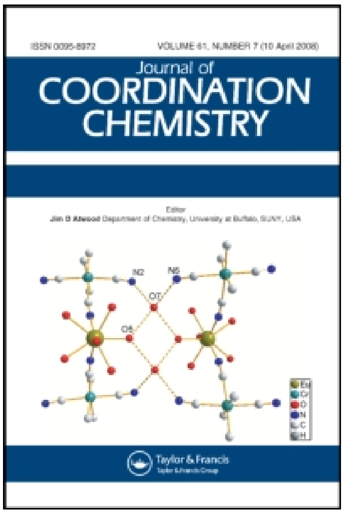

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HYDROGEN-BONDED TETRAMETHYLETHYLENEDIAMMONIUM AND TRIPHENYLPHOSPHONIUM COMPLEXES DERIVED FROM LIQUID CLATHRATE MEDIA

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Reactions of $M(CO)_6$ with $HCl_{(g)}$ in the presence of tetramethylethylenediamine (= tmeda) and H_2O (M=W) or in the presence of triphenylphosphine and H_2O (M=Mo) have been investigated. These reactions were performed in aromatic media and were promoted by UV radiation; solutions immediately separated into two layers indicative of liquid clathrate formation. In both, a M^V species was obtained, the former being $[(H^+)_2tmeda][H^+\cdot HNMe_2][WOCl_4(H_2O)^-]$-$[Cl^-]_2$, **1**, while for the latter $[H^+\cdot PPh_3]_2[MoOCl_5^{2-}]$, **2** resulted. X-ray crystal structures were performed on each compound. The structure of **1** showed two distinct structural features, $\{[(H^+)_2tmeda][Cl^-]\}_2^{2+}$dimers with Cl^- ions hydrogen-bonded through $N{-}H\cdots Cl\cdots H{-}N$ bridges and $\{[H^+\cdot HNMe_2][WOCl_4(H_2O)^-][Cl^-]\}_2^{2-}$ dimers where Cl^- ions bridge through $O(H_2O){-}H\cdots Cl\cdots H{-}N$ hydrogen bonds. Another interesting feature of this compound is the cleavage of the tmeda ligand to form the $H^+\cdot HNMe_2$ cation. In complex **2** both of the triphenylphosphine ligands are protonated and are bound to the $[MoOCl_5^{2-}]$anion through $P{-}H\cdots Cl$ hydrogen bonds.

Keywords: Liquid clathrate; hydrogen bonds; tungsten carbonyl; crystal structure

INTRODUCTION

Our group[1–5] and others[6,7] have recently been interested in stabilization of transition metal anionic complexes in liquid clathrate media by utilizing the

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lipophilic cation, [$H_3O^+ \cdot$ 18-crown-6].[8–18] The cavity of the 18-crown-6 ligand is of sufficient size to accommodate the oxonium ion (H_3O^+) in either a planar or pyramidal geometry.[19] Furthermore, in these compounds we have been able to isolate unusual coordination complexes.[3,5] In moving to smaller crown ethers, *e.g.* 15-crown-5 and 12-crown-4, however, the cavities of these macrocyclic ligands are not large enough for the oxonium ion to reside inside the cyclic ether. In these systems we found that $H_3O^+, H_5O_2^+, H_7O_3^+$ and $H_9O_4^+$ ions formed hydrogen-bonded networks either spanning between the crown ethers through hydrogen bonds, or linked metal centers.[20] In the larger cavity crown ethers 21-crown-7 and dibenzo-30-crown-10, we found 21-crown-7 snugly accommodated an $H_5O_2^+$ ion while dibenzo-30-crown-10 molecule encapsulated two H_3O^+ ions.[2,21] In several reactions with *aza*-18-crown-6 molecules we found either protonation at the N-heteroatom, or binding of an H_3O^+ occurs.[4,22] This prompted us to explore reactions of acyclic N and P donors to ascertain the possibility of oxonium ion binding by these types of Lewis bases.

As part of our study of liquid clathrate systems,[23–25] particularly of the [$H_3O^+ \cdot$ 18-crown-6] ion, we have now investigated the formation of anionic molybdenum and tungsten complexes which also contain the bidentate tetramethylethylenediamine (tmeda) ligand or the monodentate triphenylphosphine ligand. Herein we report the synthesis and crystal structures of [$(H^+)_2$tmeda][$H^+ \cdot HNMe_2$][$WOCl_4(H_2O)^-$][Cl^-]$_2$, **1**, and [$H^+ \cdot PPh_3$]$_2$ [$MoOCl_5^{2-}$], **2**, both of which were isolated from aromatic media and both devoid of oxonium ions. Complex **1** has an interesting feature, *viz* the cleavage of the tmeda ligand to form the $H^+ \cdot HNMe_2$ cation. Complex **2** is the first report of a compound containing the [$MoOCl_5^{2-}$] ion, and involves P–H $\cdots$ Cl hydrogen bonding to form discrete [$H^+ \cdot PPh_3$]$_2$[$MoOCl_5^{2-}$] units.

EXPERIMENTAL

$Mo(CO)_6$, $W(CO)_6$, tmeda and triphenylphosphine were obtained from Aldrich Chemical Co. and HCl gas was purchased from Atlas Co. Complexes **1** and **2** were prepared exposed to air, prior to the reaction mixture being sealed in an air-tight, screw-top tube.

Preparation of [$(H^+)_2$*tmeda*][$H^+ \cdot HNMe_2$][$WOCl_4(H_2O)^-$][Cl^-]$_2$, **1** To a sample of tmeda (1.26 g, 10.86 mmol) in toluene, was added H_2O (0.065 g, 3.62 mmol) and $W(CO)_6$ (1.27 g, 3.62 mmol) and the mixture was stirred rapidly for 15 min. $HCl_{(g)}$ was then rapidly bubbled through the mixture for approx. 1 h while irradiating with UV radiation. A yellow liquid clathrate separated from the solvent and overnight deep blue crystals of the *title complex* deposited from the clathrate layer.

