

# Valence Tautomeric Behavior of Tri-nuclear Mixed-Valence Co<sup>III</sup>/Co<sup>II</sup> Complex containing 2,3,6,7,10,11-Hexahydroxytriphenylene(H<sub>6</sub>L)

Yusaku Suenaga<sup>a), b)</sup>, Masataka Inomata<sup>a)</sup>, Shiomi Yabumoto<sup>a)</sup>, Ryotaro Yamaguchi<sup>a)</sup>, Takashi Okubo<sup>a), b)</sup>, Masahiko Maekawa<sup>b)</sup> and Takayoshi Kuroda-Sowa<sup>a), b)</sup>

<sup>a)</sup> Department of Science, Kindai University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan, E-mail:

[suenagay@chem.kindai.ac.jp](mailto:suenagay@chem.kindai.ac.jp)

<sup>b)</sup> Science and Technology Research Institute, Kindai University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

(Received, January 15, 2018)

## Abstract

Three tri-nuclear cobalt complexes  $[\text{Co}_3(\text{tpa})_3(\text{L})](\text{BF}_4)_4$  (1) (tpa=*tris*(2-pyridylmethyl)amine),  $[\text{Co}_3(\text{Metpa})_3(\text{L})](\text{BF}_4)_4$  (2) (Metpa=(6-methyl-2-pyridylmethyl)*bis*(2-pyridylmethyl)amine) and  $[\text{Co}_3(\text{Me}_2\text{tpa})_3(\text{L})](\text{BF}_4)_3$  (3) (Me<sub>2</sub>tpa=*bis*(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine)) with 2,3,6,7,10,11-hexahydroxytriphenylene (H<sub>6</sub>L) and three spieces ancillary ligands have been prepared. Tri-nuclear mixed-valence Co complex (3) is prepared from methanol solution. Complex (3) has consist in that the valence of two cobalt ions have +III, one cobalt ion has +II and the *tris*-dioxolene bridging ligand is formally in the -5 [cat,cat,sq] oxidation state. Complex (3) shows evidence of temperature dependence of the charge distribution, displaying thermally induced valence tautomeric transition from  $\{(ls\text{-Co}^{\text{III}})_2(hs\text{-Co}^{\text{II}})\}\text{-L}(\text{cat},\text{cat},\text{sq})$  to  $\{(ls\text{-Co}^{\text{III}})(hs\text{-Co}^{\text{II}})_2\}\text{-L}(\text{cat},\text{sq},\text{sq})$  in both solid and solution states. On the other hand, complex (1) and complex (2) are stable in the entire temperature range investigated. Various-temperature magnetic susceptibility data for the compound displayed little variation in the range 2-380 K, and the reason caused the distinct charge distribution on Co-L (L: bridging ligand) by the natural rigidity of the tripodal ligands. These results appeared methylation of the 6-position of the pyridine rings in ancillary ligand effect on redox state in the complex, occuring the distribution of electrons between the cobalt centers and the bridging ligand.

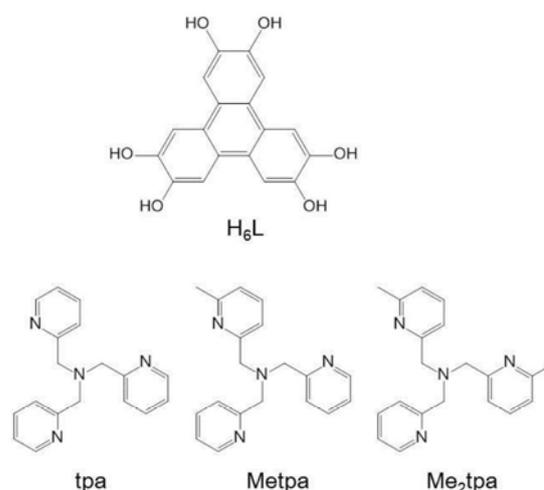
**Key words**; Tri-nuclear Co complex, Hexahydroxy triphenylene, Valence tautomeric behavior, Electrochemical behavior, Magnetic property

**Key words;** Tri-nuclear Co complex, Hexahydroxy triphenylene, Valence tautomeric behavior, Electrochemical behavior, Magnetic property

