

**Syntheses and Characterization of Co(III) Binuclear
Complexes Linked by Bis(catecholate);
[Co₂(dmbpy)₄(thBu)]²⁺ and [Co₂(dcbpy)₄(thBu)]²⁺ (dmbpy =
4,4'-dimethyl-2,2'-bipyridine, dcbpy = 4,4'-
diethylcarboxylate-2,2'-bipyridine, thBu = 3,3',4,4'-
tetrahydroxylate-5,5'-di-*tert*-butylbenzaldazine)**

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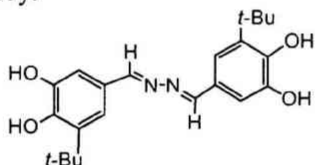
Abstract

Binuclear complexes of cobalt(III) have been prepared with 3,3',4,4'-tetrahydroxy-5,5'-di-*t*-butylbenzaldazine (H₄thBu) as bis(catecholate) ligand and ancillary ligand, 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and 4,4'-diethylcarboxylate-2,2'-bipyridine (dcbpy). The complexes were characterized by ¹H-NMR spectra, electrochemical measurements and UV-Vis spectra. In [Co₂(dmbpy)₄(thBu)]²⁺, electrochemical oxidation of the complexes occurs at the bridges as two closely spaced one-electron couples (*E*_{1/2}=74 mV and 236 mV vs. Fc/Fc⁺). Chemical oxidation of [Co₂(dmbpy)₄(thBu)]²⁺ using Ag⁺ is observed new absorbance peak at 526 nm however, is not remarkable change as [Co₂(dpa)₄(thBu)]²⁺ (dpa = 2,2'-dipyridylamine) that have been described in our later paper. On the other hand, [Co₂(dcbpy)₄(thBu)]²⁺ has never appeared new absorbance peaks under the same oxidation condition. Thus the chemical oxidation behavior and electrochemical property were correlated with the *p*K_a of the N-N ancillary ligands. In this report we discuss the effect of two different nitrogen-donor ancillary ligands on the oxidation behavior of binuclear Co(III) complexes.

Keywords: Biscatecholate; Binuclear Co(III) complexes; ¹H-NMR with various temperature; Oxidation behavior; Nitrogen-donor ancillary ligand

1. Introduction

Interests in the coordination chemistry of catecholate and semiquinonate ligands have been extended to studies on complexes containing tethered dioxolene groups. The small energy-gap between dioxolene orbitals and metal d orbitals results in significant sensitivity of the charge distribution within the metal complexes towards the molecular environment. Ligands containing saturated attachments linked to a common terminus have been developed for studies on polycatecholate chelates.¹ Direct attachment between dioxolenes has been used in studies on ligands that bridge different metal ions,² and unsaturated connections between dioxolene groups may be used to induce electronic and magnetic coupling between bridged complex units.³ The strength of intermetallic coupling for this latter class of bis(dioxolene) ligands has been found to be a function of the separation between metals, but also dependent upon the electronic structure of the bridge between dioxolene rings. In this report we describe the results of an study carried out to investigate the coordination properties of 3,3',4,4'-tetrahydroxy-5,5'-di-*t*-butyl-benzaldazine (H_4thBu) continue to our later study.⁴

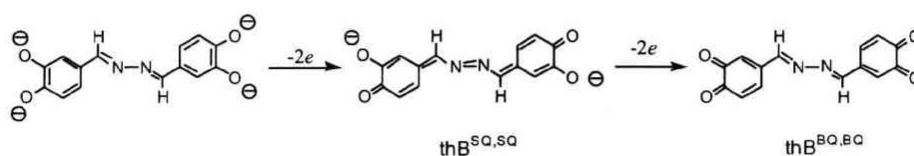


We describe the synthesis and characterization of binuclear cobalt complex with H_4thBu and N-N donor ligands. Coordination of metals at the catecholate oxygens would place them approximately 16 Å apart, with M(Cat) units linked by the conjugated hydrazone bridge. Each of the ligands may undergo oxidation by four electrons to give the bis(benzoquinone) form of the ligand ($thBu^{BQ,BQ}$). However, the bis(semiquinonate - $thBu^{SQ,SQ}$) formed by two-electron oxidation will

be of greatest interest in studies on the coordination chemistry of the ligand with redox-active transition metal ions. While each SQ may exist as a paramagnetic radical, electronic coupling between SQ regions through the planar bridge should be strong, resulting in a spin singlet ground state. Differences in ligand charge should appear with characteristic C=C, C=O, and C=N bond lengths and spectroscopic properties.

