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Synthesis, molecular structure and physicochemical properties of $M_2(\text{form})_4$ ($M = \text{nickel, palladium; form} = \text{N,N'-Di-p-tolylformamidinato}$). Attempts to generate a palladium (III) dimer

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F. Albert Cotton, Marek Matusz, Rinaldo Poli. Synthesis, molecular structure and physicochemical properties of $M_2(\text{form})_4$ ($M = \text{nickel, palladium; form} = \text{N,N'-Di-p-tolylformamidinato}$). Attempts to generate a palladium (III) dimer. *Inorganic Chemistry*, 1987, 26 (10), pp.1472-1474. 10.1021/ic00257a003. hal-03545081

HAL Id: hal-03545081

<https://hal.science/hal-03545081>

Submitted on 27 Jan 2022

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Synthesis, Molecular Structure, and Physicochemical Properties of $M_2(\text{form})_4$ ($M = \text{Ni, Pd}$; form = N,N' -Di-*p*-tolylformamidinato). Attempts To Generate a Palladium(III) Dimer

Sir:

Many dinuclear compounds of platinum(III) containing four bidentate bridging ligands and a metal-metal interaction through an electron-rich single bond of electronic configuration $\sigma^2\pi^4\delta^2\delta^*2\pi^{*4}$ are known.^{1,2} A few dinuclear compounds with the Pt atoms in the 2.5 average oxidation state and a formal bond order of 0.5 between the two metals have also been prepared.^{3,4} On the other hand, analogous compounds for nickel and palladium have never been reported. Only one Ni_2^{5+} compound, $\text{Ni}_2(\text{S}_2\text{C}-\text{CH}_3)_4\text{I}$, has been described.⁵

Since many dinuclear, quadruply bridged compounds of nickel(II) and palladium(II) are known, we thought that we might have a chance to generate oxidized species from these provided we could find the right combination of ligands and oxidizing material. We decided to test the N,N' -di-*p*-tolylformamidinato (form) ligand for the following reasons. First, the nitrogen donors are expected to increase the electronic charge on the metal atoms as compared, for example, to that obtained with carboxylato ligands, thereby decreasing the oxidation potential. Such a trend has been well established for compounds of the Rh_2^{4+} core.⁶

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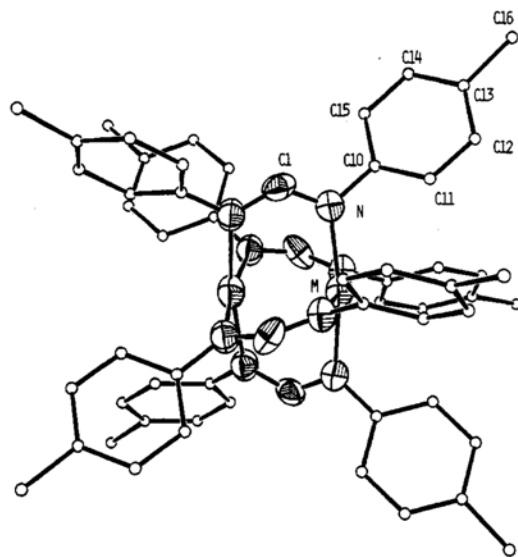


Figure 1. ORTEP view of the $M_2(\text{form})_4$ ($M = \text{Ni}, \text{Pd}$) molecule. Distances: $M-M = 2.485$ (2) Å (Ni), 2.622 (3) Å (Pd); $M-N = 1.904$ (5) Å (Ni), 2.06 (1) Å (Pd). Torsional $N-M-M'-N'$ angle: 16.82° (Ni), 15.1° (Pd).

Second, the geometry and the steric bulkiness of the ligand should favor the bridging dinuclear structure over the possible mononuclear or oligonuclear structures that are known to be formed with other bidentate ligands.⁷ Finally, $\text{Rh}_2(\text{form})_4$ ^{6c} and $\text{Ir}_2(\text{form})_4$ ⁸ which are isoelectronic with a hypothetical Pd_2^{6+} compound, have been recently described.

$\text{Ni}_2(\text{form})_4$ has been obtained by interaction of anhydrous NiBr_2 with Li^+form^- , the latter being obtained in situ from Hform and LiBu , in THF as solvent. It crystallizes as a dark green diaqua adduct from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ when the crystallization is carried out in the air.⁹ $\text{Pd}_2(\text{form})_4 \cdot 2\text{H}_2\text{O}$ has been obtained as orange crystals by a similar procedure from $\text{Pd}_3(\text{OAc})_6$ and Li^+form^- . Crystallization from dry THF gave $\text{Pd}_2(\text{form})_4 \cdot 2\text{THF}$,¹⁰ while $\text{Pd}_2(\text{form})_4 \cdot \text{C}_6\text{H}_5\text{CH}_3$ was obtained from toluene.¹¹

