Covalent Compounds of Quadrivalent Transition Metals. Part VI.† Spectroscopic Studies on Titanium, Vanadium, and Zirconium Diethyldithiocarbamates

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Data on the electronic, i.r., Raman, e.s.r., and mass spectra, and magnetochemistry of the compounds $M(S_2CNEt_2)_4$ (M = Ti, V, or Zr), $V(S_2CNEt_2)_3$, $VO(S_2CNEt_2)_3$, and $VO(S_2CNEt_2)_2$ are reported and discussed. It is deduced that the compound $V(S_2CNEt_2)_4$, which readily dissociates on heating to $V(S_2CNEt_2)_3$, is eight-co-ordinate (dodecahedral). The electronic and anisotropic e.s.r. spectra of the compound $V(S_2CNEt_2)_4$ are interpreted in terms of crystal-field splitting of *d* orbitals in the V^{4+} ion.

PREVIOUSLY [1] we described the preparation of tetrakis-*NN*-dialkyldithiocarbamates $M(S_2CNR_2)_4$ of the early transition elements by means of the insertion reaction (1). From i.r. and n.m.r. studies it was suggested that

$$M(NR_2)_4 + 4CS_2 \longrightarrow M(S_2CNR_2)_4 \qquad (1)$$

these compounds might involve eight-co-ordinate metals[1] and *X*-ray crystal-structure analysis has since proved that $Ti(S_2CNEt_2)_4$ contains discrete eight-co-ordinate (dodecahedral) molecules.[2] The zirconium analogue is isomorphous. Preliminary accounts of the magnetochemistry [3] and e.s.r. spectra [4] of the compound $V(S_2CNMe_2)_4$ and the e.s.r. spectra [4] of $V(S_2CNEt_2)_4$ have appeared, and it was postulated for the latter compound that stereoisomers occurred. We now report further work on $V(S_2CNEt_2)_4$ which shows that this compound is thermally unstable and has necessitated a reinvestigation of the magnetic properties and e.s.r. spectra. Full details of the spectroscopic work on the *NN*-diethyldithiocarbamates of titanium, vanadium, and zirconium are also reported.

RESULTS AND DISCUSSION

NN-*Diethyldithiocarbamatovanadium Compounds*.—Variable-temperature magnetic-susceptibility measurements on the compound $V(S_2CNEt_2)_4$ (I), prepared by the original method,[1] revealed the presence of $V(S_2CNEt_2)_3$ (II) due to thermal instability of the V^{IV} compound. Thus over the range 98—323 K compound (I) gave $\mu_{eff.}$ 2·24 B.M. compared with the expected value of $\leqslant$1·73 B.M. for a V^{IV} d^1 species. After heating compound (I) at 100 °C for 1 h redetermination of χ_g at 298 K gave a much higher value for $\mu_{eff.}$ corresponding to an increase in the proportion of (II). A sample of the red-brown compound (I) was heated under reflux in toluene for several hours and gave a yellow-

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† Part V, D. C. Bradley and M. H. Chisholm, *J. Chem. Soc.* (*A*), 1971, 2741.

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[2] D. C. Bradley, M. Colapietro, M. B. Hursthouse, I. F. Rendall, and A. Vaciago, *Chem. Comm.*, 1970, 743; *J.C.S. Dalton*, 1972, 1052.

[3] E. C. Alyea and D. C. Bradley, *J. Chem. Soc.* (*A*), 1969, 2330.

[4] D. C. Bradley, R. H. Moss, and K. D. Sales, *Chem. Comm.*, 1969, 1255.

brown product (II) which was shown by elemental analysis to be $V(S_2CNEt_2)_3$ and gave $\mu_{eff.}$ 2·70 B.M. at 298 K, decreasing slightly to 2·57 B.M. at 98 K. These results clearly showed that the original method of preparing compound (I), which involved heating, would inevitably lead to contamination by (II) and we have now developed a method of preparing (I) under milder conditions. The realization that previous work on (I) had involved an impure compound led us to reconsider the earlier interpretation of the e.s.r. and i.r. spectra.[4]

