Alkoxo-bridged Cobalt(II) Cube and Its Radical Adduct

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Tetranuclear cubic complexes of $[Co_4(heip)_4(MeOH)_4]$ (**1**) and $[Co_4(heip)_4(nit\text{-}p\text{-}py)_4]$ (**2**) (H_2heip = 1,1,1,5,5,5-hexafluoro-4-[(2-hydroxyethyl)imino]-2-pentanone and nit-*p*-py = 2-(*p*-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) were prepared. Complexes **1** and **2** have alkoxo-bridged cubic core structures. Magnetic susceptibility measurements revealed the occurrence of ferromagnetic interactions among Co^{II} ions in **1**, while antiferromagnetic interactions were operative in **2**.

Multinuclear metal complexes with high-spin ground states have attracted intense research interests from the viewpoints of superparamagnetism.[1–4] Such molecules act as single domain magnets showing magnetic hysteresis and slow magnetization relaxation, and they are called single molecule magnets (SMMs). SMMs require relatively high-spin ground states with uniaxial magnetic anisotropy. Alkoxo-bridged tetranuclear complexes with a cubic structure (M_4O_4) are an important class of compounds, because cubes tend to have high-spin ground states due to intramolecular ferromagnetic interactions.[5] We have reported alkoxo-bridged high-spin cubes with Fe^{2+}, Ni^{2+}, and Cu^{2+} ions, among which ferrous cubes were turned out to be SMMs with a spin ground state of $S = 8$.[5d,5e] On the other hand, nitronylnitroxide have been often used to build molecule-based magnets,[6] and the combination of cubes with nitronylnitroxide can give an opportunity to build new high-spin molecules. We report here syntheses, structures, and magnetic properties of a Co^{II} cube and its radical adduct.

The reaction of $CoCl_2$ with H_2heip[7] yielded a cobalt cube of $[Co_4(heip)_4(MeOH)_4]$ (**1**), and $[Co_4(heip)_4(nit\text{-}p\text{-}py)_4]$ (**2**) was prepared by the reaction of **1** with nitronylnitroxide.[8,9] Dark red and dark blue crystals of **1** and **2** crystallized in tetragonal space groups of $P\bar{4}2_1c$ and $I4_1/a$,[10,11] respectively, and ORTEP diagrams are shown in Figure 1. Complexes **1** and **2** have alkoxo-bridged tetranuclear cores composed of alternating aligned four cobalt ions and four oxygen atoms. Complex molecules have crystallographic S_4 axis passing through the middle of $Co1\cdots Co1^{\#1}$ and $Co1^{\#2}\cdots Co1^{\#3}$ vectors (Figure 1), hence, the asymmetric unit contains a quarter of the complex molecule. Coordination geometries of cobalt ions in **1** and **2** are both axially elongated octahedrons, where the Jahn–Teller axes lie on the $O3–Co1–O2^{\#1}$ and $N2–Co1–O2^{\#1}$ vectors, respectively. The six coordination sites of Co^{II} ions in **1** are occupied by five oxygen and one nitrogen atoms from $heip^{2-}$ and methanol, while in **2** each cobalt ion has a coordinated nitrogen atom of nit-*p*-py molecule instead of methanol. In **1** and **2**, the average coordination bond lengths involving the axial atoms (O3, $O2^{\#1}$ for **1** and N2, $O2^{\#1}$ for **2**) are 2.1973(16) and 2.235(3) Å, and the equatorial coordination bond lengths with O1, N1, O2, and $O2^{\#3}$ atoms are in the range of 2.008(2)–2.056(2) and 2.001(3)–2.070(3) Å, respectively. The Co^{II} ions are bridged by the alkoxo oxygen atoms with bond angles of 93.24(6)–100.54(6)° for **1** and 94.8(1)–101.9(1)° for **2**. Note that dihedral angles between equatorial coordination planes of Co1 and $Co1^{\#1}$ ions, defined as O1–N1–O2 and $O1^{\#1}–N1^{\#1}–O2^{\#1}$, are 44.28(6) and 50.75(10)° for **1** and **2**, respectively. Note that positional disorders on radical moiety (O3–N3–C13–N4–O4 and O5–N5–C13–N6–O6) were observed.

