

Synthesis and reactivity of a very strong reducing agent containing a quadruple bond: structures of $W_2(hpp)_4$ and $W_2(hpp)_4Cl_2 \cdot 4CH_2Cl_2$

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Abstract

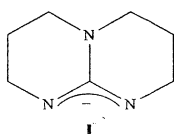
The preparation and structural characterization of the very strong reducing agent $W_2(hpp)_4$, hpp = the anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine, **1**, has been accomplished. It has a short distance of 2.1617(4) Å for the quadruply-bonded W_2^{4+} unit. Compound **1** is very reactive and gives the triple bonded $W_2(hpp)_4Cl_2 \cdot 4CH_2Cl_2$, **2** upon crystallization after mere contact with the haloalkane CH_2Cl_2 . The change in electronic configuration from the $\sigma^2\pi^4\delta^2$ in **1** to the $\sigma^2\pi^4$ system in **2** increases the W–W distance by ca. 0.09 to 2.2497(8) Å. $W_2(hpp)_4$ also reduces C_{60} and 7,7',8,8'-tetracyanoquinodimethide, TCNQ. The latter is reduced to the $TCNQ^{2-}$ anion while the W_2^{4+} unit is oxidized to the W_2^{6+} state.

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1. Introduction

In the long history of paddlewheel compounds containing metal-to-metal bonds, few ligand types have had an impact so crucial as to deserve consideration as a special group. Undoubtedly halides, carboxylates and amidinates, e.g., formamidinates, rank high in importance [1]. More recently, guanidinates, especially those derived from the anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (hpp), **1**,



have been shown to possess an extraordinary ability to stabilize higher oxidation numbers in the dimetal units

and therefore, to shift oxidation potentials to less positive values by very large amounts [2]. For example, for $Mo_2(formamidinate)_4$ compounds, as the donor ability of the substituents increases, the oxidation potentials for the $Mo_2^{4+/5+}$ couple vary over the wide range of +795 to +244 mV [3]. However, they are all positive, whereas the corresponding couple for $Mo_2(hpp)_4$ appears at –1.271 V. More remarkably, the couple $Mo_2^{6+/5+}$, which appears at –444 mV, has never been observed for the corresponding formamidinates and carboxylates [2].

Very recently, the hpp ligand has allowed us to isolate and crystallographically characterize the first dimetal units of the type M_2^{7+} . In these compounds **M** is either Os [4] or Re [5]. Surprisingly, in both cases there are reversible waves in the cyclic voltammograms that indicate the existence of M_2^{8+} units in solution, and we are actively seeking synthetic procedures for these.

It is evident that the use of the hpp ligand has opened a new window for the study of previously unknown highly oxidized species that are stable, although the increased stability of compounds in the higher oxidation states means that the lower oxidation states are more reactive and difficult to handle. It is to be noted that

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before hpp, the structural characterization of paddle-wheel compounds with an Mo_2^{6+} core was confined to only two types of species, namely, $\text{Mo}_2[\text{M}(\text{CO})_4(\text{PhPO}_2)_2]_2^{2+}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [6] and $\text{Mo}_2(\text{HEO}_3)_4^{2+}$, where $\text{E} = \text{P}$ [7] and As [8], and there are only a handful with an Mo_2^{5+} core [9]. In contrast, there are over 1,100 dimolybdenum compounds that have an Mo_2^{4+} core [10].

We have initiated studies on W analogs. A few months ago, we reported the structures of series of $\text{W}_2(\text{hpp})_4\text{Cl}_n$ ($n = 0, 1, 2$) compounds [11]. For $n = 0$, the compound was isolated as $\text{W}_2(\text{hpp})_4 \cdot 2\text{NaHBEt}_3$. Here we report the structure of pure $\text{W}_2(\text{hpp})_4$, and discuss its reactivity towards haloalkanes, C_{60} and 7,7', 8,8'-tetracyanoquinodimethide, TCNQ. Such studies were not possible on the compound $\text{W}_2(\text{hpp})_4 \cdot 2\text{NaHBEt}_3$ because of the presence of the highly reducing NaHBEt_3 .

2. Experimental

General considerations. $\text{W}_2(\text{hpp})_4\text{Cl}_2$ was synthesized as described before [12], potassium metal and TCNQ were obtained from Aldrich, and C_{60} from MTR, Inc. Toluene, THF and hexanes were dried by distillation over Na/K, and were degassed by the freeze-pump-thaw method just before use. All manipulations were carried out using standard vacuum line technique under an argon atmosphere. The IR spectra were recorded on a Perkin–Elmer 16PC FT-IR spectrometer using KBr pellets.

