

This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.

Author(s): Kolari, Kalle; Laurila, Elina; Chernysheva, Maria; Hirva, Pipsa; Haukka, Matti

Title: Self-assembly of square planar rhodium carbonyl complexes with 4,4-disubstituted-2,2'-bipyridine ligands

Year: 2020

Version: Accepted version (Final draft)

Copyright: © 2020 Elsevier B.V.

Rights: CC BY-NC-ND 4.0

Rights url: <https://creativecommons.org/licenses/by-nc-nd/4.0/>

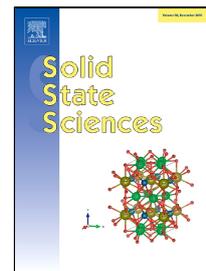
Please cite the original version:

Kolari, K., Laurila, E., Chernysheva, M., Hirva, P., & Haukka, M. (2020). Self-assembly of square planar rhodium carbonyl complexes with 4,4-disubstituted-2,2'-bipyridine ligands. *Solid State Sciences*, 100, Article 106103. <https://doi.org/10.1016/j.solidstatesciences.2019.106103>

Journal Pre-proof

Self-assembly of square planar rhodium carbonyl complexes with 4,4-disubstituted-2,2'-bipyridine ligands

Kalle Kolari, Elina Laurila, Maria Chernysheva, Pipsa Hirva, Matti Haukka



PII: S1293-2558(19)30724-1
DOI: <https://doi.org/10.1016/j.solidstatesciences.2019.106103>
Reference: SSSCIE 106103
To appear in: *Solid State Sciences*
Received Date: 21 June 2019
Accepted Date: 23 December 2019

Please cite this article as: Kalle Kolari, Elina Laurila, Maria Chernysheva, Pipsa Hirva, Matti Haukka, Self-assembly of square planar rhodium carbonyl complexes with 4,4-disubstituted-2,2'-bipyridine ligands, *Solid State Sciences* (2019), <https://doi.org/10.1016/j.solidstatesciences.2019.106103>

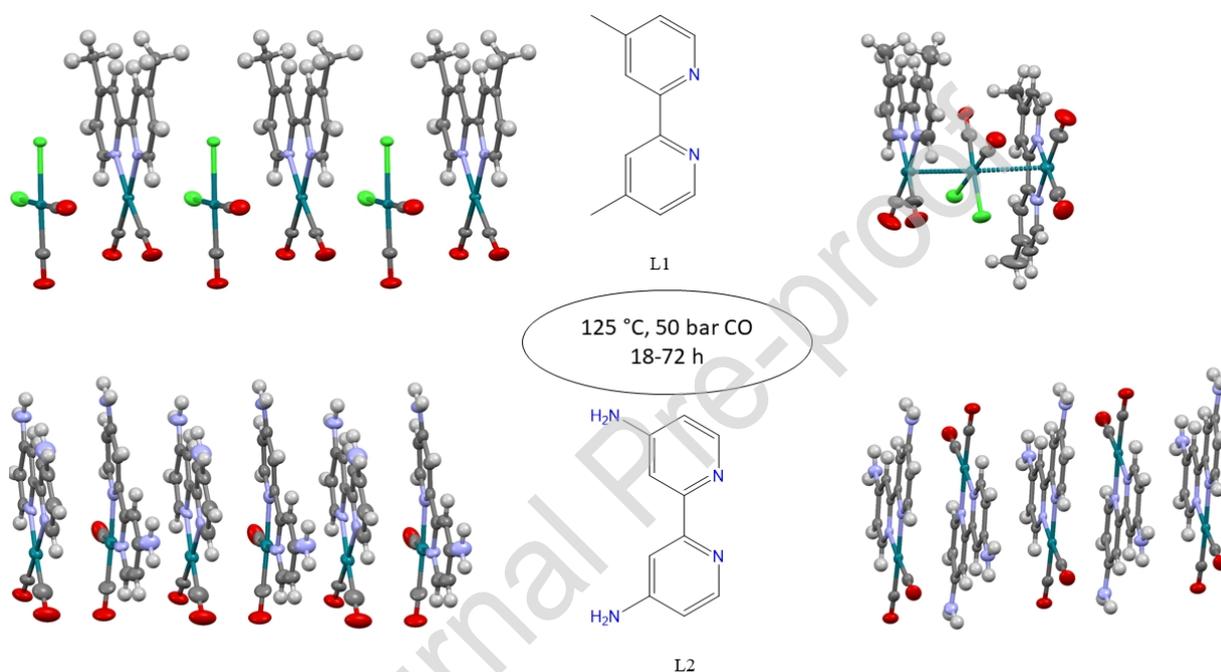
This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier.

TOC Entry for

Self-assembly of square planar rhodium carbonyl complexes with 4,4'-disubstituted-2,2'-bipyridine ligands

Kalle Kolari, Elina Laurila, Maria Chernysheva, Pipsa Hirva, Matti Haukka*

^aUniversity of Jyväskylä, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland^bUniversity of Eastern Finland, Department of Chemistry, P.O.Box 111, FI-80101, Joensuu, Finland

The impact and the role of non-covalent interactions and reaction conditions on formation and self-assembly of ionic pairs of Rh complexes with 4,4'-disubstituted bipyridine ligands bipyridine have been investigated.

Self-assembly of square planar rhodium carbonyl complexes with 4,4'-disubstituted-2,2'-bipyridine ligands

Kalle Kolari^a, Elina Laurila^a, Maria Chernysheva^a, Pipsa Hirva^b, Matti Haukka^{a*}

^aUniversity of Jyväskylä, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland

^bUniversity of Eastern Finland, Department of Chemistry, P.O.Box 111, FI-80101, Joensuu, Finland

Keywords: rhodium, bipyridine, carbonyl, reductive carbonylation, metallophilicity

ABSTRACT

The impact of non-covalent interactions and reaction conditions on formation and self-assembly of ionic pairs of Rh complexes with 4,4'-disubstituted bipyridine ligands ($[\text{Rh}(\text{L}1)(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]_n$ **(1)**, $[\text{Rh}(\text{L}1)_2\text{Cl}_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ **(2)**, $([\text{Rh}(\text{L}1)(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2][\text{Rh}(\text{L}1)(\text{CO})_2]_n([\text{Rh}(\text{CO})_2(\text{Cl})_2]_n)$ **(3)**, $([\text{Rh}(\text{L}2)\text{CO}_2][\text{Rh}(\text{CO})_2\text{Cl}_2]_n \cdot \text{EtOH}$ **(4)**, $([\text{Rh}(\text{L}2)(\text{CO})_2]_n([\text{Rh}(\text{CO})_2\text{Cl}_2]_n)$ **(5)** (L1 = 4,4'-dimethyl-2,2'-bipyridine, L2 = 4,4'-diamine-2,2'-bipyridine) have been studied. Packing of square planar Rh complexes favor formation of one-dimensional chains. In structure **1**, the polymeric chain is formed by the alternating cationic $[\text{Rh}(\text{L}1)(\text{CO})_2]^+$ and the anionic $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ units leading to a neutral pseudo linear 1D chain with metallophilic contacts. In compound **2**, the square planar

$[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ anions form only dinuclear anion pairs instead of polymeric chains. Structure **3** consists of an alternative arrangement of cations and anions compared to **1**, the repeating sequence of ions being $[\text{Rh}(\text{L1})(\text{CO})_2]^+[\text{Rh}(\text{CO})_2\text{Cl}_2]^- [\text{Rh}(\text{L1})(\text{CO})_2]^+$. The overall positive charge is balanced by outlying $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ counterion. In structures **4** and **5**, only the cationic $[\text{Rh}(\text{L2})(\text{CO})_2]^+$ units are involved in formation of the polymeric chains and the positive charge of the chain is balanced by the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ (**4** and **5**). In structures **1** and **3** the metallophilic interactions have an important role in chain formation. In **4** and **5**, the arrangement of the square planar building blocks is dominated by the hydrogen bonding between the NH_2 -substituents of the bipyridine ligand and the chlorides of the anion or solvent of crystallization.

