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Building Metallacrown Topology around a Discrete $[M_3(\mu_3\text{-O})]$ (M = Ni(II) and Pd(II)) Core Using Oximato Oxygen Linkers: Synthesis, Structures, and Spectroscopic Characterization of a New Family of Compounds with an Inverse-9-MC-3 Motif

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A family of trinuclear oximato complexes $[(M^{II}L)_3(\mu_3\text{-O})]ClO_4$ (M = Ni, **1**−**3**; Pd, **4** and **5**) (HL = 2-alkylamino-3-oximobutane) involving a discrete $[M_3(\mu_3\text{-O})]^{4+}$ core have been synthesized in moderate to high yields by a simple one-pot reaction. The products were characterized by ESI-mass and ^1H NMR spectroscopy as well as by single-crystal X-ray diffraction analysis of representative compounds viz., **1**, **2**, and **4**. The oximato oxygen atoms from the ligands and the central μ_3-O atom connect the metal centers, forming an inverse metallacrown topology in these complexes. In the isostructural nickel compounds (**1**, **2**), the metal centers are situated at the vertices of an equilateral triangle with its centroid position being occupied by the μ_3-O atom; the Ni−O−Ni angles vary in the range 119.0(2)−120.2(2)°. In the palladium complex **4**, the geometry of the Pd_3O core is better described as a regular trigonal pyramid with the metal centers and the μ_3-O atom occupying the apexes; the Pd−O−Pd angles are close to 109°. The coordination square planes around the individual palladium centers bend appreciably from each other (dihedral angles vary in the range 28.62−34.53°), providing more of a bowl shape compared to the overall metallacrown topology that remains virtually planar in the nickel complexes. The μ_3-oxygen atom in **4** is displaced by 0.687 Å from the center of the triangular plane with corners occupied by the Pd(II) ions. The protons of the metallacrown peripheral rings in **4** and **5** are more deshielded compared to their nickel(II) counterparts, as revealed from their ^1H NMR spectra in dichloromethane-d_2 solution.

Introduction

Much effort has been made in recent years in the syntheses and characterization of triangular ensembles involving the $[M_3(\mu_3\text{-O})]$ core. The most well-investigated compounds of this sort are the so-called "basic carboxylates" of general composition $[M_3O(O_2CR)_6L_3]^{n+}$ with metal ions in readily accessible +3 oxidation states ($n = 1$, M = V^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Ru^{3+}, Rh^{3+}, and Ir^{3+});[1] the corresponding Co^{3+} and Ni^{3+} compounds are only scantily investigated,[2,3] eluding all attempts of their crystal structure determination by single-crystal X-ray diffraction analysis. Interestingly, compounds with similar core structures are hard to achieve entirely with bivalent metal ions[4,5] as well as in carboxylate-free ligand environments. In the case of group 10 metal ions, the situation is even more intriguing, as no molecule with a discrete $[M_3(\mu_3\text{-O})]$ core (M^{II} = Ni^{II}, Pd^{II}, or Pt^{II}) structure has been synthesized thus far, even though compounds with $[M^{II}_3(\mu_3\text{-OH})]$ (M = Ni and Pd),[6,7] $[M^{II}_3(\mu_3\text{-S})]$ (M = Ni and Pd),[8,9]

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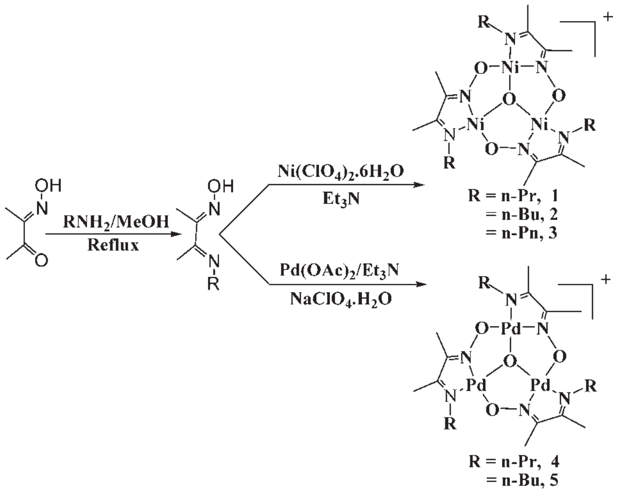
and $[Ni^{II}_3(\mu_3\text{-}F)]$[10] cores are well documented in the literature. Considering the softer nature of the higher transition metals, particularly in lower oxidation states, their interactions with the hard oxo-ligand are expected to be unfavorable.[11] Aligned with such expectations, complexes of palladium(II) with an oxo-ligand are extremely rare[12] and include two μ_4-oxo-bridged compounds involving Pd_4O and Pd_3CuO cores.[13,14] as well as two μ_3-oxo-bridged heterometal complexes involving $Pd_2Au_2O_2$ and Pd_4AuO_2 cores.[15]

