**Table IV.** Raman Frequencies for $BiCl_3$ and $BiCl_3$-Containing Melts $(cm^{-1})^a$

| BiCl₃ | | | 67:33 mol % molten BiCl₃-KCl | Aqueous BiCl₄⁻ c | 50:50 mol % molten BiCl₃-KCl | Aqueous BiCl₆³⁻ c | 25:75 mol % molten BiCl₃-KCl |
|---|---|---|---|---|---|---|---|
| Gas^b | Aqueous^c | Molten | | | | | |
| 342 s, P | 307 s, P | 304 s, P | 300 s, P | 293 s, P | 294 s, P | 263 s, P | 276 s, P |
| 322 w, sh | 272 m | 277 m | 272 m, sh, b | 256 m | 252 m, sh, b | 220 w | 236 m, sh, b |
| 123 m, P | 120 m | 122 m | 116 m | 115 w | 108 m | 110 w | 80 m, sh, b |
| 107 mw | | | | | | | |

$^a$ Key: s, strong; m, medium; w, weak; b, broad; sh, shoulder; P, polarized. $^b$ Reference 16. $^c$ Reference 11.

From the comparison with the results in aqueous media,[11] as shown in Table IV, and the spectra of solid $(N_2H_5)_3$-$BiCl_6$ and $C_6H_{13}N_2BiCl_4$,[11] we believe that the anionic species $BiCl_4^-$ and $BiCl_6^{3-}$ are formed by mixing appropriate amounts of $BiCl_3$ and KCl. Their structures are similar to the species in aqueous solution, i.e., $C_{2v}$ or distorted $T_d$ for $BiCl_4^-$ and $O_h$ for $BiCl_6^{3-}$. The presence of $BiCl_4^-$ and $BiCl_6^{3-}$ in those systems is also supported by the phase diagram studies.[14] Oertel and Plane[11] have made a considerable case for a $BiCl_5^{2-}$ ion in aqueous solution and such an ion might be postulated here. Certainly the evidence is not conclusive, but we tend to favor the simpler picture without $BiCl_5^{2-}$, since such a structure would produce more complex Raman spectra. The melting temperatures of the various $BiCl_3$-KCl mixtures varied considerably, and it was not possible entirely to eliminate the possibility that differences in the spectra were caused by the shifting of chemical equilibria with temperature changes. Observations on the lower melting mixtures made at higher temperatures, however, showed no appreciable changes in the spectra. In addition, in several cases, glassy solids were formed upon cooling rather than the usual polycrystalline solids, and the spectra of these glasses were indistinguishable from the melt spectra. Our main conclusions are that there is a remarkable similarity between the aqueous and molten Raman data and that $BiCl_3$ in both cases forms higher species of the type $BiCl_n^{(n-3)-}$.

**Molten $BiCl_3$-$AlCl_3$.** The Raman spectrum of the molten equimolar $BiCl_3$-$AlCl_3$ mixture is shown in Figure 2D. As with $SbCl_3$, the absence of a band at $186\ cm^{-1}$ shows that there is very little $AlCl_4^-$ present. The spectrum is poorer than the $SbCl_3$-$AlCl_3$ spectrum and may be interpreted as being produced by a mixture of $BiCl_3$ and $Al_2Cl_6$, although we see only the strongest $Al_2Cl_6$ bands. In contrast to the $SbCl_3$ case, we do not find evidence of $AlCl_3$ monomer or complex production. The congruently melting solid compound obtained in the phase studies[15] does not seem to be present in the melt.

**Registry No.** Bismuth trichloride, 7787-60-2; antimony trichloride, 10025-91-9; potassium chloride, 7447-40-7; aluminum trichloride, 7446-70-0; $BiCl_6^{3-}$, 15977-99-8; $BiCl_4^-$, 20057-70-9.

