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Basicity of the Solvent as the Main Factor Determining the Stability of $[Fe_4S_4(SR)_4]^-$ Cluster Ions in Solution

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Four-iron ferredoxins are redox enzymes that contain a cubane-like [4Fe-4S] cluster core at their active site(s). These sites switch either between the 2+ and + core oxidation levels (Fd sites) or between the 3+ and 2+ levels (HP sites):[2]

$$\begin{array}{ccccc} [\text{4Fe-4S}]^{+} & \rightleftarrows & [\text{4Fe-4S}]^{2+} & \rightleftarrows & [\text{4Fe-4S}]^{3+} \\ [\text{Fd}_{\text{red}}] & & [\text{Fd}_{\text{ox}}, \text{HP}_{\text{red}}] & & [\text{HP}_{\text{ox}}] \end{array}$$

X-ray crystallographic data indicate that the structural differences between the cluster cores in Fd_{ox} and HP_{red} sites are minimal. Nevertheless, HP_{ox} sites contain a stable $[4Fe\text{-}4S]^{3+}$ core, while oxidation of the $[4Fe\text{-}4S]^{2+}$ core in a an Fd_{ox} site leads to the loss of an iron atom and the formation of a three-Fe cluster.[3] The X-ray structural data suggest that the greater stability of the $[4Fe\text{-}4S]^{3+}$ core in HP proteins is due to a hydrophobic environment and protection of the core from solvent attack.[4] This idea is supported by the properties of the low-molecular-weight monoanionic cluster species $[Fe_4S_4(SR)_4]^-$, which can be considered to be models for HP_{ox} sites.[2] These species, when generated in solution, are stabilized by sterically encumbered terminal ligands that create a hydrophobic core environment.[5-9] Furthermore, the only monoanionic compound that has been isolated and structurally characterized so far contains the bulky 2,4,6-triisopropylbenzenethiolate ligand (tibt).[10] The stability of the cluster ions $[Fe_4S_4(SR)_4]^-$ (R = alkyl, aryl) in solution is also strongly dependent on the solvent. On the CV time scale, $[Fe_4S_4(SPh)_4]^{2-}$ shows a reversible 2−/− oxidation wave in the special solvent medium $n\text{-}Bu_4NBF_4\cdot 3$ toluene,[11] but not in DMF. Millar et al.[10] found the following order of stability for $[Fe_4S_4(tibt)_4]^-$: dichloromethane > acetonitrile ≫ DMF. This variation in stability was attributed to the polarity of the solvent. A similar result was obtained by Ohno et al. for three different solvents.[12]

In order to examine more carefully the solvent dependence of the stability of the $[Fe_4S_4(SR)_4]^-$ cluster ions in solution, we have recorded cyclic voltammograms of the cluster compounds $[Fe_4S_4(SPh)_4]^{2-}$ and $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ in eight different solvents, i.e. acetonitrile (AN), benzonitrile (BN), acetone (ACN), dichloromethane (DC), *N*,*N*-dimethylformamide (DMF), nitrobenzene (NB), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO), and cyclic voltammograms of the cluster compounds $[Fe_4S_4(SR)_4]^{2-}$ (R = Et, *n*-Pr, CH_2Ph, $p\text{-}C_6H_4Cl$, $p\text{-}C_6H_4Me$, and CH_2CH_2OH) in dichloromethane and benzonitrile.

Table I. Half-Wave Potentials (in Volts vs $Fc^{+/0}$) for the $[Fe_4S_4(SR)_4]^{2-}$ Cluster Compounds

R	solvent[a]	redcn 2−/3−	oxidn (s) 2−/−	oxidn (s) −/0
Ph	DC	−1.46	−0.32	0.04[d]
	NB	*b*	−0.31	0.01[d]
	BN	−1.49	−0.33	
	AN	−1.39	*c*	
	ACN	−1.49	−0.35	
	THF	−1.47	−0.40	
	DMF	−1.52	*c*	
	DMSO	−1.36	*c*	
t-Bu	DC	−1.90	−0.65	−0.07[d]
	AN	−1.73	−0.55	
	BN	−1.89	−0.62	
	DMF	−1.92	−0.70	
CH_2CH_2OH	DC	−1.60	−0.47[d]	
	BN	−1.62	−0.43[d]	
$p\text{-}C_6H_4CH_3$	BN	−1.56	−0.40	
$CH_2C_6H_5$	BN	−1.72	−0.47[d]	
C_2H_5	BN	−1.80	−0.53[d]	

