Structures and Properties of Divalent Metal Complexes of an N_2O_2 Type Ligand, 6,6′-Bis(benzoylamino)-2,2′-bipyridine

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Complex formations of an N_2O_2 tetradentate ligand, 6,6′-bis(benzoylamino)-2,2′-bipyridine (babpH_2) with various divalent metal ions were investigated. BabpH_2 complexes of Ni(II), Co(II), and Zn(II) were obtained as dinitrate and/or diacetate, and their deprotonated complexes, [Ni(babp)], [Co(babp)], and [Zn(babp)], where babp represents the deprotonated form of amide protons of babpH_2, were also isolated. The deprotonated complexes were shown to have high thermal stability up to 300 °C. The structures, stabilities, and spectral properties of these complexes were discussed in relation to the copper(II) complexes of babpH_2 and babp.

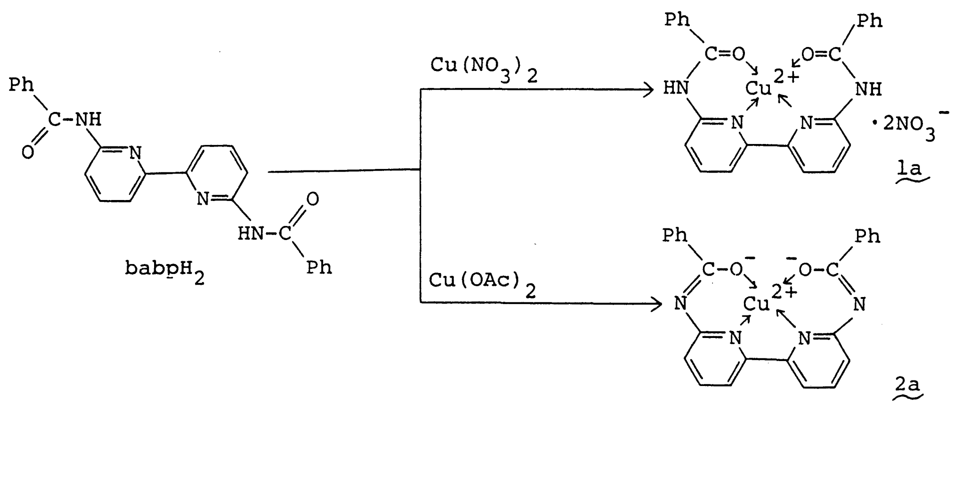
Recently we reported the syntheses, structures, and some properties of a new type of tetradentate N_2O_2 ligand, 6,6′-bis(acylamino)-2,2′-bipyridines and their copper(II) complexes.[1] Deprotonation of the amide protons of copper(II) complex **1a** takes place in weakly acidic to neutral pH range, giving the deprotonated complex **2a** which have a similar structure to those of salen complexes in their N_2O_2 tetradentate coordination sites, square-planar structure, and the anionic sites on oxygens. In addition, our preliminary results showed that the deprotonated type of the cobalt(II) complex of 6,6′-bis(benzoylamino)-2,2′-bipyridine (babpH_2), [Co(babp)], serves as a better catalyst for oxygenation of phenols by molecular oxygen compared to cobalt(II)-salen complexes.[2,3] In this report, complex formations of babpH_2 with various divalent metal ions including cobalt(II) and the structural elucidation of the complexes are described.

