N-Bonding of the hydroxamic function in nickel(II) and copper(II) complexes with 2-(hydroxyimino)propanohydroxamic acid

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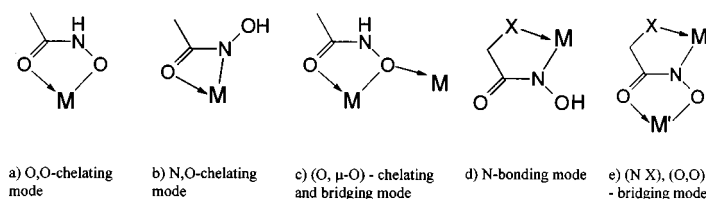[b] *Department of Chemistry, Shevchenko University, 252017 Kiev, Ukraine*
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Potentiometric, spectroscopic and X-ray studies of 2-(hydroxyimino)propanohydroxamic acid (H_2L) and its complexes with Ni^{2+} and Cu^{2+} showed that the ligand is a strong chelating agent forming a series of stable complex species with remarkably higher formation constants compared to those of either aminohydroxamic acids or oximinocarbonic acids. In the Cu^{2+}–H_2L system three dinuclear species $[Cu_2HL_2]^+$, $[Cu_2L_2]$ and $[Cu_2H_{-1}L_2]^-$ with different donor atom sets were found to be dominant at pH 3.5–7.5. In both Cu^{2+} and Ni^{2+} systems the mononuclear species $[MHL_2]^-$, $[ML_2]^{2-}$ and $[MH_{-1}L_2]^{3-}$ are formed in neutral and alkaline solutions which have, according to the UV-VIS spectral data, square-planar structure with a $M\{N_{2(oxime)}N_{2(hydrox)}\}$ core. Thus, the ligand studied represents a new example in which the adjacent oxime donor group facilitates the N-bonding of the hydroxamic function. The crystal structures of two complexes, $Na_2[NiL_2]\cdot4H_2O$ **1** and $[Cu(phen)(hpa)(H_2O)]\cdot4H_2O$ **2** [H_2hpa = 2-(hydroxyimino)propanoic acid] have been determined by single-crystal X-ray analysis. In **1** the central atom is situated at the centre of symmetry and in square-planar surroundings of four nitrogen atoms belonging to the deprotonated oxime and hydroxamic groups. The *trans*-disposed ligands are additionally linked by short intra-molecular hydrogen bonds featuring the oxime and hydroxamic oxygen atoms. Complex **2** was crystallised from an alkaline solution containing $[Cu(phen)Cl_2]$ and H_2L and formed as a result of ligand hydrolysis. The copper(II) ion is in distorted square-pyramidal surrounding, the basal plane being formed by two nitrogen atoms of 1,10-phenanthroline, an oxime nitrogen and a carboxylic oxygen atom of the dianion hpa and the water molecule occupies the apical position. Both organic ligands are co-ordinated in a bidentate chelate mode.

Hydroxamic acids represents a very important class of chelating agents.[1] Most current research on their co-ordination properties is dedicated to modeling of the biological function (in particular, microbial transport of iron[2] and inhibition of urease activity[3]) while earlier they have been extensively used in analytical chemistry for the detection of a variety of metal ions.[4] In the majority of reported metal complexes (characterised both structurally and in solution) the {O,O} chelating mode was observed (Scheme 1, a) suggesting substitution of the OH hydroxamic proton by metal ion. The N,O-chelating mode (Scheme 1, b), despite its suggestion in solution studies with aminohydroxamic acids,[5] has not been structurally evidenced in the solid state.[6] The {O, μ-O} bridging function of the hydroxamic moiety (Scheme 1, c) was observed in a series of di-nuclear complexes used as structural models of the urease active centre, in particular obtained by substitution of carboxylate ligands by hydroxamates in species with preorganised dimeric structure.[7] The N-bonding mode (suggesting deprotonation of the nitrogen hydroxamic atom) was first observed by Brown *et al.*[8] in 1982 in a nickel(II) complex with glycine hydroxamic acid, and since then only a few new examples have been reported (in all cases with aminohydroxamic acids[9]). Realisation of this mode surely must be supported by the presence of an additional adjacent strong donor X thus the ligand would be able to form 5- or 6-membered chelate rings (Scheme 1, d). Co-ordination through N also occurred in polynuclear complexes with bridging hydroxamic functions (Scheme 1, e) where it is combined with the {O,O} chelating mode. All of the reported complexes exhibiting this co-ordination mode belong to so-called metallacrown compounds.[10] These systems contain bridging hydroxamic repeat units that form cyclic structures with a cavity and are able to incorporate an additional metal ion of the appropriate size due to the hydroxamic oxygen atoms oriented towards the centre of the cavity. The hydroxamic ligands capable of forming metallacrown structures are sali-cylohydroxamate and related 2-hydroxyphenyl hydroxamates (that can form tri-,[11] tetra-[12] and penta-meric units[13]), picolinyl hydroxamate[14] [2-Pyr C(O)NHOH] forming pentameric units, β-alanine hydroxamate (pentameric units[15]) and L-α-alanine hydroxamate (tetrameric units[16]). Thus, two types of additional

a) O,O-chelating mode b) N,O-chelating mode c) (O, μ-O) - chelating and bridging mode d) N-bonding mode e) (N X), (O,O) - bridging mode

Scheme 1 Co-ordination modes of the hydroxamic group in metal complexes.

donor groups facilitating N-bonding or bridging co-ordination mode were known to date: *ortho*-phenolic and amine (both aliphatic and aromatic) groups (X = O or N).