[a] For abbreviations, see Table II. [b] Outside potential window. [c] No discrete 2−/− wave. [d] Anodic peak potential.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere. Solvents were degassed before use by means of the pump–freeze–thaw method. All solvents were purified according to standard procedures. All thiols were purchased from Janssen Chimica. Ethanethiol (97%), 1-propanethiol (98%), 2-methyl-2-propanethiol (99%), and benzylmercaptan (99%) were distilled from CaH_2 under nitrogen and stored under nitrogen. Benzenethiol (99+%) and 2-hydroxyethanethiol (98%) were stored under nitrogen and used as received. *p*-Chlorobenzenethiol (98%) and *p*-thiocresol (98%) were used as received. Sodium (Riedel de Haen, 99.5%), lithium (Merck, 99+%), iron(III) chloride (Merck), benzoyl chloride (Janssen Chimica, 99%), tetrabutylammonium bromide (Eastman Kodak), and tetraethylammonium chloride (Merck or Fluka) were used as received. The $[Fe_4S_4(SR)_4]^{2-}$ compounds were prepared in the form of their tetrabutylammonium and/or tetraethylammonium salts by direct tetramer synthesis using elemental sulfur as the source of sulfide,[13] by the ligand substitution reaction of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ with the appropriate thiol,[14] or by the ligand substitution reaction of $[Fe_4S_4Cl_4]^{2-}$ with the appropriate thiolate.[15] Elemental analyses were satisfactory. The cyclic voltammetric experiments were performed in a glovebox in which a dry and oxygen-free nitrogen atmosphere was maintained. A conventional three-electrode cell with platinum working and auxiliary electrodes and an appropriate reference electrode was used. The working electrode was always cleaned before use by polishing it with finely grinded aluminum oxide and immersing it in an ultrasonic bath for 1 min. All voltammograms were recorded in the first scan to prevent pollution of the working electrode. Solvents were purified according to standard procedures. The supporting electrolyte was 0.1 M KPF_6 in case of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ in acetone and either 0.1 M tetrabutylammonium hexafluorophosphate (TBAH), 0.1 M tetraethylammonium perchlorate (TEAP), or 0.1 M tetraethylammonium tetrafluoroborate (TEAB) in all

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Table II. Dielectric Constants (ϵ) and Donor Numbers (DN) for the Solvents Used

solvent	abbr	ϵ^a	DN^b
dichloromethane	DC	9.09^c	0.0^g
nitrobenzene	NB	35.73^c	4.4
benzonitrile	BN	25.22^d	11.9
acetonitrile	AN	37.45^d	14.1
acetone	ACN	21.19^c	17.0
tetrahydrofuran	THF	7.54^e	20.0
N,*N*-dimethylformamide	DMF	37.65^d	26.6
dimethyl sulfoxide	DMSO	47.09^f	29.8

^{a}At 293.15 K. ^{b}Data were taken from ref 16. ^{c}From ref 21. ^{d}From ref 22. ^{e}From ref 23. ^{f}From ref 24. ^{g}From ref 25.

other cases. The concentration of the electroactive species was always between 0.1 and 1.0 mM. The scan rate was 0.1 V/s. *iR* compensation was applied to minimize uncompensated solution resistance. The equipment consisted of a PAR 173 potentiostat, a PAR 176 iE converter, and a PAR 175 universal programmer or a PAR 273 potentiostat. The recording device was either a Kipp BD30 or a Kipp BD90 XY-recorder. All potentials are given against the ferrocenium/ferrocene couple measured under the same conditions.

