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Unusual binding mode of the biimidazolate bridging ligand in two novel heteropolynuclear complexes with an M_2Ag_2 [M = Ru(II) or Os(II)] core†

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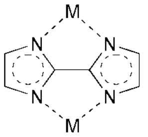
Two novel examples of heteronuclear tetrametallic M_2Ag_2 (M = Ru, Os) complexes are described which show strong argentophilic interactions.

The coordination ability of 2,2′-biimidazole is varied and interesting.[1] As a bidentate chelate it can bind as a neutral molecule H_2Biim, the monoanion $[HBiim]^-$ or the dianion $[Biim]^{2-}$. In addition, the mono- and the di-anions also can act as bridging ligands leading to the synthesis of di- and polynuclear complexes. Such polynuclear ruthenium complexes of 2,2′-biimidazolate and its derivatives[2] have received much attention in recent years. Usually the biimidazolate dianion coordinates as a bis-chelating tetradentate ligand (type I). The ligand can also behave as a tetradentate bridge attached to three metal centers (type II). However, the latter coordination mode of bridging $[Biim]^{2-}$ is very limited. As far as we are aware, the rhodium complex, $Rh_4(CO)_8(Biim)_2$ is the only structurally authenticated compound[3] which belongs to this category.



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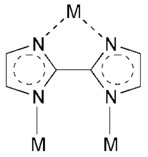

II

This communication deals with the isolation and characterisation of two novel heterometallic tetranuclear compounds with Ru_2Ag_2 and Os_2Ag_2 cores where the bridging $[Biim]^{2-}$ attaches to three metal atoms (type II).

In a recent publication[4] we have shown that in the presence of a strong π-acid co-ligand 2-(phenylazo)pyridine (pap), the complexes $[M(pap)_2(BiimH_2)]^{2+}$ (M = Ru, Os), exhibit relatively low pK_a values (pK_a: M = Ru, 4.2 and 8.0; M = Os, 3.8 and 6.5). The neutral conjugate bases, $[M(pap)_2(Biim)]$, behave as potential chelating ligands and react with appropriate metal complexes to yield di- and tri-metallic complexes.[4,5] In an attempt to prepare heteropolymetallic M–Ag complexes, methanolic solutions of $[M(pap)_2(BiimH_2)]^{2+}$ were reacted with ammoniacal silver nitrate (Tollen's reagent) in 1 : 1 molar proportion. It was anticipated that the alkalinity of the Tollen's reagent would be strong enough for the dissociation of biimidazole protons from the above ruthenium/osmium building units. The reaction mixture became blue–violet in an hour. Upon crystallisation of the crude product from acetonitrile–water (1 : 1), dark crystals of the tetrameric cationic M_2Ag_2 compounds were obtained as their perchlorate salts in high yields (*ca.* 80%) [eqn. (1), M = Ru, Os].

$$[M(pap)_2(BiimH_2)]^{2+} + 2[Ag(NH_3)_2]^{+} \longrightarrow [\{M(pap)_2(Biim)\}_2Ag_2]^{2+} \qquad (1)$$

The mass spectra of M_2Ag_2 compounds fully corroborate with their formulations. For example, the weak peak at 1514 in the ESIMS spectrum of $[\{Ru(pap)_2(Biim)\}_2Ag_2](ClO_4)_2$ is assigned to $[M_c - X]$, where M_c and X represent the molecule and ClO_4, respectively. The experimental isotopic distributions for the above molecular ions corresponded with the simulated patterns. Representative ESIMS spectra (Fig. S1–S4) are deposited as electronic supplementary information.†