Recent studies on complex formation in solution with 2-(hydroxyimino)propanohydroxamic acid [$CH_3C(=NOH)C(O)$-$NHOH$, H_2L] have shown that it may form very stable complex species with Cu^{2+} and Ni^{2+} ions above pH 7 with formation constants much higher than those of corresponding species observed for analogous ligands 2-hydroxyiminopropanoic (H_2hpa) and L-α-alanine hydroxamic (aha) acids.[17] Spectroscopy data suggested unambiguously the presence of species with $2 \times \{N_{ox}, N_{hydrox}\}$ bonding mode in both Cu^{2+} and Ni^{2+} systems thus demonstrating that the oxime nitrogen is an efficient adjacent donor for chelate formation with the nitrogen of the hydroxamic function. The present paper reports a detailed description of Cu^{2+} and Ni^{2+} speciation in aqueous solution with the mentioned ligand as well as the first structural evidence of N-co-ordination of a hydroxamic group in 2-hydroxyiminohydroxamic acids thus providing a new example of the adjacent donor function facilitating this bonding mode.

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.

2-(Hydroxyimino)propanohydroxamic acid (H_2L). The ligand was synthesized according to ref. 18. Ethyl pyruvate oxime, $H_3CC(=NOH)C(O)OC_2H_5$, (1.31 g, 10 mmol) dissolved in 5 ml of methanol was added to a solution obtained by dissolving sodium (0.23 g, 10 mmol) in 10 ml of methanol with addition of hydroxylamine hydrochloride (0.69 g, 10 mmol). The mixture was stirred for 3 h and then added dropwise to a solution of sodium methoxide [obtained by dissolving sodium (0.23 g, 10 mmol) in 10 cm³ of anhydrous methanol]. In 2–3 h the white crystalline precipitate which formed was filtered off, dissolved in water (20 cm³) with addition of several drops of diluted hydrochloric acid to adjust the pH to 4–5. The crude product was obtained by extraction with ethyl acetate (3 × 20 cm³) followed by solvent removal on a rotary evaporator. Yield after recrystallisation from ethyl acetate 0.71 g (60%). The compound is soluble in water, alcohols and acetone (Found: C, 30.39; H, 5.20; N, 23.93. Calc. for $C_3H_6N_2O_3$: C, 30.51; H, 5.12; N, 23.72%). ^{1}H NMR (dmso-d_6, 300 MHz): δ 1.864 (s, 3 H, CH_3), 8.957 (br s, 1 H, NH), 10.672 (br s, 1 H, OH) and 11.568 (s, 1 H, C=NOH). IR (cm^{-1}): 891 (N–O$_{hydroxamic}$); 1020 (N–O$_{oxime}$); 1546 (C=N$_{hydroxamic}$); 1630 (C=O, Amide I); 1679 (C=N$_{oxime}$) and 3250 (br) (O–H).

$Na_2[NiL_2]\cdot4H_2O$ 1. The compound $Ni(CH_3CO_2)_2\cdot4H_2O$ (0.249 g, 1 mmol) dissolved in water (10 cm³) was added to an aqueous solution (10 cm³) of H_2L (0.236 g, 2 mmol). To the dark green mixture obtained, sodium hydroxide (0.160 g, 4 mmol) dissolved in 5 cm³ of water was added. The resulting solution in 24 h produced dark orange needle shaped crystals that were separated by filtration (Found: C, 17.55; H, 4.20; N, 13.58; Ni, 14.61. Calc. for $C_6H_{16}N_4Na_2NiO_{10}$: C, 17.63; H, 3.94; N, 13.70; Ni, 14.35%). IR (cm^{-1}): 947 (N–O$_{hydroxamic}$); 1140 (N–O$_{oxime}$); 1551 (C=N$_{hydroxamic}$); 1583 (C=O, Amide I); 1662 (C=N$_{oxime}$) and 3400 (br) (O–H).

[Cu(phen)(hpa)(H_2O)]$\cdot4H_2O$ 2. The compound [Cu(phen)-Cl_2] (0.315 g, 1 mmol) dissolved in water (15 cm³) was added to aqueous solution (10 ml) of H_2L (0.118 g, 1 mmol) and then potassium hydroxide (0.224 g, 4 mmol) dissolved in 10 cm³ of water was added. The resulting clear solution was set aside at room temperature, and after 72 h the dark green prismatic crystals formed were isolated by filtration, washed with water and air-dried (Found: C, 41.77; H, 4.63; Cu, 14.55; N, 9.95. Calc. for $C_{15}H_{21}CuN_3O_8$: C, 41.42; H, 4.87; Cu, 14.61; N, 9.66%). IR (cm^{-1}): 1143 (N–O$_{oxime}$); 1431 [ν_{sym}(COO$^-$)]; 1590 [ν_{sym}(COO$^-$)]; 1670 (C=N$_{oxime}$) and 3450 (br) (O–H).

Potentiometric studies

Titrations involved an ionic background of 0.1 mol dm^{-3} KNO$_3$, a pro-ligand concentration of 3×10^{-3} mol dm^{-3} and metal-to-pro-ligand ratios of 1:2, 1:3 and 1:5. Alkali was added from a 0.250 cm³ micrometer syringe which had been calibrated by weight titrations and the titration of standard materials. The pH-metric titrations were performed at 25 °C in pH range 2.5–11 using a MOLSPIN automatic titration system with a microcombined glass–calomel electrode calibrated daily in hydrogen-ion concentration using HNO$_3$.[19] Titrations were performed in triplicate and the SUPERQUAD computer program was used for calculations of stability constants ($\beta_{pqr} = [M_pH_rL_q]/[M]^p[H]^r[L]^q$).[20] Standard deviations quoted refer to random errors only.

