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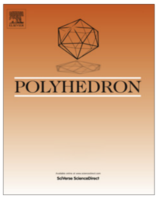

Syntheses, thermal analyses, crystal structures, FT-IR and Raman spectra of 2D $[Zn(NH_3)_2(\mu\text{–}ampy)M'(\mu\text{–}CN)_2(CN)_2]_n$ (M′ = Ni(II), Pd(II) or Pt(II)) complexes

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ABSTRACT

Three new cyano-bridged heteronuclear polymeric complexes, $[Zn(NH_3)_2(\mu\text{–}ampy)Ni(\mu\text{–}CN)_2(CN)_2]_n$ (**1**), $[Zn(NH_3)_2(\mu\text{–}ampy)Pd(\mu\text{–}CN)_2(CN)_2]_n$ (**2**) and $[Zn(NH_3)_2(\mu\text{–}ampy)Pt(\mu\text{–}CN)_2(CN)_2]_n$ (**3**) (ampy = 4-aminomethylpyridine) have been synthesized and characterized by vibrational spectroscopy (FT-IR and Raman), thermal (TG, DTG and DTA) and elemental analyses. The crystal structures of complexes **1** and **2** have been determined by the X-ray single crystal diffraction technique. Complexes **1** and **2** crystallize in the triclinic system with the space group $P\bar{1}$. Structural studies reveal that the Ni(II) or Pd(II) ions are four coordinate with four cyanide–carbon atoms in a square planar geometry and the Zn(II) ion exhibits a distorted octahedral coordination geometry completed by the six N atoms from two ammine, one ampy and two cyano ligands. The adjacent metal centers are bridged by bis-monodentate cyano ligands to form a one-dimensional linear chain. These chains are linked by ampy ligands into a 2D sheet structure. The 2D units are connected together via intramolecular C–H···N and intermolecular N–H···N hydrogen bonding to form 3D supramolecular networks. In additional, there are also interactions between the Ni(II) or Pd(II) ion and the aromatic π-system. Vibrational spectral data indicate the presence of two $\nu(C{\equiv}N)$ bands for the complexes, which can be assigned to the terminal and bridging cyanide ligands. Decomposition reactions take place in the temperature range 40–900 °C in a static air atmosphere.

1. Introduction

Cyanometallates are used as building blocks for various kinds of 1D-, 2D- and 3D-polymeric networks with transition metal ions, which have useful functional properties such as clathrate hosts [1], spin-crossover phenomena [2–4] and molecular magnet [5]. These types of materials are packed to form crystal structures because of bridging groups and intermolecular interactions [6]. The tetracyanometallate(II) anion can use a different number of cyano groups to connect to other metal atoms and it exists in a wide range of solid state structures. The bridging character of two cyano groups of $[M'(CN)_4]^{2-}$ (M′ = Ni(II), Pd(II) or Pt(II)) anions has been shown to product several types of structures in the solid state [7]. The well-known Hofmann-type complexes, with the general formula $[ML_2M'(CN)_4]$ (M(II) = Mn, Fe, Co, Ni, Cu, Zn or Cd; M′(II) = Ni, Pd or Pt), have been shown to form 1D-, 2D- or 3D-polymeric structures by metal–ligand–metal bridge connections [8–11]. The cyanide anion can behave as a bridging ligand at both ends, with the carbon and nitrogen atoms acting as Lewis bases between two coordination centers, which have generally metal cations acting as Lewis acids. The $[Ni(CN)_4]^{2-}$ moiety may adopt a number of catenation modes to build up 1D-, 2D- or 3D-structures [12]. The square planar $[Ni(CN)_4]^{2-}$ anion has been extensively used as a building block for the synthesis of expanded cyano bridged structures [13–18], but studies of coordination polymer compounds using $[Pd(CN)_4]^{2-}$ or $[Pt(CN)_4]^{2-}$ as building blocks are scarce [6,19,20]. Based on this structure, tetracyanometallate(II) complexes have been developed using N-donor ligands [7,9,16,19,21]. In general, the cyano ligand in cyano-bridged complexes acts as a bridging ligand in creating two-dimensional layers. In the synthesized cyano-bridged title complexes, the ampy ligand acts as a bridging ligand to form the two-dimensional layers. Therefore, the ampy ligand shows a bridging character, which is rare in the literature [22,23].