## 1. Introduction

Facile metal-ligand electron transfer is become a unique feature of dioxolene complexes of redox-active first-row transition metals. Complexes that exhibit VT (valence tautomerism) characteristically consist of a thermodynamically inert donor/acceptor, in most examples a dioxolene ligand, and a metal center that undergoes a tight/floppy interconversion with electron transfer. This change is primarily responsible for defining the thermodynamic properties and temperature dependence of the equilibrium [1-16]. In almost all of the examples of this class reported to date, the interconversion involves an intramolecular electron transfer between a six-coordinate diamagnetic cobalt(III) metal ion and a coordinated catecholate ligand yielding a cobalt(II)-semiquinonate species, the metal ion being in the high spin electronic configuration. These compounds have attracted great attention because of their potential applications as sensors, information storage and display devices and so on. Electron-transfer properties may be easily controlled by external stimuli such as temperature, light and pressure. However, catecholate complexes involving tri-nuclear cobalt ions still remain rare [17,18]. Recently, we reported tri-nuclear cobalt(II) complexes with conjugated bis(catecholate)

ligands ( $[\text{Co}_3(\text{phen})_3(\text{Hthba})_2]$  (phen=1,10-phenanthroline,  $\text{H}_4\text{thba}=2,2',3,3'$ -tetrahydroxybenzaldazine)) [19]. Three cobalt ions are six coordinated, phen ligand is bound to each cobalt ion, and  $\text{Hthba}^{3-}$  acts as a bridging ligand. Therefore this complex is kept electrically neutral by combining three  $\text{Co}^{2+}$  ions and two  $\text{Hthba}^{3-}$  ions. In this study we described a new tri-nuclear cobalt complex prepared with 2,3,6,7,10,11-hexahydroxytriphenylene ( $\text{H}_6\text{L}$ ) using tripodal ancillary ligand. Herein we describe the synthesis and property of the tri-nuclear mixed-valence Co complex  $[\text{Co}_3(\text{tpa})_3(\text{L})](\text{BF}_4)_4$  (1) [20],  $[\text{Co}_3(\text{Metpa})_3(\text{L})](\text{BF}_4)_4$  (2) and  $[\text{Co}_3(\text{Me}_2\text{tpa})_3(\text{L})](\text{BF}_4)_3$  (3) using three species ancillary ligands.



## 2. Experimental Section

### **Materials and Methods**

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 IR spectra were measured as KBr disks on a JASCO FT/IR-8000 spectrometer,  $^1\text{H}$  NMR spectra were recorded on a JEOL ECA-500 spectrometer. FT-NMR spectrometer at 23 °C. UV-Vis spectra were recorded on a SHIMADZU UV-2450 spectrometer, and cyclic voltammetric measurements were made under a flow of nitrogen using a ALS/CHI 660A instrument. Solutions of the complex was prepared in  $\text{CH}_3\text{CN}$  containing  $(\text{NBu}_4)(\text{PF}_6)$  (ca. 0.1 M) as supporting electrolyte. Platinum wire working and counter electrode were used with  $\text{Ag}/\text{AgNO}_3$  reference electrode. The  $\text{Fc}/\text{Fc}^+$  couple appeared at  $+0.08\text{V}(\Delta E_{1/2} = 65 \text{ mV})$  versus  $\text{Ag}/\text{AgNO}_3$  with this experimental arrangement, and the ferrocene couple was used as an internal reference.

### **Syntheses**

**Tris(2-pyridylmethyl)amine (tpa).**  $\text{CH}_2\text{Cl}_2$  solution (20 mL) of pyridine-2-carboxy aldehyde (0.899 g, 8.4 mmol) was dropwised to a stirred mixture of 2-aminomethylpyridine (0.453 g, 4.2 mmol) and sodium triacetoxyborohydride (2 g) in dichloromethane (30 mL). After the resulting reaction mixture was stirred for 18 hr, a saturated

aqueous solution of sodium hydrogencarbonate (20 mL) was added. The reaction mixture was stirred for 0.5 hr and then extracted with dichloromethane. The organic fraction was separated, dried over  $\text{MgSO}_4$ , and the solvent was removed under reduced pressure. The residue was recrystallized with hexane to give **tpa** as colorless needles (0.881 g, 72.3%). IR (KBr,  $\text{cm}^{-1}$ ) 3410w, 3080m, 3054m, 3015s, 2924m, 2817s, 2707w, 2362w, 2343m, 1590s, 1570s, 1474s, 1436s, 1366s, 1312m, 1243m, 1221m, 1154m, 1124s, 1089m, 1047m, 996s, 983s, 899m, 884m, 840w, 766s, 631m, 607m, 516m, 471w; EI-MS,  $m/z=290$ ;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ , ppm) 3.881(s, 6H), 7.188(t, 3H), 7.589-7.655(m, 6H), 8.524(d, 3H); Anal. Calc. for  $\text{C}_{18}\text{H}_{18}\text{N}_4$ : C, 74.46; H, 6.25; N, 19.30%. Found: C, 74.90; H, 6.34; N, 18.98%.

