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Ligand-Substitution Reaction of Bis(acetylacetonato)copper(II) and Bis(acetylacetonato)zinc(II) with 2-(2-Pyridyl)benzimidazole

Michio Kondo

Central Research Laboratories, Sankyo Co., Ltd., Hiromachi 1-2-58, Shinagawa-ku, Tokyo 140

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Synopsis. The reaction of bis(acetylacetonato)copper(II) with 2-(2-pyridyl)benzimidazole (**1**) in ethanol was studied by means of absorption, fluorescence, and ^{1}H NMR spectroscopies, and it was found that one of the acetylacetonate anions in the complex is replaced by the anion of **1**. Bis(acetylacetonato)zinc(II) reacts with **1** in a similar manner. Neither acetylacetonate reacts with 2-(3-pyridyl)- or 2-(4-pyridyl)benzimidazole.

It is well known that bis(β-diketonato)copper(II) complexes behave as Lewis acid and form addition compounds with nitrogen bases.[1] Several five-coordinate addition compounds of square planar bis(β-diketonato)copper(II) complexes with heterocyclic nitrogen bases have been isolated.[2] A stable 2,2′-bipyridine adduct of bis(hexafluoroacetylacetonato)copper(II)[3] and a reaction product of bis(acetylacetonato)copper(II) with ethylenediamine[4] have been isolated, and their structures were determined by means of X-ray analysis. It has been reported that bis(acetylacetonato)zinc(II) forms stable addition compounds with 4,4′-bipyridine and pyrazine.[5] In all these cases no ligand-substitution occurs. This paper describes a new mixed ligand copper(II) complex formed by ligand-substitution between bis(acetylacetonato)copper(II) and 2-(2-pyridyl)benzimidazole.

Experimental

Three 2-pyridylbenzimidazoles 2-(2-pyridyl)- (**1**), 2-(3-pyridyl)- (**2**), and 2-(4-pyridyl)benzimidazole (**3**), were prepared according to the literature.[6] Commercial bis(acetylacetonato)copper(II) and -zinc(II) (**4** and **5**) were purified by recrystallization from chloroform and ethanol, respectively. To a hot ethanol solution (50 ml) of **1** (0.98 g, 1/200 mol), was added a hot ethanol solution (500 ml) of **4** (1.31 g, 1/200 mol). The resulting green solution was concentrated to about 200 ml in a water bath, giving almost black crystals upon cooling. Found: C, 57.19; H, 4.09; N, 11.78%. Calcd for substitution product, $CuC_{17}H_{15}N_3O_2$: C, 57.19; H, 4.21; N, 11.77%. Calcd for adduct, $CuC_{22}H_{23}N_3O_4$: C, 57.82; H, 5.07; N, 9.20%.

The absorption, fluorescence, and ^{1}H NMR spectra were recorded with Hitachi spectrophotometers, Model 356, and MPF-2, at 25 °C and a Varian XL-100 spectrometer at 28 °C, respectively.

Results and Discussion

Figure 1 shows the absorption spectra of ethanol solutions of **1** in the presence of various amounts of **4**. Two isosbestic points are observed at 327 and 304 nm, indicating the existence of a stoichiometric complex-forming equilibrium. A new absorption band at about 350 nm can be ascribed to the complex formed, because neither **1** nor **4** has an absorption band in this region.

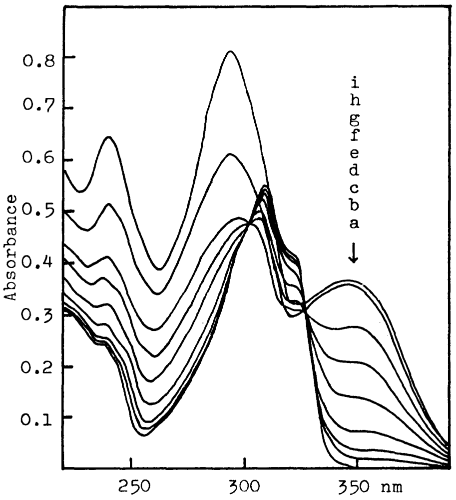

Fig. 1. The absorption spectral change of **1** (2.43×10^{-5} M) in ethanol in the presence of various amounts of **4**. The values of molar ratio, **4**/**1**, are: a, 0; b, 0.044; c, 0.088; d, 0.176; e, 0.352; f, 0.528; g, 0.704; h, 1.056; i, 1.408.

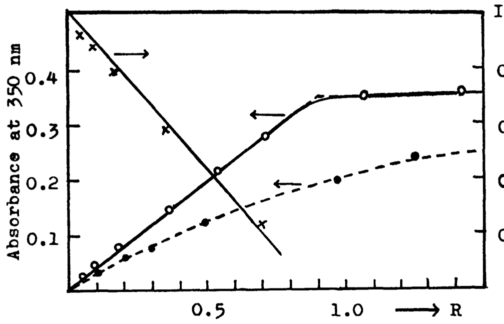

Fig. 2. Plots of absorbance at 350 nm and of relative fluorescence intensity (I/I_0; I_0 is the intensity observed in the absence of **4**), against the molar ratio, **4**/**1**:——, **1**—**4**;----, **1**—**5**.