Results and Discussion

The cyclic voltammograms of $[Fe_4S_4(SPh)_4]^{2-}$ are shown in Figure 1. In each voltammogram the chemically fully reversible 2-/3- transition ($i_b/i_f = 1.0$) has been included as reference (see also Table I). In nitrobenzene, this transition lies outside the potential window. The bad quality of the voltammogram in THF is due to the low solubility of the $[Fe_4S_4(SPh)_4]^{2-}$ salts in this solvent. In DMF, DMSO, and AN the first oxidation that is observed is a multielectron process that can be associated with the total breakdown of the cluster structure. In ACN, BN, and THF the multielectron process shifts to more positive potentials, and a more or less reversible one-electron wave becomes visible. In NB and DC the multielectron process shifts to even more positive potentials, and the 2-/- transition is a fully reversible wave ($i_b/i_f = 1.0$) well resolved from subsequent oxidation waves. In these solvents also a second, though irreversible ($i_b/i_f = 0.0$), oxidation wave is seen before the final multielectron wave. Its peak current is equal to the peak current of the 2-/- wave, suggesting that also in this process one electron is involved. Therefore this wave can tentatively be attributed to oxidation to the neutral cluster compound ("the all-ferric state").

From the data assembled here it is clear that there exists no correlation between the dielectric constant of the solvent and the stability of the $[Fe_4S_4(SPh)_4]^-$ ion (Figure 1; Table II). For instance NB and DMF both have a dielectric constant of about 35, but $[Fe_4S_4(SPh)_4]^-$ is only stable on the CV time scale in NB. On the other hand, a correlation does seem to exist between the basicity of the solvent and the stability of the monoanionic cluster species. The donor number (DN) has proven to be a useful measure of basicity.[16] In NB and DC, the solvents with the lowest donor numbers, $[Fe_4S_4(SPh)_4]^-$ is stable on the CV time scale. In all other solvents the 2-/- transition either is immediately followed by the multielectron wave (ACN, BN, THF) or is not present as a discrete wave at all (AN, DMF, DMSO). These results strongly suggest that the first step in the decomposition of a monoanionic cluster ion is a nucleophilic attack of a solvent molecule on an iron atom in the core. This interpretation of the data also rationalizes the observation that $[Fe_4S_4(SPh)_4]^-$ is relatively stable in THF, the solvent with the third highest donor number. Oxidation of the [4Fe-4S] core to the 3+ level increases the ferric character of the iron atoms, but due to the sulfide ligands, these iron atoms will still be relatively soft. According to the HSAB principle,[17] ligand substitution of a benzenethiolate by a hard THF molecule will be less favorable. On the other hand $[Fe_4S_4(SPh)_4]^-$ is somewhat less stable than expected from the donor number in acetonitrile. This is not surprising since acetonitrile is known to be a soft donor.[18] An additional reason for the high reactivity of this solvent could be the small size of the acetonitrile molecule.

