Hetero-hexametal ruthenium-nickel complexes containing 2,2'-biimidazolate dianion. Synthesis, ESI-MS and X-ray structure characterization

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Efficient and direct synthesis of hexametallic complexes, [((pap)2Ru(biim)I]M2[A153(CIO4)2] (pap = 2-(phenylazo)pyridine; M = Ni [2a] and Cu [2b]) based on the reaction of hydrated MC12 and [((pap)2Ru(biim)I]Ag2[CIO4]2 is elaborated. Synthesis of the 2,2'-bipyridine (bpy) analogue of [2a] is also described. Electrospray mass spectra of the complexes are analyzed which fully corroborate with their formulations. X-ray structure of a representative complex [{(bpy)2Ru(biim)I]Ni2[A153(CIO4)2} [3a] is reported. The structure consists of four octahedral [{(bpy)2Ru(biim)I] units arranged around the Ni2-centre in a propeller type arrangement. The separation between the two nickel (II) ions in this complex is 2.803(7) Å. The dependence of network topology on coordinations is also reported, which ultimately gives rise to a 2D sheet structure. The two nickel complexes [2a] and [3a] are diamagnetic and display resolved 1H NMR spectra in dmso-d6. These are intensively colored and their visible range spectra are dominated by an intense transition (c. 37,000-38,000 M-1 cm-1) due to Ru dia-σ* (ligand) transition. These complexes display multiple cyclic voltammetric responses, of which the responses at anodic potentials are ascribed to oxidations of the ruthenium centres.

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One of the current challenges for synthetic inorganic chemists is the controlled synthesis of high nuclearity metal complexes because of their versatile structures and useful properties. In this respect designed synthesis of coordination complexes of polydentate ligands in which fewer than the maximum possible number of donor atoms are bonded to metal centers can play a crucial role by making the possibility of controllable building of polymetallic complexes or supramolecular aggregates. The present work stems from our interest in the mononuclear ruthenium complexes of 2,2'-biimidazolate dianion, [(N4N)2Ru(biim)]+, [N4N = 2-(phenylazo)pyridine{pap} and 2,2'-bipyridine (bpy)] which can act as excellent building units due to their ability to enter into various modes of coordination (I and II). We, however, wish to note here that trimetallic coordination mode of the bridging ligand is uncommon in the literature.

Recently we have reported4-6 two heteropolymetallic complexes having Ru2Ag2 and Ru2Cu2 cores using trimetallic coordination of the biim dianion.

During the recent years we have also been actively engaged in developing direct and general procedures for the synthesis of transition metal complexes based on silver(I) assisted metal exchange2 reactions. Using this strategy we have reported successful synthesis of some compounds of acknowledged importance from the corresponding metal chloride salts. The synthetic strategy (Eq. 1) is based on the fact that Ag+ has a very strong affinity for Cl- to form insoluble AgCl, which allows concomitant coordination of L to M.

M-Cl + Ag-L \rightarrow M-L + AgCl

Our success in this area prompted us to explore the possibility of using the tetramesmetal silver complex, [((pap)2Ru(biim)I]2Ag2[CIO4]2 as a reagent for the synthesis of heteropolymetallic systems from the corresponding metal chloride salts. Accordingly, we have investigated its reactions with the two metal chlorides viz. NiCl2,6H2O and CuCl2,6H2O, respectively. Two hexametallic complexes having Ru4Ni2 and Ru4Cu2 core have been isolated from the
above reactions and these have been characterized fully. X-ray structure of a closely related compound, ([bpy]Ru(biim))₂Ni₂(ClO₄)₄ is also reported here for comparison.

Materials and Methods

The starting complexes [([bpy]Ru(biim))][ClO₄]₂₃n
(L = pap or bpy) and [[(pap)]Ru(biim)]₂Ag₂][ClO₄]₂₃n were synthesized following reported procedures. Solvents and chemicals used for the synthesis were of analytical grade.

Caution: Perchlorate salts of metal complexes containing organic ligands are potentially explosive and should be handled with care.

A JASCO V-570 spectrophotometer was used to record electronic spectra. The IR spectrum was obtained with a Perkin-Elmer 783 spectrophotometer. A Perkin-Elmer 240C elemental analyser was used to collect microanalytical data (C, H, N). Electrochemical measurements were performed under a dry nitrogen atmosphere on a PAR model (370-4) electrochemistry system. All potentials reported herein are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution. The value for the ferrocenium-ferrocene couple under our condition was 0.40 V. Electrical conductivity was measured by using a Systronics Direct Reading Conductivity Meter 304. The mass spectrum was recorded on a Micromass LCT electrospray mass spectrometer equipped electrospray (ESI) system.