INTRODUCTION

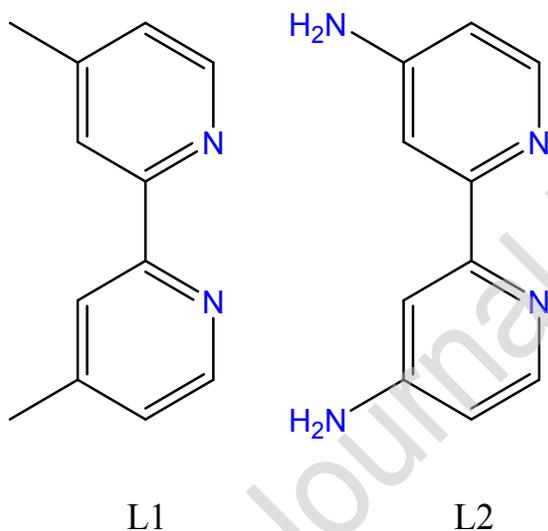
Supramolecular self-assembly [1],[2] is defined as a process where molecular entities are aggregated via reversible [3] non-covalent interactions [4],[5] such as π -stacking [6], electrostatic interactions [7], halogen bonding [8], hydrogen [9] bonding and metallophilic interactions [10,11]. Hydrogen bonding is classified as a directional and notable non-covalent interaction in strength [12] and has been widely utilized in crystal engineering [13]. Preparation of organic non-covalent polymers from diamidopyridines and uracil derivatives is an early example of systematic utilization of hydrogen bonding in self-assembly of molecules [10],[14]. Similar strategy by modulating the secondary coordination sphere [15] *via* hydrogen bonding has been implemented to self-assembly of discrete metal complexes to form from one-dimensional metallopolymers [9], [16],[17],[18],[19] to metal-organic frameworks [20],[21],[22]. Due to reversibility and the dynamic nature of the hydrogen bond interactions between monomers these polymeric compounds

express the variety of properties [23]. Closely related halogen bonds have also been used to link metal complexes into extended polymeric structures [24], [25]. It has been shown that halogen bonds can also be used to fine-tune the properties of metal complexes [26]. In the case of square planar metal complexes, metallophilic interactions or metal- π -interactions provide alternative non-covalent tools that can be utilized in building extended structures, especially linear chain compounds [10,11]. It is established that square-planar monomeric units will self-assemble *via* d_z^2 -orbital overlap of d^8 metal centers whereas in d^{10} metal ions interactions occur *via* $d_{x^2-y^2}$ [27, 28]. Magnus green salts and Krogman salts are classic examples of metallophilic Pt and Pd chain structures [29], [30]. However, metallophilicity is known to occur in a range of metal compounds including iridium and rhodium chains, known as iridium and rhodium blues.[31] Metallophilic contacts have been used for example, to generate semiconductive crystalline materials [30]. Similar chain-like structures have also been obtained with square planar rhodium complexes [10,11]. In these systems intermetallic contacts have an impact on the photophysical properties of the polymeric chains.

Derivatives of 2,2'-bipyridine are commonly used as chelating ligands in coordination chemistry. These types of ligands are able to form strongly coordinated and nearly planar groups, which makes them useful especially for building extended stacks of square planar metal complexes [10,11], [32],[33]. By decorating the polypyridine ligand with suitable substituents, such ligand can be used for changing the electronic properties of the metal complex as well as supporting secondary non-covalent contacts in the supramolecular assemblies for example *via* π -interactions or *via* hydrogen bonds. Complexes with disubstituted-2,2'-bipyridine ligands containing hydrogen bond donor/acceptor substituents such as hydroxyl [34],[35] amino [36], dicarboxylic acid [37], hydroxymethyl [38], hydroxyl [39], and pyrrole [40] groups 4,4'-disubstituted ligands, metal

complexes have been used to assemble extended hydrogen bonding networks with co-crystallants [34],[35],[41] or solvent of crystallization [42].

In the current paper we have investigated the impact of metallophilic interactions, hydrogen bonds, metal- π -interactions and Coulombic interactions as well as the influence of reaction conditions in formation of supramolecular assemblies of square planar pairs of cationic and anionic Rh-complexes $[\text{Rh}(\text{L1})(\text{CO})_2]/[\text{Rh}(\text{CO})_2\text{Cl}_2]$ and $[\text{Rh}(\text{L2})(\text{CO})_2]/[\text{Rh}(\text{CO})_2\text{Cl}_2]$ (Scheme 1).



Scheme 1. Schematic presentation of the substituted bipyridine ligands 4,4'-dimethyl-2,2'-bipyridine (L1) and 4,4'-diamino-2,2'-bipyridine (L2).

EXPERIMENTAL SECTION

All reagents were used as received. Ethanol solvent (95%) was purchased from Altia Oy, 4,4'-dimethyl-2,2'-bipyridine (99%) from Sigma-Aldrich, and 4,4'-diamino-2,2'-bipyridine (>97%) from Carbosynth. The rhodium reagent was obtained from Alfa Aesar and its Rh content was 38 – 41 %. The reduction gas carbon monoxide (100%) was obtained from AGA. All reductive carbonylation syntheses were performed in 100 mL Berghof autoclaves equipped with PTFE liner. IR-spectrum were recorded with the Bruker Alpha spectrometer with the ATR platinum diamond compartment. Elemental analyses were carried out with Elementar Vario EL III analyzer.

Crystal structure determination

The crystals of **1** – **5** were immersed in cryo-oil, mounted in a MiTeGen loop and measured at 100-200 K. The X-ray diffraction data were collected on a Rigaku Oxford Diffraction Supernova diffractometer using Mo K α radiation ($\lambda = 0.70173$ Å, compounds **1** and **2**) or Cu K α ($\lambda = 1.54184$ Å, compounds **3-5**). The CrysAlisPro [43] program package was used for cell refinements and data reductions. The structures were solved by charge flipping (SUPERFLIP) [44] or intrinsic phasing method (SHELXT) [45]. An analytical, gaussian or multi-scan absorption corrections (CrysAlisPro [43]) were applied to all data. Structural refinements were carried out using SHELXL [45] with the Olex2 [46] and SHELXLE [47] graphical user interfaces. The ethanol of crystallization in **5** was disordered resulting in high anisotropic displacement parameters. However, no disorder model was applied to the solvent molecules during the final refinement. In **5** the NH₂ hydrogen atoms were located from the difference Fourier map and refined isotropically. The OH hydrogen atoms in **4** were located from the difference Fourier map but constrained to ride on their parent oxygen with $U_{\text{iso}} = 1.5 \cdot U_{\text{eq}}$ (parent atom). Other hydrogen atoms were positioned

geometrically and constrained to ride on their parent atoms, with C–H = 0.95–0.98 Å, N–H = 0.88 Å, and $U_{\text{iso}} = 1.2\text{--}1.5 \cdot U_{\text{eq}}$ (parent atom). The crystallographic details are summarized in Table 1.

