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Unusual Cationic Trinuclear Nickel Clusters Incorporating Oxazolines or *N*,*N*,*N*′,*N*′-Tetramethylethylene-1,2-diamine: Applications in Olefin Polymerization

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Supporting Information

ABSTRACT: The synthesis and characterization of two rare examples of the nickel(II)-containing trinuclear clusters of the general formula μ_3-halido-μ_3-hydroxotris(μ-halido) tris(L) trinickel(II) halide [halide = Cl (**2**), Br (**3**); L = 4, 4-dimethyl-2-(*o*-anilinyl)-2-oxazoline] are described. These materials are compared and contrasted to the "parent" chloride salt (**1**) of this series (L = *N*,*N*,*N*′,*N*′-tetramethylethylene-1,2-diamine and halide = Cl) and its congeners; **2** and **3** represent the first oxazoline-containing clusters of this structural class. Both **1** and **2** are shown to be active catalysts for the polymerization of olefins (styrene, methyl methacrylate, etc.) using a stoichiometric equivalent of methylaluminoxane as the copromoter, a situation that gives good yields of syndiotactic rich polymers. Density functional theory (B3LYP/6-31G*/LANL2DZ) is employed to hypothesize the likely origin of the activity demonstrated by these compounds.

Metal cluster compounds have long been recognized for their unique ability to activate unsaturated organic molecules in both a stoichiometric and a catalytic fashion. Such chemistry often produces structurally unusual metal-containing products due to such factors as the nature of the original (if any) metal—metal bonds, μ- or κ^n-ligand bonding motifs, and/or the potential for significant cluster rearrangement processes.[1] This area of coordination chemistry and catalysis has, for many decades, been dominated by low-valent late transition metals of (typically) the second- and third-row transition series. Of these, π-ligand (e.g., CO, PR_3) complexes of the platinum group metals, especially ruthenium, rhodium, platinum, and iridium, are of noteworthy relevance.[1] Many years ago, an unusually reactive material was reported by Sacconi et al. that resulted from the treatment of solutions of nickel(II) chloride with *N*,*N*,*N*′,*N*′-tetramethylethylene-1,2-diamine (tmeda).[2] The resulting green-colored product was atypically air-sensitive in relation to a wide range of other stable nickel complexes incorporating chlorido and N-donor ligands. This product was assumed to contain tetrahedrally coordinated Ni^{II}, viz., $NiCl_2$(tmeda),[2] despite the characteristics usually attributed to octahedral Ni^{II} centers. The reaction product of this material, upon exposure to air, was not unequivocally elucidated until almost a decade later when Turpeinen and Pajunen[3] revealed (X-ray) that Sacconi et al.'s "$NiCl_2$(tmeda)" complex likely reacts with opportunistic water to produce the trinuclear cluster (μ_3-Cl-μ_3-[OH]-[μ-{Cl}-(Ni{tmeda-κ^2N,N'}]$_3$)Cl (**1**) presumably via the release of HCl.[4] This rare trinickel(II) cationic coordination cluster was, at the time, the only nickel example displaying this unique capping OH and Cl arrangement in addition to the three bridging Cl atoms around the Ni_3 core (Figure 1).

More recent reports of single examples by Zangrando et al.[5] and an intriguing dihydroxy-capped species by Fossey et al.,[6] containing chelating hydroxamates or benzylamines, respectively, have since appeared (Chart 1). This latter material promotes the Lewis acid catalyzed nucleophilic addition of enecarbamates to ketones, presumably involving substrate coordination to an intact cluster species.[6]

