

Copper(II) and nickel(II) complexes with oxime analogues of amino acids. Potentiometric, spectroscopic and X-ray studies of complexes with 2-cyano-2-(hydroxyimino)acetic acid and its ethane-1,2-diamine derivative

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2-Cyano-2-(hydroxyimino)acetic acid was found to be an effective ligand for Cu²⁺ and Ni²⁺ ions over a very broad pH range. Potentiometric and spectroscopic data indicate the formation of dimeric complexes with Cu²⁺ ions and the first X-ray evidence for dimer formation is obtained. Conjugation of the oximic moiety with ethane-1,2-diamine leads to another very effective family of chelating agents, although metal ion co-ordination may induce amide bond hydrolysis as indicated by the crystal structure.

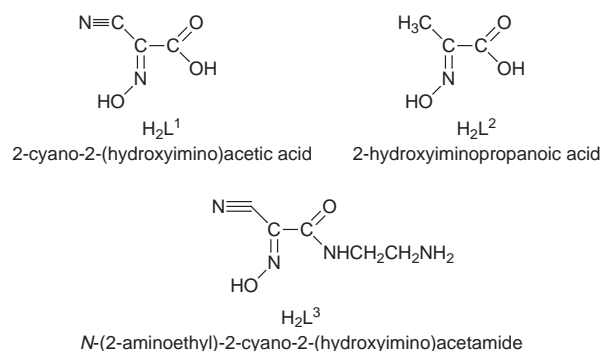
Our recent studies have shown that oximes of amino acids and peptides are very specific and efficient ligands for Cu^{II} and Ni^{II} ions.¹⁻⁴ The complex species formed are stable and water-soluble, and extensive oligomerisation is usually observed above pH 5. The oligomer complex formation results from the two alternative donor centres at the oxime group (N and O), which both have high affinity for metal ions and cannot co-ordinate simultaneously to be the same metal ion. The co-ordination ability of the oxime group donors may be critically dependent on the substituents on the adjacent α -carbon and the set of the other available binding sites. The stability constants of the respective Cu²⁺ complexes with 2-(hydroxyimino)propanamide and 2-cyano-2-(hydroxyimino)acetamide may differ by as much as four orders of magnitude in the case of CuL species.^{1,2} The cyano-substituent at the α -carbon with its strongly electron-withdrawing ability changes distinctly both the complex stability and its structure. Bis-complexes with amino acid oximes have two ligand molecules bound usually in a *cis* position due to the effective hydrogen bond between two oxime oxygens, while in the case of cyano-substitution, ligands are easily completely deprotonated and they are bound to the metal ion in a *trans* position.² Deprotonation of the oxime unit allows the {N,O_{ox}} donor set to form dimeric species both for amino acid and dipeptide derivatives. This oligomerisation was suggested by potentiometric and spectroscopic data for Cu²⁺ ions.^{1,2} However, there was no X-ray crystallographic evidence for dimer formation available. Detailed studies on metal-oxime group co-ordination are also needed to elucidate the effect of metal ion co-ordination on the reactivity of oxime-containing metal complexes.⁵

In this work solution studies on Cu²⁺ and Ni²⁺ complexes with 2-cyano-2-(hydroxyimino)acetic acid as well as the first X-ray evidence for dimeric complex formation are presented. Solution and X-ray studies are also presented for the copper(II)-*N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide system.

Experimental

Potentiometric studies

Stability constants for complexes of H⁺ and Cu^{II} were calculated from titration curves obtained using total volumes of about 2 cm³. Alkali was added from a 0.25 cm³ micrometer



syringe which had been calibrated by both weight titration and the titration of standardised materials. Experimental details were ligand concentration 0.003 mol dm⁻³, metal-to-ligand ratios 1:1, 1:2 and 1:3 for binary systems and 1:1:1 for ternary system; ionic strength 0.1 mol dm⁻³ (KNO₃); pH-metric titrations on a MOLSPIN pH-meter system using a micro combined glass-calomel electrode (Russell, CMAWL) calibrated in hydrogen-ion concentration using HNO₃; temperature 25 °C. Calculations were made with the aid of the SUPERQUAD computer program⁶ which allows for the refinement of total ligand concentrations. Titration data confirmed the ligands to be almost 100% pure.

