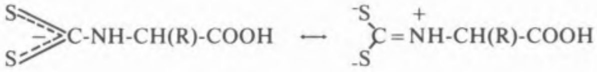
-1615 cm^{-1} and 1410-1400 cm^{-1}, respectively, while for compounds **B** only one band at 1700-1695 cm^{-1}, due to ν_{CO} in COOH groups, is recorded. ν_{NH} and ν_{CN} bands are recorded in both series of compounds **A** and **B** at the expected positions 3330-3270 and 1545-1500 cm^{-1} and do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

The position of the band corresponding to the ν_{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 cm^{-1} in compounds similar to those studied here, although other authors argue that it is recorded around 1000 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 ($\epsilon = 8000$ $dm^3mol^{-1}cm^{-1}$ 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 ν_1 and ν_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 ν_4 and ν_5 are due to d-d transitions (Laporte-forbidden), while band ν_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 ν_4 and ν_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, *^1H 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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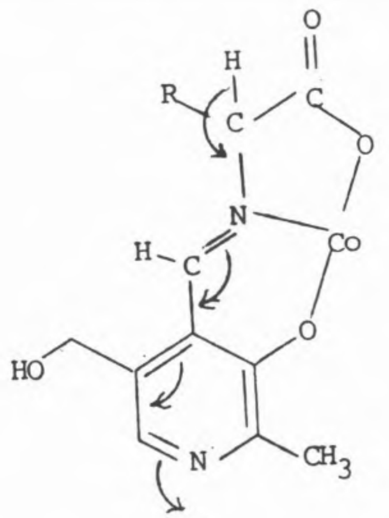
PREFERENTIAL CATALYSIS OF MODEL REACTIONS IN THE COBALT(III) COMPLEX OF THE VITAMIN B-6 SCHIFF BASE OF GLYCINE

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 pyridoxal can catalyze non-enzymic reactions of amino acids and that these reactions are often subject to strong additional catalysis by metal ions [1]. Such model reactions have provided a wealth of mechanistic information which has been of great assistance in determining the mechanism of the enzymic reactions.

The vitamin B-6 catalyzed reactions are based on transformations of a schiff base formed from the amino acid and pyridoxal. They occur through electron shifts cleaving a substituent to the amino acid α-carbon atom as illustrated in I.



I

Dunathan has suggested that selective catalysis of bond breaking at the amino acid will occur when the bond to be broken is oriented so that it best overlaps with the π orbital terminating at the azomethine nitrogen [2].

Using amino acid glycine, it is possible to synthesize cobalt(III) complexes of vitamin B-6 schiff bases which can be used to test Dunathan's hypothesis and determine the magnitude of catalysis resulting from the proper orientation of the bond to be broken [3]. The complex tetramethylammonium bis(pyridoxylideneglycinato)cobaltate(III) has been synthesized and its structure determined by X-ray crystallographic methods. The complex crystallizes in a triclinic unit cell and belongs to the space group $P\overline{1}$. 3,007 reflections were collected. The position of the cobalt ion was revealed by a Patterson synthesis and the positions of all non-hydrogen atoms were determined by least squares refinement. With anisotropic thermal parameters for all non-hydrogen atoms, the structure refined to an R value of 0.117. The magnitude of the R values is a consequence of disorder associated with the tetramethylammonium cation and from hydrogen bonding involving the waters of crystallization. The standard deviations of the bond lengths and angles are quite satisfactory and agree closely for the two independent but identical ligands. Formula I illustrates the coordination of the cobalt ion by one of two ligands. Complete crystallographic data are available upon request from the author.

The structure reveals a distortion of the chelate rings which renders the glycine protons strongly non-equivalent and places them at different dihedral angles with respect to the azomethine π system. The distortion is illustrated in fig. 1.

