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Organization of the Ru_2Na Moiety of a Phenazine Ligand Into a New Coordination Network Promoted by ClO_4–Aromatic-π Interactions

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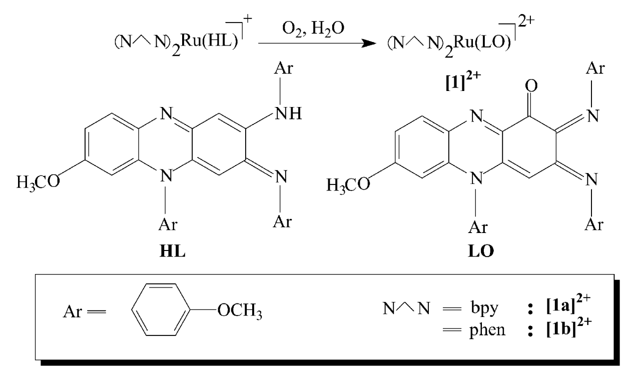
A unique supramolecular network of the trimetallic building unit $[(bpy)_2Ru(LO)Na(LO)Ru(bpy)_2](ClO_4)_5\cdot 3H_2O$ {bpy = 2,2′-bipyridine, LO = 7-methoxy-5-(4-methoxyphenyl)-2,3-bis-(4-methoxyphenylimino)-3,5-dihydro-2*H*-phenazin-1-one} is described. Crystal growth is driven by several synergistic intermolecular interactions including ClO_4–π, π–π, C–H···π and hydrogen bonding. Optical properties of the supramolecule are modified due to aggregation.

The rational design and isolation of new metal–organic[1,2] hybrid complexes through self assembly is currently an interesting and challenging area of research in modern chemistry. Organization of suitable molecular building blocks by means of noncovalent interactions into a complex arrangement is an area of research for the development of novel materials with useful functional properties. Study of the geometry of such aggregates of small molecules is significant in the context of understanding the principles that are operative in supramolecular chemistry. In this communication, we wish to introduce an example of a superstructure possessing a new heterocyclic phenazine ligand containing a Ru_2Na building unit. In this structure, the trimetallic building units aggregate into a supramolecular structure supported by several noncovalent interactions,[3] including strong interactions between perchlorate oxygen atoms[4–6] and π–aromatic rings.

Recently, we have been interested[7] in the coordination chemistry of the phenazine ligand (HL). The deprotonated ligand, upon coordination to a $[Ru\ (N^{\wedge}N)_2]^{2+}$ moiety {$N^{\wedge}N$ = 2,2′-bipyridine (bpy), 1,10-*ortho*-phenanthroline (phen)}, undergoes an oxygenation reaction spontaneously to produce ruthenium complexes of a new ligand [LO] (Scheme 1).



Scheme 1.

The above chemical transformation and the X-ray structure of the representative complex $[\mathbf{1b}](CF_3SO_3)_2$ was recently reported[7a] by us. The two apparently similar complexes $[\mathbf{1a}]^{2+}$ and $[\mathbf{1b}]^{2+}$ displayed identical solution properties. However, the spectrum of $[\mathbf{1a}]^{2+}$ in the solid state was found to be different. For example, the compound is nonemissive in solution, whereas it shows moderately strong emission in the solid state. To determine the reason behind this, we obtained the X-ray structure of the $[\mathbf{1a}](ClO_4)_2$ complex and identified an interesting supramolecular structure of the trimetallic unit, $[(bpy)_2Ru(LO)Na(LO)Ru(bpy)_2]$-$(ClO_4)_5\cdot 3H_2O$. Several synergistic intermolecular interactions are operative in the structure; chief among these is the ClO_4···π (LO) interactions. Though anion recognition is an important process in biological systems, intuitively anions are not expected to interact with the aromatic π cloud owing to repulsive effects. Incorporation of sufficient π acidity in the chemical systems, however, can lead to effective anion–π binding.[5,8–10] In this respect, metal–heterocyclic ligand systems are important because electronegative heteroatoms and positively charged metal ions together impart perturbation effects on the ligand–π cloud. Thus, the metal complexes of triazine- and tetrazine-based ligands have been studied[11] in this area.

