

intensity loss at the A resonances; (iii) broadening and intensity loss at the C resonance; (iv) above 300 K reappearance of the A and C intensity as a single narrowing line, AC, at intermediate chemical shift. The chemical shift of the fast-exchanging B resonance is almost halide-independent. The spectra of **2** in the temperature range 243–276 K show also that there is not interchange of the sites responsible for the Aa and Ab lines but rather separate exchange of each of them with the type (η) site, line C.

Therefore, it appears that the Cd site interconversion processes occurring in **5**, **6**, and **2** in solution are as follows: (1) The $S_3Cd^{eq}(OH)$ (δ) and $S_3Cd^{eq}(OH)_2$ (ϵ) sites average their stereochemistries without interchange with sites of other types. (2) $X^iCd^iS_3$ (α) sites interchange with $S_3Cd^{eq}(OH)_3$ (η) sites. The geometry of Cd(3) in 6_{cryst} demonstrates clearly the geometry intermediate in this interconversion. (3) The $S_3Cd^{eq}X^o$ (β) sites interchange with $S_3Cd^{eq}(OH)_3$ (η) sites. (4) The $S_3Cd^{eq}X^o$ (β) and $X^iCd^iS_3$ (α) sites do not interchange in the temperature range studied; that is, the $\alpha \leftrightarrow \beta$ interchange is not faster than the separate $\alpha \leftrightarrow \eta$ and $\beta \leftrightarrow \eta$ exchanges.

We have examined the spectra of mixtures of **2** with Cl^- in DMF in the slow-exchange temperature regime. At a molar ratio $Cl^-/2$ of 3 the Aa resonance is very weak, all B and C lines have

disappeared, and the major resonance is a series of at least five sharp lines in the Ab region, 573–599 ppm. At a ratio of 5 there are six sharp lines in this region only. These lines are due to Cd atoms with terminal halide coordination, types β and γ . It is not possible to assign individual resonances unequivocally, but it is clear that they arise from different combinations of Cl and I as X^i and X^o in the sites S_3CdX^o (β) and $X^iCdS_3X^o$ (γ). Evidently halide ions displace terminal OH ligands, exchange (slowly) into the central position, and reduce the rate of exchange of Cd sites. At $Cl^-/2$ ratios ≥ 8 additional resonances appear at higher chemical shift, indicative of cage fragmentation and the formation of species such as $[Cd(SCH_2CH_2OH)_3Cl]^{2-}$.

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Supplementary Material Available: Tabulations of d spacings in the powder diffraction patterns and of all atomic parameters (5 pages); tabulations of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Synthetic, Structural, and Physical Studies of Tris(2,4-pentanedionato)vanadium(IV) Hexachloroantimonate(V) and Tris(1-phenyl-1,3-butanedionato)vanadium(IV) Hexachloroantimonate(V)

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The complexes $[V(acac)_3][SbCl_6]$ (**1**) and $[V(bzac)_3][SbCl_6] \cdot CH_2Cl_2$ (**2**) have been prepared by reaction of $[V(acac)_2Cl_2]$ and $[V(bzac)_2Cl_2]$, respectively, with $SbCl_5$ in acetic acid solution. Their crystal structures are described. Crystals of **1** are orthorhombic, space group $Pcab$, with $a = 14.167$ (9) Å, $b = 18.774$ (3) Å, $c = 19.670$ (6) Å, $Z = 8$, and $R_w = 3.3\%$. Crystals of **2** are triclinic, space group $P\bar{1}$, with $a = 12.070$ (6) Å, $b = 14.110$ (4) Å, $c = 15.792$ (2) Å, $\alpha = 66.46$ (2)°, $\beta = 69.08$ (2)°, $\gamma = 65.90$ (2)°, $Z = 2$, and $R_w = 5.6\%$. The geometry about vanadium in each structure approximates octahedral with trigonal twist angles of 51.9 and 52.3°, respectively. The chelate rings are not planar, with two chelate rings in each complex possessing boat conformations. Corresponding hexafluorophosphates were also prepared. The results of optical and infrared spectroscopy, magnetic susceptibility, conductance, and electrochemical studies are reported.

Introduction

The chemistry of vanadium(IV) is dominated by the vanadyl ion, VO^{2+} .² Many complexes have been structurally and spectroscopically characterized with square-pyramidal or trigonal-bipyramidal five-coordination or distorted-octahedral six-coordination.² In contrast, only a few non-vanadyl vanadium(IV) species are well-characterized. These include complexes with dithiolenate,³ 2,4-pentanedione benzoylhydrazone,⁴ catecholate,⁵ bis(salicylaldehyde)ethylenediimine,^{6,7} and cage-like hexamine ligands.⁸

Von Dreele and Fay have reported the preparation of $[V(acac)_3][SbCl_6]$ by reaction of $[V(acac)_2Cl_2]$ with $SbCl_5$ in dichloromethane.^{9,10} However, the reported synthesis could not be repeated successfully in this laboratory, but, with acetic acid as solvent, pure products were obtained in excellent yield for the 2,4-pentanedionato and 1-phenyl-1,3-butanedionato complexes. The molecular structures of $[V(acac)_3][SbCl_6]$ and $[V(bzac)_3][SbCl_6] \cdot CH_2Cl_2$ are described and various spectroscopic and physical properties presented.

Experimental Section

Materials. Oxobis(2,4-pentanedionato)vanadium(IV), $[VO(acac)_2]$,¹¹ and oxobis(1-phenyl-1,3-butanedionato)vanadium(IV), $[VO(bzac)_2]$,¹² were prepared by the literature procedures and recrystallized twice from chloroform. Triethylammonium tris(catecholato)vanadate(IV)-acetonitrile, $[Et_3NH]_2[V(cat)_3] \cdot CH_3CN$, was prepared by the method of Cooper and coworkers.⁵ The three complexes gave satisfactory C, H, N, and V analyses. 1-Phenyl-1,3-butanedione was recrystallized twice from ethanol. 2,4-Pentanedione was dried by refluxing over P_4O_{10} for 24 h and distilled under reduced pressure. All solvents were reagent grade. Dichloromethane and acetonitrile were refluxed for at least 24 h with

- (1) (a) University of Sydney. (b) University of Queensland. (c) On leave from the University of Ioannina, Ioannina, Greece.
- (2) Selbin, J. *Coord. Chem. Rev.* **1966**, *1*, 293. Nicholls, D. *Coord. Chem. Rev.* **1966**, *1*, 379. Rice, D. A. *Coord. Chem. Rev.* **1981**, *37*, 61. Rice, D. A. *Coord. Chem. Rev.* **1982**, *45*, 67. Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. Page, E. M. *Coord. Chem. Rev.* **1984**, *57*, 237.
- (3) Stiefel, E. I.; Dori, Z.; Gray, H. B. *J. Am. Chem. Soc.* **1967**, *89*, 3353.
- (4) Diamantis, A. A.; Snow, M. R.; Vanzo, J. A. *J. Chem. Soc., Chem. Commun.* **1976**, 264.
- (5) Cooper, S. P.; Koh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092.
- (6) Pasquali, M.; Marchetti, F.; Floriani, C. *Inorg. Chem.* **1979**, *18*, 2401.
- (7) Seangprasertkij, R.; Riechel, T. L. *Inorg. Chem.* **1986**, *25*, 3121.
- (8) Comba, P.; Engelhardt, L. M.; Harrowfield, J. M.; Lawrance, G. A.; Martin, L. L.; Sargeson, A. M.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 174.