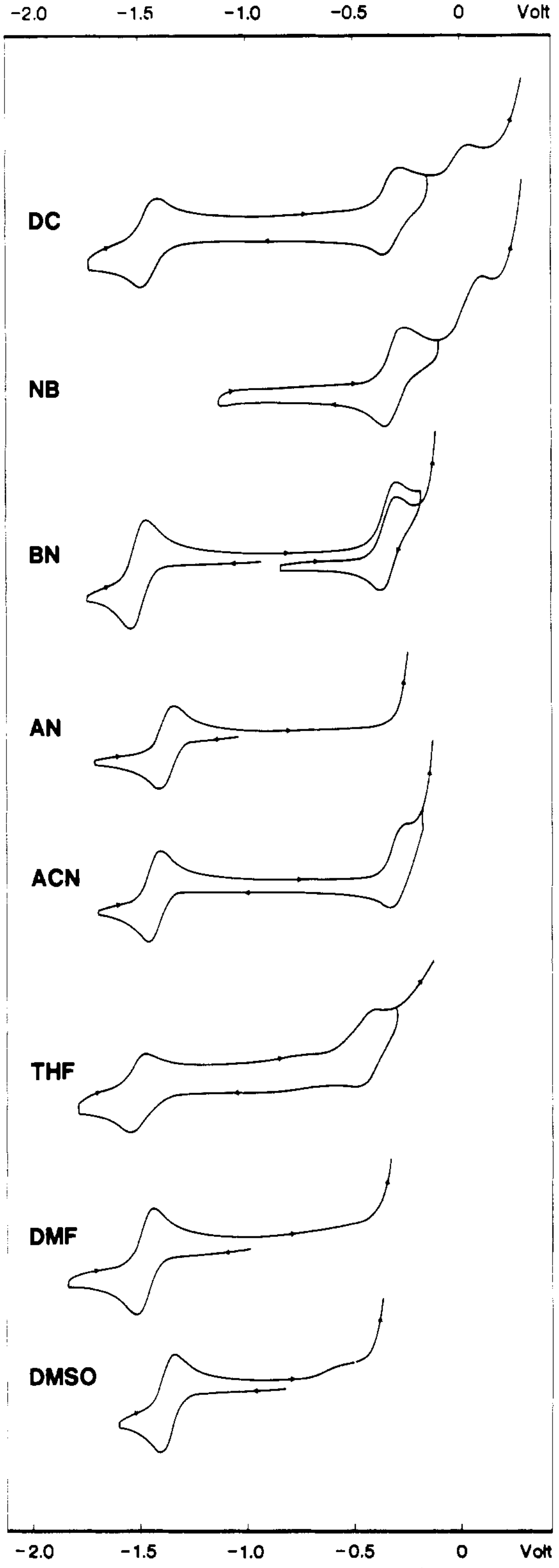

Figure 1. Cyclic voltammograms of $[Fe_4S_4(SPh)_4]^{2-}$ in eight different solvents. The voltammograms are from top to bottom in order of increasing solvent donor number. Potentials are in volts vs the Fc^+/Fc couple. Current scales are arbitrary and can not be compared.

The cyclic voltammetric behavior of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ confirms the findings for $[Fe_4S_4(SPh)_4]^{2-}$. $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ shows a fully

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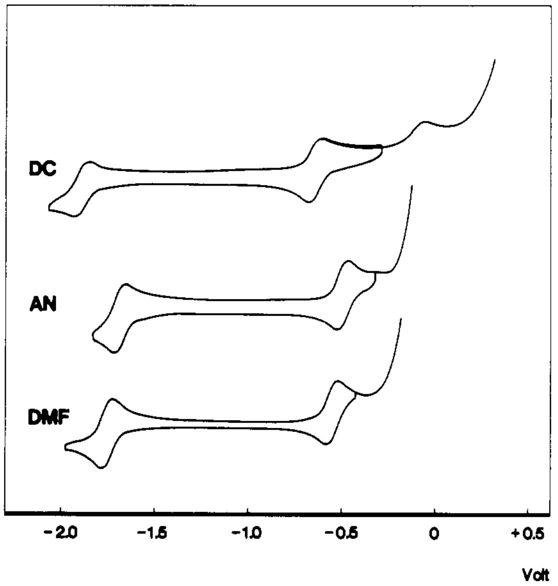

Figure 2. Cyclic voltammograms of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ in DC, AN, and DMF.

reversible 2−/− transition in all solvents, but in the less basic solvents, the voltage gap between this transition and the multielectron process is much larger (Figure 2).

