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Synthesis and crystallographic characterization of the 'sometimes'-chiral dirhenium polyoxotungstate salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]_2[W_6O_{19}]$

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Summary — Reaction of the chiral racemic carbonyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)][BF_4]$ and $[(n\text{-}C_4H_9)_4N]_2[W_6O_{19}]$ in DMF, followed by addition of CH_2Cl_2 and hexane, gives the title compound as yellow prisms (78%). A crystal structure (triclinic, $P\bar{1}$, $a/b/c$ = 9.545(2)/9.687(2)/16.226(1) Å, $\alpha/\beta/\gamma$ = 102.16(2)/105.88(2)/87.79(2)°, Z = 1) shows opposite enantiomers of the cations arrayed about a dianion-based inversion center — a *meso* assembly. The enantiomerically pure carbonyl complex gives crystals with the same unit cell, but $P1$ space group. This is possible due to the comparable sizes of the nitrosyl and carbonyl ligands. Metrical parameters are close to those of related compounds in the literature.

polyoxotungstate / chiral rhenium / crystal structure

Résumé — Synthèse et caractérisation cristallographique du 'parfois' sel chiral polyoxotungstate de dirhénium $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]_2[W_6O_{19}]$. La réaction du complexe carbonyle chiral $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)][BF_4]$ et de $[(n\text{-}C_4H_9)_4N]_2[W_6O_{19}]$ dans le DMF, suivie par l'addition de CH_2Cl_2 et d'hexane, conduit au composé $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]_2[W_6O_{19}]$ sous la forme de prismes jaunes (78%). La structure cristalline (triclinique, $P\bar{1}$, $a/b/c$ = 9.545(2)/9.687(2)/16.226(1) Å, $\alpha/\beta/\gamma$ = 102.16(2)/105.88(2)/87.79(2)°, Z = 1) montre que les deux énantiomères des cations sont alignés autour du polyanion qui présente un centre d'inversion — assemblement *méso*. Le complexe carbonyle énantiomériquement pur donne des cristaux de même maille mais de groupe d'espace $P1$. De semblables assemblements sont possibles du fait de la taille comparable des ligands carbonyle et nitrosyle. Les paramètres métriques sont proches de ceux de composés similaires de la littérature.

polyoxotungstate / rhénium chiral / structure cristalline

Introduction

We have had an active interest in the synthesis and detailed structural, spectroscopic, and chemical characterization of compounds in which elemental sp carbon chains span two transition metals [1]. To date, all of our studies have featured at least one chiral rhenium endgroup of the formula $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$ (**1**-Me_5), which carries seventeen valence electrons when neutral [2]. Interestingly, C_4 complexes with two **1**-Me_5 endgroups can be isolated in three oxidation states [2a]. The crystal structures of the neutral butadiynyl (Re-C≡C-C≡C-Re) and dication cumulenic (Re=C=C=C=C=Re^{2+}) complexes have been determined, and exhibit a number of unusual features.

For comparative purposes, we have sought to crystallographically characterize the intermediate radical cation. However, extensive efforts to obtain suitable single crystals of BF_4^-, PF_6^-, and SbF_6^- salts have been unsuccessful. Lapinte has reported a complementary series of diiron complexes, and has determined the crystal structure of the PF_6^- salt of the corresponding radical cation [3]. Encouraged by his success, we set out to evaluate anions with distinctly different geometric properties, in the hope that better packing motifs might be achieved.

Accordingly, our attention was drawn to polyoxotungstate anions $[W_xO_y]^{n-}$ [4]. These feature extensively delocalized negative charges, and most are poorly coordinating [5]. However, such species are commonly soluble only in very polar solvents. Thus, we chose to attempt mixed crystallizations with the dianion $[W_6O_{19}]^{2-}$ first. This octahedral species is often viewed as an oxide dianion (O^{2-}) encapsulated by a neutral W_6O_{18} framework, and the $[(n\text{-}C_4H_9)_4N^+]_2$ salt is readily available [6].

The carbonyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)][BF_4]$ (**1**-$H_5$$BF_4$) was selected for the cation. This compound can be prepared in three steps from $Re_2(CO)_{10}$, is easily obtained in enantiomerically pure form, and is the starting point for all chemistry of the chiral Lewis acid **1**-H_5 [7]. Furthermore, in contrast to some cationic adducts of **1**-H_5, $[\mathbf{1}\text{-}H_5][BF_4]$ is both soluble and stable in the polar solvent DMF.

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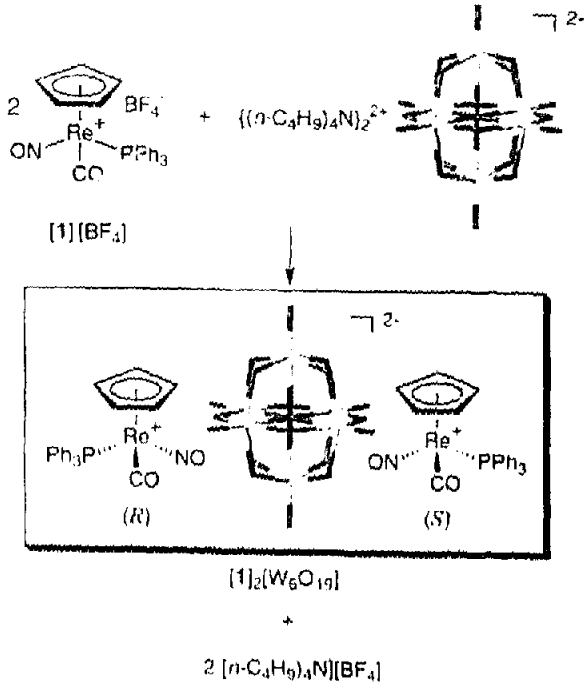
Results and discussion

As shown in scheme 1, racemic $[1][BF_4]$ and $[(n\text{-}C_4H_9)_4N]_2W_6O_{19}$ were combined in a 2:1 molar ratio in DMF. Then CH_2Cl_2 was added, and the solution was layered with hexanes. Yellow prisms formed, and were isolated in 78% yield. IR spectra showed carbonyl and nitrosyl bands characteristic of the cation **1**. These were doubled in KBr (2029/2002 and 1771/1743 cm^{-1}), but not in DMF (2019 and 1755 cm^{-1}). Bands diagnostic of the dianion $[W_6O_{19}]^{2-}$ were also present (1058, 980 cm^{-1}). The microanalysis was in agreement with the formula $[1]_2[W_6O_{19}]$. The compound was stable to >300 °C in the solid state, and survived extended periods in DMF at 130 °C (5 h) or 90 °C (48 h), as assayed by IR.



Scheme 1. Synthesis of $[1]_2[W_6O_{19}]$.

The crystal structure was determined as outlined in table I and described in the experimental section. Importantly, refinement distinguished the nitrosyl and carbonyl ligands. Bond lengths and angles are listed in table II. As shown in figure 1 (bottom), the unit cell consists of just one molecule. The cations are of opposite chirality and related by inversion centers, one of which is W_6O_{19}-based. Hence, $[1]_2[W_6O_{19}]$ crystallizes as a *meso* diastereomer. However, there is almost certainly an equilibrium with the opposite diastereomer, which is chiral, in solution.

When the structure is viewed on a stereoscopic screen, two tangential van der Waals contacts between each cation and the dianion are evident. As can be visualized from figure 1, neighboring dianions are bridged by two cations, the PPh_3 ligands of which are joined in a 'sextuple phenyl embrace' [8]. In this common packing motif, each phenyl ring on one phosphorus has a perpendicular counterpart on the other.

Not unexpectedly, the Re–NO and Re–CO bond lengths are similar (1.819(9) vs 1.864(12) Å). The former appears to be slightly shorter, in accord with the π acceptor strengths (NO > CO). At the same time, it constitutes the longest Re–NO bond found in any adduct of **1** to date [9]. This reflects the fact that most other one- or two-electron donor ligands are poorer π acceptors than carbon monoxide, allowing more rhenium–nitrosyl backbonding. Otherwise, the general geometric features about rhenium are similar to those described previously for related compounds [10].

