186 reflections
10 parameters
$w = 1/\sigma^2F$
$(\Delta/\sigma)_{\max} \leq 0.001$
$\Delta\rho_{\max} = 1.56$ e Å^{-3}

Extinction coefficient: 0.034 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional coordinates* (*x*,*x*,*x*) *and anisotropic displacement parameters* ($\times\ 10^{-2}$ Å^2) *with data of Colominas* (1967) *in square brackets*

$$u_{11} = u_{22} = u_{33},\ u_{12} = u_{13} = u_{23},\ T = \exp(-2\pi^2\sum_{i=1}^{3}\sum_{j=1}^{3} u_{ij}h_ih_ja_i^*a_j^*).$$

	Site	x	u_{11}	u_{12}
Cu	8(*a*) ($\bar{4}3m$)	1/8	0.48 (4) [0.5 (2)]	0.0
Cr	16(*d*) ($.\bar{3}m$)	1/2	0.29 (4) [0.5 (2)]	0.02 (3)
Se	32(*e*) ($.3m$)	0.25739 (5) [0.2576 (3)]	0.32 (3) [0.5 (2)]	−0.05 (1)

Table 2. *Geometric parameters* (Å, °)

Se—Cu	2.3703 (8)	Se—Se	3.8706 (1)
Se—Cr	2.5100 (4)	Cr—Cr	3.6553 (1)
Se—Se	3.4384 (1)	Cu—Cu	4.4758 (0)
Se—Se	3.6577 (1)		
Se—Cu—Se	109.47 (3)	Se—Cr—Se	86.46 (1)
Se—Cr—Se	180.0	Cu—Se—Cr	122.79 (1)
Se—Cr—Se	93.54 (1)	Cr—Se—Cr	93.43 (2)

Single crystals of $CuCr_2Se_4$ [as well as those of $(Cu,Ga)Cr_2Se_4$ mixed crystals] were grown by the chemical vapor transport method using $CrCl_3$ as transporting agent. Silica ampoules of 20 mm inner diameter and 150-180 mm length containing powdered substrates (CuSe, Ga_2Se_3, $CrCl_3$, Cu, Ga and Se) were evacuated to about 10^{-3} Pa and sealed. A horizontal zone furnace with melting zone temperatures of 1053-1253 K and crystallization zone temperatures of 935-1101 K was used. The samples were slowly cooled after 6 d of heating. Pyramidal monocrystals 0.2-4.0 mm in diameter were obtained. Unit-cell parameters were obtained by least squares. Data were corrected for Lorentz and polarization effects using *NRCVAX* (Gabe, Lee & Le Page, 1985). Empirical absorption corrections were applied using nine reflections in the range $13.7 < 2\theta < 49.2°$. Standard reflections were 084, 804 and 10,2,2. The structure was refined by full-matrix least-squares techniques including the positional and anisotropic thermal parameters, the extinction coefficient, and the scale factor ($N_p = 10$). Initial parameters for the atomic positions were taken from the literature (Colominas, 1967).

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71104 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1039]

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Structure of Bis[(*S*)-prolinamidato]-copper(II) Dihydrate

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Abstract

Crystals of bis[(*S*)-prolinamidato]copper(II) have been prepared and their structure determined by X-ray crystallography. The Cu coordination is tetrahedrally distorted square planar. An O atom of a molecule related by a twofold screw axis interacts weakly with Cu^{II}, serving as a bridging element to form a polymeric structure. A new chiral centre of (*S*) configuration is produced at the amino N atom on coordination to Cu^{II}.

