Table IV. Absorption Spectral Data[a,b]

solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
acetonitrile	680 (1300), 555 (1350), 455 (3200), 315 sh[c] (13 000)
DMF	670 (650), 565 (1200), 420 (3650), 330 sh (12 000)
DMSO	570 (1200), 418 (4400), 335 sh (11 500)
methanol	565 (1100), 420 (3600), 325 sh (12 000)

[a] In solution, **2** is sensitive to oxygen. [b] Measurements were performed on freshly prepared solution. [c] Shoulder.

shorter than that noted for nickel(II) acetylacetonate[25] (average value 2.01 Å) and $[NiBr_2(S(CH_2CH_2OH)_2)_2]$ (2.046 (2) Å).[26] The bite angles of the 2-mercaptopropionate ligand at Ni2 are close to 90°. At Ni1, two S1–Ni–S2 angles are, however, quite smaller (82.5 (1)°). The Ni–Ni distance in **2** (2.783 (1) Å) is very similar to that observed for **3** (2.733 (7) Å).

In **2**, the NiS_4 and two NiS_2O_2 coordination planes form a "chair" conformation with the two symmetry-related NiS_2O_2 planes being parallel. The angle between the NiS_4 and NiS_2O_2 planes is 115°. This arrangement is quite similar to that found in **3**, where the corresponding angle is 109°. Coordination of S to the two adjacent nickel atoms through two different lone pairs, followed by steric adjustment, gives rise to this typical dihedral angle of ca. 110°.

It has been pointed out by Busch and co-workers[27] that the ready formation of **3** from $[NiL_2]$ species is suggestive of a cis structure for the monomeric complex. Trinuclear nickel(II) complexes could therefore be isolated only when the steric repulsion requirements of the ligand are relatively limited. Indeed, *N*,*N*-dimethyl-β-mercaptoethylamine forms only a monomeric nickel(II) complex in which the two bidentate ligands are in a trans configuration.[28] Clearly, limited steric requirements in the case of the 2-mercaptopropionate anion lead to the facile formation of **2** in the present work. Successful isolation of **2** also suggests that the monomeric complex anion $[Ni(SCH(CH_3)COO)_2]^{2-}$ (eq 1), not yet isolated, will adopt a cis configuration.

Properties. In the solid state, **2** is diamagnetic and relatively air-stable. When dissolved in deaerated acetonitrile, the trimeric complex exhibits band maxima (ϵ, M^{-1} cm^{-1}) at 680 (1300), 555 (1350), 455 (3200), and 315 nm (shoulder, 13 000) (Figure 2, Table IV) and obeys Beer's law in the concentration range 0.01–0.3 mM. We assign the ~680-nm band to transition(s) associated with the NiS_4 chromophore.[29,30] The unusually high extinction coefficient might arise from pseudo-tetrahedral distortion of the NiS_4 chromophore in solution.[8a,30] Addition of up to 20 equiv of pyridine to a solution of **2** in acetonitrile does not bring about any change in the absorption spectrum. The trimeric structure appears to remain intact in such solution. However, when **2** is dissolved in DMF, the low-energy-band maximum shifts to 670 nm and the extinction coefficient drops to 650 (Figure 2). Addition of ~50% DMF to a solution of **2** in acetonitrile brings about a similar change in the electronic spectrum. The low-energy band is virtually absent in DMSO and methanol solution (Figure 2, Table IV). Variation in intensity of the ~680-nm band indicates that the trimeric complex decomposes readily in solvents like DMSO and MeOH. Similar behavior has been observed with **3** and **4**.[14,15] Clearly, the trimeric structure is stable in acetonitrile, and it is this solvent from which **2** has been isolated as microcrystalline solid. In the recrystallization step, diffusion of diethyl ether into DMF solution presumably causes preferential crystallization of the trimer.[31]

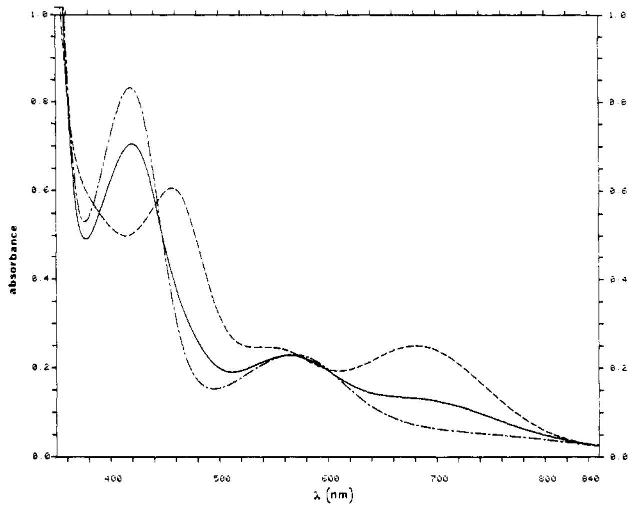

Figure 2. Absorption spectra of **2** (0.189 mM) in acetonitrile (---), DMF (—), and DMSO (-·-).

