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A New Type of Tetradentate Square-Planar N_2O_2 Ligands. Copper(II) Complexes of 6,6′-Bis(acylamino)-2,2′-bipyridines

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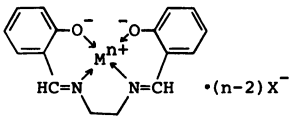
A new type of N_2O_2 tetradentate ligands, 6,6′-bis(acylamino)-2,2′-bipyridines, was synthesized and their complex formations with copper(II) were investigated. They form two types of 1:1 complexes; one is the non-deprotonated type having external counter anions and the other is the deprotonated type having no external counter anions. They serve as square planar N_2O_2 tetradentate ligands in either case and the structures of the complexes are very similar to salen complexes. The structures and properties of these complexes were investigated and discussed.

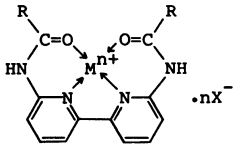
The complexes of tetradentate square-planar N_2O_2 ligands, *N,N′*-di(salicylidene)ethylenediamine (salen) and its derivatives, have been the subject of intense studies because of their ability to activate various molecules, especially, molecular oxygen coordinated to the axial positions of the complexes.[1] Property-control (tuning) by modification of diimine moiety and/or ring substitution of salen is limited in versatility, and exploitation of the complexes of analogous structure has been demanded.

We have been investigating chemistry of 6,6′-diamino-2,2′-bipyridine (dabp).[2,3] The amino groups of dabp are easily modifiable, and, in previous papers, we reported alkylation of the amino groups of dabp and application of these alkyl-substituted derivatives to metal-ion transport.[3] Here, we wish to report another type of derivatives, 6,6′-bis(acylamino)-2,2′-bipyridines, obtained by acylation of the amino groups of dabp, which are found to serve as a new type of N_2O_2 ligands.

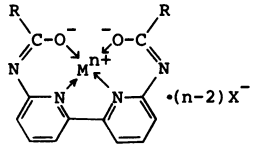
The coordination sites in these ligands are expected to be ring-nitrogens and amide-oxygens serving as N_2O_2 tetradentate planar ligands. Dissociation of amide protons upon complex formation may afford the complexes analogous to the salen complexes. Furthermore, the complexes are expected to be more stable than the salen complexes, especially in an acidic solution, because the easily hydrolyzable Schiff base moieties of the salen complexes are replaced by the bipyridine moiety. Two ligands, 6,6′-bis(benzoylamino)-2,2′-bipyridine ($babpH_2$) and 6,6′-bis(hexanoylamino)-2,2′-bipyridine ($habpH_2$) were prepared, and their complexations with copper(II) were investigated. The results were discussed in comparison with the coordination chemistry of salen and its derivatives, and also with that of analogous ligands, 2-(benzoylamino)pyridine (bapH) and 2-(acetylamino)-pyridine (aapH) reported by Nonoyama et al.[4-7]



Salen Complex



Non-Deprotonated Complex



Deprotonated Complex

Complexes of 6,6'-Bis(acylamino)-2,2'-bipyridine

Results

Syntheses. 6,6′-Bis(acylamino)-2,2′-bipyridines ($babpH_2$ and $habpH_2$) were prepared by acylation of amino groups of dabp with the corresponding acyl chlorides (Scheme 1). 2,9-Bis(benzoylamino)-1,10-phenanthroline ($baptH_2$) was also prepared from 2,9-diamino-1,10-phenanthroline.[8] Elemental analyses agreed well with the calculated values within a permitted experimental error ($\leq\pm0.3\%$, Table 1). Chemical shifts in ^{13}C and ^{1}H NMR spectra of the ligands in dimethyl-d_6 sulfoxide (DMSO-d_6) (Tables 2 and 3, respectively) confirmed their structures, most of which were quite similar to those of corresponding 2-(acylamino)pyridines.[9]

