Formation of a Ligand-based Mixed-valence Cluster Triggered by Dehydration Condensation of Semiquinonates with *o*-Phenylenediamines

Ho-Chol Chang,[†,††] Nao Nishida,[†] and Susumu Kitagawa*[†]
[†] *Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University,*
Katsura, Nishikyo-ku, Kyoto 615-8510
[††] *PRESTO, Japan Science and Technology Agency, 4-1-8, Honcho, Kawaguchi, Saitama 332-0012*

(Received December 16, 2004; CL-041550)

A tetrameric $[Co^{II}(phenSQ)_2]_4$ with homovalent semiquinonates reacts with *o*-phenylenediamines to give a ligand-based mixed-valence pentanuclear cluster $[\{Co^{II}_5(phenSQ)_4(phenCat)_3(THF)_3(H_2O)\}{\cdot}THF]$, containing two differently charged ligands, whose formation is triggered by a dehydration condensation reaction between the semiquinonates and *o*-phenylenediamines.

For over a decade, the mixed-valence clusters of transition metal ions have attracted considerable attention as multi-electron transfer systems, single-molecule magnets and active centres of enzymes in biological systems.[1] Although most of the mixed-valence states occur on the transition metal sites in the reported clusters, the ligands have paramount importance because they dominate not only the structures, but also electronic communication and magnetic interaction between two differently charged metal sites. An alternative mixed-valence state has been known for a family of complexes with electronically labile *o*-quinones.[2] Coexistence of two differently charged ligands among the known three different forms, benzoquinone (BQ), semiquinonate ($SQ^{\bullet -}$), and catecholate (Cat^{2-}) leads to a ligand-based mixed-valence (LBMV) state.[3a–3d] Clusters with a LBMV state seem to be promising candidates for developing, for example, multi-electron transfer systems based on interligand electron transfer,[3e] high-spin clusters, and single-molecule magnets.[1b] It is, however, surprising that quite a few synthetic studies have been carried out on these candidates with the highest nuclearity being limited to tetranuclear in, for example, $Fe^{III}_4(DBSQ)_4$ $(DBCat)_4$ (DB = 3,5-di-*t*-butyl).[3d] Here we focus on a new role of redox-active ligands, and show that the ligands act not only as linkers for connecting the adjacent metal ions, but also as trigger sites for initiating the cluster-to-cluster transformation accompanying the increase of the nuclearity.

18.6 mg (0.105 mmol) of 4,5-dichloro-1,2-phenylenediamine (Cl_2pda) was added to a 15-mL THF suspension containing 50 mg (0.0263 mmol) of $[Co(phenSQ)_2]_4$[4] (phenSQ = 1,10-phenanthrenesemiquinonate) under a dinitrogen atmosphere. The suspension became green after overnight stirring, then, *n*-hexane was layered onto the THF solution after filtration. The green, plate-like single crystals with stoichiometry of $[\{Co_5(phenQ)_7(THF)_3(H_2O)\}{\cdot}THF]$ (**1**) were obtained after several weeks.[5–7] The molecular structure of **1** depicted in Figure 1 is composed of five Co atoms, seven independent dioxolene ligands **a**–**g** as well as three THF and one H_2O coordinating to the Co atoms. The central core forms an incomplete double cuboidal Co_5O_8 skeleton, missing two vertices of an ideal double cubane, where the eight O atoms come from the four dioxolene ligands. Five Co atoms form a distorted tetrahedron, where the Co···Co distances fall in the range of 3.06–3.16 Å. Five independent Co atoms show three kinds of distorted geometric environments, namely, a tetrahedron (Co(1)), an octahedron (Co(2) and Co(4)), and a trigonal bipyramid (Co(3) and Co(5)), while all of the Co–O distances found in **1** are in the range of 1.976(8)–2.177(8) Å, typical values for a *high*-spin Co^{II} ion.[9] These structural parameters require a +10 positive charge for the five Co atoms, and it forces the distributing −10 anionic charges over the seven dioxolene ligands to achieve neutrality.

An alternative view of **1** (Figure 1) shows two sets of intramolecular $\pi\cdots\pi$ interactions between ligands **d**···**e** and ligands **f**···**g** with extremely short interplanar distances of ca. 3.0 Å. The dihedral angle between the ligand planes is ca. 13°, and the shortest interatomic contacts can be found in C(56)···C(70) and C(84)···C(98) at ca. 2.8 Å. The formation of intramolecular $\pi\cdots\pi$ interactions seems significant for stabilizing the structure of **1**.[10] The C–O bond distances of each dioxolene ligand can be useful in assigning the formal oxidation state.[2] The observed bond distances for ligands **a**–**c** are 1.33–1.39 Å, which seems to be longer than 1.26–1.30 Å for ligands **d**–**g**. These structural aspects suggest that ligands **a**–**c** located at the centre of the molecule possess dianionic character, $phenCat^{2-}$, while ligands **d**–**g**,

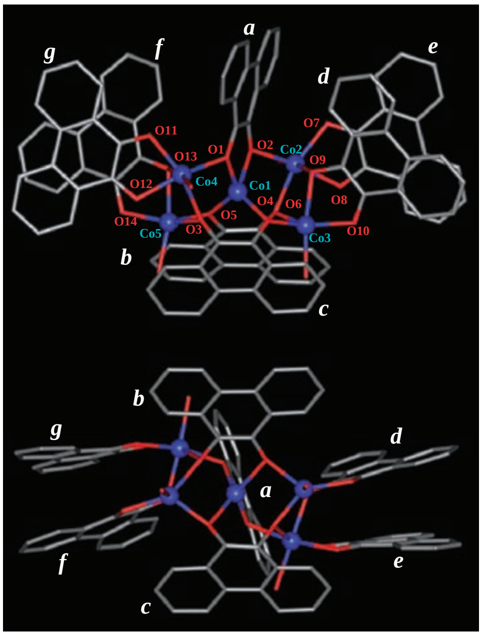

Figure 1. Top and side views of **1**. Non-coordinating THF, C atoms of THFs and H atoms are removed for clarity. The blue, red and grey coloured atoms are Co, O, and C, respectively.

