**Supplementary Information**

Electrostatic bending and outer-sphere intervalence transfer in a flexible ligand-bridged ruthenium(III)-iron(II) complex

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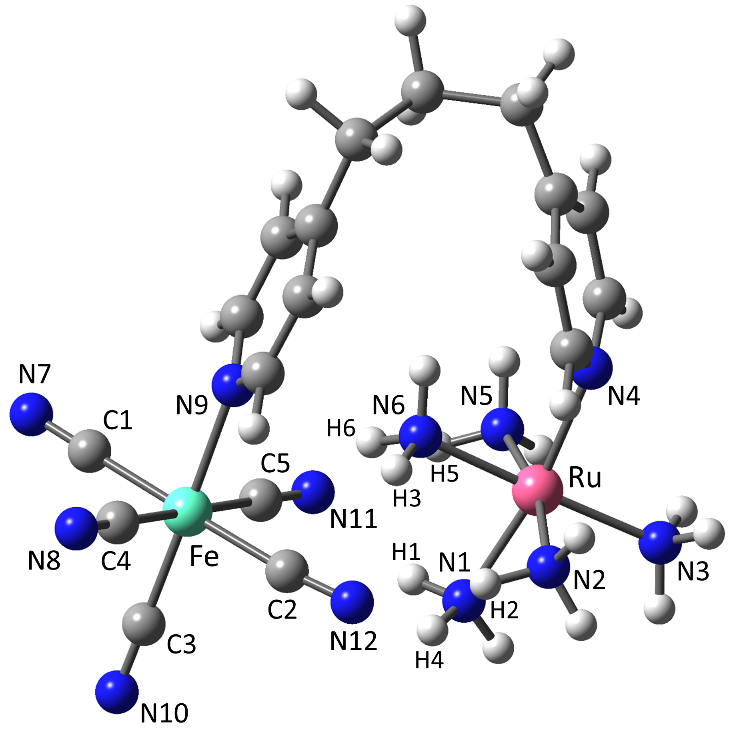


Table S1. Selected bond distances (Å) and angles (deg) for the DFT optimized molecular geometry of [RuIII(NH3)5(μ-dpypn)FeII(CN)5]. Experimental data from the crystal structures of [RuIII(NH3)5(pyridine)]Cl3 and (Et4N)3[FeII(CN)5(pyridine)] are also included for comparison.

|  |  |  |  |
| --- | --- | --- | --- |
| Bond/angle | Calculated*a* | Experimental*b* | |
| [Ru(NH3)5(py)]Cl3 | (Et4N)3[Fe(CN)5(py)] |
| Ru–N1 | 2.12 | 2.08—2.12 |  |
| Ru–N2 | 2.14 |
| Ru–N3 | 2.15 |
| Ru–N4 | 2.16 |
| Ru–N5 | 2.15 |
| Ru–N6 | 2.09 |
| Fe–C1 | 1.95 |  | 1.88—1.93 |
| Fe–C2 | 1.96 |
| Fe–C3 | 1.93 |
| Fe–C4 | 1.95 |
| Fe–C5 | 1.95 |
| Fe–N9 | 2.14 |  | 2.04 |
| C1–N7 | 1.17 |  | 1.16 (average) |
| C2–N12 | 1.18 |
| C3–N10 | 1.17 |
| C4–N8 | 1.17 |
| C5–N11 | 1.18 |
| Fe–Ru | 5.36 |  |  |
| H1···N11 | 2.07 |  |  |
| H2···N12 | 2.04 |
| H3···N12 | 2.15 |
| H4···N12 | 2.26 |
| H5···N11 | 2.04 |
| H6···N11 | 2.14 |
| N1–Ru–N2 | 83.3 | 88.8—92.0  177.9—179.8 |  |
| N1–Ru–N3 | 93.1 |
| N1–Ru–N4 | 170.2 |
| N1–Ru–N5 | 85.8 |
| N1–Ru–N6 | 88.4 |
| N2–Ru–N3 | 91.2 |
| N2–Ru–N4 | 97.5 |
| N2–Ru–N5 | 168.0 |
| N2–Ru–N6 | 89.2 |
| N3–Ru–N4 | 96.6 |
| N3–Ru–N5 | 94.3 |
| N3–Ru–N6 | 178.5 |
| N4–Ru–N5 | 92.4 |
| N4–Ru–N6 | 81.8 |
| N5–Ru–N6 | 85.6 |
| C1–Fe–C2 | 178.8 |  | 88.7—91.4  178.6—179.3 |
| C1–Fe–C3 | 90.5 |
| C1–Fe–C4 | 90.3 |
| C1–Fe–C5 | 91.2 |
| C1–Fe–N9 | 88.5 |
| C2–Fe–C3 | 90.0 |
| C2–Fe–C4 | 90.8 |
| C2–Fe–C5 | 87.6 |
| C2–Fe–N9 | 91.1 |
| C3–Fe–C4 | 90.5 |
| C3–Fe–C5 | 90.7 |
| C3–Fe–N9 | 178.9 |
| C4–Fe–C5 | 178.1 |
| C4–Fe–N9 | 89.2 |
| C5–Fe–N9 | 89.7 |