The crystal structures of the H_2O adducts of both compounds have been determined by X-ray diffraction methods.¹² The two compounds are isostructural. The molecules (see Figure 1) have imposed D_4 symmetry and contain, as expected, two metal atoms bridged by four formamidinate ligands, with four nitrogen atoms around each metal atom in a square-planar configuration. The $M-M$ distances [2.485 (2) Å ($M = \text{Ni}$); 2.622 (3) Å ($M = \text{Pd}$)]

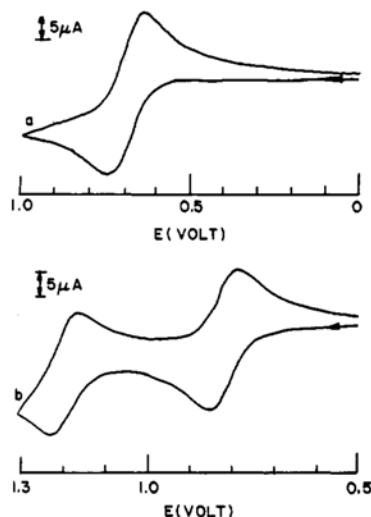


Figure 2. Cyclic voltammograms of $M_2(\text{form})_4$ in CH_2Cl_2 (ca. 0.1 M $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$) at a platinum electrode: (a) $M = \text{Ni}$; (b) $M = \text{Pd}$. Reference electrode: Ag/AgCl . Scan speed = 200 $\text{mV}\cdot\text{s}^{-1}$. The $\text{FeCp}_2/\text{FeCp}_2^+$ couple had $E_{1/2} = +0.49$ V under the same conditions.

are comparable to, although a little longer than, those of $M_2(\text{dpt})_4$ ($\text{dpt} = 1,3\text{-diphenyltriazine}$).¹³

The cyclic voltammograms of $M_2(\text{form})_4$ are reported in Figure 2. Neither compound shows any reduction process, but both undergo interesting oxidation processes. $\text{Ni}_2(\text{form})_4$ exhibits a reversible ($\Delta E_p = 78$ mV at 200 $\text{mV}\cdot\text{s}^{-1}$) oxidation with $E_{1/2} = +0.73$ V and a second irreversible oxidation with $E_{pc} = \text{ca. } +1.25$ V. $\text{Pd}_2(\text{form})_4$ shows two reversible waves, the first one centered at $E_{1/2} = +0.81$ V ($\Delta E_p = 61$ mV at 200 $\text{mV}\cdot\text{s}^{-1}$) and the second one with $E_{1/2} = +1.19$ V ($\Delta E_p = 55$ mV at the same scan speed). These two waves have the same limiting current, and they are therefore associated with the same number of electrons. Controlled-potential coulometry carried out at +1.00 V for both $\text{Pd}_2(\text{form})_4 \cdot 2\text{THF}$ and $\text{Ni}_2(\text{form})_4 \cdot 2\text{H}_2\text{O}$ established the nature of the oxidized species as $[\text{M}_2(\text{form})_4]^+$ ($M = \text{Ni}$, dark emerald green; $M = \text{Pd}$, dark brown). The amount of charge consumed in the processes was slightly higher than one electron per dimer, perhaps because of water present in the system. The $[\text{M}_2(\text{form})_4]^+$ ($M = \text{Ni}, \text{Pd}$) ions are actually able to oxidize water with production of the neutral $M(\text{II})$ dimers, although such a reaction (monitored by visible spectroscopy) is quite slow in CH_2Cl_2 . After the coulometric experiment, cyclic voltammetry on the resulting solutions confirmed the completion of the oxidation processes.

We tried to obtain salts of the oxidized species in crystalline form, but we have so far been unsuccessful: when the CH_2Cl_2 solutions from the bulk electrolysis are evaporated to dryness and the residues dissolved in acetonitrile, immediate formation of the neutral $M(\text{II})$ dimers occurs. The same behavior was observed when we tried to precipitate the cations from CH_2Cl_2 as the BPh_4^- salts (by using the CH_2Cl_2 soluble $n\text{-Bu}_4\text{N}^+\text{BPh}_4^-$).¹⁴

The solutions from bulk electrolysis were more fully characterized by EPR and visible spectroscopy. The EPR spectra are reported in supplemental Figure 3. The nickel species shows a spectrum consistent with axial symmetry, with $g_{\perp} = 2.210$ and $g_{\parallel} = 2.038$. The only other known Ni_2^{5+} compound of similar configuration, $\text{Ni}_2(\text{S}_2\text{CCH}_3)_4$, is said to be EPR silent.⁵ The palladium compound, on the other hand, shows only a symmetric line at liquid-nitrogen temperature. No other Pd_2^{5+} compound seems to have been described in the literature. A Pt_2^{5+} compound has been characterized by EPR, and it is reported to have a spectrum typical of axial symmetry with $g_{\perp} = 2.079$ and $g_{\parallel} = 2.008$.⁴

