Differential Reactivity Pattern for the Condensation Reactions of Copper(II) Complexes of DL- and L-Amino Acids†

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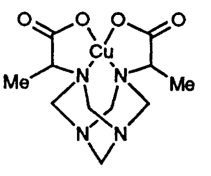
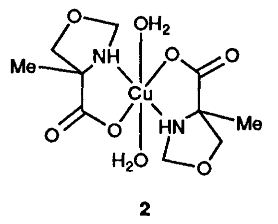
The condensation reactions of copper(II) complexes of DL and L forms of alanine, serine and threonine with aliphatic aldehydes reveal differential reactivity for the bis(amino acidato)copper(II) complexes. The reaction of [Cu(DL-ala)$_2$] (where ala = alaninato anion) with formaldehyde and ammonia, at an acidic pH of 5, yields a pentamethylenediaza group containing product, [($\alpha R,\alpha'S$)-N^3,N^7-(1,3,5,7-tetraazabicyclo[3.3.1]nonane)di(2-methylacetato)]copper(II) **1**, but at higher pH conditions (pH > 8.0), yields the known oxazolidine group containing product, diaquabis(4-methyloxazolidine-4-carboxylato)-copper(II) **2**. However, the reaction of [Cu(L-ala)$_2$] with formaldehyde and ammonia at pH 8.5 is known to yield an optically active isomer of **1**, *viz.* [($\alpha S,\alpha'S$)-N^3,N^7-(1,3,5,7-tetraazabicyclo-[3.3.1]nonane)di(2-methylacetato)]copper(II) **1a**. Though the latter reaction also yields the oxazolidine group containing product **2** at very basic pH (>10), the formation of **2** reveals racemization during the reaction process. Similarly, whereas the copper(II) complexes of DL-serine and DL-threonine readily undergo condensation reactions with aldehydes such as formaldehyde, propionaldehyde, butyraldehyde and valeraldehyde, yielding oxazolidine group containing products, the corresponding L-amino acidatocopper(II) complexes do not undergo condensation under the same experimental conditions except in the case of formaldehyde, demonstrating differential reactivity of DL- and L-amino acidatocopper(II) complexes. The crystal structures of the products obtained from the reactions of [Cu(DL-ser)$_2$] (ser = serinato anion) and [Cu(DL-thr)$_2$] (thr = threoninato anion) with formaldehyde, aqua[*N,N'*-(2-oxapropanediyl)bis(oxazolidine-4-carboxylato)]copper(II) sesquihydrate **3** and [*N,N'*-(2-oxapropanediyl)bis(5-methyloxazolidine-4-carboxylato)]copper(II) monohydrate **4**, respectively, have been determined. Complex **3** crystallizes in the triclinic space group $P\bar{1}$, a = 10.802(2), b = 11.039(2), c = 13.460(3) Å, α = 75.14(3), β = 69.57(3), γ = 87.53(3)° and Z = 4. Complex **4** also crystallizes in the triclinic space group $P\bar{1}$, a = 7.388(2), b = 10.017(2), c = 11.485(2) Å, α = 115.27(3), β = 101.89(3), γ = 91.79(3)° and Z = 2.

Reactions of copper(II) complexes of optically active α-amino acids are important in the area of biomimetic chemistry. The naturally occurring L-amino acids have also been used as precursors in the syntheses of various types of chiral ligands.[1-3] It is well known that various transition-metal ions such as copper(II) activate the amino acidato ligand units through bond polarization,[4-7] thereby enhancing the reactivity of the complex molecules. A large amount of literature is available on the reactions of copper(II) and nickel(II) complexes of various amino acids.[8-18] Interestingly, in some cases influence of chirality of the α-amino acidato ligands in the reaction process has been noticed.[15,17,18] However, the role of chirality in these reactions has not been studied in detail. For example, it is known that [Cu(L-ala)$_2$] and [Cu(DL-ala)$_2$] (ala = alaninato anion) react with formaldehyde and ammonia at pH 8.5 to yield two different products, *viz.* [($\alpha S,\alpha'S$)-N^3,N^7-(1,3,5,7-tetraazabicyclo[3.3.1]nonane)di(2-methylacetato)]copper(II) **1a** and diaquabis(4-methyloxazolidine-4-carboxylato)-copper(II) **2**.[15,17] Similarly, we have previously observed that the copper(II) complexes of DL and L forms of serine and threonine undergo condensation with formaldehyde yielding different products.[18] Therefore, it seemed appropriate to investigate these reactions more thoroughly towards understanding the role of chirality in these reactions. For this purpose, we have examined the reactions of copper(II) complexes of DL and L forms of alanine, serine and threonine under various experimental conditions with formaldehyde and ammonia and with various other aliphatic aldehydes. In this paper, we present our results and discuss differential reactivity of the DL- and L-amino acidatocopper(II) complexes observed in the reactions.



