# Dalton Transactions

## PAPER

View Article Online

Cite this: DOI: 10.1039/c3dt33011g

Received 16th December 2012, Accepted 31st January 2013 DOI: 10.1039/c3dt33011g

www.rsc.org/dalton

## Introduction

Cobalt(II) and nickel(II) complexes have attracted much attention as potential catalysts for various reductive reactions such as hydrogen evolution,  $^{1a-e,2a,b}$  CO<sub>2</sub> reduction,  $^{1f-i,2c}$  reductive dehalogenation<sup>1j,2d,2e</sup> and others.<sup>1k,2f</sup> In designing such complexes, the 2,2':6',2"-terpyridine (trpy) ligand is especially useful<sup>1f</sup> because of its well-defined coordination geometry. In order to utilize such complexes in catalytic redox reactions, we need to introduce vacant coordination sites into the metal center (Fig. 1). However, in the case of 3d metals, it is often difficult to synthesize polypyridyl complexes with a vacant site, because they tend to form homoleptic, coordination saturated complexes through fast ligand exchange. In order to solve this problem, we previously designed and synthesized binary ligands consisting of terpyridine and bipyridine (bpy) (10 in Fig. 2).<sup>3</sup> By using these binary ligands, we prepared "heteroleptic" polypyridine cobalt(II) mononuclear complexes that are stable even under repetitive electrochemical redox cycles.

## New ternary ligands consisting of an N4 bridging ligand and two terpyridines, and their Co(II) and Ni(II) dinuclear complexes. Structure, redox properties, and reaction with acid†

Hiroki Kon and Toshi Nagata\*

Two ternary ligands consisting of two 2,2':6',2''-terpyridines and one N4-quadridentate  $\mu_{2,\eta}^{2}$ -bridging ligand were synthesized. The N4 bridge is 1,4-bis(2-pyridyl)phthalazine in ligand **1**, and 3,6-bis(2-pyridyl)pyridazine in ligand **2**. Two Co(II) dinuclear complexes  $[(1)Co_2(\mu-OH)]^{3+}$  and  $[(2)Co_2(\mu-OH)]^{3+}$ , and one Ni(II) dinuclear complex  $[(1)Ni_2(\mu-CI)]^{3+}$  were obtained. In the crystal structures of  $[(1)Co_2(\mu-OH)]^{3+}$  and  $[(1)Ni_2(\mu-CI)]^{3+}$ , two pyridine rings are twisted around the pyridine–phthalazine bonds to avoid steric repulsion between the hydrogen atoms. The pyridine rings also showed a significant tilt from the octahedral coordination plane, which causes the large positive shift of the first reduction potentials. Upon the addition of a proton, the cobalt dinuclear complexes can release one cobalt ion selectively, and the dinuclear complexes can be easily restored by the addition of a tertiary amine.

Furthermore, we successfully utilized such cobalt complexes in photoreactions using porphyrins as the photosensitizer.<sup>4</sup>

As the next step, we considered expansion of this "binary ligand" concept to dinucleating ligands. Since we are particularly interested in redox catalysis with two proximal vacant sites, we planned to use an N4-quadridentate  $\mu_2$ , $\eta^2$ -bridging



**Fig. 1** Possible designs of dinuclear complexes with N4 bridging ligands: (a) desired structure with two vacant sites pointing inwards, (b) reported structures with two facing N4 ligands, (c) reported structures with one or two extra chelating ligands, and (d) the design in this work.

Research Center for Molecular Scale Nanoscience, Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan. E-mail: toshi-n@ims.ac.jp; Fax: +81-564-59-5531; Tel: +81-564-59-5531

<sup>†</sup>Electronic supplementary information (ESI) available: Synthetic procedures for compounds **2**, **5**, **6b**, **7b**, and **8b**; the X-ray structures of the dinickel complex (Fig. S1 and S2, Table S1); supplementary electrochemical results (Fig. S2–S6, S8); acid-dependent change of the ESI-MS (Fig. S7). CCDC 915668 and 915669. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33011g



Fig. 2 Chemical structures of the ternary ligands (1 and 2) prepared in this study, and the binary ligand (10) from ref. 3.

motif, namely 1,4-bis(2-pyridyl)phthalazine or 3,6-bis-(2-pyridyl)pyridazine (Fig. 1a). Such kinds of N4 ligands have been extensively used for studies of dinuclear metal complexes including cobalt and nickel complexes.<sup>5</sup> In designing these complexes, it is important to block the open coordination sites selectively to avoid uncontrollable polymerization while retaining the vacant sites for reactions. In preceding work, this was achieved either by using two N4-bridging ligands in a face-toface manner (Fig. 1b) or by appending one or two extra chelating ligands at each end of the N4 ligands (Fig. 1c). However, in both cases, at least two coordination sites are left open for each metal ion, which could cause complicated results when applied to catalytic reactions. On the other hand, our approach with "binary ligands" will leave only one open site for each metal ion (Fig. 1d), thereby providing better control of the reactivity.

It is also notable that recent reports have revealed interesting chemistry of dinuclear complexes including polypyridyl ligands,<sup>6</sup> especially ruthenium complexes.<sup>7</sup> Although synthesis of similar compounds with 3d metals would suffer from ligand exchange, our "linked ligand" approach can overcome such a problem. There are also other reports of dinuclear cobalt and nickel complexes with intriguing catalytic properties.<sup>8,9</sup> However there is only one known well-characterized example including terpyridine,  $[[Co(trpy)(bpy)]_2(\mu-O_2)](PF_6)_4$ .<sup>10</sup>

In this paper, we wish to report the syntheses of new "ternary" ligands 1 and 2, which consist of two terpyridines and one N4 bridge which is 1,4-bis(2-pyridyl)phthalazine in 1 and 3,6-bis(2-pyridyl)pyridazine in 2. They form stable dinuclear complexes  $[(1)Co_2(\mu-OH)]^{3+}$ ,  $[(1)Ni_2(\mu-Cl)]^{3+}$  and [(2)-

 $Co_2(\mu$ -OH)]<sup>3+</sup>, and the former two complexes were characterized by X-ray crystallography. The cyclic voltammograms of the dicobalt complexes revealed interesting changes in comparison with the mononuclear cobalt( $\pi$ ) complex. Furthermore, we examined the reaction of these dinuclear complexes with acid, and observed reversible formation of the mononuclear cobalt complexes by acid-induced elimination of one cobalt ion.