The April 1997 release of the Cambridge crystallographic database contains nineteen other structures of salts of the dianion $[W_6O_{19}]^{2-}$ [11]. Only one features an 'organometallic' cation in a reasonably low oxidation state, $[W(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$ [11b]. None contains chiral monocations. All exhibit bond lengths and angles very close to those in $[1]_2[W_6O_{19}]$. For example, the average W–O(central) and W=O bond lengths in $[1]_2[W_6O_{19}]$ and $[W(CN\text{-}t\text{-}C_4H_9)_7][W_6O_{19}]$ are 2.326 vs 2.315 Å and 1.688 vs 1.694 Å, respectively.

We thought it would be interesting to repeat the preceding synthesis with enantiomerically pure (*S*)-$[1][BF_4]$ [5]. This compound is configurationally stable for periods of years. Thus, a *meso* product would no longer be possible. However, since the nitrosyl and carbonyl ligands are essentially isostructural, there would be a good chance that lattice packing would be unaffected. In other words, the *S* enantiomer of the cation should be able to replace the *R* enantiomer of the cation in the racemate. Indeed, single crystals of $[(S)\text{-}1]_2[W_6O_{19}]$ could be obtained. Unfortunately, they were of poorer quality. The unit cell was identical, requiring the space group $P1$ as opposed to $P\bar{1}$. However, refinement could not distinguish the nitrosyl and carbonyl ligands, although in principle their positions are known from the cation configuration.

In solution, $[1]_2[W_6O_{19}]$ and $[(S)\text{-}1]_2[W_6O_{19}]$ should give different equilibrium mixtures of ion pairs. Thus, ^1H and ^{31}P NMR spectra were recorded at identical concentrations in CD_3CN. However, no chemical shift differences could be detected. The IR spectrum of $[(S)\text{-}1]_2[W_6O_{19}]$ also showed doubled nitrosyl and carbonyl bands in KBr.

In summary, this study establishes that polyoxotungstates are suitable anions for the crystallographic characterization of cationic adducts of **1** and presumably **1**-Me$^+$. Apart from potential solubility issues, we believe that the dianion $W_6O_{19}^{2-}$ should be broadly useful for crystallizing low-oxidation-state organometallic cations. Extensions to radical cations derived from Re(C≡C)$_n$ Re assemblies, and other unusual species, are under active investigation.

Table I. Summary of crystallographic data for $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]_2[W_6O_{19}]$ ($[\mathbf{1}]_2[W_6O_{19}]$).

Molecular formula	$C_{78}H_{60}N_2O_{23}P_2Re_2W_6$
Molecular weight	2550.26
Crystal system	triclinic
Space group	$P\bar{1}$
Cell dimensions (16 °C)	
a, Å	9.545(2)
b, Å	9.687(2)
c, Å	16.226(4)
α, deg	102.46(2)
β, deg	105.88(2)
γ, deg	87.79(2)
V, Å^3	1408.8(5)
Z	1
d_{calc}, g/cm^3	3.006
d_{obs}, g/cm^3 (CH_2I_2/CH_3I)	3.01
Crystal dimensions, mm	0.31 × 0.25 × 0.40
Diffractometer	CAD4
Radiation, Å	Mo K_α (0.71073)
Data collection method	$\theta - 2\theta$
Scan speed, deg/min	Variable
Reflections measured	5284
Range/indices (*h,k,l*)	0 11, −11 11, −19 18
2θ limit, deg	4.0 – 50.0
Standard reflections check	1 X-ray hour
Total unique data	1956
Abs coefficient, cm^{-1}	166.08
Min transmission, %	25.90
Max transmission, %	99.90
No of variables	377
Goodness of fit	1.071
$R = \sum \|\|F_o\| - \|F_c\|\| / \sum \|F_o\|$	0.0355
$wR2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w F_o^2)^2])^{1/2}$	0.0943
$\Delta\sigma$ (max)	−0.01
$\Delta\rho$ (max), e/Å^3	2.410 (about 0.98 Å from W1)

Experimental section

General data

Instrumental protocols and solvent and reagent purifications were identical to those in earlier papers [2a]. DMF was used without purification.

