Reactions of Tetrasulphur Tetranitride with Titanium and Vanadium Tetrachlorides; Crystal Structure of $VCl_2(S_2N_3)$ †

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Tetrasulphur tetranitride reacts with excess of VCl_4 in CH_2Cl_2 to form a mixture of $VCl_2(S_2N_3)$ (2) and $S_2N_2 \cdot VCl_4$ (3), whereas with excess of $TiCl_4$ only $S_4N_4 \cdot TiCl_4$ (1) is formed. Crystals of (2) are triclinic, space group $P\bar{1}$, with a = 571.3(2), b = 695.7(3), c = 772.9(3) pm, α = 95.38(3), β = 99.62(3), γ = 97.58(3)°, and Z = 2. The structure was refined to R = 0.053 for 1 601 unique observed diffractometer data. It consists of chlorine-bridged dimers, linked by additional weak V–N interactions to form polymeric chains. The six-membered VNSNSN ring is effectively planar.

The complexes $S_4N_4 \cdot TiCl_4$, $S_4N_4 \cdot VCl_4$, $S_4N_4 \cdot 2SnCl_4$, and $S_4N_4 \cdot 2TiCl_4$ were described by Goehring and co-workers,[1] but it was not until 1969 that the i.r. spectra of $S_4N_4 \cdot TiCl_4$, $S_4N_4 \cdot 2TiCl_4$, and $S_4N_4 \cdot VCl_4$ were reported.[2] These i.r. spectra differ appreciably from those of other known adducts of S_4N_4,[3] which prompted us to reinvestigate the reactions of S_4N_4 with VCl_4 and $TiCl_4$ under similar experimental conditions to those previously employed. Further details of the reactions of S_4N_4 with Lewis acids may be found in the review by Heal.[4]

Experimental

Due to the moisture sensitivity of the materials all manipulations were performed in a vacuum line or nitrogen dry-box. Infrared spectra were recorded in the range 4 000—250 cm^{-1} on a Perkin-Elmer 180 spectrometer. Solid samples were prepared as Nujol mulls pressed between CsI plates. Mass spectra were obtained with a Varian CH5 spectrometer. Melting points (uncorrected) were determined in nitrogen-filled sealed capillaries. Elemental analyses were performed commercially by Beller in Göttingen.

Vanadium tetrachloride was prepared from VCl_3 in a stream of dry chlorine at 450 °C and atmospheric pressure, and distilled twice (b.p. 148 °C; lit.,[5] 148.5 °C) before use. Titanium tetrachloride (E. Merck, Darmstadt) was used as received. Tetrasulphur tetranitride was prepared according to Villena-Blanco and Jolly [6] and recrystallised several times from carbon tetrachloride. Dichloromethane and toluene were refluxed over P_4O_{10} and Na respectively for 6—10 h and distilled prior to use.

The Preparation of $S_4N_4 \cdot TiCl_4$ (1).—Tetrasulphur tetranitride (3 g, 16.3 mmol) was dissolved in CH_2Cl_2 (300 cm^3) and added dropwise over 2 h to a stirred solution of $TiCl_4$ (8 cm^3) in CH_2Cl_2 (100 cm^3). The yellow precipitate was filtered off, washed several times with CH_2Cl_2, and dried *in vacuo*. Yield 86%, m.p. 145 °C (decomp.) (Found: Cl, 38.2; N, 14.9; S, 34.0; Ti, 12.8. $Cl_4N_4S_4Ti$ requires Cl, 37.9; N, 15.0; S, 34.2; Ti, 12.8%). The mass spectrum of compound (1) shows peaks at m/e = 32 (45%, S), 46 (100%, NS), 83 (18%, TiCl), 92 (40%, S_2N_2), 138 (85%, S_3N_3), 153 (92%, $TiCl_3$), 184 (43%, S_4N_4), and 188 (85%, $TiCl_4$). The i.r. spectrum shows absorptions at 957s, 810m, 759s, 722s, 701s, 550s, 529w, 410s (sh), 397s, 384s, 372s, and 300w cm^{-1}.