## **Results and discussion**

### Design and syntheses

The structures of the new ternary ligands 1 and 2 are shown in Fig. 2. Both ligands consist of an N4 bridge and two terpyridines linked by a butylene linker. The N4 bridge can bind two metal ions in close proximity and two terpyridines can fill the coordination sites in meridional tridentate mode, leaving one coordination site open for each ion. Furthermore, the butylene linker has appropriate length and freedom for the N4 bridge and terpyridines to adapt the octahedral geometry.

The synthetic routes of the ternary ligands **1** and **2** are shown in Scheme **1**. The stannylpyridine **5** was synthesized from 2,5-dibromopyridine according to the procedure reported in previous literature<sup>11</sup> except that the protecting group of the aldehyde was different. The protected dialdehyde **6** of the N4



**Scheme 1** Syntheses of ligands **1** and **2**, and their Co/Ni complexes.

bridge was synthesized by the Stille coupling reaction of 5 and 1,4-dichlorophthalazine or 3,6-dichloropyridazine in the presence of catalytic amounts of CuI.<sup>7*a*,12</sup> The acetal protecting group was removed using trifluoroacetic acid, and the dialdehyde 7 was oxidized by the reaction with NaClO<sub>2</sub> to give the dicarboxylic acid **8**. Finally, the ternary ligand **1** or **2** was prepared by the condensation reaction with **8** and the amino terpyridine **9**<sup>13</sup> using EDC·HCl.

Syntheses of the dinuclear cobalt(II) and nickel(II) complexes  $[(1)Co_2(\mu-OH)]^{3+}$ ,  $[(1)Ni_2(\mu-Cl)]^{3+}$  and  $[(2)Co_2(\mu-OH)]^{3+}$  are also shown in Scheme 1. The complexes  $[(1)Co_2(\mu-OH)]^{3+}$  and  $[(2)Co_2(\mu-OH)]^{3+}$  were synthesized by the reaction of 1 or 2 and  $Co(OAc)_2 \cdot 4H_2O$  in EtOH. The nickel dinuclear complex  $[(1)-Ni_2(\mu-Cl)]^{3+}$  was synthesized by the reaction of 1 and  $NiCl_2 \cdot 6H_2O$ . Interestingly, the nickel complex with the ternary ligand 2 was not obtained, in spite of many trials under various conditions and starting materials. Furthermore, neither a  $\mu$ -chloro dicobalt(II) complex nor a  $\mu$ -hydroxo dinickel(II) complex was obtained. Although we do not yet fully understand the cause of this sharp selectivity, it is likely that one of the reasons is the overcrowding caused by the close location of the N4 ligand and two terpyridine ligands (see below).

#### **Crystal structures**

The structures of  $[(1)Co_2(\mu$ -OH)]^{3+} and  $[(1)Ni_2(\mu$ -Cl)]^{3+} were examined by X-ray crystallography. Details of the crystallographic parameters and the structure refinements are listed in Table 1. The structure of the complex cation  $[(1)Co_2(\mu$ -OH)]^{3+} is shown in Fig. 3, and the selected bond distances and angles are given in Table 2. The structure of  $[(1)Ni_2(\mu$ -Cl)]^{3+} is roughly similar to the dicobalt complex, and is shown in the ESI (Fig. S-1<sup>†</sup>).

	[( <b>1</b> )Co <sub>2</sub> (μ-OH)](PF <sub>6</sub> ) <sub>3</sub> · 5CH <sub>3</sub> COCH <sub>3</sub>	$\begin{array}{l} [(1)Ni_2(\mu\text{-}Cl)](PF_6)_3\cdot\\ 2CH_3COCH_3\cdot C_6H_5CH_3\end{array}$	
Formula	C <sub>85</sub> H <sub>87</sub> N <sub>12</sub> O <sub>10</sub> CO <sub>2</sub> P <sub>3</sub> F <sub>18</sub>	C104H100N12O6Ni2ClP3F18	
Formula weight	1989.46	2201.74	
Temperature/°C	-150	-150	
Crystal system	Monoclinic	Monoclinic	
Space group	$P2_1/n$	C2/c	
a/Å	19.817(3)	17.106(3)	
b/Å	23.206(3)	27.459(4)	
c/Å	19.702(3)	21.567(3)	
$\alpha / ^{\circ}$	90	90	
β/°	93.073(2)	101.727(2)	
$\gamma/^{\circ}$	90	90	
$V/Å^3$	9047(2)	9919(2)	
Ζ	4	4	
$\mu/\mathrm{cm}^{-1}$	5.204	5.510	
$d_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.460	1.474	
No. of obsd reflns	69 421	38 445	
$(I > 2\sigma(I))$			
No. of unique	20 404 (0.0308)	11 155 (0.0613)	
reflns $(R_{int})$			
No. of parameters	1183	710	
GOF	1.044	1.079	
$R_1, WR_2$	0.0622, 0.1837	0.0625, 0.1273	

The complex cation  $[(1)Co_2(\mu-OH)]^{3+}$  has an approximate  $C_s$  symmetry. The cobalt ions are octahedral six-coordinate and are bridged by the phthalazine and one hydroxo ligand. The bond distances of Co–N are 2.07–2.19 Å, which are in a similar range as in the Co(II) mononuclear complex we reported previously (2.08–2.19 Å)<sup>3</sup> and other phthalazine or pyridazine bridged Co(II) dinuclear complexes with acyclic ligands.<sup>5a,b,d</sup>



**Fig. 3** Drawings of the X-ray structure of the complex cation  $[(1)Co_2(\mu-OH)]^{3+}$ : (a) an ORTEP side view, (b) bottom view, (c) space-filling model. The dotted arrows in (c) indicate the 3-hydrogens causing steric repulsion with the phthala-zine *peri* hydrogens.

**Table 2** Selected bond distances (Å) and angles (°) for  $[(1)Co_2(\mu-OH)]^{3+}$ 

Bond distances		Bond angles			
Co1-O1 Co1-N1 Co1-N2 Co1-N3 Co1-N4 Co1-N5	$\begin{array}{c} 1.960(2)\\ 2.199(3)\\ 2.071(3)\\ 2.172(3)\\ 2.130(3)\\ 2.168(3) \end{array}$	C01-O-C02 O-C01-N1 O-C01-N2 O-C01-N3 O-C01-N4 O-C01-N5	$\begin{array}{c} 125.85(10)\\ 102.10(9)\\ 96.84(9)\\ 94.34(9)\\ 87.21(9)\\ 161.08(9) \end{array}$	N1-Co1-N2 N1-Co1-N3 N1-Co1-N4 N1-Co1-N5 N2-Co1-N3 N2-Co1-N4 N2-Co1-N5	$75.58(9) \\ 147.85(9) \\ 98.04(9) \\ 83.62(9) \\ 75.16(9) \\ 173.01(9) \\ 102.06(9) $
(a)	23.5°	(b)	1.6° (	(c) 8	3.6°
N(5 N(1) Co(1)	N(2)	(3) • •			

**Fig. 4** Partial structures around the metal ion in (a)  $[(1)Co_2(\mu-OH)]^{3+}$ , (b)  $[(10)-CoCI]^+$  (ref. 3), and (c) the phthalazine-bridged diruthenium complex reported by Thummel (ref. 7*a*).

