sentially the same, while the Re–Re distance in the Re_2Cl_4-$(dppp)_2$ molecule (with a cis arrangement) is notably longer.

Interestingly, the magnitudes of the lengthening of the W–W and Re–Re bonds are the same, i.e., 0.022 [3] Å. [It is noteworthy that the W_2^{4+} dimers possess $\sigma^2\pi^4\delta^2$ electronic configurations and quadruple M–M bonds, while the Re_2^{4+} dimers possess $\sigma^2\pi^4\delta^2\delta^{*2}$ configurations and triple bonds. This would seem to indicate that the lengthening of M–M distances on going from trans to cis $MX_2(Phos)_2$ geometry is *not* due to a weakening of the δ bond. Most likely, the origin is a destabilization of metal–metal π-bonding orbitals. It would be worthwhile to determine whether or not this phenomenon also exists in quadruply bonded molybdenum dimers.

Registry No. $Re_2Cl_4(dppp)_2$, 86436-61-5; Re, 7440-15-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, all bond distances and angles, least-squares planes for all phenyl rings, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Structural Characterization of the Nonachloroditungsten(II,III) Ion

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The reduction of WCl_4 by Na/Hg in THF, in the presence of $(Ph_3PNPPh_3)Cl$, produces a 40–50% yield of $(Ph_3PNPPh_3)_2[W_2Cl_9]$, which can be recrystallized from CH_2Cl_2/Et_2O to give dark violet crystals. The structure was solved and refined in the space group $I2/a$ with the following unit cell dimensions: $a = 21.258$ (10) Å; $b = 12.962$ (5) Å; $c = 25.684$ (12) Å; $\beta = 101.04$ (4)°; $V = 6946$ (6) $Å^3$; $Z = 4$. The $[W_2Cl_9]^{2-}$ anions are disordered about the twofold axis. The structure was refined to $R_1 = 0.0438$ and $R_w = 0.0566$ with a quality-of-fit indicator of 1.103. The $[W_2Cl_9]^{2-}$ ion has the following principal dimensions: W–W = 2.540 (1) Å; W–Cl_t(av) = 2.358 [6] Å; W–Cl_b(av) = 2.453 [5] Å, W–Cl–W(av) = 62.4 [2]°. The increase in the W–W distance of 0.122 (9) Å compared to that in the $[W_2Cl_9]^{3-}$ ion is attributed mainly to the increased mean oxidation state of the metal atoms whereby the metal d orbitals are contracted, thus weakening the W–W σ bond. Support for this view is provided by the $[Re_2Cl_9]^-$ ion, which is isoelectronic with the $[W_2Cl_9]^{3-}$ ion but has a metal–metal distance about 0.29 Å greater than that in $[W_2Cl_9]^{3-}$.

Introduction

While we were searching for a preparative route to isolable salts of the $[W_2Cl_8]^{4-}$ ion (a goal that has subsequently been attained[2]), reduction of WCl_4 by sodium amalgam was carried out under a variety of conditions. With tetrahydrofuran as solvent at room temperature and with the very large cation $[Ph_3PNPPh_3]^+$ (PNP^+) present, a violet solid was formed. Upon recrystallization, this gave crystals suitable for X-ray study, and such a study was undertaken in hope of showing the presence of the $[W_2Cl_8]^{4-}$ ion. However, the initial phases of the X-ray work gave results at variance with this, and an elemental analysis was obtained that also disagreed with the postulated formula, $(PNP)_4[W_2Cl_8]$. Further work has shown that the compound obtained, in 40–50% yield, is the PNP salt of the $[W_2Cl_9]^{2-}$ ion, a species that had previously been made and characterized (except structurally) by Saillant and Wentworth.[3] In this paper we report and discuss the structure of this ion in the compound $(PNP)_2[W_2Cl_9]$.

Experimental Procedures

Preparation. A mixture of WCl_4 (3.26 g, 10 mmol), Na/Hg (100 g, 0.46%), and $(Ph_3PNPPh_3)Cl$ (11.5 g, 20 mmol) in THF (40 mL) was shaken at room temperature for 0.75 h. A dark red to purple product precipitated along with sodium chloride. The reaction mixture was poured over a column of Celite, leaving most of the mercury behind. The column, with reaction solids on top, was then washed through with several portions of CH_2Cl_2 to extract all of the colored material, and the extracts were filtered. The combined liquid was taken to dryness under vacuum and the solid residue recrystallized from a 1:1 mixture of CH_2Cl_2/Et_2O. The yield was 3.76 g (43% on