Spectroscopic studies

Absorption spectra were recorded on a Beckman DU 650 spectrophotometer. The metal-ion concentrations were 3×10^{-3} mol dm^{-3} and metal-to-pro-ligand ratios of 1:2 and 1:5. 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). Concentrations used in the spectroscopic measurements were similar to those given for potentiometric titrations. Infrared spectra (KBr pellets) have been recorded on a Perkin-Elmer 180 spectrometer in the range 400–4000 cm^{-1}, ^{1}H and ^{13}C NMR spectra on a Bruker (300 MHz) spectrometer in dmso-d_6 using TMS as an internal standard. The results of potentiometric, UV-VIS and EPR spectroscopy studies are given in Table 1.

Crystallography

Details of the crystal data and refinement for compounds **1** and **2** are given in Table 2. The accurate unit cell parameters and the orientation matrices were calculated using the least-squares technique. 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 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 and refined by full-matrix least squares on all F_o^2 using SHELXL 97.[21] The non-hydrogen atoms were refined anisotropically. The O–H hydrogen atoms were found on the Fourier-difference map but were not included in the refinement; the C–H atoms of the methyl and aromatic groups were set in calculated positions and allowed to ride on the atoms to which they were linked.

CCDC reference number 186/1308.

See http://www.rsc.org/suppdata/dt/1999/743/ for crystallographic files in .cif format.

Results and discussion

Solution studies

The ligand, H_2L, exhibits two dissociation constants corresponding to ionisation of hydroxamic and oxime groups ($pK_{a1} = 8.16$ and $pK_{a2} = 11.00$), respectively. The first constant is about one order lower than the typical values for aliphatic hydroxamic acids[22] which is consistent with the relatively small electron withdrawing effect of the oxime group. The second one is very close to the values observed for the deprotonation of the hydroxyimino group in 2-hydroxyiminopropanoic acid and its amide derivatives.[23]

Table 1 Spectroscopic (UV-VIS and EPR) and potentiometric data for H_2L–Cu^{2+} and H_2L–Ni^{2+} systems at 25 °C and $I = 0.1$ mol dm^{-3} KNO$_3$

Species	log β	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	10^4 $A_{\parallel}$/T	$g_{\parallel}$
HL	11.00				
H_2L	19.16				
Cu^{2+} complexes					
$CuHL_2$	29.91(6)	556[a]	110	205	2.273
		335[b]	2349		
CuL_2	22.65(5)	551[a]	128	210	2.227
		465[a]	239		
		323[b]	4867		
$CuH_{-1}L_2$	12.16(5)	552[a]	127	204	2.231
		465[a]	241		
		329[b]	4352		
Cu_2HL_2	37.13(3)	689[a]	59	[c]	[c]
		341[b]	1523		
Cu_2L_2	31.84(8)	656[a]	64	[c]	[c]
		338[b]	2054		
$Cu_2H_{-1}L_2$	26.66(6)	557[a]	94	[c]	[c]
		338[b]	2073		
Ni^{2+} complexes					
NiH_2L_2	32.71(2)	504[a]	132	—	—
		346[b]	2349		
$NiHL_2$	27.48(1)	435[a]	1114	—	—
		411[a]	1276		
		374[b]	2034		
		343[b]	4504		
NiL_2	22.16(1)	437[a]	1520	—	—
		417[a]	1579		
		343[b]	5160		
$NiH_{-1}L_2$	10.56(3)	438[a]	1505	—	—
		416[a]	1561		
		343[b]	5368		

[a] d–d Transition. [b] Ligand to metal CT transition. [c] EPR silent.

Table 2 Crystal data and structure refinement for complexes **1** and **2**

| Empirical formula	$C_6H_{16}N_4Na_2NiO_{10}$	$C_{15}H_{21}CuN_3O_8$
M	408.92	434.89
λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	3.620(1)	7.118(10)
b/Å	21.122(4)	11.377(2)
c/Å	9.505(2)	12.616(3)
α/°		70.91(3)
β/°	95.77(3)	82.79(3)
γ/°		78.15(3)
U/Å^3	723.1(3)	943.0(3)
Z	2	2
D_c/Mg m^{-3}	1.878	1.532
μ/cm^{-1}	1.462	1.206
$F(000)$	420	250
Crystal size/mm	0.20 × 0.20 × 0.15	0.18 × 0.20 × 0.25
θ range/°	2.36 to 25.05	3.25 to 28.76
Range hkl	−4 to 0, −25 to 24, −11 to 11	−5 to 9, −14 to 14, −16 to 16
Reflections collected	2528	6936
Data/parameters	1287/109	4305/246
Goodness of fit on F^2	1.082	1.022
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0263, 0.0696	0.0385. 0.1056
(all data)	0.0306, 0.0722	0.0442, 0.1129
Extinction coefficient	0.008(2)	0.0015(16)
Maximum, minimum electron density/e Å^{-3}	0.344, −0.291	0.648, −0.552

The complex species evaluated from the potentiometric calculations for Cu^{2+} and Ni^{2+} are given in Table 1 and the corresponding species distribution diagrams are presented in Fig. 1. In both systems the concentration of the metal ions starts to drop at considerably lower pH values than in the case of aha (L-α-alanine hydroxamic acid)[24] and H_2hpa [2-(hydroxy- imino)propanoic acid][25] (at pH < 3 for Cu^{2+} and pH < 5 for Ni^{2+}). This indicates that H_2L is a noticeably stronger chelating agent than the two parent ligands. The formation constants of the complexes are remarkably higher for H_2L-containing species (1–6 log units for Cu^{2+} and 4–8.5 for Ni^{2+}) as compared to aha and H_2hpa.