### **Bis(2-pyridylmethyl)(6-methyl-2-pyridylmethyl)amine (Metpa).**

**Metpa** are prepared same method with tpa except for 6-methyl-2-aminomethylpyridine (0.26 g, 2.1 mmol) in place of 2-aminomethylpyridine. The residue was recrystallized with hexane to give **Metpa** as colorless needles (0.31 g, 48%). IR (KBr,  $\text{cm}^{-1}$ ) 3422w, 3072m, 3011s, 2926m, 2819s, 2712w, 2361w, 2343m, 1589s, 1569s, 1469s, 1437s, 1369s, 1311m, 1296m, 1249m, 1154m, 1124s, 1089m, 1044m, 986s, 973s, 917m, 880m, 840w, 793m, 760s, 734m, 608m, 511m, 488m;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ , ppm) 2.52(s,

3H), 3.87(s, 6H), 7.01(d, 1H), 7.13(t, 2H), 7.18(t, 1H), 7.39(d, 1H), 7.57(m, 4H), 8.50(d, 2H).

**Bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine (Me<sub>2</sub>tpa).** Me<sub>2</sub>tpa was prepared in the same way as tpa except for 6-methyl-pyridine-2-carboxy aldehyde (1.016 g, 8.4 mmol) in place of pyridine 2-carboxy aldehyde.<sup>2</sup> After the reaction solution was filtrate and added water, the aqueous solution was extracted three times with diethyl ether, and solvent was removed to give Me<sub>2</sub>tpa as colorless needles (69.9 %). IR (KBr, cm<sup>-1</sup>) 3424w, 3068w, 2996m, 2927m, 2870m, 2818m, 1654m, 1590s, 1465s, 1445s, 1368s, 1355m, 1161m, 1121m, 1088m, 995s, 982s, 970m, 877m, 800m, 756s, 710m; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm) 2.514(s, 6H), 3.851(s, 6H), 7.004(d, 2H), 7.145(t, 1H), 7.423(d, 2H), 7.516-7.648(m, 4H), 8.515(dd, 1H); Anal. Calc. for C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>: C, 74.46; H, 6.25; N, 19.30%. Found: C, 74.90; H, 6.34; N, 18.98%.

**Tris(6-methyl-2-pyridylmethyl)amine (Me<sub>3</sub>tpa).** CH<sub>2</sub>Cl<sub>2</sub> solution (10 mL) of 6-methyl-pyridine-2-carboxy aldehyde (0.508 g, 4.2 mmol) was dropwised to a stirred mixture of 6-methyl-2-pyridylmethylamine (0.256 g, 2.1 mmol) and sodium triacetoxyborohydride (1 g) in dichloromethane (30 mL). The resulting reaction mixture was stirred for 18 hr, after which a saturated aqueous solution of sodium hydrogencarbonate (20 mL) was added. The reaction mixture was stirred for 0.5 hr and then extracted with dichloromethane. The organic fraction was separated, dried over MgSO<sub>4</sub>, and

the solvent was removed under reduced pressure. The residue was recrystallized with hexane to give Me<sub>3</sub>tpa as colorless needles (0.350 g, 50.2%). IR (KBr, cm<sup>-1</sup>) 3422w, 3062m, 2996m, 2957m, 2918m, 2878m, 2822m, 1592s, 1577s, 1464s, 1362s, 1272m, 1121m, 977s, 804m, 794m, 759m, 624m; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm) 2.51(s, 3H), 3.84(s, 2H), 7.01(d, 1H), 7.45(d, 1H), 7.53(t, 1H).

**[Co<sub>3</sub>(tpa)<sub>3</sub>(L)](BF<sub>4</sub>)<sub>4</sub> (1).** A solution of Co(BF<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (102.4 mg, 0.3 mmol) in dry methanol (10 mL) was added to a solution of tpa (87.6 mg, 0.3 mmol). The resulting solution was stirred for 1 hr, and then 30 mL of 2,3,6,7,10,11-hexahydroxytriphenylene (H<sub>6</sub>L, 32.5 mg, 0.1 mmol) dissolved in methanol containing triethylamine was added dropwise. The resulting solution was stirred for 1 hr. Diethylether was added to the solution slowly to obtain the complex. This solution was cooled to -5 °C and over the period of 10 days a deep green microcrystals of [Co<sub>3</sub>(tpa)<sub>3</sub>(L)](BF<sub>4</sub>)<sub>4</sub> separated from the solution in 69% (119.3 mg) yield. IR (KBr, cm<sup>-1</sup>) 3423s, 3033m, 2925m, 1609s, 1485s, 1445s, 1380s, 1294s, 1259s, 1226s, 1158s, 1055s, 978m, 883m, 818m, 771m, 732w, 645m, 606m, 532m, 521m; UV-vis (acetonitrile, λ<sub>max</sub>(nm)) 1020 (ε = 1.62 × 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>), 920sh (ε = 7.41 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 656 (ε = 7.92 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 609 (ε = 7.55 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 447 (ε = 1.56 × 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>), 346 (ε = 4.69 × 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>); Anal. Calc. for C<sub>72</sub>H<sub>60</sub>N<sub>12</sub>O<sub>6</sub>Co<sub>3</sub>B<sub>4</sub>F<sub>16</sub> ·

3CH<sub>3</sub>OH: C, 49.73; H, 4.12; N, 9.28%. Found: C, 49.74; H, 4.23; N, 9.29%.

