The Crystal Structure of Bis(L-serinato)copper(II)*

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The crystal structure of bis(L-serinato)copper(II), $CuC_6H_{12}O_6N_2$, has been determined and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group $P2_1$, with a = 9.924, b = 8.413, c = 5.651 Å and $\beta = 90.6^{\circ}$. The final R value for 946 reflections is 0.040; the standard deviations are about 0.006 Å for the light-atom positions. The compound is not isostructural with either the Ni or the Zn complex of L-serine. The copper surroundings are a square pyramid. Both serine molecules have the same configuration for the hydroxyl group, being the one found in DL-serine. The only influence of chelation of the serine molecules seems to be a small rotation of the amino group out of the plane of the acid group. All active protons are used for hydrogen bonding.

Introduction

The structure of the Cu^{II} chelate of L-serine was determined as one of a series of L-serine chelates to obtain information about the relative influence of transition metal ions on the configuration of an amino acid. None of the Cu^{II} , Zn^{II} or Ni^{II} complexes of L-serine are isomorphous. Another point of interest was the Cu^{II} coordination, in view of the multitude of different Cu^{II} surroundings which have been reported in the literature.

Experimental

The compound bis(L-serinato) copper(II) was prepared by reacting L-serine, copper sulfate and barium hydroxide in the molar proportions of 2:1:1. Barium sulfate was removed by filtration. The resulting solution was about 0.05 M in concentration of the complex. Crystals of the complex were obtained by diluting the solution 100 times with absolute ethanol. Blue crystalline rectangular plates appeared on standing for two or three days at room temperature. The plate face is the (001) plane while the crystals are elongated along the b axis. Extinctions, using polarized light, of a crystal lying on its plate face were not sharp.

The preliminary X-ray investigation showed it to be unnecessary to recrystallize the original crop of crystals. The crystals are monoclinic and belong to the space group $P2_1$ (systematic absences: 0k0, k=2n+1). The space group $P2_1/m$ is excluded because the compound contains L-serine. The 2θ -values of 26 reflections, measured at 22 °C, were used in a least-squares calculation to determine the cell dimensions, which were calculated to be $a=9.924\pm0.003$ Å, $b=8.413\pm0.002$ Å, c= 5.651 ± 0.001 Å and $\beta=90.6^{\circ}\pm0.1^{\circ}$. The F.W. for Cu(L-serine)₂ is 271.72 yielding $\varrho_c=1.91$ g.cm³ while ϱ_0 is 1.90 g.cm³ measured by the flotation method. There are two formula units in the unit cell. The crystals showed a rather large mosaic spread (1°). This observation, together with the fact that the monoclinic angle is to close to 90°, made it necessary to investigate the possibility of twinning. Four different crystals were mounted. The intensities of nine h0l and corresponding $h0\overline{l}$ reflections were measured for each crystal. From the measurements the conclusion could be drawn that the twinning was necessarily less than 5% and therefore most likely not existent at all. No indication of twinning was observed in the subsequent structure investigation.

A crystal cut to dimensions $0.50 \times 0.17 \times 0.09$ mm was used as the data crystal. The integrated intensities were taken on a G.E.-X.R.D.-5 diffraction unit by the θ -2 θ scan method with Ni-filtered Cu K α radiation. The diffraction unit was equipped with an SPG Single Crystal Orienter, a scintillation counter and pulse height analyzer. All reflections with a 2 θ -value below 140° were measured. Of the 946 reflections within this 2 θ -limit, 10 were below the threshold of observation. Lorentz, polarization and absorption corrections (μ = 36.43 cm⁻¹) were applied to the data.

Structure determination

The location of the copper atom was obtained from a sharpened Patterson synthesis. Further interpretation yielded two sets of locations for all carbon, nitrogen and oxygen atoms. The two sets are related by a pseudo-mirror plane. One set showed the L-configuration for both serine molecules and was taken as the trial structure.

The initial structure factor calculation had an $R(=\Sigma ||kF_o|-|F_c||/\Sigma |kF_o|$ of 0.20. The structure was refined by block-diagonal least-squares computations with anisotropic temperature factors, which led to an R value of 0.06. Approximate positions of the hydrogen atoms were obtained from a difference-Fourier synthesis which was calculated at this stage of the refinement. At the same time all the observed amplitudes were corrected for anomalous dispersion (Patterson,

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1963). The parameters of the copper, carbon, nitrogen and oxygen atoms were further refined by least-squares until the parameter shifts were less than $\frac{1}{3}$ the calculated standard deviations. At this point another difference-Fourier synthesis was calculated, based on a structure factor calculation wich did not include the hydrogen atom contributions and the hydrogen coordinates were revised. The location of the hydrogen atom attached to O(3 A) could not be ascertained from this map; the locations and peak heights of the other hydrogen atoms are given in Table 1. The maximum spurious peaks in the difference Fourier were -1.0 and +1.2e.Å⁻³ which occurred close to the position of the copper atom. The new hydrogen atom locations were included in more least-squares cycles but not refined. The refinement was completed when the shifts for all parameters became lower than $\frac{1}{2}$ the calculated standard deviations. The final weighting was $|w| = |F_o|/P$ if $|F_o| \le P$, and $\sqrt{w} = P/|F_o|$ if $P < |F_o|$, with P = 17.0 electrons. The final parameters and their estimated standard deviations are shown in Table 2. All coordinate parameters were refined including the polar coordinate of the Cu atom. In a block-diagonal least-squares refinement of a structure in a polar space group it is not necessary to fix the coordinate of one of the atoms in the polar direction, because this least-squares matrix is not singular. Table 2, therefore, shows e.s.d.'s for the positional coordinates of all atoms. The R value for all data is 0.040. A list of the observed and calculated structure factors is given in Table 3. A final electron density map is shown in Fig. 1. The peak heights (Table 4) are comparatively large, reflecting the relatively small temperature factors; electron counts of the peaks yielded the expected values. The atomic scattering factors used were from International Tables for X-ray Crystallography (1962), for Cu²⁺, O, N and C. The scattering factors for hydrogen atoms used were those of Stewart, Davidson & Simpson (1965).

Table 1. Positional parameters and peak heightsof hydrogen atoms

The parameters are expressed as fractions of cell edges. An isotropic temperature factor of 3.5 Å^2 was assigned to the hydrogen atoms. Parameters for H(O3A) are not shown (see text).

