Inorganica Chimica Acta, 8 (1974) 29–32

Preparation and Properties of Copper(II) Complexes with Schiff Bases Obtained from Pyridoxal and Amines

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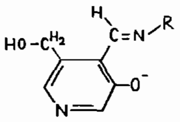
Received June 14, 1973

With Schiff bases obtained from pyridoxal and various amines (RNH_2) and glycine, many new copper(II) complexes were isolated as crystals. The 1:2 type complexes were obtained with $R = CH_3$, C_2H_5, $n\text{–}C_3H_7$, $n\text{–}C_4H_9$, $CH_2CH(CH_3)_2$, $i\text{–}C_3H_7$, $t\text{–}C_4H_9$, *Ph*, $2{,}6\text{–}(CH_3)_2\text{–}Ph$ *and* $2{,}6\text{–}(C_2H_5)_2\text{–}Ph$, *Ph being a phenyl group. They are square-planar, except for the compound with* $R = t\text{–}C_4H_9$, *wihch has a configuration distorted from the planar one. The 1:1 type complexes were obtained with* $R = CH_2CH_2O$, $n\text{–}(CH_2)_3O$ *and* CH_3COO. *The first two presumably have a multinuclear structure, while the third is uninuclear, the Schiff base acting as a terdentate ligand. The results are discussed in comparison with those of the copper(II) salicylaldiminates.*

Introduction

Extensive studies have so far been carried out about metal complexes with Schiff bases obtained from salicylaldehyde derivatives and various amines, RNH_2. Pyridoxal, which bears some resemblance to salicylaldehyde, also reacts with various amines and aminoacids to form Schiff bases (abbreviated as Pdx-R, I) and plays an important part in some enzymatic reactions in the presence of metal ions.[1]



(I)

Although the interaction of these Schiff bases with metal ions has been extensively studied in solution, the detailed characterization of the metal chelates.[2,3] The study of this sort is expected to yield information of fundamental significance even in discussing the precise mechanism of reaction in the presence of pyridoxal and the metal ions, as well as in elucidating the interaction of the metal ions with the Schiff bases obtained from pyridoxal.

The present paper describes preparation and characterization of their copper(II) complexes.

Experimental

Materials

Bis(N-alkyl- and bis(N-aryl-pyridoxaldiminato)copper(II)

A solution of pyridoxal hydrochloride (0.022 mole) and an appropriate amine (0.022 mole) in ethanol (20 ml) was heated with stirring for about ten minutes on a water-bath at about 50°. To the resulting solution were added potassium ethoxide (0.04 mole) and copper acetate (0.01 mole), and the mixture was heated with stirring at about 50° for a few hours. A precipitate obtained was filtered and recrystallized from methanol or ethanol to give pure crystals of the compound. Analytical data of the complexes prepared are shown in Table I. They are soluble in methanol, ethanol and chloroform, although the solubility is not high, and insoluble in water, benzene and acetone.

In the method described above, free pyridoxal may be used instead of the combination of pyridoxal hydrochloride and potassium ethoxide. This was successful particularly for the preparation of the N-methyl- and the N-carboxymethyl-complexes *(vide infra).*

N-Ethoxy- and N-n-propoxy-pyridoxaldiminato-copper(II)

The two complexes were synthesized in a similar manner to that described above, except that sodium acetate was employed instead of potassium ethoxide, using 0.02 mole of copper acetate. Green crystals were obtained. These two complexes are insoluble in common solvents, and recrystallization was not carried out. However, they are crystalline and no impurity was recognized, when viewed under the microscope.

TABLE I. Analytical data of bis(N-alkyl- and bis(N-aryl-pyridoxaldiminato)copper(II) complexes, $Cu(Pdx\text{-}R)_2$.

R	Calc., %			Found, %			Colour
	C	H	N	C	H	N	
CH_3	51.24	5.26	13.28	51.49	5.22	13.36	green
C_2H_5	53.38	5.82	12.45	53.24	5.73	12.68	green
$n\text{-}C_3H_7$	55.27	6.33	11.72	55.16	6.41	11.49	green
$i\text{-}C_3H_7$	55.27	6.33	11.72	54.73	6.58	11.54	green
$n\text{-}C_4H_9$	56.97	6.77	11.07	56.41	6.84	10.88	green
$CH_2CH(CH_3)_2$	56.97	6.77	11.07	56.34	6.91	10.69	green
$t\text{-}C_4H_9$	56.97	6.77	11.07	57.11	6.86	10.75	gr-br[a]
Ph[b]	59.61	5.00	9.94	60.10	4.51	9.56	gr-br
$2,6\text{-}(CH_3)_2\text{–}Ph$[b]	61.97	5.85	9.03	61.89	5.31	8.92	gr-br
$2,6\text{-}(C_2H_5)_2\text{–}Ph$[b]	65.68	6.43	8.51	65.73	6.45	8.89	gr-br

[a] gr-br: greenish brown. [b] monohydrate.

