Reaction of the Anion $[WCl_4(CBu^t)]^-$ with Tetrasulphur Tetranitride. Formation and Crystal Structure of $[AsPh_4][WCl_3O(OS_2N_2)]$†

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The reaction of $[AsPh_4][WCl_4(CBu^t)]$ with S_4N_4 in dichloromethane leads to $[AsPh_4][WCl_4(S_2N_3)]$, and, if traces of water are present, to the salt $[AsPh_4][WCl_3O(OS_2N_2)]$. The latter has been characterized by i.r. and u.v.-visible spectroscopy and by *X*-ray crystallography. It crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.077(1)$, $b = 12.675(2)$, $c = 13.480(2)$ Å, $\alpha = 88.49(1)$, $\beta = 82.13(1)$, $\gamma = 87.98(1)°$, and $Z = 2$.

Heterocyclic compounds of formulae $[(Cl_2VS_2N_3)_2]_x$ (1), $(Cl_3MoS_2N_3)_2$ (2), and $(Cl_3WS_2N_3)_2$ (3) have recently been prepared[1,2] by a variety of reactions between early transition metals and sulphur–nitrogen compounds. Crystal structures of these interesting heterocycles, or of derivatives of them, have been determined and published recently.[3] Subsequently we have attempted a substitution of one of the nitrogens, adjacent to the metal, by a carbon atom. The best approach was suggested to be the reaction of derivatives of the trichlorotungsten(VI) alkylidyne compound $(Cl_3W{\equiv}C{-}R)_x$ with S_4N_4. The salt $[AsPh_4][WCl_4(CBu^t)]$ (4) was chosen as precursor.

Experimental

All reactions and operations were carried out in a nitrogen atmosphere, *i.e.* on a vacuum line or in a dry-box, flushed with nitrogen. Dichloromethane and hexane were dried under rigorous conditions. The compound S_4N_4 was prepared according to the literature;[4] (4) was obtained as described by Schrock *et al.*,[5] except that $AsPh_4Cl$ instead of NEt_4Cl was used. Crystals of (4) are pale turquoise blue (m.p. 218 °C). The i.r. spectrum shows $\nu(W{\equiv}C)$ at 986 cm^{-1} (Raman 982 cm^{-1}).

Spectroscopic measurements were performed on Perkin-Elmer 180 (i.r., KBr discs) and 320 (u.v.–visible) spectrophotometers.

Formation of $[AsPh_4][WCl_4(S_2N_3)]$ (3a) *and* $[AsPh_4][WCl_3O(OS_2N_2)]$ (5).—A sample of S_4N_4 (0.6 g, 3.3 mmol) was added to a vigorously stirred solution of compound (4) (2 g, 2.6 mmol) in CH_2Cl_2 (70 cm^3). The colour of the solution changed rapidly to brown then to deep red. After stirring overnight and filtration, the solution was layered with hexane (160 cm^3) and kept at -5 °C for 20 d. During this time brown crystals of compound (3a) and red crystals of (5) were depositing on the walls; after decantation of the supernatant liquid, these were washed with hexane and vacuum-dried. The crystals (yield 0.75 g) could be separated by hand. Compound (3a) was identified by its melting point, i.r. spectrum,[2] and by cell-constant determination.[6] Crystals of (5) [m.p. 138 °C (decomp.)] show i.r. bands (cationic bands omitted) at 1 076s, 1 017m (sh), 1 000s, 990s, 940s, 920s, 658s, 638m (sh), 615s, 549s, 400s, 369vs, and 312vs cm^{-1}. The u.v.–visible spectrum of a dichloromethane solution (4.7×10^{-4} mol dm^{-3}) displays bands at $\lambda_{max.} = 512$ ($\varepsilon = 6.5 \times 10^2$), 380 ($5 \times 10^2$), 340 ($5.6 \times 10^2$), 272 ($2.8 \times 10^3$), 264 ($3.5 \times 10^3$), 246 ($4.2 \times 10^3$), and 234 nm ($6.2 \times 10^3$ dm^3 mol^{-1} cm^{-1}).

Crystal Structure Determination of Compound (5).—Red crystals of compound (5) were mounted in glass capillaries using polyurethane varnish and sealed with wax. A crystal of approximate dimensions $0.26 \times 0.45 \times 0.50$ mm was used for the measurements. The cell constants were refined from the setting angles of 25 reflections with $12 < \theta < 19°$.

Crystal data. $C_{24}H_{20}AsCl_3N_2O_2WS_2$, triclinic, $M = 797.70$, space group $P\bar{1}$, $a = 8.077(1)$, $b = 12.675(2)$, $c = 13.480(2)$ Å, $\alpha = 88.49(1)$, $\beta = 82.13(1)$, $\gamma = 87.98(1)°$, $U = 1\,365.9(5)$ Å^3, $Z = 2$, $D_c = 1.939$ g cm^{-3}, $F(000) = 768$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 59.9 cm^{-1}.