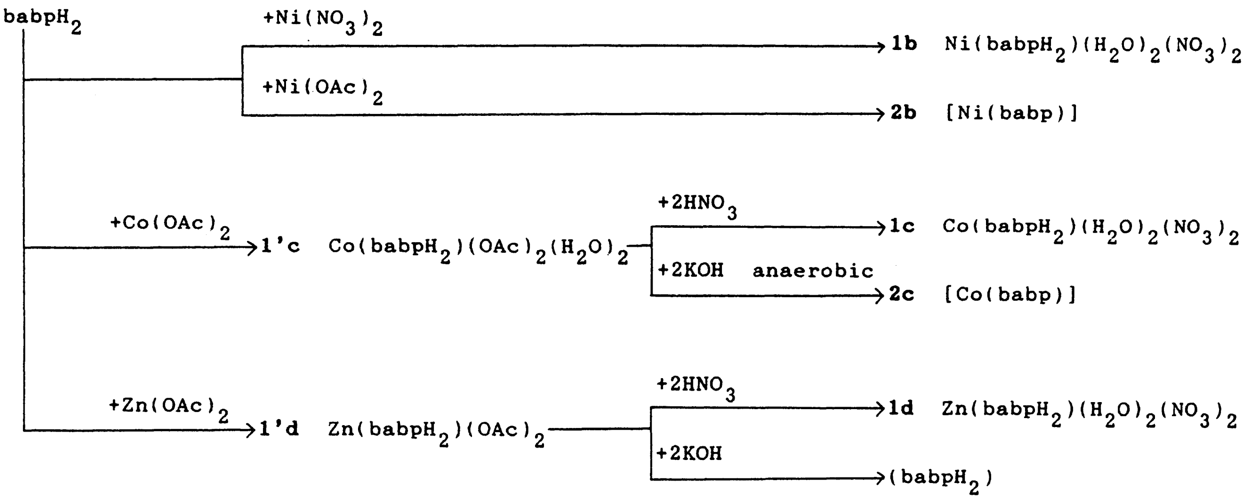
Results

Syntheses of Complexes. Syntheses of 1 : 1 complexes of babpH_2 with various divalent metal ions are shown in Scheme 1, and their characterization data are summarized in Table 1. BabpH_2 complexes of nickel(II) as a nitrate (**1b**), cobalt(II) and zinc(II) as acetates (**1′c** and **1′d**, respectively), were obtained by mixing babpH_2 with corresponding metal salts. The cobalt(II) (**1c**) and zinc(II) (**1d**) complexes were also obtained in nitrate form from **1′c** and **1′d**, respectively (see experimental section). All of the non-deprotonated complexes were soluble in water. The nitrate of the non-deprotonated nickel(II) complex **1b** was very stable in water even under highly acidic conditions, while the non-deprotonated complexes of cobalt(II) and zinc(II) acetates (**1′c** and **1′d**, respectively) or nitrates (**1c** and **1d**, respectively) released the metal ions in weakly acidic or even in neutral water to give metal-free babpH_2 quantitatively.

In the case of nickel(II), use of nickel(II) acetate directly yielded the deprotonated-type complex [Ni(babp)] (**2b**), being similar to the case of copper (II).[1] The deprotonated-type of cobalt(II) complex [Co(babp)] (**2c**) was obtained as a precipitate by addition of twice molar amount of KOH to **1′c** in methanol under anaerobic atmosphere.[4] Similar attempt to obtain the deprotonated-type complexe of zinc(II) from **1′d** resulted in recovery of metal-free babpH_2 (see experimental section). But the thermolysis of **1′d** (see thermal properties section) successfully afforded the zinc(II) complex [Zn(babp)] (**2d**). These deprotonated complexes, **2b**—**2d**, are insoluble in water and not release metal ions in acid-free water.

IR Spectra. The nitrates of the non-deprotonated complexes, **1b**, **1c**, and **1d**, showed quite similar IR spectra to that of the corresponding copper(II) complex **1a**,[1] and the deprotonated complexes, **2b**, **2c**, and **2d** to that of the corresponding copper(II) complex **2a** (Table 2),[1] showing that either babpH_2 or babp serves as a tetradentate N_2O_2 ligand in those complexes similarly to **1a** and **2a**.[1,5,6]





Scheme 1.