Magnetic susceptibility measurements for **1** and **2** were performed in the temperature range of 1.8–300 K, and $\chi_m T$

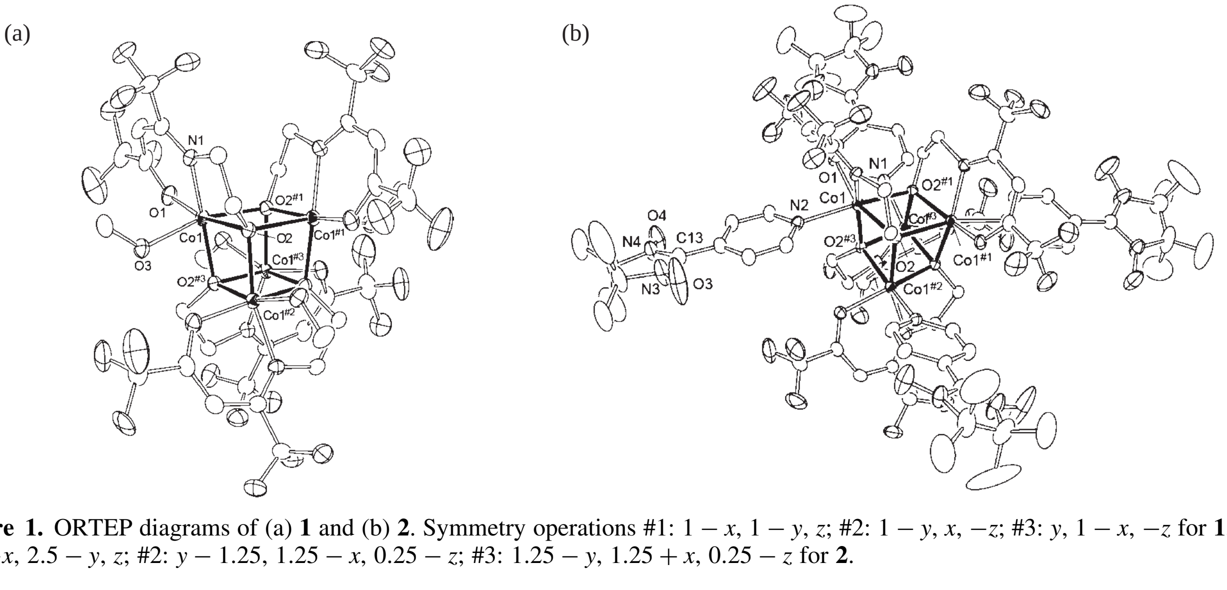

Figure 1. ORTEP diagrams of (a) **1** and (b) **2**. Symmetry operations #1: $1 - x$, $1 - y$, z; #2: $1 - y$, x, $-z$; #3: y, $1 - x$, $-z$ for **1**, and #1: $-x$, $2.5 - y$, z; #2: $y - 1.25$, $1.25 - x$, $0.25 - z$; #3: $1.25 - y$, $1.25 + x$, $0.25 - z$ for **2**.

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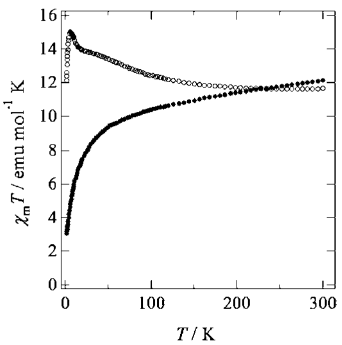

Figure 2. $\chi_m T$ versus T plots of **1** (○) and **2** (●).