TABLE 1

E.s.r. data for vanadium(IV) *NN*-diethyldithiocarbamates

Compound	Sample conditions	g_0 [a]	A_0 [b]	$g_{\parallel}$ [a]	$A_{\parallel}$ [b]	$g_{\perp}$ [a]	$A_{\perp}$ [a]
$V(S_2CNEt_2)_4$	Powder (298 K)	*ca.* 1·990	unresolved	← unresolved →			
$V(S_2CNEt_2)_4$	Toluene soln. (298 K)	1·9748	66·4				
$V(S_2CNEt_2)_4$	Doped [c] in $Ti(S_2CNEt_2)_4$ (298 K)	1·9746 [d]	66·6 [d]	1·9556	123·2	1·9841 [e]	38·3 [e]
$V(S_2CNEt_2)_4$	Toluene soln. [f] (298 K)	1·9746	66·6				
$V(S_2CNEt_2)_4$	Toluene soln. [f] (153 K)	1·9746 [d]	66·6 [d]	1·9576	123·5	1·9831 [e]	37·8 [e]
$VO(S_2CNEt_2)_2$	Powder (298 K)	*ca.* 1·987	unresolved	← unresolved →			
$VO(S_2CNEt_2)_2$	Toluene soln. (298 K)	1·9794	83·5				
$VO(S_2CNEt_2)_2$	Toluene soln. (153 K)	1·9794 [g]	83·3 [g]	1·9640	147·6	1·9871 [e]	51·2 [e]

[a] All g values quoted to four decimal places are estimated to be accurate to ± 0·0005. [b] 10^{-4} × Nuclear-hyperfine coupling, constants in cm^{-1}; estimated to be accurate to ± 0·3. [c] *Ca.* 7 mol % $V(S_2CNEt_2)_4$ in $Ti(S_2CNEt_2)_4$. [d] Assumed to be the same values as given [f] at 298 K. [e] Calculated from g_0, $g_{\parallel}$, A_0. and $A_{\parallel}$ values using the expressions $g_0 = 1/3(g_{\parallel} + 2g_{\perp})$ and $A_0 = 1/3(A_{\parallel} + 2A_{\perp})$. [f] This is a toluene solution of the doped sample *c*. [g] Assumed to be the same values as given at 298 K.

We now present evidence which suggests that: (i) only one form of compound (I) occurs; (ii) it is the tetrachelated eight-co-ordinate (dodecahedral) species; and (iii) the earlier e.s.r. and i.r. results can be explained by the presence of traces of $VO(S_2CNEt_2)_3$ (III) and $VO(S_2CNEt_2)_2$ (IV). Compound (IV) was prepared by a modification of McCormick's method[5] and an impure sample of the thermally unstable compound (III) was obtained from the reaction of $VOCl_3$ with LiS_2CNEt_2.

Referring to the e.s.r. data in Table 1, it is now clear that the signal reported[4] (g_0 1·975, A_0 0·00668 cm^{-1}) for the fresh benzene solution must be due to compound (I) and the slowly developing signal (g_0 1·977, A_0 0·00844 cm^{-1}) due to compound (IV) as an impurity. Our data for compound (IV) (Table 1) agree within experimental error with those reported independently.[6,7] No signal was given by compound (III) because it is diamagnetic and the weak signal given by (II) could be assigned to a trace of (IV) as impurity. Although compound (II) is paramagnetic, the absence of e.s.r. signals under our experimental conditions was consistent with the presence of a d^2 octahedral species.

Features of the i.r. spectra are to be found in Supplementary Publication No. SUP 20808 (5 pp.).* First it is noteworthy that the spectra of the compounds $M(S_2CNEt_2)_4$ (M = Ti, V, and Zr) are very similar and, since the titanium and zirconium compounds are known to be eight-co-ordinate,[2] this suggests that compound (I) is also tetrachelated. Secondly, it is evident that the sharp band at 953 cm^{-1}, which slowly developed in the spectrum of compound (I),[4] is most probably due to formation of traces of (III) as impurity, since the latter gives a very intense band at 951 cm^{-1} which we assign to the V=O stretching vibration. Exposure of compounds (I) and (II) to air led to a dramatic increase in intensity of a band at 952 cm^{-1} in (I), and to a lesser extent in (II), due to formation of (III), but the strong band at 989 cm^{-1} due to (IV) did not appear. However, it was also observed that compound (III) was thermally unstable and was slowly converted to (IV). Therefore, it seems that measurement of the physical properties of the compound $V(S_2CNEt_2)_4$ is fraught with difficulties due to thermal instability and sensitivity to oxygen. Some possible reaction paths are indicated in equations (2)—(4). Reaction

