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Synthesis and Structures of Dinuclear Silver(I) and Copper(II) Complexes of a Semirigid Naphthalene-Bridged Bipyrazolyl Ligand

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Abstract Reactions of a semirigid bipyrazole, 2,7-bis (4'-methylene-1*H*-3',5'-diphenylpyrazole) naphthalene (H₂L) with Ag(I) or Cu(II) salts yielded four dinuclear complexes, namely, $[Ag_2(H_2L)_2(NO_3)_2]$ (1), $[Ag_2(H_2L)_2](CIO_4)_2$ (2), $[Ag_2(H_2L)_2](BF_4)_2$ (3), and $[Cu_2(H_2L)_2Cl_4]$ (4). X-ray analysis illustrates that the three Ag(I) complexes are structurally similar and exhibit a rectangular shape, while the Cu(II) complex features an intramolecular π -stacking between two naphthalene-moieties and is much more compressed compared with those Ag(I) complexes. Two different conformations, namely *cis, cis-* and *trans, trans-*, have been observed for this bipyrazolyl ligand in its Ag(I) and Cu(II) complexes, respectively.

Keywords Crystal structure · Bipyrazole · Dinuclear complex · Silver · Copper

Introduction

The use of bipyrazoles has attracted immense attention in recent years in the field of construction of metal–organic frameworks (MOFs) and discrete supramolecular assemblies [1-5]. Bipyrazole, in which two pyrazolyl moieties are bridged via an organic linker, behave in a much more

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complicated way than a single pyrazole does upon binding to metals, as demonstrated in several recent publications [4, 5]. It has been becoming clear that the separation distance and relative orientation between two pyrazolyl moieties are two key structure-determining factors among others to dictate the assembling of the bipyrazoles and metal ions.

We have recently reported the syntheses and structures of a series of semi-rigid C⁴-linked bipyrazolyl ligands, as well as their metal complexes (Scheme 1) [6–8]. As one might readily see, this type of bipyrazoles can be easily shaped to meet the requirement of assembling; 3,5-substituents of pyrazolyl ring and the central spacer are the locations which can be modified or replaced if need be. Following up with our previous work, we designed and prepared a new bipyrazolyl ligand with a naphthalene group as the linker (H₂L, Scheme 2), which is structurally similar to H₂L¹ (Scheme 1) and others reported previously [6].

Replacement of the *m*-xylylene group in H_2L^1 with a naphthalene-2,7-dimethylene linker yielded a new bipyrazole (H₂L) with a longer distance between two pyrazolyl moieties. In the meantime the relative orientation for them in H₂L remains almost the same as in H₂L¹. Herein we report the synthesis of the new bipyrazole—2,7-bis (4'-methylene-1*H*-3',5'-diphenylpyrazole)-naphthalene (H₂L), together with the crystal structures of its Ag(I) or Cu(II) complexes, namely [Ag₂(H₂L)₂](NO₃)₂ (1), [Ag₂(H₂L)₂] (ClO₄)₂ (2), [Ag₂(H₂L)₂](BF₄)₂ (3), and [Cu₂(H₂L)₂Cl₄] (4).

Experimental

Materials and Physical Measurements

Silver salts were purchased from Alfa Aesar and other commercially available reagents used without further

Scheme 1 Three types of bipyrazoles previously reported by us

Scheme 2 Synthetic route for the bipyrazole— H_2L



Ph'purification. The bipyrazolyl ligand 2,7-bis(4'-methylene-1*H*-3',5'-diphenylpyrazole)naphthalene (H₂L) was prepared according to the synthetic route shown in Scheme 2. IR spectra were recorded on a Nicolet Impact 420 FT-IR spectrometer as KBr pellets in the range of 500–4,000 cm⁻¹. C, H, N and S microanalyses were determined on a Flash EA 1112 elemental analyzer. ¹H NMR spectra were recorded on a Bruker DPX-400 spectrometer. Luminescence spectra were measured on a PTI Fluorimeter utilizing a photomultiplier to measure light intensity and Xe-lamp as radiation source.