(1) (a) Texas A&M University. (b) Massachusetts Institute of Technology.
(2) Cotton, F. A.; Mott, G. N.; Schrock, R. R.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 6781.
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Table I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $(PNP)_2[W_2Cl_9]$

formula	$W_2Cl_9P_4C_{72}H_{60}N_2$
formula weight	1764.0
space group	$I2/a$
a, Å	21.258 (10)
b, Å	12.962 (5)
c, Å	25.684 (12)
β, deg	101.04 (4)
V, $Å^3$	6946 (6)
Z	4
d_{calcd}, g/cm³	1.686
cryst size, mm	0.50 × 0.30 × 0.25
μ(Mo Kα), cm^{-1}	39.8
data collection instrument	Syntex $P\bar{1}$
radiation	Mo Kα ($\lambda_{\bar{\alpha}} = 0.71073$ Å); graphite monochromated
scan method	ω-scan
data collection range	$4 \leqslant 2\theta \leqslant 50°$; $+h,+k,\pm l$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	3312
no. of parameters refined	441
R^a	0.0438
R_w^b	0.0566
quality-of-fit indicator^c	1.103
largest shift/esd, final cycle	0.25

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. ^{c} Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

WCl_4) of dark crystals, appearing red or blue depending on size and orientation. We believe that the presence of the PNP^+ ion is critical to obtaining a product containing the $W_2Cl_9^{2-}$ ion, since the preparation conditions are otherwise similar to those reported for preparing $Na_4(TMEDA)_4W_2Cl_8$.[2]

Anal. Calcd for $C_{72}H_{60}P_4N_2Cl_9W_2$: C, 49.03; H, 3.43; Cl, 18.09. Found: C, 50.7; H, 3.65; Cl, 20.5.

Table II. Positional and Isotropic-Equivalent Thermal Parameters and Their Estimated Standard Deviations for $(PNP)_2[W_2Cl_9]$

atom	x	y	z	$B, \text{Å}^2$
W(1)	0.28358 (3)	0.13858 (5)	0.02821 (3)	3.06 (1)
W(2)	0.18471 (3)	0.20961 (5)	−0.03269 (3)	2.86 (1)
Cl(1)	0.1823 (2)	0.1633 (4)	0.0587 (2)	5.2 (1)
Cl(2)	0.2422 (2)	0.0575 (4)	−0.0577 (2)	4.5 (1)
Cl(3)	0.2860 (2)	0.3074 (3)	−0.0143 (2)	4.5 (1)
Cl(4)	0.2813 (3)	−0.0270 (4)	0.0647 (2)	5.1 (1)
Cl(5)	0.3293 (2)	0.2167 (4)	0.1104 (2)	5.1 (1)^a
Cl(6)	0.3867 (2)	0.1139 (4)	0.0072 (2)	5.2 (1)
Cl(7)	0.1736 (2)	0.2570 (4)	−0.1224 (2)	5.0 (1)^a
Cl(8)	0.1338 (2)	0.3627 (4)	−0.0140 (2)	5.6 (1)
Cl(9)	0.0903 (2)	0.1125 (4)	−0.0529 (2)	4.9 (1)
P(1)	0.6162 (1)	0.3268 (2)	−0.20876 (9)	3.26 (4)
P(2)	0.5128 (1)	0.3541 (2)	−0.14358 (9)	3.58 (5)
N(1)	0.5535 (3)	0.3559 (5)	−0.1882 (3)	4.2 (2)
C(1)	0.6125 (4)	0.3895 (6)	−0.2714 (3)	3.0 (2)
C(2)	0.6691 (4)	0.4089 (6)	−0.2905 (3)	3.9 (2)
C(3)	0.6648 (5)	0.4535 (7)	−0.3412 (4)	4.7 (2)
C(4)	0.6057 (5)	0.4803 (7)	−0.3709 (4)	5.3 (3)
C(5)	0.5488 (5)	0.4642 (8)	−0.3519 (4)	5.2 (2)
C(6)	0.5528 (4)	0.4188 (6)	−0.3010 (4)	4.1 (2)
C(7)	0.6880 (4)	0.3670 (7)	−0.1650 (3)	3.6 (2)
C(8)	0.6902 (4)	0.4695 (7)	−0.1456 (4)	4.6 (2)
C(9)	0.7439 (5)	0.5037 (8)	−0.1089 (5)	5.7 (3)
C(10)	0.7945 (5)	0.4363 (9)	−0.0920 (4)	6.5 (3)
C(11)	0.7913 (5)	0.3345 (9)	−0.1131 (4)	6.5 (3)
C(12)	0.7388 (4)	0.3009 (7)	−0.1487 (3)	4.6 (2)
C(13)	0.6247 (4)	0.1892 (6)	−0.2190 (4)	3.7 (2)
C(14)	0.6437 (5)	0.1533 (6)	−0.2640 (4)	4.5 (2)
C(15)	0.6526 (5)	0.0462 (8)	−0.2689 (4)	5.6 (3)
C(16)	0.6443 (5)	−0.0201 (7)	−0.2290 (4)	5.0 (2)
C(17)	0.6245 (5)	0.0166 (7)	−0.1837 (4)	5.1 (2)
C(18)	0.6143 (5)	0.1230 (7)	−0.1789 (4)	5.3 (2)
C(19)	0.4376 (4)	0.2936 (6)	−0.1699 (4)	3.9 (2)
C(20)	0.3847 (5)	0.3073 (8)	−0.1462 (5)	6.4 (3)
C(21)	0.3255 (5)	0.2587 (9)	−0.1712 (6)	8.2 (4)
C(22)	0.3230 (6)	0.1968 (8)	−0.2145 (7)	9.7 (4)
C(23)	0.3755 (6)	0.1850 (8)	−0.2372 (5)	7.3 (3)
C(24)	0.4329 (5)	0.2349 (8)	−0.2158 (4)	5.7 (3)
C(25)	0.5495 (4)	0.2843 (7)	−0.0845 (3)	3.9 (2)
C(26)	0.5180 (5)	0.2003 (7)	−0.0653 (4)	5.5 (3)
C(27)	0.5506 (6)	0.1414 (8)	−0.0232 (5)	6.9 (3)
C(28)	0.6147 (6)	0.1658 (9)	−0.0012 (5)	7.1 (3)
C(29)	0.6452 (5)	0.249 (1)	−0.0190 (4)	7.8 (3)
C(30)	0.6106 (5)	0.314 (1)	−0.0612 (4)	6.4 (3)
C(31)	0.4997 (4)	0.4852 (6)	−0.1239 (4)	4.4 (2)
C(32)	0.5093 (4)	0.5649 (7)	−0.1570 (4)	5.0 (2)
C(33)	0.5033 (5)	0.6664 (8)	−0.1401 (5)	6.4 (3)
C(34)	0.4840 (7)	0.6879 (9)	−0.0942 (6)	8.4 (4)
C(35)	0.4700 (7)	0.6054 (9)	−0.0620 (5)	9.1 (4)
C(36)	0.4781 (6)	0.5010 (9)	−0.0762 (5)	7.6 (3)

