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SYNTHESIS, MOLECULAR STRUCTURE AND MAGNETIC PROPERTIES OF π-CYCLOPENTADIENYLVANADIUM BIS(TRIFLUOROACETATE) DIMER

G. M. LARIN, V. T. KALINNIKOV, G. G. ALEKSANDROV, Yu. T. STRUCHKOV, A. A. PASNSKII AND N. E. KOLOBOVA

Lenin's Order Institute of Organo Element-Compounds, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.) and Lenin's Order Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

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SUMMARY

The complex π-cyclopentadienylvanadium bis(trifluoroacetate) has a dimeric structure with four bridged trifluoroacetate groups without the metal–metal bond bond (V...V 3.7 Å). The probable explanation for the absence of latter may be the steric interaction between oxygen atoms of the bridged groups and carbon atoms of the cyclopentadienyl ligands. The complex and its acetate analogue have abnormally low magnetic moments which decrease with decreasing temperature. Possible explanation for such a phenomenon may be interaction of vanadium atoms via the π-system of carboxylate bridges.

INTRODUCTION

The following criteria are usually employed to conclude the presence of a metal–metal bond in the transition metal complexes:

(1). The metal atom separation in a molecule is almost equal to the sum of the metal covalent atomic radii.

(2). Magnetic moment of the molecule is less than the expected value for the given oxidation state since the metal–metal bond formation requires electron spin coupling.

(3). Binuclear fragments appear in the mass spectra.

However, interpretation of results is rather complicated when the groups capable of forming bridges are joined to the metal atoms. Thus it seems at a first glance, that different methods may provide inconsistent information. For example, π-cyclopentadienylvanadium diacetate, $C_5H_5V(OCOCH_3)_2$, reported by King[1] had only the mononuclear fragments (including $C_5H_5V^+$) in the mass spectrum while magnetic moment of the solid complex (1.49 B.M. per vanadium atom) is much less than the spin value for the V^{III} compound (2.83 B.M.). It has been assumed that in crystalline complex the vanadium atoms of the dimer are bonded by four acetate bridges and by a direct partially multiple bond which cleaves on sublimation of the complex. Dissociation of this bond is least probable because the vanadium binuclear complex $(C_5H_5)_2V_2(CO)_5$ showed only the $(C_5H_5)_2V_2^+$ fragment in its mass spectrum[2] and no $C_5H_5V^+$ fragment.

RESULTS AND DISCUSSION

It was of interest to elucidate the nature of vanadium–vanadium bond in such complexes and to explain their unusually low magnetic moments. Unfortunately the difficulty in obtaining good crystals prevents the structural investigation of complex (I). Thus in the present work we investigated the X-ray and magnetochemical studies of its analogue, π-cyclopentadienylvanadium bis(trifluoroacetate) $C_5H_5V(OCOCF_3)_2$ (II) being more stable in air and better soluble than (I).

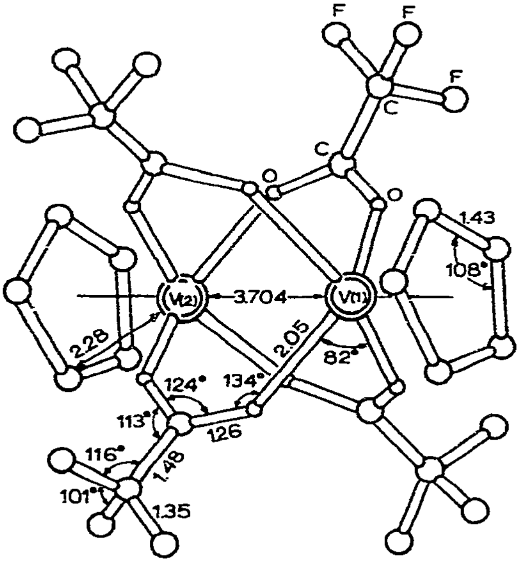

Fig. 1. Molecular structure of $[C_5H_5V(OCOCF_3)_2]_2$.