The pyridine rings attached to phthalazine are not coplanar with the phthalazine ring to avoid the steric hindrance between the hydrogen atoms at the 3-positions of pyridine and the peri (5,8-) positions of phthalazine. This situation is visualized in the space-filling drawing (Fig. 3c). Similar distortion was also observed in the dinuclear ruthenium complex by Thummel.<sup>7a</sup> In the present case, the pyridine rings connected to the phthalazine ring are not only twisted from the phthalazine plane but also significantly tilted from the octahedral coordination plane. Fig. 4 shows the partial structures around one metal ion with coordination atoms and one pyridine ring of the N4 bridge. For comparison, the corresponding partial structures of the mononuclear complex and the phthalazinebridged dinuclear ruthenium complex reported by Thummel<sup>7a</sup> are also shown. In the dinuclear complexes  $[(1)Co_2(\mu-OH)]^{3+}$ , the dihedral angle between the pyridine ring and the Co-O1-N2-N5 plane is 23.5°. This dihedral angle is much larger than the small angle of 1.6° in the cobalt mononuclear complex or 8.6° in the phthalazine-bridged diruthenium complex. The unusual tilting in the present complexes is likely to be caused by the steric repulsion between the terpyridine ligand and the ortho (2-) hydrogen of the pyridine ring. Indeed, the estimated distances between the planes of the central rings of the terpyridine and the ortho hydrogens are 2.781(2) and 2.772(2) Å in  $[(1)Co_2(\mu-OH)]^{3+}$ , which are less than the sum of the van der Waals radii of hydrogen (1.20 Å) and carbon (1.70 Å). This tilted structure causes a decrease of the electronic donation

from pyridine nitrogens to the metal ions, which results in the decrease of the electron density on the metal ions and hence the positive shift of the first reduction potential in comparison with the mononuclear complex (see below).

The dinickel complex  $[(1)Ni_2(\mu-Cl)]^{3+}$  showed bond lengths and angles commonly observed in other nickel(II) polypyridine complexes.<sup>14</sup> The structure was similar to that of [(1)- $Co_2(\mu-OH)$ <sup>3+</sup>, however there was a characteristic difference in the manner in which the pyridine rings were twisted. In the cobalt complex, both the 3-hydrogens were on the same side (the nearer side in Fig. 3) of the phthalazine plane, whereas in the nickel complex, they were on opposite sides (Fig.  $S-1^{+}$ ). These different conformations resulted in the longer Ni…Ni distance (3.754 Å) in  $[(1)Ni_2(\mu-Cl)]^{3+}$  than the Co…Co distance (3.484 Å) in  $[(1)Co_2(\mu-OH)]^{3+}$  (Fig. S-2<sup>+</sup>). This observation is consistent with the different bridging anion; the nickel complex needs to have longer Ni-Ni distance to accommodate the larger chloride bridging anion. These M···M distances are similar to those reported in the pyridazine-bridged  $Co_2(\mu-OH)$ complex  $(3.477 \text{ Å})^{5b}$  and the phthalazine-bridged Ni<sub>2</sub>(µ-Cl) complex (3.678 Å).<sup>5g</sup>

#### Cyclic voltammograms

The cyclic voltammograms (CVs) of  $[(1)Co_2(\mu-OH)]^{3+}$ ,  $[(1)-Ni_2(\mu-Cl)]^{3+}$  and  $[(2)Co_2(\mu-OH)]^{3+}$  are shown in Fig. 5. In the CV of  $[(1)Co_2(\mu-OH)]^{3+}$ , reversible waves were observed at -1.02, -1.43 and -1.81 V. The first two waves were confirmed as a one electron process by controlled potential coulometry (ESI, Fig. S-3†). By comparison with the voltammogram of ligand 1, the most negative wave can be tentatively assigned to the reduction of the ligand, and the more positive two waves to the redox couples of  $Co_2(I,II)/Co_2(I,II)$  and  $Co_2(I,II)/Co_2(I,II)$ .

The potentials of the first two reduction waves were significantly separated (0.41 V), which indicates that the electronic interaction between the two cobalt ions is relatively strong in comparison with other pyridazine/phthalazine-bridged dicobalt complexes previously reported (0.14-0.29 V).<sup>1e,5b,d,f</sup> Such strong interaction can be partly attributed to the hydroxo bridge; however, there is also a report of another µ-hydroxo- $\mu_2, \eta^2$ -pyridazine Co<sub>2</sub> complex with separation as small as 0.11 V.<sup>5b</sup> At present, we cannot give a totally satisfactory explanation for this exceptionally strong electronic coupling between the Co centers, which should be a subject of future studies. The first reduction potential of  $[(1)Co_2(\mu-OH)]^{3+}$  was shifted to the positive (0.22 V) in comparison with that of the mononuclear Co(II) complex.<sup>3</sup> This positive shift can be attributed to the decrease in the electronic donation from the pyridine nitrogen, which was caused by the tilted coordination of the pyridine (see above).

Although the first two reduction waves were well separated from the subsequent ones, it may be the case that the ligand is not completely "innocent" (*i.e.* redox inactive), as suggested from the spectroelectrochemical results (ESI, Fig. S-4†). Controlled-potential electrolysis of ligand **1** at -2.10 V showed characteristic peaks at 540 and 800 nm ( $\varepsilon = 14\,000$  and 11 000  $M^{-1}$  cm<sup>-1</sup> respectively). On the other hand, controlled-



**Fig. 5** Cyclic voltammograms (negative side) for (a) ligand **1**, (b)  $[(1)-Co_2(\mu-OH)]^{3+}$ , (c)  $[(1)Ni_2(\mu-CI)]^{3+}$ , (d) ligand **2**, and (e)  $[(2)Co_2(\mu-OH)]^{3+}$  in DMF with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>.

potential electrolysis of the dicobalt complex at -1.20 V caused the appearance of two peaks at 480 and 710 nm ( $\varepsilon = 8000$  and 5000 M<sup>-1</sup> cm<sup>-1</sup> respectively). The spectrum is quite different from the reduced ligand, which is consistent with the metalcentered reduction. However, even after electrolysis of the dicobalt complex at -2.10 V, the characteristic peak at 800 nm did not appear. This result suggests that there is significant interaction between the metal center and the ligand  $\pi$  system in the reduced state.

