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^{1}H NMR, Electron Paramagnetic Resonance, and Density Functional Theory Study of Dinuclear Pentaammineruthenium Dicyanamidobenzene Complexes

Mark L. Naklicki,[†] Serge I. Gorelsky,[‡] Wolfgang Kaim,[§] Biprajit Sarkar,[§] and Robert J. Crutchley*[,†]

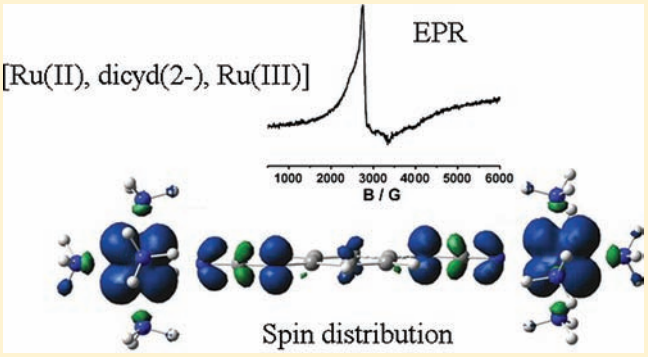
[†]Chemistry Department, Carleton University, Ottawa, Ontario K1S 5B6, Canada

[‡]Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

[§]Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

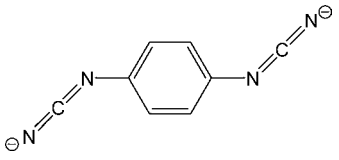
Supporting Information

ABSTRACT: Paramagnetic ^{1}H NMR and electron paramagnetic resonance (EPR) spectroscopies and density functional theory (DFT) spin density calculations were selectively performed on the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+,\ 4+,\ 5+}$ complexes, where L is 2,3,5,6-tetrachloro-, 2,5-dichloro-, 2,5-dimethyl-, and unsubstituted 1,4-dicyanamidobenzene dianion, to characterize the electronic structure of these complexes. EPR spectra of the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ complexes in *N*,*N*′-dimethylformamide at 4 K showed a ruthenium axial signal, and thus the complexes are [Ru(II),L^{2-}, Ru(III)] mixed-valence systems. DFT spin density calculations of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ where L = 1,4-dicyanamidobenzene dianion gave mostly bridging-ligand centered spin distribution for both vacuum and implicit solvent calculations, in poor agreement with EPR, but more realistic results were obtained when explicit electrostatic interactions between solute and solvent were included in modeling. For the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes, EPR spectroscopy showed no signal down to 4 K. Nevertheless, solvent-dependent ^{1}H NMR data and analysis support a [Ru(III),L^{2-}, Ru(III)] state. Hyperfine coupling constants (A_c/h) of *trans*- and *cis*-ammine and phenyl hydrogens were determined to be 17.2, 3.8, and −1.5 MHz respectively. EPR studies of the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{5+}$ complexes showed a metal-radical axial signal and based on previously published ^{1}H NMR data, a [Ru(IV),L^{2-}, Ru(III)] state is favored over a [Ru(III),L^{-}, Ru(III)] state.



INTRODUCTION

The bridging ligand 1,4-dicyanamido-benzene dianion (dicyd^{2-})



is redox active and an efficient mediator of antiferromagnetic[1] and resonance exchange[2] in dinuclear pentaammineruthenium complexes. The reason for this efficiency is the close match in energy between the Ru(III) dπ-orbitals and the π-HOMOs of the bridging ligand which permits hole-transfer superexchange. In previous studies, ammine ligands have been replaced with pyridine moieties to decrease the Ru(III)-π(dicyd^{2-}) energy gap and hence increase metal−metal coupling.[3] However, at some point, metal dπ orbitals should become lower in energy the highest occupied orbitals of the bridging ligand. In such case the redox state of the complex would change to correspond to a configuration with a reduced ruthenium ion, Ru(II), and radical anion dicyd^{-}. An example of this situation is the complex $[\{Ru(tpy)(thd)\}_2(\mu\text{-dicyd})]^+$ where tpy = 2,2′:6,2″-terpyridine and thd = 2,2,6,6-tetramethyl-3,5-heptanedione monoanion, whose electron paramagnetic resonance (EPR) spectrum showed an organic radical signal, and so the complex oxidation states are best described by [Ru(II)-dicyd^{-}-Ru(II)].[4] The redox ambivalence of the dicyd^{2-} ligand has been referred to as noninnocent behavior, and in general the proper description of the electronic structure is fundamental to an understanding of electronic properties of complexes with redox active ligands that have application to biological electronic transfer (ET) processes,[5] molecular electronics, and molecular computing.[6] EPR spectroscopy provides the easiest way by which organic radicals can be distinguished from metal radicals, but this requires an observable EPR signal which is not always possible even at liquid helium temperatures. In such instances, paramagnetic NMR spectroscopy can provide unambiguous proof of complex oxidation states.

