d⁸...d¹⁰ Rh¹...Au¹ Interactions in Rh 2,6-Xylylisocyanide Complexes with [Au(CN)₂]⁻: Bond Analysis and Crystal Effects

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The well known [RhL₄]ₙ(anion)ₙ structures, with Rh¹...Rh¹ d⁸...d⁸ interactions, are replaced by others with Rh¹...Au¹ d⁶...d¹⁰ interactions such as [(RhL₄)[Au(CN)₃]] (L = 2,6-Xylylisocyanide) or [(RhL₄)[Au(CN)₃][RhL₄][Au₂(CN)₃]·4(CHCl₃)] when the anion is [Au(CN)₂]⁻. Orbital (Rh...Au), coulombic, and inter-unit π-π aryl stacking interactions stabilize these crystal structures.

The linear dicyanooxalato(l) anion, commercially available as K[Au(CN)₂], has tendency to form [Au(CN)₂]ₙ oligomers with Au...Au interactions in concentrated solutions. These oligomers are colourless but display interesting photochemical properties.¹ Au...Au interactions are also produced in Magnus-type gold salts such as [Au(NHC₃)][Au(CN)₂].²

Similarly, although for different reasons, isocyano rhodium(Ⅰ) complexes [Rh(CNAr)₄][A] (A = anion; Ar = aryl) show a marked tendency to cation association, producing dimeric [Rh₂(CNAr)₈]³⁺ or trimeric [Rh₃(CNAr)₁₂]⁴⁺ cations with Rh...Rh interactions, both in concentrated solutions and/or in solid-state structures. There is plenty of information about these associations,³ which give rise to dramatic colour changes, often evolving from yellow in the monomers to orange-red in the dimers and green or deep blue in the trimers. Larger associations can be induced: [Rh(CNXYlyl)₄][A] (A⁻ = Cl⁻, SO₄²⁻, F⁻; XYlyl = 2,6-Xylyl) complexes self-assemble in water into ultra-long electronically active crystalline nanowires.⁴

Since the appropriate Rh¹ (d⁸) and Au¹ (d¹⁰) complexes have this tendency to establish homometallic interactions, it looked interesting to us to examine their possible combination. Complex [Rh(CNXXYlyl)₄] BF₄⁻ (1) was synthesized from [Rh(COD)₂] BF₄ and CNXYlyl. Yellow crystals of 1 were obtained by slow diffusion of diethyl ether into a chloroform solution of the compound. The most prominent feature of the square-planar structure of 1 is that three of the aryl rings are almost coplanar with the coordination square plane, while the fourth aryl arranges orthogonal to this plane, forced by steric congestion (Figure 1, left).⁵ The non-coplanarity in 1 facilitates a structural void to host the BF₄⁻ counteranion.

The reported crystal structure of the blue complex (597 nm absorption) [Rh(CNC₃H₄F₂)₂Cl·(OH₂)] (Figure 1, right),⁶ shows coplanar C₈H₄F ary1 aryls favouring intra-unit π-π stacking. In contrast [Rh(CNC₃H₄F₂)₂][ClO₄] is yellow and its structure contains monomeric complex units. Thus, the crystallographic structure controls the formation of Rh...Rh interaction and the appearance of colour. The energy due to π-π stacking dispersion stabilizes the close packing of the Rh cations by pairs (Rh...Rh = 3.293 Å), while the Rh...Rh interaction affords only 10-20% of the total binding energy.⁷,⁸

A product with [Rh(CNXXYlyl)₄][Au(CN)₂] (2) stoichiometry was prepared according to eqn. 1.

\[\text{[Rh(CNXXYlyl)₄]BF₄}^- + \text{K[Au(CN)₂]} \rightarrow \text{[Rh(CNXXYlyl)₄][Au(CN)₂]BF₄} + \text{KBF₄} \]  

Crystallisation of 2 yielded three kinds of differently coloured crystals and structures (Figure 2), depending on the crystallisation conditions: orange crystals (2a), very predominant from CHCl₃ solutions; blue crystals (2b), from acetone solutions; and green crystals (2c) mixed with blue crystals (2b), from CH₂Cl₂ solutions. Their competitive formation suggests similar overall stability for the three.