- *$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]_2[W_6O_{19}]$ ($[\mathbf{1}]_2[W_6O_{19}]$)*

A flask was charged with a solution of $[(n\text{-}C_4H_9)_4N]_2[W_6O_{19}]$ (0.095 g, 0.050 mmol) [6] in DMF (1 mL). A solution of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)][BF_4]$ ($[\mathbf{1}][BF_4]$ [7], 0.066 g, 0.100 mmol) in DMF (1 mL) was added. Then CH_2Cl_2 (10 mL) was added, and after mixing the solution was layered with hexanes (10 mL). Yellow prisms formed, which after 14 h were collected by filtration, washed with CH_2Cl_2/hexane, and dried under oil pump vacuum to give $[\mathbf{1}]_2[W_6O_{19}]$ (0.099 g, 0.039 mmol, 78%), mp > 300 °C.

Anal. calc for $C_{78}H_{60}N_2O_{23}P_2Re_2W_6$: C, 22.61; H, 1.58. Found: C, 22.44; H, 1.59.

IR (cm^{-1}): KBr, ν_{CO} 2029/2002 s, ν_{NO} 1771/1743 s, ν_{WO} 980 s; DMF, ν_{CO} 2019 s, ν_{NO} 1755 s.

NMR (CD_3CN): ^{1}H (δ), 7.69–7.54, 7.43–7.33 (2m, 3Ph), 5.88 (d, J_{HP} = 0.6 Hz, C_5H_5); ^{31}P{^{1}H} (ppm), 12.4 (s).

- *$[(S)\text{-}\mathbf{1}]_2[W_6O_{19}]$*

A flask was charged with a solution of $[(n\text{-}C_4H_9)_4N]_2[W_6O_{19}]$ (0.095 g, 0.050 mmol) in DMF (1 mL). A solution of $[(S)\text{-}\mathbf{1}][BF_4]$ (0.066 g, 0.100 mmol) [7] in DMF (1 mL) was added. Then CH_2Cl_2 (10 mL) was added, and after mixing the solution was layered with hexanes (10 mL). Yellow prisms formed, which after 14 h were collected by filtration, washed with CH_2Cl_2/hexane, and dried under oil pump vacuum to give $[(S)\text{-}\mathbf{1}]_2[W_6O_{19}]$ (0.070 g, 0.0275 mmol, 55%), mp > 300 °C.

Anal. calc for $C_{78}H_{60}N_2O_{23}P_2Re_2W_6$: C, 22.61; H, 1.58. Found: C, 22.85; H, 1.61.

$[\alpha]_{546}^{24}$ = 100 ± 4 (*c* 0.89 mg/mL, DMF) [12].

IR (cm^{-1}): KBr, ν_{CO} 2020/2002 s, ν_{NO} 1771/1743 s, ν_{WO} 1098 m, ν_{WO} 980 s; DMF, ν_{CO} 2019 s, ν_{NO} 1755 s.

NMR (CD_3CN): ^{1}H (δ), 7.69–7.54, 7.43–7.33 (2m, 3Ph), 5.88 (d, J_{HP} = 0.6 Hz, C_5H_5); ^{31}P{^{1}H} (ppm), 12.4 (s).

Crystallography

Data were collected as outlined in table I. Cell constants were obtained from 25 reflections with 22.0° ≤ 2θ ≤ 28.0°. The space group was determined by subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structure

Table II. Bond lengths (Å) and angles (°) in $[Et_4N]_2[W_2O_{10}]$.