Reflections were measured in a full sphere of reciprocal space on an Enraf–Nonius CAD4 diffractometer (graphite monochromator, ω-scan mode, $2\theta_{max.} = 46°$). 6 869 Reflections were obtained, 3 782 of which were independent. Three standard reflections remeasured every 5 500 s decreased in intensity by 10.6% due to decay of the crystal. The data were therefore rescaled with respect to the standards. An empirical absorption correction was made, based on azimuth scans of five reflections. Equivalent reflections were averaged ($R_{internal} = 0.016$). 3 557 Reflections with $F^2 > 0.5\sigma(F^2)$ were used in the structure determination and refinement.

The structure was determined by Patterson and Fourier methods and refined by full-matrix least squares. Positions for the H atoms of the phenyl groups were calculated but not refined. Oxygen and N atoms could be distinguished by *R*-factor tests and the value of their thermal parameters. Scattering and anomalous dispersion factors were taken from ref. 7. Use of a weighting scheme of the form $w(F) = 1/[\sigma^2(F) + (0.015F)^2]$ led to R $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and R' $\{= \Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ values of 0.033 and 0.033. A final difference synthesis yielded a peak of 1.0 e Å^{-3} within 1 Å of the W atom but was otherwise featureless.

The calculations were performed with the SDP program system.[8] The resulting positional parameters are given in Table 1.

Results and Discussion

The preparation of the starting compound $[AsPh_4][WCl_4(CBu^t)]$ (4) involves the reaction of $WCl_3(OMe)_3$ with neopentylmagnesium chloride (mol ratio 1:6), extraction of the mixture with hexane, sublimation of the intermediate product $[W(CH_2Bu^t)_3(CBu^t)]$, and conversion of the latter into (4) by

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† Tetraphenylarsonium trichlorooxo[1-oxo-catenadi(azathiane)-1-ene-4,4-diyl]tungstate (1 –).

Supplementary data available: Further crystallographic details can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, Federal Republic of Germany by quoting the Deposition Number, CSD-51254, and the exact literature reference.

Table 1. Positional parameters of compound (**5**) and their estimated standard deviations

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.251 06(3)	0.249 49(2)	0.254 15(2)	C(8)	0.169 8(8)	0.894 6(5)	0.112 8(5)
As	0.015 51(6)	0.750 31(4)	0.262 46(4)	C(9)	0.292 9(9)	0.923 7(5)	0.035 5(5)
Cl(1)	0.245 2(2)	0.303 6(1)	0.424 4(1)	C(10)	0.416 4(8)	0.853 1(5)	−0.000 6(5)
Cl(2)	0.184 9(2)	0.078 7(1)	0.322 8(1)	C(11)	0.423 6(9)	0.752 9(6)	0.039 5(6)
Cl(3)	0.226 4(2)	0.431 2(1)	0.206 7(1)	C(12)	0.303 5(8)	0.721 5(5)	0.116 5(5)
S(1)	−0.176 9(2)	0.258 7(1)	0.256 7(2)	C(13)	−0.140 0(7)	0.863 6(4)	0.303 2(4)
S(2)	0.034 1(2)	0.190 2(2)	0.080 3(1)	C(14)	−0.144 7(8)	0.909 2(5)	0.393 7(5)
O(1)	0.462 5(4)	0.234 5(3)	0.229 4(3)	C(15)	−0.263 5(9)	0.989 3(5)	0.420 8(5)
O(2)	−0.028 9(5)	0.277 1(3)	0.304 8(3)	C(16)	−0.374 7(9)	1.020 9(5)	0.355 9(6)
N(1)	0.189 6(6)	0.210 2(4)	0.134 8(4)	C(17)	−0.370 8(9)	0.974 2(5)	0.266 1(5)
N(2)	−0.143 4(6)	0.217 8(5)	0.151 5(4)	C(18)	−0.251 8(8)	0.894 9(5)	0.238 3(5)
C(1)	−0.119 6(7)	0.642 2(4)	0.223 0(4)	C(19)	0.146 3(7)	0.707 4(4)	0.364 8(4)
C(2)	−0.090 1(8)	0.604 1(5)	0.127 3(5)	C(20)	0.132 8(8)	0.610 2(5)	0.412 1(5)
C(3)	−0.202 5(9)	0.533 8(6)	0.098 2(5)	C(21)	0.237 8(8)	0.582 3(5)	0.480 4(5)
C(4)	−0.336 7(9)	0.501 7(5)	0.164 4(6)	C(22)	0.356 3(8)	0.649 9(5)	0.500 8(5)
C(5)	−0.366 3(8)	0.541 5(6)	0.259 4(5)	C(23)	0.371 0(8)	0.746 7(5)	0.453 7(5)
C(6)	−0.256 1(8)	0.611 9(5)	0.289 5(5)	C(24)	0.267 8(7)	0.777 3(4)	0.384 8(5)
C(7)	0.174 7(7)	0.793 4(4)	0.152 6(4)				

