X-Ray and Potentiometric Studies on a Pentanuclear Copper(II) Complex with β-Alaninehydroxamic Acid†

Barbara Kurzak,[*,a] **Etelka Farkas,**[b] **Tadeusz Glowiak**[c] **and Henryk Kozlowski**[*,c]
[a] *Institute of Chemistry, Pedagogical University, Siedlce, Poland*
[b] *Department of Inorganic and Analytical Chemistry, University of Debrecen, H-4010 Debrecen, Hungary*
[c] *Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland*

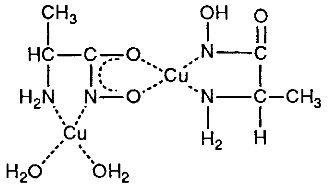
Potentiometric and X-ray studies on the system copper(II)–L-β-alaninehydroxamic acid have shown the formation of a very stable pentanuclear complex $[Cu_5A_4H_{-4}]^{2+}$ at pH around 4. In this species all donor atoms of the aminohydroxamic acid are involved in the metal ion co-ordination. Four peripheral metal ions form an almost planar structure and the central metal ion is 0.4 Å above this plane. There are twelve five- and six-membered chelate rings with different conformations. The X-ray structure results support earlier suggestions based on potentiometric and spectroscopic data for the formation of oligomeric structures at relatively low pH.

Recent spectroscopic and potentiometric studies have shown that copper(II) ions may form a variety of complex species with aminohydroxamic acids.[1–4] At relatively low pH (4–6) a dinuclear complex is formed with involvement of mixed donor sets as shown in Scheme 1. The co-ordination mode in this molecule was proposed on the basis of spectroscopic data.[4] Its stability is relatively high though the monomeric MA_2 and MAH_{-1} complexes are the major species at pH >6. The high stability of these monomeric complexes results from very effective chelation by the two nitrogen donors of the amino and hydroxamic groups, which in α-amino acid derivatives form five-membered rings. The X-ray crystal structures of planar bis(glycinehydroxamato)nickel(II) complexes[5,6] and two *trans*-bis(glycinehydroxamato)copper(II) complexes[7,8] provide clear evidence for such co-ordination. In the present work we have studied the complex formation in the copper(II)–L-β-alaninehydroxamic acid (3-amino-*N*-hydroxypropanamide) system in which the amino and hydroxamic nitrogens are one more carbon apart from each other than in the α derivatives and potentially they may form six-membered chelate rings.

Experimental

L-β-Alaninehydroxamic acid was prepared *via* the methyl ester of L-β-alanine as described in ref. 9. Its purity and the exact concentrations of the ligand stock solutions were determined by Gran's method.[10]

Potentiometric Studies.—The concentration of the ligand in the samples was varied in the range $1 \times 10^{-3} - 4 \times 10^{-3}$ mol dm^{-3}. The metal-to-ligand molar ratios were adjusted in the range 1:1 to 1:5 and measurements were performed at six different ratios. Titrations were carried out with carbonate-free KOH solutions of known concentration (*ca.* 0.2 mol dm^{-3}). The ionic strength was adjusted to 0.2 mol dm^{-3} with KCl and the temperature was 25 ± 0.1 °C. Measurements were carried out on a Radiometer pH-M64 instrument with 62040B glass and K4040 calomel electrodes, using a TTA 80 titration unit. The electrode system was calibrated by the method of Irving *et al.*,[11] so that the pH-meter readings could be converted into hydrogen-ion concentrations. The calculations of the pH-metric data were performed with the aid of the PSEQUAD computer program.[12]



$[Cu_2A_2H_{-1}]^+$

Scheme 1

Crystallographic Measurements.—The approximate unit-cell dimensions were determined from rotation and Weissenberg photographs. A specimen of 0.38 × 0.40 × 0.47 mm was selected for diffraction studies. More accurate unit-cell dimensions and the orientation matrix used for data collection were obtained from a least-squares fit of the observed setting angles for 15 high-order Mo-Kα reflections measured with a Syntex $P2_1$ computer-controlled four-circle diffractometer, equipped with a scintillation counter and graphite monochromator.

