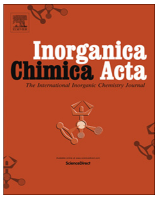
Inorganica Chimica Acta 459 (2017) 63–72

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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



Research paper

Azide-rich complexes of cobalt(III) with the rare 5-phenyl-2,2′-bipyridine ligand

Damir A. Safin [a,*], Koen Robeyns [a], Christophe M.L. Vande Velde [b], Mike Thijs [b], Mariusz P. Mitoraj [c,*], Filip Sagan [c], Yaroslav Filinchuk [a]

[a] Institute of Condensed Matter and Nanosciences, Molecules, Solids and Reactivity (IMCN/MOST), Université catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium
[b] Faculty of Applied Engineering, Advanced Reactor Technology, University of Antwerp, Groenenborgerlaan 171, 2018 Antwerpen, Belgium
[c] Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland

ARTICLE INFO

Article history:
Received 30 October 2016
Received in revised form 21 December 2016
Accepted 27 January 2017
Available online 30 January 2017

Keywords:
Cobalt
Azide
X-ray crystallography
Thermal analysis
DFT

ABSTRACT

Reaction of one or two equivalents of 5-phenyl-2,2′-bipyridine (**L**) with a mixture of one equivalent of $CoCl_2$ and two equivalents of NaN_3 leads to mononuclear heteroleptic cobalt(III) complexes $[CoL_2(N_3)_2](N_3)_{0.55}Cl_{0.45}\cdot EtOH$ (**1**) and $[CoL_2(N_3)_2]N_3\cdot 2.5EtOH$ (**2**), respectively. Both structures reveal that cobalt (III) atom is linked to the six nitrogen atoms of two **L** and two N_3^- anions. Both structures are stabilized by intermolecular C—H···N and $\pi\cdots\pi$ stacking interactions. TG and DSC analyses reveal **1** being stable up to 63 °C and decomposing in three steps, **2** on the other hand decomposes at 84 °C in two steps. Both decomposition pathways start with an endothermic loss of the lattice ethanol molecules. The second step in **1** (177 °C) and **2** (196 °C) is related to the "jet" effect, seen as an abrupt weight loss due to a drastic energy release upon heating. In **2** this is the result of a release of N_2 gas from the azides and decomposition of the ligands **L** followed by the full reduction of cobalt(III) to cobalt(0). In **1** there is a loss of one azide accompanied by the reduction of cobalt(III) to cobalt(II). The final decomposition step of **1** at 215 °C is attributed to the exothermic decomposition of **L** and remaining azide with the formation of a mixture of $CoCl_2$ and Co_2N. DFT calculations are performed in order to shed additional light on possible spin states of cobalt complexes as well as to rationalize the stability of the synthesized materials.

1. Introduction

Azide (N_3^-) is an important constituent of the compounds that play a pivotal role as propellants in air bags [1]. In particular, lead and copper azides are of importance as explosives [2,3]. Intuitively, a better energy source may be achieved through enrichment of the azide content in a metal complex. As such, thermal decomposition of the metal azide seems to be a powerful tool in the design and fabrication of materials for the controlled release of thermal energy. This can be achieved by varying not only the azide content but also its binding mode. Particularly, the azide anion is known to bind metal ions in a number of bonding modes varying from terminal, end-on bridging to end-to-end bridging modes or ionic. The binding mode of the azide ligand, obviously, depends on the nature and the oxidation state of a central metal ion, as well as the nature of other coordinated ligands. An additional role of the latter is to uphold the different stability of the metal azide.

Cobalt forms stable azide complexes [4–6] and has different stable oxidation states. This makes cobalt azide complexes promising materials for tunable heat energy release during their thermal degradation. Even more telling is that the first ever structurally characterized metal azide was the azidopentamminecobalt(III) azide, $[Co(NH_3)_5(N_3)](N_3)_2$ [7].

