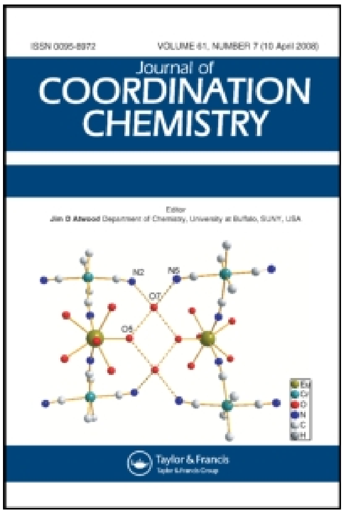

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STEREOCHEMICAL FEATURES OF TRIS(CHELATE) COMPLEXES. SYNTHESIS, CHARACTERIZATION, AND X-RAY CRYSTAL STRUCTURE OF TRIS(DIISOBUTYLDITHIOCARBAMATO)V(III)

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STEREOCHEMICAL FEATURES OF TRIS(CHELATE) COMPLEXES. SYNTHESIS, CHARACTERIZATION, AND X-RAY CRYSTAL STRUCTURE OF TRIS(DIISOBUTYLDITHIOCARBAMATO)V(III)

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The synthesis and characterization of a tris(dialkyldithiocarbamate)V(III) complex is described, including the results of a single crystal X-ray diffraction investigation. The V atoms are surrounded by the six sulfur atoms of the chelating diisobutyldithiocarbamate ligands and have structures that are quite compressed with geometries intermediate between that of an octahedron and a trigonal prism. An analysis of specific structural features of these complexes suggests the distortions observed have their origins largely in electronic effects, as opposed to steric constraints imposed by the ligands. The structure crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent molecules in the asymmetric unit and lattice parameters $a = 11.629(3)$ Å, $b = 17.773(6)$ Å, $c = 18.947(8)$ Å, $\alpha = 80.25(3)^\circ$, $\beta = 88.86(3)^\circ$, $\gamma = 76.29(2)^\circ$, $V = 3748(2)$ Å^3. Convergence to conventional R values of $R = 0.048$ and $R_w = 0.059$ was obtained for 667 variable parameters and 3306 reflections with $I>3\sigma(I)$.

KEYWORDS: Vanadium, dithiocarbamates, X-ray structure

INTRODUCTION

Tris(dithiocarbamate) complexes of a large number of transition metals have been prepared and investigated. Several have been shown to be stereochemically non-rigid on the NMR time scale, isomerizing via a metal-centered rearrangement in which a trigonal twist mechanism has been implicated.[1] In instances where crystallographic investigations have been carried out, substantial distortions from octahedral geometry have frequently been observed owing to steric constraints imposed by the small bite angle of the dithiocarbamate ligands.

Tris(dithiocarbamate) complexes of V(III) have also been reported, however, their crystal structures have not been investigated.2–4 Magnetic susceptibility data show

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that tris(dithiocarbamate) complexes of V(III) have room temperature moments close to the spin-only value of 2.83 B.M. consistent with the presence of two unpaired electrons.[4] ^{1}H NMR studies indicate that these complexes are also stereochemically non-rigid in non-coordinating solvents.[3] For the vanadium(III) complex, V(Et_2NCS_2)$_3$, X-ray powder pattern diffraction data suggest that it is isomorphous with Fe(Et_2NCS_2)$_3$ whose crystal structure has been determined and shown to be distorted toward trigonal prismatic geometry.[4,5] Our interest in the structures of complexes possessing geometries characterized by substantial distortions from octahedral coordination geometries led to the synthesis of a V(III) complex containing diisobutyldithiocarbamate ligands. In this paper we report the preparation of a tris(dithiocarbamato)V(III) complex involving an improved synthetic procedure, its characterization, and describe the results of a single crystal X-ray diffraction investigation.