The influence of steric protection from the solvent on the stability of the $[4Fe\text{-}4S]^{3+}$ core is probably best visible when a moderately basic solvent like benzonitrile is used. The cyclic voltammograms of the cluster compounds $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$, $[Fe_4S_4(S\text{-}p\text{-}C_6H_4Me)_4]^{2-}$, $[Fe_4S_4(SCH_2Ph)_4]^{2-}$, and $[Fe_4S_4(SEt)_4]^{2-}$ in this solvent are shown in Figure 3. The ratio i_b/i_f for the 2−/− transition gives information about the stability of the monoanionic cluster species on the time scale of the experiment. For the cluster compounds $[Fe_4S_4(SR)_4]^{2-}$, where R is ethyl or *n*-propyl, and for $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ this ratio lies inbetween 0.0 and 0.3, which is indicative of a high degree of chemical irreversibility. For the $[Fe_4S_4(SR)_4]^{2-}$ compounds with R an aromatic group (R = Ph, $p\text{-}C_6H_4Cl$, $p\text{-}C_6H_4Me$) and for $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$, i_b/i_f is (almost) equal to 1.0. The observation of a reversible 2−/− transition for $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ in DMF was attributed before to the electron-releasing properties of the *t*-Bu substituent.[19] The order of stability of the $[Fe_4S_4(SR)_4]^{-}$ species, R = ethyl, *n*-propyl, CH_2Ph < R = aryl, *t*-Bu, suggests, however, that steric factors are at least as important, since the primary alkyl groups are more electron-releasing than the aromatic groups. Assuming that the first step in the decomposition of a monoanionic cluster is a nucleophilic attack by a solvent molecule, this means that the activation barrier contains both steric and electronic contributions.

A deviating cyclic voltammetric behavior is exhibited by $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$. The first oxidation process that is observed in dichloromethane and benzonitrile is irreversible ($i_b/i_f = 0$; Figure 4). So for $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$, the use of a less basic solvent does not help in stabilizing the monoanionic cluster species. This suggests that upon oxidation an intramolecular nucleophilic attack of the OH function on an iron atom takes place, which ultimately leads to an irreversible oxidation and degradation of the cluster like in the case of nucleophilic attack by a basic solvent molecule. This point needs further attention, however, since a recently reported cluster compound with both a tridentate thiolate ligand and a single, deprotonated *o*-hydroxybenzenethiol ligand exhibits a fully reversible one-electron 2−/− transition in DMSO solution.[20]

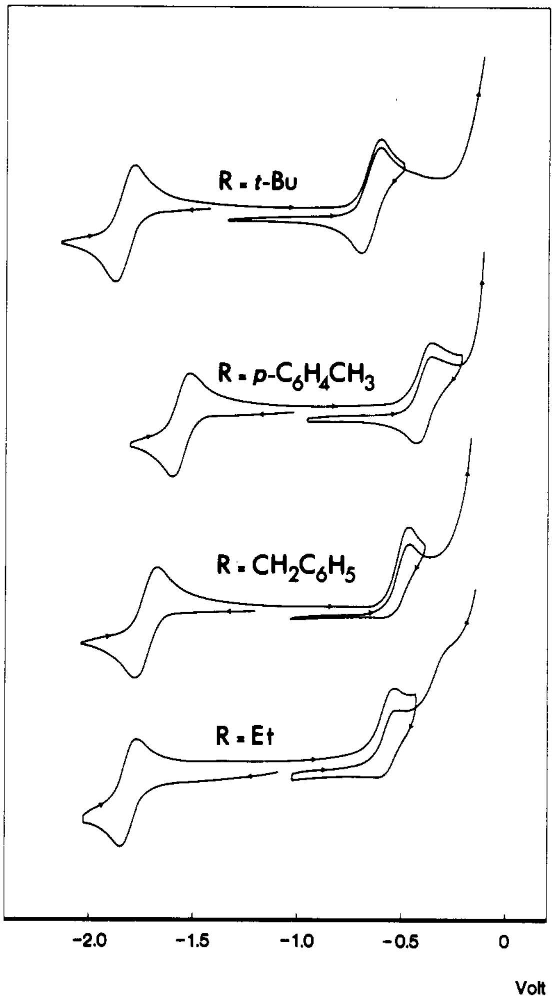

Figure 3. Cyclic voltammograms of the cluster compounds $[Fe_4S_4(SR)_4]^{2-}$ (R = *t*-Bu, $p\text{-}C_6H_4Me$, CH_2Ph, Et) in benzonitrile.