$$V(S_2CNEt_2)_4\ (I) \xrightarrow{\text{heat}} V(S_2CNEt_2)_3\ (II) + \tfrac{1}{2}(Et_2NCS_2)_2 \quad (2)$$

$$2V(S_2CNEt_2)_4 + O_2 \longrightarrow 2VO(S_2CNEt_2)_3\ (III) + (Et_2NCS_2)_2 \quad (3)$$

$$VO(S_2CNEt_2)_3 \xrightarrow{\text{heat}} VO(S_2CNEt_2)_2\ (IV) + \tfrac{1}{2}(Et_2NCS_2)_2 \quad (4)$$

(2) constitutes the major source of impurity in the absence of air. Both reactions (2) and (3) cause loss of the e.s.r. signal of (I), but reaction (4) produces the intense e.s.r. signal of compound (IV) and reaction (3) produces the intense i.r. band at *ca.* 951 cm^{-1} due to (III). However, we cannot exclude the possibility that oxygen is introduced at an earlier stage than reaction (3), namely by reaction with the compound $V(NEt_2)_4$ used in the preparation of (I).

Attempts to grow single crystals of compound (I) have not yet been successful but a comparison of *X*-ray powder diffraction patterns has shown that (I) is isomorphous with $Ti(S_2CNEt_2)_4$ and $Zr(S_2CNEt_2)_4$ and therefore contains eight-co-ordinate (dodecahedral) vanadium. This structural assignment is supported by the e.s.r. data on compound (I) (Table 1). Although

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue (items less than 10 pp. are supplied as full size copies).

[5] B. J. McCormick, *Inorg. Chem.*, 1968, **10**, 1965.

[6] B. J. McCormick and E. M. Bellot, *Inorg. Chem.*, 1970, **9**, 1779.

[7] N. S. Garif'yanov and B. M. Kozyrev, *Teor. i eksp. Khim.*, 1965, **1**, 525.

compound (I) as a powder gave a broad unresolved e.s.r. signal at room temperature, a sample doped in $Ti(S_2CNEt_2)_4$ showed *g*-anisotropy corresponding to an axially symmetric species with resolved ^{51}V nuclear-hyperfine splitting. The anisotropic data were confirmed by measurements on frozen toluene solutions at low temperatures. The *g* values are consistent with a $^2B_1$ ($d_{x^2-y^2}$) ground state which, from the following discussion, appears to be a likely possibility for a dodecahedral (D_{2d}) V^{IV} ion.[8,9]

Crystal-field calculations by Garner and Mabbs[10] have shown that the *d*-orbital energy levels in dodecahedral complexes are sensitive to the ratio a ($=R_A/R_B$, where R_A and R_B are the metal–donor atom distances for the A and B positions respectively), the angular parameters θ_A and θ_B (θ is the angle between the S_4 axis and the metal–donor atom vector), and the crystal-field parameters Dq and Cp. Assuming the geometry for compound (I) to be the same as for $Ti(S_2CNEt_2)_4$,[2] the energies of the *d* orbitals are obtained as shown in Table 2, where n is the ratio $Cp : Dq$. The parameter Dq ($=Ze^2r^4/6R_A{}^5$) (ref. 10) should be a positive quantity, and n lie somewhere in the range 2—8.[10] Certainly for a wide range of values of n, Table 2 indicates that for compound (I) $d_{x^2-y^2}$ should be the lowest-energy orbital; as it is very improbable that the simple crystal field will be wildly incorrect, we conclude that $^2B_1$ ($d_{x^2-y^2}$) is the ground state. Reference to Table 3 shows that compound (I) gave a broad weak band at 13 600 cm^{-1}, which is probably due to a *d–d* transition, and strong bands at higher energies, which are probably c.t. or intraligand transitions (*cf.* the spectrum of the d^0 Ti compound). The assignment of the 13 600 cm^{-1} band is not definitive, although it is probably due to the transition $^2B_1 \longrightarrow {}^2E$ as this is the only one of the three possible transitions which is allowed by the selection rules. A detailed consideration of the e.s.r. parameters supports this assignment.

