes in these systems are subject to equilibria [eqn. (2)].



(2)

Thus, formation of bimetallamacrocyclic complexes **1a** and **1b** may be regarded as a spontaneous self-assembly process with formation of the short intermolecular H-bond being the

Table 3 Selected bond lengths (Å) and angles (°) for **1b**[a]

Cu–N(1)	1.934(2)	Cu–O(2)	1.968(2)
Cu–N(4)^1	1.957(2)	Cu–O(3)^1	1.977(2)
		Cu–O(5)	2.189(3)
N(1)–Cu–N(4)^1	95.98(10)	O(2)–Cu–O(3)^1	99.94(9)
N(1)–Cu–O(2)	81.35(9)	N(1)–Cu–O(5)	98.52(13)
N(4)^1–Cu–O(2)	169.19(10)	N(4)^1–Cu–O(5)	94.88(11)
N(1)–Cu–O(3)^1	166.88(10)	O(2)–Cu–O(5)	95.87(11)
N(4)^1–Cu–O(3)^1	80.30(10)	O(3)^1–Cu–O(5)	94.35(13)

[a] Symmetry transformation used to generate equivalent atoms: 1 $-x, -y + 1, -z$.

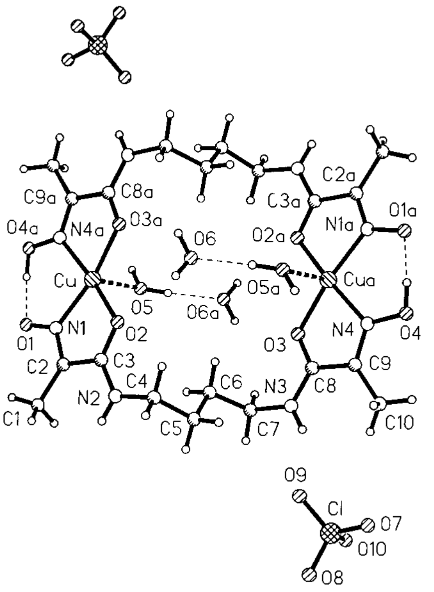


Fig. 1 Structure and numbering scheme for complex **1b**.

dominating factor in determination of the structure of the oxime complexes.

Compounds **2a** and **2b** contain trinegatively charged anions of the ligands co-ordinated in a pseudo-macrocyclic N_4-tetradentate mode with a short intramolecular H-bond between oxime oxygen atoms. The complex anion of **2a** contains three fused five-membered rings (Fig. 3) while **2b** contains alternating 5,7,5 chelate rings; both co-ordination fashions are known for tetradentate diamine–dioxime ligands.[15] The electronic spectra display bands typical for Ni^{II} square planar complexes[1,4] (Table 1). The ^1H NMR spectra of diamagnetic **2a** and **2b** in $(CD_3)_2SO$ show resonances at δ 18.866 and 18.842, respectively, disappearing upon addition of D_2O which is very characteristic of the oxime proton incorporated in the short H-bond.[16] As shown before,[1] the bridging oxime proton can be removed without changing of co-ordination mode upon increasing the pH, to give dinegatively charged anions.

Solid-state X-ray studies of complexes

$Cu(Hpab)(ClO_4)\cdot 2H_2O$ 1b. A view of the dimeric molecule and the numbering scheme is shown in Fig. 1 and selected bond lengths and angles are shown in Table 3. The ionic solid consists of complex cations $[Cu(Hpab)]_2^{2+}$, perchlorate anions and water molecules (one of which is co-ordinated to the central atom and the other is solvate of crystallisation). The ligand is co-ordinated in a bis(bidentate fashion) *via* the hydroxyimino nitrogen and amide oxygen atoms forming five-membered chelate rings. A similar chelating co-ordination mode of this ligand [N(oxime),O(amide)] was observed earlier in a Cu^{II} cationic complex with *N*-pyruvyl-L-methionine oxime[17] and a manganese(II) co-ordination polymer with *N*-pyruvyl-L-alanine oxime.[18] As there are two chelating centres within one ligand molecule separated by the tetramethylene chain, the resulting complex cation is a centrosymmetric dimer with a 22-membered metallamacrocyclic cavity. The Cu···Cu ($-x$, $1 - y$, $-z$) separation in the dimer is 7.231(2) Å. The Cu^{II} ion co-ordination geometry is distorted tetragonal pyramidal constructed by two oxime nitrogen, two amide oxygen atoms and an apical water molecule. The copper atom lies 0.201 Å above the basal plane towards the axial O(5) atom. Both five-membered chelate rings CuN(1)C(2)C(1)O(1) and CuN(4a)C(9a)C(8a)-O(3a) are noticeably non-planar: the deviations of the carbon atoms from the planes of the chelate angles being 0.111 and 0.247 Å, respectively. The co-ordination sphere is additionally stabilised by formation of a short intermolecular H-bond between *cis*-situated hydroxyimino groups with parameters typical for Cu^{II} *cis*-(bis-oximato) complexes[19] [O(4a)–H 0.930, H···O(1) 1.554, O(1)···O(4) 2.483(3) Å; O(1)–H···O(4) 175.5°].