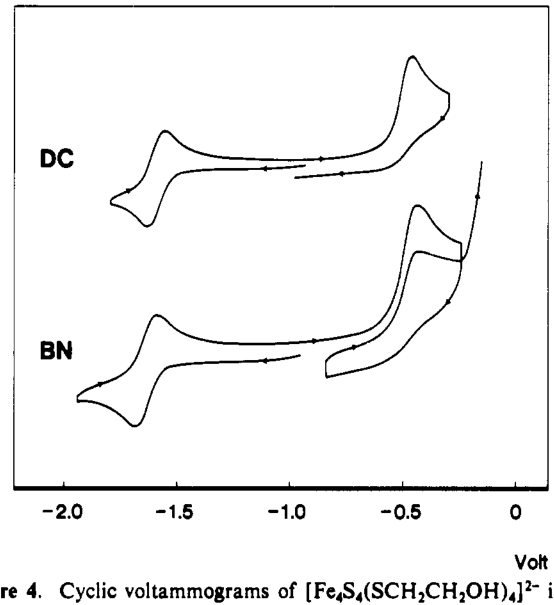

Figure 4. Cyclic voltammograms of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ in dichloromethane and benzonitrile.

The conclusion may thus be that the stability of the $[Fe_4S_4(SR)_4]^{-}$ cluster species is determined by the basicity of the solvent

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rather than by its polarity. The influence of the solvent basicity is reduced when the substituent R becomes more bulky. Because of the basic properties of water, these results imply that a hydrophobic environment and protection from solvent attack are indeed essential factors for the stabilization of the [4Fe-4S]$^{3+}$ core in HP proteins. Another conclusion may be that a low-molecular-weight thiolate cluster compound when dissolved in a low-donor-number solvent like NB or DC can be regarded to be a good model system for the active site of HP proteins.

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Registry No. AN, 75-05-8; BN, 100-47-0; ACN, 67-64-1; DC, 75-09-2; DMF, 68-12-2; NB, 98-95-3; THF, 109-99-9; DMSO, 67-68-5; $[Fe_4S_4(SPh)_4]^{2-}$, 52325-39-0; $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$, 51913-87-2; $[Fe_4S_4(SEt)_4]^{2-}$, 52261-51-5; $[Fe_4S_4(S\text{-}n\text{-}Pr)_4]^{2-}$, 52325-40-3; $[Fe_4S_4(SCH_2Ph)_4]^{2-}$, 52349-82-3; $[Fe_4S_4(S\text{-}p\text{-}C_6H_4Cl)_4]^{2-}$, 55787-38-7; $[Fe_4S_4(S\text{-}p\text{-}C_6H_4CH_3)_4]^{2-}$, 51899-68-4; $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$, 62851-99-4; $[Fe_4S_4(SPh)_4]^-$, 97365-72-5; $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^-$, 126752-32-7; $[Fe_4S_4(SEt)_4]^-$, 134566-32-8; $[Fe_4S_4(S\text{-}n\text{-}Pr)_4]^-$, 134566-33-9; $[Fe_4S_4(SCH_2Ph)_4]^-$, 134593-43-4; $[Fe_4S_4(S\text{-}p\text{-}C_6H_4Cl)_4]^-$, 134566-34-0; $[Fe_4S_4(S\text{-}p\text{-}C_6H_4CH_3)_4]^-$, 134566-35-1; $[Fe_4S_4(SCH_2CH_2OH)_4]^-$, 134566-36-2; Pt, 7440-06-4; $[Fe_4S_4(SPh)_4]^{3-}$, 52627-89-1; $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{3-}$, 91294-54-1; $[Fe_4S_4(SCH_2CH_2OH)_4]^{3-}$, 134566-37-3; $[Fe_4S_4(S\text{-}p\text{-}C_6H_4CH_3)_4]^{3-}$, 67724-72-5; $[Fe_4S_4(SCH_2C_6H_5)_4]^{3-}$, 63138-11-4; $[Fe_4S_4(SEt)_4]^{3-}$, 52499-30-6; $[Fe_4S_4(SPh)_4]$, 134566-38-4; $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$, 134566-39-5.

