A New Type of Isomerism among Coordination Compounds

Yasuo NAKAO, Shôichi SASAKI, Ken-ichi SAKURAI and Akitsugu NAKAHARA
Institute of Chemistry, College of General Education, Osaka University, Toyonaka

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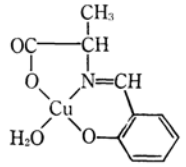
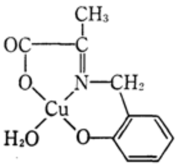
The copper(II) chelates of the Schiff bases derived from α-alanine and salicylaldehyde, I, and from pyruvic acid and salicylamine, II, have been newly-prepared in the crystalline state in this laboratory. Since the structures of the two chelates are very much alike in many respects, it is of interest to determine the delicate differences in their properties. A comparison of their properties may also be significant for an investigation of the non-enzymatic transamination reaction in which a metal ion plays an important role, because the relationship between the two chelates is similar to that between the well-known metal-pyridoxal-alaninate- and the metal-pyridox-amine-pyruvate-chelate.(1)



I



II

The chelates, I and II, isolated in the crystalline state revealed similar but distinctly different infrared spectra and X-ray powder diffraction patterns. The electronic spectra and the polarograms of aqueous solutions of the two chelates also displayed significant differences, as Table 1 indicates. Further, it was disclosed by an amino acid analyzer that a slight but appreciable transamination reaction from II to I occurs, even in a freshly-prepared solution at room temperature.

The results of elemental analyses of the two chelates are listed in Table 1. The I chelate appears blue-green or dark-green, like salicylideneglycinatoaquocopper(II),(2) and decomposes at 210°C, while the II chelate appears yellow-green or light-green and decomposes at 205°C. The II chelate is much less soluble than the I chelate in water, although both the chelates are considerably soluble in dimethylsulfoxide.

The light absorptions of the two chelates are greatly different from one another in the ultraviolet region, whereas they differ only slightly as to the ligand field band. This may suggest that there is a close resemblance between the two chelates, in spite of the quite different electronic states of the respective ligands. This may reasonably be explained by taking into account the fact that the donor atoms around copper(II) are exactly the same in both the chelates and that the location of the $\rangle$C=N– double bond allows the completion of the conjugate system in I, but not in II.

Although many types of isomerism among coordination compounds have been known, none of them always precisely describes the present kind of isomerism. Thus we want to propose a new term, "*fused chelate ring isomerism,*" though the respective Schiff base ligands of the two chelates belong to a type of isomerism quite familiar in organic chemistry.

TABLE 1. THE COMPARISONS BETWEEN THE CHELATES I AND II

Chelate		Elemental analysis			Absorption maximum*1		Half-wave potential *vs.* SCE at 25°C*2	
		C	H	N			Cu^{2+}	$\rangle$C=N–
I	*3 F.	40.90	4.24	5.05	ν_{max}	45.1	−0.28V	−1.4V
	C.	41.31	4.47	4.82	$\log \varepsilon_{max}$	1.93		
II	*3 F.	39.18	5.27	4.17	ν_{max}	44.5	−0.22V	−1.01V −1.29V
	C.	38.90	4.86	4.54	$\log \varepsilon_{max}$	1.96		

*1 ν_{max} in 10^{13} sec^{-1}

*2 Supporting electrolyte, 0.1 M KNO_3; Maximum suppressor, methylred; All reductions were irreversible.

*3 F., Found; C., Calcd for monohydrate of I and dihydrate of II, respectively.

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1) D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **74**, 979 (1952); D. E. Metzler, M. Ikawa and E. E. Snell, *ibid.*, **76**, 648 (1954).

2) A. Nakahara, This Bulletin, **32**, 1195 (1959).