Intramolecular Change Distribution and Related Properties in a Series of 3,6-Di-*tert*-butylbenzoquinonatocobalt Complexes Containing Piperidine

Ok-Sang Jung,* Young-A Lee, Sung Ho Park, Yun Ju Kim, Kyung Ho Yoo,† and Dong Chan Kim†

Materials Chemistry Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

† Medicinal Chemistry Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

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A series of cobalt-benzoquinone complexes containing piperidine derivatives as a coligand, $[Co(3,6\text{-dbq})_2(N\text{-}N)]$, (N-N = 1,1′-methylenedipiperidine (mdp), 1,1′-methylenebis(3-methylpiperidine) (mbmp), 1-methyl-4-(methylamino)piperidine (mmap); 3,6-dbq = 3,6-di-*tert*-butyl-1,2-benzoquinone) have been prepared and characterized. The crystal structure of $[Co(3,6\text{-dbq})_2(mmap)]\cdot 0.5Me_2CO$ ($P\bar{1}$, a = 11.524(2) Å, b = 12.565(4) Å, c = 14.160(3) Å, α = 80.65(2)°, β = 82.15(2)°, γ = 87.39(2)°, V = 2003.6(8) Å^3, R = 0.0763) proves that the molecule exists as low-spin $[Co^{III}(3,6\text{-dbsq})(3,6\text{-dbcat})(mmap)]$ (3,6-dbsq = 3,6-di-*tert*-butyl-1,2-semiquinonato; 3,6-dbcat = 3,6-di-tert-butylcatecholato) in the solid state. According to magnetic, spectroscopic, and thermal analyses, $[Co^{III}(3,6\text{-dbsq})(3,6\text{-dbcat})(mmap)]$ is locked up to 431 K while $[Co^{II}(3,6\text{-dbsq})_2(mdp)]$ and $[Co^{II}(3,6\text{-dbsq})_2(mbmp)]$ are changed to their corresponding low spin Co^{III} forms at (below) $T_{1/2}$ = 215 K and 271 K, respectively. The transition temperature ($T_{1/2}$) between Co^{III}/Co^{II} varies as mbmp < mdp << mmap, which appears to be associated with electronic versus steric effects of the piperidine coligands. In particular, $[Co(3,6\text{-dbq})_2(mdp)]$ reveals a two-step spin conversion centered at 208 K and 298 K with a plateau of 90 deg.

Memory and storage materials, sensors, and molecular switches are some of the important facets of molecular electronics.[1–3] Devices for such purposes contain bistable components with two stable or metastable states.[4–7] Reversible transformation of transition metal complexes offer some potential for the design of bistable inorganic and organometallic materials. Transition metal complexes containing *o*-semiquinonato (sq^-, S = 1/2) and catecholato (cat^{2-}, S = 0) ligands have shown a unique facility for intramolecular electron transfer between the metal and quinone ligand around room temperature.[8] This has been most remarkably illustrated for the cobalt complexes where temperature- and photo-dependent equilibria between the following Co^{III} and Co^{II} valence tautomers have been observed both in solution and in the solid state (Eq. 1).[9,10]

$$[Co^{III}(sq)(cat)(N\text{-}N)] \rightleftharpoons [Co^{II}(sq)_2(N\text{-}N)] \quad (1)$$

In relation to the valence tautomerism, unique physicochemical properties such as the presence of the characteristic band near 2500 nm (4000 cm^{-1}) for Co^{III} form,[11] crystal bending effect,[12] and huge hysteresis[13] have been observed. These phenomena are a consequence of charge localization within the molecule and the close energy separation between localized quinone and cobalt electronic levels.[14] Our previous papers reported that the tautomerism is very sensitive to light, solvent, or state as well as partial change of the diimine coligands.[11,13,15–17]

In an effort to expand and scrutinize the chemistry, we describe the results on the valence tautomerism and related characteristic properties for a series of complexes, $[Co(3,6\text{-dbq})_2(N\text{-}N)]$, where N-N means piperidine derivatives such as mdp, mbmp, and mmap, and 3,6-dbq is 3,6-di-*tert*-butyl-1,2-benzoquinone.