The intensities of 4368 independent reflections were measured at room temperature by the θ–2θ scan technique up to $2\theta_{max}$ 50°. Two standards were monitored after every 50 reflections. The maximum variation of an intensity value was 6%. The intensities were corrected for Lorentz and polarization effects but not for absorption; 3784 such data for which $I > 3.5\sigma(I)$ were used in the analysis.

The structure was solved by direct methods using the SHELXS program,[13] and refined by full-matrix least squares. The positions of all hydrogen atoms were determined from successive Fourier difference maps. Several cycles of refinement of coordinates and anisotropic thermal parameters for non-H atoms, fixed with coordinates and isotropic thermal parameters for H atoms, reduced R to 0.038 and R' to 0.049. Neutral atomic scattering factors for all atoms were taken from ref. 14 and all calculations were performed with a Syntex XTL/XTLE structure determination system.[15] A summary of the data collection and processing parameters is given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Summary of data collection and processing parameters

Formula	$C_{36}H_{24}Cl_4Cu_5N_8O{\cdot}5H_2O$
M	1015.52
Space group	$P\bar{1}$
a/Å	10.568(2)
b/Å	11.800(2)
c/Å	13.742(3)
α/°	94.49(3)
β/°	110.58(3)
γ/°	99.81(3)
U/Å^3	1563.0(7)
Z	2
D_m (flotation, CCl_4–$CHBr_3$)/g cm^{-3}	2.15(2)
D_c/g cm^{-3}	2.16
$F(000)$	1018
$\bar{\lambda}$(Mo-Kα)/Å	0.710 69
μ(Mo-Kα)/cm^{-1}	37.5
Unique data collected	4368
Data with $I > 3.5\sigma(I)$	3784
Total variables	433
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.038
$R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$	0.049
$S = [w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{\frac{1}{2}}$ *	4.56
Function minimized ($w = 1/\sigma^2$)	$\Sigma w(F_o - F_c)^2$
Final $\Delta\rho$/e Å^{-3}	$\pm$0.35 Å^2
Final $(\Delta/\sigma)_{max}$	0.01

* n = No. of observations, p = no. of parameters

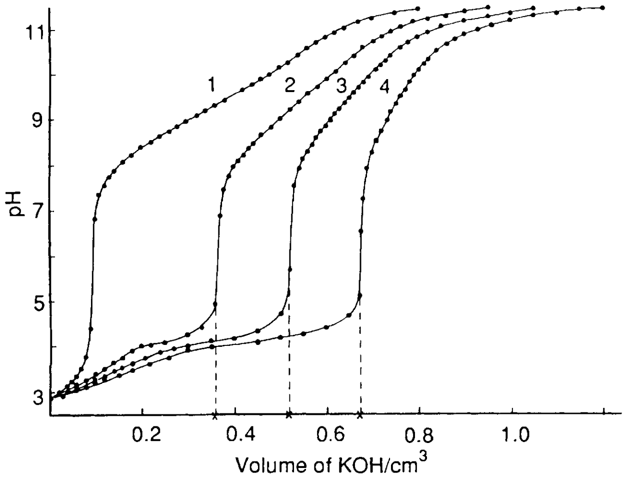

Fig. 1 Titration curves for β-alaninehydroxamic acid and copper(II)–β-alaninehydroxamic acid systems (× on the horizontal axis denotes the consumption of 2.40 equivalents of base per metal for the particular sample): $c_A = 4 \times 10^{-3}$ mol dm^{-3} for all samples; $c_M = 0$ (1), 1.9×10^{-3} (2), 2.9×10^{-3} (3) and 3.9×10^{-3} mol dm^{-3} (4)

