Tungsten–organoimido chemistry. The crystal and molecular structures of $[(n\text{-}C_4H_9)_4N][W(NC_6H_4CH_3)Cl_5]$ and $[(n\text{-}C_4H_9)_4N][C_7H_7NH_3][W_2OCl_8(NC_6H_4CH_3)_2]$

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Abstract

The reaction of $[(n\text{-}C_4H_9)_4N]_4[H_3PW_{11}O_{39}]$ with $[W(NC_5H_4CH_3)Cl_4]_2$ yields a mixture of $[(n\text{-}C_4H_9)_4N]$-$[W(NC_6H_4CH_3)Cl_5]$ (**1**) and $[(n\text{-}C_4H_9)_4N][C_7H_7NH_3][W_2OCl_8(NC_6H_4CH_3)_2]$ (**2**). Crystal data: **1**, monoclinic space group $P2_1/c$, $a=10.950(2)$, $b=11.254(3)$, $c=12.920$ Å, $\beta=108.96(2)°$, $V=1506.0(6)$ Å^3, $Z=2$, $D_{calc}=1.56$ g cm^{-3}, solution and refinement based on 2190 reflections converged at a conventional discrepancy value of 0.069; **2**, monoclinic space group $P2_1/c$, $a=14.001(8)$, $b=26.68(1)$, $c=15.278(9)$ Å, $\beta=104.28(4)°$, $V=5534(3)$ Å^3, $Z=4$, $D_{calc}=1.47$ g cm^{-3}, 4187 reflections, $R=0.069$.

Introduction

The chemistry of transition metal complexes containing oxo, imido and nitrido ligands has attracted considerable contemporary interest because of the relationship of these species to diverse industrial processes and to biological activation of small molecules [1–5]. Metal–imido species, specifically, have been evoked as models for industrial ammoxidation, a process catalyzed by metal oxides and thought to proceed through a key metal–imido intermediate [6]. Although complexes containing both oxo and imido functionalities are of particular interest in this regard, such mixed coordination species are relatively rare [7, 8]. In an attempt to exploit the chemistry of lacunary Keggin anions in the systematic synthesis of complexes of this type, we reacted $(TBA)_4[H_3PW_{11}O_{39}]$ (TBA = $(n\text{-}C_4H_9)_4N$ cation) with $[W(NR)Cl_4]_2$, expecting to isolate the Keggin species $(TBA)_3[PW_{12}(NR)O_{39}]$. However, the products of the reaction were found to be the mononuclear W(VI) species $(TBA)[W(NR)Cl_5]$ (**1**) and the binuclear W(VI) complex $(TBA)(C_7H_7NH_3)[W_2OCl_8(NR)_2]$ (**2**), whose structures are reported in this work.

Experimental

All reactions were carried out under an atmosphere of purified argon. The complexes $(TBA)_4[H_3PW_{11}O_{39}]$ and $[W(NR)Cl_4]_2$ were prepared by the literature methods [9, 10]. The following instruments were used in the study: IR, Perkin-Elmer 283B IR spectrophotometer; X-ray crystallography, Rigaku AFC-5S four-circle diffractometer; electrochemistry, BAS electroanalytical system.

Synthesis of (TBA)[W(NR)Cl$_5$] and (TBA)(C$_7$H$_7$NH$_3$)[W$_2$O(NR)$_2$Cl$_8$]

$(TBA)_4[H_3PW_{11}O_{39}]$ (1.32 g, 0.362 mmol) was added to $[W(NR)Cl_4]_2$ (0.30 g, 0.33 mmol) in 30 ml of 1,2-dichloroethane. The solution turned dark green and was heated with stirring at 60 °C for 1 h followed by refluxing for an additional 2 h. The solution was cooled to room temperature and the light brown solid which formed was filtered and discarded. The dark brown filtrate was concentrated to 15 ml and layered with 20 ml of heptane. After two weeks, brown plates of $(TBA)(C_7H_7NH_3)[W_{20}Cl_8(NR)_2]$ (**2**) were collected in 25% yield. The resulting brown–green filtrate was allowed to stand for an additional three weeks, whereupon dark green crystals of $(TBA)[W(NR)Cl_5]$ (**1**) were collected in 15% yield. *Anal.* Calc. for $C_{23}H_{43}N_2Cl_5W$ (**1**): C, 39.0; H, 6.07; N, 3.95. Found: C, 38.7; H, 5.99; N, 3.74%. *Anal.* Calc. for $C_{37}H_{60}N_4OCl_8W_2$ (**2**): C, 36.2; H, 4.89; N, 4.56. Found: C, 35.8; H, 4.55; N, 4.47%.

