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Solvent Dependence of Metal–Metal Coupling in a Dinuclear Pentaammineruthenium Complex Incorporating the Bridging Ligand 1,4-Dicyanamido-2,5-dimethylbenzene Dianion

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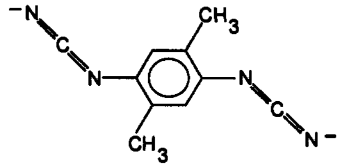
The design of molecular switching devices based on dinuclear metal systems is a major synthetic challenge.[1] The control of signal transfer depends on control of metal–metal coupling, which should be exquisitely sensitive to modest environmental stimuli and yet not result in decomposition. Chemical approaches that demonstrate the principle such as protonation of the bridging ligand[2–5] or outer-sphere coordination of crown ethers[6] involve conditions which are technically difficult to incorporate into a molecular device. We now report a dinuclear system in which the degree of metal–metal coupling is remarkably affected by the nature of its outer coordination sphere. This high sensitivity brings the reality of a molecular switching device one step closer and in addition permits a comprehensive examination of the electronic factors governing superexchange metal–metal coupling.

Solid-state temperature dependent magnetic susceptibility measurements[7] of the [3,3] complex $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)][ClO_4]_4$, where Me_2dicyd^{2-} is 1,4-dicyanamido-2,5-dimethylbenzene dianion,



have shown that the Ru(III) ions are strongly antiferromagnetically coupled with an exchange integral $-J \geq 400$ cm^{-1} (where $H = -2JS_1 \cdot S_2$). The magnitude of this interaction at a separation between Ru(III) ions of 13 Å was suggested to be the result of highly favorable superexchange between the πd-orbitals of the Ru(III) ions and the π HOMO of Me_2dicyd^{2-}. The ligand to metal charge transfer (LMCT) transition which figures prominently in the superexchange mechanism is the dominant feature in the absorption spectrum of [3,3] and is highly solvent dependent (Figure 1). The corresponding solution magnetic susceptibility measurements (Table 1) showed the [3,3] complex to be diamagnetic in nitromethane and strongly paramagnetic in aqueous or dimethyl sulfoxide solutions.[8] ^{1}H-NMR spectroscopy of the [3,3] complex in the solvents of this study (see Figure 2 and Table 2) demonstrate maintenance of complex integrity and show solvent dependent chemical shifts which reflect the paramagnetism of the system.[9]

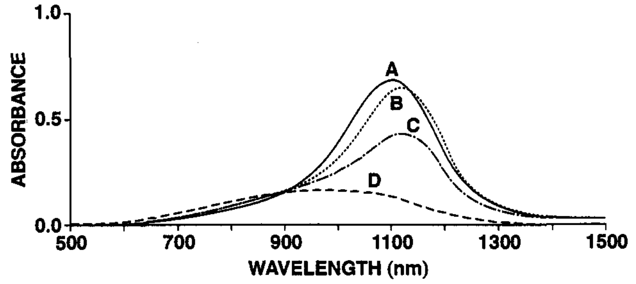


Figure 1. Lowest energy LMCT band of $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)][PF_6]_4$, 9.925×10^{-6} M in (A) nitromethane, (B) acetonitrile, (C) acetone, and (D) dimethyl sulfoxide.

Table 1. Solvent Dependent Properties of the Complex $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)][PF_6]_4$

	solvents[a]				
	nitromethane (2.7)	acetonitrile (14.1)	acetone (17.0)	DMSO (29.8)	H_2O (18.0)
LMCT f[b]	0.718	0.684	0.550	0.372	0.388
μ_{eff}/Ru^{3+} (μ_B)[c]	diamagnetic	0.725	0.751	1.16	1.27[e]
ΔE (mV)[d]	368[f]	340	325	198	85[g]

[a] The number in parentheses is the solvent donor number. See ref 10. [b] The oscillator strengths of the LMCT absorption bands in Figure 1 were obtained by fitting band profiles with Jandel PeakFit software. [c] Determined by using the Evans method (see ref 8); Bruker AMX-400 NMR spectrometer; digital resolution 0.041 Hz; complex concentration was 11 mM except in deuterated nitromethane, where the concentration was 1.8 mM. [d] ΔE is the difference between Ru(III/II) reduction couples for the dinuclear complex, 0.1 M tetrabutylammonium hexafluorophosphate, platinum working electrode. [e] Chloride complex salt. [f] Tetraphenylborate complex salt. [g] From ref 7.

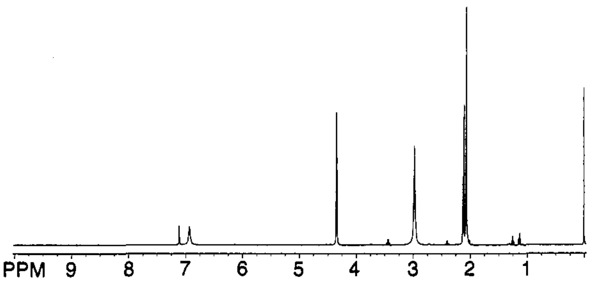


Figure 2. ^{1}H-NMR spectrum of $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)][PF_6]_4$, 1.8 mM in deuterated nitromethane. The singlets at 2.10 and 4.34 ppm and the weak multiplets are background from CD_3NO_2. The singlet at 2.06 ppm is due to acetone solvent of recrystallization. Assignments are given in Table 2.