TABLE 2

One-electron *d*-orbital energy levels in D_{2d} symmetry

3*d* Orbital	Energy (units of Dq) [a,b]	Energy [c] cm^{-1}
$d_{x^2-y^2}$ (b_1)	$-4\cdot948 - 0\cdot126n$	$-13\,175$
$d_{xz,yz}$ (e)	$-0\cdot266 + 0\cdot063n$	$+272$
d_{z^2} (a_1)	$0\cdot298 + 0\cdot126n$	$+2\,688$
d_{xy} (b_2)	$5\cdot080 - 0\cdot126n$	$+9\,939$

[a] $n = Cp : Dq$. [b] Calculated using crystallographic data[2] for the compound $Ti(S_2CNEt_2)_4$ which correspond to $a = 0\cdot971$, $\theta_A = 77\cdot5$, and $\theta_B = 35\cdot1°$. It is to be noted that the expressions quoted in ref. 10 require $a < 1$; this definition of A and B is, in this case, the reverse of the conventional crystallographic nomenclature. Crystallographic data[14] for the compound $V(S_2CCH_2C_6H_5)_4$ are equivalent to $a = 0\cdot978$, $\theta_A = 76\cdot0$, and $\theta_B = 37\cdot6°$. [c] Calculated for $n = 6\cdot1$ and $Dq = 2\,305$ cm^{-1}; values derived for the compound $V(S_2CNEt_2)_4$.

TABLE 3

Electronic absorption spectra

Compound [a]	Electronic spectra [b]
TiL_4 [c]	25·3; 29·2; 36·9
VL_4 [c]	13·6; 31·7; 34·8; 44·1
VL_4 [d,e]	13·6(22)
VL_3 [c]	14·0sh; 24·0; 30·5; 40·7
VL_3 [d]	14·0(23); 24·4sh; 31·8 (21 000)
VOL_2 [c]	18·0; 22·5sh; 32·8; 45·0
VOL_2 [d,f]	16·9sh; 18·5sh

[a] $L = S_2CNEt_2$. [b] $10^{-3} \times$ Band maxima in cm^{-1}. [c] Reflectance spectra. [d] Absorption spectra in toluene; ε (l mol^{-1} cm^{-1}) in parentheses. [e] Recorded only from 5 000 to 19 600 cm^{-1}. [f] Recorded only from 5 000 to 22 200 cm^{-1}.

The *g* and *A* values for a ground state of $d_{x^2-y^2}$ are given,[11] to first order in λ/Δ, by expressions (5)—(8),

$$g_{\parallel} = 2\cdot0023 - (8\lambda/\Delta_{xy}) \quad (5)$$

$$g_{\perp} = 2\cdot0023 - (2\lambda/\Delta_{xz,yz}) \quad (6)$$

$$A_{\parallel} = P[-\kappa - (4/7) - (8\lambda/\Delta_{xy}) - (6/7)\lambda/\Delta_{xz,yz}] \quad (7)$$

$$A_{\perp} = P[-\kappa + (2/7) - (11/7)\lambda/\Delta_{xz,yz}] \quad (8)$$

where $P = 2\cdot0023g_N\beta_N\beta\langle r^{-3}\rangle_{av}$, λ is the spin–orbit coupling parameter in the complex, κ the isotropic contribution to the hyperfine coupling constant, and Δ_q represents the excitation energy from the ground state to state q. These equations are derived with the neglect of all terms involving ligand orbitals, *i.e.* with similar assumptions to those used for deriving the orbital energies given in Table 2. Using Δ_{xy}, which is independent of n, from Table 2 in conjunction with the experimental value for $g_{\parallel}$ gives $\lambda/Dq = 0\cdot0560$, whereupon the experimental value for $g_{\perp}$ enables n to be evaluated as 6·1. Equations (7) and (8), assuming the experimental values to be negative, give rise to $\kappa = 0\cdot690$ and $P = 0\cdot0089$ cm^{-1}. Both P and λ are proportional to $\langle r^{-3}\rangle_{av}$ and for the V^{4+} ion it has been estimated[12] that $\lambda \simeq 1\cdot45 \times 10^4P$; use of this relation gives λ *ca.* 129·1 cm^{-1} and therefore a Dq value of 2 305 cm^{-1}. Hence we predict the electronic transitions to be: $^2B_1 \longrightarrow {}^2E$ at 13 450; $^2B_1 \longrightarrow {}^2A_1$ at 15 865; and $^2B_1 \longrightarrow {}^2B_2$ at 23 115 cm^{-1}. The allowed transition is very close to the observed band at 13 600 cm^{-1} and could easily mask a forbidden transition at 15 865 cm^{-1}, while the band at 23 115 cm^{-1} is in the c.t. region.