(*a*). *X-ray study**

The crystalline structure has been shown to consist of the discrete dimeric molecules (Fig. 1), the dimerization being due to the four bridged trifluoroacetate groups. But probably there is no direct vanadium–vanadium interaction, since the innermolecular V...V separation (3.70 Å) exceeds the double covalent radius of vanadium (3.06 Å)[3]. In this respect the structure of the complex principally differs from those of the earlier described carboxylates of chromium, $Cr_2(CH_3COO)_4 \cdot 2\,H_2O$ (III)[4], molybdenum, $Mo_2(CH_3COO)_4$ (IV)[5], rhenium, $Re_2(C_6H_5COO)_4Cl_2 \cdot 2\,CH_3Cl$ (V)[6], ruthenium, $Ru_2(C_3H_7COO)_4Cl$ (VI)[7], rhodium, $Rh_2(CH_3COO)_4 \cdot 2\,H_2O$ (VII)[8], and copper, $Cu_2(CH_3COO)_4 \cdot 2\,H_2O$ (VIII)[9]. The molecules (III)–(VIII) have the metal–metal bond which is usually of higher multiplicity.

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* For technique see Experimental.

In discussing the possible reasons for absence of the V–V bonds in the complex (II) one should take into account that probably the character of interaction of the vanadium atoms with each separate ligand does not hinder the metal–metal bond formation. Actually geometry of the fragment $CpVO_4$, distance V–C 2.28 Å, and the C–C bond length in the planar cyclopentadienyl ligand (1.43 Å) are identical to those of $CpV(CO)_4$[10]. Thus V–C_5H_5 bond in the complex (II) resembles that in the usual π-cyclopentadienylvanadium complexes including probably $Cp_2V_2(CO)_5$[2] containing the vanadium–vanadium bond.

Apparently an interaction of vanadium with acetate groups is also similar to the metal–carboxylate bonding in the above mentioned dimers containing the metal–metal bond. Thus like in other complexes the dihedral angles between planes of bridges V–OCO–V are close to 90° and a mean V–O bond length of 2.05 Å agrees with the metal–oxygen bond lengths in complexes (III) (1.97 Å), (IV) (2.09 Å), (V) (2.02 Å), (VI) (2.00 Å)[3,11]. The mean length of the C–O bond in (II) (1.26 Å) is also close to that in the complexes (IV)–(VI). The geometry of bridged carboxylate is always equivalently rigid and the OCO valence angles approach an ideal value of 120° [124° for (II)].

On the other hand, significant difference is observed between the V–O–C (mean 134°) and M–O–C (120°) angles. Moreover the V...V–O (mean 68°) angles are considerably smaller with respect to M–M–O (90°). Such differences may be explained by a steric hindrance resulting from the repulsion of bridged acetate oxygen atoms and the cyclopentadienyl carbon atoms. Actually even at such a molecular geometry the O...C distances are 2.76–3.12 Å *i.e.* essentially shorter with respect to the sum of Van der Waals radii (3.2 Å). This excludes formation of the vanadium–vanadium bond in complex (II), since at the vanadium–vanadium separation close to the double covalent vanadium radius (3.06 Å) the O...C distance should decrease to 2.5–2.7 Å.

(*b*). *Magnetic properties*

Investigation of magnetic susceptibility of the complexes (I) and (II) by the Faraday method showed that their magnetic properties are rather identical, *i.e.* the effect of the nature of substituent at the bridged carboxylate grouping is relatively small.

Most significant is the fact that at room temperature the magnetic moments of both the compounds (μ_{eff} = 1.71 B.M./V atom for (I)* and 1.55 B.M./V atom for (II) (Table 1) are much below the spin value for electron configuration d^2 (2.83 B.M./V atom).

In principle such a low magnetic moment may be due to the following reasons:
(1). Direct interaction of the vanadium atomic orbitals in dimer molecule (direct exchange).
(2). Effect of spin–orbital interaction on the ground state.
(3). Thermal equilibrium between the populations of ground level and the first excited level with other multiplicity (singlet–triplet equilibrium).

