Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 29 Oct 2010

To cite this article: Adelino Vieira De Godoy Netto, Regina Célia Galvão Frem & Antonio Eduardo Mauro (2002): Synthesis and Spectroscopic Characterization of a Novel Coordination Polymer of Palladium(II) with Pyrazole and Azido Ligands, Molecular Crystals and Liquid Crystals, 374:1, 255-260

To link to this article: http://dx.doi.org/10.1080/713738305

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 255-260

1058-725X/02 $12.00 + .00

Synthesis and Spectroscopic Characterization of a Novel Coordination Polymer of Palladium(II) with Pyrazole and Azido Ligands

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The one-dimensional coordination polymer of palladium(II) with pyrazolato (Pz^-) and azide (N_3^-) as bridging ligands, of formula $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$, has been prepared. From IR and Raman studies it was evidenced the exobidentate nature of pyrazole ligands as well the μ-1,1-bridging coordination of azido groups. NMR experiments showed two sets of broadened signals with different intensities indicating the presence of pyrazolato groups in distinct chemical environments. The proposed structure of $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$ consists of a zigzag ribbon in which each $(Pz)_2Pd(Pz)_2$ entity is bound to two stacked planar units [Pd(μ-Pz)(μ-N_3)Pd core] with very weak Pd-Pd interaction, based on UV-Vis spectroscopy.

Keywords: pyrazole; palladium(II); azide; coordination polymer; IR spectroscopy; NMR spectroscopy

INTRODUCTION

The construction of coordination polymers via spontaneous self-assembly of known transition metal coordination environments and multifunctional exodentate ligands is one of the most important research areas of current synthetic chemistry and molecular material science [1]. The interest in these novel species arises from their potential properties

such as non-linear optic, magnetism and electrical conductivity [2]. Within this context, pyrazolato [3] and azide anions [4] exhibit a rich coordination chemistry and display the ability to bond to different metal units as exopolydentate ligands, yielding oligo- and polymeric metal complexes with peculiar properties. In addition, bimetallic d^8 compounds containing pyrazolato and azido group as bridging ligands [M(μ-Pz)(μ-N_3)M' core] showed columnar stacking with extended M-M interactions which can provide interesting anisotropic electrical effects [5]. In the framework of our current research in the coordination chemistry of pyrazoles and pseudohalides [6], we report herein the synthesis and spectroscopic studies of a new 1-D coordination polymer of Pd(II) with pyrazole and azido ligand with very weak Pd-Pd interactions.

EXPERIMENTAL

General Comments

The materials used in the syntheses were all commercially available and were used without purification. All solvents were dried and kept over molecular sieves prior to use. Literature procedures were followed for the synthesis of [$PdCl_2(MeCN)_2$][7]. Elemental analysis (C, H, N) were conducted by the Central Analítica of IQ-USP (Brazil). Raman and Infrared spectra were recorded on a Renishaw spectrometer and on a Nicolet FTIR-Impact 400 spectrophotometer, respectively. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker AC-200 spectrometer, using $SiMe_4$ as internal standard. UV-Vis spectrum was recorded using a Hewlett Packard 852 A spectrometer.

Synthesis of $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$

To a deep orange solution of [$PdCl_2(MeCN)_2$] in MeOH it was added pyrazole and NaN_3 in a 1:2:2 molar ratio, respectively, affording a yellow suspension. The solid was isolated and purified by conventional techniques. The compound is soluble in $CHCl_3$. Yield 75%. *Anal.* Calcd. for $C_{15}H_{15}N_{13}Pd_3$(%): C, 25.85; N, 26.13; H, 2.05. Found: C, 25.30; N, 26.24; H, 2.17.

RESULTS AND DISCUSSION

Vibrational Spectroscopy

The IR spectrum of the compound (Table 1) shows a strong band at 2086 cm^{-1}, assigned to $\nu_{as}N_3$ mode. The shift to higher wavenumber of ν_{as} with respect to the free azide strongly supports the bridging nature of the ligand. In addition, it is well known [4] that the ν_sN_3 vibration is only IR active for the cases where the azido group exhibits the terminal or end-on bridging mode. So, the appearance of ν_s in the IR at 1248 cm^{-1} as well the ν_{as} band in the Raman spectrum at 2089 cm^{-1} (Table 1) suggest the presence of the end-on bridging mode. Infrared evidence for the exobidentate pyrazolato groups includes a strong band at 742 cm^{-1} due to the out-of-plane bending of the ring hydrogens and the absence of a broad and intense νNH band at *ca.* 3250 cm^{-1} [8].

TABLE 1 IR and Raman frequencies (cm^{-1}) of $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$

IR $\bar{\nu}$ (cm^{-1})	Raman $\bar{\nu}$ (cm^{-1})	Assignment
3121 *w*		νCH
2086 *s*	2089 *mw*	$\nu_{as}N_3$
1486 *mw*, 1425 *mw*, 1384 *m*	1424 *mw*, 1384 *m*	ν_{ring}
1287 *mw*, 1185 *m*	1287 *s*, 1170 *m*	$\nu_{ring} + \delta CH$
1248 *mw*		ν_sN_3
1063 *s*	1067 *m*	δCH
	969 *m*, 919 *m*	ν_{ring}
870 *w*, 742 *s*		γCH
622 *m*		δ_{ring}
551 *w*		δNNN
460 *w*, 398 *w*		νPdN

w = weak, m = medium, s = strong

NMR Spectroscopy

The ^1H and ^{13}C NMR spectra of the complex, with the assignments, are shown in Figure 1.

