



PS5.11 — TU

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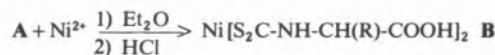
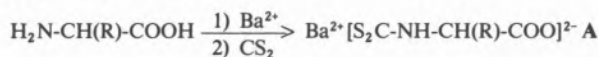
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### NEW NICKEL(II) COMPLEXES WITH DITHIOCARBAMATE-DERIVATIVES OF $\alpha$ -AMINOACIDS

Although little is known about the role of nickel *in vivo*, it has been recognized that it is essential in the growth of experimentation animals [1] and its deficiency impairs iron absorption, reducing the haemoglobin level; on the other hand, its ability in changing its coordination geometry ( $D_{4h}$ ,  $T_d$ ,  $O_h$ ) may make it important in a fine control over metabolic activity, and is also useful as a substituent for  $Mg^{2+}$  because of their close radii [2,3].

In an attempt to fathom its biochemistry, complexes formed by Ni(II) and dithiocarbamate derivatives of  $\alpha$ -aminoacids have been synthesized according to:



All reagents were from Fluka (*p.a.*) and were used without any further purification.

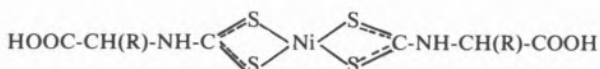
Synthesis of compounds **A** has been described elsewhere [4,5]. To obtain compounds **B**, an aqueous solution of  $NiCl_2 \cdot 6H_2O$  is dropwise added on **A** dissolved in  $H_2O$  ( $Ni:Ba = 1:2$  molar ratio). Addition of  $Et_2O$  and then  $HCl$  0.1 M

(stoichiometrically to yield  $BaCl_2$  formation) leads to extraction of compounds **B** in the organic phase. A fine olive-green powder is obtained after room temperature evaporation of  $Et_2O$ . The product is purified by recrystallization in  $Et_2O$  and acetone (final yield 70%). However, when glycine is used, if addition of  $HCl$  and  $Et_2O$  is not carried out, evaporation of water yields  $Ba[Ni(S_2C-NH-CH_2-COO)_2]$ , while decomposition products are obtained with alanine and 2-aminobutyric acid ( $R = Me, Et$ ).

Chemical analysis (C, H, N, S, Ni) data agree with the expected formula. Characterization of the complexes has been carried out by IR spectroscopy (KBr pellets, Beckman Acculab-10), UV-Vis spectroscopy (in  $H_2O$  or  $Et_2O$ , Shimadzu UV-240),  $^1H$  NMR (Hitachi Perkin-Elmer R-24B) and magnetic measurements (at room temperature, Stanton MC-5 Gouy-type balance).

Nickel(II) ( $d^8$ ) complexes may exhibit three different geometries: square planar ( $D_{4h}$ ), octahedral ( $O_h$ ) and tetrahedral ( $T_d$ ), the former being diamagnetic.

Compounds **B** are diamagnetic, and our IR results (see below) indicate the presence of free  $-COOH$  groups. With these results, the structure below can be suggested.



The main features of the IR spectra have been collected in the Table.

Table

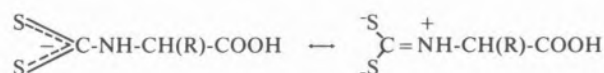
Compound	$\nu_{COOH}$	$\nu_{COO^-}$		$\nu_{CS}$	$\nu_{NiS}$
		$\nu_a$	$\nu_s$		
Ba(gly dtc)	—	1620(s)	1410(s)	620(m)	—
Ni(gly dtc) <sub>2</sub>	1700(s)	—	—	615(m)	380(w)
Ba[Ni(gly dtc) <sub>2</sub> ]	—	1580(s)	1410(s)	645(m)	380(w)
Ba(DL-ala dtc)	—	1615(s)	1405(s)	620(m)	—
Ni(DL-ala dtc) <sub>2</sub>	1700(s)	—	—	625(m)	370(w)
Ba(DL-2-am.but dtc)	—	1625(s)	1400(s)	635(m)	—
Ni(DL-2-am.but dtc) <sub>2</sub>	1695(s)	—	—	655(m)	370(w)

s = strong; m = medium; w = weak.