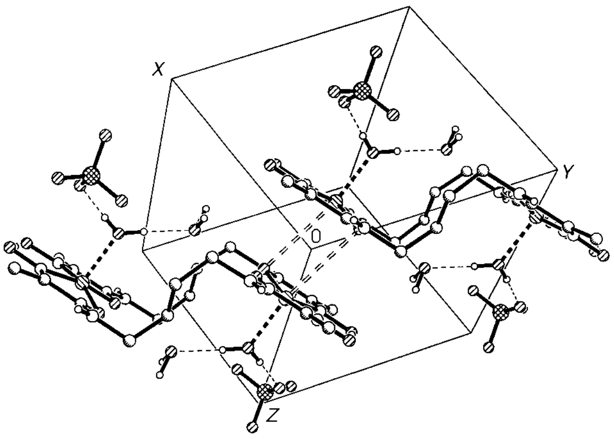


Fig. 2 Fragment of crystal packing for **1b**.

The co-ordinated ligand induces a folded geometry of the two planar moieties involving oxime and amide groups. The conformation of the 22-membered macrocyclic fragment formed as a result of dimeric co-ordination of the two ligands can be described as chair-like (Fig. 2). There are two relatively planar fragments in the dimer parallel to each other linked by the folded fragment of tetramethylene groups. The dihedral angle between the mean planes of co-ordination spheres and the C(5)C(6)C(5a)C(6a) mean plane is 75.2°.

The complex cations are packed in a 'stairway' mode so that the square pyramids of the copper atoms belonging to different dimers are stacked base-to-base with Cu···Cu separations of 4.111(2) Å with a very long axial contact Cu···O(3) (x, $-1 + y$, z) 3.535(2) Å (Fig. 2). The translational 'stairways' interact with each other *via* the solvate water molecule O(6) forming an acceptor H-bond with the apical water molecule O(5) and a donor H-bond with the translational oxime oxygen atom O(1).

Complex **1b** is paramagnetic with $\chi_M T$ equal to 0.768 cm^3 K mol^{-1} at room temperature, as expected for two uncoupled copper atoms. The temperature dependence of the magnetic susceptibility of **1b** displays no maximum but the value of $\chi_M T$ starts to decrease rapidly upon cooling to *ca.* 25 K, reaching a value of 0.364 cm^3 K mol^{-1} at 1.73 K. This is indicative of a very weak intermolecular antiferromagnetic interaction taking place at low temperatures and is consistent with the long Cu···Cu separations in the crystal structure. The magnetic behaviour of **1b** was analysed with the help of a simple Bleaney–Bowers expression[20] for two local Cu^{II} ions [eqn. (3)] where J is

$$\chi_M T = (2N\beta^2 g^2/k)[3 + \exp(-J/kT)]^{-1} \qquad (3)$$

the singlet–triplet energy gap, g the average g factor and N, β and k have their usual meanings. Fitting of the experimental data by the least-squares technique gave $J = -2.2$ cm^{-1} and $g = 2.05$.