**[Co<sub>3</sub>(Metpa)<sub>3</sub>(L)](BF<sub>4</sub>)<sub>4</sub> (2).** A solution of Co(BF<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (51.1 mg, 0.15 mmol) in dry methanol (5.0 mL) was added to a solution of Metpa (45.6 mg, 0.15 mmol). The resulting solution was stirred for 1 hr, and then 10 mL of 2,3,6,7,10,11-hexahydroxytriphenylene (H<sub>6</sub>L, 16.2 mg, 0.05 mmol) dissolved in methanol containing triethylamine was added dropwise. The resulting solution was stirred for 1 hr. Diethylether was added to the solution slowly to obtain the complex. This solution stand room temperature and over the period of 14 days a deep green microcrystals of [Co<sub>3</sub>(Metpa)<sub>3</sub>(L)](BF<sub>4</sub>)<sub>4</sub> separated from the solution in 17% (14.5 mg) yield. IR (KBr, cm<sup>-1</sup>) 3422m, 1610s, 1449s, 1381m, 1267m, 1158w, 1083s, 1060s, 1036m, 772m; UV-vis (acetonitrile, λ<sub>max</sub>(nm)) 1018 (ε = 6.68 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 910sh (ε = 3.77 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 653 (ε = 5.24 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 605 (ε = 5.51 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 439 (ε = 1.77 × 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>); Anal. Calc. for C<sub>75</sub>H<sub>66</sub>N<sub>12</sub>O<sub>6</sub>Co<sub>3</sub>B<sub>4</sub>F<sub>16</sub> · 2H<sub>2</sub>O: C, 50.28; H, 3.94; N, 9.38%. Found: C, 50.24; H, 3.76; N, 8.47%.

**[Co<sub>3</sub>(Me<sub>2</sub>tpa)<sub>3</sub>(L)](BF<sub>4</sub>)<sub>3</sub> (3).** A solution of Co(BF<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (51.1 mg, 0.15 mmol) in dry methanol (10 mL) was added to a solution of Me<sub>2</sub>tpa (47.7 mg, 0.15 mmol). The resulting solution was stirred for 1 hr, and then 30 mL of

2,3,6,7,10,11-hexahydroxytriphenylene (H<sub>6</sub>L, 16.2 mg, 0.05 mmol) dissolved in methanol containing triethylamine was added dropwise. The resulting solution was stirred for 1 hr. Diethylether was added to the solution slowly to obtain the complex. This solution stand room temperature and over the period of 14 days a deep green microcrystals of [Co<sub>3</sub>(Me<sub>2</sub>tpa)<sub>3</sub>(L)](BF<sub>4</sub>)<sub>3</sub> separated from the solution in 23.2% (19.9 mg) yield. IR (KBr, cm<sup>-1</sup>) 3433m, 1608s, 1576m, 1469s, 1379m, 1270m, 1123w, 1083s, 1037m, 788m, 533m; UV-vis (acetonitrile, λ<sub>max</sub>(nm)) 1024 (ε = 3.90 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 899sh (ε = 3.05 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 607 (ε = 7.29 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>), 419 (ε = 1.14 × 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>), 346 (ε = 4.69 × 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>); Anal. Calc. for C<sub>78</sub>H<sub>72</sub>N<sub>12</sub>O<sub>6</sub>Co<sub>3</sub>B<sub>3</sub>F<sub>12</sub> · 8H<sub>2</sub>O: C, 50.51; H, 4.78; N, 9.06%. Found: C, 50.59; H, 4.37; N, 8.99%.

### Crystallography

**Crystal data for Complex(1):** A crystal suitable for crystallographic data collection was coated with an amorphous resin and cooled in the nitrogen stream of a Rigaku/MSC Mercury CCD diffractometer. A full sphere of intensity data was measured, and the structure was solved using direct methods. CIF data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 950672 (Complex (1)). Copies of this information may be obtained free charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033); email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)

### 3. Result and Discussion

#### Crystal Structure of complex(1)

A view of the complex(1) cation is shown in Figure 1. The three cobalt ions are six-coordinate in a *cis*-distorted pseudo-octahedral coordination, and each of tripodal ligand adopts a folded conformation around the metal ion. The average Co-O and Co-N bond lengths are 1.88(3) Å and 1.92(2) Å for all three Co ions. These indicate the low-spin Co<sup>III</sup> state at 126 K as the bond lengths is shorter than reported Co-O (2.008(7), 2.086(7) Å) and Co-N (2.295(10), 2.212(9), 2.165(9), 2.091(9) Å) values for high-spin Co<sup>II</sup> [21].