(9) Abbreviations: acac, 2,4-pentanedionato; bzac, 1-phenyl-1,3-butanedionato; cat, catecholate.

(10) Von Dreele, R. B.; Fay, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 7935.

(11) Rowe, R. A.; Jones, M. M. *Inorg. Synth.* **1957**, *5*, 113.

(12) Morgan, G. T.; Moss, H. W. *J. Chem. Soc.* **1913**, 78.

powdered CaH₂. Acetic acid was refluxed for 2 h with acetic anhydride¹³ and then with potassium permanganate for 4 h. Ether was dried with LiAlH₄. Thionyl chloride was distilled. All the above distillations were carried out under dried high-purity argon just prior to use. Antimony pentachloride was fractionally distilled under reduced pressure, and the middle fraction was used. Tetraethylammonium perchlorate was purified by recrystallization twice from ethanol.

Analyses for C, H, and N were carried out by the University of Queensland's microanalytical service and P and F analyses by Amdel. Chloride analyses were carried out by potentiometric titration and V and Sb analyses by atomic absorption.

For the synthesis of the complexes, all operations were carried out under dry, oxygen-free dinitrogen in a VAC Dri-Lab, Model MO40-1.

Tris(1-phenyl-1,3-butanedionato)vanadium(IV) Hexachloroantimonate(V). Antimony pentachloride (1.34 g, 0.0045 mol) in acetic acid (5 mL) was added dropwise with stirring to a suspension of dichlorobis(1-phenyl-1,3-butanedionato)vanadium(IV) (2.00 g, 0.0045 mol) in acetic acid (100 mL). During the addition, the solution's color changed from light blue-green to deep green. As both the starting material and the product had limited solubility, the stirring was continued for about 5 h to ensure completion of the reaction. The black precipitate was filtered off, washed with three 10-mL portions of ether, and dried in vacuo over P₄O₁₀; yield 2.40 g (92%). Anal. Calcd for C₃₀H₂₇Cl₆O₆SbV: C, 41.5; H, 3.1; Cl, 24.5; Sb, 14.0; V, 5.9. Found: C, 41.4; H, 3.2; Cl, 24.2; Sb, 14.0; V, 5.8.

Crystals for X-ray diffraction studies were prepared by dissolving the complex in dichloromethane, by adding 3 volumes of acetic acid, and by allowing spontaneous evaporation of dichloromethane for 12 h at 25 °C. A molecule of dichloromethane was incorporated in the crystal lattice.

Tris(1-phenyl-1,3-butanedionato)vanadium(IV) Hexafluorophosphate(V). 1-Phenyl-1,3-butanedione (0.83 g, 0.0051 mol) was added to a suspension of dichlorobis(1-phenyl-1,3-butanedionato)vanadium(IV) (2.00 g, 0.0045 mol) in acetonitrile (50 mL). When silver hexafluorophosphate (2.42 g, 0.0096 mol) in acetonitrile (20 mL) was added dropwise with stirring, the solution cleared and changed color from pale green to a deep green-black and a white precipitate of silver chloride formed. After the solution was stirred for a further 5 h at room temperature, the silver chloride was removed by filtration. The filtrate was allowed to evaporate to dryness. When the gum was dissolved in dichloromethane (25 mL), ether (25 mL) was added slowly with stirring, and the solution was frozen for 12 h at -20 °C, black crystals were formed. These crystals were recrystallized by the same procedure as above to give the pure product, yield 1.60 g (52%). Anal. Calcd for C₃₀H₂₇F₆O₆PV: C, 53.0; H, 4.0; F, 16.8; P, 4.6; V, 7.5. Found: C, 52.9; H, 4.1; F, 16.5; P, 4.5; V, 7.5.

Dichlorobis(1-phenyl-1,3-butanedionato)vanadium(IV). The dichloro compound was prepared by a modification of the method of Floriani.⁶ Thionyl chloride (11.92 g, 0.100 mol) was added to a suspension of oxobis(1-phenyl-1,3-butanedionato)vanadium(IV) (26.00 g, 0.067 mol) in dichloromethane (130 mL) with vigorous magnetic stirring. Upon addition of the thionyl chloride, the light blue-green color of the solution changed to green-black. The solution was stirred for about 4 h and then filtered to yield a black solid, which was washed with three 30-mL portions of ether and dried in vacuo over P₄O₁₀; yield 28.50 g (96%). Anal. Calcd for C₂₀H₁₈Cl₂O₄V: C, 54.1; H, 4.1; Cl, 16.0; V, 11.5. Found: C, 54.1; H, 4.1; Cl, 15.9; V, 11.6.

Tris(2,4-pentanedionato)vanadium(IV) Hexachloroantimonate(V). The complex was prepared by the same method as for the above tris complex; yield 80%. Anal. Calcd for C₁₅H₂₁Cl₆O₆SbV: C, 26.4; H, 3.1; Cl, 31.2; Sb, 17.8; V, 7.5. Found: C, 26.0; H, 3.1; Cl, 31.1; Sb, 17.8; V, 7.7.

Tris(2,4-pentanedionato)vanadium(IV) Hexafluorophosphate(V). The hexafluorophosphate salt was prepared by the same method as above for the salt with this anion; yield 30%. Anal. Calcd for C₁₅H₂₁F₆O₆PV: C, 36.5; H, 4.2; F, 23.1; P, 6.3; V, 10.3. Found: C, 36.2; H, 4.1; F, 23.1; P, 6.3; V, 10.4.

Dichlorobis(2,4-pentanedionato)vanadium(IV). The dichloro complex was prepared by the same method as for [V(bzac)₂Cl₂]; yield 95%. It crystallized with 0.25 molecule of dichloromethane per complex. Anal. Calcd for C_{10.25}H_{14.5}Cl_{2.5}O₄V: C, 36.1; H, 4.3; V, 14.9. Found: C, 36.0; H, 4.3; V, 14.8.