The Reaction of S_4N_4 *with* VCl_4.—A sample of S_4N_4 (3 g, 16.3 mmol) was dissolved in CH_2Cl_2 (300 cm^3) and added dropwise to a stirred solution of VCl_4 (10 cm^3) in CH_2Cl_2 (100 cm^3). The solution turned green, and a brown precipitate formed which was filtered off, washed with three 60-cm^3 portions of CH_2Cl_2, and dried *in vacuo*. The i.r. spectrum of this product shows absorptions at 969s, 935w, 920w (sh), 845m,br, 738m, 691vw, 670vw, 520m (sh), 504m, 465m, 360m (sh), 316vs (sh), 300vvs, and 290s (sh) cm^{-1} (Found: Cl, 42.0; N, 15.9; S, 28.2; V, 14.6%). The i.r. spectrum and elemental analysis are not consistent with a simple $S_4N_4 \cdot VCl_4$ adduct.

Preparation of $VCl_2(S_2N_3)$ (2) *from the Reaction of* S_4N_4 *and* VCl_4.—The brown crude product from the previous reaction was placed in a sublimer fitted with a −196 °C trap and held at 110 °C under vacuum (1 Pa) for 6 h. Black needles collected on the water-cooled cold-finger, whilst in the nitrogen trap greater amounts of VCl_4 and sulphur chlorides appeared. From a temperature-controlled mass spectrometric analysis of the needles (electron impact and field ionisation) the molecular ion of composition $VCl_2(S_2N_3)$ was obtained at m/e 227 as well as the following fragment ions 32 (S^+), 46 (SN^+), 51 (V^+), 65 (VN^+), 78 (S_2N^+), 121 (VCl_2^+), 167 (VCl_2SN^+), and 192 ($VClS_2N_3^+$). The sublimed needles dissolved readily in hot toluene. The resulting deep green solution was filtered and concentrated over a period of 20 d on a vacuum line yielding black needles of compound (2) which then were quite insoluble in toluene; m.p. 157 °C without decomposition. The i.r. spectrum showed absorptions at 956s, 940s, 825m, 814m, 669s, 652s, 580s, 560ms, 504s, 417s, 388s, 375ms, and 343s cm^{-1}. The mass spectrum was identical with that quoted above.

Preparation of $S_2N_2 \cdot VCl_4$ (3) *from the Reaction of* S_4N_4 *and* VCl_4.—When the black $VCl_2(S_2N_3)$ (2) sublimed off (110 °C) the residue became lighter in colour. After 16 h the sublimation was stopped, whereupon the i.r. spectrum of the residue showed weakening of the bands due to compound (2), whereas those at 844 and 465 cm^{-1} became stronger. After further heating of the sample at 110 °C *in vacuo* (6 h) only traces of (2) continued to sublime out. The i.r. spectrum of the

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† *Supplementary data available* (No. SUP 23557, 14 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

residue was essentially unchanged, but the band at 969 cm^{-1} had decreased further in intensity. However, despite further sublimation it proved impossible to obtain a sample completely free of compound (2) and other impurities. On the other hand the spectrum of the sublimed material showed no bands due to the residue (*i.e.* at 844 and 465 cm^{-1}). From a field-ionisation mass spectrum (120 °C) of the residue the following ions were detected: $S_2N_2^+$, VCl_4^+, $VCl_2S_2N_3^+$, and some S_8^+. On the basis of the mass spectrum, elemental analysis, and a comparison of the i.r. spectrum with that of $S_2N_2{\cdot}AlCl_3$ [7] and other S_2N_2 adducts,[8] we believe that the residue consisted of an impure sample of $S_2N_2{\cdot}VCl_4$ (3).

Crystal Data.—$VCl_2(S_2N_3)$, $M = 227.96$, Triclinic, space group $P\bar{1}$, $a = 571.3(2)$, $b = 695.7(3)$, $c = 772.9(3)$ pm, $\alpha = 95.38(3)$, $\beta = 99.62(3)$, $\gamma = 97.58(3)°$, $U = 0.298\ 11$ nm^3, $Z = 2$, $D_c = 2.539$ mg m^{-3}, $F(000) = 220$, $\lambda(\text{Mo-}K_\alpha) = 71.069$ pm, $\mu = 3.08$ mm^{-1}, crystal dimensions 0.77 × 0.15 × 0.08 mm.