^{a} Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The infrared spectrum (mineral oil mull) showed all the bands characteristic of the $Ph_6P_2N^+$ ion.

The ^{31}P NMR spectrum in CH_2Cl_2 had a singlet at 21.4 ppm. The electronic absorption spectrum (in CH_2Cl_2) had the following absorption bands (nm with molar ϵ in parentheses): 740 (875); 580 (1330); 390 sh.

X-ray Structure Determination. A general description of the methods used in the crystal structure analysis has been given previously.[4] A detailed description of the diffractometer data collection,[4] data processing and corrections,[5,6] and least-squares refinement is available as supplementary material. Table I presents a summary

(4) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(5) Calculations were processed by the PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, with software from the SDP-PLUS package.

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Table III. Important Bond Distances (Å) and Their Estimated Standard Deviations for $(PNP)_2[W_2Cl_9]^a$

W(1)–W(2)	2.540 (1)	W(2)–Cl(1)	2.434 (5)
–Cl(1)	2.449 (5)	–Cl(2)	2.468 (4)
–Cl(2)	2.450 (5)	–Cl(3)	2.465 (4)
–Cl(3)	2.451 (4)	–Cl(7)	2.352 (6)
–Cl(4)	2.346 (5)	–Cl(8)	2.354 (5)
–Cl(5)	2.375 (6)	–Cl(9)	2.341 (5)
–Cl(6)	2.378 (5)		
W–Cl$_t$(av)^b	2.358 [6]		
W–Cl$_b$(av)^b	2.453 [5]		

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits. ^{b} The estimated deviation in square brackets is given as

$$[\sum_n \Delta_i^2/n(n-1)]^{1/2}$$

in which Δ_i is the deviation of the ith of n values from the arithmetic mean of the set.