Spectroscopic measurements

Absorption spectra were recorded on a Beckman DU 650 spectrophotometer. The metal-ion concentrations were 3 × 10⁻³ mol dm⁻³ and metal-to-ligand ratios 1:1, 1:2 and 1:3 for binary and 1:1:1 for the ternary systems. 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).

Ligand synthesis

2-Cyano-2-(hydroxyimino)acetic acid was synthesised as described earlier.² Synthesis of *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide was performed as follows: a mixture of 5.1 g (35.9 mmol) of 2-cyano-2-(hydroxyimino)acetate in 80 ml of propan-2-ol and 3.1 ml of 70% ethane-1,2-diamine aqueous solution was heated to 80 °C and under continuous

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

	1	2
Formula	(C ₇ H ₈ CuN ₂ O ₇) ₂	C ₇ H ₁₀ CuN ₄ O ₄
<i>M</i>	495.3	253.71
<i>T</i> /K	298(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>Pcab</i> ^a
<i>a</i> /Å	16.445(3)	7.447(2)
<i>b</i> /Å	6.497(2)	15.032(3)
<i>c</i> /Å	17.330(3)	16.602(4)
β /°	117.62(4)	
<i>U</i> /Å ³	1640.6(7)	1858.5(6)
<i>Z</i>	4	8
<i>D_c</i> /g cm ⁻³	2.005	1.814
μ /mm ⁻¹	2.675	2.665
<i>F</i> (000)	1000	1032
Crystal size/mm	0.6 × 0.5 × 0.4	0.15 × 0.2 × 0.2
No. of data collected	2224	1861
No. of data with <i>I</i> > 2 σ (<i>I</i>)	2179	1548
No. of parameters varied	151	128
<i>R</i> 1 ^b	0.0297	0.0360
<i>wR</i> 2 ^c	0.0835	0.1045

^a Non-standard setting of the orthorhombic space group *Pbca* (no. 61).

^b $R1 = \sum(F_o - F_c)/\sum F_o$, ^c $wR2 = \{\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)]\}^{1/2}$.

stirring maintained at this temperature for 4 h. The solution was cooled to room temperature and after 24 h the formed precipitate was filtered off and washed with ice water, propan-2-ol, acetone, diethyl ether and dried *in vacuo* in a desiccator with KOH. The crude product was recrystallized from propan-2-ol. This compound is a white crystalline powder, soluble in water, alcohol, DMSO, DMF, insoluble in acetone and diethyl ether; *T*_{decomp.} 195–197 °C. Yield 4.4 g (78%). IR (cm⁻¹): 3340 ν(N–H), 3300, 3060 ν(N–H, NH₂), 2220 ν(C≡N), 1648 ν(C=O, Amide I), 1552 (Amide II), 1130 ν(N=O). ¹H NMR [(CD₃)₂SO]: δ 8.15 (s, 1 H, NH), 6.65 (s, 2 H, NH₂), 3.44 (m, 2 H, CH₂NH), 2.93 (m, 2 H, CH₂NH₂).

Synthesis and crystallisation of the dimeric Cu²⁺ complex with 2-cyano-2-(hydroxyimino)acetate 1

The sodium salt of 2-cyano-2-(hydroxyimino)acetic acid (2 mmol) in 20 ml of water was added to 10 ml of 0.1 M Cu(NO₃) and then 20 ml of 0.1 M HNO₃ was added to the resulting mixture. In 2 d green crystals were grown from solution, the product was filtered off, washed with a small amount of water and dried over CaCl₂. Yield 45%.

Synthesis and crystallisation of the monomeric Cu²⁺ complex with *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide 2

To 1.13 ml of 2 M copper(II) acetate aqueous solution, 0.352 g (2.3 mmol) of *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide suspended in 40 ml of water was added. The resulting mixture was heated to complete dissolution of ligand (80–90 °C) and cooled to room temperature. The formed precipitate was filtered off and the resulting green solution was allowed to stand at room temperature for 48 h. A blue crystalline product precipitated from solution, was filtered off, washed with a small amount of water and dried over CaCl₂. Yield 0.165 g (35%).