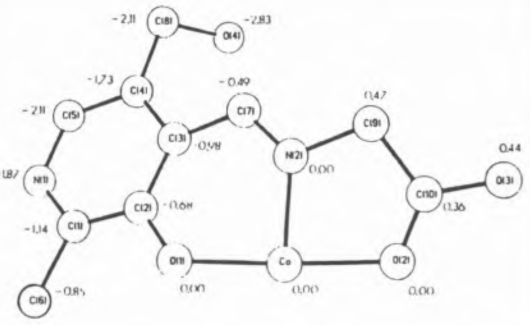


Fig. 1

Location of ligand atoms with respect to the plane determined by the cobalt ion and the atoms coordinated to it. Distances are in angstroms. C-9 is the α-carbon atom of the amino acid. This is a partial structure

Different dihedral angles for the two methylene protons is supported by their different four-bond, pseudoallylic NMR coupling to the proton on the azomethine carbon atom. Values of 1.95 Hz and 1.17 Hz are observed.

Chemically, there is an important consequence of the non-equivalence of the methylene protons on the amino acid α-carbon atom. The rates of deuteration were measured for these two protons as a mean for evaluating the kinetic differences in breaking each bond. The carbon-hydrogen bond which best overlaps the π orbital of the azomethine nitrogen is the one most easily broken. For the fast proton $\Delta H^{\neq}=9.9$ Kcal/M and $\Delta S^{\neq}=-28$ eu. For the slower reacting proton $\Delta H^{\neq}=14.5$ Kcal/M and $\Delta S^{\neq}=-17$ eu. This shows that the stereochemistry of the schiff base plays an important role in the reactivity of the amino acid substituents and that proper orientation of the bond to be broken results in a lower barrier for the reaction and shows how the enzyme might bring about its rapid rates of reaction.

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PS5.13 — MO

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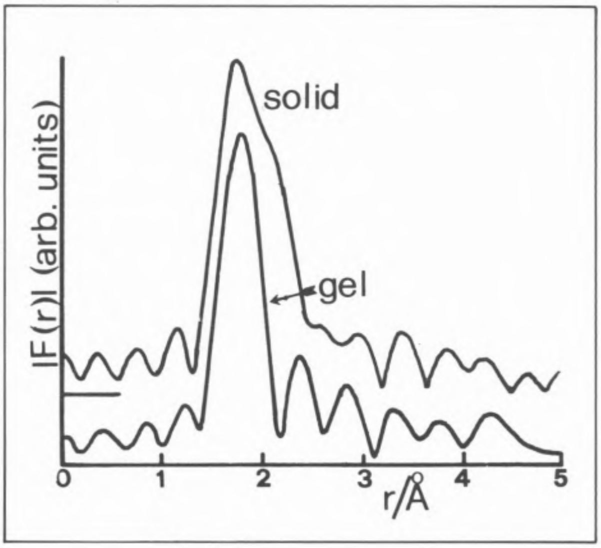
EXAFS STUDIES OF GEL AND SOLID FORMS OF Ca^{2+}-α-D-POLYGALACTURONATE

Knowledge of the structural assemblies involved in the biologically important Ca^{2+} polysaccharides is still fragmentary. We have measured the EXAFS spectra of the gel and solid forms of Ca^{2+}-α-D-polygalacturonate, the major intercellular component of deacetylated pectin [1]. Calcium ascorbate dihydrate and the 2-keto-D-gluconate were used as model compounds [2]. Filtered Fourier transforms of the extracted EXAFS (widest common k range possible; k^3-weighted; not phase-shift corrected) are shown in the figure.



The first shell peak is clearly different in the two materials, *i.e.* the Ca-O bond distance distributions differ. The gel gives a well-defined peak, whereas the solid has a shoulder at higher Ca-O distance. (EXAFS of the models confirm that an asymmetry can be identified when the spread of Ca-O bond distances is at least 0.2 Å, as in the 2-keto-D-gluconate).

Further structure is visible out to 3.5 Å, and is again different in the two forms. Full parameter fits are in course and should provide information on the possible 2_1 and 3_1 configurations put forward in the literature [3].

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