Re–N(1)	1.8196(9)	O(2)–W(1)^a	2.3246(7)	O(11)^a–W(1)–O(2)	76.3(2)
N(1)–C(21)	1.1660(11)	O(2)–W(3)^a	2.3331(6)	O(4)–W(1)–O(2)	76.2(2)
Re–C(41)	1.864(12)	O(6)–W(3)^a	1.928(8)	O(5)–W(1)–O(2)	75.7(2)
C(41)–O(41)	1.176(14)	O(10)–W(3)^a	1.926(7)	O(7)–W(2)–O(4)	103.0(4)
Re–C(5)	2.273(10)	O(11)–W(1)^a	1.913(8)	O(7)–W(2)–O(8)	102.7(3)
Re–C(1)	2.287(10)			O(4)–W(2)–O(8)	86.8(3)
Re–C(2)	2.301(11)	N(1)–Re–P	91.8(3)	O(7)–W(2)–O(1)	104.7(4)
Re–C(4)	2.302(11)	N(1)–Re–C(41)	95.5(5)	O(4)–W(2)–O(11)	152.3(3)
Re–C(3)	2.311(10)	C(41)–Re–P	90.5(3)	O(8)–W(2)–O(11)	86.4(3)
Re–P	2.391(2)	Re–N(1)–O(1)	178.8(8)	O(7)–W(2)–O(10)	104.1(3)
P–C(41)	1.815(10)	Re–C(41)–O(41)	177.9(10)	O(4)–W(2)–O(10)	87.1(3)
P–C(21)	1.818(10)	C(5)–C(1)–C(2)	108.1(10)	O(8)–W(2)–O(10)	153.2(3)
P–C(31)	1.822(10)	C(1)–C(2)–C(3)	108.3(10)	O(11)–W(2)–O(10)	86.9(3)
C(1)–C(5)	1.40(2)	C(2)–C(3)–C(4)	107.0(9)	O(7)–W(2)–O(2)	178.7(3)
C(1)–C(2)	1.41(2)	C(5)–C(4)–C(3)	108.5(10)	O(4)–W(2)–O(2)	76.1(2)
C(2)–C(3)	1.41(2)	C(1)–C(5)–C(4)	108.0(10)	O(8)–W(2)–O(2)	76.3(2)
C(3)–C(4)	1.42(2)	C(11)–P–Re	113.2(3)	O(11)–W(2)–O(2)	76.1(2)
C(4)–C(5)	1.41(2)	C(21)–P–Re	112.8(3)	O(10)–W(2)–O(2)	76.9(2)
C(11)–C(12)	1.385(14)	C(31)–P–Re	115.1(3)	O(9)–W(3)–O(5)	103.9(4)
C(11)–C(16)	1.39(2)	C(11)–P–C(21)	106.3(5)	O(9)–W(3)–O(10)^a	102.6(3)
C(12)–C(13)	1.39(2)	C(11)–P–C(31)	104.3(5)	O(5)–W(3)–O(10)^a	87.0(3)
C(13)–C(14)	1.35(2)	C(21)–P–C(31)	104.1(5)	O(9)–W(3)–O(6)^a	104.8(4)
C(14)–C(15)	1.40(2)	C(12)–C(11)–P	121.8(8)	O(5)–W(3)–O(6)^a	151.3(3)
C(15)–C(16)	1.36(2)	C(16)–C(11)–P	119.7(8)	O(10)^a–W(3)–O(6)^a	86.5(3)
C(21)–C(22)	1.38(2)	C(12)–C(11)–C(16)	118.5(9)	O(9)–W(3)–O(8)	105.0(3)
C(21)–C(26)	1.39(2)	C(11)–C(12)–C(13)	120.3(10)	O(5)–W(3)–O(8)	86.9(3)
C(22)–C(23)	1.38(2)	C(14)–C(13)–C(12)	120.0(12)	O(10)^a–W(3)–O(8)	152.4(3)
C(23)–C(24)	1.34(2)	C(13)–C(14)–C(15)	120.8(11)	O(6)^a–W(3)–O(8)	86.1(3)
C(24)–C(25)	1.38(2)	C(16)–C(15)–C(14)	118.8(11)	O(9)–W(3)–O(2)	179.0(3)