Crystallographic analysis of [(bpy)₂Ru(biim)]₂Ni₂[ClO₄]₄ [3a]

X-ray quality crystals (0.20 x 0.10 x 0.10 mm) of [3a] were obtained by slow diffusion of aetonitrile solution of the compound into toluene. The data were collected at 120(2) K in the range 2.92° < θ < 25.03° on a Bruker Nonius Kappa CCD diffractometer equipped with a rotating anode X-ray generator using MoKα radiation (λ = 0.71073 Å). A total of 47661 reflections were collected of which 19186 were unique. The structure was solved by direct methods and refined by Full-matrix least-squares procedures on F². All hydrogen atoms were placed in idealized positions and refined using a riding model. All rings were restrained to regular geometry, as were the perchlorates. C, O, Cl, N were left isotropic.

Crystal data for C₆₀H₄₆Cl₉Ni₂O₂₈Ru₄ [3a]: M = 2697.50, Triclinic, P-1, a = 16.8682(19),

b = 20.677(2), c = 21.017(3) Å, α = 61.925(7),

β = 75.545(7), γ = 66.950(7)°, V = 5932.4 Å³,

T = 120(2) K, Z = 2. μ(Mo-Kα) = 0.71073 Å. Reflections collected = 47661. Independent Refinements = 19186(Rm = 0.1509), R1 (I > 2σ(I)) = 0.1741. wR2 (all data) = 0.4978. CCDC reference number 217728.

Synthesis of [(pap)₂Ru(biim)]₂M₂[ClO₄]₆ [2] (M = Ni2a) and Cu2b)

These were synthesized following a general procedure using the tetrametallic silver complex, [(pap)₂Ru(biim)]₂Ag₂[ClO₄]₂ as a reagent. Specific details for a representative complex, [2a] are given below.

To a 20 ml methanolic solution of

[(pap)₂Ru(biim)]₂Ag₂[ClO₄]₂ (0.1 g, 0.034 mmol) an aqueous solution of Ni(ClO₄)₂·6 H2O (12.5 mg, 0.034 mmol) was added and the resulting mixture was heated to reflux on a steam bath for 1 h. The solution was then cooled and filtered through a G-4 sintered glass funnel to remove insoluble AgCl. The filtrate was then concentrated to 10 ml and the dried product was crystallized from acetonitrile-toluene solvent mixture (Yield: 75-78%). Anal.: Calcul. for C₁₀₂H₆₆N₁₄Cl₁₀Ni₂Ru₄: C 46.12, H 3.02, N 19.22%. Found: C 46.16, H 3.02, N 19.19%. Its copper analogue, [(bp)₂Ru(biim)]₂Cu₂[ClO₄]₄ was synthesized similarly (Yield: 80-82%). The physicochemical properties corresponded exactly with those of the previously reported samples.

Synthesis of [(bpy)₂Ru(biim)]₂Ni₂[ClO₄]₆ [13a]

A methanolic solution of NaOMe was added dropwise to the 30 ml methanolic solution of

[(bpy)₂Ru(H₂biim)][ClO₄]₂ (0.1 g, 0.134 mmol) to deprotonate it. To this Ni(ClO₄)₂·6 H2O (25 mg, 0.068 mmol) in 10 ml of methanol was added and the mixture was heated on a steam bath at reflux for 2 h. The resultant reddish-pink solution was then concentrated to 10 ml and an aqueous solution of NaClO₄ (ca. 1 g in 5 cm³ water) was added to precipitate the cationic complex as its perchlorate salt. The precipitate was then filtered and dried in vacuum over P₂O₅. Recrystallization of the product from acetonitrile-toluene solvent mixture yielded a
crystalline compound in 80% yield. Anal.: Calcld. for C_{19}H_{30}N_{2}ClO_{4}Ni_{2}Ru. C. 46.26; H. 2.96; N. 16.60%. Found: C. 46.22; H. 3.02; N. 16.65%.