Complexation of $babpH_2$ with copper(II) nitrate and acetate gave different types of complexes, i.e., the non-deprotonated complex **1a** and the deprotonated one **2a** respectively (Table 1). A blue complex $Cu(babpH_2)(H_2O)_2(NO_3)_2$, **1a** was obtained by complexation with copper(II) nitrate in methanol (Scheme 1). The IR spectrum of complex **1a** showed the presence of amide carbonyl and N–H stretching bands (Table 4). The change in IR spectrum upon complexation was quite similar to those of 2-(acylamino)-pyridines.[4-6] On the other hand, a green complex [Cu(babp)], **2a** was obtained by complexation with copper(II) acetate (Scheme 1). This showed neither amide carbonyl nor N–H stretching bands in its IR spectrum (Table 4), indicating the deprotonation of both of the two amide protons. The characteristic IR

Table 1. Analytical and Physical Data of Ligands and Their Copper(II) Complexes

Material[a]	Appearance	Mp(θ_m/°C)	Elemental analysis/% (Calcd)
$babpH_2$	White flake	289—291	C, 72.94; H, 4.54; N, 14.04 ($C_{24}H_{18}N_4O_2$: C, 73.08; H, 4.60; N, 14.20)
$habpH_2$	White flake	220—223	C, 69.00; H, 7.89; N, 14.67 ($C_{22}H_{30}N_4O_2$: C, 69.08; H, 7.91; N, 14.65)
$baptH_2$	Pale yellow needle	250—253	C, 74.39; H, 4.27; N, 13.73 ($C_{26}H_{18}N_4O_2$: C, 74.63; H, 4.34; N, 13.79)
$Cu(babpH_2)(H_2O)_2(NO_3)_2$ (**1a**)	Light blue plate	ca. 250[c]	C, 46.70; H, 3.42; N, 13.50 ($C_{24}H_{22}CuN_6O_{10}$: C, 46.64; H, 3.59; N, 13.60)
[Cu(babp)][b] (**2a**)	Green needle	>300	C, 63.10; H, 3.32; N, 12.36 ($C_{24}H_{16}CuN_4O_2$: C, 63.22; H, 3.54; N, 12.29)
$Cu(habpH_2)(H_2O)(NO_3)_2$ (**1b**)	Blue plate	ca. 250[c]	C, 45.22; H, 5.38; N, 14.11 ($C_{22}H_{32}CuN_6O_9$: C, 44.93; H, 5.48; N, 14.29)

a) $BabpH_2$, 6,6′-bis(benzoylamino)-2,2′-bipyridine; $habpH_2$, 6,6′-bis(hexanoylamino)-2,2′-bipyridine; $baptH_2$, 2,9-bis(benzoylamino)-1,10-phenanthroline. b) Babp, the deprotonated form of $babpH_2$ (both of amide protons). Similar abbreviations are used for other deprotonated ligands. c) Decomposition.

Table 2. Chemical Shifts in ^{13}C NMR Spectra of Metal-Free Ligands

Material[a]	Chemical shift/ppm (from TMS)										
	C=O	Heteroaromatic ring (Position)						Others			
$aapH$[b]	169.30	—	147.82 (6)	119.13 (5)	137.92 (4)	113.53 (3)	152.25 (2)	23.60 (Methyl Group)			
$bapH$[b]	169.98	—	147.81 (6)	119.73 (5)	138.05 (4)	114.77 (3)	152.18 (2)	127.94 (Benzene Ring)	128.32	130.85	
$babpH_2$	166.15	—	151.60 (2)	116.52 (3)	139.03 (4)	115.18 (5)	153.50 (6)	128.00 (Benzene Ring)	128.34	131.99	134.10
$habpH_2$	172.36	—	151.60 (2)	115.67 (3)	138.95 (4)	113.73 (5)	153.40 (6)	13.81 36.05 (Alkyl Chain)	21.85	24.59	30.83
$baptH_2$	166.02	124.81 (5, 6)	143.46 (10a, b)	126.44 (4a, 6a)	138.24 (4, 7)	116.97 (3, 8)	151.21 (2, 9)	127.95 (Benzene Ring)	128.38	132.07	133.70

a) AapH, 2-(acetylamino)pyridine; bapH, 2-(benzoylamino)pyridine. Other abbreviations, see Table 1. b) Ref. 9a.

