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Structures of Tetraphenylarsonium 1,1,1,1-Tetrachlorocyclo-1λ^6-molybdata-3,5-dithia-2,4,6-triazine and 1,1,1-Trichloro-1-acetonitrilo-cyclo-1λ^6-tungsta-3,5-dithia-2,4,6-triazine: Pseudo-Jahn-Teller Distortions of Cyclic 8π Systems

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The dithiatriazenes $[Cl_3MS_2N_3]_x$ [M = Mo, W] are formed in the reactions of S_4N_4 with Mo_2Cl_{10} and WCl_6 in dichloromethane [1]. Addition of tetraphenylarsonium chloride and acetonitrile respectively leads to crystals of the derivatives $[Ph_4As]^+[Cl_4MoS_2N_3]^-$ (**1**) and $CH_3CN{\cdot}Cl_3WS_2N_3$ (**2**), for which the X-ray structural elucidation is reported here. At the same time but independent of our work, the crystal structures of the related $[Ph_3PNPPh_3]^+[Cl_4WS_2N_3]^-$ [2], $[Ph_4As]^+[Cl_4WS_2N_3]^-$ [3] and $[Ph_4P]_2{}^+[(Cl_3MoS_2N_3)_2]^{2-}$ [4] have been determined.

Experimental

A dark red crystal 0.7 × 0.5 × 0.3 mm^3 of **1** was obtained from CH_2Cl_2/hexane and mounted in a Lindemann glass capillary. Intensities were collected by profile-fitting on a Stoe-Siemens 4-circle diffractometer with graphite monochromated MoK$_\alpha$ radiation (λ = 0.71069 Å) for $2\theta < 45°$. After Lp, crystal decay and empirical absorption corrections, 2864 unique reflections with $F > 4\sigma(F)$ were used for all calculations. Data were similarly collected for $2\theta < 50°$ from a dark yellow crystal 0.55 × 0.4 × 0.25 mm^3 of **2** grown from CH_3CN/toluene. The collection was interrupted at h = 9 when three repeatedly measured check reflections had lost *ca.* 65% of their initial intensity. There resulted 1126 unique data with $F > 4\sigma(F)$.

Crystal Data

1: $C_{24}H_{20}AsCl_4MoN_3S_2$, M = 727.2, monoclinic space group $P2_1/n$, a = 13.483(3), b = 9.629(3), c = 21.928(7) Å, β = 99.24(3)°, U = 2809.9 Å^3, Z = 4, d_{calc} = 1.72 g cm^{-3}, μ(MoK$_\alpha$) = 2.17 mm^{-1}.

TABLE 1. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for **1**.

	x	*y*	*z*	U^a
Mo	3623(1)	7275(1)	5272(1)	45(1)
As	242(1)	4809(1)	2923(1)	43(1)
Cl(1)	2970(4)	7187(4)	6215(2)	66(2)
Cl(4)	2414(3)	5510(3)	4851(2)	60(2)
Cl(2)	4166(4)	7345(4)	4267(2)	60(2)
Cl(3)	2292(3)	8939(3)	4878(3)	66(2)
S(1)	5614(4)	8992(4)	5702(3)	64(2)
S(2)	5772(4)	6013(4)	5777(3)	79(2)
N(1)	4471(10)	8782(10)	5498(7)	52(5)
N(2)	4602(10)	6032(10)	5537(7)	52(5)
N(3)	6203(12)	7557(13)	5863(10)	87(7)
C(11)	1493(11)	4953(10)	2643(7)	40(5)
C(12)	1646(13)	4397(13)	2088(8)	50(6)
C(13)	2568(13)	4452(15)	1876(8)	53(6)
C(14)	3360(12)	5071(13)	2271(7)	46(6)
C(15)	3241(13)	5644(14)	2820(9)	57(7)
C(16)	2333(13)	5590(15)	3016(9)	53(6)
C(21)	−613(13)	3827(14)	2291(9)	52(6)
C(22)	−973(12)	4430(15)	1737(8)	53(6)
C(23)	−1494(15)	3610(14)	1245(8)	61(7)
C(24)	−1595(14)	2231(19)	1331(11)	72(8)
C(25)	−1218(12)	1614(15)	1887(10)	67(8)
C(26)	−743(11)	2379(13)	2381(8)	47(5)
C(31)	−265(11)	6624(14)	3124(7)	38(5)
C(32)	−1116(14)	7118(15)	2786(10)	62(7)
C(33)	−1467(15)	8443(14)	2949(9)	63(7)
C(34)	−902(14)	9152(15)	3447(10)	64(8)
C(35)	−48(14)	8638(14)	3756(9)	58(7)
C(36)	297(13)	7330(15)	3614(8)	56(6)
C(41)	406(10)	3744(11)	3681(8)	36(5)
C(42)	−288(12)	3808(15)	4041(9)	57(6)
C(43)	−164(18)	3026(20)	4577(12)	86(10)
C(44)	677(13)	2102(16)	4693(9)	58(6)
C(45)	1372(13)	2083(15)	4335(10)	65(7)
C(46)	1267(12)	2898(13)	3809(8)	50(6)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

2: $C_2H_3Cl_3N_4S_2W$, M = 437.4, orthorhombic space group *Pbca*, a = 9.825(3), b = 18.943(7), c = 11.250(5) Å, U = 2093.8 Å^3, Z = 8, d_{calc} = 2.77 g cm^{-3}, μ(MoK$_\alpha$) = 12.39 mm^{-1}.