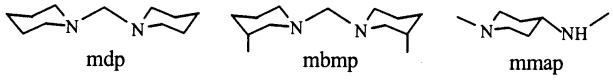


Chart 1.

Experimental

Materials and Measurements. 3,6-Di-*tert*-butyl-1,2-benzoquinone (3,6-dbq) was prepared according to the literature procedure.[18] Octacarbonyldicobalt $[Co_2(CO)_8]$ was purchased from Strem, and 1,1′-methylenedipiperidine (mdp), 1,1′-methylenebis(3-methylpiperidine) (mbmp), and 1-methyl-4-(methylamino)piperidine (mmap) were purchased from Aldrich. Elemental analysis (C,H,N) was carried out at the Advanced Analysis Center, KIST. Infrared spectra were obtained in 5000–400 cm^{-1} range on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellets. Temperature-dependent magnetic measurements were made on a Quantum Design MPMS-5 SQUID magnetometer. Electronic spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed by using a Stanton Red Croft TG 100 with a scanning rate of 10 °C min^{-1}.

Synthesis of $[Co(3,6\text{-dbq})_2(mmap)]$. $[Co_2(CO)_8]$ (171 mg, 0.5 mmol) and 5,5′-mmap (128 mg, 1.0 mmol) were combined in

30 mL of toluene. The mixture was stirred for 5 min, and 3,6-dbq (440 mg, 2.0 mmol) in 30 mL of toluene was then added. The mixture was next stirred under nitrogen atmosphere for 2 h at room temperature. Evaporation of the solvent produced a dark blue solid. Recrystallization from acetone gave dark blues crystals as the acetone solvate in 81% yield. Found: C, 66.30; H, 9.21; N, 4.31%. Calcd for $C_{35}H_{56}N_2O_4Co{\cdot}0.5C_3H_6O$: C, 66.75; H, 9.05; N, 4.27%. IR (KBr) 4312 (br, s), 2948 (s), 1548 (m), 1406 (m), 1276 (m), 1150 (m), 954 (br, s), 734 (m), 654 (m), 608 cm^{-1} (m).

[Co(3,6-dbq)$_2$(mdp)]. The complex was prepared by the above method. 83% yield. Found: C, 68.30; H, 9.31; N, 4.21%. Calcd for $C_{39}H_{62}N_2O_4Co$: C, 68.70; H, 9.16; N, 4.11%. IR (KBr) 4048 (br, s), 2946 (s), 1546 (m), 1472 (s), 1438 (s), 1348 (m), 1282 (m), 994 (m), 954 (br, s), 824 (m), 806 (m), 656 (m), 608 cm^{-1} (m).

[Co(3,6-dbq)$_2$(mbmp)]. The complex was prepared by the method of [Co(3,6-dbq)$_2$(mmap)]. 80% yield. Found: C, 69.10; H, 9.31; N, 4.02%. Calcd for $C_{41}H_{66}N_2O_4Co$: C, 69.37; H, 9.37; N, 3.95%. IR (KBr) 3998 (br, s), 2954 (s), 1546 (m), 1474 (s), 1436 (s), 1386 (m), 1354 (m), 1204 (m), 954 (br, s), 822 (s), 654 cm^{-1} (m).

X-ray Crystal Analysis of [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO. The crystal was obtained from acetone. A crystal was wedged in a Lindemann capillary with mother liquor. The X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo $K\alpha$ (λ = 0.71073 Å) at ambient temperature. Unit cell dimension was based on 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected for by the empirical φ-scan method. The structure was solved by the Patterson method (SHELXS-97), and was refined by the full-matrix least squares techniques (SHELXL-97).[19] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in their positions calculated with the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collection and structure refinement are listed in Table 1.

