1830 © 1990 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 63, 1830—1831 (1990) [Vol. 63, No. 6

Synthesis and Magnetic Property of Binuclear Oxovanadium(IV) Complex of 2,6-Diformyl-4-methylphenol Bis(benzoylhydrazone)

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(Received January 12, 1990)

Synopsis. Binuclear oxovanadium(IV) complex, $[(VO)_2L(OCH_3)]$, has been synthesized, where H_3L denotes 2,6-diformyl-4-methylphenol bis(benzoylhydrazone). Two metal ions are bridged by the phenolic oxygen of L^{3-} and a methoxide oxygen. Cryomagnetic measurements (80—300 K) indicated the operation of an antiferromagnetic spin-exchange interaction ($J=-191.3$ cm^{-1}) between the oxovanadium(IV) ions.

In our series of papers[1–8] we have shown that 2,6-diformyl-4-methylphenol and its Schiff bases can incorporate two metal ions by the use of the phenolic oxygen as the endogenous bridge. In those studies our main interest was forcussed on the spin-exchange in binuclear copper(II) complexes with respect to the nature of the exogenous bridge and the geometrical feature of the complexes. Studies on the spin-exchange of dinuclear oxovanadium(IV) complexes in comparison with those of dinuclear copper(II) complexes are of interest for gaining further insight into the spin-exchange mechanism, since copper(II) (d^9) and oxovanadium(IV) (d^1) ions have one unpaired electron, but differ regarding their electronic configurations; in the former case with square planar and square pyramidal geometries the unpaired electron, generally, resides in the $d_{x^2-y^2}$ orbital and the spin coupling is effected by a superexchange mechanism; in the latter, however, the unpaired electron resides in the d_{xy} orbital (x- and y-axes being taken on the donor atoms in equatorial plane, hence the spin coupling is caused by direct overlapping of magnetic orbitals). Studies along this line, however, are still very limited.[7]

We recently reported the synthesis, structure, and magnetic properties of copper(II) complexes of 2,6-diformyl-4-methylphenol bis(benzoylhydrazone) (abbreviated as H_3L, see Fig. 1).[9] As an extension of this study, we report here on the synthesis and magnetic properties of an oxovanadium(IV) complex of H_3L.

Experimental

Syntheses. 2,6-Diformyl-4-methylphenol was synthesized by a method found in the literature.[4] Dinucleating ligand, H_3L, was obtained by condensation of 2,6-diformyl-4-methylphenol and benzoylhydrazine in ethanol according to a method reported previously.[9]

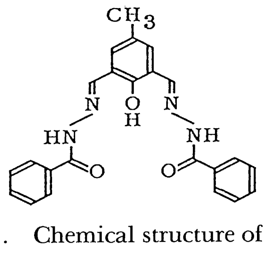

Fig. 1. Chemical structure of H_3L.

$[(VO)_2L(OCH_3)]$. An aqueous solution (10 cm^3) of oxovanadium(IV) sulfate hydrate (2.2 mmol) was added to a hot methanolic solution (50 cm^3) of H_3L (1 mmol). The solution was warmed under stirring for 30 min to afford a greenish microcrystalline product. It was collected on a glass filter, washed with hot water and then with a small amount of hot methanol, and dried in the open air. The yield was 55%. Found: C, 51.29; H, 3.59; N, 10.03%. Calcd for $V_2C_{24}H_{20}O_6N_4$: C, 51.26; N, 3.58; N, 9.96%.

Measurements. Elemental analyses were carried out at the Advanced Instrumentation Center for Chemical Analysis, Ehime University. Infrared spectra were recorded on a JASCO IR-810 Spectrophotometer. Reflectance spectra were measured on a Shimadzu MPS-5000 Spectrophotometer. The magnetic susceptibilities were determined by the Faraday method in the range from liquid-nitrogen temperature to room temperature. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$. Pascal's constants were used for a diamagnetic correction. The effective magnetic moments were calculated from the equation $\mu_{eff}=2.828\sqrt{\chi_A \cdot T}$, where χ_A is the magnetic susceptibility per metal ion.

Results and Discussion

A free ligand shows two sharp IR bands at 3400 and 3175 cm^{-1} attributable to the ν(OH) of the phenolic hydroxyl group and the ν(NH) of the hydrazone moiety, respectively; these bands disappear in $[(VO)_2L(OCH_3)]$. It is presumed that the ligand in the trinegative form (L^{3-}) acts as a hexadentate ligand to incorporate two oxovanadium(IV) ions in a similar way as demonstrated for $[Cu_2L(OCH_3)]$ by a single-crystal X-ray analysis,[9] and that the methoxide ion probably functions as an exogenous bridging group. The V=O stretching vibration is located near 1000 cm^{-1}, indicating no intermolecular V=O...V=O... bonding in this complex. Some oxovanadium(IV) complexes are known to have a polymeric structure by such intermolecular bonding; those complexes show the V=O stretching mode at a lower wavenumber (850—902 cm^{-1}).[7,10–13] The reflectance spectrum of the complex shows d-d components around 600 and 470 nm as discernible shoulders of an intense band at 420 nm that may be assigned to a charge-transfer transition.[12,14,15]

All our efforts to obtain a single crystal suitable for X-ray analysis have so far been in vain.

The temperature-dependences of the magnetic susceptibility and effective magnetic moment (per one metal ion) are given in Fig. 2. The magnetic moment at room temperature is subnormal (1.18μ_A)

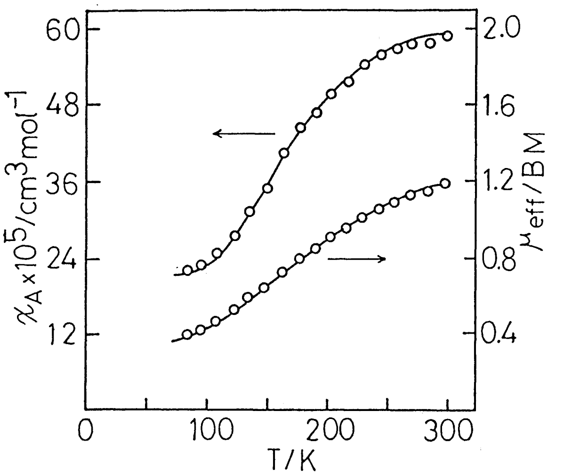

Fig. 2. Temperature dependences of magnetic susceptibilities and effective magnetic moments.

and decreases with lowering the temperature to $0.39\mu_B$ at 84.6 K. This must be due to an antiferromagnetic spin exchange within a complex molecule. An analysis of the magnetic susceptibility has been made on the basis of the Bleaney-Bowers equations[16] including a correction term for paramagnetic impurity,

$$\chi_A = \frac{Ng^2\beta^2}{3kT}[1+\frac{1}{3}\exp(-2J/kT)]^{-1}(1-p)+\frac{0.45p}{T}+N\alpha.$$

Here, p is the mole fraction of the paramagnetic contaminant and the other symbols have their usual meanings. The best-fit is attained with magnetic parameters of $g=1.95$, $J=-191.3$ cm^{-1}, $N\alpha=60\times10^{-6}$ cm^3 mol^{-1}, and $p=0.03$. The result is shown by the trace in Fig. 2. The exchange integral ($J=-191.3$ cm^{-1}) is significantly smaller (in absolute value) than that (-301 cm^{-1}) of [$Cu_2L(OCH_3)$].[9] This result is in line with that found for the complexes of a similar ligand, 2,6-bis[(2-hydroxyphenylimino)methyl]-4-methylphenol, and its homologs.[7]

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