The above interpretation of the e.s.r. parameters and electronic spectrum of compound (I) entirely in terms of crystal-field theory appears to have worked rather well. The κ value of 0·69 may be compared with values of 0·63 for tetrakis(t-butoxo)vanadium(IV)[12] and 0·53 for tetrakis(diethylamino)vanadium(IV);[13] these V^{IV} compounds both have D_{2d} symmetry and the results were interpreted using equations for the e.s.r. parameters which included the effect of ligand orbitals. In both cases λ was found to be 156 cm^{-1} compared with the value obtained here of 129 cm^{-1}. This comparison suggests the shortcomings of our model, because a

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[8] B. R. McGarvey, *Inorg. Chem.*, 1966, **5**, 476.

[9] R. G. Hayes, *J. Chem. Phys.*, 1966, **44**, 2210.

[10] C. D. Garner and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1970, 1711.

[11] B. R. McGarvey, *Transition Metal Chem.*, 1966, **3**, 89.

[12] G. F. Kokoszka, H. C. Allen and G. Gordon, *Inorg. Chem.*, 1966, **5**, 91.

[13] C. E. Holloway, F. E. Mabbs, and W. R. Smail, *J. Chem. Soc.* (*A*), 1968, 2980.

smaller λ value is usually taken to indicate a greater degree of covalent bonding. On the other hand, to analyse the results in terms of the equations involving overlap between ligand and metal orbitals would not seem to be justified with the data available. We conclude that the crystal-field model fits the data reasonably well but that the low value of λ compared to the free-ion value (250 cm^{-1}) is indicative of covalent bonding.

A major assumption in the above calculations concerned the geometrical parameters for the VS_8 group in compound (I). It is encouraging to find that *X*-ray crystal-structure analysis of the compound $V(S_2CCH_2C_6H_5)_4$[14] has shown that it also has the dodecahedral VS_8 group with parameters (V–S$_A$ 2·524 ± 0·007; V–S$_B$ 2·470 ± 0·007 Å; θ_A 37·6 ± 0·2; θ_B 76·0 ± 0·2°) close to those used in our calculations. In terms of covalent bonding in the compound $V(S_2CNEt_2)_4$, we note that the 3*d* orbitals ($a_1 + b_2 + e$), which could be hybridized with the 4*s* (a_1) and 4*p* ($b_2 + e$) to give dodecahedrally directed σ-bonds, are just those which are destabilized according to the crystal-field treatment (Table 2). Moreover, the d_{xy} (b_2) orbital is clearly involved to a much greater degree than the $d_{xz,yz}$ (e) or d_{z^2} (a_1) orbitals, in accord with the crystal structure[2] which shows significantly shorter Ti–S$_B$ bonds (2·522 ± 0·008 Å) than Ti–S$_A$ bonds (2·606 ± 0·008 Å). Furthermore, the $d_{x^2-y^2}$ (b_1) orbital which is not involved in Ti–S σ-bonding could by symmetry be involved in π-bonding with a b_1-symmetry combination of π-acceptor orbitals of the S$_B$ atoms thus enhancing the stabilization of the $d_{x^2-y^2}$ orbitals.