In the positive region, an irreversible wave was observed at 1.47 V (ESI, Fig. S-6<sup>†</sup>). This corresponds to the oxidation of the cobalt ion, and is shifted to the positive direction by more than 1 V in comparison with that of the mononuclear cobalt complex.<sup>3</sup> This large positive shift cannot be fully explained by the decrease of the electron donation; one additional cause may be the steric overcrowding provided by two terpyridine groups, which would be even more severe for the more compact Co(m) state.

The CV of  $[(1)Ni_2(\mu-Cl)]^{3+}$  showed a similar behavior with the dicobalt complex. The positive shift of the oxidation potential was smaller than the dicobalt case (*ca*. 0.2 V). Such a difference can be reasonably explained by smaller changes in bond

lengths for Ni(II)/Ni(III) (typically 0.03–0.05 Å)<sup>15</sup> compared with those for Co(II)/Co(III) (*ca*. 0.2 Å).<sup>3</sup>

The CV of  $[(2)Co_2(\mu-OH)]^{3+}$  also showed a similar voltammogram with  $[(1)Co_2(\mu-OH)]^{3+}$ , except that the reduction potentials are shifted to the negative by about 0.2 V. Although we can only speculate about the structure of  $[(2)Co_2(\mu-OH)]^{3+}$ , it is highly possible that the N4 bridge in  $[(2)Co_2(\mu-OH)]^{3+}$  is closer to coplanar than in  $[(1)Co_2(\mu-OH)]^{3+}$  because of the lack of steric repulsion by the *peri* hydrogens. Consequently, the pyridine rings would be coplanar with the coordination plane, resulting in "normal" reduction potential.

#### Reaction with acid

Peters and co-workers examined the reaction of some dicobalt complexes (of type b in Fig. 1) with a proton source and revealed that the reduction of protons occurred.<sup>1e</sup> During our examination of redox reactions of these dinuclear complexes in the presence of various additives, we found that the reaction of  $[(1)Co_2(\mu-OH)]^{3+}$  with H<sup>+</sup> showed interesting behavior. Fig. 6 shows the change of the CVs of  $[(1)Co_2(\mu-OH)]^{3+}$  when CF<sub>3</sub>SO<sub>3</sub>H was added. Initially, the CV of  $[(1)Co_2(\mu-OH)]^{3+}$  shows the redox couples at -1.03 V and -1.42 V as shown in Fig. 6a. After the addition of 1 eq. of CF<sub>3</sub>SO<sub>3</sub>H to the solution, a new peak at -1.20 V appeared with a decrease of the peaks



Fig. 6 The changes of the CVs of  $[(1)Co_2(\mu$ -OH)]^{3+} with the addition of CF<sub>3</sub>SO<sub>3</sub>H (a) 0 eq., (b) 1.0 eq., (c) 2.0 eq. and (d) after the addition of 5 eq. iPr<sub>2</sub>EtN.



**Fig. 7** Two possible structures formed from  $[(1)Co_2(\mu-OH)]^{3+}$  by the addition of CF<sub>3</sub>SO<sub>3</sub>H.

at -1.03 V and -1.42 V (Fig. 6b). When one more equiv. of CF<sub>3</sub>SO<sub>3</sub>H was added, the original redox couples completely disappeared and the peak at -1.20 V increased with the appearance of a new peak at -0.24 V (Fig. 6c). When 5 eq. of N,N-diisopropylethylamine (iPr<sub>2</sub>EtN) was added to the solution, the original redox waves were restored as shown in Fig. 6d.

We performed the reaction tracking by ESI-MS spectra (ESI, Fig. S-7<sup>†</sup>). In the initial state, only one main peak was observed at m/z = 421.1, which was assigned to the trication [1 + 2Co + 1] $OH^{3+}$ . After the addition of 10 eq. of  $CF_3SO_3H$ , a new peak appeared at m/z = 427.1, which was assigned to [1 + 2Co + OH] $+ H_2O^{3+}$ . After the addition of 30 eq. of CF<sub>3</sub>SO<sub>3</sub>H, another new peak at m/z = 396.1 became most prominent, which was assigned to  $[1 + Co + H^{+}]^{3+}$ . There are two possible structures for this formula, one is "Co(trpy)<sub>2</sub>" and another is "Co(trpy)-(bpy)" (Fig. 7). For the " $Co(trpy)_2$ " type to be produced, at least one ligand substitution reaction must take place. On the other hand, the "Co(trpy)(bpy)" type can be produced by simply releasing one cobalt ion. We therefore propose that the latter one is more likely. The CV observations also support this speculation. The voltammetric waves at -1.20 and -0.24 V were very similar to those of the mononuclear Co<sup>II</sup>(trpy)(bpy) complex which we reported previously.<sup>3</sup> Furthermore, the CV almost turned back to the initial shape after the addition of excess iPr2EtN, and the ESI-MS spectrum also showed one major peak at m/z = 421.1, which is the same as in the initial state. This observation is also consistent with the "Co(trpy)-(bpy)" type, because this structure can easily restore the original dinuclear complex by simply picking up one Co(II) ion.

The other cobalt dinuclear complex  $[(2)Co_2(\mu-OH)]^{3+}$  also showed a similar change of the CV after addition of CF<sub>3</sub>SO<sub>3</sub>H

(Fig. S-8<sup>+</sup>), which indicates that the same reaction occurred in  $[(2)Co_2(\mu-OH)]^{3+}$ . On the other hand, the CV of  $[(1)Ni_2(\mu-CI)]^{3+}$ was unchanged upon the addition of  $CF_3SO_3H$  (Fig. S-9<sup>†</sup>), which indicates that the nature of the bridging anion is important for the reaction with CF<sub>3</sub>SO<sub>3</sub>H. That is, the hydroxobridged dinuclear complex releases the second metal ion more easily upon protonation than the chloride-bridged complex.