Syntheses

Preparation of 2,7-Bis(4'-methylene-1H-3',5'- diphenylpyrazole)naphthalene

Step A A mixture of *N*-bromosuccinimide (2.50 g, 14.08 mmol), 2,7-dimethylnaphthalene (1.00 g, 6.4 mmol), AIBN (0.10 g, 0.58 mmol) in carbon tetrachloride (100 mL) was stirred at reflux for 10 min after which the mixture was cooled to 0 °C, the precipitated succinimide was filtered off and the filtrate evaporated under reduced pressure. The residue was recrystallized from absolute ether to give the desired product as a white solid. Yield: 85 %.

¹H NMR (400 MHz, CDCl₃): $\delta = 4.67$ (s, 4H, –CH₂Br), 7.52–7.85 (m, 6H, naphthyl) ppm.

Step B Potassium (0.19 g, 4.9 mmol) was dissolved in *tert*-butyl alcohol (50 mL), to this solution, dibenzoylme-thane (1.19 g, 5.3 mmol), 2,7-di(bromomethyl)naphthalene (0.77 g, 2.45 mmol) and KI (0.5 g) were added successively. The mixture was refluxed for 72 h under nitrogen.

White precipitate was obtained after *tert*-butyl alcohol being removed with rotary evaporation, which was dissolved in CHCl₃, and washed with water for several times to remove inorganic salts. The resulted solution was dried by anhydrous magnesium sulfate. Then the residue was recrystallized from THF–methanol to give the desired product as blocks. Yield: 75 %.

¹H NMR (400 MHz, CDCl₃): δ = 3.587–3.603 (d, 4H, –CH₂–), 5.604–5.637 (t, 2H, –CH–), 7.284–7.942 (m, 26H, Ph and naphthyl) ppm.

Step C The obtained bis-diketone was dissolved in $CHCl_3$ (50 mL), a solution of hydrazine (80 % N_2H_4 · H_2O , 0.8 mL) in methanol (8 mL) was added slowly. The mixture was refluxed for 12 h and then the solvent removed off under reduced pressure, the residue was recrystallized from THF–methanol to give the desired product as needles. Yield: 70 %.

¹H NMR (400 MHz, DMSO): $\delta = 4.186$ (s, 4H, –CH₂–), 7.20–7.75 (m, 26H, Ph and naphthyl) ppm. IR (KBr pellet): 3205(s), 3049(s), 2923(m), 1633(w), 1604(m), 1494(s), 1445(s), 1292(w), 1264(w), 1220(m), 1171(m), 974(s), 916(m), 837(m),763(s), 696(s) cm⁻¹. MS: m/z = 593.4[M + H]⁺.

Synthesis of $[Ag_2(H_2L)_2](NO_3)_2$ (1)

A solution of AgNO₃ (0.01 mmol, 1.7 mg) in CH₃CN (4 mL) was layered on the surface of a solution of H₂L (0.01 mmol, 6 mg) in THF (2 mL) in a test tube. Colorless crystals were obtained in 70 % yield within three days.

Anal. Calc. for $C_{42}H_{32}AgN_5O_3 \cdot 1.5CH_3CN \cdot THF$ (894.5) (%): C 65.74; H 4.97; N 10.17, Found: C 65.46; H 5.07; N 10.32. IR (KBr pellet): 3432(vs), 2924(w), 1635(m), 1491(w), 1425(m), 1384(m) (NO₃⁻), 1303(w), 1128(m), 1036(w), 982(m), 918(w), 835(w), 768(w), 695(s) cm⁻¹.

Synthesis of $[Ag_2(H_2L)_2](ClO_4)_2$ (2)

This complex was prepared in a similar way as for 1, using $AgClO_4$ (0.01 mmol, 2.3 mg) instead of the $AgNO_3$. Yield: 75 %.