Preparation of $[H^+\cdot PPh_3]_2[MoOCl_5^{2-}]$, **2** A sample of triphenylphosphine (2.85 g, 10.86 mmol) was moistened with distilled water (0.065 ml, 3.62 mmol) and approx. 100 ml of toluene added. $Mo(CO)_6$ (1.00 g, 3.62 mmol) was then added and $HCl_{(g)}$ was rapidly bubbled through the mixture for approx. 1 h while irradiating with UV radiation. A red liquid clathrate separated from the solvent and yellow crystals of the *title complex* deposited from the clathrate layer after approx 72 h.

Collection of X-ray diffraction data, and solution and refinement of the structures Single crystals of **1** and **2** were sealed in thin-walled glass capillaries. Final lattice parameters as determined from the least-squares refinement of the angular settings of 24 high angle reflections ($2\theta > 30°$) accurately centered on an Enraf-Nonius CAD4 diffractometer are given in Table I. A summary of data collection parameters is also given in Table I. An empirical absorption correction based on psi scan data was performed. Calculations were carried out using the SHELX system of computer programs.[26]

TABLE I Crystal data and summary of data collection for complexes **1** and **2**

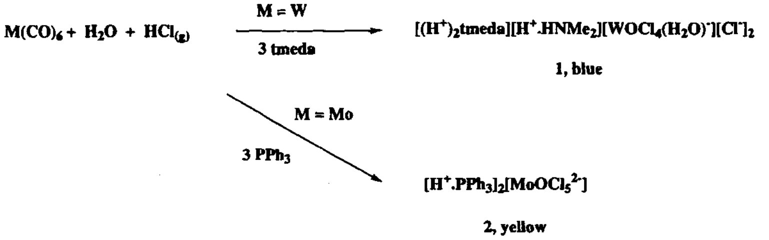
Compound	$[(H^+)_2\cdot tmeda][H^+\cdot HNMe_2]$ $[WOCl_4(H_2O)^-][Cl^-]_2$	$[H^+\cdot PPh_3]_2[MoOCl_5^{2-}]$
Mol. wt.	594.9	784.8
Space group	C2/m	$P2_1/c$
Cell constants		
a, Å	15.309(3)	11.044(3)
b, Å	20.019(4)	20.812(3)
c, Å	7.451(3)	16.168(4)
α, deg	90	90
β, deg	107.66(2)	93.34(2)
γ, deg	90	90
V, Å^3	2176(4)	3710(5)
Molecules/unit cell	4	4
D_c, g cm^{-3}	1.823	1.410
μ, cm^{-1}	61.9	7.79
Radiation	Mo Kα	Mo Kα
Scan width, deg	$0.80 + 0.20 \tan\theta$	$0.80 + 0.20 \tan\theta$
2θ range, deg	2–50	2–50
No. reflcns collcd	2152	7069
No. of obsd reflcns	1716	3243
No. of params varied	100	414
Sigma cutoff	3σ	3σ
Weighting scheme	Unit weights	Unit weights
Temp of data colln, deg	296	296
R	0.036	0.038
R_w	0.042	0.041

Positions of heavy atoms were determined from a three-dimensional Patterson function. All other non-hydrogen atoms were located from a difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom on the tmeda ligand in **1** was located but was not refined. The hydrogen atoms on the phosphine ligands in 2 were both located and refined isotropically. All other hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinements converged with $R = 0.036$ for 1716 observed reflections for **1** and $R = 0.038$ for 3243 observed reflections for **2**.

RESULTS

Preparation of Complexes

Complexes studied in this investigation were prepared according to Scheme 1. In both reactions the mixture quickly separated into two phases yielding colored liquid clathrate species. The upper layer in these reactions was toluene, while the metal complexes formed were completely dissolved within the clathrate layer. Reactions were performed in contact with air, followed by sealing the reaction vessel from aerial contact. Promotion of CO removal was aided by irradiating the reaction mixtures with UV light. It is possible that UV light may have some influence in the formation of tmeda cleaved products in **1** (where a radical mechanism may prevail in the formation of products; as discussed later). In both reactions oxidation of the metal center, from [0] to [5+], for both **1** and **2** occurred. In other reactions where we have performed the experiment with exclusion of oxygen, no oxidation of the metal center takes place. Instead, complexes of the type $[M(CO)_5Cl^-]$ are formed.[3] In preparation of **1** and **2** no oxonium ion cations were isolated. Instead, for **1** a diprotonated tmeda ligand is formed along with $H^+ \cdot HNMe_2$ ions. In **2** protonated triphenylphosphine ions balance the 2^- charge of the anions.



SCHEME 1

Reaction conditions throughout were optimized to yield liquid clathrates and X-ray quality crystals. To identify the species present in the liquid clathrate layers, both compounds investigated were structurally authenticated using X-ray crystallography. The complexes were obtained in moderate yields, and no attempts were made to maximize the yields.

Structural Results

Fractional coordinates and selected bond distances and angles for complexes **1** and **2** are shown in Tables II–V. Details for the diffraction experiments are given in the Experimental Section.

$[(H^+)_2tmeda][H^+{\cdot}HNMe_2][WOCl_4(H_2O)^-][Cl^-]_2$, **1** This complex crystallizes as discrete $\{[(H^+)_2\text{tmeda}][Cl^-]\}_2^{2+}$ and $\{[H^+{\cdot}HNMe_2][WOCl_4(H_2O)^-][Cl^-]\}_2^{2-}$ ions which both involve hydrogen bonding forming dimeric complex ions (see Figure 1). There are no interactions of less than *ca.* 3.5 Å between the two fragments.

