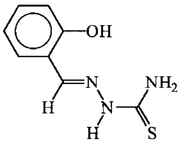
Synthesis, Structure, and Properties of a Novel Heterooctametallic Complex Containing a Cyclic Ru_4Ni_4 Core**

Indrani Pal, Falguni Basuli, Thomas C. W. Mak, and Samaresh Bhattacharya*

There is considerable current interest in the chemistry of polynuclear complexes, largely because of their fascinating properties.[1] Mononuclear transition metal complexes of multidentate ligands in which some of the donor sites are unoccupied often serve as efficient building blocks for the construction of polynuclear assemblies.[2] In our attempts to generate new heteropolynuclear systems, we planned a stepwise synthetic strategy, and salicylaldehyde thiosemicarbazone (H_3saltsc, **1**) was chosen as the multidentate ligand for this study. This ligand has five potential donor sites: three N, one O, and one S atom. However, in its reaction with ruthenium and osmium, we observed an apparently unusual coordination mode in which the H_2saltsc ligand utilizes only one N and one S donor site and forms a four-membered chelate ring (**2**).[3] Further studies showed that this type of coordination mode is in fact quite normal not only for H_2saltsc but also for benzaldehyde thiosemicarbazones.[4] The three unused donor sites in **2** and their relative dispositions in space suggested that complexes containing this moiety should be able to bind to a second metal ion as a tridentate N,N,O donor ligand, and such a possibility is explored in the present study.



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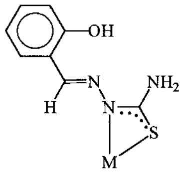

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The mononuclear mixed-ligand ruthenium(II) complex $[Ru(bpy)_2(H_2saltsc)]^+$ (bpy = 2,2′-bipyridine) was prepared first. 2,2′-Bipyridine was chosen as the coligand because it is a recognized stabilizer of bivalent ruthenium, and complexes containing the $Ru(bpy)_2$ chromophore exhibit interesting luminescence properties,[5] so that a polynuclear complex constructed from $[Ru(bpy)_2(H_2saltsc)]^+$ building blocks may also be expected to display such behavior. $[Ru(bpy)_2(H_2saltsc)]ClO_4$ was obtained from the reaction of H_3saltsc with $[Ru(bpy)_2(EtOH)_2]^{2+}$, formed in situ from $[Ru(bpy)_2Cl_2]$ and $AgNO_3$ in warm ethanol in the presence of a base [Eq. (1)]. The crystal structure of $[Ru(bpy)_2(H_2saltsc)]ClO_4$ is

$$\begin{gathered}[Ru(bpy)_2Cl_2] \xrightarrow[EtOH]{AgNO_3} [Ru(bpy)_2(EtOH)_2]^{2+} \xrightarrow[NEt_3]{H_3saltsc} \\ [Ru(bpy)_2(H_2saltsc)]^+ \xrightarrow{NaClO_4} [Ru(bpy)_2(H_2saltsc)]ClO_4\end{gathered} \quad (1)$$

displayed in Figure 1.[6] The H_2saltsc ligand is coordinated to ruthenium as a bidentate N,S donor in a four-membered chelate ring. The N_5S coordination sphere around ruthenium is distorted from ideal octahedral geometry. The phenolic oxygen atom O1, the imine nitrogen atom N5, and the amine nitrogen atom N7 of the H_2saltsc ligand remained uncoordinated, and the $Ru(H_2saltsc)$ fragment is almost planar. The $[Ru(bpy)_2(H_2saltsc)]^+$ complex cation thus appears to be a suitable building block for the construction of polynuclear complexes, and to test this hypothesis, $[Ru(bpy)_2(H_2saltsc)]ClO_4$ was treated with one equivalent of $Ni(ClO_4)_2 \cdot 6H_2O$ in warm acetonitrile/ethanol. This reaction indeed afforded a polynuclear complex, namely $[\{Ru(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4$ [Eq. (2)].