Contribution from the Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65401

# The Synthesis and Spectroscopic Properties of Vanadium(III) Squarate Trihydrate

S. M. CONDREN and H. O. McDONALD*

Vanadium(III) squarate trihydrate has been prepared; and the infrared, X-ray diffraction, and electronic spectra of the complex indicate that the central metal atom is in a slightly distorted octahedral field. A thermogravimetric study has shown that the complex loses three water molecules upon heating. A hydroxy-bridged, dimeric structure has been proposed from these data.

The preparation and spectroscopic properties of several metal complexes of diketocyclobutenediol[1] (1,2-dihydroxy-3,4-diketocyclobutene) have been previously reported.[2-4] These reports have usually presented preparations and little spectral data. In this report the preparation is similar to the one reported by West and Niu.[2] Also, the powder X-ray diffraction, thermogravimetric, magnetic, and infrared and electronic spectral data are presented and discussed.

## Experimental Section

**Materials.** Squaric acid and hexachloropropene were purchased

from Aldrich Chemical Co., Milwaukee, Wis. Vanadium pentoxide was purchased from Alfa Inorganics, Beverly, Mass. Vanadium trichloride hexahydrate was prepared by the hydrolysis of vanadium trichloride.[5] Vanadium trichloride was prepared by the chlorination of vanadium pentoxide with hexachloropropene according to published procedure.[5]

**Preparation of Vanadium(III) Squarate Trihydrate.** A solution containing 0.76 g (2.9 mmol) of vanadium trichloride hexahydrate was mixed with a solution containing 0.50 g (4.5 mmol) of squaric acid. The dark brown color of the vanadium trichloride solution was almost immediately replaced by an olive green precipitate. The solution was stirred for about 24 hr before the precipitate was filtered, washed with acetone and ether, and dried in a vacuum desiccator over calcium chloride. *Anal.* Calcd for $V^{III}(OH)C_4O_4 \cdot 3H_2O$: V, 21.8; C, 20.5; H, 2.99. Found: V, 20.2; C, 20.7; H, 3.17.

(1) Hereafter, diketocyclobutenediol will be referred to by its accepted common name, squaric acid, and the dianion, diketocyclobutenediolate will be referred to as the squarate anion.
(2) R. West and H. Y. Niu, *J. Amer. Chem. Soc.*, **85**, 2589 (1963).
(3) G. Doyle and R. S. Tobias, *Inorg. Chem.*, **7**, 2484 (1968).
(4) P. H. Tedesco and H. F. Walton, *Inorg. Chem.*, **8**, 933 (1969).
(5) W. W. Porterfield and S. Y. Tyree, Jr., *Inorg. Syn.*, **9**, 133 (1967).

**Table I.** Lattice Spacings (Å) for $V^{III}(OH)(C_4O_4)\cdot3H_2O$

| | | | | | |
|---|---|---|---|---|---|
| 7.72 | 5.17 | 3.44 | 2.76 | 2.39 | 1.980 |
| 6.61 | 4.53 | 3.23 | 2.66 | 2.29 | 1.852 |
| 6.37 | 4.24 | 3.14 | 2.58 | 2.15 | 1.826 |
| 6.18 | 3.96 | 3.03 | 2.49 | 2.10 | 1.712 |
| 5.72 | 3.70 | 2.84 | 2.46 | 2.05 | |

**Table II.** Thermogravimetric Data for $V^{III}(OH)(C_4O_4)\cdot3H_2O$

| Atm | Max temp, °C | Dta peaks,[a] °C | Wt loss Steps | Wt loss % | Residue |
|---|---|---|---|---|---|
| Air | 1020 | 230 (endo) 330 (exo) | 2 | 85.4 | $V_2O_5$ |
| Air | 300 | 200 (endo) 240 (exo) | 1 | 62.5 | $V_2O_5$ |
| Air | 140 | 140 (endo) | 1 | 20.5 | $V^{III}(OH)(C_4O_4)$ |
| Argon | 710 | 200 (endo) 340 (exo) | 2 | 88.1 | $V_2O_3$ |
| Argon | 360 | 200 (endo) 340 (exo) | 2 | 52.4 | Unidentified |
| Argon | 160 | 160 (endo) | 1 | 21.2 | $V^{III}(OH)(C_4O_4)$ |

[a] Endo refers to endotherm and exo refers to exotherm.