Anal. Calc. for $C_{42}H_{32}AgClN_4O_4\cdot 2H_2O\cdot THF$ (908.19) (%): C 60.83; H 4.88; N 6.17, Found: C 61.17; H 4.72; N 6.03. IR (KBr pellet): 3426(vs), 3051(w), 2991(w), 1636(s), 1564(w), 1499(w), 1452(m), 1384(w), 1296(m), 1113(vs)(ClO₄⁻⁻), 964(m), 921(w), 768(m), 698(s), 621(s) cm⁻¹.

Synthesis of $[Ag_2(H_2L)_2](BF_4)_2$ (3)

A solution of $AgBF_4$ (0.03 mmol, 5.7 mg) in CH_3CN (2 mL) was mixed with a 2 mL of THF solution of H_2L (0.03 mmol, 18 mg). The resulting solution was allowed to

Table 1Crystallographic dataand structure refinement for 1,2, 3 and 4

evaporate slowly to produce colorless blocks in 30 % yield within one week.

Anal. Calc. for $C_{42}H_{32}AgBF_4N_4 \cdot 1/2CH_3CN \cdot THF \cdot 1.5H_2O$ (907.06) (%): C 62.23; H 4.94; N 6.95, Found: C 62.34; H 4.69; N 6.93. IR (KBr pellet): 3423(vs), 3060(w), 2922(w), 1707(m), 1636(m), 1561(w), 1481(w), 1450(m), 1384(w), 1200(w), 1113(s)(BF_4^-), 980(w), 929(w), 836(m), 773(m), 702(s), 619(w) cm^{-1}.

Synthesis of $[Cu_2(H_2L)_2Cl_4]$ (4)

This complex was prepared in a similar way as for 1, using $CuCl_2$ (0.01 mmol, 1.7 mg) instead of the AgNO₃. Yield: 80 %.

Anal. Calc. for $C_{42}H_{32}CuCl_2N_4$ (727.18) (%): C 69.37; H 4.44; N 7.70,Found: C 69.15; H 4.58; N 7.51. IR (KBr pellet): 3424(vs), 3053(w), 2923(w), 1634(m), 1557(w), 1482(s), 1450(s), 1385(w), 1293(m), 1179(s), 1130(m), 1074(w), 906(w), 834(w), 769(m), 697(vs), 624(w), 584(w) cm⁻¹.

	$1.2THF.6CH_3CN$	$2 \cdot 2 \text{THF} \cdot 6 \text{CH}_3 \text{CN}$	3	4
Formula	$C_{104}H_{98}Ag_2N_{16}O_8$	$C_{104}H_{98}Ag_2Cl_2N_{14}O_{10}$	$C_{84}H_{64}Ag_2B_2F_8N_8$	C42H32Cl2CuN4
Mr	1915.72	1990.62	1574.79	727.18
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Crystal group	$P2_{1}/c$	C2/m	C2/c	<i>P</i> -1
a (Å)	13.075(3)	18.775(4)	27.321(9)	11.018(2)
b (Å)	26.306(5)	26.360(5)	13.142(3)	12.568(3)
c (Å)	18.806(6)	12.949(3)	27.915(11)	13.641(3)
α (°)				82.92(3)
β (°)	132.846(18)	131.76(3)	121.36(3)	66.69(3)
γ (°)				73.98(3)
V (Å)	4742(2)	4780.4(28)	8559(5)	1667.2(6)
Z	2	2	4	2
T (K)	153(2)	153(2)	153(2)	153(2)
D _{calcd} (Mg/m ³)	1.342	1.350	1.222	1.449
$m (mm^{-1})$	0.479	0.531	0.519	0.854
F (000) (e)	1984	2008	3200	750
hkl range	$-17 \leq h \leq 17$	$-25 \leq h \leq 21$	$-25 \leq h \leq =33$	$-14 \leq h \leq 14$
	$-35 \le k \le 36$	$-33 \le k \le 35$	$-15 \leq k \leq 13$	$-15 \leq k \leq 16$
	$-19 \le l \le 25$	$-15 \leq l \leq 17$	$-33 \le 1 \le 29$	$-17 \leq l \leq 17$
Refl. collected	40,326	20,396	16,052	15,719
Refl. unique	12,499	$6,523 \ [R_{int} = 0.0427]$	7,758	7,533
	$[R_{int} = 0.0476]$		$[R_{int} = 0.1039]$	$[R_{int} = 0.0471]$
Param. refined	568	403	546	442
Restrains	4	138	564	0
Final R indices	R1 = 0.0859	R1 = 0.0535	R1 = 0.0976	R1 = 0.0603
$[I > 2\sigma]$	wR2 = 0.2163	wR2 = 0.1209	wR2 = 0.2917	wR2 = 0.1373
GoF (F ²)	1.188	1.022	1.006	0.972
$\begin{array}{c} \Delta \rho_{fin}(max, \\ min) e \text{\AA}^{-3} \end{array}$	1.139, -1.174	2.101, -0.949	1.453, -1.250	0.738, -0.524

