

Pt^{II}-Promoted [2 + 3] Cycloaddition of Azide to Cyanopyridines:
Convenient Tool toward Heterometallic StructuresSuman Mukhopadhyay,[†] Bhaswati Ghosh Mukhopadhyay,[†] M. Fátima C. Guedes da Silva,^{†,‡}
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The [2 + 3] cycloaddition reactions (which are greatly accelerated by microwave irradiation) of the di(azido)platinum(II) compounds *cis*-[Pt(N₃)₂(PPh₃)₂] (**1**) with cyanopyridines NCR (**2**) (R = 4-, 3-, and 2-NC₅H₄) give the corresponding bis(pyridyltetrazolato) complexes *trans*-[Pt(N₄CR)₂(PPh₃)₂] (**3**) [R = 4-NC₅H₄ (**3a**), 3-NC₅H₄ (**3b**), and 2-NC₅H₄ (**3c**)]. Compound **3c** has been characterized as the N¹N²-bonded isomer in the solid state by X-ray crystallography and represents the first bis(tetrazolato) complex of this kind. Complexes **3a** and **3b** have been used as metallaligands to generate heteronuclear coordination polymers in the presence of copper nitrate. A one-dimensional supramolecular architecture was obtained as the exclusive product, {*trans*-[Pt₂(N₄CR)₄(PPh₃)₄Cu]_n(NO₃)_{2n}·nH₂O (**4**·nH₂O) (R = 4-NC₅H₄), when **3a** was employed, whereas with **3b** the heteronuclear square complex *trans*-[Pt(N₄CR)₂(PPh₃)₂Cu(NO₃)₂(H₂O)]₂ (**5**) (R = 3-NC₅H₄), composed of Pt/Cu ions, was obtained. All the isolated complexes were characterized by IR, elemental, and (for **3b**, **3c**, **4**, and **5**) X-ray structural analyses. Complexes **3** were additionally characterized by ¹H, ¹³C, and ³¹P {¹H} NMR spectroscopies.

Introduction

Syntheses of homo- and heterometallic coordination polymers using organic and inorganic linkers to develop new materials with interest in several areas (such as electronic devices and materials as single-molecule transistors¹ and single-molecule magnets,² catalysis,³ sensors, storage, and separation devices⁴) have attracted much attention. Of particular synthetic relevance to generate such structures is the attempt to get control over the whole process. In most

of the cases, self-assembly of organic ligands with inorganic metal ions are a key step and is a widely used approach where the success depends on the availability of programmed metal-based building blocks. Among several synthetic schemes, the in situ generation of tetrazole-based ligands to produce coordination polymers by a hydrothermal process where the cycloaddition reaction between an azide and a nitrile takes place has recently been studied,⁵ but this procedure is hitherto confined to the generation of homometallic supramolecular aggregates. Tetrazolato ligands with a pyridyl sidearm have been successfully used to generate a porous body-centered cubic type framework with copper ions.⁶ Moreover, among the numerous coordination polymeric structures reported so

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far, heterometallic coordination networks are not very common but can be synthesized by using, for example, cyanide, oxalate, or nitrite as bridging units.⁷ The use of metal complexes as building blocks (metallaligands), apart from those with such bridging ligands,⁷ to get a better control over the tuning of the desired heterometallic coordination polymer structure is still sparse in comparison with the application of pure organic ligands.⁸ Examples of formation of discrete heterometallic clusters, namely of the molecular square type, by using metallaligands are even rarer in literature.⁹

In our previous studies we have shown that the diazido-platinum(II) complexes *cis*-[Pt(N₃)₂(PPh₃)₂] react with a variety of nitriles to undergo [2 + 3] cycloaddition reactions producing *trans*-5-substituted tetrazolato complexes [Pt(N₄CR)₂(PPh₃)₂].¹⁰ In continuation of that study we have used different cyanopyridines to form cycloaddition platinum complexes, *trans*-[Pt(N₄CR)₂(PPh₃)₂] (**3**), which themselves can be used as metallaligands, providing a convenient methodology toward the synthesis of heteronuclear complexes of platinum with interesting molecular architectures. Hence, herein we also report the syntheses of a molecular square structure and a one-dimensional (1D)-supramolecular architecture with a rhombus-like grid, composed by Pt^{II} and Cu^{II} ions bridged by pyridyltetrazolato ligands.

Experimental Section

General, Materials, and Measurements. Solvents were purchased from Aldrich and were dried by usual procedures. *Cis*-[Pt(N₃)₂(PPh₃)₂] (**1**)¹¹ was prepared according to a published procedure. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ¹H, ¹³C, and ³¹P{¹H} NMR spectra (in CDCl₃ and in *d*₆-DMSO) were measured on a Varian Unity 300 spectrometer at ambient temperature. ¹H, ¹³C, and ³¹P chemical shifts (δ) are expressed in ppm relative to Si(Me)₄ (¹H and ¹³C) or 85% H₃PO₄ (³¹P). *J* values are in Hertz. Infrared spectra (4000–400 cm⁻¹) were recorded on a Bio-Rad FTS 3000MX and a Jasco FT/IR-430 instruments in KBr pellets, and the wavenumbers are in cm⁻¹. The microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter, 300 W) that is fitted with a rotational system and an IR detector for temperature.