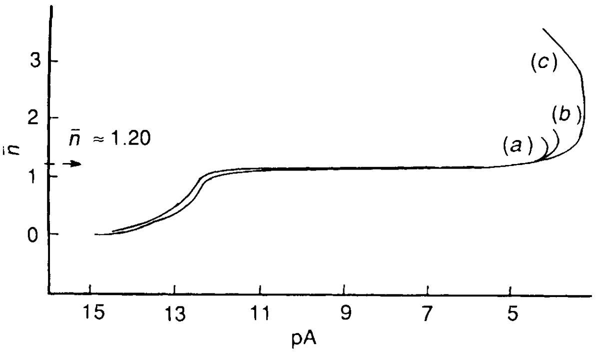

Fig. 2 Formation curves for the copper(II)–β-alaninehydroxamic acid system: $c_A = 3.75 \times 10^{-3}$ mol dm^{-3} for all samples; $c_M = 3.0 \times 10^{-3}$ (a), 2.0×10^{-3} (b) and 1×10^{-3} mol dm^{-3} (c)

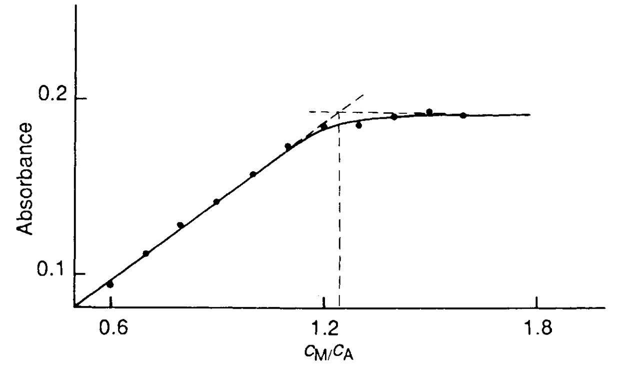

Fig. 3 Dependence of the absorbance of the d–d transition at 616 nm on metal-to-ligand molar ratio; $c_A = 5 \times 10^{-3}$ mol dm^{-3}

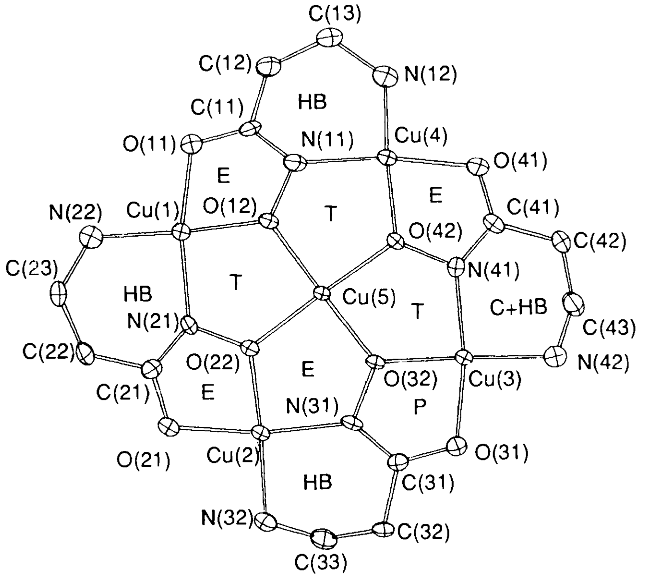

Fig. 4 Perspective view, atom numbering and assignment of the chelate-ring conformations for the complex $[Cu_5A_4H_{-4}][ClO_4]_2{\cdot}5H_2O$. Thermal ellipsoids scaled to 50% probability. The letters indicate the approximate conformations of the rings: E = envelope, T = twist, C = chair and HB = half-boat; P = planar

Results and Discussion

Potentiometric Study in Aqueous Solutions.—The fully protonated form of the ligand ($H_3N^+CH_2CH_2CONHOH$) can release two protons in the range 7.5–10.5, one from the amino group and one from the hydroxamic acid group. These two dissociation processes may overlap with each other. This means that the dissociation constants calculated from the pH-metric data are macroconstants and they are equal to 8.45 (pK_1) and 9.74 (pK_2).

Some of the titration curves registered for β-alaninehydroxamic acid and for the copper(II)–β-alaninehydroxamic acid system are shown in Fig. 1. As can be seen each sample can be titrated without precipitation up to pH 11 even at 1 : 1 metal-to-ligand molar ratio. The colour of the solution becomes greenish above pH 4.5. This finding, taking into account our previous results obtained for copper(II)–α-alaninehydroxamic acid[2] and copper(II)–aspartic acid-β-hydroxamic acid,[16] suggests that in addition to the nitrogens the oxygens of the hydroxamate moiety take part in the co-ordination in the copper(II)–β-alaninehydroxamic acid system.