Synthesis of (TBA)$_2$[W$_4$O$_4$(NR)$_4$Cl$_{10}$] (3)

The reaction of one equivalent of **1** with one equivalent of H_2O yields **3** in quantitative yield. In a similar fashion

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TABLE 1. Summary of crystal data and experimental conditions for the X-ray study of (TBA)[W(NC$_7$H$_8$)Cl$_5$] (**1**) and (TBA)(C$_7$H$_8$NH$_3$)[W$_2$O(NC$_7$H$_8$)$_2$Cl$_8$] (**2**)

	1	**2**
Crystal data		
Empirical formula	$C_{23}H_{43}N_2Cl_5W$	$C_{37}H_{60}N_4OCl_8W_2$
Color, habit	dark brown plate	dark green plate
Crystal size (mm)	0.25 × 0.23 × 0.09	0.27 × 0.35 × 0.11
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/c$
Unit cell dimensions		
a (Å)	10.950(2)	14.001(8)
b (Å)	11.253(3)	26.68(1)
c (Å)	12.920(2)	15.278(9)
α (°)	90.00	90.00
β (°)	108.96(1)	104.28(2)
γ (°)	90.00	90.00
Volume (Å^{-3})	1506.0(6)	5534(3)
Z	2	4
Formula weight	708.2	1227.4
Density (calc.) (g cm^{-3})	1.56	1.47
Absorption coefficient (cm^{-1})	4.42	4.71
F(000)	1416	3296
Data collection		
Diffractometer	Rigaku AFC5S	
Radiation	Mo Kα (λ = 0.71073 Å)	
Temperature (K)	295	
Monochromator	highly oriented graphite	
2θ Range (°)	2–45	2–55
Scan speed (°/min)	6	6
Background measurement	stationary counts, peak/background counting time = 2:1	
Standard reflections	3 collected every 400 data	
Index ranges		
h	−11 to 12	−13 to 14
k	0 to 12	0 to 29
l	0 to 13	0 to 11
Reflections collected	2962	7769
Reflections observed	2190	4187
Absorption correction	based on Ψ scans for 5 reflections with χ near 90° or 270°	
Transmission factor range	0.73–0.91	0.69–0.82
Solution and refinement		
System used	TEXSAN	
Solution	Patterson method	
Refinement method	full matrix least-squares	
Quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
Hydrogen atoms		
Weighting scheme	$w = 4(F_o^2)/\sigma^2(F_o)^2$ [a]	
Final R indices (obs. data)		
R	0.069	0.069
R_w	0.072	0.069
Goodness of fit	1.93	1.63
Max. shift/error in final cycle	0.009	0.007
Data to parameter ratio	11.8	13.6
Largest hole (e$^-$/Å^3)	0.15	0.23
Largest peak (e$^-$/Å^3)	0.33	0.15

[a] $\sigma^2(F_o^2) = [S^2(C + R^2B) + pF_o^2)]/Lp^2$ where S = scan time, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, p = p factor (0.03).

the reaction of **2** (0.12 g, 0.10 mmol) with H$_2$O in CH$_2$Cl$_2$ gives brown crystals of **3** in low yield (*c*. 5%). *Anal.* Calc. for $C_{60}H_{90}N_6O_4Cl_{10}W_4$ (**3**): C, 35.2; H, 4.39; N, 4.10. Found: C, 35.1; H, 4.25; N, 4.01%.