<i>x y z i</i>	зак
$(\times 10^3)$ $(\times 10^3)$ $(\times 10^3)$ hei	ghts
H(1)(NA) 375 620 110 0.5 c	e.Å-3
H(2)(NA) 490 640 260 0.4	
H(C2A) 460 390 -020 0.5	
H(1)(C3A) = 670 = 400 = -080 = 0.5	
H(2)(C3A) 650 610 -090 0.5	
H(1)(NB) 120 500 340 0.7	
H(2)(NB) 130 680 400 0.3	
H(C2B) 110 700 800 0.5	
H(1)(C3B) - 110 610 810 0.3	
H(2)(C3B) - 110 690 580 0.4	
H(O3B) - 170 500 460 0.7	



Fig.1. Composite electron density map. First contour at 2 e.Å⁻³. Contours around light atoms every 2 e.Å⁻³ and around the Cu atom at every 10 e.Å⁻³.

Table 2. Parameters of copper, oxygen, nitrogen and carbon atoms bis(L-serinato)copper(II)

Positional parameters are expressed as fractions of cell edges. Anisotropic temperature factors are expressed as $\exp \left\{-(h^2b_{11}+k^2b_{22}+l^2b_{33}+klb_{13}+hkb_{12})\right\}.$

Standard deviations are given in parentheses.

	x	у	Z	<i>b</i> ₁₁	b22	b33	b23	b13	b ₁₂
	(×104)	(×104)	(×104)	(×104)	(×104)	(×104)	(×104)	(×104)	(×104)
Cu	3182 (1)	4999 (2)	4861 (1)	38 (1)	46 (1)	133 (2)	39 (5)	32 (2)	18 (3)
$\tilde{O}(1A)$	4667 (5)	3448 (7)	5018 (10)	63 (6)	79 (8)	151 (16)	71 (20)	73 (16)	73 (11)
O(2A)	6169 (5)	2188 (6)	2780 (9)	62 (5)	53 (7)	147 (17)	9 (19)	19 (14)	33 (10)
$\tilde{C}(1A)$	5356 (6)	3282 (8)	3147 (13)	28 (6)	45 (9)	178 (23)	5 (24)	-1(18)	22 (13)
C(2A)	5103 (7)	4503 (8)	1150 (12)	42 (6)	52 (9)	103 (20)	11 (20)	13 (18)	4 (11)
N(A)	4202 (6)	5785 (7)	2088 (10)	47 (6)	35 (8)	120 (18)	10 (20)	- 10 (16)	2 (11)
C(3A)	6419 (6)	5125 (12)	0223 (11)	53 (6)	52 (9)	177 (19)	2 (34)	45 (18)	-15 (18)
O(3A)	7180 (5)	5791 (7)	2098 (10)	57 (6)	78 (8)	250 (20)	5 (22)	- 49 (16)	- 53 (11)
O(1B)	2403 (5)	3960 (6)	7615 (9)	57 (5)	62 (7)	156 (16)	60 (18)	38 (14)	27 (10)
O(2B)	0747 (6)	4153 (8)	10186 (10)	95 (7)	107 (9)	161 (17)	72 (23)	105 (18)	22 (14)
C(1B)	1313 (7)	4585 (8)	8367 (13)	44 (7)	73 (14)	176 (22)	-23(23)	66 (19)	- 39 (13)
C(2B)	0714(7)	5956 (9)	6901 (12)	44 (7)	70 (11)	106 (20)	-3(24)	50 (18)	4 (14)
N(B)	1388 (6)	6002 (7)	4571 (10)	49 (6)	37 (8)	119 (18)	22 (20)	29 (16)	22 (11)
C(3B)	-0793 (8)	5895 (10)	6737 (13)	63 (8)	61 (11)	172 (24)	-48 (27)	37 (21)	- 19 (16)
O(2R)	- 1191 (5)	4496 (6)	5537 (11)	70 (6)	63 (8)	256 (20)	21 (19)	-91(18)	-12(10)

Table 3. Observed and calculated structure factors

The listing shows for each reflection k, $|10F_o|$, $|10F_c|$ and the phase angle in degrees. The reflections for which the intensity could not be distinguished from the background are indicated by a star.