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Fine, block-shaped, dark-coloured crystals of $[Ru_2Na(LO)_2(bpy_4](ClO_4)_5\cdot 3H_2O$ were obtained by slow diffusion of an acetonitrile solution of the compound into toluene. The X-ray crystallographic study revealed that two $[Ru(bpy)_2(LO)]^{2+}$ units are bridged across an octahedral Na atom to form a trimetallic unit. Two water molecules occupy the axial positions (Figure 1, ORTEP and crystallographic data are submitted as Figure S1 and Table S1 in the Supporting Information). The octahedral coordination environment around the central Na metal is heavily distorted. The coordinating N7 and O5 atoms of one LO ligand occupy the two equatorial positions, and the symmetry-related N7* and O5* atoms of the second LO ligand bind to the same metal centre in the *trans* equatorial positions. The two planes formed by Na1–N7–O5 and Na1–N7*–O5*, respectively, are inclined to each other at an angle of 169°, which gives the whole asymmetric unit a bowl shape.

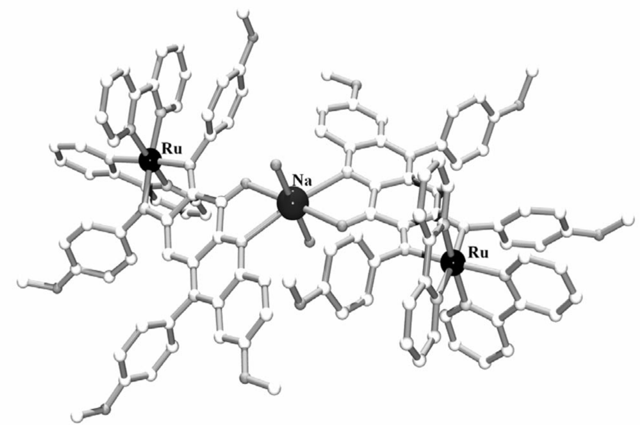

Figure 1. Molecular view of the Ru_2Na building block.

The packing diagram of the compound exhibits a 3D supramolecular network. The trimetallic units are locked by weak C–H···π interactions (C–H···π angular range 140–118° and C···π distance range 3.419–3.679 Å) together with face-to-face π–π interactions [perpendicular distance between the centroids (C_g) of the interacting bipyridine rings is 3.309 Å; dihedral angle 3.04°] (Figure 2; Supporting Information, Tables S2 and S3).

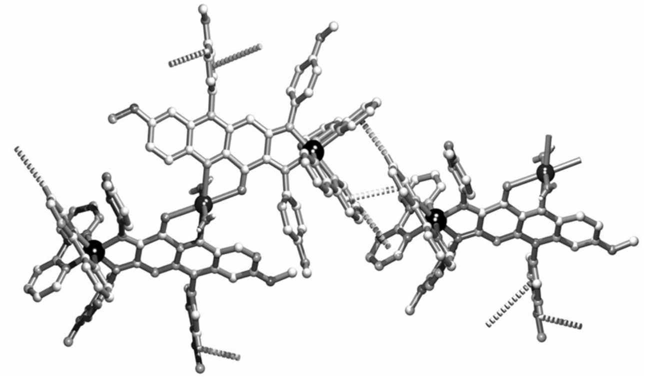

Figure 2. π–π and C–H···π interactions in trimetallic units assembled in the *ab* plane (weak interactions are shown as dotted lines).