Comment

Chiral discrimination of amino acids and derivatives in HPLC has been obtained by using copper(II) complexes of amino acids, according to a mechanism of ligand exchange [ligand exchange chromatography, LEC (Davankov, Navratil & Walton, 1988)]. (*S*)-Proline, in particular, has been selected as the chiral ligand on account of its rigid cyclic structure, either bound to the stationary phase (Davankov & Zolotarev, 1978) or added to the eluent associated to an ion-exchange resin (Hare & Gil-Av, 1979) or to a reversed-phase column (Gil-Av, Tishbee & Hare, 1980). As part of a general project aimed at

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studying enantioselective interactions in copper(II) complexes (Marchelli, Dossena, Casnati, Dallavalle & Weinstein, 1985), we reported that copper(II) complexes of amino acid amides were able to give enantiomeric separation of dansyl-amino acids (Armani, Barazzoni, Dossena & Marchelli, 1988) and unmodified amino acids (Galaverna, Corradini, Dossena & Marchelli, 1993) in HPLC (reversed phase).

The equilibria of complex formation in aqueous solutions of copper(II) and (*S*)-prolinamide were studied by potentiometry (Dallavalle, Fisicaro, Corradini & Marchelli, 1989). Among the species present in the pH range utilized in HPLC (5–8.0), CuL_2H_{-2} was particularly relevant to the discrimination process. Thus, the knowledge of its structural features may provide very useful information about the stereochemical requirements for chiral recognition. We report here the preparation and the X-ray crystal structure determination of bis[(*S*)-prolinamidato]copper(II). We were able to prepare and to determine the crystal structures of strictly related complexes with (*S*)-phenylalaninamide, methyl- and dimethylphenylalaninamide. Besides the coordination parameters concerning the Cu ion, there were two very interesting features in these structures: the position of the side chain of phenylalanine, which changed according to the presence and the number of substituents on the amino N atom, and the stereochemistry of the methyl-substituted N atom coordinated to the metal ion (Corradini, Gasparri Fava, Belicchi Ferrari, Dossena, Marchelli & Pelosi, 1992).

Crystals of $[Cu(ProNH)_2].2H_2O$ were obtained from (*S*)-prolinamide hydrochloride and $CuCl_2.5H_2O$ in absolute ethanol. The crystal structure is shown in Fig. 1, and the atomic numbering and final atomic parameters are reported in Table 1 with selected bond distances and angles in Table 2. Two prolinamide molecules are *trans*-coordinated to a Cu atom through imino and amidato N atoms. The tetrahedrally distorted coordination completes a very elongated square pyramid by a long interaction [3.014 (7) Å] between the Cu atom and an O atom O2′ ($-x, y+\frac{1}{2}, -z-1$) of a twofold-screw-axis related molecule. The Cu atom is displaced 0.10 Å from the basal plane towards O2′, which serves as a bridging element to form a polymeric structure (Fig. 2).

The Cu—O2′ direction forms an angle of 7.8 (2)° with the normal to the coordination plane. The absolute configuration of the structure was established in the early stages of the refinement from the (*S*) configuration of the prolinamide ligand. The new chiral centre formed on the imino N atom on coordination to the metal atom shows an (*S*) configuration. In contrast, in the analogous complex of copper(II) with *N*-methylphenylalaninamide [Cu(Me-Phe-NH)$_2$].H$_2$O (Corradini, Gasparri Fava, Belicchi Ferrari, Dossena, Marchelli & Pelosi, 1992) the corresponding N atoms are in the (*R*) configuration. It is interesting to note that in both cases the *N*-alkyl substituent is axial, though they have opposite configurations. The Cu—N distances between the metal and the anionic amidato N atoms are shorter than the other two and are comparable with those found in bis(phenylalaninamidato)copper(II) complexes (Corradini, Gasparri Fava, Belicchi Ferrari, Dossena, Marchelli & Pelosi, 1992), falling in the usual range of values reported for other amino acid derivatives.