Non-covalent interactions are very important in biological structures, supramolecular chemistry and molecular recognition. Although cyano bridged complexes have been studied extensively,

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both structurally and spectroscopically, for many years [24,25], Ni(II)···π or Pd(II)···π interactions have rarely been reported for this type of complex [21]. The M···π interactions are probably weak; however, they are very import in stabilizing the polymeric structure of the complexes. Transition-metal-directed self-assembly is also a powerful approach for the construction of different supramolecular architectures with unusual and interesting properties.

We have recently reported the polymeric complexes $[Cd(NH_3)(\mu\text{–ampy})Ni(\mu\text{–CN})_4]_n$ and $[Cd(NH_3)_2(\mu\text{–ampy})Pd(\mu\text{–CN})_2(CN)_2]_n$, which are the first examples of tetracyanonickellate(II) and tetracyanopalladate(II) complexes with 3-aminomethylpyridine or 4-aminomethylpyridine ligands as blocking ligands [22,23]. As an extension of these works, we are reporting the results of our study on the preparation, vibrational spectral and thermal properties of three new cyano-bridged heteronuclear polymeric complexes, $[Zn(NH_3)_2(\mu\text{–ampy})Ni(\mu\text{–CN})_2(CN)_2]_n$ (**1**), $[Zn(NH_3)_2(\mu\text{–ampy})Pd(\mu\text{–CN})_2(CN)_2]_n$ (**2**) and $[Zn(NH_3)_2(\mu\text{–ampy})Pt(\mu\text{–CN})_2(CN)_2]_n$ (**3**). The molecular and crystal structures of the cyano bridged heteronuclear polymeric complexes **1** and **2** have been determined by X-ray single crystal diffraction.

2. Experimental

2.1. Material and instrumentation

Zinc(II) chloride ($ZnCl_2$), nickel(II) chloride hexahydrate ($NiCl_2\cdot6H_2O$), palladium(II) chloride ($PdCl_2$), platinum(II) chloride ($PtCl_2$), potassium cyanide (KCN) and 4-aminomethylpyridine were purchased from commercial sources and were used without further purification. The FT-IR spectra of the complexes were recorded as KBr pellets in the range 4000–400 cm^{-1} (2 cm^{-1} resolution) on a Perkin Elmer 100 FT-IR spectrometer which was calibrated using polystyrene and CO_2 bands. The Raman spectra of the complexes were recorded in the range 4000–100 cm^{-1} on a Bruker Senterra Dispersive Raman instrument using 785 nm laser excitation. A Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in a static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range 40–900 °C using platinum crucibles. Elemental analyses were carried out on a LECO, CHNS-932 analyzer for C, H and N at the Middle East Technical University Central Laboratory.

2.2. Syntheses of the complexes

$K_2[M'(CN)_4]\cdot H_2O$ (M' = Ni(II), Pd(II) or Pt(II)) was prepared by mixing stoichiometric amounts of the metal(II) chloride (1 mmol, $NiCl_2\cdot6H_2O$ = 0.237 g, $PdCl_2$ = 0.177 g or $PtCl_2$ = 0.265 g) in water (10 mL) with KCN (4 mmol, 0.260 g) also in water (10 mL). To this $K_2[M'(CN)_4]\cdot H_2O$ (M' = Ni(II), Pd(II) or Pt(II)) solution, $ZnCl_2$ (1.0 mmol, 0.136 g) dissolved in water (10 mL) was added with continuous stirring for approximately 4 h at 50 °C in a temperature-controlled bath. The compounds obtained were filtered and washed with water and dried in air.

Table 2
Crystallographic data and structure refinement parameters for complexes.