From a structural viewpoint some of these triangular ensembles, reported in recent times, particularly with oxime-type ligands, have topologies of a metallacrown (MC),[16] the inorganic structural analogue of crown ethers. Specific nomenclature of a nine-membered metallacrown ring holding three metal centers is 9-MC-3, for which two structural motifs, regular[17] and inverse,[18] are known. In the relatively rare *regular* motif, the oxygen atoms of the repeating [−O−N−M−] moieties are oriented toward the center of the cavity, while for the *inverse* motif, the metal atoms are directed toward the center. In general, a regular MC prefers to host a cation in the central cavity, while the inverse one prefers an anionic species as its guest, although there also exist several examples of 9-MC-3 complexes with a vacant cavity site.[19]

Scheme 1. Syntheses of Complexes **1**−**5**



For quite some time, we have an ongoing project on the coordination chemistry of group 10 metal ions [mainly Ni(II) and Pd(II)] under a variety of coordination environments.[20−25] Herein, we report the synthesis of a family of trinickel compounds $[(Ni^{II}L)_3(\mu_3\text{-}O)]ClO_4$ (**1**−**3**) involving a discrete $[Ni^{II}_3(\mu_3\text{-}O)]$ core, HL being a member of a series of tridentate monoprotic Schiff-base ligands (Scheme 1) based on 2,3-butanedionemonoxime. This also gives us an opportunity to extend this work to the corresponding tripalladium compounds $[(Pd^{II}L)_3(\mu_3\text{-}O)]ClO_4$ (**4**, **5**) involving an

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unprecedented homometallic [$Pd^{II}_3(\mu_3\text{-}O)$] core.[15] The compounds have been characterized by single-crystal X-ray diffraction analysis as well as by ^1H NMR and ESI mass spectroscopy, providing evidence for the existence of inverse 9-MC-3 topology in the compounds **1−5**.

Experimental Section

Materials. All reactions were carried out in aerobic environment with chemicals available from commercial sources and used as received. Solvents were reagent grade, dried by standard methods,[26] and distilled under nitrogen prior to their use.

Preparation of Complexes. **[$(NiL^1)_3(\mu_3\text{-}O)$]$ClO_4$, 1.** 2,3-Butanedionemonoxime (0.10 g, 1 mmol) and *n*-propylamine (0.059 g, 1 mmol) were mixed together in 30 mL of methanol, and the solution was refluxed for 30 min to get a pale yellow solution. To this were then added Et_3N (0.10 g, 1 mmol) and $Ni(ClO_4)_2\cdot6H_2O$ (0.37 g, 1 mmol), and the resulting solution was refluxed further for an additional hour to get a deep red solution. It was then filtered, and the filtrate was kept in the open air for slow evaporation. A dark red crystalline compound was obtained within a couple of days. Some of these crystals appeared to be of diffraction grade and were used directly for X-ray data collection. Yield: 0.19 g (80%). Anal. Calcd for $C_{21}H_{39}N_6O_8Ni_3Cl$: C, 35.24; H, 5.45; N, 11.74. Found: C, 34.79; H, 5.41; N, 11.58. FT-IR bands (KBr pellet, cm^{-1}): 2968m, 2933m, 2875m, 1602w, 1519s, 1386m, 1344m, 1224m, 1091sb, 750m, 622m. ESI-MS (positive) in CH_3CN: *m*/*z* 615 [$M - ClO_4$]$^+$. ^1H NMR (500 MHz, CD_2Cl_2, 298 K, δ/ppm): 2.77 (t, 2H, J = 7.75 Hz, H(3)); 1.83 (s, 3H, H(1)); 1.64 (s, 3H, H(2)); 1.51−1.45 (m, 2H, H(4)); 0.87 (t, 3H, J = 7.25 Hz, H(5)).

[$(NiL^2)_3(\mu_3\text{-}O)$]$ClO_4$, 2. This compound was synthesized using the same procedure as that described above for **1**, the only change being the use of *n*-butylamine as a replacement for *n*-propylamine. A red, crystalline compound was obtained following a similar workup. Yield: 75%. Diffraction grade crystals were grown by slow diffusion of methanol into a red dichloromethane solution of the compound. Anal. Calcd for $C_{24}H_{45}N_6O_8Ni_3Cl$: C, 38.03; H, 5.94; N, 11.09. Found: C, 38.12; H, 5.76; N, 10.96. FT-IR bands (KBr pellet, cm^{-1}): 2958m, 2929m, 2871m, 1612w, 1521s, 1382m, 1342m, 1226m, 1097sb, 750m, 621m. ESI-MS (positive) in CH_3CN: *m*/*z* 657 [$M - ClO_4$]$^+$. ^1H NMR (500 MHz, CD_2Cl_2, 298 K, δ/ppm): 2.79 (t, 2H, J = 7.75 Hz, H(3)); 1.83 (s, 3H, H(1)); 1.63 (s, 3H, H(2)); 1.46−1.40 (m, 2H, H(4)); 1.30−1.23 (m, 2H, H(5)); 0.90 (t, 3H, J = 7.50 Hz, H(6)).

