

Synthesis and Properties of Tris(dithioacetylacetonato)vanadium(III)

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The reaction of reduced 3,5-dimethyl-1,2-dithiolium iodide with vanadium trichloride leads to the preparation of tris(dithioacetylacetonato)vanadium(III), $[V(\text{SacSac})_3]$. The electrochemical, spectroscopic, and magnetic properties of $[V(\text{SacSac})_3]$ have been measured and compared with those of the tris chelates of vanadium(III) with acetylacetonate, $[V(\text{acac})_3]$, and monothioacetylacetonate, $[V(\text{Sacac})_3]$. All three complexes show one-electron reductions at a platinum electrode in acetone with the ease of reduction being in the order $[V(\text{SacSac})_3] > [V(\text{Sacac})_3] > [V(\text{acac})_3]$. Proton n.m.r. spectra of the tris chelates show increasing delocalisation of the vanadium(III) unpaired electrons to the ligand with increasing sulphur in the ligand $[V(\text{SacSac})_3] > [V(\text{Sacac})_3] > [V(\text{acac})_3]$. Magnetic susceptibility measurements in the range 4.2–300 K show a near Curie law behaviour for $[V(\text{SacSac})_3]$ and a near constant magnetic moment whilst for $[V(\text{acac})_3]$ the 3A ground state of the molecule is split by 8.0 cm^{-1} leading to a decreasing moment with decreasing temperature.

A wide range of complexes of the ligand dithioacetylacetonate, HSacSac (pentane-2,4-dithione, $\text{C}_5\text{H}_8\text{S}_2$) with both divalent and trivalent transition metals has been reported.¹ The synthesis of these compounds has been carried out, using the method of Martin and Stewart,² by the reaction of a solution of the metal ion, acetylacetonate, and HCl in ethanol with hydrogen sulphide at 0°C . Of the trivalent first-row transition metal complexes, $[M^{\text{III}}(\text{SacSac})_3]$, those for $M = \text{Cr}, \text{Fe},$ and Co have been reported.^{3–5} The preparation of $[\text{Cr}(\text{SacSac})_3]$, however, was performed by the chromium(II) chloride reduction of 3,5-dimethyl-1,2-dithiolium iodide to the corresponding dithioacetylacetonate anion.⁵ The reduction of dithiolium salts to the unstable dithioacetylacetonate anion using alkaline tetrahydroborate solution has also been reported as a possible method of complex preparation.⁶

In this work the preparation of the previously unreported tris(dithioacetylacetonato)vanadium(III), $[V(\text{SacSac})_3]$ (**1a**), is reported. A comparative study of donor atom effects on the electrochemical, magnetic, and spectroscopic properties of $[V(\text{SacSac})_3]$ is made with the tris chelates of vanadium(III) with acetylacetonate (Hacac), $[V(\text{acac})_3]$ (**1b**),⁷ and monothioacetylacetonate (HSacac), $[V(\text{Sacac})_3]$ (**1c**).⁸

Experimental

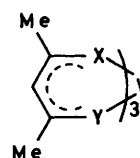
The preparation of all complexes was carried out in a nitrogen-filled glove box using deoxygenated solvents.

$[V(\text{acac})_3]$ (**1b**).—This complex was prepared by literature methods.⁷

3,5-Dimethyl-1,2-dithiolium Iodide.—This was prepared by the method of Hendrickson and Martin.⁹

Monothioacetylacetonate (HSacac).—This was prepared by the methods of both Mayer *et al.*¹⁰ and Duus and Anthosen¹¹ and purified using the lead salt.¹²

$[V(\text{Sacac})_3]$ (**1c**).—Vanadium trichloride (1.5 g) was dissolved in deoxygenated water (150 cm^3). Monothioacetyl-