X-ray structure determinations

Full details of the crystallographic methodologies may be found in ref. 11. The crystal data and experimental conditions are summarized in Table 1.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	U_{eq}[a]
W(1)	1450(1)	0	3489(1)	41(1)
Cl(1)	1704(7)	1336(7)	2190(6)	55(3)
Cl(2)	−629(8)	796(9)	3202(8)	72(4)
Cl(3)	3355(8)	−955(9)	3494(8)	71(4)
Cl(4)	1037(8)	−1550(9)	4581(8)	72(4)
Cl(5)	369(9)	−1339(8)	1921(7)	73(4)
N(1)	2231(25)	919(25)	4569(21)	57(7)
C(1)	2802(25)	1628(24)	5462(22)	45(10)
C(2)	2016(33)	2164(35)	5972(28)	71(15)
C(3)	2660(31)	2909(35)	6817(24)	61(13)
C(4)	4060(34)	3162(37)	7076(25)	68(14)
C(5)	4594(33)	2256(69)	6728(29)	151(39)
C(6)	4127(34)	1797(34)	5779(30)	73(16)
C(7)	4402(45)	4293(53)	7901(34)	153(31)
N(2)	625(18)	285(20)	8326(15)	44(5)
C(11)	−332(24)	−132(36)	7255(20)	51(8)
C(12)	−1331(28)	−628(29)	6470(25)	54(7)
C(13)	−2105(24)	−188(28)	5575(20)	49(7)
C(14)	−3172(48)	731(49)	5707(42)	127(19)
C(15)	−145(29)	977(29)	9017(26)	57(8)
C(16)	−1167(25)	252(31)	9180(22)	58(8)
C(17)	−1808(49)	1182(47)	9890(43)	114(17)
C(18)	−4115(101)	1323(204)	9797(109)	0(115)
C(19)	1344(30)	−778(33)	8868(27)	63(9)
C(20)	2370(41)	−505(37)	10038(34)	77(12)
C(21)	2866(86)	484(67)	10004(67)	56(24)
C(22)	3098(42)	1715(40)	10446(37)	100(13)
C(23)	1477(27)	1272(30)	8133(25)	53(8)
C(24)	2496(30)	848(29)	7595(27)	56(9)
C(25)	2407	−765	7435	371(143)
C(26)	3304(38)	−1908(38)	7477(35)	85(12)

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

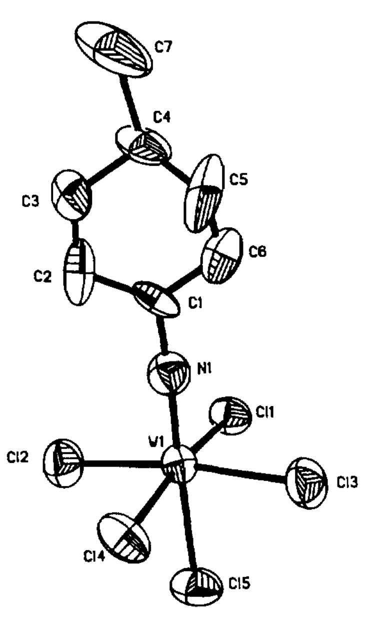

Fig. 1. ORTEP view of the structure of $[W(NC_7H_7)Cl_4]^-$.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) for **2**