[$(NiL^3)_3(\mu_3\text{-}O)$]$ClO_4$, 3. This compound was synthesized using the same procedure as that described above for **1** using *n*-pentylamine as a replacement for *n*-propylamine. The compound was recrystallized from a dichloromethane/methanol mixture as a dark red, crystalline solid. Yield: 68%. Anal. Calcd for $C_{27}H_{51}N_6O_8Ni_3Cl$: C, 40.53; H, 6.38; N, 10.51. Found: C, 40.22; H, 6.08; N, 10.32. FT-IR bands (KBr pellet, cm^{-1}): 2956m, 2927m, 2862m, 1612w, 1523s, 1382m, 1344m, 1228m, 1108sb, 1089sb, 746m, 622m. ESI-MS (positive) in CH_3CN: *m*/*z* 699 [$M - ClO_4$]$^+$. ^1H NMR (500 MHz, CD_2Cl_2, 298 K, δ/ppm): 2.82 (t, 2H, J = 7.00 Hz, H(3)); 1.87 (s, 3H, H(1)); 1.65 (s, 3H, H(2)); 1.50−1.43 (m, 2H, H(4)); 1.35−1.28 (m, 2H, H(5)); 1.25−1.19 (m, 2H, H(6)); 0.90 (t, 3H, J = 7.25 Hz, H(7)).

[$(PdL^1)_3(\mu_3\text{-}O)$]$ClO_4.CH_3OH$, 4. 2,3-Butanedionemonoxime (0.1 g, 1 mmol) and *n*-propylamine (0.059 g, 1 mmol) were mixed together in 30 mL of methanol, and the solution was refluxed for 30 min to get a pale yellow solution. To this were then added Et_3N (0.1 g, 1 mmol), $Pd(O_2CCH_3)_2$ (0.22 g, 1 mmol), and $NaClO_4\cdot H_2O$ (0.28 g, 2 mmol) in a stepwise manner. The resulting solution was refluxed for an additional one hour to get a deep yellow-brown solution. It was then filtered and the filtrate was kept in the open air for slow evaporation. Orange-yellow, block-shaped crystals were obtained after about one week. Some of these crystals appeared to be of diffraction grade and were used directly for X-ray data collection. Yield: 0.16 g (55%). Anal. Calcd for $C_{22}H_{43}N_6O_9Pd_3Cl$: C, 29.67; H, 4.83; N, 9.44. Found: C, 29.12; H, 4.48; N, 9.42. FT-IR bands (KBr pellet, cm^{-1}): 3425wb, 2964m, 2933m, 2875m, 1596w, 1512s, 1384m, 1344m, 1226m, 1145m, 1093sb, 1006m, 700m, 622m. ESI-MS (positive) in CH_3CN: *m*/*z* 758 [$M - ClO_4 - CH_3OH$]$^+$. ^1H NMR (500 MHz, CD_2Cl_2, 298 K, δ/ppm): 3.37 (t, 2H, J = 7.50 Hz, H(3)); 2.15 (s, 3H, H(1)); 1.96 (s, 3H, H(2)); 1.71−1.63 (m, 2H, H(4)); 0.97 (t, 3H, J = 7.25 Hz, H(5)).

[$(PdL^2)_3(\mu_3\text{-}O)$]$ClO_4\cdot CH_3OH$, 5. This compound was synthesized following an identical procedure to that described above for **4** using *n*-butylamine as a replacement for *n*-propylamine. An orange crystalline compound was obtained following a similar workup. Yield: 50%. Anal. Calcd for $C_{25}H_{49}N_6O_9Pd_3Cl$: C, 32.19; H, 5.25; N, 9.01. Found: C, 32.04; H, 5.08; N, 9.24. FT-IR bands (KBr pellet, cm^{-1}): 3434wb, 2958m, 2929m, 2871m, 1596w, 1515s, 1386m, 1346m, 1226m, 1147m, 1091sb, 1008m, 700m, 622m. ESI-MS (positive) in CH_3CN: *m*/*z* 800 [$M - ClO_4 - CH_3OH$]$^+$. ^1H NMR (500 MHz, CD_2Cl_2, 298 K, δ/ppm): 3.39 (t, 2H, J = 7.50 Hz, H(3)); 2.12 (s, 3H, H(1)); 1.94 (s, 3H, H(2)); 1.64−1.58 (m, 2H, H(4)); 1.42−1.36 (m, 2H, H(5)); 0.96 (t, 3H, J = 7.50 Hz, H(6)).

Caution! *Perchlorate salts of metal complexes containing organic ligands are potentially explosive*[27] *and should be handled in small quantity with sufficient care.*

Physical Measurements. IR spectroscopic measurements were made on samples pressed into KBr pellets using a Shimadzu 8400S FT-IR spectrometer, whereas for UV−visible spectral measurements a Perkin-Elmer Lambda 950 UV/vis/NIR spectrophotometer was employed. The ^1H NMR (500 MHz) spectra were recorded on a Bruker model Avance 500 spectrometer using $SiMe_4$ as the internal reference. The ESI-MS in positive ion mode were measured on a QTOF model YA 263 Micromass spectrometer. A standard built-in software package, Masslynx.4.0 supplied by Micromass, has been used for data simulation. Elemental analyses (for C, H, and N) were performed at IACS on a Perkin-Elmer model 2400 Series II CHNS analyzer.