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Long-Range Antiferromagnetic Coupling between Two Ruthenium(III) Ions Bridged by a 1,4-Dicyanamidobenzene Dianion Ligand

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The study of polymetallic complexes in which coupling between metals is propagated via a bridging molecule has clear application to the design of novel magnetic and electronic solid-state materials and to the role of polymetallic sites in biological processes.[1,2] A fundamental property to be understood is the distance dependence of metal–metal interactions. Researchers[3] have proposed the relation

$$|2J_{\mathrm{lim}}| = 1.35 \times 10^7 \exp(-1.80R) \tag{1}$$

for the limiting value of J (cm^{-1}),[4] the magnetic exchange coupling constant, and R (Å), the distance between metal ions. In approximate agreement with eq 1, a study of the distance dependence of the magnetic coupling between two Cu(II) complexes bridged by 4,4′-bipyridine (metal ions separated by 11.1 Å) found $2J = -0.9$ cm^{-1}.[5] The authors pointed out that at this magnitude of coupling it would be difficult to distinguish between intermolecular and intramolecular mechanisms. In contrast, a later study found moderately strong intramolecular antiferromagnetic coupling ($2J = -140$ cm^{-1}) between Cu(II) ions separated by 11.25 Å in $[X_2Cu_2(OH_2)(\mu\text{-terephthalato})][ClO_4]_2$, where X = 1,4,7-trimethyl-1,4,7-triazacyclononane.[6] The difference in magnetic coupling between these two results is clearly dependent on the nature of the interaction of the magnetic orbitals with the bridging ligand. For maximum resonance exchange of the magnetic orbitals,[1,7] the bridging ligand should possess a HOMO delocalized on its donor atoms with the correct symmetry and energy to optimize its interaction with the magnetic orbitals. Even if the bridging ligand's HOMO has improper symmetry to interact with the magnetic orbitals, the spin polarization mechanism can still induce antiferromagnetic coupling.[1,8]

Table I. Crystal Data for the Tetraphenylarsonium Salt of the 1,4-Dicyanamido-2,3,5,6-tetramethylbenzene Dianion ($[AsPh_4]_2[L]$)

formula	$As_2N_4C_{60}H_{52}$	MW	966.84
space group	$P2_1/n$	Z	2
cryst syst	monoclinic	D_c; g/cm^3	1.323
a, Å	12.6115 (24)	temp, °C	22
b, Å	14.3029 (17)	radiation (λ, Å)	Mo (0.709 30)
c, Å	13.6986 (14)	R factor[a]	0.051
β, deg	100.820 (10)	R_w factor[b]	0.051
V, Å^3	2427.0 (6)		

[a] $R = \sum||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

The possibility that long-range antiferromagnetic coupling might occur between magnetic orbitals bridged by an easily oxidized, extended π HOMO system led us to prepare the dinuclear complex $[\mu\text{-}L\{(NH_3)_5Ru\}_2][ClO_4]_4$ (**1**), where L^{2-} = 1,4-dicyanamido-2,3,5,6-tetramethylbenzene dianion. The physical characterization of this complex, including its temperature-dependent magnetic properties, is the subject of this report.

Experimental Section

Physical Measurements. The equipment used to perform cyclic voltammetry and UV–vis spectroscopy has been described in a previous paper.[9] Temperature-dependent magnetic measurements were performed on a Quantum Design SQUID magnetometer from 5 to 300 K in a 1.0-T field. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

Materials. All solvents and solid chemicals were reagent grade or better. $[(NH_3)_5Ru(OH_2)][PF_6]_2$ was prepared by literature methods.[10] Protonated 1,4-dicyanamido-2,3,5,6-tetramethylbenzene was prepared from its thiourea precursor.[9,11]

Preparation of Bis(tetraphenylarsonium) 1,4-Dicyanamido-2,3,5,6-tetramethylbenzene(2−) ($[AsPh_4]_2[L]$). The protonated ligand LH_2 (0.68 g) and NaOH (3 g) were placed in a 100-mL round-bottom flask and purged with argon. A previously degassed 30-mL aliquot of water was transferred to the reaction flask under argon. The mixture was stirred until complete dissolution. Tetraphenylarsonium chloride monohydrate (2.6 g) was dissolved into 30 mL of 2.5 M NaOH aqueous solution. This solution was degassed and then transferred under argon to the basic solution of the ligand. The resulting yellow precipitate was filtered out,

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