

sidered (Table II). It should be noted that although the AB pattern of the *p*-tolyl ring is highly resolved, the lines attributed to H<sub>5,8</sub> and H<sub>6,7</sub> are rather broad and did not show any fine structure (Figure 3). These phenomena are in good agreement with the small HOMO-LUMO energy gap of this dianion (0.18β (Table IV)). This relatively narrow energy gap is also manifested in the <sup>13</sup>C NMR of 6<sup>2-</sup>/2Na<sup>+</sup>. The <sup>13</sup>C NMR of 6<sup>2-</sup>/2Na<sup>+</sup> at 213 K in THF-*d*<sub>8</sub> gave the expected eight bands in the range of 164–100 ppm. At 273 K only seven bands were detected after a short accumulation. Accumulation of 1000–2000 scans enabled us to observe the eight lines which appear as broad ones. These phenomena can be rationalized in terms of local paramagnetic contributions in the region of the high charge density. Such a contribution may cause line broadening of <sup>1</sup>H and <sup>13</sup>C NMR bands and in extreme cases may even lead to a total disappearance of these lines.

## Conclusions

A new class of dianions derived from polycyclic systems containing two nitrogen atoms has been prepared and its NMR parameters were determined. The resulting dianions are, as expected, paratropic and show moderate stability. From calculations and carbon NMR spectroscopy it is concluded that a significant portion of the charge resides on the nitrogen atoms. The charging experiments were carried out with sodium and lithium, and the spectra were measured at various temperatures. The temperature-dependent spectra of the lithium and the sodium salts contradict the trend expected due to the ion-solvation equilibrium. A different mode of bonding is suggested for the lithium and the sodium salts, viz., a covalent contribution to the structure of the lithium salts vs. an ionic nature of the sodium salts.

## Experimental Section

**Materials.** The benzo[*c*]cinnoline **3** was purchased from Aldrich Co. and used without further purification. Dibenzo[*a,c*]phenazine (**4**) and the quinoxaline derivatives **5** and **6** were prepared from the corresponding diamine and dicarbonyl compounds according to the following general procedure (as demonstrated for dibenzo[*a,c*]phenazine (**4**)): A mixture of 1 mmol of 9,10-phenanthrenequinone, 1 mmol of orthophenylenediamine, and a catalytic amount of HCl in 20 mL of ethanol was placed in a 50-mL flask equipped with a reflux condenser. The mixture was heated to reflux for 2 h with magnetic stirring. The precipitate was collected on a Büchner funnel. The resulting solid was crystallized from EtOH/CHCl<sub>3</sub>.

**Dibenzo[*a,c*]phenazine (4):** light brown needles, mp 223–224 °C (lit.<sup>20</sup> 227–228 °C); <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 8.21, 7.62 (*J*<sub>1</sub> = 7.8, *J*<sub>2</sub> = 1.5, 2 H), 8.53 (dd, *J*<sub>1</sub> = 7.7, *J*<sub>2</sub> = 1.5, 2 H), 8.38, 7.84 (AA'BB', 4 H), 7.75 (m, 4 H); <sup>13</sup>C NMR (THF) δ 141.9, 141.8, 131.7, 130.0, 129.8, 129.2, 129.0, 127.6, 125.7, 122.5. Anal. Calcd for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>: C, 85.69; H, 4.31; N, 10.0. Found: C, 85.93; H, 4.24; N, 10.16.

**2,3-Di-*p*-tolylbenzo[*g*]quinoxaline (5):** yellow needles, mp 197–198 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.76 (s, 2 H), 8.21, 7.62 (AA'BB', 4 H), 7.60, 7.23 (AB, 8 H), 2.44 (s, 6 H); <sup>13</sup>C NMR (THF) δ 154.4, 139.2, 138.7, 137.6, 134.6, 130.4, 129.0, 129.0, 127.7, 126.8, 20.9. Anal. Calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.35; H, 5.98; N, 7.47.

**2,3-Di-*p*-tolylquinoxaline (6):** light brown needles, mp 145–146 °C; <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 8.16, 7.82 (AA'BB', 4 H), 7.54, 7.21 (AB, 8 H), 2.42 (s, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.5, 141.2, 138.7, 136.5, 129.7, 129.6, 129.2, 129.0, 21.3. Anal. Calcd for C<sub>22</sub>N<sub>18</sub>N<sub>2</sub>: C, 85.1; H, 5.84; N, 9.02. Found: C, 84.84; H, 5.54; N, 9.23.

**General Procedure for Metal Reduction Process.** Lithium, sodium wire, or potassium chips are introduced to the upper part of an extended NMR tube containing the polyheterocyclic compound, dissolved in THF-*d*<sub>8</sub> or DME-*d*<sub>10</sub> (Aldrich). The frozen solution was degassed and sealed under vacuum. The solution was brought into contact with the metal solution by turning the tube upside down.