X-ray Crystal Structure Determination

Diffraction intensities were collected at 153(2) K on a Rigaku Saturn 724 + CCD diffractometer with graphite-monochromated Mo-Ka radiation (0.71073 Å). Absorption corrections were applied using the multiscan program. The structures were solved by direct methods and refined by least squares techniques using the SHELXS-97 and SHELXL-97 programs [9]. All non-hydrogen atoms were refined with anisotropic displacement parameters expect for the disorder solvents; hydrogen atoms were generated geometrically. SQUEEZE program in PLATON was used in the refinement of 3 to cope with the unidentifiable solvent molecules [10]. A phenyl group and the tetrafluoroborate anion in 2 and the perchlorate anions in 3 are disorder and were modeled by splitting them into two parts, each with the site occupancy factor of 0.5 or 0.25. The high wR2 values for compound 1 and 3 may possibly originate from the highly disordered solvent molecules. The crystal data and the selected bond lengths and angles for these complexes are listed in Tables 1 and 2, respectively.

Results and Discussion

Synthesis and Characterization

Complexes 1, 2 and 4 were prepared by slow diffusion of solutions of metal salts into a solution of ligand, while the

crystals of **3** were obtained by slow evaporation of a mixture of $AgBF_4$ and bipyrazole.

The microanalyses demonstrated the molar ratio of metal to ligand is 1:1 for all of the four complexes. The IR spectra of these complexes showed the characteristic peaks of the anions (NO_3^- , CIO_4^- , or BF_4^- ; Figs. S6–S8).

Crystal Structure Description

The solvated complex, 1.2THF·6CH₃CN, crystalizes in the monoclinic space group of $P2_1/c$. The asymmetric unit consists of one Ag atom, one bipyrazole, one nitrate, two halves of THF molecules and three CH₃CN molecules (Fig. S10).

1 actually exists as a dinuclear molecular rectangle of M_2L_2 type, which is generated by a symmetric operation of inversion on the asymmetric unit of **1**. As shown in Fig. 1, the Ag(I) atom is linearly two-coordinated by two pyrazolyl N^2 atoms in a *cis*-fashion. The bipyrazolyl ligand, in the *cis*, *cis*-conformation (Scheme 3), behaves as a μ_2 -N,N' bridge linking two Ag(I) atoms. The shape of **1** resembles that of $[Ag_2(H_2L^1)_2](NO_3)_2$, H_2L^1 being a bipyrazole similar to H_2L , however, with *m*-xylylene as the linker between two pyrazolyl moieties [6]. The rectangle thus formed possesses a rather large cavity as exemplified by the intramolecular Ag...Ag distance of 8.264(3) Å, which is much longer than that [5.825(3) Å] in $[Ag_2(H_2L^1)_2](NO_3)_2$. The nearest distance between Ag and O atom from