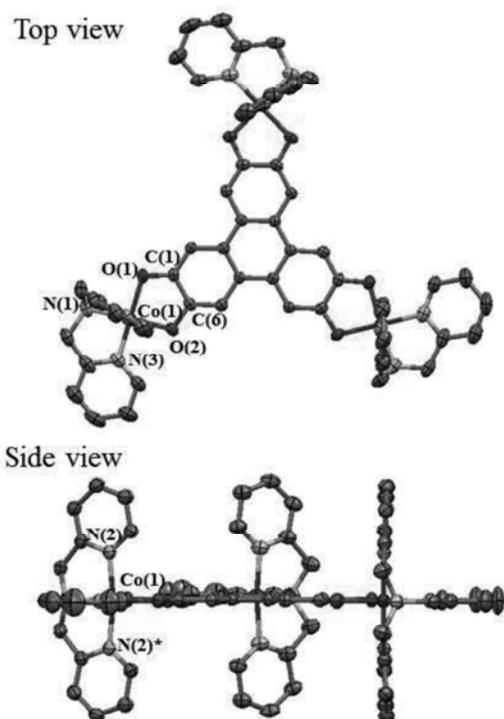


Figure 1. Perspective view of the complex cation in  $[\text{Co}_3(\text{tpa})_3(\text{L})](\text{BF}_4)_4$  (1) showing 50% thermal ellipsoids. Hydrogen atoms and  $\text{BF}_4$  anions are omitted for the sake of clarity.

The range of C-O bond lengths for structurally characterized first-row transition-metal quinone complexes is quite narrow: 1.29(1) Å and 1.35(1) Å, respectively, for coordinated semiquinonate(-

1) and catecholate(-2) ligands [22-25]. As a complex containing three low-spin Co<sup>III</sup> ions, the overall change of +4 for the ion requires regional differences in change for the the central ligand [cat,cat,sq], and the three-fold symmetry of the cation implies charge delocalization within the ligand. Consistent with this delocalization C-O (1.325(9) Å, 1.327(6) Å) and C(1)-C(6) (1.435(7) Å) bond lengths of the dioxolene ligand are intermediate between semiquinonate and catecholate values.

#### Spectroscopic properties

The electronic spectrum of the complex was measured in acetonitrile solution (Figure 2).

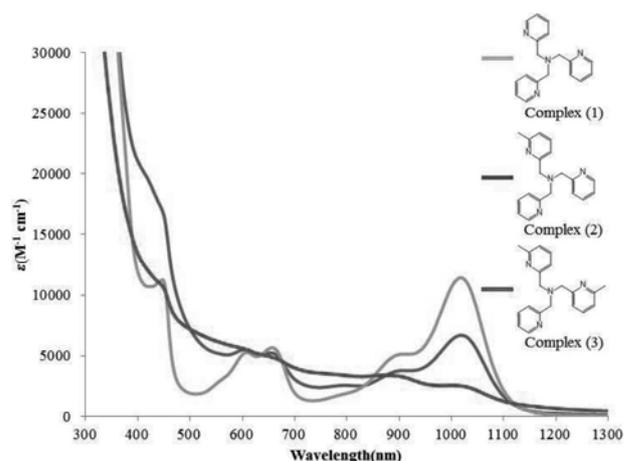


Figure 2. Electronic absorption spectra of complexes in acetonitrile solution.

$[\text{Co}_3(\text{tpa})_3(\text{L})](\text{BF}_4)_4$  (1) was isolated in the +4 state, the internal oxidation state distribution is  $\text{Co}^{\text{III}}_3(\text{cat},\text{cat},\text{sq})$  and the intense near-IR absorption maximum at 1020 nm may be ascribed to a SOMO originating from the bridging ligand [27]. The UV-Vis-NIR spectrum of  $[\text{Co}_3(\text{Metpa})_3(\text{L})](\text{BF}_4)_4$  (2) is almost same. But in

[Co<sub>3</sub>(Me<sub>2</sub>tpa)<sub>3</sub>(L)](BF<sub>4</sub>)<sub>3</sub> (**3**), the intensity of 1020 nm absorption peak is observed weakly. Upon heating from -30 degree celsius, the broad MLCT bands around 500 nm gradually increase in intensity, while 1020 nm band shows a decrease. On increasing temperature the change of the spectra with isosbestic points at 460 nm and 700 nm, respectively, were noticed. These spectral changes are consistent with the intramolecular electron transfer between a metal centre and ligand resulting in a transformation of Co<sup>III</sup><sub>2</sub>Co<sup>II</sup>-L<sup>5-</sup> (L<sup>5-</sup>; cat-cat-sq) to its isomeric form Co<sup>III</sup>Co<sup>II</sup><sub>2</sub>-L<sup>4-</sup> (L<sup>4-</sup>; cat-sq-sq). Both the heating and cooling modes of the spectral scan suggested that the thermal processes is well reversible, and shows valence tautomerism in solution too (Figure 3).