Facile metal-ligand electron transfer has become a unique feature of dioxolene complexes of redox active first-row transition metals.⁶ A number of studies reported to date have investigated the equilibrium between localized $M^I(SQ)$ and $M^{II}(Cat)$ redox isomers as valence tautomerism (VT).⁷ Complexes that exhibit VT 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.⁶ The shift between tight and floppy redox isomers is mainly due to a change in the occupancy of antibonding $d\sigma$ orbitals. The earliest and most widely studied examples of VT are dioxolene complexes of Co, where the *tight* component is a $ls-Co^{III}(Cat)$ species and the *floppy* redox isomer is $hs-Co^{II}(SQ)$ formed as the product of intramolecular electron transfer and spin transition. The donor atoms of the dioxolene ligand have been varied with nitrogen and sulfur donors in place of the ring oxygens.⁸ The model can be extended to systems other than the dioxolene complexes.

The choice of a metal for the initial study on the coordination chemistry of the conjugated bis(catecholate) ligands was based on the strong tendency of complexes of cobalt to exhibit VT. This has been emphasized by Dei and Sato in



recent work on cobalt-dioxolene complexes that might show the properties of a molecular switch.⁹ In our work Co(III) binuclear complexes with bis(catecholate) have shown unique electrochemical

properties. In this report we describe the oxidation behavior in cobalt complexes with two different nitrogen-donor ancillary ligands.

2. Experimental Section

Materials and Methods:

Preparations were performed using Schlenk techniques. All solvents were dried and distilled by standard methods before use. Reagents were obtained from Wako Chemical Co. and used without further purification. IR spectra were measured as KBr disks on a JASCO IR-8000 FT-IR spectrometer, and ¹H-NMR spectra were recorded on a Varian Mercury-300 spectrometer and JEOL-500 spectrometer. UV-visible spectra were recorded on a SHIMAZU UV-2450 spectrometer, and cyclic voltammetric measurements were made under a flow of nitrogen using a ALS/CHI 660A. Solutions of the complexes were prepared in CH₃CN containing N(*n*-Bu)₄(PF₆) (ca. 0.1 M) as supporting electrolyte. Platinum wire working and counter electrode were used with a Ag/AgNO₃ reference electrode. The Fc/Fc⁺ couple appeared at +0.083 V (ΔE = 65 mV) vs. SCE with this experimental arrangement, and the ferrocene couple was used as an internal reference.

3,3',4,4'-tetrahydroxy-5,5'-di-*tert*-butylbenzaldazine (H₄thBu):^{5,12}

Hydrazine dihydrochloride (0.37 g, 3.5 mmol) was placed in a flask with 5 ml of conc. NH₃ and 30 ml of distilled water under a flow of Ar. 3,4-dihydroxy-5-*tert*-butylbenzaldehyde (1.37 g, 0.007 mol) dissolved in 30 ml of methanol was added to this solution with stirring. The solution was stirred for 3 hrs at room temperature as the color changed from light brown to yellow. The solution was then neutralized with conc. acetic acid to remove excess ammonia and kept at 5°C for 18 hrs. During this time, yellow needles of H₄thBu separated from the solution and they were isolated by filtration. The product was recrystallized from methanol-H₂O (1:1) and dried under vacuum.

Yield: light yellow needles of 3,3',4,4'-tetrahydroxy-5,5'-di-*tert*-butylbenzaldazine (2.06 g, 76 %), IR (KBr, cm⁻¹), 3467s, 2953m, 1617s, 1593m, 1428s, 1365m, 1328m, 1292s, 1183m, 1029m, 922w, 868w, 799w, 721w, 612w, 533w; ¹H NMR (300 MHz, d₆-dmsO, ppm) 1.352 (9 H, s), 7.18 (1 H, s), 7.23 (1 H, s), 8.448 (1 H, s); EI-Mass m/z=384; (Found: C, 63.37; H, 8.18; N, 6.20. Calc. for C₂₂H₂₈N₂O₄·2CH₃OH: C, 64.20; H, 8.03; N, 6.24 %).