The $\{[(H^+)_2\text{tmeda}][Cl^-]\}_2$ ion exists essentially as a dimeric unit through bridging chloride ions which are bound through N–H···Cl···H–N hydrogen bonds (Figure 2). The protons on the nitrogen atoms were located at 0.8(1) Å from the N-atom and the HN···Cl(3) and N(1)···Cl(3) distances are 2.30(1) and 3.14(1) Å respectively. The N–C–C–N dihedral angle through the ethylene unit is 99.4(1)° which indicates a *syn* configuration rather than *anti* about the ethylene backbone allowing the chlorides to doubly bridge two tmeda groups rather than to reside in terminal H-bonded positions.

TABLE II Final fractional coordinates for $[(H^+)_2{\cdot}\text{tmeda}][H^+{\cdot}HNMe_2][WOCl_4(H_2O)^-]$-$[Cl^-]_2$, **1**

Atom	*x/a*	*y/b*	*z/c*	*U (eqv)*
W	0.0000	0.21170(2)	0.5000	0.032(4)
Cl(1)	0.0810(2)	0.1944(1)	0.8231(3)	0.049(6)
Cl(2)	−0.1396(1)	0.8019(1)	0.5712(3)	0.053(15)
Oxo	0.0000	0.7057(4)	0.5000	0.048(6)
Wat	0.0000	0.0984(4)	0.5000	0.065(37)
C(1)	0.0255(5)	0.3394(4)	0.105(1)	0.037(11)
N(1)	0.1079(4)	0.3841(3)	0.154(1)	0.039(6)
Me (1)	0.1358(7)	0.4025(5)	354(1)	0.055(8)
Me(2)	−0.3146(6)	−0.8504(5)	0.106(1)	0.058(20)
Cl(3)	0.4150(2)	0.0000	0.1420(4)	0.042(4)
Cl(4)	0.3467(2)	0.5000	0.3166(4)	0.037(4)
N(2)	0.1289(7)	0.0000	0.084(1)	0.054(19)
C(2)	0.176(1)	0.0607(6)	0.182(2)	0.076(30)

TABLE III Final fractional coordinates for $[H^+ \cdot PPh_3]_2[MoOCl_5^{2-}]$, **2**

Atom	*x/a*	*y/b*	*z/c*	*U (eqv)*
Mo(1)	0.20146(6)	0.06221(3)	0.21319(4)	0.045(1)
Oxo	0.1205(5)	0.0337(2)	0.1326(3)	0.054(7)
Cl(1)	0.3220(2)	0.12855(9)	0.1281(1)	0.050(5)
Cl(2)	0.0677(2)	0.1517(1)	0.2318(1)	0.060(10)
Cl(3)	0.0983(2)	0.0030(1)	0.3121(1)	0.084(24)
Cl(4)	0.3557(2)	−0.01826(9)	0.2118(1)	0.063(13)
Cl(5)	0.3298(2)	0.1087(1)	0.3362(1)	0.056(16)
P(1)	0.1913(2)	0.23129(9)	0.4351(1)	0.040(2)
C(11)A	0.1850(6)	0.1813(4)	0.5230(5)	0.049(9)
C(12)A	0.1352(8)	0.1212(4)	0.5143(6)	0.069(18)
C(13)A	0.121(1)	0.0847(5)	0.5842(8)	0.103(38)
C(14)A	0.154(1)	0.1070(6)	0.6598(7)	0.105(19)
C(15)A	0.207(1)	0.1657(6)	0.6683(6)	0.097(26)
C(16)A	0.2227(8)	0.2040(4)	0.6008(5)	0.068(8)
C(11)B	0.0722(6)	0.2897(3)	0.4313(4)	0.040(3)
C(12)B	0.0421(7)	0.3233(4)	0.5003(5)	0.052(3)
C(13)B	−0.0480(7)	0.3684(4)	0.4949(5)	0.062(6)
C(14)B	−0.1098(7)	0.3802(4)	0.4215(6)	0.059(23)
C(15)B	−0.0806(8)	0.3485(4)	0.3523(6)	0.067(1)
C(16)B	0.0089(7)	0.3017(4)	0.3575(5)	0.059(6)
C(11)C	0.3360(6)	0.2699(3)	0.4342(4)	0.042(3)
C(12)C	0.3457(8)	0.3306(4)	0.4033(5)	0.057(4)
C(13)C	0.458(1)	0.3594(5)	0.3992(6)	0.083(18)
C(14)C	0.559(1)	0.3263(6)	0.4266(7)	0.090(21)
C(15)C	0.5519(8)	0.2665(6)	0.4589(6)	0.081(33)
C(16)C	0.4404(7)	0.2377(4)	0.4624(5)	0.062(8)
P(2)	0.6199(2)	0.1148(1)	0.2395(1)	0.048(12)
C(21)A	0.6448(7)	0.1953(4)	0.2110(5)	0.055(7)
C(22)A	0.5563(9)	0.2405(5)	0.2244(5)	0.076(7)
C(23)A	0.572(1)	0.1950(5)	0.7022(6)	0.092(12)
C(24)A	0.690(1)	0.3226(5)	0.1702(6)	0.094(30)
C(25)A	0.770(1)	0.2771(5)	0.1580(6)	0.091(6)
C(26)A	0.7518(9)	0.2130(5)	0.1773(6)	0.076(8)
C(21)B	0.6862(6)	0.0610(4)	0.1676(4)	0.042(2)
C(22)B	0.6262(7)	0.0517(4)	0.0909(4)	0.050(3)
C(23)B	0.6769(8)	0.0124(4)	0.0349(5)	0.057(6)
C(24)B	0.7850(8)	−0.0181(4)	0.0551(5)	0.056(8)
C(25)B	0.8432(7)	−0.0093(3)	0.1309(5)	0.052(14)
C(26)B	0.7942(6)	0.0303(3)	0.1875(4)	0.047(6)
C(21)C	0.6756(8)	0.0987(6)	0.3416(5)	0.075(36)
C(22)C	0.769(1)	0.1338(6)	0.3788(6)	0.108(45)
C(23)C	0.808(2)	0.117(1)	0.4600(9)	0.162(72)
C(24)C	0.763(2)	0.070(1)	0.5003(9)	0.174(92)
C(25)C	0.671(2)	0.036(1)	0.4641(8)	0.168(66)
C(26)C	0.626(1)	0.0496(6)	0.3841(6)	0.100(26)
H(1)	0.174(5)	0.199(3)	0.381(3)	0.029(15)
H(2)	0.551(7)	0.112(3)	0.231(4)	0.054(24)