Preparation of $\text{W}_2(\text{hpp})_4$, 1. To black crystals of $\text{W}_2(\text{hpp})_4\text{Cl}_2$ (0.200 g, 0.202 mmol) was added 15 ml of THF. This was followed by addition of 0.5 g of potassium metal. The mixture was degassed by the freeze-pump-thaw method and then warmed up and heated to 80–85 °C, giving a brown solution within 30 min. After 1 h, a red crystalline solid was obtained. The mixture was further refluxed for 1 h, and the THF was removed under vacuum, leaving a red crystalline solid with some white solid and potassium metal. The solid mixture was extracted with 30 ml of warm benzene giving a deep red filtrate with some brown solid on the frit which was discarded. Benzene was removed under vacuum, and a red solid was obtained. Yield: 74%. IR (cm^{-1} , KBr): 2934 (m), 2805 (m), 1711 (w), 1653 (w), 1628 (w), 1511 (s), 1438 (w), 1378 (w), 1309 (w), 1275 (w), 1243 (w), 1206 (s), 1077 (w), 1027 (s), 835 (m), 793 (m), 672 (w). X-ray quality crystals were obtained by slowly cooling a hot saturated THF solution to room temperature.

Reaction between $\text{W}_2(\text{hpp})_4$ and CH_2Cl_2 . To 50 mg of **1**, 15 ml of CH_2Cl_2 was added. This resulted in the immediate formation of a brown solution. After about 10 min, a dark brown precipitate formed. After filtration, the brown solution was layered with hexanes and dark brown crystals of $\text{W}_2(\text{hpp})_4\text{Cl}_2 \cdot 4\text{CH}_2\text{Cl}_2$, **2** $\cdot 4\text{CH}_2\text{Cl}_2$ grew within 2 days.

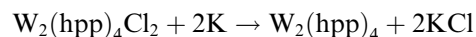
Reaction between $\text{W}_2(\text{hpp})_4$ and C_{60} . C_{60} (23.5 mg, 0.033 mmol) was dissolved with the aid of a sonicator in 40 ml toluene, giving a reddish purple solution. Separately, **1** (30 mg, 0.033 mmol) was dissolved in 20 ml toluene. The solution of **1** was transferred to the solution of C_{60} via cannula, resulting in a dark purplish red precipitate within 5 min. The nearly colorless liquid phase was discarded. The solid was dried under vacuum. It was insoluble in THF, DMSO and other common organic solvents. The solid was air-sensitive and turned to dark brown when exposed to air. IR (cm^{-1} , KBr): 2937 (w), 2836 (w), 1735 (w), 1696 (m), 1681 (m), 1646 (s), 1540 (s), 1452 (m), 1379 (s), 1308 (m), 1256 (w), 1199 (m), 1137 (w), 1059 (m), 1029 (m), 803 (s), 735 (w), 672 (m), 571 (w), 517 (w), 467 (w).

Reaction between $\text{W}_2(\text{hpp})_4$ and TCNQ. Solutions of **1** (30 mg, 0.033 mmol) in 25 ml THF, and TCNQ (6.7 mg, 0.033 mmol) in 15 ml THF were prepared. The THF solution of TCNQ was transferred to the solution of **1** by cannula. A transient green color was observed. Within 1 min, a cloudy off-white suspension formed. The colorless liquid was discarded, and the remaining solid was washed with 10 ml of dichloromethane, and then dried under vacuum. The solid was air-sensitive and turned pinkish brown when exposed to air. The yield was essentially quantitative. IR (cm^{-1} , KBr): 3422 (br, m), 2937 (w), 2858 (w), 2157 (s), 2097 (s), 1539 (m), 1496 (m), 1447 (w), 1379 (m), 1309 (s), 1215 (m), 1131 (w), 1031 (w), 823 (br, s), 750 (w).

X-ray crystallography. Each of the single crystals of **1** and **2** $\cdot 4\text{CH}_2\text{Cl}_2$ was attached to a quartz fiber with a minimum of silicone grease and mounted on a goniometer head. Data were collected at 213 K on a Bruker SMART 1000 CCD diffractometer. Cell parameters were determined using the program SMART [13]. Data reduction and integration were performed with the software package SAINTPLUS [14]. The crystal structures were solved via direct methods and refined using the SHELXL-97 program [15]. Hydrogen atoms were placed at calculated positions. Non-hydrogen atoms were refined with anisotropic displacement parameters. Some crystallographic disorder was found in the conformation of the CH_2 groups of the hpp ligands in **2** $\cdot 4\text{CH}_2\text{Cl}_2$ but not in **1**. Crystal data and structure refinement results for both compounds are listed in Table 1.