Further details concerning the crystal structure investigation of [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, (U.K.). The complete F_o–F_c data have been deposited as Document No. 74004 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Crystallographic Data for [Co(3,6-dbq)$_2$-(mmap)]·0.5Me$_2$CO

Formula	$C_{35}H_{56}N_2O_4Co{\cdot}0.5C_3H_6O$
Formular weight	656.81
Space group	$P\bar{1}$(No. 2)
a, b, c/Å	11.524(2), 12.565(4), 14.160(3)
α, β, γ/deg	80.65(2), 82.15(2), 87.39(2)
V/Å^3	2003.6(8)
Z	2
D_{cal}/Mg m^{-3}	1.089
Absorption coeff./mm^{-1}	0.464
F(000)	710
Crystal size/mm	0.40 × 0.20 × 0.03
θ_{max}/deg	25
Index ranges	h, ±k, ±1
Reflections collected	3717
Independent reflections	3530
Parameters refined	416
Goodness of fit	1.138
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0763
	$wR2$ = 0.1879
R indices (all data)[a]	$R1$ = 0.0823
	$wR2$ = 0.1930
Largest diff. peak and hole/eÅ^{-3}	0.634, −0.350

a) $R1 = \| F_o| - |F_c \| / |F_o|$, $wR2 = \{(F_o^2 - F_c^2)^2 / wF^4\}^{1/2}$.

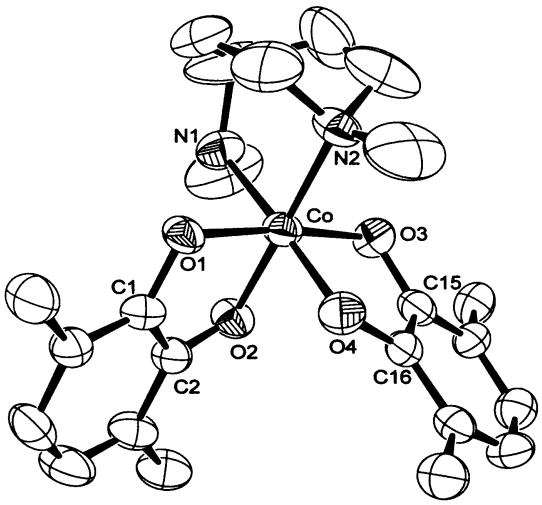


Fig. 1. ORTEP drawing of [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO showing the atomic labeling scheme and thermal ellipsoids at the 50% level. Methyl carbon atoms of *tert*-butyl group, solvate acetone molecule, and hydrogem atoms are omitted for clarity.

Results and Discussion

Synthetic procedures described in earlier studies have been used to prepare the series of [Co(3,6-dbq)$_2$(N-N)][11]: the reaction between [$Co_2(CO)_8$] and 3,6-dbq in the presence of the respective piperidine coligand afforded the present complexes in toluene at room temperature. The solid products gave satisfactory chemical analyses, and were soluble in common solvents such as toluene, benzene, tetrahydrofuran, acetone, and dimethylformamide. This solubility supports the conclusion that the complexes are discrete molecules. The complexes were characterized based on spectral, thermal, and magnetic properties along with a crystal structure.

Crystal Structure of [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO. A view of the molecule is shown in Fig. 1, and relevant bond distances and angles are listed in Table 2. The structural data suggest that the molecule exists as [Co^{III}(3,6-dbsq)(3,6-dbcat)(mmap)] in the solid state. In the figure, oxygen atoms O(1) and O(2) are associated with the 3,6-di-*tert*-butyl-1,2-semiquinonato (3,6-dbsq$^-$, S = 1/2), O(3) and O(4) belong to the 3,6-di-*tert*-butylcatecholato (3,6-dbcat^{2-}, S = 0) ligand. This is apparent from the Co^{II}–O lengths. The bond lengths of Co–O (1.872(5)–1.883(5) Å) are also shorter than general Co^{II}–O bonds (≥ 2.00 Å). The radius of low spin Co^{III} is roughly 0.2 Å shorter than the radius of high spin Co^{II}.[13] The low spin Co^{III}