1a



2

Experimental

The α-amino acids, DL and L forms of alanine, serine and threonine (Sisco), and the aliphatic aldehydes, formaldehyde (37% solution, w/v), propionaldehyde, butyraldehyde (Sisco) and valeraldehyde (Fluka), were obtained from commercial sources. Copper(II) complexes of the α-amino acids were synthesised by a known general procedure.[19]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Reactions of [Cu(DL-ala)$_2$]·H$_2$O *with Formaldehyde and Ammonia.*—To an aqueous solution (25 cm^3) of [Cu(DL-ala)$_2$]·H$_2$O (1.2 g, 5 mmol) were added solutions of formaldehyde (10 cm^3) and ammonia (5 cm^3, 25% w/v) with stirring. The pH of the solution was adjusted to 5 by the addition of dilute hydrochloric acid. The dark blue solution was filtered and the filtrate was allowed to stand at room temperature for 7 d. The blue microcrystalline product **1** formed was separated by filtration, washed with ethanol (96%) and acetone and dried under reduced pressure at 50 °C for 12 h. Yield: 1.2 g (72%).

The above reaction at pH > 8.0 yielded the dark blue crystalline product, diaquabis(4-methyloxazolidine-4-carboxylato)copper(II), **2** as reported.[15]

Reactions of [Cu(L-ala)$_2$] *with Formaldehyde and Ammonia.*—To an aqueous solution (25 cm^3) of [Cu(L-ala)$_2$] (1.15 g, 5 mmol) was added formaldehyde solution (10 cm^3) with stirring. The pH of the solution was adjusted to 10 by the addition of ammonia (25% w/v). The dark blue solution was filtered and allowed to stand at room temperature for 7 d. The blue crystals formed were separated by filtration, washed with ethanol (96%) and acetone and dried under reduced pressure at 50 °C for 12 h. These crystals were identified as **2** from their IR spectral and analytical data. Unit-cell dimensions and the space group were also determined for a single crystal of the complex, which further confirmed the identity of the product.

The above reaction in the pH range 5–9 yields the optically active complex, [(αS,$\alpha' S$)-N^3,N^7-(1,3,5,7-tetraazabicyclo[3.3.1]nonane)di(2-methylacetato)]copper(II), **1a** as reported.[17]

Reactions of Copper(II) *complexes of* DL *and* L *Forms of Serine and Threonine with Aliphatic Aldehydes.*—Reactions of [Cu(DL-ser)$_2$] and [Cu(DL-(thr)$_2$] (ser = serininato anion, thr = threoninato anion) with propionaldehyde, butyraldehyde and valeraldehyde were carried out by the same procedure as for the reactions with formaldehyde and acetaldehyde reported by us previously.[18] In a typical reaction, to an aqueous solution (25 cm^3) of [Cu(DL-ser)$_2$] (1.35 g, 5 mmol) was added propionaldehyde (1 cm^3, 13.9 mmol) with stirring and the reaction mixture was allowed to stand at room temperature for 6 h. The blue crystalline product formed was separated by filtration, washed with water and acetone and dried under reduced pressure at 50 °C for 12 h. Yield: 1.1 g (62%).

The reaction of [Cu(DL-ser)$_2$] with formaldehyde yielded blue rectangular prismatic crystals **3** suitable for X-ray analysis. The reactions with propionaldehyde, butyraldehyde and valeraldehyde yielded the products **5**, **6** and **7** respectively. Similarly the reactions of [Cu(DL-thr)$_2$] with formaldehyde yielded blue, needle-like crystals **4** suitable for X-ray analysis. The reactions with propionaldehyde, butyraldehyde and valeraldehyde yielded the products **8**, **9** and **10** respectively. Analytical and important IR spectral data are presented in Table 1.

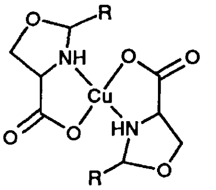
Similar reactions of [Cu(L-ser)$_2$] and [Cu(L-thr)$_2$] with the aldehydes did not yield any products. The starting copper(II) complexes crystallized from the reaction mixtures after 2 d, indicating that these complexes do not undergo condensation similar to [Cu(DL-ser)$_2$] and [Cu(DL-thr)$_2$].