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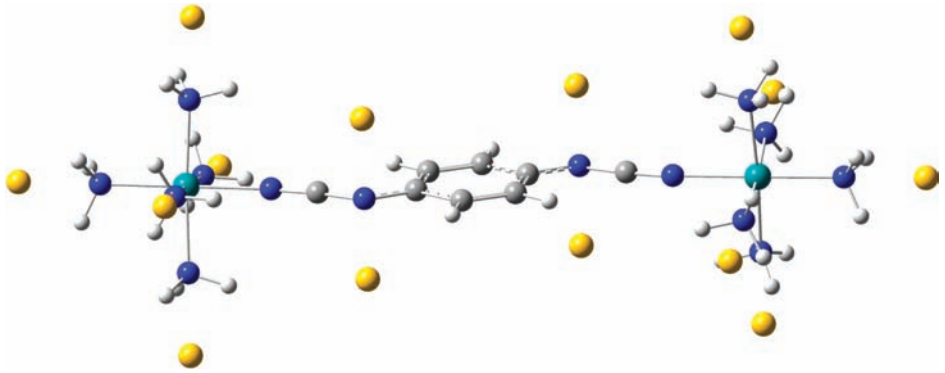

Figure 1. Structure of the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complex with the point charges (yellow spheres) shown.

In this study, EPR and ^{1}H NMR spectroscopies and Density Functional Theory (DFT) methods are selectively applied to the complex ions $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+,\,4+,\,5+}$, where L = 2,5-dimethyl (Me_2dicyd^{2-}), unsubstituted ($dicyd^{2-}$), 2,5-dichloro-(Cl_2dicyd^{2-}), and 2,3,5,6-tetrachloro-1,4-dicyanamidobenzene dianion (Cl_4dicyd^{2-}), to establish their oxidation states. In addition, the magnitude of antiferromagnetic coupling and hence paramagnetism seen in the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes can be selectively "tuned" by solvents possessing a range of electron donor properties.[1b] This in turn, permits a unique opportunity to examine experimentally the relationship between proton isotropic shifts as derived from solution ^{1}H NMR spectra and the magnitude of spin at constant temperature.

EXPERIMENTAL SECTION

Reagents. Nitromethane-d_3 (99 atom % D, 1% v/v TMS), acetonitrile-d_3 (99.5 atom % D, 1% v/v TMS), acetone-d_6 (99.9 atom % D, 1% v/v TMS and deuterium oxide (99.9 atom % D) were purchased from Aldrich. Dimethylsulfoxide-d_6 (99.9 atom % D) was purchased from Norell Inc. Tetramethylsilane (TMS, 99.9+%) and the sodium salt of 2,2-dimethyl-2-silapentane-5-sulfonate (DSS, 99%) were purchased from Aldrich.

Complexes. The ruthenium dimer complexes have been previously prepared as chloride or perchlorate salts.[1a] In this study, the complexes' counteranion was usually hexafluorophosphate, however, solubility in nitromethane was significantly improved if tetraphenyl borate was selected. In either case, the appropriate complex was metathesized from an aqueous solution of the complex halide salt by the addition of excess $NaBPh_4$ or NH_4PF_6.[7] The mononuclear complex $[(NH_3)_5Ru(2\text{-chlorophenylcyanamide})](PF_6)_2$ was prepared by the addition of NH_4PF_6 to an aqueous solution of the complex bromide salt.[7,8] $[(NH_3)_5CoCl]Cl_2$ was prepared according to the method of Schlessinger[9] and converted to a hexafluorophosphate salt by metathesis with NH_4PF_6 in slightly acidic aqueous solution.

Magnetic Studies. ^{1}H NMR spectra were obtained at 300 K by using a Bruker AMX-400 NMR spectrometer and reference to TMS (0.00 ppm) in nonaqueous solutions and DSS (0.00 ppm) in D_2O solutions. Solution magnetic susceptibility measurements were determined by the Evans method[10] and have been reported previously.[1b] Special stem coaxial insert tubes (dimensions: 203 mm × 4 mm OD) with a capillary reference volume of 60 μL (capillary dimensions: 50 mm × 2.5 mm OD) were made of precision grade Pyrex by the Wilmad Glass company. The Evans method expression[11] for mass susceptibility is

$$\chi_g = \frac{-3\Delta f}{4\pi\nu m} + \left[\chi_0 + \frac{\chi_0(d_0 - d_s)}{m}\right] \tag{1}$$

where Δf is the observed frequency shift in hertz (Hz) of the reference resonance; ν is the fixed probe frequency in Hz of the NMR spectrophotometer; χ_0 is the mass susceptibility in cm^3 g^{-1} of the solvent; m is the mass in grams of the complex per cm^3 of solution; d_0 and d_s are the densities in g cm^{-3} of the solvent and solution, respectively. The term in the square brackets is a correction to the solvent's density and hence diamagnetism because of the addition of solute. The complex concentration for all the solutions studied was 11.0 mM, except in nitromethane where the solubility of the complexes limited the concentration to 1.8 mM. At these concentrations, the solution density is approximated by $d_0 + m$,[12] and the gram susceptibility simplifies to

$$\chi_g = \frac{-3\Delta f}{4\pi\nu m} \tag{2}$$

Molar susceptibility can be calculated

$$\chi_M = M\chi_g - \chi_D \tag{3}$$

where M is the molecular weight of the complex and χ_D is the diamagnetic correction determined from Pascal's constants.

In our treatment of the magnetic moment of these dinuclear Ru(III) systems, we have ignored orbital angular momentum. Mononuclear Ru(III) complexes possess magnetic moments which range from 1.90 to 2.07 μ_B[13] suggesting only a small contribution from orbital angular momentum. In agreement, the magnetic moment of $[(NH_3)_5Ru(2\text{-chlorophenylcyanamide})][PF_6]_2$ in acetonitrile-d_3 was determined by using the Evans' method to be 2.05 μ_B. Finally, the solid state temperature dependence of magnetic susceptibility for the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes could be successfully modeled by using the spin-only Bleaney–Bowers expression.[1a]

EPR Spectroscopy. EPR spectra of the complexes were recorded in dimethylformamide (DMF) at 4 K by using a Bruker system EMX. A continuous flow cryostat ESR 900 of Oxford Instruments was used for this purpose.