versus T plots are shown in Figure 2. Complex **1** has a $\chi_m T$ value of 11.67 emu mol^{-1} K at 300 K, which corresponds to magnetically uncorrelated cobalt ions ($S = 3/2$ and $g_{Co} = 2.50$). In **2**, each Co^{II} ion has a coordinated pyridyl group of nitronylnitroxide, magnetic interactions between Co^{II} ion and radical are, therefore, considered to be weak and these two paramagnetic moiety act as noncorrelated spins at 300 K.[12] The $\chi_m T$ value for **2** is 12.15 emu mol^{-1} K at 300 K. Subtracting the contribution of four radicals from the $\chi_m T$ value at 300 K, the Co^{II} cube in **2** has a $\chi_m T$ value of 10.65 emu mol^{-1} K ($= 12.15 - 4 \times 0.375$), which corresponds to a g_{Co} value of 2.38. Temperature dependences of $\chi_m T$ values for **1** and **2** are quite different. The $\chi_m T$ values for **1** increased as the temperature was lowered, reaching the maximum value of 15.02 emu mol^{-1} K at 6.0 K. This magnetic behavior is indicative of the occurrence of ferromagnetic interactions among the Co^{II} ions. On the other hand, the gradual decrease of $\chi_m T$ values for **2** was observed as lowering temperature, suggesting antiferromagnetic interactions being operative among the Co^{II} ions. Although distinct differences in coordination geometries about Co^{II} ions and bridging modes were not observed in **1** and **2**, slight differences should be responsible for different orbital contributions on Co^{II} ions and different intra-core magnetic interactions. Note that neither **1** nor **2** showed out-of-phase signals in AC magnetic susceptibility measurements.

In conclusion, we prepared two Co^{II} cubes with and without nitronylnitroxides and they showed quite different magnetic behaviors. Slightly different core structures, including bridging bond angles (Co–O–Co) and tilted magnetic orbitals on the Co^{II} ions, must be responsible for the intra-core magnetic interactions, and the orbital contributions to the magnetic moments cannot be ignored.

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9 Synthesis of **1**: To a stirred solution of NaH (53.8 mg, 2.2 mmol) in THF (20 mL) at 0 °C was added a THF (20 mL) solution of H$_2$heip (501 mg, 2.0 mmol) slowly, turning the solution from white to yellow. After stirring for 10 min at 0 °C and further stirring at room temperature for 30 min, the solution was added to a THF (20 mL) solution of CoCl$_2$ (130 mg, 1.0 mmol), and the resulting red solution was stirred at room temperature for 4 h. After the solvent was evaporated, the residue was extracted into diethyl ether, which was washed with distilled water and dried (MgSO$_4$). The red solution was concentrated to 10 mL, slow evaporation under dry nitrogen atmosphere gave red crystal of **1** (119 mg) in 35% yield. Anal. Calcd (Found) for **1** ($C_{32}H_{36}N_4Co_4F_{24}O_{12}$): C, 28.25 (28.26); H, 2.67 (2.64); N, 4.12 (4.07). Synthesis of **2**•4CH$_3$CN•2CH$_3$OH: To solution of **1** (20 mg, 0.015 mmol) in acetonitrile (1 mL) was added nit-*p*-py (13 mg, 0.060 mmol). The mixture was concentrated to 0.3 mL and then cooled to room temperature. Dark blue crystal of **2** was obtained. Yield 16 mg (50%). Anal. Calcd (Found) for **2** ($C_{76}H_{84}N_{16}Co_4F_{24}O_{16}$): C, 42.08 (42.04); H, 3.90 (3.97); N, 10.33 (10.16).

10 Crystallographic data for **1**: red blocks ($0.3 \times 0.3 \times 0.3$ mm^3) $C_{32}H_{36}N_4Co_4F_{24}O_{12}$, $M_r = 1360.352$, tetragonal, space group $P\bar{4}2_1c$, $a = 14.197(3)$, $c = 12.052(3)$ Å, $V = 2429.2(9)$ Å^3, $Z = 2$, $T = 200$ K. A total of 11464 were collected ($6° < 2\theta < 46°$) of which 1745 unique reflections ($R_{int} = 0.0191$) were measured. $R_1 = 0.0189$, $wR_2 = 0.0518$ ($I > 2\sigma(I)$). **2**•4CH$_3$CN•2CH$_3$OH: dark bule plate ($0.4 \times 0.3 \times 0.2$ mm^3) $C_{88}H_{84}N_{20}Co_4F_{24}O_{18}$, $M_r = 2401.47$, tetragonal, space group $I4_1/a$, $a = 18.723(2)$, $c = 30.706(5)$ Å, $V = 10764(2)$ Å^3, $Z = 4$, $T = 200$ K. A total of 21857 were collected ($4° < 2\theta < 47°$) of which 3874 unique reflections ($R_{int} = 0.0349$) were measured. $R_1 = 0.0481$, $wR_2 = 0.1361$ ($I > 2\sigma(I)$).

11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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