Physical Measurements.—Elemental analyses were performed on a Perkin-Elmer 240C elemental analyser. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer as KBr pellets. For pH measurements an EC 5651 pH meter was used. Cyclic voltammograms were recorded for aqueous solutions of the complexes (*ca.* 0.001 mol dm^{-3}) containing NaClO$_4$ supporting electrolyte (0.1 mol dm^{-3}) using a PARC 370 electrochemistry system consisting of model 174 polarographic analyser, model 175 universal programmer, RE 0074 XY-recorder and a three-electrode cell system. A metrohm E410 hanging mercury-drop electrode was used as the working electrode together with a platinum-wire auxiliary electrode and a saturated calomel reference (SCE) electrode.

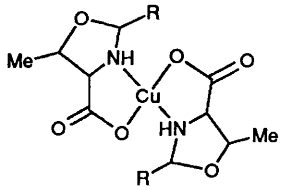
Table 1 Analytical and IR data for the complexes

Complex	Analysis* (%) C	H	N	IR bands/cm^{-1}
1	39.4 (39.6)	5.3 (5.4)	16.9 (16.8)	—
3	31.2 (31.3)	5.1 (5.0)	7.2 (7.3)	1174, 1138, 1172; 3512
4	35.7 (35.8)	5.3 (5.5)	7.1 (7.0)	1118, 1152, 1186; 3444, 3576
5	36.8 (37.2)	5.9 (6.2)	6.7 (7.2)	1100, 1142, 1156; 3244, 3490
6	39.6 (40.4)	6.4 (6.7)	6.6 (6.7)	1112, 1156, 1172; 3234, 3544
7	43.2 (43.3)	7.0 (7.2)	6.4 (6.3)	1098, 1146, 1162; 3252, 3502
8	41.9 (42.3)	6.4 (6.5)	6.8 (7.0)	1108, 1146, 1158; 3246, 3494
9	45.2 (45.1)	6.8 (7.1)	6.5 (6.6)	1102, 1144, 1184; 3248, 3518
10	49.3 (49.6)	7.6 (7.3)	6.5 (6.4)	1106, 1152, 1162; 3256, 3490

* Calculated values in parentheses.



	R
5	Et
6	Pr
7	Bu



	R
8	Et
9	Pr
10	Bu

X-Ray Structure Determinations.—The structures of the complexes **3** and **4** were determined at room temperature (23 °C) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [λ(Mo-Kα_1) = 0.709 26 Å; λ(Mo-Kα_2) = 0.713 54 Å] and a graphite monochromator. Cell constants and the orientation matrix for intensity data collection for each crystal were determined by least-squares fits to the scattering parameters of 50 independent reflections. The intensity data were collected in the 2θ range 4–45 and 4–50° respectively, for **3** and **4**. The intensities of three standard reflections, measured after every 100, showed no significant decay. The data were corrected for Lorentz–polarization effects and absorption. The structures were solved by direct methods or Patterson techniques and refined by least-squares techniques; the programs used were from the SHELXTL PLUS system.[20] The weighting schemes, $w = [\sigma^2(F) + 0.0005F^2]^{-1}$ and $w = [\sigma^2(F) + 0.0004F^2]^{-1}$ respectively, for **3** and **4**, gave satisfactory analyses. All non-hydrogen atoms were refined anisotropically. Non-hydrogen atom coordinates are listed in Tables 2 and 3. Selected bond distances and angles are listed in Tables 4 and 5.

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

Aqua[N,N′-(2-*oxapropanediyl*)*bis*(*oxazolidine*-4-*carboxylato*)]*copper*(II) *Sesquihydrate* **3**. $C_{10}H_{19}CuN_2O_{9.5}$, M = 382.8, triclinic, space group $P\bar{1}$, a = 10.802(2), b = 11.039(2), c = 13.460(3) Å, α = 75.14(3), β = 69.57(3), γ = 87.53(3)°, U = 1451.8(5) Å^3, D_c (Z = 4) = 1.751 g cm^{-3}, $F(000)$ = 732,