Physical Measurements. Infrared spectra were obtained with the compounds dispersed in KBr pellets and in Nujol with CsI windows by using a Mattson Sirius 100 FT-IR spectrophotometer with polystyrene as frequency calibrant. UV-visible spectra were measured with solutions in septum-sealed quartz cuvettes with a Hewlett-Packard 8450A spec-

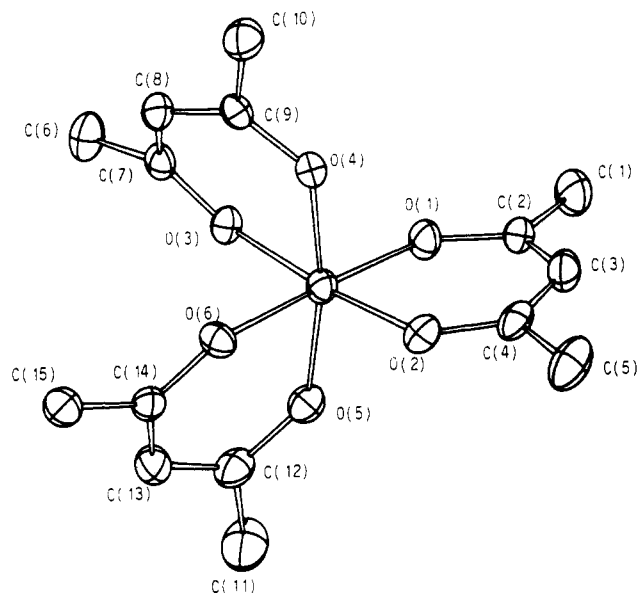


Figure 1. View of the [V(acac)₃]⁺ cation down the "C₃" axis giving the atom numbering.

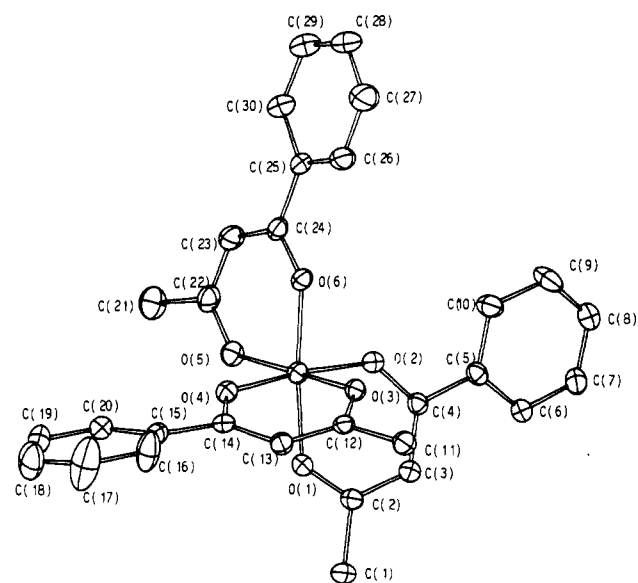


Figure 2. View of the [V(bzac)₃]⁺ cation giving the atom numbering.

trophotometer. Sample preparation was carried out in the Dri-Lab. Electrochemical experiments were performed with a Metrohm E506 Polarecord, E612 VA-scanner apparatus connected to a Houston 2000 XY recorder. All cyclic voltammetry was undertaken with the electrochemical cell in a N₂-filled Dri-Lab. The working electrode was a platinum disk, and a platinum wire was used as the auxiliary electrode. The reference was a calomel electrode in tetraethylammonium perchlorate saturated dichloromethane. Dichloromethane solutions of the complexes (10⁻³ M) were 0.1 M in tetraethylammonium perchlorate. All potentials are given relative to the normal hydrogen electrode with ferrocene (+0.400 V vs NHE) as a standard.¹⁴ Magnetic moments were measured at room temperature by the Gouy method with tris(ethylenediamine)nickel(II) thiosulfate as the susceptibility standard. Diamagnetic corrections were made by using Pascal's constants. Conductivity measurements were carried out with a TPS Model 3102 bridge and a cell of standard constant, which was calibrated with a 0.0200 M KCl solution.

X-ray Diffraction Data Collection, Structure Solution, and Refinement. Crystals were mounted in thin-walled quartz capillaries to preclude decomposition. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. The crystallographic data are summarized in Table I. Data were reduced, and Lorentz, polarization, and decomposition corrections

(13) Because acetic anhydride was used as drying agent, the acetic acid contained traces of the anhydride, but this did not prove to be a problem for the preparations.

Table I. Crystallographic Data

formula	[V(acac) ₃][SbCl ₆]	[V(bzac) ₃][SbCl ₆] CH ₂ Cl ₂
fw	682.7	953.9
space group	<i>Pcab</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	14.167 (9)	12.070 (6)
<i>b</i> , Å	18.774 (3)	14.110 (4)
<i>c</i> , Å	19.670 (6)	15.792 (2)
α , deg		66.46 (2)
β , deg		69.08 (2)
γ , deg		65.90 (2)
vol, Å ³	5231.7	2189.5
<i>Z</i>	8	2
λ	Mo K α (0.71073 Å)	Mo K α (0.71073 Å)
μ , cm ⁻¹	19.67	13.00
cryst color	black	black
cryst habit	needles	needles
cryst size, mm	0.55 × 0.13 × 0.13	0.50 × 0.28 × 0.20
faces	±100, ±012, ±0 $\bar{1}$ 2	100, $\bar{1}0\bar{1}$, ±010, ±001
<i>F</i> (000), electrons	2680	946
transmission	0.83–0.70	0.80–0.65
factor range		
cryst degradation	10%	<2%
scan mode	ω - θ	ω - θ
2 θ range, deg	1.0–50.0	1.0–50.0
range of <i>hkl</i>	0 ≤ <i>h</i> ≤ 16, 0 ≤ <i>k</i> ≤ 22, 0 ≤ <i>l</i> ≤ 23	0 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ +16, -18 ≤ <i>l</i> ≤ +18
rflns collected	3908	6742
rflns used (<i>I</i> > 2.5 σ (<i>I</i>))	2903	5094
no. of variables	335	482
final <i>R</i> , %	2.9	4.8
final <i>R</i> _w , %	3.3	5.6
<i>w</i> [= <i>g</i> /($\sigma^2 F_o$ + <i>kF</i> _o ²)], <i>g</i>	1.11, 0.000 58	3.84, 0.000 38
shift/esd	<0.5	<0.5
residual extreme in final diff map, e Å ⁻³	+0.4, -0.6	±0.6

Table II. Positional Parameters (×10⁴) for [V(acac)₃][SbCl₆]

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{mean} ^a , Å ²
V(1)	798 (1)	2912 (1)	-318 (1)	0.051
O(1)	1991 (2)	3238 (2)	16 (2)	0.062
O(2)	424 (2)	2829 (2)	613 (2)	0.062
O(3)	1198 (2)	3097 (2)	-1236 (2)	0.053
O(4)	213 (2)	3817 (2)	-365 (2)	0.055
O(5)	1253 (2)	1979 (2)	-427 (2)	0.064
O(6)	-382 (2)	2536 (2)	-646 (2)	0.056
C(1)	3276 (6)	3633 (4)	655 (5)	0.094
C(2)	2278 (4)	3395 (3)	617 (3)	0.062
C(3)	1719 (4)	3320 (3)	1179 (3)	0.071
C(4)	829 (4)	3026 (3)	1161 (3)	0.063
C(5)	277 (7)	2918 (5)	1799 (4)	0.098
C(6)	1226 (5)	3456 (4)	-2385 (3)	0.077
C(7)	806 (3)	3489 (3)	-1686 (2)	0.053
C(8)	80 (3)	3957 (2)	-1540 (2)	0.055
C(9)	-145 (3)	4145 (2)	-883 (2)	0.053
C(10)	-777 (5)	4767 (4)	-727 (4)	0.080
C(11)	1593 (7)	816 (4)	-810 (4)	0.116
C(12)	944 (4)	1445 (3)	-779 (3)	0.073
C(13)	98 (4)	1457 (3)	-1107 (3)	0.073
C(14)	-556 (3)	1989 (2)	-1013 (2)	0.055
C(15)	-1507 (4)	1967 (4)	-1328 (3)	0.072
Sb(1)	2317 (1)	693 (1)	1658 (1)	0.055
Cl(1)	2608 (1)	4766 (1)	4120 (1)	0.070
Cl(2)	1634 (1)	4849 (1)	2585 (1)	0.092
Cl(3)	3800 (1)	5490 (1)	2833 (1)	0.089
Cl(4)	812 (1)	5885 (1)	3815 (1)	0.103
Cl(5)	2981 (1)	6512 (1)	4107 (1)	0.092
Cl(6)	2043 (2)	6604 (1)	2543 (1)	0.104