On the other hand *N*-heterocyclic ligands, in particular polypyridine compounds, serve as multidentate ligands that give characteristic properties to the metal complexes that they form. These ligands can be easily modified by introducing different substituents, imposing a variety of electronic, steric and conformational effects on both the coordinated chelate and coordination core. *N*-heterocyclic compounds such as 2,2′-bipyridine, 1,10-phenanthroline and 2,2′:6′,2″-terpyridine seem to be the most widely used polypyridine ligands for metal complexes as well as building units in coordination and supramolecular chemistry. In particular, these compounds are known to be efficient ligands for dye-sensitized solar cells [8]. Furthermore, the renaissance of a highly attractive ligand, owing to the presence of three fused terpyridine-like coordination pockets, 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine has recently been announced [9]. Although 2,4,6-tris(2-

---

[*] Corresponding authors.
E-mail addresses: damir.a.safin@gmail.com (D.A. Safin), mitoraj@chemia.uj.edu.pl (M.P. Mitoraj).

http://dx.doi.org/10.1016/j.ica.2017.01.020
0020-1693/

pyrimidyl)-1,3,5-triazine has been known for almost 60 years [10], its coordination chemistry remains vastly underexplored. Indeed, until recently only two coordination compounds of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine were known in the literature [11,12]. However, during the last two years the number of reported complexes built from 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine has quadrupled [13–19].

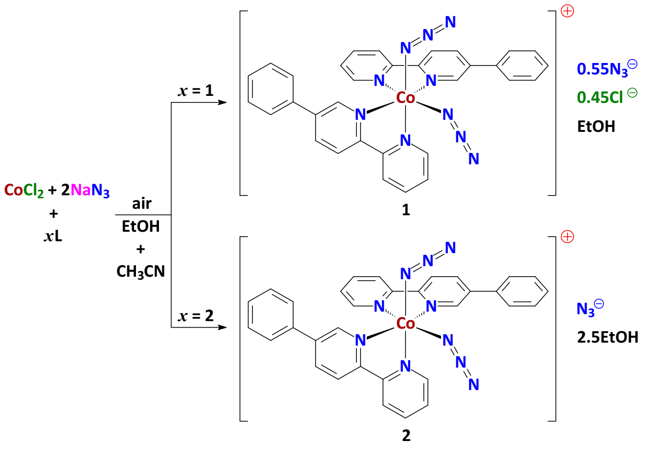
With this in mind, we have recently directed our attention to the 5-phenyl-2,2′-bipyridine (**L**), which was synthesized according to a known procedure [20,21]. It was established, that the reaction of **L** with a mixture of CuHal (Hal = Cl^-, Br^-, I^-) or $[Cu(CH_3CN)_4]BF_4$ and PPh_3 leads to the mononuclear heteroleptic complexes $[CuL(PPh_3)Hal]$ and $[CuL(PPh_3)_2]BF_4$, respectively [22,23]. All compounds were found to be emissive in the solid state. DFT calculations have shown that, while emission of **L** is due to the ligand-centered $\pi \rightarrow \pi^*$ transition, luminescence of $[CuL(PPh_3)Hal]$ and $[CuL(PPh_3)_2]BF_4$ is attributed to (M + Hal)LCT and MLCT excited states, respectively. We have also described the synthesis and complete structural investigation of Ag^I complexes of **L**, namely $[AgL_2]NO_3{\cdot}0.5H_2O$ and $[AgLPPh_3NO_3]{\cdot}0.5CH_2Cl_2$, which were obtained through the direct reaction of **L** with $AgNO_3$ or with a mixture of $AgNO_3$ and PPh_3, respectively [24]. Furthermore, conversion of the first complex into the second one upon reacting with PPh_3 was also described.

In this contribution, we continue our comprehensive research of the complexation properties of **L**. We describe the synthesis and complete structural investigation of the mononuclear heteroleptic cobalt(III) complexes $[CoL_2(N_3)_2](N_3)_{0.55}Cl_{0.45}{\cdot}EtOH$ (**1**) and $[CoL_2(N_3)_2]N_3{\cdot}2.5EtOH$ (**2**) as well as their thermal decomposition.

2. Results and discussion

The complexes **1** and **2** were prepared by reacting $CoCl_2$ with two equivalents of NaN_3, followed by the addition of one or two equivalents of **L**, respectively, in an ethanol/acetonitrile mixture under ambient conditions (Scheme 1). The obtained red crystals are soluble in most polar solvents. It should be noted, that the composition of **2** was suggested based on the elemental analysis data, which best fit corresponds to the presence of about two and a half molecules of ethanol per one $[CoL_2(N_3)_2]N_3$ species. This finding is further supported by the ^1H NMR spectroscopy and TGA data (see below) as well as by the presence of cavities with non-discrete solvent molecules account for the 69 electrons as evidenced from single crystal X-ray diffraction.