Crystal-structure determination

Intensity data collections were carried out on a KUMA KM-4 four-circle diffractometer⁷ using graphite-monochromated Mo-K α radiation (0.710 73 Å). An absorption correction following the DIFABS⁸ procedure was applied to complex 1 (minimum and maximum absorption corrections were 0.8496 and 1.2477). The structures were solved by direct methods

Table 2 Protonation constants and complex-formation constants of 2-cyano-2-(hydroxyimino)acetic acid, 2-(hydroxyimino)propanoic acid, *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide at 25 °C and *I* = 0.1 mol dm⁻³ KNO₃

Species	log β		
	H ₂ L ¹	H ₂ L ^{2*}	H ₂ L ³
HL	6.607(2) (=NOH)	11.61 (=NOH)	9.22(1) (NH ₃ ⁺)
H ₂ L	7.86(5)	14.86	14.11(2)
log <i>K</i> (H ₂ L)	1.25(5) (CO ₂ H)	3.25 (CO ₂ H)	4.89(2) (=NOH)
Nickel(II) complexes			
NiL	—	—	—
NiH ₋₁ L	—	—	-4.00(1)
NiH ₋₂ L	—	—	-12.70(1)
NiH ₂ L ₂	—	28.86	—
NiHL ₂	14.79(1)	23.66	—
NiL ₂	9.67(2)	13.49	—
NiH ₋₁ L ₂	-1.10(3)	—	—
Copper(II) complexes			
CuL	—	—	6.50(3)
CuH ₋₁ L	—	—	0.29(1)
CuH ₋₂ L	—	—	-11.04(1)
CuH ₂ L ₂	—	31.76	—
CuHL ₂	17.14(4)	29.00	—
CuL ₂	12.38(4)	18.84	—
CuH ₋₁ L ₂	—	—	—
Cu ₂ L ₂	—	27.15	—
Cu ₂ H ₋₁ L ₂	12.59(8)	21.64	12.12(1)
Cu ₂ H ₋₂ L ₂	3.03(9)	11.67	—
Cu ₂ H ₋₃ L ₂	-7.01(9)	—	—

* Data from refs. 1 and 3.

(SHELXS 86)⁹ and refined on *F*² by full-matrix least-squares using SHELXL 93.¹⁰ Positions of carbon-bonded hydrogen atoms were calculated based on the geometry of the molecules. Other H atoms were located from a Fourier-difference map. Crystal data and the details of data collection and the refinement procedure are given in Table 1.

CCDC reference number 186/963.

Results and Discussion

Solution studies

Protonation constants. 2-Cyano-2-(hydroxyimino)acetic acid behaves as an H₂L molecule with two dissociation constants corresponding to oxime OH and carboxylate functions (Table 2). The log *K*(CO₂H) 1.25(5) is too low to be precisely evaluated with the potentiometric data obtained within this work and it should be treated with caution. The comparison with 2-(hydroxyimino)propanoic acid clearly shows the strong withdrawing effect of the cyano substituent. The oxime OH group becomes five orders of magnitude more acidic than that of the methyl-substituted ligand, while the p*K* value of the carboxylic group decreases by two orders of magnitude.

N-(2-Aminoethyl)-2-cyano-2-(hydroxyimino)acetamide also behaves as an H₂L acid with protonation constants corresponding to the oxime OH group (p*K* = 4.89) and the terminal amine group of ethane-1,2-diamine (9.22). The oxime OH of the amide form of the 2-cyano-ligand is usually more acidic than that of the acid form (Table 2).

Copper(II) and Ni²⁺ complexes with 2-cyano-2-(hydroxyimino)acetic acid. Potentiometric and spectroscopic data obtained for Cu²⁺-containing solutions suggest formation of several species including monomeric CuHL₂ and CuL₂ as well as the dimeric Cu₂H₋₁L₂, Cu₂H₋₂L₂ and Cu₂H₋₃L₂ complexes (Tables 2 and 3, Fig. 1). It is noteworthy that the formation of

Table 3 Spectral parameters (visible and EPR) for metal(II)-2-cyano-2-(hydroxyimino)acetic acid (A) and *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide (B) systems at 25 °C and $I = 0.1 \text{ mol dm}^{-3} \text{ KNO}_3$