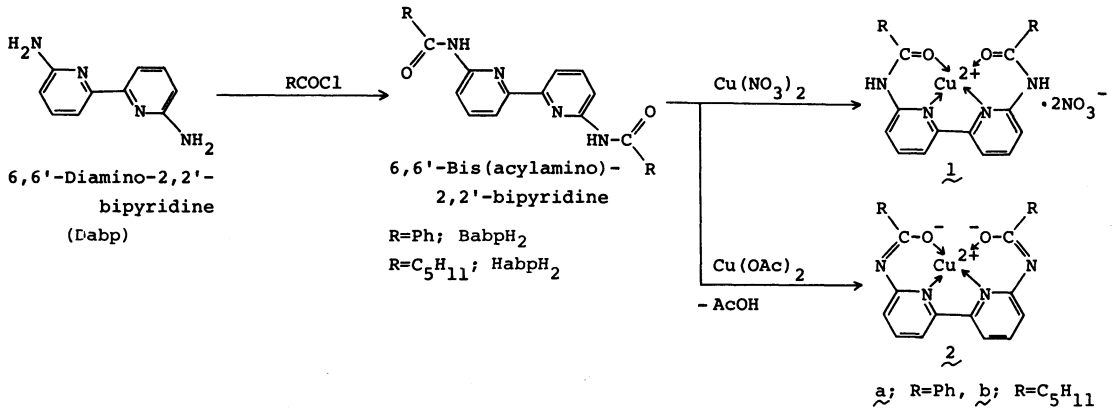
Table 3. Chemical Shifts in ^1H NMR Spectra of Metal-Free Ligands

Material	Chemical shift/ppm (from TMS)						
	N-H	Heteroaromatic ring (Position)					Others
$aapH$[a]	10.48	—	8.31 (6)	7.08 (5)	7.76 (4)	8.08 (3)	2.10 (Methyl Group)
$bapH$[a]	10.81	—	8.40 (6)	7.18 (5)	7.86 (4)	8.21 (3)	8.05, 7.60, 7.52 (Benzene Ring)
$babpH_2$	10.75	—	—	8.20 (3)	8.02 (4)	8.23 (5)	8.07, 7.60, 7.55 (Benzene Ring)
$habpH_2$	10.43	—	—	7.99 (3)	7.90 (4)	8.13 (5)	2.42, 1.60, 1.30, 0.87 (Alkyl Chain)
$baptH_2$	10.98	7.94 (5, 6)	—	—	8.49 (4, 7)	8.56 (3, 8)	8.15, 7.64, 7.56 (Benzene Ring)

a) Ref. 9a.

bands of **2a** at 1555 and 1366 cm^{-1} were quite similar to those of the palladium complex of 2-(acetylamino)-pyridine [Pd(aap)] (1568 and 1393 cm^{-1}).[4] The ligand $habpH_2$ also gave a blue complex **1b** of similar structure to **1a** by complexation with copper(II) nitrate (Tables 1 and 4). Furthermore, $habpH_2$ gave a green complex **2b** with copper(II) acetate which showed a similar IR bands to **2a** (1554 and 1380 cm^{-1}), suggesting the formation of the deprotonated complex. However, the complex **2b** could not be isolated in a pure form (from elemental analysis).

The ESR spectra of the complexes obtained were also measured (Fig. 1). The spectrum of **1b** was quite similar to that of **1a** (Fig. 1-A).



Scheme 1.