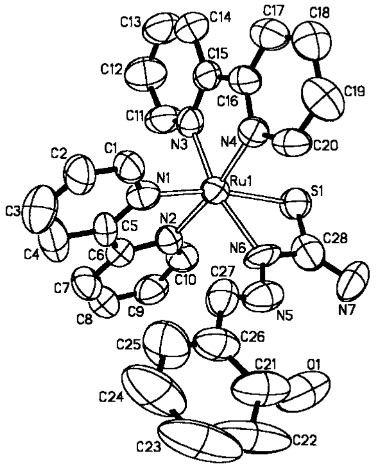

Figure 1. ORTEP plot of the structure of $[Ru(bpy)_2(H_2saltsc)]^+$. Selected bond lengths [Å] and angles [°]: Ru1-S1 2.430(5), Ru1-N6 2.068(12), S1-C28 1.70(2), C28-N7 1.33(2), C28-N6 1.41(2), N6-N5 1.41(2), N5-C27 1.24(2), C27-C26 1.47(3), C26-C21 1.40(4), C21-O1 1.28(4); N6-Ru1-S1 66.7(5), Ru1-S1-C28 82.6(7), N6-C28-S1 107.1(15), N7-C28-S1 125.6(17), C28-N6-N5 118.5(17), N6-N5-C27 119.3(19), N5-C27-C26 123(2), C27-C26-C21 121(3), O1-C21-C26 123(3).

$$4\,[Ru(bpy)_2(H_2saltsc)]ClO_4 + 4\,Ni(ClO_4)_2 \cdot 6\,H_2O \longrightarrow [\{Ru(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4 \quad (2)$$

Formation of the centrosymmetric, octametallic complex cation was confirmed by X-ray crystallography (Figure 2).[7] The coordinated H_2saltsc ligand of $[Ru(bpy)_2(H_2saltsc)]ClO_4$ has lost two further protons, one from the phenolic OH and the other from the NH_2 group, and the resulting saltsc ligand exhibits N,N,O coordination to the nickel(II) ion. The fourth coordination site of the nickel ion is occupied by the sulfur

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[*] Dr. S. Bhattacharya, I. Pal, F. Basuli
Department of Chemistry
Inorganic Chemistry Section
Jadavpur University
Kolkata 700032 (India)
Fax: (+91) 33-473-4266
E-mail: samaresh_b@hotmail.com
Prof. Dr. T. C. W. Mak
Department of Chemistry
The Chinese University of Hong Kong
Shatin, New Territories (Hong Kong)

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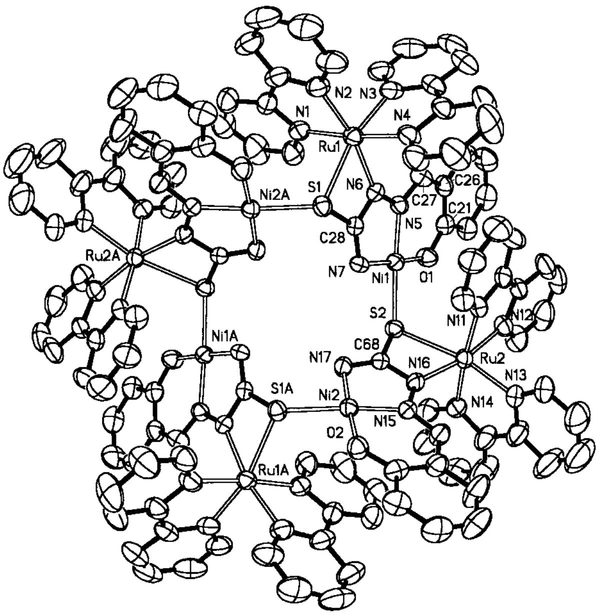

