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Synthesis, Structures, and Properties of Nickel(II) Mixed-Ligand Complexes Containing Various *β*-Diketonates and a Phosphorus Donor Bidentate Ligand

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New mixed-ligand nickel(II) complexes containing *β*-diketonates and 1,2-bis(diphenylphosphino)ethane, [Ni(dike)(dppe)]X (X = BF_4, ClO_4, and NO_3) were synthesized and characterized. Since the ligand field strength of the phosphorus donor is very strong, the complexes [Ni(dike)(dppe)]X studied in this work are as stable as the square-planar both in solid state and in solutions.

Nickel(II) complexes have mainly two types of structures depending on ligand field strength and steric properties of the ligands; one is diamagnetic square-planar structure with yellow-red-pink colors, the other is paramagnetic octahedral structure with purple-blue-green colors, so their general structures can be easily expected from UV–vis spectra and magnetic behaviors.[1,2] In previous papers, we reported the chromotropic properties of many mixed-ligand nickel(II) complexes in solutions.[3] Our success in obtained stable mixed-ligand complexes (ternary system) is due to suitable combinations of the ligands with different stereo-chemical properties, i.e., one ligand is a sterically hindered ligand and the partner is slim one. The donor set of these complexes is mostly N2O2 such as [Ni(acac)(tmen)]BPh_4.[3] If we use the stronger coordinating ligand containing phosphorus as the partner ligand of *β*-diketonate, it is interesting that whether we can observe or can not observed the solvatochromic behavior in the new system. In this paper, we have used 1,2-bis(diphenylphosphino)ethane (dppe) and four *β*-diketonates shown in Fig. 1, to be the nickel(II) mixed-ligand complexes; Ni(acac)(dppe)BF_4 (**1a**), Ni(acac)(dppe)ClO_4 (**1b**), Ni(acac)(dppe)NO_3 (**1c**), Ni(bzac)(dppe)ClO_4 (**2**), Ni(dibm)(dppe)ClO_4 (**3**), and Ni(dipm)(dppe)ClO_4 (**4**). As the previous work related to this type of the system, only one mixed-ligand complex, [Ni(acac)(dppe)]BPh_4, was reported with the tetraphenylborate counter anion.[4] But no other complexes with different anions have been reported. The solution behavior of the obtained complexes was investigated by UV–vis spectra and NMR spectra. For acac complex **1a**, **1b**, and dibm complex **3**, their crystal structures have been determined by the method of the X-ray single crystal analysis.

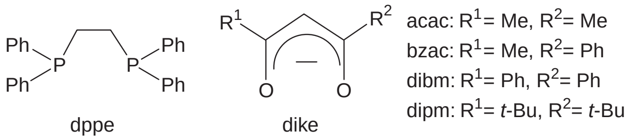

Fig. 1. Ligands dppe and dike.

Results and Discussion

Synthesis of the Mixed-Ligand Complexes. Only one Ni^{II} mixed-ligand complex containing acac and dppe with the tetraphenylborate counter anion, [Ni(acac)(dppe)]BPh_4, has been synthesized in the way showed in Eq. 1 by Favero et al.[4]

$$[\mathrm{Ni(acac)_2}] \xrightarrow{\text{dppe}} \xrightarrow{\mathrm{NaBPh_4}} [\mathrm{Ni(acac)(dppe)}]\mathrm{BPh_4}. \qquad (1)$$

But any other complexes containing different kinds of counter anions (such as BF_4^-, ClO_4^-, and NO_3^-) have not been reported so far. We have re-tried to synthesize the perchlorate in the same way,[3] and confirmed the presence of mixed-ligand complex [Ni(acac)(dppe)]ClO_4 in the dilute solution by UV–vis spectra. But after concentration for obtaining crystals at room temperature, the disproportionation products, the bis-dppe complex $[\mathrm{Ni(dppe)_2}](\mathrm{ClO_4})_2$ and the bis-acac complex $[\mathrm{Ni(acac)_2(Solvent)_2}]$ were obtained (see Eq. 2).