1 726 Unique reflections were measured using a profile-fitting procedure [9] on a Stoe-Siemens four-circle diffractometer, of which 1 601 with $F > 3\sigma(F)$ were used after Lorentz, polarisation, and semi-empirical absorption corrections for all calculations. Calculations were performed using the SHELXTL programs (written by G. M. S.). The structure was solved by direct methods and refined with complex neutral-atom scattering factors and all atoms anisotropic to $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0.058$ and $R = 0.053$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.001\ 64\ F^2$. Final co-ordinates are given in Table 1, bond lengths and angles in Table 2.

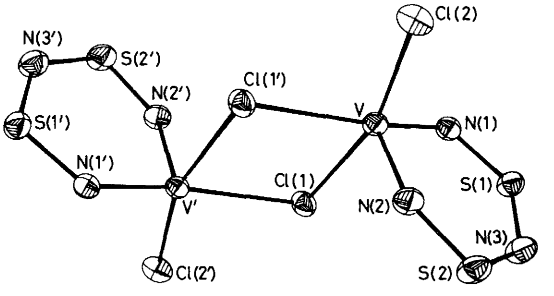

Figure 1. The dimer unit in compound (2) with 50% probability thermal ellipsoids. Atoms generated by the centre of symmetry are primed

Results and Discussion

The dropwise addition of a dilute solution of S_4N_4 in CH_2Cl_2 to excess of $TiCl_4$ in CH_2Cl_2 does not lead to the expected [1] 1 : 2 adduct $S_4N_4{\cdot}2TiCl_4$, but rather to the 1 : 1 adduct (1). The i.r. spectrum of (1) differs considerably from that reported by Ashley and Torrible [2] for a compound of the same empirical formula, indicating a structural difference. In the Ti–Cl stretching region of compound (1) we found three

Table 1. Atom co-ordinates (× 10^4) with standard deviations in parentheses for compound (2)

Atom	x	y	z
V	2 422(1)	1 502(1)	9 846(1)
Cl(1)	3 741(1)	−1 237(1)	8 243(1)
Cl(2)	1 966(2)	3 770(1)	12 017(1)
S(1)	−1 831(2)	1 262(1)	6 713(1)
S(2)	2 559(2)	3 705(1)	6 538(1)
N(1)	−655(5)	780(4)	8 591(4)
N(2)	3 392(5)	3 044(4)	8 423(4)
N(3)	−147(5)	2 660(5)	5 792(4)

Table 2. Bond lengths (pm) and angles (°) for compound (2)

V–Cl(1)	244.5(1)	V–N(1)	184.1(3)
V–Cl(2)	226.6(1)	V–N(2)	171.4(3)
V–Cl(1′)	246.9(1)	V–N(1′)	231.2(3)
S(1)–N(1)	158.0(3)	S(1)–N(3)	157.8(3)
S(2)–N(2)	158.5(3)	S(2)–N(3)	160.6(3)
Cl(1)–V–Cl(2)	162.6(1)	Cl(1)–V–N(1)	90.4(1)
Cl(2)–V–N(1)	103.0(1)	Cl(1)–V–N(2)	90.7(1)
Cl(2)–V–N(2)	98.7(1)	N(1)–V–N(2)	96.3(1)
Cl(1)–V–Cl(1′)	78.0(1)	Cl(2)–V–Cl(1′)	85.8(1)
N(1)–V–Cl(1′)	159.2(1)	N(2)–V–Cl(1′)	101.0(1)
Cl(1)–V–N(1′)	86.5(1)	Cl(2)–V–N(1′)	86.2(1)
N(1)–V–N(1′)	75.5(1)	N(2)–V–N(1′)	171.3(1)
V–Cl(1)–V′	102.0(1)	N(1)–S(1)–N(3)	115.3(1)
N(2)–S(2)–N(3)	108.1(2)	V–N(1)–S(1)	130.3(2)
V–N(1)–V′	104.5(1)	S(1)–N(1)–V′	124.5(1)
V–N(2)–S(2)	140.9(2)	S(1)–N(3)–S(2)	128.6(2)

