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Mixed Complexes of Aminoacids with Transition Metals.

I. Preparation and Characterization of the New Mixed Complex Cu^{II}(L-Tryptophanate)(DL-Methioninate)·$1.5H_2O$

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Introduction

The study of the compounds formed by ions of transition metals with aminoacids is of great interest, since these compounds can be used as models of metal–protein interaction. Moreover, some of them possess biological activity.

While simple complexes formed by copper and aminoacids have been amply studied, mixed ligand complexes are not so well known. Laurie [1] reported the preparation and properties of complexes of the type [CuAB] in which A is acetylacetone, salicylaldehyde, oxin, *etc.* and B an 'aromatic' aminoacid. Freeman *et al.* [2] determined the structure of the mixed complex Cu(histidinate)(threoninate) by X-Ray diffraction.

Till now few systems containing Cu–tryptophanate have been described [3]. This has prompted us to investigate mixed complexes of the type Cu(L-Trp)(aminoacid). In this paper we describe for the first time the preparation and characterization of the complex Cu(L-Tryptophanate)(DL-Methioninate) (abbreviated Cu(L-Trp)(DL-Met)) and study it comparatively with the simple complexes Cu(L-Trp)$_2$ and Cu(DL-Met)$_2$.

Experimental

Synthesis

An aqueous solution containing 0.0025 mol of L-tryptophane, 0.0025 mol of DL-methionine and a few drops of HCl was added slowly to another aqueous solution containing 0.0025 mol of copper acetate. The resulting intense blue mixture was shaken at a temperature of 50 °C for 1 hr. 0.1 N NaOH was then carefully added to pH = 6. The solution was left standing for several hours, and the deposit formed was filtered and washed, first with hot water and then with a mixture of EtOH/cold acetone. The product was taken to dryness in a current of dry air and in a vacuum desiccator using P_4O_{10}.

The bright blue product is not very soluble in water or in normal organic solvents. It is slightly soluble in DMSO. All attempts to obtain crystals for X-ray diffraction were unsuccessful, so the study was carried out with samples in powder form. The complexes Cu(L-Trp)$_2$ and Cu(DL-Met)$_2$ were prepared by methods previously described [4, 6]. Crystals of the simple complex Cu(L-Trp)$_2$ could not be obtained.

Analysis

The Cu was determined by gravimetry and the C, H, N with a Carlo Erba Mod. 1102 automatic analyser. Calcd. for $Cu(C_{11}H_{11}N_2O_2)(C_5H_{10}NO_2S)\cdot 1.5H_2O$: Cu, 14.38; C, 43.48; H, 5.47; N, 9.51. Found: Cu, 14.78; C, 43.59; H, 5.31; N, 9.48.

Physical Measurements

The powder diffractograms of the compounds were carried out in a Philips X-ray diffractometer PW 1720 using $CuK_{\alpha 1}$ (λ = 1.5405 Å). Cr_2O_3 was used as the external reference in the correction of the angular positions of the reflections observed in the diffractograms. The densities were measured by the picnometric method.

The infrared spectra of the products were obtained with a Perkin Elmer Mod. 457 in KBr pellets in the 4000–250 cm^{-1} spectral range.

The visible–ultraviolet spectrum was recorded with a Beckman DU-2 spectrophotometer. The sample was dispersed in $BaSO_4$ (diffuse reflectance).

Magnetic susceptibility measurements were taken at room temperature by the Gouy method with $Hg(Co(SCN)_4)$ as the calibrating substance.

Mass spectra were recorded on a VG Micromass ZAB-2F spectrometer. Ionization voltage was 70 eV and the temperature 453 K. The samples were introduced directly into the ionization chamber.

Results and Discussion

From the results obtained by Laurie [1] on mixed-ligand complexes of Cu(II) with bidentate ligands, it is inferred that in order to be stable these complexes must be similar: first, overall acid dissociation constants of the ligands; second, formation constants and solubility product of the simple complexes. Another important factor must be the value of the formation constant of the mixed complex.

In accordance with the above the system Cu(L-Trp)(DL-Met) should be expected to be stable, considering the similarity of the acid dissociation constants of the ligands and formation constants of the simple complexes [5].

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TABLE I. Crystal Data.

Molecular formula	$Cu(DL\text{-}Met)_2$	$Cu(L\text{-}Trp)_2$	$Cu(L\text{-}Trp)(DL\text{-}Met)\cdot 1.5H_2O$
Crystal system	Monoclinic	Monoclinic	Triclinic
Cell dimensions *a*, Å	9.482(5)	10.113(9)	8.729(5)
b, Å	5.018(4)	4.673(2)	6.502(9)
c, Å	16.035(13)	20.206(6)	16.818(2)
α deg.			89.42
β deg.	93.78(4)	84.50	98.36
γ deg.			102.09
V, Å^3	761.3	950.65	923.41
Z	2	2	2
Reliability index M_{20}	–	12.4	11.5
Calculated density	1.57	1.64	1.59
Observed density (g/cm^3)	1.60	1.61	1.61

TABLE II. Magnetic Data.

Compound	T K	χ_M 10^3 cgsu	μ_{eff} (BM)	Ref.
$Cu(DL\text{-}Met)_2$	270	1.67	1.90	6
$Cu(L\text{-}Trp)_2$	290	1.47	1.85	This work
$Cu(L\text{-}Trp)(DL\text{-}Met)\cdot 1.5H_2O$	298	1.71	2.02	This work

χ_M includes diamagnetic corrections. μ_{eff} calculated by the relationship $\mu_{eff} = 2.828\,(\chi_M \cdot T)^{1/2}$.