Table 2 Selected bond distances (\mathring{A}) and hend angles	Complex 1			
(°) for 1, 2, 3 and 4	Ag(1)–N(1) 2.117(3)	N(3)-Ag(1)#1 2.117(3)		
	C(13)-N(3)-Ag(1)#1 135.7(3)	N(1)-Ag(1)-N(3)#1 165.93(13)		
	N(4)-N(3)-Ag(1)#1 118.2(2)	N(2)-N(1)-Ag(1) 118.3(2)		
	Complex 2			
	Ag(1)–N(1) 2.130(2)	O(3)–Cl(1)–O(2) 109.0(5)		
	C(1)-N(1)-Ag(1) 135.25(17)	O(3)–Cl(1)–O(1) 109.1(4)		
	N(2)-N(1)-Ag(1) 118.76(15)	O(2)–Cl(1)–O(1) 110.1(5)		
	N(1)#1-Ag(1)-N(1) 165.61(11)			
	Complex 3			
	Ag(1)–N(1) 2.147(7)	N(1)-Ag(1)-N(3)#1 170.5(3)		
	Ag(1)-N(3)#1 2.156(7)	C(7)-N(1)-Ag(1) 134.0(7)		
	C(29)-N(3)-Ag(1)#1 133.4(6)	N(2)-N(1)-Ag(1) 120.8(6)		
	N(4)-N(3)-Ag(1)#1 120.8(6)	N(4)-C(36)-C(28) 106.4(7)		
		N(4)-C(36)-C(37) 121.2(7)		
	Complex 4			
	Cu(1)–N(1) 2.008(3)	N(1)-Cu(1)-N(3) 91.41(12)		
	Cu(1)–N(3) 2.009(3)	N(1)-Cu(1)-Cl(2) 89.27(9)		
	Cu(1)–Cl(2) 2.232(13)	N(3)-Cu(1)-Cl(2) 158.96(10)		
	Cu(1)–Cl(1) 2.266(12)	N(1)-Cu(1)-Cl(1) 141.48(10)		
	C(9)–N(1)–Cu(1) 135.2(2)	N(3)-Cu(1)-Cl(1) 93.53(9)		
Symmetry codes: $1 \# 1 - x + 1$,	N(4)-N(3)-Cu(1) 117.5(2)	Cl(2)-Cu(1)-Cl(1) 98.98(5)		
-y, -z + 1; 2 #1) x, -y + 1, z; 3 #1) $-x + 1, y, -z + 1/2$	C(36)–N(3)–Cu(1) 135.3(3)	N(2)-N(1)-Cu(1) 118.8(2)		



Fig. 1 Ball-and-stick diagram of **1**, showing the coordination environment around the Ag atom and the *cis*, *cis*-conformation of the μ_2 -bridging bipyrazolyl ligand. The solvent molecules have been omitted for clarity. Selected distances (Å) and angles (°): Ag1–N1 = 2.117(3), Ag1–N3a = 2.117(3); N1–Ag–N3a = 165.93(13). Symmetry code: a) -x + 1, -y, -z + 1

nitrate is 2.895(8) Å, indicative of no coordination to metals. However, H-bonding is found between O atom of nitrate and pyrazole N atoms, with O…N distances being 2.934(6) and 2.981(6) Å (Fig. 1).

Extensive $\pi - \pi$ interactions are observed in the crystal structure of 1, which may contribute to the formation or stabilization of the present structure. Within the dinuclear complex, it can be clearly found that some of phenyl H atoms are pointing to the faces of naphthalene. The distances of $H(phenyl)\cdots C(naphthalene)$ for bipyrazole in 1 fall in the range of 2.559(5)-2.952(3) Å, indicative of the presence of C–H··· π interactions (Fig. S11) [11]. Moreover, we noticed that the H···H distances are 2.673(1) Å between two phenyl groups from two bipyrazoles within 1, implying some kind of weak interactions. However, the orientation and the centroid separation for the phenyl groups are somehow different from the well-defined face-to-face π stacking and the edge-to-face C–H··· π interaction (Fig. S12) [12, 13]. Between neighboring dinuclear rectangles exist the C–H··· π interactions, as evident by the fact that one naphthalene H atom points to a phenyl ring of an adjacent dinuclear complex with the shortest distance of H(naphthalene)…C(phenyl) being 2.66(3) Å (Fig. 2).



