Correspondence of $Ru^{III}Ru^{II}$ (d^5d^6) and $Ru^{IV}Ru^{III}$ (d^4d^5) Mixed Valent States in a Small Dinuclear Complex

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The recent advancement of application potential of mixed valent diruthenium complexes in information transfer, energy-relevant research, and optical devices[1] has initiated the systematic developments of newer molecular frameworks with well defined electrochemical and optical features.[2] In this context structural and electronic properties of the newly designed $\{(\mu\text{-oxa})[Ru(acac)_2]_2\}^n$ ($\mathbf{1}^n$) (n = +, 0, –; oxa^{2-} = oxamidato(2–) and $acac^-$ = 2,4-pentanedionato) has been explored via experimental and theoretical investigations. **1** exhibits an S = 1 ground state with intramolecular as well as intermolecular antiferromagnetic spin-spin coupling. The molecular structure of **1** reveals a notable asymmetry within the bridging ligand. The stepwise facile electron-transfer processes lead to the generation of paramagnetic mixed valent intermediates: $Ru^{IV}Ru^{III}$ ($\mathbf{1}^+$) and $Ru^{III}Ru^{II}$ ($\mathbf{1}^-$) of similar thermodynamic stability with K_c = comproportionation constant = $10^{5.9}$ and broad near-infrared absorption bands corresponding to intramolecular metal-to-metal (intervalence) charge transfer (IVCT) transitions. The spin density distributions establish little participation of the ligand bridge in the spin accommodation for all paramagnetic states. Although only one broad NIR band (IVCT) is observed for the $Ru^{III}Ru^{II}$ ($4d^5/4d^6$) system in $\mathbf{1}^-$, the unusual $Ru^{IV}Ru^{III}$ ($4d^4/4d^5$) form in $\mathbf{1}^+$ exhibits extended absorbance over the UV-vis-NIR range due to the presence of multiple holes.

References

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