Results and Discussion

The starting material used [{((pap)Ru(H-biim))}_{2}]^{2+}, is known to have low $pK_a$ values: 4.2 and 8.0 respectively. The conjugate base of this complex usually acts as a bidentate ligand forming di-metallic system where biim diation coordinates in its chelating fashion. Its trimetallic coordination mode is uncommon and is being explored in our laboratory. For example, the ruthenium complex reacts freely with the Tollen’s reagent ([Ag(NH_{3})_{2}]^{+}) forming a tetrametallic Ru$_4$Ag$_2$ complex, [{((pap)Ru(biim))}_{2}Ag$_2$][ClO$_4$]. [1] which has been used as the reagent for this work. The reactions of hydrated MCl$_2$nH$_2$O [M = Ni(II) and Cu(II)] with equimolar quantity of the complex reagent, [1] were carried out in boiling methanol which produced [{((pap)Ru(biim))}_{2}M$_2$][ClO$_4$]. [2] directly together with insoluble AgCl. The synthetic reaction is shown in Eq 2. Compound numbering scheme for [{((L)Ru(biim))}_{2}M$_2$][ClO$_4$]. (L = pap/bpy) complexes is shown below:

\[
2\text{MCl}_2\text{nH}_2\text{O} + 2\text{[((pap)Ru(biim))}_{2}\text{Ag}_2][\text{ClO}_4]\rightarrow 2\text{[((pap)Ru(biim))}_{2}M$_2$][\text{ClO}_4] + 4\text{AgCl} \quad \text{(2)}
\]

Ancillary ligand | Metal (M) | Comp. No. 
--- | --- | --- 
| pap | Ni | 2a 
| pap | Cu | 2b 
| bpy | Ni | 3a 

The resultant hexametallic complexes were isolated as their perchlorate salts in high yields (75-80%). The complex [2b] with the Ru$_4$Cu$_2$ core is identical in all respect to that reported recently by us. We were, however, unsuccessful in isolation of the bpy analogue of [1] from the reaction of [Ru(bpy)$_2$(biimH$_2$)]$^{2+}$ and the Tollen’s reagent. This is not unexpected since magnitudes of $pK_a$ values of the bpy compound are high for which strongly alkaline conditions are necessary for deprotonation. The fact that silver is precipitated as its oxide from highly alkaline conditions precludes the synthesis of the bpy analogue of [2a]. The complex [{((bpy)Ru(biim))}_{2}Ni$_2$][ClO$_4$]. [3a] was thus synthesized following the conventional synthetic route, from the reaction of the conjugate base [{(bpy)Ru(biim)}], generated in situ, by the addition of excess of NaOMe, with hydrated salt Ni(ClO$_4$)$_2$$\cdot$H$_2$O. The Ag(I) assisted synthetic route seems to be a general one for the Ru-pap complexes. The reactions are fast and experimentally more facile than the conventional synthesis. Since the $pK_a$’s of H-biim are high, synthesis of di- and trimetallic systems containing biim as the bridging ligand usually requires strongly alkaline conditions. In contrast, the silver assisted synthesis, reported herein, does not require addition of base. This may be advantageous for the synthesis of heteromeric systems of those metal ions, which are precipitated as hydrated oxide even from a weakly alkaline solution.

Elemental analysis of the Ru$_2$Ni$_2$ complexes match well with their formulations. These complexes are highly soluble in polar solvents like acetonitrile and their solutions behave as $1:4$ electrolytes ($\lambda_{\text{M}}$ ca. 420 $\Omega^{-1}$ cm$^2$ mol$^{-1}$).

ESI mass spectra

One of the major problems in the synthesis of polynuclear complexes is to show a clear identification of the structure of a complex synthesized. Herein we have found that the electrospray mass spectrum is a powerful and informative tool for the identification of the present hexametallic complexes. The general formula of the complexes are [{((N^N)Ru(biim))}_{2}Ni$_2$][ClO$_4$].[1] where N^N= pap/bpy. The charge state distribution ranging from +1 to +4 can be clearly observed for both complexes, which exactly corroborated with the complex formation equilibrium in acetonitrile solution. Mass spectral data are collected in Table 1, segmented spectra of a representative complex, [2a] are shown in Fig. 1. These multiply charged ions are produced from loss of negative counterions which is denoted by $[Y-nX]^n$ where Y and X represent the molecule and perchlorate ion respectively. The equilibrium can be described as follows:

\[
[Y][\text{ClO}_4]^n \leftrightarrow [Y][\text{ClO}_4][Y]^n \leftrightarrow [Y]^n
\]

The most abundant peak, called a base peak, was obtained for $[Y-4X]^+ \text{ at } m/z$ 629 amu for [2a] and 575 amu for [3a]. The fact that the charge state of +4 is the base peak in both mass spectra clearly indicate that the species $[Y-4X]^+$ exist predominantly in solution. Two additional weak peaks for [2a] were
Table 1 — Characterization data for the complexes