Preliminary results from magnetic susceptibility measurements on dilute solutions of **2** in CD_3CN indicate that the complex is diamagnetic in such solution. Marginal solubility of **2** in CD_3CN has restricted attempts to record high-quality NMR spectra and to obtain reliable solution susceptibility data.

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Registry No. **2**, 111004-82-1; $(Ph_4P)_2NiCl_4$, 111004-83-2.

Supplementary Material Available: Thermal parameters for non-hydrogen atoms (Table S1), hydrogen atom parameters (Table S2), bond distances and angles associated with the cation (Table S3), and perpendicular distances of the core atoms from the molecular planes (Table S5) (5 pages); values of $10|F_o|$ and $10|F_c|$ (Table S4) (7 pages). Ordering information is given on any current masthead page.

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(31) The IR spectrum of the crude product from the reaction mixture (see Experimental Section) is identical with that of the recrystallized product. Analytical data for these two samples also confirm that the trimer can be recrystallized from DMF/ether.

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Electron-Transfer Reactions of Encapsulated Ruthenium, Manganese, Iron, and Nickel: Self-Exchange Rates for (3,6,10,13,16,19-Hexaazabicyclo[6.6.6]eicosane)metal(3+/2+) Couples

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The question of nonadiabaticity in electron-transfer (et) reactions of transition-metal complexes is continuing to attract attention,[1] and approaches to the "electronic factor" have been made experimentally[2] and theoretically.[3] The interest has been particularly stimulated by the fact that there exist some (large) discrepancies between observed and calculated et rate constants and that the classical, adiabatic theories of Marcus[4] and Hush[5] could not account for the large negative entropies of activation observed. Equally important has been the early realization that the ground-state electron self-exchange in most Co^{3+}–Co^{2+} systems is spin-forbidden.[6]

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Table I. Observed and Calculated Electron-Transfer Rate Constants[a]