Preparations. Complexes 3a–c. These complexes can be prepared by two different methods. The first method is by refluxing a solution of the starting complex **1** along with an excess of the corresponding cyanopyridine in DMF, and the second one is by using focused microwave irradiation.

i. Refluxing. A solution of **1** (0.080 g, 0.10 mmol) and 4-cyanopyridine (**2a**) (0.104 g, 1.00 mmol) in DMF (8 mL) was refluxed for 12 h, whereupon the solvent was removed in vacuo. The oily residue was treated with diethyl ether to obtain, upon stirring, a white semicrystalline solid. The solid was washed repeatedly with 5 mL portions of diethyl ether, and the resultant compound was recrystallized from a dichloromethane/diethyl ether mixture to produce the off-white crystalline compounds *trans*-[Pt{5-(4-pyridyl)-tetrazolato}₂(PPh₃)₂] (**3a**).

Complexes **3b** and **3c** were prepared analogously, but by using 3-cyanopyridine and 2-cyanopyridine, respectively.

ii. Focused Microwave Irradiation. In this method, identical amounts of the reagents described above were added to a cylindrical Pyrex tube that was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 °C. The solvent was then removed in vacuo, and the resulting oily residue was treated in a manner similar to that described above to obtain the white crystalline solid of **3a**. Complexes **3b** and **3c** were synthesized in an identical way.

Trans-[Pt{5-(4-pyridyl)-tetrazolato}₂(PPh₃)₂] (3a**).** 60% (method i) and 62% (method ii) yields. IR (cm⁻¹): 1634 (C=N). ¹H NMR (CDCl₃), δ 7.22–8.54 (m, 38H, aromatic). ¹³C{¹H} NMR (CDCl₃), δ 120.22–149.86 (C_{aromatic}) and 162.12 (C=N). ³¹P{¹H} NMR (CDCl₃), δ 16.58 (*J*_{Pt–P} = 2673 Hz). Anal. calcd for PtC₄₈H₃₈N₁₀P₂: C, 56.91; H, 3.75; N, 13.83; found: C, 56.12; H, 3.67; N, 13.97.

Trans-[Pt{5-(3-pyridyl)-tetrazolato}₂(PPh₃)₂] (3b**).** 65% (method i) and 60% (method ii) yields. IR (cm⁻¹): 1656 (C=N). ¹H NMR (CDCl₃), δ 7.19–8.70 (m, 38H, aromatic). ³¹P{¹H} NMR (CDCl₃), δ 16.71 (*J*_{Pt–P} = 2693 Hz). Anal. calcd for PtC₄₈H₃₈N₁₀P₂: C, 56.91; H, 3.75; N, 13.83; found: C, 55.45; H, 3.90; N, 13.75. Due to poor solubility, reliable results were not obtained for ¹³C NMR spectroscopy.

Trans-[Pt{5-(2-pyridyl)-tetrazolato}₂(PPh₃)₂], N¹N²-bonded isomer (3c**).** 55% (method i) and 60% (method ii) yields. IR (cm⁻¹): 1617 (C=N). ¹H NMR (CDCl₃), δ 7.44–8.66 (m, 38H, aromatic). ¹³C{¹H} NMR (CDCl₃), δ 121.57–151.09 (C_{aromatic}). ³¹P{¹H} NMR (CDCl₃), δ 4.79 (*J*_{Pt–P} = 2430 Hz). Due to the poor solubility, the obtained signals were very weak and could not be properly analyzed. Anal. calcd for PtC₄₈H₃₈N₁₀P₂: C, 56.91; H, 3.75; N, 13.83; found: C, 55.45; H, 3.90; N, 13.75.

Complex 4. A solution of 0.012 g (0.050 mmol) of Cu(NO₃)₂·3H₂O in 10 mL of methanol was added dropwise to a solution of 0.101 g (0.100 mmol) of complex **3a** in 20 mL of dichloromethane with constant stirring until a clear blue solution was obtained. It was stirred for 1 h and then filtered. The resultant solution was left in the air for slow evaporation. After ca. 4–5 days, a blue crystalline compound was obtained along with X-ray diffraction quality

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Table 1. Relevant Crystal Data for **3b**, **3c**, **4**, and **5**