TABLE IV Selected (i) bond distances (Å) and (ii) angles (°) for $[(H^+)_2\text{tmeda}][H^+\cdot HNMe_2][WOCl_4(H_2O)^-][Cl^-]_2$, **1**

Atoms	*Distance*	*Atoms*	*Distance*
(i)			
W–Oxo	1.651(8)	W–Wat	2.266(8)
W–Cl(1)	2.375(2)	W–Cl(2)	2.369(2)
N(1)–HN	0.8(1)	N(1)–C(1)	1.492(9)
C(1)–C(1′)	1.52(1)	Me(1)–N(1)	1.47(1)
Me(2)–N(1)	1.48(1)	C(2)–N(2)	1.48(1)
HN···Cl(3)	2.30(1)	N(1)···Cl(3)	3.14(1)
Wat···Cl(4)	3.05(1)	N(2)···Cl(4)	3.11(1)
(ii)			
Wat–W–Oxo	179.92(1)	Oxo–W–Cl(1)	98.38(5)
Wat–W–Cl(1)	81.62(5)	Cl(1)–W–Cl(2)	88.92(8)
Oxo–W–Cl(2)	96.59(6)	Wat–W–Cl(2)	83.41(6)
Me(1)-N(1)-HN	119(9)	Me(2)-N(1)-HN	111(9)
Me(1)–N(1)–C(1)	111.4(6)	Me(2)–N(1)–C(1)	111.0(6)
Me(1)-N(1)-Me(2)	110.5(7)		

TABLE V Selected (i) bond distances (Å) and (ii) angles (°) for $[H^+\cdot PPh_3]_2[MoOCl_5{}^{2-}]$, **2**

Atoms	*Distance*	*Atoms*	*Distance*
(i)			
Mo–Oxo	1.647(5)	Mo–Cl(1)	2.405(2)
Mo–Cl(3)	2.364(2)	Mo–Cl(2)	2.406(2)
Mo–Cl(5)	2.563(2)	Mo–Cl(4)	2.390(2)
P(1)–C(11)A	1.768(7)	P(2)–C(21)A	1.764(8)
P(1)–C(11)B	1.790(7)	P(2)–C(21)B	1.798(7)
P(1)–C(11)C	1.790(7)	P(2)–C(21)C	1.761(8)
P(1)–H(1)	1.08(5)	P(2)–H(2)	0.77(7)
H(1)···Cl(2)	2.81(1)	H(1)···Cl(5)	2.70(1)
P(1)···Cl(2)	3.86(1)	P(1)···Cl(5)	3.42(1)
H(2)···Cl(1)	2.86(1)	H(2)···Cl(5)	2.81(1)
P(2)···Cl(1)	3.66(1)	P(2)···Cl(5)	3.64(1)
(ii)			
Cl(1)–Mo–Oxo	92.7(2)	Cl(2)–Mo–Oxo	94.0(2)
Cl(3)–Mo–Oxo	95.0(2)	Cl(4)–Mo–Oxo	95.3(2)
Cl(5)–Mo–Oxo	178.5(2)	Cl(1)–Mo–Cl(2)	89.56(7)
Cl(1)–Mo–Cl(3)	172.30(8)	Cl(1)–Mo–Cl(4)	88.76(7)
Cl(1)–Mo–Cl(5)	85.84(7)	Cl(2)–Mo–Cl(3)	89.71(9)
Cl(2)–Mo–Cl(4)	170.58(7)	Cl(2)–Mo–Cl(5)	85.82(6)
Cl(3)–Mo–Cl(4)	90.72(9)	Cl(3)–Mo–Cl(5)	86.46(8)
C(11)A–P(1)–H(1)	106(3)	C(21)A–P(2)–H(2)	103(5)
C(11)B–P(1)–H(1)	106(3)	C(21)B–P(2)–H(2)	106(5)
C(11)C–P(1)–H(1)	112(3)	C(21)C–P(2)–H(2)	114(5)
C(11)A–P(1)–C(11)B	111.3(3)	C(21)A–P(2)–C(21)B	110.3(3)
C(11)A–P(1)–C(11)C	110.3(3)	C(21)A–P(2)–C(21)C	112.0(5)
C(11)B–P(1)–C(11)C	110.5(3)	C(21)B–P(2)–C(21)C	110.8(4)