Figure 2. ORTEP plot of the structure of $[\{Ru(bpy)_2(saltsc)\}_4Ni_4]^{4+}$. Selected bond lengths [Å] and angles [°]: Ru1-S1 2.450(2), Ru1-N6 2.0936, S1-C28 1.789(8), C28-N7 1.303(9), C28-N6 1.319(10), N6-N5 1.390(9), N5-C27 1.301(10), C27-C26 1.406(12), C26-C21 1.402(12), C21-O1 1.321(10), Ni1-O1 1.831(6), Ni1-N7 1.868(7), Ni1-N5 1.853(6), Ni1-S2 2.213(2); N6-Ru1-S1 66.55(19), Ru1-S1-C28 80.0(3), N6-C28-S1 106.8(5), N7-C28-S1 132.2(6), C28-N6-N5 110.4(6), N6-N5-C27 119.5(7), N5-C27-C26 125.0(8), C27-C26-C21 122.3(8), O1-C21-C26 123.2(7), Ni1-O1-C21 128.3(5), O1-Ni1-N5 94.3(3), N5-Ni1-N7 83.6(3), Ni1-N7-C28 111.2(5), O1-Ni1-S2 83.53(18).

atom of another $Ru(bpy)_2(saltsc)Ni$ fragment, and the bridging sulfur atoms result in the formation of the cyclic octametallic $[\{Ru(bpy)_2(saltsc)\}_4Ni_4]^{4+}$ complex cation. It is noteworthy that in this complex all five available donor sites of the thiosemicarbazone ligand are involved in coordination, and this is unprecedented in the literature. The N_2OS coordination sphere around nickel is distorted from ideal square-planar geometry. While bond lengths within the NiN_2OS core are quite normal,[8] those in the Ru(saltsc) fragment of $[\{Ru(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4$ are slightly different to the corresponding bond lengths in the $Ru(H_2saltsc)$ fragment of $[Ru(bpy)_2(H_2saltsc)]ClO_4$ owing to coordination to nickel. The significant elongation of the C28−S1 bond is attributable to the bridging nature of the sulfur atom.

Both the mononuclear and octametallic complexes are diamagnetic; this indicates the presence of Ru^{II} (low-spin d^6, $S = 0$) in both of them, and of Ni^{II} (square-planar d^8, $S = 0$) in the octametallic complex. The ^1H NMR, conductance, and analytical data of the two complexes support their formulations. The cyclic voltammograms of $[Ru(bpy)_2(H_2saltsc)]ClO_4$ and $[Ru\{(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4$ recorded in $(Et_4N)ClO_4$/MeCN are shown in Figure 3. For $[Ru(bpy)_2(H_2saltsc)]ClO_4$ two oxidation waves are observed on the positive side of the saturated calomel electrode (SCE), and four successive reduction waves on the negative side. The first oxidation is reversible ($E_{1/2} = 0.62$ V, $\Delta E_p = 60$ mV, $i_{pa} = i_{pc}$) and is assigned to $Ru^{II} \rightarrow Ru^{III}$ oxidation. The second oxidation is irreversible ($E_{pa} = 1.38$ V) and is probably ligand-centered. The reduction waves ($E_{pc} = -1.50, -1.70, -1.87$, and -2.39 V) are due to reductions of the two coordinated bpy ligands. Each bpy ligand is known to undergo two one-electron reductions.[9] Hence, four successive one-electron reductions are expected for $[Ru(bpy)_2(H_2saltsc)]^+$, and all of them were observed experimentally. Cyclic voltammetric behavior of $[Ru\{(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4$ is qualitatively similar to that of $[Ru(bpy)_2(H_2saltsc)]ClO_4$. However, both oxidations are shifted to more positive values. The first oxidation is now irreversible ($E_{1/2} = 0.75$ V, $i_{pa} > i_{pc}$), and the second remained irreversible ($E_{pa} = 1.56$ V). All four reductions of the two bpy ligands in the $Ru(bpy)_2$ fragments were also observed ($E_{pc} = -1.55, -1.81, -2.06$, and -2.37 V) in this complex. The cyclic voltammetric results clearly indicate that there are no detectable metal–metal interactions in the octametallic complex.

