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Inorganica Chimica Acta 360 (2007) 1661–1668

Inorganica Chimica Acta

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A structural study of late transition metal diethylenetriamine complexes

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Received 13 April 2006; received in revised form 29 August 2006; accepted 1 September 2006
Available online 23 September 2006

Abstract

The synthesis and X-ray crystal structures of *u-fac*-[Ni(dien)$_2$](NO$_3$)$_2$, *s-fac*-[Ni(dien)$_2$](tos)$_2$, *fac-fac*-[(H$_2$O)(dien)Ni(μ-Cl)$_2$(dien)(H$_2$O)]Cl$_2$, *s-fac*-[Ni(dien)$_2$][ZnCl$_4$], *mer*-[Ni(dien)$_2$][CdCl$_4$] · H$_2$O, *fac*-[Ni(dien)(H$_2$O)$_3$](tos)$_2$ · (H$_2$O), *mer*-[Cu(dien)(H$_2$O)](tos)$_2$, *fac*-[Zn(dien)(H$_2$O)$_2$](tos)$_2$ (dien = bis(2-aminoethyl)amine = diethylenetriamine; tos = *p*-toluenesulfonate) are described. The mode of binding of the tridentate amine is examined in detail.

Keywords: Diethylenetriamine; Nickel; Copper; Zinc; Coordination complexes; X-ray crystal structures

1. Introduction

Transition metal coordination complexes involving tridentate amines as ligands have attracted solid attention for their role as model compounds for bioinorganic systems, as building blocks in supramolecular assemblies and as catalysts [1]. On a more fundamental note, the stereochemistry of these compounds have been studied with respect to their preference towards facial or meridional binding [2]. For octahedral complexes that have two tridentate ammine ligands, there are three possible configurations: (i) meridional (*mer*), (ii) unsymmetrical-facial (*u-fac*) and (iii) symmetrical-facial (*s-fac*) (Fig. 1). A previous detailed study on the equilibrium distribution of the three geometric isomers of [Co(dien)$_2$]$^{3+}$ in solution suggested this distribution depended considerably on solvation, ion association and temperature, but more generally a ratio of *mer*:*u-fac*:*s-fac* of approximately 10:3:1 was found. These reactions were performed using a variety of anions at varying concentrations and isomer ratios were determined spectrometrically in solution [3]. Thus, a preference for the *mer* isomer was found for the [Co(dien)$_2$]$^{3+}$ system, while the *u-fac* isomer was favoured over the *s-fac* isomer on statistical grounds (after the facial coordination of one dien ligand, there are three possible ways the second ligand can bind leading to the distribution *s-fac*:*u-fac* = 1:2) [3]. This evidence has been supported by the findings of Kepert where geometric considerations of the ligands spatially distributed about a metal are considered [2]. More recently, a theoretical report on the bis-diethylenetriamine complexes of Ni^{2+} has stated the *mer* isomer is 18.8 kJ mol^{-1} lower in energy than the *s-fac* isomer [4]. A Cambridge Structural Database search on [Ni(dien)$_2$]$^{2+}$ cations revealed 30 hits suitable for comparison [5]. Of these, 13 structures have solely a *mer* stereochemistry [4,6], 8 have *s-fac* stereochemistry [4,7] while only four compounds adopt the *u-fac* geometry [8]. Five compounds have multiple cations of different stereochemistry [6f,9]. This latter analysis shows that for Ni^{2+} in the solid state, the predictions/observations quoted above may not be relevant. However, it must be kept in mind that the distribution observed in crystal structures is not necessarily relevant to solution distribution and indeed sometimes it is the least stable isomers in solution that crystallize [10]. Although this assumption is based on a limited number of solid state structures it would be beneficial for more structural work to be performed to increase the amount of archived data.

Structural studies on compounds where there is a 1:1 dien:metal ratio, viz [M(dien)L$_n$]$^{2+}$ (M = Ni, Cu, Zn;

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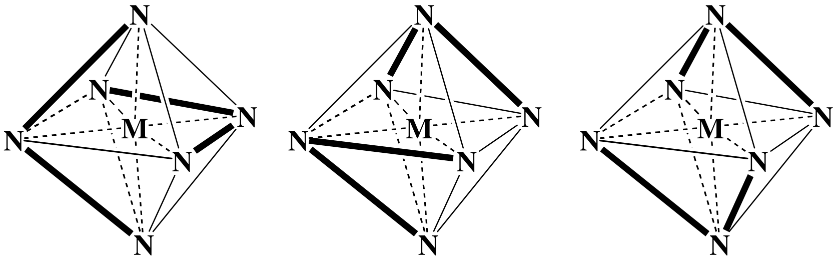
doi:10.1016/j.ica.2006.09.001



(i) (ii) (iii)

Fig. 1. Configurations for the (i) meridional (*mer*), (ii) unsymmetrical-facial (*u-fac*) and (iii) symmetrical-facial (*s-fac*) isomers.

