

Review

Compounds formed by Mannich reaction of a coordinated amine with an α -methylene nitro compound and formaldehyde – Syntheses and structures



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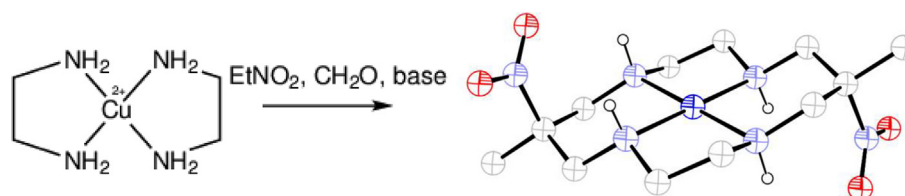
 α -Methylene nitro-compounds

Nitro-substituted tetraaza-macrocycles

Crystal structures

ABSTRACT

This review covers compounds formed by Mannich-like reactions of coordinated amine-compounds with an α -methylene nitro-compound (usually nitroethane) and an aldehyde (predominantly formaldehyde) to form a compound with two primary amine functions joined by a $-\text{NH}-(\text{CH}_2)-\text{C}(\text{NO}_2)(\text{CH}_3)-(\text{CH}_2)-\text{NH}-$ link, forming a new chelate ring. Most reported compounds have tetraaza-macrocyclic ligands. Copper(II) is the usual “templating” metal ion, with compounds of nickel(II), palladium(II), platinum(II) and gold(III) also reported. The refcodes of compound with structures in the Cambridge Crystallographic Data Centre files are listed and structural figures of representative examples shown.



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1. Introduction

This review is concerned with compounds formed by Mannich-like condensations of two coordinated amine groups with an α -methylene nitro compound, $R-(CH_2)_2-NO_2$, usually nitroethane, and an aldehyde, almost exclusively formaldehyde, to form compounds of polydentate ligands with the two amine groups linked by a $-NH-CH_2-C(R)(NO_2)-CH_2-NH-$ bridging group.

Alan Sargeson in 1977 reported the facile reaction of tris(ethane-1,2-diamine)cobalt(III) with formaldehyde and ammonia, resulting in the formation of clathrochelate compounds with the $N(CH_2-NH-)_3$ capping group [1,2]. He followed this with reports of the reaction of tris(ethane-1,2-diamine)cobalt(III) with the triprotic carbon acid nitromethane and formaldehyde, F, under basic conditions leading to the formation of clathrochelate compounds with the tripodal capping group $O_2N-C(CH_2-N-)_3$ [3–9].

During a period of sabbatical leave at Sargeson's laboratories in the Chemistry Department of the Australian National University in Canberra in 1980 the author attempted to extend these reactions to amine compounds of the labile nickel(II) and copper(II) ions. Facile reactions occurred and products incorporating nitromethane and formaldehyde were isolated but these did not have clathrochelate or macrocyclic ligands. The studies moved to reactions of diprotic carbon acids with ionisable methylene groups, initially with nitroethane, NE, which were immediately successful. Rapid reaction of bis(ethane-1,2-diamine)copper(II) with formaldehyde, F, and one mole proportion of NE in refluxing methanol, with triethylamine as base, formed a compound with a tetradentate ligand cation with two ethane-1,2-diamine residues linked by a $-NH-CH_2-C(Me,NO_2)-CH_2-NH-$ linking group, which formed a new six-membered chelate ring (Scheme 1.1). With excess NE the reaction continued to link the second amine functions of the diamines by a second bridging link to form a [14]-membered, di-nitro substituted tetraaza-macrocyclic ligand cation [10]. Analogous, but slower, reactions of $[Ni(en)_2]^{2+}$ with NE and F formed the analogous di-nitro-substituted macrocyclic cation, but with more poly-

meric by-products – the tetradentate mono-nitro nickel(II) cation was not isolated [11]. The nitro functions of these macrocyclic cations were readily reduced to amine functions, thus providing a synthetic route to a range of novel ligands with pendant primary amine functions.

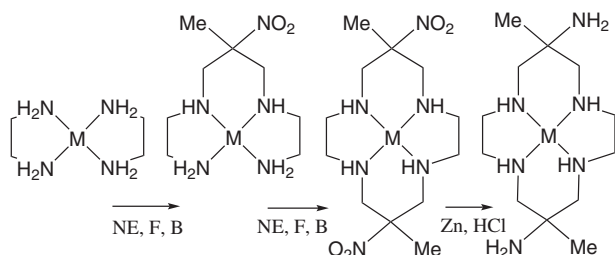
This review covers the subsequent extensions of these reactions to compounds of other amines and to amine compounds of other metal ions. Many of the publications reporting these reactions have emanated from the Chemistry Department of the Australian National University, with Geoffrey Lawrance as the most prolific author.

Reactions of compounds of diamines which form non-cyclic tetradentate ligands with a single NE, F link are described in Section 2. Reactions of compounds of diamines to form two NE, F links forming a tetraaza macrocyclic ligand are described in Section 3, including the extension of the reaction to propane-1,3-diamine and butane-1,4-diamine compounds, which form products with [16]- and [18]-membered macrocycles, respectively. Macrocyclic compounds formed from C-substituted diamines are described in Section 4. For compounds of linear tetraamines a single link forms a mono-nitro-substituted tetraaza-macrocyclic cation and products with [13]- to [18]-membered macrocycles are described in Section 5. Compounds formed from C-substituted linear tetraamines are described in Section 6. Compounds with tetraaza-bicyclic ligands formed from linear tetraamines with an included bicyclic link are described in Section 7. The combination of the NE, F linking reaction with other ring-closing mechanisms to form a variety of macrocyclic products are described in Section 8. More diverse reactions with other amine ligands to yield a variety of products are described in Sections 9–14.

Most reported reactions have copper(II) as the “templating” metal ion, though reactions of nickel(II), palladium(II), gold(III) and molybdenum(0) compounds have been reported. The reactions for palladium(II) compounds often give higher yields than for the copper(II) compound, with less non-cyclic by-products, particularly for the larger ring-sized macrocycles [12]. Attempted reactions for compounds of other metal ions have generally been unsuccessful.

The reaction conditions; copper(II)-(amine) starting compound, usually as the perchlorate salt, an α -methylene nitro compound (usually nitroethane), aqueous formaldehyde (or paraformaldehyde), with triethylamine as base, in refluxing (m)ethanol apply to the synthesis of most of the reported compounds of this type. The reactions in the electrolyte solvent 1-butyl-3-methylimidazolium tetrafluoroborate produce the same products, with fewer non-macrocyclic by-products and with higher yields of larger ring macrocyclic compounds [13].

The first step of this synthesis is the facile and reversible reaction of a coordinated amine group with formaldehyde to form an iminol function, which can dehydrate to form the imine. The imine function can undergo a Mannich-type reaction with a nucleophile,



Scheme 1.1. Showing the reaction of a bis(ethane-1,2-diamine)metal ion, $[M(en)_2]^{2+}$, with formaldehyde, F, and nitroethane, NE, with base, B, and subsequent reduction of the nitro-groups to form amine substituents.

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