None of these complexes has hitherto been tested for their polymerization potential nor have any extensive reactivity studies been carried out on such clusters.[3−7] As part of our systematic studies of bi-[8] and multidentate oxazolines,[9] we have been investigating the coordination chemistry, modification, and catalytic potential of the aniline—oxazoline hybrid ligand 4,4-dimethyl-2-(*o*-anilinyl)-2-oxazoline ($\mathbf{L_{ox}}$, Chart 1). In this Communication, we reveal that the major products of the reaction of $\mathbf{L_{ox}}$ with hydrated NiX_2 (X = Cl or Br) are, in fact, examples of such clusters (**2**, X = Cl; **3**, X = Br) that are structurally analogous to that of **1**. In addition, complexes **1** and **2** are shown to be active catalysts for the stereospecific polymerization of olefins such as styrene. This specificity is surmised to be due to the unique structural aspects of an intact methylated cluster in addition to the relative positioning of the backbone of the bidentate N-donor ligands and favorable orientation of both the highest occupied and lowest unoccupied molecular orbitals of an active catalytic form.

The treatment of aqueous EtOH solutions of hydrated NiX_2 (X = Cl or Br) with 1 equiv or an excess of $\mathbf{L_{ox}}$ leads to the formation of an analytically pure product material in the form of air-stable green powders for both X = Cl (**2**) and X = Br (**3**).[10] Crystallization of both halide congeners is difficult but can be carried out using solutions of the complexes via the slow evaporation (**2**, CH_3CN; **3**, EtOH) technique.[11] A representation of the cationic component of **2** is shown in Figure 2.

Elemental analysis data of materials in powder form are consistent to the structures determined by single-crystal X-ray diffraction.[10] Both complexes contain a cationic Ni_3 core unit with a capping OH and halido (X) group in addition to three bridging

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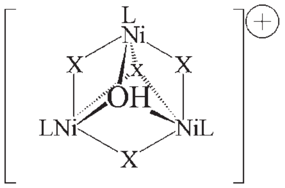
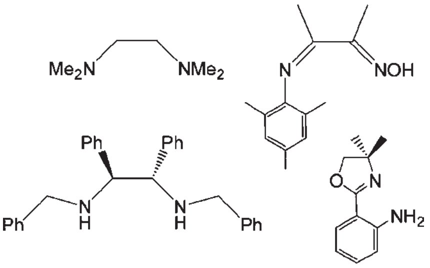


Figure 1. General schematic of the clusters described herein.

Chart 1. N,N′-Ligands "L", Including L_{ox} (Bottom, Right), That Are Known To Give the Class of Nickel Clusters Described Here



halides; a noncoordinated halide counterion completes the unit cell contents. The structural parameters of the core metal−X−OH units are comparable to other structurally characterized examples (see the Supporting Information, SI).[3−6,11] All three molecules of $\mathbf{L_{ox}}$ are oriented with the aniline groups located on the upper hemisphere of a hypothetical μ_3-X-μ_3-OH-μ-X_3-Ni_3 core in which the hydroxide is located on the northern vector aligning the two capping groups. This situation can be compared with the only other example of a non-C_2-symmetric N,N′-donor ligand complex, the hydroxamate complex of Zangrando et al.[5] Both materials reported here represent the first such nickel clusters with a six-membered chelating ring motif and are also the first such oxazoline derivatives. The general bond lengths and angles of both cores of **2** and **3** are similar to that of **1**; the remaining metal−oxazoline interactions are similar to other such Ni^{2+} materials[12] and, hence, are otherwise unsurprising.[3−6,11] As in the case of **1**, the three $\mathbf{L_{ox}}$ ligands (and, hence, the three Ni atoms and their bridging halido counterparts) are not symmetry-related in the solid state because of the torsion angle formed between the aniline and oxazoline rings of each $\mathbf{L_{ox}}$ unit. This creates a situation in which the three bridging halides are flanked by ligand backbones that allow either a wide, narrow, or rhomboid-shaped spacing above the halide atom relative to that of the capping OH group (Figure S-1 in the SI). Using **1** as the model complex, examination of the cationic component of this cluster by density functional theory (DFT; B3LYP/6-31G*/LANL2DZ level) was carried out. These results (Figure S-2 in the SI)[10] clearly distinguish the three unique Ni centers and resulting inequivalent bridging Cl atoms and provide quite a reasonable depiction of the cation found in the solid state of **1**.[3,4,10]