cross-reaction						
no.	reacn	orbital sym	$\Delta E'$, V	k_{exptl}, $M^{-1}\ s^{-1}$	k_{calcd}, $M^{-1}\ s^{-1}$	f_{12} (eq Ib)
1	$(NH_3)_5Ru(py)^{3+}$–$Ru(sar)^{2+}$	$t_{2g} \rightarrow t_{2g}$	0.012	$(1.05 \pm 0.08) \times 10^5$	1.4×10^5	1.00
2	$(NH_3)_5Ru(nic)^{3+}$–$Ru(sar)^{2+}$	$t_{2g} \rightarrow t_{2g}$	0.072	$(2.8 \pm 0.1) \times 10^5$	4.4×10^5	0.92
3	$(NH_3)_5Ru(isn)^{3+}$–$Ru(sar)^{2+}$	$t_{2g} \rightarrow t_{2g}$	0.094	$(5.2 \pm 0.9) \times 10^5$	6.6×10^5	0.87
4	$Ru(tacn)_2^{3+}$–$Ru(sar)^{2+}$	$t_{2g} \rightarrow t_{2g}$	0.076	$(7.3 \pm 2.5) \times 10^{5\,b}$	3.4×10^5	0.91
5	$Mn(sar)^{3+}$–$(NH_3)_5Ru(py)^{2+}$	$t_{2g} \rightarrow e_g$	0.217	$(3.7 \pm 0.6) \times 10^4$	7.2×10^4	0.58
6	$Mn(sar)^{3+}$–$(NH_3)_5Ru(isn)^{2+}$	$t_{2g} \rightarrow e_g$	0.135	$(1.4 \pm 0.1) \times 10^4$	1.7×10^4	0.81
7	$Mn(sar)^{3+}$–$Ru(tacn)_2^{2+}$	$t_{2g} \rightarrow e_g$	0.153	$(2.9 \pm 0.2) \times 10^4$	1.6×10^4	0.77
8	$Ni(tacn)_2^{3+}$–$Mn(sar)^{2+}$	$e_g \rightarrow e_g$	0.429	$(1.2 \pm 0.2) \times 10^5$	2.6×10^5	0.15
9	$Ni(tacn)_2^{3+}$–$Ni(sar)^{2+}$	$e_g \rightarrow e_g$	0.093	$(3.9 \pm 0.6) \times 10^3$	9.0×10^3	0.90
10	$(NH_3)_5Ru(py)^{3+}$–$Fe(sar)^{2+}$	$t_{2g} \rightarrow t_{2g}$	0.209	$(6.4 \pm 1.5) \times 10^{5\,b}$	6.3×10^5	0.53
11	$(NH_3)_5Ru(isn)^{3+}$–$Fe(sar)^{2+}$	$t_{2g} \rightarrow t_{2g}$	0.291	$\sim 2 \times 10^{6\,b}$	2.3×10^6	0.29
12	$Fe(sar)^{3+}$–$Ru(NH_3)_6^{2+}$	$t_{2g} \rightarrow t_{2g}$	0.031	$(8.2 \pm 0.8) \times 10^3$	1.1×10^4	0.99
13	$Fe(sar)^{3+}$–$Co(azacapten)^{2+}$	$e_g \rightarrow t_{2g}$	0.113	$(4.6 \pm 1.0) \times 10^4$	5.4×10^4	0.85
14	$Mn(sar)^{3+}$–$Ru(sar)^{2+}$	$t_{2g} \rightarrow e_g$	0.229	$(1.7 \pm 0.2) \times 10^5$	9.0×10^4	0.54
15	$Ni(sar)^{3+}$–$Mn(sar)^{2+}$	$e_g \rightarrow e_g$	0.336	$(1.0 \pm 0.1) \times 10^5$	6.5×10^4	0.32
16	$Mn(sar)^{3+}$–$Fe(sar)^{2+}$	$t_{2g} \rightarrow e_g$	0.426	$\sim 10^{6\,b,c}$	2.7×10^5	0.14
17	$Fe^{3+}{}_{aq}$–$Ru(sar)^{2+}$	$t_{2g} \rightarrow t_{2g}$	0.450	$(7.2 \pm 0.6) \times 10^4$	6.7×10^4	0.15
18	$Fe^{3+}{}_{aq}$–$Mn(sar)^{2+}$	$e_g \rightarrow t_{2g}$	0.221	$(1.2 \pm 0.1) \times 10$	2.0×10^1	0.69
19	$Ni(sar)^{3+}$–$Fe^{2+}{}_{aq}$	$t_{2g} \rightarrow e_g$	0.115	$(4.3 \pm 0.3) \times 10$	2.8×10^1	0.90

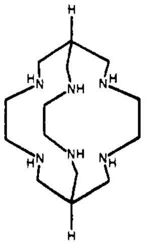
[a] $T = 25\ °C$, $\mu = 0.10$ M (CF_3SO_3H, $LiCF_3SO_3$). [b] Only two values of k_{obsd}. [c] Relatively poor data.

Table II. Electron Self-Exchange Rate Constants[a]

	el config	k, $M^{-1}\ s^{-1}$	E',[c] V
(a) Deduced Self-Exchange Rate Constants[b]			
$Ru(sar)^{3+/2+}$	$(t_{2g})^5/(t_{2g})^6$	1.2×10^5	0.290
$Mn(sar)^{3+/2+}$	$(t_{2g})^3(e_g)^1/(t_{2g})^3(e_g)^2$	1.7×10	0.519
$Fe(sar)^{3+/2+}$	$(t_{2g})^5/(t_{2g})^6,(t_{2g})^4(e_g)^{2\,d}$	6.0×10^3	0.093
$Ni(sar)^{3+/2+}$	$(t_{2g})^6(e_g)^1/(t_{2g})^6(e_g)^2$	1.7×10^3	0.855
$(Fe_{aq})^{3+/2+}$	$(t_{2g})^3(eg)^2/(t_{2g})^4(eg)^2$	6.2×10^{-3}	0.740
(b) Calibrant Self-Exchange Rate Constants[e]			
$(NH_3)_5Ru(L)^{3+/2+}$	$(t_{2g})^5/(t_{2g})^6$	$1.1 \times 10^{5\,f}$	0.302 (py)
(L = py, nic, isn)			0.362 (nic)
			0.384 (isn)
$Ru(NH_3)_6{}^{3+/2+}$	$(t_{2g})^5/(t_{2g})^6$	$2.0 \times 10^{3\,g}$	0.062
$Ru(tacn)_2{}^{3+/2+}$	$(t_{2g})^5/(t_{2g})^6$	$5.4 \times 10^{4\,h}$	0.366
$Ni(tacn)_2{}^{3+/2+}$	$(t_{2g})^6(eg)^1/(t_{2g})^6(eg)^2$	$1.4 \times 10^{3\,i}$	0.948
$Co(azacapten)^{3+/2+}$	$(t_{2g})^6/(t_{2g})^6(e_g)^1$	$2.4 \times 10^{3\,k}$	–0.020