Table 1. Analytical Data of Isolated Complexes

Code	Appearance	Composition[a)]	E.A./%(Found(Calcd)) C	H	N
1b	Pale green plates	$Ni(babpH_2)(NO_3)_2(H_2O)_2$	46.84 (47.01)	3.88 (3.62)	13.63 (13.71)
2b	Orange needles	[Ni(babp)]	64.12 (63.90)	3.44 (3.57)	12.26 (12.42)
1′c	Pink powder	$Co(babpH_2)(OAc)_2(H_2O)_2$	55.73 (55.36)	4.15 (4.64)	8.64 (9.22)
1c	Pale brown powder	$Co(babpH_2)(NO_3)_2(H_2O)_2$	46.91 (46.99)	3.60 (3.61)	13.33 (13.70)
2c	Red needles	[Co(babp)]	63.54 (63.87)	3.42 (3.57)	12.43 (12.41)
1′d	White plates	$Zn(babpH_2)(OAc)_2$	58.01 (58.19)	4.07 (4.19)	9.58 (9.69)
1d	White needles	$Zn(babpH_2)(NO_3)_2(H_2O)_2$	46.85 (46.51)	3.40 (3.58)	13.13 (13.56)
2d	Yellow powder	[Zn(babp)]	63.52 (62.97)	3.53 (3.52)	12.30 (12.24)

a) Abbrebiation babp representates deprotonated (both of two amide protons) form of $babpH_2$.

Table 2. Characteristic IR Bands of Complexes in KBr Disks

Material	IR band/cm^{-1} ν(N-H)	Amide band I	II	III	Others
$babpH_2$[a)]	3310	1651	1521	1245	—
1a[a)]	3430	1615	1535	1323	1381 (ν(N-O) of nitrate)
1b	3406	1620 1647sh[b)]	1541	1317	1385 (ν(N-O) of nitrate)
1c	3284	1616 1645sh	1541	1315	1385 (ν(N-O) of nitrate)
1d	3398	1619 1640sh	1542	1317	1384 (ν(N-O) of nitrate)
2a[a)])	—	(1555)	(1366)	—	—
2b	—	(1562)	(1382)	—	—
2c	—	(1557)	(1381)	—	—
2d	—	(1562)	(1378)	—	—
1′c	3290	1653 1675	1537	1238	1579 (ν(C-O) of acetate)
1′d	3334	1658 1694	1538	1266	1578 (ν(C-O) of acetate)

a) Ref. 1. b) Shoulder peak.

On the other hand, IR spectra of the acetates of the non-deprotonated complexes, **1'c** and **1'd**, are quite different in amide carbonyl region (amide I) from those of nitrates (Table 2). The amide I bands of the acetates appear at higher wavenumber compared with that of metal-free babpH_2. Similar blue shift of the amide I band was reported for the non-deprotonated palladium(II) complex of 2-(acetylamino)pyridine in which the ligand coordinates only with its ring nitrogen but not with its amide oxygen.[6] Therefore, it may be implyed that babpH_2 in **1'c** and **1'd** coordinates to metal ions only with its ring nitrogens but not with its amide oxygens. The structures of the acetates are remained uncertain.

Electronic Spectra. The electronic spectra of the complexes in dimethyl sulfoxide (DMSO) are shown in Fig. 1. The acetates of the non-deprotonated complexes, **1'c** and **1'd**, showed the similar spectra to those of the corresponding deprotonated-type complexes (**2c** and **2d**, respectively). Therefore, it is quite likely that the amide protons of these complexes were dissociated under the measured conditions.

Dropwise addition of nitric acid to the solution of the deprotonated nickel(II) complex **2b** in DMSO up to twice molar amount caused gradual spectral change to that of **1b** in two-steps (Fig. 2). This result shows

$$[\mathrm{Ni(babpH_2)}]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [\mathrm{Ni(babpH)}]^{+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [\mathrm{Ni(babp)}]$$

Scheme 2.