EXPERIMENTAL

Materials and Methods

All manipulations were carried out under oxygen-free nitrogen using standard Schlenk techniques or in an inert atmosphere glove box. All solvents were freshly distilled prior to use with appropriate drying agents. NMR spectra were obtained on a Bruker 360 MHz spectrometer, and IR spectra were recorded as nujol mulls between CsI plates.

Synthesis of Na(^{i}Bu$_2$NCS$_2$)

A solution of diisobutylamine (17.4 mL, 100 mmol) and sodium hydroxide (10.0 g, 250 mmol) in 50 mL of H_2O was cooled to 0°C. Carbon disulfide (30 mL, 500 mmol) was added dropwise with stirring, and the mixture was stirred for an additional two hours. The reaction mixture was filtered and the crude product was recrystallized from an acetone/diethyl ether solution yielding 17.5 g (77 mmol, 77% yield) of a white crystalline product. IR: 1440, 1412, 1380, 1378, 1345(sh), 1300, 1242, 1210, 1180, 1160, 1100, 990, 948, 930, 920, 880, 830, 815, 730, 645(w), 610, 560(w), 475(w), 450(w), 415(w), 340(w), 280(w) cm^{-1}. ^{1}H NMR (CD_3CN): 0.876 ppm (d, C*H*$_3$), 2.416 ppm (sept., C*H*), 3.875 ppm (d. C*H*$_2$)

Synthesis of tris(^{i}Bu$_2$NCS$_2$)V(III)

To a solution of Na(^{i}Bu$_2$NCS$_2$) (9.08 g, 40 mmol) in 30 mL of THF was added VCl_3(THF)$_3$ (4.9 g, 13.3 mmol). After 1 day the solution was filtered and washed with 30 mL of fresh THF. After evaporation of the solvent, 8.30 g (12.5 mmol, 95% yield) of an orange microcrystalline product was obtained. IR: 1340, 1250, 1205, 1150, 1100, 990, 920, 885, 820(w), 625(w), 530(w), 375, 310 cm^{-1}. Anal. Calcd. for C, 48.48; H, 8.20; N, 6.33%. Found: C, 48.18; H, 8.16; N, 6.14%.

Crystal Data

$C_{27}H_{54}N_3S_6V$, $M = 664.0$, triclinic, space group P$\bar{1}$, $a = 11.629(3)$ Å, $b = 17.773(6)$ Å, $c = 18.947(8)$ Å, $\alpha = 80.25(3)^0$, $\beta = 88.86(3)^0$, $\gamma = 76.29(2)^0$, $V = 3748(2)$ Å^3,

$D_{(calc)}$ = 1.436 Mg m^{-3}, $Z = 4$, $\mu = 0.596$ mm^{-1}, λ(Mo Kα) = 0.71073 Å, $F(000) = 1424$, $T = 298$ K.

Crystal Structure Solution and Refinement

Crystals suitable for X-ray analysis were obtained by slow evaporation from hexane. A regularly shaped dark brown crystal having approximate dimensions 0.20 × 0.30 × 0.30 mm was selected and mounted on the end of a glass fiber in a random orientation. Triclinic symmetry was suggested on the basis of the interaxial angles and confirmed by a Delaunay reduction. Refined cell parameters were determined from the setting angles of 25 reflections with $15° < 2\Theta < 30°$. Data collection was carried out at ambient temperature using the ω-scanning technique in bisecting geometry on a Nicolet R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation. Scan rate variable, 3–20° min^{-1}; scan range, 1.6° in ω. Three standard measured every 100 data showed no significant variation over the period of data collection. A total of 10456 reflections (±h, ±k, +l; $h_{max} = 12$, $k_{max} = 19$, $l_{max} = 20$) with $3.5° < 2\Theta < 45°$ were obtained and corrected for Lorentz and polarization effects, but not absorption. This led to 9871 unique reflections (R_{int} = 2.14%). Structure solution was carried out using the *SHELXTL-PC* collection of crystallographic software.[6] Intensity statistics favored a centrosymmetric cell which was assigned to the $P\bar{1}$ space group. The structure was solved using direct methods and all non-hydrogen atoms were refined anisotropically using scattering factors that included terms for anomalous dispersion.[7] Hydrogen atoms were included in idealized positions with fixed isotropic U = 0.080 Å^2. Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0015(F^2)]$. One intense low-angle reflection (−1 0 1) appeared to suffer from some form of extinction, and was therefore omitted during the later stages of redinement. For the final cycle, maximum shift/σ = 0.031 with minimum and maximum residual electron densities of -0.24 e Å^{-3} and +0.25 e Å^{-3}. Convergence to conventional R values of $R = 0.048$ and $R_w = 0.059$ with a goodness-of-fit of 1.08 was obtained for 667 variable parameters and 3306 reflections with $I > 3\sigma(I)$.

