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# Syntheses, structure and properties of dinuclear Co complexes with *bis* (catecholate) ligands – Effect of a quinoline ring in the terminal group



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# ABSTRACT

Two types of biscatechol, namely H<sub>4</sub>L1 (5,5'-(buta-1,3-diyne-1,4-diyl)bis(3-t-butylcatechol)) and H<sub>4</sub>L2 (5.5'-(ethyne-1.2-diyl)bis(3-t-butylcatechol)) were synthesized. In these ligands, two redox active catechol moieties are connected by one or two triple bonds. Also, tpa (tris(2-pyridylmethyl) amine), bpqa (bis(2-pyridylmethyl)(2-quinolylmethyl)amine) and pbqa ((2-pyridylmethyl)bis(2-quinolylmethyl) amine) were synthesized as terminal ligands of the tetracoordinated tripod type. In total, six dinuclear Co complexes were synthesized from these biscatechol and terminal ligands as follows:  $[Co_2(L1)(tpa)_2]$  $(BF_4)_2$  (1),  $[Co_2(L1)(bpqa)_2](PF_6)_2$  (2),  $[Co_2(L1)(pbqa)_2](PF_6)_2$  (3),  $[Co_2(L2)(tpa)_2](BF_4)_2$  (4),  $[Co_2(L2)(tpa)_2](PF_6)_2$  (4),  $[Co_2(L2)(tpa)_2](PF_6)_2$  (4),  $[Co_2(L2)(tpa)_2](PF_6)_2$  (4),  $[Co_2(L2)(tpa)_2](PF_6)_2$  (5),  $[Co_2(L2)(tpa)_2](PF_6)_2$  (7),  $[Co_2(L2)(tpa$  $(bpqa)_2](PF_6)_2$  (5),  $[Co_2(L2)(pbqa)_2](PF_6)_2$  (6). Of the six dinuclear Co complexes, complex 6, which was isolated as a mixed valent state Co<sup>II</sup>(HS)-[SQ-Cat]-Co<sup>III</sup>(LS) compound, showed an absorption intensity at around 703 nm (MLCT bands) that increased with increasing temperature in acetonitrile solution. In addition, an investigation of the magnetic properties of the complex 6 with SQUID showed that the  $\chi_M T$  value gradually increased as the temperature increased from 150 to 380 K. This suggests that a transition from  $Co^{III}(LS)$  (S = 0) to  $Co^{II}(HS)$  (S = 3/2) accompanies the temperature rise. This means the steric hindrance and electronic effect of the quinolyl groups around the Co ion produce a coordination atmosphere weaker than that of pyridyl groups, with the result that the Co<sup>III</sup> ions easily convert to Co<sup>II</sup> ions. © 2019 Elsevier Ltd. All rights reserved.

# 1. Introduction

There has been great interest in studying the magnetic properties of molecular compounds. A particularly important subject in the field is the preparation of tunable molecular magnetic materials. Tunable materials are those in which the magnetic properties can be switched by some external perturbation. This is an important objective, because such tunable materials can be used for future molecular memory and switching devices [1–5]. In complexes composed of a redox active organic ligand and a transition metal, electron transfers occur because the *d* orbital of the metal ion and the  $\pi^*$  orbital of the organic molecules are physically close to each other, resulting in a change in the valence of the metal ion complex, which affects the magnetic properties. Complexes containing Co ions as the transition metal ion and catechols as the redox active organic ligands have been well studied. Studies by C. G. Pierpont and colleagues showed that some mononuclear Co complexes coordinated to two 3,5-di-t-butylcatechol molecules, undergo a VT (valence tautomerism) change via a simple bending