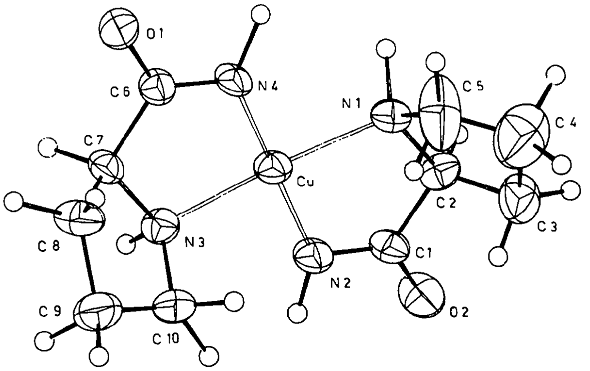

Fig. 1. *ORTEP* view of the complex with thermal ellipsoids at 40% probability.

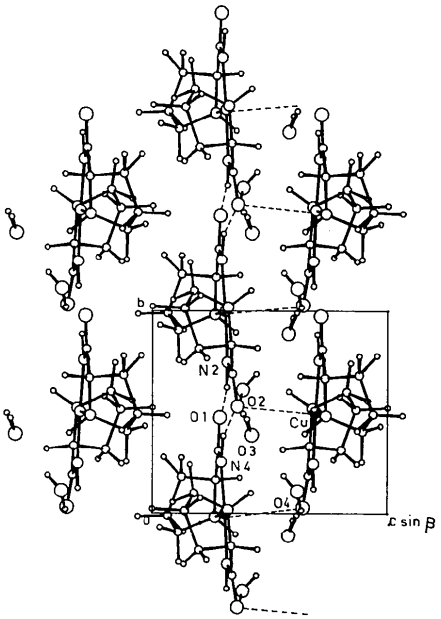

Fig. 2. The packing arrangement on the (100) plane showing polyhedral chains along the *b* axis.

The two non-planar pyrrolidine rings are on the same side of the coordination plane (Fig. 2), as found in bis(L-prolinamidato)nickel(II) dihydrate (Tsukihara, Katsube, Fujimori & Ishimura, 1972) and in bis(*N*-Bz-L-Pro)Cu^{II} (Aleksandrov, Struchkov, Kurganov, Rogozhin & Davankov, 1972), in contrast to bis(L-prolinato)palladium(II) (Ito, Marumo & Saito, 1971). The conformation of the two pyrrolidine rings is not identical; one (C2, N1, C5, C4, C3) is in envelope form [q_2 = 0.256 (15) Å, φ_2 = −111 (3)° (Cremer & Pople, 1975)], the other (C7, N3, C10, C9, C8) shows a twist-envelope (C_2) conformation (Dale, 1978) [q_2 = 0.363 (13) Å, φ_2 = −120 (2)°]. The nearly planar five-membered chelate rings show a twist [moiety defined by N3; q_2 = 0.107 (8) Å, φ_2 = −165 (6)°] and a twist-envelope [moiety defined by N1; q_2 = 0.057 (10) Å, φ_2= 134 (9)°] conformation.

The long interaction between Cu and O2′ [3.014 (7) Å] is shorter than that in the structure of the isomorphous complex bis(L-prolinamidato)nickel(II) [distance of 3.493 Å determined, but not considered, by Tsukihara, Katsube, Fujimori & Ishimura (1972)]. The packing is governed by the Cu—O2′ interaction which determines the formation of zigzag chains running along the crystallographic *b* axis (Fig. 2). The water molecules are not coordinated to Cu and occupy interstitial polar sites between the polyhedral chains. Hydrogen bonds, involving the N atoms of amine and amidic groups, and O atoms of water molecules and imino carbonyl groups, run along the chains, which are also linked by van der Waals interactions between the pyrrolidine rings.

