



Copper complexes with dithiocarbamates derived from natural occurring amino acids. Crystal and molecular structure of $[\text{Cu}(\text{en})(\text{EtOH})(\text{H}_2\text{O})_3][\text{Cu}(\text{dtc-pro})_2]$

Benigno Macías^{a,*}, María V. Villa^a, Eduardo Chicote^a, Silvia Martín-Velasco^a, Alfonso Castiñeiras^b, Joaquín Borrás^c

^a Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Salamanca, Campus Unamuno, E-37007 Salamanca, Spain

^b Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Santiago de Compostela, Compostela, Spain

^c Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Valencia, Valencia, Spain

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Abstract

Reaction of Cu(II) salts with dithiocarbamates derived from the amino acids asparagine, glutamine, serine, threonine and tyrosine leads to reduction of the metallic cation and formation of Cu(I) complexes, whereas reaction with proline dithiocarbamate takes place without reduction, leading to formation of a Cu(II) coordination compound. Simultaneous reaction of proline dithiocarbamate and ethylenediamine with Cu(II) leads to the formation of the mixed complex $[\text{Cu}(\text{en})(\text{EtOH})(\text{H}_2\text{O})_3][\text{Cu}(\text{dtc-pro})_2]$. In the anion, the Cu(II) centre possesses a D_{2h} local symmetry, coordinated by two bidentate dithiocarbamate ligands, while the Cu(II) centre is in a distorted octahedral coordination in the cationic unit. The spectroscopic and magnetic properties of the complexes synthesised are also investigated. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dithiocarbamates; Cu(II) complexes; Ethylenediamine; Mixed-ligands Cu(II) chelates; Crystal structures

1. Introduction

Among the ligands coordinating through sulfur atoms, dithiocarbamates are deserving of much attention in recent years, and a large number of dithiocarbamate complexes have been synthesised so far; these compounds are being investigated in order to gain insight into the nature of the sulfur–metal bond in many biomolecules [1,2] and also because of their potential role in cancer disease treatment [3,4]. One of the variables which we can control is the effect of the organic chain linked to the dithiocarbamate unit, as it controls the ability of the ligand to reduce the metal cation and to favour solubility of the complexes formed.

We have reported several studies on the preparation of dithiocarbamates derived from α -amino acids and their coordination compounds with several metal cations [5–7]. Unfortunately, due to their limited stability,

crystallisation of these compounds in order to determine their structure via X-ray diffraction studies has been achieved only in a very few cases.

Nevertheless, from the studies carried out so far, we have concluded that the dithiocarbamate from proline is more stable and has a lower reduction power than those prepared from other amino acids; it forms coordination compounds with Mo(VI) [8], while other dithiocarbamates derived from α -amino acids lead to reduction and formation of compounds of Mo(V) and even Mo(IV) [9,10].

In the present study, we have selected several natural amino acids, i.e. asparagine (asn), glutamine (gln), serine (ser), threonine (thr), tyrosine (tyr) and proline (pro) and we have prepared their dithiocarbamates and the corresponding coordination compounds with copper. Our aim is to study the effect of the hydrocarbon chain on the ability of the dithiocarbamate to coordinate to copper cations, and we succeeded in preparing a complex with Cu(II) in the crystalline state, thus

* Corresponding author. Tel.: +34-23-294524; fax: +34-23-294515
E-mail address: bmacias@gugu.usal.es (B. Macias).

Table 1
Elemental analyses ^a for the copper complexes (%)

Complex	C	H	N	Cu
1 Ba[Cu(dtc-asn)] ₂ ·4H ₂ O	15.8(16.0)	2.6(2.7)	7.3(7.5)	17.3(17.0)
2 Ba[Cu(dtc-gln)] ₂ ·4H ₂ O	18.2(18.5)	2.9(3.1)	7.0(7.2)	16.7(16.4)
3 Ba[Cu ₂ (dtc-ser)] ₂ ·2H ₂ O	12.2(12.2)	1.4(1.5)	3.4(3.6)	31.3(32.4)
4 Ba[Cu ₂ (dtc-thr)] ₂ ·3H ₂ O	14.8(14.5)	1.9(2.2)	3.3(3.4)	29.1(30.6)
5 Ba[Cu ₂ (dtc-tyr)] ₂ ·3H ₂ O	24.0(25.1)	2.2(2.3)	2.7(2.9)	25.5(26.6)
6 Ba[Cu(dtc-pro)] ₂ ·3H ₂ O	21.1(22.2)	2.9(3.2)	4.1(4.4)	10.8(10.1)
7 [Cu(dtc-pro)] ₂ [Cu(en)(EtOH)(H ₂ O) ₃]	28.6(28.8)	4.8(5.1)	9.5(8.4)	19.8(19.1)

^a Calculated values in parentheses.

allowing determination of its structure by X-ray diffraction.