К РО РСАЦРНА К РО РСАЦРНА ни о. 1.4 0 8 31 30 56.09	R FO FC ALPHA 0 346 347 0.0	к FO FC АЦРНА В 146 173 205.37	Е FO FC ALPHA 6 65 69 357-19 м	К FD ·FC АЦРНА 14 5, 14 5	K FO PC ALPHA 7 206 205 270,19	R FO FC ALPHA
9 102 132 94.63 2 1062 992 159.24 1	t 446 435 247.09 2 332 324 4.83 3 267 256 255.82 4 48 47 41.85 5 223 219 283.16 6 64 58 267.18 7 246 245 286.70	Hr 3, L+ 4 0 378 386 0,0 1 168 177 86.33 2 271 269 16.30 3 192 193 59.62	7 119 114 274.68 40 4, Le -4 0 50 54 140.00 1 218 206 259.03 2 130 128 199.08	0 228 227 0.0 1 51 51 240.58 2 215 211 356.74 3 56 57 244.97 4 83 77 12.89 5 45 38 268.49	8 59 65 249.03 1 H+ 7, L= 1 0 173 176 180.00 1 275 296 60.21 2 106 114 150.44	•• 8, L* 3 0 96 103 0.0 1 52 50 270.90 2 113 115 352.02 3 61 62 71.35 4 182 178 8.46
H= 0, Le 1 3 200 286 182.56 0 605 596 180.00 5 118 135 121.26 1 87 87 100.76 5 118 135 121.26 7 337 190 192.75 5 118 120.21 7 337 190 192.75 5 108 101 192.51 6 118 120 705.82 9 121 124 83.39	8 51 49 9.89 9 134 140 288.56 H= 2, L= 4 0 298 295 180.00 1 121 114 118.72	4 227 217 1.38 5 153 154 67.20 6 83 81 2.49 7 100 102 83.83 H= 3, 1= -4	3 334 320 257.34 4 228 220 159.11 - 5 218 208 244.00 6 110 105 167.99 7 142 147 286.21	5, L5 0 105 105 0.0 1 219 218 277.99 2 103 101 5.23 3 146 145 260.35	3 129 351 38.71 4 157 156 123.40 5 307 317 47.34 6 228 20 213.48 7 204 210 87.40 8 65 64 198.94	5 106 109 345,48 6 177 174 14.93 54 8, Le -3 0 103 100 0.0 1 101 98 239,44
5 70 58 100.40 557 736 174.00 H* 1. L* 4 7 54 57 271.33 7 246 256 171.30 0 44 33 180.00 9 87 73 98.67 1 338 322 288.62 0 141 131 180.44 2 70 71 378.40	2 278 258 175.75 5 118 109 63.67 4 269 257 170.30 5 124 123 100.31 6 141 139 188.15 7 40 40 96.60 8 99 106 161.57	n 176 169 0.3 1 113 116 277.79 2 306 301 351.25 3 99 56 127.96 4 350 349 341.55 5 24 21 319.03 6 207 208 351.90	0 67 63 180.00 1 267 261 91.77 2 123 125 126.90 3 186 188 115.09 4 73 77 135.91 5 78 74 104.60	4 118 119 52.42 5 103 103 271.28 4- 5, 1= 6 0 203 210 180.00 1 25 24 24.36	H= 7, L= -1 0 75 87 180.00 1 430 436 95.63 2 107 107 140.56 3 213 222 111.86 4 20 16 246.14	2 132 132 7.19 3 97 85 294.75 4 226 721 7.57 5 153 149 288.63 6 181 181 14.46 He 8, Le 4
Image Or L= Z 4 81 45 260.47 0 36.7 5 185 182 267.44 0 36.7 5 185 182 267.44 1 174 170 119.7 7 109 105 289.45 2 6.22 548 313.24 8 1.4 21 212.72 3 3 34.3 354.01 109 289.453 1.4 21 212.72	He Z, La -4 0 A0 77 1A0.00 1 259 246 84.38 2 180 175 197.54	7 100 103 144.48 He 3, Le 5 0 160 164 180.00 1 181 180 254.46	6 77 85 159.79 He 4, Le -5 P 0 10P 62 0.0 1 120 134 120.99 1 120 134 127.90	2 136 138 184,27 4 5, 1 -6 0 62 69 180,00 1 126 131 93,08 2 35 151 197,91	5 121 130 124.91 6 93 101 114.95 7 122 125 69.94 8 24 19 48.49 H- 7, 1- 2	0 150 153 180.00 1 49 50 297.61 2 166 168 166.37 3 66 65 284.65 4 155 139 182.84
4 402 184 186.17 rm 1, 1 1.2 5 1/2	5 214 207 71.33 4 40 44 161.53 5 270 274 92.12 6 53 50 105.13 7 158 150 72.24 8 70 72 199.54	3 147 156 271.04 4 105 111 158.50 5 69 72 260.51 8 37 41 174.03	3 170 180 109.96 4 99 100 330.77 5 161 169 97.53 8 33 39 49.29 He 4, L= 6	4+ 6, L= 0 0 104 126 0.0 1 137 145 72,91 2 231 239 347.95	0 234 1 0.0 1 257 271 258.03 2 43 41 105.58 3 145 149 244.78 4 61 69 373.89 5 223 218 288.72	X* 8, L= -4 0 140 135 180.00 1 203 209 74.86 2 166 165 187.63 3 102 105 80.07
Her 3 10/2 10/	0 23 20 180.00 1 111 114 267.40 2 129 128 9.48 3 88 90 225.89 4 159 100 4.57	0 58 59 180.00 1 29 32 19.53 2 153 155 270.39 3 61 58 21.61 4 237 240 178.46 9 71 76 64.76	0 54 58 0.0 1 70 82 278.91 2 20 15 25.68 3 98 102 301.45 H= 4. La -6	4 379 325 356.24 5 144 151 87.06 6 313 318 357.16 7 185 184 90.10 8 159 167 3.80	7 145 142 280.21 H= 7, L= -2 0 24 8 0.0 1 426 444 264.59	H4 4, L4 9 0 49 100 0.0 1 43 52 80.48
5 63 66 222,80 0 55 9 0.0 6 217 214 144,80 1 141 177 98,78 7 56 45 164,07 3 271 177 98,78 103 107 274,80 4 177 99,42 9 103 107 274,80 4 10 272 99,42 9 103 107 274,80 4 10 212 94,88 9 10 212 94,88 9 78 55,20	3 64 68 294.08 6 138 143 11.17 H+ 3, L= -5 0 61 61 0.0 1 210 217 270.66	H= 3, L+ 6 0 28+ 17 0.0 1 36 24 134.21 2 120 120 3.69	0 131 140 180-00 1 167 172 265,97 2 144 152 179.16 3 136 142 239-09 He 5, L= 0	0 256 274 180.00 1 240 254 265.41 2 260 275 170.75 3 36 37 261.88 4 152 153 216.31	5 215 211 240.97 4 49 47 167.44 5 202 206 271.17 6 51 47 265.07 7 159 157 245.76	0 127 125 0.0 1 113 112 246444 2 133 141 12.83 H= 9. L= 8
0 511 507 0.0 H= 1, L+ -3 1 735 719 144.03 270 719 10 120 221 776 0.0 3 709 70 100.021 1 200 209 107.70 3 709 701 153 14.75 7 144 149 15.69 5 91 66 700.76 3 98 104 104.29.74	3 210 214 254 30 4 124 125 125 525.62 5 240 8 17.45	3 103 107 44.75 4 111 116 352.06 H= 3, L+ ~6 0 209 212 0.0 1 70 72 199.60	0 593 629 179.99 1 189 188 150.11 2 470 496 171.49 3 206 211 124.09 4 156 168 174.23 5 188 198 91.17	5 00 55 282.02 6 164 168 177.42 7 109 118 254.29 8 85 91 185.61 H= 0, L= -1	0 158 160 180-00 1 299 300 83-81 2 171 167 215-16 3 164 150 76-01 4 106 100 750-30	0 124 119 0.0 1 178 172 85.30 2 168 161 532.41 3 209 108 93.51 4 122 118 2.74 5 179 172 85.68