[a] $T = 25\ °C$, $\mu = 0.1$ M (CF_3SO_3H, $LiCF_3SO_3$). [b] Reference 19b. [c] Vs NHE. [d] K(high spin/low spin) ~2.[16] [e] Extrapolated, where necessary, to $\mu = 0.1$ M as in ref 15. [f] Reference 15. [g] Reference 17. [h] Preliminary value from a NMR study, to be published. [i] Reference 18. [k] Reference 7b.

In recent papers[7] on encapsulated cobalt amine complexes it was shown that et rate constants for the Co(III)/Co(II) couples could be rationalized well and correlated in terms of the Marcus–Hush theories, regardless of the spin-state conditions; the conclusion, therefore, was that the reactions are essentially adiabatic. In this paper we wish to report and discuss a series of reactions involving similar complexes of ruthenium, manganese, iron, and nickel displaying a variety of spin states (c.f. Table II). They include $M(sar)^{3+/2+}$ (M = Ru, Mn, Fe, Ni; sar (**1**) = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane), $(NH_3)_5RuL^{3+/2+}$ (L = NH_3, pyridine (py), nicotinamide (nic), isonicotinamide (isn)), $M(tacn)_2{}^{3+/2+}$ (M = Ru, Ni; tacn (**2**) = 1,4,7-triazacyclononane), $Co(azacapten)^{3+/2+}$ (azacapten (**3**) = 1-methyl-3,13,16-trithia-6,8,10,19-tetraazabicyclo[6.6.6]eicosane), and $Fe(H_2O)_6{}^{3+/2+}$. The purpose of the study was (a) to obtain, from the Marcus cross-relation,[4] estimates for the $M(sar)^{3+/2+}$ self-exchange rates to correlate with (known) structural data and (b) to examine whether there was any systematic dependence of the rates upon the symmetry of the donor and of the acceptor orbital. The estimated self-exchange rate constants should also be important in the design of experiments aimed at the direct measurement of the electron self-exchange rates.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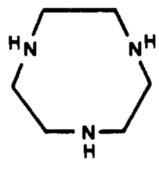
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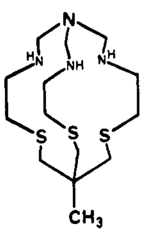
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Experimental Section

Syntheses. The following complexes were synthesized as reported or with slight modifications (e.g. isolated with a different counterion): $[(NH_3)_5RuL](CF_3SO_3)_2$ and $[(NH_3)_5RuL](CF_3SO_3)_3$ (L = py, nic, isn);[8] $[Ru(sar)](CF_3SO_3)_2$,[9] $[Ni(tacn)_2](ClO_4)_3$.[10] $[Ru(NH_3)_6](CF_3SO_3)_2$ was isolated at 0 °C after electrochemical reduction of $[Ru(NH_3)_6](CF_3SO_3)_3$[11] in 1 M $NH_4CF_3SO_3$ (pH ~7). Solutions of (a) $Co(azacapten)^{2+}$, (b) $Fe(H_2O)_6{}^{3+}$, and (c) $Fe(H_2O)_6{}^{2+}$ were prepared as follows: (a) reduction of $[Co(azacapten)](CF_3SO_3)_3$[12] over Zn(Hg); (b) dissolution of Fe-powder (Halewood Chem 99.9999%) in CF_3SO_3H, followed by oxidation with H_2O_2; (c) electrochemical reduction of $Fe(H_2O)_6{}^{3+}$. Detailed syntheses of the compounds $[M(sar)](CF_3SO_3)_2$ (M: Mn, Fe, Ni), $[M(sar)](CF_3SO_3)_3$ (M = Fe, Ni), and $[Mn(sar)](PF_6)_3$[13] as well as of $[Ru(tacn)_2](CF_3SO_3)_z$ (z = 2, 3)[14] will be published shortly.

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Elemental analyses were in good agreement with the calculated values. $Fe^{3+}{}_{aq}$ was analyzed by atomic absorption spectroscopy.