## Conclusions

We synthesized ternary ligands consisting of two terpyridines and one N4 bridge which is either 1,4-bis(2-pyridyl)phthalazine or 3,6-bis(2-pyridyl)pyridazine. These ligands exclusively formed cobalt(II) and nickel(II) dinuclear complexes with OH or Cl as the bridging anion respectively. The structures of the phthalazine-bridged complexes revealed characteristic deformation caused by the steric hindrance within the organic ligands. The electrochemistry of these dinuclear complexes was qualitatively similar to the reported compounds with the pyridazine/phthalazine bridge; however, some of the redox potentials were significantly different from the reported values, which is (at least partly) caused by the presence of the nearby terpyridine groups. The cobalt dinuclear complexes reacted with a proton and released one cobalt ion selectively, and the dinuclear complexes were restored by the addition of a small excess of amine. This easy restoration is derived from the effect of the partial structure (like the binary ligands) which can readily pick up the free cobalt ions. These characteristic reactions can be useful to design and synthesize more intriguing compounds such as heterodinuclear metal complexes.

## Experimental section

### General

Reagents were purchased from Wako, Nacalai, and Aldrich, and used as received unless otherwise noted. The syntheses of compounds 2, 5, 6b, 7b and 8b are described in the ESI.<sup>†</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured at room temperature with JEOL LA400 and LA500 spectrometers; tetramethylsilane was used as the internal reference. ESI-MS spectra were recorded on a Waters Micromass LCT.

#### Syntheses

1,4-Bis[5-(1,3-dioxane-2-yl)-2-pyridyl]phthalazine (6a). A mixture of 5 (1.07 g, 2.35 mmol), 1,4-dichlorophthalazine (196 mg, 0.98 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (24.3 mg, 0.021 mmol) and CuI (8.1 mg, 0.043 mmol) in DMF (10 ml) was heated to reflux for 24 h under N<sub>2</sub>. Dichloromethane and sat. NaHCO<sub>3</sub> aq. were added, and the mixture was extracted with CH2Cl2. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The product was purified by column chromatography (alumina,  $CH_2Cl_2$ -MeOH = 100:0 - 99:1). The residual solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane and the pale brown solid was

Downloaded by Cape Breton University on 02 March 2013

obtained by filtration. Yield: 325 mg (0.711 mmol, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 8.92 (d, <sup>4</sup>*J*(H,H) = 1.6 Hz, 2H; py-6-H), 8.79 (dd, <sup>3</sup>*J*(H,H) = 6.4 Hz, <sup>4</sup>*J*(H,H) = 3.2 Hz, 2H; phthalazine-6,7-H), 8.28 (d, <sup>3</sup>*J*(H,H) = 8.0 Hz, 2H; py-3-H), 8.08 (dd, <sup>3</sup>*J*(H,H) = 8.0 Hz, <sup>4</sup>*J*(H,H) = 2.0 Hz, 2H; py-4-H), 7.88 (dd, <sup>3</sup>*J*(H,H) = 6.4 Hz, <sup>4</sup>*J*(H,H) = 3.4 Hz, 1H; phthalazine-5,8-H), 5.71 (s, 2H; dioxane-2-H), 4.32–4.37 (m, 4H; dioxane-4,6-H), 4.05–4.11 (m, 4H; dioxane-4,6-H), 2.25–2.34 ppm (m, 2H; dioxane-5-H).

2,2'-(1,4-Phthalazinediyl)dipyridine-5,5'-dicarbaldehyde (7a). Compound 6a (258 mg, 0.565 mmol) was dissolved in CHCl<sub>3</sub> (6 ml), and H<sub>2</sub>O (6 ml) and trifluoroacetic acid (4 ml) were added and stirred at 80 °C. After 8 h, the reaction mixture was neutralized by the addition of the sat. NaHCO<sub>3</sub> aq. and extracted with CH2Cl2. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The <sup>1</sup>H NMR of the reaction mixture was examined, and if the deprotection of the cyclic acetal was incomplete, this operation was repeated once again. The residual solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane and the pale yellow solid was obtained by filtration. Yield: 156 mg (0.458 mmol, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 10.29 (s, 2H; -CHO), 9.31 (d,  ${}^{4}J(H,H)$  = 2.0 Hz, 2H; py-2-H), 8.93 (dd,  ${}^{3}J(H,H) = 6.4$  Hz,  ${}^{4}J(H,H) = 3.2$  Hz, 2H; phthalazine-6,7-H), 8.55 (d,  ${}^{3}$ /(H,H) = 8.0 Hz, 2H; py-5-H), 8.46 (dd,  ${}^{3}$ /(H,H) = 8.0 Hz,  ${}^{4}J(H,H)$  = 2.2 Hz, 2H; py-4-H), 8.00 ppm (dd,  ${}^{3}J(H,H)$  = 6.4 Hz,  ${}^{4}J(H,H) = 3.2$  Hz, 1H; phthalazine-5,8-H).  ${}^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 190.4 (-CHO), 173.1 (py-6-C), 156.1 (Pht-1-C, Pht-4-C), 150.7 (py-2-C), 137.2 (py-4-C), 132.9 (Pht-6-C, Pht-7-C), 131.1 (py-3-C), 126.9 (py-5-C), 126.2 (Pht-5-C, Pht-8-C), 126.0 (Pht-4a-C, Pht-8a-C).

2,2'-(1,4-Phthalazinediyl)dipyridine-5,5'-dicarboxylic acid (8a). Compound 7a (365 mg, 1.07 mmol), NaClO<sub>2</sub> (80%, 373 mg, 3.31 mmol) and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O (509 mg, 3.26 mmol) were suspended in a mixture of CH<sub>3</sub>CN (30 ml)–H<sub>2</sub>O (9 ml)– H<sub>2</sub>O<sub>2</sub> (35%, 2 ml), and the mixture was stirred for 16 h at room temperature. The reaction mixture was poured into 10% HCl aq. (100 ml) and stirred for 10 min. The white powder was isolated by suction filtration, washed with H<sub>2</sub>O, and dried *in vacuo* at 80 °C. Yield: 315 mg (0.846 mmol, 79%). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO, 25 °C):  $\delta$  = 9.32 (s, 2H; py-2-H), 8.65 (dd, <sup>3</sup>*J*(H,H) = 6.4 Hz, <sup>4</sup>*J*(H,H) = 3.4 Hz, 2H; phthalazine-6,7-H), 8.57 (dd, <sup>3</sup>*J*(H,H) = 8.0 Hz, <sup>4</sup>*J*(H,H) = 2.0 Hz, 2H; py-4-H), 8.32 (d, <sup>3</sup>*J*(H,H) = 8.0 Hz, 2H; py-5-H), 8.08 ppm (dd, <sup>3</sup>*J*(H,H) = 6.4 Hz, <sup>4</sup>*J*(H,H) = 3.2 Hz, 1H; phthalazine-5,8-H).

