

DICYANIDO Ru(III) COMPLEXES: SYNTHESIS AND CRYSTAL STRUCTURES

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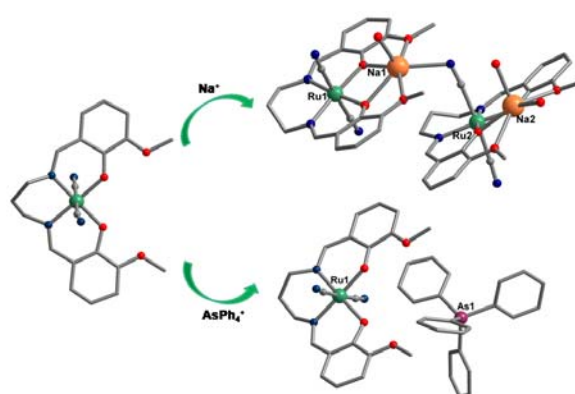
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Three new coordination compounds, $[\text{Ru}(\text{valpn})(\text{CN})_2\text{Na}(\text{H}_2\text{O})(\mu\text{-CN})\text{Ru}(\text{valpn})(\text{CN})\text{Na}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**), $\text{AsPh}_4[\text{Ru}(\text{valpn})(\text{CN})_2]\cdot 11\text{H}_2\text{O}$ (**2**), and $\text{AsPh}_4[\text{Ru}(\text{valdmcx})(\text{CN})_2]\cdot 6.5\text{H}_2\text{O}$ (**3**), have been synthesized and their structures have been solved by single-crystal X-ray diffraction (H_2valpn and $\text{H}_2\text{valdmcx}$ are Schiff base proligands resulted from the condensation reactions of *o*-vanillin with 1,3-propanediamine and 1,2-diaminocyclohexane, respectively). Compound **1** is a tetranuclear complex, assembled as $\{\text{RuNa}\}_2$ dimers where the association takes place by the coordination of a cyanido nitrogen atom to a sodium ion. The ruthenium(III) ion is located into the (N_2O_2) coordination site and sodium ion into the open $(\text{O}_2\text{O}'_2)$ compartment. The single-crystal X-ray diffraction investigation of **2** and **3** reveals the formation of discrete mononuclear Ru^{III} anionic complexes, $[\text{Ru}^{\text{III}}(\text{L})(\text{CN})_2]^-$, and tetraphenylarsphonium counteranions.



INTRODUCTION

Discrete cyanido complexes of various 3d-5d metal ions are very attractive and useful as metalloligands to prepare polynuclear compounds.¹⁻³ Interesting magnetic molecular materials were obtained due to the excellent ability of the cyanido ligand to connect different metal ions and to mediate strong exchange interactions.¹⁻⁴ Homoleptic $[\text{M}(\text{CN})_x]^{n-}$ ($\text{M} = \text{Fe}, \text{Cr}, \text{Ru}, \text{Os}, \text{Mo}, \text{W}$) and heteroleptic $[\text{M}_a(\text{L})_y(\text{CN})_x]^{n-}$ cyanidometallates ($\text{M}_a =$ divalent or trivalent metal ion, $\text{L} =$ polydentate ligand) have been successfully used in the construction of discrete and multidimensional

magnetic materials.¹⁻⁶ Nevertheless, the dicyanido building-blocks are poorly represented in literature.^{3b,7} Dicyanido-based heteroleptic Ru(III) building-blocks are rare examples: $[\text{Ru}(\text{Q})_2(\text{CN})_2]^-$ and $[\text{Ru}(\text{acac})_2(\text{CN})_2]^-$, ($\text{HQ} = 8\text{-hydroxyquinoline}$, $\text{Hacac} = \text{acetylacetonate}$),⁸ $[\text{Ru}(\text{salen})(\text{CN})_2]^-$ ($\text{H}_2\text{salen} = \text{N,N}'\text{-bis(salicylidene)ethylenediamine}$).^{8b,9} In these units the charge of the precursor depends not only on the oxidation state of metal ions, but also on the nature of organic ligand (neutral or anionic). In a previous paper, we have reported a new heteroleptic dicyanido-Schiff base complex $[\text{K}(\text{H}_2\text{O})_2\text{Ru}^{\text{III}}(\text{valen})(\text{CN})_2]\cdot\text{H}_2\text{O}$ which has been employed as a building-block to design

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heterometallic $\text{Ru}^{\text{III}}\text{-Ln}^{\text{III}}$ complexes (H_2valen = Schiff base derived from *o*-vanillin and ethylenediamine).¹⁰ The organic ligand has the ability to accommodate two metal ions simultaneously, given the different compartments it possesses. The inner compartment (N_2O_2) hosts the Ru^{III} ion, while the outer one, ($\text{O}_2\text{O}'_2$), can accommodate another metal ion.

Herein we report three new Ru(III) heteroleptic dicyanido-based complexes, $[\text{Ru}(\text{valpn})(\text{CN})_2\text{Na}(\text{H}_2\text{O})(\mu\text{-CN})\text{Ru}(\text{valpn})(\text{CN})\text{Na}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**), $\text{AsPh}_4[\text{Ru}(\text{valpn})(\text{CN})_2]\cdot 11\text{H}_2\text{O}$ (**2**), and $\text{AsPh}_4[\text{Ru}(\text{valdmcx})(\text{CN})_2]\cdot 6.5\text{H}_2\text{O}$ (**3**), together with their spectral and crystallographic characterization.