The tris(*NN*-diethyldithiocarbamato)vanadium compound (II) is expected to be a distorted (D_3) octahedral d^2 complex. Three *d–d* transitions are expected in O_h symmetry [$\nu_1 = {}^3T_{1g}(F) \longrightarrow {}^3T_{2g}$; $\nu_2 = {}^3T_{1g} \longrightarrow {}^3T_{1g}(P)$; $\nu_3 = {}^3T_{1g} \longrightarrow {}^3A_{2g}$], but Table 3 shows only two bands (14 000 and 24 400 cm^{-1}) which are probably due to *d–d* transitions. The low-energy band (14 000 cm^{-1}) is weak (ε *ca* 23 l mol^{-1} cm^{-1}) and is most probably due to ν_1, but the higher-energy band is a shoulder on a very intense band at 31 800 cm^{-1} and is in the region where c.t. or intraligand transitions are expected (*cf.* spectrum of d^0 Ti^{IV} compound). Assuming that the transitions are ν_1 14 000 cm^{-1} and ν_2 24 400 cm^{-1} gives $Dq = 1\,541$, $B = 787$ cm^{-1}, and $\beta = 0{\cdot}92$. However, this value for β seems high compared with those deduced for the compounds $V\{S_2P(OEt)_2\}_3$[15] ($Dq = 1\,400$, $B = 420$ cm^{-1}, $\beta = 0{\cdot}49$) and $Cr(S_2CNEt_2)_3$ ($Dq = 1\,550$, $B = 430$ cm^{-1}, $\beta = 0{\cdot}50$)[16] which should have values comparable with (II). The assumptions $\beta = 0{\cdot}50$ ($B = 430$ cm^{-1}) and $\nu_1 = 14\,000$ cm^{-1} lead to the following values: $Dq = 1\,495$; ν_1 14 000; ν_2 19 514; and ν_3 28 957 cm^{-1}.

The electronic spectral data for the compound $VO(S_2CNEt_2)_2$ (IV) are in reasonable agreement with those reported by previous workers[5,17] who were in disagreement on the assignment of the bands. Apart from suggesting that the band at 23 000 cm^{-1} seems too intense for a *d–d* transition, we cannot resolve the disagreement and further work such as crystal-structure determination and single-crystal spectral measurements are required.

I.r. and Raman Spectra of Ti, V, *and* Zr NN-*Diethyldithiocarbamates*.—The more important i.r. bands (1 500—200 cm^{-1} region) for all of the compounds studied and also the stronger Raman bands (1 000—200 cm^{-1}) for $Ti(S_2CNEt_2)_4$ and $Zr(S_2CNEt_2)_4$ are listed in the Supplementary Publication. It was not possible to obtain Raman spectra on the vanadium compounds. We have discussed the i.r. bands in the 1 000 cm^{-1} region earlier in this paper in explaining the behaviour of compound (I). Whilst there is little doubt that the compound $VO(S_2CNEt_2)_2$ (IV) has bidentate dithiocarbamato-ligands, the structure of $VO(S_2CNEt_2)_3$ (III) is uncertain. Since compound (III) exhibits extra bands in the 'thioureide' $C\overset{...}{-}N$ (*ca.* 1 500 cm^{-1}), $C\overset{...}{-}S$ (*ca.* 1 000 and 850 cm^{-1}), and M–S (*ca.* 360 cm^{-1}) stretching regions, this could be indicative of the presence of both uni- and bi-dentate ligands. Alternatively, some of the 'extra' bands at 1 515, 989, 847, and 373 cm^{-1} in the spectrum of compound (III) could be due to (IV). Attempts to assign the spectra in the 400—200 cm^{-1} region, in terms of M–S vibrations of the MS_8 unit in D_{2d} symmetry, were inconclusive.

The vanadium tris-dithiocarbamate (II) gave a strong V–S stretching vibration (T_{1u} in O_h symmetry) at 363 cm^{-1} in the i.r. spectrum and a medium band at 244 cm^{-1}, which could be due to an extra stretching vibration caused by a lowering of symmetry [$O_h(T_{1u}) \longrightarrow D_3(A_2 + E)$] or to the V–S bending mode.

Mass Spectra.—Fairly high temperatures (see Supplementary Publication) were required to obtain mass spectra of these metal dithiocarbamates. Parent ions were given by the compounds $Zr(S_2CNEt_2)_4$, $V(S_2CNEt_2)_3$, and $VO(S_2CNEt_2)_2$. In most cases, the base peak corresponded to the ligand fragment ion $(SCNEt_2)^+$ and in the other cases it was a major constituent of the spectrum. Considering the tetrakis-dithiocarbamates, the most striking feature is the predominance of the fragment ion $[M(S_2CNEt_2)_3]^+$ which constituted the base peak for the zirconium compound and is by far the most abundant metal-containing fragment ion for the titanium and vanadium compounds.