Species {binding mode}	UV/VIS		EPR	
	λ/nm	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$10^4 A_{\parallel}/T$	g_{\parallel}
A				
[NiHL ₂]	929 ^a	5.1		
2x{N _{ox} ,CO ₂ ⁻ }	736 ^a	4.2		
	633 ^a	5.3		
	465 ^a	15		
[NiL ₂]	940 ^a	12		
2x{N _{ox} ,CO ₂ ⁻ }	511 ^a	67		
	378 ^a	310		
[NiH ₋₁ L ₂]	940 ^a	11		
2x{N _{ox} ,CO ₂ ⁻ }{OH ⁻ }	800 ^a	7.3		
[CuHL ₂]	704 ^a	56.5	153	2.31
2x{N _{ox} ,CO ₂ ⁻ }	360 ^b	1636		
	280 ^b	9515		
[CuL ₂]	620 ^a	161	181	2.24
2x{N _{ox} ,CO ₂ ⁻ }	360 ^b	4197		
[Cu ₂ H ₋₁ L ₂]	623 ^a	160	<i>c</i>	
2x{N _{ox} ,CO ₂ ⁻ }{O _{ox} ⁻ }	360 ^b	4048		
[Cu ₂ H ₋₂ L ₂]	632 ^a	127	<i>c</i>	
2x{N _{ox} ,CO ₂ ⁻ ,O _{ox} ⁻ }	356 ^b	3311		
[Cu ₂ H ₋₃ L ₂]	660 ^a	65	<i>c</i>	
2x{N _{ox} ,CO ₂ ⁻ ,O _{ox} ⁻ }{OH ⁻ }	352 (sh) ^b	746		
B				
[CuL] {(OH _{ox})N _{ox} ,N ⁻ ,NH ₂ }	627 ^a	70	144	2.2
	361 ^b	1569		
[CuH ₋₁ L] {(O _{ox} ⁻)N _{ox} ,N ⁻ ,NH ₂ }	566 ^a	157	185.9	2.1
	347 ^b	1631		
[CuH ₋₂ L] {N _{ox} ,N ⁻ ,NH ₂ ,OH ⁻ }	577 ^a	149	185.9	2.1
	347 ^b	1588		
[Cu ₂ H ₋₁ L ₂]	588 ^a	153	<i>c</i>	
2x{N _{ox} ,N ⁻ ,NH ₂ }{O _{ox} ⁻ } _{bridge}	347 ^b	1880		

^a d-d transition. ^b N_{ox}→Cu²⁺ charge-transfer transition. ^c EPR spectrum not observed.

the monomeric 1:1 species was not observed at low pH which is probably due to the high acidity of the hydroxyimino group in the cyanooximes. The formation of dimeric complexes is supported by the EPR spectra, which diminish in intensity when dimeric species are formed. In equimolar solutions dimeric species predominate above pH 3.5 [Fig. 1(A)]. It is interesting to note that the oxime ligand binds to Cu²⁺ ions at very acidic pH and the concentration of the complexed metal exceeds that of the aqua ion at pH > 2 for molar ratio 1:2 [Fig. 1(B)] and above pH 3 for equimolar solutions [Fig. 1(A)]. The lower basicity of the oximic moiety causes the respective complexes of the 2-cyano-2-(hydroxyimino)-derivative to be less stable than those of 2-(hydroxyimino)propanoic acid. The hydrolysis of the dimeric Cu₂H₋₂L₂ species with log *K* 10.04 suggests deprotonation of the apically metal-bound water (the crystal structure shows that two or three water molecules may be bound to the metal ion in dimeric species, see below). According to the EPR spectra, above pH 11 only totally hydrolysed Cu(OH)₄²⁻ is observed. This indicates that the formation of Cu₂H₋₃L₂ marks the beginning of the total hydrolysis of the metal complex.

Nickel(II) ions form monomeric complex species only: NiHL₂, NiL₂ and NiH₋₁L₂ (Fig. 2). The latter complex is not found for 2-(hydroxyimino)propanoic acid. According to the absorption spectra (Table 3) all these species are octahedral and deprotonation of the NiL₂ species may be attributed to proton loss from the metal-bound water (p*K* = 10.77). Also Ni²⁺ complexes with 2-cyano-2-(hydroxyimino)acetic acid are dis-

