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In(III), Tl(III) and V(IV) Tris-chelates of the Heterocyclic Dithiolene and Diselenolene Ligands 1,3-Dithiole-2-thione-4,5-dithiolate (dmit), 1,2-Dithiole-3-thione-4,5-dithiolate (dmt) and 1,3-Diselenole-2-selone-4,5-diselenolate (dsis). Crystal and Molecular Structure of $(Bu_4N)_2[V(dmt)_3]$

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Abstract

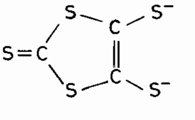
Synthesis and characterization of the first tris-chelates of the dichalcogenolene ligands 1,3-dithiole-2-thione-4,5-dithiolate (dmit), 1,2-dithiole-3-thione-4,5-dithiolate (dmt) and 1,3-diselenole-2-selone-4,5-diselenolate (dsis) with the central ions In(III), Tl(III) and V(IV) are reported. On $(Bu_4N)_2[V(dmt)_3]$ the first X-ray structure of a dithiolene tris-chelate containing unsymmetric ligand was carried out: the compound crystallizes monoclinic, space group $P2_1/c$, with four molecules in the unit cell; $a = 16.264(3)$, $b = 17.319(4)$, $c = 21.554(4)$ Å, $\beta = 103.03(2)°$. The ligand dmt causes a very low symmetry of the VS_6 moiety in $[V(dmt)_3]^{2-}$ having pseudo-meridional arrangement of the three ligands.

The EPR parameters of the compounds $(Bu_4N)_2[V(dmit)_3]$ and $(Bu_4N)_2[V(dmt)_3]$ measured in liquid and frozen acetonic solution are compared with those of the tris(maleonitriledithiolato)vanadate(IV) anion supporting a geometry of the anion being between octahedral and trigonal prismatic.

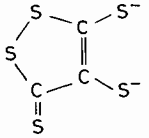
Introduction

Since the early work of King [1], Schrauzer *et al.* [2] and Hoyer and Schroth [3] it is well known that classical dithiolene ligands form bis- and tris-complexes. The number of central metal ions in dithiolene tris-chelates [4–9] is huge, and transition as well as main group elements are involved. Main group ions, such as indium(III), form essentially octahedral dithiolene complexes [10] whereas transition metal compound structures are varying between ideal trigonal prismatic and octahedral symmetry, obviously depending on the total charge of the complexes, *i.e.* on the formal oxidation state of the central metal ion. Lower total charge favours coordination spheres more trigonal prismatically oriented whereas higher charge favours octahedral geometry [11, 12]. The sulfur-rich dithiolene ligands '4,5-dimercapto-isotrithione' (dmit, **1**) and '4,5-dimercapto-trithione' (dmt, **2**) could not be checked in this respect until now because, surprisingly enough, no tris-compounds of these ligands were known in contrast to a lot of bis-chelates which have been intensively studied in the last years [13]. In particular the solid state electrical conductivity of some planar compounds $[M(dmit)_2]^{n-}$ with $0 < n \leq 1$ has grown in interest [14].

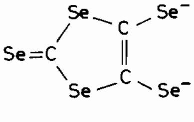
Contrary to other dithiolene ligands (e.g. maleonitriledithiolate, mnt) the tendency to form tris-chelates is obviously smaller for the ligands under study, especially with three-valent transition metal ions. None of the corresponding compounds with dmit, dmt and the all-selenium ligand dsis could be isolated whereas $[Fe(mnt)_3]^{3-}$ and $[Co(mnt)_3]^{3-}$ are known [15]. In addition the proper choice of the precipitation cation seems to be more critical for getting crystallized samples (diffraction quality) as with other dithiolene ligands.



(dmit)
1



(dmt)
2



(dsis)
3

Although the chemistry of diselenolene ligand complexes is closely related to that of dithiolenes there are only a few publications about this subject [16]. This is mainly due to the unpleasant odour of the starting material and the lower stability of the ligands towards oxidation. Only the structure of $Mo[Se_2C_2(CF_3)_2]_3$ was published [17], until more recently when diselenolene mixed ligand complexes

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were prepared by reactions via coordinated ligands [18]. As we have shown [19] 4,5-dibenzoylseleno-1,3-diselenole-2-selone is a useful precursor for preparation of complexes of the genuine diselenolene ligand '4,5-diselenolato-isotriselone' (dsis, **3**).

Due to the topology of the dmt ligand a 'pseudo-facial' as well as a 'pseudo-meridional' structure of tris-chelates could be expected. Therefore we studied the crystal and molecular structure of $(Bu_4N)_2[V(dmt)_3]$ which is the first structure investigation on a tris-chelate containing unsymmetric dithiolene ligand at all to our knowledge.