W(1)	−441(1)	3854(1)	7847(1)	28(1)
W(2)	−1870(1)	5010(1)	7037(1)	29(1)
O(1)	−1225(12)	4433(6)	7551(10)	39(6)
N(1)	431(16)	4017(8)	7252(13)	43(8)
N(2)	−2439(15)	4734(7)	6029(14)	35(8)
Cl(1)	525(5)	4187(3)	9221(4)	37(2)
Cl(5)	−3176(5)	4901(3)	7741(5)	51(3)
Cl(7)	−978(5)	5399(3)	8552(4)	42(2)
Cl(6)	−2468(5)	5825(3)	6609(4)	49(3)
Cl(2)	349(5)	3060(3)	8291(4)	48(3)
Cl(3)	−1578(6)	3605(3)	8820(5)	55(3)
Cl(4)	−1515(5)	3425(3)	6648(4)	49(3)
Cl(8)	−451(5)	5232(3)	6547(5)	46(3)
C(11)	1311(16)	4062(8)	6958(14)	22(5)
C(12)	2142(18)	3840(10)	7424(16)	40(6)
C(13)	2977(20)	3879(11)	7106(18)	50(7)
C(14)	2953(20)	4117(11)	6308(18)	45(7)
C(15)	2091(20)	4339(11)	5772(19)	50(8)
C(16)	1235(18)	4304(10)	6125(16)	38(7)
C(17)	3858(23)	4174(13)	5907(21)	77(10)
C(21)	−2993(17)	4512(9)	5260(15)	31(6)
C(22)	−2483(21)	4301(11)	4686(18)	53(8)
C(23)	−3084(26)	4053(14)	3896(24)	86(11)
C(24)	−4111(23)	4036(12)	3696(20)	58(8)
C(25)	−4564(26)	4268(13)	4261(22)	77(10)
C(26)	−4067(21)	4506(11)	5021(20)	55(8)
C(27)	−4730(27)	3755(14)	2894(24)	95(12)
N(3)	1256(15)	5394(8)	9943(13)	41(6)
C(31)	2031(17)	5340(9)	9446(15)	33(6)
C(32)	1838(17)	5161(9)	8588(15)	32(6)
C(33)	2580(18)	5081(10)	8154(17)	43(7)
C(34)	3596(19)	5143(10)	8636(17)	42(7)
C(35)	3765(20)	5344(10)	9492(17)	46(7)
C(36)	3018(19)	5433(10)	9939(18)	44(7)
C(37)	4402(20)	5034(12)	8182(19)	63(8)
N(4)	1260(16)	2856(9)	1337(15)	47(6)
C(40)	2025(36)	2722(20)	2202(33)	134(18)
C(41)	2675(49)	2727(27)	2768(46)	215(32)
C(42)	3167(28)	2506(15)	3556(25)	91(12)
C(43)	3579(37)	2908(18)	4219(32)	156(21)
C(44)	474(34)	3073(19)	1646(31)	127(17)
C(45)	−320(47)	3233(28)	1178(42)	227(32)
C(46)	−1108(26)	3466(13)	1601(24)	81(11)
C(47)	−1632(47)	3083(22)	2047(41)	237(34)
C(48)	1036(41)	2569(21)	522(35)	159(21)
C(49)	424(35)	2178(17)	583(30)	127(17)
C(50)	−173(30)	1797(16)	−224(26)	104(14)
C(51)	652(32)	1684(18)	−586(30)	133(17)
C(52)	1841(44)	3229(23)	949(41)	194(26)
C(53)	2639(35)	3425(19)	796(32)	128(17)
C(54)	3103(33)	3737(18)	372(31)	124(16)
C(55)	3719(46)	3996(23)	175(41)	208(31)

In no instance was an extinction correction applied to the data. Idealized hydrogen atom positions were used throughout the analysis, with the C–H distances set at 0.96 Å. All non-hydrogen atoms were refined anisotropically.

Atomic positional parameters for **1** and **2** are presented in Tables 2 and 3, respectively.