$$2[\mathrm{Ni(acac)(dppe)}]\mathrm{ClO_4} \rightleftharpoons [\mathrm{Ni(acac)_2(Solvent)_2}] + [\mathrm{Ni(dppe)_2}](\mathrm{ClO_4})_2. \qquad (2)$$

We can conclude that the equilibrium shown as Eq. 2 exists in the solution and this equilibrium shifts to the right hand side at room temperature because the solubility of $[\mathrm{Ni(dppe)_2}](\mathrm{ClO_4})_2$ is less than that of [Ni(acac)(dppe)]ClO_4 at the temperature. Then, we have succeeded in the isolation of mixed-ligand complexes with the ClO_4 or BF_4 anion at low temperature. In detail, as shown in Scheme 1, to a green ethanol solution of $[\mathrm{Ni(dike)(H_2O)_4}]$X (dike = acac, bzac, dibm, and dipm, X = BF_4, ClO_4, and NO_3) in ice bath, an equimolar amount of dppe solution was added and then color changed to brown. UV–vis spectra of this brown solution of all complexes have the similar absorption peak at around 425 nm, which is the characteristic shape of the square-planar Ni^{II} complex.[1] For comparison, the absorption of the bis-dppe complex shows a shoulder around 400 nm. The solution was kept in a freezer for several hours; then the yellow crystals could be observed. Although formations of the square-planar acac-nitrate complex **1c** and bzac-perchlorate complex **2** were confirmed by the absorption peaks in UV–vis spectra and ^{31}P NMR in EtOH solutions, it could not be obtained as a crystal but only as an oily product. In the IR spectra of obtained complexes, the characteristic bands due to $\nu_{C=O}$ and $\nu_{C=C}$ of coordinated *β*-diketonate in the regions of 1600–1400 cm^{-1} and free anion around 1100 cm^{-1} for both perchlorate and tetrafluoroborate were observed,[5] and all complexes were diamagnetic which imply that they have square-planar structures in solid state.

X-ray Crystal Structures of 1a, 1b, and 3. Figure 2 show the new crystal structure of complex [Ni(dibm)(dppe)]ClO_4 (**3**). Because the complexes [Ni(acac)(dppe)]BF_4 (**1a**) and

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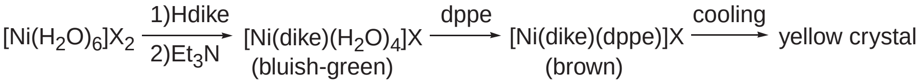

$$[Ni(H_2O)_6]X_2 \xrightarrow[2)Et_3N]{1)Hdike} \underset{\text{(bluish-green)}}{[Ni(dike)(H_2O)_4]X} \xrightarrow{dppe} \underset{\text{(brown)}}{[Ni(dike)(dppe)]X} \xrightarrow{cooling} \text{yellow crystal}$$

Scheme 1. Synthesis of mixed-ligand complexes [Ni(dike)(dppe)]X.

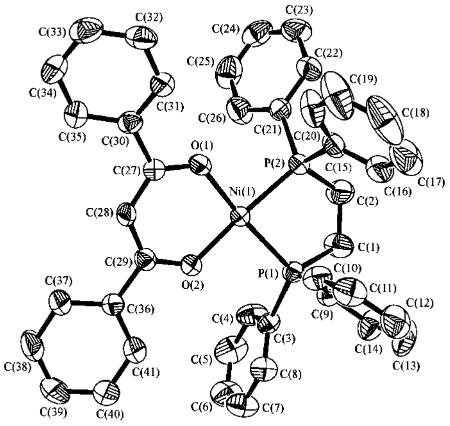

Fig. 2. An ORTEP view of the [Ni(dibm)(dppe)]ClO$_4$ (**3**). Perchlorate anion is omitted for clear viewing. Thermal ellipsoids are at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (°) for Complex **3**