Computational Details. DFT calculations have been performed using the Gaussian 09 program. In all calculations, the spin-unrestricted molecular orbital approximation was employed. Wave function stability calculations were performed to confirm that the calculated wave functions corresponded to the electronic ground state. The structures of all species were optimized using the B3LYP exchange-correlation functional[14,15] with the DZVP[16] basis set for all atoms unless indicated otherwise. To test the basis set dependence of the results, several calculations were repeated using the triple-ζ basis set (TZVP)[17] on all atoms except Ru (for which the DZVP basis set was kept). Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. Harmonic frequency calculations with the analytic evaluation of force constants were used to determine the nature of the stationary points.

Implicit solvent effects (geometry optimization and electronic structure calculations) in water were evaluated using the PCM model[18] with the UFF atomic radii. Water was selected as a solvent to probe the effects of the highly dielectric medium on the electronic structure of the complexes. Explicit solvent–solvent effects were probed by the model calculations where 14 point charges (with the charges from 0.0

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to 0.5 au in magnitude) were places near the gas-phase structure of the complex: one negative charge was placed next to each of the NH_3 ligands (2.0 Å away from the N atoms of the ammonia ligands) while four positive charges were placed next to the 1,4-dicyanamido-benzene ligand (2.0 Å away from the proximal N atoms of the NCN groups) as shown in Figure 1. Atomic spin densities were evaluated using the natural population analysis (NPA).[19]

RESULTS AND DISCUSSION

EPR Studies. The $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes showed no EPR signal in DMF solution down to 4 K. However, reduction or oxidation to form the complexes $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ and $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{5+}$, respectively, gave spectra at 4 K that were consistent with an axially symmetric Ru(III) ion in which $g_\perp > g_\parallel$ and $g_\parallel$ lies along the Ru-cyanamide bond . Similar EPR spectra were observed for the mononuclear complexes $[(NH_3)_5Ru(pcyd)]^{2+}$ where pcyd is a phenylcyanamide ligand except that $g_\parallel > g_\perp$.[20] A representative spectrum of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ in DMF at 4 K is shown in Figure 2, and the complexes' g-values have been

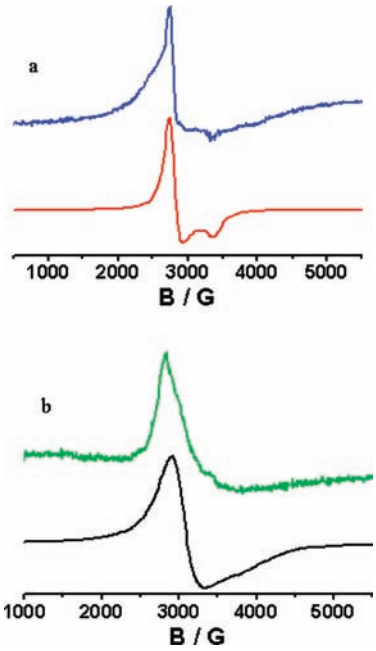

Figure 2. EPR spectra of a) $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ experiment (blue lines) and simulated (red lines) and b) $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)]^{5+}$ experiment (green lines) and simulated (black lines), in DMF at 4 K.

Table 1. EPR g-Values for the Complexes $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ and $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{5+}$ in DMF at 4 K

	$[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$		$[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{5+}$	
L	$g_\perp$	$g_\parallel$	$g_\perp$	$g_\parallel$
Me_2dicyd^{2-}	2.432	2.001	2.282	1.780
$dicyd^{2-}$	2.421	2.003	2.291	1.770
Cl_2dicyd^{2-}	2.440	2.002	2.285	1.785
Cl_4dicyd^{2-}	2.461	2.000	2.298	1.788

placed in Table 1. For the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ complexes, the observation of a metal centered radical is consistent with a [Ru(II), L^{2-}, Ru(III)] mixed-valence complex. This should be contrasted with the study[4] of $[\{Ru(tpy)(thd)\}_2(\mu\text{-dicyd})]^+$ where tpy = 2,2′:6,2″-terpyridine and thd = 2,2,6,6-tetramethyl-3,5-heptanedione monoanion, for which EPR spectroscopy showed an organic radical EPR signal that is due to the structure in which two Ru(II) ions bridged by radical $dicyd^-$. The noninnocent behavior of the $dicyd^{2-}$ bridging ligand in the latter complex is undoubtedly related to a combination of inner and outersphere electronic perturbations of both the Ru(II) ions and the $dicyd^{2-}$ ligand. For example, the $[\{Ru(tpy)(thd)\}_2(\mu\text{-dicyd})]^{2+/+}$ couple is shifted approximately 358 mV to more positive potentials compared to $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{4+/3+}$, and it can be argued that this positive shift in potential is responsible for the oxidation of $dicyd^{2-}$ over that of Ru(II). However, as we will show in this study, solvent effects can play a dramatic role in determining the formal oxidation state of the redox centers in the dinuclear pentaammine complexes.