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO

Co–O(1)	1.874(5)	Co–O(2)	1.873(5)
Co–O(3)	1.883(5)	Co–O(4)	1.872(5)
Co–N(1)	1.995(7)	Co–N(2)	2.016(6)
C(1)–O(1)	1.333(8)	C(2)–O(2)	1.305(8)
C(15)–O(3)	1.333(8)	C(16)–O(4)	1.319(8)
O(2)–Co–O(4)	87.8(2)	O(3)–Co–O(4)	86.5(2)
O(2)–Co–O(3)	88.5(2)	O(1)–Co–O(4)	89.2(2)
O(1)–Co–O(2)	86.2(2)	O(1)–Co–O(3)	173.3(2)
N(1)–Co–O(4)	177.7(3)	N(1)–Co–O(2)	90.2(3)
N(1)–Co–O(3)	94.5(3)	O(1)–Co–N(1)	89.5(3)
N(2)–Co–O(4)	92.3(3)	N(2)–Co–O(2)	178.3(3)
N(2)–Co–O(3)	93.2(2)	N(2)–Co–O(1)	92.1(2)
N(1)–Co–N(2)	89.7(3)		

would be expected to be in a rigidly octahedral arrangement[20] in contrast to a few examples of the high-spin Co^{II} trigonal prismism.[11,21] Thus, for the present complex, a distorted octahedral geometry around the cobalt atom may be additional evidence of Co^{III} species. In contrast to the known [Co(3,6-dbq)$_2$(N-N)] with a symmetric diimine coligand, the C–O bond length of the benzoquinone seems to be not significant for discerning its bonding mode.[14] This fact may be affected by the *trans* effect of the asymmetric mmap coligand. On the other hand, the asymmetric mmap ligand is chelated to the cobalt(III) in *cis* position. The Co–N(1) (1.995(7) Å) involving the secondary amine is shorter than Co–N(2) (2.016(6) Å) involving the tertiary amine. The tertiary amine group is *trans* to the 3,6-dbsq and the secondary amine group is *trans* to the 3,6-dbcat.

Magnetic Properties. Magnetic measurements are an effective means of following the equilibrium due to the change in metal spin state as well as the shift in charge distribution.[2,22] The temperature-dependent magnetic moments recorded on solid samples are depicted in Fig. 2. The magnetic moments of [Co(3,6-dbq)$_2$(mdp)] and [Co(3,6-dbq)$_2$(mbmp)] convert in the 140–350 K region, while the magnetic moments of mmap analogue are nearly invariant up to 400 K. That is, [Co(3,6-dbq)$_2$(mmap)] species is locked in a charge distribution of [Co^{III}(3,6-dbsq)(3,6-dbcat)(mmap)] with 1.7–1.8 μ_{eff}. For [Co(3,6-dbq)$_2$(mdp)] and [Co(3,6-dbq)$_2$(mbmp)], the magnetic moments retain approximately 1.7–1.8 μ_B in the temperature range of 10–140 K, increase in the temperature range 140–350 K, and finally approach 5.2 μ_{eff} at 400 K, indicating that the valence tautomerism shown in Eq. 2 occurs in the solid state. In an earlier report we noted that the [Co^{II}(3,6-dbq)$_2$(Py$_2$Se)] species exhibits a similar value of 5.2 μ_{eff}.[13] From the magnetic data, the transition temperature ($T_{1/2}$) increases in the order of mbmp < mdp << mmap. The magnetic values of 1.7–1.8 μ_{eff} are approximately the value expected for a S = 1/2 molecule, which is characteristic of low-spin [Co^{III}(3,6-dbsq)(3,6-dbcat)(N-N)]. Electron transfer from the 3,6-dbcat to the Co of Co^{III} was accompanied by spin transition of the resulting Co^{II} ion. The S = 3/2 Co^{II} center couples with the two S = 1/2 radical semiquinonato ligands to give spin states of S = 5/2, 3/2, and 1/2. At high temperatures, 5.2 μ_{eff} is due to weak antiferromagnetic exchange between the S = 3/2 metal center and the two S = 1/2 ligands. In particular, the spin crossover of [Co(3,6-dbq)$_2$-(mdp)] takes place in two steps, centered at 208 and 298 K, with a plateau of 90 deg. Its magnetic moment is 3.2 μ_{eff} at 250 K and 5.2 μ_{eff} at 400 K. Two-step spin crossover has been reported for only a few iron^{II} and iron^{III} complexes,[23,24] and is very rare for cobalt complexes. The two-step spin transition may come from the existence of two slightly nonequivalent sites in the unit cell. The two step spin process rules out the cooperativity of the molecules due to the bulkiness of *tert*-butyl groups.