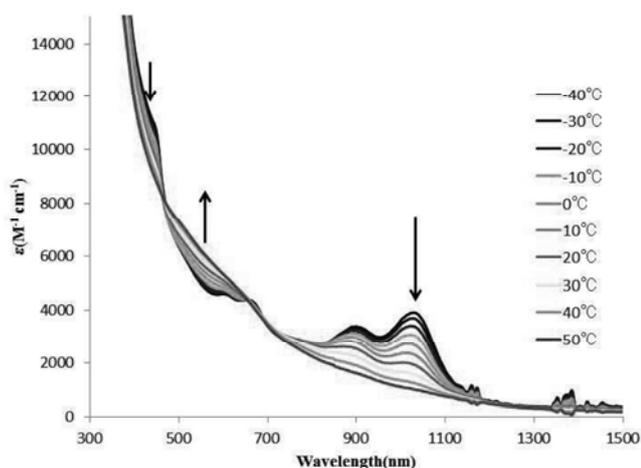


Figure 3. Electronic absorption spectra depend on temperature of complex (**3**) in acetonitrile solution.

### Electrochemical property

The electrochemical properties of the complexes were studied in acetonitrile solution, and the representative spectra of complex (**1**) and (**2**) are displayed in Figure 4(b).

The voltammetric response for complex (**1**) exhibits three well-separated oxidation process

having formal potential  $\Delta E_{1/2}$  of -0.33, 0.05 and 0.41 V vs. Fc-Fc<sup>+</sup>. These three oxidation processes are due to the redox activity of the triphenylene ligand, and assigned to the consecutive oxidation of coordinated L(cat,cat,sq) to L(cat,sq,sq) and L(sq,sq,sq). Complex (**3**) is almost similarly to complex (**1**) in that it is three cat-sq processes for ligand-based redox waves. However, irreversible wave was observed in reduction side (potential -0.51 V). This may be a reduction wave from Co(III) to Co(II). Electrochemical characterization failed to show clear structural differences for the charge distributions between cobalt ion and the ligand(L) in complex (**3**). Also it may be indicating a dependence on the electron-transfer rate.

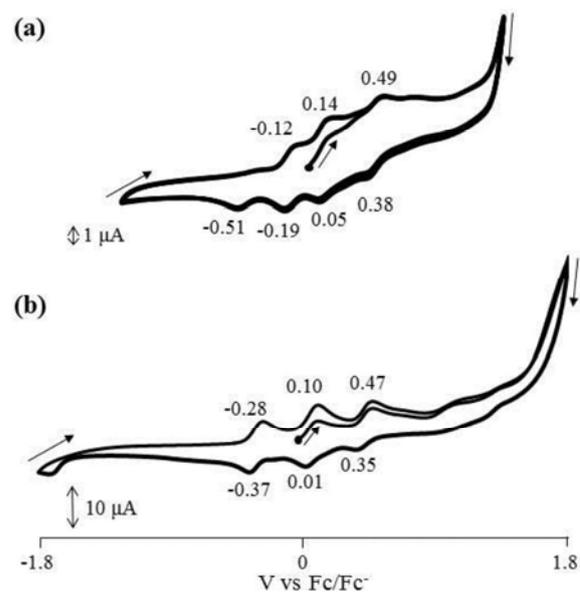


Figure 4. Cyclic voltammetry of tri-nuclear Co complexes (a) Complex (**3**) (b) Complex (**1**) at 20°C in acetonitrile solution, 1.0 mM with 0.1 M [N(n-Bu)<sub>4</sub>]PF<sub>6</sub> supporting electrolyte; platinum working electrode; scan rate 100 mV/s.

### Magnetic property

Solid state magnetic measurements for polycrystalline sample of [Co<sub>3</sub>(Me<sub>2</sub>tpa)<sub>3</sub>(L)](BF<sub>4</sub>)<sub>3</sub>