TABLE 4. Selected bond lengths (Å) and angles (°) for **1**

W(1)–Cl(1)	2.336(8)	W(1)–Cl(2)	2.361(9)
W(1)–Cl(3)	2.344(9)	W(1)–Cl(4)	2.377(10)
W(1)–Cl(5)	2.495(9)	W(1)–N(1)	1.724(25)
N(1)–C(1)	1.375(36)	C(1)–C(2)	1.382(51)
C(1)–C(6)	1.387(44)	C(2)–C(3)	1.376(47)
C(3)–C(4)	1.486(49)	C(4)–C(5)	1.325(78)
C(4)–C(7)	1.625(65)	C(5)–C(6)	1.274(56)
N(2)–C(11)	1.514(30)	N(2)–C(15)	1.613(43)
N(2)–C(19)	1.478(40)	N(2)–C(23)	1.522(40)
C(11)–C(12)	1.347(37)	C(12)–C(13)	1.290(36)
C(13)–C(14)	1.610(64)	C(15)–C(16)	1.455(47)
C(16)–C(17)	1.688(67)	C(19)–C(20)	1.593(47)
C(20)–C(21)	1.247(90)	C(21)–C(22)	1.487(89)
C(23)–C(24)	1.568(52)	C(24)–C(25)	1.826(33)
C(25)–C(26)	1.608(43)		
Cl(1)–W(1)–Cl(2)	88.7(3)	Cl(1)–W(1)–Cl(3)	89.0(3)
Cl(2)–W(1)–Cl(3)	170.4(3)	Cl(1)–W(1)–Cl(4)	171.3(3)
Cl(2)–W(1)–Cl(4)	90.6(3)	Cl(3)–W(1)–Cl(4)	90.2(3)
Cl(1)–W(1)–Cl(5)	86.6(3)	Cl(2)–W(1)–Cl(5)	85.5(3)
Cl(3)–W(1)–Cl(5)	85.0(3)	Cl(4)–W(1)–Cl(5)	84.7(3)
Cl(1)–W(1)–N(1)	93.0(10)	Cl(2)–W(1)–N(1)	95.7(10)
Cl(3)–W(1)–N(1)	93.8(10)	Cl(4)–W(1)–N(1)	95.8(10)
Cl(5)–W(1)–N(1)	178.7(11)	W(1)–N(1)–C(1)	176.5(24)
N(1)–C(1)–C(2)	118.0(26)	N(1)–C(1)–C(6)	118.4(30)
C(2)–C(1)–C(6)	123.6(28)	C(1)–C(2)–C(3)	114.0(30)
C(2)–C(3)–C(4)	121.4(34)	C(3)–C(4)–C(5)	108.2(35)
C(3)–C(4)–C(7)	107.4(34)	C(5)–C(4)–C(7)	142.4(34)
C(4)–C(5)–C(6)	123.7(39)	C(1)–C(6)–C(5)	113.3(38)
C(11)–N(2)–C(15)	108.9(19)	C(11)–N(2)–C(19)	106.6(23)
C(15)–N(2)–C(19)	115.0(23)	C(11)–N(2)–C(23)	110.9(21)
C(15)–N(2)–C(23)	101.4(22)	C(19)–N(2)–C(23)	114.0(21)
N(2)–C(11)–C(12)	165.5(29)	C(11)–C(12)–C(13)	130.7(33)
C(12)–C(13)–C(14)	116.1(31)	N(2)–C(15)–C(16)	112.0(25)
C(15)–C(16)–C(17)	101.9(30)	N(2)–C(19)–C(20)	113.3(28)
C(19)–C(20)–C(21)	108.7(47)	C(20)–C(21)–C(22)	147.2(86)
N(2)–C(23)–C(24)	114.4(26)	C(23)–C(24)–C(25)	109.5(23)
C(24)–C(25)–C(26)	141.4(18)		