Table 1. Crystal Data.

	1	2	3	4	5
empirical formula	$\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_4\text{Rh}$ ²	$\text{C}_{26}\text{H}_{24}\text{Cl}_4\text{N}_4\text{O}_2\text{Rh}_2$	$\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_4\text{Rh}_2$	$\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_4\text{O}_4\text{Rh}_2$	$\text{C}_{32}\text{H}_{32}\text{Cl}_4\text{N}_8\text{O}_{10}\text{Rh}_4$
fw	573.00	772.11	573.00	574.98	1242.09
temp (K)	120(2)	120(2)	200(2)	100(2)	120(2)
λ (Å)	0.71073	0.71073	1.54184	1.54184	1.54184
cryst syst	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	P-1	P-1	C2/c	P2 ₁ /c	P-1
<i>a</i> (Å)	6.73607(15)	7.8652(2)	10.2239(5)	6.65090(11)	6.7517(5)
<i>b</i> (Å)	6.1636(3)	12.1823(3)	17.6662(11)	23.3367(4)	15.8847(9)
<i>c</i> (Å)	17.6273(3)	16.4622(5)	42.6639(17)	12.01598(18)	20.7118(9)
α (°)	97.2875(14)	100.175(2)	90	90	72.782(5)
β (°)	94.0227(16)	102.055(3)	92.484(5)	99.3009(15)	85.895(5)
γ (°)	97.4129(17)	105.096(3)	90	90	78.957(6)
<i>V</i> (Å ³)	1880.51(6)	1444.04(8)	7698.6(7)	1840.48(5)	2082.2(2)
<i>Z</i>	4	2	16	4	2
ρ_{calc} (Mg/m ³)	2.024	1.776	1.977	2.075	1.981
μ (K α) (mm ⁻¹)	2.063	1.544	16.645	17.442	15.511
No. reflns.	67614	23622	12999	21392	13765
Unique reflns.	19097	7466	7771	3883	8392
GOOF (F ²)	1.073	1.032	1.027	1.062	1.041
<i>R</i> _{int}	0.0530	0.0427	0.0554	0.0239	0.0659
<i>R</i> 1 ^a (<i>I</i> ≥ 2σ)	0.0364	0.0351	0.0638	0.0205	0.0694
w <i>R</i> 2 ^b (<i>I</i> ≥ 2σ)	0.0792	0.0671	0.1608	0.0493	0.1815

^a $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^b $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Syntheses

Compounds 1 and 2

A mixture of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (50 mg, 0.2 mmol), 4,4'-dimethyl-2,2'-bipyridine (L1) (20 mg, 0.1 mmol) and 2 mL of ethanol were placed into a Berghof autoclave with PTFE liner. Mixture was stirred for 15 min and then of 2 mL of ethanol was added. The autoclave was pressurized with CO gas to 50 bar and heated at 125 °C for 72 h. After reaction, the autoclave was ramped down with two steps. The first temperature was decreased 10 °C/h for 7h. Then starting from 55°C cooling rate was increased to 15°C/h until room temperature was reached. The orange, crystalline product of $[\text{Rh}(\text{L1})(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ (**1**) (17 mg, 24 %) was filtered off and dried in the air overnight. X-Ray quality crystalline material was collected directly from the reaction solution after cooling and no separate crystallization steps were used. Despite drying, the bulk material contained some moisture, which was confirmed by IR-spectroscopy. Elemental analysis for $[\text{Rh}(\text{L1})(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ (**1**): calculated C: 32.52 %, H: 2.39 % and N: 4.74 % found C: 32.22 % H: 2.13 % and N: 4.56 %. IR $\nu(\text{ATR})/\text{cm}^{-1}$: 1966 and 1987 ($\nu(\text{CO})$, the anionic unit), 2021 and 2067 ($\nu(\text{CO})$, the cationic unit). In addition to **1**, few yellow crystals of $[\text{Rh}(\text{L1})_2\text{Cl}_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ were obtained as a side product (**2**).

Compound 3

Modification of reaction time and vessel cooldown yielded a few dark orange-red crystals of $[\text{Rh}(\text{L1})(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2] \cdot \text{EtOH}$ (**3**). This crystalline material was obtained in 3d reaction and upon cooling reaction vessel first in powered off heating system for 2h and then in ice bath for additional 2h. X-Ray quality crystalline material was collected directly from the reaction solution

after cooling and no separate crystallization steps were used. Even with fast cooling the compound **1** was the dominating product and compound **3** was obtained only as a minor product. No further analysis of **3** could be carried out due to the low yield of **3**.

Compounds **4** and **5**

Synthesis was performed following similar procedure as in the case of **1** with slight modifications. The amounts of 0.2 mmol (50 mg) of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ and 0.1 mmol (21 mg) of 4,4'-diamino-2,2'-bipyridine (L2) was stirred in 2 mL of ethanol for 15 min. Then 2 mL of ethanol was added into the mixture. The autoclave was pressurized with CO gas to 50 bar and heated at 125 °C for 20 h. Again, the reaction vessel was allowed to cool down in two steps (from 125°C to 65°C with the cooling rate of 10 °C/h and from 65°C to room temperature with cooling rate of 15 °C/h). The yellow crystals (11 mg, 75 %) with metallic luster were filtered off and dried in the air overnight. Single-crystal X-Ray diffraction showed that the crystals of **5** contained ethanol of crystallization. However, the bulk samples used for elemental analysis contained only some moisture matching with $[\text{Rh}(\text{L}2)(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$. Presence of moisture was confirmed by IR-spectroscopy. Calculated: C: 28.36 %, H: 2.04 % and N: 9.45 % found C: 28.64 %, H: 1.99 %, and N: 9.76 %. IR ν (ATR)/cm⁻¹: 2016 and 2017 ($\nu(\text{CO})$, the cationic unit), 1983 ($\nu(\text{CO})$, the anionic unit). When the reaction mixture was cooled down in a similar way as in the case of **2**, few orange crystals of solvent free $[\text{Rh}(\text{L}2)(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ (**4**) were obtained. The crystalline product **5** was found to be unstable compared to compound **4** without solvent of crystallization at the ambient conditions due to the slow loss of solvent of crystallization. Again, X-Ray quality crystalline material was collected directly from the reaction solution after cooling and no separate crystallization steps were used.

RESULTS AND DISCUSSION

All syntheses were performed as a one-pot reductive carbonylation of RhCl_3 in the presence of the bipyridine ligands in ethanol. With 4,4'-dimethyl-2,2'-bipyridine (L1) linear arrangement of the reduced alternating cationic and anionic square planar Rh-units was preferred (Figure 1).