Final authentication of these unusual M_2Ag_2 species, however, were made by X-ray crystallographic characterization‡ of the representative Ru_2Ag_2 compound. The complex cation consists of two approximately octahedral $[Ru(pap)_2(Biim)]$ units which are linked by two silver atoms in a head-to-tail fashion. The asymmetric unit consists of half of the molecule. The other half of the molecule is related by the crystallographic two-fold axis passing through the two silver atoms. The local geometry around each silver atom is nearly linear (N–Ag–N *ca.* 179°). The Ag–Ag distance is 2.8899(19) Å, which is similar to that observed[6] in metallic silver (2.89 Å). An ORTEP plot of $[\{Ru(pap)_2(Biim)\}_2Ag_2]^{2+}$ is shown in Fig. 1. In the solid state the cations are arranged in chains with water molecules present between alternate layers. The small Ag–Ag separation in the compound indicates the presence of argentophilic interactions between the two Ag(I) ($4d^{10}$) ions. The present M_2Ag_2 compounds clearly demonstrate the unique feature of $[M(pap)_2(Biim)]$ as building units, *viz.* their ability to encapsulate two Ag(I) such that these come in proximity giving rise to metallophilic interactions.[7] Heterometallic compounds with

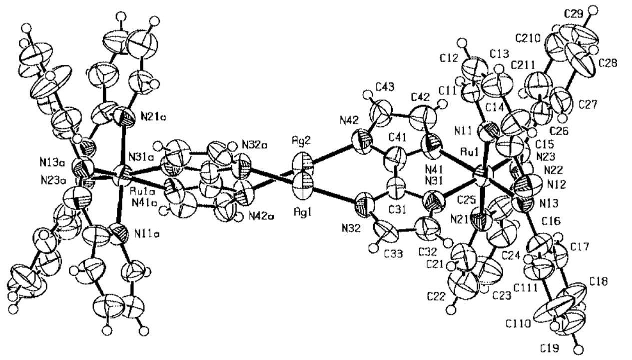

Fig. 1 An ORTEP plot and atom numbering scheme of $[\{Ru(pap)_2(Biim)\}_2Ag_2]^{2+}$ in $[\{Ru(pap)_2(Biim)\}_2Ag_2](ClO_4)_2 \cdot H_2O$. Selected bond distances (Å) and angles (°): Ag(1)–Ag(2) 2.8899(19), C(41)–N(41) 1.329(14), C(41)–N(42) 1.349(14), Ru(1)–N(41) 2.093(10), Ru(1)–N(11) 2.042(9), Ru(1)–N(13) 1.980(9), Ag(1)–N(32) 2.081(10); N(32)–Ag(1)–N(32a) 179.3(5), N(41)–C(41)–C(31) 115.0(11), N(42)–C(41)–C(31) 131.2(11).

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† Electronic supplementary information (ESI) available: details of crystal structure solution and refinement: Fig. S1–S4: representative ESIMS spectra. See http://www.rsc.org/suppdata/cc/b1/b100171j/

such small Ag–Ag separations[8] are unprecedented in the literature. Attractive interactions between formally closed shell (d^{10}) metal centres containing coinage monovalent metals have been known predominantly for gold.[9] In comparison, argentophilic compounds are rare and the M_2Ag_2 compounds, described here are the first examples of heterometallic Ru–Ag and Os–Ag compounds which show metallophilic interactions. In the recent past, however, there have been a few reports[10] on tetranuclear Ru_2Ag_2 compounds in which the Ag–Ag separations are large.