Ni(1)–O(1)	1.866(2)	O(1)–Ni(1)–O(2)	94.83(11)
Ni(1)–O(2)	1.858(2)	P(1)–Ni(1)–P(2)	85.23(4)
Ni(1)–P(1)	2.1650(11)	P(1)–Ni(1)–O(2)	89.79(8)
Ni(1)–P(2)	2.1645(11)	P(2)–Ni(1)–O(1)	90.85(8)
		P(1)–Ni(1)–O(1)	170.63(8)
		P(2)–Ni(1)–O(2)	172.87(9)

[Ni(acac)(dppe)]ClO$_4$ (**1b**) were almost same structures as [Ni(acac)(dppe)]BPh$_4$,[4] we describe only complex **3** in this report. Table 1 lists selected bond distances and angles around the metal center in complex **3**. Two phenyl substituent groups of dibm have no direct steric influence to the partner ligand dppe. For all complexes, the anion BF_4^- or ClO_4^-, does not coordinate to the central metal ion and the coordination geometry of the nickel(II) is a distorted square-planar geometry involving two oxygen atoms of the β-diketonate and two phosphorus atoms of the dppe ligand. The bite angles of dppe and Ni–P bond lengths are almost same as the literature.[6] On the other hand, comparing Ni–O bond lengths of Ni–dike in dppe complexes with those of [Ni(acac)(tmen)]BPh$_4$,[7] one can see that the former bond distances (1.866(2) and 1.858(2) Å for complex **3**) are longer than the latter tmen complex (1.848(2) and 1.840(2) Å) due to the strong coordination power of phosphorus donors in dppe ligand. It is also noteworthy that the variations in the bond lengths C–O and C–C of the acetylacetonate chelate ring were observed in all complexes.[8]

Solution Behavior of the Complexes. Figure 3 shows UV–vis spectra of the analogous square-planar systems, [Ni(acac)(tmen)]BPh$_4$ in DCE,[3] [Ni(acac)(dppe)]ClO$_4$ (**1b**) and [Ni(dppe)$_2$](ClO$_4$)$_2$ in ACN. For the tmen complex, the spectra depended on the donor strength of the solvents, that is, structures and colors changed with the donor strength of the solvents (solvatochromism). However, for the dppe mixed-ligand complex **1b**, dissolving into five solvents with different donor numbers shown in respective parentheses, i.e., DCM (0), ACN (14), ACO (17), DMF (27), and DMSO (30), the yellow color of the complex solutions did not change any more, in fact UV–vis spectra were the same shape, as shown in Fig. 3b. Comparing d–d transition spectra of the dppe complexes containing the different β-diketonates, we could not observe any important differences in their spectral peaks, which mean that there is no substituent effect of β-diketonates on the ligand field strength of these dike–dppe complexes. From these results, the complexes obtained in this study, [Ni(dike)(dppe)]X, do not show any solvatochromism and keep their square-planar structures stably due to the strong ligand field strength of dppe ligand.

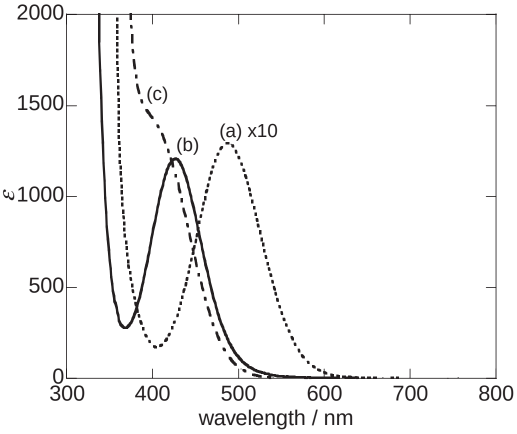

Fig. 3. UV–vis spectra of (a) [Ni(acac)(tmen)]BPh$_4$/DCE (ten times $\mathcal{E}$), (b) [Ni(acac)(dppe)]ClO$_4$ (**1b**)/ACN, and (c) [Ni(dppe)$_2$](ClO$_4$)$_2$/ACN.