2. Experimental

2.1. Materials and methods

All amino acids were used in the L form and were purchased from Fluka. Other reagents (i.e. Ba(OH)₂, CS₂, Cu(NO₃)₂·3H₂O, CuCl₂·2H₂O) and the organic solvents were from Fluka (pa) as well. Chemical analyses for carbon, hydrogen and nitrogen were performed on a 2400 elemental analyser from Perkin–Elmer. Barium and copper were determined on an ICP spectrometer Perkin–Elmer model 2380 Plasma 2. IR spectra were recorded using KBr mulls and a Perkin–Elmer instrument. Electronic spectra were recorded in aqueous solution on Shimadzu UV-240 double beam and Hewlett–Packard 8452A diode spectrophotometers. The room temperature (r.t.) magnetic moment was measured by the Faraday method on a AZTEC DSM8 pendulum-type susceptometer and electron paramagnetic resonance spectra were recorded at X-band frequencies with a Bruker ER200D. The water content in the complexes was determined by thermal analysis using a Perkin–Elmer TGA-7 thermobalance and a DTA-7 differential thermal analysis apparatus, both operating at a heating rate of 5 °C min⁻¹ and under oxygen as the reaction atmosphere.

2.2. Preparation of the barium dithiocarbamates

The dithiocarbamate ligands have been prepared in the form of the barium salts through reaction of the corresponding amino acid with CS₂ in a basic medium (Ba(OH)₂), following the method described elsewhere [3]. The use of the barium salts permits larger yields (ca. 85%) than if sodium salts are used, due to their low solubility in ethanol. The general formula of the salts is Ba(dtc-a.a.)·H₂O, where a.a. stands for the amino acid; the existence of the crystallisation water molecule has been checked by thermogravimetric and differential

thermal analysis of the barium salts. These salts are very soluble in water, but insoluble in organic solvents.

2.3. Preparation of the copper complexes

The copper complexes have been prepared by direct reaction between the dithiocarbamate barium salts and soluble Cu(II) salts (nitrate or chloride), results being different depending on the precise nature of the amino acid (with an alcohol or an amide group, or proline). The method was as follows: 0.8 mmol of the dithiocarbamate are dissolved in 25 ml H₂O and dropwise added to a magnetically stirred solution containing 0.4 mmol Cu(II) soluble salt in 25 ml H₂O. For compounds 1–5 (see Table 1) the solution immediately darkens when addition starts, finally giving a dark brown precipitate, which is separated by filtration. Elemental chemical analysis results are given in Table 1; yields ranged between 40 and 45% in all cases.

The proline derived compound (6) behaves differently. The solution changes to a dark green colour and precipitation only takes place after strong concentration, by slow evaporation of water or in a vacuum dessicator; the yield was 70–75% in this case. Unfortunately, we failed to crystallise this compound, despite its solubility in water. However, well defined crystals were obtained upon addition of a second ligand, ethylenediamine (en), leading to formation of a mixed, more stable complex. This was obtained as follows: 2.2 mmol of the barium salt of the proline derived dithiocarbamate are dissolved in 25 ml H₂O; the solution is strongly magnetically stirred and 2.2 mol Cu, dissolved in 25 ml H₂O, and 2.2 mmol ethylenediamine are added. After completing the addition, a green precipitate is formed (compound 7), which is separated by filtration. After standing for 3 days at r.t., the supernatant liquid forms green, needle-like, crystals whose elemental chemical analysis data and FTIR spectrum coincide with those of the precipitate. It is worth noting the presence of an ethanol molecule in the composition of this compound as evidenced by X-ray diffraction (see below), which probably was present in the starting barium salt (precipitated in ethanol medium). The presence of crystal-

lisation water molecules has been checked in all cases by thermogravimetric and differential thermal analyses.