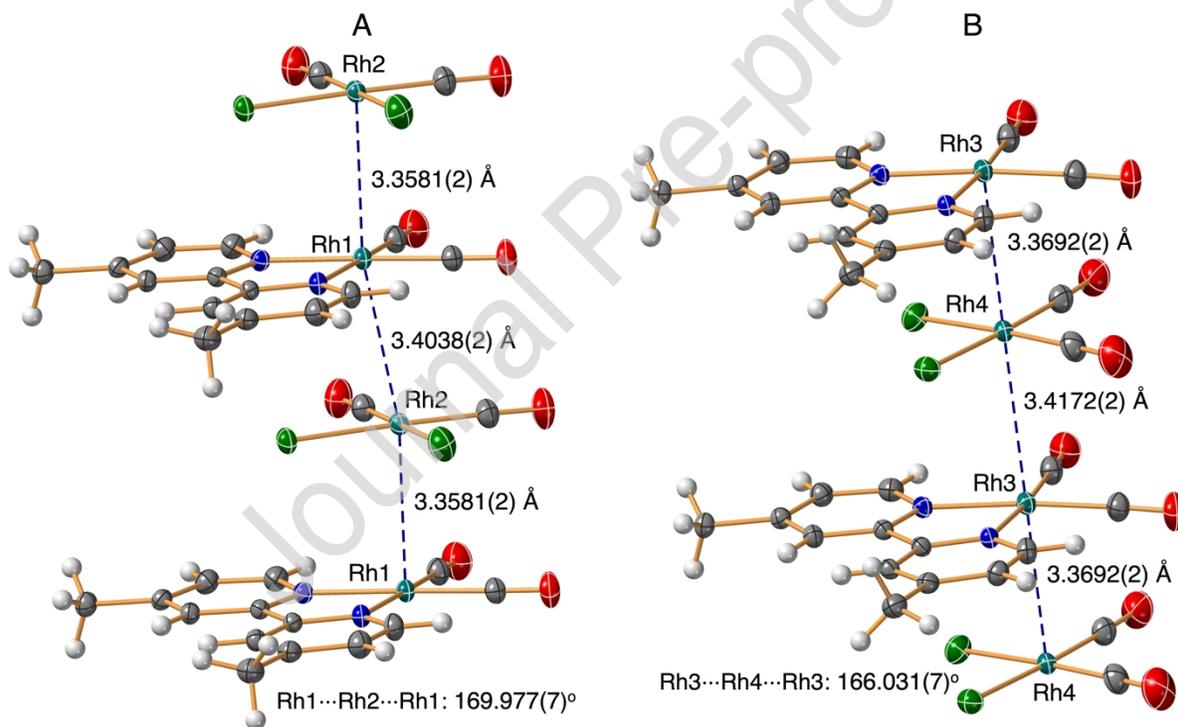


Figure 1. The two crystallographically independent cation-anion chains, A and B, in **1**.

The crystal structure of **1** contained two independent cation-anion chains (A and B in Fig. 1) with metallophilic contacts between the Rh-atoms. The $\text{Rh}\cdots\text{Rh}$ distances varied between 3.3581(2) Å and 3.4172(2) Å. Both chains were nearly linear with $\text{Rh}\cdots\text{Rh}\cdots\text{Rh}$ angles of 169.977(7)° and

166.031(8)° respectively (Fig. 1). The structures resemble closely the previously reported cation-anion chains of $[\text{Rh}(\text{bpy})(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ [11], indicating that the methyl substituents on 4,4'-positions on the bipyridine ligands did not have significant impact on stacking cationic and anionic units. However, the shortest intermetallic distance of 3.3174(5) Å, found in $[\text{Rh}(\text{bpy})(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$, is somewhat shorter than the corresponding distance in **1**. Just like the $[\text{Rh}(\text{bpy})(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ crystals, also the crystals of **1** had metallic luster indicating the existence of continuous metal-metal contacts. In addition to polymeric chain structures, few crystals of $[\text{Rh}(\text{L1})_2\text{Cl}_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ (**2**) ion pairs (Fig. 2) were also obtained in all reactions as a minor side product. It shows that even if the reaction was carried out under 50 bar CO pressure and the reaction time was 72 h, the reduction of RhCl_3 was not complete. In **2**, the square planar $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ anions did form stacked pairs with long $\text{Rh}\cdots\text{Rh}$ distances (3.9729(5) Å) but not continuous chains (Fig. 2).

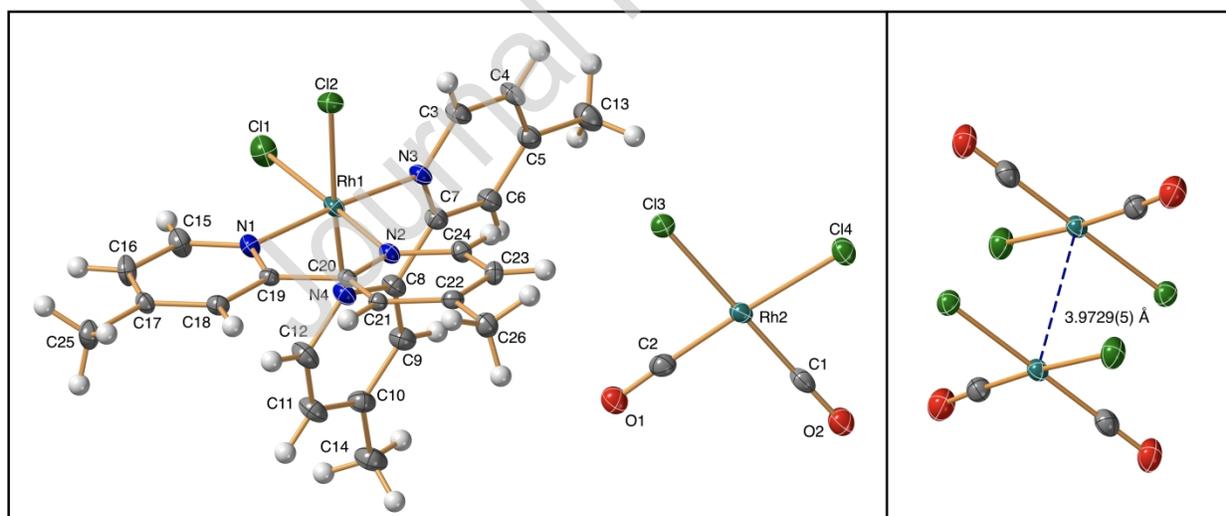


Figure 2. Left: the asymmetric unit of $[\text{Rh}(\text{L1})_2\text{Cl}_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ (**2**). Right: The stacked anion pairs in **2**.

The reduction process and the arrangement on the reduced products in crystals were strongly dependent on reaction conditions. The chain compound **1** was obtained only when the reaction solution was cooled down slowly from the reaction temperature of 125°C to room temperature. If the reaction solution was cooled down rapidly (see the experimental section) the arrangement of Rh-complexes was changed (Fig. 3). Instead of having regular cation-anion chains, the obtained crystalline product consisted of chains with repeating trinuclear cation-anion-cation units with metallophilic contacts between the Rh centers. The positive charge of the repeating trinuclear units were balanced by the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ anions which were not part of the main chain. The anions formed again stacked pairs with relatively long $\text{Rh}\cdots\text{Rh}$ contacts of 3.6198(17) Å and interactions between the anionic units are weak (Fig. 3).