EXPERIMENTAL

Materials

All chemicals and solvents were of reagent grade and purchased from commercial sources. The organic pro-ligands (H_2L) have been synthesized by the condensation reaction of *o*-vanillin with 1,3-propanediamine (H_2valpn) and, 1,2-diaminocyclohexane ($\text{H}_2\text{valdmcx}$), respectively, in ethanol. The starting compound, $[\text{Ru}(\text{L})(\text{PPh}_3)\text{Cl}]$, was synthesized following the Murray's procedure, with minor modifications.¹¹ The dicyanido-Ru(III) precursors were synthesized by adapting the procedure reported by Leung.¹²

Synthesis of $[\text{Ru}(\text{valpn})(\text{CN})_2\text{Na}(\text{H}_2\text{O})(\mu\text{-CN})\text{Ru}(\text{valpn})(\text{CN})\text{Na}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (1**):** Complex **1** has been obtained by adapting the procedure reported for the salen derivative.¹² $[\text{Ru}(\text{valpn})(\text{PPh}_3)\text{Cl}]$ (1 mmol) was refluxed with NaCN (3.3 mmol) in methanol for 2 hours. The green solution was cooled and then evaporated to dryness. Distilled water (25 mL) was added to the green residue and then filtered. Slow evaporation of the resulting green solution at room temperature over a period of several weeks produced dark green crystals (yield 75%). IR data (KBr, cm^{-1}): 3397m, 2958m, 2931m, 2873m, 2836w, 2096s (νCN), 2057vw (νCN), 1600vs, 1598vs, 1538m, 1465m, 1434s, 1361w, 1313s, 1245vs, 1220vs, 1170m, 1089w, 1072s, 995w, 956w, 854m, 782w, 740s, 694wm, 619w, 559m, 428m. Elemental analysis: Calcd. for $\text{C}_{42}\text{H}_{48}\text{Na}_2\text{N}_8\text{O}_{12}\text{Ru}_2$: C, 45.61; H, 4.34; N, 10.13; Found: C, 45.05; H, 4.89; N, 10.98.

Synthesis of $\text{AsPh}_4[\text{Ru}(\text{valpn})(\text{CN})_2]\cdot 11\text{H}_2\text{O}$ (2**):** $[\text{Ru}(\text{valpn})(\text{PPh}_3)\text{Cl}]$ (1 mmol) was refluxed with KCN (3.3 mmol) in methanol for 2 hours. The resulted green solution was cooled and then the solvent was removed using a rotary evaporator. The dark green residue was dissolved in 10 mL water and then filtered. AsPh_4Cl (1.5 mmol) was added to the green filtrate to give a dark green precipitate, which was filtered and collected (yield 55%). The green filtrate was let to crystallize at room temperature. After one week, dark green crystals suitable for X-ray diffraction have been obtained. IR data (KBr, cm^{-1}): 3399s, 2927m, 2834m, 2090s (νCN), 1627w, 1600vs, 1538s, 1488vs, 1435w, 1315s, 1247vs, 1220s,

1172m, 1079s, 997m, 894m, 854s, 795w, 744vs, 690s, 605w, 525w, 466s. Elemental analysis: Calcd. for $\text{C}_{45}\text{H}_{62}\text{AsN}_4\text{O}_{15}\text{Ru}$: C, 50.23; H, 5.76; N, 5.21; Found: C, 51.09; H, 5.03; N, 4.98.

Synthesis of $\text{AsPh}_4[\text{Ru}(\text{valdmcx})(\text{CN})_2]\cdot 6.5\text{H}_2\text{O}$ (3**):** This compound was prepared following the same procedure described for **2** using $\text{H}_2\text{valdmcx}$ instead of H_2valpn . In this case, dark green crystals suitable for X-ray crystallography were obtained by slow evaporation of the green filtrate, at room temperature over a period of several days (yield 45%). IR data (KBr, cm^{-1}): 3421s, 2933m, 2861w, 2094s (νCN), 1635w, 1594vs, 1535s, 1457m, 1427s, 1299s, 1243vs, 1214s, 1170w, 1078s, 997m, 857m, 784w, 742vs, 690m, 565w, 464s. Elemental analysis: Calcd. for $\text{C}_{48}\text{H}_{56.75}\text{AsN}_4\text{O}_{10.5}\text{Ru}$: C, 55.72; H, 5.49; N, 5.41; Found: C, 54.98; H, 6.02; N, 5.98.

Physical measurements

Elemental analyses of C, N and H were performed on a EuroEa Elemental Analyzer. IR spectra were recorded on a Jasco FTIR 4100 spectrophotometer (KBr pellets) in the range of 4000–400 cm^{-1} . UV–Vis spectra were recorded on a JASCO V-670 spectrophotometer.

Crystallographic Data Collection and Structure Determination

X-ray diffraction measurements for compounds **1** and **2** were performed on a STOE IPDS II diffractometer operating with Mo-K α ($\lambda = 0.71073$ Å) X-ray tube with graphite monochromator.

For compound **3** X-ray diffraction measurements were performed on Bruker APEX-II CCD diffractometers. Single crystal was positioned at 63 mm from the detector and 1026 frames were measured each for 80 s over 1° scan width. The data were processed using SAINT software. SAINT-Plus, version 7.06a and APEX2; Bruker-Nonius AXS Inc.: Madison, WI, 2004. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F₂. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-2013/2014/2015 crystallographic software package. A summary of crystallographic data and the structure refinement for crystals **1-3** are given in Table 1. CCDC reference numbers: 1869644 - 1869646.