X-ray Crystallography. Suitable crystals of **1** (red block, 0.48 × 0.22 × 0.12 mm^3) and **2** (red block, 0.40 × 0.24 × 0.16 mm^3) were mounted on glass fibers without any protection, whereas that of **4** (orange-yellow block, 0.30 × 0.18 × 0.10 mm^3) was coated with perfluoropolyether oil before mounting. Intensity data for the compounds were measured employing a Bruker SMART APEX II CCD diffractometer equipped with a monochromatized Mo Kα radiation (λ = 0.71073 Å) source using the $\omega/2\theta$ scan technique at 298(2) K (100(2) K for **4**). No crystal decay was observed during the data collections. The intensity data were corrected for empirical absorption. In all cases, absorption corrections based on multiscans using the SADABS software[28] were applied.

The structures were solved by direct methods[29] and refined on F^2 by a full-matrix least-squares procedure[29] based on all data minimizing $wR = [\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2]^{1/2}$, $R = \sum\|F_o| - |F_c\|/\sum|F_o|$, and $S = [\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$. SHELXL-97 was used for both structure solutions and refinements.[30] A summary of the relevant crystallographic data and the final refinement details is given in Table 1. For both **1** and **4**, the emerging structures show clearly that one of the end carbon atoms, C(21), of the propyl chains is disordered over two sites, C(21A) and C(21B), with occupancy factors of 0.56, 0.44 and

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Table 1. Summary of the Crystallographic Data for the Complexes **1**, **2**, and **4**

	1	**2**	**4**
composition	$C_{21}H_{39}N_6$-O_8Ni_3Cl	$C_{24}H_{45}N_6$-O_8Ni_3Cl	$C_{22}H_{43}N_6$-O_9Pd_3Cl
fw	715.15	757.24	890.27
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.1919(12)	11.7618(10)	11.677(3)
b, Å	12.6867(15)	12.3220(11)	12.398(3)
c, Å	12.8474(16)	12.4946(10)	12.821(6)
α, deg	107.846(3)	76.802(3)	102.305(4)
β, deg	90.380(3)	76.656(3)	103.702(4)
γ, deg	107.024(3)	78.646(3)	115.661(3)
V, Å^3	1503.5(3)	1695.4(2)	1516.1(9)
ρ_{calc}, Mg m^{-3}	1.578	1.483	1.948
temp, K	298(2)	298(2)	100(2)
λ (Mo Kα), Å	0.71073	0.71073	0.71073
Z	2	2	2
$F(000)/\mu$, mm^{-1}	742/1.999	792/1.778	886/1.906
$2\theta_{max}$, deg	49.62	50.76	49.98
reflections collected/unique	14 028/5144	16 158/6160	14 084/5328
R_{int}/GOF on F^2	0.0426/0.942	0.0316/0.998	0.0256/0.776
no. of params	361	388	381
$R1(F_o)$, $wR2(F_o)$ (all data)[a]	0.0731, 0.1546	0.0737, 0.1581	0.0396, 0.1180
largest diff peak and deepest hole, e Å^{-3}	0.662, −0.445	0.603, −0.367	1.350, −1.154

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR = [\sum[w((F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

0.58, 0.42, respectively, for these compounds. All non-hydrogen atoms (excluding C(21)) were refined anisotropically. The hydrogen atoms were calculated and isotropically fixed in the final refinement [d(C−H) = 0.95 Å, with the isotropic thermal parameter of $U_{iso}(H) = 1.2U_{iso}(C)$]. The SMART and SAINT software packages[31] were used for data collection and reduction, respectively. Crystallographic diagrams were drawn using the DIAMOND software package.[32]

Results and Discussion

Syntheses. Discrete μ_3-oxo-bridged trimetallic $[(ML)_3(\mu_3\text{-O})]ClO_4$ [M = Ni(II) and Pd(II)] complexes (**1**−**5**) have been synthesized through a single-pot synthesis. In the preparative procedure as outlined in Scheme 1, stoichiometric amounts of 2,3-butanedione monoxime, corresponding alkylamine, and the metal perchlorate (or acetate for Pd(II)) (in 1:1:1 mol ratio) were refluxed together in methanol in the presence of added triethylamine. The tridentate monoprotic Schiff-base ligands (2-alkylimino-3-oximobutane, HL) generated *in situ* in solution combine with the metal ion in the subsequent step to form crystalline compounds (**1**−**5**) in moderate to high yields. The oximato oxygen atoms from the ligands and the central μ_3-O bridge connect the metal centers together, providing a 9-MC-3 type of metallacrown topology[16−19] in the complexes **1**−**5**. Control experiments under a nitrogen atmosphere have confirmed that the presence of aerial oxygen is not mandatory for the syntheses of these compounds. This establishes our view that the source of μ_3-oxide in the present series of compounds is the traces of water present in the reaction mixtures. Hay et al.[6d] have isolated a μ_3-OH-bridged trinickel(II) compound under similar basic reaction medium using *N*,*N*′-bis(2-carbamoylethyl)ethylenediamine as ligand. With copper(II), however, many trinuclear complexes involving an μ_3-O or μ_3-OH bridge have been reported in recent time using derivatives of pyrazole as ancillary connecting ligands.[33,34] In certain cases, reversible transformations are possible between the μ_3-oxo-bridged compound and its hydroxo counterpart under appropriate conditions of pH of the solution.[33] In acidic medium, compounds **1**−**5** are, however, resistant to similar transformation, leading only to an intractable mass of unknown composition(s). Incidentally, it is pertinent to mention here that the Cu(II) complexes of HL^1 and HL^2 are also μ_3-oxo-bridged trinuclear species[5] and are reluctant to form the corresponding hydroxo-bridged product under acidic conditions.

