Inorganica Chimica Acta 478 (2018) 118–124

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Variations in the molecularity of bis(formylpyrrolyl)cobalt(II) complexes

Tiago F.C. Cruz [a], Pedro M.M. Machado [a], Clara S.B. Gomes [a], Laura C.J. Pereira [b], Pedro T. Gomes [a],*

[a] Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal
[b] C^{2}TN-Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, 2695-066 Bobadela LRS, Portugal

ARTICLE INFO

Article history:
Received 1 February 2018
Received in revised form 29 March 2018
Accepted 4 April 2018
Available online 5 April 2018

Dedicated to Professor Malcolm L. H. Green in recognition of his inspiration and outstanding contribution to inorganic and organometallic chemistry.

Keywords:
Cobalt(II) complexes
2-Formylpyrrolyl ligands
Tetranuclear cubane complexes

ABSTRACT

This work aims to extend the coordination chemistry of Co(II) with bis(2-formylpyrrolyl) ligands to different donor molecules. Treatment of a mixture of anhydrous $CoCl_2$ and excess of pyridine in THF with two equivalents of sodium 2-formylpyrrolyl gives rise to complex $[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2(Py)_2]$ (**1**) in good yields, after standard work-up procedures. By contrast, the reaction of two equivalents of sodium 2-formylpyrrolyl with anhydrous $CoCl_2$ in neat THF or MeCN solutions systematically led, after standard work-up, to the identification of the tetrameric complex $[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2]_4$ (**2**) and other unknown contaminations. Analytically pure samples of complex **2** were only prepared when the synthesis reaction was performed in toluene at 90 °C. Complexes **1** and **2** are paramagnetic and were characterized by elemental analysis, magnetic susceptibility measurements (Evans method) and X-ray diffraction. Complex **1** is a hexacoordinated octahedral complex with a low-spin ($S = 1/2$) electronic configuration. On the other hand, the tetrameric complex **2** results from the self-assembling of the elusive and highly unsaturated complex "$[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2]$" giving rise to a tetranuclear distorted cubane structure, comprising two hexacoordinated octahedral and two pentacoordinated trigonal bipyramidal Co(II) centers. Complex **2** revealed an overall high-spin ($S = 3/2$ per Co center) nature, as suggested in solution by the Evans method and in the solid state by SQUID magnetometry.

1. Introduction

The coordination chemistry of bidentate chelating ligands has had numerous reports in a wide array of applications, from catalysis to materials. Pyrrolyl-based ligand systems coordinated to cobalt are reminiscent of the corrinic compounds of vitamin B12 complex (Chart 1, **A**), which have a key role in cellular metabolism [1].

In one aspect, complexes of bis(2-formiminopyrrolyl) ligands often give rise to *N,N* bidentate chelates and have been reported with many elements of the periodic table, such as main-group elements [2], early [3] and late [4] transition metals and rare earth elements [5]. Most of these complexes have found applications in polymerization or luminescence.

The preparation of 2-formiminopyrrolyl ligand precursors is often accomplished via a condensation reaction of an appropriate aniline and 2-formylpyrrole. The latter compound is the precursor of the 2-formylpyrrolyl *N,O* chelating ligand, which is a poorer electron donor and provides very reduced stereochemical protection to the metal when compared to the 2-formiminopyrrolyl ligands. Given this fact, the coordination chemistry of 2-formylpyrrolyl ligands is quite scarce, being limited to vanadium [6] and to some examples with late transition metals [7]. In particular, Lewiński and co-workers were able to control the molecularity of the resulting zinc complexes by changing the nature of the bis(alkyl) zinc precursor [8]. With cobalt, Jablonski *et al.* prepared and characterized a family of diamagnetic Co(III) three-legged piano stool cyclopentadienyl complexes containing a chelating 2-formylpyrrolyl and a phosphorus(III) ligands [9].

In a previous work, we reported that stable Co(II) complexes containing the bis(2-formylpyrrolyl) Co(II) framework could only be isolated in the presence of an additional strongly donating ligand. The use of trimethylphosphine allowed the synthesis and characterization of the 19-electron paramagnetic complex $[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2(PMe_3)_2]$ (Chart 1, **B**) [10]. In this case, the coordination of the two trimethylphosphine ligands stabilized the extremely unsaturated and unobserved tentative synthon "$[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2]$". In fact, the isolation of tetracoordinated Co(II) complexes of unhindered oxygen-based ligands is not straightforward (Chart 1, **C**). An example of this observation is the tendency of bis(acetylacetonate) Co(II) complexes to form co-solvates or multinuclear structures upon crystallization in the absence of strongly coordinating solvents (Chart 1, **D**) [11].

---

* Corresponding author.
E-mail address: pedro.t.gomes@tecnico.ulisboa.pt (P.T. Gomes).

https://doi.org/10.1016/j.ica.2018.04.004
0020-1693/

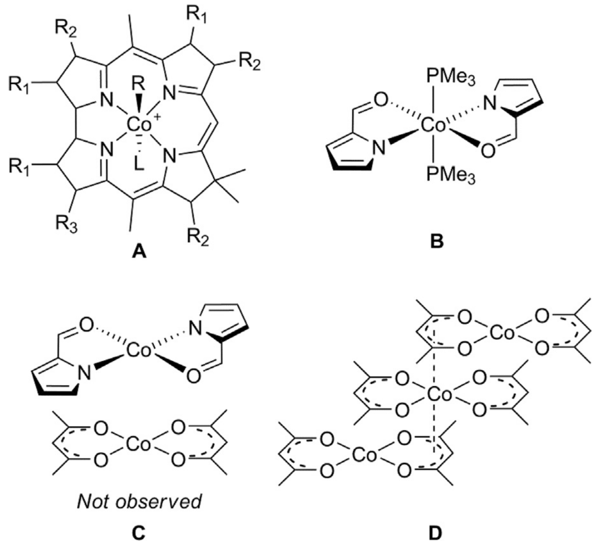


Chart 1. General representation of the corrinic Co(III) complexes of vitamin B12 (**A**). Structural diversity in Co(II) complexes bearing unhindered oxygen-based bidentate ligands (**B**–**D**).