RESULTS AND DISCUSSION

The asymmetric unit of this structure contains two crystallographically independent molecules, each consisting of a six-coordinate V(III) center with three chelating ^{i}Bu$_2$NCS$_2$ ligands. Pertinent bond distances and angles are given in Table 2, and a view of both molecules illustrating the atomic numbering scheme is shown in Figure 1.

In both molecules the V centers are surrounded by six S atoms with V-S bond lengths that range from 2.413(3) Å to 2.449(5) Å (mean 2.432 Å). Interaxial S-V-S angles range from a minimum of 72.6(1)° to 102.5(1)°, and the dithiocarbamate ligands display an average bite angle of 72.7°, similar to that observed in a square-pyramidal V(IV) oxo complex containing bis(diethyldithiocarbamate) ligands.[8] The ^{i}Bu$_2$NCS$_2$ ligand groups display no particularly unusual structural features; the C-N-CS$_2$ atoms are essentially planar and the N atoms possess trigonal-planar geometries. The C-S and C-N bonds display average lengths of 1.714 Å and 1.335 Å, respectively, and the average bite distance, as defined by the

Table 1 Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3).

	x/a	*y/b*	*z/c*	*U*(eq)
V(1)	666(2)	2482(1)	9313(1)	64(1)
V(2)	5759(2)	2484(1)	4180(1)	66(1)
S(1)	-325(2)	1439(2)	9189(2)	72(1)
S(2)	-1400(3)	2948(2)	9564(2)	83(1)
S(3)	1200(3)	3534(2)	9814(2)	71(1)
S(4)	1433(3)	1931(2)	10511(2)	76(1)
S(5)	2508(2)	1886(2)	8777(1)	71(1)
S(6)	638(3)	3151(2)	8074(2)	72(1)
S(7)	6679(3)	1707(2)	3291(1)	70(1)
S(8)	6424(3)	3371(2)	3228(2)	74(1)
S(9)	7511(2)	2045(2)	4957(2)	72(1)
S(10)	5520(3)	3337(2)	5075(2)	96(2)
S(11)	3719(2)	2894(2)	3722(2)	72(1)
S(12)	4718(3)	1518(2)	4763(2)	89(2)
N(1)	-2669(8)	1923(5)	9373(4)	60(4)
N(2)	2165(8)	2986(5)	11129(5)	67(4)
N(3)	2635(6)	2587(5)	7416(4)	68(4)
N(4)	7550(7)	2592(4)	2222(4)	61(4)
N(5)	7394(7)	2935(4)	5975(4)	64(4)
N(6)	2372(7)	1952(4)	4417(4)	67(4)
C(1)	-1592(9)	2082(5)	9370(5)	55(4)
C(2)	-3720(10)	2476(6)	9575(6)	67(5)
C(3)	-4546(13)	2921(9)	8972(8)	125(9)
C(4)	-4131(14)	3251(10)	8365(8)	196(12)
C(5)	-5583(12)	3433(9)	9274(7)	157(9)
C(6)	-2865(10)	1234(7)	9155(6)	82(6)
C(7)	-3384(12)	696(8)	9701(9)	108(8)
C(8)	-3638(12)	19(8)	9376(9)	162(10)
C(9)	-2673(15)	395(9)	10347(8)	179(11)
C(10)	1666(9)	2837(6)	10566(6)	64(5)
C(11)	2411(9)	3758(6)	11159(5)	72(5)
C(12)	1599(16)	4229(9)	11610(10)	153(10)
C(13)	671(17)	4211(11)	11834(14)	377(27)
C(14)	1940(15)	5025(9)	11544(9)	191(12)
C(15)	2547(9)	2368(6)	11754(5)	70(5)
C(16)	3729(14)	1871(10)	11732(10)	162(10)
C(17)	4565(14)	1995(11)	11375(10)	231(14)
C(18)	3991(12)	1237(8)	12393(8)	135(8)
C(19)	2043(9)	2546(6)	8015(5)	67(5)
C(20)	2256(10)	3185(7)	6784(5)	79(6)
C(21)	2852(14)	3882(9)	6704(8)	115(8)
C(22)	2608(14)	4334(9)	7287(8)	147(10)
C(23)	2532(14)	4383(8)	5979(8)	161(10)
C(24)	3793(9)	2037(7)	7350(5)	77(5)
C(25)	3757(13)	1390(9)	6943(7)	107(8)
C(26)	3117(13)	806(10)	7305(10)	177(12)
C(27)	4962(13)	963(9)	6776(7)	167(10)
C(28)	6969(8)	2566(6)	2827(5)	56(4)
C(29)	7825(9)	3318(6)	1853(6)	73(5)
C(30)	7059(14)	3721(7)	1198(7)	96(7)
C(31)	5800(13)	4019(9)	1361(7)	146(9)
C(32)	7547(13)	4387(8)	819(7)	142(8)
C(33)	7981(9)	1874(6)	1896(5)	69(5)
C(34)	9304(11)	1517(8)	1984(8)	96(7)
C(35)	9704(11)	1322(10)	2731(9)	169(11)