	3b	3c	4	5
empirical formula	C ₄₈ H ₃₈ N ₁₀ P ₂ Pt	C ₄₈ H ₃₈ N ₁₀ P ₂ Pt	C ₉₆ H ₇₆ CuN ₂₀ P ₄ Pt ₂	C ₉₆ H ₈₀ Cu ₂ N ₂₄ O ₁₄ P ₄ Pt ₂
formula weight	1011.90	1011.90	2087.36	2434.99
cryst system	Triclinic	Triclinic	Orthorhombic	Triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbcn</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.3626(3)	12.153(8)	27.0000(15)	13.4734(3)
<i>b</i> (Å)	11.6149(4)	12.336(8)	17.135(1)	14.0405(2)
<i>c</i> (Å)	11.6592(3)	16.907(11)	21.9480(13)	15.9240(3)
α (deg)	69.129(1)	88.584(15)	90	83.711(1)
β (deg)	83.727(1)	74.856(13)	90	71.975(1)
γ (deg)	81.956(1)	72.836(14)	90	75.227(1)
<i>V</i> (Å ³)	1045.59(6)	2334(3)	10154.1(10)	2768.32(9)
<i>Z</i>	1	2	4	1
ρ_{calcd} (g cm ⁻³)	1.607	1.440	1.365	1.4561
<i>F</i> (000)	504	1008	4148	1210
N ^o reflections coll.	8493	15642	39880	27350
No. reflections unique	3596	8331	9235	10109
R ₁ , wR ₂ (obs refts)	0.0259, 0.0576	0.0577, 0.1216	0.0315, 0.0732	0.0370, 0.0889
R ₁ , wR ₂ (all data)	0.0264, 0.0579	0.1022, 0.1349	0.0483, 0.0777	0.0476, 0.0926
GOF	1.041	0.899	1.016	1.081
Largest diff. peak (hole) (e Å ⁻³)	0.951 (-0.483)	2.516 (-1.446)	0.728 (-1.217)	1.337 (-1.214)

crystals. It was separated by filtration, washed with diethyl ether, and dried in vacuo.

[Pt₂{5-(4-pyridyl)-tetrazolato}₄(PPh₃)₄Cu]_n(NO₃)_{2n}·nH₂O (4·n-H₂O). 60% yield. IR (cm⁻¹): 1617 (C=N), 1384 (NO₃). Anal. calcd for Pt₂CuC₉₆H₇₈N₂₂O₇P₄: C, 51.71; H, 3.50; N, 13.82; found: C, 51.36; H, 3.59; N, 13.36.

Complex 5. A solution of 0.024 g (0.10 mmol) of Cu(NO₃)₂·3H₂O in 10 mL of methanol was added dropwise to a suspension of 0.101 g (0.10 mmol) of complex **3b** in 20 mL of dichloromethane with constant stirring, giving a clear blue solution after five minutes. This was further stirred for 1 h and then filtered. The resultant solution was left in air for slow evaporation. A blue crystalline compound was obtained along with X-ray diffraction quality crystals after standing for ca. one week. The solid was separated by filtration, washed with diethyl ether, and dried in vacuo.

[Pt{5-(3-pyridyl)-tetrazolato}₂(PPh₃)₂Cu(NO₃)₂(H₂O)]₂·CH₃OH·H₂O (5·CH₃OH·H₂O). 60% yield. IR (cm⁻¹): 1656 (C=N), 1384 (NO₃). Anal. calcd for Pt₂Cu₂C₉₇H₈₆N₂₄O₁₆P₄: C, 45.71; H, 3.38; N, 13.20; found: C, 46.68; H, 3.31; N, 13.06.

Complex 6. Treatment of complex **3c** with copper nitrate by a similar method to that described above for **4** and **5** furnished an insoluble sky-blue powder that could not be properly characterized due to its poor solubility and noncrystalline nature.

Crystal Structure Determination of 3b, 3c, 4, and 5. Single crystals of **3b** and **3c** were obtained by diffusing diethyl ether in chloroform solutions of the respective complexes. Crystals of **4** and **5** that were suitable for X-ray diffraction were obtained from the reaction mixture. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo K α radiation. Data were collected 150 K using ω scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and were refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS. Structures were solved by direct methods by using the SHELXS-97 package¹² and were refined with SHELXL-97¹³ with the WinGX graphical user interface.¹⁴ All hydrogens were inserted in calculated positions.

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Least square refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed.

For **3c**, **4**, and **5** there are disordered solvent in the structures. Attempts were made to model them, but were unsuccessful. PLATON/SQUEEZE¹⁵ was used to correct the data. Potential solvent volumes of 332.6 (**3c**), 2246.1 (**4**), and 518.0 (**5**) Å³ were found. A total of 146.2 (**3c**), 296.5 (**4**), and 28.9 (**5**) electrons per unit cell of scattering were located in the voids. The stoichiometries were tentatively calculated as 1CHCl₃ + 1MeOH (**3c**), 2NO₃⁻ + 1H₂O (**4**), and 1MeOH + 1H₂O (**5**) molecules, which result in 152 (**3c**), 296 (**4**), and 28 (**5**) electrons per unit cell. The modified data set improved the R₁ values by ca. 10% (**3c**), 64% (**4**), and 46% (**5**). The maximum and minimum peaks in the final difference electron density map are generally located close to the platinum atoms. Additionally, a disorder model was included for two of the phenyl rings of the phosphines in **5**, which are disordered between two positions.