\* Corresponding author. E-mail address: suenagay@chem.kindai.ac.jp (Y. Suenaga). motion of the *N,N*'-ligand [6–8]. A. Dei and colleagues used the tetracoordinated tripod **tpa** (*tris*(2-pyridylmethyl)amine) as a terminal ligand to introduce a methyl group at the 6-position and focused on the change in the valence of the Co ions due to the difference in the ligand bulkiness [9–12]. The structure of a dinuclear Co complex having 1,4-dihydroxy-2,5-benzoquinone as a ligand and **tpa** as a terminal ligand was clarified by Sato et al. and it showed that VT behavior is instigated by heat and also by light [13,14]. A quinoline ring containing a tetradentate terminal ligand is sterically bulky compared with pyridine and is expected to show weak metal coordination. Therefore, terminal tripod ligands containing quinolyl groups are expected to produce pseudo-state Co<sup>II</sup> ion species.

We synthesized a biscatechol linked by a —C=N— bond in 2005 and published the properties of its dinuclear Co complex [15]. Since then, this biscatechol ligand has been synthesized by a different method and its dinuclear Co complex has been successfully isolated, but so far it has not been possible to synthesize a complex exhibiting VT behavior. In this paper, as a result of a new synthesis of biscatechols linked by triple bonds and research aimed at clarifying the properties of their dinuclear Co complexes, we found that when a part of the pyridine ring of **tpa** was substituted with a



terminal quinoline ring, we obtained a novel dinuclear Co complex having a reversible spin transition from the Co<sup>III</sup> low spin state to the Co<sup>II</sup> high spin state.



# 2. Experimental

Preparations were performed using the usual Schlenk techniques. All solvents were dried and distilled by standard methods before use. The standard chemicals were obtained from Wako Chemical Co., Japan, and used without further purification. The terminal ligands **tpa** (*tris*(2-pyridylmethyl) amine), **bpga** (*bis*(2pyridylmethyl)(2-quinolyl methyl)amine) and pbqa ((2-pyridylmethyl)bis(2-quinolylmethyl)amine) were synthesized according to the literature [16]. These organic chemicals were identified by IR, <sup>1</sup>H NMR and elemental analysis. The IR spectra were measured as KBr disks on a JASCO FT/IR-8000 spectrometer and <sup>1</sup>H NMR spectra with a JEOL JMS-ESC 400 FT-NMR spectrometer at 23 °C. UV-Vis spectra were recorded on a SHIMADZU UV-2450 spectrometer and cyclic voltammetric measurements were made using an ALS/CHI 660A instrument. Solutions of the complexes were prepared in CH<sub>3</sub>CN containing (NBu<sub>4</sub>)(BF<sub>4</sub>) (ca. 0.1 M) as a supporting electrolyte. Platinum wire working and counter electrodes were used with an Ag/AgNO<sub>3</sub> reference electrode. The Fc/Fc<sup>+</sup> couple appeared at +0.08 V ( $\Delta E = 65 \text{ mV}$ ) versus Ag/AgNO<sub>3</sub> with this experimental arrangement and the ferrocene couple was used as an internal reference. Magnetic susceptibility data were collected on fresh microcrystalline samples on a Quantum Design MPMSXL7 SQUID magnetometer within the temperature range 5-380 K. EPR spectra were obtained on a JEOL JES-FA200 spectrometer.

# 2.1. Synthesis of H<sub>4</sub>L1 and H<sub>4</sub>L2

The two biscatechols were synthesized according to Scheme S1 (described in the Supporting Information). For **H**<sub>4</sub>**L1**, compound **7** (3.281 g, 9.15 mmol), triethylamine (50 mL), dichloro*bis*(triphenylphosphine)palladium (401 mg, 0.572 mmol) and copper(I) iodide (54 mg, 0.286 mmol) were added to a 100 mL flask under an Ar atmosphere. The mixture solution was stirred and refluxed (100 °C) overnight. After filtration, the reaction solution was concentrated and the obtained crude mixture was purified by column chromatography (silica gel: 250 ml, hexane:ethyl acetate =  $20:1 \rightarrow 5:1$ ) to get a reddish yellow solid compound (**8**) (1.477 g, 2.07 mmol). Compound **8** (1.477 g, 2.06 mmol) was then dissolved in chloroform (30 mL) in a 100 ml flask, 2 M HCl (10 mL) and MeOH (30 mL) were added sequentially to make the solution