**Compound 1.** Compounds **8a** (104 mg, 0.279 mmol), **9**<sup>13</sup> (307 mg, 0.772 mmol), *N*,*N*-dimethyl-4-aminopyridine (DMAP, 173 mg, 1.42 mmol), 1-hydroxybenzotriazole monohydrate (HOBt·H<sub>2</sub>O, 190 mg, 1.41 mmol) and 1-ethyl-3-(3-dimethyl-aminopropyl)carbodiimide hydrochloride (EDC·HCl, 269 mg, 1.41 mmol) were dissolved in  $CH_2Cl_2$  (8 ml) and stirred at room temperature. After 16 h, the reaction mixture was extracted with saturated NaHCO<sub>3</sub> aq. and the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The residual oily compound was purified by column chromatography (alumina,  $CH_2Cl_2$ -MeOH = 100:0 – 97:3). Finally, the product was recrystallized from  $CH_2Cl_2$ -hexane and obtained as a white

powder. Yield: 277 mg (0.246 mmol, 88%). Elemental analysis calcd (%) for 1.2H<sub>2</sub>O (C<sub>70</sub>H<sub>60</sub>N<sub>12</sub>O<sub>6</sub>): C 72.15, H 5.19, N 14.42; found: C 72.41, H 5.09, N 14.44. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 8.95 (d, <sup>4</sup>*J*(H,H) = 2.4 Hz, 2H; py-2-H), 8.67-8.69 (m, 6H; phthalazine-6,7-H, trpy-3'-H, trpy-5'-H), 8.60-8.62 (m, 8H; trpy-3-H, trpy-6-H, trpy-3"-H, trpy-6"-H), 8.13  $(d, {}^{3}J(H,H) = 8.0 \text{ Hz}, 2H; \text{ py-5-H}), 7.89 (dd, {}^{3}J(H,H) = 8.0 \text{ Hz}, {}^{4}J$  $(H,H) = 2.2 Hz, 2H; py-4-H), 7.84 (dd, {}^{3}J(H,H) = 6.4 Hz, {}^{4}J(H,H)$ = 3.2 Hz, 2H; phthalazine-5,8-H), 7.77 (td, <sup>3</sup>J(H,H) = 7.6 Hz, <sup>4</sup>J  $(H,H) = 2.0 Hz, 4H; trpy-4-H, trpy-4''-H), 7.53 (dd, {}^{3}_{J}(H,H) = 7.6$ Hz,  ${}^{4}$ /(H,H) = 2.0 Hz, 2H; Ar-6-H), 7.40 (td,  ${}^{3}$ /(H,H) = 8.0 Hz,  ${}^{4}$ / (H,H) = 1.6 Hz, 2H; Ar-5-H), 7.25 (overlapping with CHCl<sub>3</sub>, 4H; trpy-5-H, trpy-5"-H), 7.04-7.09 (m, 4H; Ar-3-H, Ar-4-H), 6.94 (t, <sup>3</sup>*J*(H,H) = 5.6 Hz, 2H; amide-H), 4.16 (t, <sup>3</sup>*J*(H,H) = 4.8 Hz, 4H;  $-NHCH_2CH_2CH_2CH_2O_-$ , 3.55 (q,  ${}^{3}J(H,H) = 6.0$  Hz, 4H;  $-NHCH_2CH_2CH_2CH_2O-),$ 1.92-1.97 ppm (m, 8H; -NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-). <sup>13</sup>C NMR (100 MHz, CDCl3, 25 °C, TMS): δ = 165.6 (-NHCO-), 157.7 (Ar-2-C), 156.4 (trpy-2'-C, trpy-6'-C), 156.2 (trpy-2-C, trpy-2"-C), 155.9 (py-6-C), 155.1 (py-2-C), 148.9 (trpy-6-C, trpy-6"-C), 148.5 (Pht-1-C, Pht-4-C), 147.3 (trpy-4'-C), 137.0 (trpy-4-C, trpy-4"-C), 135.4 (py-3-C), 132.4 (Pht-6-C, Pht-7-C), 130.8 (Ar-4-C), 130.3 (Ar-6-C), 130.2 (py-4-C), 128.2 (Pht-5-C, Pht-8-C), 126.9 (Ar-1-C), 125.9 (Pht-4a-C, Pht-8a-C), 125.1 (py-5-C), 123.8 (trpy-5-C, trpy-5"-C), 121.9 (trpy-3-C, trpy-3"-C), 121.5 (trpy-3'-C, trpy-5'-C), 121.1 (Ar-5-C), 112.2 (Ar-3-C), 67.6 (-NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-), 39.7 (-NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-), 26.7  $(-NHCH_2CH_2CH_2CH_2O-),$ 26.4ppm (-NHCH<sub>2</sub>- $CH_2CH_2CH_2O-$ ).

**Compound**  $[(1)Co_2(\mu-OH)]^{3^+}$ . Compound 1 (20.0 mg, 0.0177 mmol) was suspended in EtOH (4 ml) and the solution was stirred at room temperature. To the suspension, an EtOH solution (4 ml) of Co(OAc)\_2·4H\_2O (14.7 mg, 0.0590 mmol) was added and stirred. After a few minutes, the solution changed to a red-brown homogeneous solution. After 8 h, a saturated NH<sub>4</sub>PF<sub>6</sub> aqueous solution (3 ml) was added to the reaction mixture, a brown precipitate was formed and collected by filtration. Yield: 27.6 mg (0.162 mmol, 92%). The orange-brown crystals were obtained from the diffusion of acetone-toluene mixed solvent. Elemental analysis calcd (%) for  $[(1)Co_2(\mu-OH)]$ -(PF<sub>6</sub>)<sub>3</sub>·4H<sub>2</sub>O (C<sub>70</sub>H<sub>65</sub>N<sub>12</sub>O<sub>9</sub>Co<sub>2</sub>F<sub>18</sub>P<sub>3</sub>): C 47.47, H 3.70, N 9.49; found: C 47.75, H 3.73, N 9.37.