(1a) $X = Y = S$

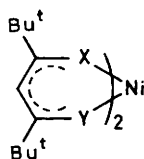
(1b) $X = Y = O$

(1c) $X = S, Y = O$

acetone (3.3 g) in methanol (40 cm^3) and sodium carbonate (1.5 g) were added to the vanadium trichloride solution and the brown mixture stirred for 15 min. Toluene (180 cm^3) was added to the solution and the mixture stirred for a further 1 h. Separation of the toluene layer, reduction in volume to 20 cm^3 , and addition of light petroleum (200 cm^3 ; b.p. $40\text{--}60^\circ\text{C}$) afforded crystals of $[V(\text{Sacac})_3]$ by filtration (Found: C, 45.45; H, 5.35; S, 24.25; V, 12.85. Calc. for $\text{C}_{15}\text{H}_{21}\text{S}_3\text{O}_3\text{V}$: C, 45.90; H, 5.25; S, 24.30; V, 12.75%). The complex is sensitive to atmospheric oxidation, giving the previously reported green vanadyl complex $[\text{VO}(\text{Sacac})_2]$.¹³

$[V(\text{SacSac})_3]$ (**1a**).—Sodium tetrahydroborate (0.3 g) was added cautiously to water (10 cm^3) containing sodium hydroxide (0.88 g) cooled in an ice-bath. On dissolution of the NaBH_4 , methanol (10 cm^3) was added and the resulting solution quickly added dropwise with stirring to freshly recrystallised 3,5-dimethyl-1,2-dithiolium iodide (2.86 g) in methanol (20 cm^3). This solution was added to a solution of vanadium trichloride (1.8 g) in deoxygenated water (50 cm^3). After stirring for 15 min toluene (100 cm^3) was added and the dark toluene layer separated from the aqueous layer. n-Heptane (200 cm^3) was added to the toluene and the mixture left to stand for 12 h. Dark crystals were isolated by filtration and recrystallised from dichloromethane–diethyl ether [Found: C, 40.50; H, 4.75; S, 43.25; V, 11.45%; M (dichloromethane), 450. Calc. for $\text{C}_{15}\text{H}_{21}\text{S}_6\text{V}$: C, 40.50; H, 4.80; S, 43.30; V, 11.20%; M , 445]. I.r. bands (cm^{-1}) at 1 475, 1 369, 1 330, 1 315, 1 157, 1 010, 849, 738, 690, 554, 358. U.v.–visible bands (cm^{-1} ; in

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(2a) X = Y = S

(2b) X = Y = O

(2c) X = S, Y = O

CH_2Cl_2) at 28 450 (ϵ 10 644), 22 967 (ϵ 8 810), 17 191 (ϵ 3 321 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

An alternative method of preparation of (1a) was attempted using an aqueous solution of vanadium(II) obtained by reduction of a vanadium(IV) solution using a Jones reductor¹⁴ in a manner similar to that used for $[\text{Cr}(\text{SacSac})_3]$.⁵ However, on addition of the vanadium(II) solution to a solution of the dithiolium salt red crystals of the zinc dithioacetylacetonate complex¹⁵ were found, the zinc ions being in the solution from the Jones reductor.

Instrumental.—Electrochemical measurements were performed in acetone, with 0.1 mol dm^{-3} $[\text{NET}_4][\text{ClO}_4]$, using PAR174 instrumentation. A three-electrode, iR compensated system with platinum auxiliary and working electrodes was used for the voltammetry measurements with a Ag–AgCl (acetone, 0.1 mol dm^{-3} LiCl) reference electrode.¹⁶

Electronic spectra of the complexes were recorded on a Cary 14 spectrophotometer. Variable-temperature magnetic susceptibilities were measured on a modified Oxford Instruments Faraday balance¹⁷ between 4.2 and 300 K. Diamagnetic corrections to the susceptibility were made using Pascal's constants.¹⁸ Proton n.m.r. spectra of the paramagnetic complexes were recorded on a JEOL C60-HL spectrometer.