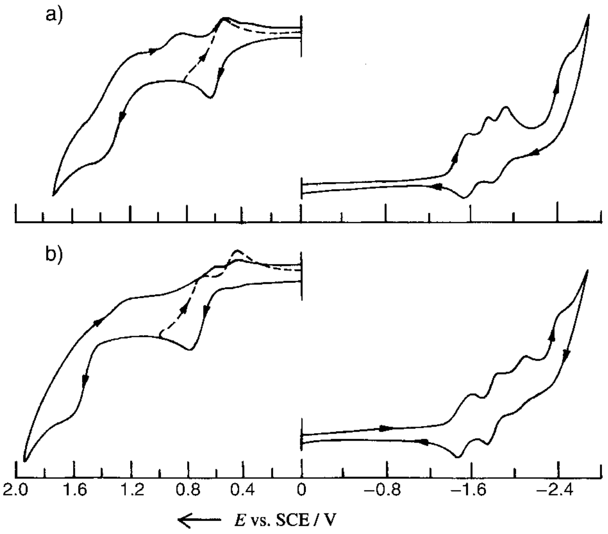

Figure 3. Cyclic voltammograms of a) $[Ru(bpy)_2(H_2saltsc)]ClO_4$ and b) $[\{Ru(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4$ in acetonitrile solution (0.1 M $(Et_4N)ClO_4$) at a scan rate of $50\ mV\,s^{-1}$.

Experimental Section

$[Ru(bpy)_2(H_2saltsc)]ClO_4$: $AgNO_3$ (65 mg, 0.38 mmol) was added to a solution of $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ (100 mg, 0.19 mmol) in ethanol (30 mL). The mixture was warmed and stirred for 30 min. The deposited AgCl was separated by filtration, and $H_3saltsc$ (40 mg, 0.21 mmol) and NEt_3 (21 mg, 0.21 mmol) were added to the filtrate. The solution was heated to reflux for 2 h. It was then concentrated to ca. 10 mL, and a saturated aqueous solution of $NaClO_4$ (0.5 mL) was added. $[Ru(bpy)_2(H_2saltsc)]ClO_4$ separated as a dark precipitate, which was collected by filtration, washed with water, and dried in vacuo over P_4O_{10}. Recrystallization from acetonitrile/benzene gave 125 mg of $[Ru(bpy)_2(H_2saltsc)]ClO_4$ (92%) as a brownish red crystalline solid. Elemental analysis (%) calcd for $C_{28}H_{24}N_7O_5SClRu$: C 47.56, H 3.40, N 13.87; found: C 47.69, H 3.49, N 13.65.

$[\{Ru(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4$: $[Ru(bpy)_2(H_2saltsc)]ClO_4$ (100 mg, 0.14 mmol) was dissolved in warm ethanol (30 mL), and NEt_3 (14 mg, 0.14 mmol) and a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (52 mg, 0.14 mmol) in acetonitrile (10 mL) were added to the stirred solution. The mixture was warmed and stirred for 5 h to afford 75 mg of $[\{Ru(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4$ (66%), which separated as a brown microcrystalline solid and was collected by filtration, washed with ethanol, and dried in air. Elemental analysis (%) calcd for $C_{28}H_{22}N_7O_5SClRuNi \cdot 2H_2O$: C 42.04, H 3.25, N 12.26; found: C 41.51, H 3.35, N 11.70.