The  $\nu_a$  and  $\nu_s$  bands of the  $COO^-$  groups in the ligands (compounds **A**) have been recorded at 1625-

-1615  $\text{cm}^{-1}$  and 1410-1400  $\text{cm}^{-1}$ , respectively, while for compounds **B** only one band at 1700-1695  $\text{cm}^{-1}$ , due to  $\nu_{\text{CO}}$  in COOH groups, is recorded.  $\nu_{\text{NH}}$  and  $\nu_{\text{CN}}$  bands are recorded in both series of compounds **A** and **B** at the expected positions 3330-3270 and 1545-1500  $\text{cm}^{-1}$  and do not change significantly between each pair of compounds **A** and **B**, while the  $\nu_{\text{NiS}}$  band is recorded at 380-370  $\text{cm}^{-1}$ .

The position of the band corresponding to the  $\nu_{\text{CS}}$  vibration in dithiocarbamates has been a matter of controversy, and largely depends on the bond order in such a moiety. Taking into account the feasibility of a resonance of the type



(i.e., lowering the C-S bond order), BECK *et al.* [4] have ascribed to this vibration a band at ca. 630  $\text{cm}^{-1}$  in compounds similar to those studied here, although other authors argue that it is recorded around 1000  $\text{cm}^{-1}$  [6].

*Electronic spectra* of compounds **A** show three very intense bands at 205, 250 and 275 nm. For compounds **B**, bands are recorded at  $\nu_1 = 230$  nm (broad, sometimes splitted) and  $\nu_2 = 320$  nm ( $\epsilon = 8000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  in both cases), with lower intensity bands at  $\nu_3 = 390$  nm ( $\epsilon = 1800$ ),  $\nu_4 = 480$ -475 nm ( $\epsilon = 20$ ) and  $\nu_5 = 640$ -630 nm ( $\epsilon = 30$ ).

Bands  $\nu_1$  and  $\nu_2$  should be originated by intra-ligand transitions, and the shift observed if compared with those of the free ligands may be originated by electronic effects. Bands  $\nu_4$  and  $\nu_5$  are due to d-d transitions (Laporte-forbidden), while band  $\nu_3$  is M-L charge transfer in origin [7].

For  $d^8$  systems in  $D_{4h}$  geometry three spin allowed, Laporte forbidden bands are expected, corresponding to transitions  $E_g(xz, yz) \rightarrow B_{1g}(x^2 - y^2)$ ,  $A_{1g}(z^2) \rightarrow B_{1g}(x^2 - y^2)$  and  $B_{2g}(xy) \rightarrow B_{1g}(x^2 - y^2)$ . Taking into account that the ligands are bidentate, the symmetry would be  $D_{2h}$  and band splitting is expected, although usually a mere broadening of the band is observed.

The lowest energy d-d transition is usually recorded above 1000 nm, and so, bands  $\nu_4$  and  $\nu_5$  at 480-475 and 640-630 nm may be ascribed to transitions  $A_{1g} \rightarrow B_{1g}$  and  $E_g \rightarrow B_{1g}$ , respectively.

Finally,  $^1\text{H}$  NMR spectra coincide with those expected for the formula above depicted. A structural (X-ray diffraction) determination of glycine-compounds **A** and **B** is under progress.

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PS5.12 — TH

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## PREFERENTIAL CATALYSIS OF MODEL REACTIONS IN THE COBALT(III) COMPLEX OF THE VITAMIN B-6 SCHIFF BASE OF GLYCINE

Vitamin B-6 is an essential cofactor to a large number of enzymes which catalyze many diverse reactions of amino acids. The heterocyclic aldehyde, pyridoxal is one of the forms of the cofactor. It has been recognized for many years that pyri-