[Co₂(dmbpy)₄(thBu)](ClO₄)₂:

A solution of cobalt(II) acetate (100 mg, 0.4 mmol) in dry methanol (48 mL) was added to a methanol solution (8 ml) of 4,4'-dimethyl-2,2'-dipyridine (147 mg, 0.8 mmol) under Ar. The resulting solution was stirred for 30 mins, and then 20 mL of H₄thBu (76.8 mg, 0.2 mmol) dissolved in methanol was added dropwise. The resulting solution was stirred for 30 mins and then an aqueous solution of NaClO₄ was added. Ether was added to the solution slowly to precipitate the complex. This solution was cooled to 20°C and over the period of 10 days a deep green powder of [Co₂(dmbpy)₄(thBu)](ClO₄)₂ separated from the solution in 72% yield. IR (KBr, cm⁻¹) 3421s, 3068m, 2952m, 1621s, 1432s, 1411s, 1338m, 1300m, 1275m, 1249s, 1143s, 1090s, 1037m, 831m, 625m; ¹H NMR (500 MHz, d₆-dmsO, ppm); 1.045 (9 H, s), 2.549 (3 H, d), 2.636 (3H, d), 6.614 (1 H, s), 6.755 (1 H, s), 7.389 (2H, d), 7.454(2H, d), 7.752 (1H, d), 7.833 (1H, d), 8.132 (1H, s), 8.452 (1H, d), 8.530 (1H, d), 8.729 (2 H, d), 8.735 (1H, s), 8.776 (1H, s)); UV-vis (acetone, λ_{max}(nm)) 416 (ε = 4.45×10⁴ M⁻¹cm⁻¹). (Found: C, 56.48; H, 5.38; N, 9.15. Calc. for C₇₀H₇₂N₁₀O₄Co₂Cl₂O₈·3H₂O: C, 56.49; H, 5.28; N, 9.41 %).

[Co₂(dcbpy)₄(thBu)](ClO₄)₂:

A solution of cobalt(II) acetate (16.4 mg, 0.07 mmol) in dry methanol (10 ml) was added to a chloroform solution (5 ml) of 4,4'-diethylcarboxylate-2,2'-bipyridine (40 mg, 0.13 mmol) under Ar. The resulting solution was stirred for 30 mins, and then 7 mL of H₄thBu (13 mg, 0.03 mmol) dissolved in dry methanol was added dropwise. The resulting solution was stirred for 30 mins and then added an aqueous solution of NaClO₄. Ether as diffusion solvent poured on this solution slowly. The solution was cooled to 20 °C and over the period of 10 days a dark green

3. Results and Discussion

¹H-NMR Spectra

¹H-NMR spectra recorded on [Co₂(dmbpy)₄(thBu)]²⁺ at room temperature were clearly resolved. Specific assignments for resonances could be made from spectra obtained on the free H₄thBu ligand. The 2-dim NMR of [Co₂(dmbpy)₄(thBu)]²⁺ is shown in Figure 1. The assignments for resonances are given in Table 1. With dmbpy the two protons of the catechol ring appear as two singlets at δ= 6.61 ppm and 6.75 ppm (with dcbpy as ancillary ligand, δ= 6.67 ppm and 6.81 ppm). These signals are significantly shifted to higher field compared with the free protonated ligands (7.18 ppm and 7.23 ppm). Resonances appeared to broaden into the baseline at the higher temperatures. This is an indication that the collapse of the spectral resonances is not associated with the formation of a paramagnetic form of the complex. Rather, the loss of resolution is more likely associated with a dynamic process that averages resonance positions, ultimately giving a coalesced time-averaged spectrum at some high temperature. In fact, from the assignments for the specific bipyridine resonances it is possible to conclude that, not only are the two unique dmbpy ligands exchanging coordination sites, but that the two unique halves of the coalesced dmbpy, with nitrogens *trans* to either oxygen or nitrogen, coalesce to give four resonances for the ring