*a* From full geometry optimization without constraints at the at the unrestricted CAM-B3LYP//6-31G\*(C,H,N)/LANL2DZ(Fe,Ru)//C-PCM(water) level. *b* X-ray crystal data for the most closely related complexes that could be found in the literature: [Ru(NH3)5(pyridine)]Cl3⋅1.4H2O [Y.G.K. Shin, D.J. Szalda, B.S. Brunschwig, C. Creutz, N. Sutin, Inorg. Chem. 36 (1997) 3190] and (Et4N)3[Fe(CN)5(pyridine)]⋅6H2O [G.M. Chiarella, D.Y. Melgarejo, S.A. Koch. *J. Am. Chem. Soc.*, **128**, 1416 (2006)].

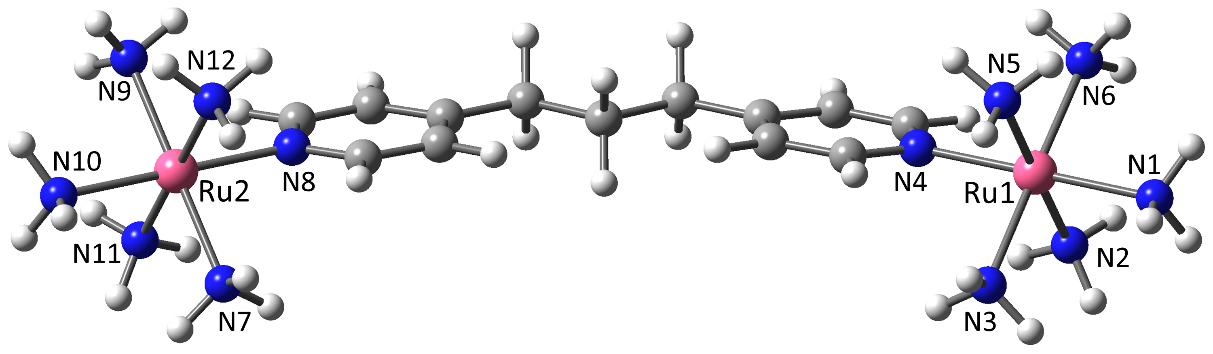


Table S2. Selected bond distances (Å) and angles (deg) for the DFT optimized molecular geometry of [RuII(NH3)5(μ-dpypn)RuIII(NH3)5]5+. Experimental data from the crystal structures of [RuIII(NH3)5(pyridine)]Cl3 and [RuII(NH3)5(pyridine)](CF3SO3)2 are included for comparison.