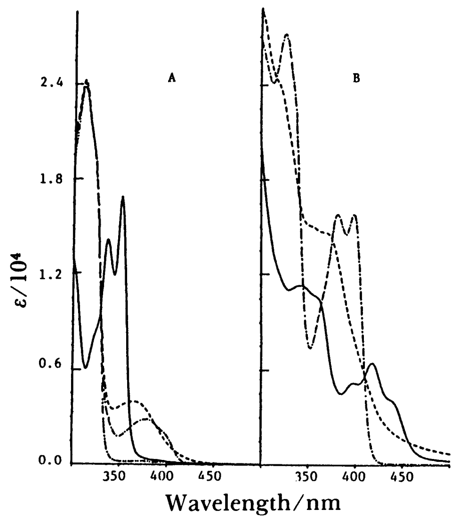


Fig. 1. The electronic spectra of (A) nitrate salts of the non-deprotonated complexes and (B) deprotonated complexes in DMSO (6.67×10^{-5} M) at 20 °C. (——): nickel(II) complexes **1b** (A) and **2b** (B), (----): cobalt(II) complexes **1c** (A) and **2c** (B), (-·-·-): zinc(II) complexes **1d** (A) and **2d** (B), and (-··-··-): metal free babpH_2 (A).

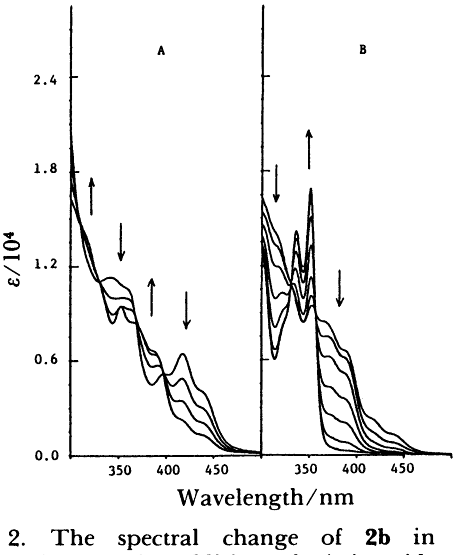


Fig. 2. The spectral change of **2b** in DMSO (6.67×10^{-5} M) by addition of nitric acid at 20 °C. Molar ratio of added nitric acid were as follows; A: 0.0, 0.2, 0.4, and 0.6, B: 0.6, 0.8, 1.0, 1.2, 1.6, 1.8, and 2.0.

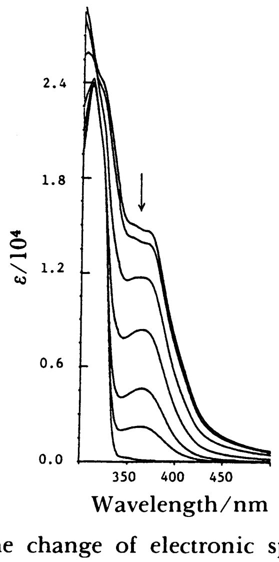


Fig. 3. The change of electronic spectra of **2c** by addition of nitric acid in DMSO (6.67×10^{-5} M) at 20 °C. Molar ratio of added nitric acid were 0.0, 0.5, 1.0, 1.5, 2.0, 2.2, and 2.5.

that protonation to the deprotonated species **2b** in DMSO takes place stepwisely via intermediacy of monoprotonated species (Scheme 2). Similar result has been observed for the copper(II) complex **2a**.[1] The spectra of the cobalt(II) and zinc(II) complexes, **2c** and **2d**, in DMSO changed to that of metal-free babpH_2 by addition of nitric acid (Fig. 3).[7]

Thermal Properties of Complexes in Solid State. Thermal properties of the complexes were analyzed by TG and DTA, and the results are summarized in Table 3. Figure 4 represents the typical TG curves of the complexes, **1b**, **1'd**, and **2b**. Those of the copper(II) complexes are also included which were not reported in the preceding paper.[1]

Table 3. Thermal Properties of Complexes[a)]

Complex	Temperature/°C
1a	63—76(−H_2O) 136—161(−H_2O) 224—238(−$2HNO_3$→**2a**)
1b	72—85(−H_2O) 166—186(−H_2O) 254—303(−$2HNO_3$→**2b**)
1c	75—166(−$2H_2O$) 228—248(−$2HNO_3$→decomp)
1d	77—110(−$2H_2O$) 238—263(−$2HNO_3$→decomp)
1′c	96—203(−$2H_2O$, −2AcOH→**2c**)
1′d	200—258(−2AcOH→**2d**)
2a	337(mp)
2b	337(mp)
2c	333(mp)
2d	b)

a) Heating rate; 5 °C min^{-1}, under aerobic atmosphere. b) See text.

