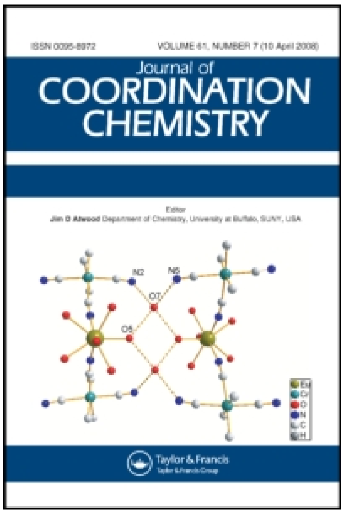

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DITHIOCARBAMATES DERIVED FROM NATURALLY OCCURING AMINO ACIDS AND THEIR COMPLEXES WITH NICKEL AND COPPER

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Dithiocarbamates of tryptophane (tryp), lysine (lys) and arginine (arg) have been synthetized by direct reaction of the corresponding amino acid with carbon sulphide in a basic medium. Barium salts isolated had formulae Ba(dtc tryp), Ba_3(dtc lys)$_2$ and Ba_3(dtc arg)$_2$. These dithiocarbamates react with nickel(II) salts forming square-planar complexes. However, reaction copper(II) salts leads to reduction to copper(I).

Keywords: Dithiocarbamates; amino acids; nickel; copper

INTRODUCTION

A very large number of coordination compounds with ligands where sulfur acts as the donor atom have been synthetized. One of the reasons for this interest has been the discovery of the existence of many biomolecules containing metal-sulfur linkages. Examples can be found in nickel enzymes,[1] copper proteins[2,3] or molybdenum enzymes.[4,5] However, it is noteworthy that the way sulfur bonds to these cations does not follow the same trend in all cases. Thus it would be interesting to design various specific ligands

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containing sulfur atoms as donors sites, as well as their coordination compounds.

In the present paper, we have prepared dithiocarbamates of three naturally occuring amino acids (tryptophane, lysine, and arginine) to obtain ligands in which the sulfur atoms in the ligands would interact in different ways with metal cations. Previous studies[6–8] concerning coordination compounds of dithiocarbamates formed with simpler amino acids have been used to understand the properties of the compounds prepared in this study.

EXPERIMENTAL

Materials and Methods

The starting amino acids *D,L*-tryptophan, *D,L*-lysine and *D,L*-arginine, and $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$, were purchased from Fluka. Chemical analyses for C, H, N were made on a 2400 Perkin Elmer instrument while Ba, Ni and Cu were determined using AAS (Perkin Elmer 2380). The magnetic study was performed by the Servicio de Magnetoquímica (Universidad de Barcelona), using a MANICS-DSM8 susceptometer. I.r. spectra were recorded in the $4000–275\,cm^{-1}$ range on a Perkin Elmer FT-IR 1730 instrument, using KBr discs. Electronic spectra were recorded on a Hewlett Packard 8452 A spectrophotometer.

Preparation of Dithiocarbamates

A method consisting in reacting the amino acid with carbon sulphide in a basic medium has been followed,[6] as follows: 50 mmol of tryptophane (80 mmol for lysine and arginine) were added to a saturated solution (55 mmol) of barium hydroxide; 60 mmol (110 mmol in the case of lysine and arginine) of carbon sulphide were added dropwise and the mixture stirred during 12 h. The resulting solution was concentrated on a rotary evaporator at 40°C to one third of the initial volume, solid impurities filtered off, and then one litre of absolute ethanol was added. A white precipitate immediately formed, which was filtered and dried over P_2O_5. The products obtained were very soluble in water, but insoluble in organic solvents. Purification to remove barium carbonate was achieved by dissolving the production in water and further precipitating with ethanol. The yield was close to 80% in all cases.