RESULTS AND DISCUSSION

Description of the crystal structures of 1-3

The structure of complex **1** is made up of neutral tetranuclear entities $[\text{Ru}(\text{valpn})(\text{CN})_2\text{Na}(\text{H}_2\text{O})(\mu\text{-CN})\text{Ru}(\text{valpn})(\text{CN})\text{Na}(\text{H}_2\text{O})_2]$ and crystallization water molecules. In this structure there are two similar crystallographically independent tetranuclear complexes (Figure 1), which crystallize together with water molecules. Both complexes contain two slightly different {RuNa} dimers. The difference between these two dimers is that one acts as a monodentate ligand through one

cyanido group towards the sodium atom belonging to the second one, whereas the other has both cyanido groups as terminal sites. The crystallographically independent ruthenium atoms (Ru1–Ru4) exhibit a distorted octahedral geometry. Each ruthenium atom is coordinated by two nitrogen and two phenoxido oxygen atoms from H₂valpn ligand, and by two cyanido carbon atoms. The Ru–N and Ru–O distances vary between: 1.981(11) and 2.073(15); 1.986(10) and 2.030(11) Å, respectively (Table 2). The Ru–C–N angles for both terminal [176.0(15)° and 179.0(11)° (Ru1); 178.8(13)° (Ru2); 175.9(15)° and 177.8(13)° (Ru3) and 177.8(14)° (Ru4)] and bridging [176.4(17)° (Ru2) and 176.3(15)° (Ru4)] cyanido groups are slightly bent. The Na1 and Na3 atoms are hexacoordinated by two phenoxido [Na1–O1 = 2.359(12), Na1–O2 = 2.451(12); Na3–O9 = 2.477(12) and Na3–O10 = 2.338(11) Å, respectively] and two methoxy [Na1–O3 = 2.498(12), Na1–O4 = 2.584(12); Na3–O11 = 2.493(12), Na3–O12 = 2.553(12) Å] oxygen atoms from the Schiff base ligand, one cyanido nitrogen atom [Na1–N9 = 2.548(16) and Na3–N13 = 2.565(17) Å], and one oxygen atom from aqua ligand [Na1–O2w = 2.300(16) and Na3–O3w =

2.282(15) Å] generating a pentagonal pyramid. The other sodium atoms, Na2 and Na4, are also six-coordinated by one O₂O₂ set and two water molecules, with bond distances varying between 2.300(15) and 2.647(12) Å (Table 2). The longest Na–O bond distances correspond to the methoxy groups, and the shortest one to the water molecules. The intramolecular Ru⋯Na distances vary between 3.503 and 3.514 Å, and Ru⋯Ru distances are 7.055 and 7.094 Å, while the intramolecular Ru⋯Na distances across the cyanido bridges are 4.679 and 4.721 Å. Selected bond lengths and angles are collected in Table 2. The crystallization water molecule contributes to the stabilization of a 2D-lattice by hydrogen-bonding interactions which involve the coordinated water molecules and the nitrogen atoms of the cyanido groups (Figure 2). The hydrogen bond distances are O(2w)⋯N(14)' = 2.922, O(1w)'⋯N(14)' = 2.997, O(1w)'⋯O(5w) = 2.862, O(5w)⋯N(7) = 3.029, N(4)''⋯O(4w) = 2.917, O(3w)'''⋯N(10)'''' = 2.943, N(10)''''⋯O(6w)'''' = 2.975, O(6w)''''⋯O(8w)' = 2.828, and O(8w)'⋯N(3)'''' = 3.015 Å, respectively [symmetry code: ' = 1+x, y, z; '' = -1+x, -1+y, z; ''' = 1+x, 1+y, z; '''' = 1+x, y, -1+z; ''''' = x, -1+y, -1+z Å].

Table 1

Crystallographic data, details of data collection and structure refinement parameters for compounds 1–3

Compounds	1	2	3
Chemical formula	C ₄₂ H ₄₈ Na ₂ N ₈ O ₁₂ Ru ₂	C ₄₅ H ₆₂ AsN ₄ O ₁₅ Ru	C ₄₈ H _{56.75} AsN ₄ O _{10.5} Ru
M (g mol ⁻¹)	1105	1074.97	1033.71
Temperature, (K)	293(2)	293(2)	130
Wavelength, (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P1</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> (Å)	11.5064(2)	9.9210(2)	9.799(3)
<i>b</i> (Å)	12.5497(3)	22.6076(4)	21.215(6)
<i>c</i> (Å)	17.0697(4)	21.8255(3)	23.331(8)
<i>α</i> (°)	101.370(3)	90	90
<i>β</i> (°)	96.428(4)	94.628(4)	96.72(2)
<i>γ</i> (°)	106.885(5)	90	90
<i>V</i> (Å ³)	2274.41(11)	4879.28(15)	4817(3)
<i>Z</i>	2	4	4
<i>D_c</i> (g cm ⁻³)	1.614	1.463	1.425
<i>μ</i> (mm ⁻¹)	0.776	1.064	3.905
<i>F</i> (000)	1124	2228	2135
Goodness-of-fit on <i>F</i> ²	1.020	0.878	1.083
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0641, 0.0716	0.1212, 0.1796	0.0842, 0.1724
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1637, 0.1754	0.3176, 0.3428	0.1172, 0.1861
Largest diff. peak and hole (eÅ ⁻³)	1.178, -1.685	1.421, -0.705	0.94, -0.74