In order to obtain more specific information about the stoichiometry of the species formed in the copper(II)–β-alaninehydroxamic acid solutions, formation curves have been calculated. Some of them are depicted in Fig. 2. A wide plateau is attained at $\bar{n}$ [= (c_A − [A])/c_M] *ca.* 1.20. This parameter

Table 2 Final atomic coordinates for non-hydrogen atoms (× 10^4) of $[Cu_5A_4H_{-4}][ClO_4]_2\cdot 5H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	1 074(1)	4 805(1)	1 850(1)	O(5)	5 972(6)	3 282(6)	5 298(6)
Cu(2)	1 239(1)	2 987(1)	4 729(1)	O(6)	3 731(5)	3 543(4)	4 764(4)
Cu(3)	2 025(1)	6 523(1)	6 754(1)	O(7)	4 233(7)	1 735(5)	5 075(5)
Cu(4)	2 282(1)	8 355(1)	4 003(1)	O(8)	4 436(9)	2 482(6)	3 620(4)
Cu(5)	1 261(1)	5 688(1)	4 221(1)	N(11)	1 733(5)	7 156(4)	2 784(3)
Cl(1)	7 411(2)	9 109(2)	469(2)	N(12)	3 383(5)	9 466(4)	3 445(4)
Cl(2)	4 610(2)	2 779(2)	4 682(2)	N(21)	757(5)	3 620(4)	2 742(4)
O(11)	1 843(5)	6 152(4)	1 331(3)	N(22)	1 140(6)	3 622(4)	767(4)
O(12)	1 012(4)	6 028(3)	2 847(3)	N(31)	1 658(5)	4 242(3)	5 869(3)
O(21)	893(4)	1 940(3)	3 449(3)	N(32)	1 662(5)	1 811(4)	5 687(3)
O(22)	705(4)	4 038(3)	3 711(3)	N(41)	1 941(5)	7 691(4)	5 809(4)
O(31)	2 237(4)	5 205(3)	7 516(3)	N(42)	2 773(6)	7 659(4)	8 049(4)
O(32)	1 618(4)	5 377(3)	5 602(3)	C(11)	2 106(6)	7 091(5)	1 975(4)
O(41)	2 921(5)	9 340(3)	5 360(3)	C(12)	2 958(6)	8 176(5)	1 800(5)
O(42)	1 411(4)	7 304(3)	4 709(3)	C(13)	2 871(7)	9 331(5)	2 288(5)
W(1)	−1 263(5)	4 753(4)	819(3)	C(21)	837(6)	2 534(5)	2 684(4)
W(2)	315(5)	9 518(4)	3 352(4)	C(22)	910(7)	1 933(5)	1 712(5)
W(3)	4 374(6)	6 639(5)	−131(4)	C(23)	311(7)	2 446(5)	708(5)
W(4)	4 206(11)	4 955(6)	2 975(5)	C(31)	2 006(6)	4 263(5)	6 876(4)
W(5)	4 284(7)	4 799(6)	1 013(5)	C(32)	2 093(7)	3 148(5)	7 320(5)
O(1)	7 040(6)	8 461(6)	−521(3)	C(33)	2 634(7)	2 292(5)	6 758(5)
O(2)	8 681(6)	8 877(6)	1 171(4)	C(41)	2 679(6)	8 753(4)	6 042(4)
O(3)	7 562(7)	10 331(5)	402(6)	C(42)	3 239(7)	9 331(5)	7 169(5)
O(4)	6 339(6)	8 766(5)	876(4)	C(43)	3 847(7)	8 620(5)	8 000(5)

increases only at high ligand concentration (high pH) where hydrolytic processes can take place. Thus bis(ligand) complexes are not formed in this system.