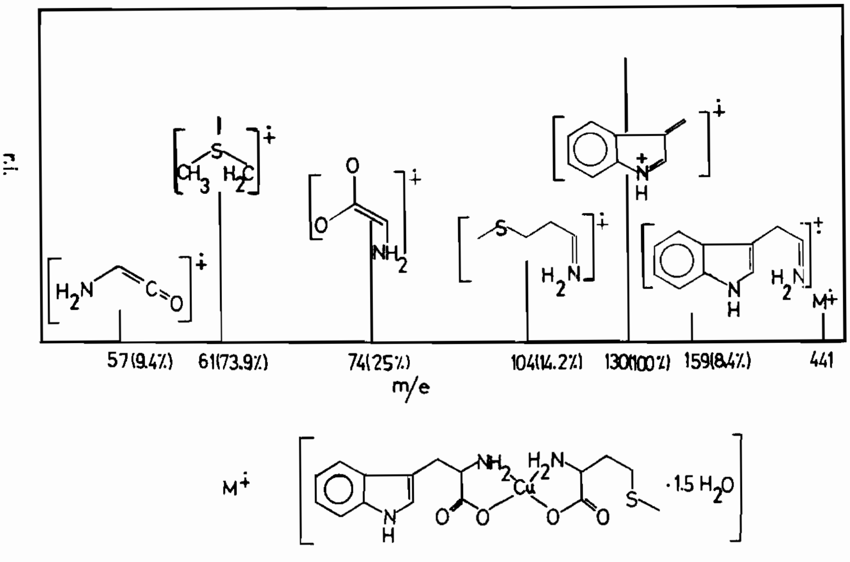

Fig. 1. Mass spectrum of compound $Cu(L\text{-}Trp)(DL\text{-}Met)\cdot 1.5H_2O$ (schematic).

Furthermore, both complexes $Cu(L\text{-}Trp)_2$ and $Cu(DL\text{-}Met)_2$ show similar solubility in water, the complex Cu(L-Trp)(DL-Met) being less soluble. Therefore it is expected that the mixed complex can be prepared free of impurities of simple complexes.

The X-ray powder diagram of the mixed complex does not show the peaks of the simple complexes or the free ligands. The diagrams of the mixed complex and of the complex $Cu(L\text{-}trp)_2$ were interpreted following the method of de Wolff [7]. Reliability indices M_{20} [8, 9] were always above 10. The dimensions of the unit cell were refined by least squares. The results obtained are shown in Table I. The data referring to the complex Cu(DL-Met)$_2$ have been taken from reference [6].

The infrared spectrum of the mixed complex is different from that of the simple complexes, but infrared spectroscopy is not appropriate for distinguishing between Cu(L-Trp)(DL-Met) and a mixture of Cu(L-Trp)$_2$ and Cu(DL-Met)$_2$. The infrared spectrum of Cu(L-Trp)(DL-Met) shows bands at 3240, 3130 and 2910 cm^{-1} corresponding to the NH$_2$ group of the ligands and indicates the coordination of this group to the metal. The band at 3400 cm^{-1} characteristic of the stretching vibration N–H of the indol group appears broadened by the presence of water in the compound.

The antisymmetric vibration of the group COO$^-$ is observed at 1600 cm^{-1}, near that at which water absorbs, and the symmetric vibration of the same group appears at 1396 cm^{-1}. This gives a value of $\Delta\nu = \nu_a - \nu_s = 204$ cm^{-1}, higher than that of the free ligands (175 cm^{-1} for L-tryptophane and 172 cm^{-1} for DL-methionine) and intermediate with regard to the simple complexes (184 cm^{-1} for the complex Cu(L-Trp)$_2$ and 214 cm^{-1} for the complex Cu(DL-Met)$_2$), indicating the monodentate nature of the carboxylate group in the mixed complex [10]. The monodentate carboxylate group is found in the complex Cu(L-Met)$_2$, whose structure is known [5], and in the complex Cu(DL-Met)$_2$ a similar behaviour is expected, considering the similarity between the infrared spectra of both complexes.

On the other hand, the stretching vibration C–S is found in the region 600–700 cm^{-1}. This band cannot be identified in the methionine or in its complexes due to the existence of other groups which absorb in the same zone of the spectrum. However, the fact that the bending vibration of the S–CH$_3$ group which appears around 1330 cm^{-1} coincides in the DL-methionine and in the complexes Cu(DL-Met)$_2$ and Cu(L-Trp)(DL-Met)·1.5H$_2$O affords indirect evidence that the sulphur atom is not involved in the coordination.

The absorptions at 480 and 335 cm^{-1} are tentatively assigned to the modes Cu–N and Cu–O, respectively. These vibrations are normally of a mixed character and do not permit the accurate deduction of the *cis* or *trans* structure of the complex.

The magnetic data are given in Table II and include the simple complexes for comparative reasons. The value obtained of the magnetic moment for the compound Cu(L-Trp)(DL-Met)·1.5H$_2$O indicates a normal behaviour at room temperature, as observed in the complexes Cu(L-Trp)$_2$ and Cu(DL-Met)$_2$.

The diffuse reflectance spectrum shows a broad band at 800–830 nm characteristic of the existence of a Jahn–Teller distortion.

Finally, the mass spectrum of the complex with the most important peaks is represented in Fig. 1 with its assignments. The peak at m/e 441 (0.4%) corresponds to the molecular ion M$^+$ of the complex. The spectrum shows peaks corresponding to L-Trp and DL-Met which can also be observed in the complexes Cu(L-Trp)$_2$ and Cu(DL-Met)$_2$, respectively, while the peaks of the molecular ions of the simple complexes are not to be found.

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