homogeneous, and it was stirred for a while. After that, a saturated NaHCO<sub>3</sub> aqueous solution (50 mL) was added. This solution was extracted three times with chloroform (1 time: 50 mL), and the organic layer was washed with brine (100 mL). After drying the organic layer with Na<sub>2</sub>SO<sub>4</sub>, filtration and concentration gave the crude product, which was purified by column chromatography (silica gel: 250 mL, hexane: ethyl acetate = 5:1) to get **H**<sub>4</sub>L1 as a dark brown solid (567 mg, 1.50 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 1.37 (s, 18H), 5.40–6.00 (m, 4H), 6.86 (s, 2H), 7.07 (s, 2H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 29.68, 34.87, 72.26, 81.91, 112.07, 116.57, 124.91, 136.89, 142.52, 145.39.

For H4L2, triethylamine (20 mL), tetrakis(triphenylphosphine)palladium(0) (485 mg, 0.420 mmol) and copper(I) iodide (28 mg, 0.145 mmol) were added to a 100 mL flask containing compound **5** (2.602 g, 7.26 mmol); a solution of compound **7** (4.399 g, 10.5 mmol) in triethylamine (30 mL) was then added and stirred. followed by stirring overnight with heating at reflux (100 °C). The reaction solution was concentrated and the obtained crude was purified by column chromatography (silica gel: 250 ml, hexane:ethyl acetate =  $20:1 \rightarrow 10:1 \rightarrow 3:1$ ) to obtain a yellow solid compound (9) (1.302 g, 1.88 mmol). In a 100 ml flask, compound 9 (1.302 g, 1.88 mmol) was dissolved in chloroform (40 mL), 2 M HCl (10 mL) was added, MeOH (40 mL) was added to make the solution homogeneous, and the mixture was stirred for 5 hours. After that, a saturated NaHCO<sub>3</sub> aqueous solution (50 mL) was added; this solution was extracted three times with chloroform (1 time: 50 mL), and the organic layer was washed with brine (100 mL). After drying the organic layer with Na<sub>2</sub>SO<sub>4</sub>, filtration and concentration gave the crude product, which was purified by column chromatography (silica gel: 250 mL, hexane:ethyl acetate = 5:1  $\rightarrow$  3:1  $\rightarrow$  1:1) to get **H<sub>4</sub>L2** as a dark brown solid (184 mg, 0.520 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.35 (s, 18H), 5.35 (br, 2H), 5.98 (br, 2H), 6.88 (s, 2H), 7.06 (s, 2H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 29.36, 34.72, 87.59, 113.78, 115.73, 123.56, 136.63, 142.32, 144.02.

# 2.2. [Co<sub>2</sub>(L1)(tpa)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, complex 1

A solution of  $Co(BF_4)_2$ ·6H<sub>2</sub>O (0.10 mmol) in dry methanol (2 mL), Ar gas aerated for 5 min, was added to a stirred solution of **tpa** (0.10 mmol) in dry MeOH solution (5 mL) and the resulting solution was stirred for 30 min. A solution of Et<sub>3</sub>N (0.20 mmol) and H<sub>4</sub>L1 (0.050 mmol) in Et<sub>2</sub>O (7 mL), Ar gas aerated for 15 min, was added to the above methanol solution slowly. The solution was allowed to stand at  $-13 \,^{\circ}$ C for 3 days to obtain the desired complex as a dark green precipitate. The yield obtained was 47%. IR (KBr, cm<sup>-1</sup>): 3420s, 3073m, 2955m, 2120w, 1635m, 1610s, 1572m, 1545w, 1482m, 1438m, 1415s, 1384m, 1349m, 1279m, 1249m, 1158m, 1083s, 1056s, 1037s, 992w, 905w, 885w, 836w, 811w, 771m, 730w, 699w, 667w, 642w, 612w, 582w, 532w, 522w, 504w; ESI-MS, [Co<sub>2</sub>(L1)(tpa)<sub>2</sub>]<sup>2+</sup> m/z: 536.1614; Anal. Calc. for C<sub>60</sub>H<sub>58</sub>N<sub>8</sub>O<sub>4</sub>Co<sub>2</sub>B<sub>2</sub>F<sub>8</sub>·6H<sub>2</sub>O: C, 53.20; H, 5.21; N, 8.27%. Found: C, 52.56; H, 4.82; N, 7.51%.