For the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{5+}$ complexes, an axial metal-centered signal must arise from the oxidation states shown below

[Ru(III), L^{2-}, Ru(IV)] [Ru(III), L^-, Ru(III)]

A **B**

For **A**, the Ru(IV) ion would be a strong π-acceptor of the pseudohalide cyanamido group and possibly diamagnetic as has been shown for bis(amido)ruthenium(IV) complexes.[21] The EPR signal would then arise from the Ru(III) ion. For **B**, antiferromagnetic exchange between Ru(III) and radical $dicyd^-$ would leave only the remaining Ru(III) ion to respond to the EPR experiment. In the case of **B**, antiferromagnetic coupling would have to be very large otherwise spin density on the bridging ligand would cause a considerable paramagnetic shift of its proton chemical shifts. In a previous ^1H NMR study[22] of the complex $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)]^{5+}$, the observed chemical shifts of ammine and phenyl protons indicated delocalized spin between the metal ions on the NMR time scale and isotropic shifts that are approximately half those seen for mononuclear $[(NH_3)_5Ru(pcyd)]^{2+}$ complexes.[20] This by analogy, indicates <1% spin density/phenyl carbon atom of the bridging ligand. Thus, with little evidence at present for radical Me_2dicyd^- formation, **A** is favored to represent the redox centers of $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)]^{5+}$.

DFT Calculations for $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$. Spin density in $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ was calculated in vacuum and in aqueous solution (Figure 3). For the calculation in the gas phase (Figure 3a), the spin density is 90% localized on the bridging ligand. Increasing the quality of basis set from the double-ζ level (DZVP) to the triple-ζ level (TZVP) did not change this result. The spin localization on the bridging ligand in $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ in the gas-phase calculation is in disagreement with EPR data in solution (Figure 2 and Table 2). This strongly suggests that the solvent plays a significant role in stabilization of the redox state of the complex with the Ru(III) ion and the reduced dicyd ligand. We also calculated the spin distribution of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ using implicit solvent calculations at the PCM level. However, the introduction of a dielectric continuum, even hightly dielectric one (ε = 78 corresponding to water), only slightly perturbed the spin distribution in the complex (Figure 3b). The spin density of the Ru atoms increases from 3% to 10%. Much greater effect on the electronic structure of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ was obtained using an explicit electrostatic model in which 10 negative and 4 positive point charges were placed in

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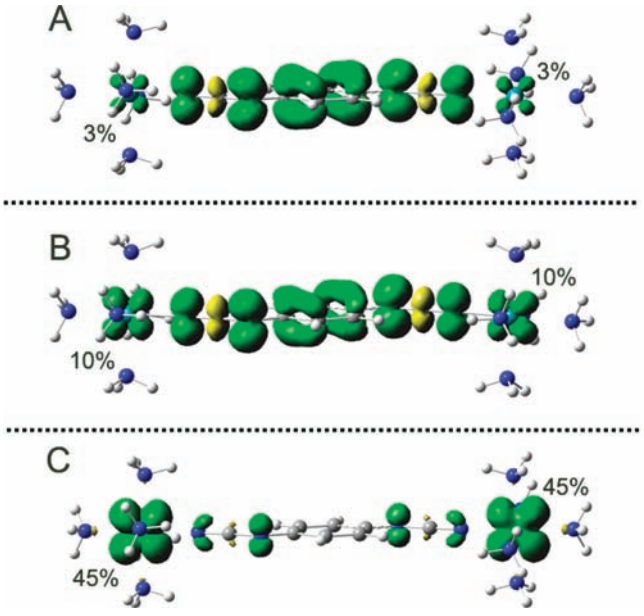

Figure 3. Spin-density distribution (isosurface values of 0.002) $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ in vacuum (a), in dielectric continuum (b), and with explicit electrostatic interactions (c). Green and yellow surfaces show regions with positive and negative spin densities, respectively. NPA-derived atomic spin densities (%) for Ru atoms are shown.

Table 2. Solvent Dependent ^{1}H NMR Chemical Shifts[a] of $[\{(NH_3)_5Ru\}_2(\mu\text{-Me}_2\text{dicyd})]^{4+}$ and the Solution Magnetic Moment/Ruthenium ion, 298 K

deuterated solvents	*trans* NH_3	*cis* NH_3	methyl	phenyl	μ_{eff}/Ru[b]
nitromethane	6.92	2.96	2.12	7.10	*c*
acetonitrile	18.75	5.58	3.75	5.27	0.73
acetone	36.87	10.49	5.91	2.91	0.75
DMSO	167.17	43.81	17.11	−8.44	1.16
water	*b*	*b*	17.04	−6.58	1.27

[a]All chemical shifts are singlets and gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) in nonaqueous solutions and DSS (0.00 ppm) in D_2O; the complex concentration was 11 mM except in nitromethane where it was 1.8 mM. [b]Evans' method calculation of the magnetic moment per ruthenium ion in B.M. [c]Diamagnetic

hydrogen bonding proximity (2.0 Å) to ammine ligands and the cyanamide groups of the bridging ligand, respectively (Figure 1), to mimic the electrostatic interactions of the complex with polar solvent molecules. The results of these calculations are shown in Figure 3c. The increasing value of point charges from ±0.1 au to ±0.5 au increases the spin density localized on the Ru atoms from 7% to 45%. Thus, in the latter case, the spin density is almost entirely localized on the ruthenium ions and the spin density is equally shared between the two metal atoms. The real solvent environment can trap the Ru(III) and Ru(II) ions and, experimentally, $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ has been shown[2] to be a Class II mixed-valence system[23] with localized charges (i.e., $[Ru(III),L^{2-}, Ru(II)]$). Of course, it is not possible to obtain such spin distribution using calculations with a symmetric $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ structure surrounded by symmetric solvent environment.