**Instrumentation.** The infrared spectra were measured with a Beckman IR 12 A spectrophotometer. Spectrophotometric grade potassium bromide pellets of a 300:1 weight ratio of potassium bromide to metal squarate complex were used in obtaining the spectra of the solids. The electronic spectra were measured with a Cary 14 spectrophotometer by use of Kel-F 90 grease mulls of the solid between quartz plates. The powder X-ray diffraction patterns were obtained using a Siemens Crystalloflex IV diffractometer, Type U-13. The magnetic susceptibility measurements were made by use of a Gouy balance composed of a Mettler H20Gd balance modified for under the pan weighing, an electromagnet Varian Model V-4005, and a Varian Associates Model V-2900 regulated power supply. The thermogravimetric studies were made by use of a Mettler Recording Vacuum Thermoanalyzer.

**Analyses.** The vanadium analysis was performed gravimetrically by igniting the complex to $V_2O_5$. The carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

## Results and Discussion

In contrast to the previously reported preparative methods for metal squarates,[2] the preparation for vanadium(III) squarate trihydrate proceeds slowly, requiring 24 hr for completion. Otherwise, the complex appears to be identical with the trivalent metal squarate trihydrates previously reported.

The X-ray powder pattern for vanadium(III) squarate trihydrate at room temperature was found to be identical within experimental error with those reported for the trivalent metal squarate trihydrates by West and Niu.[2] Table I contains the lattice spacings which were calculated from the powder X-ray diffraction patterns for vanadium(III) squarate trihydrate.

The thermogravimetric patterns indicated that the vanadium(III) squarate trihydrate lost weight stepwise upon heating. Therefore, a comprehensive study was made of the thermal decomposition reaction by stopping the reaction after each step and analyzing the product. The product was identified by powder X-ray diffraction and infrared spectral analysis. The results of that study are given in Table II.

The infrared spectra of the product of the first step of the reaction contained all the characteristic bands of the squarate anion. This indicated that the weight loss was not the result of the decomposition of the squarate anion. Therefore, the first step must involve the endothermic loss of the three waters of hydration, since loss of three water molecules would result in a weight loss of 23.1%, which compares favorably with the experimental values of 20.5% in air and 21.2% in argon.

**Table III.** Infrared Spectral Data $(cm^{-1})$ for $V^{III}(OH)(C_4O_4)\cdot3H_2O$

| | | | |
|---|---|---|---|
| 450 s | 720 w, sh | 1090 m, sp | 1615 s |
| 520 w, sh | 750 m | 1108 m, sp | 1801 w |
| 535 m | 875 m | 1145 vw | 2500 w, sh |
| 645 w | 1048 w | 1515 vs, b | 3280 s, vb |
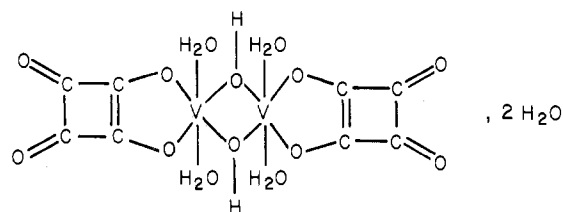


**Figure 1.** Dimeric structure of $V^{III}(OH)(C_4O_4)\cdot3H_2O$.

Bailey, Mills, and Tangredi have reported that the divalent metal squarate dihydrates thermally decompose by a two-step weight loss, the first step of which is the loss of two water molecules.[6]

Attempts at preparing the dehydrated material by vacuum dehydration techniques at 80° have shown that the dehydrated material was quite hygroscopic, going to a complex with an apparent empirical formula of $V^{III}(OH)(C_4O_4)\cdot2H_2O$.