Table 1 *Continued.*

C(36)	9628(11)	809(7)	1619(7)	118(7)
C(37)	6876(9)	2790(6)	5414(5)	66(5)
C(38)	6965(15)	4338(9)	6122(10)	136(10)
C(39)	6776(10)	3555(6)	6355(5)	80(6)
C(40)	8051(19)	4507(9)	6050(10)	227(17)
C(41)	6142(14)	4943(8)	6496(9)	175(10)
C(42)	8561(9)	2473(6)	6239(6)	75(5)
C(43)	8590(19)	1803(14)	6802(12)	209(14)
C(44)	7857(19)	1572(12)	7147(12)	252(17)
C(45)	9850(15)	1391(10)	7023(9)	200(12)
C(46)	3444(9)	2105(6)	4318(5)	105(5)
C(47)	1375(9)	2432(6)	3968(6)	74(5)
C(48)	450(16)	2906(10)	4379(11)	157(11)
C(49)	890(16)	3412(10)	4765(11)	205(14)
C(50)	-497(14)	3410(10)	3874(10)	205(13)
C(51)	2172(10)	1321(7)	4970(5)	85(6)
C(52)	1768(12)	671(8)	4721(8)	100(7)
C(53)	2542(15)	296(8)	4235(8)	164(10)
C(54)	1582(13)	87(8)	5355(8)	145(9)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