powder of [Co₂(dcbpy)₄(thBu)](ClO₄)₂ separated from the solution in 82% yield. IR (KBr, cm⁻¹) 3423s, 2981m, 1731s, 1637m, 1617m, 1560m, 1410s, 1369m, 1297m, 1252s, 1121s, 1090m, 1016m, 861w, 766m, 625m; ¹H NMR (500 MHz, d₆-dmsO, ppm) 1.077 (9 H, s), 1.366-1.404 (12H, m), 4.441-4.502 (8H, m), 6.673 (1 H, s), 6.812 (1 H, s), 7.904 (2H, d), 7.953-8.007 (2H, m), 8.158(1H, s), 8.382 (1H, d), 8.513 (1H, d), 8.775 (1H, d), 8.922 (1H, d), 9.421 (1H, s), 9.457 (1H, s), 9.496 (2H, s); UV-vis (acetone, λ_{max}(nm)) 401 (ε = 5.06 × 10⁴ M⁻¹cm⁻¹).

protons. The temperature-dependence of the spectra is shown in Figure 2.

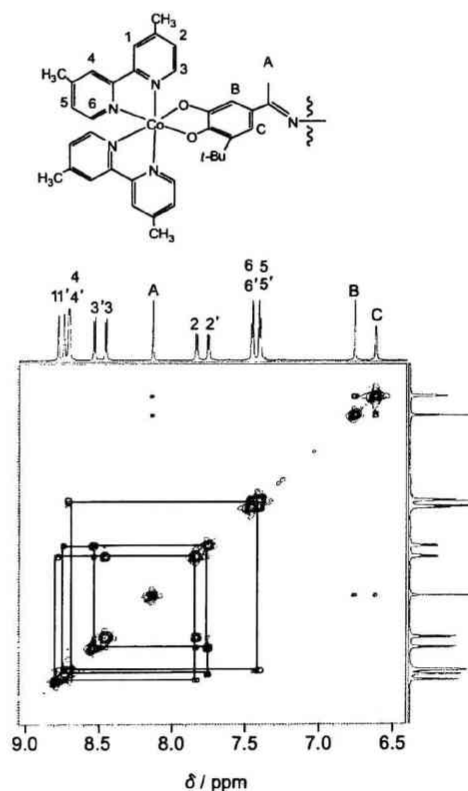


Figure 1 2-D ¹H-NMR spectrum of [Co₂(dmbpy)₄(thBu)](ClO₄)₂ Solv.:d₆-dmsO.

As temperature is increased to the upper temperature limit of 100°C for dmsO, resonances for the 1, 4, 1', and 4' protons coalesce to a singlet at 8.7 ppm, and the 5, 6, 5', and 6' resonances coalesce to a broad resonance at 7.4 ppm. The 3 and 3' resonances collapse to a broad at 8.5 ppm and the 2 and 2' resonances at 7.7 ppm. Resonances for the ring protons of the thBu ligand

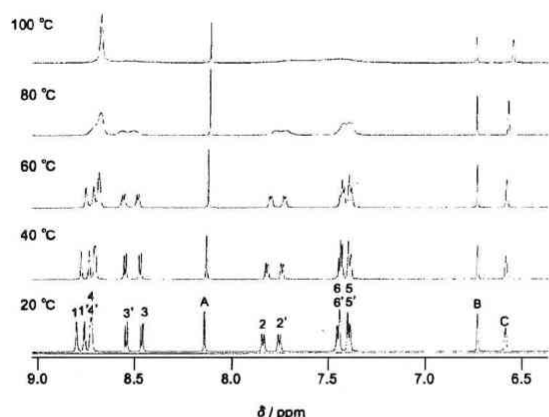


Figure 2 $^1\text{H-NMR}$ spectra with various temperature with $[\text{Co}_2(\text{dmbpy})_4(\text{thBu})](\text{ClO}_4)_2$. Solv.: $\text{d}_6\text{-dmsO}$.

appear as two separated resonances near 6.6-6.7 ppm at 20°C. They are observed to move apart as temperature is increased, while resonances for the imine proton group remain essentially fixed in position but the *tert*-butyl protons are shifted to low field through the temperature range.

