Syntheses and Properties of β-Diketone Vanadium(II) Complexes

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In this communication, some novel syntheses and some physical properties of bis(acetylacetonato)dipyridinevanadium(II): $V(acac)_2py_2$,[1] bis(trifluoroacetylacetonato)dipyridinevanadium(II): $V(tfaa)_2py_2$, and bis(dibenzoylmethanato)dipyridinevanadium(II): $V(dbme)_2py_2$ are reported. All the procedures for syntheses and for physical measurements were performed in a nitrogen atmosphere, and all the solvents used were carefully saturated with pure nitrogen. $V(acac)_2py_2$ was synthesized by the following procedure. To an aqueous solution containing 2.55 g of $VSO_4 \cdot 7H_2O$ and a small amount of sulfuric acid, 2.0 m*l* of acetylacetone was added. After stirring this mixture, 5.0 m*l* of pyridine was added to it. The solution turned blue, and then a dark blue crystalline material was precipitated. The crude product was dissolved in ethanol containing a small amount of pyridine and recrystallized by adding water to this solution. The dark blue prismatic crystalline material thus obtained is soluble in usual organic solvents such as chloroform, benzene, pyridine, and alcohol, and gives a blue solution, while it is insoluble in water. In the air this compound is readily oxidized, absorbs moisture, and becomes viscous.

Found: V, 12.1; C, 58.5; H, 5.99; N, 6.11%. Calcd: V, 12.5; C, 59.0; H, 5.90; N, 6.88%.

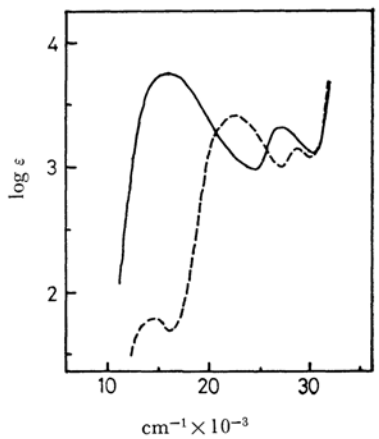

Fig. 1. Electronic absorption spectra in pyridine solution. ——$V(acac)_2py_2$, ···$Fe(acac)_2py_2$

$V(tfaa)_2py_2$ and $V(dbme)_2py_2$ were synthesized by means of procedures analogous to that described above.

Magnetic susceptibility measurements gave 3.4 B. M. for both $V(acac)_2py_2$ and $V(tfaa)_2py_2$.

The visible and near-ultraviolet absorption spectra were measured in a pyridine solution. As is shown by Fig. 1, the V(II)-complex gives an absorption curve similar to that of the corresponding Fe(II)-complex. The fact that in Fig. 2, three points make a straight line suggests similar origins for the corresponding bands in both V(II)- and Fe(II)-complexes.[2]

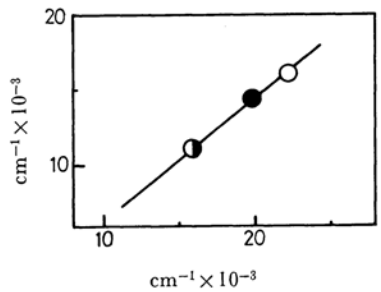

Fig. 2. Comparison of the bands at the lowest wave number.

The vertical axis indicates the band positions of V(II)-complexes and the horizontal axis indicates those of Fe(II)-complexes.

○ acac-complex, ● tfaa-complex, ◑ dbme-complex

In the case of trifluoroacetylacetone, the inductive effect due to the CF_3 group is expected to increase the electron affinity of the π-conjugated system, while in the case of dibenzoylmethane the conjugated effect due to the phenyl group operates as well. On the other hand, the ionization potential of the central metal ion decreases on going from iron(II) to vanadium(II). These considerations and the experimental facts lead to the conclusion that the band at the lowest wave number of $V(acac)_2py_2$ shifts towards an even lower wave number as the ionization potential of the central metal ion decreases and as the electron affinity of the ligand increases, and therefore can be assigned to electron transitions from dπ orbitals of the central metal ion to the lowest vacant π molecular orbitals of ligand acetylacetones.

1) The stabilities of V(II)-acetylacetonato-complexes in aqeuous solution have already been studied: W. P. Schaefer, *Inorg. Chem.*, **4**, 642 (1965).

2) R. J. P. Williams, *J. Chem. Soc.*, **1955**, 137.