**Compound**  $[(1)Ni_2(\mu-Cl)]^{3^+}$ . This compound was synthesized by the same procedure as for  $[(1)Co_2(\mu-OH)]^{3^+}$  by using **1** (25.0 mg, 0.0221 mmol) and NiCl<sub>2</sub>·6H<sub>2</sub>O (24.5 mg, 0.103 mmol). Yield: 32.0 mg (0.019 mmol, 86%). The pale yellow-brown crystals were obtained from the diffusion of acetone-toluene mixed solvent. Elemental analysis calcd (%) for  $[(1)Ni_2(\mu-Cl)](PF_6)_3\cdot 4H_2O$  ( $C_{70}H_{64}N_{12}O_8Ni_2ClF_{18}P_3$ ): C 46.99, H 3.61, N 9.40; found: C 46.70, H 3.58, N 9.39.

**Compound**  $[(2)Co_2(\mu-OH)]^{3+}$ . This compound was synthesized by the same procedure as for  $[(1)Co_2(\mu-OH)]^{3+}$  by using 2 (18.4 mg, 0.017 mmol) and Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (14.3 mg, 0.057 mmol). Yield: 26.6 mg (0.016 mmol, 94%). Elemental analysis calcd (%) for  $[(2)Co_2(\mu-OH)](PF_6)_3\cdot 6H_2O$  (C<sub>66</sub>H<sub>67</sub>N<sub>12</sub>O<sub>11</sub>Co<sub>2</sub>F<sub>18</sub>P<sub>3</sub>): C 45.12, H 3.84, N 9.57; found: C 45.05, H 3.63, N 9.36.

#### X-ray diffraction studies

Suitable single crystals of  $[(1)Co_2(\mu-OH)]^{3+}$  and  $[(1)Ni_2(\mu-Cl)]^{3+}$ were obtained from the diffusion of acetone–toluene mixed solvent. The measurements were performed at -150 °C. Data collection was made on a Mercury CCD area detector coupled with a Rigaku/MSC diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å) by use of the Crystal-Clear software.<sup>16</sup> Calculations were carried out on CrystalStructure<sup>17</sup> and ShelXle<sup>18</sup> program packages. The structures were solved by direct methods and expanded by Fourier and difference Fourier techniques. The crystals contained acetone and toluene molecules as crystal solvents. Details of crystal parameters and structure refinement are given in Table 1.

#### **Electrochemical methods**

Cyclic voltammograms were measured with an ALS/CHI Model 660 voltammetric analyzer at a scan rate of 100 mV s<sup>-1</sup>. The working and counter electrodes were a platinum disk and a platinum wire, respectively. The sample solutions (*ca*. 0.001 M) in DMF with 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> were deoxygenated with a stream of nitrogen gas. All values of redox potentials are reported with reference to Fc/Fc<sup>+</sup> (Fc = ferrocene); in practice, an Ag/Ag<sup>+</sup> electrode was used as a reference (-0.32 V *vs*. Fc/Fc<sup>+</sup>). Spectroelectrochemistry was performed with an Ocean Optics DH-2000-BAL light source and a USB2000-UV-Vis spectrometer, in a quartz cell (path length 1 mm) with a platinum mesh electrode.

## Acknowledgements

The authors thank Prof. Koji Tanaka (IMS) for his permission to use the X-ray diffractometer and the ESI-MS spectrometer, Mr Seiji Makita for performing elemental analysis, and the Instrument Center of IMS for use of the NMR spectrometer. This work was financially supported by IMS, a Grant-in-aid for Scientific Research (C) (no. 22550133) from the Japan Society for Promotion of Science (JSPS), a Grant-in-aid for Scientific Research on Innovative Areas (no. 21200057) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), and the Nanotechnology Support Project by MEXT.

## References

 (a) P. Du, K. Knowles and R. Eisenberg, J. Am. Chem. Soc., 2008, 130, 12576; (b) C. V. Krishnan and N. Sutin, J. Am. Chem. Soc., 1981, 103, 2141; (c) B. Probst, M. Guttentag, A. Rodenberg, P. Hamm and R. Alberto, Inorg. Chem., 2011, 50, 3404; (d) C. Creutz, N. Sutin and B. S. Brunschwig, J. Am. Chem. Soc., 1979, 101, 1298; (e) N. K. Szymczak, L. A. Berben and J. C. Peters, Chem. Commun., 2009, 6729; (f) T. Ogata, S. Yanagida, B. S. Brunschwig and E. Fujita, J. Am. Chem. Soc., 1995, 117, 6708; (g) T. Ogata,

Y. Yamamoto, Y. Wada, K. Murakoshi, M. Kusaba,
N. Nakashima, A. Ishida, S. Takamuku and S. Yanagida, *J. Phys. Chem.*, 1995, 99, 11916; (*h*) C. Arana, M. Keshavarz,
K. T. Potts and H. D. Abruña, *Inorg. Chim. Acta*, 1994, 225,
285; (*i*) M. Isaacs, J. C. Canales, M. J. Aguirre, G. Estiú,
F. Caruso, G. Ferraudi and J. Costamagna, *Inorg. Chim. Acta*, 2002, 339, 224; (*j*) J. E. Argüello, C. Costentin,
S. Griveau and J.-M. Savéant, *J. Am. Chem. Soc.*, 2005, 127,
5049; (*k*) I. Iwakura, M. Hatanaka, A. Kokura, H. Teraoka,
T. Ikeno, T. Nagata and T. Yamada, *Chem.-Asian J.*, 2006, 1,
656.
2 (*a*) II. L. Kilgore, I. A. Poherts, D. H. Pool, A. M. Appel