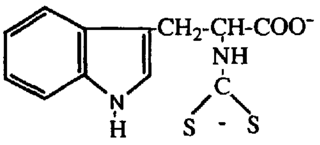
Preparation of the Complexes

Nickel complexes were prepared by direct reaction of the barium dithiocarbamates with dissolved nickel salts in different stoichiometric ratios. Ten cm^3 of a fresh tryptophane dithiocarbamate solution containing 8×10^{-4} mol, were slowly added dropwise to a stirred solution containing 4×10^{-4} mol of $NiCl_2 \cdot 6H_2O$ (8×10^{-4} mol for lysine and arginine) in $20\,cm^3$ of 0.1 M HCl (better results were obtained for the arginine derivative with 0.5 M HCl). Dark green precipitates were obtained with the tryptophane and lysine derivatives, while for the arginine derivative the precipitate was brown. The precipitates were filtered and washed three times with $5\,cm^3$ of 0.1 M HCl and two $5\,cm^3$ portions of distilled water, and were finally dried over P_2O_5. Yields ranged from 50% (arginine derivative) to 70% (lysine derivative).

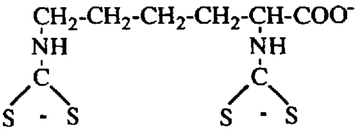
Copper complexes were prepared in a similar way, with a copper : dithiocarbamate ratio of 1 : 3 for tryptophane and 2 : 1 for lysine and arginine derivatives. Complexes obtained with the tryptophane and lysine derivatives were olive-green, and that with the arginine derivative dark brown; yields were 45–50%.

RESULTS AND DISCUSSION

Satisfactory analytical data were obtained for all compounds isolated. Empirical formulae for the barium salts were Ba(dtcaa) for aa = tryp and $Ba_3(dtcaa)_2$ (aa = lys, arg). Thus two carbon sulphide molecules were added to both arginine and lysine; for tryptophane only one molecule would be added. Corresponding formula are shown below.

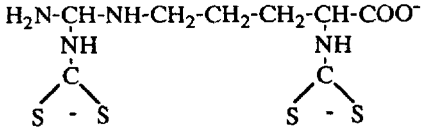


dtctrp



$\underset{\underset{\underset{S\;-\;S}{C}}{NH}}{CH_2}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{\underset{S\;-\;S}{C}}{NH}}{CH}\text{-}COO^-$

dtclys



$H_2N\text{-}\underset{\underset{\underset{S\;-\;S}{C}}{NH}}{CH}\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{\underset{S\;-\;S}{C}}{NH}}{CH}\text{-}COO^-$

dtcarg

Formation of the nickel and copper complexes follow a different pattern. The stoichiometry of the complexes was 1 : 2 for Ni : dtctryp and otherwise 1 : 1. However, the stoichiometry for the copper complexes was 1 : 1 for Cu : dtctryp and 2 : 1 for the other ligands. Bearing in mind the charge on these ligands, these results suggests a reduction from Cu(II) to Cu(I) upon reaction with the dithiocarbamate. Magnetic susceptibility measurements show that all complexes (Ni and Cu) are diamagnetic, suggesting square-planar geometry around the central metal cation for the Ni(II) complexes, and reduction of Cu(II) to Cu(I). For the latter with dtctrp the ligand shown above will be protonated for charge balance.

I.R. Spectra

The positions of the most relevant bands in the i.r. spectra of the complexes are given in Table I. A band close to 1500 cm^{-1} is recorded in all spectra, thus suggesting a multiple character for the C–N bond, probably because of electron delocalization in the dithiocarbamate group.[9–11] Although differences among the different spectra are not very large, this band shifts toward lower wavenumbers in the tryptophane compounds, due to electron withdrawal from the C–N bond by the aromatic rings. A band at 1650 cm^{-1} is recorded in the spectra of all arginine complexes (and also in the spectrum of the free amino acid), due to the CN double bond.