Complex	1	2
Empirical formula	$C_{10}H_{14}N_8NiZn$	$C_{10}H_{14}N_8PdZn$
Color/shape	purple/block	yellow/block
Formula weight	370.37	418.06
T (K)	293	293
Radiation used, graphite monochromator	Mo Kα (λ = 0.71073 Å)	
Crystal system	$P\bar{1}$	$P\bar{1}$
Space group	triclinic	triclinic
a (Å)	8.4953 (8)	8.5445 (12)
b (Å)	8.6323 (11)	8.7026 (12)
c (Å)	11.1956 (12)	11.4451(17)
α (°)	77.359 (10)	77.009 (12)
β (°)	78.221 (8)	76.965 (13)
γ (°)	68.144 (10)	67.398 (14)
V ($Å^3$)	736.68 (14)	756.36 (19)
Z	2	2
Absorption coefficient (mm^{-1})	2.91	2.78
D_{calc} ($Mg\ m^{-3}$)	1.670	1.836
Max. crystal dimen. (mm)	0.21 × 0.18 × 0.11	0.34 × 0.21 × 0.13
θ (max) (°)	30.5	30.5
Reflections measured	4472	4617
Range of h, k, l	$-10 < h < 12$, $-12 < k < 12$, $-15 < l < 15$	$-12 < h < 11$, $-12 < k < 12$, $-16 < l < 16$
Diffractometer/scan	Bruker Kappa APEXII/φ and w	
No of reflections with $I > 2\sigma(I)$	2006	1413
Corrections applied	Lorentz-polarization	
Source of atomic scattering factor	Int. Table for X-ray Cryst. Vol. IV, 1974 [44]	
Structure solution	Direct methods	
Treatment of hydrogen atoms	Geometric calculation & difference map.	
Goodness-of-fit (GOF) on F^2	0.97	1.03
$R = \lVert F_o\rvert - \lvert F_c\rVert/\lvert F_o\rvert$	0.0750	0.112
R_w	0.127	0.304
(Δ/ρ) max ($e\ A^{-3}$)	1.082	2.44
(Δ/ρ) min ($e\ A^{-3}$)	−0.65	−0.06

The $[Zn(NH_3)_2(\mu\text{–ampy})M'(\mu\text{–CN})_2(CN)_2]_n$ (M' = Ni(II), Pd(II) or Pt(II)) complexes were prepared by mixing together a 50 mL of water solution of $K_2[M'(CN)_4]\cdot H_2O$ (1 mmol, $K_2[Ni(CN)_4]\cdot H_2O$ = 0.259 g, $K_2[Pd(CN)_4]\cdot H_2O$ = 0.306 g or $K_2[Pt(CN)_4]\cdot H_2O$ = 0.395 g) with ampy (2 mmol, 0.216 g) dissolved in ethanol and ammonia

Table 1
The wavenumbers of the $[M'(CN)_4]$ (M' = Ni(II), Pd(II) or Pt(II)) vibrations in the complexes (cm^{-1}).

Assignment [32–34]	$K_2[M'(CN)_4]\cdot H_2O$			**1**	**2**	**3**
	M' = Ni	M' = Pd	M' = Pt			
A_{1g}, $\nu(C\equiv N)$	(2160) vs	(2169) vs	(2173) vs	(2186) s, (2166) s	(2201) s, (2185) s	(2206) s, (2196) s
B_{1g}, $\nu(C\equiv N)$	(2137) m	(2159) s	(2153) m	(2146) vs	(2162) vs	(2165)vs
E_u, $\nu(C\equiv N)$	2122 vs	2135 m	2136 vs	2159 s, 2138 s, 2122 vs	2173 s, 2154 s, 2137 s	2170 s, 2155 s, 2136 s
E_u, $\nu(C^{13}N)$	2084 w	2097	2085 w	2082 sh	2096 sh	2096 sh
E_u, $\nu(M'\text{–}C)$	540 w	486 w	504 m	543 w	508 vw	506 w
A_{2u}, $\pi(M'\text{–}CN)$	443 w	–	428 vw	487 m	485 m	484 m
A_{1g}, $\nu(M'\text{–}C)$	–	(436) w	(477) w	–	(436) m	(485) m
E_u, $\delta(M'\text{–}CN)$	417 s	400 m	407 s	425 vs	414 w	418 m

Abbreviations used: s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very. The symbols ν, δ and π refer to valence, in-plane and out-of-plane vibrations, respectively. Raman bands are given in parenthesis.