

A Study of Six-Coordinate Oxime-Imine Cobalt(III) Complexes with Amino Acid Co-Ligands; Synthesis and Characterisation



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Abstract :

In this publication, several six coordinate Co(III)-complexes are reported. The reaction of 2,3-butanedione monoxime with ethylenediamine or o-phenylenediamine in mole ratios of 2:1 gave the tetradentate imine-oxime ligands diaminoethane-N,N'-bis(2-butyldine-3-onedioxime) H₂L₁ and o-phenylenediamine-N,N'-bis(2-butyldine-3-onedioxime), respectively. The reaction of H₂L₁ and H₂L₂ with Co(NO₃)₂, and the amino acid co-ligands (glycine or serine) resulted in the formation of the required complexes. Upon complex formation, the ligands behave as a neutral tetradentate species, while the amino acid co-ligand acts as a monobasic species. The mode of bonding and overall geometry of the complexes were determined through physico-chemical and spectroscopic methods. These studies revealed octahedral geometry about Co(III) complexes in which the co-ligands bound through the amine and the carboxylate groups. Molecular structure for the complexes have been optimised by CS Chem 3D Ultra Molecular Modelling and Analysis Program and supported six coordinate geometry.

Introduction

The coordination chemistry of metal complexes of α -dioxime has been investigated widely [1]. Approaches such as synthetic routes to obtain vicinal imine-oxime complexes and analytical and structural applications of these oxime species have been reviewed extensively [2]. Schiff-base oxime species based on transition metal compounds and polydentate ligands has been the subject of extensive research due to their potential applications in materials science [3, 4] and environmental chemistry and medicine [2] and biomimetic model including the preparation and molecular structure of Co(III)-complexes called cobaloxime. The interesting feature of these complexes is due to their relevance to

the chemistry of vitamin B12. As models for coenzyme B12, cobaloxime have been subjected to extensive studies including their electrochemical [7] and structural properties [8]. Furthermore, a new family of cobalt and nickel complexes with tetradentate ligands providing a diimine-dioxime coordination sphere was reported as efficient and stable electrocatalysts for hydrogen evolution from acidic nonaqueous solutions with lower over-voltages [9]. Recently, we reported the formation of phenoxo-bridged binuclear transition metal ions with the Schiff-oxime ligand -((E)-(hydroxyimino)methyl)-5-methylbenzylideneamino) ethylimino)m ethyl)-5- methylbenzaldehyde oxime [10]. As part of our continuing efforts to explore the use of mixed ligands based on the multidentate Schiff-base oxime ligands and amino acid co-ligands, we describe here the formation and the spectral investigations of Co(III)-complexes with the mixed ligands; the amino acids (glycine or serine) and the tetradentate imin-oxime ligands diaminoethane-N,N'-bis(2-butylidene-3-onedioxime) H2L1 and o-phenylenediamine-N,N'-bis(2-butylidene-3-onedioxime) H2L2.

Materials and methods

All reagents were obtained commercially (Aldrich) and used without further purification. Solvents used in the synthesis were distilled from appropriate drying agent immediately prior to use.

2.2. Physical measurements

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer from 4000-400 cm⁻¹. Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Electronic spectra were measured from 200-900 nm for 10⁻³ M solutions in H₂O at 25°C using a Shimadzu 160 spectrophotometer. ¹H NMR spectra were acquired in DMSO-d₆ solution using a Jeol 270 MHz spectrometers with tetramethylsilane (TMS) as an internal standard. Mass spectra obtained by positive Electron Impact (EI) recorded on a VG autospec micromass spectrometer. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Conductivity measurements were made with DMF solutions using a Jenway 4071 digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Jonson Matthey Catalytic System Division).

Synthesis

The preparation of the ligands was adopted according to a method published in [11], and as follows:

Preparation of H2L1

A solution of ethylenediamine (0.5 g, 8 mmol) in methanol (20 mL) was added slowly to a mixture of diacetylmonoxime (1.68 g, 16.6 mmol) dissolved in methanol (20 mL). The reaction mixture was allowed to reflux for 2 h, and then stirred at room temperature for a further 1 h. A white solid was collected by filtration, recrystallised from a mixture of hot methanol:H₂O, and dried under vacuum for 24 hr to give H2L1 as a white solid (yield 56%), m.p. = 166 °C. ¹H NMR data (ppm), δ H (270 MHz,

Molecular modelling

3D molecular modelling of the proposed structure of the complexes was performed using CS Chem 3D Ultra Molecular Modelling and Analysis Program [12]. It is an interactive graphics program that allows rapid structure building, geometry optimization with minimum energy and molecular display. It is well known program and has the ability to handle transition metal complexes. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries.

Results and Discussion

4.1. Chemistry

The reaction of 2,3-butanedione monoxime with ethylenediamine or o-phenylenediamine in mole ratios of 1:2 gave the tetradentate imine-oxime ligands diaminoethane-N,N'-bis(2-butyldine-3-onedioxime) H2L1 and o-phenylenediamine-N,N'-bis(2-butyldine-3-onedioxime), H2L2 respectively in moderate yield (Scheme 1). The Schiff-base oxime ligands were characterised by elemental analysis (Table 1), IR (Table 2), UV-Vis (Table 3) spectroscopy, ¹H NMR and mass spectrometry. The ¹H NMR and the EI (+) mass spectra of the ligands were consistent with the proposed structural formula (see experimental section).

The di-electrolyte Co(III)-complexes were synthesised by mixing at RT 1 mmole of the appropriate ligand with 1 mmole of the cobalt nitrate in methanol followed by a solution of the appropriate amino acid, glycine or serine, (1 mmol) in methanol, and then a saturated solution of NaIO₄ in water was added to above solution. The mixture was stirred vigorously with bubbling air for 3 h. Bubbling air was introduced to facilitate the oxidation of Co(II) to Co(III). Complexes of the general formulae [Co(H₂L_n)(A⁻)]₂ (where n = 1 or 2; A⁻ = amino acid, glycine or serine) was obtained (Scheme 1). The complexes are air-stable solids, soluble in H₂O, and partially in DMSO and DMF. The complexes are sparingly soluble in EtOH and not soluble in other common organic solvents. The coordination geometries of the complexes were deduced from their spectra. The analytical data (Table 1) agree well with the suggested formulae. Conductivity measurements of the Co(III) mixed complexes lie in the 142.7-150 cm²Ω⁻¹mol⁻¹ range.

Conclusion

In this paper, we have explored the synthesis and coordination chemistry of some imine-oxime Co(III)-complexes derived from the tetradentate Schiff-base oxime ligands H₂L₁ and H₂L₂ and the amino acid co-ligands. The ligands behave as a neutral species upon complexation with the involvement of the nitrogen atoms of the oxime groups in coordination for all complexes. The magnetic susceptibilities and electronic spectra of the complexes indicated that they are low-spin d⁶ octahedral.

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