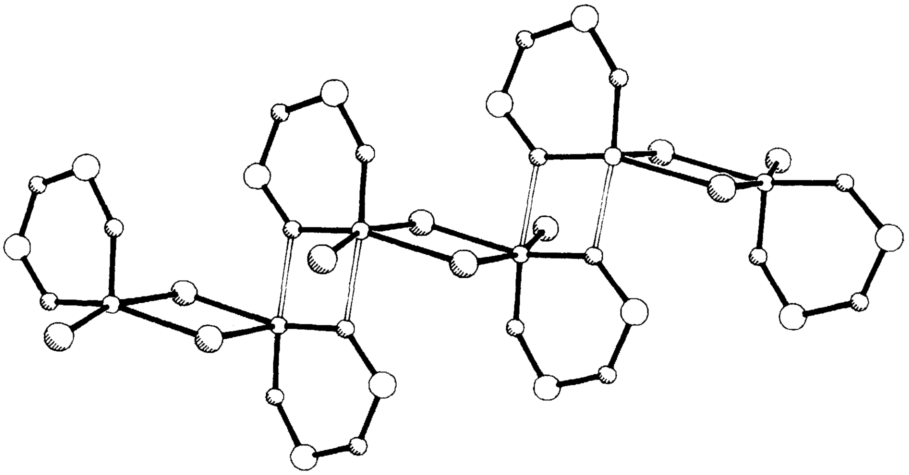

Figure 2. A three-dimer section of the polymeric chain in compound (2). The longer V–N interactions which link the dimers are indicated by open bonds

bands at 397, 384, and 372 cm^{-1}, which indicate *cis* co-ordination of one bidentate ligand to Ti (presumably *via* N).[7] Bands at 1 040 and about 790 cm^{-1}, characteristic of the unidentate S_4N_4 ligand,[4] are not observed. Unfortunately the yellow product (1) was too insoluble in inert solvents for us to determine a molecular weight.

It is remarkable that the reaction of S_4N_4 with VCl_4 proceeds quite differently under similar conditions. The S_4N_4 ligand could not be detected in the products, and a complex of S_2N_2 was formed only as a by-product. The VCl_4 reaction may involve the initial formation of an S_2N_2 complex (perhaps $2S_2N_2{\cdot}VCl_4$), analogous to the reactions of S_4N_4 with $AlCl_3$ [8,10] and $CuCl_2$; [11] in the case of vanadium, there is then a further redox reaction, with $VCl_2(S_2N_3)$ (2) as the primary product. The i.r. bands at 844 and 465 cm^{-1} of the residue can be identified as the two asymmetric stretching modes of a co-ordinated bidentate S_2N_2 ring.[12] Since it is involatile, $S_2N_2{\cdot}VCl_4$ (3) probably has a polymeric structure with octahedrally co-ordinated vanadium and bridging S_2N_2 rings bonded through N.

To a first approximation, the structure of compound (2) consists of centrosymmetric dimers (Figure 1), in which the vanadium atoms are each co-ordinated by two bridging chlorines, one terminal chlorine, and the two terminal N atoms of an NSNSN chain. The four S–N bond lengths in the six-membered VS_2N_3 ring are approximately equal, and the ring is effectively planar, with a root-mean square deviation of 3 pm from the mean plane. The bridging V–Cl distances [244.5(1) and 246.9(1) pm] are longer than the terminal V–Cl distance [226.6(1) pm]. If an additional V–N interaction of 231.2(3) pm [appreciably longer than the other two V–N bonds of 171.4(3) and 184.1(3) pm] is considered, then the co-ordination of V becomes octahedral, and the dimers link together to form polymeric chains. A section of such a chain is shown in Figure 2. This additional interaction of one of the two terminal N atoms accounts for the difference in V–N bond lengths.

Acknowledgements

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Results and Discussion

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