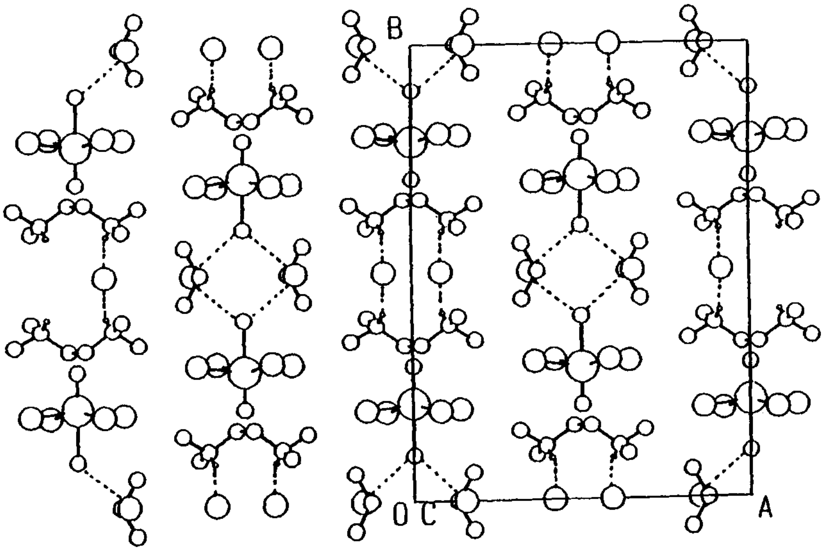


FIGURE 1 Packing diagram for $[(H^+)_2\cdot tmeda][H^+\cdot HNMe_2][WOCl_4(H_2O)^-][Cl^-]_2$ **1**, showing internuclear hydrogen bonding.

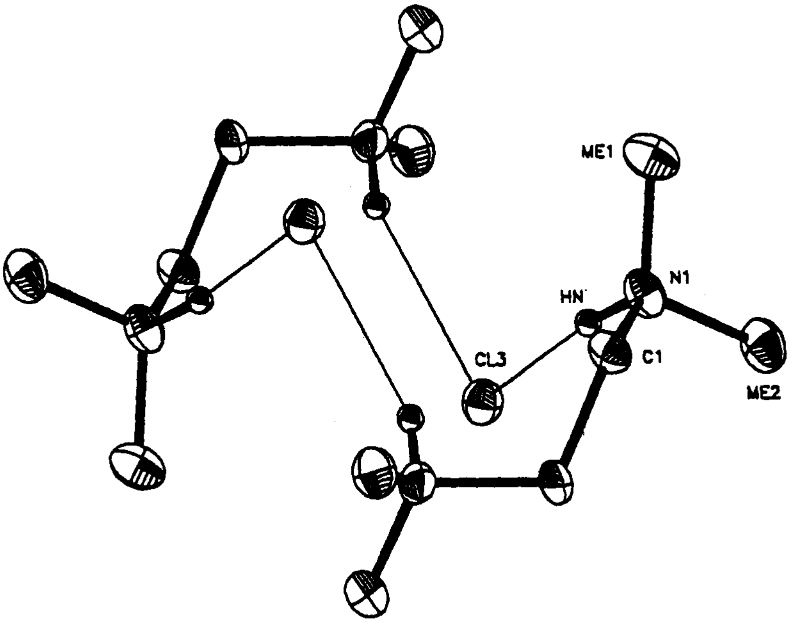


FIGURE 2 The hydrogen bonded $\{[(H^+)_2\cdot tmeda]_2[Cl^-]_2\}^{2+}$ dimer. H(N)···Cl(3), 2.30(1); N(1)···Cl(3), 3.14(1) and Cl(3)···Cl(3), 3.820 Å.

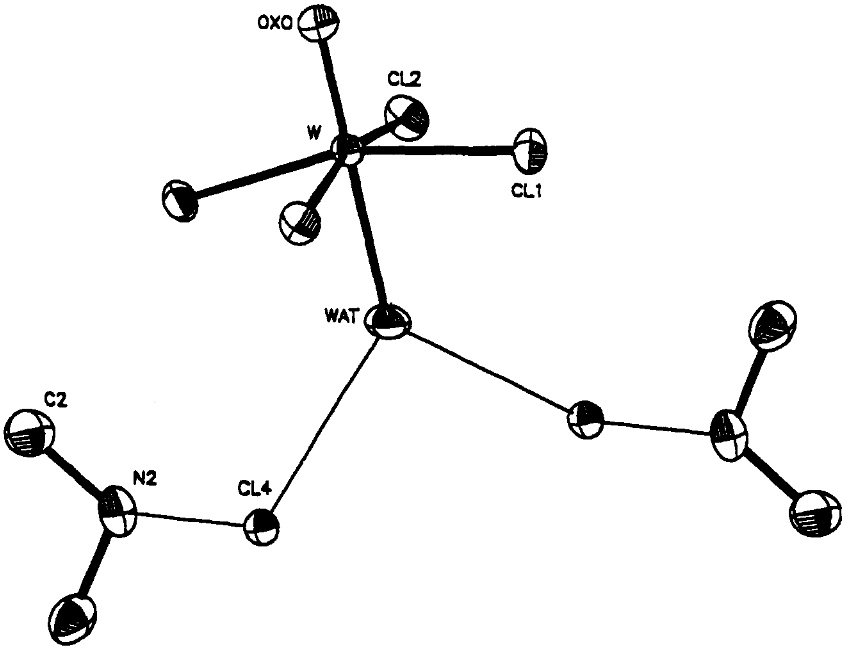


FIGURE 3 Hydrogen bonding interactions between the $[H^+{\cdot}HNMe_2]$ cations and the $[WOCl_4(H_2O)^-]$ and chloride atoms. Wat···Cl(4), 3.05(1) and N(2)···Cl(4), 3.11(1) Å.

