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Dielectric anomalies on mixed-valence vanadium complex $K_3[V_2O_3(nta)_2]\cdot 3H_2O$ and mixed-valence cobalt complex $[Co\{(\mu\text{-}L)(\mu\text{-}OAc)Co(NCS)\}_2]$

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Recently, we succeeded in the development of a single-molecule electret, which exhibits dielectric hysteresis on one molecule, based on a Preyssler-type polyoxometalate (POM). This POM molecule has a cavity with two stable ion sites, and contains one metal ion inside. Using this molecule, we could control the direction of the molecular polarization by applying an electric field, and observed the dielectric hysteresis without long-range order of the polarization. In this study, we aimed to develop the single-molecule electret with a new mechanism, which shows the behavior of single-molecule electret by electron transfer in the molecule. Especially, we focused on electron transfer of mixed-valence complex.

As such mixed-valence complexes, we found $K_3[V_2O_3(nta)_2]\cdot 3H_2O$ (Figure 1) and $[Co\{(\mu\text{-}L)(\mu\text{-}OAc)Co(NCS)\}_2]$ (Figure 2), and these complexes were prepared according to the previously reported literature. [1][2] The oxidation states were determined by a single crystal X-ray diffraction analysis (SCXRD) and magnetic susceptibility measurements. On the crystal structure of $K_3[V_2O_3(nta)_2]\cdot 3H_2O$, two V-O bonds in this cluster were crystallographically equivalent and its length was estimated to be 1.802 Å. The χT value of this compound corresponds with the magnetic moment of S = 1/2 spin. These results indicate that this compound contains V^{IV} and V^{V} and the oxidation states of the both V atoms are +4.5. On the other hand, crystallographically independent two Co-O bonds in $[Co\{(\mu\text{-}L)(\mu\text{-}OAc)Co(NCS)\}_2]$ are determined, and their lengths were to be 1.894 and 2.132 Å. The χT value of this compound corresponds with the calculated value of one S = 3/2 spin. These results allow that the compound contains one Co^{II} and two Co^{III}. From the results of permittivity measurements, the dielectric anomalies were observed.

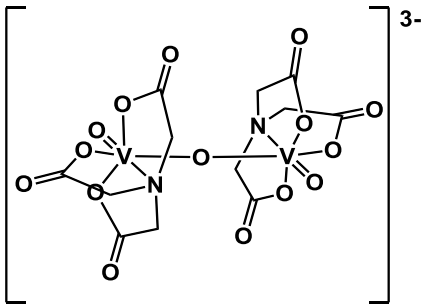

Figure 2 Structural formula of $[V_2O_3(nta)_2]^{3-}$

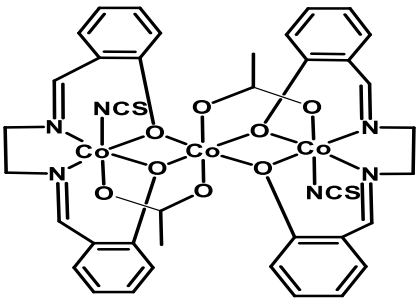

Figure 2 Structural formula of **$[Co\{(\mu\text{-}L)(\mu\text{-}OAc)Co(NCS)\}_2]$**

[1] J. M. Shi *et al.*, *Polish J. Chem.*, **75**, *1695*(2001)
[2] S. Chattopadhyay *et al.*, *Inorg. Chem. Comm.*, **9**, 1053(2006)