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www.rsc.org/
Structure 2a consists of binuclear Rh⋯Au units, with d(Rh⋯Au) = 3.089 Å. Structure 2b shows an infinite arrangement of \([\text{RhL}_4\cdots\text{Au}⋯\text{RhL}_4]\) trinuclear units with d(Rh⋯Au) = 3.071 Å, reasonably aligned with \([\text{NC}⋯\text{Au}⋯\text{CN}]^–\) anions at d(Rh⋯Au) = 4.175 Å. Finally, 2c features an infinite 1D \([\cdots\text{RhL}_4⋯\text{Au}⋯\cdots]\) sequence with very similar d(Rh⋯Au) distances: 3.403 and 3.417 Å. In 2c, two Xylyl aryls are out of the coordination plane. The change from polymorph 2b to 2c could be considered a structural symmetrisation under compensated crystalline forces in the two crystal packing patterns.

The fourth compound displaying Rh⋯Au interactions is \(\{\text{L}_4\text{Rh}[\text{Au(CN)}_3]\}\{\text{RhL}_4[\text{Au(CN)}_3]\}⋯4\text{CHCl}_3\) (\(3\)), which was crystallized as a very minor product from the CHCl\(_3\) solutions prepared to obtain single crystals of 2a (Figure 3).

A most striking feature of 3 is the appearance of the \([\text{Au}_2(\text{CN})_4]^2–\) anion bridging \([\text{RhL}_4⋯\text{Au}⋯\text{RhL}_4]\) units and making an infinite \((\cdots\text{RhL}_4⋯\text{Au}⋯\text{RhL}_4⋯\text{CN}⋯\text{Au}⋯\text{RhL}_4⋯\cdots)\) zigzag chain. Compounds with anions \([\text{Au}_2(\text{CN})_4]^2–\) are common, and there is also one report of encapsulated \([\text{Au}_2(\text{CN})_4]^2–\), but \([\text{Au}_2(\text{CN})_4]^2–\) has never been reported before.\(^{10}\)

The crystal of 3 contains CHCl\(_3\) molecules, which are connected by N⋯H hydrogen bonds to the cyano groups of \([\text{Au}⋯\text{CN}]^+\) and to the terminal ones of \([\text{Au}_2(\text{CN})_4]^2–\). The X-ray study cannot individualize the C or the N atom in the bridging cyano group of \([\text{Au}_2(\text{CN})_4]^2–\) because they are submitted to non resoluble disorder (this is represented as Au⋯(C–N)⋯Au). The two different Rh⋯Au distances observed in 3, whether to \([\text{Au}⋯\text{CN}]^+\) (3.209 Å) or to \([\text{Au}_2(\text{CN})_4]^2–\) (3.377 Å), are somewhat shorter than in the other polymeric species 2c, but longer than in 2a and 2b.

\([\text{Au}_2(\text{CN})_4]^2–\) is not formed by adventitious traces of acid in the solvent removing the missing CN\(^{–}\) as HCN, since the crystals of 2a are resistant to fairly concentrated hydrochloric acid. A very plausible alternative is that the missing CN\(^{–}\) is captured by \([\text{RhL}_4]^2+\) (Equation 2). As a matter of fact, reaction of \([\text{RhL}_4]\)Cl with NaCN gives quantitatively \([\text{Rh}⋯\text{CN}L]\) (4) + L + NaCl (see ESI). Considering the scarcity of crystals of 3 formed, the small accompanying mass of \([\text{Rh}⋯\text{CN}L]\) expected to be formed according to Equation 3, would hardly be detected.

\[
3 \rightarrow \text{L}_4\text{Rh}⋯\text{Au}[\text{CN}_3] \rightarrow \text{L}_4\text{Rh}⋯\text{Au}[\text{CN}_3]⋯\text{RhL}_4⋯\text{Au}[\text{CN}_3] + \text{L}_4\text{Rh}[\text{CN}] + \text{L}
\]  