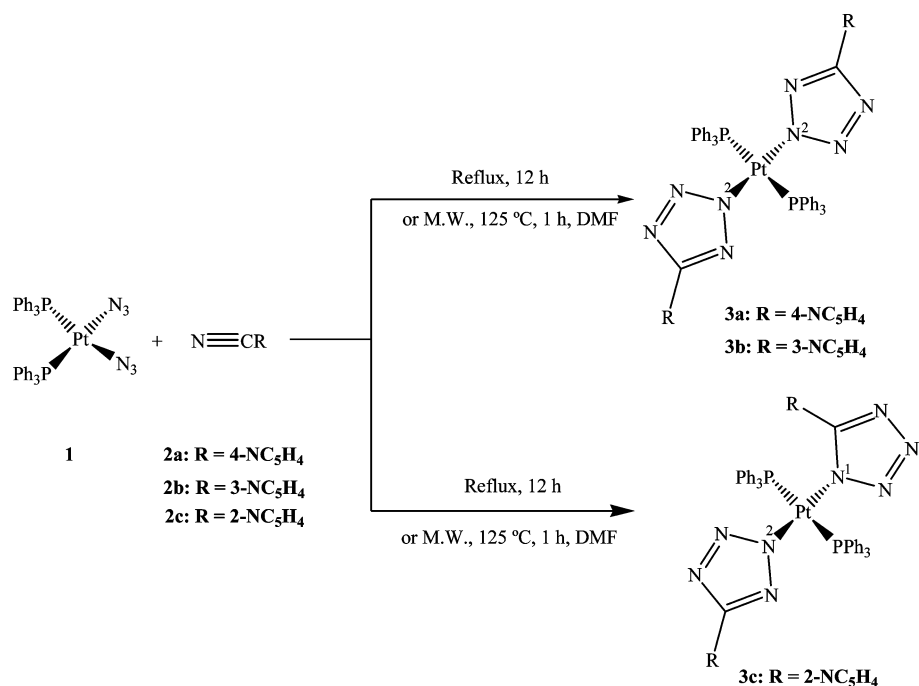
Crystallographic parameters and residuals are given in Table 1.

Results and Discussions

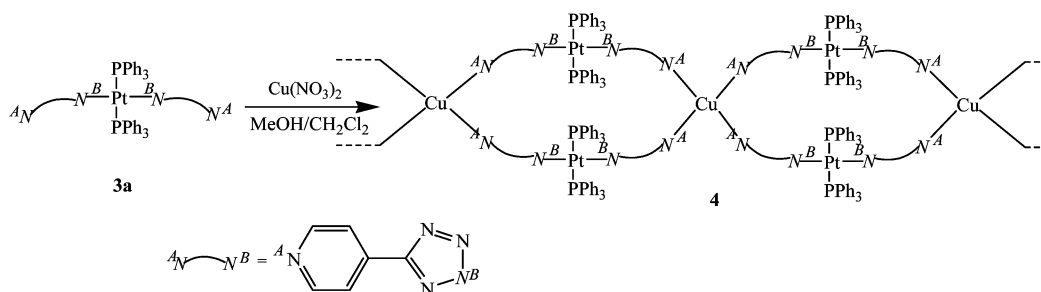
Treatment of the diazidoplatinum(II) complex **1** with a cyanopyridine **2** [R = 4-NC₅H₄ (**2a**), 3-NC₅H₄ (**2b**), and 2-NC₅H₄ (**2c**)] in refluxing DMF for 12 h furnishes the corresponding bis(pyridyltetrazolato) complexes **3**, isolated as white crystalline solids in moderate yields (ca. 60–55%) (Scheme 1). These reactions could be greatly accelerated under microwave irradiation (100 °C, 300 W), leading only in 1 h to yields that are comparable to those obtained after 12 h under conventional heating, as we have observed¹⁰ in other cases. The tetrazolato complexes were obtained via [2 + 3] cycloaddition of the organonitriles with the ligated azides. Cis-to-trans isomerization also occurred upon heating, indicating that the trans isomer of the bis(tetrazolato) product is thermodynamically more favorable than the cis one.

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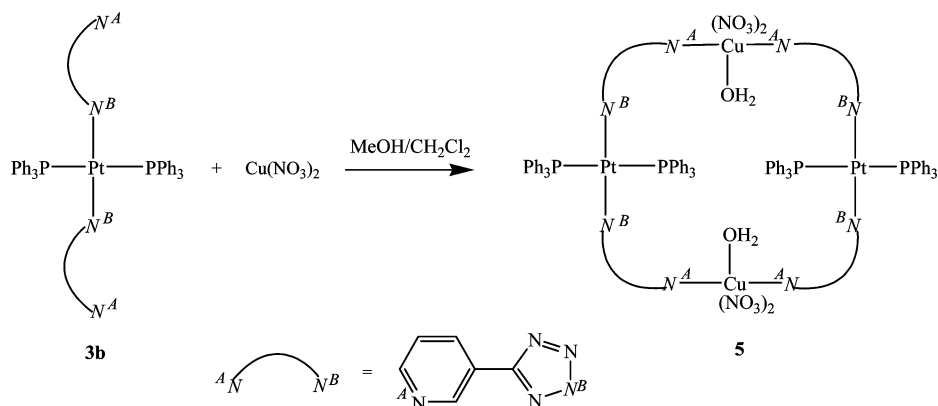
Scheme 1



Scheme 2



Scheme 3



Related thermal isomerizations of *cis*-[PtCl₂(RCN)₂] into *trans*-[PtCl₂(RCN)₂] have been reported previously.¹⁶