On the other hand the 2-dim NMR of $[\text{Co}_2(\text{dcbpy})_4(\text{thBu})]^{2+}$ is shown in Figure 3. The assignments for resonances are given in Table 1. N-N ligand has two carboxylic acid ethylester group at para-position for N atom. Therefore, the chemical shifts values of dcbpy protons observed to lower field than the case of dmbpy. Also, from exist of couple proton signals for 5 or 6 proton, isomer products (Δ or Λ -form) may be mixed in this compound. The temperature-dependence of the spectra is shown in Figure 4. All most protons signal not only dcbpy protons but also, thBu proton are disappeared at 100°C and these temperature dependence spectra are not reversible behavior. From this observation $[\text{Co}_2(\text{dcbpy})_4(\text{thBu})]^{2+}$ were degenerated at high temperature.

Differences in the coordination chemistry of the two common ions of cobalt are striking. Octahedral complexes of Co(II) are generally high spin and both kinetically and stereochemically labile, while corresponding complexes of Co(III) are low-spin, diamagnetic, and inert to ligand exchange and stereodynamic shifts in structure.¹⁰ Optically active complexes of Co(III) may be resolved in solution without evidence for racemization, and this is particularly true for complexes containing diimine ligands like 2,2'-bipyridine and 1,10-phenanthroline.¹⁰ This is due to the enormous disfavor of the trigonal prismatic intermediate associated with nondissociative racemization and the high energy required for dissociation of a chelating nitrogen or oxygen ligand.¹¹ Electron transfer from one or both catechol groups to the cobalt center(s) would produce labile Co(II) in a process that appears coupled with the change in electronic spectrum in

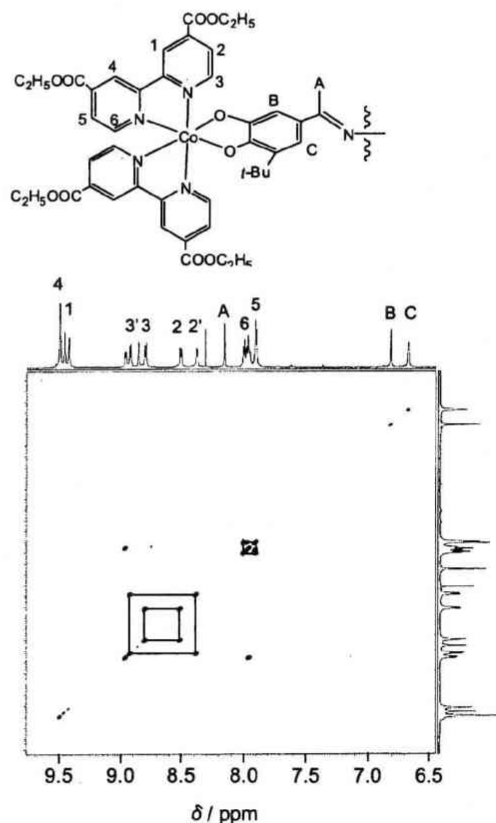


Figure 3 2-D $^1\text{H-NMR}$ spectrum of $[\text{Co}_2(\text{dcbpy})_4(\text{thBu})](\text{ClO}_4)_2$, Solv.: $\text{d}_6\text{-dmsO}$.

solution. However, there is no evidence in the NMR for the formation of a *hs*-Co(II) species that is stable on a timescale that would produce the paramagnetically shifted NMR spectrum that is generally observed for octahedral Co(II).⁷ It is likely that the transition temperature for the equilibrium between Co^{III}(Cat) and Co^{II}(SQ) redox isomers is well above the temperature range accessible in this solution. At the upper experimental temperature range the equilibrium still favors the Co^{III}(Cat) isomer, with Co^{II}(SQ) present at low concentration, but sufficiently long-lived to permit equilibration of the bpy ligands in a dynamic process.