Both structures were solved by the heavy atom method and refined anisotropically with weights $w^{-1} = \sigma^2(F) + gF^2$ (g = 0.001 for **1** and 0.0005 for **2**). Riding isotropic hydrogens [C–H 0.96 Å on external C–C–C bisectors, U(H) = 1.2 U_{eq}(C)] were employed for **1**, whereas in **2** the hydrogens were not located and C and N were refined isotropically. The refinements converged to R = 0.93, R_w = 0.089 for **1** and R = 0.062, R = 0.053 for **2**.

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TABLE II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **2**.

	x	*y*	*z*	*U*
W	1044(1)	6658(1)	5135(1)	$27(1)^a$
Cl(2)	2960(6)	6800(3)	6436(4)	$40(2)^a$
Cl(1)	−807(6)	6247(3)	4014(4)	$44(2)^a$
Cl(3)	2304(6)	5673(3)	4342(4)	$41(2)^a$
S(2)	−56(7)	8079(3)	6213(4)	$40(2)^a$
S(1)	1601(7)	8191(3)	4111(4)	$42(2)^a$
N(2)	73(19)	7247(7)	6104(12)	31(4)
N(3)	711(18)	8478(9)	5187(13)	44(5)
N(1)	1657(18)	7360(8)	4169(12)	34(4)
N(4)	345(18)	5819(7)	6503(12)	31(4)
C(1)	−72(23)	5475(9)	7202(14)	31(5)
C(2)	−624(22)	5027(9)	8182(15)	37(5)

[a]Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

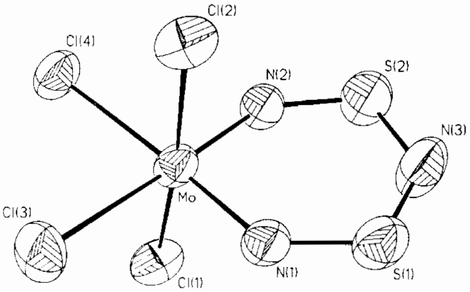

Fig. 1. The anion of **1**, showing 50% probability thermal ellipsoids and atom labelling scheme. Selected bond lengths (Å) and angles (°) are: Mo–N(2) 1.807(11), N(2)–S(2) 1.581(14), S(2)–N(3) 1.597(13), N(3)–S(1) 1.605(14), S(1)–N(1) 1.548(14), N(1)–Mo 1.865(11), Mo–Cl(1) 2.375(6), Mo–Cl(2) 2.432(5), Mo–Cl(3) 2.457(4), Mo–Cl(4) 2.431(4), N(1)–Mo–Cl(1) 95.4(5), N(2)–Mo–Cl(1) 92.9(5), N(1)–Mo–Cl(2) 87.6(5), N(2)–Mo–Cl(2) 89.9(5), N(1)–Mo–N(2) 92.6(5).

Final atomic coordinates and selected bond lengths and angles are given in Tables I and II and the legends to Figs. 1 and 2*.

Results and Discussion

In both compounds the N and S atoms of the ring lie in a plane (deviations less than 0.02 Å) with W about 0.09 Å and Mo about 0.12 Å out of the best plane through the other five ring atoms. A similar geometry has been observed in $Ph_3E=NS_3N_3$ (E = P, As) [5, 6] and in the monomeric unit of $(Cl_2VS_2N_3)_x$ [7]. Despite the unsymmetrical substitution at tungsten the ring geometry is symmetrical, with W–N and S–N bonds, respectively, equal within experimental error. The ring dimensions in **1** are less regular, though they agree within experimental error with those observed in $[Cl_4WS_2N_3]^-$ [3]; in each case a long M–N bond is adjacent to a short N–S bond and vice versa. In both **1** and **2**, one chlorine atom [Cl(1)] which lies *cis* to the ring is appreciably closer (0.06 Å) to the metal atom than the others, and (as can clearly be seen in the Figures) bends away from the ring plane. This distortion is correlated with the displacement of the metal out of the ring plane, which is in the direction away from Cl(1).

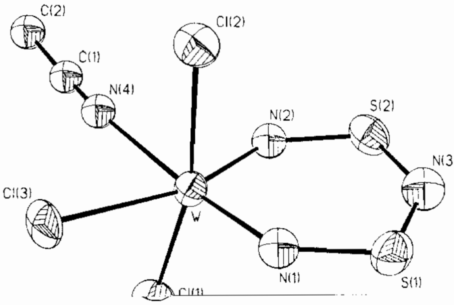

Fig. 2. The molecule of **2**, showing 50% probability thermal ellipsoids and atom labelling scheme. Selected bond lengths (Å) and angles (°) are: W–N(2) 1.827(14), N(2)–S(2) 1.585(15), S(2)–N(3) 1.571(17), N(3)–S(1) 1.590(17), S(1)–N(1) 1.575(16), N(1)–W 1.820(15), W–Cl(1) 2.346(6), W–Cl(2) 2.400(6), W–Cl(3) 2.411(5), W–N(4) 2.317(14), N(1)–W–Cl(1) 100.3(5), N(2)–W–Cl(1) 96.9(6), N(1)–W–Cl(2) 91.3(5), N(2)–W–Cl(2) 88.7(5), N(1)–W–N(2) 94.7(7).

If the metal atom is considered to have the oxidation state +6, then there are 8 π-electrons associated with the ring. There will thus be two almost degenerate ring π-orbitals to be occupied by one electron pair. The distortions from C_{2v} symmetry will split this degeneracy further, enabling the lower lying π-orbital to be occupied by both electrons, resulting in a diamagnetic electronic structure. By analogy with the corresponding one-electron effect involving degenerate orbitals, this may be termed a 'pseudo-Jahn-Teller' distortion.

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*Full Tables of bond lengths, angles, hydrogen atom coordinates, anisotropic temperature factors, and observed and calculated structure factors are obtainable from author GMS on request.

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