3. Results and discussion

Synthesis of $\text{W}_2(\text{hpp})_4$. This red compound was prepared in good yield by reduction of $\text{W}_2(\text{hpp})_4\text{Cl}_2$ by potassium sand in THF according to:



These conditions are similar to those employed to reduce some neutral complexes with low electron affin-

Table 1
Crystal data and structure refinement for $W_2(hpp)_4$, **1** and $W_2(hpp)_4Cl_2 \cdot 4CH_2Cl_2$, **2**· $4CH_2Cl_2$

Compound	$W_2(hpp)_4$	$W_2(hpp)_4Cl_2 \cdot 4CH_2Cl_2$
Formula	$C_{28}H_{48}N_{12}W_2$	$C_{32}H_{56}Cl_{10}N_{12}W_2$
fw	920.48	1331.09
Space group	$P\bar{1}$ (No. 2)	$I4/mmm$ (No. 139)
<i>a</i> (Å)	8.4358(6)	13.7468(9)
<i>b</i> (Å)	9.6540(7)	13.7468(9)
<i>c</i> (Å)	10.1217(7)	12.3118(8)
α (°)	88.283(1)	90
β (°)	71.180(1)	90
γ (°)	80.367(1)	90
<i>V</i> (Å ³)	769.0(2)	2326.6(3)
<i>Z</i>	1	2
ρ_{calcd} (g/cm ³)	1.988	1.900
μ (mm ⁻¹)	7.515	5.555
λ (Å)	0.71073	0.71073
<i>T</i> (K)	213(2)	213(2)
<i>R</i> 1 ^a , <i>wR</i> 2 ^b (all data)	0.0373, 0.0637	0.0226, 0.0886
Goodness-of-Fit ^c	1.022	1.120

^a $R1 = \sum \|F_o| - |F_c|\| / \sum |F_o|$.

^b $wR2 = [\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, where $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

^c Goodness-of-Fit = $[\sum [w(F_o^2 - F_c^2)]^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$, based on all data.

ities such as $[V(\eta^6\text{-arene})_2]$ [16], $[Ce(\eta\text{-}C_8H_8)_2]$ [17], $[VCp_2]$ [18] to their monoanions. An interesting feature of alkali metal reductants is that their reducing potentials depend very much on solvents [19]. In this case, the coordination of THF to the potassium cation plays an important role in its extremely strong reducing power. By contrast, sodium amalgam and potassium amalgam were not sufficient to reduce $W_2(hpp)_4Cl_2$ to **1**. Earlier we had shown that when an excess of NaHBET₃ was used it cocrystallized along with **1** [11], thus hindering further reactivity studies. Compound **1** is extremely air and moisture-sensitive. It is soluble in toluene and benzene, and less so in THF.

Structures and reactivity. A thermal displacement ellipsoid plot of **1** is shown in Fig. 1. The two W atoms are spanned by four hpp ligands forming a paddlewheel structure. The hpp anions adopt a puckered conformation and are perfectly ordered. This represents one of the very few examples where the hpp ligands are not disordered, thus providing an excellent opportunity to obtain unambiguous, reliable structural data for the hpp ligands.

The core of hpp, namely the three N atoms and the central C atom, is essentially coplanar. The three C–N bond lengths of 1.34(1) Å, 1.35(1) Å and 1.38(1) Å, are considerably shorter than those typical for a C–N single bond, of ca. 1.46 Å. This is indicative of the electron delocalization that spans over the four coplanar atoms, facilitating the electronic interaction between the ligands and the metal atoms. The W–W distance of 2.1617(4) Å