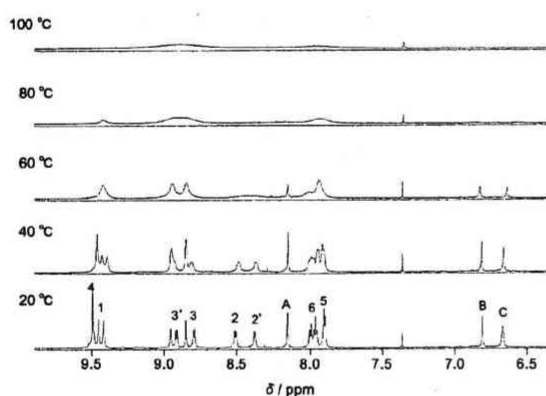


Figure 4 ¹H-NMR spectra with various temperature of $[\text{Co}_2(\text{dcbpy})_4(\text{thBu})](\text{ClO}_4)_2$, Solv.: d_6 -dmso.

Electrochemistry

Assigning features in the cyclic voltammograms of our Biscat bridged complexes should be more straightforward due to the relative redox stability of the metal ions we have employed. Electrochemical data and the CV traces from which they derive are given in Table 2 and Figure 5, respectively. The data reveal that each compounds undergoes two reversible one-electron redox process for $[\text{Co}_2(\text{dmbpy})_4(\text{thBu})]^{2+}$. The first redox electrode potential is 74 mV and second redox electrode potential is 236 mV (vs. Fc/Fc^+). The two oxidations electrode potential are separated by approximately 160 mV, suggesting that they correspond to stepwise Cat-Cat/Cat-SQ and Cat-SQ/SQ-SQ redox complexes of the bridging ligands. The electronic structure of the bridging ligand of

$[(\text{N-N})_2\text{Co}^{\text{III}}(\text{SQ-SQ})\text{Co}^{\text{III}}(\text{N-N})_2]^{2+}$ would have significantly carbonyl character at the C-O bond and *trans* conformation to the carbon of the azine bridge (scheme1). In contrast, $[\text{Co}_2(\text{dcbpy})_4(\text{thBu})]^{2+}$ has no clearly reversible redox waves. Thus it is interesting N-N donor ancillary ligand effect on redox behavior of Biscat into binuclear complex. The $E_{1/2}$ of the complexes were correlated with the pK_a of the ancillary. This result is correspondent to chemical oxidation next paragraph.

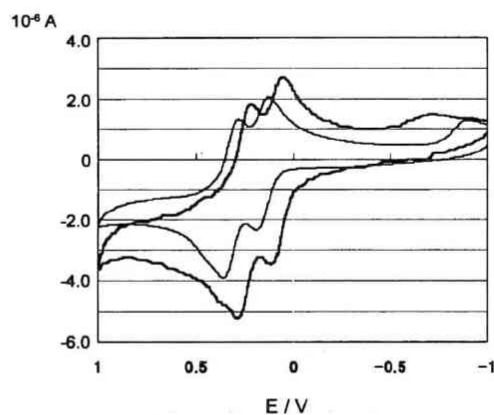
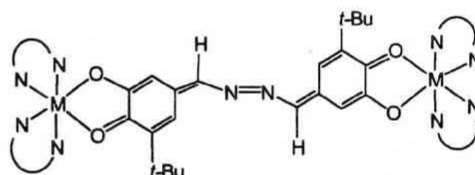


Figure 5 Cyclic voltammogram of $[\text{Co}_2(\text{dmbpy})_4(\text{thBu})]^{2+}$ (red line) and $[\text{Co}_2(\text{dpa})_4(\text{thBu})]^{2+}$ (black line) Electrolyte reagent: 0.1 M $\text{N}(\text{n-Bu})_4\text{PF}_6$, Concentration: 1 mM, Solv.: CH_3CN , Scan rate: 100mV/s.



Scheme 1

Chemical Oxidation of $[\text{Co}_2(\text{dmbpy})_4(\text{thBu})](\text{ClO}_4)_2$.

Chemical oxidation reactions were carried out using $\text{Ag}(\text{PF}_6)$ in an effort to isolate oxidized forms of the binuclear complexes containing semiquinonate ligands. A reaction was carried out with binuclear complexes dissolved in dry acetone at room temperature. Time-dependent changes in UV-Vis spectra are shown in Figure 6. Upon addition of 1.3 equivalent of Ag^+ to $[\text{Co}_2(\text{dpa})_4(\text{thBu})]^{2+}$ the yellow solution was observed to immediately turn red, and then gradually purple. Oxidation with Ag^+ occurs as a *thBu* ligand-based one-electron process forming the SQ-Cat trication,