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- (8) Cotton, F. A.; Poli, R. *Polyhedron*, in press.
- (9) $\text{Ni}_2(\text{form})_4 \cdot 2\text{H}_2\text{O}$. Anal. Calcd for $\text{C}_{60}\text{H}_{64}\text{N}_8\text{Ni}_2\text{O}_2$: C, 68.9; H, 6.2; Ni, 11.2. Found: C, 70.3; H, 6.4; Ni, 10.5. IR (Nujol mull/ cm^{-1}): 1620 m, 1590 s, 1535 m, 1500 s, 1345 s, 1230 s, 970 m, 830 m, 820 m, 535 m, 525 m, 475 w, 465 m. Visible [CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 630 (800), 482 (2700)]. ^1H NMR (CDCl_3 , δ): 1.53 (s, H_2O , 4 H), 2.52 (s, CH_3 , 24 H), 6.14 (s, $\text{N}-\text{CH}-\text{N}$, 4 H), 7.08 (m, aromatic, 32 H). The peak at δ 1.53 disappeared upon treatment with D_2O .
- (10) $\text{Pd}_2(\text{form})_4 \cdot 2\text{THF}$. IR (Nujol mull/ cm^{-1}): 1620 m, 1585 s, 1540 m, 1500 s, 1345 s, 1230 s, 1070 m, 965 m, 835 sh, 820 m, 545 w, 520 m, 450 m. Visible [CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 492 (2600)]. ^1H NMR (CDCl_3 , δ): 1.84 (m, THF, 8 H), 2.24 (s, CH_3 , 24 H), 3.74 (m, THF, 8 H), 6.87 (m, aromatic, 32 H), 7.05 (s, $\text{N}-\text{CH}-\text{N}$, 4 H).
- (11) $\text{Pd}_2(\text{form})_4 \cdot \text{C}_6\text{H}_5\text{CH}_3$. The IR (Nujol mull) spectrum was identical with that of $\text{Pd}_2(\text{form})_4 \cdot 2\text{THF}$, with the exception of the band at 1070 cm^{-1} , not present in the toluene adduct. ^1H NMR (CDCl_3 , δ): 2.25 (s, CH_3 , 24 H), 2.35 [s, CH_3 (toluene), 3 H], 6.88 (m, aromatic, 32 H), 7.05 (s, $\text{N}-\text{CH}-\text{N}$, 4 H), 7.19 [m, aromatic (toluene), 5 H].
- (12) Crystal data: Cubic, space group $Pn\bar{3}m$; $a = 20.841$ (5) Å (Ni), 21.067 (4) Å (Pd); $V = 9052$ (5) Å³ (Ni), 9350 (5) Å³ (Pd); $Z = 6$; $R = 0.0492$ (Ni), 0.0520 (Pd) [$R_w = 0.0620$ (Ni), 0.0649 (Pd)] for 521 (Ni) or 401 (Pd) data having $F_o^2 > 3\sigma(F_o^2)$.

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- (14) Note added in Proof: Both $[\text{M}_2(\text{form})_4]^+$ cations have now been isolated in salts and structurally characterized.

Both $[M_2(\text{form})_4]^+$ ($M = \text{Ni}, \text{Pd}$) solutions have strong absorptions in the near-infrared. The spectra are reported in supplementary Figure 4 and contrasted with those of the corresponding neutral species. An assignment of such bands will be presented following a molecular orbital study under way.

A bulk electrolysis was attempted for the palladium species at +1.35 V in order to electrogenerate the $[\text{Pd}_2(\text{form})_4]^{2+}$ species, but more than two electrons per molecule were consumed in the process and a following cyclic voltammetric experiment showed that most of the electroactive species had been destroyed. We attribute this instability to a slow process that follows the generation of the $[\text{Pd}_2(\text{form})_4]^{2+}$ species, since the peak separation and the peak currents in the process centered at $E_{1/2} = +1.19$ V in the cyclic voltammogram of $\text{Pd}_2(\text{form})_4$ (see Figure 2b) do not show any significant deviation from reversibility. Such a slow process may involve either the solvent or the formamidinato ligand.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supplementary Material Available: Tables of crystallographic data, atomic fractional coordinates, bond distances and angles, and temperature factors for $\text{Ni}_2(\text{form})_4 \cdot 2\text{H}_2\text{O}$ and $\text{Pd}_2(\text{form})_4 \cdot 2\text{H}_2\text{O}$ and figures showing EPR spectra of $M_2(\text{form})_4^+ \text{PF}_6^-$ (Figure 3) and visible spectra of $[M_2(\text{form})_4]^{n+}$ (Figure 4) (10 pages). Ordering information is given on any current masthead page.

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Received December 16, 1986