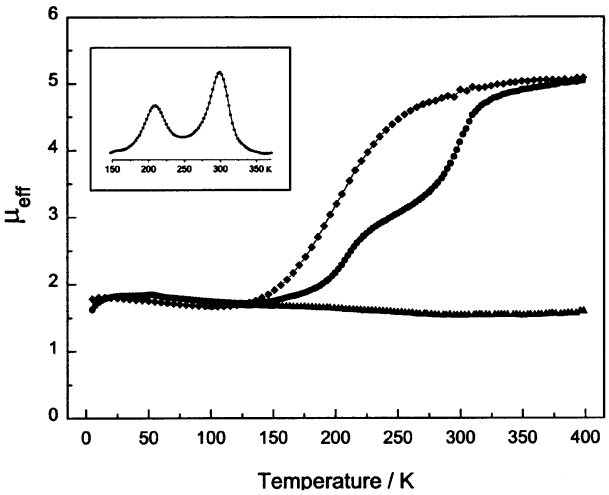
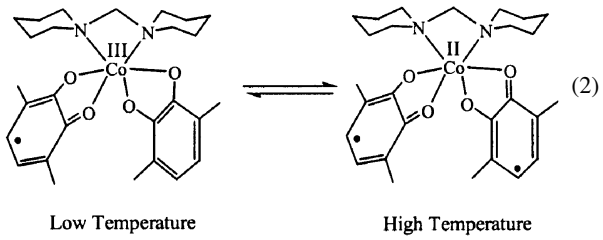


Fig. 2. Changes in the magnetic moment of [Co(3,6-dbq)$_2$(mmap)] (▲, 100–400 K), [Co(3,6-dbq)$_2$(mdp)] (●, 10–400 K) and [Co(3,6-dbq)$_2$(mbmp)] (◆, 10–400 K). Inset: the first derivative of the μ_{eff} vs T for [Co(3,6-dbq)$_2$(mmap)] (150–350 K).



(2)

IR and UV Spectra. IR spectra in the region of 5000–2500 cm^{-1} at room temperature are designated in Fig. 3. The complexes shows the characteristic band around 4000 cm^{-1} along with ν_{C-H} of *tert*-butyl group around 3000 cm^{-1} for comparison of intensity. The broad band around 4000 cm^{-1} indicates the presence of Co^{III} species.[11] The bands of mmap, mdp, and mbmp complexes appear at 4312 cm^{-1}, 4048 cm^{-1}, and 3998 cm^{-1}, respectively. The band intensity increases in the order of mbmp ≈ mdp << mmap, which is roughly consistent with the results of magnetic moments at room temperature. However, no significant difference between mbmp and mdp complexes could be observed since the intensity of mbmp and mdp complexes is much weaker than that of mmap analogue.