Analysis for $Cu(Pdx\text{–}CH_2CH_2O)$. Calcd.: C, 44.19; H, 4.45; N, 10.31%. Found: C, 43.59; H, 4.45; N, 10.11%.

Analysis for $Cu(Pdx\text{-}CH_2CH_2CH_2O)\cdot 3/4\ H_2O$. Calcd.: C, 44.29; H, 5.24; N, 9.39%. Found: C, 45.18; H, 5.78; N, 9.24%.

N-Carboxymethylpyridoxaldiminatoaquocopper(II)

This complex was obtained as green crystals by the general method described above. The crystals were washed several times with ethanol. The complex is insoluble in water and common organic solvents.

Analysis for $Cu(Pdx\text{–}CH_2COO)\cdot H_2O$. Calcd.: C, 39.54; H, 3.98; N, 9.22% Found: C, 38.74; H, 3.55; N, 9.12%.

Measurements

Electronic absorption spectra of the complexes in solution and in the solid state were recorded on a Hitachi EPS–4T and a Hitachi EPU–2 spectrophotometer.

Magnetic measurements were carried out by the Gouy method at room temperature using $CoHg(SCN)_4$ as a calibrant.

Infrared spectra were measured in Nujol mulls on a Hitachi EPI–C–2 IR spectrophotometer.

Results and Discussion

As shown in Table I, the 1:2 type complexes were obtained as crystals for R = alkyl and aryl groups. For R = n-alkyl and $CH_2CH(CH_3)_2$, the complexes of the type $Cu(Pdx\text{-}R)_2$ show spectra, which are similar to each other and also to the spectra of the corresponding salicylaldiminatocomplexes.[4,5] Some of the typical data are shown in Fig. 1. Their first d–d bands are located in the frequency region almost as high as, or slightly higher than, those of the N-alkyl-salicylaldiminatocopper(II) complexes. It is considered, therefore, that these copper(II) complexes may have an essentially planar configuration, their ligand field being only slightly stronger than that of the salicylaldiminates.

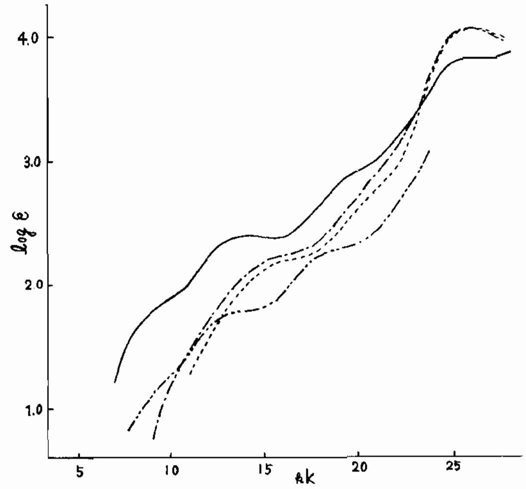


Figure 1. Electronic absorption spectra of $Cu(Pdx\text{-}R)_2$: 1, R = $n\text{-}C_3H_7$, in $CHCl_3$ (------); 2, R = $t\text{-}C_4H_9$, in $CHCl_3$ (——); 3, R = $i\text{-}C_3H_7$, in $CHCl_3$ (—-—); 4, R = $i\text{-}C_3H_7$, in the solid state (——-——). The solid spectrum is shown in arbitrary scale.