6 170 171 34.78 6 171 172 324.21 7 36 47 147.45 5 107 111 107.50 8 153 159 2.14 6 170 174 335.56 w= 0, L+ 5	0 32 28 180.00 1 10 16 39.48 2 159 156 144.52 3 55 52 138.93 4 180 182 169.69 He 2, L6	2 184 185 10.44 3 74 75 204.67 4 119 120 357.61 H= 4, 1= 0 0 260 283 180.00	6 189 203 140.11 7 104 106 42.77 8 112 120 144.55 9 61 62 70.66	0 305 314 180.00 1 66 77 269.25 2 189 201 178.44 3 140 144 320.44 4 202 205 166.49 3 91 98 312.20 6 151 160 210.00	5 177 171 107.74 5 55 55 111.94 7 81 91 75.55 He 7. L= -3 0 248 245 180.00	e 130 194 397.10 He 9, Le 3 0 74 72 180.00 1 71 68 290.00 2 118 119 184.19
1 137 136 299.31 1 176 179 390.34 2 106 107 172.40 2 47 47 26.39 3 134 155 112.41 3 166 172 236.50 4 130 152 188.71 4 38 34 267.97 5 41 34 260.45 6 170 175 175.46 H+ 1, L+ -6	0 22* 5 0.0 1 116 124 94.81 2 76 74 257.17 3 116 120 109.36 4 75 78 170.19	1 279 293 247.53 2 299 295 240.01 3 403 428 248.78 4 213 215 154.29 5 333 354 255.13 6 49 51 74.52 7 315 245 274.33	0 448 487 0.0 1 215 231 287.95 2 312 341 352.38 3 259 200 105.41 4 160 157 75.95 5 35 32 281.72 4 210 215 137.91	7 94 93 267.28 6 186 188 188.74 H= 6, L= 2 0 252 233 0.0 1 327 347 103.76	1 162 161 73.34 2 91 82 211.51 3 127 122 89.74 4 61 54 22.42 5 249 243 100,43 6 124 3.10 7 205 201 87.57	3 126 124 240.81 4 102 102 175.28 5 185 182 267.59 6 97 95 167.77 H= 9, t= -1
0 129 129 129 180.00 4 0 1 6 103.47 2 131 137 164.67 0 100 206.75 3 96 100 206.75 5 5 5 5 100 206.75 2 150 120.22 2 15 156.15 5 9 100 206.75	H= 3, L= 0 0 170 173 359,94 1 240 241 340,49 2 420 431 35,36 3 253 240 52,65 4 10 41	8 59 64 120.54 9 157 157 292.88 He 4, Le 1 0 120 118 0.0	7 00 102 287.41 8 159 160 351.93 9 124 119 279.10 H= 5, L= -1 0 744 159 0.0	2 103 191 16.64 3 141 144 163.39 4 191 177 53.86 5 174 170 146.87 6 174 171 34.47 7 101 106 52.21 8 118 135 4.04	H= 7, L= 4 0 75 80 0.0 1 136 135 253.94 2 82 83 10.77 3 163 145 260.77	0 305 304 180.00 1 131 125 252.00 2 216 217 154.69 3 146 189 259.85 4 120 124 174.39 5 137 133 237.35 6 86 88 176.65
111 10.00 0.00 10.00 111 10.00 0.00 24 100.00 14 10.10 0.00 1.237 730.121.78 14 10.10 2.356 160.100 100.121.78 1 2.01 2.00 2.00 2.00 100.122.43 1 4.01 2.00 2.73.70 100.122.43 100.122.43	5 164 175 55.75 6 243 255 27.72 7 160 165 105.55 8 247 251 16.93 9 64 64 146.17	2 295 316 61.79 5 413 429 104.57 4 28 34 113.26 5 229 236 97.28 6 158 164 203.01 7 296 305 111.04 8 54 348.29	1 254 285 284.79 2 268 281 25.16 3 154 167 257.78 4 293 312 5.99 5 169 177 245.24 6 204 209 358.35 7 119 115 297.40	H= 6. L= -2 0 527 569 0.0 1 152 151 81.98 2 343 403 17.77 3 45 37 30.50	4 63 59 54.26 5 144 153 242.48 H# 7. L# -4 0 70 68 180.00 1 227 225 259.70	H= 9, L= 2 D 190 193 0.0 1 208 212 90.98 2 157 159 21.18 3 210 209 65.11
5 Jor 103 227.20 6 115 16 201.95 4 261 28 2125.20 7 124 125 85.20 5 217 216 271.36 8 191 211 223.74 7 105 194 274.51 10 129 136 104 73.49 7 165 194 274.51 10 129 136 107.66 78 6 155.74	0 308 316 179.98 1 300 310 253.27 2 525 556 186.84 3 301 108 210.97 4 233 247 182.06	 201 202 98.05 He 4, Le -1 0 113 131 0.0 1 458 485 113.71 	8 156 154 339.74 9 158 167 289.27 H= 5, L+ 2 0 469 498 180.00	4 100 193 6.09 5 169 172 120.88 6 81 85 354,21 7 107 113 88.50 8 105 164 379.12	2 04 103 115.11 3 180 180 281.06 4 18 40 153.03 5 157 160 276.15 H= 7. L= 5	4 110 111 344,19 4 131 134 70,59 6 30 27 379,44 H= 9, 14 -7 0 153 149 0.0
0 [00 /20 /20 /20 /1 ++ 2, L = 1 0 41 40 /22 /1 4 ++ 1, L = 1 1 /1 4 750 /20 /0 0 190 145 0.0 3 570 550 217.40 1 860 563 95.12 4 /25 765 318.05	6 89 90 180.72 6 89 90 187.09 7 39 33 301.49 8 146 146 203.94 9 33 36 227.25 H= 3, 1= -1	2 111 107 304-37 3 410 433 99.71 4 185 182 301.13 5 391 417 90.30 6 69 292.94 7 189 190 60.70 8 18 21 297.81	2 318 326 157,87 3 154 157 114,73 4 243 248 157,27 5 87 94 312,07 6 174 175 176,69 7 37 34 128,63	0 176 1A1 1A0.00 1 206 212 267.19 2 108 103 169.79 3 119 119 271.22 4 113 117 151.14	0 24 18 180.00 1 93 99 80.50 2 49 60 105.30 3 113 114 97.52 H= 7, L= -5	1 105 102 81.74 2 49 98 31.84 3 208 207 64.02 4 161 159 20.09 5 132 131 64.43 8 134 130 13.90
2 404 149 28.00 5 316 11 224.57 3 596 137 134.20 5 316 11 224.57 5 796 137 134.20 5 168 228.01 5 795 216 110.01 8 145 146 23.67 6 211 200 33.98 9 89 93 316.98 7 262 236 66.20 8 90 82 19.44 Me 7, Le -1	0 36 16 0.51 1 187 202 262.97 2 176 174 163.88 3 174 155 203.54 4 575 603 161.53 5 78 74 222.09	H- 4, L- 2 0 54 62 180.00 1 441 458 279.57 2 170 169 157.71	 H= 131 133 136.08 H= 5, L= -2 0 280 285 179.09 1 122 123 133.67 2 204 200 152.72 	6 79 80 203.17 7 138 143 224.99 H= 6. L= -3 0 347 356 180.20	0 132 128 0.0 1 176 182 84.95 2 56 57 47.67 3 126 129 91.00 H= A, L= 0	He 9, L+ 3 0 135 133 170.30 1 80 77 293.64 7 65 94 174.30 3 159 155 287.74
• [1,7] 144 446.16 1,77 140 0.7 10 • 73 40.7 1,70 0.7 140 0.277.70 *** 1, L* -1 270 160 277.70 *** 1, L* -1 270 163 277.70 *** 1, L* -1 170 163 275.75 10 164 170 164 354 310 310.57 1 201 164 105.25 317 326.45 310.57	4 341 355 174.91 7 46 46 133.64 8 180 181 177.90 9 199 10 356.33 Mm 3, Le 2	4 405 411 272.41 4 87 78 37.76 5 154 157 250.11 6 55 60 40.76 7 100 111 282.44 8 83 94 242.18 9 141 144 253.75	5 184 188 119.07 6 237 230 152.80 5 106 105 93.73 6 131 139 712.91 7 142 141 198.42 8 122 123 159.44	1 115 110 718.70 2 317 316 182.69 3 179 127 141.89 4 148 144 186.39 5 59 65 308.22 6 156 147 152.35 7 66 61 251.13	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9 80 80 277.29 He 9, Le -3 0 161 151 180.00 1 83 81 321.70