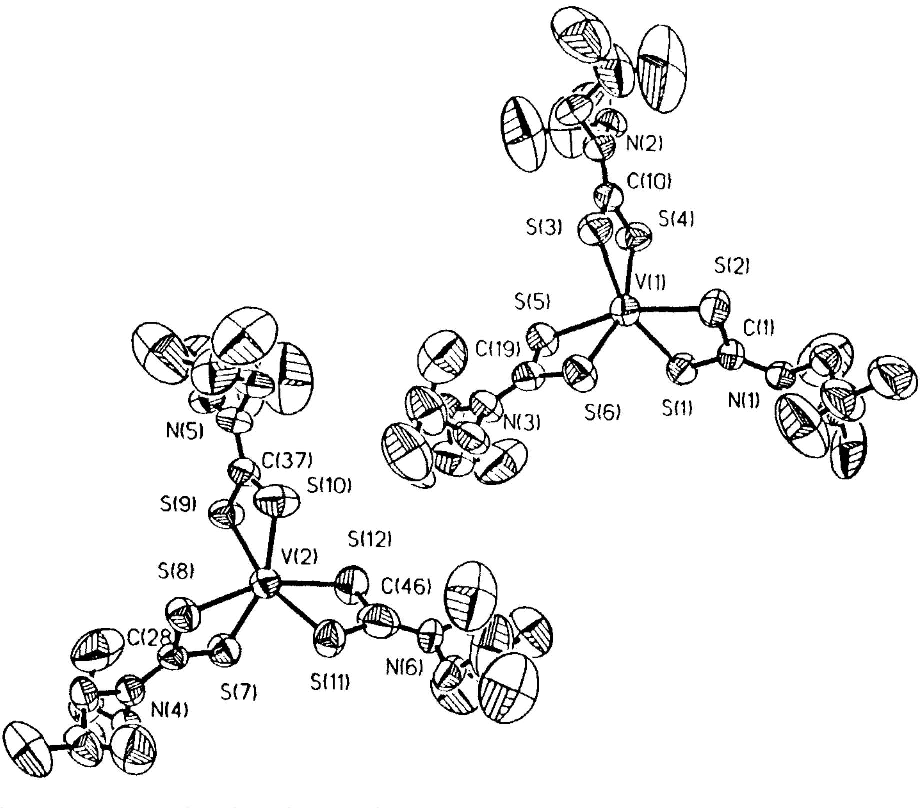

Figure 1 A perspective view of the two independent molecules with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2 Bond lengths and angles for the complex.