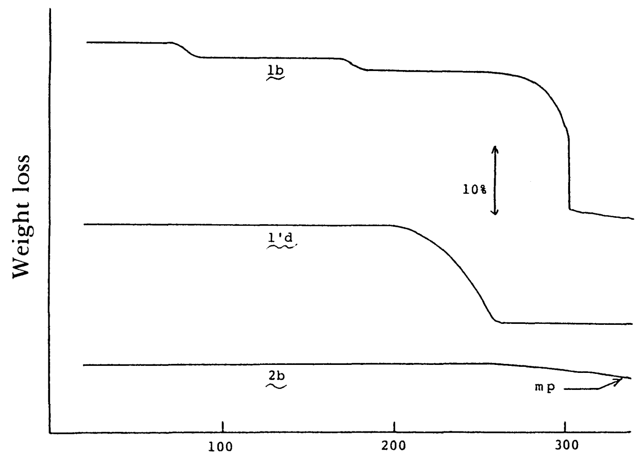


Fig. 4. Typical TG curves of the complexes, **1b**, **1′d**, and **2b**.

In the case of the nitrate salts of the non-deprotonated complexes, **1a—1d**, small weight loss during 50—190 °C accounted for loss of two water molecules took place endothermically. Further heating caused gradual weight decrease endothermically at above 220 °C, followed by abrupt weight loss with sharp exothermic peak in DTA. In the case of **1a** and **1b**, these weight losses were accounted for the loss of nitric acid, and IR spectra of the residual solids were identical to those of **2a** and **2b**, respectively. While, weight of **1c** and **1d** decreased much more than those accounted for loss of two nitric acid molecules indicating the thermal decomposition of the ligand, and, indeed, IR spectra of the residues were different from those of the deprotonated complexes. Instead, heating the acetate salts, **1′c** and **1′d**, up to 260 °C successfully afforded the deprotonated complexes of cobalt(II) and zinc(II), respectively, by elimination of acetic acid, though elimination took place more slowly in these cases. IR spectra of the residual solids were characteristic to those of the deprotonated complexes. Thus, it was shown that thermolysis of the non-deprotonated complexes yielded the corresponding deprotonated complexes. It is worth to note that the deprotonated complex **2d**, [Zn(babp)] was isolated only by thermolysis of **1′d** but not by deprotonation in solution under basic conditions.

The deprotonated complexes **2a—2c** showed clear melting points near 330 °C, and were stable up to these temperatures. Decomposition of these complexes were only observed when they were heated above their melting points. The deprotonated complex of zinc(II) **2d** did not show any weight loss up to 370 °C, and decomposed without showing any apparent melting above this temperature.

Discussion

Structure and Stability of the Complexes. The ligand babpH_2 is shown to coordinate as N_2O_2 tetradentate ligand to form two types of the complexes, one is the non-deprotonated type (nitrate salts), **1a—1d**, and the other the deprotonated ones, **2a—2d**. The structure of the complexes were elucidated by their IR spectra[1,5,6] and elemental analyses. In the case of acetates of the non-deprotonated complexes, **1′c** and **1′d**, however, babpH_2 was suggested to serve as an N_2 bidentate ligand from their IR spectra.

The non-deprotonated complexes of copper(II)[1] and nickel(II) were stable even in acidic aqueous solution, while those of cobalt(II) and zinc(II) were not stable in water. This difference in the stability of the non-deprotonated complexes were in agreement with Irving-Williams'[8] and Mellor-Malley's[9] laws. The deprotonated complexes, **2a—2d**, were stable enough not to suffer any change in neutral acid-free water.