$$^a U_{\text{mean}} = (U_{11}U_{22}U_{33})^{1/3}.$$

were applied by using a local data reduction program. Both structures were solved by conventional Patterson and Fourier synthesis techniques and were refined by full-matrix least-squares analysis with SHELX.¹⁵

Table III. Positional Parameters (×10⁴) for [V(bzac)₃][SbCl₆]-CH₂Cl₂

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{mean} ^a , Å ²
V(1)	8141 (1)	2439 (1)	7046 (1)	0.071
O(1)	7722 (3)	3193 (3)	7956 (2)	0.077
O(2)	7449 (3)	3837 (3)	6245 (2)	0.074
O(3)	6508 (3)	2255 (3)	7527 (2)	0.076
O(4)	8662 (3)	1085 (3)	7960 (2)	0.074
O(5)	9830 (3)	2451 (3)	6625 (3)	0.088
O(6)	8496 (3)	1882 (3)	6032 (2)	0.075
C(1)	6586 (7)	4314 (6)	8956 (4)	0.111
C(2)	6897 (5)	4097 (5)	8029 (4)	0.081
C(3)	6329 (5)	4850 (5)	7314 (4)	0.079
C(4)	6666 (4)	4723 (4)	6428 (4)	0.069
C(5)	6176 (5)	5582 (4)	5618 (4)	0.076
C(6)	5570 (5)	6649 (5)	5631 (4)	0.087
C(7)	5144 (6)	7459 (6)	4853 (5)	0.097
C(8)	5257 (6)	7209 (6)	4090 (5)	0.106
C(9)	5806 (8)	6175 (7)	4065 (5)	0.129
C(10)	6315 (7)	5331 (5)	4814 (4)	0.103
C(11)	4665 (5)	1924 (6)	8594 (4)	0.097
C(12)	6058 (4)	1675 (5)	8340 (3)	0.076
C(13)	6775 (5)	861 (5)	8953 (4)	0.078
C(14)	8063 (5)	537 (4)	8727 (3)	0.072
C(15)	8827 (5)	-432 (5)	9306 (4)	0.076
C(16)	8338 (7)	-1205 (6)	9981 (6)	0.125
C(17)	9077 (11)	-2064 (9)	10529 (2)	0.173
C(18)	10269 (10)	-2197 (8)	10441 (7)	0.138
C(19)	10775 (7)	-1471 (7)	9733 (6)	0.116
C(20)	10071 (6)	-567 (5)	9171 (4)	0.089
C(21)	11958 (6)	2224 (7)	5853 (6)	0.132
C(22)	10688 (5)	2187 (5)	5930 (5)	0.091
C(23)	10518 (6)	1900 (6)	5264 (5)	0.105
C(24)	9426 (5)	1754 (4)	5322 (4)	0.070
C(25)	9264 (5)	1460 (5)	4600 (4)	0.080
C(26)	10174 (7)	1369 (5)	3777 (4)	0.104
C(27)	9981 (8)	1100 (7)	3104 (6)	0.127
C(28)	8920 (10)	920 (8)	3252 (6)	0.157
C(29)	8018 (8)	944 (9)	4083 (7)	0.167
C(30)	8187 (6)	1252 (7)	4736 (5)	0.122
Sb(1)	4720 (1)	1395 (1)	2315 (1)	0.084
Cl(1)	5931 (2)	2515 (2)	1996 (2)	0.128
Cl(2)	6526 (2)	70 (2)	1797 (2)	0.140
Cl(3)	2933 (2)	2747 (2)	2803 (2)	0.112
Cl(4)	3517 (2)	271 (2)	2672 (2)	0.150
Cl(5)	4943 (3)	629 (2)	3884 (2)	0.184
Cl(6)	4496 (4)	2194 (4)	768 (2)	0.190
Cl(1')	3461 (23)	922 (21)	1780 (19)	0.159
Cl(2')	4009 (34)	455 (27)	3752 (24)	0.210
Cl(3')	6035 (18)	2027 (16)	2467 (14)	0.132
Cl(4')	6477 (17)	-160 (14)	2428 (13)	0.121
Cl(5')	5271 (41)	2720 (37)	839 (32)	0.271
Cl(6')	3066 (32)	2885 (27)	2275 (22)	0.166
C(31)	210 (20)	4855 (17)	3793 (16)	0.201
Cl(7)	-216 (14)	5132 (13)	2847 (12)	0.325
Cl(8)	0 (1)	5000 (1)	5000 (1)	0.401
C(32)	-2530 (40)	4417 (32)	1915 (33)	0.214
Cl(9)	7360 (17)	4886 (14)	958 (14)	0.349
Cl(10)	8728 (31)	4223 (26)	1614 (23)	0.540
Cl(7')	8674 (28)	4896 (23)	2181 (21)	0.090
Cl(8')	-2593 (21)	3952 (18)	2710 (17)	0.090
Cl(9')	-887 (37)	4783 (32)	416 (29)	0.090
Cl(10')	-774 (24)	4459 (20)	2793 (19)	0.090
Cl(11)	-42 (38)	4732 (32)	2135 (30)	0.090
Cl(12)	-1756 (26)	5385 (22)	-31 (19)	0.090
Cl(13)	-1510 (17)	3412 (15)	1562 (12)	0.090

$$^a U_{\text{mean}} = (U_{11}U_{22}U_{33})^{1/3}.$$

Scattering factors and anomalous dispersion corrections for V and Sb were taken from ref 16 and for Cl, O, C, and H from the SHELX data. Absorption correction was by numerical integration.¹⁷ Non-hydrogen

- (15) Sheldrick, G. M. "SHELX-76, A Program for X-ray Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.
- (16) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.
- (17) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1985**, *18*, 1035.