The relevant common feature of the four structures is that the Rh⋯Au interactions are absent in favour of Rh⋯Au orbital and ionic interactions. Probably the steric difficulty of the Xylyl groups to become coplanar contributes to disfavour the formation of Rh2 species and opens the opportunity to RhAu species. The structures observed differ in the roles played by the \([\text{Au}_2(\text{CN})_4]^2–\) or \([\text{Au}_2(\text{CN})_4]^2–\) moieties, which are not that of a simple anion such as BF\(_4^–\) does in 1: they participate in formation of Rh⋯Au interactions at different lengths in the range 3.0–3.5 Å. Average, the linear \([\text{Au}⋯\text{CN}]^2+\) or \([\text{Au}_2(\text{CN})_4]^2–\) groups are located with the Au centre on the Rh atom (or close to it for the anionic \([\text{Au}_2(\text{CN})_4]^2–\) in 2b), and in a plane approximately bisecting the cis–(L⋯Rh⋯L) angles. The crystal colours, and the Rh⋯Au distances for 1, 2a–c, and 3 are gathered in Table 1.

### Table 1. Rh⋯Au interaction lengths [Å]

<table>
<thead>
<tr>
<th>Compound (crystal colour)</th>
<th>L = CN–2-6-Xylyl</th>
<th>Rh⋯Au [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>{L,Rh}<a href="1">BF(_4)</a> [Yellow]</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>{L,Rh}<a href="2a">Au(CN)(_3)</a> [Orange]</td>
<td>3.089</td>
<td></td>
</tr>
<tr>
<td>{L,Rh}<a href="2b">Au(CN)(_3)</a> [Blue]</td>
<td>3.071, 4.175</td>
<td></td>
</tr>
<tr>
<td>{L,Rh}<a href="2c">Au(CN)(_3)</a> [Green]</td>
<td>3.403, 3.417</td>
<td></td>
</tr>
<tr>
<td>{L,Rh}<a href="3">Au(CN)(_3)</a> [Violet]</td>
<td>3.209, 3.377</td>
<td></td>
</tr>
</tbody>
</table>

All the Rh⋯Au distances observed are below the sum of van der Waals radii (4.89 Å), but also well above the sum of covalent radii Rh\(^+\)Au\(^+\) (2.75 Å). They range from short...
distances close to 3.1 Å, where significant orbital overlapping and some orbital Rh···Au contribution to the stability of the crystal can be presumed, to long distances of 4.175 Å, where the Rh···Au bond orbital contribution to crystal stabilization must be negligible.

At variance with [Rh2(CNAr)2]2+ dimers,7 in this collection of RhAu complexes the Au moiety does not bear aryl substituents, hence intra-unit π-π stacking interactions to support the Rh···Au interactions cannot be formed. However, we should keep in mind that we are discussing structures only existing in the tridimensional crystal, where multiple inter-units π-π stacking interactions observed in the X-ray structures (involving aryls of neighbouring Rh···Au units in the crystal and not susceptible to simple description and analysis; see Figure ESI9) on one hand, and the sum of Coulombic interactions on the other are probably the higher contributors to the structure adopted in the crystal.11,12 Although the Rh···Au short distances are powerfully catching the eye in Figures 2 and 3, the small Rh···Au orbital contribution is not determining of the structure, but determined by the structure.

Regardless of their strength, DFT MO examination of the d8···d10 Rh···Au orbital interactions is interesting, and is needed to understand the colours observed. This study can be qualitatively approached at low computational cost on a simplified model in gas-phase. The condition is that the Rh···Au distance is an experimental fact that must be respected.13 This condition was applied first to 2a, applying single-point calculations to the X-ray structure, with a fixed 3.089 Å Rh···Au distance (details in ESI). The resulting orbitals more heavily involved in the intermetallic interactions are shown in Figure 4.