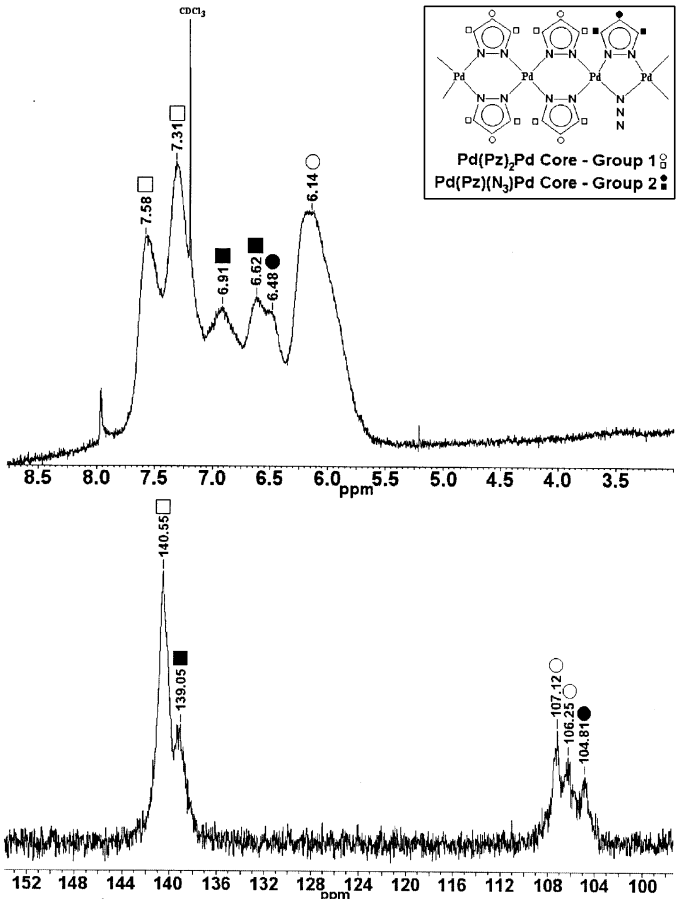

FIGURE 1 ^{1}H (A) and ^{13}C NMR (B) spectra of $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$. (Inset) Proposed monomer structure with the assignment legends

The broadening of signals observed in the NMR spectra is characteristic of polymeric systems. In the Figure 1 it is observed two sets of signals, with different intensities, which indicate the presence of pyrazolato rings in distinct chemical environments (see Inset of Figure 1).

UV-Vis Spectroscopy

The existence of metal-metal interactions in this compound was inferred on the basis of UV-Vis spectroscopy. The electronic spectrum of $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$ showed, besides the IL and LF transitons, at UV

region and 458 nm, respectively, a band at 737 nm which is characteristic of metal-metal electronic interactions among stacked planar coordination entities [9].

Proposed Structure

Some important features of the five- and six-membered metallocycles {M(μ-Pz)(μ-N_3)M and M(μ-$Pz)_2$M}, obtained from crystallographic data [5,10], indicate that the former presents a planar conformation suitable for stacking arrangements whereas the later framework has a boat configuration with high flexibility.

Therefore on basis of these above statements and spectroscopic results as well with the support of analytical data we proposed the following structure for $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$ in the solid state (Figure 2):

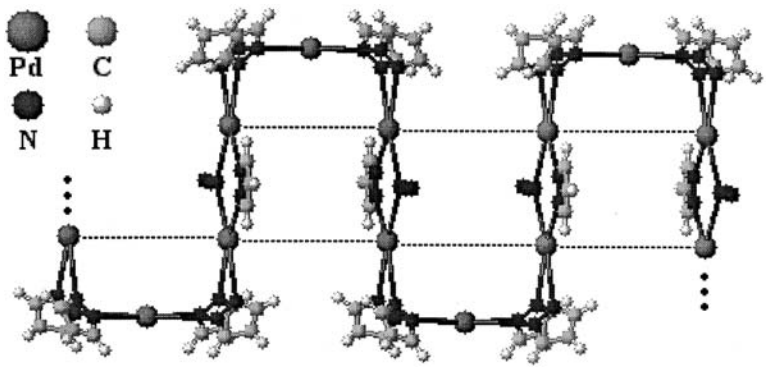

FIGURE 2 Proposed structure of $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$

The proposed structure of $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$ (Figure 2) consists of a one-dimensional zigzag molecular ribbon in which each $(Pz)_2Pd(Pz)_2$ entity is bounded to two stacked planar units {Pd(μ-Pz)(μ-N_3)Pd core}. The columnar stacking of the planar units takes place along one axis *via* Pd-Pd interactions (dotted lines).

CONCLUSIONS

The synthesis and characterization of the novel one-dimensional coordination polymer have been presented. The self-assembly of

$[PdCl_2(HPz)_2]$ complex and azide ion giving rise to the $[Pd_3(\mu\text{-}N_3)(\mu\text{-}Pz)_5]_n$ compound takes place without the need of any deprotonating agent. The spectroscopic data are in agreement with the proposed structure in which it is suggested the existence of very weak metal-metal interactions among the stacked coordination entities.

ACKNOWLEDGMENTS

The authors wish to thanks for the financial support from FAPESP, Capes and CNPq.

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