<table>
<thead>
<tr>
<th>Infrared (v/cm$^{-1}$) $^a$</th>
<th>Infra-red (v/cm$^{-1}$) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(C=N) 1590; v coordinated pap 1600, 1245; v (breathing vibration of bim) 765; v(ClO$_4$) 1100, 630</td>
<td>v(C=N) 1590; v coordinated bpy 1585, 1460, 1405; v (breathing vibration of bim) 765; v(ClO$_4$) 1100, 630</td>
</tr>
<tr>
<td>540(37100), 440(12000), 360(66500), 320(89900), 220(139800)</td>
<td>520(37880), 460(23940), 380(35080), 340(44320), 295(20340), 245(104500)</td>
</tr>
<tr>
<td>Cyclic voltammetry $^b$</td>
<td>Cyclic voltammetry $^b$</td>
</tr>
<tr>
<td>$E_r/N$ $^c$</td>
<td>$E_r/N$ $^c$</td>
</tr>
<tr>
<td>1.42$^a$, 0.98$^a$, -0.45$^a$, -0.84$^a$, -1.25$^a$</td>
<td>1.55$^a$, 1.05$^a$, 0.8$^a$, -1.67$^a$</td>
</tr>
<tr>
<td>ESIMS (amu)</td>
<td>629, 872, 1358 and 2809</td>
</tr>
<tr>
<td>575, 799, 1248 and 2593</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In KBr disk;
$^b$ Solvent: acetonitrile solvent;
$^c$ Shoulder;
$^d$ Solvent: acetonitrile, Supporting electrolyte: TEAP;
$^e$ Irreversible anodic response;
$^f$ Reversible cathodic response;
$^g$ Irreversible cathodic response.

Fig. 1 — ESI mass spectra of the complexes: (a) $\{[(pap)_2Ru(bim)]_1Ni_2[ClO_4]_4\}^{1+}$; (b) $\{[(pap)_2Ru(bim)]_2Ni_2[ClO_4]_4\}^{1+}$; (c) $\{[(pap)_2Ru(bim)]_3Ni_3\}^{1+}$. 

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observed at m/z 872 and 1358 amu respectively due to +3 and +2 ions, which were accompanied by a very weak signal at m/z 2809 amu for the +1 ion. The spectral nature thus indicates that the intermediate cationic complexes, formed due to partial dissociation of counteranion(s), are unstable with respect to dissociation in solution. The compound, [3a], also exhibited similar peaks at 799, 1248 and 2593 amu respectively. The experimental spectral features exactly correspond to the isotopic distribution pattern for the given formulations. Simulated spectra for the above ions are submitted as supplementary material (Fig. S1).

X-ray structure

The Ru₂Ni₂ compounds. [2a] and [3a] appear to be crystalline but after several trials only weakly diffracting X-ray quality crystals of [3a] could be obtained. The structure determination of [3a], which was derived from poor quality diffraction data, suffices to establish the identity, connectivity of the molecule and gross feature of the system. But it would not be appropriate to use these results in fine comparisons with similar entities. A view of the complex cation of [3a] is displayed in Fig. 2 and selected bond distances are collected in Table 2. The structure consists of four octahedral ruthenium centers arranged around a bi-metallic Ni₂-core. The coordination geometry around the ruthenium(II) is distorted octahedral involving the bpy ligand and a biim ligand bridging to the Ni₂ center. Both Ni(1) and Ni(2) are square planar and deviate from the root mean square plane of the four nitrogen atoms [N(1), N(11), N(30), N(31)], [N(6), N(20), N(21), N(36)] by 0.0045 and 0.0044 Å, respectively. The four biim ligands are arranged such that they bridge both Ni(1) and Ni(2) resulting in a propeller type arrangement. The tilts of the four ligands to the Ni(1)-Ni(2) axis are 25.41(77), 23.21(81), 26.37(74) and 26.54(62)°. The molecule sits approximately at 1/4 and 3/4 along the 'a' axis and is arranged in a close packed manner in the bc plane.