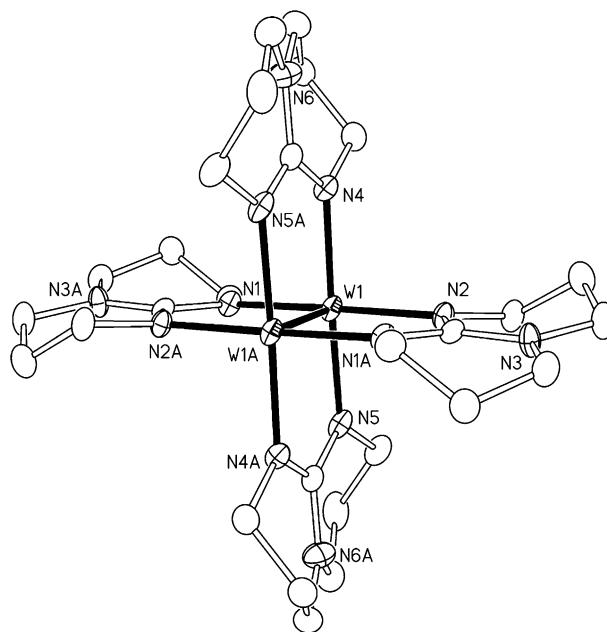


Fig. 1. An ellipsoid plot of $W_2(hpp)_4$, **1**, with atoms drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

is essentially the same as that of 2.1608(5) Å in $1 \cdot 2NaHBET_3$ [11]. As shown in Table 2, for the $W_2(hpp)_4Cl_n$ molecules, $n = 0, 1, 2$ the W–W distance increases by ca. 0.04 Å as the oxidation state of the W_2 unit changes from 4 to 5 and from 5 to 6, consistent with the decrease in bond order from 4 to 3.5 to 3. The W–N distances, however, decrease as the oxidation state increases as expected from the increase in electrostatic attraction. For **1**, the W–W distance is exceedingly short compared to those in other known W_2^{4+} complexes. There are only five other W_2^{4+} paddlewheel compounds (out of several dozen) in which the W–W bond lengths are comparably short. These are $W_2(mhp)_4$ (2.161(1) Å) [20], $W_2(map)_4$ (2.164(1) Å) [21], $W_2(dmhp)_4$ (two forms, with 2.155(2) Å and 2.163(1) Å) [22], $W_2(dmhp)_2$ (triaz)₂ (2.169(1) Å) [23] and $W_2(PhNpy)_4$ (2.165(2) Å) [24].

It is also noteworthy that all corresponding distances and angles in **1** and $1 \cdot 2NaHBET_3$ are essentially the same, thus indicating that the interstitial Na atoms, which are located in pockets formed by the hpp ligands do not interact in any important way with the ligands, as was true also for the pair $Nb_2(hpp)_4/Nb_2(hpp)_4 \cdot 2NaHBET_3$ [25].

Upon addition of CH_2Cl_2 to red crystals of **1**, a brown solution immediately forms. On standing this solution produces a precipitate of $W_2(hpp)_4Cl_2$, **2**. By layering a saturated solution with hexanes, crystalline $2 \cdot 4CH_2Cl_2$ can be obtained. The structure shown in Fig. 2 is similar to that of **1** but here the puckered hpp ligands are disordered. The W–W distance of 2.2497(8) Å for the triply-bonded W_2^{6+} unit is ca. 0.09 Å longer

Table 2

Selected dimensions of $W_2(hpp)_4Cl_n$ molecules, $n = 0, 1, 2$

Compound	W–W (Å)	W–N (Å) (av)	W···Cl (Å)	Torsion angle (°)	Ref.
$W_2(hpp)_4$	2.1617(4)	2.13		1.0	This work
$W_2(hpp)_4 \cdot 2NaHBEt_3$	2.1608(5)	2.14		0.1	[11]
$W_2(hpp)_4Cl_{0.5}Cl_{0.5}^a$	2.209(1)	2.12	2.84	0.0	[11]
$W_2(hpp)_4Cl$	2.2131(8)	2.12	2.94	0.2	[11]
$W_2(hpp)_4Cl_2$	2.250(2)	2.08	3.06	0.0	[11]
$W_2(hpp)_4Cl_2 \cdot 4CH_2Cl_2$	2.2497(8)	2.09	2.95	0.0	This work

^a This nomenclature is intended to indicate that the Cl atom in this W_2^{5+} species is disordered over two positions.