Bands due to the carboxylate group are also informative. In the case of the barium salts, two bands are recorded close to 1570 and 1400 cm^{-1}. The difference between the positions of these two bands suggests strong ionic character of the metal–ligand bond.[12] However, these bands are absent in the spectra of the nickel and copper complexes and instead a strong band is recorded close to 1720 cm^{-1}, characteristic of the carbonyl group, *i.e.*, this group does not participate in bonding to the metal cations; the ligand exists in the carboxylic acid form.

The positions of bands ascribed to metal–sulfur bonds[13,14] are also given in Table I. The values are slightly larger for the copper complexes than for the nickel ones, probably because of the lower oxidation state of the former.

Electronic Spectroscopy

A summary of data is given in Table II. Five bands are recorded in the ultraviolet range for the barium salts, which positions agree with those reported in the literature for similar compounds.[15,16] The two weaker bands recorded in the visible range for the nickel compounds can be related to *d–d*

TABLE I Characteristic I.R. bands of the ligands and their complexes (cm^{-1})

Compound	ν_{C-N}	$\nu_{C'-N}$	ν_{asC-S}	ν_{sC-S}	ν_{N-H}	ν_{asCOO^-}	ν_{sCOO^-}	$\nu_{C=O}$	$\nu_{C-O}+\delta_{O-H}$	ν_{M-S}
Ba(dtc tryp)	1474	1101	976	661	3403	1572	1407			
Ba_3(dtc lys)$_2$	1494	1145	955	661	3382	1568	1408			
Ba_3(dtc arg)$_2$	1485	1140	958	652	3328	1569	1407			
Ni(dtc tryp)$_2$	1510	1099	963	619	3304			1723	1386	385
Ni(dtc lys)	1520	1127	964	625	3231			1719	1397	383
Ni(dtc arg)	1510	1129	966	638	3176			1719	1398	381
Cu(dtc tryp)	1489	1097	954	609	3302			1719	1342	425
Cu_2(dtc lys)	1500	1121	911	610	3165			1719	1398	449
Cu_2(dtc arg)	1501	1102	939	607	3186			1720	1376	467

TABLE II Electronic spectroscopy data for the ligands and their complexes

Compound[a]	λ (nm)	*log* ϵ[b]	*Transition*
Ba dtc a.a.[c]	330–345	2.60–4.20	$n \rightarrow \pi$
	285–300	4.00–4.35	$\pi \rightarrow \pi^*$
	255–265	3.95–4.35	$\pi \rightarrow \pi^*$
	230–240	4.40–4.45	$\pi \rightarrow \pi^*$
	210–220	4.40–4.45	$\sigma \rightarrow \sigma^*$
Ni dtc a.a.[d]	636–650	1.73–1.92	$dx^2-y^2 \rightarrow dxy$
	480–495	2.10–2.20	$dz^2 \rightarrow dxy$
	380–388	3.66–3.71	$dxz,dyz \rightarrow \pi^*(L)$
	324–326	4.25–4.35	$\pi(L) \rightarrow \pi^*(L)$
	270–285	3.77–4.25	$\pi(L) \rightarrow \pi^*(L)$
Cu dtc a.a.[d]	424–432	2.75–3.49	$d \rightarrow \pi^*(L)$
	300–320	4.00–4.95	$\pi(L) \rightarrow \pi^*(L)$
	278–280	3.95–4.95	$\pi(L) \rightarrow \pi^*(L)$

[a] Here, a.a. represents the amino acids, tryptophane, lysine and arginine.
[b] Units are $M^{-1} cm^{-1}$.
[c] In water.
[d] In DMF.

transitions; the band close to 385 nm (slightly stronger) could be due to ligand to metal cation charge transfer and the two very intense bands in the ultraviolet range to transitions in the ligands. These results confirm square planar geometry for the nickel complexes.[6,17–19]

Finally, no medium intensity band is recorded in the visible region for the copper complexes, as expected if the metal ions have been reduced to the Cu(I), d^{10}, state. Only charge transfer bands, and others due to intraligand transitions are recorded.

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