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* The μ_{eff} of (I) somewhat differs from that of King[1] (1.49 B.M.) which is probably due to the certain differences in the conditions of sample preparation. In any case the absence of ferromagnetic impurities in (I) and (II) has been confirmed by susceptibility independence of the magnetic field intensity.

(4). Interaction between the neighbouring vanadium atoms through the π-system of carboxylate bridges (superexchange).

Apparently the found V...V distance, 3.70 Å, makes it possible to ignore the contribution from direct exchange. For investigating the other three factors the magnetic susceptibility against the temperature was investigated at 356–83°K and 299–80°K for the complexes (I) and (II) respectively (Table 1). It was shown that the susceptibility does not obey the Curie law. It does not increase with decreasing temperature, but sharply falls and the magnetic moments gradually decrease to 0.5 B.M. on cooling the samples to 80°K.

TABLE 1

MAGNETIC SUSCEPTIBILITY OF V^{III} COMPOUNDS[a]

$[C_5H_5V(COOCH_3)_2]_2$ (I)				$[C_5H_5V(COOCF_3)_2]_2$ (II)			
Temp. (°K)	$\chi_r \cdot 10^6$	$\chi'_m \cdot 10^6$	μ_{eff} (B.M.)	Temp. (°K)	$\chi_r \cdot 10^6$	$\chi'_m \cdot 10^6$	μ_{eff} (B.M.)
356	3.38	1286	1.92	299	3.84	1009	1.55
294	3.24	1242	1.71	270	3.63	960	1.45
262	3.06	1175	1.56	266	3.59	949	1.36
221	2.75	1071	1.38	240	3.31	886	1.31
194	2.44	968	1.23	176	2.36	665	0.97
160	1.98	812	1.02	153	2.02	586	0.86
125	1.44	625	0.79	109	1.19	392	0.59
83	0.98	469	0.56	80	0.84	303	0.44

[a] Calculation of diamagnetic correction for determination of χ'_m (ref. 19); μ_{eff} was calculated using the formula $\mu=2.84\,(\chi'_m \cdot T)^{\frac{1}{2}}$ B.M.

According to the theory[12] only in case of compounds with almost octahedral symmetry the second factor, *e.g.* effect of a spin–orbital interaction on the ground state may cause "diamagnetizing" at lower temperature. Since the symmetries of the compounds studied are below octahedral (each vanadium atom has its local symmetry C_{4v}) contribution of the spin–orbital effects is probably small.

Apparently an observed abnormal magnetism can not be explained by the effect of the third factor, singlet–triplet equilibrium, because usually such cases have the following specificities:

(1). The magnetic properties depend essentially upon any changes in the ligand compositions[13–15].

(2). The change of μ_{eff} with temperature is not the same for different compounds[15].

(3). The colour of complexes is sufficiently temperature dependent[15].

(4). The compounds are monomers[15].

(5). The μ_{eff} is pressure dependent[15].

In the given case the complexes do not satisfy the conditions 1–4 (the μ_{eff} against the pressure was not studied). Besides there is yet no information on the singlet–triplet equilibrium $(b_2)^2(e) \rightleftarrows (b_2)'(e)'$ for compounds of V^{III} (for example, for the complexes Cp_2VR, the μ_{eff} increases with temperature[16]). Thus an abnormal magnetism of complexes (I) and (II) can be explained only by a superexchange interaction between the vanadium atoms through the π-system of carboxylate bridges[17]:

$$-\ddot{V}-O{=}C{=}O-\ddot{V}-$$

This is confirmed by good coincidence of the experimental effective magnetic moments with the theoretical values calculated for a linear chain of n interacting ions with spin $S = 1$[18] and $n = 2$ [the exchange integrals are -110 and $-130\ \text{cm}^{-1}$ respectively for complexes (I) and (II) (Table 2)].