Physical Measurements. Cyclic voltammograms were recorded at 22 °C by using a PAR 170 or BAS 100 electrochemistry system. All the complexes exhibited reversible behavior on the voltammetric timescale (scan rate = 0.1 V s^{-1}) in 0.10 M CF_3SO_3H ($Ru(sar)^{3+/2+}$ = 0.5 V s^{-1}). Reduction potentials E' (Table II) were obtained in the usual way ($E' = (E_{ox} + E_{red})/2$). $E'(Fe^{3+/2+}{}_{aq})$ was taken from ref 15. All the kinetic experiments were performed at 25.0 ± 0.2 °C at an ionic strength μ = 0.10 M (CF_3SO_3H, $LiCF_3SO_3$) under pseudo-first-order conditions. Solutions were prepared by the addition of known amounts of the reactants, and the measurements were carried out within 5 min. For the slower reactions 18 and 19 (Table I), a HP 8450 rapid-scan spectrophotometer was used; all of the other reactions were followed on a Gibbs-Durrum D-110 stopped-flow reactor, equipped with a D-131 photometric log amplifier and a Biomation 805 waveform recorder. To exclude all oxygen from the reactions the reservoir syringes were placed in a continuously flushed nitrogen atmosphere. In addition, a piece of amalgamated Zn was added to solutions containing $Fe(sar)^{2+}$, $Co(azacapten)^{2+}$, $Ru(sar)^{2+}$, or $Ru(NH_3)_6{}^{2+}$, all of which were extremely O_2-sensitive. With these precautions, the rates were reproducible to ±10% (for reactions 4, 10, 11, and 16 ~±30%). Absorbance–time or transmittance–time (for very small changes) data were acquired at three different concentrations of the excess reagent unless indicated otherwise (c.f. Table I). First-order rate constants k_{obsd} were obtained from nonlinear least-squares fits of the curves to the equation $A(t) = A(\infty) + (A(0) - A(\infty)) \exp(-k_{obsd}t)$ by using a VAX 11/750 computer. The values k_{exptl} (Table I) are the average second-order rate constants.

Results and Discussion

Experimental rate constants (k_{exptl}) are given in Table I, together with the driving force ($\Delta E'$) and the symmetries of the donor and of the acceptor orbital. The electronic configurations are given in Table II. A multiparameter least-squares fit[19a] of the experimental rate constants to the Marcus cross-relation[4] (eq I) was

$$\log k_{12} = 0.5 \log (k_{11}k_{22}K_{12}f_{12}) \qquad \text{(Ia)}$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)} \qquad \text{(Ib)}$$

$$\log K_{12} = 16.913\ \Delta E'$$

performed, neglecting any differences in work terms (which are known to be small[7a]) between the reactions. The six parameters allowed to float were the electron self-exchange rate constants (k_{11}) of the $M(sar)^{3+/2+}$ (M = Ru, Mn, Fe, Ni) couples and of $Fe(H_2O)_6{}^{3+/2+}$ (for reasons discussed later) and Z; the self-exchange rate constants of the other systems (Table II, lower part) were used to "calibrate" the cross-reaction matrix. This procedure immediately converged to the values given in Table II (upper part) and Z = 1.9 × 10^{10} M^{-1} s^{-1}. Correlation coefficients[19a] were ≤0.16 between the $M(sar)^{3+/2+}$ couples. The fit was relatively insensitive to the value of Z due to the small to moderate driving forces in our reactions. When Z was fixed at the frequently used value of 10^{11} M^{-1} s^{-1} [4] the shifts in the other parameters were <5%. Nevertheless, it is important to note that Z did converge to a meaningful value. Correlation coefficients were 0.1–0.6 between Z and the other parameters. From the deduced values, the rate constants k_{calcd} (Table I) were then calculated.

In general, the scatter around this best fit is small; only for one reaction (16) is there a difference of a factor of 3 between k_{exptl} and k_{calcd} and only for four reactions (4, 5, 8, and 9) is there a factor of 2. The scatter is not correlated with the orbital symmetries involved; i.e., it is not the case, for instance, that $e_g \rightarrow e_g$ and $t_{2g} \rightarrow t_{2g}$ reactions tend to be fast ($k_{exptl} > k_{calcd}$) and $e_g \rightarrow t_{2g}$ ($t_{2g} \rightarrow e_g$) reactions slow ($k_{exptl} < k_{calcd}$), nor does the conservation of total spin seem to be important. This implies that all the reactions are either adiabatic or nonadiabatic to about the same extent. Even so, it is likely that the degree of nonadiabaticity is small since there is no evident correlation between rate and orbital symmetry and the discrepancy between k_{12}(exptl) and k_{12}(calcd) does not increase as the net free energy change increases.[20] A further "improvement" of the fit by introducing small electronic correction factors into eq I would be meaningless at this stage since we do not know the directly measured self-exchange rates for some couples. However, it is relevant to discuss the deduced self-exchange rates in terms of known structural and kinetic data.