Because the end product of the reaction in air was identified as vanadium pentoxide, the second step of the decomposition must involve the decomposition of the squarate anion. The calculated weight loss for the complex decomposing to $V_2O_5$ is 61.1%. The experimental weight losses of 85.4 and 62.5% are greater than the calculated value probably because the complex burns rather violently, resulting in some loss due to splattering. Bailey, *et al.*, reported the second step of the thermal decomposition of the divalent squarates was the oxidation of the squarate anion to CO and $CO_2$ and of the metal to its oxide.[6]

The trivalent vanadium, having a $d^2$ configuration, should have an effective magnetic moment of 2.83 BM for the free metal ions. A $d^2$ metal ion in an octahedral crystal field has a $^3T_{1g}$ ground state and should have a temperature-dependent magnetic moment. However, the magnetic moments of 2.81 BM at 295°K and 2.84 BM at 103.0°K, which were obtained from magnetic susceptibilities of $3340 \times 10^{-6}$ cgsu and $9830 \times 10^{-6}$ cgsu, respectively, did not show any temperature dependence. The lack of temperature dependence could be the result of a large, low-symmetry component as compared to the spin-orbit coupling component as has been shown to be the reason for the lack of temperature dependence of the magnetic moment of $(NH_4)V(SO_4)_2\cdot12H_2O$.[7]

The infrared spectral data for $V^{III}(OH)(C_4O_4)\cdot3H_2O$ are given in Table III. The spectrum of this complex contains bands at 1615 $cm^{-1}$, assigned to a C=C conjugated system, and 1801 $cm^{-1}$, assigned to a C=O band, which have been previously reported to indicate the presence of uncoordinated oxygen atoms on the squarate anion.[2,3,8] In his dissertation, Niu[8] proposed a dimeric structure for the trivalent metal squarates with the metal atoms connected by two hydroxyl bridges as shown in Figure 1. Such bridges in iron complexes have been shown to contain bands in the infrared spectrum at approximately 500 $cm^{-1}$, the stretch of the metal-oxygen bond, and 1050 $cm^{-1}$, the bending O-H vibration

(6) R. A. Bailey, W. N. Mills, and W. J. Tangredi, *J. Inorg. Nucl. Chem.*, 33, 2387 (1971).

(7) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 252.

(8) H. Y. Niu, "New Aromatic Anions and Their Complexes," Ph.D. Dissertation, University of Wisconsin, 1962.

in the hydroxyl bridge.[9] The bands at 520 and 1048 cm$^{-1}$, respectively, have been assigned to these vibrations. The band at 450 cm$^{-1}$ is in the region of the vanadium-oxygen single-bond stretch in vanadium complexes.[10] The band at approximately 1500 cm$^{-1}$ in vanadium(III) squarate trihydrate and all other trivalent metal squarate trihydrates is assigned to be a mixture of the C-C and C-O stretch vibrations.[2,8,11] The spectrum contained a very broad band at approximately 3200 cm$^{-1}$ which was assigned to the O-H stretch in water and the hydroxyl radical where there is considerable hydrogen bonding.

The vanadium(III) ion is a $d^2$ configuration with a $^3T_{1g}$ (F) ground state in an octahedral crystal field. The band in the electronic spectrum of $V^{III}(OH)(C_4O_4)\cdot3H_2O$ at 17,900 cm$^{-1}$ can be assigned to the d-d transition of $^3T_{2g}$ (F) $\leftarrow$ $^3T_{1g}$ (F). The $^3T_{2g}$ (F) $\leftarrow$ $^3T_{1g}$ (F) transition in a $V(H_2O)_6^{3+}$ solution appears at 17,200 cm$^{-1}$.[12] The band in the electronic spectrum at 26,000 cm$^{-1}$ can be assigned to the d-d transition of $^3T_{1g}$ (F) $\leftarrow$ $^3T_{1g}$ (F). This band in a $V(H_2O)_6^{3+}$ solution appears at 25,000 cm$^{-1}$.[12] By using these assignments for d-d transitions, it was possible to estimate the crystal field splitting parameter $10Dq = 18,900$ cm$^{-1}$ and the Racah parameter $B = 611$ cm$^{-1}$. These values compare favorably to the values of $10Dq = 18,600$ cm$^{-1}$ and $B = 665$ cm$^{-1}$ for $V(H_2O)_6^{3+}$ [12] and suggest that the vanadium ion could be in a slightly distorted octahedral field.

