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Overcoming the chelate effect: hypodentate coordination of common multidentate amine ligands

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Abstract

The concept of hypodentate coordination, in which a multidentate ligand binds to a transition metal using fewer than the maximum number of donor atoms, is briefly reviewed, with particular reference to common aliphatic, alicyclic and aromatic amine ligands. ***To cite this article: A.G. Blackman, C. R. Chimie 8 (2004)***.

Résumé

Surmonter l'effet chélatant : coordination hypodentée des ligands aminés multidentés usuels. Le concept de la coordination hypodentée, dans lequel un ligand multidenté se lie à un métal de transition sans utiliser tous les atomes donneurs, est succinctement revu, avec une attention particulière portée sur les ligands aminés usuels aliphatiques, alicycliques et aromatiques. ***Pour citer cet article : A.G. Blackman, C. R. Chimie 8 (2004)***.

Keywords: Hypodentate; Transition-metal complex; Amine ligand

Mots clés : Hypodenté ; Complexe de métaux de transition ; Ligand aminé

Abbreviations: abba, *N*-(4-aminobutyl)-*N,N*-bis(2-aminoethyl)amine; ahba, *N*-(6-aminohexyl)-*N,N*-bis(2-aminoethyl)amine; apba, *N*-(5-aminopentyl)-*N,N*-bis(2-aminoethyl)amine; baep, *N,N*-bis(2-aminoethyl)-*N*-3-aminopropylamine; bipy, 2,2′-bipyridine; cyclam, 1,4,8,11-tetraazacyclotetradecane; cyclen, 1,4,7,10-tetraazacyclododecane; dien, diethylenetriamine; EDTRA, ethylenediaminetriacetate; en, ethylenediamine; linpen, pentaethylenehexaamine; mnt, maleonitriledithiolato-S,S′; tacn, 1,4,7-triazacyclononane; tdt, 3,4-toluenedithiolato-*S,S*′;; terpy, 2,2′:6′,2″-terpyridine; tpen, *N,N,N*′;*N*′;-tetrakis(2-pyridylmethyl)ethylenediamine; tren, tris(2-aminoethyl)amine; trien, triethylenetetraamine.

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1. Introduction

Reaction of a solvated transition-metal ion with a multidentate ligand generally results in coordination of all suitably-disposed ligand donor atoms to form a metal complex containing the maximum possible number of chelate rings. Thus, ligands such as ethylenediamine (1,2-ethanediamine) and 2,2′-bipyridine almost invariably coordinate to transition metals in a bidentate fashion and the number of metal complexes containing these chelated ligands is legion. This propensity for coordination of all donor atoms is usually rationalised in terms of the Chelate Effect, a subject on which much has been written [1]. However, there is a small but steadily growing number of complexes in which multidentate ligands are coordinated through fewer than the maximum number of donor atoms. Although such complexes have been known for decades, it is only relatively recently that the word 'hypodentate' has been coined by Constable to describe a ligand "in which fewer than the maximum number of donor atoms are involved in interactions with metal centres" [2], and this terminology is now being increasingly used in the chemical literature[1]. Although the term "hypodentate" was originally introduced to refer to a particular mode of ligand binding, its use has also extended to complexes containing hypodentate ligands, and thus it is common to see reference to a 'hypodentate complex'. Both usages will be found herein. Hypodentate coordination of multidentate ligands is more common than might at first be thought; monodentate coordination of potentially chelating oxoanion ligands such as carbonate, phosphate, sulfate and any number of carboxylates is not at all uncommon, and such ligands lie outside the scope of this discussion. Even amongst amine ligands, hypodentate coordination is encountered surprisingly frequently, and thus the following article is restricted to complexes containing common multidentate amine ligands bound in a hypodentate fashion. Important factors in the rational syntheses of such complexes are also detailed.

2. Hypodentate complexes

2.1. Nomenclature

The nomenclature of hypodentate coordination merits comment, as a variety of methods have appeared in the literature, and a consistent approach to the naming of such complexes is obviously to be preferred. As an example of the confusion that can occur, protonated monodentate ethylenediamine is often abbreviated as enH (for example, in the complex cation $[Co(NH_3)_5enH]^{4+}$), but ambiguity can arise when the monodentate ethylenediamine is not protonated; the complex *fac*-$[Re(CO)_3(en)_2](O_2PPh_2)$ (section 2.2) contains both chelated and monodentate ethylenediamine ligands, a fact not immediately obvious from this simple formula. Thus, a more complete notation is required in such cases and IUPAC recommends one of two possible unambiguous nomenclature schemes [3]. The first involves specifying the bound donor atoms of the ligand in italics; in this case, monodentate ethylenediamine would be designated (using the correct IUPAC naming) as 1,2-ethanediamine-*N*, whereas the chelated ligand would be 1,2-ethanediamine-*N*,*N*′. The kappa convention is recommended for more complicated ligands; the italicised donor atom is in this case preceded by κ, and is placed immediately following the portion of the ligand to which it directly applies. Thus the two possible tridentate modes of binding of triethylenetetramine (Fig. 5) would be designated as *N*-(2-amino-κ*N*-ethyl)-*N*′-(2-aminoethyl)-1,2-ethanediamine-κ^2*N*,*N*′ (bound through one primary and two secondary N atoms) and *N*,*N*′-bis(2-amino-κ*N*-ethyl)-1,2-ethanediamine-κ*N* (bound through one secondary and two primary N atoms). Even for simple ligands, such notation often becomes unwieldy and cumbersome (the Re complex above, for example, would be *fac*-$[Re(CO)_3$(1,2-ethanediamine-*N,N*′)(1,2-ethanediamine-*N*)$](O_2PPh_2)$ or *fac*-$[Re(CO)_3$(1,2-ethanediamine-κ^2*N,N*′)(1,2-ethanediamine-κ*N*)$](O_2PPh_2)$ under the two systems), and, in many cases, a picture is worth (literally) a thousand words.

2.2. Hypodentate aliphatic amine ligands

Every undergraduate textbook uses ethylenediamine as the archetypal example of a chelating ligand, and the possibility that it can bind in a hypodentate fash-

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[1] He also proposes the term *sundentate* to describe a ligand in which all donor atoms are coordinated to the metal, although this does not appear to have yet been used in the chemical literature.