Fig. 2 The intermolecular C–H··· π interactions in 1, involving the naphthalene rings and the phenyl groups

One of the two solvated THF molecules is located within the cavity, which is disordered to two opposite positions with the distance of Ag \cdots O(THF) being 2.733(13) Å.

The complexes 2 and 3 crystalize in the monoclinic space groups, C2/m and C2/c, respectively. Their structures are similar to that of 1, therefore no further discussion is made of these complexes (Figs. S13–S16).

A few rectangular dinuclear silver complexes of M_2L_2 type, based on the bipyrazole ligands and various metals, have been recently reported by us [6–8]. The sizes of these rectangular structures can be defined by their intramolecular Ag...Ag distances, which are 5.825(3), 8.264(3), 8.898(2) and 12.153(2) Å for [Ag₂(H₂L¹)₂](NO₃)₂, [Ag₂(H₂L)₂] (NO₃)₂, [Ag₂(H₂L²)₂](BF₄)₂ and [Ag₂(H₂L³)₂](ClO₄)₂ (Scheme 1), respectively. It is worthy of note that except [Ag₂(H₂L¹)₂](NO₃)₂, all other three complexes hold solvent molecules in their cavities, indicating a longer linker between the two pyrazolyl moieties of the bipyrazoles leads







cis, trans



to a larger cavity within the complex, which is inclined to show the inclusion phenomena.

The complex **4** crystalizes in the triclinic P-1 space group. The asymmetric unit consists of one Cu(II) atom, one ligand and two chloride ions, which is related to its other half by a crystallographically imposed inversion center located midway between two metals in the dinuclear complex **4** (Fig. S17).

The Cu(II) atom is four-coordinated by two Cl⁻ ions and two pyrazolyl N^2 atoms from two ligands in a N₂Cl₂ geometry between tetrahedron and square planar. The ligand, in the *trans*, *trans*-conformation, acts as a μ_2 -N,N' bridge linking the two Cu(II) atoms in **4**, as depicted in Fig. 3. This *trans*, *trans*-conformation has not been observed for its analogue—H₂L¹, a *m*-xylylene bridged bipyrazole, while the *cis*, *cis*- and the *cis*, *trans*-conformations for this ligand have been reported in our previous paper [6].

Intramolecular hydrogen bonds of N_{pz} -H···Cl are presented with N···Cl distances of 3.013(4) and 3.070(4) Å. Similar to **1**, the intramolecular C–H··· π interactions



Fig. 3 Ball-and-stick diagram of **4**, showing the coordination environment around the Cu atom and the *trans*, *trans*-conformation of the μ_2 -bridging bipyrazolyl ligand. The intramolecular H-bonds of N_{pz}-H···Cl are represented as *dashed lines*. Selected distances (Å) and angles (°): Cu1–N1 = 2.008(3), Cu1–N3 = 2.009(3), Cu1–Cl2 = 2.232(1), Cu1–Cl1 = 2.266(2); N1–Cu1–Cl2 = 89.27(9), N1–Cu1–N3 = 91.41(12), N3–Cu1–Cl1 = 93.53(9), Cl1–Cu1–Cl2 = 98.98(5), N1–Cu1–Cl1 = 141.48(10), N3–Cu1–Cl2 = 158.96(10). Symmetry code: a) -x + 2, -y + 1, -z

Fig. 4 A chain formed by molecules of **4** through the weak intermolecular Cu…Cl bonds

involving the phenyl H atoms and the naphthalene faces are observed in **4**, as evident by the distances of H(phenyl)····C (naphthalene) for bipyrazole falling in the range of 2.676(3)–2.769(4) Å. Interestingly, the two naphthalene rings in **4** are parallel with a face-to-face distance of 3.484(4) Å, revealing the presence of intramolecular offset π ··· π stacking interaction (Fig. S18) [12], which together with other structural determinants (e.g. the coordination geometry of Cu²⁺) may contribute to the formation of the somewhat compressed structure compared with that of **1**.