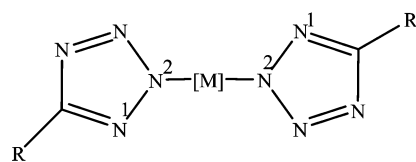
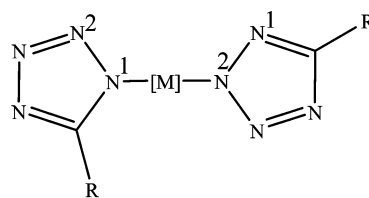
The use of a metal complex with a free potential coordinating center is a known strategy to generate mixed-

metal coordination polymers with different topologies.¹⁷ For this purpose we have used the bis(pyridyltetrazolato) complexes **3**, which bear two uncoordinated pyridyl

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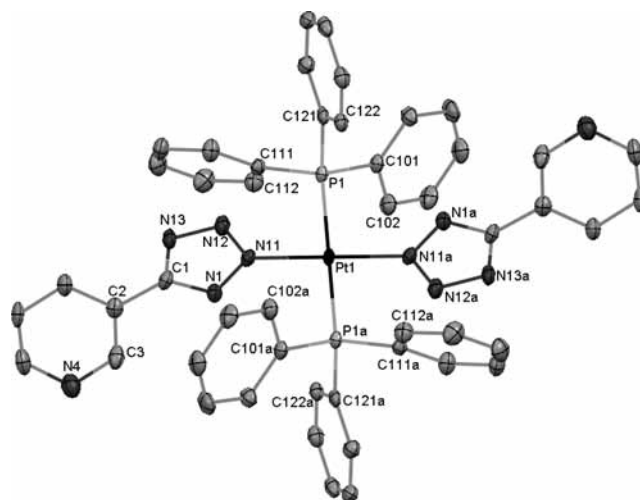
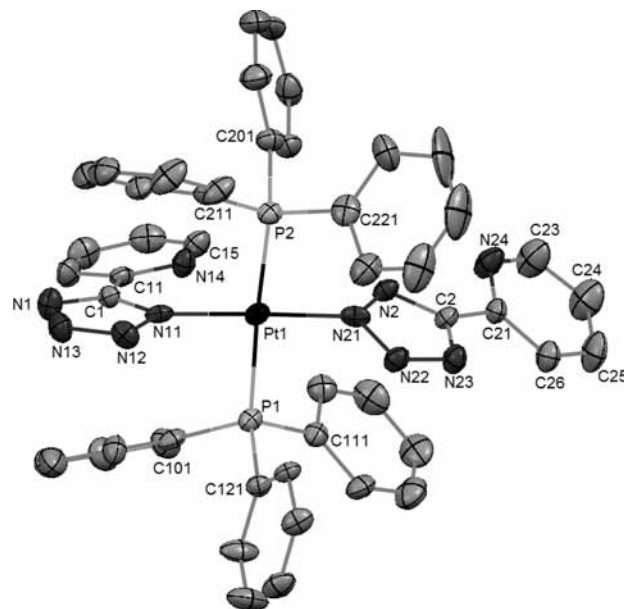
Scheme 4

(a) N^2N^2 -coordination(b) N^1N^2 -coordination**Table 2.** Selected Bond Distances and Angles for **3b**, **3c**, **4**·*n*H₂O and **5**·CH₃OH^a

	3b	3c	4	5
Bond Lengths (Å)				
Pt1–P1	2.3234(9)	2.350(3)	2.3273(11)	2.3140(13)
Pt1–P1a	2.3234(9)	2.343(3)	2.3235(11)	2.3298(13)
Pt1–N11	1.995(3)	1.971(8)	2.001(3)	2.005(4)
Pt1–N21		1.989(8)	2.008(3)	2.002(4)
Cu1–N14			2.037(3)	2.002(4)
Cu1–N24a			2.033(3)	2.009(4)
Cu1–O10				2.167(4)
Cu1–O11				2.007(4)
Cu1–O12				2.907(6)
Cu1–O21				2.032(4)
Cu1–O22				2.593(5)
Bond Angles (°)				
P1–Pt1–P2		174.43(9)	168.66(4)	173.96(4)
P1–Pt1–N11	89.49(10)	89.3(2)	92.83(10)	89.58(13)
P1–Pt1–N21		88.3(2)	86.05(10)	90.34(13)
P2–Pt1–N11		93.2(2)	92.23(10)	89.35(13)
P2–Pt1–N21		89.5(2)	90.30(10)	90.92(13)
N11–Pt1–N21		176.9(3)	172.08(13)	178.26(18)
P1b–Pt1–N11	90.52(10)			
P1b–Pt1–N11b	89.49(10)			
N14–Cu1–N24a			92.31(13)	165.20(17)
N14–Cu1–N24c			179.45(14)	
N24a–Cu1–N24c			87.21(13)	
O10–Cu1–O11				113.16(19)
O10–Cu1–O12				69–90(18)
O10–Cu1–O21				85.67(19)
O10–Cu1–O22				139.97(19)
O10–Cu1–N14				99.75(17)
O11–Cu1–O12				73.7(4)
O11–Cu1–O21				106.0(4)
O11–Cu1–O22				81.3(3)
O11–Cu1–N14				123
O11–Cu1–N24a				106
O12–Cu1–O21				129
O12–Cu1–O22				103.5(4)
O12–Cu1–N14				103.5(4)
O12–Cu1–N24a				116.8(5)
O21–Cu1–O22				119.6(7)
O21–Cu1–N14				123.6(6)
O21–Cu1–N24a				123.5(3)
O22–Cu1–N14				124.0(4)
O22–Cu1–N24a				112.3(4)

^a Symmetry operation to generate the atom: (a) $x, -1 + y, z$ (**4**) and $-x, -y, 2 - z$ (**5**); (b) $2 - x, 2 - y, -z$; (c) $1 - x, -1 + y, 1/2 - z$.