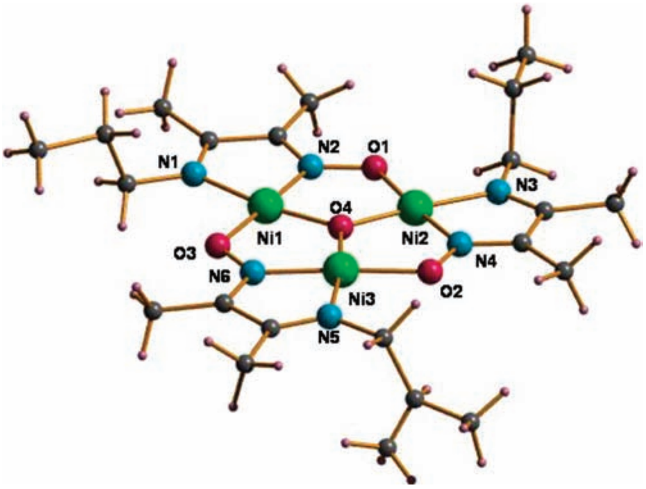

Figure 1. Partially labeled POV-Ray (in ball-and-stick form) diagram showing atom-labeling scheme for complex **1**.

The IR spectra of the nickel(II) complexes (**1**−**3**) display a strong band at ca. 1520 cm^{-1} due to the ν(C=N) vibrational mode of the alpha diimine moiety of the oxime ligands.[5] The corresponding band for the palladium complexes (**4**, **5**) appears at 1515 cm^{-1}. Also an expected twin pattern due to ν(N−O) stretching modes[35] appears in the form of an overlapping strong band at ca. 1095 cm^{-1} along with ionic perchlorate.

Description of Crystal Structures. The molecular structures and the atomic labeling schemes for **1**, **2**, and **4** are displayed in Figures 1, 2, and 3, respectively, which provide confirmatory evidence in support of their μ_3-oxo-bridged discrete trinuclear structures. Selected metrical parameters of these structures are summarized in Table 2. The isostructural nickel complexes (**1** and **2**) crystallize in the triclinic space group $P\bar{1}$ with two molecular

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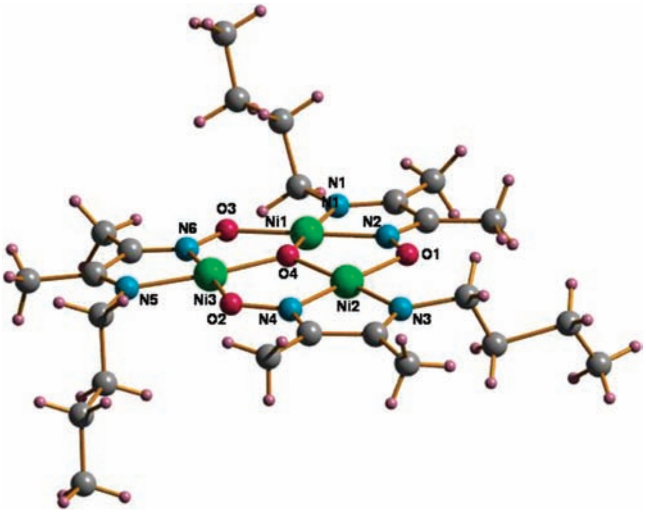

Figure 2. Partially labeled POV-Ray plot (in ball-and-stick form) of the cation in complex **2**.

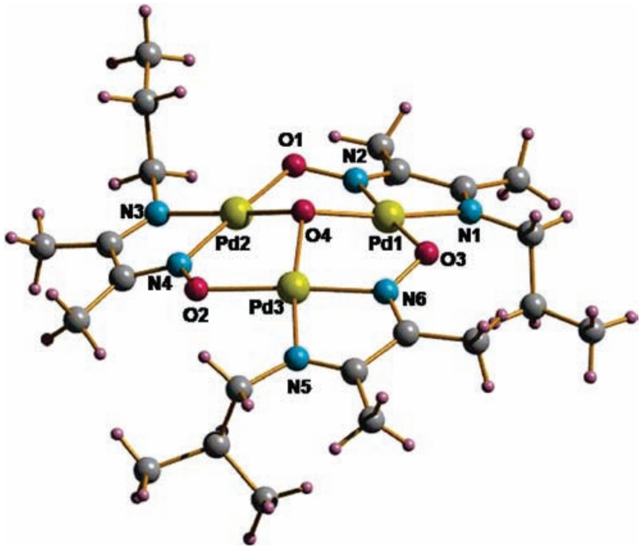

Figure 3. Partially labeled POV-Ray (in ball-and-stick form) diagram showing atom-labeling scheme for complex **4**.