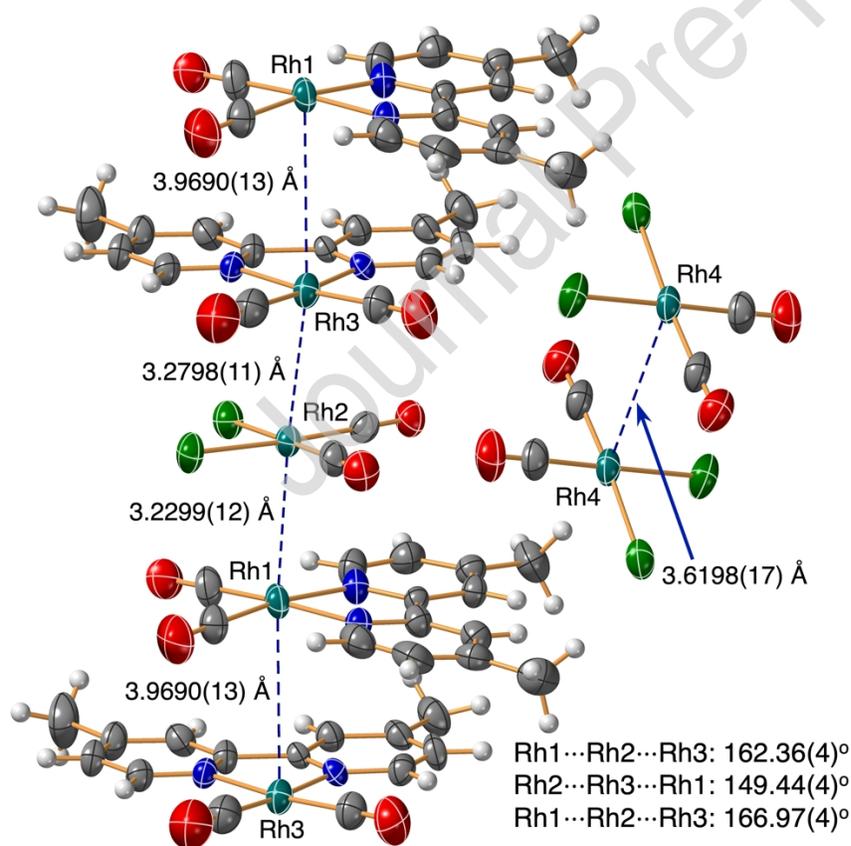


Figure 3. The chains structure of **3**.

The arrangement of ions in **3** is somewhat unusual. Typically, cationic chains consist only of cationic units. The counter anions are then simply balancing the charge as separated anions. In **3** the cationic repeating trinuclear unit $\text{Rh1}\cdots\text{Rh2}\cdots\text{Rh3}$ contains two square planar cations and one counter anion giving a net charge of +1 to the trinuclear unit. Despite the unusual order of charged building blocks the metal-metal distances in the repeating trinuclear units are comparable with the metal-metal distances in typical metallophilic Rh-chains [45]. The metal-metal distance between the repeating trinuclear units is clearly longer (3.960(13) Å) than the intermetallic distance within the trinuclear unit (3.2299(12)-3.2798(11)Å) indicating lack of significant metallophilic contacts between the repeating trinuclear units. The separate counter anions in **3** formed dinuclear entities in the crystalline state with the $\text{Rh}\cdots\text{Rh}$ distance of 3.6198(17) Å. Such a distance is only slightly longer than those reported in the literature for typical anionic dinuclear or polymeric $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ -systems [46-48]. The possible metallophilic interaction between the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ anions is expected to be at most weak. The directing effect of the metal-metal interactions and formation of metallophilic cation-anion chains seems to be favored by a slow crystallization process. In fast crystallization non-directional coulombic forces and weaker van der Waals interactions start to have a significant role in arranging ionic complexes.

The NH_2 substituent (L2) is not only a stronger electron donor compared to CH_3 -group (L1) but also a good H-bond donor. When the Me-substituted bipyridine was replaced with NH_2 -substituted bipyridine, formation of hydrogen bonds favored purely cationic chains (Figs. 4 and 5). The hydrogen bonding between the chlorido ligands of the anion became the dominating directional force instead of the metallophilicity pushing the anions away from the chain structure (Fig. 4). The steric hindrance affected the arrangement of the cations and instead of metallophilic contacts. Due

to the hydrogen bonds the bipyridine ligands of the cationic units are now facing opposite directions and the cation chain is formed *via* metal- π -interactions.

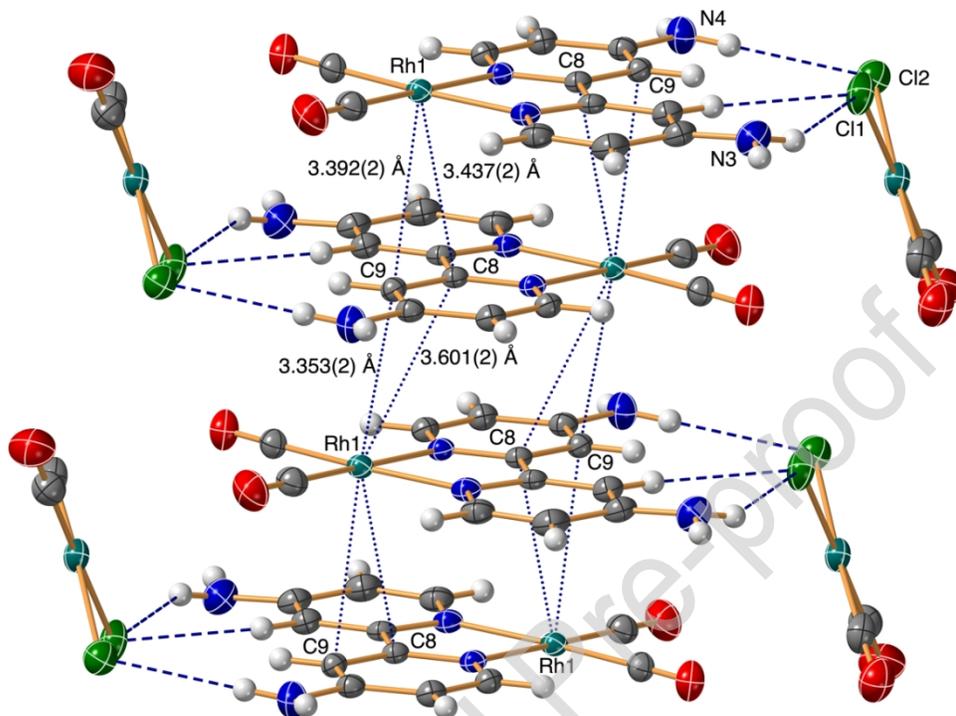


Figure 4. The chain structure of **4**. Heavy atom distances in selected H-bonds: N3 \cdots C11#1: 3.669(3) Å, N3 \cdots C11#2: 3.272(2) Å, N4 \cdots C12#1: 3.333(2) Å, C9 \cdots C11#2: 4.044(2) Å. Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+1, -z+2$, #2: $-x+1, y+1/2, -z+3/2$.