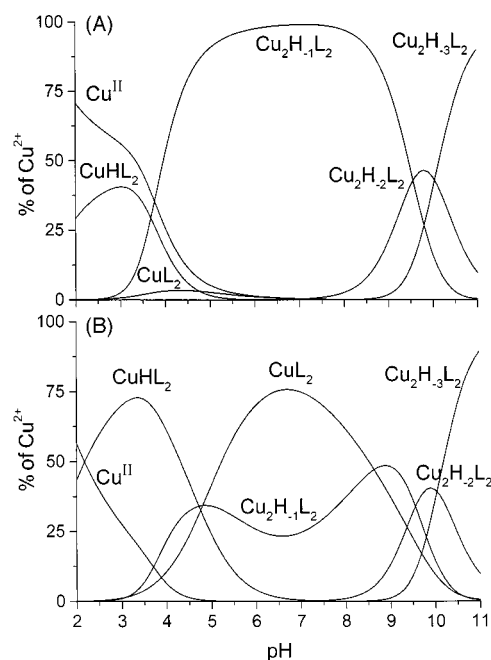


Fig. 1 Species distribution curves for the complexes formed in the Cu²⁺-2-cyano-2-(hydroxyimino)acetic acid system for 1:1 (A) and 1:2 (B) metal-to-ligand molar ratios as a function of pH

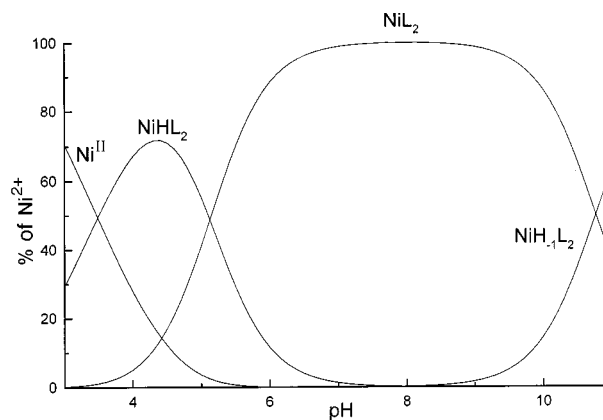


Fig. 2 Species distribution curves for the complexes formed in the Ni²⁺-2-cyano-2-(hydroxyimino)acetic acid system (1:5) as a function of pH

tinctly less stable than those of 2-(hydroxyimino)propanoic acid (Table 2).

Copper(II) complexes with *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide in solution. The combination of two effective chelating agents, oxime and ethane-1,2-diamine, in one molecule leads to a potent terdentate chelating agent for Cu²⁺ ions. There are two major complexes formed in solution, including the dimeric form Cu₂H₋₁L₂ predominant at lower pH (Table 2, Fig. 3). The latter complex dominates between pH 4.5 and 9, while above pH 9 the monomeric CuH₋₁L species is a major complex. The spectroscopic data (Table 3) with the d-d transition energy around 580 nm indicate that in both major complexes the metal ion is bound to three nitrogen donors.¹¹ In the dimeric complex one of the oxime oxygens undergoes deprotonation and bridges two Cu²⁺ ion species. Deprotonation of the second oxime OH group leads to formation of the monomeric species with same {N_{ox},N⁻,NH₂} binding mode.

Solid-state X-ray studies

Crystal structures of the dimeric Cu²⁺ complex with 2-cyano-2-(hydroxyimino)acetic acid 1. The crystal structure consists of