Table 2. Selected Bond Distances and Angles for **1**, **2**, and **4**

	1	2	4
		Bond Distances (Å)	
M(1)−O(4)	1.809(4)	1.801(3)	1.976(4)
M(1)−N(2)	1.836(4)	1.832(4)	1.962(4)
M(1)−O(3)	1.859(4)	1.848(3)	2.032(4)
M(1)−N(1)	1.903(4)	1.889(3)	2.005(4)
M(2)−O(4)	1.791(4)	1.795(4)	1.975(4)
M(2)−N(4)	1.838(4)	1.832(4)	1.956(4)
M(2)−O(1)	1.849(4)	1.855(3)	2.047(4)
M(2)−N(3)	1.884(4)	1.875(4)	2.012(4)
M(3)−O(4)	1.797(4)	1.803(4)	1.989(3)
M(3)−N(6)	1.834(5)	1.832(4)	1.952(4)
M(3)−O(2)	1.866(4)	1.857(3)	2.044(4)
M(3)−N(5)	1.894(4)	1.882(4)	2.007(4)
		Bond Angles (deg)	
O(4)−M(1)−N(2)	89.73(18)	89.58(15)	92.38(16)
O(4)−M(1)−O(3)	92.08(17)	93.02(15)	90.69(14)
N(2)−M(1)−O(3)	178.15(19)	177.28(15)	176.85(16)
O(4)−M(1)−N(1)	171.47(19)	172.14(17)	171.56(16)
N(2)−M(1)−N(1)	82.45(19)	83.18(16)	79.93(18)
O(3)−M(1)−N(1)	95.77(19)	94.26(15)	96.97(16)
O(4)−M(2)−N(4)	90.06(18)	90.32(16)	92.18(17)
O(4)−M(2)−O(1)	93.27(17)	92.49(14)	91.91(15)
N(4)−M(2)−O(1)	176.20(18)	177.14(16)	174.16(16)
O(4)−M(2)−N(3)	172.93(18)	172.30(17)	169.53(16)
N(4)−M(2)−N(3)	82.90(19)	82.42(18)	79.66(18)
O(1)−M(2)−N(3)	93.76(17)	94.76(16)	96.72(17)
O(4)−M(3)−N(6)	89.53(19)	90.26(16)	91.59(17)
O(4)−M(3)−O(2)	92.66(17)	92.45(15)	91.84(14)
N(6)−M(3)−O(2)	177.16(17)	176.63(16)	176.52(17)
O(4)−M(3)−N(5)	172.8(2)	172.83(17)	169.96(17)
N(6)−M(3)−N(5)	83.3(2)	82.82(17)	80.16(19)
O(2)−M(3)−N(5)	94.48(19)	94.53(17)	96.50(18)

weight units accommodated per cell. The cationic species in **2** contains three tridentate monoanionic ligands $(L^2)^-$ $[(L^1)^-$ in the case of **1**], one μ_3-O atom, and three Ni(II) centers. The individual metal centers are planar, tetracoordinated with N_2O_2 donor sites. The N-donors, both imino N and oximino N, are contributed by L^2 (or L^1), while an oximato oxygen atom from an adjacent ligand molecule together with the central μ_3-O atom O(4) complete the remaining donor sites of each of the three equivalent Ni(II) centers, which are displaced only negligibly, 0.002−0.017 Å (0.020−0.024 Å), from these least-squares mean planes. The C−N and N−O distances of the oxime moieties are in the ranges 1.286(6)−1.304(5) [1.300(7)−1.315(6)] and 1.331(5)−1.350(5) Å [1.336(5)−1.346(5) Å], respectively, consistent with the coordinated oximato ligand in deprotonated form.[36] The Ni−O(4) distances in the central Ni_3O core are adjacent to each other, while the Ni(1)−O(4)−Ni(2), Ni(2)−O(4)−Ni(3), and Ni(3)−O(4)−Ni(1) angles are close to 120°. The Ni centers are almost equidistant from each other (Ni(1)···Ni(2), 3.100 [3.108]; Ni(2)···Ni(3), 3.100 [3.110]; and Ni(3)···Ni(1), 3.106 Å [3.129 Å]), forming an equilateral triangle, and the μ_3-O atom O(4) is displaced marginally by 0.176 Å [0.026 Å] from the center of this Ni_3 least-squares plane. The bond angles O(3)−Ni(1)−N(2), O(1)−Ni(2)−N(4), and O(2)−Ni(3)−N(6) are slightly short of linearity and vary in the range 176.20(18)−178.15(19)°, forcing the metal centers to drift marginally toward the central O(4) atom, thus generating precisely an inverse metallacrown topology[18] in this case.