Experimental

Preparation of Compounds

4,5-Dibenzoylthio-1,3-dithiole-2-thione, 4,5-dibenzoylthio-1,2-dithiole-3-thione and 4,5-dibenzoylseleno-1,3-diselenole-2-selone were synthesized as described earlier [13c, e, 19].

$(Ph_4As)_3[In(dmit)_3]$. 2.03 g (5 mmol) of 4,5-dibenzoylthio-1,3-dithiole-2-thione are saponified by adding 6 ml (2 M) methanolic sodium methanolate solution and leaving the mixture for 10 min. The resulting solution of the 1,3-dithiole-2-thione-4,5-dithiolate dianion is combined with 1.47 g (3 mmol) tetraphenylarsonium chloride dissolved in 50 ml methanol. Drop by drop addition of a solution of indium(III) chloride (1 mmol prepared from 115 mg indium metal) in 10 ml ethanol under heavily stirring yields 1.45 g (0.78 mmol, 78%) of deep red needles. The crude product can be recrystallized from acetonitrile, melting point (m.p.) 228–230 °C.

$(Ph_4As)[Tl(dmit)_3]$. This compound can be synthesized similarly to the indium complex by adding 982 mg (2 mmol) Ph_4AsCl and 729 mg (1 mmol) $Ph_4As[TlCl_4]$*, dissolved in 20 ml methanol/acetone (1:1), to the ligand solution (see above). Recrystallization from acetonitrile yields 1.25 g (0.64 mmol, 64%) red–brown needles, m.p. 189–190 °C.

$(Bu_4N)_2[V(dmit)_3]$. 487 mg (1.2 mmol) 4,5-dibenzoylthio-1,3-dithiole-2-thione are hydrolyzed using 3 ml (1 M) methanolic sodium methanolate solution as described above. After addition of 10 ml methanol and subsequently of 62 mg (0.39 mmol) anhydrous vanadium(III) chloride (Merck sample, synthetic quality), dissolved in 10 ml methanol under vigorous stirring, the stirring is continued for another 15 min. 386 mg (1.2 mmol) tetrabutylammonium bromide, dissolved in 20 ml methanol, precipitate a green crude product. The complex salt can be purified by dissolving in acetone followed by slow addition of isopropanol in the cold. Reprecipitation yields 528 mg (0.23 mmol, 59%) dark green needles, m.p. 166–168 °C. UV–Vis (acetone, 1 mM): $\bar{\nu}$ 28 000 cm^{-1} (ϵ 1150 cm^{-1} M^{-1}); 22 700 (1550); 19 400 (1800); 14 300 (850).

K_2dmt. 4.06 g (10 mmol) 4,5-dibenzoylthio-1,2-dithiole-3-thione are solvolyzed by 40 ml (1 M) methanolic potassium methanolate solution. After 10 min the reaction is finished. Adding of 20 ml diethylether precipitates the dipotassium trithione-dithiolate as an orange–red powder. The product is reprecipitated and purified by dissolving in 15 ml of water at 60 °C and adding 100 ml acetone. The procedure is repeated giving 2.3 g (8.4 mmol, 84%) of the orange–red potassium salt.

$(Ph_4As)_3[In(dmt)_3]$. 1.47 g (3 mmol) tetraphenylarsonium chloride, dissolved in 15 ml methanol, are dropped slowly into a solution of 822 mg (3 mmol) dipotassium trithione-dithiolate in 2 ml water. Dilution with 150 ml acetone and filtration gives a clear solution to which 1 mmol indium(III) chloride (prepared from 115 mg indium metal) in 10 ml ethanol is added yielding fine crystals. The complex salt is filtered off and recrystallized twice from 150 ml acetonitrile (60 °C) in the presence of some charcoal. The yield of the pure complex salt is 700 mg (0.38 mmol), orange needles, m.p. 169–171 °C.

$(Ph_4As)_3[Tl(dmt)_3]$. The compound is prepared like the corresponding indium complex starting with 982 mg (2 mmol) Ph_4AsCl, dissolved in 10 ml methanol, and 729 mg (1 mmol) $Ph_4As[TlCl_4]$ in 20 ml methanol/acetone (1:1). 300 mg (0.15 mmol, 15%) red needles are obtained, m.p. 132–133 °C.

$(Bu_4N)_2[V(dmt)_3]$. 2.19 g (5.4 mmol) 4,5-dibenzoylthio-1,2-dithiole-3-thione are saponified during 10 min using 10 ml (1 M) methanolic sodium methanolate solution. This solution is diluted with 15 ml methanol and rapidly combined with a solution of 283 mg (1.8 mmol) anhydrous vanadium(III) chloride in 20 ml methanol. Dropwise addition of 1.74 g (5.4 mmol) tetrabutylammonium bromide, dissolved in 20 ml methanol, yields 100 mg (0.09 mmol, 5%) dark green prisms. The complex salt can be recrystallized from acetone, m.p. 157–158 °C. UV–Vis (acetone, 1.2 mM): $\bar{\nu}$ 29 400 cm^{-1} (ϵ 2350 cm^{-1} M^{-1}); 24 000 (2050); 21 500 (2250); 14 500 (650).

