Inorganica Chimica Acta 362 (2009) 5224–5230

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

The synthesis, structure, and characterization of three novel 1D nitrogen-heterocyclic copper(I)-diphosphine polymers

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ARTICLE INFO

Article history:
Received 10 June 2009
Received in revised form 19 September 2009
Accepted 21 September 2009
Available online 24 September 2009

Keywords:
Copper(I) polymer
Diphosphine
Nitrogen-heterocyclic
1D polymer

ABSTRACT

At ambient temperature, three 1D nitrogen-heterocyclic Cu(I)-diphosphine polymers, $\{[Cu_2(dppm)_2(BF_4)_2(pyz)](CH_2Cl_2)_2\}_n$ (**1**), $\{[Cu_2(dppm)_2(4,4'\text{-bpy})(CF_3SO_3)](CF_3SO_3)(CH_3OH)\}_n$ (**2**), $\{[Cu_2(dppe)_2(phen)_2](ClO_4)_2(CH_2Cl_2)\}_n$ (**3**) (dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane, pyz = pyrazine, 4,4′-bpy = 4,4′-bipyridine, phen = 1,10-phenanthroline) have been synthesized and characterized by X-ray crystallography, luminescence, IR, ^1H, and ^{31}P NMR. Structure analysis shows that **1** is a 1D linear polymer, **2** is a 1D stair-shaped polymer, and **3** is a 1D W-shaped polymer. A photoluminescent study of them shows that they exhibit fluorescent emission bands at ca. 555 nm, 535 nm and 557 nm, respectively.

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1. Introduction

Various transition metal complexes with bridging phosphines or functionalized phosphines have been an important part of coordination chemistry and organometallic chemistry, and have drawn much attention in recent years for their special structures, novel reactivity performances, catalytic properties and luminescence [1–4]. The diphosphine ligands known in the literature with the general formula $R_1R_2P\text{-}(X)_n\text{-}PR_3R_4$ (X = CH_2, NR) [5] are extensively studied. Among them, dppm has been confirmed to be a very efficient bridging bidentate ligand [6], and its chelating tendency is very suitable to lock two metal atoms together in close proximity [7]. Generally speaking, the complexes consisting of bridging dppm can give a M_2P_4 (that is, $M_2(dppm)_2$) framework with the two metal atoms held in close distance (regardless of whether a metal–metal bond is present or not) [8]. For some complexes with M_2P_4 framework, both metal atoms in M_2P_4 are coordinatively unsaturated or weakly coordinated [9,10], so they are versatile precursor complex, and are always used to react with additional ligands to get various complexes [8,11–15]. However, most of them are zero dimensional mono, bi, tri, and tetra nuclear complexes, and polymers are not common.

$Cu_2(dppm)_2$ framework is symmetrical, and we introduced a symmetrical linking ligand, pyrazine, to dinuclear precursor complexes $[Cu(dppm)(NO_3)]_2$ [9] and $[Cu_2(\mu\text{-}dppm)_2(CH_3CN)_2]X_2$ (X = ClO_4 or BF_4) [10], and got three 1D linear Cu(I)-dppm polymers $\{[Cu_2(dppm)_2(NO_3)_2(pyz)](pyz)\}_n$ [16], $\{[Cu_2(dppm)_2(ClO_4)_2(pyz)](CH_2Cl_2)\}_n$ [17], and $\{[Cu_2(dppm)_2(BF_4)_2(pyz)](CH_2Cl_2)_2\}_n$ (**1**). In a similar synthetic procedure to that of $[Cu_2(\mu\text{-}dppm)_2(CH_3CN)_2]X_2$ (X = ClO_4 or BF_4), we got the triflate analogue $[Cu_2(\mu\text{-}dppm)_2(CH_3CN)_2](CF_3SO_3)_2$, used it as a precursor complex and introduced 4,4′-bipyridine as linking ligand. Finally, we got a 1D stair-shaped polymer $\{[Cu_2(dppm)_2(4,4'\text{-bpy})(CF_3SO_3)](CF_3SO_3)(CH_3OH)\}_n$ (**2**). When engineering idea was expanded to Cu(I)-dppe analogue, we found a versatile dppe precursor complex $[Cu_2(\mu\text{-}dppe)(dppe)_2(CH_3CN)_2](ClO_4)_2$ [18], and used it as starting material to react with the chelating ligand 1,10-phenanthroline. Interestingly, we got a 1D W-shaped polymer $\{[Cu_2(dppe)_2(phen)_2](ClO_4)_2(CH_2Cl_2)\}_n$ (**3**). Herein, we report the synthesis, crystal structure and characterization of the three polymers, $\{[Cu_2(dppm)_2(BF_4)_2(pyz)](CH_2Cl_2)_2\}_n$ (**1**), $\{[Cu_2(dppm)_2(4,4'\text{-bpy})(CF_3SO_3)](CF_3SO_3)(CH_3OH)\}_n$ (**2**), and $\{[Cu_2(dppe)_2\text{-}(phen)_2](ClO_4)_2(CH_2Cl_2)\}_n$ (**3**).