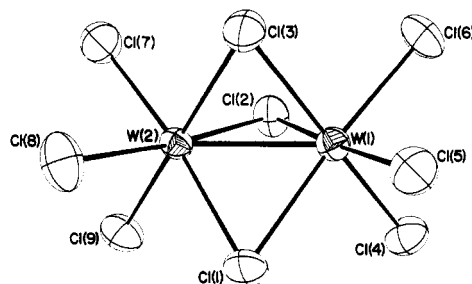**Table IV.** Important Bond Angles (deg) and Their Estimated Standard Deviations for $(PNP)_2[W_2Cl_9]^a$

W(2)–W(1)–Cl(1)	58.4 (1)	Cl(1)–W(2)–Cl(2)	99.0 (2)
–Cl(2)	59.3 (1)	–Cl(3)	97.0 (2)
–Cl(3)	59.2 (1)	–Cl(7)	173.1 (2)
–Cl(4)	120.0 (1)	–Cl(8)	85.1 (2)
–Cl(5)	122.8 (2)	–Cl(9)	84.6 (2)
–Cl(6)	126.8 (2)	Cl(2)–W(2)–Cl(3)	90.2 (2)
Cl(1)–W(1)–Cl(2)	99.1 (2)	–Cl(7)	85.2 (2)
–Cl(3)	96.9 (2)	–Cl(8)	175.2 (2)
–Cl(4)	84.6 (2)	–Cl(9)	87.6 (2)
–Cl(5)	84.0 (2)	Cl(3)–W(2)–Cl(7)	88.5 (2)
–Cl(6)	174.5 (2)	–Cl(8)	86.9 (2)
Cl(2)–W(1)–Cl(3)	90.9 (2)	–Cl(9)	177.5 (2)
–Cl(4)	86.3 (2)	Cl(7)–W(2)–Cl(8)	90.9 (2)
–Cl(5)	176.9 (2)	–Cl(9)	90.1 (2)
–Cl(6)	85.8 (2)	Cl(8)–W(2)–Cl(9)	95.2 (2)
Cl(3)–W(1)–Cl(4)	177.0 (2)	W(1)–Cl(1)–W(2)	62.7 (1)
–Cl(5)	88.6 (2)	–Cl(2)–W(2)	62.2 (1)
–Cl(6)	85.4 (2)	–Cl(3)–W(2)	62.2 (1)
Cl(4)–W(1)–Cl(5)	94.1 (2)		
–Cl(6)	93.3 (2)	W–W–Cl$_b$(av)^b	58.8 [1]
Cl(5)–W(1)–Cl(6)	91.2 (2)	W–W–Cl$_t$(av)^b	124 [1]
W(1)–W(2)–Cl(1)	58.9 (1)	W–Cl–W(av)^b	62.4 [2]
–Cl(2)	58.6 (1)		
–Cl(3)	58.6 (1)		
–Cl(7)	127.9 (1)		
–Cl(8)	122.6 (1)		
–Cl(9)	120.9 (1)		

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits. ^{b} The estimated deviation in square brackets is given as

$$[\sum_n \Delta_i^2/n(n-1)]^{1/2}$$

in which Δ_i is the deviation of the ith of n values from the arithmetic mean of the set.

Figure 1. Structure and atom-labeling scheme for the $W_2Cl_9^{2-}$ anion found in $(PNP)_2[W_2Cl_9]$. Atoms are represented by their 40% probability ellipsoids.

of crystal data and basic information about the data collection and structure refinement. Table II gives the atomic coordinates for all

atoms, and Tables III and IV list the important bond distances and angles, respectively, with their estimated standard deviations. The structure of the $W_2Cl_9^{2-}$ unit, along with the atom-labeling scheme, is shown in Figure 1. Full tables of bond distances and angles, anisotropic thermal parameters, and observed and calculated structure factors are available as supplementary material.

Discussion

The structure of the $[W_2Cl_9]^{2-}$ ion is of considerable interest because it can be compared with that of the $[W_2Cl_9]^{3-}$ ion to see the effect of removing one electron. The structure of the $[W_2Br_9]^{2-}$ ion, in which the W-W distance is 2.601 (2) Å, was reported several years ago.[7] However, it is well-known that in $[M_2X_9]^{n-}$ ions a change of the halogen from Cl to Br will cause an appreciable, though not regular or predictable, increase in the M-M bond length. Thus, no unambiguous comparison of $[W_2Cl_9]^{3-}$ and $[W_2Br_9]^{2-}$ was possible. The comparison of the two 2- ions that is now possible shows that the W-W distance increases by 0.061 (3) Å on replacing Cl by Br. This is typical and may presumably be attributed to the fact that a greater W-W distance is necessary in order that the W-(μ-X)-W angle not be too small when X is Br. In fact the average bridge angles are 62.4 [2]° and 60.0° for Cl and Br, respectively.