Figure 4 shows the electronic spectra in the range of

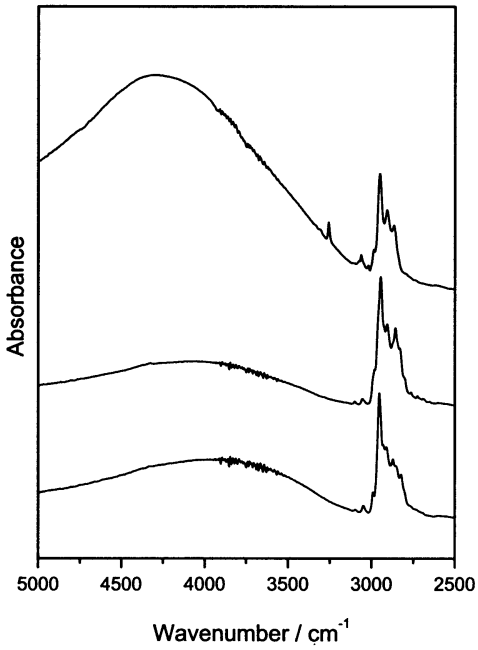


Fig. 3. IR spectra of [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO (top), [Co(3,6-dbq)$_2$(mdp)] (middle) and [Co(3,6-dbq)$_2$(mbmp)] (bottom) in the range from 5000 to 2500 cm^{-1} showing a broad band around 4000 cm^{-1} along with ν_{C-H} of *tert*-butyl group.

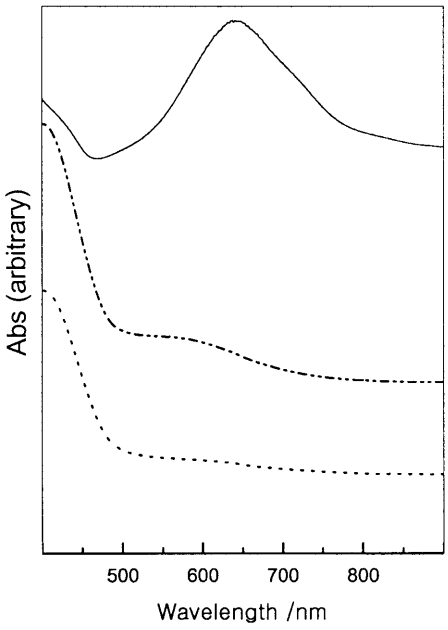


Fig. 4. Electronic spectra of [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO (top), [Co(3,6-dbq)$_2$(mdp)] (middle) and [Co(3,6-dbq)$_2$(mbmp)] (bottom) in toluene solution in the range from 400 to 900 nm.

400–900 nm in toluene. The electronic spectra have been found to be a proof for the equilibrium between Co^{III}/Co^{II} species in solution. For [Co(3,6-dbq)$_2$(mmap)], the strong band at 640 nm indicates that the low spin Co^{III} species is still predominant even in solution.[11] The molar extinction coefficient is about 1.3×10^3 M^{-1} cm^{-1} (1 M = mol dm^{-3}). Catecholate complexes have been reported to typically show ligand to metal charge-transfer bands in this region.[25] For [Co(3,6-dbq)$_2$(mdp)] and [Co(3,6-dbq)$_2$(mbmp)], each corresponding band is very weak, indicating that Co^{II} is predominant in solution at room temperature. Thus, the transition temperature ($T_{1/2}$) varies as mbmp < mdp << mmap in toluene, which is consistent with the results of solid state.

Thermal Analysis. The DSC and TGA curves of [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO are shown in Fig. 5. The typical TGA curve discloses that the skeletal structure dose not degrade up to 200 °C. A mass loss around 70 °C corresponds to the desolvation of the solvate acetone molecule (obsd 4.5%, calcd 4.4%). A strong endothermic peak around 200 °C is due to the degradation of the compound, and the compound was completely decomposed at 515 °C. The weak endothermic peaks at 158 and 172 °C seem to be associated with the transition between Co^{III}/Co^{II} species. Of course, the endothermic peaks via the transition are not accompanied by mass-loss. The spin transition processes including the enthalpy and entropy change could be evaluated from thermal analysis.[16,22]