$[\text{Co}_2(\text{dmbpy})_4(\text{thBu}^{\text{SQ,Cat}})]^{3+}$. This appears as an absorption peak at 543 nm in Figure 6(a). Upon addition of Ag^+ , $^1\text{H-NMR}$ signals become broad but with no evidence of a paramagnetic shift. After oxidation with Ag^+ , second-oxidation reaction occurs immediately. Then the Cat-Cat dication changes to the SQ-SQ tetracation through the Cat-SQ trication. Two radicals in SQ-SQ that obtained by auto-oxidation are coupling each other through conjugated bond and stable SQ-SQ tetracation are

forms like scheme 1. Therefore this may be interpreted to no detect paramagnetic shifts in $^1\text{H-NMR}$. In contrast, $[\text{Co}_2(\text{dmbpy})_4(\text{thBu})](\text{ClO}_4)_2$ and $[\text{Co}_2(\text{dcbpy})_4(\text{thBu})](\text{ClO}_4)_2$ shows no change in UV-Vis spectrum upon addition of Ag^+ (Figure 6(b)(c)) during oxidation reaction. It is likely associated with the difference in ligand field strength ($\text{p}K_a$) of N-N donor and the planar/folded change in conformation of the dpa ligand.

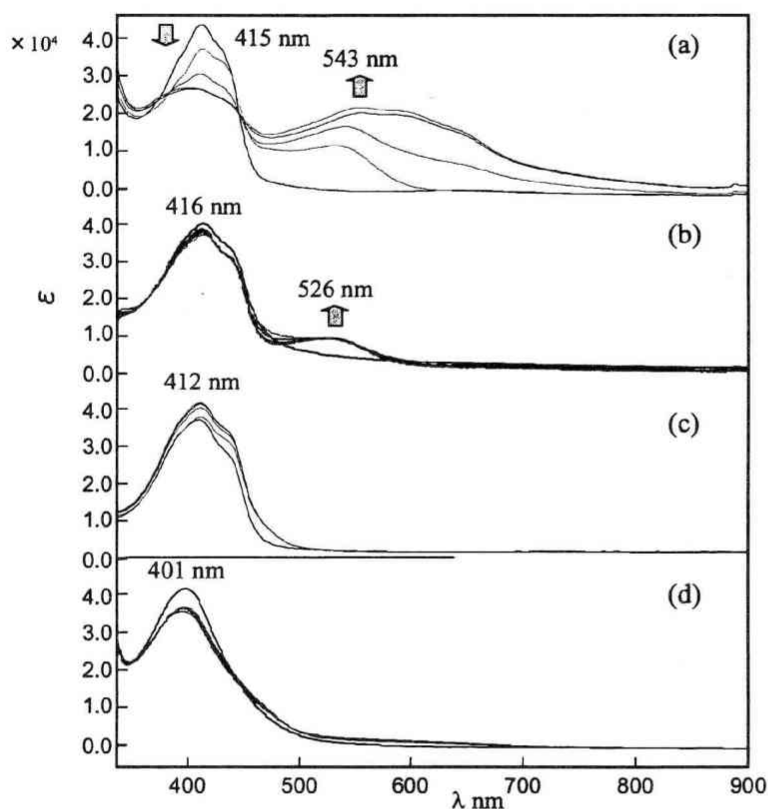


Figure 6 Time-dependent changes in the UV-visible spectra of $[\text{Co}_2(\text{N-N})_4(\text{thBu})](\text{ClO}_4)_2$ in acetone solution with addition of 1.3 eq. AgPF_6 . (a) $[\text{Co}_2(\text{dpa})_4(\text{thBu})](\text{ClO}_4)_2$ (b) $[\text{Co}_2(\text{dmbpy})_4(\text{thBu})](\text{ClO}_4)_2$ (c) $[\text{Co}_2(\text{bpy})_4(\text{thBu})](\text{ClO}_4)_2$ (d) $[\text{Co}_2(\text{dcbpy})_4(\text{thBu})](\text{ClO}_4)_2$