C(25)–C(26)	1.40(2)	C(15)–C(16)–C(11)	121.6(11)	O(5)–W(3)–O(2)	75.6(2)
C(31)–C(32)	1.37(2)	C(22)–C(21)–P	121.0(8)	O(10)^a–W(3)–O(2)	76.6(2)
C(31)–C(36)	1.408(11)	C(26)–C(21)–P	120.7(8)	O(6)^a–W(3)–O(2)	75.8(2)
C(32)–C(33)	1.38(2)	C(22)–C(21)–C(26)	118.2(10)	O(8)–W(3)–O(2)	75.9(2)
C(33)–C(34)	1.34(2)	C(21)–C(22)–C(23)	121.3(12)	W(2)^a–O(2)–W(2)	180.0
C(34)–C(35)	1.40(2)	C(24)–C(23)–C(22)	119.4(14)	W(2)^a–O(2)–W(1)	90.00(3)
C(35)–C(36)	1.35(2)	C(23)–C(24)–C(25)	122.3(12)	W(2)–O(2)–W(1)	90.00(3)
W(1)–O(3)	1.700(8)	C(24)–C(25)–C(26)	117.9(12)	W(2)^a–O(2)–W(1)^a	90.00(3)
W(1)–O(6)	1.907(7)	C(21)–C(26)–C(25)	120.8(12)	W(2)–O(2)–W(1)^a	90.00(3)
W(1)–O(11)^a	1.913(8)	C(32)–C(31)–P	121.6(8)	W(1)–O(2)–W(1)^a	179.999(2)
W(1)–O(4)	1.914(8)	C(36)–C(31)–P	120.5(8)	W(2)^a–O(2)–W(3)^a	90.24(2)
W(1)–O(5)	1.920(8)	C(32)–C(31)–C(36)	117.5(10)	W(2)–O(2)–W(3)^a	89.76(2)
W(1)–O(2)	2.3246(7)	C(31)–C(32)–C(33)	121.2(12)	W(1)–O(2)–W(3)^a	89.83(3)
W(2)–O(7)	1.678(7)	C(34)–C(33)–C(32)	121.3(14)	W(1)^a–O(2)–W(3)^a	90.17(2)
W(2)–O(4)	1.924(7)	C(33)–C(34)–C(35)	118.9(12)	W(2)^a–O(2)–W(3)	89.76(2)
W(2)–O(8)	1.925(8)	C(36)–C(35)–C(34)	120.5(13)	W(2)–O(2)–W(3)	90.24(2)
W(2)–O(11)	1.927(8)	C(35)–C(36)–C(31)	120.5(12)	W(1)–O(2)–W(3)	90.17(2)
W(2)–O(10)	1.928(7)	O(3)–W(1)–O(6)	103.6(4)	W(1)^a–O(2)–W(3)	89.83(3)
W(2)–O(2)	2.3192(6)	O(3)–W(1)–O(11)^a	103.5(4)	W(3)^a–O(2)–W(3)	180.0
W(3)–O(9)	1.687(7)	O(6)–W(1)–O(11)^a	87.4(3)	W(1)–O(4)–W(2)	117.7(4)
W(3)–O(5)	1.917(8)	O(3)–W(1)–O(4)	104.1(4)	W(3)–O(5)–W(1)	118.5(4)
W(3)–O(10)^a	1.926(7)	O(6)–W(1)–O(4)	87.2(3)	W(1)–O(6)–W(3)^a	118.1(4)
W(3)–O(6)^a	1.928(8)	O(11)^a–W(1)–O(4)	152.4(3)	W(2)–O(8)–W(3)	117.6(3)
W(3)–O(8)	1.929(8)	O(3)–W(1)–O(5)	104.3(4)	W(3)^a–O(10)–W(2)	116.8(3)
W(3)–O(2)	2.3332(6)	O(6)–W(1)–O(5)	152.1(3)	W(1)^a–O(11)–W(2)	117.6(3)
O(2)–W(2)^a	2.3192(6)	O(11)^a–W(1)–O(5)	86.1(3)		
		O(4)–W(1)–O(5)	86.1(3)		
		O(3)–W(1)–O(2)	179.7(4)		
		O(6)–W(1)–O(2)	76.4(2)		