Table 2 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*
Cu(1)	1561(1)	13(1)	3691(1)
O(1)	−58(3)	908(3)	4007(3)
O(7)	755(4)	−1500(3)	3674(3)
N(1)	2438(4)	1608(4)	3630(4)
N(2)	3241(4)	−938(4)	3484(4)
O(1w)	1905(4)	811(3)	1699(3)
C(1)	108(6)	2093(5)	3823(4)
C(2)	1511(5)	2626(5)	3477(5)
C(3)	1655(6)	3508(6)	4154(6)
C(4)	2584(6)	1676(5)	4670(5)
C(5)	3743(5)	1906(5)	2722(5)
C(6)	4383(6)	−145(5)	2585(5)
C(7)	3614(6)	−1450(6)	4473(5)
C(8)	3587(6)	−3150(5)	3851(6)
C(9)	3007(6)	−2101(5)	3176(5)
C(10)	1546(6)	−2358(5)	3431(5)
O(2)	−793(4)	2828(3)	3906(3)
O(3)	2646(4)	2978(4)	4592(4)
O(4)	4604(4)	936(4)	2879(3)
O(5)	4326(4)	−2524(4)	4280(4)
O(6)	1233(5)	−3386(4)	3371(4)
Cu(2)	765(1)	4122(1)	8352(1)
O(8)	−307(3)	5491(3)	8776(3)
O(14)	−818(3)	3007(3)	8924(3)
N(3)	2333(4)	5233(4)	8153(3)
N(4)	1770(4)	2531(4)	8282(3)
O(2w)	813(4)	4655(3)	6634(3)
C(11)	319(5)	6451(5)	8766(4)
C(12)	1786(5)	6344(5)	8592(5)
C(13)	2645(5)	7484(6)	7735(6)
C(14)	3192(6)	5835(5)	6999(5)
C(15)	3167(6)	4536(5)	8768(5)
C(16)	2746(6)	2424(5)	8860(5)
C(17)	2431(6)	2362(5)	7150(5)
C(18)	1211(6)	581(6)	8023(5)
C(19)	779(5)	1435(5)	8816(5)
C(20)	−633(6)	1842(5)	9044(5)
O(9)	−179(4)	7444(4)	8914(3)
O(10)	3735(4)	6946(4)	7043(3)
O(11)	3644(4)	3470(3)	8393(3)
O(12)	2503(4)	1049(3)	7309(3)
O(13)	−1516(4)	1012(4)	9329(3)
O(3w)	6984(11)	4563(10)	8615(9)
O(4w)	5286(19)	3643(13)	133(14)
O(5w)	5722(6)	1276(7)	9777(5)

Table 3 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*
Cu	1924(1)	3916(1)	4901(1)
O(1)	3510(1)	5802(1)	5789(1)
O(7)	249(1)	4500(1)	3696(1)
N(1)	3712(1)	3323(1)	6138(1)
N(2)	547(1)	1859(1)	3742(1)
C(1)	5032(1)	5884(1)	6591(1)
C(2)	5355(1)	4527(1)	6854(1)
C(3)	5668(1)	4884(1)	8333(1)
C(4)	3035(1)	3239(1)	7253(1)
C(5)	7664(1)	5075(1)	9045(1)
C(6)	4352(1)	1869(1)	5366(1)
C(7)	1796(1)	673(1)	3491(1)
C(8)	−1047(1)	1500(1)	4214(1)
C(9)	−2321(1)	832(1)	2028(1)
C(10)	−426(1)	1828(1)	2453(1)
C(11)	−635(1)	3399(1)	2594(1)
C(12)	−2610(1)	−554(1)	733(1)
O(2)	6270(1)	6948(1)	7141(1)
O(3)	4648(1)	3599(1)	8289(1)
O(4)	2816(1)	736(1)	4702(1)
O(5)	−2268(1)	383(1)	3080(1)
O(6)	−1617(1)	3530(1)	1661(1)
O(1w)	7201(1)	1655(1)	8964(1)