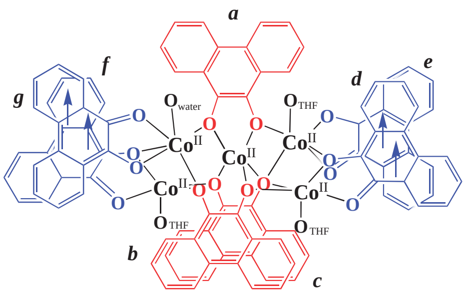

Figure 2. Schematic representation of plausible charge distribution in **1**. Blue and red colours represent phenSQ$^{\bullet-}$ and phenCat^{2-} forms, respectively.

located at both sides of the molecule, could be the phenSQ$^{\bullet-}$ form rather than phenCat^{2-}, giving a formulation of [$Co^{II}_5(phenSQ)_4(phenCat)_3(THF)_3(H_2O)$] with an LBMV state (Figure 2). This charge distribution could be rationalized by the fact that ligands **a**–**c** interact with three or four Co atoms, while ligands **d**–**g** interact only with two independent Co atoms, indicative of the weaker anionic nature of phenSQ$^{\bullet-}$.

The transformation of [$Co^{II}(phenSQ)_2$]$_4$ to **1** leads to (1) the increase of nuclearity and (2) the LBMV state. It should be mentioned that [$Co^{II}(phenSQ)_2$]$_4$ is known to react with pyridines to give a mononuclear complex [$Co^{II}(phenSQ)_2(py)_2$], but does not form a cluster.[4] In order to understand qualitatively the formation of **1**, the reaction was traced by the use of UV–vis absorption spectroscopy after the addition of Cl_2pda to a solution containing [$Co^{II}(phenSQ)_2$]$_4$. As demonstrated in Figure 3, [$Co^{II}(phenSQ)_2$]$_4$ shows absorption maxima at 698, 505, 469, and 399 nm, while new absorption bands were observed at 1164, 786, 598, 404, and 383 nm after the addition of Cl_2pda. Furthermore, insoluble yellowish–green precipitates were obtained from the reaction mixture after several hours. The precipitates were crystallographically and spectroscopically identified as 2,3-dichlorophenanthraphenazine ($\lambda_{max} = 404$ and 383 nm in THF). Therefore, the formation of **1** is associated with a dehydration condensation reaction between Cl_2pdas and phenBQs,[11] where the phenBQs could be generated by reductive elimination of the phenSQ$^{\bullet-}$s from [$Co^{II}(phenSQ)_2$]$_4$. Additional experiments are in progress to study the reaction mechanism in detail.

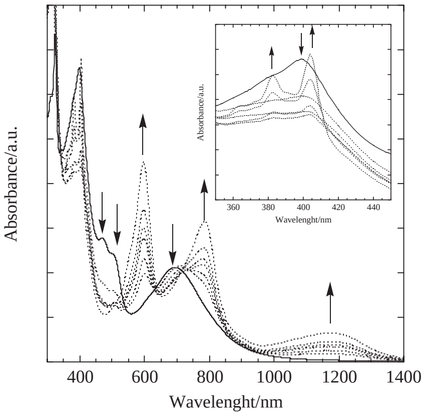

Figure 3. UV–vis–NIR absorption spectrum of [$Co^{II}(phenSQ)_2$]$_4$ (solid line) and those after the addition of Cl_2pda (dashed line) in THF at room temperature (1–192 h). No isosbestic point was observed.

In conclusion, we have found a new approach to fabricate clusters with mixed-valence ligands. The unexpected formation of **1** shows that the complexes with SQs serve as reactive precursors that can be useful for the synthesis of high-nuclearity clusters. The success of this example of cluster-to-cluster transformation triggered by dehydration condensation of the SQs will be applicable to other transition metal complexes, and augurs well for the future use in generation of a variety of novel mixed-valent and high-spin clusters.

This work was supported by a Grant-in-Aid for Young Scientists (No. 14740362) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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5 The single crystal easily loses the crystallinity and the THFs to give a polycrystalline sample with nine H_2O molecules ([$Co_5(phenQ)_7 \cdot 9H_2O$]). Anal. Calcd. For $C_{98}H_{74}Co_5O_{23}$; C, 61.49; H, 3.90%. Found: C, 61.75; H, 3.88%. Yield 25 mg.

6 PhenQ is used for the ligands without assignments of oxidation states.

7 Crystal Data for **1**: $C_{114}H_{88}Co_5O_{19}$, fw = 2056.60, orthorombic, *Pbca*, $a = 23.109(1)$ Å, $b = 26.160(1)$ Å, $c = 36.850(1)$ Å, $V = 22276(1)$ Å^3, $T = 223$ K, $Z = 8$, 9632 unique, $R = 0.104$, $R_w = 0.265$ ($I > 2\sigma(I)$). Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-249603. Copies of the data can be obtained free of charge via 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 336033; or deposit@ccdc.cam.ac.uk).

8 In addition, O(4) and O(5) atoms weakly interact with the Co(1) atom, with the bond distances being 2.30 and 2.24 Å, respectively.

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Published on the web (Advance View) February 12, 2005; DOI 10.1246/cl.2005.402