Absorption spectra in the d–d region at pH <3 exhibit a transition around 820 nm characteristic for the copper(II) aqua ion. An increase in pH above 3 leads to the appearance of a new d–d band at 616 nm which increases in intensity up to pH 9 without any changes in energy ($\varepsilon = 55$ at pH 4.2 and 67 $dm^3\ mol^{-1}\ cm^{-1}$ at pH 9). This indicates that the major species at pH 4–9 is the same although its amount can vary slightly. The charge-transfer (c.t.) band centred at 325 nm is broad and most likely contains at least two transitions as was the case for the dimeric species reported earlier.[2] In the latter case the circular dichroism spectra were resolved enough to show that the c.t. band observed in the absorption spectra around 330 nm consists in fact of three transitions at 430, 355 and 315 nm. The first of these can be assigned as the hydroxamic oxygen to metal c.t. transition. The other two correspond to the hydroxamic nitrogen to Cu^{II} c.t. transitions.[2] Since the ligand is not optically active the c.t. band at 325 nm remains, unfortunately, unresolved. The major complex formed at pH 4–9 does not show any EPR spectrum at liquid-nitrogen temperature or above.

According to the experimental results outlined above, the formation of a polynuclear species at pH >4 is strongly suggested. It is obvious from the potentiometric results that only one complex species exists at measurable concentration in the range pH 4.5–9 (see Figs. 1 and 2). At the same time, from the spectroscopic data (Fig. 3) a plot of absorption coefficient *vs.* c_M/c_A indicates a metal-to-ligand ratio of 1:0.8 in this species. The contradiction between the pH-metric ($\bar{n} = 1.2$) and spectroscopic results (ligand:metal = 0.8:1) can be resolved if we consider the jumping on the titration curves at 2.4 equivalents of base consumption per Cu^{II} ion. This suggests the occurrence of 'extra' deprotonation of the hydroxamate group by the copper(II) ion already in acidic solution with the formation of the AH_{-1} form of the ligands.[2,16] Polynuclear species have been found in which all of the three donor atoms of the hydroxamate group are co-ordinated.[2,16]

Consequently, the most likely explanation of our pH-metric results is that the β-alaninehydroxamic acid in its polynuclear copper(II) complex may release three protons. Taking this into account, a 1:0.8 copper(II) to AH_{-1} ratio arises also from the pH-metric results. The simplest possible formula corresponding to this ratio is $[Cu_5(AH_{-1})_4]^{2+}$ [$A = NH_2(CH_2)_2CONHO^-$].

From the considerations presented above it is possible that the major species in solution at pH 4.5–9 is a pentanuclear species $[Cu_5A_4H_{-4}]^{2+}$. The pH-metric data for this pH range (about 100 experimental points) could be evaluated satisfactorily by assuming this complex with a stability constant log β = 46.66(7). The formation of other complexes has to be presumed below pH 4.5. A fairly good fit was found assuming the species CuA with log β = 12.85(3).

X-Ray Studies.—From titrated solutions (pH around 9) left to stand for some hours single crystals were obtained of sufficient quality for the diffraction study. The X-ray structure (Fig. 4) confirms the formation of a pentanuclear species. All the donor groups of four ligand molecules are involved in the metal ion co-ordination. The nitrogen atoms chelate one copper ion while the oxygen donors are bound to another metal ion. This co-ordination leads to formation of the tetrameric unit $Cu_4A_4H_{-4}$ having at its centre the fifth metal ion bound to four oxygens of the hydroxamic groups. The latter oxygen donors bridge the central metal ion and the four peripheral metal ions. The central metal ion fits very well into the space between the four oxygens, being almost in their plane. The unusual structure consists of 12 chelate rings. The NH_2,N^- co-ordination leads to the formation of four six-membered rings which have distorted half-boat conformations (Fig. 4). The CO,O^- donors form four five-membered chelate rings of which only that with Cu(3) is planar while the others have envelope-like conformations. The inclusion of copper ion at the central position of the pentamer leads to the formation of four further five-membered rings. Most of these rings are twisted as indicated in Fig. 4.