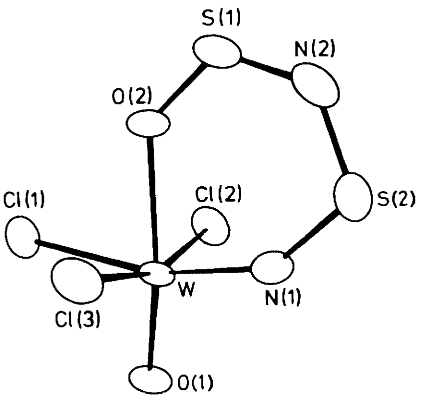


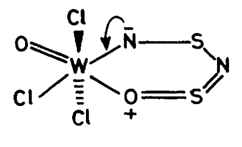
Figure. Perspective view of the anion in compound (**5**)

Table 2. Bond distances (Å) and angles (°) in the anion

W–Cl(1)	2.406(1)	W–N(1)	1.833(4)
W–Cl(2)	2.380(1)	S(1)–O(2)	1.464(3)
W–Cl(3)	2.382(1)	S(1)–N(2)	1.509(5)
W–O(1)	1.699(3)	S(2)–N(2)	1.644(5)
W–O(2)	2.288(3)	S(2)–N(1)	1.570(4)
Cl(1)–W–Cl(2)	86.36(5)	Cl(3)–W–O(2)	81.1(1)
Cl(1)–W–Cl(3)	88.15(5)	Cl(3)–W–N(1)	90.8(1)
Cl(1)–W–O(1)	95.8(1)	O(1)–W–O(2)	173.4(2)
Cl(1)–W–O(2)	77.6(1)	O(1)–W–N(1)	100.8(2)
Cl(1)–W–N(1)	163.3(1)	O(2)–W–N(1)	85.8(2)
Cl(2)–W–Cl(3)	161.67(5)	W–O(2)–S(1)	132.4(2)
Cl(2)–W–O(1)	99.7(1)	O(2)–S(1)–N(2)	115.9(2)
Cl(2)–W–O(2)	80.7(1)	S(1)–N(2)–S(2)	130.6(3)
Cl(2)–W–N(1)	89.5(1)	N(2)–S(2)–N(1)	112.0(2)
Cl(3)–W–O(1)	98.2(1)	W–N(1)–S(2)	143.2(3)

means of anhydrous HCl and $AsPh_4Cl$ in diethyl ether–dichloromethane.[5] It is most likely that during the conversion of the intermediate parts of the material are hydrolysed by traces of moisture in the reaction mixture. We believe that thereby oxo-complexes of tungsten(VI) are partially formed, which react with S_4N_4 to give (**5**). The reaction between the original alkylidyne complex (**4**) and S_4N_4, leading to (**3a**), involves exchange of the ≡CBu^t group at tungsten by unsaturated sulphur–nitrogen ligands; the resulting intermediate complexes are thence converted into the appreciably stable[2] S_2N_3 ring system of (**3a**).

The structure of compound (**5**) consists of tetraphenylarsonium cations and $[WCl_3O(OS_2N_2)]^-$ anions. The anion is shown in the Figure. Bond distances and angles are listed in Table 2. The co-ordination geometry around the metal may be regarded as distorted octahedral. A weak *trans* effect of the =NSNSO ligand is indicated by the different axial and equatorial metal–chlorine bond lengths. The W–N(1) distance of 1.833(4) Å can be related to a formal bond order of 2,[2,3] W–O(2) of 2.288(3) Å to a long single bond.[9] The W–O(1) distance of 1.699(3) Å is in the range shown by W=O double bonds. The metal atom and the chelating =NSNSO ligand form a six-membered ring, in which NSNSO is planar within the experimental accuracy. The O–S and N–S bond lengths indicate an appreciable degree of bond fixation in the ring, expressed by resonance structures such as that shown below. The effective



planarity of the ring [the metal atom lies only 0.083(5) Å out of the plane, defined by the NSNSO ligand atoms] is probably due to the shift of the π-electron density from the ligand into unoccupied tungsten 5*d* orbitals. Structural distortions of the ring geometry, known in PS_2N_3 ring systems,[10] are not necessary. This point of view is supported by the electronic spectrum of compound (**5**). The first band in the visible region at $\lambda_{max.}$ = 512 nm indicates a larger gap between the highest occupied and lowest unoccupied molecular orbitals as compared to (**3a**) ($\lambda_{max.}$ = 540 nm);[2] concomitantly the intensity of this band is lower.

Acknowledgements

We are grateful to the Alexander von Humboldt Foundation for a fellowship (to Z. A. S.) and the Deutsche Forschungsgemeinschaft for financial support.

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Received 8th February 1985; Paper 5/231