The C–H···π and π–π interactions form a pseudosquare to facilitate strong interactions in the *ab* plane. The separations between the pyridine ring planes are notably shorter than those usually observed[10] in other pyridyl-ring-containing systems. The relative orientation of the interacting pyridine rings in the present example is nearly *anti*, which leads to superior[11] electrostatic interactions. Furthermore, the C–H···π interactions, operative in the same part of the structure, also contribute in bringing the pyridyl rings close to each other. Perpendicular to the above *ab* plane, two perchlorate anions position themselves on diametrically opposite sides of a phenazine ring, which results in Cl–O···π interactions (Table 1; Supporting Information, Table S4). Notably, two types of such interactions exist in the present structure. Whereas one phenazine plane interacts with only one oxygen atom of a (ClO_4) unit, all four oxygen atoms of the second (ClO_4) unit are recognized by the opposite side of the phenazine plane and the neighbouring symmetry-related phenazine ring plane (Figure 3) so as to develop a sandwich-type anion–π interaction. The self assembly thus grows in the *c* direction through the bridging oxyanion–π interactions. Notably, the ring centroid···O distances in the present system vary from 2.866(3) to 2.982(3) Å, and they are significantly shorter[11,12] than those reported in the oxyanion–π complexes of N-heterocyclic ligands (3.335–3.671 Å).

Moreover, the angles of the O···centroid axis to the plane of different rings are (80 ± 1)°. As a result of these interactions, the trimetallic units assemble into a 3D supramolecular network, which traps a square-shaped (Figure 4a) solvent-filled channel propagating along (001). In the channel, a helical perchlorate–water assembly was identified, and it repeats four times per unit *c* lattice distance and rotates 90° down the 4_1 screw axis to form a helical 1D chain (Figure 4b). The volume of void space encapsulated by the network is 4355.71 $Å^3$, that is, 10% of the unit-cell volume (Supporting Information, Figure S2). The helical chains are hydrogen bonded to the supramolecular framework (Table 2).

Table 1. Cl–O···π interactions in the complex.

Cl–O··· π	O···Cg[a] [Å]	O–Perp. on R(*i*)[a] [Å]	Cl–O···Cg [°]	Cl···Cg [Å]	R(*i*) plane···Cg(*i*)-O(*j*) axis[°]
Cl1–14···R(5)a[b]	2.866(3)	2.765(3)	120.95(15)	3.805(1)	79.7
Cl2–21···R(6)a	2.982(3)	2.904(2)	123.15(12)	3.953(1)	81.2
Cl2–O22···R(5)a	2.971(3)	2.841(3)	101.34(11)	3.551(1)	78.9

[a] Cg = ring centroid, R(*i*) = ring plane. [b] Symmetry code (a) = *x*, *y*, *z*; where R(5) = C35–C36–C37–C38–C39–C40; R(6) = N7–C37–C38–N8–C46–C41.

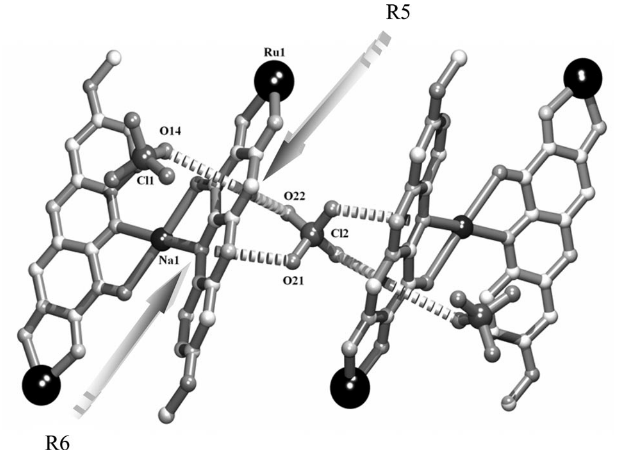

Figure 3. Sandwiched anion–π interactions between trimetallic units that assemble along the crystallographic *c* axis; coordinated water molecules to Na atom have been omitted for clarity (weak interactions are shown as dotted lines).

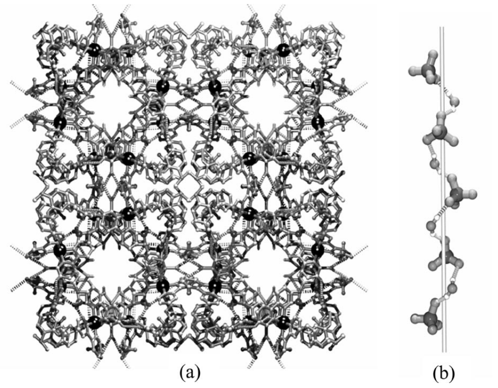

Figure 4. (a) Crystal packing in the *ab* plane with channels and (b) the helical assembly of water–perchlorate anions within the channel space in (a).