Table 4. Characteristic IR Bands of Ligands and Complexes in KBr Disks

Material	IR Band/cm^{-1}				
	$\nu_{(N-H)}$	Amide band			$\nu_{(N-O)}$[a]
		I	II	III	
aapH[b]	3183	1693	1531	1242	—
bapH[c]	3200	1675	1580	1245	—
$babpH_2$	3310	1651	1521	1245	—
$habpH_2$	3242	1655	1519	1247	—
$baptH_2$	3410	1673	1509	1243	—
$[Cu(aapH)_2]Cl_2$[b]	2872	1645	1537	1346	—
$[Cu(bapH)_2][NO_3]_2$[c]	3230	1660sh[d]	1570	1331	1280
1a	3430	1615	1535	1323	1381
1b	3380	1635	1527	1317	1373
$[Pd(aap)_2][H_2O]_4$[b]	—	(1568)	(1393)	—	—
2a	—	(1555)	(1366)	—	—

a) Nitrate anion, b) Ref. 4, c) Ref. 6, d) shoulder.

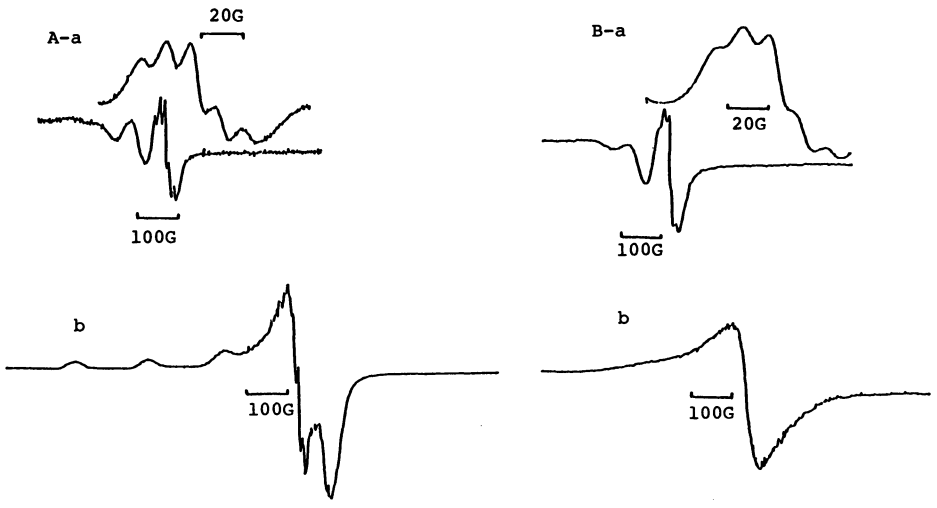


Fig. 1. ESR spectra of copper(II) complexes (1×10^{-3} mol dm^{-3}). A: **1a** in methanol (a) at room temperature (g=2.15) and (b) at 77 K ($g_{//}$=2.26, $g_{\perp}$=2.10), B: **2a** in DMSO (a) at room temperature (g=2.12) and (b) at 77 K (g=2.07).

