



Nickel scorpionate complexes containing poly(aryl ether) dendritic substituents



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ABSTRACT

Novel dinitratonickel(II) complexes with bis(pyrazolyl)methane ligands at the focal point of poly(aryl ether) Fréchet dendrons of up to the third generation are reported. The complexes are accessible by direct reaction of the corresponding scorpionate ligand with Ni(NO₃)₂, or by treatment of the dibromidonickel derivatives with AgNO₃, although they reversibly convert to the dibromidos in the presence of KBr. The paramagnetic compounds could be characterized by ¹H NMR in solution. The molecular structure of metallodendrimers G0 and G1 [Ni(NO₃)₂{(Gn-dend)CH(3,5-Me₂pz)₂}] have been determined by X-ray diffraction methods. Both structures show an almost identical three-dimensional organization of the –ArCH₂CH(3,5-Me₂pz)₂Ni(NO₃)₂ moieties, with the nickel atoms exhibiting a distorted octahedral structure with a scorpionate-κ² and two bidentate nitrate ligands.

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1. Introduction

The fruitful chemistry of scorpionates was initiated with the introduction of poly(pyrazol-1-yl)borates by Trofimenko half a century ago [1]. Subsequent widespread research in the area raised these versatile di- or tridentate N-donors to the major league of useful ligands in coordination and organometallic chemistry, resulting in a plethora of reported complexes of most metals, which were found suitable for a wide range of applications [2]. More recently, significant advances in the synthesis of poly(pyrazol-1-yl) alkanes [3] have decisively facilitated numerous advances with this new generation of isoelectronic and isosteric, but neutral, scorpionate ligands [4].

We have contributed to the field with studies on dendrimers of different topologies decorated with scorpionate complexes. The preparation strategy for the ligands was based on the well known facile substitution of the respective reactive proton in the methine [5] or methylene [6] group of tri- or bis-(pyrazolyl)methanes, and consisted in the functionalization of the bridging carbon atom with a dendritic scaffold. Other different approaches have been reported to synthesize carbosilane dendrimers anchoring peripheral bis- or tris(pyrazolyl)borate complexes of rhodium [7]. Thus, we have also

described carbosilane dendritic cores grafting tris- or bis(pyrazolyl) methane complexes of molybdenum [8a] or palladium at their periphery, respectively, and evaluated the latter as polymetallic catalysts for the Mizoroki-Heck coupling [8b]. We have also reported monometallic dendrimers based on poly(aryl ether) dendrons (Fréchet dendrons) functionalized at the focal point with dibromido[bis(pyrazolyl)methane]nickel complexes [9], neutral and cationic derivatives of palladium(II) [10], and with bis- and tris(pyrazolyl)methane scorpionates of molybdenum in low and high oxidation state [11]. The Pd(II) compounds were explored as catalysts for the Heck reaction [10b], the Ni(II) complexes for ethylene polymerization [9], and the Mo(VI) metallodendrimers for catalytic olefin epoxidation [11]. Additionally, the single-crystal structures of a series of Pd(II) complexes from zeroth (G0) to the second (G2) generation, showed a similar 3D organization, layer by layer, on going from the G0 to the G2 structure, with the dendritic wedges progressively engulfing the metal center [10a]. Similarly, ¹H NMR studies performed with nickel(II) dibromido complexes in CDCl₃ solution, and using the nickel center as a paramagnetic probe to gather structural information, also led to the conclusion that the dendrons tend to wrap up the metal center in this solvent [9]. Herein we report on the synthesis and characterization, including ¹H NMR data, of the paramagnetic complexes [Ni(NO₃)₂{(Gn-dend)CH(3,5-Me₂pz)₂}] (Gn = G0–G3; pz = pyrazol-1-yl).

