Notes

CONTRIBUTION FROM THE MELLON INSTITUTE,
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Organometallic Chemistry of the Transition Metals. XVII. Cyclopentadienylvanadium Diacetate[1]

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Cyclopentadienyltetracarbonylvanadium, $C_5H_5V(CO)_4$ has been shown to react with dimethyl disulfide[3] and bis(trifluoromethyl)dithietene[4] to give the compounds $[C_5H_5V(SCH_3)_2]_2$ and $[C_5H_5VS_2C_2(CF_3)_2]_2$. Both of these compounds appear to have structures with four sulfur bridges.

Further reactions of $C_5H_5V(CO)_4$ have been investigated in an attempt to prepare other types of complexes with four bridging groups. This note discusses the nature of the product obtained from $C_5H_5V(CO)_4$ and acetic acid.

Experimental Section

Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. The mass spectrum was recorded on an Associated Electrical Industries MS-9 mass spectrometer at 70-ev electron energies. Magnetic susceptibility measurements were carried out on a Faraday balance. Microanalyses were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Cyclopentadienyltetracarbonylvanadium was prepared by the published procedure.[5]

Cyclopentadienylvanadium Diacetate.—A mixture of 1.0 g (4.39 mmoles) of $C_5H_5V(CO)_4$, 5 ml of glacial acetic acid, and 20 ml of acetic anhydride was refluxed 16 hr under nitrogen with magnetic stirring. After the reaction period was over, the reaction mixture was allowed to cool to room temperature. The resulting gray precipitate was filtered, washed with five portions of water, two portions of ethanol, and two portions of diethyl ether, and dried. The crude product weighed 1.09 g.

For final purification a 0.80-g sample of the crude product was sublimed at 125° (0.1 mm) for 18 hr to give 0.49 g of a gray-purple sublimate, mp 239–240° dec, identified by its analysis and mass spectrum as $C_5H_5V(CO_2CH_3)_2$. The recovery of sublimed product based on crude product was 61% and the yield based on $C_5H_5V(CO)_4$ was 65%. However, in other experiments the yield was rather erratic. Often much insoluble and nonvolatile gray-green material, apparently a vanadium acetate no longer containing cyclopentadienyl groups, was obtained.[6]

Anal. Calcd for $C_9H_{11}O_4V$: C, 46.1; H, 4.7; O, 27.3; V, 21.8. Found: C, 45.6; H, 4.5; O, 27.6; V, 21.7.

Mass Spectrum.—The following ions (with $m/e > 115$), m/e values, and relative intensities, respectively, were observed: $C_5H_5V(CO_2CH_3)_2^+$, 234, 120; $C_5H_5V(OH)(CO_2CH_3)^+$, 192, 740; $C_5H_5VCO_2CH_3^+$, 175, 270; $C_5H_5V(OH)_2^+$, 150, 830; $C_5H_5VO^+$, 132, 350; $C_5H_5V^+$, 116, 50.

Infrared Spectrum.—ν_{CH} at 3060 (w) and 2890 (vw) cm^{-1}; ν_{CO} (acetate) at 1610 (s) cm^{-1}; other bands at 1435 (s), 1345 (vw), 1335 (w), 1017 (m), 820 (m), and 799 (s) cm^{-1}.

Magnetic Susceptibility Measurements.—$\chi_{mole}^{23°} = +878 \times 10^{-6}$ cm^3/mole (sample I) and $+859 \times 10^{-6}$ cm^3/mole (sample II) corresponding to magnetic moments of 1.47 BM (sample I) and 1.51 BM (sample II), respectively.

Discussion

The new purple compound $C_5H_5V(CO_2CH_3)_2$ is unusual in being completely insoluble in organic solvents but yet volatile at 125° (0.1 mm). The mass spectrum of $C_5H_5V(CO_2CH_3)_2$ vapor clearly confirms the *monomeric* formulation (I) in the vapor phase. This contrasts with the mass spectrum[7] of the compound[4] $[C_5H_5VS_2C_2(CF_3)_2]_2$ (II) which exhibits ions containing two vanadium atoms such as the parent $[C_5H_5VS_2C_2(CF_3)_2]_2^+$ demonstrating that vaporization of the binuclear $[C_5H_5VS_2C_2(CF_3)_2]_2$ does not result in fission to mononuclear species.