Table 4 Selected bond lengths (Å) and bond angles (°) for complex **3**

Molecule A		Molecule B	
Cu(1)–O(1)	1.939(4)	Cu(2)–O(8)	1.944(4)
Cu(1)–O(7)	1.925(4)	Cu(2)–O(14)	1.951(4)
Cu(1)–N(1)	2.006(5)	Cu(2)–N(3)	2.034(5)
Cu(1)–N(2)	2.026(4)	Cu(2)–N(4)	2.030(4)
Cu(1)–O(1w)	2.495(4)	Cu(2)–O(2w)	2.218(4)
O(1)–Cu(1)–O(7)	95.4(2)	O(8)–Cu(2)–O(14)	90.4(2)
O(1)–Cu(1)–N(1)	85.3(2)	O(8)–Cu(2)–N(3)	85.5(2)
O(7)–Cu(1)–N(1)	177.3(2)	O(14)–Cu(2)–N(3)	165.9(2)
O(1)–Cu(1)–N(2)	175.5(2)	O(8)–Cu(2)–N(4)	167.0(2)
O(7)–Cu(1)–N(2)	85.8(2)	O(14)–Cu(2)–N(4)	85.1(2)
N(1)–Cu(1)–N(2)	93.6(2)	N(3)–Cu(2)–N(4)	95.9(2)
O(1)–Cu(1)–O(1w)	88.4(1)	O(8)–Cu(2)–O(2w)	95.1(2)
O(7)–Cu(1)–O(1w)	88.1(2)	O(14)–Cu(2)–O(2w)	95.3(2)
N(1)–Cu(1)–O(1w)	89.3(2)	N(3)–Cu(2)–O(2w)	98.5(2)
N(2)–Cu(1)–O(1w)	96.0(2)	N(4)–Cu(2)–O(2w)	97.5(2)

Table 5 Selected bond lengths (Å) and bond angles (°) for complex **4**

Cu–O(1)	1.925(2)	Cu–O(7)	1.955(3)
Cu–N(1)	2.028(3)	Cu–N(2)	2.005(3)
O(1)–Cu–O(7)	93.8(1)	O(1)–Cu–N(1)	85.4(1)
O(7)–Cu–N(1)	178.7(1)	O(1)–Cu–N(2)	169.9(1)
O(7)–Cu–N(2)	85.3(1)	N(1)–Cu–N(2)	95.2(1)

$\mu = 15.44$ cm^{-1}. Specimen: blue rectangular prism of size $0.08 \times 0.22 \times 0.22$ mm, $N = 3792$, $N_o = 2771$ [$F > 6.0\sigma(F)$], range of *hkl*: 0–11, −11 to 11, −13 to 14, $R = 0.0375$, $R' = 0.0472$, $S = 1.47$, $n_v = 406$.

[N,N′-(2-*Oxapropanediyl*)*bis*(5-*methyloxazolidine*-4-*carboxylato*)]*copper*(II) *Monohydrate* **4**. $C_{12}H_{22}CuN_2O_9$, $M = 401.9$, triclinic, space group $P\bar{1}$, $a = 7.388(2)$, $b = 10.017(2)$, $c = 11.485(2)$ Å, $\alpha = 115.27(3)$, $\beta = 101.89(3)$, $\gamma = 91.79(3)$°, $U = 745.3(3)$ Å^3, D_c ($Z = 2$) $= 1.791$ g cm^{-3}, $F(000) = 418$, $\mu = 15.20$ cm^{-1}. Specimen: blue needle of size $0.08 \times 0.10 \times 0.22$ mm, $N = 2631$, $N_o = 1911$ [$F > 6.0\sigma(F)$], range of *hkl*: 0–8, −11 to 11, −13 to 13, $R = 0.0327$, $R' = 0.0383$, $S = 1.12$, $n_v = 208$.

Results

Details of the reactions of copper(II) complexes of DL and L forms of alanine, serine and threonine with formaldehyde and ammonia at different pH conditions and with various other aliphatic aldehydes are described in the Experimental section. The reaction of [Cu(DL-ala)$_2$] with formaldehyde and ammonia at pH 5 yielded a microcrystalline product **1**. Identical IR spectra, analytical data and redox behaviour (irreversible reduction at −0.51 V *vs.* SCE[18]) show the product to be identical to the known[17] optically active complex, [(α*S*,α′*S*)-N^3,N^7-(1,3,5,7-tetraazabicyclo[3.3.1]nonane)di(2-methylacetato)]copper(II), **1a**, and hence **1** must be the optical isomer of **1a**, *viz.* [(α*R*,α′*S*)-N^3,N^7-(1,3,5,7-tetraazabicyclo[3.3.1]nonane)di(2-methylacetato)]copper(II). The product obtained from the condensation reaction of [Cu(L-ala)$_2$] with formaldehyde and ammonia at pH 10 has been identified as diaquabis(4-methyloxazolidine-4-carboxylato)copper(II), **2**, by comparing the IR spectrum and unit-cell dimensions and space group of the product with those of the complex synthesised