Table 4 Selected bond lengths (Å) and angles (°) for complex 1

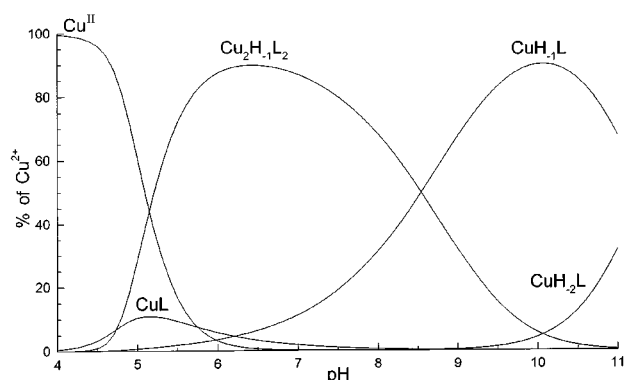
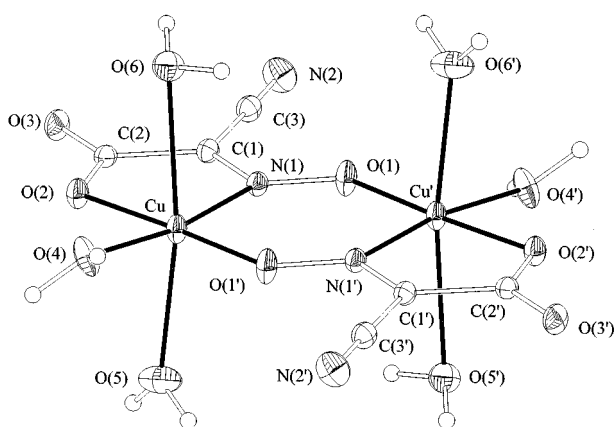
Cu–O(1')	1.921(2)	O(1)–N(1)	1.306(2)
Cu–O(2)	1.972(2)	O(2)–C(2)	1.268(3)
Cu–O(4)	1.959(2)	O(3)–C(2)	1.233(3)
Cu–O(5)	2.392(2)	N(1)–C(1)	1.298(3)
Cu–O(6)	2.495(2)	N(2)–C(3)	1.132(3)
Cu–N(1)	2.008(2)	C(1)–C(3)	1.433(3)
Cu–Cu'	3.795(1)	C(1)–C(2)	1.490(3)

Primed atoms are related to unprimed by: $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

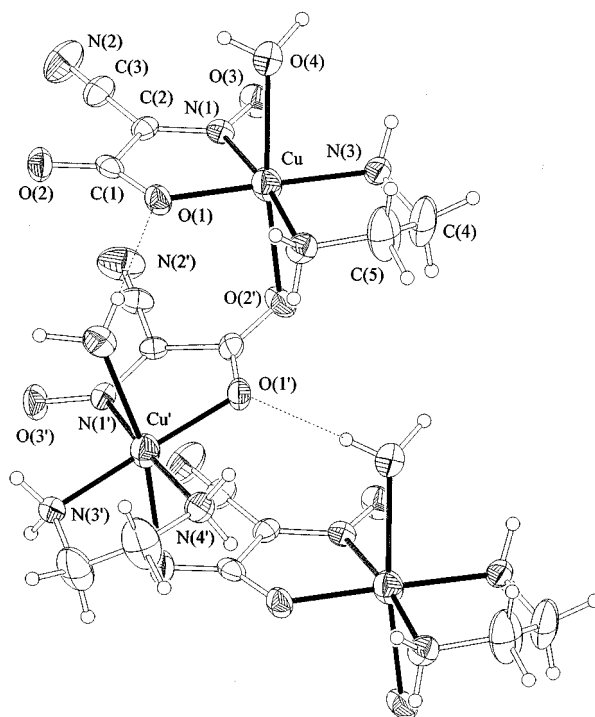
Table 5 Selected bond lengths (Å) and angles (°) for complex 2

Cu–O(1)	1.967(2)	O(3)–N(1)	1.281(2)
Cu–O(4)	2.501(2)	N(1)–C(2)	1.317(3)
Cu–O(2')	2.665(2)	N(2)–C(3)	1.138(3)
Cu–N(3)	1.987(2)	N(3)–C(4)	1.470(4)
Cu–N(4)	1.987(2)	N(4)–C(5)	1.466(4)
Cu–N(1)	1.991(2)	C(1)–C(2)	1.491(3)
Cu–Cu'	5.092(1)	C(2)–C(3)	1.423(3)
O(1)–C(1)	1.281(3)	C(4)–C(5)	1.455(5)
O(2)–C(1)	1.224(3)		

Primed atoms are related to unprimed by: $0.5 + x, 0.5 - y, z$.

**Fig. 3** Species distribution curves for the complexes formed in the Cu^{2+} –*N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide system (1:2) as a function of pH**Fig. 4** Molecular structure of complex 1 with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. Primed atoms are related to those not primed by: $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$

centrosymmetric dimers. The dimer structure is composed of two octahedra, which do not share a common edge (Fig. 4). The distance between copper atoms is 3.795(1) Å. The oxygen atoms of carboxylate [O(2)], bridging deprotonated oxime group [O(1')] and water [O(4)] as well as the oxime nitrogen are involved in equatorial co-ordination with Cu–O bonds of 1.921(2)–1.972(2) Å and a Cu–N bond of 2.008(2) Å (Table 4). Both axial copper sites are occupied by water molecules [O(5)]

**Fig. 5** The polymeric structure of complex 2 with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. Primed atoms are related to those not primed by: $0.5 + x, 0.5 - y, z$. Intramolecular hydrogen bonds are shown as dashed lines

and [O(6)] with much longer Cu–O bonds of 2.392(2) and 2.495(2) Å, respectively. The structure is stabilised by intermolecular hydrogen bonds involving all metal-bound water protons, which are especially effective in the case of equatorially bound H_2O molecule.