$(Ph_4As)_3[In(dsis)_3]$. 175 mg (0.27 mmol) 4,5-dibenzoylseleno-1,3-diselenole-2-selone are saponified during 5 min using 2 ml (1 M) methanolic sodium methanolate solution. Successive adding of 133 mg

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*Prepared by a similar method to ref. 20, starting with K_3TlCl_6.

(0.27 mmol) Ph_4AsCl, dissolved in 8 ml methanol, 5 ml acetone and indium(III) chloride (prepared from 20 mg indium metal) in 6 ml ethanol/methanol (1:5) under vigorous stirring precipitates the complex which is filtered off and dissolved in 50 ml of hot acetonitrile (60 °C). Slow addition of diethylether gives 144 mg (0.056 mmol, 63%) deep red crystals, m.p. 141–143 °C.

Crystal Data, Intensity Data, Structure Determination and Refinement of $(Bu_4N)_2[V(dmt)_3]$

Suitable crystals of $(Bu_4N)_2[V(dmt)_3]$ were grown by slow evaporation of its acetonic solution.

For structure determination data were collected on an Enraf-Nonius CAD-4 automated single crystal diffractometer. Graphite-monochromated Mo Kα radiation ($\lambda(\alpha_1) = 0.70926$ Å) was used to determine the cell dimensions from 74 accurately centered reflections with $10° < \theta < 14°$ at 293(1) K. Integrated intensities were measured in the reciprocal space $\pm h +k +l$ with equality test up to θ_{max} 25°. Crystal stability was monitored by periodic measuring of three standard reflections every 216 reflections; there was no evidence of crystal deterioration. A summary of the crystal data and data collection parameters is given in Table I. The space group was determined from systematic absences. $\sigma(I)$ based on counting statistics, intensities greater than $2.5\sigma(I)$ were considered as observed. Intensities were corrected for background and change in the standards and converted to structure amplitudes after applying Lorentz and polarization corrections. No absorption correction was made.

The structure was solved in a routine way by direct method with MULTAN80 [21]. E map with the highest combined figure of merit, using 250 phases ($|E| > 2.27$), resulted in initial coordinates for V and S atoms, successive Fourier syntheses gave coordinates for all non-hydrogen atoms. An isotropic full-matrix least-squares refinement proceeded to $R = 0.114$. A subsequent three-blocks matrix refinement with anisotropic temperature factors for anion's atoms, with isotropic temperature factors for two cations' atoms using empirical weighting function gave $R = 0.081$. A summary of refinement parameters is presented in Table II. Positions of hydrogen atoms were calculated and included with an isotropic temperature factor U of 0.06 Å^2 as fixed atom contribution. Mo Kα value of 0.71069 Å, atomic scattering factors for neutral V, S, N and C atoms from [22], for H atoms from [23] and dispersion correction for V, S, N and C [24] were used in calculations.

TABLE I. Crystal and Data Collection Summary

Empirical formula	$[(C_4H_9)_4N]_2[V(S_5C_3)_3]$
Formula weight	1124.94
Crystal system	monoclinic
Space group	$P2_1/c$
Temperature (K)	293(1)
Unit cell parameters:	
a (Å)	16.264(3)
b (Å)	17.319(4)
c (Å)	21.554(4)
β (°)	103.03(2)
Volume (Å^3)	5914.9
Z	4
$F(000)$	2380
D_m (g cm^{-3})	1.263
μ(Mo Kα) (cm^{-1})	6.99
Size of crystal (mm)	$0.20 \times 0.46 \times 0.57$
Scan method	$\omega - 2\theta$
θ_{max} (°)	25
θ scan width (°)	$0.7 + 0.3$ tg θ
Scan rate (° min^{-1})	min. 2.0, max. 20.1
Maximum scan time (s)	40
Aperture	$2.4 + 0.9$ tg θ
Background	1/4 of the scan time at each of the scan limit
Reference reflections	$\bar{9}06$, 158, $\bar{3}68$
Intensity change (%)	0.14
Measured reflections	10840
Averaged reflections	10367
Mean discrepancy on I (%)	3.2
Observed reflections	4266
Unobserved reflections	6101