The$\{[H^+{\cdot}HNMe_2][WOCl_4(H_2O)^-][Cl^-]\}_2^{2-}$ ion has a distorted octahedral geometry about the tungsten(V) center (see Figure 3). The W–Cl(ave), W–oxo and W–wat separations are 2.37(1), 1.651(8) and 2.266(8) Å, respectively. The Cl ligands are equatorial and bent down and away from the oxo ligand at an average of 97.5(1)°. The oxo–W–wat angle is 179.92(1)°. The axial water ligand hydrogen bonds through the Cl ions to the protonated $HNMe_2$ groups (O···Cl, 3.05(1) and N(2)···Cl(4), 3.11(1) Å).

$[H^+{\cdot}PPh_3]_2[MoOCl_5^{2-}]$, **2** In this complex both of the triphenylphosphine groups are protonated and form internuclear hydrogen bonds through P–H···Cl to the $[MoOCl_5]^-$ anions (see Figure 4).

In the anion, the geometry around the Mo center is a distorted octahedron (see Figure 4). The average bonding parameters are Mo–$Cl_{(eq.)}$ = 2.39(1), Mo–$Cl_{(axial)}$ = 2.563(2) and Mo–O = 1.647(5) Å. The equatorial Cl ligands are bent down and away from the oxo group (ave O(oxo)–Mo–Cl = 94.3(1)°) and the O(oxo)–Mo–Cl(5) angle is 178.5(2)°. There are hydrogen bonds between the protonated PPh_3 groups

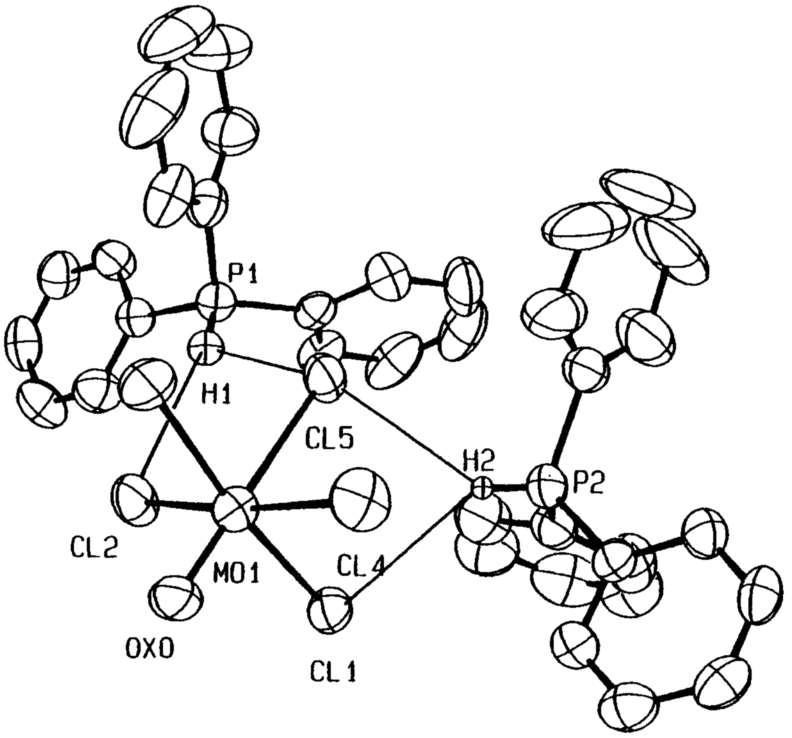
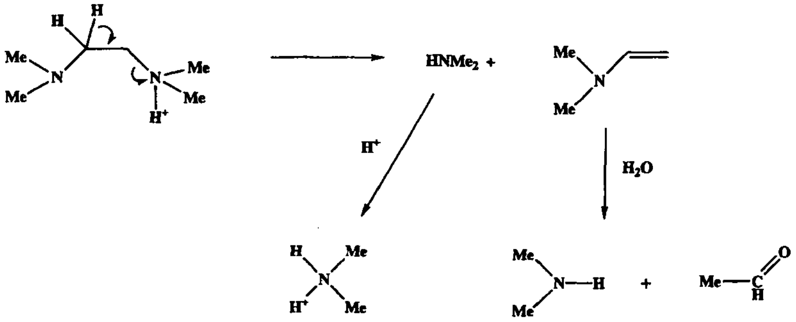


FIGURE 4 Structure of $[H^+ \cdot PPh_3]_2[MoOCl_5^{2-}]$ showing the hydrogen bonding between H(1) and Cl(2), Cl(5) and H(2) and Cl(1), Cl(5). H(1)-Cl(2), 2.81(1); H(1)-Cl(5), 2.70(1); H(2)-Cl(1), 2.86(1), Cl(5)-H(2), 2.81(1); P(1)-Cl(5), 3.42(1); P(1)-Cl(2), 3.86(1); P(2)-Cl(1), 3.66(1) and P(2)-Cl(5), 3.64(1) Å.

and the $[MoOCl_5^{2-}]$ anions (P(1)···Cl(2), 3.86(1); P(1)···Cl(5), 3.42(1); P(2)···Cl(1), 3.66(1) and P(2)···Cl(5), 3.64(1) Å, P-H, 1.08(5) and 0.77(7) Å).

