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INTERMEDIATE SPECIES ABSORBING IN THE 500-nm REGION IN METAL ION MEDIATED NONENZYMATIC TRANSAMINATION*

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A key step in the action of almost all pyridoxal enzymes is the formation of a quinonoid species, in which the α-carbon in a Schiff base (aldimine) is deprotonated. Several enzymes have been reported to exhibit an intense absorption band in the 500-nm region of the spectrum, which has been ascribed to the species. We reported previously that in methanolic solutions pyridoxal (PL) and ethyl alaninate with Al (III) gave an intense absorption band at the 500-nm region and the species should serve as a model of the enzymatic intermediate.

We now report that the 500-nm species were observable with divalent transition ions. The species was formed in the isomerization between the ketimine from ethyl pyruvate and pyridoxamine (PM) and the aldimine from ethyl alaninate and PL catalyzed by the 1:1 Cu (II) chelates of ethylenediamine (en), dipyridyl (dipy) and tripyridyl (tripy). The species was hardly observable without the di- or tridentate ligands such as en. The quinonoid species were stabilized in the ternary complexes such as Cu (II) -quinonoid-en. The ternary complex was formed with a planar tridentate ligand, tripy, but a similar ternary complex was hardly formed with diethylenetriamine (dien). The fact should indicate the coplanarity of the quinonoid species. Tripy is a tridentate planar ligand, while dien is tridentate and coordinates with Cu (II) mostly in a nonplanar form.

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