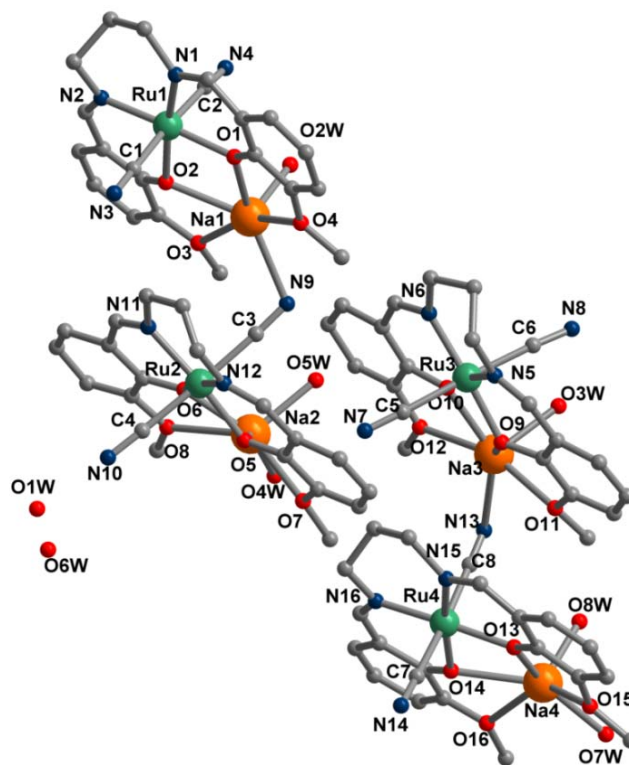


Fig. 1 – Perspective views of the two crystallographically independent tetranuclear complexes in crystal **1**, $[\text{Ru}(\text{valpn})(\text{CN})_2\text{Na}(\text{H}_2\text{O})(\mu\text{-CN})\text{Ru}(\text{valpn})(\text{CN})\text{Na}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$, (the hydrogen atoms were omitted for clarity).

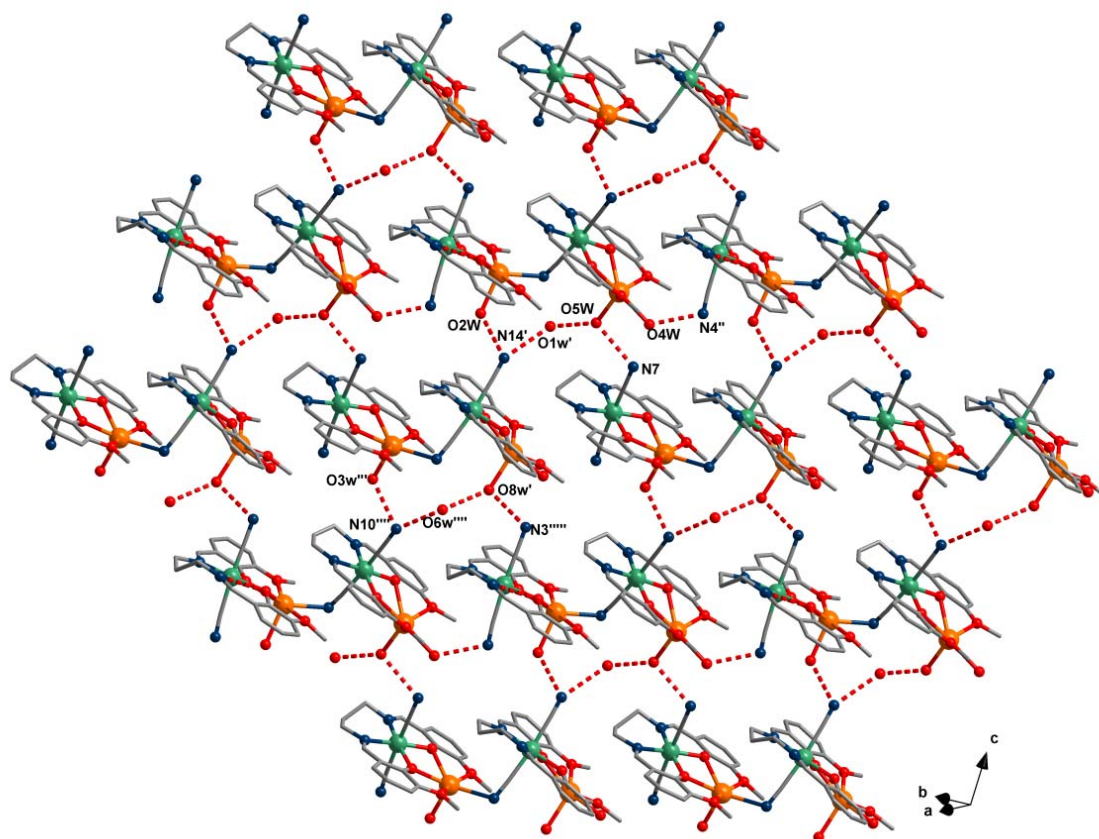


Fig. 2 – View of a 2D-lattice formed by tetranuclear complexes through hydrogen bonds (dashed lines) in crystal **1**.