Comparing the mass spectra of the vanadium compounds, it is not surprising to find similar fragmentation patterns for compounds (I) and (II) since (I) is known to undergo facile thermal dissociation into (II). However, detailed comparison shows that the spectra are quantitatively different. In particular the ion $[V(S_2CNEt_2)_3]^+$ is significantly more intense for compound (II) (where it is the parent molecular ion) than for (I). The instability of the compound

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[16] C. Furlani, E. Cervone, and F. D. Camassei, *Inorg. Chem.*, 1968, **7**, 265.

[17] G. Vigee and J. Selbin, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3187.

$VO(S_2CNEt_2)_3$ (III) is reflected in the general similarity of its fragmentation pattern to that of the more stable $VO(S_2CNEt_2)_2$ (IV) and the absence of a parent molecular ion for (III). The presence of the ion $(VL_3)^+$ in the spectrum of compound (III) shows that some major rearrangements have taken place in the mass spectrometer because the V=O bond is very stable. Nevertheless the two compounds do show significant quantitative differences in their spectra. Compound (IV) is characterized by a very strong parent molecular ion $[VO(S_2CNEt_2)_2]^+$ which could be considered as a cation of quinquevalent vanadium.

EXPERIMENTAL

All reactions were carried out under an atmosphere of carefully dried deoxygenated nitrogen.

Preparations.— *Tetrakis*(NN-*diethyldithiocarbamato*)-*titanium* and -*zirconium*. These were prepared by a previously described method.[1]

Tetrakis(NN-*diethyldithiocarbamato*)*vanadium*. CS_2 (18 cm^3) was added dropwise to a stirred solution of the compound $V(NEt_2)_4$ (2·2 g) in benzene (55 cm^3) at −10 °C. The solution was allowed to attain room temperature slowly and then stirred for 2 days, after which it was reduced in volume *in vacuo* to *ca.* 10 cm^3 and then pentane (15 cm^3) was added. The red-brown precipitate was filtered off, washed with pentane, and finally dried *in vacuo* at 25 °C. This product gave $(\chi_M')^{298} = 1{\cdot}823 \times 10^{-3}$ c.g.s.u. corresponding to $\mu_{eff.}$ 2·08 B.M.

Tris(NN-*diethyldithiocarbamato*)*vanadium*. CS_2 was added to the compound $V(NEt_2)_4$ under the conditions used by Bradley and Gitlitz,[1] but with toluene replacing benzene as solvent. After heating under reflux for 15 h the solution was cooled, filtered, and washed to remove $(Et_2NCS_2)_2$ and gave the compound $V(S_2CNEt_2)_3$ as a pale brown powder (m.p. 172—174 °C) [Found: C, 36·3; H, 6·25; N, 8·50; S, 38·95; V, 10·3. $V(S_2CNEt_2)_3$ requires C, 36·35; H, 6·10; N, 8·50; S, 38·75; V, 10·3%].

Bis(NN-*diethyldithiocarbamato*)*oxovanadium*(IV). Anhydrous vanadyl sulphate (7·3 g) was slowly added at 0 °C to a stirred slurry of lithium *NN*-diethyldithiocarbamate [obtained by dropwise addition of a solution of CS_2 (8 cm^3) in benzene (15 cm^3) to a stirred solution of lithium diethylamide (7 g) in tetrahydrofuran–light petroleum at 0 °C]. Ethanol (30 cm^3) was added to increase the solubility of the vanadyl sulphate and the reaction mixture was heated under reflux for 1 h. The grey precipitate was washed first with water (3 × 30 cm^3), then with ethanol (40 cm^3), and finally with light petroleum (40 cm^3). The grey powder obtained by drying at 70 °C *in vacuo* had a m.p. of 217—220 °C [Found: C, 31·95; H, 5·50; N, 7·55; V, 13·9. $VO(S_2CNEt_2)_2$ requires C, 33·05; H, 5·55; N, 7·70; V, 14·0%].