V(1)—S(1)	2.44(4)	V(1)—S(2)	2.415(3)
V(1)—S(3)	2.44(4)	V(1)—S(4)	2.413(3)
V(1)—S(5)	2.43(3)	V(1)—S(6)	2.441(3)
V(2)—S(7)	2.42(4)	V(2)—S(8)	2.428(4)
V(2)—S(9)	2.43(3)	V(2)—S(10)	2.430(4)
V(2)—S(11)	2.44(3)	V(2)—S(12)	2.434(4)
S(1)—C(1)	1.70(10)	S(2)—C(1)	1.707(11)
S(3)—C(10)	1.72(10)	S(4)—C(10)	1.714(12)
S(5)—C(19)	1.70(9)	S(6)—C(19)	1.743(9)
S(7)—C(28)	1.73(10)	S(8)—C(28)	1.717(10)
S(9)—C(37)	1.71(10)	S(10)—C(37)	1.717(9)
S(11)—C(46)	1.73(10)	S(12)—C(46)	1.735(9)
N(1)—C(1)	1.34(15)	N(1)—C(2)	1.465(13)
N(1)—C(6)	1.426(16)	N(2)—C(10)	1.318(16)
N(2)—C(11)	1.47(15)	N(2)—C(15)	1.469(13)
N(3)—C(19)	1.31(12)	N(3)—C(20)	1.458(12)
N(3)—C(24)	1.48(12)	N(4)—C(28)	1.317(11)
N(4)—C(29)	1.46(13)	N(4)—C(33)	1.488(13)
N(5)—C(37)	1.32(13)	N(5)—C(39)	1.457(13)
N(5)—C(42)	1.45(12)	N(6)—C(46)	1.341(14)
N(6)—C(47)	1.45(12)	N(6)—C(51)	1.458(13)
Bond angles (°)			
S(1)—V(1)—S(2)	72.6(1)	S(1)—V(1)—S(3)	159.2(1)
S(2)—V(1)—S(3)	91.9(1)	S(1)—V(1)—S(4)	95.8(1)
S(2)—V(1)—S(4)	99.8(1)	S(3)—V(1)—S(4)	72.8(1)
S(1)—V(1)—S(5)	95.2(1)	S(2)—V(1)—S(5)	163.4(1)
S(3)—V(1)—S(5)	102.5(1)	S(4)—V(1)—S(5)	92.4(1)
S(1)—V(1)—S(6)	101.4(1)	S(2)—V(1)—S(6)	98.4(1)
S(3)—V(1)—S(6)	94.3(1)	S(4)—V(1)—S(6)	157.9(1)
S(5)—V(1)—S(6)	72.6(1)	S(7)—V(2)—S(8)	72.8(1)
S(7)—V(2)—S(9)	92.4(1)	S(8)—V(2)—S(9)	100.8(1)
S(7)—V(2)—S(10)	160.2(1)	S(8)—V(2)—S(10)	96.6(1)
S(9)—V(2)—S(10)	72.8(1)	S(7)—V(2)—S(11)	100.4(1)
S(8)—V(2)—S(11)	92.5(1)	S(9)—V(2)—S(11)	163.8(1)
S(10)—V(2)—S(11)	96.8(1)	S(7)—V(2)—S(12)	95.2(1)
S(8)—V(2)—S(12)	159.2(1)	S(9)—V(2)—S(12)	96.5(1)
S(10)—V(2)—S(12)	99.4(1)	S(11)—V(2)—S(12)	72.6(1)
V(1)—S(1)—C(1)	85.6(4)	V(1)—S(2)—C(1)	86.7(4)
V(1)—S(3)—C(10)	86.1(4)	V(1)—S(4)—C(10)	87.2(4)
V(1)—S(5)—C(19)	87.3(3)	V(1)—S(6)—C(19)	86.4(3)
V(2)—S(7)—C(28)	86.6(3)	V(2)—S(8)—C(28)	87.0(3)
V(2)—S(9)—C(37)	86.5(3)	V(2)—S(10)—C(37)	86.5(4)
V(2)—S(11)—C(46)	87.1(4)	V(2)—S(12)—C(46)	87.3(4)
C(1)—N(1)—C(2)	121.1(9)	C(1)—N(1)—C(6)	122.7(8)
C(2)—N(1)—C(6)	116.2(9)	C(10)—N(2)—C(11)	122.9(8)
C(10)—N(2)—C(15)	120.5(9)	C(11)—N(2)—C(15)	116.6(9)
C(19)—N(3)—C(20)	124.0(7)	C(19)—N(3)—C(24)	121.4(7)
C(20)—N(3)—C(24)	114.5(7)	C(28)—N(4)—C(29)	121.8(8)
C(28)—N(4)—C(33)	121.1(8)	C(29)—N(4)—C(33)	117.1(8)
C(37)—N(5)—C(39)	119.6(8)	C(37)—N(5)—C(42)	121.7(8)
C(39)—N(5)—C(42)	118.7(8)	C(46)—N(6)—C(47)	119.5(8)
C(46)—N(6)—C(51)	121.6(7)	C(47)—N(6)—C(51)	118.9(8)
S(1)—C(1)—S(2)	115.0(7)	S(1)—C(1)—N(1)	123.2(8)
S(2)—C(1)—N(1)	121.8(7)	S(3)—C(10)—S(4)	113.9(7)
S(3)—C(10)—N(2)	123.0(8)	S(4)—C(10)—N(2)	123.2(8)
S(5)—C(19)—S(6)	113.7(5)	S(5)—C(19)—N(3)	124.8(7)
S(6)—C(19)—N(3)	121.4(6)	S(7)—C(28)—S(8)	113.5(5)
S(7)—C(28)—N(4)	122.7(8)	S(8)—C(28)—N(4)	123.8(8)
S(9)—C(37)—S(10)	114.2(6)	S(9)—C(37)—N(5)	122.8(7)
S(10)—C(37)—N(5)	123.0(7)	S(11)—C(46)—S(12)	112.6(6)
S(11)—C(46)—N(6)	124.0(7)	S(12)—C(46)—N(6)	123.4(7)

distance spanned by two S atoms, measures 2.884 Å. Structural details of the alkyl side chains are unexceptional and will not be discussed further, except to note that several atoms exhibit some degree of high-amplitude thermal motion. In addition to contributing to an increase in the standard deviation associated the derived bond length and angle parameters, this motion leads to apparent shortening of the derived bond lengths. As a result, these parameters are of limited precision and no particular significance can be attached to variations in the associated C-C bond lengths.