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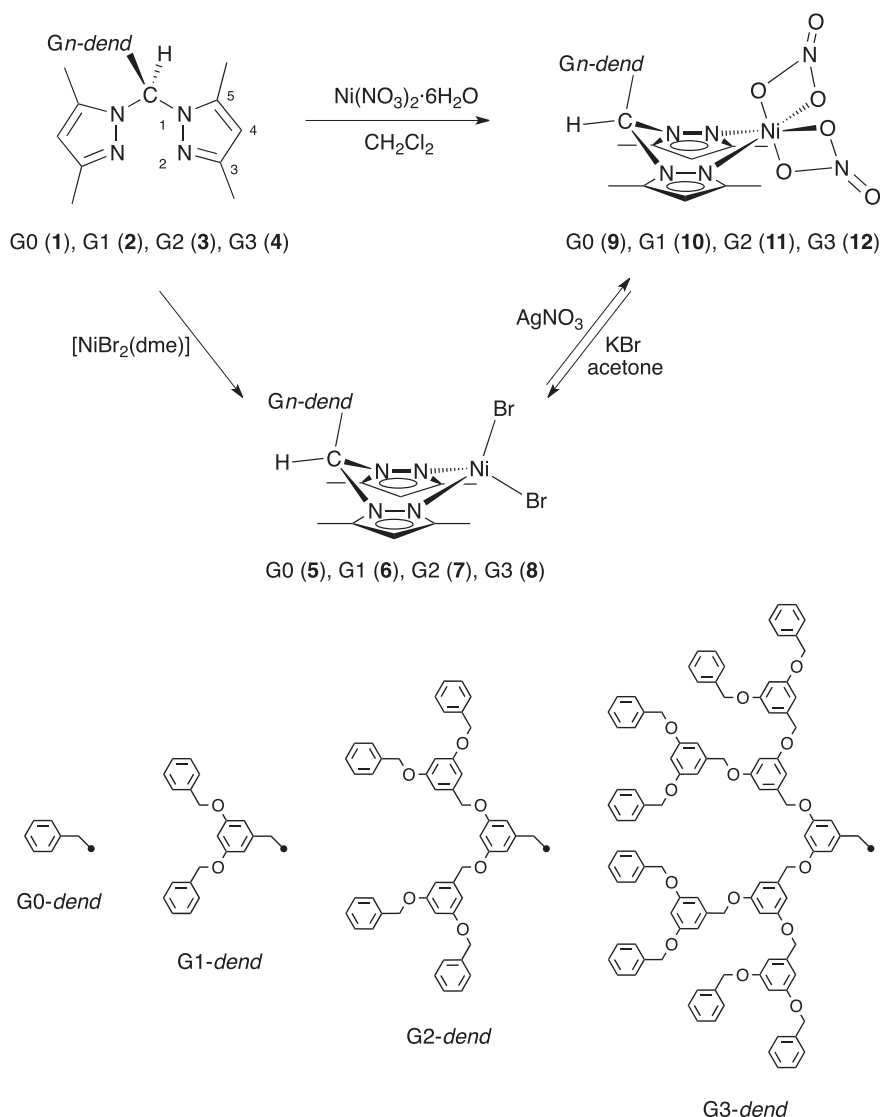
2. Results and discussion

2.1. Synthesis and characterization of nickel complexes

The nitrate complexes **9–12** can be readily prepared using the procedure reported by Baho and Zargarian for the synthesis of a related compound with interesting chromic properties in solution [12] (i.e., $[\text{Ni}(\text{NO}_3)_2(\text{Ph}_2\text{C}(\text{pz})_2)]$). Accordingly, addition of 1 equiv of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to a dichloromethane solution of chelates **1–4** [9], followed by reflux (Scheme 1), resulted in the steady disappearance of the insoluble nickel precursor with concomitant formation of a vivid lime-green solution. After workup (see Experimental Section), complexes **9–12** were isolated as dark green solids (yields ca. 90%), they are stable to air in the solid and in solution, and are insoluble in alkanes but soluble in chlorinated and aromatic solvents or in acetone, and slightly soluble in diethyl ether.

The complexes **9–12** can alternatively be synthesized from the corresponding nickel dibromido complexes **5–8** by reaction with two equivalents of AgNO_3 (Scheme 1). Interestingly, no progress of the reaction was observed using the conditions applied in direct

reactions between nickel nitrate and ligands **1–4** (i.e., CH_2Cl_2 , reflux, 4 h). Nevertheless, the reactions proceed to completion in acetone at room temperature after 6 h, with a striking color change of the solution from the deep blue of the dibromidos to a green solution for the nitrates, and with simultaneous precipitation of AgBr . The reaction is also quite straightforward in this solvent and the products are isolated in high yields (ca. 90%), although it is obvious that a direct synthesis of the nitrates from **1–4** is more convenient than the two steps procedure. The formation of compounds **9–12** from the dibromidos **5–8** is fully reversible by simply stirring the acetone solutions of the nitrates in the presence of an excess of KBr (Scheme 1), in a transformation that is evident to the naked eye by the corresponding drastic color change. Whilst the conversion between the two series of complexes is driven by the precipitation of AgBr on going to the nitrates, the shift back to dibromidos **5–8** is in agreement with the relatively labile coordination of the nitrate ligand described for compounds of same type [12,13]. This lability involves a flexible denticity through the oxygen atoms of the nitrate ion ($-\kappa^2$, $-\kappa^1$, or $-\kappa^0$), as has been observed for related $\text{Ni}(\text{II})$ [12,14] and $\text{Cu}(\text{II})$ [15] compounds. In fact, we have found—either at preparative or at NMR-tube scale—that the



Scheme 1. Synthesis of dendronized dinitratonickel scorpionate complexes.

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