$Ru(sar)^{3+/2+}$. Six rates of oxidation of $Ru(sar)^{2+}$ were measured, but unfortunately the instability of $Ru(sar)^{3+}$ in aqueous solutions[9] obviated any measurements involving this complex as a reactant. Reaction 4, when corrected for the driving force, is itself a good approximation to the electron self-exchange. The value of 1.2 × 10^5 M^{-1} s^{-1} represents the fastest known self-exchange rate for a saturated hexaamine Ru^{3+}–Ru^{2+} couple and implies that the structures of the two $Ru(sar)^{3+/2+}$ ions are virtually identical. Data from X-ray structure determinations are not yet available although the problem is being examined.

$Mn(sar)^{3+/2+}$. Five rates of reduction of $Mn(sar)^{3+}$ and three rates of oxidation of $Mn(sar)^{2+}$ were measured, exhibiting a somewhat larger scatter than for the $Ru(sar)^{3+/2+}$ systems. The discrepancies are, however, not easy to rationalize. It seems surprising, for example, that the reactions with the complexes $(NH_3)_5RuL^{2+}$ (L = py, isn) are slow compared to those with $Ru(sar)^{2+}$ and $Ru(tacn)_2{}^{2+}$. On the basis of a slight difference in mechanism, we can speculate that a specific interaction between the unsaturated ligands leads to a particularly fast self-exchange rate for $(NH_3)_5RuL^{3+/2+}$—an interaction that is not possible with a saturated system like $Mn(sar)^{3+/2+}$. This situation would qualitatively account for the relatively slower et rates observed. It is worth noting that the rates for $(NH_3)_5RuL^{3+}$ with $Ru(sar)^{2+}$ are also slow with respect to k_{calcd}.

Except for a crude estimate of ~10^{-4} M^{-1} s^{-1} for $Mn(H_2O)_6{}^{3+/2+}$,[21] we are unaware of any reported self-exchange rate constants for Mn^{3+}–Mn^{2+} systems. The low value of 17 M^{-1} s^{-1} reflects large structural differences between the $Mn(sar)^{3+}$ and $Mn(sar)^{2+}$ ions. X-ray structure determinations of the compounds $[Mn^{II}(sar(NH_3)_2)](NO_3)_4$[22] and $[Mn(sar)](NO_3)_3$[23] revealed a trigonally twisted coordination around Mn^{2+} (average Mn^{II}–N bond length $\langle d \rangle$ = 2.24 (1) Å) and a strongly Jahn–Teller-distorted coordination around Mn^{3+} (d = 2.18, 2.08, 2.13 Å).

$Fe(sar)^{3+/2+}$. Two rates of reduction of $Fe(sar)^{3+}$ and three rates of oxidation of $Fe(sar)^{2+}$ were measured. The relatively large deduced value of the self-exchange rate constant, 6 × 10^3 M^{-1} s^{-1}, implies that the electron is transferred between low-spin Fe^{2+} and Fe^{3+} since this route involves the minimum reorganization energy. The X-ray structure determination of $[Fe(sar)](NO_3)_3$[22] revealed an almost octahedral coordination around the Fe^{3+} ($\langle d \rangle$ = 2.01 (2) Å). Structural data on Fe^{2+} coordination in the cages are only available for the high-spin compound $[Fe(sar(NH_2)_2](NO_3)_4$ ($\langle d \rangle$ = 2.20(2) Å)[22] at present. However, for the complex $[Fe(2\text{-picolylamine})_3]^{2+}$ it has been shown[24a] that the high-spin to low-spin transition is accompanied by decreases in the Fe^{II}–N bond lengths of 0.16 and 0.21 Å for saturated and unsaturated nitrogen atoms, respectively. A Fe^{II}–N bond length of ~2.04 Å for low-spin $Fe(sar)^{2+}$ would therefore be entirely

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(19) (a) Levenberg-Marquart algorithm (using 1st derivatives); correlation coefficients describe the interdependence of the parameters. (b) Taking into consideration the errors of the calibrant self-exchange rate constants and the standard deviations of the fit, we estimate an overall error of ~30% for the deduced self-exchange rate constants.