The HOMO of [Rh(CNxylyl)4]2+ is a 4dz(Rh) orbital and the HOMO of [Au(CN)]− is mostly 5d2 + 6s (Au) provide in 2a the bonding σ*-HOMO-3(RhAu) and the antibonding σ+-HOMO(RhAu) combinations, which resemble those of Rh1···Rh1 or Au1···Au1 systems.3,13,14 Overall, they give rise to some net Rh1···Au1 bonding interaction, even if this stabilizing effect is modest. Since the participation of Au in the bonding HOMO-3 is larger than that of Rh (see computational details in ESI), this interaction produces some neat electron transfer from Rh to Au, as suggested by the Mulliken charges (in caption to Fig. 4). The UV-vis spectra of the solids were recorded on drop-cast films and follow the typical trends of Rh1 oligomers with Rh1···Rh1 interactions.3 Representative spectra are plotted in Figure 5. Possibly these films contain more than one structure but they are sufficient to examine the effect of Rh1···Au1 interactions. In similarity with the Rh1···Rh1 systems, bands at higher wavenumbers are seen when structures with Rh1···Au1 short distances are present, and the effect increases the higher the involvement of these interactions.

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Figure 4. σ-HOMO-3 and σ+-HOMO orbitals for the intermetallic interaction, from the HOMO orbitals of the two interacting ions. The energies are arbitrary but we assume that the HOMO of [Au(CN)]− is somewhat more stable than that of [RhL4]2−, since: a) in the starting reagents the Mulliken positive charge on Au (0.516 e) is larger than that on Rh (0.369 e); b) in complex 2a the charges are 0.477 e for Au and 0.403 e on Rh, supporting neat electron transfer from Rh to Au.

Figure 5. UV-vis absorptions in drop-cast films from solutions of 1 and 2a-c.
The calculated gap values for 2a (6.91 eV) and 2b (6.15 eV) follow the expected trend but are clearly overestimated. They should be only about 2.6 and 1.9 eV, respectively, to justify the colours observed. However, the gap between 2a and 2b is quite similar, whether from DFT calculation (0.76 eV) or from colours (about 0.7 eV) suggesting that this difference is meaningful. This indicates that forces further stabilizing the LUMO energy, relatively similar for 2a and 2b, are missing in the calculation. Obviously these forces must be the inter-unit π-π aryl stacking interactions in the crystal, which should stabilize the respective LUMOs by 4.3 eV for 2a and 4.2 eV for 2b in order to bring the σ*-HOMO → LUMO transition in the crystal into the wavelength range of orange and, respectively, blue colours. Although in an indirect way, the result that the effect on the LUMOs of these inter-unit π-π stacking contributions is energetically quite similar keeps well with the fact that these structures coexist, as mentioned above.

In conclusion, the combination of $d^8 \{\text{Rh(CNXYlyl)}\}_4^+ \text{ with } d^{10} \{\text{Au(CN)}\}_2^+ \text{ gives rise to formation of different crystals where } \text{(RhAu), (RhAuRh), or (RhAu)}_n \text{ interactions totally prevail on alternative } d^8 \cdots d^8 \text{ (RhRh) + d}^{10}\cdots d^{10} \text{ (AuAu) interactions. These compounds are not supported by intra-unit π-π aryl stacking, which suggests that the ionic contribution is taking this role to induce cation/anion Rh···Au approximation in the crystal. The orbital M-M' interactions are quite comparable, so that the effect of Au as modifier of MLCT transitions in Rh···Au complexes is qualitatively similar to the effect of a second Rh in Rh···Rh complexes. The crystals stabilization must have a large ionic contribution, but much stabilization in the crystal comes also from inter-unit π-π aryl stacking of the isocyani de aryls. This inter-unit π-π aryl stacking in the crystal is also responsible notable stabilization of the LUMO orbitals, which reduces the σ*-HOMO → LUMO energy, bringing these electron transfers into the range orange-to-blue colours.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

5) An alternative structure of the cation, with the four Xyl rings making dihedral angles with the coordination plane in the range 19.3–45.6°, was found in the yellow (BPh$_4$) salt: T. V. Ashworth, D. C. Liles, H. E. Oosthuizen and E. Singleton, Acta Cryst., 1984, C40, 1169 – 1172.
8) As an example, DFT calculations for [Rh$_3$(CNPh)$_3$]$_2$PF$_6$ in the gas-phase (reference 7) show that the contribution of Rh···Rh interactions to stabilization of the dimer is small (about 10-15% relative to the total binding energy).
13) The dispersion corrected hybrid functional ωB97X-D was used. If free geometry relaxation in gas phase is allowed, the two metal centres separate (see ESI). Thus, the restriction imposed is needed to account for the structure existing in the crystals.