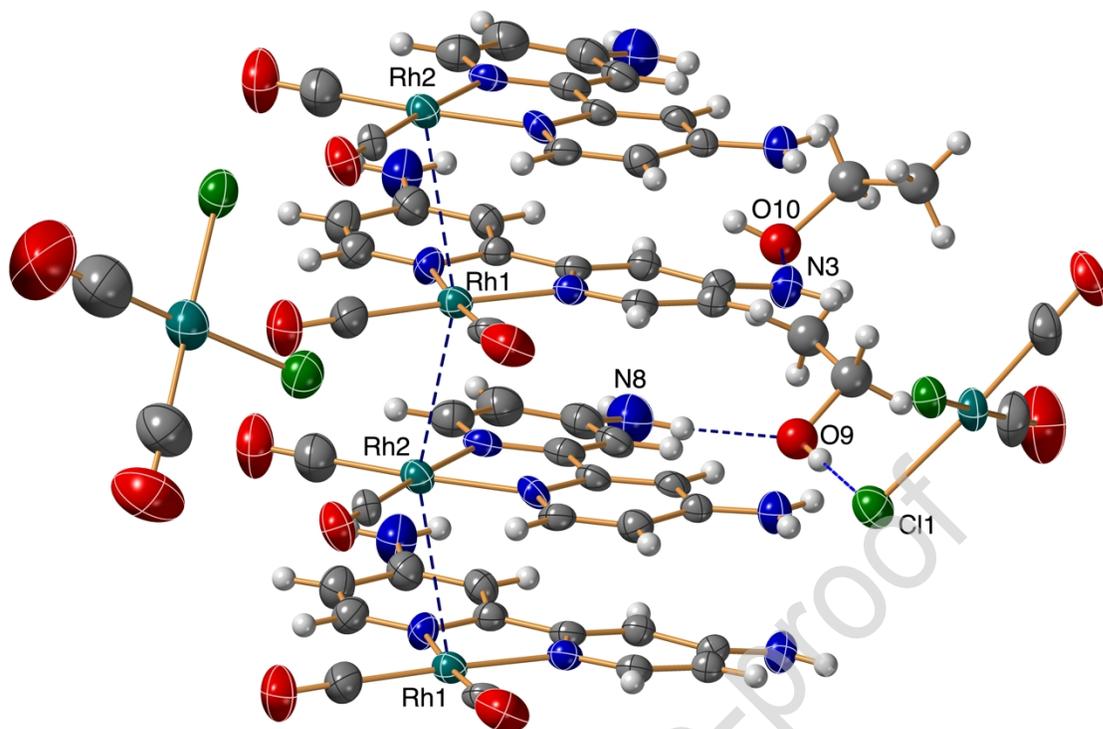


Figure 5. The chain structure of **5**. Rh1 \cdots Rh2: 3.5216(10) Å. Rh1 \cdots Rh2#1: 3.3840(10) Å, Rh2#1 \cdots Rh1 \cdots Rh2: 155.76(3) $^\circ$. Heavy atom distances in selected H-bonds: N3 \cdots O10: 2.80(2) Å, N8 \cdots O9: 2.83(3) Å, O9 \cdots Cl1: 3.167(18) Å.

Because of the good H-bond properties of the cations with NH₂-substituted bipyridine ligands, solvent of crystallization had also an important role in the arrangement of ionic units in crystalline state. A strong H-bond acceptor/donor, such as ethanol, could replace the weaker NH \cdots Cl contacts with stronger NH \cdots O and OH \cdots Cl interactions. This pushed the anions further away from the cations allowing the cations to approach differently compare to structure **4**. Now the Rh centers in **5** are nearly linearly aligned and they do form weak metal-metal contacts throughout the crystal (Fig. 5).

Conclusions

The organization of the cation/anion pairs of $[\text{Rh}(4,4'\text{-dimethyl-2,2'}\text{-bipyridine})(\text{CO})_2]/[\text{Rh}(\text{CO})_2\text{Cl}_2]$ and $[\text{Rh}(4,4'\text{-diamine-2,2'}\text{-bipyridine})(\text{CO})_2]/[\text{Rh}(\text{CO})_2\text{Cl}_2]$ depend on the interplay between various directional and non-directional non-covalent interactions. In general, the square planar structure of the Rh(I) ions tends to favor stacking of these ionic molecules. In the case of $[\text{Rh}(4,4'\text{-dimethyl-2,2'}\text{-bipyridine})(\text{CO})_2]/[\text{Rh}(\text{CO})_2\text{Cl}_2]$ system, the metallophilic interactions are favoring linear stacks with alternating cations and anions in slow crystallizations. The stacks are further supported by Coulombic forces. In fast crystallizations the non-directional Coulombic forces and other weak van der Waals forces reduces the directing role of the metal-metal interactions. When the 4,4'-dimethyl-2,2'-bipyridine ligand is replaced with a much better H-bond donor ligand 4,4'-diamine-2,2'-bipyridine, hydrogen bonding takes the dominating role in the arrangement of the molecular units. Hydrogen bond formation between the cation and anion leads to linear stacks where the cationic units are facing opposite direction. This prevents sterically the metal-metal contacts and they are replaced with metal- π -interactions. Simultaneously, the anions are pushed away from the chain structure. The solvent of crystallization may also have a strong impact on the arrangement of ionic units. Presence of a good H-bond acceptor/donor, such as ethanol, may replace the hydrogen bonds between the cation and anion with cation-solvent contacts. In such a case the anions may be pushed even further away from the cation stacks allowing metal-metal interactions and aligned stacking of the cationic units. All in all, design of a supramolecular systems is challenging. To be able to fabricate predictable structures requires that all significant interactions must be considered as the potential directing forces.

ACKNOWLEDGMENT

Financial support of Magnus Ehrnrooth foundation (K.K), Academy of Finland, project no. 295581 (M.H) as well as the European Network on Smart Inorganic Polymers (SIPs) COST CM1302 project.

ASSOCIATED CONTENT

Supporting Information. CCDC 1935018-1935022 contain the crystallographic data for **1-5**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

REFERENCES

- [1] K.C. Bentz, S.M. Cohen, Supramolecular Metallopolymers: From Linear Materials to Infinite Networks, *Angew. Chemie Int. Ed.* **57** (2018) 14992–15001. doi:10.1002/anie.201806912.
- [2] L. Yang, X. Tan, Z. Wang, X. Zhang, Supramolecular Polymers: Historical Development, Preparation, Characterization, and Functions, *Chem. Rev.* **115** (2015) 7196–7239. doi:10.1021/cr500633b.
- [3] M. Schmittel, K. Mahata, Diversity and Complexity through Reversible Multiple Orthogonal Interactions in Multicomponent Assemblies, *Angew. Chemie Int. Ed.* **47** (2008) 5284–5286. doi:10.1002/anie.200800583.
- [4] T. Aida, E.W. Meijer, S.I. Stupp, Functional Supramolecular Polymers, *Science* (80-.). **335** (2012) 813 LP – 817. doi:10.1126/science.1205962.