TABLE II. Refinement Parameters

Scale factor	1.011
Number of contributing reflections (m)	7768
Number of variables (n)	362
m/n ratio	21.5
Weighting function	empirical
($w = W_f \times W_s$)	
$W_f(\lvert F_o\rvert < 20.0)$	$(\lvert F_o\rvert/20.0)^{2.0}$
$W_f(20.0 < \lvert F_o\rvert < 35.0)$	1.0
$W_f(35.0 < \lvert F_o\rvert)$	$(35.0/\lvert F_o\rvert)^{1.0}$
$W_s(\sin\theta < 0.23)$	$(\sin\theta/0.23)^{2.0}$
$W_s(0.23 < \sin\theta < 0.36)$	1.0
$W_s(0.36 < \sin\theta)$	$(0.36/\sin\theta)^{2.0}$
$[\Sigma w(\Delta F)^2/(m-n)]^{1/2}$	1.842
R	0.081
R_w	0.100
Average shift/error	0.28
Maximum shift/error	3.32 (U C(84))
Final difference map:	
$\Delta\delta_{max}$ (e Å^{-3})	1.09
$\Delta\delta_{min}$	−0.48

All calculations were performed on the DEC-10 computer at RCU Ljubljana with the XRAY-76 system [25] of crystallographic programs.

Although the crystal was perfect, large and stable during the measurement there are 59% of unobserved reflections using $2.5\sigma(I)$ as criterion. Even at a maximum value of $\theta = 20°$ there are still 41% unobserved data, pointing out a structure with high vibration. The structure shows a remarkable libration

TABLE III. Molar Conductivities (10^{-4} M Solutions, CH_3NO_2, $T = 20$ °C) and Important IR Frequencies of the Tris-complexes

Compound	Λ (ohm^{-1} cm^2 mol^{-1})	Electrolyte type [30]	IR frequencies (ν(C=S))
$(Ph_4As)_3[In(dmit)_3]$	181	3:1	1040, 1065
$(Ph_4As)_3[Tl(dmit)_3]$	187	3:1	1040, 1065
$(Bu_4N)_2[V(dmit)_3]$	131	2:1	1030, 1055
$(Ph_4As)_3[In(dmt)_3]$	180	3:1	1045
$(Ph_4As)_3[Tl(dmt)_3]$	169	3:1	1045
$(Bu_4N)_2[V(dmt)_3]$	101	2:1	1050
$(Ph_4As)_3[In(dsis)_3]$	195	3:1	895 (C=Se)

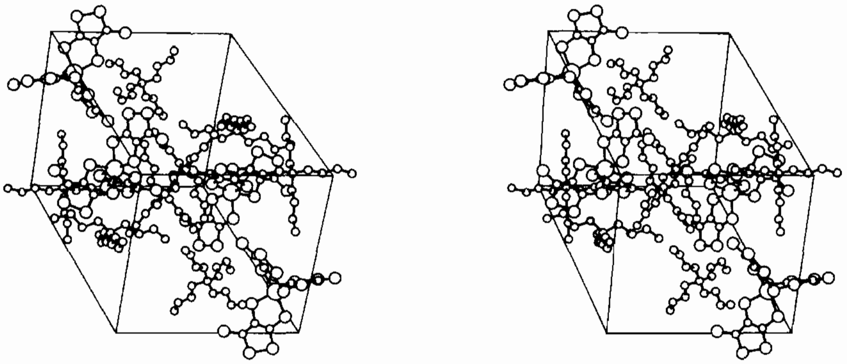

Fig. 1. Stereo view of the unit cell of $(Bu_4N)_2[V(dmt)_3]$.

of cations (this is indicated also by the maxima from the difference map around the N(2) atom). Due to this fact particularly the terminal C–C bonds and conformation are unusual.

Physical Measurements

EPR spectra were recorded from acetonic solutions at $T = 295$ and 133 K using an E-112 spectrometer (Varian) in the X-band. Conductivity measurements were performed at 10^{-4} M in nitromethane (293 K) using a conductivity bridge type LM 301 (VEB Hydromat, G.D.R.).

Infrared spectra (see Table III) were taken with an UR 20 spectrometer (VEB Carl Zeiss, Jena, G.D.R.). UV–Vis spectra were recorded using a spectrometer 'Specord' (VEB Carl Zeiss, Jena, G.D.R.).

Discussion

Preparation of Compounds

There is no sharp classification of central metal ions in those which form bis- and/or tris-chelates with dithiolene ligands. Indium(III) or thallium(III) for example yield bis- as well as tris-compounds with the same dithiolene ligands (e.g., mnt [10, 26, 27]). Also transition metal ions like manganese, iron or cobalt in different oxidation states show that behaviour [4, 15, 28].

We succeeded in preparing tris-chelates of In(III) and Tl(III) containing the ligands dmit and dmt, respectively, and an In(III) chelate of dsis. No preparative evidence was found for the existence of bis-complexes. Thus, it seems that all three ligands prefer an octahedral arrangement around the ions In(III) and Tl(III). With Ga(III) we could isolate a bis-chelate $Ph_4As[Ga(dmt)_2]$ only [29], although with other dithiolene ligands (mnt [27]) also bis- as well as tris-compounds have been formed.