Results and Discussion

The vanadium(III) tris chelate of dithioacetylacetonate, $[\text{V}(\text{SacSac})_3]$ (1a), was prepared by the reaction of an aqueous alkaline solution of 3,5-dimethyl-1,2-dithiolium iodide, reduced with sodium tetrahydroborate, with an aqueous solution of vanadium(III) chloride. The complex is a dark crystalline solid with a room-temperature magnetic moment (μ_{eff}) of 2.79 corresponding to a d^2 vanadium(III) complex with a triplet ($S = 1$) ground state. The i.r. and u.v.-visible spectra are very similar to those previously reported for other octahedral $[\text{M}^{\text{III}}(\text{SacSac})_3]$ ($M = \text{Cr}$ or Fe) complexes.^{4,5,19}

The d.c. and a.c. cyclic voltammograms of (1a) in acetone solution at platinum disc electrodes show three redox processes. An irreversible oxidation at +0.77 V, a reversible reduction at -0.45 V ($i_p^f/i_p^r = 1.00$, $\Delta E_p = 57$ mV)* and an irreversible reduction at -1.19 V ($i_p^f/i_p^r = 0.98$, $\Delta E_p = 70$ mV). This behaviour is similar to that found for the analogous $[\text{Cr}^{\text{III}}(\text{SacSac})_3]$.⁵ In contrast, the d.c. and a.c. cyclic voltammograms of (1c) show both a reversible oxidation at +0.82 V ($i_p^f/i_p^r = 1.00$, $\Delta E_p = 70$ mV) and a reduction at -0.84 V ($i_p^f/i_p^r = 0.83$, $\Delta E_p = 68$ mV)* whilst those of (1b) show a reversible oxidation at +0.94 V ($i_p^f/i_p^r = 0.98$, $\Delta E_p = 67$ mV)* and a reversible reduction at -1.33 V ($i_p^f/i_p^r = 1.01$, $\Delta E_p = 70$ mV) as reported previously by Nawi and Riechel.²⁰ The ease of reduction of these complexes increases monotonically with the increasing number of sulphur donor ligands.

* D.c. cyclic voltammograms recorded at 200 mV s^{-1} .

Table. Isotropic shifts (p.p.m.) for (1a)–(1c) at 292 K

Complex	$\Delta\nu_{\text{A}}(\text{CH})$	$\Delta\nu_{\text{B}}(\text{CH}_3)$	$\Delta\nu_{\text{C}}(\text{CH}_3)$
$[\text{V}(\text{acac})_3]^a$	36.1	45.6	—
$[\text{V}(\text{Sacac})_3]^b$	62.6	58.1	56.4
$[\text{V}(\text{SacSac})_3]^{c,d}$	101.6	98.4	—

^a Relative to $[\text{Co}(\text{acac})_3]$; $\delta(\text{CH})$ 5.29, $\delta(\text{CH}_3)$ 1.91 p.p.m.; ref. 4.

^b Relative to $[\text{Co}(\text{Sacac})_3]$; $\delta(\text{CH})$ 6.0, $\delta(\text{CH}_3)$ 1.97, $\delta(\text{CH}_3)$ 1.85 p.p.m.; ref. 4. ^c Temperature dependence of contact shifts $\Delta\nu_{\text{A}}, \Delta\nu_{\text{B}}, \Delta\nu_{\text{C}}$ (p.p.m.) = $(0.38 \times 10^5)/T - 29.2$, $\Delta\nu_{\text{B}}$ (p.p.m.) = $(0.34 \times 10^5)/T - 18.0$. ^d Relative to $[\text{Co}(\text{SacSac})_3]$; $\delta(\text{CH})$ 6.85, $\delta(\text{CH}_3)$ 2.32 p.p.m.; ref. 4.