In the Cu²⁺–H₂L system three stable dimeric species, $[Cu_2HL_2]^+$, $[Cu_2L_2]$ and $[Cu_2H_{-1}L_2]^-$ are formed and dominate at pH region 3.5–7.5 [Fig. 1 (a)]. Their formation is clearly indicated by vanishing of the EPR spectra at pH around 4. Electronic spectra for the first two species (Table 1) suggest the presence of only two nitrogen atoms in the co-ordination sphere, the values of absorption maxima being close to those observed for Cu{2N, 2O} species formed by 2-hydroxy-iminopropanamide (688 nm) and N-pyruvoylglycine oxime, $H_3CC(=NOH)C(O)NHCH_2CO_2H$, (666 nm).[25] In the present case two copper ions can be linked by a {N,N; O,O} chelating and bridging hydroxamic group (Scheme 2, a) in both species. The absorption maximum for $[Cu_2H_{-1}L_2]^-$ (557 nm) having maximum abundance (>80%) at pH 6.5 is consistent with the presence of a CuN₄ chromophore, so that in both ligands the hydroxamic groups are deprotonated, and the second metal ion can be bridged by the oxygen atoms of the hydroxamic group (Scheme 2, b). At higher pH (above 6.0) the monomeric species start to be formed, $[CuHL_2]^-$, $[CuL_2]^{2-}$ and $[CuH_{-1}L_2]^{3-}$. Their EPR and absorption spectral data are consistent with a 2 × {N$_{ox}$, N$_{hydrox}$} co-ordination core for all three species (Table 1).
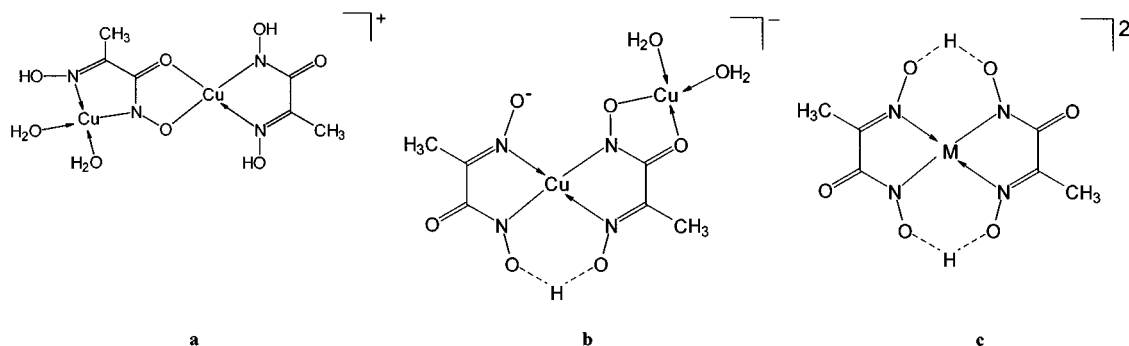
Formally, both series of dimeric and monomeric species contain ligands in the same degree of deprotonation. In both cases the protons taking part in stepwise dissociation $[CuHL_2]^{3-}$ ⟶ $[CuL_2]^{4-}$ ⟶ $[CuH_{-1}L_2]^{5-}$ belong to OH moieties of the oxime or hydroxamic groups (NH hydroxamic protons start to dissociate when Cu²⁺ ions bind). However, comparison of the corresponding stepwise dissociation constants within both series reveals the different nature of these processes. For the dimeric series the values $pK([Cu_2L_2]/[Cu_2HL_2]^+)$ = 5.29(8) and $pK([Cu_2H_{-1}L_2]^-/[Cu_2L_2])$ = 5.18(8) are several orders of magnitude lower than the dissociation constants for the 'free' ligand which is the normal trend for oxime and hydroxamic OH protons in the presence of Cu²⁺ ions. The higher value of the first pK could result from hydrogen bond involvement which is possible within the hydroxamic group in one of the ligands (Scheme 2, a).[6]

For the monomeric series $pK([CuL_2]^{2-}/[CuHL_2]^-)$ = 7.26(6) and $pK([CuH_{-1}L_2]^{3-}/[CuL_2]^{2-})$ = 10.49(8). The second value is more than 5 orders of magnitude higher than that observed for the dimeric series. Such a remarkable increase is connected, in our opinion, with two factors: important stabilisation of $[CuL_2]^{2-}$ species by a pair of short intramolecular hydrogen bonds (Scheme 2, c) observed in the crystal structure of $Na_2[NiL_2]·4H_2O$ (see below) and high negative charge (3−) of the resulting species. Note, that in Ni²⁺ monomeric series with the same co-ordination mode the values of the dissociation constants are very close, $pK([NiH_{-1}L_2]^{3-}/[NiL_2]^{2-})$ = 11.60(3), which confirms the above conclusion.

In the Ni²⁺–H₂L system the species distribution is simpler [Fig. 1 (b)]. The major species dominating in the wide range of pH (6.0–10.5) is $[NiL_2]^{2-}$. In the pH range 5–7 the minor species $[NiH_2L_2]$ and $[NiHL_2]^-$ are detected as well; their maximum abundance does not exceed 20%. The $[NiH_2L_2]$ species is octahedral, with the absorption spectral characteristics (Table 1) typical for a NiN(oxime)₂O₄ chromophore, thus the ligands are co-ordinated in chelating mode via the oxime nitrogen and the oxygen of the deprotonated hydroxamic group. The species $[NiHL_2]^-$, $[NiL_2]^{2-}$ and $[NiH_{-1}L_2]^{3-}$ (the last one starts to be noticeable only above pH 11), according to the UV-VIS spectral data, have a square-planar structure with a NiN₄ core. This is consistent with N,N-chelating co-ordination of the ligand via the oxime and hydroxamic nitrogen atoms with different degrees of deprotonation of the oximic and hydroxamic groups (Scheme 2, c).