Table 2. Solvent Dependent ^{1}H-NMR Chemical Shifts of the Complex $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)][PF_6]_4$

	proton chemical shifts[a]			
deuterated solvents	*trans*-NH_3	*cis*-NH_3	2,5-methyl	3,6-phenyl
nitromethane	6.92	2.97	2.12	7.10
acetonitrile	18.75	5.58	3.75	5.27
acetone	36.87	10.49	5.91	2.91
DMSO	167.17	43.81	17.11	–8.44
water	*b*	*b*	17.04	–6.58

[a] Bruker AMX-400 NMR spectrometer; all chemical shifts are singlets and gave the correct integration for their assignment. The values in ppm are referenced to TMS (0.00 ppm) for nonaqueous solutions and to DSS (0.00 ppm) for D_2O. The concentration of the complex was 11 mM except in nitromethane, where it was 1.8 mM. [b] Not observed, probably because of rapid deuterium exchange.

We interpret the onset of paramagnetism with a reduction in metal–metal antiferromagnetic coupling and the thermal population of the triplet excited state. This results from a decoupling of Ru(III) ions from the cyanamide groups of the bridging ligand (and hence the superexchange pathway) because of an outer-

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(1) For example, see: (a) Joachim, C.; Launay, J. P. *Chem. Phys.* **1986**, *109*, 93. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (c) Bissell, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maquire, G. E. M.; Sandanayake, K. R. A. S. *Chem. Soc. Rev.* **1992**, *12*, 187.

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sphere donor–acceptor interaction between the solvent's nonbonding electron pairs and the protons of the ammine ligands. Dimethyl sulfoxide has the largest donor number[10] in Table 1, and solutions of [3,3] in dimethyl sulfoxide show the largest paramagnetism in comparison to the other aprotic solvents. In aqueous solution, protonation of the bridging ligand is an additional complication. Outer-sphere donor–acceptor interactions have been invoked to rationalize solvent[11] and crown ether[6] induced valence trapping of mixed-valence ruthenium ammine complexes.

In studies of mononuclear pentaammineruthenium(III) phenylcyanamide complexes, we showed that LMCT oscillator strength increased with increasing overlap between cyanamide anion π-donor and Ru(III) π-acceptor orbitals.[12] Both inner-sphere[13] and outer-sphere[14] perturbations of the Ru(III)–cyanamide bond obeyed this qualitative relationship. As illustrated by the trend in oscillator strengths and paramagnetism in Table 1, the overlap in the Ru(III)–cyanamide π-bond parallels metal–metal coupling.

Cyclic voltammetry studies of complex [3,3] (see supplementary material) also show evidence of solvent dependent metal–metal coupling of the mixed-valence complex [3,2] by the increasing separation between Ru(III/II) couples with decreasing solvent donor number (Table 1). The separation between Ru(III/II) couples in nitromethane (ΔE = 368 mV) is close to that seen for strongly coupled class III complexes. For example, the Creutz–Taube ion $[\{(NH_3)_5Ru\}_2(\mu\text{-pyrazine})]^{5+}$ in nitromethane solution has ΔE = 430 mV, which is largely independent of solvent.[15] This suggests that the [3,2] complex of this study must be close to the boundary between localized and fully delocalized properties. The separation between Ru(III/II) couples in aqueous solution does not follow the trend in solvent donor number. This may be due to protonation of the cyanamide group bound to Ru(II),[16] which would significantly perturb the bridging ligand HOMO and reduce metal–metal coupling.

At this time, the near-IR absorption spectrum of the mixed valence complex [3,2] (see supplementary material) has been obtained by spectroelectrochemical methods in only one solvent, acetonitrile. Unfortunately, the intervalence (IT) band (λ_{max} = 1405 nm, ϵ = 20 300 M^{-1} cm^{-1}) overlaps the LMCT band (λ_{max} = 1211 nm, ϵ = 18 000 M^{-1} cm^{-1}) and requires deconvolution to obtain meaningful spectral information. In solvents where metal–metal coupling is smaller, the IT band intensity will drop and the IT band properties will become increasingly dependent on the appropriateness of the deconvolution model. A full analysis will be described in a later study.

We have demonstrated a remarkable sensitivity of metal–metal coupling on the nature of the outer coordination sphere. This effect arises from a preferential solvent donor–acceptor interaction with the pentaammineruthenium(III) moiety which decouples the Ru(III) ions from the cyanamide groups of the bridging ligand and hence the superexchange pathway. Dinuclear tetraammine- and pentaammineruthenium(III) complexes of substituted 1,4-dicyanamidobenzene dianion bridging ligands have been synthesized in order to perform a comprehensive evaluation of solvent-perturbed superexchange in these systems.

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Supplementary Material Available: Absorption spectra of [3,3] and [3,2] complexes in acetonitrile and table of cyclic voltammetry data (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(9) Phenyl and methyl protons are subject to pseudocontact shifts while ammine ligands experience contact shifts. The significant anisotropy of contact shifts between *cis*- and *trans*-ammines suggests preferential spin delocalization onto the trans ammine. Because the odd electron resides in a Ru(III) πd-orbital, it seems likely that spin density is delocalized via a π hyperconjugation mechanism. We hope to explore this effect in a future study.

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(12) The oscillator strength of a charge-transfer band can be given by $f \approx (1.085 \times 10^{-5})G\bar{\nu}S^2R^2$ where G is the degeneracy of the transition, $\bar{\nu}$ is the energy of the transition in cm^{-1}, R is the transition dipole moment length in angstroms, and S is the overlap integral between donor and acceptor wave functions. See refs 13 and 14 for details.

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