

The coordination chemistry of tripodal tetraamine ligands

Allan G. Blackman *

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

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Abstract

The coordination chemistry of tripodal tetraamine ligands is reviewed. These ligands contain a tertiary N atom bonded to three arms, each of which contains an N-donor atom, via at least one methylene group on each arm, and generally bind to a single transition metal or lanthanide ion using all four N-donor atoms. Fifty-four such ligands, not including substituted derivatives, are described. References are given to methods for the synthesis of these, and the coordination chemistry of each ligand with both transition metals and lanthanide ions is detailed, with emphasis being placed on structural features of the resulting metal complexes. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Tetradentate tripodal ligands have the general structure depicted in Fig. 1 and consist of a central donor atom X attached to three arms, each of which also contains at least one methylene group and a donor atom Y.

A large number of such ligands containing identical sets or combinations of the donor atoms N, S, O and P are known, but this paper will discuss only those ligands having four N donor atoms and which normally bind to a single metal ion using all of these. These tetradentate tripodal tetraamine ligands thus contain a single tertiary N atom, which ‘caps’ the tripod, and one N-donor atom on each arm. The ligands can differ both in the lengths of the arms and in the nature of the N-donor atoms on each arm and there are at least 54 such ligands (not including their alkylated and substituted derivatives) known. The majority of these ligands have been prepared only in the last 20 years and much of their coordination chemistry remains to be explored in detail. This paper presents a review of the chemistry of tripodal tetraamine ligands. It

aims not to be comprehensive in terms of a discussion of every known complex containing a tripodal tetraamine ligand (such a task would fill a book for the complexes of tris(2-aminoethyl)amine (tren) alone!); rather, it aims to provide the reader some idea of the range of chemistry that has been carried out (and indeed remains still to do) with these ligands. Each section details the synthesis of the ligand, and discusses some of its more important transition metal and (where applicable) lanthanide complexes, with particular emphasis being placed on structural aspects of these.

2. General remarks

2.1. Nomenclature

As is the case with many organic ligands, most tripodal tetraamine ligands are known by an abbreviation, usually of three or four letters, nominally derived from the full name of the ligand. Thus, the systematically named ligand *N,N*-bis(2-aminoethyl)ethane-1,2-diamine is better known as tren (Section 3.1.1), the abbreviation being derived from the non-systematic name

* Tel.: +64 3 479 7931; fax: +64 3 479 7906.

E-mail address: blackman@alkali.otago.ac.nz.

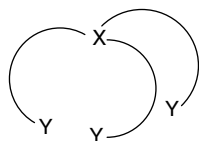


Fig. 1. General structure of a tetradentate tripodal ligand.

tris(2-aminoethyl)amine, and the name tren is in fact part of the 2004 provisional IUPAC recommendations on ligand abbreviations. However, this is the only tripodal tetraamine ligand for which IUPAC has proposed such a recommendation, and the abbreviations of other tripodal tetraamine ligands are somewhat haphazard and confusing. For example, the common ligand tris(2-pyridylmethyl)amine (Section 3.2.9) is variously abbreviated as tpa or tmpa, while the abbreviation bppa has been used for both bis(1-pyrazolylmethyl)(2-pyridylmethyl)amine (Section 4.2.8) and bis(2-(3,5-dimethylpyrazol-1-yl)ethyl)(pyrazol-1-yl)methyl)amine (Section 4.2.9). Obviously, this is an unsatisfactory situation and ideally a systematic abbreviation system should be developed. However, in what follows, the ligand abbreviations given are those used most commonly in the literature (in some cases, more than one), and, where no abbreviation exists, a suitable one is proposed.

2.2. Synthesis

While the majority of tripodal tetraamine ligands discussed herein have been synthesised in the laboratory, some have been found in natural systems. Trpn (Section 3.1.4) and abbp (Section 3.1.8) have been found in the aquatic plants *Potamogeton distinctus* and *Sagittaria trifolia* L. [1], and also in the thermophilic eubacteria *T. thermophilus* HB8, *T. filiformis* Wai33 A1, *T. flavus* AT-62 and *T. caldophilus* GK24 [2].

Various methods are available for the synthesis of tripodal tetraamine ligands, with the route of choice generally dictated by the nature of the donor atoms on the three arms. All routes have in common the alkylation of the N atom of ammonium ion, or a primary or secondary amine precursor, with this N atom becoming the tertiary N atom of the resulting tripodal ligand. Bromo- and chloroalkylphthalimides are useful for the synthesis of ligands having aliphatic donor atoms as these can alkylate both primary and secondary N atoms at elevated temperatures, and deprotection using acid then gives the amine directly. Aliphatic N-donor atoms can also result from reduction of nitrile precursors with such reagents as $\text{LiAlH}_4/\text{H}_2\text{SO}_4$ or $\text{NaBH}_4/\text{Raney nickel}$, with the nitrile precursors generally being prepared from the reaction of acrylonitrile with the appropriate protected amine. Ligands having aromatic amine donor atoms are often prepared using haloalkylpyridines, imidazoles or pyrazoles as alkylating agents, while 2-vinylpyridine has proven useful as a reagent for the

introduction of 2-(pyridylethyl) arms and 1-hydroxymethylpyrazole has been used in the synthesis of a number of pyrazole-containing tripodal ligands. The Mannich reaction has also been used in the synthesis of a number of tripodal tetraamine ligands.

2.3. Stereochemistry

The so-called “symmetric” tripodal ligands, in which all three arms are identical, usually have nominal C_{3v} symmetry about the central N atom, providing all the arms have the same conformations about the C–C and C–N bonds. Ligands in which the lengths of the arms differ, or which have N-donors of different types on each arm, are usually termed “asymmetric” and are of C_s symmetry or lower. Crystal structures of the free ligands show a variety of geometries, ranging from a “splayed” arrangement of the three arms, to internally H-bonded structures in which the three arms are folded to form a cavity into which an anion can bind. The latter arrangement is often found in protonated salts of the ligands.

Coordination to a metal ion generally results in a complex having a lower symmetry than the free ligand, depending on the coordination number of the metal ion. Four-coordinate complexes of tripodal amine ligands, in which all four N atoms are coordinated to a single metal ion, are relatively rare, as the ligands are often too constrained to be able to accommodate the square planar or tetrahedral geometries preferred by such complexes. Thus, four-coordinate complexes of tripodal tetradentate ligands often display either a very distorted tetrahedral geometry, or a trigonal pyramidal geometry, with the tertiary N atom occupying the apical position. Five-coordinate complexes are much more common, and the geometries of these occupy a continuum between the idealised trigonal bipyramidal and square pyramidal geometries. Such complexes are characterised by their τ value, where $\tau = 1$ for perfect trigonal bipyramidal geometry and $\tau = 0$ for perfect square pyramidal geometry [3]. It has been found that complexes having trigonal bipyramidal geometries are significantly more numerous than those having square pyramidal geometries. Indeed, five-coordinate complexes containing ligands such as tren (Section 3.1.1) and tpa (Section 3.2.9), almost invariably display trigonal bipyramidal geometries with the tertiary N atom at an apical position, reflecting the low-energy conformation of the ligand in such complexes. However, when the ligand arm lengths differ, such that a mixture of five- and six-membered chelate rings are present in the complex, square pyramidal geometries become more common, due presumably to the increased strain resulting from the accommodation of larger chelate rings in a trigonal bipyramidal geometry. Six-coordinate complexes containing tripodal amine ligands usually adopt distorted octahedral geometries, while seven coordinate

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