Structural studies

The molecular structure of complex **1** and the numbering scheme is shown in Fig. 2, and selected bond lengths and angles are listed in Table 3. Compound **1** is ionic and consists of the complex anions $[NiL_2]^{2-}$, counter ions (Na⁺) and the solvating water molecules.

The complex anion comprises a square-planar nickel(II) ion co-ordinated to four nitrogen atoms belonging to the deprotonated oxime and hydroxamic groups of the ligand. It is

Fig. 1 Species distribution diagrams for Cu²⁺–H₂L (a) and Ni²⁺–H₂L (b) at 25 °C and I = 0.1 mol dm⁻³. Concentration of ligand 0.003 mol dm⁻³ and concentration of metal ions 0.0015 mol dm⁻³.

Scheme 2 Suggested structures for $[Cu_2HL_2]^+$ (a), $[Cu_2H_{-1}L_2]^-$ (b) and $[ML_2]^{2-}$ (M = Cu²⁺ or Ni²⁺) (c) in solution.
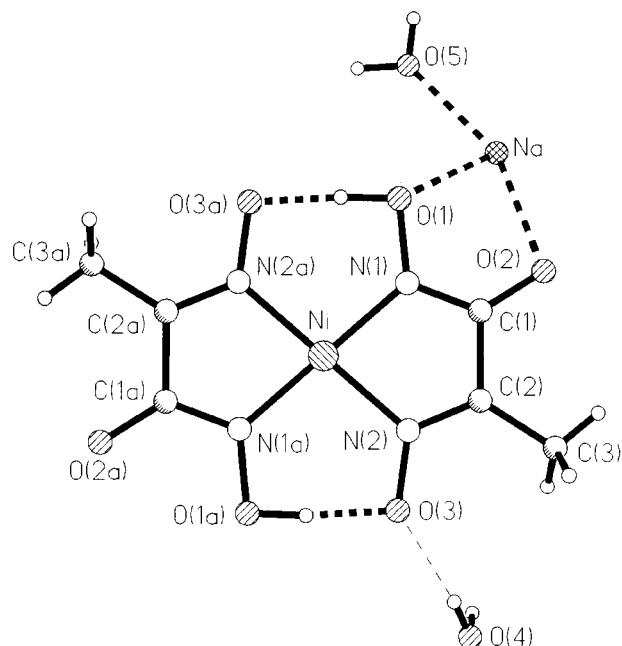
Fig. 2 Molecular structure and the numbering scheme for complex **1**.

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

Ni–N(1)	1.855(2)	Na–O(2²)	2.345(2)
Ni–N(2)	1.881(2)	Na–O(5)	2.344(3)
		Na–O(1)	2.378(2)
N(1)–Ni–N(1¹)	180.0	Na–O(2³)	2.442(2)
N(1)–Ni–N(2)	82.13(8)	Na–O(2)	2.482(2)
N(1¹)–Ni–N(2)	97.87(8)	Na–O(1⁴)	2.585(2)
O(1)–N(1)	1.408(2)	C(1)–N(1)–O(1)	116.2(2)
O(2)–C(1)	1.269(3)	C(2)–N(2)–O(3)	120.3(2)
O(3)–N(2)	1.339(2)	O(2)–C(1)–N(1)	127.4(2)
N(1)–C(1)	1.309(3)	O(2)–C(1)–C(2)	122.2(2)
N(2)–C(2)	1.297(3)	N(1)–C(1)–C(2)	110.4(2)
C(1)–C(2)	1.493(3)	N(2)–C(2)–C(3)	125.1(2)
C(2)–C(3)	1.476(3)	N(2)–C(2)–C(1)	112.7(2)
		C(3)–C(2)–C(1)	122.2(2)

[a] Symmetry transformations used to generate equivalent atoms (indicated by superscript): 1 $-x, -y, -z$; 2 $-x - 1, -y, -z + 1$; 3 $-x, -y, -z + 1$; 4 $x - 1, y, z$.
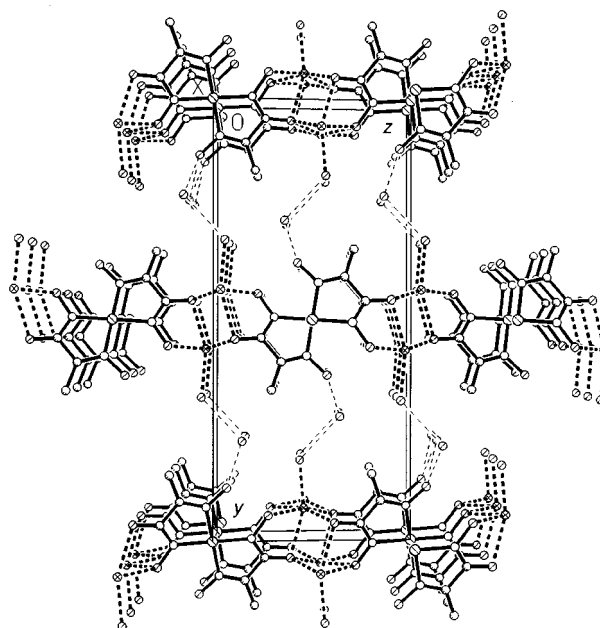
noteworthy that in the hydroxamic function the nitrogen atom is deprotonated while the oxygen retains its proton and does not take part in the co-ordination of the central atom, similarly to the nickel(II) and copper(II) square-planar complexes with 2-aminohydroxamic acids.[8,9] The nickel ion is situated in the specific position (0,0,0) so that the anion is centrosymmetric, and the central and four donor atoms define the same plane. In the five-membered chelate ring NiN(1)C(1)C(2)N(2) carbon atoms C(1) and C(2) deviate from the basal plane by 0.107 and 0.053 Å, respectively. The Ni–N distances [Ni–N(2)$_{oxime}$ 1.881(2), Ni–N(1)$_{hydroxamate}$ 1.855(2) Å] are normal when compared to those of related square-planar nickel(II) complexes of 2-hydroxyiminopropanamide derivatives[23] and 2-amino-hydroxamic acids.[8,9] The bite angle N(1)–Ni–N(2) is decreased to 82.13(8)°.