TABLE 2

COMPARISON OF THE EXPERIMENTAL AND THEORETICAL VALUES μ_{eff} FOR COMPOUNDS (I) AND (II)

$[C_5H_5V(CH_3COO)_2]_2$ (I)			$[C_5H_5V(CF_3COO)_2]_2$ (II)		
$I = -110\ \text{cm}^{-1}$ $(S=1, n=2)$			$I = -130\ \text{cm}^{-1}$ $(S=1, n=2)$		
Temp. (°K)	μ_{theor} (B.M.)	μ_{exp} (B.M.)	Temp. (°K)	μ_{theor} (B.M.)	μ_{exp} (B.M.)
294	1.72	1.71	299	1.55	1.55
262	1.59	1.56	240	1.34	1.31
194	1.28	1.23	176	1.05	0.97
125	0.89	0.79	109	0.54	0.59
83	0.61	0.56	80	0.38	0.44

Finally it can be concluded that in the presence of μ-bridged ligands in the π-complexes it is not necessary that a metal–metal exchange interaction occurs via direct exchange but it can also involve a superexchange through the π-systems of the ligands.

EXPERIMENTAL

1. Synthesis of complexes

Bis(π-cyclopentadienylvanadium) tetrakis(μ-trifluoroacetate) (II). A solution of 0.60 g (2.63 mmoles) of $CpV(CO)_4$ in 15 ml of trifluoroacetic acid was refluxed for 24 h. In the course of reaction the colour slowly changed from orange to dark-red. The hot solution was filtrated. The dark-violet crystals precipitated on cooling the filtrate to room temperature. The mother liquor was decanted and the product recrystallized from ether/hexane (2/1). Dark-violet crystals were obtained, 0.27 g (30%), m.p. 217–218°. (Found: C, 31.83; H, 1.50; F, 33.07. $G_9H_5F_6O_4V$ calcd.: C, 31.6; H, 1.5; F, 33.3%.)

IR spectrum (cm^{-1}, in KBr): 725 s, 790 s, 820 vs, 855 m, 1025 m, 1080 w, 1130 w, 1160 vs, 1208 vs, 1335 w, 1450 w, 1475 m, 1720 vs.

Bis(π-cyclopentadienylvanadium) tetra-μ-acetate (I). A solution of 0.40 g (1.78 mmoles) of $CpV(CO)_4$ in 10 ml of an equal mixture of glacial acetic acid and acetic anhydride was refluxed for 3 h. The colour of the solution gradually changed from orange to dark-red and finally to light green. After cooling to +5° the dendrite-like violet crystals slowly precipitated from the solution. After decanting the solvent, crystals were washed with benzene and hexane and dried *in vacuo*. Yield 0.25 g (60%). M.p. 238–239°) (lit.[1] 239–240°).

X-ray study

Crystals of investigated complex (II) are elongated prisms and belong to a triclinic singonic structure: $a = 9.00 \pm 0.01$, $b = 8.75 \pm 0.01$, $c = 8.88 \pm 0.01$ Å, $\alpha = 65.9 \pm 0.3°$, $\beta = 105.5 \pm 0.3°$, $\gamma = 102.8 \pm 0.3°$, $d_{exp} = 1.78$ g/cc, $d_{calcd} = 1.81$ g/cc, $N = 1$ (dimeric molecule), steric group $P\bar{1}$. Intensities of 750 independent nonzero reflections (equisloped Weissenberg X-ray spectrometer, unfiltered copper radiation) were visually estimated, correction was introduced for the spot expansion and contraction. No account of an absorption factor was taken. The structure was recognized by the heavy atom method and corrected by the least squares procedure in the full matrix isotropic approximation. Final value of divergence factor being $R = 13.9\%$. Standard deviations are 0.01–0.07 Å for bond lengths, and 3–5° for valence angles depending upon the atomic numbers. Low accuracy of investigation was associated probably with some structural nonuniformity and large unaccounted anisotropy of the atomic thermal vibrations of cyclopentadienyl rings and trifluoromethyl groups.

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