Experimental

Crystal data

$[Cu(C_5H_9N_2O)_2].2H_2O$
M_r = 325.85
Monoclinic
$P2_1$
a = 10.897 (1) Å
b = 7.427 (1) Å
c = 9.516 (1) Å
β = 112.88 (1)°
V = 709.6 (2) Å^3
Z = 2.00
D_x = 1.5252 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 10–45°
μ = 2.2914 mm^{-1}
T = 293.00 K
Rhomboidal plates
0.24 × 0.10 × 0.05 mm
Red-orange

Data collection

Siemens AED diffractometer
θ-2θ scans
Absorption correction: none
1515 measured reflections
1515 independent reflections
998 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0259

$\theta_{\rm max}$ = 70°
h = −13 → 12
k = 0 → 9
l = 0 → 10
1 standard reflection monitored every 50 reflections
intensity variation: none

Refinement

Refinement on F
Final R = 0.043
wR = 0.048
S = 1.09
996 reflections
182 parameters

H-atom parameters not refined
Unit weights applied
$(\Delta/\sigma)_{\rm max}$ = 0.69
$\Delta\rho_{\rm max}$ = 0.14 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.18 e Å^{-3}

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	−0.0123 (1)	0.00000	−0.6921 (2)	0.0369 (4)
O1	0.1557 (6)	0.4772 (14)	−0.7150 (9)	0.0518 (35)
O2	−0.1709 (7)	−0.4683 (12)	−0.6392 (9)	0.0572 (37)
N1	−0.1950 (8)	0.0216 (19)	−0.6804 (10)	0.0440 (36)
N2	−0.0381 (9)	−0.2498 (13)	−0.6829 (11)	0.0395 (43)
N3	0.1569 (7)	−0.0141 (18)	−0.7357 (8)	0.0372 (29)
N4	0.0124 (9)	0.2596 (12)	−0.7084 (12)	0.0400 (45)
C1	−0.1462 (10)	−0.3083 (14)	−0.6619 (12)	0.0376 (47)
C2	−0.2441 (10)	−0.1630 (13)	−0.6670 (12)	0.0366 (46)
C3	−0.3755 (11)	−0.1833 (16)	−0.8023 (15)	0.0607 (50)
C4	−0.4105 (14)	0.0143 (31)	−0.8643 (18)	0.1019 (73)
C5	−0.2946 (13)	0.1053 (19)	−0.8240 (19)	0.0918 (71)
C6	0.1198 (10)	0.3121 (15)	−0.7203 (12)	0.0366 (41)
C7	0.2151 (10)	0.1708 (13)	−0.7325 (12)	0.0344 (40)
C8	0.2403 (12)	0.1861 (15)	−0.8776 (13)	0.0528 (52)
C9	0.2325 (11)	−0.0050 (27)	−0.9362 (13)	0.0663 (53)
C10	0.1313 (11)	−0.0913 (16)	−0.8918 (13)	0.0590 (49)
O3	0.3775 (7)	−0.1119 (12)	−0.4226 (10)	0.0695 (36)
O4	0.4060 (8)	−0.3888 (16)	−0.6166 (14)	0.1123 (57)

Table 2. *Geometric parameters* (Å, °)

Cu—N1	2.04 (1)	N3—C10	1.51 (1)
Cu—N2	1.88 (1)	N4—C6	1.28 (1)
Cu—N3	2.044 (9)	C1—C2	1.51 (1)
Cu—N4	1.962 (9)	C2—C3	1.52 (1)
O1—C6	1.28 (1)	C3—C4	1.57 (2)
O2—C1	1.26 (1)	C4—C5	1.35 (2)
N1—C2	1.50 (1)	C6—C7	1.51 (1)
N1—C5	1.51 (1)	C7—C8	1.51 (1)
N2—C1	1.34 (1)	C8—C9	1.52 (2)
N3—C7	1.51 (1)	C9—C10	1.47 (2)
N3—Cu—N4	82.6 (5)	O2—C1—C2	119 (1)
N2—Cu—N4	178.3 (4)	N1—C2—C1	112.8 (9)
N2—Cu—N3	97.0 (4)	C1—C2—C3	112.3 (9)
N1—Cu—N4	95.4 (5)	N1—C2—C3	105.7 (8)
N1—Cu—N3	172.0 (3)	C2—C3—C4	104 (1)
N1—Cu—N2	84.8 (5)	C3—C4—C5	107 (1)
Cu—N1—C5	110.8 (8)	N1—C5—C4	108 (1)
Cu—N1—C2	108.7 (7)	O1—C6—N4	124 (1)
C2—N1—C5	107 (1)	N4—C6—C7	118 (1)
Cu—N2—C1	118.8 (8)	O1—C6—C7	117 (1)
Cu—N3—C10	112.4 (6)	N3—C7—C6	109.7 (8)
Cu—N3—C7	110.8 (6)	C6—C7—C8	113.1 (9)
C7—N3—C10	106.3 (9)	N3—C7—C8	105.9 (8)
Cu—N4—C6	117.7 (8)	C7—C8—C9	105 (1)
O2—C1—N2	126 (1)	C8—C9—C10	104 (1)
N2—C1—C2	115 (1)	N3—C10—C9	104 (1)