Dissociation of Amide Protons. Amide proton is very weak acid and the pK_a is higher than 13 in most cases.[10] Complexation of metal ions at amide oxygen is known to increase their acidity.[10] Spectrometric titration of the nitrate salt of the non-deprotonated nickel(II) complex, **1b**, in water with pottasium hydroxide solution indicated that the two amide protons dissociated almost simultanously at pH 5.8 and the deprotonated complex **2a** precipitated. Titration of copper(II) complex **1a** by similar method showed that dissociation of both of its amide protons took place at pH 5.2.[1] Titration of the cobalt(II) complex could not be carried out because of its instability in water. Complexation of babpH_2 and cobalt(II) acetate gave the non-deprotonated complex, though complexation with nickel(II) or copper(II) acetate gave the deprotonated complex, suggesting that the acidity of the amide protons of the cobalt(II) complex is lower than that of copper(II) or nickel(II) complex. Thus acidities of the amide protons of the babpH_2 complexes follow the order, Co(II)<Ni(II)<Cu(II). Acidities of metal-chelated amide protons in peptides were also known to follow this order.[10]

In most cases amide groups are known to coordinate to metal ions by their oxygens, while, amide groups in deprotonated form by their nitrogens. In the cases of babpH_2, however, both babpH_2 and babp served as an N_2O_2 tetradentate ligand, and high acidity of amide protons in nitrate salts of the non-deprotonated complexes were observed. One of the reason why the amide protons in the complexes of babpH_2 have high acidity might be due to the high stability of the deprotonated complexes. They are thought to be stabilized by intramolecular charge transfer because they contain strong O-donor (deprotonated amide oxygens) and heteroaromatic N-donor having relatively strong π-electron accepting abilities (2,2′-bipyridine moiety).[11] This effect has been proposed as "intramolecular mixed ligand" effect[10,12] to explain the stability of the complexes of 8-quinolinol[13] and the deprotonated palladium(II) complex of 2-(acetylamino)pyridine.[6,10]

Thermal Properties. The results of thermal analyses of the non-deprotonated complexes indicated that dissociation of amide protons took place by heating in solid state. In some cases, thermolysis is an effective process to obtain deprotonated complexes, because dissolution of the complexes in aqueous solution sometimes causes the release of the metal ions from the complexes.

It is noteworthy that the deprotonated complexes **2a—2d** are thermally stable up to 300°C under aerobic atmosphere. This also enable thermal dissociations of acid moieties of the non-deprotonated complexes to give deprotonated ones.[14]

Experimental

Materials. 6,6′-Bis(benzoylamino)-2,2′-bipyridine (babpH_2) was prepared from 6,6′-diamino-2,2′-bipyridine[15] and benzoyl chloride according to the method previously reported.[1] Other chemicals were obtained commercially, and some of them were purified by conventional methods prior to use.

Spectral Measurements. IR spectra were measured by JASCO IR-700 spectrophotometer. Electronic spectra were recorded on a JASCO UVIDEC-505 spectrophotometer at 20 °C. Measurement of cobalt(II) complexes in this report were carried out under anaerobic conditions because they interact with molecular oxygen in solution.[2,3]

Thermal Analyses. TG and DTA curves were recorded simultanously on Shimadzu DTG-30 Thermal Analyzer with heating rate of 5 °C min^{-1} under aerobic conditions.

Nickel(II) Complex 1b: This was obtained from 78 mg (0.2 mmol) of babpH_2 and 58 mg (0.2 mmol) of $Ni(NO_3)_2\cdot6H_2O$ by complexation in methanol in a similar manner to the preparation of copper(II) complex **1a.**[1] Recrystallization from water gave 83 mg (68%) of pale green plates of Ni(babpH_2)$(H_2O)_2(NO_3)_2$.