The ligands in the complex anion are situated in *trans* position with respect to each other due to the symmetry of the anion. The latter exhibits a closed pseudo-macrocyclic conformation on account of short intramolecular hydrogen bonds between the oximino oxygen atom and OH group of the hydroxamic function. This is unlike nickel(II) square-planar anionic complexes with 2-hydroxyiminopropanamide derivatives,[23] where one intracomplex hydrogen bond is formed by two oximino groups of *cis*-situated ligands. In **1** such a bond could be formed provided the *cis* arrangement of the ligands is realised. However, due to the capacity of both oximic and hydroxamic OH moieties to form hydrogen bonds, and the difference in acidity of the corresponding protons, the *trans* arrangement of the co-ordination sphere appears preferable, and the formed hydrogen bond incorporates both oxime and hydroxamic functions. The parameters O(1)–H 0.98, H···O(3a) 1.53 and O(1)···O(3a) 2.503(3) Å, O(1)–H···O(4) 172.5° are close to those characteristic of square-planar *cis*-bis(oximato)nickel(II) complexes,[23] although the O···O separation is somewhat longer than the typical values 1.43–1.48 Å.[23,26]

The bond lengths and angles of the ligands in complex **1** are typical for N-co-ordinated hydroxamic and oxime groups. In the hydroxamic group the C(1)–O(2) [1.269(3)], C(1)–N(1) [1.309(3)] and N(1)–O(1) [1.408(2) Å] distances are very close to those observed in the nickel(II) complex with glycine hydroxamic acid[8] and clearly indicate that this group is in hydroxamic rather than hydroxooximic form. Although the C=O bond length is somewhat longer than the values typical

Fig. 3 Packing diagram for complex **1**.

for amide bonds, the C–N bond length and the bond angles are consistent with sp² hybridisation due to considerable delocalisation of π-electron density from the nitrogen. The C–N bond lengths in the oxime and hydroxamic groups coincide [C(2)–N(2) 1.297(3) and C(1)–N(1) 1.309(3) Å, respectively] while the N–O distances differ significantly [N(2)–O(3) 1.339(2) and N(1)–O(1) 1.408(2) Å] which is consistent with an O-protonated hydroxamic function.

The planar complex anions related by the inversion centres in the points ($\frac{1}{2}$ 0 0) are packed in columns perpendicularly to the x axis with Ni···Ni($1 + x, y, z$) separations of 3.620(1) Å and Ni···N(2)($1 + x, y, z$) of 3.383(2) Å between the neighbouring anions (Fig. 3). The sodium cation is co-ordinated in chelate mode to the O(1) and O(2) oxygen atoms of the basic complex anion forming a five-membered ring. Thus, the hydroxamic groups are bridging between nickel and sodium atoms. The sodium ion is also co-ordinated to the O(1) atom of the neighbouring translational anions thus forming edge-shared centrosymmetric dimers with Na···Na($-1 + x, -y, 1 + z$) separations of 3.242(2) Å which unite the anions into strips along the z direction. The sodium environment is complemented to distorted octahedral by Na···O(1) contacts with two anions related by translations along the x axis, and with water molecule O(5). Thus, each sodium cation participates in the linkage of four complex anions. The Na–O distances (Table

3) are normal for sodium cations.[27] The sodium cationic dimers interact in *x* directions with other dimers by sharing the edges, thus forming frameworks consisting of Na₃O₄ distorted face-shared cubic fragments with a vacancy (Fig. 4). Note, that each O(2) atom participates in co-ordination of three sodium atoms. The sodium frameworks inserted between the nickel anionic columns form walls parallel to the *xz* plane. The walls are interlinked by means of hydrogen bonds formed by water molecules O(4) and O(5) (Fig. 3).

Crystal structure of complex 2 obtained from the alkaline solution containing [Cu(phen)Cl₂] and 2-(hydroxyimino)-propanohydroxamic acid. Crystallisation of the complex from the aqueous solution containing Cu(phen)²⁺ and H₂L in the presence of an excess of alkali (KOH) leads to hydrolysis of the ligand (Scheme 3). The formed compound **2** is a quaternary complex incorporating two neutral ligands (1,10-phen-anthroline and water) and the two-charged anion of 2-hydroxyiminopropanoic acid (H₂hpa) with deprotonated carboxylic and oxime groups. The molecular structure of **2** is shown in Fig. 5; selected bond lengths and angles are listed in Table 4. The structure consists of neutral complex molecules [Cu(phen)(hpa)(H₂O)] and four solvate water molecules linked by hydrogen bonds. The latter are formed