# 2.3. [Co<sub>2</sub>(L1)(bpqa)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, complex 2

A solution of  $Co(OAc)_2 \cdot 4H_2O$  (0.10 mmol) in dry MeOH solution (2 mL), Ar gas aerated for 5 min, was added to **bpqa** (0.10 mmol) in dry MeOH solution (5 mL) and the resulting solution was stirred for 30 min. A solution of KPF<sub>6</sub> (0.20 mmol), Et<sub>3</sub>N (0.20 mmol) and **H<sub>4</sub>L1** (0.050 mmol) in dry MeOH (7 mL), Ar gas aerated for 15 min, was added to above methanol solution. The resultant solution was allowed to stand at -13 °C for 3 days, resulting in a dark green precipitate, which was filtered to obtain the desired complex. The yield obtained was 18%. IR (KBr, cm<sup>-1</sup>): 3435m, 3079m, 2956m, 2145w, 1609m, 1569m, 1541m, 1517m, 1435s, 1414s,

1369m, 1279s, 1249s, 1160m, 1128m, 1055w, 1037w, 994w, 970m, 846s, 767m, 669w, 558 m; ESI-MS,  $[Co_2(L1)(bpqa)_2](PF_6)^+$  *m/z*: 1318.3697; *Anal.* Calc. for  $C_{68}H_{62}N_8O_4Co_2P_2F_{12}$ ·CH<sub>3</sub>OH: C, 55.43; H, 4.45; N, 7.49%. Found: C, 55.96; H, 4.75; N, 7.00%.

# 2.4. [Co<sub>2</sub>(L1)(pbqa)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, complex 3

Complex **3** was synthesized using almost the same procedure as for complex **2**. The resulting dark green precipitate was filtered to obtain the desired complex. The yield obtained was 34%. IR (KBr, cm<sup>-1</sup>): 3404s, 3080m, 2957m, 2155w, 1619s, 1604s, 1568s, 1514s, 1461s, 1435s, 1415s, 1364s, 1342s, 1301s, 1252s, 1210m, 1158m, 1127m, 1053w, 1022w, 960w, 846s, 781m, 759m, 662w, 636w, 617w, 604, 558s, 526w, 512w; ESI-MS,  $[Co_2(L1)(pbqa)_2]$  (PF<sub>6</sub>)<sup>+</sup> *m/z*: 1417.3524; *Anal.* Calc. for C<sub>76</sub>H<sub>66</sub>N<sub>8</sub>O<sub>4</sub>Co<sub>2</sub>P<sub>2</sub>F<sub>12</sub>·5H<sub>2</sub>O: C, 55.21; H, 4.63; N, 6.78%. Found: C, 55.66; H, 4.86; N, 7.47%.