(3) were investigated using a SQUID magnetometer over the temperature range 2-380 K using an external field of 10 kOe (Figure 5). Upon heating the sample from 2 K, the onset of the first step of the VT transition occurs at ca 310 K. Below this temperature, almost plateau  $\chi_M T$  value of  $1.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  in the range 100-300 K indicates a trapped a parts of fraction of *hs*-Co(II) in three cobalt ions. However, the observed value of  $\chi_M T$  is lower than  $2.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  with the presence of an  $S=3/2$  paramagnet and an  $S=1/2$  of one spin distribution on the triphenylene(L) ring. A parts of  $\text{Co}^{\text{III}}\text{-L}$  species may be containing in the polycrystalline sample. As the temperature is increased from 300 to 380 K, VT transition occurs, with  $\chi_M T$  increasing to a value of a ca.  $2.7 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 380 K. This step shows change from  $(ls\text{-Co}^{\text{III}})_2(\text{hs-Co}^{\text{II}})$  to  $(ls\text{-Co}^{\text{III}})(\text{hs-Co}^{\text{II}})_2$  as shown in Scheme, but incomplete at 380 K, with the  $\chi_M T$  value of  $2.7 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  indicating a parts of  $\text{Co}^{\text{III}}\text{-L}$  species in complex (1). On the other hand, the data of  $\chi_M T$  versus  $T$  for  $[\text{Co}_3(\text{tpa})_3(\text{L})](\text{BF}_4)_4$  (1) indicate a  $\text{Co}^{\text{III}}\text{-L}(\text{cat}, \text{cat}, \text{sq})$  charge distribution up to 300 K, as expected on the basis of the molecular structure determined by X-ray analysis. These results lead to the conclusion that in the solid state the  $\text{Co}^{\text{II}}$  species is favoured by increasing the number of methyl groups on the ancillary ligand, as Beni *et al.*, [22] discribed in their paper. The frozen-solution EPR spectra of complex (1) is typical for semiquinonate based mono-radical structure in  $\Delta m_s = 1$  region. Complex (1) exhibit

weak  $\Delta m_s = 2$  features near half-field, indicating  $S=3/2$   $\text{Co}(\text{II})$  present, signal should occur at  $g = \sim 4.4$ . However, there is no evidence of  $^{59}\text{Co}$  ( $I=7/2$ ) hyperfine coupling that appears prominently for semiquinonate ligands chelated with  $\text{Co}(\text{II})$ . This may be the result of electron transfer between the three electronic regions of the ligand taking place on the EPR time scale.

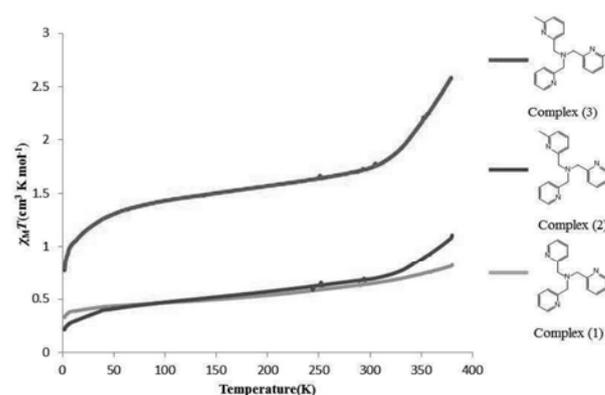


Figure 5. Polts of  $\chi_M T$  versus  $T$  for tri-nuclear Co complexes. Green line; Complex (1), Blue line; Complex (2), Red line; Complex (3).

In conclusion tri-nuclear mixed-valence cobalt complex containing  $[\text{Co}(\text{Me}_2\text{tpa})(\text{sq})]^+$  fragments linked by a conjugated polydioxolene bridging ligand, has prepared. The assignments are supported by spectroscopic studies and SQUID measurements, which show: (i) magnetic property which confirm the presence of mixed-valence  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  centers; (ii) the presence of fully delocalized ligand-centered mixed-valence states such as *cat/cat/sq* for trinuclear cobalt complex; (iii) there are occurrence intramolecular electronic transfer between *ls*- $\text{Co}(\text{III})$  and *hs*- $\text{Co}(\text{II})$ . Complex (3) is first example tri-nuclear cobalt complex showing valence tautomeric behaviour.

## Acknowledgments

We thank Prof. Ho-Chol Chang in Chuo University for measuring UV-Vis-NIR spectrum depend on temperature.