between water molecules and with acceptor oxygen atoms of oxime and carboxylic groups. Both organic ligands are co-ordinated in a bidentate chelate mode. The copper(II) ion is in a distorted square-pyramidal environment, the basal plane being formed by two nitrogen atoms of 1,10-phenanthroline, an oxime nitrogen and a carboxylate oxygen atom of the dianion of 2-hydroxyiminopropanoic acid. Note that the Cu–N(1) [1.966(2) Å] and Cu–O(1) [1.964(2) Å] distances with donor atoms of hydroxamate are noticeably shorter than Cu–N distances with phenanthroline nitrogens [Cu–N(2) 2.032(2), Cu–N(3) 2.003(2) Å]. The water molecule O(4) occupies the apical position, the Cu–O(4) distance [2.258(2) Å] being sig-nificantly longer than the basal bond lengths. The angular distortions are mostly connected with decreasing bite angles [O(1)–Cu–N(1) 82.23(8), N(3)–Cu–N(2) 82.03(8)°] and severe distortion of the equatorial plane with a dihedral angle of 18.70(9)° and the central atom ascending by 0.213(1) Å from the mean plane of the four donor atoms towards the apical water molecule O(4). Both five-membered chelate rings CuN(1)C(2)C(1)O(1) and CuN(2)C(8)C(13)N(3) deviate from planarity and exhibit a distorted envelope conformation with dihedral angles of 3.3(1)° along N(2)–N(3) and 4.8(2)° along N(1)–O(1). The co-ordinated residue of 2-hydroxyimino-propanoic acid approaches a planar conformation with a
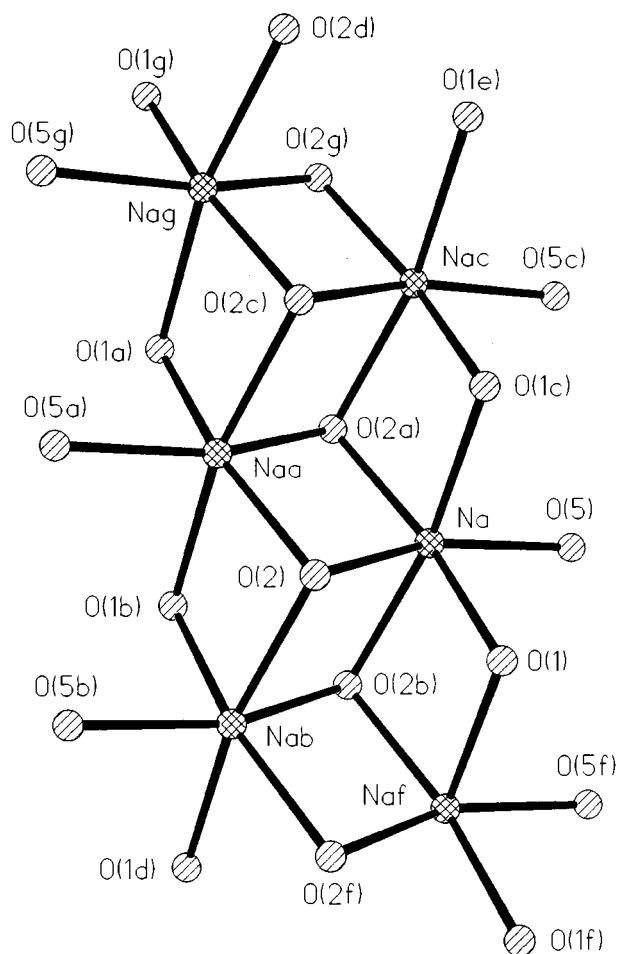
Table 4 Selected bond lengths (Å) and angles (°) for complex **2**

Cu–O(1)	1.964(2)	Cu–N(2)	2.032(2)
Cu–N(1)	1.966(2)	Cu–O(4)	2.258(2)
Cu–N(3)	2.003(2)		
O(1)–Cu–N(1)	82.23(8)	N(1)–Cu–N(2)	101.34(8)
O(1)–Cu–N(3)	92.39(8)	N(3)–Cu–N(2)	82.03(8)
N(1)–Cu–N(3)	172.34(7)	O(1)–Cu–O(4)	100.48(7)
O(1)–Cu–N(2)	161.13(8)	N(1)–Cu–O(4)	94.40(7)
O(1)–C(1)	1.282(3)	N(2)–C(8)	1.360(3)
O(2)–C(1)	1.239(3)	N(3)–C(9)	1.325(3)
O(3)–N(1)	1.329(2)	N(3)–C(13)	1.356(3)
N(1)–C(2)	1.300(3)	C(1)–C(2)	1.494(3)
N(2)–C(4)	1.327(3)	C(2)–C(3)	1.488(3)
C(2)–N(1)–O(3)	120.0(2)	N(1)–C(2)–C(3)	123.5(2)
O(2)–C(1)–O(1)	123.9(2)	N(1)–C(2)–C(1)	113.4(2)
O(2)–C(1)–C(2)	119.6(2)	N(2)–C(4)–C(5)	122.4(2)
O(1)–C(1)–C(2)	116.6(2)		

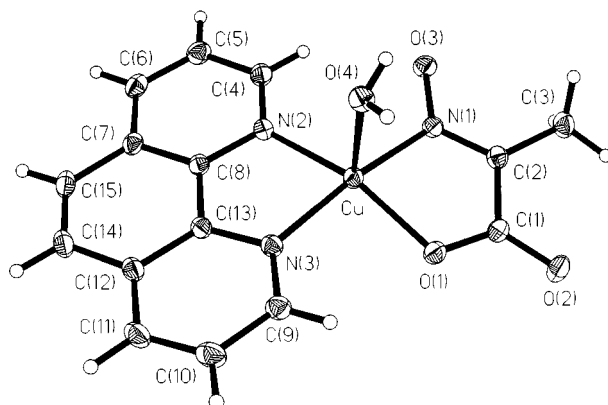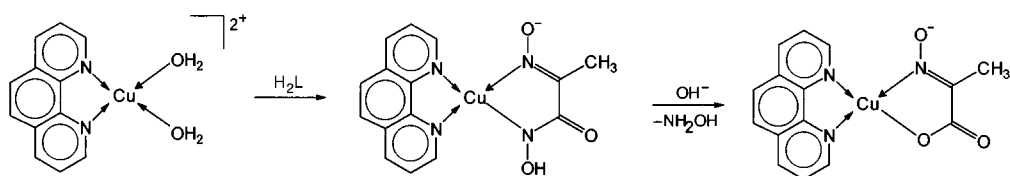**Fig. 4** Fragment of the sodium cation framework in complex **1**.