Tris(NN-*diethyldithiocarbamato*)*oxovanadium*(V). $VOCl_3$ (5·9 g) in benzene (20 cm^3) was added dropwise to a stirred solution of LiS_2CNEt_2 (15·4 g) in benzene–tetrahydrofuran–light petroleum at 0 °C. The mixture was stirred for 12 h, heated under reflux for 1½ h, and the solvent then evaporated off *in vacuo*. After drying the brown residue at 70 °C *in vacuo*, it was extracted with C_6H_6–CS_2 (1 : 1, 120 cm^3) and the extract reduced in volume to 10 cm^3. Pentane (25 cm^3) was added and the solution filtered. The orange-brown precipitate was washed with pentane (3 × 20 cm^3) and dried at 70 °C *in vacuo* (Found: C, 34·7; H, 5·80; N, 8·10; V, 11·7%). The product was contaminated with some $VO(S_2CNEt_2)_2$. Heating the product under reflux in toluene for 6 h converted more $VO(S_2CNEt_2)_3$ to $VO(S_2CNEt_2)_2$ (Found: C, 33·9; H, 5·70; N, 7·90; V, 13·45%).

I.r. spectra were obtained using Perkin-Elmer 337 (4 000—400 cm^{-1}) and Grubb-Parsons DM-4 (500—200 cm^{-1}) instruments. Raman spectra were obtained using a Cary 81 instrument fitted with a SP 125 He–Ne laser at Imperial College through the University of London Intercollegiate Research Service. Data are given in the Supplementary Publication. A Beckman DK-2A instrument (50 000—4 000 cm^{-1}) was used to measure electronic spectra, with 1 cm path silica cells (fitted with B10 standard joints for solution measurements), and with a DK-2A Reflectance attachment for reflectance measurements. Data are given in Table 3. A Decca X3 spectrometer with a Newport 11 in magnet type M4X was used to measure e.s.r. spectra, with the Decca cavity insert MW 235 and a stream of nitrogen to control the temperature in the range −175 to +100 °C. Samples were sealed *in vacuo* in Pyrex or Spectrosil tubes (0·4 cm bore). Results are given in Table 1. An A.E.I. MS 902 instrument was used to record mass spectra, operating at 70 eV. Samples were introduced by direct insertion. Metal-containing ions were identified by their characteristic isotope patterns. Results are given in the Supplementary Publication.

A Newport Magnets variable-temperature Gouy balance was used to measure magnetic susceptibilities at three field strengths (3 785, 5 750, and 6 675 G) over the temperature range 98—373 K. Gouy tubes of silica were fitted with B-5 standard joints and calibrations were made with mercury tetrathiocyanatocobaltate(II) ($\chi_g = 16{\cdot}44 \times 10^{-6}$ c.g.s.u. at 298 K) and methylcyclohexane ($\chi_g = -0{\cdot}8038 \times 10^{-6}$ c.g.s.u.). The compounds studied obeyed the Curie–Weiss law and magnetic moments were calculated from the formula $\mu_{eff.} = 2{\cdot}828[\chi_M'(T + \theta)]^{\frac{1}{2}}$, where χ_M' is the molar susceptibility after correcting for diamagnetism of the

TABLE 4

Magnetic-susceptibility data for the compound $V(S_2CNEt_2)_3$

T/K	$10^6\chi_g$/c.g.s.u.	$10^6\chi_M'$/c.g.s.u.	$\mu_{eff.}$/B.M.
298	5·608	3 036	2·70
223	7·730	4 087	2·70
173	10·09	5 257	2·70
98	16·48	8 422	2·57

Diamagnetic correction, 258 × 10^{-6} c.g.s.u.; θ = 12°.

TABLE 5

Magnetic-susceptibility data for the compound $VO(S_2CNEt_2)_2$

T/K	$10^6\chi_g$/c.g.s.u.	$10^6\chi_M'$/c.g.s.u.	$\mu_{eff.}$/B.M.
298	2·879	1 227	1·71
273	3·109	1 310	1·69
223*	3·729	1 535	1·65
123*	6·255	2 454	1·55

Diamagnetic correction, 180 × 10^{-6} c.g.s.u.; θ = 45°.

* The susceptibility was slightly field-dependent at temperatures below 273 K and the average value from the three field strengths was used.

ligand atoms (Pascal's constants). Measurements on the compound $V(S_2CNEt_2)_4$ were carried out over the whole temperature range but the results were high due to the presence of $V(S_2CNEt_2)_3$. Results for the compounds $V(S_2CNEt_2)_3$ and $VO(S_2CNEt_2)_2$ are recorded in Tables 4 and 5.

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