2 241 217 271.47 92 99 1.65 3 322 309 90.44 7 150 163 244.67 4 161 151 27.50 8 107 108 4.12 5 411 4.27 104.65 9 128 128 128 28.13 7 10 267 104.65 9 128 128 28.13 6 101 103 14.14 2.46 8 101 103 14.14 2.46	0 141 184 0.0 1 268 250 142.57 2 430 437 347.41 3 331 325 95.05 4 388 340 347.89 5 216 209 64.71 4 305 303 351.13	H= 4, L= -2 0 287 283 180.00 1 383 401 279.57 2 287 271 179.61 3 321 327 265.82	H= 5, L= 3 0 294 300 0.0 1 157 154 297,29 2 240 241 7.41 3 131 132 203,40 4 230 249 345.42	H= 6, L= 4 0 37 33 0.0 1 115 123 55.19 2 114 120 49.68 3 139 139 71.47	6 163 158 187.00 7 83 86 133.91 H= 8.1= 1 D 192 202 0.0 1 23 21 224.27	3 124 125 264.61 4 163 159 169.17 5 103 103 252.15 H+ 9, L+ 4
9 261 257 101.07 0 49 70 0.0 10 36 35 70.74 1 217 210 22.36 10 36 35 70.749 219.91 219.91 14* 14 2 3 103 107 93.04 10 142 160 0.0 5 264 255 92.45	7 32 54 26.76 8 198 194 24.80 9 70 73 28.35 H= 3, L= -2	4 85 78 245,85 5 197 190 277,08 6 47 46 186,48 7 121 125 300,80 8 56 57 217,63 9 186 166 273,10	5 61 61 248.23 6 183 182 366.55 7 60 60 321.42 8 131 142 327.52 H= 5, L= -3	4 151 151 20.43 5 148 148 75.76 6 126 126 23.21 He A, Le -4	2 240 245 15.79 3 10% 109 31% 45 4 250 249 0.%3 5 66 67 297.46 4 174 173 0.06 7 89 83 283.27	0 47 70 0.9 1 73 70 91.38 2 69 60 379.40 3 146 144 96.71 H= 9.14
2 40 46 71.61 7 210 224 90.07 3 301 310 314.64 8 174 165 167.11 4 167 160 740.84 9 370 20 163.43 5 220 207 7874.22 6 213 200 199.56 Ht 2, Lt -7 7 311 200 209.56	1 3+5 354 162,43 2 374 376 356,92 3 249 241 142,10 4 337 337 17,45 5 142 133 118,04 6 288 286 10,63	H= 4, L= 3 0 147 150 140.00 1 198 222 147.19 2 90 85 196.35 3 293 293 106.61	0 223 231 0.0 1 273 275 277.55 2 236 233 333.96 3 323 325 279.49 4 199 193 347.94 5 135 129 223.17	1 177 105 01.73 2 172 171 6.99 3 121 122 161.99 4 179 179 24.05 5 66 70 149.47 6 212 213 357.77	H- R, LP -1 0 730 237 0.0 1 137 136 257.70 7 235 235 2357.60 3 112 123 216.23 1 12 123 216.23	n 118 117 0.n 1 128 130 104.44 2 165 165 951.47 3 115 114 102.38 He 10.1= 0
* 1/2 1/2 201/0 U 200 (* 180.00) * 1/2 1/2 201/0 U 201 (* 180.00) ** 1/2 1/2 201/0 U 201 (* 180.00) ** 1/2 1/2 201/0 U 201 (* 180.00) ** 1/2 1/2 1/2 1/2 1/2 1/2 1/2 1/2 1/2 1/2	7 78 73 322-21 8 198 202 73.45 9 66 62 33.28 N= 3, L= 3 0 103 107 180.00	4 24 19 210.36 5 315 314 07.40 6 43 41 313.32 7 103 102 08.62 8 78 28 124.99 He 4, Le -3	6 183 183 4,94 7 100 100 267.22 8 112 118 14.37 H+ 5. L- 4 p 216 214 180.00	H= 6. 1= 5 0 31 35 190.00 1 112 122 259.73 2 47 75 159.63 3 95 100 244.68	5 138 134 287.85 6 217 226 354.78 7 82 83 292.51 H= 8, L= 2	0 52 61 0.5 1 267 228 271.31 2 91 79 23.88 5 217 200 294.24 4 106 103 337.54 5 139 111 241.36
1 411 179 295.45 20 211 74.91 4 211 270 195.45 4 112 221.51 5 226 210 296.41 4 71 42.75 5 235 125 105.49 He 2, 1 3 7 185 177 295.10 152 117 141 0 276 26 0.2	1 97 90 201.12 2 141 135 200.98 3 286 280 216.17 4 284 270 176.90 5 198 108 243.91 6 216 212 176.72 7 101 93 296.84	0 118 129 0.0 1 217 208 71.40 7 204 194 14.54 3 404 401 74.89 4 81 77 0.33 5 273 264 55.70	1 55 55 700.85 2 220 223 181.65 3 55 58 67.40 4 136 141 179.77 5 96 99 84.57 6 109 112 184.94 7 188 1 38.97	H* 6, L* -5 0 312 310 140.00 1 28 27 228.87 2 217 223 163.71	1 32 29 66.70 2 170 175 156.21 3 64 64 224.28 4 236 239 156.50 5 61 61 179.07 6 154 153 197.10	H= 17, L= 1 0 148 147 180.70 1 05 84 105.81 2 105 101 201.42 4 108 107 112.56 4 108 107 185.57
V 100 107 233.03 1 240 777 294.51 H= 1 1 1 1 1 1 1 100 20.34 H= 1<	8 178 110 184.89 H= 3. L= -3 0 148 150 179.94 1 17 15 134.34 2 323 318 181.50	6 104 99 287.36 7 197 201 106.98 8 46 42 299.27 H= 6, L= 6 0 57 52 180.00	H= 5, 14 -4 0 89 87 180.00 1 125 134 152.19 2 118 121 100.02 3 218 227 132.16	3 30 41 348.55 4 140 140 163.46 H= 7, L= 0 0 260 10 0.0 1 251 254 283.05	ү 20 г 34.44 н= 8. L= -2 п 216 225 180.00 1 101 100 44.53 2 174 168 142.75	5 141 145 103.14 No 10, Le -1 0 25 30 0.0 1 169 170 90.90
2	3 116 105 194.95 4 241 217 208.69 5 126 119 141.87 6 208 206 195.73 7 56 55 30.44	1 187 177 281.87 2 90 89 288.17 3 157 144 273.96 4 37 37 275.65 5 148 135 277.65	4 94 95 218.69 5 116 116 98.37 6 139 141 176.75 7 109 114 82.43	2 105 101 54.64 3 295 294 200.15 4 36 57 62.08 5 210 207 266.03 5 59 57 201.31	3 107 102 25.81 4 181 179 162.94 5 140 160 99.54 6 160 161 191.06 7 72 71 91.64	3 164 161 04,45 4 113 110 137,43 5 77 72 76,74
		Table	3 (cont.)			
E FO FC ALPHA K TO FC ALPHA He 10+ L Z 0 40 00 7.0 1 95 95 120.92 115 10 204.01 2 57 41 328.41	K FT FC ALPHA 0 94 94 180.00 1 188 182 106.96 2 135 139 197.40 3 125 123 107.14	K FO FC ALPHA 2 37 39 231.76 3 180 179 82.63 He 11. Le D	E FG FC ALPHA 4 150 L41 154.93 H= 11, L+ 1	x FO FC ALPHA M= 11, L= -1 0 116 115 0.0 1 57 52 8.43	K FO FC ALPHA D 118 106 180-00 1 63 56 271-92 2 94 82 200-15 3 104 50 548-53	K FO FC ALPHA 1 67 51 158.27 2 165 170 195.14 3 51 58 70.89
1 115 118 107.41 3 140 18 280.77 1 12 120 120 77.55 4 20 17 372.67 4 92 97 114.19 mm 10, L 3 mm 10, L7	H= 10, L+ -3 0 46 46 183,00 1 183 179 107.66	0 161 155 180.00 1 67 66 71.00 2 196 185 179.43 3 18 71 175.70	0 198 189 0.0 1 34 28 177.09 2 169 160 20.68 3 18 5 140.50	2 187 185 4.78 3 87 81 324.21 M= 11. L= 2	H- 11, 14 -7 0 160 162 180.00	H- 17, L- 0 0 36 28 7.7 1 198 178 44.45