Fig. 5 Molecular structure of the complex [Cu(phen)(hpa)(H₂O)] **2**.

Scheme 3 Reaction occurring in [Cu(phen)]²⁺–H₂L in aqueous solution.

slight twist of the carboxylate group with respect to the oxime moiety and a dihedral angle of 3.8(2)°.

Conclusion

The obtained results show that 2-(hydroxyimino)propano-hydroxamic acid is a powerful chelating agent towards Cu^{2+} and Ni^{2+} ions. The presence of the adjacent oxime group facilitates N-binding of the hydroxamic function and thus formation of dimeric species through hydroxamic bridges. This capacity can be utilised in design and synthesis of metallacrown compounds and polynuclear assemblies based on oxime hydroxamic acids.

Acknowledgements

References

1 *Chemistry and Biology of Hydroxamic Acids*, ed. H. Kehl, Karger, New York, 1982.
2 K. N. Raymond, *Coord. Chem. Rev.*, 1990, **105**, 135.
3 M. A. Pearson, L. O. Michel, R. P. Hausinger and P. A. Karplus, *Biochemistry*, 1997, **36**, 8164.
4 B. Kurzak, H. Kozłowski and E. Farkas, *Coord. Chem. Rev.*, 1992, **114**, 169.
5 E. Farkas, D. A. Brown, R. Cittaro and W. K. Glass, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 3903.
6 D. A. Brown, R. A. Coogan, N. J. Fitzpatrick, W. K. Glass, D. E. Abukshima, L. Shiels, M. Ahlgren, K. Smolander, T. T. Pakkanen, T. A. Pakkanen and M. Perakyla, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 2673.
7 A. J. Stemmler, J. W. Kampf, M. L. Kirk and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1995, **117**, 6368.
8 D. A. Brown, A. L. Roche, T. A. Pakkanen, T. T. Pakkanen and K. Smolander, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 676.
9 M. Julien-Pouzol, S. Jaulmes, P. Laruelle, S. Carvalho and E. D. Paniago, *Acta Crystallogr.*, *Sect. C*, 1985, **41**, 712; C. O. B. de Miranda-Pinto, E. B. Paniago, S. Carvalho, M. Tabak and Y. P. Mascarenhas, *Inorg. Chim. Acta*, 1987, **137**, 145; T. T. Pakkanen, T. A. Pakkanen, K. Smolander, D. A. Brown, W. K. Glass and A. L. Roche, *J. Mol. Struct.*, 1987, **162**, 313; T. Głowiak and B. Kurzak, *J. Crystallogr. Spectrosc. Res.*, 1992, **22**, 341.
10 M. S. Lah and V. L. Pecoraro, *Comments Inorg. Chem.*, 1990, **11**, 59.
11 V. L. Pecoraro, *Inorg. Chim. Acta*, 1989, **155**, 171; B. R. Gibney, A. J. Stemmler, S. Pilotek, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 1993, **32**, 6008; Myoung Soo Lah, M. L. Kirk, W. Hatfield and V. L. Pecoraro, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1606.
12 Myoung Soo Lah and V. L. Pecoraro, *Inorg. Chem.*, 1991, **30**, 878; *J. Am. Chem. Soc.*, 1989, **111**, 7258; B. R. Gibney, Hsin Wang, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 1996, **35**, 6184; B. R. Gibney, D. P. Kessissoglou, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 1994, **33**, 4840.
13 D. P. Kessissoglou, J. Kampf and V. L. Pecoraro, *Polyhedron*, 1994, **13**, 1379.
14 A. J. Stemmler, J. F. Kampf and V. L. Pecoraro, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 2841.
15 B. Kurzak, E. Farkas, T. Głowiak and H. Kozłowski, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 163.
16 A. J. Stemmler, A. Barwinski, M. J. Baldwin, V. Young and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1996, **118**, 11962.
17 A. Dobosz, I. O. Fritsky, A. Karaczyn, H. Kozłowski, T. Yu. Sliva and J. Świątek-Kozłowska, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1089.
18 G. Ponzio and I. De Paolini, *Gazz. Chim. Ital.*, 1927, **57**, 633.
19 H. M. Irving, M. H. Miles and L. D. Pettit, *Anal. Chim. Acta*, 1967, **68**, 475.
20 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 1195.
21 G. M. Sheldrick, SHELXL 97, University of Göttingen, 1997.
22 L. Bauer and O. Exner, *Angew. Chem.*, *Int. Ed. Engl.*, 1974, **13**, 376.
23 T. Yu. Sliva, T. Kowalik-Jankowska, V. M. Amirkhanov, T. Głowiak, C. O. Onindo, I. O. Fritsky and H. Kozłowski, *J. Inorg. Biochem.*, 1997, **65**, 287; A. M. Duda, A. Karaczyn, H. Kozłowski, I. O. Fritsky, T. Głowiak, E. V. Prisyazhnaya, T. Yu. Sliva and J. Świątek-Kozłowska, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3853.
24 E. Farkas, J. Szöke, T. Kiss, H. Kozłowski and W. Bal, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 2247.
25 C. O. Onindo, T. Yu. Sliva, T. Kowalik-Jankowska, I. O. Fritsky, P. Buglyo, L. D. Pettit, H. Kozłowski and T. Kiss, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3911.
26 M. S. Hussain and E. O. Schlemper, *Inorg. Chem.*, 1979, **18**, 2275.
27 I. O. Fritsky, R. D. Lampeka, V. V. Skopenko, Yu. A. Simonov, A. A. Dvorkin and T. I. Malinowsky, *Z. Naturforsch.*, *Teil B*, 1993, **48**, 270.