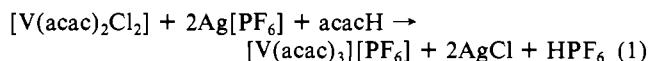
Table IV. Interatomic Distances (Å) and Angles (deg) Relevant to the Vanadium Coordination Sphere in [V(acac)₃][SbCl₆] and [V(bzac)₃][SbCl₆]-CH₂Cl₂

[V(acac) ₃][SbCl ₆]			
O(1)-V(1)	1.914 (2)	O(2)-V(1)	1.917 (2)
O(3)-V(1)	1.924 (2)	O(4)-V(1)	1.894 (2)
O(5)-V(1)	1.878 (2)	O(6)-V(1)	1.927 (2)
O(2)-V(1)-O(1)	86.6 (1)	O(3)-V(1)-O(1)	90.3 (1)
O(3)-V(1)-O(2)	174.1 (1)	O(4)-V(1)-O(1)	96.7 (1)
O(4)-V(1)-O(2)	89.9 (1)	O(4)-V(1)-O(3)	85.5 (1)
O(5)-V(1)-O(1)	92.0 (1)	O(5)-V(1)-O(2)	97.4 (1)
O(5)-V(1)-O(3)	87.7 (1)	O(5)-V(1)-O(4)	169.0 (1)
O(6)-V(1)-O(1)	177.2 (1)	O(6)-V(1)-O(2)	92.8 (1)
O(6)-V(1)-O(3)	90.5 (1)	O(6)-V(1)-O(4)	86.1 (1)
O(6)-V(1)-O(5)	85.4 (1)		
[V(bzac) ₃][SbCl ₆]-CH ₂ Cl ₂			
O(1)-V(1)	1.927 (5)	O(2)-V(1)	1.898 (3)
O(3)-V(1)	1.928 (4)	O(4)-V(1)	1.896 (3)
O(5)-V(1)	1.910 (4)	O(6)-V(1)	1.899 (5)
O(2)-V(1)-O(1)	84.9 (2)	O(3)-V(1)-O(1)	89.4 (2)
O(3)-V(1)-O(2)	88.9 (2)	O(4)-V(1)-O(1)	90.4 (2)
O(4)-V(1)-O(2)	173.2 (1)	O(4)-V(1)-O(3)	86.1 (1)
O(5)-V(1)-O(1)	93.1 (2)	O(5)-V(1)-O(2)	97.1 (2)
O(5)-V(1)-O(3)	173.7 (2)	O(5)-V(1)-O(4)	88.1 (2)
O(6)-V(1)-O(1)	172.4 (1)	O(6)-V(1)-O(2)	87.6 (2)
O(6)-V(1)-O(3)	91.5 (2)	O(6)-V(1)-O(4)	97.1 (2)
O(6)-V(1)-O(5)	86.8 (2)		

atom coordinates are listed in Tables II and III. The atomic nomenclature is defined in Figures 1 and 2.¹⁸

Results and Discussion

Syntheses. The choice of acetic acid as the solvent for the reaction of [V(acac)₂Cl₂] with excess SbCl₅ to yield [V(acac)₃][SbCl₆] was based on its use in the preparation of [Ti(acac)₃][SbCl₆].¹⁹ It gave a high yield of pure product. For the electrochemical studies [V(β-diketonato)₃][PF₆] was prepared by the reaction



Structures. Both structures consist of cationic vanadium(IV) complexes and hexachloroantimonate(V) anions and, in the case of the 1-phenyl-1,3-butanedionato complex, there is also disordered solvent. Bond lengths and angles for the coordination spheres are given in Table IV. There are no contacts between the molecules significantly shorter than the van der Waals radii sum. The [SbCl₆]⁻ anions are regular octahedra (average Sb-Cl 2.352 Å).

The average V-O bond length in both structures is 1.909 Å, slightly shorter than that for [V(cat)₃]²⁻, 1.942 Å,⁵ and is 0.07 Å shorter than the value reported for [V(acac)₃], 1.980 Å,²⁰ a reduction also observed for the corresponding catecholato complexes.⁵ The VO₆ units in [V(acac)₃]⁺ and [V(cat)₃]²⁻ show distinct tetragonal distortions. In the former complex V-O_{av} values for the three axes of the octahedron are 1.886 ± 0.008, 1.921 ± 0.004, and 1.921 ± 0.007 Å, whereas in the latter the values are 1.966 ± 0.005, 1.923 ± 0.002, and 1.937 ± 0.007 Å.⁵ For the catecholato complex, the elongation results from hydrogen bonding to the donor oxygens by the triethylammonium cations. In the acetylacetonato complex, the cause of the compression is not clear. For [V(bzac)₃]⁺ a similar but reduced distortion is observed: 1.897 ± 0.001, 1.919 ± 0.009, and 1.913 ± 0.014 Å. The tetragonal distortion is attenuated by the influence of the three meridional phenyl groups to reduce their adjacent V-O bonds relative to those adjacent to the methyl groups as a consequence of delocalization from the phenyl group into the chelate ring.²¹

The other bond lengths within the 2,4-pentanedionato chelate rings also show some differences from those reported for [V(acac)₃]. The average C-O distance is 1.284 Å, significantly longer than the 1.259 Å in [V(acac)₃],²⁰ indicative of a stronger V-O interaction in the present structure. The intraring C-C carbon bond and C-Me carbon bond distances, 1.374 and 1.493 Å, are slightly shorter than those in the vanadium(III) analogue.

The trigonal twist angles of 51.9 and 52.3° for [V(acac)₃]⁺ and [V(bzac)₃]⁺, respectively, can be compared with the idealized octahedron and trigonal prism values of 60 and 0°, respectively, with the values for other tris(2,4-pentanedionato)metal complexes that range from 47.4 to 67.9°²² and with the value of 41.8° for the closely related complex [Et₃NH]₂[V(cat)₃]-CH₃CN.⁵ A comparison of the structures of [V(acac)₃]⁺ and [V(acac)₃],²⁰ and of [V(cat)₃]²⁻⁵ and [V(cat)₃]³⁻,⁵ shows that for both ligands the +IV oxidation state has a twist angle approximately 4° less than that for the +III state.

The O--O bite distances for the bidentate ligands were found to be 2.722 and 2.724 Å for [V(acac)₃]⁺ and [V(bzac)₃]⁺, respectively. With use of Kepert's model,²³ the above twist angles for these complexes correspond to a bite of 2.62 Å. Avdeef and Fackler's relationship^{22,24} between the ratio of the bite to the M-L bond length and the twist angle would predict a bite of 2.52 Å.

Least-squares planes through the five carbon atoms and two oxygen atoms of the ligand in [V(acac)₃]⁺ show deviations of up to 0.21 Å from planarity. The vanadium atom lies between 0.11 and 0.42 Å out of these planes. For [V(bzac)₃]⁺ least-squares planes through the five carbon and two oxygen atoms again show significant deviations from planarity (up to 0.10 Å) with the vanadium atom 0.08–0.39 Å out of plane. The benzene rings are all rotated slightly with respect to these planes, resulting in deviations of carbons up to 0.51 Å.