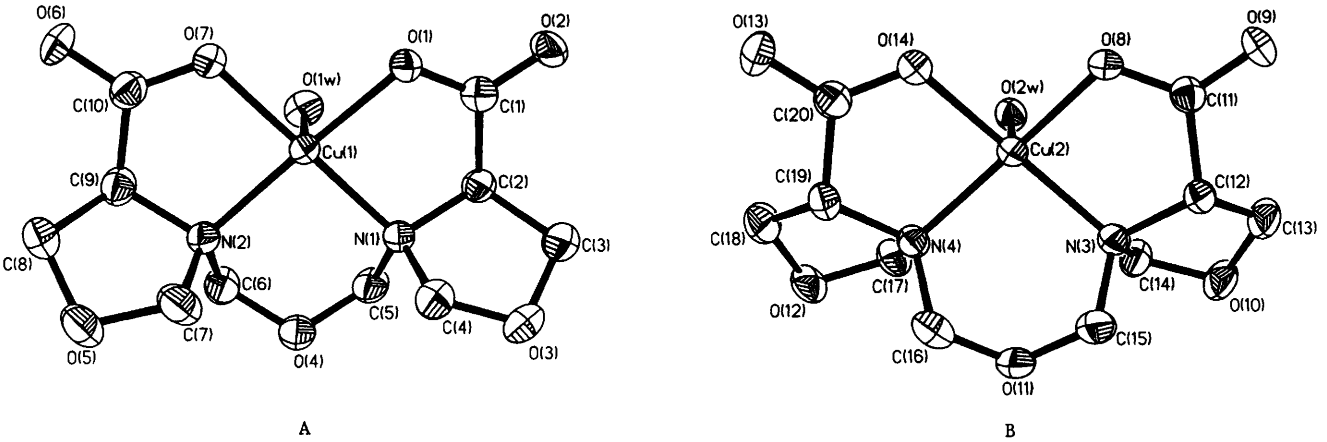


Fig. 1 View of the two crystallographically independent complex molecules A and B of 3, with their atom-numbering scheme. Hydrogen atoms are omitted for clarity

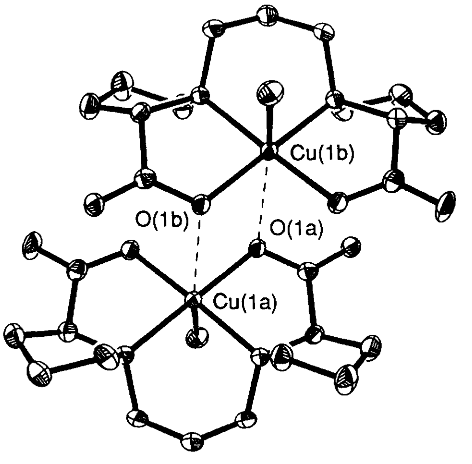


Fig. 2 Dimeric association in molecule A of complex 3

from the known condensation reaction of [Cu(DL-ala)$_2$] with formaldehyde and ammonia at pH 8.[15]

The reactions of [Cu(DL-ser)$_2$] and [Cu(DL-thr)$_2$] with formaldehyde yielded crystalline products. The products were assigned to structures 3 and 4 respectively by us previously on the basis of various experimental data without crystal structures.[18] In this study crystal structures of the complexes have been determined. The reactions of [Cu(DL-ser)$_2$] and [Cu(DL-thr)$_2$] with propionaldehyde, butyraldehyde and valeraldehyde yielded blue crystalline products as described in the Experimental section. However, the crystals were not suitable for X-ray analysis and our best attempts to grow single crystals of the complexes were unsuccessful. On the basis of the following data and elemental analyses (Table 1) the products have been assigned to structures **5**–**10**. All these complexes exhibit three closely spaced IR bands in the region 1200–1080 cm^{-1}, similar to **3** and **4** and the condensation products of [Cu(DL-ser)$_2$] and [Cu(DL-thr)$_2$] with acetaldehyde,[18] indicating the presence of oxazolidine ring in these complexes. However, the IR spectra of these complexes exhibit a sharp band at *ca.* 3250 cm^{-1}, indicating the presence of an NH group and the absence of formation of ether-bridged products analogous to **3** and **4**. The absence of further condensation may be due to the steric effects of alkyl substituents on the oxazolidine rings, which could disallow the *trans* to *cis* arrangement of the ligand units, essential for the formation of bridged products. The complexes **5**–**9** also exhibit bands at *ca.* 3450 cm^{-1} indicating the presence of water molecules. Analytical data (Table 1) reveal that the complexes **5**–**7** are dihydrates, **8** and **9** are monohydrates and **10** is anhydrous. Reactions of [Cu(L-ser)$_2$] and [Cu(L-thr)$_2$] with the above aldehydes were also carried out by the same procedure but the reactions did not yield any products.