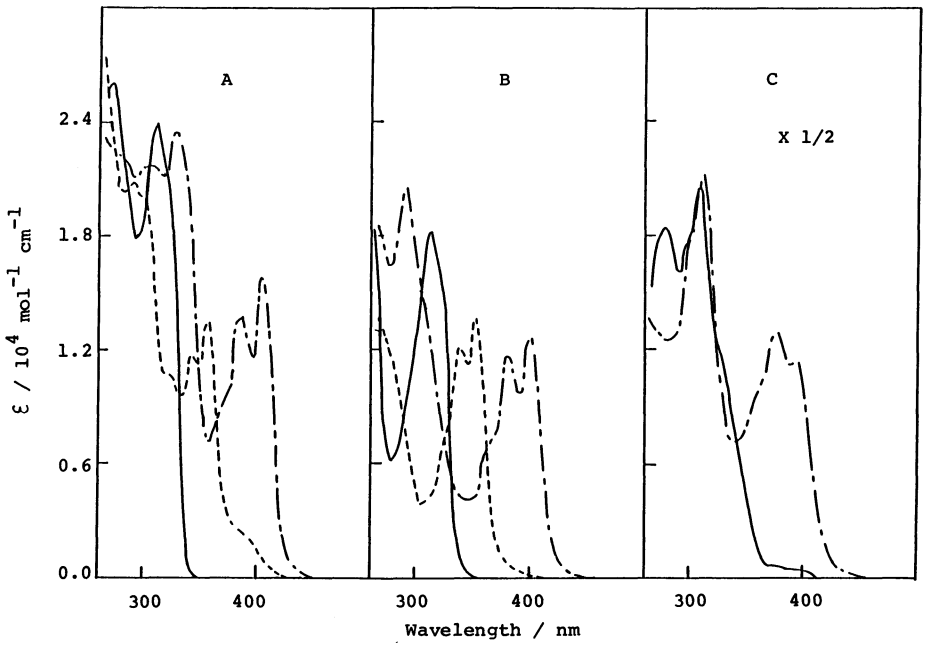


Fig. 2. The electronic spectra of (A) babpH$_2$, (B) habpH$_2$, and (C) baptH$_2$ and their copper(II) complexes in DMSO (6.67×10^{-5} mol dm^{-3}) at 20 °C; (——): metal-free ligands, (------): non-deprotonated complexes in the presence of HNO_3, and (—·—): fully-deprotonated complexes. The spectra of the fully-deprotonated complexes for habpH$_2$ (B) and baptH$_2$ (C) are those of the 1:1 mixture of Cu(OAc)$_2$ with corresponding ligands.

Properties. The electronic spectra of metal-free ligands and their copper(II) complexes are shown in Fig. 2. The spectral changes of the metal-free ligands in DMSO (6.67×10^{-5}mol dm^{-3}) by addition of various amounts of copper(II) acetate indicated the quantitative formation of the 1:1 complexes. The spectra of the equimolar solutions of the ligands and copper(II) acetate in DMSO were quite similar to that of **2a**, indicating the formation of deprotonated complexes, [Cu(babp)], [Cu(habp)], and [Cu(bapt)], in a DMSO solution. The spectra of the equimolar solutions of the ligands and copper(II) nitrate with an excess amount of HNO_3 in DMSO were also almost the same as those of the complexes **1a** and **1b**. The apparent complex-formation constants were too large to measure by the Rose-Drago's method[10] (concentration of ligads; ca. 10^{-5} mol dm^{-3}), and the complexations proceeded completely in the presence of an excess amount of HNO_3 (non-deprotonated complexes) and in the presence of acetic acid produced upon deprotonation (deprotonated complexes) (Scheme 1).

The spectra at 260—500 nm region of the copper(II) complexes of babpH$_2$ and habpH$_2$ in DMSO were sensitive to their concentrations or presence of an acid or a base (Fig. 3). The spectral changes indicated that the two types of the complexes **1** and **2** were in equilibrium. In the course of transformation between the two types of the complexes, two different set of isosbestic points appeared successively, i.e., one is the

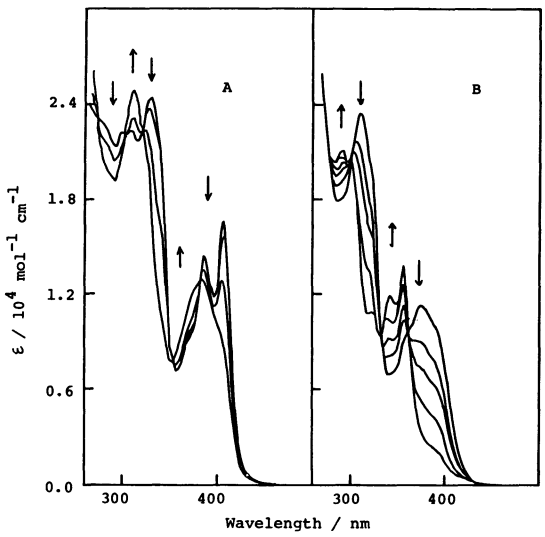
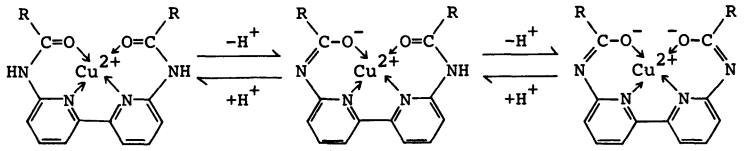