- 2 (a) U. J. Kilgore, J. A. Roberts, D. H. Pool, A. M. Appel, M. P. Stewart, M. R. DuBois, W. G. Dougherty, W. S. Kassel, R. M. Bullock and D. L. DuBois, J. Am. Chem. Soc., 2011, 133, 5861; (b) M. Fontecave, Y. Oudart, V. Artero and J. Pecaut, Inorg. Chem., 2006, 45, 4334; (c) V. S. Thoi and C. J. Chang, Chem. Commun., 2011, 47, 6578; (d) C. J. Campbell, J. F. Rusling and C. Bueckner, J. Am. Chem. Soc., 2000, 122, 6679; (e) D. Lexa, J.-M. Savéant, K. B. Su and D. L. Wang, J. Am. Chem. Soc., 1987, 109, 6464; (f) J. Y. Yang, M. Bullock, W. Dougherty, W. S. Kassel, B. Twamley, D. L. DuBois and M. R. DuBois, Dalton Trans., 2010, 39, 3001.
- 3 H. Kon and T. Nagata, Inorg. Chem., 2009, 48, 8593.
- 4 H. Kon and T. Nagata, Chem.-Eur. J., 2012, 18, 1781.
- 5 (a) S. Roggan, C. Limberg, C. Knispel and T. D. Tilley, Dalton Trans., 2011, 40, 4315; (b) P. G. Plieger, A. J. Downard, B. Moubaraki, K. S. Murray and S. Brooker, Dalton Trans., 2004, 2157; (c) U. Beckmann and S. Brooker, Coord. *Chem. Rev.*, 2003, **245**, 17; (d) Y. Lan, Kennepohl, B. Moubaraki, K. S. Murray, D. К. J. D. Cashion, G. B. Jameson and S. Brooker, Chem.-Eur. J., 2003, 9, 3772; (e) S. Brooker, P. G. Plieger, B. Moubaraki and K. S. Murray, Angew. Chem., Int. Ed., 1999, 38, 408; (f) S. Brooker, R. J. Kelly and P. G. Plieger, Chem. Commun., 1998, 1079; (g) T. Wen, L. K. Thompson, F. L. Lee and E. J. Gabe, Inorg. Chem., 1988, 27, 4190; (h) L. Rosenberg and L. K. Thompson, J. Chem. Soc., Dalton Trans., 1986, 625.
- 6 (a) C. Baffert, S. Romain, A. Richardot, J.-C. Leprêtre, B. Lefebvre, A. Deronzier and M.-N. Collomb, J. Am. Chem. Soc., 2005, 127, 13694; (b) C. W. Cady, K. E. Shinopoulos, R. H. Crabtree and G. W. Brudvig, Dalton Trans., 2010, 39, 3985; (c) M. G. Barandika, R. Cortés, L. Lezama, M. K. Urtiaga, M. I. Arriortua and T. Rojo, J. Chem. Soc., Dalton Trans., 1999, 2971.
- 7 (a) Z. Deng, H.-W. Tseng, R. Zong, D. Wang and R. Thummel, *Inorg. Chem.*, 2008, 47, 1835; (b) C. Sens, I. Romero, M. Rodríguez, A. Llobet, T. Parella and J. Benet-Buchholz, *J. Am. Chem. Soc.*, 2004, **126**, 7798; (c) V. Catalano and T. J. Craig, *Inorg. Chem.*, 2003, **42**, 321; (d) E. L. Lebeau, S. A. Adeyemi and T. J. Meyer, *Inorg. Chem.*, 1998, **37**, 6476; (e) L. Francàs, X. Sala, E. Escudero-Adán, J. Benet-Buchholz, L. Escriche and A. Llobet, *Inorg. Chem.*, 2011, **50**, 2771; (f) T. Wada and K. Tanaka, *Eur. J. Inorg. Chem.*, 2005, 3832; (g) Y. Xu, A. Fischer,

L. Duan, L. Tong, E. Gabrielsson, B. Åkermark and L. Sun, *Angew. Chem., Int. Ed.*, 2010, **49**, 8934.

- 8 (a) J. Luo, N. P. Rath and L. M. Mirica, *Inorg. Chem.*, 2011, 50, 6152; (b) S. K. Sharma, P. S. May, M. B. Jones, S. Lense, K. I. Hardcastle and C. E. MacBeth, *Chem. Commun.*, 2011, 47, 1827; (c) Q. Khamker, Y. D. M. Champouret, K. Singh and G. A. Solan, *Dalton Trans.*, 2009, 8935; (d) J.-M. Chen, X.-M. Zhuang, L.-Z. Yang, L. Jiang, X.-L. Feng and T.-B. Lu, *Inorg. Chem.*, 2008, 47, 3158; (e) H. Shimakoshi, S. Hirose, M. Ohba, T. Shiga, H. Okawa and Y. Hisaeda, *Bull. Chem. Soc. Jpn.*, 2005, 78, 1040; (f) H. Harada, M. Kodera, G. Vučković, N. Matsumoto and S. Kida, *Inorg. Chem.*, 1991, 30, 1190.
- 9 (a) S. Lin and T. Agapie, Synlett, 2011, 1; (b) M. Ito, M. Kotera, T. Matsumoto and K. Tatsumi, Proc. Natl. Acad. Sci. U. S. A., 2009, 106, 11862; (c) T. C. Harrop, M. M. Olmstead and P. K. Mascharak, Inorg. Chem., 2006, 45, 3424; (d) E. Simon-Manso and C. P. Kubiak, Organometallics, 2005, 24, 96; (e) M. Gomez, G. Muller, D. Panyella and M. Rocamora, Organometallics, 1997, 16, 5900; (f) K. Mochizuki, H. Gotoh, M. Suwabe and T. Sakakibara, Bull. Chem. Soc. Jpn., 1991, 64, 1750; (g) J.-P. Collin, A. Jouaiti and J.-P. Sauvage, Inorg. Chem., 1988, 27, 1986.

- 10 D. Ramprasad, A. G. Gilicinski, T. J. Markley and G. P. Pez, *Inorg. Chem.*, 1994, 33, 2841.
- 11 (a) F. J. Romero-Salguero and J.-M. Lehn, *Tetrahedron Lett.*, 1999, 40, 859; (b) G. Zoppellaro, A. Ivanova, V. Enkelmann, A. Geies and M. Baumgarten, *Polyhedron*, 2003, 22, 2099.
- 12 V. Farina, S. Kapadia, B. Krishnan, C. Wang and L. S. Liebeskind, *J. Org. Chem.*, 1994, **59**, 5905.
- 13 T. Nagata and K. Tanaka, Inorg. Chem., 2000, 39, 3515.
- 14 (a) E. C. Constable, J. Lewis, M. C. Liptrot and P. R. Raithby, *Inorg. Chim. Acta*, 1990, **178**, 47; (b) C. Stroh, P. Turek, P. Rabu and R. Ziessel, *Inorg. Chem.*, 2001, **40**, 5334; (c) M. L. Calatayud, J. Sletten, M. Julve and I. Castro, *J. Mol. Struct.*, 2005, **741**, 121; (d) A. Wada, N. Sakabe and J. Tanaka, *Acta Crystallogr.*, 1976, **32**, 1121; (e) C. Ruiz-Pérez, P. A. Lorenzo-Luis, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 2002, **336**, 131.
- 15 K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe and Y. Moro-oka, *J. Am. Chem. Soc.*, 2000, **122**, 254.
- 16 CrystalClear, Rigaku Corp., Tokyo, 1999.
- 17 CrystalStructure ver. 3.8.2, Rigaku Corp., Tokyo, 2007.
- 18 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, J. Appl. Crystallogr., 2011, 44, 1281.