# 2.5. [Co<sub>2</sub>(**L2**)(**tpa**)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, complex **4**

Complex **4** was synthesized using almost the same procedure as for complex **1**. Complex **4** was isolated as a dark green precipitate. The yield obtained was 55%. IR (KBr, cm<sup>-1</sup>) 3423s, 3073m, 2953m, 2146w, 1610s, 1572w, 1541w, 1483m, 1439m, 1414s, 1385m, 1349m, 1281m, 1247m, 1210m, 1157m, 1123m, 1083s, 1056s, 1037s, 905w, 886w, 817w, 770m, 665w, 647w, 533w, 520w, 505w; ESI-MS,  $[Co_2(L2)(tpa)_2]^{2+}$  m/z: 524.1624; Anal. Calc. for C<sub>58</sub>-H<sub>58</sub>N<sub>8</sub>O<sub>4</sub>Co<sub>2</sub>B<sub>2</sub>F<sub>8</sub>·5H<sub>2</sub>O: C, 53.07; H, 5.22; N, 8.54%. Found: C, 53.29; H, 5.13; N, 8.40%.

# 2.6. [Co<sub>2</sub>(L2)(bpqa)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, complex 5

Complex **5** was synthesized using almost the same procedure as for complex **2**. The resulting dark green precipitate was filtered to obtain the desired complex. The yield obtained was 17%. IR (KBr, cm<sup>-1</sup>): 3421s, 3079m, 2956m, 2868m, 2145s, 1609s, 1569s, 1541s, 1517s, 1481s, 1436s, 1414s, 1386s, 1359s, 1341s, 1287s, 1247s, 1209m, 1159m, 1129m, 1095m, 1056w, 1038w, 1002w, 924w, 845s, 768m, 739m, 721m, 668w, 644w, 558s, 528w, 504w; ESI-MS,  $[Co_2(L2)(bpqa)_2](PF_6)^+ m/z$ : 1293.3451; *Anal.* Calc. for  $C_{66}H_{62}N_8O_4Co_2P_2F_{12}$ ·1.5CH<sub>3</sub>OH: C, 54.52; H, 4.61; N, 7.54%. Found: C, 55.11; H, 4.72; N, 7.00%.

# 2.7. [Co<sub>2</sub>(L2)(pbqa)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, complex 6

Complex **6** was synthesized using almost the same procedure as for complex **2**. The resulting dark green precipitate was filtered to obtain the desired complex. The yield obtained was 55%. IR (KBr, cm<sup>-1</sup>): 3424s, 3079m, 2957m, 2147m, 1619s, 1603, 1568s, 1515s, 1481s, 1435s, 1414s, 1388s, 1361s, 1340s, 1312s, 1247s, 1207m, 1179m, 1159m, 1146m, 1128m, 1098m, 1053w, 1036w, 1022w, 960w, 926w, 844s, 781m, 756m, 676w, 659w, 636w, 604w, 558s, 531w, 500w; ESI-MS,  $[Co_2(L2)(pbqa)_2](PF_6)^+$  *m/z*: 1393.3567; *Anal.* Calc. for C<sub>74</sub>H<sub>66</sub>N<sub>8</sub>O<sub>4</sub>Co<sub>2</sub>P<sub>2</sub>F<sub>12</sub>·4H<sub>2</sub>O: C, 54.55; H, 4.70; N, 6.88%. Found: C, 54.72; H, 4.53; N, 6.41%.

# 3. Crystallography

Data collection for  $[Co_2(L1)(tpa)_2](ClO_4)_2$  (1') were performed on a Rigaku/MSC Mercury CCD area detector coupled with a Rigaku XtaLAB P200 diffractometer with graphite-monochromated Mo K $\alpha$ (0.71073 Å) radiation. The structure was solved by a direct method [17] and expanded using Fourier techniques [18]. The final cycle of full-matrix least-squares analysis [19] on  $F^2$  was based on 9096 observed reflections and 435 variable parameters, and converted with unweighted and weighted agreement factors of R1 = 0.0496 and wR2 = 0.1439. All the full-occupancy non-hydrogen atoms were refined anisotropically. The positions of all the hydrogen atoms were determined from difference electron density maps and included, but not refined. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources. Computations were carried out using the CrystalStructure [20] crystallographic software package, except for refinement which was performed using SHELXL 2015 [21]. Selected bond lengths and bond angles for (**1**') are listed in Table S2.