Crystal Structure of Aqua[N,N′-(*2-oxapropanediyl*)*bis*(*oxazolidine-4-carboxylato*)]*copper*(II) *Sesquihydrate* **3**.—The asymmetric unit consists of two crystallographically independent complex molecules and three water molecules of solvation. One of the complex molecules (molecule A) exists as a 'dimer' as a result of mutual long 'axial' interactions between carboxyl oxygens and coppers of two neighbouring molecules, whereas the other molecule (molecule B) exists as a monomer. Views of both molecules with their atom-numbering scheme are shown in Fig. 1. The dimeric association in molecule A is shown in Fig. 2. Selected bond distances and angles are listed in Table 4.

In molecule A, the co-ordination polyhedron around each copper atom has a tetragonally elongated octahedral geometry, the four equatorial ligands being two nitrogens and two carboxyl oxygens of the tetradentate ligand, while the axial sites are occupied by a water molecule and a carboxyl oxygen that is equatorial to the other copper centre in the dimer. The Cu–O bond distances associated with the bridging carboxyl oxygens differ considerably, the axial distance being 2.879 Å and the equatorial distance being 1.939(4) Å. The Cu ··· Cu separation is 3.931 Å and the bond angle involving the co-ordinated water molecule, copper and the bridging carboxyl oxygen is 167.22°. The other Cu–N and Cu–O$_{\text{carboxyl}}$ bond distances are normal, in the range 1.925(4)–2.026(4) Å and are comparable to those of molecule B (Table 4), whereas the Cu–O$_{\text{aqua}}$ bond distance of 2.495(4) Å is considerably longer than that of the molecule B [2.218(4) Å], which may be due to the dimeric nature of molecule A. Similar dimeric-type structures have also been reported for 2,2′-bipyridine(phthalato)copper(II) dihydrate[21] and (2,7-diacetyl-3,6-dimethylnaphthalene-1,8-diolato)ethylenediaminecopper(II).[22] The long 'axial' Cu–O distances are 2.58 and 2.848(12) Å for the two complexes respectively. In molecule B, the geometry about the copper is roughly tetragonal pyramidal with the base plane formed by the two nitrogens and two carboxyl oxygens of the ligand and the fifth (apical) site being occupied by a water molecule. The four basal atoms are nearly coplanar, with no atom deviating from the least-squares plane by more than 0.0106 Å. The copper sits 0.2292 Å above this plane, toward the apical water molecule, as is expected for this geometry.[23–26] The Cu–N and Cu–O$_{\text{carboxyl}}$ bond distances are in the range 1.944(4)–2.034(5) Å and are comparable to those of related complexes.[9,10]

The geometry of the tetradentate ligand is similar in both molecules. The oxazolidine rings are disposed *trans* to the –CH$_2$OCH$_2$– linkage. However, the co-ordination of the water molecule is different for the two molecules. In molecule A, the water molecule is disposed *anti* to the oxazolidine rings, whereas in molecule B the water molecule is disposed *syn* to the oxazolidine rings. The six-membered chelate ring involving the

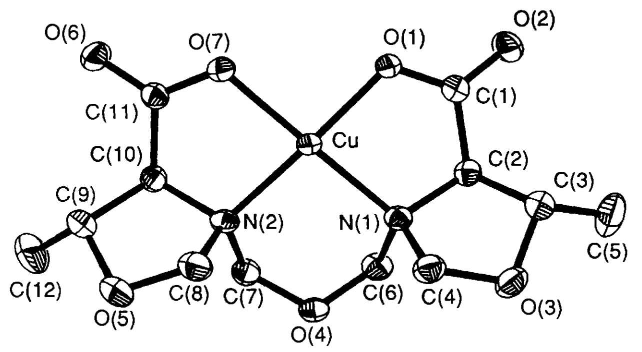


Fig. 3 View of the complex molecule **4** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity

$-CH_2OCH_2-$ linkage adopts a chair conformation in both molecules. The solvate water molecules in the crystal are involved in extensive hydrogen bonding with the free carboxyl oxygens of both molecules.