Of particular interest are the distortions from ideal octahedral geometry present in the two crystallographically independent vanadium molecules. Excluding distortions arising from either compression or elongation, and considering only distortions of the twist type, the limiting extremes are an octahedron, which may be regarded as a trigonal antiprism when viewed down the C_3 axis, and a trigonal prism. If the twist angle in an octahedron is defined as the angle ϕ between the triangles formed by ligands as viewed down the C_3 axis, ϕ equals 60° in a perfect octahedron, decreasing to 0° in the case of the trigonal prism (Figure 2).[9]

These extremes are exemplified in the structures of $V(acac)_3$ where the twist angle is 56° in accordance with the nearly octahedral geometry,[10] and the V(III) dithiolene complex, $V(S_2C_2(Ph)_2)_3$ exhibiting a nearly trigonal prismatic structure with $\phi = 3$.[11] With an average twist angle of 35° calculated for the two independent molecules in the asymmetric unit, the coordination geometry of the V(III) complex

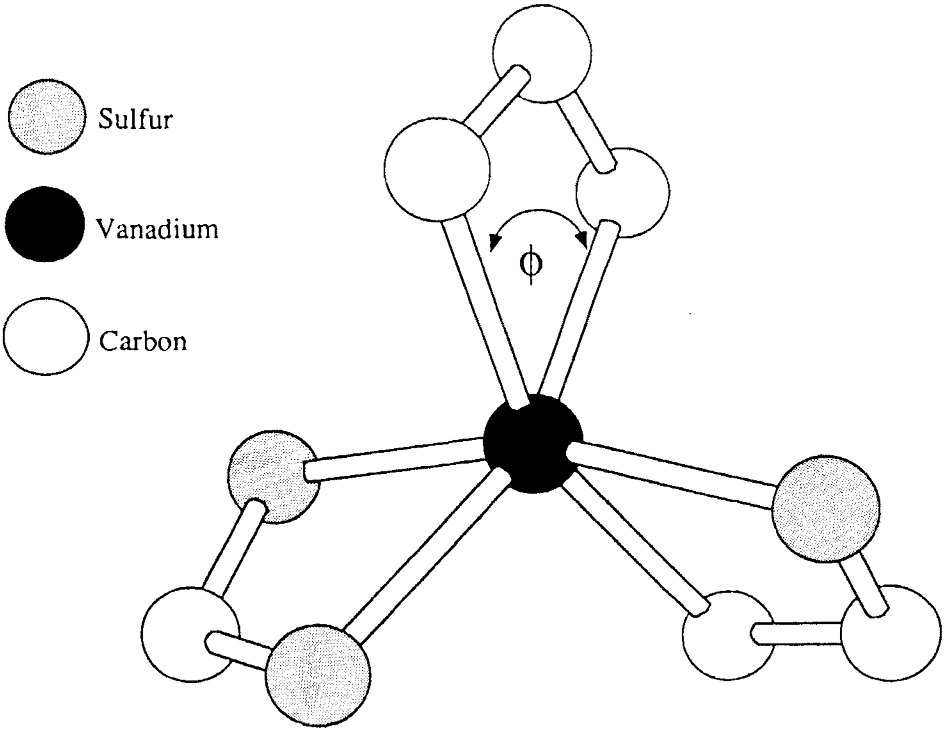

Figure 2 A view of the coordination sphere defining the twist angle θ.