**Quenching of the Anions.** All anions were quenched with oxygen. The quenching experiments were carried out by bubbling oxygen gas into the NMR sample under anhydrous conditions. Oxygen gas is bubbled via a syringe into the anion solution at a slow rate at –78 °C. The deep color disappears and the <sup>1</sup>H NMR of the solution is then recorded. In each case the only product observed was the starting material.

In one case a quench experiment was carried out with methyl bromide. To the anion of **3** was bubbled methyl bromide at –78 °C. The product was analyzed by CI mass spectrometry. The appearance of the *m/e* 211 is a proof of the dianionic nature of 3<sup>2-</sup>.

The NMR spectra were obtained on Bruker WH-300 pulsed FT spectrometer operating at 300.133 and 75.46 MHz for <sup>1</sup>H and <sup>13</sup>C NMR, respectively. The field/frequency regulations were maintained by <sup>2</sup>H locking. The free induction decay signals were digitalized and accumulated on an Aspect-2000 computer (32K).

**Registry No.** **3**, 230-17-1; 3<sup>2-</sup>, 94370-25-9; 3-2Li, 94370-20-4; 3-2Na, 94404-04-3; **4**, 215-64-5; 4<sup>2-</sup>, 94370-26-0; 4-2Na, 94370-21-5; **5**, 94370-19-1; 5<sup>2-</sup>, 94404-05-4; 5-2Li, 94370-22-6; 5-2Na, 94370-23-7; **6**, 3719-84-4; 6<sup>2-</sup>, 94370-27-1; 6-2Na, 94370-24-8; 9,10-phenanthrenequinone, 84-11-7; *o*-phenylenediamine, 95-54-5; lithium, 7439-93-2; sodium, 7440-23-5; oxygen, 7782-44-7; methyl bromide, 74-83-9; potassium, 7440-09-7.

(20) Hall, D. M.; Huaun-Yong, H.; Bhanthumnavin, B. *J. Chem. Soc. Perkin Trans. 2* 1973, 2131.

# Mn(CNR)<sub>6</sub><sup>+2+</sup> Electron Self-Exchange in Acetonitrile. A Possible Distance Dependence for a Bimolecular Electron-Transfer Reaction in Solution

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**Abstract:** The electron self-exchange of Mn(CNR)<sub>6</sub><sup>+2+</sup> has been measured, for five alkyl R groups by <sup>55</sup>Mn NMR, as a function of concentration, temperature, and added *n*-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub>. The results (0.1 M *n*-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub>, 26 °C) are the following: R = CH<sub>3</sub>, *k* (M<sup>-1</sup> s<sup>-1</sup>) = 2.06 × 10<sup>7</sup>, Δ*H*<sup>‡</sup> (kcal/mol) = 1.79, Δ*S*<sup>‡</sup> = –19.5 cal/mol-deg; CH<sub>3</sub>CH<sub>2</sub>, 1.97 × 10<sup>6</sup>, 3.61, –17.7; (CH<sub>3</sub>)<sub>2</sub>CH, 2.61 × 10<sup>5</sup>, 4.85, –17.7; (CH<sub>3</sub>)<sub>3</sub>C, 6.51 × 10<sup>4</sup>, 5.38, –18.5; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, 1.30 × 10<sup>6</sup>, 1.97, –24.0. All rate constants increase with ionic strength. The data are analyzed in terms of a current semiclassical theory of electron transfer by estimating precursor complex formation constants and inner-sphere and outer-sphere reorganization energies. It is concluded that, within the assumptions, the rate variation is due to a decrease in electron-transfer rate constant with distance. The possibility, more consistent with the activation parameters, that the rate variation arises from a decrease in the precursor complex stability due to a requirement to attain a common, short electron-transfer distance, is also discussed.

The study of the electron-transfer reactions of transition metal complexes has been an especially active field in recent years

because improved theoretical treatments and refined experimental work have developed cooperatively.<sup>1-4</sup> This is especially apparent