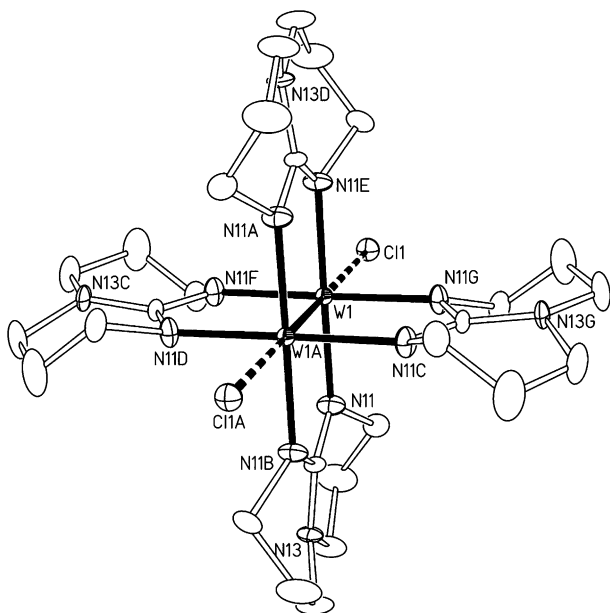


Fig. 2. Displacement ellipsoid plot of one orientation of the disordered $W_2(hpp)_4Cl_2$ molecule in $2 \cdot 4CH_2Cl_2$. Atoms are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

than that in quadruply-bonded **1**. There are long $W \cdots Cl$ separations of 2.952(3) Å indicating that there is no significant axial bonding. All corresponding metrical parameters are similar to those found in the unsolvated form [11].

What is most important here is the fact that mere contact of **1** with CH_2Cl_2 is capable of oxidizing the W_2^{4+} core to the W_2^{6+} state. A similar reaction with the Mo analog also oxidizes the Mo_2^{4+} core promptly and quantitatively but only to the Mo_2^{5+} state [2]. In order to take the $Mo_2(hpp)_4Cl$ molecule to $Mo_2(hpp)_4Cl_2$ or another $Mo_2(hpp)_4^{2+}$ species, an additional, and stronger, oxidizing agent such as O_2 or Ag^+ is required. It should be noted that CH_2Cl_2 and other haloalkanes are known to be highly toxic to living organisms and the toxicity has been associated with reduction via generation of free radicals [26]. Thus, the ability of CH_2Cl_2 to act as an oxidizing agent towards **1** can be explained.

Because of the evident high reactivity of **1** and its facile oxidation we decided to investigate its reactivity towards two other well-known reducible species, TCNQ

and C_{60} . Solutions of **1** and TCNQ react very rapidly generating a transient green solution and then an insoluble precipitate, which was found to be diamagnetic. TCNQ is a mild oxidant, which can accept one or two electrons depending on the reduction potentials of the reductants [27]. Its cyclic voltammogram shows two reduction waves centered around -0.30 and -0.88 V (referred to $FeCp_2/FeCp_2^+$). The oxidation state of TCNQ as well as its coordination mode to metals can be conveniently and conclusively determined by IR spectroscopy. The IR peaks of some complexes containing TCNQ with different charges and coordination modes [28] are listed in Table 3. The $C \equiv N$ vibration frequency is sensitive to the charges on TCNQ, because the added electrons occupy the antibonding orbital of the CN group, which attenuates the force constant, and results in a lowering of the frequency. The $\nu(C \equiv N)$ of $[TCNQ]^0$, $[TCNQ]^{1-}$ and $[TCNQ]^{2-}$ are above 2200 cm^{-1} , between 2150 and 2200 cm^{-1} , and around 2100 cm^{-1} , respectively [a]. The IR spectrum of the off-white solid obtained from the reaction between $W_2(hpp)_4$ and TCNQ (1:1 ratio) shows a peak at 2097 cm^{-1} , which strongly indicates that the charge on TCNQ in this product is -2 . This is also consistent with the solid being diamagnetic, and not green ($[TCNQ]^{1-}$ is typically green, as is the color of the transient solution that forms before the precipitate). Thus, we believe that the product is $[W_2(hpp)_4]^{2+} [TCNQ]^{2-}$. Efforts to crystallize this compound are underway. The nature of the product of the reaction between **1** and C_{60} (1:1) in toluene is not as clear and will require further work. However, some inferences can be made. The precipitate formed upon mixing the solutions strongly implies that a redox reaction occurs, because C_{60} can be easily reduced, anions up to $[C_{60}]^{6-}$ have been obtained up to date [29], and $W_2(hpp)_4$ is such a strong reducing species. Unfortunately the product is rather insoluble in most organic solvents and the IR spectrum of the product appears to be devoid of signals from $[C_{60}]^{n-}$, probably because of their low intensities, and the shielding by the many strong peaks from the hpp anion.

