The Crystal Structure of Disulphido-tris(N,N,-diethyldithiocarbamato)tantalum(V): A Monomeric and Eight Co-ordinate Species Containing a Novel Tantalum–Disulphide Moiety

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There has been a growing interest in the chemistry of the dialkyldithiocarbamate compounds formed by the elements of Group Va [1]. Of particular importance is the species $[Ta(S)(S_2CN(C_2H_5)_2)_3]$ which was first isolated as a green compound from the reaction of $TaCl_5$ with $[Na(S_2CN(C_2H_5)_2]$ in benzene [2]. A band in the infra-red spectrum at 483 cm^{-1} was attributed to the stretching mode of a terminally bonded Ta=S fragment. Repeating the reaction in MeCN rather than benzene led to a yellow compound that was shown by single-crystal X-ray methods to be $[Ta(S)(S_2CN(C_2H_5)_2)_3]$ with a terminal Ta=S moiety of 2.181(1) Å [3] but whose stretch was assigned to a vibration at the surprisingly high frequency of 905 cm^{-1}.

It was decided to clarify these discrepancies in colour and infra-red spectra by alllowing the sulphido–halide $TaSBr_3$ to react with $[Na(S_2CN(C_2H_5)_2)]$ (1:3 molar ratio) in CS_2 under anaerobic conditions. The NaBr that was initially precipitated was removed by filtration and the resulting filtrate was allowed to stand for 6 months at 50 °C during which period two types of crystal were deposited, one being green the other yellow. The yellow product was shown by X-ray methods to be identical to the crystals of $[Ta(S)(S_2CN(C_2H_5)_2)_3]$ which had been previously characterised [3]. The green crystals were shown by single-crystal X-ray analysis to be $[Ta(S_2)(S_2CN(C_2H_5)_2)_3]$.

Crystal Data. $C_{15}H_{30}N_3S_8Ta$; $M = 689.67$; monoclinic; space group $C2/c$; systematic absences hkl (h + k = 2n + 1), h0l (l = 2n + 1), $a = 16.319(8)$ Å, $b = 10.887(7)$ Å, $c = 30.215(21)$ Å, $B = 88.00(5)°$; $Z = 8$; $U = 5383.75$ Å^3; $d_m = 1.75$ g cm^{-3}, $d_c = 1.70$ g cm^{-3}. The intensities of 3359 independent reflections were measured on a Stoe STADI2 diffractometer, of which 1814 with $I > 3\sigma(I)$ were used in the final refinement. The general techniques employed for the solution of the structure were as previously reported [4]; By the use of techniques involving a Patterson function, Fourier methods, and an empirical absorption correction in association with least squares methods the structure was refined to a value of $R = 0.099$ (Table I).

TABLE I. Atomic Coordinates (×10 000) with Estimated Standard Deviations in Parentheses.

Atom	*X*	*Y*	*Z*
Ta	3686(1)	5(2)	1196(0)
S(1)	2157(6)	178(14)	1404(4)
S(2)	2833(7)	931(11)	569(3)
S(3)	5195(6)	−149(11)	1348(3)
S(4)	4648(6)	766(9)	558(3)
S(5)	3669(8)	356(9)	2016(3)
S(6)	3814(9)	2294(11)	1399(4)
S(7)	3559(8)	−2063(11)	1509(4)
S(8)	3651(7)	−1918(11)	827(4)
N(1)	1258(21)	1449(35)	802(15)
N(2)	6213(18)	847(31)	744(11)
N(3)	3439(39)	2833(49)	2252(13)
C(1)	2020(23)	869(42)	893(14)
C(2)	1171(28)	2027(59)	361(21)
C(3)	895(32)	1227(43)	−23(20)
C(4)	462(39)	1205(57)	1159(17)
C(5)	14(34)	213(24)	1128(14)
C(6)	5438(35)	477(36)	872(13)
C(7)	6353(25)	1425(37)	305(13)
C(8)	6323(28)	2896(37)	387(15)
C(9)	6935(23)	667(41)	1012(16)
C(10)	7486(63)	−307(81)	835(26)
C(11)	3719(54)	1885(43)	1900(22)
C(12)	3504(50)	4192(45)	2140(20)
C(13)	2752(40)	4638(92)	1994(24)
C(14)	3266(40)	2432(60)	2725(16)
C(15)	3944(50)	2666(62)	3043(20)

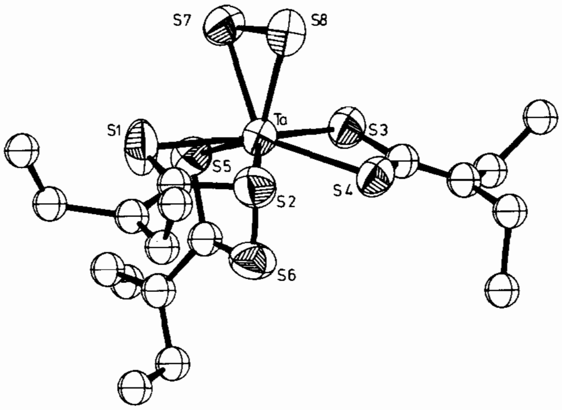

Fig. 1. Structure of $[Ta(S_2)(S_2CN(C_2H_5)_2)_3]$ showing the atom labelling scheme and 50% probability ellipsoids. The C and N atoms are given arbitrary small isotropic thermal parameters for reasons of clarity.