Crystal data for (1'): M = 1436.12, crystal size  $0.4 \times 0.2 \times 0.2$  mm, trigonal, space group *R*-3, *a* = 32.9851(11) Å, *b* = 32.9851(11) Å, *c* = 16.2797(5) Å, *V* = 15339.5(11) Å<sup>3</sup>, *Z* = 9, *F* (0 0 0) = 6714,  $D_{\text{calc}} = 1.399 \text{ g cm}^{-1}$ ,  $\mu = 0.635 \text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 55.0^{\circ}$ , reflection collected 9096, independent reflection 7047 ( $R_{\text{int}} = 0.0$ ), GOF ( $F^2$ ) = 1.028,  $R_1 = 0.0496$  [ $I > 2\sigma$  (I)], w $R_2 = 0.1439$  (all data), largest diff. peak and hole 1.032 and  $-1.271 \text{ e} \text{Å}^{-3}$ .

CCDC reference number 1919513 is available as a file in .cif format.

## 4. Results and discussion

#### 4.1. Syntheses of the dinuclear Co complexes

Six dinuclear Co complexes were synthesized using biscatechols (H<sub>4</sub>L1 and H<sub>4</sub>L2) and terminal ligands (tpa, bpga and pbga). They are [Co<sub>2</sub>(L1)(tpa)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (1), [Co<sub>2</sub>(L1)(bpqa)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (2), [Co<sub>2</sub>(L1)  $(pbqa)_2](PF_6)_2$  (3),  $[Co_2(L2)(tpa)_2](BF_4)_2$  (4),  $[Co_2(L2)(bpqa)_2]$  $(PF_6)_2$  (**5**) and  $[Co_2(L2)(pbqa)_2](PF_6)_2$  (**6**). First, a methanol solution of Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and **tpa** were well mixed. After preparing the methanol solution, which immediately changed from pink to green for  $[Co(tpa)](BF_4)_3$ , a methanol solution containing  $H_4L1$  (or  $H_4L2$ ) and triethylamine as a deprotonating agent was gently added to the methanol solution so as not to disturb the interface. The solution was allowed to stand at -13 °C for 3 days. The precipitates that formed were washed with cold methanol to obtain pale green precipitates. When **bpga** and **pbga**, having quinoline rings, were used in place of **tpa** as the terminal ligand, Co(OAc)<sub>2</sub>·4H<sub>2</sub>O was used as a starting material instead of Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Lastly, KPF<sub>6</sub> was added and anion exchange was carried out. The reason for this is to prevent the formation of a red dinuclear Co<sup>II</sup> complex in which F<sup>-</sup> ions are doubly-crosslinked due to dissociated F<sup>-</sup> ions accompanying the hydrolysis of the BF<sub>4</sub><sup>-</sup> ions [22,23]. From the elemental analysis of the obtained compounds, they were found to be dinuclear Co complexes containing two counter anions. IR and ESI-MS data are shown in the Supporting Information. For complex (1), we replaced the BF<sub>4</sub><sup>-</sup> ion by the ClO<sub>4</sub><sup>-</sup> ion and succeeded in crystallizing the complex (as 1') and determined its molecular structure. Thus, its structure is described in the next section.

# 4.2. Crystal structure of [Co<sub>2</sub>(L1)(tpa)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (1')

X-ray data collection was performed at 100 K to increase the apparent low diffracting power of the crystals obtained. Even if the final X-ray crystal structure determination is not of excellent quality, it provides a strong enough framework to describe the different magnetic and electronic properties. The crystallographic data and selected atomic distances and angles are presented in Tables S1 and S2, respectively. The two cobalt ions are six-coordinated in a *cis*-distorted pseudo-octahedral coordination, and each of the tripodal ligands adopts a folded conformation around the metal ion (Figs. 1, S12 and S13). The average Co–O and Co–N bond lengths are 1.870 and 1.928 Å for both Co ions, values which are consistent with a low-spin Co<sup>III</sup> state. The metal-donor atoms lengths strongly indicate that a Co<sup>III</sup>-Cat (Cat = catechol) charge distribution at 100 K. This suggestion is confirmed by analysis of