The extent of the distortions from planarity of the chelate rings can also be evaluated by the distances of the chelate ring carbons from the OVO plane for each ring (Å). [V(acac)₃]⁺: O(1)V(1)O(2), C(2) 0.122, C(3) 0.236, C(4) 0.139; O(3)V(1)O(4), C(7) 0.455, C(8) 0.841, C(9) 0.514; O(5)V(1)O(6), C(12) 0.316, C(13) 0.602, C(14) 0.391. [V(bzac)₃]⁺: O(1)V(1)O(2), C(2) -0.402, C(3) -0.632, C(4) -0.361; O(3)V(1)O(4), C(12) -0.387, C(13) -0.592, C(14) -0.314; O(5)V(1)O(6), C(22) 0.020, C(23) 0.155, C(24) 0.147. The dihedral angles between the OVO and OCCO planes for the six chelate rings are 18.5, 17.2, 4.6, 6.9, 24.5, and 17.4°.

Two of the three chelate rings in [V(acac)₃]⁺ are markedly distorted away from planarity with boat conformations. Marked distortions have also been reported for [Fe(acac)₃],²⁵ [Sc(acac)₃],²⁶ and [V(acac)₃].²⁰ These four complexes have trigonal twist angles less than 60°, whereas [Mn(acac)₃],²⁷ [Cr(acac)₃],²⁸ [Al(acac)₃],²⁹ and [Co(acac)₃]³⁰ which have more planar chelate rings, have twist angles between 60 and 70°. The OVO angles for the chelate rings have the ranges 80–90 and 90–100° for these two sets of metals.

UV-Visible Spectra. The electronic absorption spectra of [V(acac)₃]⁺, [V(bzac)₃]⁺, and [V(cat)₃]²⁻ are given in Figure 3 for acetonitrile and dichloromethane solutions. Intense absorptions at 562 nm (ε 5200) and 351 nm (ε 4400) in dichloromethane and at 562 nm (ε 4800) and 348 nm (ε 4600) in acetonitrile give [V(acac)₃]⁺ a deep violet color in solution. The deep green [V(bzac)₃]⁺ solutions absorb at 596 nm (CH₂Cl₂, ε 6600; CH₃CN, ε 5000). For (β-diketonato)vanadium(IV) complexes, including [V(acac)₃]⁺, Von Dreele and Fay assigned bands at 660–550 nm to diketonate (π) → metal (d) charge transfer and bands at about

(18) Figures were drawn with ORTEP (Johnson, C. K. "ORTEP, A Thermal Ellipsoid Plotting Program"; Oak Ridge National Laboratory: Oak Ridge, TN, 1965).

(19) Cox, M.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1964**, 6113.

(20) Morosin, B.; Montgomery, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 1354.

(21) Hon, P. K.; Pfluger, C. E.; Belford, R. L. *Inorg. Chem.* **1967**, *6*, 730.

(22) Avdeef, A.; Fackler, J. P. *Inorg. Chem.* **1975**, *14*, 2002.

(23) Kepert, D. L. *Inorg. Chem.* **1972**, *11*, 1561. Bite and twist angles used here are twice the parameters used by Kepert.

(24) Avdeef, A.; Costamagna, J.; Fackler, J. P. *Inorg. Chem.* **1974**, *13*, 1854.

(25) Iball, J.; Morgan, C. H. *Acta Crystallogr.* **1967**, *23*, 239.

(26) Anderson, T. J.; Neuman, M. A.; Melson, G. A. *Inorg. Chem.* **1973**, *12*, 927.

(27) Morosin, B.; Brathovde, J. R. *Acta Crystallogr.* **1964**, *17*, 705.

(28) Morosin, B. *Acta Crystallogr.* **1965**, *19*, 131.

(29) Hon, P. K.; Pfluger, C. E. *J. Coord. Chem.* **1973**, *3*, 67.

(30) Kruger, G. J.; Reynhardt, E. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 822.

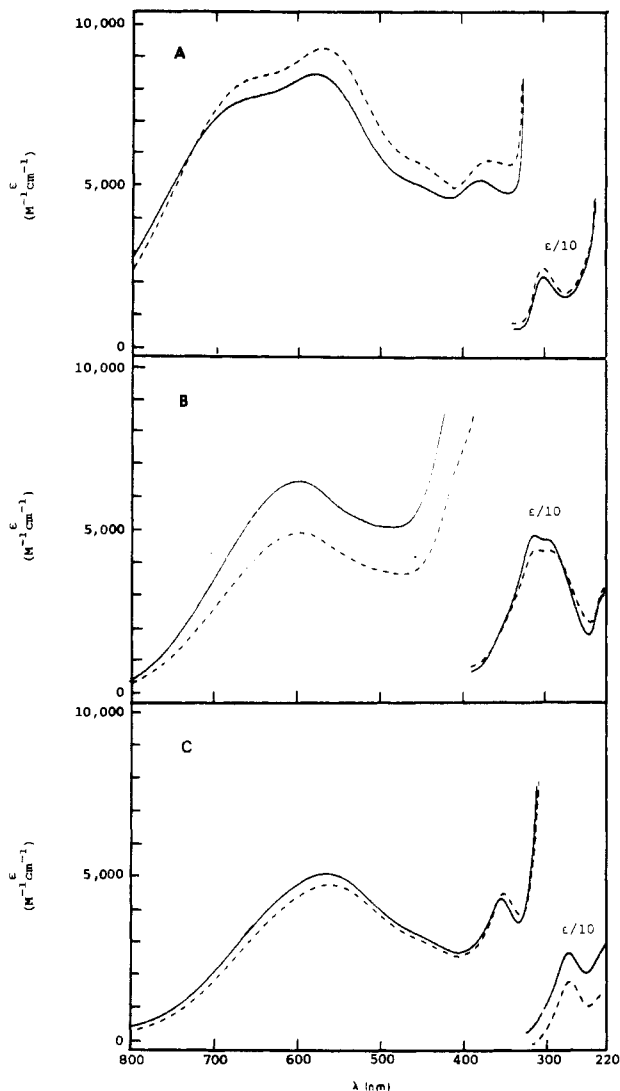


Figure 3. Optical spectra of (A) $[\text{Et}_3\text{NH}]_2[\text{V}(\text{cat})_3]\cdot\text{CH}_3\text{CN}$, (B) $[\text{V}(\text{bzac})_3][\text{SbCl}_6]$, and (C) $[\text{V}(\text{acac})_3][\text{SbCl}_6]$ in CH_2Cl_2 (—) and CH_3CN (---).

