



Review

Compounds with carboxy-substituted ligands formed by Mannich reactions of a coordinated amine with diethyl malonate and formaldehyde – Syntheses and structures

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ABSTRACT

This review covers compounds formed by Mannich-like reactions of coordinated amine-compounds with diethyl malonate and formaldehyde to form compounds with two primary amine functions joined by a $-\text{NH}-(\text{CH}_2)-\text{C}(\text{OEt})_2-(\text{CH}_2)-\text{NH}-$ link. Most reported compounds have tetraaza-macrocyclic ligands, with copper(II) as the usual “templating” metal ion. The refcodes of compounds with structures in the Cambridge Crystallographic Data Centre files are listed and structural figures of representative examples shown.

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1. Introduction

Coordinated amine functions readily and reversibly react with carbonyl compounds to form iminol and imine functions. These are generally readily hydrolysed and seldom isolated. However, they can undergo aldol-like reactions with other carbonyl

compounds, and Mannich-like reactions with nucleophiles, to form compounds with elaborated ligands which are more stable.

Sargeson's observation of the Mannich reaction of $[\text{Co}(\text{en})_3]^{3+}$ with formaldehyde and the carbon acid nitromethane led to extensive chemistry of clathrochelate ligands [1]. During a period of Sabbatical leave in Sargeson's laboratory at the Australian National University in Canberra in 1980 the author attempted to extend these reactions to the labile metal ions nickel(II) and copper(II). Reactions with nitromethane were unsuccessful, so studies moved to the diprotic carbon acid nitroethane. These were productive, and

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the extensive chemistry of nitro-methyl substituted ligands resulting from these reactions has been reviewed [2–6]. The studies included similar reactions for the di-protic carbon acid diethyl malonate. Reaction of $[\text{Cu}(\text{en})_2]^{2+}$ with formaldehyde and diethyl malonate in basic solution formed a product with a carboxyethyl-substituted tetradentate ligand. This review covers subsequent developments of this reaction, much of it from the Chemistry Department of the Australian National University, with Geoffrey Lawrance as the most prolific author.

The compounds formed by the diethyl malonate, formaldehyde (DEM, F) reaction of amine compounds have bis(carboxyethyl) substituted ligands with two amine functions joined by a $-\text{NH}-(\text{CH}_2)-\text{C}(\text{OEt})_2-(\text{CH}_2)-\text{NH}-$ link. For bis(diamine) compounds the formation of two such links forms a tetrakis(carboxyethyl) substituted macrocyclic ligand. Hydrolysis of the ester functions forms the bis(carboxyl) substituted ligand, which readily decarboxylates to form the carboxyl-substituted ligand. Decarboxylation of the tetrakis(carboxyl) substituted macrocyclic ligand forms both the *syn* and *anti* isomeric macrocyclic carboxyl substituted ligands, see Scheme 1.

For each section, Schemes show numbered structural formulae of reported carboxy-substituted cations generated by these reactions.

Section 2 includes compounds with tetradentate ligands, formed by a single DEM, F linking reaction. Section 3 includes compounds with tetraaza-macrocyclic ligands, formed by a single DEM, F reaction for a linear tetraamine compound. Section 4 includes tetraaza macrocyclic ligand compounds formed from bis(diamine) compounds by two DEM, F linking reactions. Section 5 includes compounds with tetraaza-macrocyclic ligands, formed from bis(diamine)copper(II) compounds by an initial DEM, F reaction to form a tetradentate ligand compound, followed by a nitroethane,