2.4. Crystal structure determination

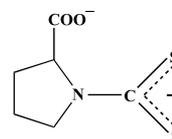
A dark green prismatic crystal of $[\text{Cu}(\text{en})(\text{EtOH})(\text{H}_2\text{O})_3][\text{Cu}(\text{dtc-pro})_2]$ was mounted on a glass fiber and used for data collection. Crystal data were collected at 291(2) K, using a Bruker SMART CCD 1000 diffractometer. Graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was used throughout. The data were processed with SAINT [11] and corrected for absorption using SADABS (transmissions factors: 1.000–0.573) [12]. The structure was solved by direct methods using the program SHELXS-97 [13] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [14]. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms of the anion and the copper atom of the cation, and isotropic displacement parameters for the other cation atoms. The cation atoms are disordered over two positions; the occupancy factor for each was initially refined, resulting in a value of 0.50(6) for each. Hydrogen atoms, except those bonded to oxygen atoms, were placed geometrically and positional parameters were refined using a riding model. Isotropic atomic displacement parameters for hydrogen atoms were constrained to be 1.2 (1.5 for methyl groups). Atomic scattering factors were obtained from ‘International Tables for X-ray Crystallography’ [15]. Molecular graphics were obtained from PLATON [16] and SCHAKAL [17]. A summary of the crystal data, experimental details and refinement results are listed in Table 2.

3. Results and discussion

Reaction of Cu(II) salts with dithiocarbamates derived from α -amino acids possessing alcohol or amide groups leads to reduction of the metal cation to Cu(I), probably through oxidation of the dithiocarbamate to the corresponding disulfide. An additional feature of the compounds prepared with serine, threonine and tyrosine arises from the presence of an alcohol group in their structures, which becomes deprotonated, thus providing a total formal charge of -3 to the corresponding ligands. However, such a reduction does not take place with the proline compound, a Cu(II) complex being formed. This result further confirms that the reduction ability of dithiocarbamates depends on the nature of the organic chain linked to the NCS_2^- moiety, as previously observed for some dithiocarbamate complexes of Mo [8,10]. Probably, the fact that the nitrogen atom belongs to the organic ring (Scheme 1) decreases its electron donor ability towards the sulfur atoms, thus decreasing their reducing ability.

Table 2
Crystal data and structure refinement for $[\text{Cu}(\text{en})(\text{EtOH})(\text{H}_2\text{O})_3][\text{Cu}(\text{dtc-pro})_2]$

Empirical formula	$\text{C}_{16}\text{H}_{34}\text{Cu}_2\text{N}_4\text{O}_8\text{S}_4$
Formula weight	665.79
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system	orthorhombic
Space group	$C222_1$ (No. 20)
Unit cell dimensions	
a (\AA)	6.560(2)
b (\AA)	28.384(9)
c (\AA)	14.927(4)
α ($^\circ$)	90
β ($^\circ$)	90
γ ($^\circ$)	90
V (\AA^3)	2779.3(14)
Z	4
Calculated density (Mg m^{-3})	1.591
Absorption coefficient (mm^{-1})	1.875
$F(000)$	1376
Crystal size (mm)	$0.43 \times 0.10 \times 0.03$
Theta range for data collection ($^\circ$)	1.98–28.08
Limiting indices	$-8 \leq h \leq 8, -36 \leq k \leq 26, -17 \leq l \leq 19$
Reflections collected/unique	8276/3243 [$R_{\text{int}} = 0.0945$]
Completeness to θ	28.08(%) 48.9
Absorption correction	SADABS
Max/min transmission	0.9459, 0.4993
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3243/0/154
Goodness-of-fit on F^2	0.974
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0914, wR_2 = 0.2032$
R indices (all data)	$R_1 = 0.1607, wR_2 = 0.2322$
Largest difference peak and hole (e \AA^{-3})	1.638 and -1.346



Scheme 1. Schematic representation of proline dithiocarbamate.

3.1. IR spectra

The positions of the main FT-IR bands recorded for all seven complexes synthesised are given in Table 3. The band close to 1490 cm^{-1} is due to the stretching of the C–N group of the NCS_2^- moiety; its position corresponds to a partial double bond character, and is recorded in the range previously reported for similar compounds [18,19]. The band designated as $\nu(\text{N–C}')$ in the table corresponds to the vibration of the two N–C bonds within the five members ring, and corresponds to single N–C bonds. The additional band at 1044 cm^{-1} in complex 7 is due to the ethylenediamine ligand.

The bands recorded in the region corresponding to the C–S vibrations are typical of a bidentate bonding of the dithiocarbamate unit to the metal cation [18,19], and

Table 3
Vibrational frequencies (cm^{-1}) for selected absorption bands in the IR spectra