Although here the overall structure is predominantly controlled by the coordination preference of the transition metal and the ligand building blocks, more subtle effects such as C-H---O weak interactions have been seen to have a profound effect upon network topology (Table 3). Most interestingly, the crystal packing diagram of [3a] reveals the existence of ClO₄⁻ at the interstices which provides sites for additional hydrogen bonding interactions C-H---O (perchlorate). Thus, they act as “molecular clips” to stitch two

![Fig. 2 — Molecular structure of the complex cation.](image-url)
adjacent molecules affording an one-dimensional zig-zag architecture (Fig. 3 and Supplementary material Fig. S2). A set of intervening ClO\(_2^\text{-}\) connects two parallel zig-zag ribbons through complementary hydrogen bonds to form an expanded 2D sheet structure (Supplementary material Fig. S3). Thus the 1D ribbons are interlocked by a second set of ClO\(_2^\text{-}\) ions. The top view of the 2D network indicates the presence of parallel channels that run through it. But the large separation between two successive sheets eliminates the possibility for the existence of any type of π-interaction between the adjacent layers or any type of interaction through the ClO\(_2^\text{-}\) ion. Thus here C-H-O like secondary interaction leads to the formation of novel supramolecular networks. This type of realistic approach to crystal engineering or synthesis leads to the identification and exploitation of reliable synthons that can control the dimensionality of the molecular assembly and therefore lead to controlled crystal structure or architecture.

### Table 3 — Hydrogen bonding (C-H—O) parameters for [(11bpy)\(_2\)Ru(biim)]\(_2\)Ni\(_2\)(ClO\(_2\))\(_4\) [3a]

<table>
<thead>
<tr>
<th>D-H—A</th>
<th>&lt; H—A (Å)</th>
<th>D—A (Å)</th>
<th>D-H—A (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C72-H72—O1</td>
<td>2.319</td>
<td>3.265</td>
<td>179.47</td>
</tr>
<tr>
<td>C57-H57—O3</td>
<td>2.340</td>
<td>3.218</td>
<td>153.59</td>
</tr>
<tr>
<td>C86-H86—O5</td>
<td>2.316</td>
<td>3.183</td>
<td>150.70</td>
</tr>
<tr>
<td>C73-H73—O7</td>
<td>2.614</td>
<td>3.260</td>
<td>125.31</td>
</tr>
</tbody>
</table>

### Spectra and redox

Both the complexes are diamagnetic at room temperature and gave resolved but very complicated \(^1\text{H NMR spectrum in dmso-}d_6\) solvent due to overlap of several unique proton resonances. Spectral characterisation data of the hexametallic complexes are collected in Table I. Diamagnetism in the complexes are due to the presence of two square planar nickel(II) ions. Solution electronic spectrum of the complex [2a] is shown in Fig. 4. It may be noted here that the absorption maxima for the lowest energy electronic transition in both the monometallic building unit and the hexanuclear complexes appear almost at the same wavelength. This is not unexpected since the tris chelated \([\text{Ni}(H_{\text{biim}})\text{]}\) displayed only weak d-d transition in the visible region. Thus the Ni-biim coordination in the hexametallic complexes have only insignificant effect on the visible range spectra. To support this and in an attempt to have an insight into the nature of the orbitals that are involved in the visible range electronic transition in the present complexes an Extended Hückel Molecular Orbital (EHMO) calculation have been done using CACAO98 program. The calculations were performed on the basis of atomic positions obtained from the crystal data analysis of the compounds. The results of this calculation reveal that in [Ru(pap)_2(H_{\text{biim}})](ClO\(_2\))\(_2\) complex. HOMO has approximately 64% metal character which is contributed by Ru \(d_{x^2-y^2}\) 18\%, \(d_{x^2}\) 3\%, \(d_{xy}\) 38\%, \(d_{z^2}\) 5\%. On the other hand, LUMO has 85% ligand (pap) character (Supplementary material Fig. S4). Thus the

![Fig. 3 — A perspective view of the formation of the 1D zig-zag structure through C-H—O hydrogen bonding. All the hydrogen atoms and counteranions except those involved in hydrogen bonding have been omitted for clarity.](image-url)
The compounds show multiple electrochemical responses in the range +2.0 to −2.0 V versus SCE. There are two broad anodic potential responses: one quasi-reversible and an irreversible near 0.80 and 1.48 V, respectively. Differential pulse voltammogram indicates that each of the above responses is actually a combination of two overlapping responses. The two nearly overlapping responses near 0.80 V may be ascribed to the successive oxidation of ruthenium(II) ions. The complex, [2a], with ancillary pap ligand shows responses also in the cathodic potential (0.0 to −1.70 V), that are due to the reductions of azo ligands.

Supplementary Material

Supplementary material. Figs S1-S5, may be obtained from the authors on request.

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References