|  |  |  |  |
| --- | --- | --- | --- |
| Bond/angle | Calculated*a* | Experimental*b* | |
| [Ru(NH3)5(py)]Cl3 | [Ru(NH3)5(py)](CF3SO3)2 |
| Ru1–N1 | 2.15 | 2.08—2.12 |  |
| Ru1–N2 | 2.14 |
| Ru1–N3 | 2.13 |
| Ru1–N4 | 2.13 |
| Ru1–N5 | 2.14 |
| Ru1–N6 | 2.14 |
| Ru2–N7 | 2.17 |  | 2.06—2.16 |
| Ru2–N8 | 2.13 |
| Ru2–N9 | 2.17 |
| Ru2–N10 | 2.18 |
| Ru2–N11 | 2.17 |
| Ru2–N12 | 2.17 |
| Ru1–Ru2 | 13.94 |  |  |
| N1–Ru1–N2 | 90.1 | 88.8—92.0  177.9—179.8 |  |
| N1–Ru1–N3 | 89.8 |
| N1–Ru1–N4 | 179.9 |
| N1–Ru1–N5 | 90.0 |
| N1–Ru1–N6 | 90.4 |
| N2–Ru1–N3 | 86.6 |
| N2–Ru1–N4 | 90.0 |
| N2–Ru1–N5 | 180.0 |
| N2–Ru1–N6 | 93.0 |
| N3–Ru1–N4 | 90.1 |
| N3–Ru1–N5 | 93.4 |
| N3–Ru1–N6 | 179.6 |
| N4–Ru1–N5 | 89.9 |
| N4–Ru1–N6 | 89.7 |
| N5–Ru1–N6 | 87.0 |
| N7–Ru2–N8 | 90.6 |  | 89.2—91.5  178.4 |
| N7–Ru2–N9 | 179.2 |
| N7–Ru2–N10 | 89.3 |
| N7–Ru2–N11 | 87.9 |
| N7–Ru2–N12 | 92.2 |
| N8–Ru2–N9 | 90.2 |
| N8–Ru2–N10 | 179.6 |
| N8–Ru2–N11 | 90.4 |
| N8–Ru2–N12 | 90.4 |
| N9–Ru2–N10 | 89.7 |
| N9–Ru2–N11 | 92.0 |
| N9–Ru2–N12 | 87.8 |
| N10–Ru2–N11 | 90.0 |
| N10–Ru2–N12 | 89.3 |
| N11–Ru2–N12 | 179.2 |

*a* From full geometry optimization without constraints at the at the unrestricted CAM-B3LYP//6-31G\*(C,H,N)/LANL2DZ(Ru)//C-PCM(water) level. *b* X-ray crystal data for the most closely related complexes that could be found in the literature: [Ru(NH3)5(pyridine)]Cl3⋅1.4H2O and [Ru(NH3)5(pyridine)](CF3SO3)2 [Y.G.K. Shin, D.J. Szalda, B.S. Brunschwig, C. Creutz, N. Sutin. *Inorg. Chem.*, **36**, 3190 (1997)].

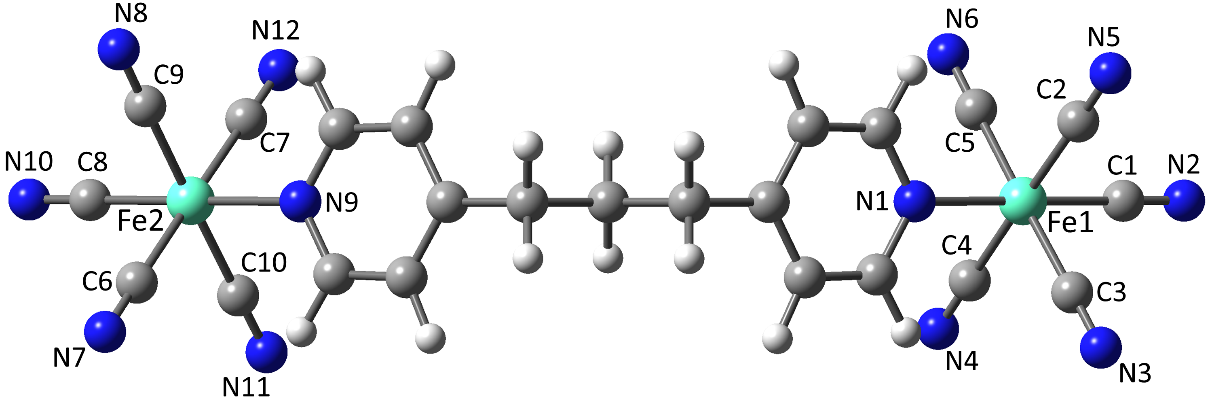


Table S3. Selected bond lengths (Å) and angles (deg) for the DFT optimized molecular geometry of [FeIII(NH3)5(μ-dpypn)FeII(CN)5]. Experimental data from the crystal structures of (Et4N)3[FeII(CN)5(pyridine)] and (*n*Bu4N)2[FeIII(CN)5(pyridine)] are included for comparison.