Fig. 1. Crystal structure of complex 1'.

the C(30)–C(25) (1.418 Å) and C–O (1.347, 1.345 Å) bond lengths of the dioxolene ligand, which gives a strong indication that the two catechol rings in complex **1**' are in the same plane. The bond distance of the C(36)–C(37) triple bond is 1.203 Å and the C (27)–C(36)–C(37) angle is 176.5°. The packing structure is shown in Fig. S13. Six molecules of the dinuclear Co complex are present in a hexagon and form a columnar structure along the *c* axis direction. However, no special interactions were found between the Co binuclear complex molecules.

# 4.3. Electronic spectra

The electronic spectra of the dinuclear Co complexes, measured in acetonitrile, are shown in Fig. 2. For  $[Co_2(L1)(tpa)_2](BF_4)_2$  (1), absorption bands appeared at 350 and 700 nm; the former is a  $\pi$ - $\pi$ \* transition from the ligand and the latter is a ligand-to-metal charge transfer (LMCT) between L1 and the Co ion. Based on SQUID results, complex 1 can be regarded as Co<sup>III</sup>(LS)-[Cat-Cat]-Co<sup>III</sup>(LS), where LS denotes a low spin state of the Co<sup>III</sup> ion, with all six of its *d* electrons occupying  $t_{2g}$  orbitals. On the other hand, in  $[Co_2(L2)(pbqa)_2](PF_6)_2$  (6), in addition to the  $\pi - \pi^*$  transition absorption band derived from the ligand at around 350 nm, a prominent absorption band at 703 nm and another weak band at 500 nm were observed. In the dinuclear Co complexes using either H<sub>4</sub>L1 or H<sub>4</sub>L2 ligands, the absorption intensity at 703 nm of the complexes containing **pbqa** is larger than that for the **tpa** complexes, and it is shifted to a longer wavelength. This indicates that the ligand field strength is weakened by the bulkiness of the quinoline ring.

The electronic spectra of complex **6** in acetonitrile solution at -40 to +50 °C are shown in Fig. 3. Interestingly, the absorption intensities at 500 and 703 nm increased with increasing

temperature, while the absorption intensity at 350 nm decreased. This behavior was reversible and represents electron transfer from Co<sup>III</sup>(LS)-Cat to Co<sup>II</sup>(HS)-SQ. Complex 6 was isolated as a mixed valence-state Co<sup>II</sup>(HS)-[SQ-Cat]-Co<sup>III</sup>(LS) with two counter anions  $(PF_{6})$ , from the results of its elemental analysis. From the spectral changes brought about by temperature changes, the absorption band at 350 nm can be assigned to the catecholate  $\pi$ - $\pi$ \* transition, while the 703 nm band is due to a metal-to-ligand charge transfer (MLCT) from the Co ion to the ligand. However, no spectral change associated with changing temperature was observed for complexes 1-3, containing H<sub>4</sub>L1, or complexes 4 and 5, containing H<sub>4</sub>L2. Judging from these results, the spectral changes in complex 6 due to temperature variation in acetonitrile solution resulted from a change from Co<sup>II</sup>(HS)-[SQ-Cat]-Co<sup>III</sup>(LS) to Co<sup>II</sup>(HS)-[SQ-SQ]-Co<sup>II</sup>(HS). This is thought to be due to the close spacing between the two Co units of complex **6** and the fact that the Co ion tends to be in the +II high spin state due to the bulkiness of the guinoline ring ligands.