N-atoms per platinum atom. Such pyridyl moieties are expected to bind to other metal sites, and copper nitrate was taken as a metal center source, keeping also in mind the coordinating ability of nitrate ion to fulfill suitable copper coordination geometry. A dichloromethane solution (or suspension) of each of complexes **3** was treated dropwise with a methanolic solution of Cu(NO₃)₂ to afford a clear blue solution from which, in the case of using **3a** and **3b**, the crystalline heteronuclear Pt^{II}/Cu^{II} compounds **4** and **5**, respectively, with bridging pyridyltetrazolato ligands (Schemes 2 and 3), could be isolated upon slow solvent evaporation in air.

**Figure 1.** Molecular structure of **3b** with atomic numbering scheme (ellipsoids are drawn at 30% probability).**Figure 2.** Molecular structure of **3c** with atomic numbering scheme (ellipsoids are drawn at 30% probability).

The obtained complexes **3** were characterized by elemental analyses; IR, ¹H, ¹³C{¹H}, (for **3a** and **3c**), and ³¹P{¹H} spectroscopies; and X-ray crystal structure analyses (for **3b** and **3c**). Their IR spectra display a band within the 1617–1656 cm⁻¹ range due to the tetrazolato ring,¹⁸ quite distinct from the typical azide band at 2055 cm⁻¹ in **1**. The

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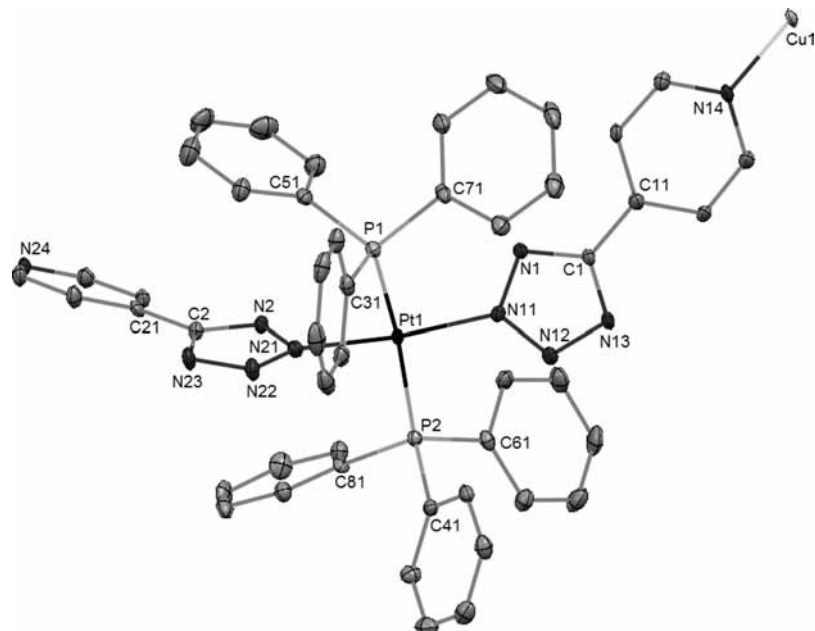


Figure 3. ORTEP diagram of the asymmetric unit of **4** with atom labeling scheme. Thermal ellipsoids are drawn at 30% probability. All hydrogens were omitted for clarity.