To look for the reason for this mode of binding in the Ru–Ag compound, we compared the separations between the coordinated nitrogen atoms of the biimidazolate ring in the present Ru–Ag heterometallic compound with those in the symmetrical cationic compound,[4] $[\{Ru(bpy)_2\}_2(Biim)]^{2+}$. The separation between the coordinating N(31) and N(41) in $[\{Ru(pap)_2(Biim)\}_2Ag_2]^{2+}$ is 2.622 Å and that between N(32) and N(42) is 3.222 Å. The first pair of nitrogens are attached to the $Ru(pap)_2{}^{2+}$ moiety as a chelate whereas the other two are coordinated linearly to two Ag(I). This effect is also reflected in the uneven C–N lengths and bond angles in the biimidazolate rings. For example, the bond lengths C(41)–N(41) [1.329(14) Å] and C(31)–N(31) [1.350(13) Å] are shorter than C(41)–N(42) [1.349(14) Å] and C(31)–N(32) [1.371(13) Å], respectively. Moreover, the bond angles N(41)–C(41)–C(31) [115.0(11)°] and N(31)–C(31)–C(41) [117.3(10)°] are narrower than the corresponding angles N(42)–C(41)–C(31) [131.2(11)°] and N(32)–C(31)–C(41) [130.7(11)°]. This wider separation between N(32) and N(42) undoubtedly favours monodentate type II coordination of the $[Ru(pap)_2(Biim)]$ bridging unit over chelate type I coordination. Interestingly, in the symmetrical compound $[\{Ru(bpy)_2\}_2(Biim)]^{2+}$, the reference C–N bond distances, the respective angles and the separation between the coordinated N atoms are very similar.[4]§ In the M–Ag compounds, one half of the bridging biimidazolate is coordinated to M(II) which are known to participate in $d\pi$–$p\pi$ interactions very effectively[11] and the other half is attached to two Ag(I) which is known to be a σ-acceptor. The presence of $[M(pap)_2]^{2+}$ moiety together with a preferential affinity of the Ag(I) for a linear coordination[12] are believed to be the two important factors for the trinuclear coordination of the $[Biim]^{2-}$ anion in $[M(pap)_2(Biim)]$.

Finally, we note here that the ESIMS spectral measurements together with experimental results on the reactions of $[M(pap)_2(Biim)]$ with Cu^{2+} indicate a similar binding mode of $[Biim]^{2-}$ resulting in the formation of heteropolymetallic compounds with M_4Cu_2 cores. However, X-ray structural authentication of the products, which are in progress, are essential to make further conclusions. These will be reported in due course.

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Notes and references

‡ The M_2Ag_2 compounds appear to be crystalline but, in general, were not suitable for X-ray study. Fortunately, after several trials X-ray quality crystals of $[\{Ru(pap)_2(Biim)\}_2Ag_2](ClO_4)_2\cdot H_2O$ could be formed. Crystals of this compound were found to be weak scatterers and thus the quality of the structure is not very high. However, the structural analysis of the reference Ru_2Ag_2 compound suffices to establish the identity and gross features of the system. Further details of the diffraction experiment are provided as ESI.†

Crystal data: $[\{Ru(pap)_2(Biim)\}_2Ag_2](ClO_4)_2\cdot H_2O$: $C_{56}H_{46}N_{20}O_9Cl_2Ag_2Ru_2$, $M = 1631.91$, orthorhombic, space group *Pnna* (No. 52), $a = 34.037(5)$, $b = 19.467(4)$, $c = 10.0362(12)$ Å, $Z = 4$, $D_c = 1.630$ Mg m^{-3}, crystal dimensions 0.25 × 0.15 × 0.15 mm. Intensity data were collected on an Enraf Nonius CAD4 automatic diffractometer using Cu-Kα radiation ($\lambda = 1.54184$ Å) and the ω-scan technique, and corrected for Lorentz and polarisation effects.[13] The number of reflections measured was 7708, of which 6955 were unique and were used for refinement. A semi-empirical absorption correction (ψ-scans) was made.[14] The structure was solved by Patterson and Fourier methods[15] and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.[16] All hydrogen atoms were located in their calculated positions (C–H 0.93 Å) and were refined using a riding model. The hydrogen atoms of one water molecule, O(1), were not located. The final R indices $[I > 2(\sigma)I]$ was 0.078 while $wR2$ for all data was 0.2514. CCDC reference number 156515. See http://www.rsc.org/suppdata/cc/b1/b100171j/ for crystallographic data in CIF or other electronic format.

§ Reference C–N bond distances[4] (Å): 1.322(10), 1.327(10), 1.327(10), 1.322(10); reference N–C–C bond angles (°) : 121.5(7), 121.7(7), 121.7(7), 121.5(7). Separation between the two pairs of coordinating N, N are identical: 2.811 Å.

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