# 4.4. Magnetic property

Changes in the magnetic susceptibility ( $\chi_M T$ ) due to temperature are shown in Fig. 4 for complex 4 and 5. Since the dinuclear complexes using tpa and pbqa as a terminal ligand do not exhibit magnetism, the atomic valence of Co is +III and can be judged to be in a low spin state. In complex 5, the biscatechol molecules are partially oxidized (**L2**<sup>-3</sup>:SQ<sup>--</sup>-Cat<sup>-2</sup>) and the  $\chi_M T$  values are almost constant, with a value of  $1.2 \text{ cm}^3 \text{ Kmol}^{-1}$ . For  $[\text{Co}_2(\text{L2})(\text{pbqa})_2]$  $(PF_6)_2$  (6), the magnetic susceptibility gradually increased from  $2.0 \text{ cm}^3 \text{ Kmol}^{-1}$  to  $2.74 \text{ cm}^3 \text{ Kmol}^{-1}$  between 50 and 380 K (Fig. 5). From the magnetic susceptibility value at 150 K or lower, assuming that complex 6 is Co<sup>II</sup>(HS)-[SQ-Cat]-Co<sup>III</sup>(LS), the value of the magnetic susceptibility obtained from the spin is 2.0 cm<sup>3</sup> Kmol<sup>-1</sup>. As the temperature rises, it is presumed that a change to Co<sup>II</sup>(HS)-[SO-SO]-Co<sup>II</sup>(HS) occurs, since the susceptibility increases from around 150 K, but at 380 K it is still not complete. The value of the magnetic susceptibility remained at 2.74 (3.75 cm<sup>3</sup> Kmol<sup>-1</sup> in the theoretical formula) since the spin transfer was not complete. EPR spectra have been measured for complex **6** in the solid state. Complex **6** display a radical at around g = 2.00, weakly (Fig. S11). With other **bpga** complexes and dinuclear Co complexes using H<sub>4</sub>L1 (complexes 4 and 5), such a spin transfer phenomenon could not be confirmed (Fig. S10).

# 5. Conclusion



A total of six dinuclear Co complexes were synthesized from two types of biscatechol ligand, having different numbers of triple

Fig. 2. UV–Vis spectra of the dinuclear Co complexes in acetonitrile solution. (a) blue line, complex 1; red line, complex 2; green line, complex 3. (b) blue line, complex 4; red line, complex 5; green line, complex 6. (Color online.)



Fig. 3. UV-Vis spectra at various temperature for complex 6. left, total spectra; right, magnification of each band.



**Fig. 4.** Magnetic susceptibility of complex **4**, blue line, and complex **5**, green line. (Color online.)

bonds, and terminal ligands (**tpa**, **bpqa** and **pbqa**), in which the pyridine ring of the tetracoordinated tripod ligand **tpa** is partially



Fig. 5. Magnetic susceptibility of complex 6.

substituted by one or two quinoline rings for the latter two ligands. The compounds were identified from elemental analysis, mass spectrometry and IR spectra.

The dinuclear Co complex obtained from the tetracoordinated tripod ligand **tpa** has a valence number of +III and showed a broad electronic absorption band in the vicinity of 700 nm, which is considered to be due to a LMCT. In the dinuclear Co complex  $[Co_2(L2) (pbqa)_2](PF_6)_2$  (**6**) the electronic absorption spectrum revealed that the valence number of the Co ion is +II valence and the absorption at 703 nm reversibly changed with temperature. Variable-temperature magnetic susceptibility measurements show solely changes from Co<sup>III</sup> low spin to Co<sup>II</sup> high spin with increasing temperature. The bulky quinolyl groups around the Co ion produce a coordination atmosphere weaker than for pyridyl groups, with the result that the Co<sup>III</sup> ions change to Co<sup>II</sup> ions easily.

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#### Appendix A. Supplementary data

CCDC 1919513 contains the supplementary crystallographic data for  $[Co_2(L1)(tpa)_2](ClO_4)_2$ . These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2019.07.035.

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