 Table 4. Peak heights of copper, oxygen, nitrogen and carbon atoms

Cu	82•0 e Å−3	O(3.4)	13-4 e Å-3
N(A)	13.0	O(3B)	12.5
N(B)	13.4	$\mathbf{C}(1\mathbf{A})$	10.6
O(1A)	.14.7	C(1B)	10.3
O(1 <i>B</i>)	15.4	C(2A)	10.2
O(2A)	13.9	C(2B)	9.9
O(2B)	13.5	C(3A)	10.1
		C(3B)	9.4

Discussion of the structure

The bond lengths and bond angles in the L-serine ligands are shown in Figs. 2 and 3. These values show a good consistency for the two independent L-serine ions. The averages of the bond lengths are given in Table 5 and compared with average values obtained from a large number of reported copper complexes of amino acids and peptides (Freeman, 1966), with the results from DL-serine (Shoemaker, Barieau, Donohue & Lu, 1953) and those from copper glutamate dihydrate (Gramaccioli & Marsh, 1966). A similar comparison for bond angles is given in Table 6. It can be concluded from the tabulated data that there are no significant changes in the bond lengths when serine is being chelated except for the expected small changes in the acid group. Some of the bond angles, however, in the present structure differ by more than 5σ from those reported for DL-serine, i.e. C(3)-C(2)-N and C(2)-C(3)-O(3) (Table 6). It is interesting to note that C(1)-C(2)-C(3) and the C(3)-C(2)-N angles are all larger than the tetrahedral angle. Furthermore both C(2)-C(3) distances are smaller than one would expect for a $C(sp^3)$ - $C(sp^3)$ bond.

Chelation of serine causes a small rotation around the C(1)-C(2) bond. In DL-serine the nitrogen atom is 0.05 Å out of the plane of the acid group, while in the present structure the nitrogen atoms are 0.16 Å and 0.31 Å removed from the planes through the acid groups (Table 8, planes 1 and 2). These observations correspond to rotations of 6.6° and 12.5° , respectively. The sense of rotation is clockwise on looking down from C(1) to C(2). The configuration around the C(2)-C(3) bond in both the serine molecules is similar to the one found in DL-serine (Shoemaker, *et al.* 1953) and L-serine phosphate (McCallum, Robertson & Sim, 1959). This particular configuration might be considered the least favorable of the three possible staggered configurations with the hydroxyl group close to both the carboxyl and amino groups. Fig.4 shows a schematic drawing of the serine molecules viewed along the C(3)-C(2) bonds.