Table 2. Hydrogen-bonding interactions in the complex.

O–H···O	O–H [Å]	H···O [Å]	O···A[a] [Å]	O–H···O [°]
O1W–H1W1···O11c	0.85	2.270	3.034(4)	149.0
O2W–H1W2···O3Wc[b]	0.78	1.880	2.646(5)	167.0
O3W–H1W3···O4W	0.87	1.780	2.651(6)	172.0

[a] A = acceptor. [b] Symmetry code (c) = *x*, 1 – *y*, 3/2 – *z*.

Finally, the solid-state optical properties of the reference supramolecule are different than its solution properties. Figure 5 shows the fluorescence spectra of the reference compound both in the solid and solution phases. Whereas the compound is nonemissive in acetonitrile solution, the solid sample shows a moderately strong emission at 555 nm upon excitation at 410 nm. The luminescence property in the crystalline state is attributed to the polymeric nature of the complex. This imparts rigidity in the ligand framework and thus reduces energy[13] loss through a nonradiative relaxation pathway. However, the compound exists as a monomer in solution as evidenced by its mass spectrum (ESI), *m*/*z* = 493 amu. Moreover, its absorption wavelengths in the solid state are redshifted by nearly 10 nm relative to those in solution (Supporting Information, Figure S3).

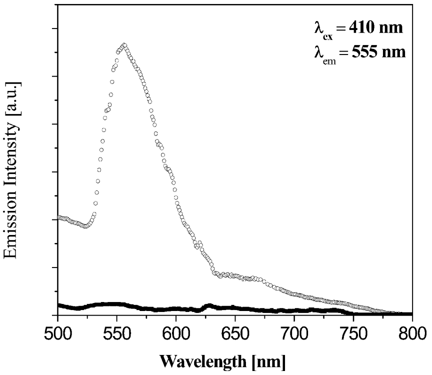

Figure 5. Emission spectra of the compound in (a) the solid state (······) and (b) in solution (−).

Conclusion

We introduced a new N-heterocyclic phenazine bridging ligand, LO, which formed a heterotrimetallic complex with a Ru_2Na core. The trimetallic building units self-organized into a supramolecular assembly, which was formed primarily through ClO_4–π (phenazine ring) interactions. It will be interesting to examine the structure and properties of related systems incorporating other metal and counteranions. Our work in this area is continuing. The magnitude of secondary interactions in our system, as evidenced by crystallographic bond parameters, appears to be strong.

Experimental Section

$[Ru_2Na(LO)_2(bpy)_4](ClO_4)_5\cdot3H_2O$: The dicationic complex, $[Ru(bpy)_2(LO)]^{2+}$, was synthesized by heating an aqueous methanolic solution of the preformed $[Ru(bpy)_2(L^1)]^+$ at reflux. It was purified on a preparative alumina TLC plate as before[7a] and isolated as its perchlorate salt. Fine, block-shaped dark-coloured crystals of $[Ru_2Na(LO)_2(bpy)_4](ClO_4)_5\cdot3H_2O$ were obtained by slow diffusion of an acetonitrile solution of the compound into toluene. Yield: 85%. $C_{108}H_{98}Cl_5N_{16}NaO_{35}Ru_2$ (2581.04): calcd. C 50.21, H 3.80, N 8.67; found C 50.20, H 3.84, N 8.60. IR (KBr): $\tilde{\nu}$ = 1670, 1605, 1550, 1504, 1460, 1445, 1278, 1250, 1115, 1090, 620 cm^{-1}.

CAUTION! *Although no problems were encountered in this work, transition-metal–perchlorate complexes with organic ligands are potentially explosive. Heating of dried samples must be avoided; handling of small quantities must proceed with great caution by using proper protection.*

Supporting Information (see footnote on the first page of this article): Crystal and structure refinement data, tables of interactions and additional figures.

Acknowledgments

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