Fig. 3. The changes of electronic spectra of the copper(II) complex **2a** by addition of HNO_3 in DMSO. Concentration of complex **2a**: 6.67×10^{-5} mol dm^{-3}, molar ratio of added nitric acid were as follows; A: 0.0, 0.4, 0.8, and 1.2, and B: 2.0, 4.0, 6.0, 10.0, and 22.0.

set at 382, 352, 322, and 303 nm (Fig. 3-A) and the other at 363, 332, and 300 nm (Fig. 3-B). This indicates the intervention of monodeprotonated species, i.e., one of the amide protons dissociated (Scheme 2). The spectral changes due to the interconversion of the three types of the complexes were also observed in an aqueous medium, though the



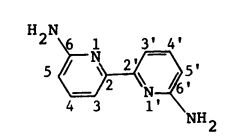
Scheme 2.

fully-deprotonated complex precipitated out in this case. The equilibrium was dependent on the pH of the solution. As the result of the spectrometric titration with concd HNO_3 or KOH (6.67×10^{-5} mol dm^{-3} of the complex), first dissociation of the amide proton in **1b** occured at pH 6.7, and second at pH 9.5. While, the complex **1a** dissociated both of the amide protons almost simultaneously at pH 5.1 in aqueous medium. The complexes themselves were stable during such treatment and neither decomplexation of metal ion nor hydrolysis of the ligands occured even in the presence of an acid or a base.

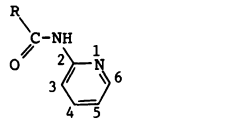
The copper(II) complexes showed additional bands due to d–d transition in their electronic spectra. The absorption maxima of **1a** and **1b** were 640 nm either in DMSO (ε=110) or in methanol (ε=121). On the other hand, a large solvent effect was observed for **2a**, the absorption maximum of which was 595 nm in DMSO (ε=167), 550 nm in chloroform (ε=227), 585 nm in tetrahydrofuran (ε=180), and 605 nm in pyridine (ε=173).

Discussion

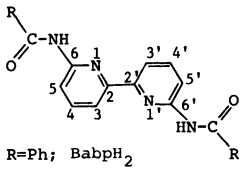
Conformation of the Metal-Free Ligands. The conformation of the metal-free ligands was confirmed to have planar structure by the ^1H NMR spectrometry (Table 3). Chemical shifts of 3,3′-protons are sensitive to the conformation of the two pyridine rings of bipyridine.[11] The large lower-field shift (ca. 0.8-1 ppm) of 3,3′-protons of the bipyridine moiety compared with that of 5-proton of 2-(acylamino)pyridines (bapH and aapH) indicates that the two pyridine rings of the bipyridine moiety are in the plane in "*transoid*" conformation.[11] The chemical shifts of the other ring-protons of $babpH_2$ and $habpH_2$ were almost the same as those of the corresponding protons of 2-(acylamino)pyridines. The large lower-field shift of 5,5′-protons (ca. 1.8 ppm) of 6,6′-bis(acylamino)-2,2′-bipyridines compared with those of dabp[2] is due to the strong deshielding effect by the amide oxygen, suggesting that the amide groups and the pyridine rings are in the plane in "*trans-cis*" conformation as reported for 2-(acylamino)pyridines.[9] Thus, it was concluded that the metal-free ligands have a planar structure as shown below.



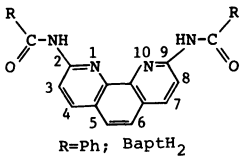
"*transoid*" Conformation of Dabp



"*trans-cis*" Conformation of 2-(Acylamino)pyridine



R=Ph; $BabpH_2$
R=C_5H_{11}; $HabpH_2$



R=Ph; $BaptH_2$

Complex Formation with Copper(II). 2-(Acetylamino)pyridine (aapH) has been reported to form two types of complexes with palladium(II), i.e., $[Pd(aapH)_2]_2^+$ gave deprotonated one, $[Pd(aap)_2]$[4] in alkaline condition. However, $[Cu(aapH)_2]^{2+}$ was decomposed in alkaline solution to give $Cu(OH)_2$ instead of $[Cu(aap)_2]$.[4] In the present case, $babpH_2$ and $habpH_2$ formed both types of copper(II) complexes as described in the previous section.