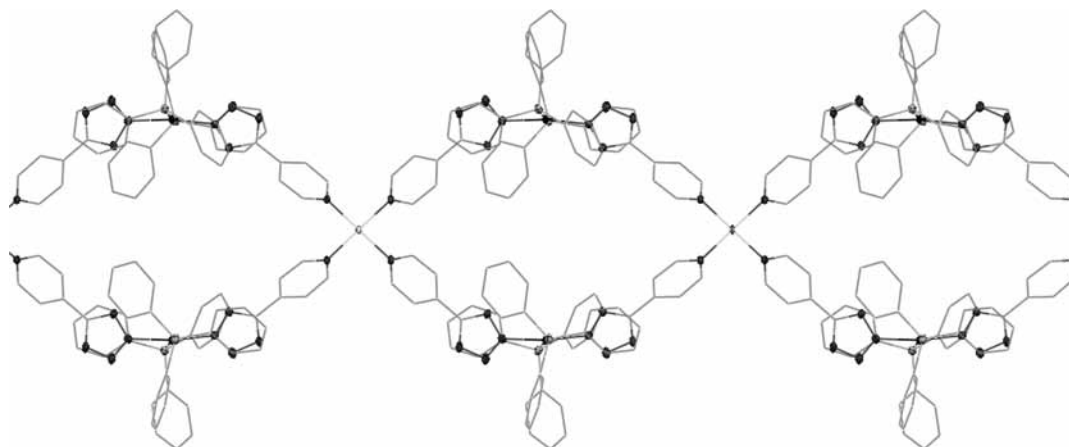


Figure 4. Extended 1D structure of **4** viewed down the crystallographic axis *c*.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3a–c** exhibit a singlet with platinum satellites, at δ 16.6, 16.7, and 4.79, with $J_{\text{Pt-P}}$ of 2673, 2693, and 2430 Hz, respectively. These coupling values clearly show the trans configuration of the phosphines,¹⁹ and the singlet resonance indicates the existence of only one type of *N*-coordination for each pyridyltetrazole ligand, contrary to the alkyl tetrazolato complexes obtained from an alkyl nitrile.¹⁰ In **3a** and **3b**, both bulky pyridyltetrazolato rings are equivalent and bind the metal only by the N^2 -atom (Scheme 4a), as shown by X-ray analysis of **3b** (see below), thus minimizing the steric congestion. However, for complex **3c**, the ^1H and ^{13}C NMR spectra (although the latter was not well-resolved due to poor solubility of the

complex in common organic solvents) show the nonequivalence of the two pyridyl groups, which was confirmed by X-ray crystallography (see below) and which revealed the asymmetric nature of the complex with the N^1N^2 -coordination mode (Scheme 4b) of the tetrazolato ligands. The elemental analyses of **3–5** confirm their analytical purity and are consistent with the formulations authenticated by the X-ray diffraction studies as indicated below.

A strong band at 1384 cm^{-1} for both complexes **4** and **5** is assigned²⁰ to the Cu^{II} -bound monodentate NO_3^- ligand. The triphenyl phosphine ligands are detected by their characteristic bands at ca. 1436 and 695 cm^{-1} . No band that could be due to N-H stretching or bending was observed, indicating the retention of the anionic nature of

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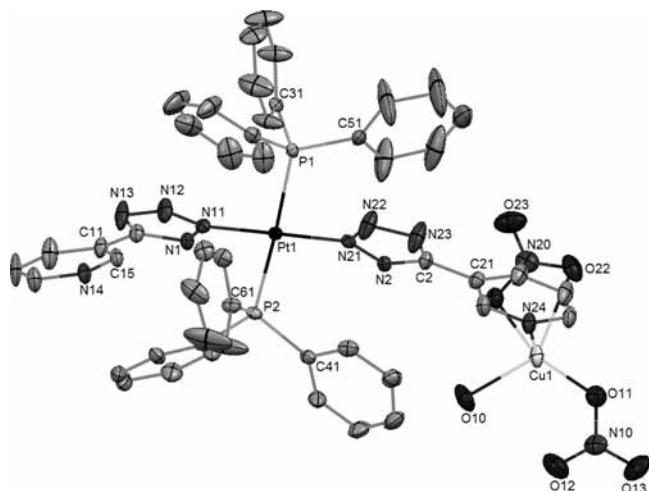


Figure 5. ORTEP diagram of the asymmetric unit of **5** with atom labeling scheme. Thermal ellipsoids are drawn at 30% probability. All hydrogens were omitted for clarity.

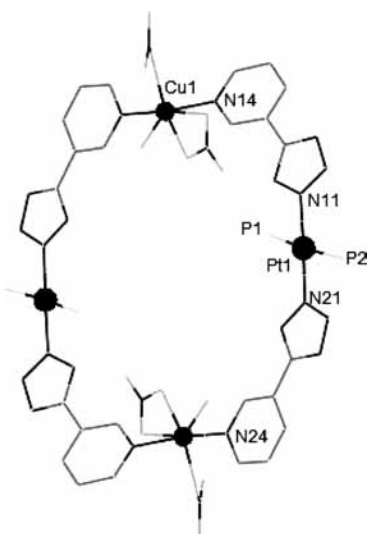


Figure 6. The heterobimetallic square of **5**. Phenyl rings of PPh_3 as well as hydrogen atoms were omitted for clarity.

the tetrazolato ligand. The IR spectra of **4** and **5** show typical broad bands in the $3260\text{--}3225\text{ cm}^{-1}$ range due to the stretching frequency of the water molecule.²¹

The single-crystal X-ray diffraction structural analyses of complexes **3b**, **3c**, **4**, and **5** confirm their formulations. Selected bond lengths and angles are reported in Table 2. In compound **3b** the platinum atom is in an inversion center and lies in a slightly distorted square-planar environment consisting of the two nitrogen atoms of the tetrazolato ligands and the two phosphorus atoms of the phosphines, in mutual trans positions (Figure 1). Both tetrazolates are coordinated to the metal center by the N^2 -nitrogen atom of the ring, as previously described for the related complex $\text{trans-[Pt(N}_4\text{CPh)}_2(\text{PPh}_3)_2]$,¹⁰ thus providing the most sterically favorable N^2N^2 -coordination mode. Moreover, the overall bond distances and angles for this analogue¹⁰ and **3b** (Table 2) are identical.