The complex $[Cu^{II}(ProNH)_2].2H_2O$ was synthesized and crystallized as follows: 2 mmol (340.94 mg) of $CuCl_2.5H_2O$ (Carlo Erba) and 4 mmol of (*S*)-prolinamide hydrochloride (Aldrich) were dissolved in 50 ml of doubly distilled water. The pH was adjusted to 9.5 by addition of concentrated NaOH and the resulting purple-red solution was evaporated to dryness under reduced pressure. The solid residue was dissolved in absolute ethanol (30 ml); the alcoholic solution was filtered and allowed to evaporate slowly in a covered beaker. After 2 d deep-red rhombohedral plates were recovered by vacuum filtration and washed with a few drops of absolute ethanol. M.p. 456-457 K. Elemental analysis for $C_{10}H_{22}CuN_4O_4$: calculated C 36.86, H 6.80, N 17.19%; found C 37.05, H 7.08, N 17.18%. IR: 3239 (N—H stretch), 2971 (C—H stretch), 1592 (C=O stretch), 1432, 1278, 1074, 930 cm^{-1}.

Intensity data were collected on a Siemens AED single-crystal diffractometer using the θ-2θ technique with a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. The structure was solved by the Patterson and Fourier methods and the refinement was carried out by full-matrix least-squares cycles using the *SHELXS*86 and the *SHELX*76 computer programs, respectively (Sheldrick, 1985, 1976). The absolute configuration was established in the early stages of the refinement by assigning the (*S*) configuration to the prolinamide ligand. All isotropic H atoms (from a ΔF map) were included in the calculations but not refined. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A and 2.3.1 for Cu, O, N and C atoms, Table 2.2C for H). All calculations were carried out on a GOULD 6040 Powernode computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma) using the *PARST* (Nardelli, 1983) program for the geometrical description of the structure and *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1976) for the structure drawings.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71099 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1038]

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Sodium Ion Complexes with Ethylenediaminetetraacetic Acid

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Abstract

The crystal structures of tetrasodium (1,2-ethanediyldinitrilo)tetraacetate pentahydrate and disodium dihydrogen (1,2-ethanediyldinitrilo)tetraacetate dihydrate have been determined. Na ions prefer to act as bridges between different edta ligands and only in the tetrasodium salt is the edta ligand hexadentate to one Na ion. Na ions display seven-coordination, when coordinated to one edta ligand (distorted pentagonal bipyramid), and six-coordination, when linked to several edta ligands (from distorted octahedral to trapezoidal bipyramidal geometry). An Na ion in the tetrasodium salt shows five-coordination, because the sixth site is blocked by the edta ligand. H atoms in the disodium salt are linked to amine groups. Only these two salts can be obtained on varying the pH of an aqueous solution containing Na^+ and ethylenediaminetetraacetic acid. The first is obtained around pH 2–5 and the second around pH 12.

Comment

The chelating capacity of the ethylenediaminetetraacetato (edta) ligand has attracted widespread interest and the literature contains a large number of