The crystal structure of the dimeric complex discussed above agrees well with the structure of Cu_2L_2 proposed earlier from the solution studies for 2-(hydroxyimino)propanoic acid.¹

Crystal structure of the complex obtained from the solution containing Cu^{2+} and *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide 2. Crystallisation of the complex from the aqueous solution containing copper(II) acetate and *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide leads to hydrolysis of the ligand. According to X-ray crystallography (Fig. 5, Table 5) the complex obtained is a ternary complex with 2-cyano-2-(hydroxyimino)acetate and ethane-1,2-diamine bound as two separate molecules. The carboxylate acts as the bridging group and the complex forms a linear polymeric structure. Copper(II) is six-co-ordinated with a water molecule co-ordinated in an apical position *trans* to the bridging carboxylate oxygen (Fig. 5). Thus, the terdentate Cu^{2+} complex with *N*-(2-aminoethyl)-2-(hydroxyimino)acetamide described in solution as CuH_{-1}L undergoes hydrolysis of the amide bond which is catalysed by the bound metal ion.

The ternary complex observed in the crystal structure is also formed in the solution containing Cu^{2+} , ethane-1,2-diamine (en) and 2-cyano-2-(hydroxyimino)acetic acid (L). The ternary $\text{Cu}(\text{en})\text{L}$ species is stable and above pH 8 the deprotonation of metal-bound water with log $K = 10.1$ occurs (Table 6).

Conclusion

Modification of an amino group into an oxime function in simple amino acids leads to a very effective chelating agent. The binding ability of the oxime nitrogen atom towards Cu^{2+} and Ni^{2+} ions may be easily modified by substituents at the vicinal 2-carbon (*e.g.* by a strongly withdrawing cyano group). The deprotonation of the oxime OH group leads to a rearrangement

Table 6 $\log \beta$ and spectroscopic parameters for ternary complexes of the Cu^{2+} -ethane-1,2-diamine (en)-2-cyano-2-(hydroxyimino)acetic (L) system

Species	$\log \beta$	UV/VIS		EPR	
		λ/nm	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$10^4 A_{\parallel}/T$	g_{\parallel}
Cu(en)L	17.09(4)	591	80	187	2.2
		328	1881		
		279	7148		
CuH ₋₁ (en)L	7.08(4)	573	101	187.5	2.2
		327	1579		
		279	7332		

of the electron density from the oxime-oxygen to the oxime-nitrogen making the latter donor very efficient in metal-ion co-ordination. The deprotonated oxime-oxygen donor leads to the formation of effective dimeric Cu^{2+} complexes. The co-ordination ability of oxime derivatives of amino acids may be effectively improved by conjugation of the oxime with other potent chelating agents such as ethane-1,2-diamine. The oxime nitrogen serves as a low pH effective metal-ion anchoring site while conjugated ethane-1,2-diamine completes the co-ordination with its two strongly bonding nitrogen donors. The bound metal may induce the hydrolysis of the amide bond in *N*-(2-aminoethyl)-2-cyano-2-(hydroxyimino)acetamide. Oxime ligands with ethane-1,2-diamine are also able to form very stable ternary complexes.

The formation of the dimeric species at very low pH may need some comment. The residual quantity of the acid in solution (2 mmol in 50 ml) gives a pH slightly less than 2, and under these conditions noticeable complex formation occurs (Fig. 1). Complex **1** (Cu_2L_2) bears no counterpart in the solution equilibrium because the concentrations of the reagents used in synthesis are about two orders of magnitude higher than those applied in the solution studies. Taking into account the fact that

even at low concentrations the dimeric species start to be formed at pH as low as 3, the crystallisation of the dimeric complex from highly concentrated solutions is then not surprising indicating the strong tendency of the ligand to form dimeric species.

Acknowledgements

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