350 nm to metal ($d \rightarrow$ diketonate (π^*) charge transfer.¹⁰ In the dichloromethane spectrum of $[\text{V}(\text{acac})_3]^+$ (Figure 3C) there is a shoulder at about 650 nm, a peak at 562 nm, a shoulder at about 450 nm, and a peak at 351 nm, in positions very similar to those of the bands observed for $[\text{V}(\text{cat})_3]^{2-}$. For the latter complex, Raymond and co-workers had also assigned the first two of these bands to ligand-to-metal charge transfer.⁵

The ligand $\pi \rightarrow \pi^*$ transitions occur at 270 nm (CH_2Cl_2 , ϵ 28 900; CH_3CN , ϵ 20 800) for $[\text{V}(\text{acac})_3]^+$, at 305 nm (ϵ 49 100) and 291 nm (ϵ 47 800) for $[\text{V}(\text{bzac})_3]^+$ in dichloromethane, and at 303 nm (ϵ 44 700) and 288 nm (ϵ 29 000) for $[\text{V}(\text{bzac})_3]^+$ in acetonitrile. These extinction coefficients and those given above are in $\text{M}^{-1} \text{cm}^{-1}$. Haigh and Thornton have concluded that, for metal β -diketonates, if the $\pi \rightarrow \pi^*$ transition for the 2,4-pentanedionato complex is at an energy higher than that for the corresponding 1-phenyl-1,3-butanedionato complex, the $d\pi$ orbitals lie between the π and π^* orbitals.³¹ This order for the $\pi \rightarrow \pi^*$ transition is observed here for $[\text{V}(\text{acac})_3]^+$ and has been observed for $[\text{VO}(\text{acac})_2]$,³¹ and consequently the $d\pi$ orbitals of vanadium(IV) would be between the π and π^* orbitals. This is consistent with the assignment of Von Dreele and Fay.¹⁰

Infrared Spectra. The spectra of $[\text{V}(\text{acac})_3][\text{SbCl}_6]$ and $[\text{V}(\text{bzac})_3][\text{SbCl}_6]$ are typical of β -diketonate complexes³² and are

Table V. Infrared Spectral Data^a (cm^{-1})

$[\text{V}(\text{acac})_3][\text{SbCl}_6]$	$[\text{V}(\text{bzac})_3][\text{SbCl}_6]\cdot\text{CH}_2\text{Cl}_2$
1531 s, 1415 w, 1361 w, 1318 m, 1289 m, 1270 m, 1173 vw, 1030 m, 1021 m, 953 vw, 933 w, 816 w, 807 vw, 788 w, 673 m, 647 vw, 579 vw, 567 vw, 544 vw, 433 m, 420 m, 344 s	1597 vw, 1527 s, 1502 s, 1488 s, 1427 m, 1364 w, 1317 s, 1291 m, 1263 m, 1208 vw, 1183 m, 1161 vw, 1108 m, 1028 w, 1009 vw, 999 m, 965 m, 849 m, 816 vw, 775 m, 704 m, 682 s, 580 m, 562 w, 452 m, 344 s

^a KBr disks.

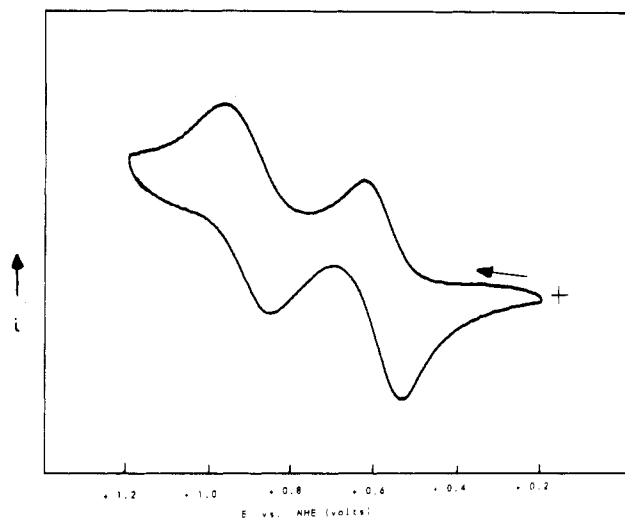


Figure 4. Cyclic voltammogram for the oxidation and reduction of $[\text{V}(\text{bzac})_3][\text{PF}_6]$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M}$ tetraethylammonium perchlorate at a platinum electrode and a scan rate of 50 mV s^{-1} .

summarized in Table V. The main difference between the $[\text{SbCl}_6]^-$ and $[\text{PF}_6]^-$ salts is the presence of a very strong band in the former at 344 cm^{-1} and the presence of a very strong band in the latter at 843 cm^{-1} , each of which is absent in the other salt, and these bands are therefore assignable to the anions. The spectra of the oxobis(β -diketonato)vanadium(IV) and dichlorobis(β -diketonato)vanadium(IV) complexes were measured and found to have $\text{V}=\text{O}^{2+}$ stretches at 999 and 998 cm^{-1} for the symmetric and unsymmetric ligand complexes, respectively, for the former and a $\text{V}-\text{Cl}$ stretch at 359 cm^{-1} for the latter complexes. These are absent in the spectra recorded for the tris complexes. The dichloro compound could only be measured in Nujol because in the KBr pellet the chloride was substituted by bromide.

Conductance Measurements. The molar conductance of the $[\text{V}(\beta\text{-diketonato})_3][\text{SbCl}_6]$ complexes in dichloromethane at 25°C and $1 \times 10^{-3} \text{ M}$ concentration is $60 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, which is characteristic of other tris(β -diketonato) 1:1 electrolytes under the same conditions, for example $[\text{Ti}(\text{acac})_3]\text{I}_3$ ($55 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and $[\text{Si}(\text{acac})_3]\text{Br}$ ($57 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).³³ As expected, the dichloro compounds $[\text{V}(\text{acac})_2\text{Cl}_2]$ and $[\text{V}(\text{bzac})_2\text{Cl}_2]$ are nonelectrolytes with molar conductances of 0.8 and $1.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively. In this solvent, $[\text{Et}_3\text{NH}]_2[\text{V}(\text{cat})_3]\cdot\text{CH}_3\text{CN}$ is also a nonelectrolyte because of strong hydrogen bonding between the counterions with no detectable conductance. In acetonitrile the molar conductances of all complexes are increased possibly due to some dissociation of a coordinated ion or of associated ions ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): $[\text{V}(\text{acac})_3][\text{SbCl}_6]$, 160; $[\text{V}(\text{bzac})_3][\text{SbCl}_6]$, 157; $[\text{V}(\text{acac})_2\text{Cl}_2]$, 37; $[\text{V}(\text{bzac})_2\text{Cl}_2]$, 37; $[\text{Et}_3\text{NH}]_2[\text{V}(\text{cat})_3]\cdot\text{CH}_3\text{CN}$, 81.

Magnetic Behavior. The magnetic moments of $[\text{V}(\text{acac})_3][\text{SbCl}_6]$ and $[\text{V}(\text{bzac})_3][\text{SbCl}_6]$ are 1.73 and $1.74 \mu_{\text{B}}$, respectively, at 25°C in accord with the spin-only value expected for d^1 , $S = 1/2$ systems.

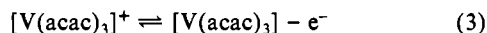
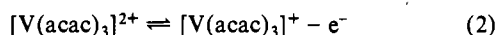
Electrochemistry. Cyclic voltammetric examination of $[\text{V}(\text{bzac})_3][\text{PF}_6]$ in 0.1 M tetraethylammonium perchlorate-di-

(31) Haigh, J. M.; Thornton, D. A. *Helv. Chim. Acta* **1971**, *54*, 2221.

(32) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; pp 249–252.