Complex	$\nu(\text{C}-\text{N})$	$\nu(\text{N}-\text{C}')$	$\nu_{\text{as}}(\text{C}-\text{S})$	$\nu_{\text{s}}(\text{C}-\text{S})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\rho(\text{COO}^-)$	$\nu(\text{S}-\text{Cu})$
1 Ba[Cu(dtc-asn) ₂ ·4H ₂ O	1484	1112	927	622	1589	1396	548	337
2 Ba[Cu(dtc-gln) ₂ ·4H ₂ O	1488	1107	939	614	1577	1396	541	328
3 Ba[Cu ₂ (dtc-ser) ₂ ·2H ₂ O	1499	1172	928	609	1602	1385	556	326
4 Ba[Cu ₂ (dtc-thr) ₂ ·3H ₂ O	1498	1177	936	608	1606	1383	556	328
5 Ba[Cu ₂ (dtc-tyr) ₂ ·3H ₂ O	1513	1233	901	612	1609	1373	538	327
6 Ba[Cu(dtc-pro) ₂ ·3H ₂ O	1472	1164	940	659	1598	1382	487	345
7 [Cu(en)(EtOH)(H ₂ O) ₃][Cu(dtc-pro) ₂]	1489	1173	952	661	1598	1381	487	339
		1152						
		1044						

the vibration of the sulfur–copper bond gives rise to a band close to 330 cm^{-1} in all complexes synthesised [18–20]. The bands close to 1600 and 1390 cm^{-1} are due to the antisymmetric and symmetric vibrations of the carboxylate groups.

3.2. Crystal structure of [Cu(en)(EtOH)(H₂O)₃][Cu(dtc-pro)₂]

In addition to the other experimental data described above, X-ray diffraction for this complex shows both the cation and the anion are coordination compounds. Most significant structural parameters are given in Table 4 and the molecular structure of both ions are shown in Fig. 1(a and b).

As shown in this figure, the copper is coordinated by four sulfur atoms in the anion [Cu(dtc-pro)₂]²⁻, giving rise to a local symmetry of D_{2h} around the metallic site, as the SCS angles are lower than 90° (otherwise the local geometry would approach D_{4h}). The four Cu–S distances are almost coincident, as well as the C–S distances, thus confirming the bidentate nature of the dithiocarbamate ligand; actually, the C–S distances are close to 1.71 \AA , similar to the values previously reported for other dithiocarbamates [21], including the barium salt of glycine dithiocarbamate [22]. The C–N distance, 1.312 \AA , is also similar and in agreement with a marked double bond character. However, the –SCS– angle is about 6° smaller in the copper complex than in the glycine dithiocarbamate (as the barium salt), i.e. the angles become somewhat closed upon coordination to copper. Overall, the bond angles and bond distances are rather similar to those reported for Cu complexes with alkyldithiocarbamates [23].

In the other complex subunit, [Cu(en)(EtOH)(H₂O)₃]²⁺, Cu(II) is hexacoordinated, with a distorted octahedral symmetry. The aquo ligands stand in a *fac* symmetry, and two of the three water molecules are in the same plane as the nitrogen atoms of the ethylenediamine ligand; the oxygen atom of the third water molecule is 0.27 \AA further out than the other two, and

Table 4
Selected bond lengths (\AA) and angles ($^\circ$) for [Cu(en)(EtOH)(H₂O)₃][Cu(dtc-pro)₂]

Bond lengths	
Cu(1)–S(12)	2.293(2)
Cu(1)–S(12)#1	2.293(2)
Cu(1)–S(11)#1	2.308(3)
Cu(1)–S(11)	2.308(3)
Cu(2)–N(21)	1.795(15)
Cu(2)–O(22)	2.011(17)
Cu(2)–O(21)	2.024(17)
Cu(2)–N(22)	2.060(18)
Cu(2)–O(23)	2.392(16)
Cu(2)–O(31)	2.571(16)
S(11)–C(5)	1.724(9)
S(12)–C(5)	1.721(10)
N(1)–C(5)	1.312(11)
Bond angles	
S(12)–Cu(1)–S(12)#1	163.22(18)
S(12)–Cu(1)–S(11)#1	103.84(10)
S(12)#1–Cu(1)–S(11)#1	78.10(10)
S(12)–Cu(1)–S(11)	78.10(10)
S(12)#1–Cu(1)–S(11)	103.84(10)
S(11)#1–Cu(1)–S(11)	167.0(2)
N(21)–Cu(2)–O(22)	91.1(7)
N(21)–Cu(2)–O(21)	170.3(7)
O(22)–Cu(2)–O(21)	81.8(7)
N(21)–Cu(2)–N(22)	88.5(7)
O(22)–Cu(2)–N(22)	175.6(8)
O(21)–Cu(2)–N(22)	99.0(7)
N(21)–Cu(2)–O(23)	95.1(6)
O(22)–Cu(2)–O(23)	91.5(7)
O(21)–Cu(2)–O(23)	91.8(6)
N(22)–Cu(2)–O(23)	84.2(7)
N(21)–Cu(2)–O(31)	79.6(6)
O(22)–Cu(2)–O(31)	95.8(7)
O(21)–Cu(2)–O(31)	94.4(6)
N(22)–Cu(2)–O(31)	88.4(6)
O(23)–Cu(2)–O(31)	171.0(6)
S(12)–C(5)–S(11)	114.6(5)