The intermolecular distance of Cu···Cl between two adjacent molecules is 3.114(15) Å, generating a 1D chain along [011] direction if this weak Cu···Cl bond is taken into consideration, as shown in Fig. 4.

Luminescence Spectra

The solid-state luminescent spectra were recorded for the ligand and silver complexes at room temperature. Upon excitations at 350, 350, 288 and 223 nm for H₂L, **1**, **2**, and **3**, the emission maxima are observed at 420, 478, 338 and



Fig. 5 Solid-state luminescent spectra of H_2L , 1, 2, and 3 at room temperature



416 nm, respectively (Fig. 5). Since the structures of 1, 2 and 3 are similar, the variation on the emission maximum seems to be related with the different anions presented in the structures.

Conclusion

In this paper, a semi-rigid naphthalene-2,7-dimethylenebridged bipyrazole together with its four Ag(I) or Cu(II) complexes were prepared and characterized. X-ray analyses revealed a novel trans, trans-conformation of the bipyrazole in its Cu(II) complex, besides the more common cis, cis-conformation observed in its Ag(I) complexes and others reported previously with similar bipyrazolyl ligands. Extensive $\pi \cdots \pi$ interactions are found in the structures, involving the 3,5-diphenyl substituents of pyrazole and the naphthalene rings. Compared with the analogue bipyrazole with *m*-xylylene as the linker between two pyrazolyl moieties, the one reported in this paper possesses a longer separation distance here, which results in a larger void within the rectangular dinuclear complex. Further research to use this bipyrazole in construction of new architectures is underway in our laboratory.

Supplementary Materials

¹HNMR, MS and IR spectra of H_2L , IR spectra of the four metal complexes, the ellipsoid diagrams of the asymmetric units of the four metal complexes, several packing

diagrams showing the $\pi \cdots \pi$ interactions in 1 and 4 are provided as supplementary material.

CCDC 918864–918867 contain the crystallographic data for the complexes **1**, **2**, **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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References

- 1. Halcrow MA (2009) Dalton Trans 2059
- 2. Zhang JP, Zhang YB, Lin JB, Chen XM (2012) Chem Rev 112:1001
- Colombo V, Montoro C, Maspero A, Palmisano G, Masciocchi N, Galli S, Barea E, Navarro JAR (2012) J Am Chem Soc 134:12830
- 4. Gao GF, Li M, Zhan SZ, Lv Z, Chen GH, Li D (2011) Chem Eur J 17:4113
- 5. Jozak T, Sun Y, Schmitt Y, Lebedkin S, Kappes M, Gerhards M, Thiel WR (2011) Chem Eur J 17:3384
- 6. Yang G, Hao SJ, Wang ZY (2010) Transition Met Chem 35:381
- 7. Wang ZY, Chen JH, Zhao LF, Zhang WH, Yang G (2011) Transition Met Chem 36:731
- Duan PC, Huang ZD, Zhang FF, Yang G (2012) Transition Met Chem 37:595
- 9. Sheldrick GM (2008) Acta Cryst A64:112
- Spek AL (2008) PLATON, a multipurpose crystallographic tool. Utrecht University, Utrecht
- 11. Suezawa H, Yoshida T, Umezawa Y, Tsuboyama S, Nishio M (2002) Eur J Inorg Chem 3148
- 12. Janiak C (2000) J Chem Soc Dalton Trans 3885
- Hunter CA, Lawson KR, Perkins J, Urch CJ (2001) J Chem Soc Perkin Trans 2 651