2. Experimental

2.1. Materials and measurements

The reagents $Cu(ClO_4)_2{\cdot}6H_2O$, $Cu(BF_4)_2{\cdot}6H_2O$, $Cu(CF_3SO_3)_2$, pyrazine, dppm and dppe were purchased from J&K Chemical Ltd. and used as received. The precursor complexes $[Cu_2(\mu\text{-}dppm)_2(CH_3CN)_2](BF_4)_2$, $[Cu_2(\mu\text{-}dppe)(dppe)_2(CH_3CN)_2](ClO_4)_2$ were prepared according to literature procedure [10,18]. $[Cu_2(\mu\text{-}dppm)_2(CH_3CN)_2](CF_3SO_3)_2$ were prepared according to literature procedure [10], and its structure was determined by elemental analyses data. All other materials were of analytical grade and used without further purification. Elemental analyses (C, H, N) were

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doi:10.1016/j.ica.2009.09.035

performed on an Elementar Vario EL (Germany) analyzer. IR spectra were recorded from KBr pellets on a Brucker EQUINOX 55 FT-spectrometer. NMR experiments were carried out on a JNM ECA-600 (JEOL) spectrometer. Emission spectra were recorded on a Hitachi F-4500 Luminescence Spectrophotometer.

Caution: Perchlorate salts are potentially explosive and should therefore be handled with appropriate care.

2.2. Synthesis of complex **1**

A mixture of $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2](BF_4)_2$ (0.3456 g, 0.3 mmol) and pyrazine (0.0325 g, 0.4 mmol) in CH_2Cl_2/CH_3OH (7 ml/3 ml) was stirred at room temperature for 7 h, then filtered. Subsequent slow evaporation of the filtrate resulted in the formation of yellow crystals of complex **1**. Crystals suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared. IR (KBr disc, cm^{-1}): 3055m, 1631w, 1588w, 1485m, 1436s, 1423m, 1400m, 1309w, 1274w, 1124s, 1084s, 1051s, 991s, 806w, 779m, 743s, 720s, 695s, 516m, 483s, 457m, 441m. *Anal.* Calc. for $[H_{26}BC_{28}Cl_2CuF_4NP_2]$ (%): C, 50.98; H, 3.97; N, 2.12. Found: C, 51.01; H, 4.04; N, 2.14%.

2.3. Synthesis of complex **2**

2.3.1. Synthesis of $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2](CF_3SO_3)_2$

A mixture of $[Cu(CH_3CN)_4][CF_3SO_3]$ and dppm (1:1 mol ratio) was stirred in dichloromethane at room temperature for 6 h. Concentration of the resulting solution and addition of diethyl ether resulted in the precipitation of an off-white solid which was washed with diethyl ether and vacuum-dried. IR (KBr disc, cm^{-1}): 3447m, 3055m, 2260w, 1960w, 1892w, 1813w, 1630w, 1587w, 1575w, 1485m, 1437s, 1383w, 1288s, 1235s, 1167s, 1099s, 1072w, 1025s, 1000w, 919w, 848w, 787m, 737s, 720m, 693s, 636s, 575m, 516s, 476m. *Anal.* Calc. for $[H_{50}C_{56}CuF_6N_2O_6P_4S_2]$ CH_2Cl_2 (%): C, 50.25; H, 3.82; N, 2.06. Found: C, 49.84; H, 3.95; N, 2.11%.