Table 4 Selected bond lengths (Å) and angles (°) for **2a**

Ni–N(3)	1.803(2)	Ni–N(1)	1.839(2)
Ni–N(2)	1.816(2)	Ni–N(4)	1.841(2)
N(3)–Ni–N(2)	87.25(8)	N(3)–Ni–N(4)	85.50(8)
N(3)–Ni–N(1)	171.73(7)	N(2)–Ni–N(4)	172.74(7)
N(2)–Ni–N(1)	84.51(7)	N(1)–Ni–N(4)	102.74(7)

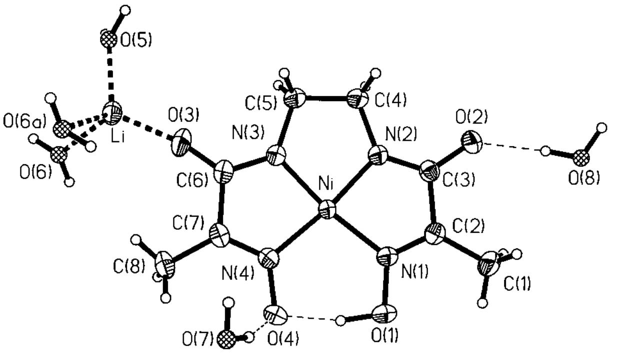


Fig. 3 Structure and numbering scheme for complex **2a**.

Li[Ni(H_{-1}pen)]·4H_2O 2a. The structure is ionic, and the unit cell comprises the complex anions [Ni(H_{-1}pen)]$^-$, lithium cations and four water molecules, two of which partake in co-ordination with the lithium cation and the other two are solvate molecules of crystallisation. Both co-ordinated and solvent water molecules in **2a** form extensive systems of multibranched H-bonds linking the elements of the structure with each other.

A view of the molecule and the numbering scheme for **2a** is shown in Fig. 3 and selected bond lengths and angles are given in Table 4. The central atom has square planar geometry, being co-ordinated to four nitrogen atoms of deprotonated hydroxyimino and amide groups and the deviations of the metal and donor atoms from the N(1)N(2)N(3)N(4) plane lie within 0.01 Å. The co-ordination mode of the ligand is similar to that found in the structure of [Ni(H_2O)$_6$][Ni(H_{-1}pap)]$_2$:[1] the ligand is triply deprotonated and forms three planar condensed chelate rings. However, in [Ni(H_{-1}pap)]$^-$ there are altering 5, 6 and 5-membered rings, whereas in the present structure all three fused chelates are five-membered. This difference leads to a noticeable shortening the Ni–N bonds {1.803(2) and 1.816(2) Å for Ni–N(amide); 1.839(2) and 1.841(2) Å for Ni–N(oxime) bonds in **2a** *vs.* 1.864(3)–1.869(3) Å for Ni–N in [Ni(H_2O)$_6$][Ni(H_{-1}pap)]$_2$}. The Ni–N(amide) bond lengths in **2a** appear to be surprisingly short compared to typical values found in related square planar Ni^{II} chelate and macrocyclic complexes (average 1.85–1.87 Å). The differences in the angular parameters of such complexes are also significant: the N(2)–Ni–N(3) bond angle value in **2a** [87.25(8)°] is noticeably reduced compared to the value in [Ni(H_{-1}pap)]$^-$ [97.6(2)°]. By contrast, the N(1)–Ni–N(2) and N(3)–Ni–N(4) bond angles values are increased {84.51(7) and 85.50(8)° in **2a**; 82.4(2) and 82.5(2)° in [Ni(H_{-1}pap)]$^-$, respectively}. The O(1)···O(4) distance in the short intramolecular H-bond between *cis*-oximino oxygens in **2a** [O(1)–H 1.06, H···O(1) 1.58, O(1)···O(4) 2.625(2) Å; O(1)–H···O(4) 176°] is markedly decreased as compared to typical values for Ni^{II} oximato complexes (average 2.43–2.48 Å).[1,4,21]

The planar complex anions are related by inversion centres at (0 0 1/2) and (1/2 0 1/2) and are packed in columns perpendicularly to the x axis with alternating Ni···Ni separations of 3.710(1) and 3.742(1) Å and Ni···N(2) separations of 3.513(2) and 3.361(2) Å, respectively, between the neighbouring anions.

Conclusion

Open chain oxime ligands are versatile upon co-ordination to Ni^{II} and Cu^{II} complexes, the mode of bonding of which depends on the pH of the solution. In acid conditions they are self-assembled into dimeric complexes with Cu^{II} ions featuring two CuN$_2$(oxime)O$_2$(amide) co-ordination spheres separated by the metallamacrocyclic cavity. This co-ordination mode is determined by the short intramolecular H-bonds between *cis*-oximino nitrogens. MN$_2$(oxime)N$_2$(amide) co-ordination occurs at higher pH upon deprotonation of amide groups and leads to formation of square planar anionic complexes with closed pseudomacrocyclic environments of the central atoms for both Ni^{II} and Cu^{II}.

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