Nickel(II) Complex 2b: This was obtained from 78 mg (0.2 mmol) of babpH_2 and 50 mg (0.2 mmol) of $Ni(OAc)_2\cdot4H_2O$ by complexation in chloroform in a similar manner to the preparation of copper(II) complex **2a.**[1] Recrystallization from benzene gave orange needles of [Ni(babp)], yield 57 mg (63%).

Cobalt(II) Complex 1′c: A mixture of 78 mg (0.2 mmol) of babpH_2 and 50 mg (0.2 mmol) of $Co(OAc)_2\cdot4H_2O$ in 100 cm^3 of chloroform was stirred at room temperature until the suspension became a homogeneous brown solution. Then the solvent was removed by evaporation to leave pink powder, which was washed by benzene, yielding 80 mg (66%) of Co(babpH_2)$(OAc)_2(H_2O)_2$.

Zinc(II) Complex 1′d: A mixture of 78 mg (0.2 mmol) of babpH_2 and 44 mg (0.2 mmol) of $Zn(OAc)_2\cdot2H_2O$ in 100 cm^3 of tetrahydrofuran was stirred at room temperature until the suspension became a homogeneous pale brown solution. Then solvent was removed by evaporation. Residual white powder was recrystallized from benzene to give 72 mg (62%) of Zn(babpH_2)$(OAc)_2$.

Cobalt(II) Complex 1c and Zinc(II) Complex 1d: A mixture of 78 mg (0.2 mmol) of babpH_2 and 50 mg (0.2 mmol) of $Co(OAc)_2\cdot4H_2O$ in 100 cm^3 of tetrahydrofuran was stirred at room temperature until the suspension became a homogeneous brown solution. Then 0.4 cm^3 of 1M HNO_3 (1 M=1 mol dm^{-3}) was added and was allowed to stand for 24 h at room temperature. The precipitated pale brown powder was collected by filtration, yielding 110 mg (90%) of **1b**, Co(babpH_2)$(H_2O)_2(NO_3)_2$. Compound **1d** was obtained from 78 mg (0.2 mmol) of babpH_2 and 44 mg (0.2 mmol) of $Zn(OAc)_2\cdot2H_2O$ in a similar manner to the preparation of **1c**, yielding 98 mg (79%) of Zn(babpH_2)$(H_2O)_2(NO_3)_2$ as white needles. Non-deprotonated complxes **1c** and **1d** were not obtained pure form by direct complexation of babpH_2 and nitrate.

Cobalt(II) Complex 2c: Under nitrogen gas bubbling, a mixture of 78 mg (0.2 mmol) of babpH_2 and 50 mg (0.2 mmol) of $Co(OAc)_2\cdot4H_2O$ in 20 cm^3 of methanol was stirred at room temperature until the mixture became a homogeneous brown solution. To this solution, 0.8 cm^3 of 0.5 M-methanolic KOH was added. The color of the solution changed to dark red followed by precipitation of red solid. After stirring another 1 h under nitrogen atmosphere at room temperature, the red solid was collected by filtration. Recrystallization from benzene gave red needles of **2c**, [Co(babp)], yield 60 mg (67%). When similar process was performed under aerobic atmosphere or oxygen bubbling, reaction mixture retained homogeneous after addition of alkali, and removal of most of methanol gave 55 mg of yellow powder, which showed almost the same IR spectrum as that of **2c** except that the former has strong absorption band at 1403 cm^{-1}.

Zinc(II) Complex 2d: Compound **1′d** (116 mg, 0.2 mmol) was heated at 280 °C under reduced pressure for 20 h. Yellow powder of [Zn(babp)], **2d**, was obtained as a residue, yield 84 mg (92%). Compound **2d** was not obtained as a precipitate by addition of potassium hydroxide to a solution of **1d** or **1′d** in methanol. Extraction by benzene from residual solid after removal of methanol gave only metal free babpH_2 as extract and $Zn(OH)_2$ as insoluble solid.

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