The palladium complex **4** has most of the structural features similar to those of compounds **1** and **2**, with some variations apparently due to the larger size of the metal ion. Individual Pd centers have square-planar geometry. For example, the trans angles N(2)−Pd(1)−O(3) and O(4)−Pd(1)−N(1) are close to linearity (Table 2) and the Pd(1) atom is also displaced marginally by 0.035 Å (0.016 and 0.042 Å for Pd(2) and Pd(3), respectively) from the least-squares plane through O(3), N(1), N(2), and O(4) atoms. Corresponding metrical parameters are almost the same around the Pd(2) and Pd(3) centers. The C−N and N−O distances for the oxime moieties are in the ranges 1.295(7)−1.307(7) and 1.333(6)−1.340(6) Å, respectively, and differ negligibly from the relevant distances in compounds **1** and **2**. The central μ_3-oxygen O(4) is almost equidistant from all three metal centers with Pd−O(4) distances varying in the range 1.975(4)−1.989(3) Å, close

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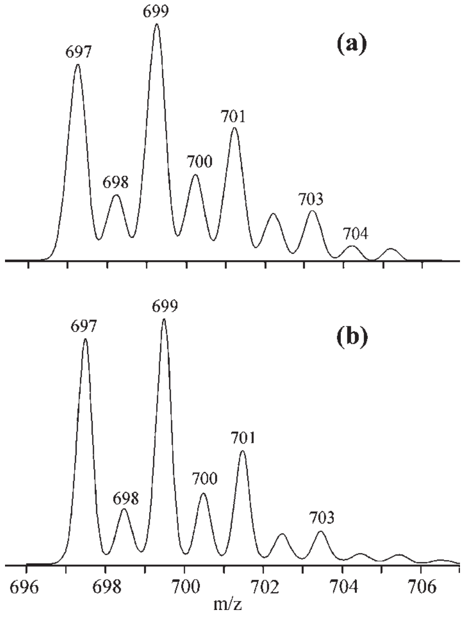

Figure 4. Molecular ion peak in the ESI mass spectrum (positive) for complex **3** in acetonitrile with (top, a) simulated and (bottom, b) observed isotopic distributions.

to what has been reported earlier for a μ_3-oxo Pd(II) complex.[15] Interestingly, the angles Pd(1)−O(4)−Pd(2) 108.85(17)°, Pd(2)−O(4)−Pd(3) 109.32(16)°, and Pd(3)−O(4)−Pd(1) 107.66(16)° are all much shorter than 120°, unlike what has been observed in the nickel(II) complexes **1** and **2**. The Pd atoms here are placed at the corners of a regular trigonal pyramid. This is reflected well in the dihedral angles (vary in the range 28.62−34.53°) between the N_2O_2 square planes around the individual palladium centers. Corresponding angles in **2** are in the range 6.25−9.31° (1.89−3.96° in **1**). This enforces the central oxygen atom O(4) to move out of the least-squares plane comprising the three Pd centers, the displacement being 0.687 Å. Comparatively large displacement (0.784 Å) of the central oxygen atom is also observed in the Pd_3O moiety of the heterometallic Pd_3AuO complex.[15] Similar to the Ni complexes, the Pd centers in **4** are also equally separated (Pd(1)···Pd(2), 3.213(9); Pd(2)···Pd(3), 3.233(1); and Pd(3)···Pd(1), 3.201(8) Å), and the included bond angles (Pd(1)···Pd(2)···Pd(3), 59.54(14)°; Pd(2)···Pd(3)···Pd(1), 59.92(2)°; and Pd(3)···Pd(1)···Pd(2), 60.54(3)°) are all close to 60°, forming an equilateral triangle. The angles O(3)−Pd(1)−N(2), 176.85(16)°, O(1)−Pd(2)−N(4), 174.16(16)°, and O(2)−Pd(3)−N(6), 176.52(17)°, are only marginally short of linearity, establishing clearly an inverse metallacrown topology but with a bowl shape (see later), unlike what has been observed with the Ni complexes **1** and **2**.

Mass Spectroscopy. ESI-MS data (in the positive ion mode) for the complexes **1**−**5** are listed in the Experimental Section. All these compounds demonstrate their respective molecular ion peak due to the $[M - ClO_4]^+$ ionic species ($[M - ClO_4 - CH_3OH]^+$ for **4** and **5**). In Figure 4 is displayed the isotope distribution pattern for the molecular ion peak for compound **3**, together with its simulation pattern. Congruous results are also obtained for the remaining compounds (Figures S1−S4 in the Supporting Information), thus providing evidence in favor of the proposed composition involving the μ_3-oxo trimetallic core in these compounds. Addition of acetic acid in trace amount to the analyte solutions before ESI-MS injections led only to the free ligand peak in the mass spectra, thus providing evidence for the decomposition of the compounds even in mild acidic conditions.