TABLE 5. Selected bond lengths (Å) and angles (°) for **2**

W(1)–O(1)	1.886(17)	W(1)–N(1)	1.750(24)
W(1)–Cl(1)	2.368(6)	W(1)–Cl(2)	2.411(7)
W(1)–Cl(3)	2.525(9)	W(1)–Cl(4)	2.355(7)
W(2)–O(1)	1.862(16)	W(2)–N(2)	1.712(19)
W(2)–Cl(5)	2.358(8)	W(2)–Cl(7)	2.557(6)
W(2)–Cl(6)	2.369(7)	W(2)–Cl(8)	2.368(7)
N(1)–C(11)	1.418(34)	N(2)–C(21)	1.370(28)
C(11)–C(12)	1.346(31)	C(11)–C(16)	1.412(33)
C(12)–C(13)	1.377(40)	C(13)–C(14)	1.371(39)
C(14)–C(15)	1.413(36)	C(14)–C(17)	1.547(46)
C(15)–C(16)	1.435(41)	C(21)–C(22)	1.376(41)
C(21)–C(26)	1.458(37)	C(22)–C(23)	1.446(42)
C(23)–C(24)	1.396(48)	C(24)–C(25)	1.339(51)
C(24)–C(27)	1.510(44)	C(25)–C(26)	1.351(42)
N(3)–C(31)	1.477(35)	C(31)–C(32)	1.355(33)
C(31)–C(36)	1.424(32)	C(32)–C(33)	1.381(39)
C(33)–C(34)	1.441(33)	C(34)–C(35)	1.376(37)
C(34)–C(37)	1.490(43)	C(35)–C(36)	1.402(42)
N(4)–C(40)	1.526(48)	N(4)–C(44)	1.423(57)
N(4)–C(48)	1.424(58)	N(4)–C(52)	1.502(70)
C(40)–C(41)	1.090(73)	C(41)–C(42)	1.369(74)
C(42)–C(43)	1.487(58)	C(44)–C(45)	1.241(74)
C(45)–C(46)	1.538(83)	C(46)–C(47)	1.520(76)
C(48)–C(49)	1.369(75)	C(49)–C(50)	1.654(58)
C(50)–C(51)	1.430(68)	C(52)–C(53)	1.308(84)
C(53)–C(54)	1.324(74)	C(54)–C(55)	1.201(83)
O(1)–W(1)–N(1)	96.2(9)	O(1)–W(1)–Cl(1)	94.6(5)
N(1)–W(1)–Cl(1)	92.7(6)	O(1)–W(1)–Cl(2)	171.3(6)
N(1)–W(1)–Cl(2)	92.2(7)	Cl(1)–W(1)–Cl(2)	87.4(2)
O(1)–W(1)–Cl(3)	86.9(6)	N(1)–W(1)–Cl(3)	175.1(6)
Cl(1)–W(1)–Cl(3)	83.3(2)	Cl(2)–W(1)–Cl(3)	84.9(3)
O(1)–W(1)–Cl(4)	89.2(5)	N(1)–W(1)–Cl(4)	96.5(6)
Cl(1)–W(1)–Cl(4)	169.7(3)	Cl(2)–W(1)–Cl(4)	87.5(2)
Cl(3)–W(1)–Cl(4)	87.4(2)	O(1)–W(2)–N(2)	95.5(8)
O(1)–W(2)–Cl(5)	93.0(6)	N(2)–W(2)–Cl(5)	96.6(8)
O(1)–W(2)–Cl(7)	82.7(5)	N(2)–W(2)–Cl(7)	178.1(6)
Cl(5)–W(2)–Cl(7)	84.2(2)	O(1)–W(2)–Cl(6)	168.9(5)
N(2)–W(2)–Cl(6)	95.0(6)	Cl(5)–W(2)–Cl(6)	89.0(3)
Cl(7)–W(2)–Cl(6)	86.6(2)	O(1)–W(2)–Cl(8)	89.2(6)
N(2)–W(2)–Cl(8)	93.7(8)	Cl(5)–W(2)–Cl(8)	169.2(2)
Cl(7)–W(2)–Cl(8)	85.6(2)	Cl(6)–W(2)–Cl(8)	86.9(3)
W(1)–O(1)–W(2)	167.0(11)	W(1)–N(1)–C(11)	163.7(16)
W(2)–N(2)–C(21)	173.2(20)	N(1)–C(11)–C(12)	120.0(21)

Results and discussion

The incorporation of metal–ligand groups into polyanion structures may be achieved by reaction of the appropriate halido complex $[RMCl_x]$ with a lacunary polyanion, such as $[H_3PW_{11}O_{39}]^{3-}$ which acts as a polydentate ligand for the RM unit in the resultant Keggin derived core, $[PW_{11}(MR)O_{39}]^{n}$. However, the reaction of $[H_3PW_{11}O_{39}]^{4-}$ with $[W(NR)Cl_4]_2$ failed to yield the desired product $[PW_{12}(NR)O_{39}]^{3-}$, giving rather a mixture of two products, the mononuclear $(TBA)[W(NC_7H_7)Cl_5]$ (**1**) and the binuclear $(TBA)(C_7H_7NH_3)[W_2O(NC_7H_7)_2Cl_8]$ (**2**). The major by-product of the reaction is the parent Keggin species $[PW_{12}O_{40}]^{3-}$. The IR spectrum of **1** exhibits a band at 1145 cm^{-1} tentatively assigned to $\nu(W{=}N)$. The spectrum of **2** exhibits an additional band at 755 cm^{-1} attributed to the bridging group W–O–W.

Both **1** and **2** react readily with excess H_2O to yield intractable products. However, careful addition of stoichiometric amounts of H_2O results in the isolation of $(TBA)_2[W_4O_4(NR)_4Cl_{10}]$ (**3**), a species whose structure has been reported by other investigators [12]. These reactions may be formally represented by the following equations:

$$4[W(NR)Cl_5]^{1-} + 4H_2O \longrightarrow [W_4O_4(NR)_4Cl_{10}]^{2-} + 8HCl + 2Cl^-$$

$$2[W_2O(NR)_2Cl_8]^{2-} + 2H_2O \longrightarrow [W_4O_4(NR)_4Cl_{10}]^{2-} + 4HCl + 2Cl^-$$