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[6] a) X-ray structure analysis of $[Ru(bpy)_2(H_2saltsc)]ClO_4 \cdot 1/2\,C_6H_6 \cdot 1/2\,CH_2Cl_2$: $C_{31.50}H_{27}Cl_2N_7O_5RuS$, $M_r = 787.63$, monoclinic, space group $P2_1/c$, $a = 9.169(1)$, $b = 16.396(2)$, $c = 24.634(3)$ Å, $\beta = 99.075(8)^\circ$, $V = 3657.0(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.431$ Mg m^{-3}; crystal dimensions $0.50 \times 0.30 \times 0.02$ mm. Data ($2\theta_{max} = 51.1^\circ$) were collected at 293(2) K on a Rigaku RAXIS-IIC imaging plate with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.597$ mm^{-1}, transmission factors 0.755–1.148. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included but not refined. $R1 = 0.1267$ for 3296 observed reflections ($I > 2\sigma(I)$) and 418 parameters; $wR2 = 0.3507$ for 4634 unique reflections. Programs used: SHELXS-97 (structure solution) and SHELXL-97 (structure refinement). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156075 and -156076. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] X-ray structure analysis of $[\{Ru(bpy)_2(saltsc)\}_4Ni_4](ClO_4)_4 \cdot 4\,C_6H_6 \cdot 2\,MeCN$: $C_{140}H_{118}Cl_4N_{30}Ni_4O_{20}Ru_4S_4$, $M_r = 3449.80$, monoclinic, space group $P2/n$, $a = 18.386(3)$, $b = 12.268(2)$, $c = 36.398(6)$ Å, $\beta = 104.219(3)^\circ$, $V = 7959(2)$ Å^3, $Z = 2$; crystal dimensions $0.60 \times 0.47 \times 0.28$ mm, intensities ($2\theta_{max} = 56.2^\circ$) were collected at 293(2) K on a Bruker SMART 1000 CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 1.020$ mm^{-1}; absorption corrections with the SADABS program yielded relative transmission factors of 0.8075–1. $R1 = 0.0795$ for 10301 observed reflections ($I > 2\sigma(I)$) and 932 parameters; $wR2 = 0.2672$ for 19288 reflections.[6b]

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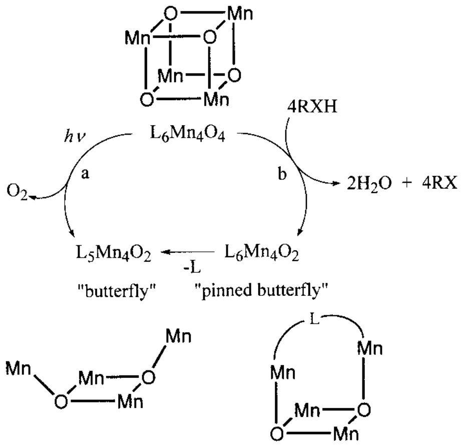
Selective Photoproduction of O_2 from the Mn_4O_4 Cubane Core: A Structural and Functional Model for the Photosynthetic Water-Oxidizing Complex[**]

Masayuki Yagi, Kurt V. Wolf, Patrick J. Baesjou, Steven L. Bernasek, and G. Charles Dismukes*

Dedicated to Dr. Peter Gabriel

Both the announcement last year by the German Federal Government to eliminate the use of nuclear power generators by 2021[1] and the recent shortage of electric power in California USA place renewed emphasis on development of socially acceptable energy sources such as solar[2] and fuel cells.[3] The latter cells rely on energy generated by the combination of H_2 (or hydrocarbons) with O_2. Both of these molecules are expected to be produced by solar-based water-splitting catalysts ($H_2O \rightarrow ½O_2 + H_2$), hence, the efforts to understand Nature's photosynthetic process of O_2 generation by water oxidation in plants,[4] and to functionally mimic the catalytic center,[5, 6] take on a pressing schedule. Key advances have occurred recently on both fronts with the first X-ray crystal structure at 3.8 Å resolution of the water-oxidizing complex (WOC) and its associated photochemical reaction center (photosystem II) from a cyanobacterium[7] and the first report of intramolecular O_2 photoproduction from the bridging oxygen atoms of a manganese–oxo cluster of cubane-type geometry, $L_6Mn_4O_4$ (**1**; L = diphenylphosphinate; $Ph_2PO_2^-$)



Scheme 1. Reactions of $L_6Mn_4O_4$ cubane complexes **1** and **1'**: a) UV photochemical reaction in the gas phase and b) reductive dehydration reaction in solution. RXH = organoammine, phenol, etc. Bridging phosphinates omitted for clarity.

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[*] Prof. Dr. G. C. Dismukes, Prof. Dr. M. Yagi, K. V. Wolf
Dr. P. J. Baesjou Prof. Dr. S. L. Bernasek
Department of Chemistry
Princeton University
Princeton, NJ, 08544-1009, NJ (USA)
Fax: (+1) 609-258-1980
E-mail: dismukes@princeton.edu

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