Our initial goal was the synthesis of heteroleptic azide-containing cobalt(II) complexes with **L** yielding new hybrid materials displaying interesting magnetic properties such as single-molecule and single-chain magnet behaviour. With respect to this, it was supposed that using two equivalents of **L** most likely lead to the formation of a discrete cobalt(II) complex $\mathbf{[CoL_2(N_3)_2]}$, exhibiting an octahedral coordination mode, while adding of one equivalent of **L** to a reaction mixture should support the formation of a polymeric cobalt(II) 1D chain structure $\mathbf{[CoL(N_3)_2]_{\mathit{n}}}$, constructed also from coordination octahedra (Chart 1). Both synthetic strategies may also afford a tetrahedral cobalt(II) structure (Chart 1). It was, however, found that both synthetic strategies yields mononuclear heteroleptic salt-like complexes of cobalt(III), each containing the same $[CoL_2(N_3)_2]^{+\cdot}$ cation, where the metal center is octahedrally coordinated (Scheme 1). Thus, the cobalt(II) cation is further oxidized to cobalt(III) under the synthetic conditions. This might be explained by the coordination of two ligands **L** with the subsequent oxidation of the metal center similar to that of the formation of the hexamminecobalt(III) salts upon reacting cobalt(II) salts with NH_3 [25].



Scheme 1. Synthesis of **1** and **2**.

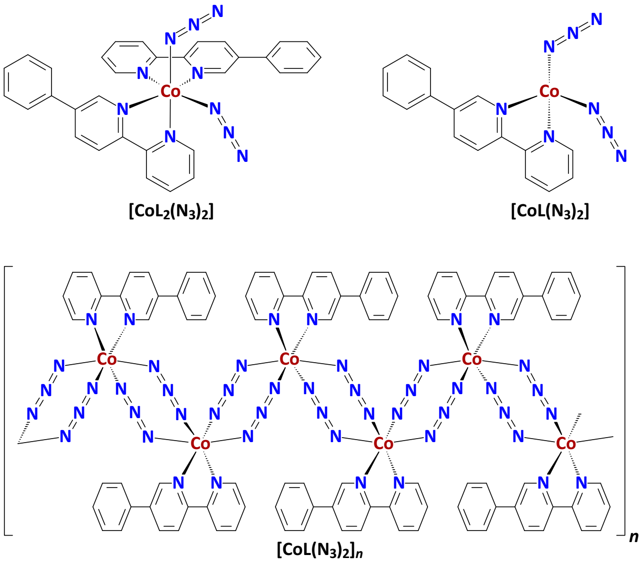


Chart 1.

The ^1H NMR spectra of **1** and **2** in DMSO-d_6 are the same and each exhibit a triplet at about 8.00 ppm and three multiplets at 7.37–7.65, 8.28–8.44 and 8.68–8.84 ppm corresponding to the ligands **L**. Besides all, the spectra contain characteristic signals for the ethanol molecules: a triplet at about 1.10 ppm and a quartet at about 3.40 ppm with coupling constants $^3J_{H,H}$ = 7.0 Hz. The relative ratio of integral intensities of the signals of **L** and ethanol supports the presence of one and about two and a half molecules of ethanol per two ligands **L** in **1** and **2**, respectively. It should be noted that the spectra exhibit signals exclusively in the diamagnetic region (0–14 ppm), testifying to the presence of low spin diamagnetic cobalt(III) species.

The coordination chemistry of DMSO to transition metals has been thoroughly studied [26]. DMSO can exhibit *S*-, *O*-, or bridging µ-*S*,*O*-bound coordination modes. In the ^1H NMR spectra, *O*- and *S*-bound DMSO ligands exhibit ^1H NMR chemical shifts at 2.60–3.05 and 3.30–3.80 ppm, respectively [27]. In the ^1H NMR spectra of both **1** and **2**, the solvent signal was exclusively observed at 2.50 ppm testifying to the presence of free DMSO. Furthermore, all the signals of **L** and DMSO in the ^1H NMR spectra of the complexes were shown as narrow signals testifying to the absence of exchange between these species, at least under experimental conditions.