Crystal Structure of [N,N′-(2-*Oxapropanediyl*)*bis*(5-*methyl-oxazolidine*-4-*carboxylato*)]*copper*(II) *Monohydrate* **4**.—The asymmetric unit consists of one complex molecule and a water molecule. This complex molecule also exists as a 'dimer' as a result of mutual long 'axial' interactions between the carboxyl oxygens and coppers of two neighbouring molecules. A view of the complex molecule with the atom-numbering scheme is shown in Fig. 3 and selected bond distances and angles are listed in Table 5.

The geometry about the copper is roughly tetragonal pyramidal, the four equatorial ligands being two nitrogens and two carboxyl oxygens of the tetradentate ligand, while the apical site is occupied by a carboxyl oxygen that is equatorial to the other copper centre in the dimer. The Cu–O bond distances associated with the bridging carboxyl oxygens differ considerably, the axial distance being 2.595 Å and the equatorial distance being 1.955(3) Å. The Cu $\cdots$ Cu separation is 3.617 Å which is considerably shorter than the separation of 3.931 Å in one of the molecules (A) of **3**. The Cu–N bond distances of 2.028(3) and 2.005(3) Å and $Cu-O_{equatorial}$ bond distances of 1.925(2) and 1.955(3) Å are normal and are comparable to those of **3** and related species.[9,10] The geometry of the ligand is similar to that of the ligand in **3**; the two oxazolidine rings are disposed *anti* to the $-CH_2OCH_2-$ linkage and the six-membered chelate ring involving the $-CH_2OCH_2-$ linkage adopts a chair conformation.

Discussion

The products **1** and **1a**, which are obtained from the condensation reactions of $[Cu(DL\text{-}ala)_2]$ and $[Cu(L\text{-}ala)_2]$ respectively with formaldehyde and ammonia at pH 5 and 8.5, contain a pentamethylenediaza group bridging the two alaninato units. It is obvious from the structures of **1** and **1a** that the above reactions involve only the deprotonation of the amino groups. The structure of complex **2**, which can be obtained from the condensation of both $[Cu(DL\text{-}ala)_2]$ and $[Cu(L\text{-}ala)_2]$ with formaldehyde and ammonia at pH 8 and 10 respectively, reveals that these reactions involve deprotonation of both amino and α-methine groups. Our present synthesis of product **1** containing the pentamethylenediaza group from $[Cu(DL\text{-}ala)_2]$ at pH 5, clearly demonstrates that at this acidic pH, the α-methine group is not deprotonated and hence the reaction leads to the formation of **1**. At pH 8, the α-methine groups are readily deprotonated leading to the formation of **2**. However, in the analogous reaction of $[Cu(L\text{-}ala)_2]$, in the pH range of 5–9, only the product **1a** is obtained implying that the α-methine group is not deprotonated even at pH 9. At pH > 10, deprotonation of the α-methine group occurs as is evident from the formation of **2**. The formation of **2**, which is optically inactive, also indicates that the deprotonation is followed by racemization. These pH-dependent reactions reveal that the α-methine groups of $[Cu(DL\text{-}ala)_2]$ are more readily deprotonated than those of $[Cu(L\text{-}ala)_2]$.

The crystal structures of complexes **3** and **4**, obtained from the condensation of $[Cu(DL\text{-}ser)_2]$ and $[Cu(DL\text{-}thr)_2]$ respectively, with formaldehyde at pH 4.5, establish the formation of tetradentate ligands in each condensation reaction as proposed by us previously.[18] The crystal structure of **3** reveals that the complex is present as two crystallographically independent complex molecules. One of them exists as a dimer with a Cu $\cdots$ Cu distance of 3.931 Å, while the other molecule is monomeric. Complex **4** exists exclusively as a dimer with a Cu $\cdots$ Cu distance of 3.617 Å. The copper(II) complexes of DL-serine and DL-threonine undergo condensation with aliphatic aldehydes such as acetaldehyde,[18] propionaldehyde, butyraldehyde and valeraldehyde yielding oxazolidine containing products. Under the same experimental conditions, the copper(II) complexes of L-serine and L-threonine do not undergo similar condensation reactions, further supporting the differential reactivity pattern for the DL- and L-amino acidatocopper(II) complexes. The reactions discussed above reveal that the copper(II) complexes of DL-alanine, DL-serine and DL-threonine are more reactive in comparison to those of the corresponding L-amino acids.

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