[a] Symmetry transformations used to generate equivalent atoms: $-x-3, -y-3, -z+2$.

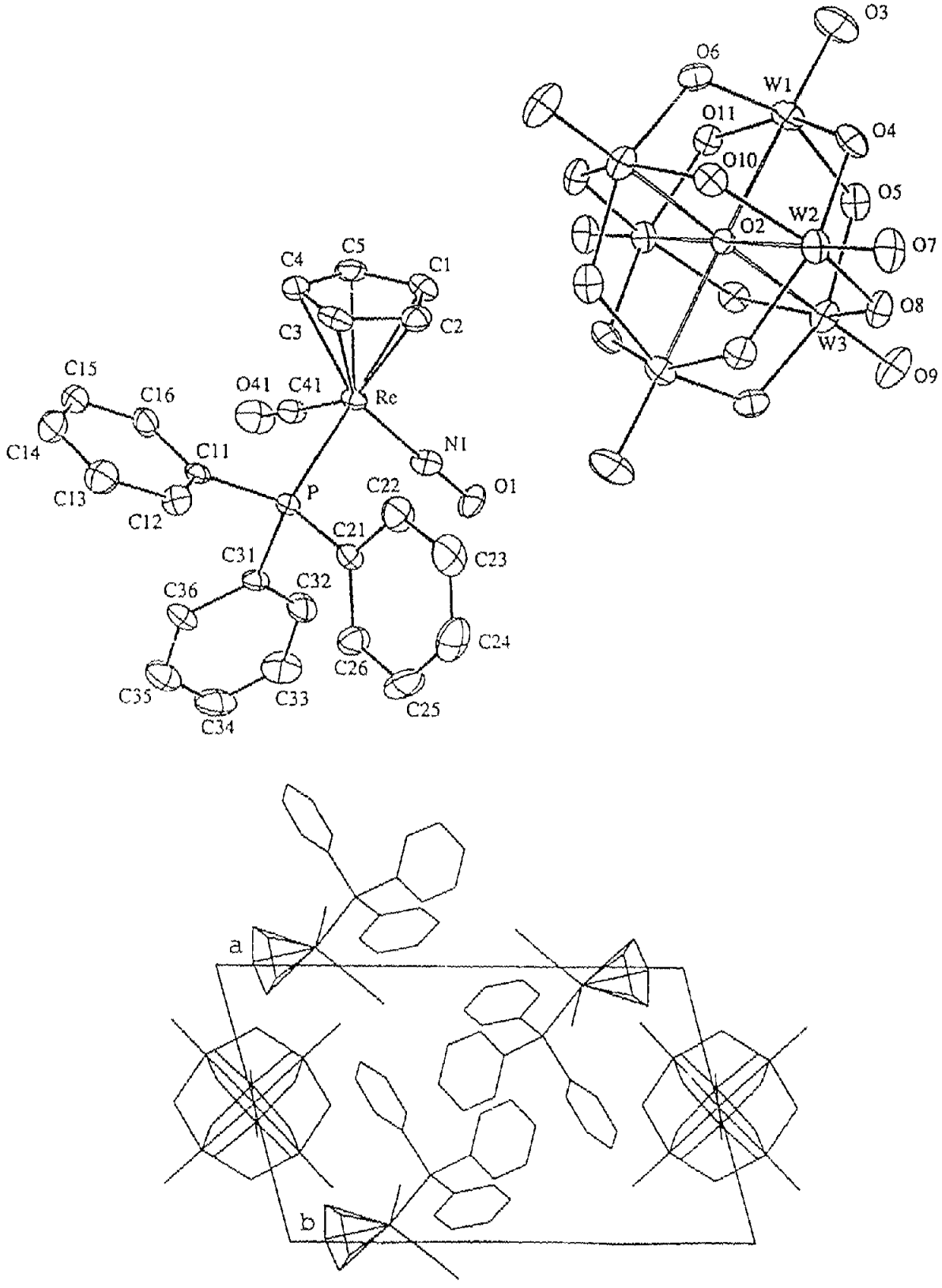


Fig. 1. Views of one cation and the dianion of $[1]_2[W_6O_{19}]$ (top), and the unit cell (bottom).