The crystallographic parameters are collected in Tables 1–4. Besides the basic planar co-ordination (four donors) each metal ion interacts with a fifth donor in apical position. All are oxygens of water, perchlorate ion, or vicinal aminohydroxamic acid ligand (Table 3) at distances between 2.363(5) and 2.675(5) Å. In addition to the bonds in the ligand plane, Cu(5) shows a long interaction with $O(5^{II})$, 2.787(7) Å, and the latter also interacts, 2.884(7) Å, with the adjacent Cu(4). Atom $O(5^{II})$, located on the opposite side with respect to W(2) (W = water

Table 3 Bond distances (Å) and angles (°) for $[Cu_5A_4H_{-4}][ClO_4]_2\cdot5H_2O$*

Copper environment

Cu(1)–O(11)	1.960(4)	Cu(2)–O(21)	1.951(4)	Cu(3)–N(41)	1.959(5)	Cu(4)–N(11)	1.952(5)
Cu(1)–O(12)	1.936(4)	Cu(2)–O(22)	1.942(4)	Cu(3)–N(42)	1.966(5)	Cu(4)–N(12)	1.982(6)
Cu(1)–N(21)	1.993(4)	Cu(2)–N(31)	1.941(5)	Cu(3)–O(22^{I})	2.675(5)	Cu(4)–W(2)	2.619(5)
Cu(1)–N(22)	1.988(5)	Cu(2)–N(32)	1.984(5)	Cu(5)–O(12)	1.898(4)	Cu(4)–O(5^{II})	2.884(7)
Cu(1)–W(1)	2.363(5)	Cu(2)–O(6)	2.585(6)	Cu(5)–O(32)	1.879(4)	Cu(5)–O(22)	1.934(4)
Cu(3)–O(31)	1.943(4)	Cu(4)–O(41)	1.948(4)	Cu(5)–O(5^{II})	2.787(7)	Cu(5)–O(42)	1.932(4)
Cu(3)–O(32)	1.873(4)	Cu(4)–O(42)	1.937(4)				

β-Alaninehydroxamic acid ligands

	n = 1	n = 2	n = 3	n = 4
O(n1)–C(n1)	1.287(7)	1.299(7)	1.293(7)	1.278(7)
O(n2)–N(n1)	1.441(6)	1.405(6)	1.420(6)	1.420(6)
N(n1)–C(n1)	1.305(8)	1.297(7)	1.298(7)	1.307(7)
N(n2)–C(n3)	1.474(8)	1.489(8)	1.467(8)	1.485(9)
C(n1)–C(n2)	1.521(9)	1.496(9)	1.497(8)	1.506(8)
C(n2)–C(n3)	1.503(9)	1.522(8)	1.525(10)	1.497(9)