^{1}H NMR Studies. The study of the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ complexes proved difficult because of the ease of ligand substitution of the pentaammineruthenium(II) coordination sphere. This is not the case for the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes and representative spectra of the complex $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{4+}$ in nitromethane-d_3 and dimethylsulfoxide-d_6 are shown in Figure 4 and ^{1}H NMR spectral data for the complexes in various deuterated solvents are compiled

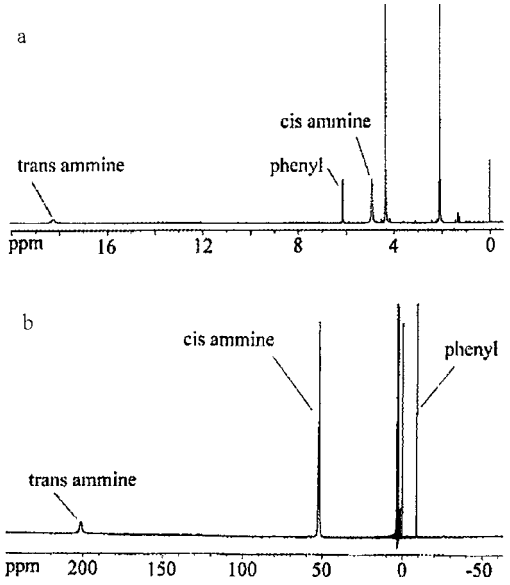

Figure 4. ^{1}H NMR spectrum of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})][PF_6]_4$ in nitromethane, 1.8 mM (a) and in dimethyl sulfoxide, 11 mM (b).

in Tables 2−5. The spectrum for a given solution consists of 2 to 4 singlet peaks whose assignments were made based on their

Table 3. Solvent Dependent ^{1}H NMR Chemical Shifts[a] of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{4+}$ and the Solution Magnetic Moment/Ruthenium ion, 298 K

deuterated solvents	*trans* NH_3	*cis* NH_3	phenyl	μ_{eff}/Ru[b]
nitromethane	18.24	4.90	6.12	0.64
acetonitrile	50.53	11.74	1.72	0.79
acetone	76.49	18.12	−1.18	0.88
DMSO	201.72	52.18	−8.99	1.25
water			−8.44	1.35

[a]All chemical shifts are singlets and gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) in nonaqueous solutions and DSS (0.00 ppm) in D_2O; the complex concentration was 11 mM except in nitromethane where it was 1.8 mM. [b]Evans' method calculation of the magnetic moment per ruthenium ion in B.M.

proton integrations. Also included in Tables 1−4 are the solution magnetic moment μ_{eff}/ruthenium values for the complexes. The experimental determination of μ_{eff} for the complexes in nitromethane-d_3 were handicapped by poor solubility, and only $[\{(NH_3)_5Ru\}_2(\mu\text{-Cl}_4\text{dicyd})]^{4+}$ showed a measurable difference between the reference resonance in the presence and absence of complex.[24] Nevertheless, the ^{1}H NMR spectra of the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes in nitromethane-d_3 showed some evidence of paramagnetic shift, particularly of the *trans*-ammine chemical shift (Table 2−5).

For these antiferromagnetically coupled dinuclear complexes, the increase in μ_{eff} reflects an increase of the triplet excited state population as the exchange constant (J) decreases. As shown in a previous study,[1b] donor−acceptor interactions between the

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Table 4. Solvent Dependent ^{1}H NMR Chemical Shifts[a] of $[\{(NH_3)_5Ru\}_2(\mu\text{-}Cl_2dicyd)]^{4+}$ and the Solution Magnetic Moment/Ruthenium ion, 298 K

deuterated solvents	*trans* NH_3	*cis* NH_3	phenyl	μ_{eff}/Ru[b]
nitromethane	85.31	20.92	−2.28	0.93
acetonitrile	140.33	34.52	−7.12	1.11
acetone	174.05	43.64	−8.74	1.19
DMSO	245.11	67.13	−8.30	1.38
water			−7.89	1.60

[a]All chemical shifts are singlets and gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) in nonaqueous solutions and DSS (0.00 ppm) in D_2O; the complex concentration was 11 mM except in nitromethane where it was 0.45 mM. [b]Evans' method calculation of the magnetic moment per ruthenium ion in B.M.

Table 5. Solvent Dependent ^{1}H NMR Chemical Shifts[a] of $[\{(NH_3)_5Ru\}_2(\mu\text{-}Cl_4dicyd)]^{4+}$ and the Solution Magnetic Moment/Ruthenium ion, 298 K

deuterated solvents	*trans* NH_3	*cis* NH_3	μ_{eff}/Ru[b]
nitromethane	182.20	37.41	1.24
acetonitrile	226.19	48.54	1.30
acetone	246.66	55.03	1.30
DMSO	275.80	72.87	1.42
water			1.86

[a]All chemical shifts are singlets and gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) in nonaqueous solutions and DSS (0.00 ppm) in D_2O; the complex concentration was 11 mM except in nitromethane where it was 0.9 mM. [b]Evans' method calculation of the magnetic moment per ruthenium ion in B.M.

solvent and the ammine ligands decreases Ru(III)-cyanamide resonance exchange and decouples the Ru(III) ions from the bridging ligand. Because the bridging ligand provides the superexchange pathway for antiferromagnetic exchange, the magnetic moment increases with increasing electron-donor properties of the solvent.

