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C–H···Pd interactions and cyano-bridged heteronuclear polymeric complexes

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ABSTRACT

Three new heterometallic complexes, $[Cu(N\text{-}Meim)_4Pd(\mu\text{-}CN)_2(CN)_2]_n$ (**1**), $[Zn(N\text{-}Meim)_3Pd(\mu\text{-}CN)_2(CN)_2]_n$ (**2**) and $[Cd(N\text{-}Meim)_2Pd(\mu\text{-}CN)_4]_n$ (**3**), have been isolated from the reactions of $M[Pd(CN)_4]$ (M = Cu(II), Zn(II) or Cd(II)) and *N-Meim* (*N*-methylimidazole) with in different molar ratios. All complexes have been characterized by X-ray analyses, vibrational (FT-IR and Raman) spectra, thermal and elemental analyses. The crystallographic analysis reveals that the crystal structures of **1** and **2** are 1D coordination polymer, while **3** presents a 2D network. In the Cu(II) and Zn(II) complexes, two cyanide groups of $[Pd(CN)_4]^{2-}$ coordinated to the adjacent M(II) ions and distorted octahedral and square pyramidal geometries of complexes are completed by four and three nitrogen atoms of *N-Meim* ligands, respectively. The Cd(II) ion is six-coordinate, completed with the two nitrogen atoms of *N-Meim* ligands in the axial positions and the four nitrogen atoms from bridging cyano groups in the equatorial plane. The most striking features of complexes **1**–**3** are the presence of obvious C–H···Pd hydrogen-bonding interactions between the Pd(II) and hydrogen atoms of *N-Meim* ligand. This weak hydrogen bonding plays a crucial role in the architecture of the network polymers. The adjacent chains are held together by C–H···Pd, C–H···π or π···π interactions, forming three-dimensional network.

1. Introduction

Today, there is an increasing interest in the synthesis and characterization of new coordination polymers due to their challenging structural features. These complexes frequently contain porous structures and can act as adsorbents for gases [1], as molecular sieves [2], in sensing devices [3], as hosts for smaller guest molecules [4], in non-linear optics devices [5] and as magnetic materials [6]. Recently, cyano complexes with various degrees of dimensionality have been the subject of structural studies. In such a case, the cyano group or cyano complex anion in addition to its structural function, also demonstrates an important function: the particular characteristics of the cyano ligand have accorded it wide-ranging interest in various research areas [7,8]. The well-known one-, two- and three-dimensional cyano-bridged metal complexes, $[MLPd(CN)_4]$, are built by stacking the two-dimensional palladium cyanide sheets in layers [9–22].

For many years there had been considerable interest in the activation of C–H bonds by transition metal complexes. In this connection, many examples of transition metal complexes showing the agostic or anagostic C–H···M interaction have been recognized [13–16]. The C–H···M interaction can be viewed as Lewis acid–Lewis base interactions, wherein the metal center in the former serves as the Lewis base while in the latter it adopts the role of the Lewis acid [16]. Recently a few examples of the three-center four-electron agostic interaction have been reported [13,17–22]. The C–H···M interactions are relevant with d^8 systems and considered to be of importance for the understanding of catalytic reactions [23]. Furthermore, the C–H···M hydrogen bond plays a crucial role in constructing the supramolecular network [24].

In the preceding studies, the complexes of imidazole and its methyl derivatives with the metal(II) ion were described in several papers [25–28]. We have recently reported the vibrational spectra, thermal properties and crystal structure results of cyano-bridged heteronuclear polymeric complexes [29–32]. As a part of our continuing research on the syntheses and characterizations of complexes, we define in this study, the syntheses, spectral (FT-IR and Raman), thermal and elemental analyses of the $[Cu(N\text{-}Meim)_4Pd(\mu\text{-}CN)_2(CN)_2]$ (**1**), $[Zn(N\text{-}Meim)_3Pd(\mu\text{-}CN)_2(CN)_2]$ (**2**) and $[Cd(N\text{-}Meim)_2Pd(\mu\text{-}CN)_4]_n$ (**3**). The molecular and crystal structures of the cyano-bridged heteronuclear polymeric complexes **1**–**3** have been designated by X-ray single crystal diffraction. The thermal decomposition behaviors of the complexes were followed up in the temperature range 30–700 °C in the static air atmosphere.