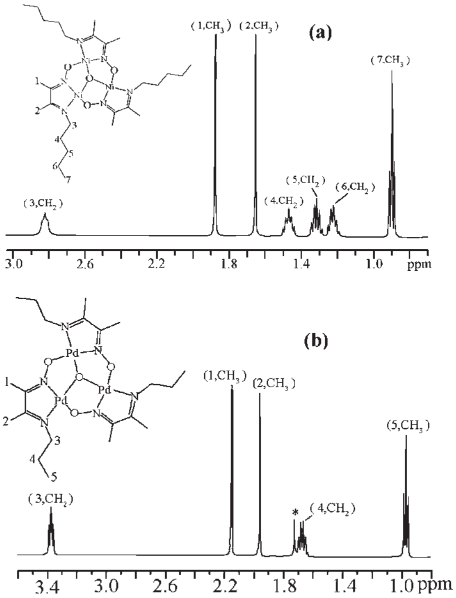

Figure 5. 500 MHz ^{1}H NMR spectra of (a) compound **3** and (b) compound **4** in dichloromethane-d_2 at 298 K. The peak marked with an asterisk denotes solvent impurity.

^{1}H NMR Spectroscopy. ^{1}H NMR spectra of **1**−**5** have been measured at room temperature in dichloromethane-d_2, and the data are summarized in the Experimental Section. The spectral profiles of **3** and **4** are displayed in Figure 5, a and b, respectively, as representatives of each type of complex along with their possible interpretations. The spectrum of **3** looks simple and straightforward. The observed signals include a pair of singlets of equal intensity appearing at 1.87 and 1.65 ppm due to the C(1) and C(2) methyl protons, respectively (atom labelings are as shown in Figure 5a). As expected, the C(3) methylene and C(7) methyl protons appear in the form of triplets at 2.82 (J = 7.00 Hz) and 0.90 ppm (J = 7.25 Hz), respectively. The remaining methylene protons involving the C(4), C(5), and C(6) atoms of the appended alkyl chain appear as multiplets in the region 1.50−1.43, 1.35−1.28, and 1.25−1.19 ppm, respectively, due to the vicinal couplings with the adjacent aliphatic protons. Thus in solution, as the spectrum confirms, the molecules of **3** possess a 3-fold axis of symmetry, in compliance with its 9-metallacrown-3 topology.

As expected, the spectral profiles of the palladium complexes are similar to those of the corresponding nickel complexes, confirming their metallacrown topology in solution. One interesting aspect, though, are the positions of the signals in **4** and **5**, which are systematically shifted downfield relative to the positions of the corresponding signals in the nickel complexes. The significant out-of-plane displacement and larger separations of the μ_3-oxo anion from the palladium centers in the trigonal-pyramidal Pd_3O core (~1.97 vs ~1.80 Å in the triangular-planar Ni_3O core) neutralize only partially the positive charges on the metal centers in **4** and **5**, which in effect draw more electron density from the surrounding ligand backbone, resulting in more deshielded spectra for these compounds. Thus, the spectrum of **4** displays a pair of singlets of nearly equal intensity appearing at 2.15 and 1.96 ppm due to the methyl protons C(1) and C(2), respectively, as labeled in Figure 5b. The C(3) methylene and C(5) methyl protons appear as triplets at 3.37 (J = 7.50 Hz) and 0.97 ppm (J = 7.25 Hz), respectively. The C(4) methylene protons, as expected, appear as a multiplet in the region 1.71−1.64 ppm due to couplings with the adjacent aliphatic protons. Thus in solution, as the ^{1}H NMR data indicate, the structures of compounds **1**−**5** possess a 3-fold axis of symmetry, in compliance with their 9-metallacrown-3 topology.

Concluding Remarks

Trinuclear oximato complexes containing a hitherto unknown discrete $[M^{II}_3(\mu_3\text{-O}]$ core (M = Ni, Pd) (**1**−**5**) in the midst of an inverse metallacrown topology have been reported. In the nickel complexes (**1**−**3**), the metal centers are situated at the vertices of an equilateral triangle with the μ_3-O atom located right at its center, thus generating a planar Ni_3O moiety (Figure 6a). In the palladium compounds (**4**, **5**) however, the Pd_3O core has a regular trigonal-pyramidal geometry with the μ_3-O atom occupying one of the apexes. This enforces the coordination planes around each Pd center to bend appreciably from each other (dihedral angles in the range 28.62−34.53°), thus providing more of a bowl shape to the overall metallacrown topology, as displayed in Figure 6b. The μ_3-O atom is shifted by 0.687 Å from the least-squares triangular plane through the Pd centers. Corresponding displacements are 0.026 and 0.176 Å for the nickel compounds that reveal almost a planar metallacrown topology. The observed structures are maintained in solution also, as confirmed by ^{1}H NMR and ESI mass spectroscopy.

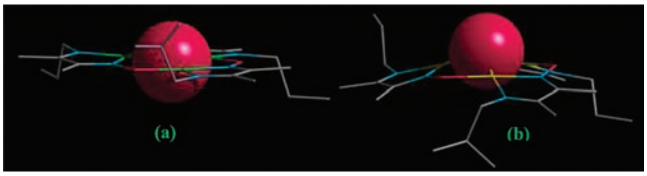

Figure 6. Relative displacement of the central μ_3-O atom from the metallacrown ring in the (a) nickel and (b) palladium complexes as depicted by a POV-Ray plot.

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Supporting Information Available: X-ray crystallographic files in CIF format and the ESI-mass spectra (Figures S1−S4) for compounds **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.