- [5] P. Xing, Y. Zhao, Multifunctional Nanoparticles Self-Assembled from Small Organic Building Blocks for Biomedicine, *Adv. Mater.* 28 (2016) 7304–7339. doi:10.1002/adma.201600906.
- [6] W.-H. Wu, M.-J. Huang, Q. Zeng, W.-R. Xian, W.-M. Liao, J. He, Electrical and magnetic properties of a radical-based Co(II) coordination complex with $\text{CH}\cdots\pi$ and $\pi\cdots\pi$ supramolecular interactions, *Inorg. Chem. Commun.* 103 (2019) 149–153. doi:https://doi.org/10.1016/j.inoche.2019.03.022.
- [7] R.O. Fuller, C.S. Griffith, G.A. Koutsantonis, K.M. Lapere, B.W. Skelton, M.A. Spackman, A.H. White, D.A. Wild, Supramolecular interactions between hexabromoethane and cyclopentadienyl ruthenium bromides: Halogen bonding or electrostatic organisation?, *CrystEngComm.* 14 (2012) 804–811. doi:10.1039/C1CE05438D.
- [8] B. Li, S.-Q. Zang, L.-Y. Wang, T.C.W. Mak, Halogen bonding: A powerful, emerging tool for constructing high-dimensional metal-containing supramolecular networks, *Coord. Chem. Rev.* 308 (2016) 1–21. doi:https://doi.org/10.1016/j.ccr.2015.09.005.
- [9] C.S.A. Fraser, D.J. Eisler, R.J. Puddephatt, Self-assembly of organometallic polymers through hydrogen bonding: A diplatinum(IV) complex with a single bridging halide ligand, *Polyhedron.* 25 (2006) 266–270. doi:https://doi.org/10.1016/j.poly.2005.08.020.
- [10] E. Laurila, R. Tatikonda, L. Oresmaa, P. Hirva, M. Haukka, Metallophilic interactions in stacked dinuclear rhodium 2,2'-biimidazole carbonyl complexes, *CrystEngComm.* 14 (2012) 8401–8408. doi:10.1039/c2ce25385b.
- [11] E. Laurila, L. Oresmaa, J. Hassinen, P. Hirva, M. Haukka, Neutral one-dimensional metal chains consisting of alternating anionic and cationic rhodium complexes, *Dalt. Trans.* 42 (2013) 395–398. doi:10.1039/c2dt31671d.

- [12] M. Tadokoro, K. Nakasuji, Hydrogen bonded 2,2'-biimidazolate transition metal complexes as a tool of crystal engineering, *Coord. Chem. Rev.* 198 (2000) 205–218. doi:[https://doi.org/10.1016/S0010-8545\(99\)00223-4](https://doi.org/10.1016/S0010-8545(99)00223-4).
- [13] B. Moulton, M.J. Zaworotko, From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids, *Chem. Rev.* 101 (2001) 1629–1658. doi:10.1021/cr9900432.
- [14] C. Fouquey, J.-M. Lehn, A.-M. Levelut, Molecular recognition directed self-assembly of supramolecular liquid crystalline polymers from complementary chiral components, *Adv. Mater.* 2 (1990) 254–257. doi:10.1002/adma.19900020506.
- [15] S.A. Cook, A.S. Borovik, Molecular Designs for Controlling the Local Environments around Metal Ions, *Acc. Chem. Res.* 48 (2015) 2407–2414. doi:10.1021/acs.accounts.5b00212.
- [16] B. Soltani, H. Nabipour, J.T. Engle, C.J. Ziegler, $\pi\cdots\pi$ and hydrogen bonding interactions in the crystal structure of trans-dichloro-tetrakis(1H-indazole-N2)-nickel(II), *Mater. Today Proc.* 5 (2018) 15845–15851. doi:<https://doi.org/10.1016/j.matpr.2018.05.083>.
- [17] K. Chkirate, S. Fettach, K. Karrouchi, N.K. Sebbar, E.M. Essassi, J.T. Mague, S. Radi, M. El Abbes Faouzi, N.N. Adarsh, Y. Garcia, Novel Co(II) and Cu(II) coordination complexes constructed from pyrazole-acetamide: Effect of hydrogen bonding on the self assembly process and antioxidant activity, *J. Inorg. Biochem.* 191 (2019) 21–28. doi:<https://doi.org/10.1016/j.jinorgbio.2018.11.006>.
- [18] M. Kose, S.E. Duman, V. McKee, I. Akyol, M. Kurtoglu, Hydrogen bond directed 1D to 3D structures of square-planar Ni(II) complexes and their antimicrobial studies, *Inorganica Chim. Acta.* 462 (2017) 281–288. doi:<https://doi.org/10.1016/j.ica.2017.04.005>.

- [19] V. Sethuraman, N. Stanley, P. Thomas Mu-thiah, C. Karunakaran, Supramolecular self-assembly via inter-ligands hydrogen bonds in $[\text{Cu}(\text{H}_2\text{O})_2(\text{NO}_3)_2(\text{tb})]$ (tb is thia-bendazole), *Acta Crystallogr. Sect. E.* 58 (2002) m392–m395. doi:10.1107/S1600536802011054.
- [20] S. Petriček, Syntheses and crystal structures of metal (Mn, Co, Ni) chloride complexes with 3-hydroxypyridin-2-one and contribution of $\text{OH}\cdots\text{Cl}$ hydrogen bonds to their structural diversity, *Polyhedron.* 167 (2019) 11–25. doi:https://doi.org/10.1016/j.poly.2019.03.050.
- [21] I.A. Baburin, V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, Interpenetrated three-dimensional hydrogen-bonded networks from metal–organic molecular and one- or two-dimensional polymeric motifs, *CrystEngComm.* 10 (2008) 1822–1838. doi:10.1039/B811855H.
- [22] T.-G. Zhan, T.-Y. Zhou, Q.-Y. Qi, J. Wu, G.-Y. Li, X. Zhao, The construction of supramolecular polymers through anion bridging: from frustrated hydrogen-bonding networks to well-ordered linear arrays, *Polym. Chem.* 6 (2015) 7586–7593. doi:10.1039/C5PY01284H.
- [23] M. Tuikka, M. Niskanen, P. Hirva, K. Rissanen, A. Valkonen, M. Haukka, Concerted halogen and hydrogen bonding in $[\text{RuI}_2(\text{H}_2\text{dcbpy})(\text{CO})_2]\cdots\text{I}_2\cdots(\text{CH}_3\text{OH})\cdots\text{I}_2\cdots[\text{RuI}_2(\text{H}_2\text{dcbpy})(\text{CO})_2]$, *Chem. Commun.* 47 (2011) 3427–3429. doi:10.1039/C0CC05726F.
- [24] X. Ding, M.J. Tuikka, P. Hirva, V.Y. Kukushkin, A.S. Novikov, M. Haukka, Fine-tuning halogen bonding properties of diiodine through halogen–halogen charge transfer – extended $[\text{Ru}(2,2'\text{-bipyridine})(\text{CO})_2\text{X}_2]\cdot\text{I}_2$ systems (X = Cl, Br, I), *CrystEngComm.* 18 (2016) 1987–1995. doi:10.1039/C5CE02396C.

