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Review

# High-valent first-row transition-metal complexes of tetraamido (4*N*) and diamidodialkoxido or diamidophenolato (2*N*/2*O*) ligands: Synthesis, structure, and magnetochemistry

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## Contents

## Abstract

Introduced approximately two decades ago, macrocyclic deprotonated tetraamido (4*N*) and, nearly a decade earlier, acyclic diamidodialkoxido or diamidophenolato (2*N*/2*O*) ligand systems have been used, among other things, for the synthesis of a wide variety of high-valent complexes of iron, manganese, cobalt, vanadium, nickel, chromium, and copper. Structural, magnetic, and catalytic properties of these mononuclear, dinuclear, and polynuclear complexes created by the Collins group are reviewed. The present account continues an overview of complexes of this type published recently and devoted to iron species exclusively [Chanda et al., J. Inorg. Biochem., 100 (2006) 606], which provide the first highly effective small molecule mimics of peroxidase enzymes, called TAML activators. The story of the reviewed first-row complexes does not include the diverse and instructive chemistry discovered for osmium, but like the osmium chemistry, it derives its greatest significance from the fact that key members of the various species mark the steps along the design pathway that led to iron-TAML activators. Consideration is given to recent questioning in the literature of the innocence of a TAML system that was designed to be innocent. The reasons underlying the now 15-year old refocusing of our research program on oxidation catalysis and green chemistry with the associated termination of research into designed molecule-based magnetic

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materials are explained. Our closing contributions from the mid-1990s to the design of molecule-based magnetic materials are reviewed. Previously reported data are discussed in conjunction with newly obtained information on the complexes using density functional theory.

*Keywords:* High-valent transition metal complexes; TAML complexes; Tetraamido macrocyclic ligand complexes; Diamidodialkoxido complexes; Diamidodiphenolato complexes; Ligand innocence; Molecule-based magnetic materials; Magnetochemistry; Green chemistry

## 1. Introduction

The powerful biological oxidizing systems of peroxidases, cytochrome P450s and similar enzymes [1,2] challenge chemists to understand and to reproduce their exceptional reactivity in synthetic mimics in related or tangential design spaces [3]. The phenomenal oxidizing power of the enzymes coexists with appreciable resistance to “self-oxidation”. This coexistence is achieved by the employment of design elements that direct the selectivity of the reactive intermediates toward rapid substrate oxidation, thus allowing oxidatively fragile components of the enzyme to be kinetically camouflaged and enabling the enzymes to perform numerous catalytic turnovers before they finally succumb to degradation under the intense reactivity pressure. Ideally, synthetic low-molecular-weight catalysts should possess similar functional properties, preferably with an easily accessible range of reactivity, diverse controllable selectivity, and even superior performance especially in terms of the turnover numbers. Now knowing what is needed, we can assert that to create such catalysts requires one to focus intently upon the design and synthesis of appropriate ligand systems that both convey what one imagines will be the required electronic structure to the chosen catalytic metal atom while also being resistant to hydrolysis (given that the most important solvent to master is water) as well as to the aggressive oxidizing conditions that the catalysts are being designed to unleash. Then, after complexation of a suitable metal, the man-made catalyst should activate the primary oxidizing agents of nature, *viz.* hydrogen peroxide and dioxygen. Their oxidizing equivalents should be delivered to target molecules avoiding rapid catalystacidal self-oxidation of both the suicidal and homicidal varieties.

The Collins group initiated such a design program more than 25 years ago with a focus on learning how to slow down the degradation processes of ligand systems conceived to be electronically capable of supporting appropriate reactive intermediates. This was seen as an alternative and more viable technological approach to the ingenuity in enzyme evolution, which focuses on speeding up the targeted reactions [3]. In recent years, we have been able to confirm that the Collins iterative design protocol, developed to understand how to protect ligand systems from rapid oxidative and hydrolytic degradation, is a sine qua non for achieving useful small molecule enzyme-like synthetic catalysts for oxidative processes [4]. At the top of our research pyramid stand iron(III) complexes of the *T*etra*A*mido *M*acrocyclic *L*igand (TAML) system [5,6]. These phenomenal activators of hydrogen peroxide in water [3,7,8] and, less usefully at present of dioxygen in weakly coordinating non-aqueous media [9], show superior activity in a variety of industrially, environmentally, and strategically important processes including persistent pollutant remediation, pulp and paper bleaching [10], chemical effluent treatment, chemical warfare and biological decontamination [11], degradation of persistent chlorinated pollutants [12], desulfurization of diesel fuel [13], fine chemical synthesis, and water purification [14].

A number of TAML systems that deliver the desired catalytic activity have been designed, synthesized and thoroughly explored. But the *P*oly*A*nionic *C*helating (PAC) ligands that were initially introduced differ noticeably from the more recent TAML systems [15]. Almost a dozen transition metals have been incorporated into PAC ligand and TAML systems. Although only iron-TAML complexes have proven to date to be powerful oxidation catalysts, manganese-TAMLs give less useful catalysts. In addition, the many different metal systems have revealed a spectrum of new features related to general aspects of coordination chemistry showing unusual geometries and coordination numbers, and magnetic properties.

This last area deserves special mention in the introduction, because our having to abandon it was especially chagrining. A design program, complementary to the catalyst design program, was aimed at contributing to developing the synthetic and related thinking required for building magnetic crystals of predetermined magnetic behavior and it was beginning to bear fruit by the early 1990s. This program arose as the unusual higher spin ground states were being found for mononuclear $M_a$PAC ligand complexes and it was realized that $M_a$PAC species could be coupled to other paramagnetic ions ($M_b$) at the $M_a(OR)_2$ moieties giving $M_a(\mu\text{-}OR)_2M_b$ multimetallic ions that had the potential to have ground state electronic configurations with high numbers of weakly coupled spins. Moreover, it was realized that high-spin ground states were to be reasonably expected in these multinuclear ions because the unpaired spin structures on $M_a$ ions are such that they should favor ferromagnetic exchange interactions with $M_b$ ions whenever $M_a$ had a d-electron count $\leq 7$, regardless of the electronic structure of $M_b$. This notion was based on the realization that the principal d$\sigma$ orbital on $M_a$ is made especially antibonding by the strong PAC ligand $\sigma$-donor system and it was this feature that was giving rise to the high-spin ground states of $M_a$PAC species with the d-electrons being distributed among the four remaining more closely grouped d orbitals. Thus, the major $M_a$ d-orbital communicating through the –OR bridges with $M_b$ could reliably be expected to be empty and therefore to interact with $M_b$ to give ferromagnetic exchange. This, it was further rationalized, meant that the PAC ligand systems offered promise, following their further development into iterated complexes capable of bridging two $M_b$ magnetic ions, for use as synthons for building magnetic crystals where one would be able to predetermine the sign of the local exchange interactions and extend these globally to the crystal and also to learn how