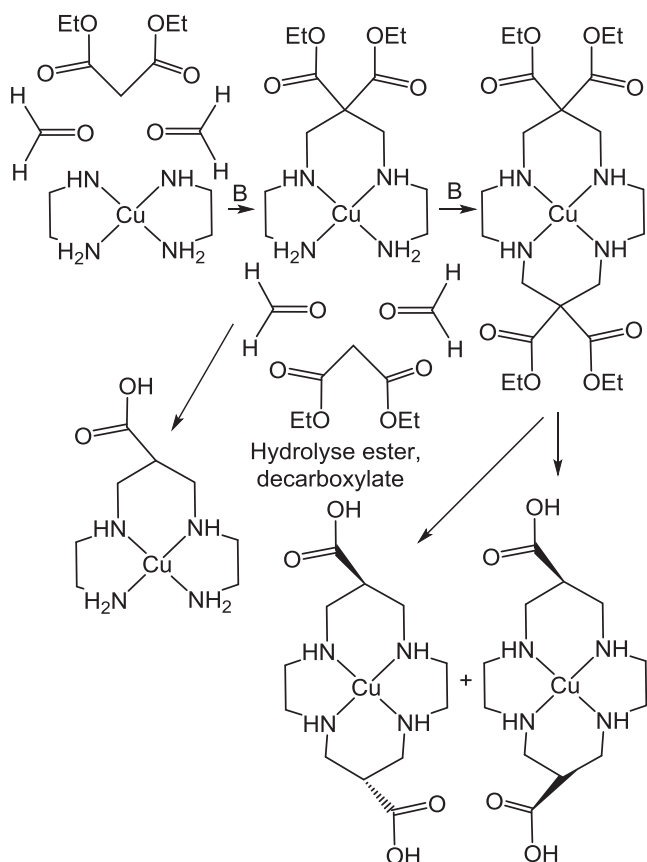
formaldehyde (NE, F) reaction to ring-close. Section 6 includes compounds with diazadithia macrocyclic ligands formed from (dithia-diamine)copper(II) compounds. Compounds which are structurally similar, but formed by other reaction mechanisms are included.

The refcodes of compounds with structures in the Cambridge Crystallographic Data Base are listed with their names and formulae, in numerical sequence, for each section. The ligands are formally esters of amino acids, or their esters, but systematically naming coordination compounds as such leads to complex names, so in this review ligands are named as substituted hydrocarbons, with carboxyethyl ($-\text{CO}_2\text{Et}$), carboxyl ($-\text{COOH}$), etc., generically carboxy, substituents. Names and formulae are otherwise as in the CDC database, so include coordinated anions and other ligands, even when distances indicate that these interactions must be very weak. Most reported structures are for tetraazamacrocyclic ligand copper(II) compounds. These generally have structures with the 1*R*,4*S*,8*R*,11*S* configuration (III) typical of copper(II) cyclam compounds, usually with a weak axial interaction and consequent square-pyramidal distortion of the CuN_4 group.

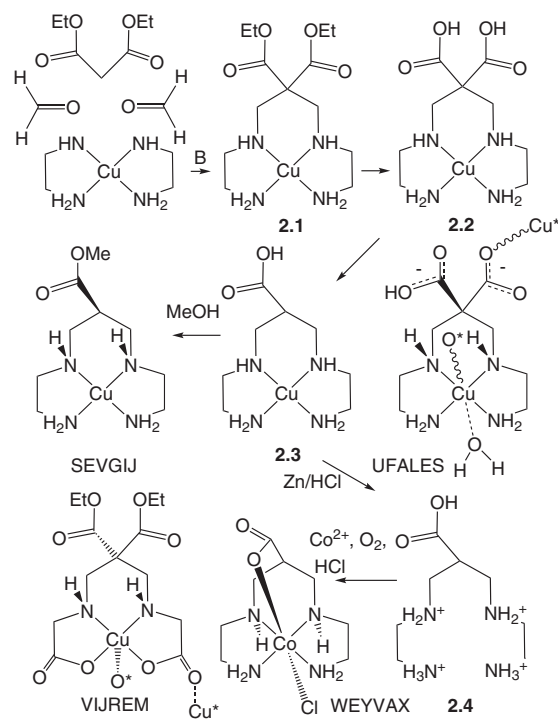
For a representative selection of the structures, indicated in the Schemes, an ORTEP figure of the cation is shown. These figures were generated from the CDC cif files, using ORTEP-32 [7] with displacement ellipsoids set at 30% probability. H(C) atoms are usually omitted for clarity and H(N) atoms shown as circles with arbitrary radius.

2. Compounds with non-macrocyclic carboxy-substituted ligands

The reaction of $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$ with DEM, F in refluxing methanol with NEt_3 as base rapidly forms the singly bridged tetradentate ligand cation $[(5,5\text{-bis}(\text{carboxyethyl})\text{-}3,7\text{-diazanonane-}1,9\text{-diamine})\text{copper(II)}]^{2+}$ **2.1**, Scheme 2.1 [8–10]. Further reaction to form



Scheme 1. Compounds formed by reaction of bis(ethane-1,2-diamine)copper(II) with DEM, F.



Scheme 2.1. Non-macrocyclic carboxy-substituted ligand compounds formed from bis(diamine) or bis(amino acid) copper(II) compounds.

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