
01 Jan 1973

The Synthesis And Spectroscopic Properties Of Vanadium(III) Squarate Trihydrate

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Recommended Citation

S. M. Condren and H. O. McDonald, "The Synthesis And Spectroscopic Properties Of Vanadium(III) Squarate Trihydrate," *Inorganic Chemistry*, vol. 12, no. 1, pp. 57 - 59, American Chemical Society, Jan 1973. The definitive version is available at <https://doi.org/10.1021/ic50119a015>

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Table IV. Raman Frequencies for BiCl₃ and BiCl₃-Containing Melts (cm⁻¹)^a

BiCl ₃			67:33 mol % molten BiCl ₃ -KCl	Aqueous BiCl ₄ ^{-c}	50:50 mol % molten BiCl ₃ -KCl	Aqueous BiCl ₆ ^{3--c}	25:75 mol % molten BiCl ₃ -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 (N₂H₅)₃-BiCl₆ and C₆H₁₃N₂BiCl₄,¹¹ we believe that the anionic species BiCl₄⁻ and BiCl₆³⁻⁻ are formed by mixing appropriate amounts of BiCl₃ and KCl. Their structures are similar to the species in aqueous solution, *i.e.*, C_{2v} or distorted T_d for BiCl₄⁻ and O_h for BiCl₆³⁻⁻. The presence of BiCl₄⁻ and BiCl₆³⁻⁻ in those systems is also supported by the phase diagram studies.¹⁴ Oertel and Plane¹¹ have made a considerable case for a BiCl₅²⁻⁻ 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 BiCl₅²⁻⁻, since such a structure would produce more complex Raman spectra. The melting temperatures of the various BiCl₃-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 spec-

tra. Our main conclusions are that there is a remarkable similarity between the aqueous and molten Raman data and that BiCl₃ in both cases forms higher species of the type BiCl_n⁽ⁿ⁻³⁾⁻⁻.

Molten BiCl₃-AlCl₃. The Raman spectrum of the molten equimolar BiCl₃-AlCl₃ mixture is shown in Figure 2D. As with SbCl₃, the absence of a band at 186 cm⁻¹ shows that there is very little AlCl₄⁻ present. The spectrum is poorer than the SbCl₃-AlCl₃ spectrum and may be interpreted as being produced by a mixture of BiCl₃ and Al₂Cl₆, although we see only the strongest Al₂Cl₆ bands. In contrast to the SbCl₃ case, we do not find evidence of AlCl₃ monomer or complex production. The congruently melting solid compound obtained in the phase studies¹⁵ 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; BiCl₆³⁻⁻, 15977-99-8; BiCl₄⁻, 20057-70-9.

Acknowledgment. We wish to thank Drs. G. P. Smith and C. R. Boston for the use of their drybox and for furnishing purified compounds.

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

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Received March 30, 1972

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 diketocyclobutenediol¹ (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

(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).

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)C₄O₄·3H₂O: V, 21.8; C, 20.5; H, 2.99. Found: V, 20.2; C, 20.7; H, 3.17.

(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 $V^{III}(OH)(C_4O_4) \cdot 3H_2O$

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 $V^{III}(OH)(C_4O_4) \cdot 3H_2O$

Atm	Max temp, °C	Dta peaks, °C	Wt loss		Residue
			Steps	%	
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_5
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.

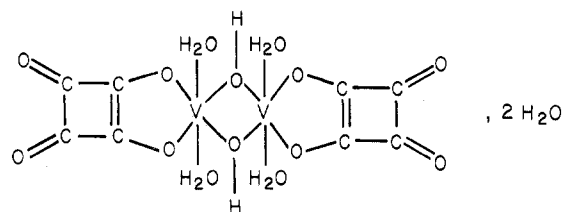
The X-ray powder pattern for vanadium(III) squarate trihydrate at room temperature was found to be identical within experimental error with those reported for the trivalent metal squarate trihydrates by West and Niu.² Table I contains the lattice spacings which were calculated from the powder X-ray diffraction 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 $V^{III}(OH)(C_4O_4) \cdot 3H_2O$

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 $V^{III}(OH)(C_4O_4) \cdot 3H_2O$.

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 $V^{III}(OH)(C_4O_4) \cdot 2H_2O$.

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 CO₂ 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 3340×10^{-6} cgsu and 9830×10^{-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 $(NH_4)V(SO_4)_2 \cdot 12H_2O$.⁷

The infrared spectral data for $V^{III}(OH)(C_4O_4) \cdot 3H_2O$ 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, Niu⁸ 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 $\text{V}^{III}(\text{OH})(\text{C}_4\text{O}_4)\cdot 3\text{H}_2\text{O}$ 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 $\text{V}(\text{H}_2\text{O})_6^{3+}$ 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 $\text{V}(\text{H}_2\text{O})_6^{3+}$ solution ap-

pears at 25,000 cm^{-1} .¹² By using these assignments for d-d transitions, it was possible to estimate the crystal field splitting parameter $10Dq = 18,900 \text{ cm}^{-1}$ and the Racah parameter $B = 611 \text{ cm}^{-1}$. These values compare favorably to the values of $10Dq = 18,600 \text{ cm}^{-1}$ and $B = 665 \text{ cm}^{-1}$ for $\text{V}(\text{H}_2\text{O})_6^{3+}$ 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 Niu⁸ 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.

Registry No. Vanadium(III) squarate trihydrate dimer, 35918-74-2.

Acknowledgments. The authors wish to acknowledge the assistance of Dr. K. G. Mayhan, Dr. G. J. Long, Dr. J. D. Bucci, and Mrs. Barbara Parmalee with various aspects of this work. National Science Foundation Grant No. GY6625 made possible the purchase of components for the magnetic susceptibility balance.

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(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.

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The Tetrafluoroiodate(III) Anion, IF_4^-

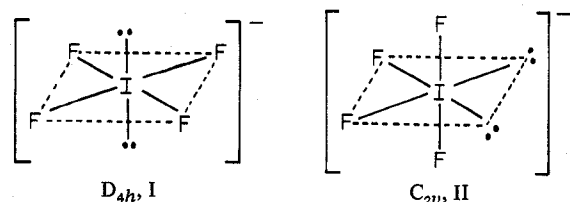
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Received May 22, 1972

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 reported¹ 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 reported¹ to be CsIF_6 whereas at ambient temperature it was believed to be CsIF_4 . In 1961, Asprey, Margrave, and Silverthorn reported² the syntheses of IF_4^- salts by direct fluorination of iodides. In 1969, Shamir and Yaroslavsky published³ the Raman spectrum of "CsIF₄" prepared by the method¹ of Hargreaves. They observed nine bands and concluded³ 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 out⁸ that



the Raman spectrum, attributed³ by Shamir and Yaroslavsky 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 method⁹ of Schmeisser, *et al.*

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