Structure of the Copper(II) Complexes. 2-(Acylamino)pyridines has been shown unambiguously to coordinate to metal ions as planar NO bidentate ligands from their spectral data[4–7] and X-ray crystal structure analysis.[7] Aap (deprotonated aapH) also serves as a planar NO bidentate ligand.[4,7] Usually deprotonated amide group is known to coordinate at its nitrogen atom,[12] but in the cases of (2-acylamino)pyridine derivatives described here the oxygen is shown to act as the coordination site to form more stable 6-membered ring structure. The shifts of the amide bands of $babpH_2$ and $habpH_2$ in IR spectra upon formation of the complexes **1** (Table 4) are similar to those of the corresponding 2-(acylamino)-pyridines, suggesting the coordination at the amide oxygens[12] (i.e., amide I; red shift, amide II and III; blue shift). The characteristic IR bands of **2** are also similar to those of the deprotonated complex of 2-(acylamino)pyridine, $[Pd(aap)_2]$.[4] Thus, the similarities of IR bands of copper(II) complexes **1a**, **1b**, and **2a** to the corresponding complexes of 2-(acylamino)-pyridines indicate that 6,6′-bis(acylamino)-2,2′-bipyridines act as the square-planar N_2O_2 tetradentate ligands.

The ESR spectra of **1a** and **2a** at room temperature (Fig. 1) were quite similar to each other. They showed the usual four-line pattern due to coupling of electron to the spin 3/2 copper nucleus, and showed five

superhyperfine splitting due to the two nitrogens in the copper coordination sphere. These pattern were almost the same as that of salen derivatives.[13] The ESR spectra at 77 K (Fig. 1), however, were quite different from each other. The complex **2a** showed no fine structure probably due to an intermolecular interaction between copper(II) ions under the measured conditions. The complex **1a** and **1b** showed a typical axial-type spectrum, confirming the structure of a square-planar symmetry. The electronic spectrum of **2a** in 260—500 nm region was similar to that of [Cu(bapt)] (Fig. 2). The ligand baptH$_2$ is regarded as a babpH$_2$ analogue and the conformation of the bipyridine moiety in baptH$_2$ is rigidly fixed in plane. The spectral similarities of the two complexes support the planar structures of the complex **2a**. The complexes **1a**, **1b**, and **2a** have the absorption maxima due to d–d transition appeared at 550—640 nm, similar to that observed in a variety of square-planar copper(II) complexes hitherto reported. The absorption maximum of **2a** in chloroform (550 nm) is similar to that of d–d transition band of copper(II) complex of *N*,*N*′-bis(1-methyl-3-oxobutylidene)ethylenediamine rather than that of salen (570 nm),[14] suggesting the presence of strong square-planar ligand field around copper(II) ion in the deprotonated complexes. Therefore, these spectral data indicate the square-planar structure of the complexes of 6,6′-bis(acylamino)-2,2′-bipyridine.

The absorption maximum of *d-d* transition band of **2a** in DMSO (Fig. 3) was markedly red-shifted (45 nm) compared with that in chloroform, while that of copper(II) complex of salen or acen showed only a small solvent effect (max. 20 nm).[14] This larger solvent effect may be interpreted in terms of coordination of the solvent molecules at the axial positions of **2a**.

In conclusion, 6,6′-bis(acylamino)-2,2′-bipyridines have been shown to form two different types of 1:1 complexes with copper(II) salt depending on the counter anions of the salts. The deprotonated complexes are similar to salen complexes in their N_2O_2 tetradentate coordination sites, square-planar structure, and the anionic sites on oxygens. Furthermore, in the ligands obtained here, the Schiff base moieties in salen complexes are replaced by bipyridine moieties which have higher chemical stability.