The asymmetric unit contains discrete monomers of $[Ta(S_2)(S_2CN(C_2H_5)_2)_3]$ (Fig. 1). The metal atom

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is bonded to eight sulphur atoms, six from the chelatingdialkyldithiocarbamate residues, and two from a 'side on' co-ordinated S_2 group. The co-ordination polyhedron is a distorted dodecahedron with the dialkyldithiocarbamate ligands occupying the m edges between adjacent A and B sites [5]. In the mmmm dodecahedron, it is usually found that bonds to the atoms in the A sites are larger than those to the atoms in the B sites. In the present compound this is true for the S_2 ligand [A 2.45(1) Å, B 2.38(1) Å] and for two out of the three dialkyldithiocarbamate groups [A 2.60(1) Å, 2.58(1) Å, 2.51(1) Å, B 2.56(1) Å, 2.53(1) Å, 2.58(1) Å]. We are unable to explain the disparities but suspect it is due to the difference in ligand 'bite' between S_2 and the dialkyldithiocarbamate as the unique dialkyldithiocarbamate is in the same trapezoid as the S_2 ligand.

For two of the dialkyldithiocarbamate ligands the disparity in Ta–S distances is reflected by differences in the C–S distances; thus for the two sulphur atoms in a given dialkydithiocarbamate group the sulphur with the shorter Ta–S distance has a longer C–S distance (approximately 0.1 Å). Similar differences in the C–S distances have been noted before [6–8] but were not seen in pentagonal bipyramidal $[Ta(S)(S_2CN(C_2H_5)_2)_3]$ [3] or in dodecahedral $[Ta(S_2CN(C_2H_5)_2)_4]^+$ [9] although both compounds exhibited differences in Ta–S distances for a given dialkyldithiocarbamate group. The most interesting feature of the present structure is the 'side on' bonded S_2 group which has only been previously noted for group Va metals in cyclopentadienyl (Cp) compounds $[(Cp)_2V(S_2)]$ [10], $[(Cp)_2lNB(S_2)X]$ [X = Me [11], Cl [12], or $S_2P(OEt)_2$ [13]]. The S_2 group is asymmetrically bound to the metal with Ta–S distances much shorter than those observed for the dialkyldithiocarbamate groups. It is the presence of this S_2 group with its short Ta–S distances, small S(7)–Ta–S(8) angle [50.9(4)°], and S–S distance of 2.07(2) Å that is the main cause of the distortion of the co-ordination polyhedron as the means of the equivalent angles and distances for the dialkyldithiocarbamate ligands are 66.7(1)° and 2.82(1) Å. The r.m.s. deviation from ideal geometry for a dodecahedron is 0.079 Å [5]. The S(7)–S(8) distance [2.07(2) Å] is longer than those seen in other group Va compounds [1.93–2.03 [10–13]] but is typical of disulphide complexes of other early transition metals [14]. However, it is shorter than that in ionic Na_2S_2 [2.13 Å] [15] and longer than in S_2 [16] thus suggesting the presence of some π^* to d_π S_2 to Ta donation.

This work has confirmed the nature of the yellow $[Ta(S)(S_2CN(C_2H_5)_2)_3]$ previously reported [3] and suggests that the 'green' $[Ta(S)(S_2CN(C_2H_5)_2)_3]$ [2] isolated earlier may have contained some $[Ta(S_2)(S_2CN(C_2H_5)_2)_3]$ as an impurity. A solution of yellow $[Ta(S)(S_2CN(C_2H_5)_2)_3]$ in benzene slowly turns green and a green powder can be isolated from the solution. The nature of this green powder is being investigated. In view of the disagreement in the literature over the position of the $\nu(Ta{=}S)$ [2, 3], we have re-examined the infra-red spectrum of the yellow species $[Ta(S)(S_2CN(C_2H_5)_2)_3]$ and assign a band in the spectrum at 479 cm^{-1} to a $\nu(Ta{=}S)$ stretch in accord with the band previously reported for the green species [2] that we believe to be slightly impure.

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References

1 R. P. Burns, F. P. McCullough and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem., 23,* 211 (1980).

2 P. R. Heckley, D. G. Holah and D. Brown, *Can. J. Chem., 49,* 1151 (1971).

3 E. J. Peterson, R. B. von Dreele and T. M. Brown, *Inorg. Chem., 17,* 1410 (1978).

4 M. G. B. Drew, D. A. Rice and D. M. Williams, *J. Chem. Soc., Dalton Trans.,* in the press.

5 M. G. B. Drew, *Coord. Chem. Rev., 24,* 179 (1977).

6 R. Bally, *Acta Crystallogr., 23,* 295 (1967).

7 M. Colapietro, A. Domenicano, L. Scaramuzza and A. Vaciago, *J. Chem. Soc., Chem. Commun.,* 302 (1968).

8 S. Husebye, *Acta Chem. Scand., 24,* 2198 (1970).

9 D. F. Lewis and R. C. Fay, *Inorg.Chem., 15,* 2219 (1976).

10 S. Gambarotta, C. Floriani, A. C. Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.,* 184 (1983).

11 R. Mercier, J. Douglade, J. Amaudrut, J. Sal-Pala and J. Guerchais, *Acta Crystallogr., 36B,* 2986 (1980).

12 R. Mattes and M. Bradtke, *Z. Kristallogr., 157,* 95 (1981).

113 R. Mercier, J. Douglade and B. Viard, *Acta Crystallogr., 37B,* 949 (1981).

14 A. Muller, W. Jaegermann and J. H. Enemark, *Coord. Chem. Rev., 15,* 2219 (1976).

15 H. Foppl, E. Busmann and F. K. Frorath, *Z. Anorg. Allg. Chem., 314,* 12 (1962).

16 B. Meyer, *Chem. Rev., 76,* 367 (1976).