DISCUSSION

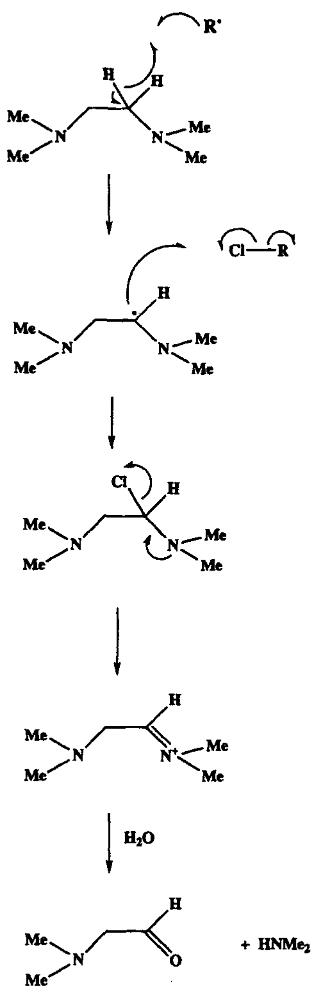
Formation of both complexes reported herein follows procedures successful in preparation of $[Mo_2Cl_9]^{3-}$, $[MoOCl_4(H_2O)]^-$, $[W(CO)_4Cl_3]^-$ and $[WOCl_4(H_2O)]^-$ anions in liquid clathrate media associated with $[H_3O^+ \cdot$ 18-crown-6$]$ cations.[3-5] Furthermore we have been able to stabilize $H_5O_2^+$ oxonium ions in 21-crown-7 molecules and even two H_3O^+ ions bound within a dibenzo-30-crown-10 macrocycle using these transition metal ions to balance the charge.[2,21] Replacement of the crown ether with tetramethylethylenediamine or triphenylphosphine allows formation of the transition metal anion but formation of an oxonium species does not occur. Instead protonation of the phosphine or amine ligand occurs. In the case of tetramethylethylenediamine, not only does the tmeda ligand get doubly protonated, but concurrent decomposition of the bidentate amine occurs. This results in formation of a complex where the tmeda is doubly protonated and forms a dimer with bridging Cl ions through N–H $\cdots$ Cl $\cdots$ H–N hydrogen bonding, and protonated dimethylamine fragments which are hydrogen bonded through N–H $\cdots$ Cl $\cdots$ H–O to lattice Cl ions to the $[WOCl_4(H_2O)^-]$ ion. The formation of the $H^+ \cdot HNMe_2$ ions in **1** could be from one of two mechanisms. Firstly the protonated dimethylamine could arise from a Hoffman elimination mechanism producing $Me_2NCH=CH_2$ which on hydrolysis would yield Me_2NH and CH_3CHO (see Scheme 2).[27] Alternatively, under the conditions involved (UV light, $HCl_{(g)}$ and presence of metal carbonyls) a radical mechanism may prevail (see Scheme 3).



SCHEME 2

The $\{[(H^+)_2\text{tmeda}][Cl^-]\}_2^{2+}$ complex ion is related to N,N,N′,N′-tetramethylethylenediammonium dibromide $([(H^+)_2\text{tmeda})]_2[Br^-]_2$.[28] The structures of these two compounds however have contrasting features which essentially involve rotation about the ethylene linkage. In the latter the *anti* configuration positions the protonated nitrogen centers at a maximal distance from each other and the bromide ions are bound through H-bonding to the protonated amines. In the present case, the N–C–C–N dihedral angle of 99.4° dictates that the two protonated N centers are not on opposite sides of the ethylene linkage and therefore allows the ion to dimerize through hydrogen-bonded bridging Cl ions.

The other structural feature of compound **1** is the formation of $\{[H^+ \cdot HNMe_2][WOCl_4(H_2O)^-][Cl^-]\}_2^{2-}$ ions where the generated



SCHEME 3

dimethylamine (see Schemes 2 and 3) is protonated and then bound in hydrogen-bonded dimers to the $[WOCl_4(H_2O)]^-$ anion. The transition metal containing anion is similar to those reported in related chemistry.[5,21] In these other complexes as well as the present case, this anion is quite often found in hydrogen-bonded arrays through either Cl or O–H linking with other centers in the structures.

In complex **2**, the triphenylphosphine ligands are protonated and form discrete anion/cation molecular units through hydrogen bonding. In other complexes where protonated PPh_3 ligands have been formed, hydrogen bonding has also been a feature, for example $[H^+ \cdot PPh_3][Br^-]$ which also forms discrete molecular units through P–H··· Br hydrogen bonds.[29] The P–H distances in the present structure (0.77(7) and 1.08(5) Å) are significantly shorter than in other structures (*cf.* P–H of 1.5(1) and 1.35 Å in $[H^+ \cdot PPh_3]_2[OsBr_6]$[30] and $[H^+ \cdot PPh_3]_2[GaBr_6]$[31] respectively), while the P··· Cl distance (3.42(1)–3.86(1) Å) is similar to other cases (*e.g.* 3.60 Å in $[H^+ \cdot PPh_3]_3[PrCl_6]$[32] and 3.65 and 3.72 Å in $[H^+ \cdot PPh_3]_2[OsCl_6]$[30]) and shorter than P··· Br (3.79 and 3.85 Å) in $[H^+ \cdot PPh_3][Br^-]$.[29] The average P–C distance of 1.78(1) Å is significantly shorter than in triphenylphosphine (1.83 Å).[33]

A search of the Cambridge Crystallographic Database showed that this is the first reported crystallographic determination of the $[MoOCl_5]^-$ ion. Related complexes such as the $[Mo_2O_2Cl_8^{2-}]$ ion[34] which has doubly-bridging chlorines, the $[MoOCl_4(H_2O)]^-$ ion,[4] which is similar to the tungsten analog in compound **1** and also the typical ion observed in similar reactions involving crown ethers, and the $[WOCl_5]^-$ ion found in $[H_5O_2^+ \cdot \text{21-crown-7}][WOCl_5^-]$which was the first reported structure of a W^{VI} ion.[2,21] In all of these cases, the metal to ligand distance of the ligand *trans* to the oxo ligand is lengthened due to the *trans* influence. It has been reported that when L = Cl for $[MoOCl_4L]^{n-}$ the degree of formation of the anion is low and dependent on the molybdenum concentration. For example with $[Et_4N^+]$ the formation of$[MoOCl_5^{2-}]$ was more favored than when $[Ph_4As^+]$ was the cation.[35]