In Figure 4b, *cis* and *trans* ammine chemical shifts appear at 52.18 and 201.72 ppm, respectively. This anisotropy in chemical shifts has been noted before in mononuclear pentaammine Ru(III) phenylcyanamide[20,22] and aquo[25] complexes and has been ascribed to a hyperconjugation mechanism which favors the delocalization of spin density from Ru(III) onto the ammine ligand *trans* to the cyanamide group. The data in Tables 2 to 5 show upfield and downfield chemical shifts out of the "normal" diamagnetic region of ^{1}H NMR spectroscopy, and this occurs because of the coupling of magnetic nuclei with an unpaired electron which gives rise to a chemical shift contribution whose magnitude depends upon the amount of spin density, the extent of coupling, and the molecule's orientation with respect to the external magnetic field. In solution, rapid molecular motion averages the shift anisotropy, yielding the isotropic shift which can be derived experimentally by taking the difference in shift of a given atom in a paramagnetic compound (observed) and that of the same atom in an analogous diamagnetic compound as shown in eq 4

$$\delta_{iso} = \delta_{obs} - \delta_{dia} \quad (4)$$

In the following analysis, the isotropic shift of the bridging ligand protons was calculated to be the difference between an observed shift and that of the appropriate resonance of the protonated free ligand in DMSO-d_6.[7,26] For the ammine protons, the isotropic chemical shifts were calculated relative to $[Co(NH_3)_5Cl]^{2+}$ (δ_{trans} =3.12 and δ_{cis} = 3.75 pm).[27]

Isotropic chemical shifts arise from two main contributions: contact and dipolar shifts

$$\delta_{iso} = \delta_{con} - \delta_{dip} \quad (5)$$

A dipolar shift results from through-space dipolar coupling and is commonly expressed in terms of the anisotropy in g values for an axially symmetric system, assuming a point dipole model,[28]

$$\delta_{dip} = \left[\frac{\mu_B^2 S(S+1)}{9kT}\right]\left[\frac{(1-3\cos^2\theta)(g_{\parallel}^2 - g_{\perp}^2)}{r^3}\right] \quad (6)$$

where μ_B is the Bohr magneton of the electron, S is the total spin, θ is the angle between the principal symmetry axis of the complex and the vector between the metal ion center and the nucleus whose NMR is being observed, and r is the distance between metal ion and nucleus. For this study, dipolar coupling occurs from each ruthenium ion with spin derived from eq 7,

$$\mu_{eff} = g_{av}\sqrt{S(S+1)} \quad (7)$$

where μ_{eff} is the effective magnetic moment per ruthenium ion and g_{av} is the average g-factor. For a given proton, the dipolar coupling from each ruthenium can be determined by using eqs 6 and 7, provided estimates of the g-values and geometric values are available. Unfortunately, the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes proved to be EPR silent but assuming that the anisotropy in g-values is due to a pentaammine ruthenium(III) cyanamido coordination sphere, it is appropriate to average $g_{\perp}$ and $g_{\parallel}$ values respectively of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ complexes (Table 1) to yield the estimates: $g_{\parallel}$ = 2.00, $g_{\perp}$ =2.40, and g_{av} = 2.30. Computer modeling was used to provide estimates of the appropriate distances and angles in close agreement with crystal structures of similar complexes.[2,3a,b] Substitution of these values together with eqs 6 and 7 yielded the dipolar shifts δ_{dip} found in Tables 6–8 as well as the contact shifts δ_{con} derived from eq 5. Comparing the magnitude of δ_{dip} to δ_{con}, it is clear that for

Table 6. Isotropic,[a] Dipolar, and Contact Shifts of *trans*-Ammine Hydrogens of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Deuterated Solvents

	L = $dicyd^{2-}$			L = Me_2dicyd^{2-}			L = Cl_2dicyd^{2-}			L = Cl_4dicyd^{2-}		
solvents	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}	δ_{dip}	δ_{con}
NO_2CD_3	15.12	−3.2	18.3	3.8	*b*	*b*	82.19	−6.7	88.9	179.08	−11.9	191.0
CD_3CN	47.41	−4.8	52.2	15.63	−4.1	19.7	137.21	−9.4	146.6	223.07	−13.0	236.1
Aacetone-d_6	73.37	−6.0	79.4	33.87	−4.4	38.3	170.93	−10.9	181.8	243.54	−13.1	256.6
DMSO-d_6	198.6	−12.1	210.7	164.0	−10.3	174.3	241.99	−14.7	256.7	276.68	−15.7	292.4

[a]$\delta_{iso} = \delta_{obs} - 3.12$ ppm. [b]Solution magnetic moment was too small to be measured.

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Table 7. Isotropic,[a] Dipolar and Contact Shifts of *cis*-Ammine Hydrogens of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Deuterated Solvents

	L = dicyd^{2-}			L = Me$_2$dicyd^{2-}			L = Cl$_2$dicyd^{2-}			L = Cl$_4$dicyd^{2-}		
solvents	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}	δ_{dip}	δ_{con}
NO_2CD_3	1.15	1.2	0	−0.79	*b*	*b*	17.17	2.5	14.7	33.66	4.4	29.3
CD_3CN	7.99	1.8	6.2	1.83	1.5	0.3	30.77	3.5	27.3	44.79	4.8	40.0
Acetone-d$_6$	14.37	2.2	12.2	6.74	1.6	5.1	39.89	4.1	35.8	51.28	4.9	46.4
DMSO-d$_6$	48.43	4.5	43.9	40.06	3.8	36.3	63.38	5.5	57.9	69.12	5.8	63.3

[a] $\delta_{iso} = \delta_{obs} - 3.75$ ppm. [b] Solution magnetic moment was too small to be measured.