The production of stereoregular polymers has represented a major arena of chemical endeavor for over 60 years.[13] Mononuclear nickel complexes are well-known to be an active class of polymerization catalysts,[14] but the resulting polymer structures rarely display controlled architecture. Brookhart and co-workers pioneered the use of cationic Pd^{2+} and Ni^{2+} α-diimine species, often in the presence of excess methylaluminoxane (MAO), for the controlled polymerization of a wide variety of polar and apolar monomers.[15] As the class of clusters described here contains Ni^{2+} centers and is inherently cationic (in addition to the fact that the related dihydroxy complex of Fossey et al. is an effective Lewis acid catalyst[6]), we chose to investigate whether complexes such as **1** and **2** can be used to produce useful quantities of desirable polymers such as polystyrene (PS) or poly(methyl methacrylate) (pMMA). The initial screening of **1** for PS syntheses[3,4] at room temperature revealed (Table S-1 in the SI),[10] in contrast to typical nickel-mediated polymerizations,[13,14,16] that activation of the precatalyst with excesses of MAO resulted in *poorer polydispersity index (PDI) values* of the resulting polymers (Table S-1 in the SI; compare run 5 to runs 8, 10, and 11 and compare run 19 to run 20). Hence, approximately 1 equiv of MAO (per Ni) was found to be optimal for good polymer yields, high M_w values (up to $\sim 2 \times 10^6$ g mol^{-1}), and low polymer polydispersities (PDI $\leq \sim 1.7$; Table S-1 in the SI, run 5).[13] It is somewhat surprising, however, that both PS and pMMA were also found to contain considerable backbone regularity (NMR: see the SI). Further examination [gel permeation chromatography (GPC) and glass transition temperature (T_g)] of these materials revealed all of the characteristics of primarily (>70%) syndiotactic polystyrene (s-PS) and 65−75% syndiotactic pMMA (s-pMMA).[10] In both cases, the residual polymer makeup was atactic[7,14] in nature.[10] Of the clusters tested here, the parent tmeda material **1** displays superior catalytic potency over that of **2** (Table S-1 in the SI, runs 7 and 8) and was tested more extensively (Table S-1 in the SI), although admittedly these preliminary results have employed a limited set of reaction conditions (<10 g of monomer; neat or C_7H_8 solutions; room temperature; ambient pressure). Further optimization involving temperature ramping, with respect to the somewhat sluggish turnover numbers (TONs; s-PS, $\sim 2 \times 10^{-1}$ mol h^{-1}/Ni; s-pMMA, $\sim 1 \times 10^{-1}$ mol h^{-1}/Ni), is underway.[7] One preliminary observation is that the addition of toluene as solvent does seem to retard the relative reaction rates (compare run 5 to