Experimental

Materials 6,6′-Diamino-2,2′-bipyridine was prepared from 2,6-dibromopyridine according to the method previously reported.[3] 2,9-Diamino-1,10-phenanthroline was prepared from 1,10-phenanthroline by the literature method.[8] Other chemicals were obtained commercially, and some of them were purified by conventional methods prior to use.

Spectral Measurements. ^{1}H and ^{13}C NMR spectra were measured with a JEOL JNM-GX270 Spectrometer at 27 °C. ESR spectra were measured with a JEOL JES-FE3X spectrometer operated at X band. Electronic and IR spectra were recorded on a JASCO UVIDEC-505 spectrophotometer at 20 °C and a IRA-1 spectrophotometer, respectively.

6,6′-Bis(benzoylamino)-2,2′-bipyridine (babpH$_2$): Into a solution of dabp (186 mg, 1 mmol) in 10 cm^3 of dry pyridine was added dropwise a solution of benzoyl chloride (1.41 g, 10 mmol) in 10 cm^3 of dry pyridine at 0 °C with stirring. The mixture was stirred for another 15 min at the temperature. Then 100 cm^3 of methanol was added to the mixture in order to precipitate a white solid, which was collected by filtration, washed successively with diluted hydroohloric acid, acetone, diluted aqueous ammonia, and methanol. Recrystallization from benzene yielded 294 mg (75%).

6,6′-Bis(hexanoylamino)-2,2′-bipyridine (habpH$_2$): This was prepared from 186 mg (1 mmol) of dabp and 1.34 g (10 mmol) of hexanoyl chloride in a similar manner to that of babpH$_2$. Yield 298 mg (78%).

2,9-Bis(benzoylamino)-1,10-phenanthroline (baptH$_2$): Into a solution of 2,9-diamino-1,10-phenanthroline (100 mg, 0.47 mmol) in 5 cm^3 of dry pyridine was added dropwise a solution of benzoyl chloride (0.66 g, 4.7 mmol) in 5 cm^3 of dry pyridine at 0 °C with stirring and the mixture was stirred for 15 min at the temperature. Then, 100 cm^3 of ether was added to the mixture to precipitate pale yellow solid, which was collected by filtration and subjected to column chromatography (Wakogel C-200–chloroform). The fraction obtained was washed with diluted aqueous ammonia. Evaporation of chloroform and recrystallization from methanol gave pale yellow needles which was dried at 80 °C under reduced pressure. Yield 84 mg (39%).

Copper(II) Complex 1a: A mixture of babpH$_2$ (78 mg, 0.2 mmol) and Cu(NO$_3$)$_2$·3H$_2$O (48 mg, 0.2 mmol) in 10 cm^3 of methanol was stirred at room temperature until the mixture became a homogeneous blue solution. Then methanol was removed by evaporation. The residual blue solid was recrystallized from water to give light blue plates of Cu(babpH$_2$)(H$_2$O)$_2$(NO$_3$)$_2$, yield 71 mg (58%).

Copper(II) Complex 2a: A mixture of babpH$_2$ (78 mg, 0.2 mmol) and Cu(OAc)$_2$·H$_2$O (40 mg, 0.2 mmol) in 100 cm^3 of chloroform was stirred at room temperature until the mixture became a homogeneous purple solution. Then chloroform was removed by evaporation. The residual green solid was washed by methanol containing KOH, and recrystallized from benzene, yielding 70 mg (76%) of [Cu(babp)].

Copper(II) Complex 1b: This was obtained from 76 mg (0.2 mmol) of habpH$_2$ and 48 mg (0.2 mmol) of Cu(NO$_3$)$_2$·3H$_2$O in a similar manner to the preparation of **1a**. Recrystallization from water gave blue plate of Cu(habpH$_2$)(H$_2$O)(NO$_3$)$_2$, yield 26 mg (18%).

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