The structure of the anion of **1** is illustrated in Fig. 1, while selected bond lengths and angles are given in Table 4. The structure consists of discrete molecular

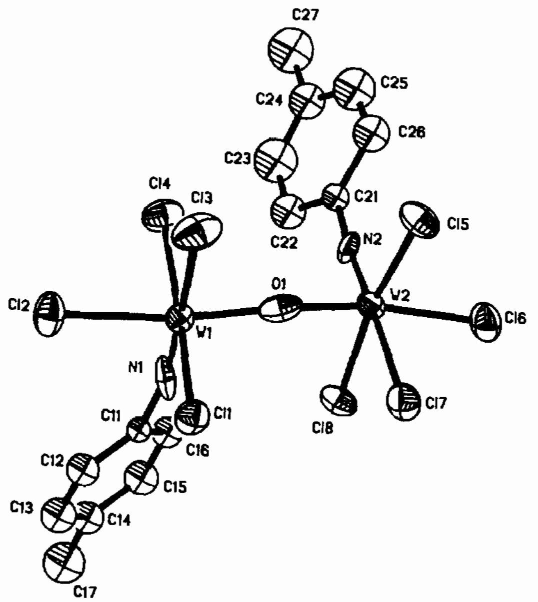

Fig. 2. ORTEP view of the structure of $[W_2O(NC_7H_7)_2Cl_8]^{2-}$.

anions $[W(NR)Cl_5]^{1-}$ with the W atom in a distorted octahedral environment as a consequence of the presence of the multiply bonded imido ligand. The short W–N distance of 1.73(3) Å and the 0.43 Å displacement of the W from the Cl1–Cl2–Cl3–Cl4 plane are consistent with the presence of significant multiple bonding. The anion structure is essentially identical to that previously reported for $[P(C_6H_5)_3(C_7H_7)][W(C_7H_7N)Cl_5]$ [13].

The structure of the anion of **2**, shown in Fig. 2, exhibits a binuclear oxo-bridged core. As illustrated by the data tabulated in Table 5, the W–Cl distances exhibit considerable variation, presumably as a consequence of the relative *trans* influences of the oxo and imido groups. Thus, while the average W–Cl distance for Cl ligands *trans* to other Cl donors is 2.362(9) Å, the average distance for those *trans* to the oxo group is 2.390(8) Å. The significant *trans* influence of the imido group is demonstrated by the W–Cl3 and W–Cl7 distances of 2.525(9) and 2.557(6) Å, respectively. The metrical parameters for **2** are similar to those previously reported for $[W_4O_4(NR)_4Cl_{10}]^{2-}$ (**3**), while the facile synthesis of **3** from **2** in the presence of trace amounts of water confirms that **2** serves as a chemical building block in the preparation of **3**.

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References

1 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988.
2 R. A. Sheldon and J. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
3 E. A. Maatta and Y. Du, *J. Am. Chem. Soc., 110* (1988) 8249.
4 R. W. Marshman and P. A. Shapely, *J. Am. Chem. Soc., 112* (1990) 8369.
5 J. Robbins, G. C. Bazan, J. S. Murdzek, M. B. O'Regan and R. R. Schrock, *Organometallics, 10* (1991) 2907.
6 J. D. Burrington, C. T. Kartisek and R. K. Grasselli, *J. Catal., 87* (1984) 363.
7 H. Kang and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, (1988) 1192.
8 J. Fletcher, G. Hogarth and D. A. Tocher, *J. Organomet. Chem., 403* (1991) 345.
9 R. K. C. Ho, *Ph.D. Thesis*, Columbia University, 1979.
10 B. R. Ashcroft, A. J. Nielson, D. C. Bradley, R. J. Errington, M. B. Hursthouse and R. L. Short, *J. Chem. Soc., Dalton Trans.*, (1987) 2059.
11 C. E. Fluger, J. Kallmerton and D. J. Plata, *Acta Crystallogr., Sect. C, 45* (1989) 1031.
12 W. Clegg, R. J. Errington, D. C. R. Hockless and C. Redshaw, *Polyhedron, 8* (1989) 1788.
13 W. Clegg, R. J. Errington and C. Redshaw, *Acta Crystallogr., Sect. C, 45* (1989) 164.