Cl–O av. 1.421(7) range 1.384–1.443

Copper environment

O(11)–Cu(1)–O(12)	81.2(2)	O(22)–Cu(2)–N(31)	90.3(2)	O(32)–Cu(3)–N(42)	170.0(3)	O(5^{II})–Cu(4)–N(11)	75.2(2)
O(11)–Cu(1)–N(22)	95.6(2)	O(22)–Cu(2)–N(32)	175.3(2)	N(41)–Cu(3)–N(42)	95.0(2)	O(5^{II})–Cu(4)–N(12)	102.7(2)
O(11)–Cu(1)–N(21)	163.9(2)	N(31)–Cu(2)–N(32)	93.5(2)	O(22^{I})–Cu(3)–O(31)	89.3(2)	O(5^{II})–Cu(4)–W(2)	169.1(2)
O(12)–Cu(1)–N(21)	90.7(2)	O(6)–Cu(2)–O(21)	84.7(2)	O(22^{I})–Cu(3)–O(32)	83.3(2)	N(11)–Cu(4)–N(12)	93.2(2)
O(12)–Cu(1)–N(22)	176.5(2)	O(6)–Cu(2)–O(22)	88.4(2)	O(22^{I})–Cu(3)–N(41)	95.4(2)	W(2)–Cu(4)–O(41)	87.4(2)
N(21)–Cu(1)–N(22)	92.8(2)	O(6)–Cu(2)–N(31)	90.5(2)	O(22^{I})–Cu(3)–N(42)	105.6(2)	W(2)–Cu(4)–O(42)	97.4(2)
W(1)–Cu(1)–O(11)	95.7(2)	O(6)–Cu(2)–N(32)	94.3(2)	Cu(3)–O(31)–C(31)	110.3(4)	W(2)–Cu(4)–N(11)	100.5(2)
W(1)–Cu(1)–O(12)	89.2(2)	Cu(2)–O(21)–C(21)	109.9(4)	O(21)–Cu(2)–O(22)	80.8(2)	W(2)–Cu(4)–N(12)	87.4(2)
W(1)–Cu(1)–N(21)	98.1(2)	Cu(2)–O(22)–N(21)	111.5(3)	O(21)–Cu(2)–N(32)	95.6(2)	Cu(4)–O(41)–C(41)	110.2(4)
W(1)–Cu(1)–N(22)	89.8(2)	Cu(2)–O(22)–Cu(5)	117.5(2)	O(21)–Cu(2)–N(31)	170.0(2)	Cu(3)–O(32)–N(31)	113.9(3)
Cu(1)–O(11)–C(11)	110.8(4)	N(21)–O(22)–Cu(5)	119.5(3)	Cu(4)–O(42)–N(41)	111.0(3)	Cu(3)–O(32)–Cu(5)	123.8(2)
Cu(1)–O(12)–N(11)	112.7(3)	Cu(2)–N(31)–O(32)	117.2(3)	Cu(4)–O(42)–Cu(5)	112.7(2)	N(31)–O(32)–Cu(5)	122.3(3)
Cu(1)–O(12)–Cu(5)	117.0(2)	Cu(2)–N(31)–C(31)	132.2(4)	N(41)–O(42)–Cu(5)	118.6(3)	Cu(3)–N(41)–O(42)	118.4(3)
N(11)–O(12)–Cu(5)	116.1(3)	Cu(2)–N(32)–C(33)	114.4(4)	Cu(4)–N(11)–O(12)	116.8(3)	Cu(3)–N(41)–C(41)	126.9(4)
Cu(1)–N(21)–O(22)	116.7(3)	O(41)–Cu(4)–O(42)	81.8(2)	Cu(4)–N(11)–C(11)	131.9(4)	Cu(3)–N(42)–C(43)	111.0(4)
Cu(1)–N(21)–C(21)	130.6(4)	O(41)–Cu(4)–N(12)	93.0(2)	Cu(4)–N(12)–C(13)	114.1(4)	O(12)–Cu(5)–O(22)	91.1(2)
Cu(1)–N(22)–C(23)	113.5(4)	O(41)–Cu(4)–N(11)	170.2(2)	O(32)–Cu(5)–O(42)	89.1(2)	O(22)–Cu(5)–O(32)	90.0(2)
O(31)–Cu(3)–O(32)	82.3(2)	O(42)–Cu(4)–N(11)	91.3(2)	O(42)–Cu(5)–O(12)	90.6(2)	O(12)–Cu(5)–O(32)	176.7(2)
O(31)–Cu(3)–N(42)	93.2(2)	O(42)–Cu(4)–N(12)	172.8(2)	O(22)–Cu(5)–O(42)	167.7(2)	O(5^{II})–Cu(5)–O(12)	87.7(2)
O(31)–Cu(3)–N(41)	169.1(2)	O(5^{II})–Cu(4)–O(41)	96.1(2)	O(5^{II})–Cu(5)–O(32)	89.1(2)	O(5^{II})–Cu(5)–O(22)	116.8(2)
O(32)–Cu(3)–N(41)	88.5(2)	O(5^{II})–Cu(4)–O(42)	73.0(2)	O(5^{II})–Cu(5)–O(42)	75.5(2)		

β-Alaninehydroxamic acid ligands

	n = 1	n = 2	n = 3	n = 4
O(n1)–C(n1)–N(n1)	124.2(6)	122.8(5)	122.9(5)	123.6(6)
O(n1)–C(n1)–C(n2)	117.4(5)	117.7(5)	118.0(5)	118.1(5)
O(n2)–N(n1)–C(n1)	109.9(5)	111.5(5)	110.6(5)	111.3(5)
N(n1)–C(n1)–C(n2)	118.4(5)	119.5(5)	119.1(5)	118.3(5)
C(n1)–C(n2)–C(n3)	117.4(5)	116.2(5)	113.9(5)	117.4(5)
C(n2)–C(n3)–N(n2)	112.7(6)	111.3(5)	112.8(5)	111.3(5)

O–Cl–O av. 109.7(4) range 108.5–111.6

* Symmetry codes: I $-x, 1-y, 1-z$; II $1-x, 1-y, 1-z$.

molecule) bridges Cu(5) and Cu(4) and completes the distorted elongated octahedral co-ordination of the latter.