Synthesis of the tris-complexes is no problem starting with alkali salts of the ligands, either isolated before or *in situ* solution obtained by saponification of the dibenzoyl compounds, and a suitable metal salt. For the vanadium(IV) compounds it seems important to start with vanadium(III) chloride. Otherwise, starting for example with vanadyl sulfate, the vanadyl bis-chelate or mixtures of vanadyl and vanadium(IV) compounds are obtained as can be followed by EPR. Elemental analyses, molar conductivities (see Table III) and EPR results (see Table V) prove the compositions of the compounds.

Description and Discussion of the Structure of $(Bu_4N)_2[V(dmt)_3]$

The structure consists of four anions and eight cations in the unit cell as shown in Fig. 1. Despite the obviously remarkable thermal motion of the cations causing unusual conformation and unusual, especially

TABLE IV. Selected Distances (Å) and Angles (°) in the $[V(dmt)_3]^{2-}$ Anion

V–S(1)	2.401(3)	S(1)–S(6)	3.670(2)
V–S(2)	2.341(2)	S(1)–S(7)	3.126(2)
V–S(6)	2.419(2)	S(1)–S(11)	3.410(3)
V–S(7)	2.342(2)	S(2)–S(6)	3.412(3)
V–S(11)	2.405(3)	S(2)–S(11)	3.758(3)
V–S(12)	2.342(3)	S(2)–S(12)	3.167(2)
S(1)–S(2)	3.150(3)	S(6)–S(12)	3.315(3)
S(6)–S(7)	3.210(3)	S(7)–S(11)	3.097(2)
S(11)–S(12)	3.228(3)	S(7)–S(12)	3.832(2)
C(1)–S(1)	1.706(8)	S(4)–S(5)	2.069(3)
C(2)–S(2)	1.736(8)	S(9)–S(10)	2.067(4)
C(6)–S(6)	1.710(8)	S(14)–S(15)	2.089(6)
C(7)–S(7)	1.745(7)		
C(11)–S(11)	1.699(10)		
C(12)–S(12)	1.745(9)		
C(1)–C(2)	1.380(12)		
C(6)–C(7)	1.367(12)		
C(11)–C(12)	1.379(15)		
S(1)–V–S(2)	83.25(8)	'*trans*-Angles'	
S(6)–V–S(7)	84.74(8)	S(1)–V–S(12)	166.34(8)
S(11)–V–S(12)	85.67(9)	S(2)–V–S(7)	164.47(10)
S(1)–C(1)–C(2)	122.8(6)	S(6)–V–S(11)	162.00(9)
S(2)–C(2)–C(1)	119.1(5)		
S(6)–C(6)–C(7)	124.0(6)		
S(7)–C(7)–C(6)	120.5(6)		
S(11)–C(11)–C(12)	123.8(7)		
S(12)–C(12)–C(11)	121.1(7)		

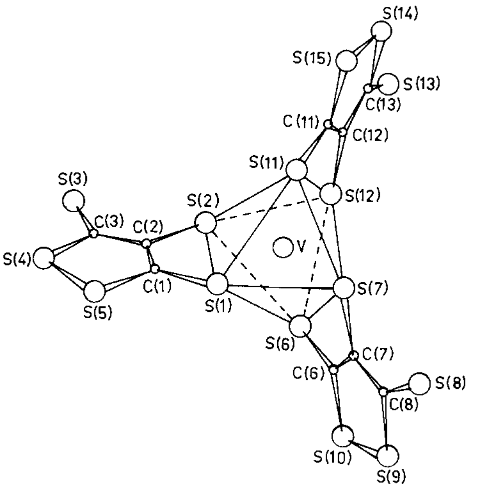

Fig. 2. Geometry of the $[V(dmt)_3]^{2-}$ anion and numbering of atoms.

terminal, C–C bonds, the structure of these tetra-n-butylammonium cations is not further discussed. Most important interatomic distances and angles of the anion $[V(dmt)_3]^{2-}$ are listed in Table IV. The numbering scheme and the coordination geomeotry of this anion are shown in Fig. 2. As expected, the symmetry of the VS_6 core is closer to an octahedron than to a trigonal prism found mainly in neutral tris-dithiolenes, that is compounds containing the metal ion in the formal oxidation state +VI [12, 31]. The six sulfur donor atoms are located around the vanadium at an average distance of 2.375 Å which is in quite good accordance with the value 2.36 Å reported for the compound $(Me_4N)_2[V(mnt)_3]$ containing also a dithiolene ligand and vanadium in the formal oxidation state +IV [31]. Contrary to this complex, however, the V–S bonds in $[V(dmt)_3]^{2-}$ can be classified in two groups: the V–S bonds neighbouring the non-coordinated C–S group have an average length of 2.342 Å, the other ones with 2.408 Å are clearly longer than expected. The polyhedra described by the six sulfur atoms are in both cases a distorted octahedron. Normally the parameters θ, the compression ratio s/h and the '*trans*-angle' S–M–S are used to characterize these distortions [12]. However, due to the very low symmetry of the VS_6 core in the compound under study* a discussion of the values which can be calculated for θ and the s/h ratio does not seem to be of any worth. The average *trans*-

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*The reason for the low symmetry of the VS_6 core (inter-ligand S–S distances from 3.097(2) to 3.832(2) Å and intra-ligand distances 3.150(3), 3.210(3), 3.228(3) Å; see Table IV) in comparison to similar anions $[M(mnt)_3]^{2-}$ (M e.g. V, Mo, W, Fe [1, 4, 5]), which contain a C_2 axis, is the asymmetry of the coordinated dmt ligand destroying such a symmetry axis.