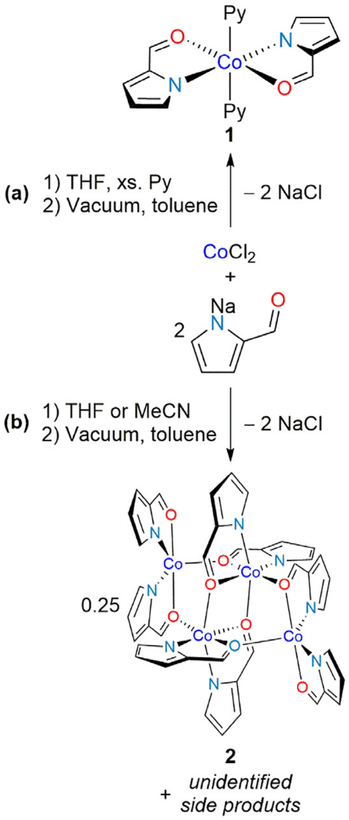
Considering our previous effort on the preparation of bis(2-formylpyrrolyl) Co(II) complexes stabilized with trimethylphosphine, and bearing in mind that monomeric tetracoordinated Co(II) complexes of sterically unprotected ligands is a challenging task, we have reactivated this chemistry. Therefore, we report herein the stabilization of the very reactive "$[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2]$" core with different donor ligands, other than trimethylphosphine, by presenting the preparation of new paramagnetic bis(2-formylpyrrolyl) Co(II) complexes. The obtained complexes were characterized by elemental analysis, X-ray diffraction, magnetic susceptibility measurements in solution (Evans method) and in solid state, in order to understand the factors that control the molecularity of the resulting species.

2. Results and discussion

2.1. Synthesis and characterization of the complexes

To explore the coordination chemistry of bis(2-formylpyrrolyl) Co(II) complexes, we used different donor molecules, such as pyridine, THF or MeCN. When a THF solution of two equivalents of *in situ* prepared sodium 2-formylpyrrolyl was added, at −20 °C, to a slurry of anhydrous $CoCl_2$ in THF with an excess of pyridine (ten equivalents), the 19-electron complex $[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2(Py)_2]$ (**1**) was obtained in good yields, after a standard work up procedure (Scheme 1 (a)). Complex **1** was isolated as a red-brown microcrystalline paramagnetic solid from a toluene/*n*-hexane solution cooled to −20 °C. Complex **1** is insoluble in *n*-hexane, partially soluble in diethyl ether and soluble in toluene. The effective magnetic moment of **1** in toluene-d_8 is 2.9 μ_B, being consistent with a low-spin ($S = 1/2$; μ_{eff} (spin only) = 1.73 μ_B) Co(II) complex [12].

On the other hand, when using neat THF or MeCN as reaction solvents, different observations are to be noted. After the overnight reaction of two equivalents of sodium 2-formylpyrrolyl and anhydrous $CoCl_2$, dark blue or dark brown-yellow cloudy solutions were observed in the cases of THF and MeCN, respectively. After evaporating all volatile materials to dryness, the formation of a brown-red solid was observed, irrespective of the solvent used in the reaction. Following a toluene extraction, a mixture of red-brown crystals and a brown powder was obtained, after cooling of a toluene/*n*-hexane solution to −20 °C. The crystalline portion was crystallographically identified as the tetrameric complex $[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2]_4$ (**2**), instead of the respective monomeric hexacoordinated complexes $[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2L_2]$, with L being THF or MeCN, analogous to complex **1**. The amorphous part remained unidentified (Scheme 1(b)). The consistently low carbon values obtained in independent CHN elemental analyses of this mixture, in relation to the formulation of complex **2**, likely point to the formation of adducts of complex **2** with the sodium chloride reaction product, promoted by the presence, at some point, of coordinating solvent molecules.



Scheme 1. Synthesis of complex **1** (a) and identification of complex **2** (b).

Complex **2** was isolated in an analytically pure form by treating a solid mixture of anhydrous $CoCl_2$ and two equivalents of sodium 2-formylpyrrolyl with toluene, and heating at 90 °C overnight. Complex **2** precipitated from a toluene/*n*-hexane solution cooled to −20 °C, as a microcrystalline brown-red paramagnetic powder (Scheme 2).

Complex **2** formally represents the synthon "$[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2]$", assembled as a tetramer, in order to compensate the coordinative and electronic unsaturation of the hypothetic 15-electron tetracoordinated monomer. Complex **2** is insoluble in *n*-hexane and soluble in toluene. The effective magnetic moment of complex **2** in toluene d_8 is 4.1 μ_B per cobalt atom ($S = 3/2$ per Co atom; μ_{eff} (spin only) = 3.88 μ_B). This result indicates a global high-spin electronic configuration, contradicting the results observed for the isolated monomeric complexes of the same ligands, $[Co\{\kappa^2 N,O\text{-}NC_4H_3\text{-}C(H){=}O\}_2L_2]$, with L = PMe_3 [10] or Py (**1**), which have low-spin behaviors in solution. This observation could be attributed to a spin state cooperation effect due to possible interactions between the different Co centers.

Complex **2** is also soluble in coordinating solvents. Magnetic susceptibility measurements of complex **2** in THF-d_8 or CD_3CN indicate the dissociation of the tetramer to form four units of