L = H_2O, $n = 1$, 2 or 3) are rather more limited [11]. There are no examples in the CSD of $[Ni(dien)(H_2O)_3]^{2+}$ or $[Zn(H_2O)_2]^{2+}$ while for $[Cu(dien)(H_2O)]^{2+}$ there are several cases [11] and these are normally Jahn–Teller distorted cations.

In this contribution, we report a structural study of diethylenetriamine complexes of the late transition ions Ni^{2+}, Cu^{2+} and Zn^{2+} with emphasis on Ni^{2+}. We report herein the X-ray crystal structures of *u-fac*-$[Ni(dien)_2](NO_3)_2$ (**2**), *s-fac*-$[Ni(dien)_2](tos)_2$ (**3**), *fac-fac*-$[(H_2O)(dien)Ni(\mu\text{-}Cl)_2(dien)(H_2O)]Cl_2$ (**4**), *s-fac*-$[Ni(dien)_2][ZnCl_4]$ (**5**), *mer*-$[Ni(dien)_2][CdCl_4] \cdot H_2O$ (**6**), *fac*-$[Ni(dien)(H_2O)_3](tos)_2 \cdot H_2O$ (**7**), *mer*-$[Cu(dien)(H_2O)](tos)_2$ (**8**), *fac*-$[Zn(dien)(H_2O)_2](tos)_2$ (**9**) (dien = bis(2-aminoethyl) amine = diethylenetriamine; tos = *p*-toluenesulfonate). The energetically favoured meridional isomer (particularly for $[M(dien)_2]^{2+}$ cations) is rarely observed.

2. Experimental

All reagents were purchased from Sigma–Aldrich and were used as received. Ethanolic solvents were used as received, while freshly deionised water was used. For all compounds, reaction conditions were used to obtain crystalline material suitable for X-ray crystallography and yields were not optimised.

2.1. Synthesis of $[Ni(dien)_2]X_2 \cdot n(H_2O)$. X = Cl, n = 1 (*1*); X = NO_3, n = 0, (*2*); X = tos, n = 0, (*3*)

The preparation of these compounds followed the published synthesis for $[Ni(en)_3]Cl_2$ (en = 1,2-diaminoethane) [12]. Thus, an aqueous solution of two molar equivalents of dien was added to an aqueous solution of the relevant metal salt. The solutions were then allowed to slowly evaporate in a desiccator until X-ray quality crystals were obtained. All compounds were deep violet.

2.2. Synthesis of $[(H_2O)(dien)Ni(\mu\text{-}Cl)_2Ni(dien)(H_2O)]Cl_2$ (*4*), $[Ni(dien)_2][ZnCl_4]$ (*5*) and $[Ni(dien)_2][CdCl_4] \cdot H_2O$ (*6*)

The preparation of these compounds followed the published synthesis for $[Ni(en)_2(\mu\text{-}Cl)]_2Cl_2$ (en = 1,2-diaminoethane) [13]. Thus, $[Ni(dien)_2]Cl_2 \cdot H_2O$ and MCl_2 were mixed in a 5% methanolic water solution and vigorously shaken until dissolution took place. The solutions were then allowed to slowly evaporate in a desiccator until X-ray quality crystals were obtained. Compound (**4**) was blue, while compounds (**5**) and (**6**) were purple.

2.3. Synthesis of fac-$[Ni(dien)(H_2O)_3](tos)_2 \cdot H_2O$ (*7*), mer-$[Cu(dien)(H_2O)](tos)_2$ (*8*), fac-$[Zn(dien)(H_2O)_2](tos)_2$ (*9*)

These compounds were prepared as for compounds (**1**), (**2**) and (**3**) except a 1:1 ratio of dien to $M(tos)_2$ was used. Compound (**7**) was blue/purple while (**8**) was blue and (**9**) was colourless.

2.3.1. Structure determinations

Compounds **3**, **7**, **8** and **9** were sealed and mounted in thin walled capillaries, with hemispheres of data collected at room temperature on a Bruker SMART CCD diffractometer using the omega scan mode with total reflections and unique data listed below. Data sets were corrected for absorption using the program SADABS [14]. Structural solution and refinement was carried out using the SHELX suite of programs [15] with the graphical interface X-Seed [16]. All non-hydrogen atoms were located and refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (riding model) with isotropic parameters 1.2 or 1.5 times the parent atom and were not refined, except those on water molecules that were located and refined using isotropic thermal parameters. Details of the X-ray data collection and refinements appear below.

Crystals of **2**, **4**, **5** and **6** were mounted on a thin glass fibre using a fast setting epoxy resin and cooled on a Nonius KappaCCD diffractometer to the temperature stated using an Oxford Cryostream low temperature attachment. A total of either 90 or 180 oscillation frames each of width either 2° or 1° in ϕ, respectively, and of 10–120 s exposure time (depending on crystal quality) were recorded, with a detector to crystal distance of 25–35 mm. Crystals were indexed from the first 10 frames using the DENZO package [17] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO, Scalepack [17]) resulted in