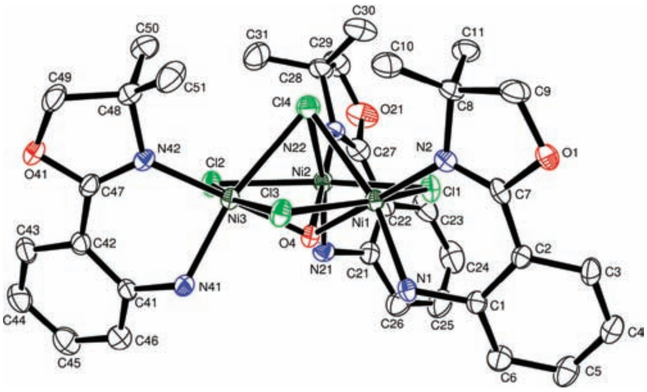


Figure 2. ORTEP representation of one of the cationic components found in the unit cell of complex **2**. Selected bond lengths (Å) and angles (deg): Cl1−Ni2, 2.4493(11); Cl1−Ni1, 2.4550(11); Cl2−Ni3, 2.4094(11); Cl2−Ni2, 2.4739(11); Cl3−Ni3, 2.4612(11); Cl3−Ni1, 2.5153(11); Cl4−Ni2, 2.5302(12); Cl4−Ni1, 2.5666(11); Cl4−Ni3, 2.5676(11); O4−Ni1, 1.976(3); O4−Ni3, 1.980(3); O4−Ni2, 1.991(3); Ni1−N2, 2.035(3); Ni1−N1, 2.067(3); Ni2−N22, 2.044(3); Ni2−N21, 2.072(3); Ni3−N42, 2.030(3); Ni3−N41, 2.079(3); Ni2−Cl1−Ni1, 76.22(3); Ni3−Cl2−Ni2, 75.85(3); Ni3−Cl3−Ni1, 75.94(3); Ni2−Cl4−Ni1, 72.86(3); Ni2−Cl4−Ni3, 72.15(3); Ni1−Cl4−Ni3, 73.23(3); Ni1−O4−Ni3, 101.46(12); Ni1−O4−Ni2, 99.46(12); Ni3−O4−Ni2, 98.22(11).

runs 10 and 11; Table S-1 in the SI) and suggests that solvent molecules may compete with the olefin for open metal coordination sites (i.e., the solvent has an inverse rate dependence on polymer production). A further observation is that the activated catalyst form appears to be unstable in the complete absence of olefin (Table S-1 in the SI, run 12).

These data suggested to us that selective single replacement of one of the chlorido groups via methylation (MAO) may result in the formation of the active catalytic species. Optimized calculations (DFT; B3LYP/6-31G*/LANL2ZD)[10] of a resulting mono-CH_3 cluster of **1** reveal that the most energetically favorable isomer likely involves the replacement of the chlorido group located *in the wide angle* between the tmeda ligands (Figures S-1−S-3 in the SI)[10] and that this now methylated position contains considerable singly occupied molecular orbital character. Conveniently, the corresponding LUMO, i.e., the likely site of olefin coordination, contains considerable orbital density in close proximity to this same methyl position and is located *directly above* this methyl group on the "top" of the cluster cation containing the OH cap (Figure S-1 in the SI).[10] Assuming this situation, the calculation of a cluster containing a unit of styrene inserted into the μ-H_3C-Ni_2 fragment was carried out. Energy minimization suggests a partially modified but intact cluster cation containing both four- and five-coordinate Ni atoms (Figure S-3 in the SI).[10] This situation may be involved when a dark-red coloration is observed in C_7H_8 solutions of **1** that have been treated with MAO/styrene.

The s-PS and s-pMMA obtained here have architectural features that rival those obtained by highly air-sensitive early-transition-metal or main-group complexes (e.g., zirconium- or aluminum-based)[14,17] but with the advantage of using several orders of magnitude lower amounts of MAO. In addition, the air-stable compounds described here incorporate ligands that are readily available and are resistant to both oxidation and nucleophilic attack (confer phosphorus ligands).[18] This situation is in sharp contrast to the many zirconium-based systems containing metallocenes, which are currently the best technology for the production of stereoregular polymers such as s-PS.[14] Encouraged by these results, we are examining a more extended series of monomers[7] for polymerization and attempting to modify (e.g., ligand exchange) these cluster frameworks for enhanced catalytic potency. In addition, aspects of the polymerization mechanism(s) are being examined to test our hypothesis concerning a coordination−polymerization[6,19] mechanism and the possible involvement and isolation of hitherto unknown monomethylated derivatives of **1** and/or **2**.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthetic details, X-ray diffraction data, CIF files, DFT calculations, polymerization data, Table S-1, and Figures S-1−S-3. This material is available free of charge via the Internet at http://pubs.acs.org.

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