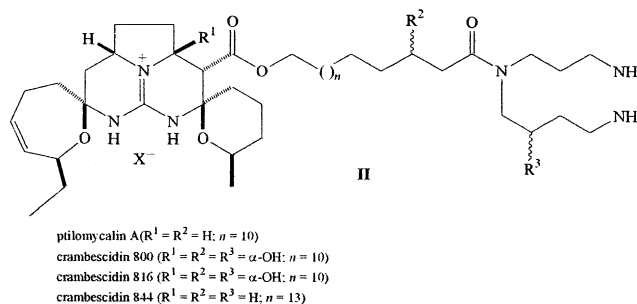
It is clear, however, that **1** is a strong reducing agent with an enormous potential for use on organic substrates in organic solvents. This is an area of great current interest [30].

Table 3
IR frequencies of some complexes containing TCNQ with different charges

Compound	Charge	IR peaks (cm ⁻¹), (νC≡N)	Ref.
TCNQ	Neutral	2222 (s)	[a]
LiTCNQ	[TCNQ] ⁻	2181 (s), 2154 (s)	[a]
Fe(TCNQ) ₂ (H ₂ O) ₂	[TCNQ] ⁻	2212 (s), 2195 (s), 2177 (m)	[a]
Co(TCNQ) ₂ (H ₂ O) ₂	[TCNQ] ⁻	2220 (s), 2201 (s), 2177 (m)	[a]
[Co ^{III} (acacen)(py) ₂] ⁺ TCNQ	[TCNQ] ⁻	2171 (s), 2145 (s)	[b]
[Co ^{III} (acacen)(py) ₂] ²⁺ TCNQ	[TCNQ] ²⁻	2151 (s), 2102 (s)	[b,c]
[W ₂ (hpp) ₄] ²⁺ [TCNQ] ²⁻	[TCNQ] ²⁻	2157 (s), 2097 (s)	This work

How does hpp stabilize high oxidation states? It has been shown that the guanidinate ligand hpp is a very strong Brønsted base and it is estimated that it is nearly 100 times more basic than tetramethylguanidine [31]. Photoelectron spectroscopy has established that the HOMO for the ionization of Hhpp corresponds to a lone pair in the unique N atom [32]. Thus, there is significant electron delocalization in the NC(N)N core that favors an increase in the basicity of the anion. This is consistent with the observation of three short C–N distances in **1** and **2** as well as in other hpp [2] and guanidinate compounds [33]. For hpp these short C–N bonds can be regarded as having partial double-bond character. Thus, each of the four atoms in the NC(N)N core can be regarded as sp² hybridized with some of the electrons occupying pπ MOs. This leads to planarity, or near planarity, in the central part of the ligand, but the two sets of three CH₂ groups need not, and do not, all lie in this plane. Furthermore, recent DFT calculations on M₂(hpp)₄ compounds, M=Mo, W, reveal that the HOMO in each of these two molecules displays δ-bond character and the δ orbitals of the metal cores strongly interact with orbitals of the hpp ligands. This interaction is much stronger than those in formamidinate ligands [34]. This leads to an extraordinary stabilization of the oxidized species such that in the gaseous phase the ionization potential of the W₂(hpp)₄ molecule is lower and that of Mo₂(hpp)₄ about the same as the ionization potential of Cs atoms, as shown by photoelectron spectroscopy.

Some additional thoughts. It should be pointed out that there might be some relationship of this work and chemistry in living organisms, in which redox chemistry is fundamental [35]. Natural guanidine derivatives are abundant in terrestrial microorganisms, marine and fresh water microorganisms, invertebrates, marine sponges and higher plants and play an important role in many vital processes [36]. Among them, a particular group of alkaloids of the crambescidin/ptilomycalin family have attracted much attention because of the range of biological activities they exhibit including hypotensive and adrenergic neuron blocking effects [37]. Some of the schematic structures are shown as **II**



where it can be seen that they incorporate the hpp core.

4. Concluding remarks

We have prepared W₂(hpp)₄, a very strong reducing agent, and have studied its reactivity toward the haloalkane CH₂Cl₂, C₆₀ and TCNQ, all of which are rapidly reduced. The structures of W₂(hpp)₄ and W₂(hpp)₄Cl₂·4CH₂Cl₂ are presented.

Supplementary material

Additional details of the crystal structure determinations and data tables have been deposited at the Cambridge Crystallographic Data Centre (CCDC Nos. 194798 for **1** and 194799 for **2**·4CH₂Cl₂). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

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