Coligand Effects for Valence Tautomerism. The potential data storage utility of complexes that exhibit valence tautomerism has been noted.[26] For [Co(3,6-dbq)$_2$(N-N)] system, the tautomerism between Co^{III}(3,6-dbcat)/Co^{II}(3,6-dbsq) species via intramolecular electron transfer has been found to be extremely dependent upon the nature of the nitrogen donating coligands.[11,13] The present works have been carried out to study the effects and differences of/between alicyclic piperidine coligands for the cobalt–quinone system. Electronic and magnetic measurements recorded for [Co(3,6-dbq)$_2$(mmap)] have not provided a value for $T_{1/2}$ between Co^{III}/Co^{II} both in solution and in the solid state due to the high transition temperature. However, the thermal analysis suggests that the mmap complex converts at the temperatures of 158–172 °C. The high transition temperature may be ascribed to the strong donor nature of mmap, with a secondary amine terminal. Actually, [Co(3,6-dbq)$_2$(mmap)] is stable even in solution, in contrast to mdp and

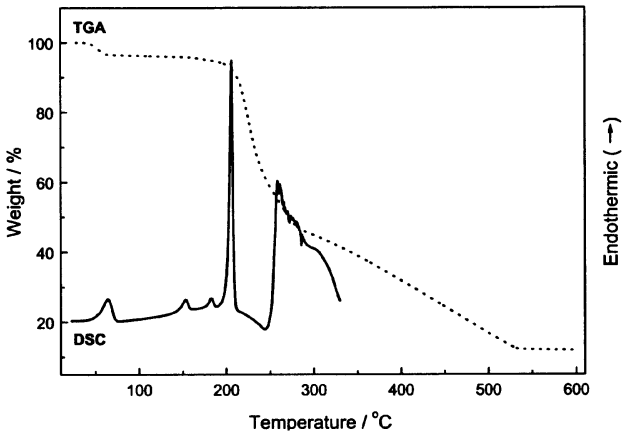


Fig. 5. Overlay of TGA and DSC traces of [Co(3,6-dbq)$_2$(mmap)]·0.5Me$_2$CO, each recorded at heating rate of 10 °C min^{-1}.

mbmp analogues. Even though the chelate ring of mdp and mbmp is essentially similar to tetramethylmethylenediamine,[15] the donor strengths of mdp and mbmp are much weaker than that of tmmda. This is presumably due to the ring constraint and steric hindrance of the two alicyclic coligands. In fact, from an electronic point of view, mbmp may be stronger donor than mdp ligand, but $T_{1/2}$ of [Co(3,6-dbq)$_2$(mdp)] is 56 K higher (from magnetic data) than that of [Co(3,6-dbq)$_2$(mbmp)] with the addition of two methyl groups to the piperazine ring. This emphasizes the steric effects of the coligand on the valence tautomerism. The subtle difference between mdp and mbmp analogues is related to the changes in both the steric and the electronic effects.

[Co(3,6-dbq)$_2$(mmap)] is the first cobalt-benzoquinone complex with asymmetric diimine coligand. In the case of [Co^{III}(3,6-dbsq)(3,6-dbcat)(mmap)] species, two different amine terminals create a new geometric character. That is, the tertiary amine terminal is *trans* to the 3,6-dbsq and the secondary amine is *trans* to the 3,6-dbcat. The 3,6-dbcat/3,6-dbsq seems to be controlled by the nature of the two different amine terminals. The coordination character results from the ligand field environment provided by the different donations of two terminal amine groups. In order to explicit the origin of two-step spin transition and the characteristic properties of the present system, efforts are now directed to obtain single crystals suitable for X-ray crystallography.

In conclusion, the valence tautomeric equilibria between Co^{III}(3,6-dbcat)/Co^{II}(3,6-dbsq) are extremely sensitive to both electronic and steric effects of coligands. Subtle changes in the nature of the N-donor coligand result in significant changes of physicochemical properties. [Co(3,6-dbq)$_2$(mdp)], that exhibits two-step spin conversion with a broad plateau of 90 K, may be used to modulate features of the associated spin conversion process.

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