The structure of the $[W_2Cl_9]^{3-}$ ion was first determined by Brosset[8] in 1935 using powder data for $K_3W_2Cl_9$, but interatomic distances were relatively inaccurate. In 1958, Watson and Waser[9] used single-crystal data to improve the accuracy, obtaining the W-W distance as 2.409 (7) Å, where the esd is our estimate. We have taken the reported data of Watson and Waser and refined the structure anisotropically by full-matrix least squares. Full details along with data for related compounds will be published elsewhere. We obtain the following bond lengths: W-W = 2.418 (8) Å; W-Cl$_t$ = 2.41 (2) Å; W-Cl$_b$ = 2.47 (3) Å. We shall use these results in subsequent discussions.

Clearly, the loss of one electron in going from $[W_2Cl_9]^{3-}$ to $[W_2Cl_9]^{2-}$ has resulted in a substantial lengthening, by 0.122 (9) Å, of the W-W bond. It is not easy to rationalize this sizable increase solely in terms of a decrease in bond order. According to SCF-Xα-SW calculations[10,11] on $[Mo_2Cl_9]^{3-}$ and $[Ru_2Cl_9]^{3-}$, the HOMO of $[W_2Cl_9]^{3-}$ should be a weakly bonding (perhaps nonbonding) MO; loss of half the little bonding that it provides might have been expected to produce little or no effect on the W-W bond strength and hence on the W-W distance.

We believe that an important cause of the 0.122-Å increase in W-W distance on going from $[W_2Cl_9]^{3-}$ to $[W_2Cl_9]^{2-}$ is to be found by considering the increase in effective charge of the metal atoms. The principle is much the same as that invoked[12] to explain some surprising M-M bond distance variations in

the case of ditechnetium[13] and dirhenium[14] species of the $[M_2Cl_8]^{n-}$ and $[M_2Cl_4(PR_3)_4]^{np}$ types. The increase in average formal oxidation number of the metal atoms causes a contraction of the 5d orbitals, and this results in a weakening of the σ bond between the metal atoms. This weakening of the σ bond is then responsible for much of the increase in the W-W distance. An alternative view, which may be more appealing to some, is that the increase in formal oxidation number causes an increase in the repulsive force between two partly cationic metal atoms, thus increasing the distance between them.

The above argument receives strong support from the fact that in the $[Re_2Cl_9]^-$ ion,[15] which is isoelectronic with the $[W_2Cl_9]^{3-}$ ion and where the atomic radii of the two metallic elements in the same oxidation state are scarcely different, the Re-Re distance, 2.703 (5) Å, is about 0.29 Å longer than the W-W distance. Here we see the effect of an increase in the formal oxidation number of the metal atoms uncomplicated by any bond-order change. The change in this case is about twice as great as in the $[W_2Cl_9]^{3-}$ to $[W_2Cl_9]^{2-}$ comparison. It should, of course, be greater since in going from $[W_2Cl_9]^{3-}$ to $[Re_2Cl_9]^-$ there is a total increase of two units of positive charge rather than one.

In their discussion of the structure of $[N(C_3H_7)_4]_2[W_2Br_9]$, Templeton, Jacobson, and McCarley[7] proposed that certain very small angular deviations from ideal D_{3h} symmetry in the anion could be attributed to a static Jahn-Teller effect. They noted that no such deviations are found in the reported structures of the $[Mo_2X_9]^{3-}$, $[Cr_2X_9]^{3-}$, or $[W_2Cl_9]^{3-}$ ions, but this aspect of their argument is nihil ad rem since all of the latter were located on positions of crystallographic D_{3h} symmetry. Moreover, since SCF-Xα-SW calculations on $[Mo_2Cl_9]^{3-}$ and $[Ru_2Cl_9]^{3-}$ (not available at the time) show that the e' "bonding" orbitals have very little if any bonding effect, it is not clear that any observable static Jahn-Teller effect is really to be expected in the $[W_2X_9]^{2-}$ ions. It is, in any case entirely inconclusive when very small distortions are observed in an entity residing on a crystallographic site lacking any symmetry. There are a number of small deviations from ideal D_{3h} symmetry in the $[W_2Cl_9]^{2-}$ ion found in (PNP)$_2$-$[W_2Cl_9]$, but we do not suggest that they can logically be attributed to autogenous internal electronic effects (i.e., Jahn-Teller distortions).

Registry No. (PNP)$_2$[W_2Cl_9], 86437-04-9; WCl$_4$, 13470-13-8.

Supplementary Material Available: A detailed description of the X-ray procedures with a figure showing ORTEP drawings of the two possible orientations and complete tables of bond lengths, bond angles, anisotropic thermal parameters, and structure factor data (27 pages). Ordering information is given on any current masthead page.

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