In conclusion, it appears that the data reported here best fit the dimeric structure first proposed by Niu[8] for the iron(III) squarate complex. The infrared spectrum appears to contain bands characteristic of hydroxyl bridges. The infrared spectrum also contains those bands associated with uncoordinated oxygen atoms on the squarate anion. The electronic spectra suggest that the vanadium atoms are in a slightly distorted octahedral field. All of these data agree well with the dimeric structure.

(9) J. R. Ferraro, R. Driver, W. R. Walker, and W. Wozniak, *Inorg. Chem.*, 6, 1586 (1967).

(10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 121.

(11) S. Cohen, J. R. Lacher, and J. D. Park, *J. Amer. Chem. Soc.*, 81, 3480 (1959).

(12) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 218.

---

# The Tetrafluoroiodate(III) Anion, IF4-

KARL O. CHRISTE* and DIETER NAUMANN

The salts $CsIF_4$ and $Cs_3IF_6$ were prepared and characterized by infrared and Raman spectroscopy. The vibrational spectra observed for $IF_4^-$ are consistent with a square-planar structure of symmetry $D_{4h}$. The Raman spectrum previously reported for $IF_4^-$ and interpreted in terms of a nonplanar structure of symmetry $C_{2v}$ can be attributed to $IF_6^-$. Force constants were computed for $IF_4^-$ and are compared to those of $BrF_4^-$, $ClF_4^-$, and $XeF_4$.

## Introduction

The existence of salts containing the $IF_4^-$ anion was first reported[1] in 1960 by Hargreaves and Peacock. When studying the reaction between CsI and $IF_5$, they obtained depending upon the reaction conditions different products. At elevated temperature the solid product was reported[1] to be $CsIF_6$ whereas at ambient temperature it was believed to be $CsIF_4$. In 1961, Asprey, Margrave, and Silverthorn reported[2] the syntheses of $IF_4^-$ salts by direct fluorination of iodides. In 1969, Shamir and Yaroslavsky published[3] the Raman spectrum of "$CsIF_4$" prepared by the method[1] of Hargreaves. They observed nine bands and concluded[3] that $IF_4^-$ is not square planar (I) but possesses structure II. These results were quite unexpected since the related $ClF_4^-$ and $BrF_4^-$ anions and the isoelectronic $XeF_4$ molecule are all square planar.[4-7] Recently, Christe pointed out[8] that



$D_{4h}$, I          $C_{2v}$, II
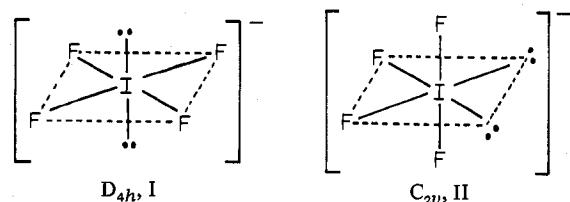
the Raman spectrum, attributed[3] by Shamir and Yaroslawsky to $IF_4^-$, closely resembles that of $IF_6^-$. Hence, it appeared interesting to study the vibrational spectrum of a sample of $CsIF_4$ which had been prepared from $IF_3$ and CsF by the method[9] of Schmeisser, *et al.*

(4) K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, 357, 125 (1968); 374, 306 (1970).

(5) A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1936 (1969).

(6) K. O. Christe and C. J. Schack, *Inorg. Chem.*, 9, 1852 (1970).

(7) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, 65, 199 (1965).

(8) K. O. Christe, *Inorg. Chem.*, 11, 1215 (1972).

(9) M. Schmeisser, W. Ludovici, D. Naumann, P. Sartori, and E. Scharf, *Chem. Ber.*, 101, 4214 (1968).

*Address correspondence to this author at Rocketdyne.

(1) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 2373 (1960).

(2) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Amer. Chem. Soc.*, 83, 2955 (1961).

(3) J. Shamir and I. Yaroslavsky, *Isr. J. Chem.*, 7, 495 (1969).