On the contrary, $Cu(Pdx\text{-}t\text{-}C_4H_9)_2$ has d–d bands in much lower frequency region than the n-alkyl complexes. This complex most probably has a configuration distorted from a square-planar one, possibly due to steric condition arising from the t-butyl groups, just as in the case of bis(N-t-butylsalicylaldiminato)copper(II).[4,5]

As far as the steric hindrance against the square-planar configuration is concerned, it is known that bis(N-isopropylsalicylaldiminato)copper(II) lies between the corresponding t-butyl and n-alkyl complexes. The spectrum of Cu(Pdx-i-C_3H_7)$_2$ in ethanol is similar to that of Cu(Pdx-n-alkyl)$_2$, as is seen in Fig. 1. Their spectra in chloroform are also similar. It is, therefore, presumed that Cu(Pdx-i-C_3H_7)$_2$ in non-donor solvents also has an essentially planar configuration. On the other hand, this compound in the solid state shows a different spectrum from that in non-donor solvents, its first d–d band being located at much lower frequency than that of the same compound in solution. It is likely that Cu(Pdx-i-C_3H_7)$_2$ in the solid state has a configuration distorted from the square-planar geometry. In fact, the colour (brown) of this complex in the solid state is different from that (green) of the same compound in solution or that of Cu(Pdx-n-alkyl)$_2$ both in solution and in the solid state. It seems to be reasonable to assume that the energy gap between the planar and the distorted tetrahedral configuration may be small for the isopropyl complex, possibly because of the steric condition arising from the presence of the isopropyl groups. Ring-substituted salicylaldiminatocopper(II) complexes with R = isopropyl were reported to have a square-planar configuration or a configuration distorted from that, depending upon the substituent X at the benzene ring,[5] and even isomers having different molecular configurations were recently isolated with some substituents for X.[6]

For R = Ph, 2,6-$(CH_3)_2$-Ph and 2,6-$(C_2H_5)_2$-Ph, the spectra of Cu(Pdx-R)$_2$ are similar to each other, all showing the first d–d band as a shoulder at about 15 kK. These spectra are also similar to those of the corresponding salicylaldiminatocopper(II) complexes,[7] the band maxima of their d–d bands being nearly the same. These copper(II) complexes may most probably have an essentially planar configuration.

The complex Cu(Pdx-$CH_2CH_2CH_2O$)·3/4 H_2O at room temperature has a magnetic moment of 1.31 B.M., which is much lower than the spin-only moment. Exchange interaction seems to exist between copper(II) ions in this complex, as in the analogous salicylaldiminatocopper(II) complexes.[8,9] It is likely that this complex may have a binuclear structure similar to that of the salicylaldiminatocomplexes. Other multinuclear structures, however, may not be excluded. The solubility of this complex is too low for the molecular weight determination.

The complex Cu(Pdx-CH_2CH_2O) also has a subnormal magnetic moment (1.37 B.M.) at room temperature. This complex may have a bi- or multi-nuclear structure, in which a sort of exchange interaction is present between copper(II) ions. The spectra of this and the preceding complexes are remarkably similar, with a well-defined d–d band at about 15.4 kK, probably indicating that they have a similar multinuclear structure. It should be noted that bis(N-hydroxyethylpyridoxaldiminato)copper(II) has not been isolated, whereas the corresponding salicylaldiminato-complex was readily obtained.[10]

The complex Cu(Pdx-CH_2COO)H_2O has a normal magnetic moment (1.83 B.M.) at room temperature, no special interaction being present between copper(II) ions. In addition to a C=N vibration at 1620 cm^{-1}, it shows an asymmetric COO vibration at 1640 cm^{-1} and a symmetric COO vibration at 1400 cm^{-1}, in agreement with the presumption that the carboxylate group may be coordinated to the copper(II) ion. It is most likely that the copper(II) ion forms a planar complex with the terdentate Schiff base and a water molecule coordinated, just as in N-carboxymethylsalicylaldiminatoaquocopper(II) previously reported.[11]

Conclusions

The pyridoxaldiminates as ligands form many copper(II) complexes, whose composition and structure are similar to those of the corresponding salicylaldiminatocopper(II) complexes. The hydroxymethyl group on the pyridine ring and the pyridine nitrogen atom are not coordinated to the copper ion in the complexes obtained in this work, although these may play some part in their reactions in solution.

One of the differences between the pyridoxaldiminato- and the salicylaldiminatocopper(II) complexes was found in their solubility. The solubility of the former complexes in organic solvents is considerably lower than that of the latter. The ligand field produced by Pdx-R, as judged from the d–d band maxima, seems to be nearly equal to, or slightly stronger than, that of the salicylaldiminates.

Acknowledgement

Financial support of this work by the Ministry of Education of Japan is gratefully acknowledged.

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