Table III. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[1_2W_6O_{19}]$.

	x	y	z	$U_{(eq)}$[a]
Re	9355(1)	8052(1)	7772(1)	29(1)
W(1)	13313(1)	11970(1)	8656(1)	36(1)
W(2)	14319(1)	12698(1)	9934(1)	33(1)
W(3)	13240(1)	15859(1)	10724(1)	35(1)
P	7529(3)	8816(3)	6636(2)	27(1)
O(1)	11350(9)	7277(10)	6626(6)	56(2)
O(2)	15000	15000	10000	29(2)
O(3)	12081(10)	14956(11)	7673(6)	64(3)
O(4)	13081(8)	13139(8)	8874(5)	40(2)
O(5)	12218(8)	15658(8)	9504(5)	39(2)
O(6)	15040(9)	14292(8)	8345(5)	40(2)
O(7)	13786(8)	11043(8)	9881(6)	45(2)
O(8)	13053(8)	13832(8)	10537(5)	42(2)
O(9)	11964(10)	16505(8)	11238(6)	54(2)
O(10)	15860(7)	12118(6)	9359(4)	32(2)
O(11)	15822(8)	13175(8)	11025(5)	38(2)
O(41)	7876(12)	5157(10)	7314(6)	69(3)
N(1)	10560(10)	7572(9)	7065(5)	36(2)
C(1)	11042(12)	8760(12)	9108(7)	43(3)
C(2)	10484(12)	9985(12)	8807(7)	41(2)
C(3)	8980(12)	10045(11)	8758(6)	37(2)
C(4)	8622(12)	8830(12)	9019(7)	40(3)
C(5)	9890(13)	8036(13)	9224(7)	45(3)
C(11)	5932(10)	9502(11)	6976(6)	29(2)
C(12)	5301(12)	10748(11)	6785(7)	38(2)
C(13)	4039(14)	11211(15)	7023(8)	52(3)
C(14)	3411(13)	10460(15)	7458(8)	51(3)
C(15)	4072(12)	9206(14)	7669(7)	46(3)
C(16)	5311(11)	8766(13)	7438(7)	42(3)
C(11)	8132(13)	6282(12)	7177(7)	41(3)
C(21)	8188(10)	10202(11)	6230(6)	31(2)
C(22)	9019(14)	11327(14)	6709(9)	53(3)
C(23)	9532(15)	12381(14)	6494(10)	61(4)
C(24)	9272(16)	12274(16)	5627(11)	69(4)
C(25)	8434(17)	11185(17)	5020(9)	65(4)
C(26)	7905(14)	10131(14)	5334(8)	48(3)
C(31)	6805(11)	7450(11)	5655(6)	32(2)
C(32)	7701(14)	6546(14)	5275(8)	53(3)
C(33)	7469(19)	5644(16)	4473(9)	69(4)
C(34)	5753(19)	5589(16)	4018(8)	66(4)
C(35)	4796(15)	6460(15)	4437(8)	58(3)
C(36)	5311(12)	7387(12)	5211(7)	42(3)

[a] $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

was solved by standard heavy-atom techniques with the MOLEN/VAX package [13] and refined with SHELXL-93 [14]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The nitrosyl and carbonyl ligands were assigned according to the configuration that refined better. Hydrogen atom positions were calculated, added to the structure factor calculations, and refined (riding model). Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature [15]. All data have been deposited in the Cambridge Crystallographic Data Base.

Supplementary crystallographic data have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication No SUP 90474 and are available upon request from the Document Supply Centre.

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