Table 8. Isotropic,[a] Dipolar and Contact Shifts of Phenyl Hydrogens of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Deuterated Solvents

	L = dicyd^{2-}			L = Me$_2$dicyd^{2-}			L = Cl$_2$dicyd^{2-}		
solvents	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}	δ_{dip}	δ_{con}
NO_2CD_3	−0.84	−0.4	−0.4	0.24	*b*	*b*	−9.50	−0.8	−8.7
CD_3CN	−5.24	−0.6	−4.6	−1.59.	−0.5	−1.1	−14.34	−1.1	−13.2
Acetone-d$_6$	−8.14	−0.7	−7.4	−3.95	−0.5	−3.5	15.96	−1.3	−14.7
DMSO-d$_6$	−15.95	−1.4	−14.6	−15.30	−1.2	−14.1	−15.52	−1.7	−13.8
D_2O	−15.4	−1.7	−13.7				−15.11	−2.3	−12.8

[a] $\delta_{iso}=\delta_{obs} - \delta_{dia}$ in ppm; for L = dicyd^{2-}, Me$_2$dicyd^{2-}, and Cl$_2$dicyd^{2-}, δ_{dia} = 6.96, 6.86, and 7.22 ppm, respectively. [b] Solution magnetic moment was too small to be measured.

these complexes contact shift makes the greatest contribution to the isotropic shift.

A contact shift results from the presence of spin density at the resonating nucleus and can be described by using the spin-only equation[28,29]

$$\delta_{con} = \frac{A_C g_{av} \mu_B S(S+1)}{g_n \mu_n 3kT} \quad (8)$$

where A_c is the hyperfine coupling constant, μ_B is the Bohr magneton of the electron, g_n is the nuclear *g*-factor, μ_n is the nuclear magneton, k is the Boltzmann constant, and T is temperature. Hyperfine coupling constants are usually determined by measuring the temperature dependence of contact shifts.[25,30] In this regard, a temperature dependent study (−50 to 25 °C in CD_3CN) of the nearly diamagnetic complex $[\{Ru(NH_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][PF_6]_4$ was attempted to see if the singlet ground state could be completely populated and a diamagnetic spectrum obtained. Instead of a diamagnetic spectrum, we observed an increase in the downfield isotropic shift of the ammine protons, presumably because the triplet state is increasingly populated with decreasing temperature. This can only occur if antiferromagnetic exchange decreases with decreasing temperature and, based on the solvent dependent magnetic properties of these complexes, it is suggested that solvent-ammine donor−acceptor interaction must be increasing with decreasing temperature. This complexity prevents the facile evaluation of hyperfine coupling constants by temperature dependent NMR; however, the solvent-dependent magnetic properties of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ at constant temperature provide an alternative method. Expressing the contact shift in terms of μ_{eff} at T = 298 K by substituting eq 7 into eq 8, and using g_{av} = 2.30 and the standard values, yields,

$$\delta_{con} = \frac{A_C \mu_B \mu_{eff}^2}{g_n \mu_n 3kTg_{av}} = 1.69 \times 10^{22} A_c \mu_{eff}^2 \quad (9)$$

For ammine ligands bonded to a given Ru(III) ion in a dinuclear complex, spin is delocalized from the metal ion onto the ammine ligands by the previously mentioned hyperconjugation mechanism. The delocalization of spin from the bridged Ru(III) ion to the ammines is assumed to be small in which case μ_{eff} is the effective magnetic moment per ruthenium ion. Thus, plots of δ_{con} versus μ_{eff}^2 should be linear with slope proportional to A_c provided A_c is constant for these complexes.[31] Plots of δ_{con} versus μ_{eff}^2 for *trans* and *cis* ammine hydrogens appear in Figures 5 and 6, respectively, and show linear behavior. The linear-least-squares fits of the data in

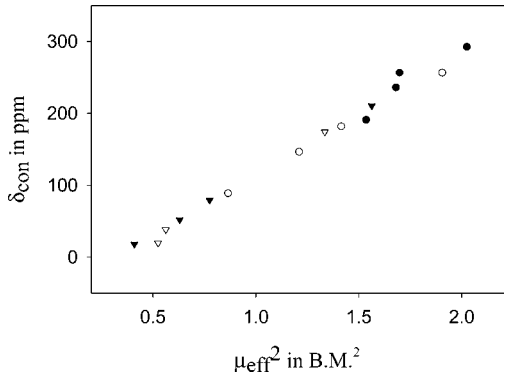

Figure 5. Plot of μ_{eff}^2 versus δ_{con} for the *trans* ammine protons of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ at a complex concentration of 11.0 mM in various solvents. L= Cl$_4$dicyd^{2-} (●), Cl$_2$dicyd^{2-} (○), dicyd^{2-} (▼), and Me$_2$dicyd^{2-} (▽). Data can be found in Tables 2−6.

Figures 5 and 6 gave the hyperfine coupling constants for *trans*- and *cis*-ammine hydrogens of A_c/h = 15.4 and 3.4 MHz, respectively.