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consistent with the fast self-exchange rate for the low-spin Fe(sar)$^{3+/2+}$ system.[16] For [Fe(tacn)$_2$]$^{3+/2+}$ (low spin) bond lengths of 1.99 (Fe^{3+}) and 2.03 Å (Fe^{2+}) have been reported.[24b]

Ni(sar)$^{3+/2+}$. Only two rates of reduction of Ni(sar)$^{3+}$ and one rate of oxidation of Ni(sar)$^{2+}$ could be measured; the reaction between [Ni(tacn)$_2$]$^{3+}$ and Ni(sar)$^{2+}$ is, as for ruthenium, a good approximation to the self-exchange reaction. Structural information is only available for Ni(sar)$^{2+}$ (octahedral, $\langle d \rangle = 2.11$ Å)[22] at present, but for [Ni(tacn)$_2$]$^{3+}$ a tetragonally distorted coordination with $d_{ax} = 2.11$ Å and $d_{eq} = 1.97$ Å has been reported.[25] The value of 1.7×10^3 M^{-1} s^{-1} thus seems to be a reasonable deduction.

Fe(H$_2$O)$_6$$^{3+/2+}$. It was not our intention to assess the electron self-exchange rate constant for this redox couple; in fact in the first refinement the directly measured value of 4 M^{-1} s^{-1} [26] (corrected to $\mu = 0.10$ M, pH 1) was used as a calibrant value but it soon became evident that reactions 17–19 did not fit the consistent picture that emerged from reactions 1–16.[27] We therefore decided to let k_{11}(Fe(H$_2$O)$_6$$^{3+/2+}$) float. Our final value for this "effective" ferric–ferrous electron self-exchange is close to the value ($\sim 10^{-3}$ M^{-1} s^{-1}) that has been derived from a large number of cross-reactions between Fe(H$_2$O)$_6$$^{3+/2+}$ and mostly inert metal complexes.[28] In a recent comparison of the Ru(NH$_3$)$_6$$^{3+/2+}$, Ru(H$_2$O)$_6$$^{3+/2+}$, and Fe(H$_2$O)$_6$$^{3+/2+}$ redox couples using structural and vibrational data,[29] it was noted that the measured Fe(H$_2$O)$_6$$^{3+/2+}$ self-exchange rate was relatively *too fast*. The "effective" self-exchange rate constant deduced here, however, would be very much in keeping with those of the two ruthenium couples. These results and arguments militate against large nonadiabatic effects and in favor of an inner-sphere pathway for the directly measured Fe(H$_2$O)$_6$$^{3+/2+}$ self-exchange reaction.

Conclusions

The analysis of a series of electron-transfer reactions between similar complexes of ruthenium, manganese, iron, and nickel in terms of the Marcus cross-relation have led to estimates of the self-exchange rate constants for the M(sar)$^{3+/2+}$ redox couples (M = Ru, Mn, Fe, Ni) that are satisfactorily interpreted in terms of known structural and kinetic data. No discrepancies were detected that indicated nonadiabatic behavior. Further insight into this problem requires direct measurements of the self-exchange rates themselves and of the temperature dependence of those rates. The classical theories of Marcus and Hush appear to hold very well for the reactions of encapsulated complexes studied so far. It is worth noting also that the largest deviations encountered involve reaction partners of labile metal–aqua systems. Such anomalies have been observed many times and specifically in ref 7, 20, and 28.

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Registry No. Ru(sar)$^{2+}$, 101482-29-5; Mn(sar)$^{2+}$, 110433-26-6; Ni(sar)$^{2+}$, 110433-27-7; Fe(sar)$^{2+}$, 110433-28-8; (NH$_3$)$_5$Ru(py)$^{3+}$, 33291-25-7; (NH$_3$)$_5$Ru(nic)$^{3+}$, 50762-76-0; (NH$_3$)$_5$Ru(isn)$^{3+}$, 46372-32-1; Ru(tacn)$_2$$^{3+}$, 110433-29-9; Ni(tacn)$_2$$^{3+}$, 86709-81-1; Ru(NH$_3$)$_6$$^{2+}$, 19052-44-9; Co(azacapten)$^{2+}$, 86161-69-5; Fe^{3+}, 20074-52-6.

Supplementary Material Available: A listing of concentrations, first-order rate constants, and experimental conditions for all reactions (Table S) (5 pages). Ordering information is given on any current masthead page.