Table 3 Selected structural data on mononuclear vanadium complexes

Complex	Bite Distance (Å)	Bite angle (°)	Twist angle (°)	s/h	b/a	Ref.
Octahedron			60	1.22	1.41	
Trigonal-prism			0	1.31	1.00	
$V(acac)_3$	2.79	88.0	56	1.21	1.39	10
$V(S_2C_2(Ph)_2)_3$	3.07	81.7	3	1.01	1.31	11
$V(^i\mathrm{Bu}_2NCS_2)_3$	2.884	72.7	35 (avg.)	1.38	1.19	this work

described here lies intermediate between that of an octahedron and a trigonal prism (*vida infra*). It is nearly identical to the 32° twist angle observed in the structure of a tris(di-*n*-butyldithiocarbamato)Fe(III) complex.[12]

V(III) is a Jahn-Teller active transition metal. In order to separate distortions having their origin in ligand steric constraints from those arising solely from electronic factors, the distortions in this complex have been analyzed in detail using an approach first articulated by Stiefel and Brown.[9] In this treatment we consider: (1) the twist angle, (2) the distance between sulfur atoms comprising one face (S_i) and (3) the distance between the planes of parallel triangular faces (h_i). In this construction, the ratio, s/h, is a measure of the compression (or elongation) of the complex. In the trigonal prism s/h equals exactly 1.00, whereas in a complex having perfect O_h symmetry, $s/h = 1.22$. Our analysis of the nature of the distortion is further enhanced by considering the ratio of the bite distance, (b), to the V-S distance, (a). For the limiting cases of the perfect octahedron (O_h) and trigonal prism (D_{3h}), these latter values are 1.41 and 1.31, respectively. In the analysis that follows we have utilized values based on averages derived from the two crystallographically independent molecules.

For $V(^i\mathrm{Bu}_2NCS_2)_3$ the ratio of the average bite distance to the V-S bond length is 1.186, roughly 32% less than the b/a value of 1.41 expected for a complex possessing perfect octahedral geometry. Calculation of the compression ratio, s/h, for this complex yields a value of 1.379. Compared with the value of 1.22 for the perfect octahedron, this parameter again suggests a more compressed structure. Thus, despite the fact that the average twist angle of $V(^i\mathrm{Bu}_2NCS_2)_3$ is between the limiting case of the octahedron and the trigonal prism, the structure exhibits a substantial degree of compression.

Stiefel and Brown have noted similar trends (ϕ values between those of an octahedron and a trigonal prism with b/a and s/h values suggestive of compression greater than that of the octahedral geometry) for tris complexes of oxalates, dialkylxanthates and dialkyldithiocarbamates.[9] In such systems they concluded that the distortion is not truly in the direction of the trigonal prism, as has been frequently suggested when only the twist angle is considered.

Steric constraints have frequently been implicated in compressions and distortions toward trigonal prismatic coordination geometry in a number of transition metal complexes of dithiocarbamates because of the limited ability of the DTC ligands to span two coordination sites. Our calculations, however, indicate that the complex is far too compressed to be accounted for simply by the ligand bite distance alone. Since $V(^i\mathrm{Bu}_2NCS_2)_3$ is Jahn-Teller active, some distortion from ideal octahedral geometry is to be expected. Symmetry considerations indicate that the nature of the distortion can either be in the form of axial elongation or compression, or a twist toward a trigonal prismatic type of geometry. The analysis we have carried out on this system allows us to separate distortions arising as a result of electronic effects from those whose origin lies in ligand steric constraints. From the results of these calculations, we conclude that the distortion in this vanadium complex has its origin largely in electronic effects with only minor, if any, contribution from steric constraints imposed by the dithiocarbamate ligands.

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Supplementary data

Lists of structure factors, anisotropic thermal parameters, and hydrogen atom coordinates, as well as bond length and angle data for the ligand *iso*-butyl groups, are available from one of the authors (LCP) upon request.

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