Table 2

Selected geometric parameters: bonds length (Å) and angles (°) in **1**

1			
<i>bonds length</i> (Å)			
Ru1-N1 = 1.981(11)	Ru2-N11 = 2.073(15)	Ru3-O9 = 1.992(10)	Ru4-N15 = 1.997(14)
Ru1-N2 = 2.059(12)	Ru2-N12 = 2.025(13)	Ru3-N6 = 2.015(14)	Ru4-O14 = 2.009(10)
Ru1-C1 = 2.072(15)	Ru2-O5 = 1.986(10)	Ru3-O10 = 2.008(9)	Ru4-O13 = 2.013(10)
Ru1-C2 = 2.095(18)	Ru2-O6 = 2.019(9)	Ru3-N5 = 2.015(11)	Ru4-N16 = 2.028(12)
Ru1-O1 = 2.030(11)	Ru2-C3 = 2.030(17)	Ru3-C5 = 2.054(15)	Ru4-C8 = 2.038(16)
Ru1-O2 = 2.012(10)	Ru2-C4 = 2.039(15)	Ru3-C6 = 2.072(17)	Ru4-C7 = 2.057(16)
Na1-O2W = 2.300(16)	Na2-O5W = 2.329(16)	Na3-O3W = 2.282(15)	Na4-O7W = 2.350(14)
Na1-O1 = 2.359(12)	Na2-O4W = 2.338(14)	Na3-O10 = 2.338(11)	Na4-O14 = 2.485(12)
Na1-O2 = 2.451(12)	Na2-O6 = 2.347(11)	Na3-O9 = 2.477(12)	Na4-O16 = 2.579(12)
Na1-O3 = 2.498(12)	Na2-O5 = 2.519(12)	Na3-O11 = 2.493(12)	Na4-O15 = 2.647(12)
Na1-N9 = 2.548(16)	Na2-O7 = 2.604(14)	Na3-O12 = 2.553(12)	Na4-O13 = 2.348(12)
Na1-O4 = 2.584(12)	Na2-O8 = 2.637(13)	Na3-N13 = 2.565(17)	Na4-O8W = 2.300(15)
<i>angles</i> (°)			
N1-Ru1-O2 = 173.1(5)	O5-Ru2-N12 = 90.4(5)	O9-Ru3-O10 = 81.8(4)	N15-Ru4-O14 = 172.6(5)
N1-Ru1-O1 = 91.2(5)	O6-Ru2-N12 = 171.8(5)	N6-Ru3-O10 = 92.4(5)	N15-Ru4-O13 = 91.2(5)
O2-Ru1-O1 = 82.3(4)	O5-Ru2-O6 = 81.7(4)	O9-Ru3-N5 = 89.9(5)	O14-Ru4-O13 = 81.5(4)
N1-Ru1-N2 = 95.2(6)	O5-Ru2-N11 = 173.5(5)	N6-Ru3-N5 = 96.0(6)	N15-Ru4-N16 = 95.5(6)
O2-Ru1-N2 = 91.3(5)	O6-Ru2-N11 = 92.5(5)	O10-Ru3-N5 = 171.4(5)	O14-Ru4-N16 = 91.8(5)
O1-Ru1-N2 = 173.1(5)	N12-Ru2-N11 = 95.6(5)	O9-Ru3-N6 = 174.0(5)	O13-Ru4-N16 = 172.9(5)
N3-C1-Ru1 = 179.0(11)	N9-C3-Ru2 = 176.4(17)	N7-C5-Ru3 = 177.8(13)	N14-C7-Ru4 = 177.8(14)
N4-C2-Ru1 = 176.0(15)	N10-C4-Ru2 = 178.8(13)	N8-C6-Ru3 = 175.9(15)	N13-C8-Ru4 = 176.3(15)
O2W-Na1-O1 = 97.1(5)	O5W-Na2-O4W = 84.2(5)	O3W-Na3-O10 = 95.2(5)	O8W-Na4-O13 = 108.6(5)
O2W-Na1-O2 = 99.4(5)	O5W-Na2-O6 = 110.4(5)	O3W-Na3-O9 = 100.7(5)	O8W-Na4-O7W = 84.9(5)
O1-Na1-O2 = 67.1(4)	O4W-Na2-O6 = 142.3(5)	O10-Na3-O9 = 65.8(4)	O13-Na4-O7W = 142.3(5)
O2W-Na1-O3 = 86.0(5)	O5W-Na2-O5 = 108.8(5)	O3W-Na3-O11 = 89.3(5)	O8W-Na4-O14 = 110.5(5)
O1-Na1-O3 = 130.0(5)	O4W-Na2-O5 = 144.7(5)	O10-Na3-O11 = 128.5(4)	O13-Na4-O14 = 65.7(3)
O2-Na1-O3 = 63.2(4)	O6-Na2-O5 = 65.0(4)	O9-Na3-O11 = 63.0(4)	O7W-Na4-O14 = 143.4(5)
O2W-Na1-N9 = 107.8(6)	O5W-Na2-O7 = 97.9(5)	O3W-Na3-O12 = 104.3(5)	O8W-Na4-O16 = 99.5(5)
O1-Na1-N9 = 140.8(5)	O4W-Na2-O7 = 85.5(5)	O10-Na3-O12 = 64.2(3)	O13-Na4-O16 = 124.9(4)
O2-Na1-N9 = 134.2(5)	O6-Na2-O7 = 124.3(5)	O9-Na3-O12 = 125.4(4)	O7W-Na4-O16 = 85.1(5)
O3-Na1-N9 = 82.5(5)	O5-Na2-O7 = 60.7(4)	O11-Na3-O12 = 161.0(5)	O14-Na4-O16 = 60.3(4)
O2W-Na1-O4 = 109.9(5)	O5W-Na2-O8 = 118.1(5)	O3W-Na3-N13 = 109.9(5)	O8W-Na4-O15 = 115.7(5)
O1-Na1-O4 = 62.4(4)	O4W-Na2-O8 = 80.2(5)	O10-Na3-N13 = 140.0(5)	O13-Na4-O15 = 62.1(4)
O2-Na1-O4 = 123.6(4)	O6-Na2-O8 = 62.2(4)	O9-Na3-N13 = 134.2(5)	O7W-Na4-O15 = 80.2(5)
O3-Na1-O4 = 159.6(5)	O5-Na2-O8 = 118.0(4)	O11-Na3-N13 = 83.7(5)	O14-Na4-O15 = 118.1(4)
N9-Na1-O4 = 80.5(5)	O7-Na2-O8 = 139.2(5)	O12-Na3-N13 = 79.4(5)	O16-Na4-O15 = 140.0(5)