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Syntheses and Phosphorus-31 NMR Studies of Five-Coordinate Platinum(II) Complexes of Tris(2-(diphenylphosphino)ethyl)phosphine and Monodentate Phosphorus Ligands

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Recently, five-coordinate complexes of Co(I) and Ni(II) containing tripodal tetradentate ligands and neutral P(OR)$_3$ or PR$_3$ ligands in the fifth positions have been prepared.[1,2] All of the complexes possess trigonal-bipyramidal coordination geometries, in which the tripodal ligand occupies one apical and three equatorial positions. The monodentate ligand occupies the second axial position. It has been shown that complexes of Pt(II) of tris(2-(diphenylphosphino)ethyl)phosphine, PP$_3$, have the same stereochemical properties.[3-5] Here the corresponding monophosphito and monophosphino derivatives of the types [Pt(PP$_3$)(P(OR)$_3$)]Cl$_2$ (R = Me = **1a**, R = Et = **1b**) and [Pt(PP$_3$)(PEt$_3$)]Cl$_2$ (**2**) are described, which are the first platinum(II) complexes containing five phosphorus ligands.

Experimental Section

Reagents and Chemicals. Reagent grade chemicals were used as received unless stated otherwise. Tris(2-(diphenylphosphino)ethyl)phosphine (PP$_3$) was purchased from Strem Chemical Co. Trimethyl phosphite was obtained from Fluka; triethyl phosphite and triethylphosphine were obtained from Merck-Schuchardt. Absolute methanol and absolute ethanol were also obtained from Merck-Schuchardt. Other organic solvents were of purum quality and received from Fluka. Et$_2$O was purified by conventional methods. K$_2$PtCl$_4$ was prepared from platinum metal.

Instrumentation. Fourier-mode, broad-band proton-decoupled ^{31}P NMR spectra were obtained by use of a Bruker WP-80 spectrometer. Positive chemical shifts are downfield from 85% H$_3$PO$_4$ used as external standard. Elemental analyses were obtained with a Heraeus EA 425 elemental analyzer.

Synthesis of Platinum(II) Complexes. A Schlenk apparatus and oxygen-free, dry Ar were used in the syntheses of all complexes. Solvents were degassed by several freeze–thaw–pump cycles prior to use.

[PtCl(PP$_3$)]Cl. The complex was prepared according to ref 6, however in a slightly different manner. To K$_2$PtCl$_4$ in water a solution of an equimolar amount of PP$_3$ in CH$_2$Cl$_2$ was added. Then EtOH was added under stirring until a clear orange solution was obtained. The solution was stirred for 12 h and [PtCl(PP$_3$)]Cl was isolated as described.

1a and 1b. [PtCl(PP$_3$)]Cl (0.187 g, 0.200 mmol) was dissolved in absolute MeOH or EtOH (10 mL). The solution was stirred at 273 K and an excess of P(OMe)$_3$ or P(OEt)$_3$ was added dropwise via a syringe, respectively. Immediate decoloring of the solution occurred. The solution was allowed to warm up to room temperature, and Et$_2$O was added until a white solid precipitated. After the mixtures were cooled to 243 K for several hours **1a** and **1b** were collected, washed with Et$_2$O, and dried in vacuo. **1a**: yield 0.091 g (43%); mp = 242–245 °C dec. Anal. Calcd for C$_{45}$H$_{51}$Cl$_2$O$_3$P$_5$Pt: C, 50.95; H, 4.85. Found: C, 50.8; H, 5.0. **1b**: yield 0.143 g (65%); mp = 167–169 °C dec. Anal. Calcd for C$_{48}$H$_{57}$Cl$_2$O$_3$P$_5$Pt: C, 52.3; H, 5.2. Found: C, 52.0; H, 5.4.

2. [PtCl(PP$_3$)]Cl (0.187 g, 0.200 mmol) was dissolved in absolute MeOH (10 mL). The solution was stirred at 273 K, and an excess of PEt$_3$ was added dropwise via a syringe. The color of the solution turned slightly yellowish. Et$_2$O was added to the cold solution and a yellowish solid precipitated. **2** was collected, washed with Et$_2$O, and dried under a stream of Ar: yield 0.116 g (55%); mp = 138–141 °C dec. Anal. Calcd for C$_{48}$H$_{57}$Cl$_2$P$_5$Pt: C, 54.65; H, 5.45. Found: C, 54.3; H, 5.4.

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