In Fig. 2, the increments in the absorbance at 350 nm are plotted *versus* the molar ratio (*R*). The absorbance increases linearly with R until it ceases to increase at $R=1$. It can be concluded, therefore, that 1 : 1 complex with a large stability constant is formed. The high stability of this complex and the result of elemental analysis of the almost black crystals obtained from an ethanol solution of the 1 : 1 mixture of **1** and **4**, indicate that it is not merely an addition product of **1** and **4**, but a mixed ligand complex in which **1** coordinates to the Cu(II) ion as a bidentate ligand replacing an acetylacetonate anion in **4**. Consistent with this conclusion, the absorption spectrum of an ethanol solution of the almost black crystals was very similar to that of the 1 : 1 mixture of **1** and **4**, though the latter shows stronger absorbance at shorter wavelengths, $\lambda < 300$ nm, because of the contribution from acetylacetone molecules liberated by the ligand-substitution.

The fluorescence spectra of these solutions showed a marked decrease in intensity without any sign of the appearance of a new band in the presence of **4**. A plot of the observed intensities at 358 nm *versus* R yielded a straight line which crosses the abscissa at about $R=1$. This observation indicates that the complex formed is nonfluorescent and that the fluorescence emission originates only from the free molecules of **1**.

The ^{1}H NMR spectrum of **1** in $CDCl_3$ gave a broad signal due to the imidazolic proton at δ 11.3 and complex signals with fine structures due to the aromatic protons over the range of δ 7.2—8.7. The addition of a few drops of a dark blue chloroform solution of **4** to this solution gave a green color and, at the same time, a broadening of the aromatic proton signals, accompanied by the appearance of new weak signals at δ 2.04, 2.22, 3.57, and 5.52. These new signals can be ascribed to acetylacetone molecules liberated by the ligand-substitution, because these δ values are very close to those assigned to acetylacetone.[7]

For the system of **1** and bis(acetylacetonato)zinc(II) (**5**) in ethanol, a very similar absorption spectral behavior was observed, a smaller complex formation constant being inferred from the plot of the absorbance increase at 350 nm *versus* R (Fig. 2). This system showed a quite different fluorescence spectral change. The zinc-complex is strongly fluorescent; the new fluorescence band at about 420 nm can be ascribed to the zinc-complex because its intensity increases linearly as the absorbance at 350 nm increases.

The nonfluorescent property of the copper-complex can be interpreted in terms of the paramagnetism of the copper(II) ion, which may induce intersystem crossing in the excited state. The zinc-complex, on the other hand, is diamagnetic and fluorescent. In this connection, Bark and Rixon have studied the application of the zinc complex of **1** to the fluorimetric determination of zinc.[8]

The corresponding mixed complexes did not appear to be formed between **4** and **2** (or **3**) in ethanol, because the absorption spectra of the mixtures are almost the same as the sums of those of their components and because the fluorescence quenching of **2** and **3** in the presence of **4** was negligible.

The acetylacetonate anion in **4** is replaced only by the anion of **1** but not by those of **2** and **3**. This fact indicates the necessity of appropriate positioning of the imidazolic NH group and the pyridine nitrogen atom in order to function as a bidentate ligand. It can also be said that the ionizable property of the imidazolic proton in **1** is very important in the ligand-substitution reaction, because such substitution reactions did not occur between **4** and ethylenediamine or between bis(hexafluoroacetylacetonato)copper(II) and 2,2'-bipyridine.[3,4]

A mixed ligand copper(II) complex, Cu(acac)-(OCH_3), was prepared directly by treating **4** with sodium hydroxide in methanol. The methoxo ligand can be replaced by a pyrazolate anion and the resultant copper(II) complex has been proposed to have a dimeric structure on the basis of its antiferromagnetic properties.[9] This fact suggests that the possibility of a dimeric structure of the present mixed ligand complex cannot be discounted.

No double coordination of the anion of **1** to the copper(II) ion was observed. This indicates the relative instability of Cu($\mathbf{1}^-$)$_2$ compared with Cu(acac)($\mathbf{1}^-$) from an energy point of view, probably because of the van der Waals' interaction between two anions of **1**, which is bulkier than the acetylacetnate anion.

The apparently smaller stability constant inferred for the zinc-complex may be ascribed to the smaller difference between the affinities of the two ligands in question to the zinc(II) ion.

References

1) D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).

2) A. F. Garito and B. B. Wayland, *J. Am. Chem. Soc.*, **91**, 866 (1969).

3) M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Am. Chem. Soc.*, **91**, 1859 (1969).

4) T. Kurauchi, M. Matsui, Y. Nakamura, S. Ooi, S. Kawaguchi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **47**, 3049 (1974).

5) S. Ambe and F. Ambe, *J. Inorg. Nucl. Chem.*, **35**, 1109 (1973).

6) *Cf.* a) T. Hisano and M. Ichikawa, *Chem. Pharm. Bull.* **22**, 1923, (1974); b) Y. Sasaki and T. Shigematsu, *Bull. Chem. Soc. Jpn.*, **46**, 3438 (1973); References cited in these.

7) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).

8) L.S. Bark and A. Rixon, *Anal. Chim. Acta*, **45**, 425 (1969).

9) C. G. Barraclough, R. W. Brookes, and R. L. Martin, *Aust. J. Chem.*, **27**, 1843 (1974).