Fig. 2. Bond lengths in both serine ions. Number in parentheses is the estimated standard deviation of the last digit.



Fig. 3. Bond angles in both serine ions. Number in parentheses is the estimated standard deviation.

Table 5. Comparison of bond lengths

Column I: Average bond lengths of L-serine in bis(L-serinato)copper(II). Column II: Average bond lengths from a tabulation on several copper chelates of amino acids and peptides (Freeman, 1966). Column III: Results of DL-serine (Shoemaker *et al.* 1952). Column IV: Results from the structure of copper glutamate dihydrate (Gramaccioli & Marsh, 1966). Numbers in parentheses are estimated standard deviations of the last digit given.

	I	II	III	IV
C(1)-C(2)	1·540 (7) Å	1•520 (5) Å	1·528 (9) Å	1·509 (6) Å
C(1) - O(1)	1.276 (7)	1.286 (7)	1.268 (9)	1.284 (6)
C(1)–O(2)	1.237 (6)	1.235 (5)	1.261 (9)	1.242 (6)
C(2)–N	1·493 (6)	1.482 (7)	1.491 (9)	1.486 (6)
C(2) - C(3)	1.502 (7)		1.513 (9)	_``
C(3)–O(3)	1.411 (7)		1.425 (9)	



Fig.4. Configuration of the hydroxyl group in DL-serine, L-serine A and L-serine B. View is along the C(3)-C(2) bond.



Fig. 5. Surroundings of the copper ion. Standard deviations of last digit in parentheses.

Table 6. Comparison of bona angles	
The column numbers refer to the sources given in Table	5.
Numbers in parentheses are estimated standard deviations	of
the last digit given.	

	I	ш	IV
O(1)-C(1)-O(2)	124.3 (5)	125.3	124.3
O(1)-C(1)-C(2)	116.8 (4)	117.4	117.5
O(2)-C(1)-C(2)	118.9 (4)	117.2	118.2
C(1) - C(2) - N	108.5 (4)	110.0	110.1
C(1)-C(2)-C(3)	111.7 (4)	110.3	110.0
C(3) - C(2) - N	113.6 (4)	111.1	111.3
C(2) - C(3) - O(3)	109.5 (4)	112.0	

The copper is coordinated to a carboxylic oxygen and the nitrogen of both L-serine ions to form two 5-membered chelate rings. Dimensions for those rings, if not shown in Figs. 2 and 3, are given in Table 7. These bond lengths and angles compare well with previously reported results. The rings are not flat. When leastsquares planes are calculated for the carboxylic acid groups, it is observed that the Cu and N atoms are on opposite sides of these planes (Table 8).

Table 7. Bond lengths and bond angles of chelate rings in bis(L-serinato)Cu^{II}

The columns A and B refer to the chelate rings formed by the serine molecules A and B respectively. Column C are average values tabulated by Freeman (1966). The numbers in parentheses are the estimated standard deviations for the last digit.

	Α	В	С
Cu–O	1·970 (5) Å	1·952 (5) Å	1·966 (12) Å
Cu–N	1.988 (6)	1.975 (6)	1.996 (5)
O(1)–Cu–N	82·4° (2)	83·9° (2)	84°
Cu - O(1) - C(1)	116.4 (4)	115.4 (4)	120 (5)
Cu-N-C(2)	110.4 (4)	109.3 (4)	111

The two serine residues are *cis* with respect to each other. The same configuration has been observed in bisglycinatocopper(II) hydrate (Tomita & Nitta, 1961, Freeman, Snow, Nitta & Tomita, 1964). The surroundings of the copper ion form a square pyramid which is shown in Fig. 5. The four atoms in the basal plane are a part of the two chelate rings and form strong bonds with the copper ion. These four atoms are not coplanar but form a very flattened tetrahedron. The copper ion is not in the center of this tetrahedron

Table 8. Equations of some least-squares planes

Equations are expressed in the form Ax + By + Cz = D where D is expressed in Å, and x, y and z are fractional coordinates.

Plane	Atoms in pla	ane	Α	В	С	D
1	O(1A) O(2A) C(1A)	4) C(2A)	7.194	4.814	2.121	6.086
2	O(1B) O(2B) C(1E)	$\dot{C}(2B)$	5.277	5.531	2.983	5.729
3	O(1A) O(1B) N(A)) N(B)	4.074	5.870	3.291	5.694
Atoms	⊿(1)	Atoms	⊿(2)	Atoms	⊿(3)
Cu	-0.360 Å	Cu	+0.1	66 Å	Cu	+0·137 Å
O(1A)	-0.005	O(1 <i>B</i>)	+0.0	01	O(1A)	-0.117
O(2A)	-0.005	O(2B)	+0.0	01	O(1B)	+0.116
C(1A)	+0.014	C(1B)	-0.0	04	N(A)	+0.101
C(2A)	-0.004	C(2B)	+0.0	01	N(B)	-0.101
N(A)	+0.164	N(B)	-0.3	13		

but displaced towards the top of the square pyramid by 0.14 Å (Table 8). The serine molecule A is bonded to two copper ions. The top of the pyramid is occupied by the carboxyl oxygen which is trans to the amino group of an A-type serine molecule. The fifth interaction is weaker than the first four. The sixth position is unoccupied, [O(2B), translated one unit in the negative c direction, is at 3.63 Å from the copper atom] where in the similar structure of bis(L-serinato)zinc(II) (van der Helm, Nicholas & Fisher, 1969) a hydroxyl oxygen is in this position (at 2.99 Å), forming a weak interaction with the metal ion. The cis configuration leads to a short non-bonded distance between O(1A)and O(1B) of 2.73 Å, which is significantly shorter than the 2.83 Å found between the two similar oxygens in the structure of bisglycinatocopper(II) hydrate (Freeman, Snow, Nitta & Tomita, 1964). The cis configuration is also present in the structure of diaquobis-(L-serinato)nickel(II) (van der Helm & Hossain, 1969) and the corresponding O-O distance in that case is 2.87 Å.

The principal axes of the thermal ellipsoids were determined and the magnitudes of their direction cosines with respect to the cell edges are listed in Table 9. The atoms of serine molecule B have in general a slightly higher temperature movement than the same atoms in serine molecule A. This is probably correlated with the fact that serine A forms a chelate ring with one copper and is also complexed to another copper ion whereas serine B forms only a chelate ring. This can be seen in Fig. 6, which shows the molecular structure as viewed down the b axis. The two serine molecules are approximately related by a twofold axis lying in the basal plane of the copper surroundings and bisecting the angle N(B)-Cu-N(A). The protons available for hydrogen bonding (two on each nitrogen atom and one on each hydroxyl oxygen atom) are all being used (Table 10) to form bonds of similar strength. All oxygen atoms accept one hydrogen bond. The coordinate and hydrogen bonds form a three-dimensional network.