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2. Experimental

2.1. Materials

High purity *N*-methylimidazole (99%), $NiCl_2 \cdot 6H_2O$ (98%), $CuCl_2$ (98%), $ZnCl_2$ (99%), $CdCl_2 \cdot H_2O$ (98%) and KCN (96%) were purchased from Aldrich Chemical Co. Inc. and used as received. All other chemicals were of AR grade.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a LECO CHNS-932 analyzer. The FT-IR spectra were recorded as KBr pellets in the range of 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 were measured in the range of 3200–100 cm^{-1} on a Bruker Senterra Dispersive Raman instrument using laser excitation of 785 nm. Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in the static air atmosphere at a heating rate of 30–700 °C using platinum crucibles.

2.3. Crystallographic data collection and refinement

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structures were solved by direct methods and refined using the programs SHELXS97 and SHELXL97 [33]. All non-hydrogen atoms were refined anisotropically by full-matrix least squares methods [33]. Some H atoms (bonded to C8 for **1**, C4 and C12 for **2** and C2 for **3**) were located in a difference map and refined freely. Other hydrogen atoms bonded to carbon were placed in calculated positions (C–H = 0.93–0.96 Å) and treated using a riding model with *U* = 1.2 times the *U* value of the parent atom for CH and CH_3. The following procedures were implemented in our analysis: data collection: X-Area, cell refinement: X-Area, data reduction: X-RED [34]; program(s) used for molecular graphics were as follows: MERCURY programs [35]; software used to prepare material for publication: WinGX [36].

Table 1
Crystal data and structure refinement parameters for complexes

	1	2	3
Empirical formula	$C_{20}H_{24}CuN_{12}Pd$	$C_{16}H_{18}N_{10}PdZn$	$C_{12}H_{12}CdN_8Pd$
Formula weight	602.45	522.17	487.10
T (K)	293 (2)		
Wavelength (Å)	0.71073 Mo Kα		
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/m$
a (Å)	8.3038 (6)	8.2748 (3)	16.4032 (10)
b (Å)	8.6157 (7)	13.9991 (4)	7.6933 (5)
c (Å)	9.9506 (7)	18.4127 (8)	7.3147 (5)
α (°)	71.776 (6)		
β (°)	73.441 (7)	104.688 (3)	115.806 (5)
γ (°)	87.798 (6)		
V ($Å^3$)	647.14 (8)	2063.22 (13)	831.02 (9)
Z	1	4	2
Absorption coefficient (mm^{-1})	1.55	2.06	2.37
D_{calc} ($Mg\ m^{-3}$)	1.546	1.681	1.947
θ Range for data collection (°)	2.5–27.9	1.9–28.1	2.8–27.3
Measured reflections	6822	23 803	4601
Independent reflections, R_{int}	2669, 0.029	4279, 0.048	938, 0.033
Observed reflections [$I > 2\sigma(I)$]	2317	3901	854
Absorption correction	Integration Stoe X-RED (Stoe & Cie, 2001)		
Refinement method	Full-matrix least-squares on F^2		
Final *R* indices (all data)	R_1 = 0.023 wR_2 = 0.056	R_1 = 0.027 wR_2 = 0.066	R_1 = 0.019 wR_2 = 0.048
Goodness-of-fit on F^2	1.02	1.08	1.15
$\Delta\rho_{max}$ ($e\ Å^{-3}$)	0.37	0.62	0.33
$\Delta\rho_{min}$ ($e\ Å^{-3}$)	−0.34	−0.54	−0.43

2.4. Synthesis

$K_2[Pd(CN)_4] \cdot H_2O$ was prepared by mixing stoichiometric amounts of palladium(II) chloride (0.71 g, 4 mmol) with potassium cyanide (1.04 g, 16 mmol) in water solution (25 mL). The mixture was refluxed with stirring for 3 h at 50 °C in a temperature-controlled bath and then the $K_2[Pd(CN)_4] \cdot H_2O$ solution was cooled to

Table 2
The bond distances and angles in the complexes (Å, °).