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References

[1] P.C. Junk and J.L. Atwood, *J. Chem. Cryst.*, **24**, 247 (1994).
[2] P.C. Junk and J.L. Atwood, *J. Chem. Soc., Chem. Commun.*, 1551 (1995).
[3] J.L. Atwood, S.G. Bott, P.C. Junk and M.T. May, *J. Organomet. Chem.*, **487**, 7 (1994).
[4] J.L. Atwood, S.G. Bott, P.C. Junk and M.T. May, *J. Coord. Chem.*, **37**, 89(1996).
[5] J.L. Atwood, P.C. Junk, M.T. May and K.D. Robinson, *J. Coord. Chem.*, **40**, 247 (1996).
[6] R. Chenevert, D. Chamberland, M. Simard and F. Brisse, *Can. J. Chem.*, **67**, 32 (1989).
[7] R. Chenevert, D. Chamberland, M. Simard and F. Brisse, *Can. J. Chem.*, **68**, 797 (1990).
[8] J.-P. Behr, P. Dumas and D. Moras, *J. Am. Chem. Soc.*, **104**, 4540 (1982).
[9] P.D.J. Grootenhuis, J.W.H.M. Uiterwijk, D.N. Reinhoudt, C.J. van Stveren, E.J.R. Sudholter, M. Bos, J. van Eerden, W.T. Klooster, L. Kruise and S. Harkema, *J. Am. Chem. Soc.*, **108**, 780 (1986).

[10] C.B. Shoemaker, L.V. McAfree, D.P. Shoemaker and C.W. Dekock, *Acta Crystallogr.*, **C42**, 1310 (1986).

[11] J.L. Atwood, S.G. Bott, A.W. Coleman, K.D. Robinson, S.B. Whetstone and C.M. Means, *J. Am. Chem. Soc.*, **109**, 8100 (1987).

[12] W. Ming, W. Boyi, Z. Peiju, H. Wenji and L. Jie, *Acta Crystallogr.*, **C44**, 1913 (1988).

[13] J.L. Atwood, S.G. Bott, C.M. Means, A.W. Coleman, H. Zhang and M.T. May, *Inorg. Chem.*, **29**, 467 (1990).

[14] J.L. Atwood, S.G. Bott, K.D. Robinson, E.J. Bishop and M.T. May, *J. Cryst. Spec. Res.*, **21**, 459 (1991).

[15] R.D. Rogers, A.H. Bond, W.G. Hipple, A.N. Rollins and R.F. Henry, *Inorg. Chem.*, **30**, 2671 (1991).

[16] V.S Sergienko, L.Kh. Minacheva, N.Kh. Ashurova, M.A. Porai-Koshits, K.G. Yakubov and V.G. Sakharova, *Russ. J. Inorg. Chem.*, **36**, 212 (1991).

[17] J.L. Atwood, P.C. Junk, M.T. May and K.D. Robinson, *J. Chem. Cryst.*, **24**, 243 (1994).

[18] P.C. Junk, L.R. MacGillivray, M.T. May, K.D. Robinson and J.L. Atwood, *Inorg. Chem.*, **34**, 5395 (1995).

[19] See Ref.[4] for a discussion of the different geometries for $[H_3O^+ \cdot 18\text{-crown-}6]$ ions.

[20] P.C. Junk and J.L. Atwood, *Chem. Comm.* (1997) submitted.

[21] P.C. Junk and J.L. Atwood, *J. Chem. Soc., Dalton Trans.* (1997) 4393.

[22] P.C. Junk and J.L. Atwood, *Supramol. Chem.* (1997), in press.

[23] J.L. Atwood, in *Inclusion Compounds*, J.L. Atwood, J.D. Davies and D.D. MacNicol (Eds.), Academic Press: London (1984), Vol. 1, pp. 375–405.

[24] J.L. Atwood, in *Chemical Separations*, C.J. King and J.D. Navratil (Eds.), Litarvan: Denver (1986), pp. 335–354.

[25] J.L. Atwood, in *Separation Technology*, N.N. Li and H. Strathmann (Eds.), United Engineering Trustees: New York (1988), pp. 46–56.

[26] G.M. Sheldrick, SHELX76; *A System of Computer Programs for X-ray Structure Determination*, University of Cambridge (1976).

[27] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, second edition, McGraw-Hill, Tokyo (1977), p. 900.

[28] T.A. Annan, R.K. Chadha and D.G. Tuck, *Acta Crystallogr.*, **C47**, 151 (1991).

[29] N. Brinklebank, S.M. Godfrey, C.A. McAuliffe and R.G. Pritchard, *Acta Crystallogr.*, **C49**, 1017 (1993).

[30] P.D. Robinson, C.C. Hinckley, M. Matusz and P.A. Kibala, *Acta Crystallogr.*, **C44**, 619 (1988).

[31] M.A. Khan, D.G. Tuck, M.J. Taylor and D.A. Rogers, *J. Cryst. Spec. Res.*, **16**, 895 (1986).

[32] R.J. Majeste, D. Chriss and L.M. Trefonas, *Inorg. Chem.*, **16**, 188 (1977).

[33] J.J. Daly, *J. Chem. Soc.*, 3799 (1964).

[34] R. Herbst-Irmer and E. Egert, *Acta Crystallogr.*, **C48**, 1843 (1992).

[35] P.M. Boorman, C.D. Garner and F.E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 1299 (1975).