Table 9. Values of anisotropic temperature factors along the principal axes

Values of the temperature factors (in $Å^2$) along the major, intermediate and minor axes of the thermal ellipsoids are given together with the direction cosines of these axes with respect to the axes of the crystallographic unit cell.

	Bi	l_1	l_2	l_3
Cu	2.20	0.539	0.464	0.697
	1.25	0.777	0.047	-0.636
	1.04	-0.324	0.884	-0.332
O(1 <i>A</i>)	4.07	0.666	0.604	0.431
	1.43	-0.226	-0.397	0.892
	1.13	-0·711	0.691	0.136
O(2A)	2.75	0.884	0.403	0.225
	1.83	-0.212	-0.102	0.974
	1.24	-0.416	0.909	0.009
C(1A)	2.28	-0.050	0.037	0.999
	1.57	0.620	0.784	-0.023
	0.80	0.784	-0.619	0.030

	B_i	l_1	l_2	l_3
C(2A)	1.72	0.846	0.383	0.361
	1.47	-0.475	0.858	0.203
	1.24	-0.242	-0.343	0.910
N(A)	1.90	0.941	0.001	-0.350
	1.51	0.333	0.198	0.918
	0.98	- 0.068	0.980	-0.185
C(3A)	2.68	0.656	-0.124	0.738
	1.79	0.608	-0.498	-0.625
	1.34	0.448	0.828	-0.256
O(3A)	3.64	-0.550	0.365	0.757
	2.74	-0.428	0.649	-0.624
	1.26	0.716	0.668	0.192
O(1 <i>B</i>)	2.95	0.639	0.510	0.569
	1.75	0.756	-0.580	-0.600
	1.27	-0·141	0.813	-0.563
O(2 <i>B</i>)	4.58	0.792	0.391	0.460
	2.89	-0.473	0.879	0.071
	1.33	-0.386	-0.274	0.885
C(1 <i>B</i>)	3.07	0.280	-0.508	0.631
	1.93	-0.068	0.749	0.659
	1.01	0.812	0.425	-0.409
C(2B)	2.14	0.794	0.268	0.537
	1.97	− 0·186	0.962	-0.199
	0.96	<i>−</i> 0·579	0.028	0.820
N(<i>B</i>)	2.25	0.829	0.330	0.442
	1.35	-0.485	0.024	0.879
	0.89	-0.278	0.944	-0.177

Table 9 (cont.)

Table 10. Hydrogen bonding

0.711

0.699

0.078

0.620

0.753

0.219

0.394

0.304

0.867

0.121

0.184

0.975

0.574

0.655

0.491

0.782

0.623

0.021

2.98

2.00

1.45

4.14

1.94

1.75

C(3B)

O(3B)

Donor (D)	Acceptor (A)	∠C- <i>D</i> A	
N(A)	O(1A)	120°	2·99 Å
N(A)	O(2A)	91	3.01
N(B)	O(3B)	91	2.95
N(B)	O(2B)	129	2.99
O(3A)	O(1B)	121	2.70
O(3B)	O(3A)	99	2.74

Although the packing below the square pyramid around the copper ions is rather open, there occur in this area two van der Waals interactions shorter than



Fig. 6. Projection of the structure down the b axis.

3.5 Å: C(3A)-C(3B): 3.48 Å and N(A)-O(1B): 3.44 Å (See Table 11). The other intermolecular distances below 3.5 Å are also listed in Table 11.

Table 11. Van der Waals interactions

The atoms listed in the first column have the parameters given in Table 2. The atoms in the second column are related by the formulas given in column 3 to the parameters for the atoms given in Table 2.

		Formula	Distance
N(A)	O(1 <i>B</i>)	- c	3∙44 Å
C(2A)	O(1B)	+ c	3.36
C(2B)	O(2A)	$1-x, y+\frac{1}{2}, 1-z$	3.27
C(1B)	O(2A)	$1-x, y+\frac{1}{2}, 1-z$	3.39
C(2A)	O(2A)	$1-x, y+\frac{1}{2}, 1-z$	3.40
N(A)	C(1A)	$1-x, y+\frac{1}{2}, 1-z$	3.44
C(2B)	O(3B)	$-x, y+\frac{1}{2}, 1-z$	3.32
C(3A)	C(3B)	-a-c	3.48
C(3B)	O(3A)	— a	3.29
O(3A)	O(1A)	$1-x, y+\frac{1}{2}, 1-z$	3.33

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The Crystal Structure of Diaquobis(L-serinato)nickel(II)*

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The crystal structure of diaquobis(L-serinato)nickel(II), NiC₆H₁₆O₈N₂, has been determined and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group C2, with a =7.776, b = 8.546, c = 8.834 Å and $\beta = 101^{\circ}31'$. The final R value for 608 reflections is 0.043; the standard deviations are about 0.006 Å for the non-hydrogen light-atom positions. The compound is not isostructural with either the Cu or the Zn complex of L-serine. The nickel environment is octahedral and the ligands are attached *cis* to the metal ion. The serine molecule has a different configuration for the hydroxyl group when compared with the one found in DL-serine. A fractional molecule of water of crystallization is present in the structure.

Introduction

The influence of transition metal ions on the conformation of peptides and amino acids prompted the investigation of a series of chelates of L-serine. A preliminary investigation showed the nickel compound to crystallize in a different space group to the Cu and Zn chelates, while the crystals apparently contained water of crystallization or complexed water in contrast to the non-hydrated Cu and Zn compounds.

Experimental

The compound was prepared in aqueous solution by adding proportional amounts of NiSO₄, Ba(OH)₂ and L-serine to form Ni(L-serine)₂. The BaSO₄ was separated from the light blue solution by centrifugation. Evaporation of the solution yielded a glass. After several unsuccessful attempts, some crystalline material was obtained from a 2-propanol-H₂O solution. Subsequently an aqueous solution was equilibrated with an ether-ethanol (2:1) mixture. Close to the saturation point the solution was seeded with a few crystals. This technique yielded a good crop of blue, well formed,

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