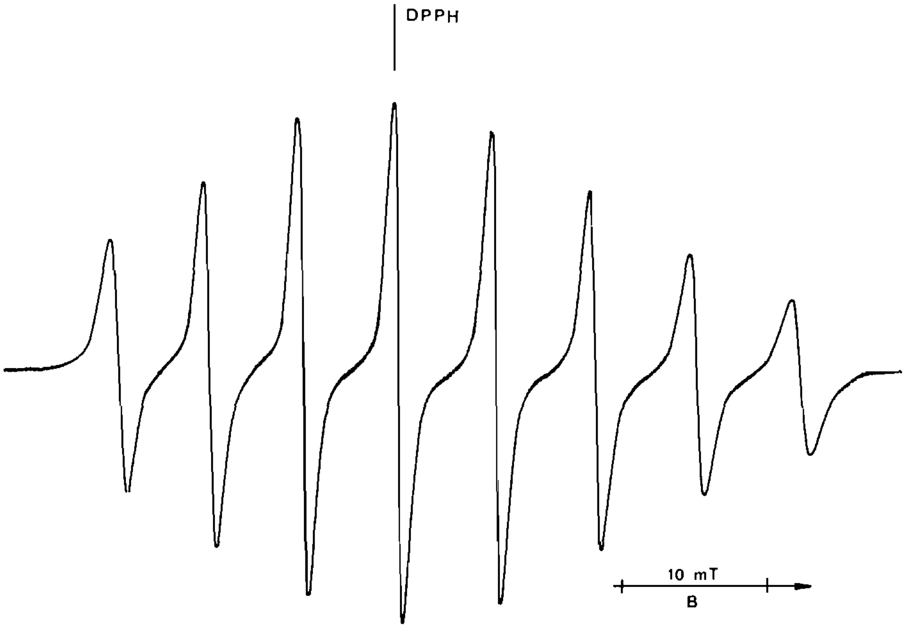

Fig. 3. Room-temperature EPR spectrum of $(Bu_4N)_2[V(dmt)_3]$ in acetone.

TABLE V. Principal Values of the $\tilde{g}$ and the ^{51}V Hyperfine Structure Tensor $\tilde{A}^V$. Hyperfine Couplings and K Given in 10^{-4} cm^{-1}, Solvent: Acetone

	$[V(dmit)_3]^{2-}$	$[V(dmt)_3]^{2-}$	$[V(mnt)_3]^{2-}$[a]
g_z	2.000 ± 0.003	2.000 ± 0.003	2.000
g_x	1.964 ± 0.002	1.960 ± 0.002	1.974
g_y	1.971 ± 0.003	1.965 ± 0.003	1.974
g_{av}	1.978	1.973	1.982
g_0[b]	1.979 ± 0.002	1.978 ± 0.002	1.980
A_z^V	+3.3 ± 3.0	+4.0 ± 3.0	+9.2
A_x^V	−113.0 ± 2.0	−113.3 ± 2.0	−91.0
A_y^V	−94.0 ± 3.0	−96.7 ± 3.0	−91.0
A_{av}^V	−67.9	−68.7	−57.7
a_0^V[b]	63.9 ± 0.5	61.9 ± 0.5	57.9
β^2	0.76	0.78	0.65
K	72.1	73.4	55.2

[a] Data taken from ref. 37. [b] Liquid solution data.

angle S–V–S is 164.3°, which is remarkably lower than the 174.6° expected for a 'corrected' octahedron formed by the constraint of rigid chelate ligands exhibiting an average bite angle (S–V–S) of 84.6° [12, 32]. Nevertheless, this value resembles more that of an octahedron than that of a trigonal prism (which is expected to be about 136°). In $(Me_4N)_2[V(mnt)_3]$ the *trans*-angle 158.6° deviates still stronger from 173° (the bite angle of the mnt ligand is about 83°) expected for the octahedral limit.

All three $VS_2C_2(CS)S_2$ units are nearly planar. The average C–S (1.723(8) Å) and C–C (1.375(18) Å) distances in the chelate rings are similar to those found for $(Me_4N)_2[V(mnt)_3]$ and $(Ph_4As)_2[Fe(mnt)_3]$ [33] and support the contention that the complex anions are formed by three dithiolato ligands and a metal(IV) central ion. Surprisingly, however, the C–C bond (chelate ring) in $(Bu_4N)_2[V(dmt)_3]$ appears to be remarkably shorter than that found for the planar $(Bu_4N)_2[Ni(dmt)_2]$ (1.42 Å) [13f].