The mononuclear complexes **2** and **3** crystallize in the monoclinic space group $P2_1/n$ and their structures consist of $[\text{Ru}^{\text{III}}(\text{L})(\text{CN})_2]^-$ anions, tetraphenylarsonium cations and crystallization water molecules (Figure 3 a,b). The ruthenium atom is six-coordinated by: two imino nitrogen and two phenoxido oxygen atoms from the tetradentate Schiff base ligands (H_2valpn and $\text{H}_2\text{valdmcx}$), in the equatorial plane and by two cyanido groups atoms into the apical positions building a distorted octahedral environment around the Ru(III) center. The distances are Ru1-N1 = 1.986(17); Ru1-N2 = 2.002(17); Ru1-O1 = 2.000(11); Ru1-O2 = 2.041(12); Ru1-C23 = 1.99(2); Ru1-C24 = 2.056(17) Å for compound **2**, and Ru1-N1 = 2.004(10); Ru1-N2 = 1.976(10); Ru1-O1 = 2.014(8); Ru1-O2 = 2.021(7); Ru1-C23 =

2.060(15); Ru-C24 = 2.060(13) Å for compound **3**, respectively. The Ru1-C23-N4 and Ru1-C24-N3 angles are 172(2)° and 176.3(13)° for **2**, and 174.3(11)° and 176.4(10)° for **3**, respectively. An inspection of the packing diagrams for **2** and **3** shows that the crystallization water molecules are involved in an extended 2-D network of hydrogen bonds with the nitrogen atoms of the cyanido groups (Figures 4 and 5). One water molecule (O1w) is hosted by a neighbouring anionic unit, through hydrogen bonds with the oxygen atoms from the open ($\text{O}_2\text{O}'_2$) site of the H_2L ligand (Figures 4a, 5a). This is in agreement with the previous structural reports where the four-oxygen compartment ($\text{O}_2\text{O}'_2$) acts as a receptor for alkaline cations (e.g. K^+) or water molecules.¹³ The tetraphenylarsonium cation exhibits the expected

tetrahedral shape and the bond distances and angles are in agreement with those observed with other AsPh_4^+ containing compounds (with an average As-C bond of 1.902 (compound **2**) and 1.898 Å (compound **3**), and an average C-As-C angle of 109.9 (compound **2**) and 109.2° (compound **3**).^{14,15} Focusing on the tetraphenylarsonium cations, they form supramolecular dimers

along the crystallographic *a* axis (Figures 4b,5b), each cation being involved in edge-to-face CH- π interactions. The intradimer As---As separation through the edge-to-face supramolecular motifs is 6.18 (for **2**) and 6.15 Å (for **3**), respectively. The main bond distances and angles together with the hydrogen bonds for compounds **2** and **3** are listed in Tables 3 and 4.

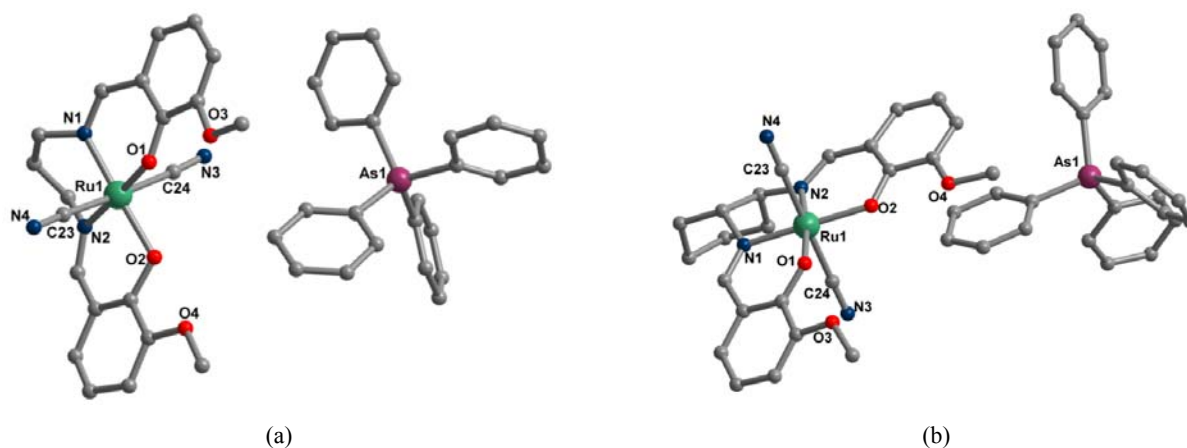


Fig. 3 – Perspective view of the (a) $\text{AsPh}_4[\text{Ru}^{\text{III}}(\text{valpn})(\text{CN})_2]$ in crystal **2** and (b) $\text{AsPh}_4[\text{Ru}^{\text{III}}(\text{valdmcx})(\text{CN})_2]$ in crystal **3**, with the atom numbering scheme (the hydrogen atoms and the water molecules have been omitted for clarity).