The monomeric formulation $C_5H_5V(CO_2CH_3)_2$ corresponds to a vanadium(III)[8] derivative which would be expected to have two unpaired electrons and a magnetic moment of about 2.83 BM. The magnetic susceptibility measurements in the solid state indicate a much lower magnetic moment of 1.49 ± 0.02 BM suggesting spin pairing in the solid state by means of vanadium–vanadium bonding. Since molecular weight measurements on the solid are not yet available, it is not possible at present to decide whether such spin pairing occurs through formation of a dimer (III) with four bridging acetate groups for two vanadium atoms or of a higher polymer with similar repeating units of type IV.

The behavior of $C_5H_5V(CO_2CH_3)_2$ resembles that of $[C_5H_5Cr(CO)_3]_2$.[9,10] The mass spectra of the vapors of both compounds exhibit only ions containing one metal atom. However, the solid materials are both sparingly soluble to insoluble in organic solvents and exhibit magnetic moments which are abnormally low for those required for the monomeric formulas $C_5H_5V(CO_2CH_3)_2$ and $C_5H_5Cr(CO)_3$. This indicates association in the solid state involving metal–metal bonding. Thus $C_5H_5V(CO_2CH_3)_2$ and $[C_5H_5Cr(CO)_3]_2$ are both compounds where metal–metal bonds are broken upon vaporization. Studies on additional such compounds are contemplated.

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[1] For Part XVI of this series see R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).

[2] Department of Chemistry, University of Georgia, Athens, Ga.

[3] R. H. Holm, R. B. King, and F. G. A. Stone, *Inorg. Chem.*, **2**, 219 (1963).

[4] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[5] R. P. M. Werner, A. H. Filbey, and S. A. Manastyrskyj, *Inorg. Chem.*, **3**, 298 (1964).

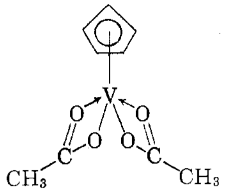
[6] Attempts to make similar $C_5H_5V(CO_2R)_2$ compounds from formic acid and propionic acid (and propionic anhydride) failed. Only insoluble and nonvolatile gray-green materials were obtained. Excess boiling acetylacetone (2,4-pentanedione) reacts with $C_5H_5V(CO)_4$ to give (after 18 hr) an 89% yield of brown vanadium(III) acetylacetonate, $V(C_5H_7O_2)_3$, mp 176–179° dec. Thus complete loss of both carbonyl and cyclopentadienyl groups occurs in this case.

[7] R. B. King, unpublished results.

[8] In determining the formal oxidation state of the vanadium atom the π-cyclopentadienyl ring is considered as the anion $C_5H_5^-$.

[9] E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 140 (1955); E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allgem. Chem.*, **282**, 47 (1955); R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 104(1963).

[10] R. B. King, *J. Am. Chem. Soc.*, **88**, 2075 (1966).



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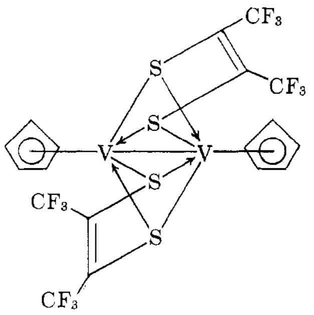

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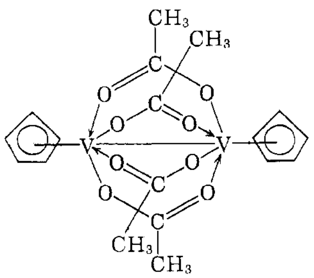

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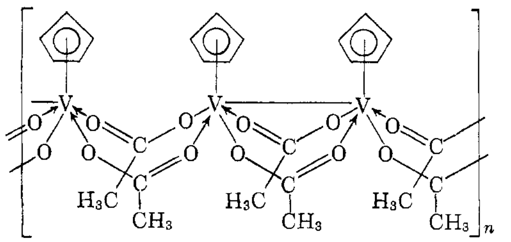