Selected atoms			
Complex **1**			
Pd1–C10	1.992 (3)	Cu1–N1	2.0270 (16)
Pd1–C9	1.9929 (19)	Cu1–N3	2.0214 (16)
		Cu1–N5	2.510 (2)
$C10–Pd1–C9^{ii}$	88.39 (9)	$N3^i–Cu1–N5$	88.49 (7)
C10–Pd1–C9	91.61 (9)	N3–Cu1–N5	91.51 (7)
N3–Cu1–N1	88.29 (7)	N1–Cu1–N5	89.78 (7)
$N3–Cu1–N1^i$	91.71 (7)	$N1^i–Cu1–N5$	90.22 (7)
Complex **2**			
Pd1–C13	1.996 (3)	Zn1–N1	2.021 (2)
Pd1–C14	2.000 (3)	Zn1–N3	1.997 (2)
Pd1–C15	1.996 (3)	Zn1–N5	2.007 (2)
Pd1–C16	1.987 (3)	Zn1–N7	2.261 (2)
		Zn1–N8	2.293 (2)
C16–Pd1–C15	92.20 (10)	N5–Zn1–N1	119.98 (10)
C16–Pd1–C13	85.79 (10)	N3–Zn1–N7	90.90 (9)
C15–Pd1–C13	177.97 (10)	N5–Zn1–N7	91.65 (9)
C16–Pd1–C14	179.12 (11)	N1–Zn1–N7	88.87 (9)
C15–Pd1–C14	88.53 (11)	N3–Zn1–N8	88.05 (9)
C13–Pd1–C14	93.47 (10)	N5–Zn1–N8	91.23 (9)
N3–Zn1–N5	122.51 (9)	N1–Zn1–N8	89.18 (9)
N3–Zn1–N1	117.49 (9)	N7–Zn1–N8	177.06 (9)
Complex **3**			
Pd1–C5	1.984 (2)	Cd1–N3	2.377 (2)
Cd1–N1	2.271 (3)		
$C5^i–Pd1–C5$	90.37 (13)	$N3^{iv}–Cd1–N3$	87.18 (12)
$C5^{ii}–Pd1–C5$	89.63 (13)	$N1–Cd1–N3^{iii}$	87.38 (8)
N1–Cd1–N3	92.68 (8)	$N3–Cd1–N3^{iii}$	92.82 (12)

Symmetry codes: (i) −*x* + 1, −*y* + 1, −*z* + 1; (ii) −*x* + 2, −*y* + 1, −*z* for **1** and (i) −*x* + 1, *y*, −*z* + 2; (ii) *x*, −*y*, *z*; (iii) −*x* + 1, −*y*, −*z* + 2; (iv) −*x* + 1, −*y* + 1, −*z* + 1 for **3**.

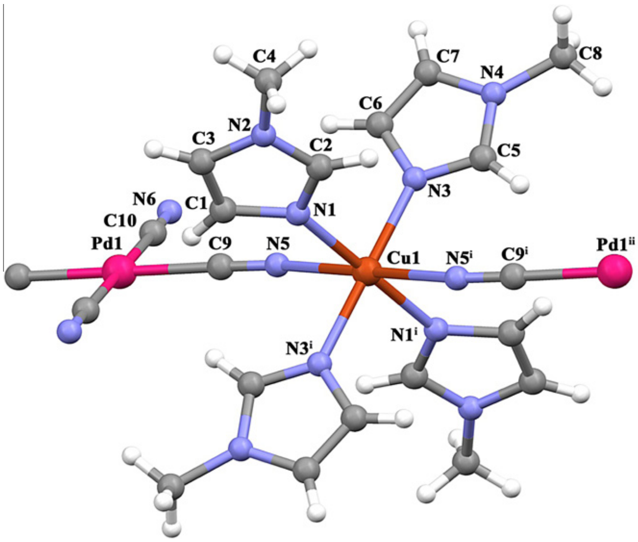

Fig. 1. The molecular structure of **1** showing the atom numbering scheme ((i) 1 − *x*, 1 − *y*, 1 − *z*; (ii) −1 + *x*, *y*, 1 + *z*).