The isovalence of the three sulfur atoms (e.g. S(1), S(2), S(3)) in the non-coordinated 'free' dmt ligand (1,2-dithiole-3-thione-4,5-dithiolate) as observed for instance in the dipotassium salt [34] is lifted by coordination to Ni(II) or V(IV). In the case of the nickel bis-chelate a *trans* position of the non-coordinated C=S groups and in the case of the vanadium tris-chelate a pseudo-meridional arrangement of the three dmt ligands has been observed, whereby the responsibility of packing requirements to this geometry cannot be excluded.

EPR Investigations

For $(Bu_4N)_2[V(dmit)_3]$ and $(Bu_4N)_2[V(dmt)_3]$ in acetone solution intense EPR spectra are observed. The room-temperature spectra consist of 8 vanadium hyperfine structure lines due to the interaction of the unpaired electron with the nuclear spin of the isotope ^{51}V ($I = 7/2$). Figure 3 shows the room-temperature spectrum of $(Bu_4N)_2[V(dmt)_3]$. The isotropic g values and hyperfine coupling parameters a_0^V are listed in Table V.

In frozen solutions the EPR spectra of both complexes are clearly non-axial and can be described by the following rhombic-symmetric spin-Hamiltonian

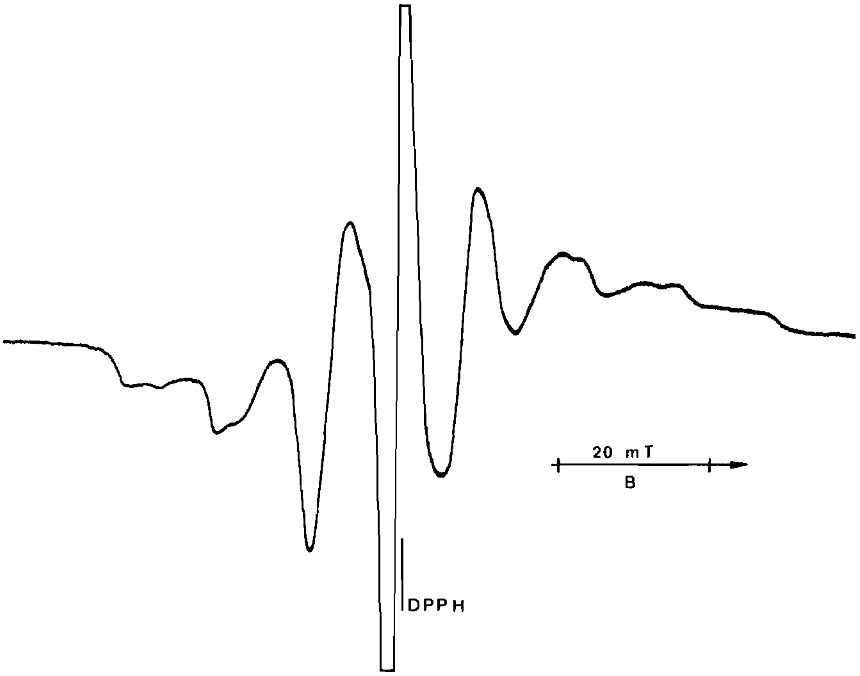

Fig. 4. EPR spectrum of $(Bu_4N)_2[V(dmit)_3]$ recorded in acetone, $T = 133$ K.

$$\hat{\mathcal{H}}_{sp} = \beta_e(g_x\mathcal{H}_x\hat{S}_x + g_y\mathcal{H}_y\hat{S}_y + g_z\mathcal{H}_z\hat{S}_z) + A_x^V\hat{S}_x\hat{I}_x + A_y^V\hat{S}_y\hat{I}_y + A_z^V\hat{S}_z\hat{I}_z \qquad (1)$$

in which all symbols have their usual meaning [35]. Quadrupole interactions have been neglected because they are expected to be small. In Fig. 4 the frozen solution spectrum of $(Bu_4N)_2[V(dmit)_3]$ recorded in acetone at $T = 133$ K is reproduced. The experimentally obtained principal values of the $\tilde{g}$ and the ^{51}V hyperfine structure tensor $\tilde{A}^V$ are given in Table V, together with those reported for tris(maleonitriledithiolato)vanadate(IV), $[V(mnt)_3]^{2-}$, for comparison. $[V(mnt)_3]^{2-}$ is the only other vanadium(IV) trisdithiolato complex which has been studied in detail in frozen solutions [36] and by single-crystal EPR technique [37, 38].