|  |  |  |  |
| --- | --- | --- | --- |
| Bond/angle | Calculated*a* | Experimental*b* | |
| (Et4N)3[Fe(CN)5(py)] | (*n*Bu4N)2[Fe(CN)5(py)] |
| Fe1–C1 | 1.93 | 1.88—1.93 |  |
| Fe1–C2 | 1.96 |
| Fe1–C3 | 1.96 |
| Fe1–C4 | 1.96 |
| Fe1–C5 | 1.96 |
| Fe1–N1 | 2.10 | 2.04 |  |
| C1–N2 | 1.17 | 1.16 (average) |  |
| C2–N5 | 1.17 |
| C3–N3 | 1.17 |
| C4–N4 | 1.17 |
| C5–N6 | 1.17 |
| Fe2–C6 | 1.95 |  | 1.91—1.95 |
| Fe2–C7 | 1.95 |
| Fe2–C8 | 1.92 |
| Fe2–C9 | 1.95 |
| Fe2–C10 | 1.95 |
| Fe2–N9 | 2.07 |  | 2.04 |
| C6–N7 | 1.16 |  | 1.15 (average) |
| C7–N12 | 1.16 |
| C8–N10 | 1.16 |
| C9–N8 | 1.16 |
| C10–N11 | 1.16 |
| Fe1–Fe2 | 13.07 |  |  |
| C1–Fe1–C2 | 90.6 | 88.7—91.4  178.6–179.3 |  |
| C1–Fe1–C3 | 90.5 |
| C1–Fe1–C4 | 90.5 |
| C1–Fe1–C5 | 90.3 |
| C1–Fe1–N1 | 179.9 |
| C2–Fe1–C3 | 90.2 |
| C2–Fe1–C4 | 178.9 |
| C2–Fe1–C5 | 89.9 |
| C2–Fe1–N1 | 89.4 |
| C3–Fe1–C4 | 89.8 |
| C3–Fe1–C5 | 179.2 |
| C3–Fe1–N1 | 89.7 |
| C4–Fe1–C5 | 90.1 |
| C4–Fe1–N1 | 89.5 |
| C5–Fe1–N1 | 89.5 |
| C6–Fe2–C7 | 178.5 |  | 86.4—92.1  176.8–177.8 |
| C6–Fe2–C8 | 89.3 |
| C6–Fe2–C9 | 87.2 |
| C6–Fe2–C10 | 92.8 |
| C6–Fe2–N9 | 90.7 |
| C7–Fe2–C8 | 89.3 |
| C7–Fe2–C9 | 92.8 |
| C7–Fe2–C10 | 87.2 |
| C7–Fe2–N9 | 90.7 |
| C8–Fe2–C9 | 89.4 |
| C8–Fe2–C10 | 89.3 |
| C8–Fe2–N9 | 180.0 |
| C9–Fe2–C10 | 178.7 |
| C9–Fe2–N9 | 90.6 |
| C10–Fe2–N9 | 90.7 |

*a* From full geometry optimization without constraints at the at the unrestricted CAM-B3LYP//6-31G\*(C,H,N)/LANL2DZ(Fe)//C-PCM(water) level. *b* X-ray crystal data for the most closely related complexes that could be found in the literature: (Et4N)3[Fe(CN)5(pyridine)]⋅6H2O and (*n*Bu4N)2[Fe(CN)5(pyridine)] [G.M. Chiarella, D.Y. Melgarejo, S.A. Koch. *J. Am. Chem. Soc.*, **128**, 1416 (2006)].

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Figure S1. Cyclic voltammetry of the [RuII(NH3)5(dpypn)](PF6)2 complex 0.01 mol L-1, KCl 0.1 mol L-1. Glassy carbon working electrode. Ag/AgCl reference electrode. Coiled platinum wire as counter electrode.



Figure S2. Cyclic voltammetry of the [FeII(CN)5(dpypn)]3- complex, 0.01 mol L-1, KCl 0.1 mol L-1. Glassy carbon working electrode. Ag/AgCl reference electrode. Coiled platinum wire as counter electrode.