- [25] V. V Sivchik, A.I. Solomatina, Y.-T. Chen, A.J. Karttunen, S.P. Tunik, P.-T. Chou, I.O. Koshevoy, Halogen Bonding to Amplify Luminescence: A Case Study Using a Platinum Cyclometalated Complex, *Angew. Chemie Int. Ed.* 54 (2015) 14057–14060. doi:10.1002/anie.201507229.
- [26] M. Fontana, H. Chanzy, W.R. Caseri, P. Smith, A.P.H.J.H.J. Schenning, E.W. Meijer, F. Gröhn, A soluble equivalent of the supramolecular, quasi-one-dimensional, semiconducting Magnus' green salt, *Chem. Mater.* 14 (2002) 1730–1735. doi:10.1021/cm0109793.
- [27] J.K. Bera, K.R. Dunbar, 23 / 2002 The Chemistry of the Antibody Molecule Chain Compounds Based on Transition Metal Backbones : New Life for an Old Topic, *Angew. Chem. Int. Ed.* 41 (2002) 4453. doi: 10.1002/1521-3773(20021202)41:23<4453::AID-ANIE4453>3.0.CO;2-1
- [28] L. H. Doerrer, Steric and electronic effects in metallophilic double salts, *Dalton Trans.* 39 (2010) 3543-3553. doi: 10.1039/b920389c.
- [29] K. Krogmann, Planar Complexes Containing Metal-Metal Bonds, *Angew. Chemie Int. Ed. English.* 8 (1969) 35–42. doi:10.1002/anie.196900351.
- [30] E. Laurila, L. Oresmaa, J. Hassinen, P. Hirva, M. Haukka, Neutral one-dimensional metal chains consisting of alternating anionic and cationic rhodium complexes, *Dalt. Trans.* 42 (2013) 395–398. doi:10.1039/C2DT31671D.
- [31] C. Tejel, M.A. Ciriano, L.A. Oro, From platinum blues to rhodium and iridium blues, *Chem. - A Eur. J.* 5 (1999) 1131–1135. doi:10.1002/(SICI)1521-3765(19990401)5:4<1131::AID-CHEM1131>3.0.CO;2-3.
- [32] P.W. DeHaven, V.L. Goedken, Crystal and molecular structure of dicarbonyl(2,4-pentanediiimine)rhodium(I) tetrafluoroborate, a structure having extended rhodium-

- rhodium interactions, *Inorg. Chem.* 18 (1979) 827–831. doi:10.1021/ic50193a058.
- [33] C. Crotti, S. Cenini, B. Rindone, S. Tollari, F. Demartin, Deoxygenation reactions of ortho-nitrostyrenes with carbon monoxide catalysed by metal carbonyls: a new route to indoles, *J. Chem. Soc. {,} Chem. Commun.* (1986) 784–786. doi:10.1039/C39860000784.
- [34] A.J. Rodríguez-Santiago, N. Cortés, K. Pham, J. Miksovská, R.G. Raptis, 4,4'-Dihydroxy-2,2'-bipyridine complexes of Co(III), Cu(II) and Zn(II); structural and spectroscopic characterization, *Polyhedron*. 150 (2018) 61–68. doi:https://doi.org/10.1016/j.poly.2018.04.039.
- [35] M.D. Stephenson, T.J. Prior, M.J. Hardie, New Network Structures from Cu(II) Complexes of Chelating Ligands with Appended Hydrogen Bonding Sites, *Cryst. Growth Des.* 8 (2008) 643–653. doi:10.1021/cg700820d.
- [36] T. Chand Vagvala, T. Ooyabe, M. Sakai, Y. Funasako, M. Inokuchi, W. Kurashige, Y. Negishi, V. Kalousek, K. Ikeue, Synthesis and characterization of metal-diaminobipyridine complexes as low-cost co-catalysts for photo-sensitized hydrogen evolution, *Inorganica Chim. Acta.* 482 (2018) 821–829. doi:https://doi.org/10.1016/j.ica.2018.07.022.
- [37] A.E. Platero-Prats, A. Bermejo Gómez, L. Samain, X. Zou, B. Martín-Matute, The First One-Pot Synthesis of Metal–Organic Frameworks Functionalised with Two Transition-Metal Complexes, *Chem. – A Eur. J.* 21 (2015) 861–866. doi:10.1002/chem.201403909.
- [38] D. Sivanesan, S. Yoon, Functionalized bipyridyl rhodium complex capable of electrode attachment for regeneration of NADH, *Polyhedron*. 57 (2013) 52–56. doi:https://doi.org/10.1016/j.poly.2013.04.011.
- [39] C.M. Conifer, R.A. Taylor, D.J. Law, G.J. Sunley, A.J.P.P. White, G.J.P.P. Britovsek, First metal complexes of 6,6'-dihydroxy-2,2'-bipyridine: from molecular wires to applications in

- carbonylation catalysis, *Dalt. Trans.* 40 (2011) 1031–1033. doi:10.1039/C0DT01526A.
- [40] P. Plitt, D.E. Gross, V.M. Lynch, J.L. Sessler, Dipyrrolyl-Functionalized Bipyridine-Based Anion Receptors for Emission-Based Selective Detection of Dihydrogen Phosphate, *Chem. – A Eur. J.* 13 (2007) 1374–1381. doi:10.1002/chem.200601514.
- [41] N. Rigby, T. Jacobs, J.P. Reddy, M.J. Hardie, Metal Complexes of 2,2'-Bipyridine-4,4'-diamine as Metallo-Tectons for Hydrogen Bonded Networks, *Cryst. Growth Des.* 12 (2012) 1871–1881. doi:10.1021/cg201512q.
- [42] E. Tomás-Mendivil, J. Díez, V. Cadierno, Palladium(II) complexes with symmetrical dihydroxy-2,2'-bipyridine ligands: Exploring their inter- and intramolecular interactions in solid-state, *Polyhedron.* 59 (2013) 69–75. doi:https://doi.org/10.1016/j.poly.2013.04.043.
- [43] Agilent, CrysAlisPro, Agilent Technologies Inc, Yarnton, Oxfordshire, England, 2013.
- [44] L. Palatinus, G. Chapuis, *{it SUPERFLIP}* *{--}* a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, *J. Appl. Crystallogr.* 40 (2007) 786–790. doi:10.1107/S0021889807029238.
- [45] G.M. Sheldrick, Crystal structure refinement with *{it SHELXL}*, *Acta Crystallogr. Sect. C.* 71 (2015) 3–8. doi:10.1107/S2053229614024218.
- [46] O. V Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *{it OLEX2}*: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.* 42 (2009) 339–341. doi:10.1107/S0021889808042726.
- [47] C.B. Hübschle, G.M. Sheldrick, B. Dittrich, *{it ShelXle}*: a Qt graphical user interface for *{it SHELXL}*, *J. Appl. Crystallogr.* 44 (2011) 1281–1284. doi:10.1107/S0021889811043202.

Declaration of Interest Statement

Ref: SSSCIE_2019_658

Self-assembly of square planar rhodium carbonyl complexes with 4,4-disubstituted-2,2'-bipyridine ligands

Kalle Kolari^a, Elina Laurila^a, Maria Chernysheva^a, Pipsa Hirva^b, Matti Haukka^{a*}

^aUniversity of Jyväskylä, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland

^bUniversity of Eastern Finland, Department of Chemistry, P.O.Box 111, FI-80101, Joensuu, Finland

There are no interests to declare.

Matti Haukka
University of Jyväskylä
Department of Chemistry
P.O. Box 35
FI-40014 University of Jyväskylä, Finland
Tel. +358 40 8054666
E-mail: matti.o.haukka@jyu.fi

Highlights for

Self-assembly of square planar rhodium carbonyl complexes with 4,4-disubstituted-2,2'-bipyridine ligands

Kalle Kolari, Elina Laurila, Maria Chernysheva, Pipsa Hirva, Matti Haukka*

^aUniversity of Jyväskylä, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland

^bUniversity of Eastern Finland, Department of Chemistry, P.O.Box 111, FI-80101, Joensuu, Finland

- Metallophilic chains can be obtained by controlling the non-covalent interactions.
- Utilization of different interactions can be used for changing the assembly of metal complexes in solid state.

Journal Pre-proof