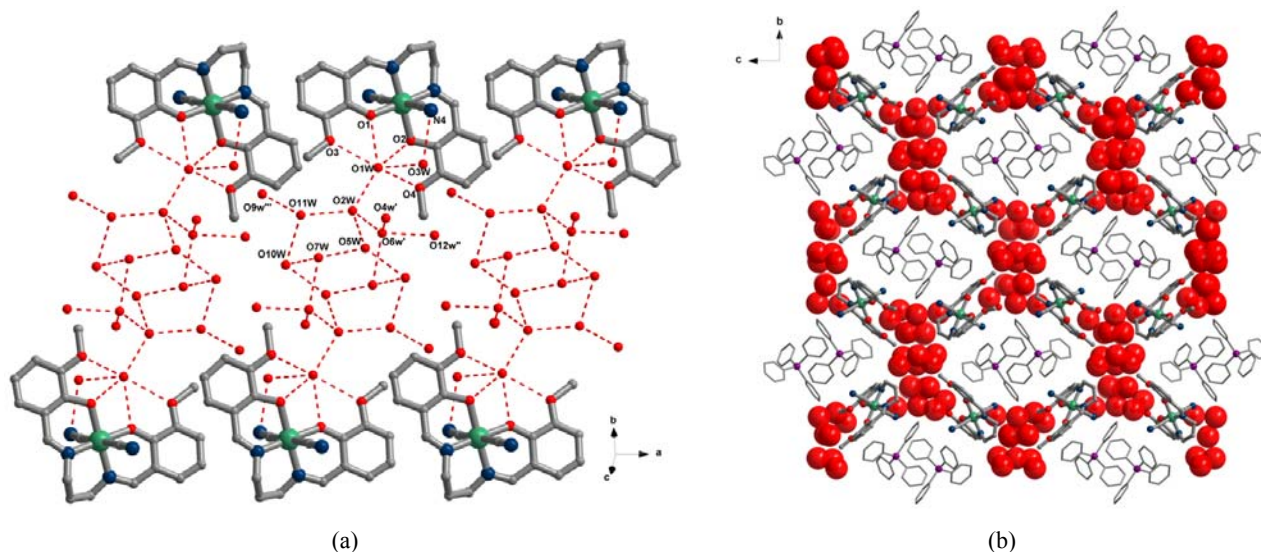


Fig. 4 – (a) Hydrogen interactions involving the crystallization water molecules in the crystals of $\text{AsPh}_4[\text{Ru}^{\text{III}}(\text{valpn})(\text{CN})_2] \cdot 11\text{H}_2\text{O}$ along the crystallographic *a* axis; (b) view of packing diagram in crystal **2** along the crystallographic *a* axis.

Spectral properties of 1–3

The IR spectra of the complexes show the characteristic bands of the Schiff base ligands, the most important being the azomethine C=N stretching that appears at 1598–1600 cm^{-1} and $\nu(\text{C}-\text{O}_{\text{phenoxido}})$ located between 1299–1315 cm^{-1} for all ruthenium(III) complexes. The $\nu(\text{C}\equiv\text{N})$ stretching vibrations are observed at 2096 and 2057 cm^{-1} for

1 – supporting two coordination modes of the cyanido group: bridging and terminal, 2090 cm^{-1} for **2**, and 2094 cm^{-1} for **3**. These values are comparable to those reported in Ru(III) dicyanides^{3e,9} Another broad and strong absorption band covering the 3500–3000 cm^{-1} region is due to an extensive network of hydrogen bonds caused by the presence of uncoordinated and lattice water molecules.