2.3.2. Synthesis of complex **2**

A mixture of $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2](CF_3SO_3)_2{\cdot}CH_2Cl_2$ (0.3828 g, 0.3 mmol) and 4,4′-bpy·$2H_2O$ (0.1153 g, 0.6 mmol) in CH_2Cl_2/CH_3OH (7 ml/3 ml) was stirred at room temperature for 7 h, then filtered. Subsequent slow evaporation of the filtrate resulted in the formation of yellow crystals of complex **2**. Crystals suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared. IR (KBr disc, cm^{-1}): 3055m, 1603m, 1532w, 1484m, 1436s, 1412w, 1278s, 1224s, 1156s, 1099s, 1068w, 1030s, 1000w, 810m, 779m, 740s, 717m, 694s, 637s, 573m, 516s, 480m. *Anal.* Calc. for $[H_{56}C_{63}Cu_2F_6N_2O_7P_4S_2]$ (%): C, 54.70; H, 4.05; N, 2.02. Found: C, 54.53; H, 4.02; N, 2.11%.

2.4. Synthesis of complex **3**

A mixture of $[Cu_2(\mu\text{-dppe})(dppe)_2(CH_3CN)_2](ClO_4)_2$ (0.2770 g, 0.173 mmol) and 1,10-phenanthroline·H_2O (0.0348 g, 0.173 mmol) in CH_2Cl_2/CH_3OH (7 ml/3 ml) was stirred at room temperature for 7 h, then filtered. Subsequent slow evaporation of the filtrate resulted in the formation of yellow crystals of complex **3**. Crystals suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared. IR (KBr disc, cm^{-1}): 3054m, 1623w, 1587w, 1510w, 1484m, 1435s, 1424m, 1307w, 1144m, 1095s, 999w, 848s, 745s, 728s, 696s, 624s, 516s, 482m. *Anal.* Calc. for $[H_{66}C_{77}Cl_4Cu_2N_4O_8P_4]$ (%): C, 58.92; H, 4.21; N, 3.57. Found: C, 59.11; H, 4.41; N, 3.42%.

2.5. X-ray crystallography

Single-crystal X-ray diffraction studies of complexes **1**–**3** were performed on a Bruker SMART diffractometer equipped with CCD area detector with a graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo Kα radi-

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**.

Cu(1)–P(1)	2.2241(15)	Cu(1)–N(1)	2.091(4)
Cu(1)–P(2)	2.2270(16)	Cu(1)–F(1)	2.608(4)
P(1)–Cu(1)–P(2)	145.50(6)	P(1)–Cu(1)–F(1)	85.07(11)
P(1)–Cu(1)–N(1)	106.22(13)	P(2)–Cu(1)–F(1)	110.93(12)
P(2)–Cu(1)–N(1)	103.79(13)	F(1)–Cu(1)–N(1)	91.38(19)

Table 1
Crystallographic data and structure refinement summary for complexes **1**–**3**.

	1	**2**	**3**
Formula	$C_{28}H_{26}Cl_2CuNP_2BF_4$	$C_{63}H_{56}Cu_2N_2P_4S_2O_7F_6$	$C_{77}H_{66}Cl_4Cu_2N_4O_8P_4$
Molecular weight	659.67	1382.18	1568.10
Temperature (K)	293(2)	93(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$C2/c$	$P\bar{1}$
a (Å)	11.090(2)	52.832(4)	13.1231(13)
b (Å)	21.270(4)	14.8628(11)	13.7760(18)
c (Å)	12.780(3)	18.0916(15)	23.114(2)
α (°)	90.00	90.00	99.3000(10)
β (°)	98.35(3)	103.3600(10)	99.7400(10)
γ (°)	90.00	90.00	111.164(2)
V (Å^3)	2982.6(10)	13821.6(19)	3726.2(7)
Z	4	8	2
D_{calc} (mg m^{-3})	1.465	1.301	1.398
Goodness-of-fit on F^2	1.004	1.092	1.023
Crystal size (mm)	0.38 × 0.27 × 0.22	0.40 × 0.33 × 0.33	0.14 × 0.12 × 0.10
θ Range (°)	25.00	27.49	25.205
Reflections collected/unique	15 117/5105	55 982/15 833	19 087/12 693
R_{int}	0.0707	0.0326	0.1425
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Final R_1 and wR_2 indices	R_1 = 0.0624, wR_2 = 0.1500	R_1 = 0.0841, wR_2 = 0.2328	R_1 = 0.0743, wR_2 = 0.1609
R_1 and wR_2 indices (all data)	R_1 = 0.1132, wR_2 = 0.1795	R_1 = 0.0892, wR_2 = 0.2373	R_1 = 0.0867, wR_2 = 0.1917
Maximum, minimum peaks (e Å^{-3})	0.656 and −0.561	2.396 and −1.892	0.894 and −0.824

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