And it is interesting to note that the value of d–d transition energy of the square-planar complex [Ni(acac)(dppe)]X (427 nm) is higher than that of corresponding tmen complex [Ni(acac)(tmen)]BPh$_4$ (486 nm, Fig. 3a). This reflects the fact that the ligand field strength of dppe is stronger than that of tmen, so the square-planar structure of the dppe ternary complex is more stable. Additionally, the intensities at λ_{max} of dppe binary and ternary complexes are ten times as large as that of the tmen complex, which is attributed to the intensity stolen from the strong CT transition in the dppe complex. $[Ni(CN)_4]^{2-}$ and $[Ni(TetraMeen)_2]^{2+}$ (TetraMeen = 2,3-dimethyl-2,3-diaminobutane) are known as the complexes which keep their square-planar structures in any solvent due to their strong ligand field strength; $[Ni(CN)_4]^{2-}$: $\lambda_{max} = 357$ nm, $[Ni(TetraMeen)_2]^{2+}$: $\lambda_{max} = 434$ nm.[9,10] The λ_{max} value of [Ni(acac)(dppe)]X in this work exists in between the values of the complex with cyano-ligand and that with TetraMeen ligand.

Experimental

The abbreviations of the solvents used are as follows: dichloromethane, DCM; 1,2-dichloroethane, DCE; acetone, ACO; acetonitrile, ACN; *N*,*N*-dimethylformamide, DMF; and dimethylsulf-

Table 2. Crystallographic Data of **1a**, **1b**, and **3**

	1a	**1b**	**3**
Crystal color	brown	brown	brown
Empirical formula	$C_{31}H_{31}BF_4NiO_2P_2$	$C_{31}H_{31}ClNiO_6P$	$C_{41}H_{35}ClNiO_6P_2$
Formula weight	643.05	655.69	779.82
Crystal dimensions/mm^3	0.80 × 0.50 × 0.30	0.50 × 0.50 × 0.30	0.40 × 0.35 × 0.20
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$
a/Å	25.934(12)	26.204(11)	17.523(4)
b/Å	10.261(3)	10.260(4)	10.288(2)
c/Å	23.587(8)	23.543(8)	20.011(4)
β/°	92.97(3)	92.53(3)	91.447(8)
V/Å^3	6268.(4)	6323.(4)	3606.4(11)
Z	8	8	4
D_{calcd}/Mg m^{-3}	1.363	1.378	1.436
μ/mm^{-1}	0.771	0.840	0.7492
θ_{max}/°	27.50	27.53	30.05
No. of observations	6467	6351	5488
Parameters	371	371	495
R_1 ($I > 2\sigma(I)$)	0.0611	0.0695	0.0681
R_w	0.1910	0.2114	0.0804
S (Fit on F^2)	1.016	1.071	1.227

oxide, DMSO.

Preparation of dppe Mixed-Ligand Complexes. The complexes Ni(dike)(dppe)X were prepared by the same general methods. To a solution of $NiX_2 \cdot 6H_2O$ (5 mmol) in ethanol (10 mL) in ice bath, a mixture of Hdike (5 mmol) and triethylamine (5 mmol) in ethanol (5 mL) was added, and then dppe (5 mmol) in dichloromethane (5 mL) was dropped into the solution. This mixture was stirred for 1 h, and after filtration, the solution was kept in a freezer (−18 °C). Four hours later, a yellow precipitate was obtained. Brown crystals for X-ray structure determination were obtained by the vapor diffusion of diethyl ether into the acetonitrile solution of the product.

X-ray Crystallography. Crystallographic data and refinement parameters are listed in Table 2. Crystal data have been submitted to Cambridge Crystallographic Data Centre; the document numbers are CCDC-288011 (**1a**), 606996 (**1b**), and 288012 (**3**). Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, by e-mailing: deposit@ccdc.cam.ac.uk, or contacting CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK [Fax: +44 1223 336033].

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Supporting Information

Materials, physical measurements, crystallographic data of **1a** and **1b**, and analytical data of all complexes. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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