4. Summary

Interests in the switching properties of metal-dioxolene complexes that exhibit valence tautomerism have been directed at members of the $\text{L}_n\text{Co}^{\text{III}}(\text{Cat})/\text{L}_n\text{Co}^{\text{II}}(\text{SQ})$ series.⁹ Differences in donor strength of the L_n ligands may be used to tune the conditions for electron transfer. The transition from $\text{ls-Co}^{\text{III}}(\text{Cat})$ to $\text{hs-Co}^{\text{II}}(\text{SQ})$ has an accompanying diamagnetic/paramagnetic change in magnetism that may facilitate detection, and

properties of ancillary ligands and counter ions may contribute to hysteretic effects. The cobalt coordination sphere are under the same circumstances, however, biscatecholate ligands are oxidized easily in $[\text{Co}_2(\text{dpa})_4(\text{thBu}^{\text{SQ,SQ}})](\text{ClO}_4)_2$. These mean it is likely associated with the ligand field strength ($\text{p}K_a$) of N-N donor and the Two $\text{Co}(\text{III})$ binuclear complexes, $[\text{Co}_2(\text{dmbpy})_4(\text{thBu})](\text{ClO}_4)_2$ and

[Co₂(dcbpy)₄(thBu)](ClO₄)₂ were successfully isolated and characterized by ¹H-NMR, UV-Vis and CV (for [Co₂(dmbpy)₄(thBu)](ClO₄)₂). The different oxidation behavior between two binuclear complexes herein and [Co₂(dpa)₄(thBu)](ClO₄)₂ is shown by UV-Vis spectrum after chemical oxidation using Ag(PF₆). This result means the difference in ligand field strength of N-N donor, dpa is more

strong than dmbpy and dcbpy. In fact *E*_{1/2} values of [Co₂(dmbpy)₄(thBu)](ClO₄)₂ are larger than the values of [Co₂(dpa)₄(thBu)](ClO₄)₂ from CV. The ligand field strength of N-N donor ancillary ligand correlates with the redox potential of biscatecholate in Co(III) binuclear complexes. planar/folded change in conformation of the dpa ligand.

Table 1. ¹H-NMR chemical shift assignments (ppm) for [Co₂(dmbpy)₄(thBu)]²⁺ and [Co₂(dcbpy)₄(thBu)]²⁺ in d₆-DMSO at 20°C (see labels in Figure 1 and Figure 2)

¹ H	[Co ₂ (dmbpy) ₄ (thBu)] ²⁺	[Co ₂ (dcbpy) ₄ (thBu)] ²⁺
thBu		
H _A	8.132	8.158
H _B	6.755	6.812
H _C	6.614	6.673
H _D	1.045	1.077
N-N ligand		
	dmbpy	dcbpy
H ₁ , H _{1'}	8.735, 8.776	9.421, 9.457
H ₂ , H _{2'}	7.752, 7.833	8.382, 8.513
H ₃ , H _{3'}	8.452, 8.530	8.775, 8.922
H ₄ , H _{4'}	8.729	9.496
H ₅ , H _{5'}	7.389	7.904
H ₆ , H _{6'}	7.454	7.980

Table 2. Electrochemical properties of [Co₂(dmbpy)₄(thBu)]²⁺, [Co₂(dcbpy)₄(thBu)]²⁺, [Co₂(bpy)₄(thBu)]²⁺ and [Co₂(dpa)₄(thBu)]²⁺

compounds		Ligands <i>pK_a</i>	3+/2+		4+/3+	
			<i>E</i> _{1/2} (V)	Δ <i>E</i> (mV) ^b	<i>E</i> _{1/2} (V)	Δ <i>E</i> (mV) ^b
[Co ₂ (dcbpy) ₄ (thBu)] ²⁺	This work	4.26	-	-	-	-
[Co ₂ (bpy) ₄ (thBu)] ²⁺	Ref.[12]	4.44	0.099	64	0.262	70
[Co ₂ (dmbpy) ₄ (thBu)] ²⁺	This work	4.92	0.074	63	0.236	79
[Co ₂ (dpa) ₄ (thBu)] ²⁺	Ref.[12]	5.00	0.001	61	0.168	67

^a All potentials are referenced to the ferrocenium/ferrocene couple (*E*_{1/2} = 0.083 V).

^b Δ*E* = *E*_{p anodic} - *E*_{p cathodic}

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