The distances between the central and peripheral metal ions vary from 3.221(2) [Cu(5) · · · Cu(4)] to 3.315(2) Å [Cu(5) · · · Cu(2)]. The distances between peripheral metal ions are in the range 4.638(2) [Cu(1) · · · Cu(4)]–4.565(2) Å [Cu(3) · · · Cu(4)]. Four such ions form an almost planar structure (±0.1 Å) and the central Cu^{II} is 0.4 Å above this plane.

The co-ordination *via* hydroxamic group oxygens suggested earlier from the spectroscopic data for dimeric complexes is now clearly seen also in the X-ray structure of the oligomeric complex. In the solid state the complex does not give any EPR spectrum, owing most likely to the strong antiferromagnetic coupling within the oligomer and between the pentameric units. The distances between the metal ions of the vicinal molecules are relatively short (3.5–3.9 Å). The finding that the hydroxamic oxygens are bound strongly to metal ions had been suggested previously for dimeric complexes formed at low pH with α-aminohydroxamic acids.[2]

Conclusion

The solution and X-ray studies on copper(II) complexes with β-alaninehydroxamic acid have shown that all donor atoms of the aminohydroxamic acids are very effective binding sites for metal ions. The binding of two copper centres through the NO^- group is very strong and it is now evident that the earlier suggestions of its involvement in dimer formation in

Table 4 Hydrogen bond distances (Å) and angles (°) with e.s.d.s in parentheses

D–H···A	D–H	H···A	D···A	Angle
W(1)–H(1)···O(11$^{\text{III}}$)	0.770	2.210	2.873(6)	145
W(1)–H(2)···O(31$^{\text{I}}$)	0.943	1.945	2.820(6)	153
W(2)–H(3)···O(21$^{\text{IV}}$)	0.910	1.968	2.801(6)	151
W(2)–H(4)···O(2$^{\text{V}}$)	1.044	1.866	2.846(7)	155
W(3)–H(5)···O(4)	0.965	1.937	2.861(8)	160
W(3)–H(6)···W(5$^{\text{VI}}$)	1.011	1.921	2.841(10)	150
W(4)–H(7)···O(6)	1.003	2.259	3.209(10)	158
W(4)–H(8)···O(5$^{\text{II}}$)	0.993	2.186	3.110(11)	154
W(5)–H(9)···W(3)	0.966	1.819	2.786(9)	179
W(5)–H(10)···W(4)	0.962	1.795	2.719(11)	160
N(12)–H(15)···O(7$^{\text{IV}}$)	0.999	2.249	3.134(8)	147
N(22)–H(21)···W(1$^{\text{III}}$)	1.000	2.188	3.035(7)	142
N(32)–H(27)···W(2$^{\text{I}}$)	0.999	2.219	3.118(7)	149
N(42)–H(34)···W(3$^{\text{VII}}$)	1.000	1.973	2.959(8)	169

Symmetry codes: I $-x, 1-y, 1-z$; II $1-x, 1-y, 1-z$; III $-x, 1-y, -z$; IV $x, 1+y, z$; V $-1+x, y, z$; VI $1-x, 1-y, -z$; VII $x, y, 1+z$.

corresponding α-aminohydroxamic acid systems were correct. This strong coupling of metal centres leads to the 'EPR silent species.'

The results obtained in this work and in the earlier study with aspartic acid–β-hydroxamic acid[16] indicate that when two aminohydroxamate ligand nitrogen donors are in a position to form six-membered chelate rings the formation of the oligomeric species becomes favourable.

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