The sign of the smallest ^{51}V hyperfine component A_z^V has been chosen to be opposite to that of the other two tensor components. This has been proposed by Kwik and Stiefel [37] for $[V(mnt)_3]^{2-}$ and appears to be reasonable also for $[V(dmit)_3]^{2-}$ and $[V(dmt)_3]^{2-}$ because it results in a better agreement between the average values A_{av}^V and the observed isotropic values a_0^V obtained from the liquid solution spectra.

The isotropic ^{51}V splittings as well as the dipolar parts of the ^{51}V hyperfine tensors obtained for $[V(dmit)_3]^{2-}$ and $[V(dmt)_3]^{2-}$ are considerably smaller than those reported for oxovanadium(IV) biscomplexes [39–41] and come close to the parameters found for $[V(mnt)_3]^{2-}$. This and the observed symmetry behaviour of the $\tilde{g}$ tensors (g_z is close to the free-electron g value) are consistent with a 'more trigonal-prismatic' arrangement of the dithiolene ligands in the complexes which is disturbed as indicated by the rhombic nature of $\tilde{g}$ and $\tilde{A}^V$. This seems to be somewhat in contradiction to the results of the structure investigations described above for $[V(dmt)_3]^{2-}$. However, this result is not surprising because as a rule the symmetry of complexes studied in solution is found to be higher than that reported for the solid state.

The low symmetry revealed for the investigated complexes does not allow a complete description of the bonding situation in the vanadium(IV) trischelates. Nevertheless, the general features of the observed tensor parameters – $g_z \approx g_e$, A_z^V very small – and the observation of small line widths in the spectra even at room temperature indicate a well-separated non-degenerate molecular orbital of a_1 symmetry containing the unpaired electron

$$\Psi(a_1) = \beta|d_{z^2}\rangle - \beta'|\Phi_L(a_1)\rangle \qquad (2)$$

where β and β' are MO coefficients; $|\Phi_L(a_1)\rangle$ represents the corresponding symmetry-adapted linear combination of the sulfur orbitals in this MO. The MO is predominantly π-type in character, thus β becomes a measure of the π-bonding in the complexes. β can be estimated using the following eqns. (3)

$$A_\parallel^V = -K + (4/7)\beta^2P - (1/7)(g_\perp - g_e)P \qquad (3a)$$

$$A_\perp^V = -K - (2/7)\beta^2P - (13/14)(g_\perp - g_e)P \qquad (3b)$$

In these equations axial symmetry (D_3) has been assumed ($A_{\parallel}^{\mathrm{V}} = A_{\mathrm{z}}^{\mathrm{V}}$; $A_{\perp}^{\mathrm{V}} = (A_{\mathrm{x}}^{\mathrm{V}} + A_{\mathrm{y}}^{\mathrm{V}})/2$; $g_{\perp} = (g_{\mathrm{x}} + g_{\mathrm{y}})/2$), K is a measure of the isotropic contact interaction, and $P = g_{\mathrm{e}}g_{\mathrm{N}}\beta_{\mathrm{e}}\beta_{\mathrm{N}} \langle r^{-3} \rangle = 172 \times 10^{-4}$ cm^{-1} [37]. The values obtained for β^2 and K are listed in Table V and therein compared to those published for $[\mathrm{V(mnt)_3}]^{2-}$. According to this, as shown by the larger β^2 and K values the covalency degree found for the $\Psi(a_1)$ MO of the two vanadium(IV) tris-complexes studied in this work turns out to be noticeably smaller than that observed for $[\mathrm{V(mnt)_3}]^{2-}$. Nevertheless, the results indicate substantial delocalization of the unpaired electron in the a_1 level and support an effective overlapping of the metal d_{z^2} orbital with the corresponding sulfur orbitals, most probably with the lone pair orbital on S which is not involved in σ bonding [37, 42]. The smaller degree of delocalization of spin-density found for the investigated chelates seems to be mainly caused by the deviations from a trigonal-prismatic symmetry making the overlapping of the d_{z^2} orbital with the corresponding S orbitals less effective than observed for $[\mathrm{V(mnt)_3}]^{2-}$; single-crystal EPR studies made on $[\mathrm{Cu(mnt)_2}]^{2-}$ [43, 44] and $[\mathrm{Cu(dmit)_2}]^{2-}$ [45] in comparable structural situations (the corresponding almost planar Ni(II) compounds have been used as host lattices) show only a small difference in the metal–ligand covalency for both complex anions. No appropriate interpretation of the g values in terms of bonding parameters for other states than that of the unpaired electron could be made on the basis of the obtained data. This would require knowledge of (a) the corresponding d–d transition energies of the electronic spectra and (b) the values of the compression ratio s/h from crystallographic studies. As shown above, the low symmetry of $[\mathrm{V(dmt)_3}]^{2-}$, however, does not allow the determination of any reasonable s/h ratio. Also, from the electronic spectra of the vanadium(IV) complexes an unambiguous attribution of d–d transitions could not be deduced.

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