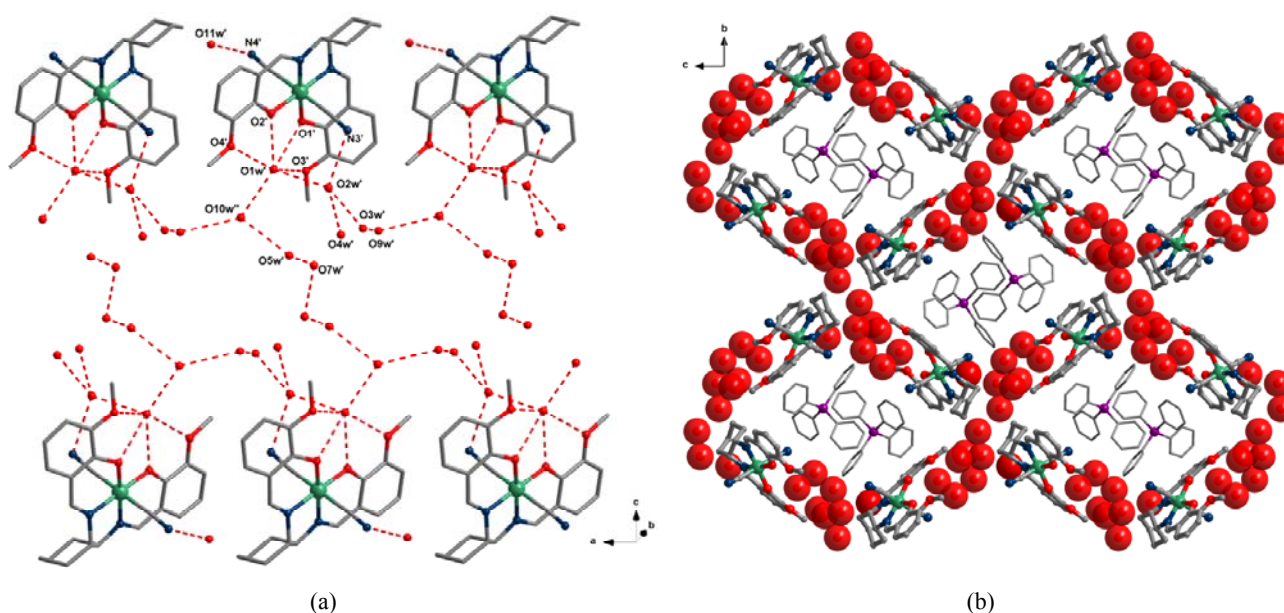


Fig. 5 – (a) Hydrogen interactions involving the crystallization water molecules in the crystals of $\text{AsPh}_4[\text{Ru}^{\text{III}}(\text{valdmcx})(\text{CN})_2] \cdot 6.5\text{H}_2\text{O}$ along the crystallographic a axis; (b) view of packing diagram in crystal **3** along the crystallographic a axis.

Table 3

Selected geometric parameters: bonds length (Å) and angles (°) in **2**

2	
bonds length (Å)	angles (°)
Ru1 - N1 = 1.986(17)	N1-Ru1-O1 = 88.8(7)
Ru1 - C23 = 1.99(2)	N1-Ru1-N2 = 89.5(7)
Ru1 - O1 = 2.000(11)	O1-Ru1-N2 = 177.9(5)
Ru1 - N2 = 2.002(17)	N1-Ru1-O2 = 178.5(5)
Ru1 - O2 = 2.041(12)	O1-Ru1-O2 = 90.4(5)
Ru1 - C24 = 2.056(17)	N2-Ru1-O2 = 91.3(6)
	N3-C24-Ru1 = 176.3(13)
	N4-C23-Ru1 = 172(2)
Hydrogen-bonds (Å)	
O1...O1w	2.795
O2...O1w	2.865
O3...O1w	2.917
O4...O1w	2.838
O1w...O3w	2.859
O1w...O2w	2.641
O3w...N4	2.847
O2w...O11w	2.726
O2w...O5w	2.741
O2w...O6w'	2.648
O6w'...O4w'	2.636
O6w'...O12w''	2.742
O5w...O7w	2.727
O7w...O10w	2.791
O10w...O11w	2.892
O11w...O9w'''	2.756
<i>symmetry code:</i> ' = 0.5+x, 0.5-y, 0.5+z; '' = 1+x, y, z; ''' = -1+x, y, z.	

Table 4

Selected geometric parameters: bonds length (Å) and angles (°) in **3**

3	
bonds length (Å)	angles (°)
Ru1 - O1 = 2.014(8)	O1 - Ru1 - O2 = 93.4(3)
Ru1 - O2 = 2.021(7)	N1-Ru1-O1 = 91.8(4)
Ru1 - N1 = 2.004(10)	N1-Ru1-O2 = 173.6(4)
Ru1 - N2 = 1.976(10)	N2-Ru1-O1 = 173.7(4)
Ru1 - C23 = 2.060(15)	N2-Ru1-O2 = 92.4(4)
Ru1 - C24 = 2.060(13)	N2-Ru1-N1 = 82.6(4)
	N4-C23-Ru1 = 174.3(11)
	N3-C24-Ru1 = 176.4(10)

Table 4 (continued)

Hydrogen-bonds (Å)			
O1'...O1w'	2.989	O2w'...O4w'	2.635
O2'...O1w'	2.854	O3w'...O9w'	2.713
O3'...O1w'	2.865	O1w'...O10w''	2.806
O4'...O1w'	3.013	O10w''...O5w'	2.904
N3'...O2w'	2.937	O5w'...O7w'	2.818
O1w'...O2w'	2.850	O11w'...N4'	2.805
O2w'...O3w'	2.816		
symmetry code: ' = x, y, -1+z; '' = 1+x, y, -1+z			

The UV-Vis spectra of all compounds contain a broad band in the range 550-1200 nm, which is due to the [Ru^{III}N₂O₂C₂] chromophore (mainly charge transfer transitions).^{11,16} The spectral profiles below 400 nm correspond to ligand transitions (π - π^* and n - π^*).^{16d}

CONCLUSIONS

In this work we reported new dicyanido ruthenium(III) complexes. Using different counteranions, Na⁺ and AsPh₄⁺, we obtained different structures: tetranuclear, [Ru(valpn)(CN)₂Na(H₂O)(μ -CN)Ru(valpn)(CN)Na(H₂O)₂] \cdot H₂O, and discrete, AsPh₄[Ru(valpn)(CN)₂] \cdot 11H₂O and AsPh₄[Ru(valdmcx)(CN)₂] \cdot 6.5H₂O species. These new compounds will be employed as metalloligands against various 3d and 4f ions. Further work is in progress in our laboratory.

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