IV

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Raman Spectra of Tetrahalozincates and the Structure of Aqueous $ZnCl_4^{2-}$

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The stereochemistry of zinc(II) may involve either tetrahedral or octahedral coordination. Small donors such as fluorine and oxygen often exhibit a sixfold coordination as is found in the solids ZnF_2 (rutile structure)[1] and $(Zn(H_2O)_6)(ClO_4)_2$.[2] Larger donors prefer tetrahedral coordination. X-Ray diffraction studies have shown solid Cs_2ZnBr_4[3] and Cs_2ZnCl_4[4] to contain tetrahedral ZnX_4^{2-} species. Raman studies by Delwaulle[5] and others[6,7] have established a tetrahedral structure for ZnI_4^{2-} and $ZnBr_4^{2-}$ in aqueous solution. However, Irish, *et al.*,[8] argue from Raman evidence that $ZnCl_4^{2-}$ in aqueous solution is actually $ZnCl_4(H_2O)_2^{2-}$, with D_{4h} symmetry. If confirmed, this would represent an unusual and interesting difference between solution and crystalline structures of a complex ion.

We have recorded the Raman spectra of a series of cesium tetrahalozincates in order to investigate the vibrations of tetrahedral ZnX_4^{2-}. Comparison of solid and solution spectra strongly indicates that the conclusion of Irish, *et al.*, is unwarranted and that $ZnCl_4^{2-}$ is tetrahedral in solution.

Experimental Section

Cs_2ZnCl_4 and Cs_2ZnBr_4 were prepared by evaporation in dry air of aqueous solutions containing stoichiometric proportions of cesium halide and zinc halide. Cs_2ZnI_4 was prepared by evaporation in dry nitrogen of a 2.5 mole ratio mixture of CsI and ZnI_2 in water. In each case, small colorless crystals were obtained.

Raman spectra, at 28 ± 1°, were recorded with a Cary Model 81 Raman spectrophotometer using the 4358-A mercury line for excitation. The compounds were ground in a mortar and tapped into a conical sample holder, constructed after the design of Busey and Keller.[9]

Results and Discussion

The observed vibrational frequencies are presented in Table I with the results of others[5-8] on aqueous solution for comparison.

Four fundamental Raman-active internal vibrations are expected for a tetrahedral XY_4 molecule. Four bands are indeed observed for each compound and are assigned in the table. In no case was splitting of degenerate modes, from site symmetry or geometric distortion, observed. The four distinct bands found for Cs_2ZnI_4 justify our assumption that ZnI_4^{2-} is tetrahedral in this compound although its crystal structure has not been determined. The observed frequencies and assignments are quite reasonable in the light of the results of Delwaulle; Clark and Dunn[10] have observed ν_3 for Cs_2ZnCl_4 in the infrared at 292 cm^{-1}, in good agreement with our result.

The Raman spectra of ZnX_4^{2-} in aqueous solution show four distinct bands for ZnI_4^{2-} and $ZnBr_4^{2-}$ and two bands for $ZnCl_4^{2-}$: a polarized band in the stretching region at 280 cm^{-1} and a broad, depolarized band in the bending region at 80–120 cm^{-1}. Irish, *et al.*,[8] argue that the observation of only two bands, and particularly only one band in the bending region, indicates a nontetrahedral structure. They contend that the two bending modes observed for ZnI_4^{2-} and $ZnBr_4^{2-}$ should be more clearly resolved for $ZnCl_4^{2-}$.

The separation of ν_2 and ν_4 is somewhat larger in the cesium salts for $ZnCl_4^{2-}$ than for $ZnBr_4^{2-}$ or ZnI_4^{2-},

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[1] A. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 337.

[2] Reference 1, p 506.

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[7] W. Yellin and R. A. Plane, *J. Am. Chem. Soc.*, **83**, 2448 (1961).

[8] D. E. Irish, B. McCarroll, and T. F. Young, *J. Chem. Phys.*, **39**, 3436 (1963).

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[10] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963).