## References

- [1] D. N. Hendrickson, C. G. Pierpont, In *Topoic in Current Chemistry*; P. Gutlich, H. A. Goodwin, Eds.; Springer-Verlag: Berlin, **2004**; Vol. 234, pp 63-95.
- [2] C. G. Pierpont, *Coord. Chem. Rev.* **2001**, *216*, 99.
- [3] D. A. Shultz, In *Magnetism: Molecules to Materials, II: Molecular-Based Materials*; J. S. Miller, M. Drillon, Eds.; Wiley-VCH: New York, **2001**; 281.
- [4] O. Sato, S. Miura, H. Maruyama, Y. Zhang, D. Wu, W. Zhang, H. Xu, R. Matsuda, H. Sun, J. Tao, *Inorg. Chim. Acta*, **2008**, *361*, 3659-3662.
- [5] I. Imaz, D. Maspoch, C. Rodriguez-Blanco, J. M. Perez-Falcon, J. Campo, D. Ruiz-Molina, *Angew. Chem. Int. Ed.*, **2008**, *47*, 1875-1860.
- [6] B. Li, L-Q, Chen, J. Tao, R.-B, Huang, and L.-S. Zheng, *Inorg. Chem.*, **2013**, *52*, 4136-4138.
- [7] A. Tashiro, S. Kanegawa, O. Sato, Y. Teki, *Polyhedron*, **2013**, *66*, 167-170.
- [8] K. G. Alley, G. Poneti, J. B. Aitken, R. K. Hocking, B. Moubaraki, K. S. Murray, B. F. Abraham, H. H. Harris, L. Sorace, C. Boskovic, *Inorg. Chem.*, **2012**, *51*, 3944-3946.
- [9] K. G. Alley, G. Poneti, P. S. D. Robinson, A. Nafady, B. Moubaraki, J. B. Aitken, S. C. Drew, C. Ritchie, B. F. Abrahams, R. K. Hocking, K. S. Murray, A. M. Bond, H. H. Harris, L. Sorace, C. Boskovic, *J. Am. Chem. Soc.*, **2013**, *135*, 8304-8323.
- [10] M. van der Meer, Y. Rechkemmer, F. D. Breitgoff, S. Dechert, R. Marx, M. Dorfel, P. Neugebauer, J. van Slageren, B. Sarkar, *Dalton Trans.*, **2016**, *45*, 8394-8403.
- [11] R. Ishikawa, Y. Horii, R. Nakanishi, S. Ueno, B. K. Breedlove, M. Yamashita, S. Kawata, *Eur. J. Inorg. Chem.*, **2016**, 3233-3239.
- [12] D. Sato, Y. Shiota, G. Juhasz, K. Yoshizawa, *J. Phys. Chem. A*, **2010**, *114*, 12928-12935.
- [13] X.-Y. Chen, R.-J. Wei, L.-S. Zheng, J. Tao, *Inorg. Chem.*, **2014**, *53*, 13212-13219.
- [14] F. Shen, W. Huang, D. Wu, Z. Zheng, X.-C. Huang, O. Sato, *Inorg. Chem.*, **2016**, *55*, 902-908.
- [15] G. Poneti, M. Mannini, B. Cortigiani, L. Poggini, L. Sorace, E. Otero, P. Sainctavit, R. Sessoli, A. Dei, *Inorg. Chem.*, **2013**, *52*, 11798-11805.

- [16] O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem. Int. Ed.*, **2007**, *46*, 2152-2187.
- [17] R. Sakamoto, T. Kambe, S. Tsukada, K. Takada, K. Hishiko, Y. Kitagawa, M. Okumura, H. Nishihara, *Inorg. Chem.*, **2013**, *52*, 7411-7416.
- [18] M. Hmadeh, Z. Lu, Z. Liu, F. Gandara, H. Furukawa, S. Wan, V. Augustyn, R. Chang, L. Liao, F. Zhou, E. Perre, V. Ozolins, K. Suenaga, X. Duan, B. Dunn, Y. Yamamoto, O. Terasaki, O. M. Yaghi, *Chem. Mater.*, **2012**, *24*, 3511-3513.
- [19] Y. Suenaga, Y. Nakaguchi, Y. Fujishima, H. Konaka, K. Okuda, *Inorg. Chem. Commun.*, **2011**, *14*, 440-444.
- [20] Y. Suenaga, H. Inada, M. Inomata, R. Yamaguchi, T. Okubo, M. Maekawa, T. Kuroda-Sowa, *Chem. Lett.*, **2014**, *43*, 562-564.
- [21] Crystal data is described in ref. [20]. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-950672. Copies of the 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, U.K.; fax +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).
- [22] A. Beni, A. Dei, S. Laschi, M. Rizzitano, L. Sorace, *Chem. Eur. J.*, **2008**, *14*, 1804-1813.
- [23] D. M. Adams, A. Dei, A. L. Rheingold, D. N. Hendrickson, *J. Am. Chem. Soc.*, **1993**, *115*, 8221-8229.
- [24] K. S. Mon, A. G. Dipasquale, J. A. Golen, A. L. Rheingold and J. S. Miller, *J. Am. Chem. Soc.*, **2007**, *129*, 2360-2368.
- [25] Y. Mulyana, K. G. Alley, K. M. Davies, B. F. Abrahams, B. Moubaraki, K. S. Murray, C. Boskovic, *Dalton, Trans.*, **2014**, *43*, 2499-2511.
- [26] K. Arora, J. K. White, R. Sharma, S. Mazumder, P. D. Martin, H. B. Schlegel, C. Turro, J. J. Kodanko, *Inorg. Chem.*, **2016**, *55*, 6968-6979.
- [27] N. Azzaroli, A. D. Lapini, M. D. Donato, A. Dei, R. Righini, *J. Phys. Chem. B*, **2013**, *117*, 15492-15502.