Interestingly, the structure of **3c** reveals (Figure 2) that, although one of the tetrazolato rings is coordinated by the N^2 -nitrogen atom, the other is coordinated via the N^1 -nitrogen atom of the ring. The less sterically favorable N^1 -coordination for one of the pyridyltetrazolato ligands conceivably results from the coordinative interaction ($2.966(9)\text{ \AA}$) between the metal and the nitrogen atom (N14) of the pyridine ring, which thus almost takes the apical position of a distorted, pseudo-square-pyramidal coordination geometry. A similar type of coordinative interaction has been reported earlier for a Mn^{II} complex.¹⁸ The measured angles of N14 , the metal, and the coordinating atoms of the basal plane lie in the $112.13\text{--}65.86^\circ$ range. Both tetrazolato rings are almost planar, but they are mutually twisted by 23.58° to each other, unlike in the related known compounds.¹⁰ To the best of our knowledge, compound **3c** provides the first example of an N^1N^2 isomer isolated in the solid state, among the bis-tetrazolato transition metal complexes reported so far.

Compound **4** is a 1D-type coordination polymer in which the metallaligand **3a** acts as a building block, thus leading to an asymmetric unit containing one Pt center (**3a**) and one Cu bound to the N -atom of a pyridyl ring (Figure 3). In the polymeric network that is thus constructed, the coordination environment of the Pt^{II} atom is square-planar, and it consists of two triphenylphosphine ligands in trans position along with two 5-substituted tetrazolato ligands that coordinate in the N^2N^2 -mode. The $\text{Cu}(\text{II})$ center in **4** also adopts a square-planar geometry, with the metal bound to the N -atoms of four pyridyl rings from the metallaligands **3a**. All the bond distances and angles are within the ranges reported earlier for comparable compounds.¹⁰ Structure **4** qualifies as a heterometallic supramolecular square: the nearest distance between two adjacent copper atoms in a chain is 17.135 \AA , the same as the unit cell parameter b , whereas the nearest $\text{Pt}\cdots\text{Pt}$ separation is 10.323 \AA . Additionally, the shortest interchain $\text{Pt}\cdots\text{Cu}$, $\text{Cu}\cdots\text{Cu}$, and $\text{Pt}\cdots\text{Pt}$ distances are 8.524 , 15.989 , and 9.221 \AA , respectively. These distances considerably exceed the sum of the van der Waals radii of two Pt or two Cu atoms, hence the chains are effectively separated, as shown in Figure 4 (additional views are shown in the Supporting Information). A van der Waals-based space filling model of the structure indicates that, although there might be room for small molecules to enter the center of the square, the pendant phenyl rings of the phosphines may block the access, not only to the central core but also to the interchain channels, thus eliminating any 3D channels that would otherwise exist. The framework contains disordered nitrate anions and water molecules, for which a reasonable refinement was not possible.

In complex **5** the metallaligand **3b** provides the required angle for bridging between platinum and copper atoms to form a molecular square-type structure (Figures 5 and 6). Unlike other molecular squares where the metal atoms are usually positioned at the vertices, here they take the positions at the midpoint of the arms (Figure 6). The platinum atoms are square planar, and the observed bond distances and angles are comparable to those for the noncoordinated metallaligand **3b**. The $\text{Pt}\text{--}\text{N}$ bonds are slightly elongated with respect to

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3b, possibly due to the stretching arising from the coordination of the N-atom of the pyridyl ring to copper. The coordination environment of the Cu(II) atom is best described as a distorted octahedron with two mutually *trans*-pyridyl ligands defining the axial positions and one water and two nitrate ligands, one of which is coordinated in the η^2 - and the other is in the η^1 -mode, defining the equatorial positions. The Pt...Pt distance in the ring is of 11.520 Å, whereas the Cu...Cu distance is 11.921 Å. Extensive intra and intermolecular contact interactions were detected. In particular, the hydrogen bonds involving the coordinated water molecule and the nitrate oxygen of a vicinal tetramer (H10B...O12, 2.2300 Å) contribute to stabilize the structure.

Conclusions

In this work we have used the cycloaddition reaction between a Pt^{II}-bound azide and different cyanopyridines as a strategic and convenient tool to generate metalla-pyridyltetrazolate ligands of the type **3**. Hence, compounds **3a** and **3b** can be used successfully as metallaligands upon reaction with copper(II) nitrate, providing heteronuclear Pt^{II}/Cu^{II} complexes with unusual structures, namely, a molecular square type structure and an 1D-supramolecular architecture. The nitrate ion appears to play a relevant role for the products syntheses, since we have failed to obtain analogous compounds using other anions whose effects are currently under investigation.

Although the presence of different linkage isomers of bis(tetrazolato) complexes had been reported in solution, on account of the ambidentate nature of the tetrazolato ligand, only the N²N² isomer had been found in the solid state. This work also shows for the first time, to our knowledge, that the N¹N² isomer can be sufficiently stable to be isolated and fully characterized by X-ray diffraction, provided the sterically unfavorable N¹ coordination component is promoted by interaction of the metal with a suitable tetrazolato substituent such as a pyridyl group, as in the case of complex **3c**.

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Supporting Information Available: An extended view of the 2-D structure **4** and a CIF file containing the above mentioned compounds are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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