(33) Fay, R. C.; Lowry, R. N. *Inorg. Chem.* **1970**, *9*, 2048.

chloromethane solution reveals an oxidation at +0.90 V (NHE) (ΔE_p 90 mV, $i_p^f/i_p^r = 1.01$) and a reduction at +0.58 V (NHE) (ΔE_p 80 mV, $i_p^f/i_p^r = 1.01$) (Figure 4). $[V(\text{acac})_3][\text{PF}_6]$ gave almost identical cyclic voltammograms. Dc voltammograms of $[V(\text{bzac})_3]^+$ and $[V(\text{acac})_3]^+$ each gave two waves with a current ratio of 1.01. These data suggest that in both steps the same number of electrons is involved. A blank run with the ligands in the same solution gave no peak in the potential range 0.0 to +1.5 V. The two couples are essentially reversible because the peak-current ratios were unity, and the ΔE_p values were almost independent of scan rate below 500 mV s⁻¹. The electrode reactions are concluded to be

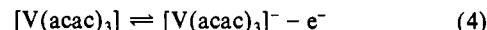


The system used was unable to detect the reduction of $[V(\text{acac})_3]$ to the divalent state.

Boyd and co-workers, who studied $[V(\text{acac})_3]$ in acetone, found a reversible oxidation at 0.94 V (Ag/AgCl, 0.1 M LiCl, acetone) and a reversible reduction at -1.33 V.³⁴ Applying a correction of +0.19 V to convert the potential to the NHE scale³⁵ yields potentials of +1.13 V (NHE) and -1.14 V (NHE), respectively, for presumably reactions 3 and 4. Earlier work in dimethyl

(34) Boyd, P. D. W.; Hope, J.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1986**, 887.

(35) Lawrence, G. A., personal communication, 1987.



sulfoxide (H₂O, 0.01%) obtained potentials of +0.73 and -1.35 V (NHE) for reactions 3 and 4, respectively.^{36,37} Reaction 2 was not observed, with $[VO(\text{acac})_2]$ and $[V(\text{acac})_3]$ both giving on oxidation the same undisclosed vanadium(V) product.

From the above potential data it is seen that $[V(\text{acac})_3]$ is very stable to reduction and oxidation. Although $[V(\text{acac})_3]^+$ is easily reduced, it is stable to disproportionation. In contrast, for the catecholato complexes the +III state is not a stable state, being readily oxidized to the +IV state (in acetonitrile $E_{1/2} = -0.84$;³⁷ in H₂O $E_{1/2} = -0.48$ V (NHE)³⁸), but this oxidation state, although stable to disproportionation, is readily oxidized to the +V state (in acetonitrile $E_{1/2} = -0.015$ V (NHE)³⁷).⁵

Acknowledgment. Financial assistance from the Australian Research Grants Scheme (C.J.H.) is gratefully acknowledged.

Supplementary Material Available: Tables SI-SVIII, listing thermal parameters, hydrogen atom positional and thermal parameters, angles and distances associated with the ligands, and deviations from least-squares planes for $[V(\text{acac})_3][\text{SbCl}_6]$ and $[V(\text{bzac})_3][\text{SbCl}_6] \cdot \text{CH}_2\text{Cl}_2$ (8 pages); Tables SIX and SX, giving calculated and observed structure factors for the two compounds (48 pages). Ordering information is given on any current masthead page.

(36) Nawi, M. A.; Riechel, T. L. *Inorg. Chem.* **1981**, *20*, 1974.

(37) Measurements have been repeated here with ferrocene (0.400 V) as reference to give potentials relative to NHE.

(38) Potentials converted from SCE to NHE scale by addition of +0.24 V for aqueous solution.

Contribution from the Laboratory of Chemistry, Faculty of Education, Kanazawa University, Kanazawa 920, Japan, and the Department of Chemistry, Faculty of Science, Ochanomizu University, Tokyo 112, Japan

Solid-Phase Thermal Square-Planar-to-Octahedral Isomeric Transformation of Nickel(II) Complexes Containing 1,2-Cyclohexanediamines

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New examples of thermal square-planar (low-spin)-to-octahedral (high-spin) isomeric transformations were discovered and studied in the thermal reactions of bis(*dl*- or *meso*-1,2-cyclohexanediamine)nickel(II) complexes, $[\text{Ni}(\text{dl- or } ms\text{-chxn})_2]\text{X}_2$ (X = Cl, Br, NO₃), in the solid phase. These transformations proceeded endothermically and were accompanied by a reversible thermochromism from yellow to violet-blue. Obvious differences in the reactivity between the *dl*-chxn complexes and the *ms*-chxn ones were observed. They indicate that this type of reaction (and the stability of the square-planar species) is strongly dominated by the steric effect of the substituent groups in the coordinated diamines. The enthalpy changes for these endothermic transformations were found to be small (<8 kJ/mol). The activation energies for them were also estimated.

Introduction

Nickel(II) complexes often show the peculiarity that their configuration can be readily converted into a different one by a change in their chemical and physical environments. This structural lability implies that the energy gap between different stereoisomers is small. Many instances of structural isomerism are known,³ and in a few cases two isomers have been found together in one crystalline unit cell.^{4,5}

Accordingly, nickel(II) complexes provide many examples of thermochromism in the solid phase, which is attributed to the change in coordination geometry.⁶⁻¹² In these complexes, small differences in the electronic properties and steric requirements of the ligand are reflected in the structures that they prefer when heated or cooled. However, a systematic knowledge is still lacking as to the factors that decide the preference of certain coordination geometries at different temperatures.

Among several kinds of solid-phase isomeric transformations already studied, the transformations between a square-planar

structure and an octahedral one seem to be of special interest and importance, particularly in relation to the problem of spin

- (1) Kanazawa University.
- (2) Ochanomizu University.
- (3) Lifschitz, I.; Bos, J. G.; Dijkema, K. M. *Z. Anorg. Allg. Chem.* **1939**, *242*, 97.
- (4) Rayner, J. H.; Powell, H. M. *J. Chem. Soc.* **1958**, 3412.
- (5) Nakano, T.; Miyoshi, T.; Iwamoto, T.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1297.
- (6) Bloomquist, D. R.; Willett, R. D. *Coord. Chem. Rev.* **1982**, *47*, 125. In this review, the authors classified the thermochromic changes of Ni(II) complexes into the following five kinds of isomeric transformations according to their origins: dimer to monomer,⁷ square planar to distorted square planar,⁸ tetragonally distorted octahedral to distorted tetrahedral,⁹ octahedral to tetrahedral,¹⁰ and square planar to tetrahedral.^{11,12}
- (7) Laskowski, E. J.; Felthouse, T. R.; Hendrickson, D. N.; Long, G. J. *Inorg. Chem.* **1976**, *15*, 2908.
- (8) Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1974**, *13*, 3019.
- (9) Goedken, V. L.; Vallarino, L. M.; Quagliano, J. V. *Inorg. Chem.* **1971**, *10*, 2682.
- (10) Ferraro, J. R.; Sherren, A. T. *Inorg. Chem.* **1978**, *17*, 2498.
- (11) Sacconi, L.; Paoletti, P.; Cini, R. *J. Am. Chem. Soc.* **1958**, *80*, 3583.
- (12) Clark, H. C.; O'Brien, R. J. *Can. J. Chem.* **1961**, *39*, 1030.

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