For the phenyl protons of the bridging ligand, the situation is more complicated as shown in Figure 7. The plot of δ_{con} versus μ_{eff}^2 shows linear behavior, with δ_{con} increasingly negative in magnitude until $\mu_{eff}^2 > 1.5$, after which δ_{con} becomes smaller in magnitude. This behavior is quite different from that seen for the ammine ligands (Figures 5 and 6) and may be due to an abrupt decrease in spin delocalization onto the phenyl ring.[32] The mechanism by which spin can be delocalized onto the dicyd^{2-} bridging ligand is optimum when the πd-orbitals of ruthenium and the π-symmetry orbitals of the cyanamide and

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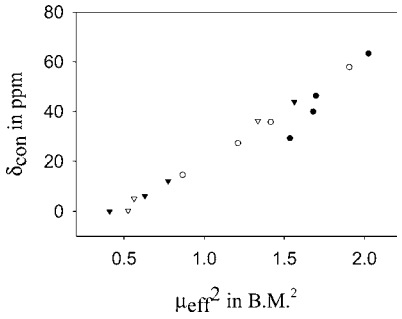

Figure 6. Plot of μ_{eff}^2 versus δ_{con} for the *cis* ammine protons of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ at a complex concentration of 11.0 mM in various solvents. L= Cl_4dicyd^{2-} (●), Cl_2dicyd^{2-} (○), $dicyd^{2-}$ (▼), and Me_2dicyd^{2-} (▽). Data can be found in Tables 2–5 and 7.

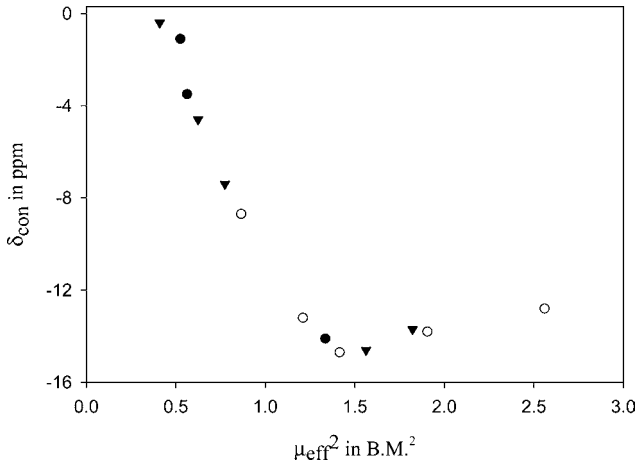

Figure 7. Plot of μ_{eff}^2 versus δ_{con} for the phenyl protons of $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ at a complex concentration of 11.0 mM in various solvents. L = Me_2dicyd^{2-} (●), Cl_2dicyd^{2-} (○), and $dicyd^{2-}$ (▼). Data can be found in Tables 2–5 and 8.

phenyl ring moieties form a continuous π interaction. The planarity of the bridging ligand and a linear Ru(III)-cyanamide bond are key geometric parameters in this regard. It is suggested that a limit to spin density transferred from Ru(III) to the bridging ligand has been reached at $\mu_{eff}^2 > 1.5$ because the solvent donor–acceptor interactions that are responsible for the increasing magnetic moment must weaken the linear Ru-cyanamide π bond toward a bent σ-bond conformation. Further increases in solvent donor properties (and hence magnetic moment), serves to increase the σ-bonding only character of the Ru-cyanamide bond and diminishes the effectiveness of the spin delocalization mechanism and so phenyl proton δ_{con} becomes smaller in magnitude. Ignoring the data points higher than $\mu_{eff}^2 = 1.5$ in Figure 7, gave for the phenyl ring hydrogens an $A_c/h = -1.3$ MHz.

The phenyl ring hydrogen atoms obtain spin density by the polarization mechanism in which π-spin density on the carbon atom (ρ_c^{π}) induces opposite spin density on the hydrogen atom according to,[28]

$$A_c(\text{hydrogen}) = \frac{Q\rho_c^{\pi}}{2S} \qquad (10)$$

where Q is the proportionality constant which has a value of approximately −70 MHz.[33] Substituting the appropriate values, ρ_c^{π} is estimated to be 1.9%. Thus, for the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes, spin density resides mostly on the ruthenium ions and so are best described by [Ru(III),L^{2-}, Ru(III)].

CONCLUSION

EPR spectroscopy of the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ complexes showed a metal-radical axial signal and thus the complexes are [Ru(II),L^{2-}, Ru(III)] mixed-valence systems. DFT calculations of these complexes gave mostly bridging-ligand centered spin for both vacuum and PCM calculations, in poor agreement with experiment, but better results were obtained using an explicit electrostatic model in which the [Ru(II),L^{2-}, Ru(III)] state is stabilized. For the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes, solvent-dependent ^{1}H NMR data and analysis support a [Ru(III),L^{2-}, Ru(III)] state. Hyperfine coupling constants (A_c/h) of *trans*- and *cis*-ammine and phenyl hydrogens were determined to be 17.2, 3.8, and −1.5 MHz, respectively. EPR studies of the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{5+}$ complexes showed a metal-radical axial signal and based on the similarity of the previously published ^{1}H NMR spectrum of $[\{(NH_3)_5Ru\}_2(\mu\text{-Me}_2\text{dicyd})]^{5+}$ to those of $[(NH_3)_5Ru(pcyd)]^{2+}$ complexes, a [Ru(III),L^{2-}, Ru(IV)] state is favored.

ASSOCIATED CONTENT

Supporting Information

XYZ atomic coordinates of optimized structures and composition (%) of frontier β-spin molecular orbitals. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: robert_crutchley@carleton.ca.

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(29) Eq 8 is valid for pure spin states but as the dinuclear complex is in singlet−triplet equilibrium only a fraction of the complex is responsible for the isotropic shift. Strictly speaking both the left and the right sides of eq 8 should be divided by this fraction.
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