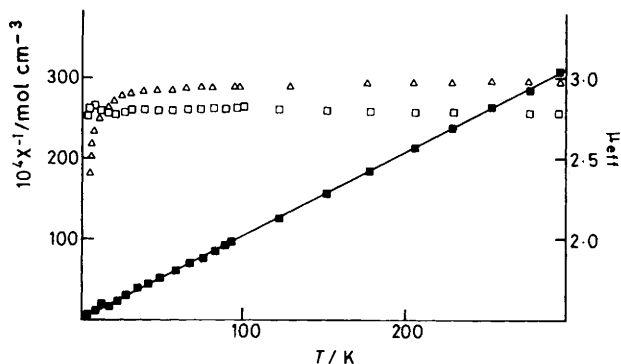


Figure. Temperature variation of inverse molar susceptibility (■), magnetic moment of $[\text{V}(\text{SacSac})_3]$ (□), and magnetic moment of $[\text{V}(\text{acac})_3]$ (△)

The increasing ease of reduction with increasing number of sulphur donor atoms has also been observed in the corresponding series of nickel(II) complexes²¹ (2a)–(2c), although the variation is less (-1.058 to -1.327 V) and the nature of the reduction site may change from ligand- to metal-based.²²

The temperature dependence of the magnetic susceptibility of (1a) in the range 4.2–300 K obeys the Curie–Weiss law ($C = 0.970 \pm 0.001$, $\theta = -0.1 \pm 0.2$ K), Figure. The magnetic moment is very nearly independent of temperature in the range 295 K (μ_{eff} 2.79) to 4.2 K (μ_{eff} 2.77). This corresponds to the magnetic moment of a d^2 vanadium(III) complex in an octahedral ligand field with an $S = 1$ ground state, $g = 1.969$. The corresponding complex (1b) shows a decrease in moment at lower temperatures due to zero-field splitting of the triplet state of 7.7 cm^{-1} , with $g = 1.84$.^{23–25} The decrease of the triplet state zero-field splitting and increase in g value for (1a) compared to (1b) correspond to an increased ligand-field splitting (Δ) or a reduction in the Racah parameter B , i.e. the ratio of Δ/B in the sulphur chelate is as observed in the analogous complexes $[\text{Fe}^{\text{III}}(\text{SacSac})_3]$ ($S = \frac{1}{2}$) and $[\text{Fe}^{\text{III}}(\text{acac})_3]$ ($S = \frac{5}{2}$).

The proton n.m.r. spectrum of (1a) shows two broad peaks from the methyl and ring protons of the SacSac ligand shifted downfield from SiMe_4 . These peaks show a linear dependence on $1/T$ over the temperature range studied (238–302 K), Table. The isotropic shifts observed for these protons in (1a) are considerably larger than those found in (1b) (Table).^{26,27} The proton n.m.r. spectrum of (1c) shows only the *cis* isomer as previously reported by Holm *et al.*⁸ with intermediate isotropic shifts between (1a) and (1b). These also show a linear dependence with inverse temperature. The isotropic shift pattern for both (1a) and (1c) has $\Delta\nu(\text{CH}) > \Delta\nu(\text{CH}_3)$ with $\Delta\nu(\text{CH})$ and $\Delta\nu(\text{CH}_3)$ having comparable magnitudes for (1a).

The absence of a significant zero-field splitting in the ground triplet state of (1a) suggests that the susceptibility will be near to

isotropic leading to negligible pseudocontact shifts. Hence in the case of (**1a**) the isotropic shifts are close to those expected for the contact shift mechanism. This may be compared with the shifts observed for the complex (**1b**) where pseudocontact shifts account for 2–4% of the isotropic shift.²⁷

Contact shifts observed in (**1b**) arise from a combination of metal-to-ligand spin transfer to empty ligand π^* orbitals and ligand-to-metal spin transfer from occupied ligand π to metal d orbitals, although the first mechanism is considered more important.^{28–31} A comparison of the electronic spectra of (**1a**) with (**1b**) shows that the metal d orbitals are closer in energy to the ligand π and π^* orbitals in the SacSac ligand than for the oxygen-containing ligand. Increasing shifts observed in (**1c**) and (**1a**) imply a greater efficacy of these spin-transfer mechanisms in the sulphur-containing ligands. A similar effect may be seen by comparison of [Ti(acac)₃], [V(acac)₃], and [Cr(acac)₃] where the CH_3 shifts decrease as the metal orbital energies decrease from Ti to Cr.²⁹ This supports the increasing importance of the metal-to-ligand π^* spin transfer mechanism with increasing ligand sulphur content.

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