Symmetry transformations used to generate equivalent atoms:
#1 $-x+2, y, -z+1/2$.

that of the ethanol molecule is even further out, probably because of the tetragonal distortion favoured for this configuration (d^9), according to the Jahn–Teller

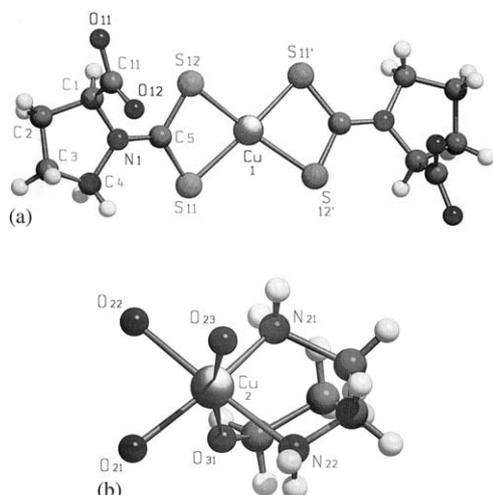


Fig. 1. Atomic structure and labelling scheme for (a) $[\text{Cu}(\text{dtc-pro})_2]^{2-}$ and (b) $[\text{Cu}(\text{en})(\text{EtOH})(\text{H}_2\text{O})_3]^{2+}$.

effect. The two Cu–N (from ethylenediamine) distances are also different, probably because of packing effects in the crystalline state and/or in order to minimise repulsions with the other ligands.

3.3. Electronic and ESR spectra

Compounds **1–5** are diamagnetic and do not show well defined bands in the visible region, but the absorption extends almost in all the visible range. On the contrary, the proline complexes show a broad, ill defined, absorption band centred at about 630 nm for compound **6** and at 615 nm for compound **7**, with an extinction coefficient of $100 \text{ M}^{-1} \text{ cm}^{-1}$, that should correspond to transits from lower energy levels to $dx^2 - y^2$ [24]. An additional band at 430 nm ($\epsilon = 3500 \text{ M}^{-1} \text{ cm}^{-1}$) is recorded for both complexes and can be assigned to a $S \rightarrow \text{Cu}$ charge transfer process. These two compounds are paramagnetic, the effective magnetic moments being 1.78 and 1.76 BM for complexes **6** and **7**, respectively, very close to the value calculated for the spin-only moment, 1.73 BM, thus suggesting only weak, if any, spin-orbit coupling [25]. Cu^{2+} possesses an orbitally non-degenerate ground state in the Jahn–Teller distorted polyhedra and hence essentially a spin-only magnetic moment; deviations are due to admixtures of very small orbital contributions of excited states via spin-orbit coupling.

The ESR spectra for both proline complexes are included in Fig. 2; no fine structure was observed in either case. That for compound **6** is axial, with ESR parameters deduced from simulation [26] of $g_{\parallel} = 2.09$, $g_{\perp} = 2.03$ and $g_o = 2.07$. The spectrum corresponding to compound **7** corresponds to a mixture of two Cu(II) ions (d^9 configuration) under two different surroundings, as it can be considered as being formed by two

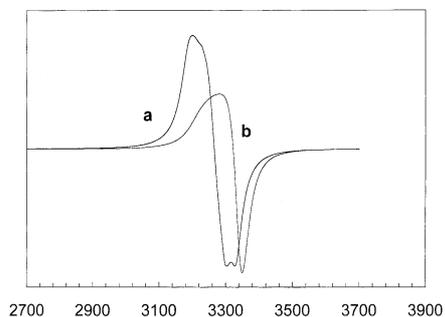


Fig. 2. Experimental polycrystalline X-band ESR spectra at 298 K of the copper complexes: (a) $[\text{Cu}(\text{en})(\text{EtOH})(\text{H}_2\text{O})_3][\text{Cu}(\text{dtc-pro})_2]$. (b) $\text{Ba}[\text{Cu}(\text{dtc-pro})_2] \cdot 3\text{H}_2\text{O}$.

axial quasi-isotropic spectra, unable to be simulated, with average values of $g_o = 2.08$ and 2.06 for both Cu atoms [25].

4. Supplementary material

Complete lists with atomic coordinates, anisotropic displacement parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre [CCDC 178510], 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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