Table I. Kinetic Parameters for  $\text{Mn}(\text{CNR})_6^{+2+}$ 

R	$k$ ( $\text{M}^{-1} \text{s}^{-1}$ ) (26 °C, 0.1 M $\text{Bu}_4\text{NBF}_4$ )	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (cal/mol-deg)	result of fit to the ionic strength dependence data	
				$k_\infty$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$r_\mu$ (Å)
$\text{CH}_3$	$2.06 \pm 0.27 \times 10^7$	$1.79 \pm 0.10$	$-19.5 \pm 1.5$	$9.24 \pm 0.17 \times 10^7$	8.75
$\text{CH}_2\text{CH}_3$	$1.97 \pm 0.06 \times 10^6$	$3.61 \pm 0.16$	$-17.7 \pm 2.6$	$9.01 \pm 0.54 \times 10^6$	8.50
$\text{CH}(\text{CH}_3)_2$	$2.61 \pm 0.09 \times 10^5$	$4.85 \pm 0.10$	$-17.7 \pm 1.0$	$8.04 \pm 0.41 \times 10^5$	10.25
$\text{C}(\text{CH}_3)_3$	$6.51 \pm 0.12 \times 10^4$	$5.38 \pm 0.10$	$-18.5 \pm 1.3$	$2.03 \pm 0.11 \times 10^5$	10.25
$\text{C}_6\text{H}_{11}^a$	$4.38 \pm 0.07 \times 10^5$	$3.36 \pm 0.10$	$-21.4 \pm 1.0$	$1.34 \pm 0.08 \times 10^6$	11.00
$\text{CH}_2\text{C}_6\text{H}_5$	$1.30 \pm 0.02 \times 10^6$	$1.97 \pm 0.26$	$-24.0 \pm 2.2$	$5.22 \pm 0.34 \times 10^6$	9.25

<sup>a</sup> From ref 12, 0.08 M  $\text{Bu}_4\text{NBF}_4$ .

with regard to predictions and observations of the distance dependence of electron-transfer efficiency.<sup>3</sup> Experimentally, the question arises often. In biological electron transport, metal ion oxidation-reduction centers are separated by significantly larger distances than occur for the typically studied coordination complexes. In such cases, there is also a significant question of the involvement of the medium, which can be peptide, membrane, or vacuum, as well as solvent, along with the distance problem.<sup>5-7</sup> Distance dependences are experimentally measurable with some precision for bimetallic complexes, for which photoelectron transfer is often observed as an intervalence absorption band,<sup>8</sup> and in the radiation chemistry of complexes or organic molecules in solution or rigid matrices.<sup>9-11</sup>

We have chosen the  $\text{Mn}^{\text{I}}$  hexakis(alkyl isocyanide) system for detailed study for several reasons. First, it is experimentally tractable in that a variety of highly symmetric complexes can be made, all are substitution inert in their oxidized and reduced forms, and the electron self-exchange process can be followed readily by  $^{55}\text{Mn}$  NMR.<sup>12,13</sup> Second, despite the inherent structural ambiguities in interpreting a bimolecular system compared to the elegant bimetallic complexes, we believe it is important to study bimolecular thermal chemistry both as a test of the electron-transfer theories and as a test of theories of bimolecular solution reactions in general. Third, it is important to test the theory on self-exchange reactions, reactions with no thermodynamic driving force. Much of what is studied to obtain distance-dependence information is from systems with large free-energy differences between reactants and products, as in the photoelectron transfer systems and the radiation chemistry examples. There is a significant debate about the reaction free-energy dependence of electron-transfer efficiency, especially at high driving forces, and this complication is avoided in treating self-exchange reactions. In addition, there are fewer parameters to consider in the theory of self-exchange reactions since the reactants and products are identical. Electron transfer at constant electrochemical potential is also important for many natural and artificial electron-transport systems. When electron-transfer mediators are needed, whether in an artificial photosynthesis cell or between cytochrome *c* and cytochrome *c* oxidase, it is important that the mediator give up an electron at the potential it receives it and not waste energy just to force the electron-transfer reaction to be faster.

This work continues from ref 12 which presented solvent, temperature, and added electrolyte studies of the  $\text{Mn}(\text{CNC}_6\text{H}_{11})_6^{+2+}$  self-exchange.

### Experimental Section

The isocyanides were prepared from the corresponding formamides using slight variations of literature methods.<sup>14,15</sup> The formamides were prepared from the amine and ethyl formate except for *N*-methylformamide which was purchased from Aldrich.

The hexakis(alkyl isocyanide) $\text{MnI}_3$  complexes were made as previously described.<sup>12</sup> These were converted to the tetrafluoroborate form using the anion exchanger Dowex 1-X8 from Bio-Rad in acetonitrile. The powder resulting from evaporation to dryness was recrystallized from hot ethanol-water, except for the methyl isocyanide and benzyl isocyanide complexes which were recrystallized from hot acetonitrile-water and hot acetone, respectively.

The hexakis(alkyl isocyanide) $\text{Mn}(\text{BF}_4)_2$  complexes were made by dissolving the corresponding  $\text{Mn}(\text{I})$  salt in acetonitrile with an excess of fluoroboric acid (Aldrich), and then bubbling with chlorine gas for 5 min. The resulting solution was evaporated nearly to dryness and ethyl ether was added to induce precipitation. The precipitate was recrystallized from acetone-ether except for the methyl isocyanide complex which was recrystallized from acetonitrile-ether.

All solids were stored on solid carbon dioxide. This was especially necessary for the  $\text{Mn}(\text{II})$  complexes. All complexes were stable for at least 8 weeks when stored this way. Analytical data for the complexes was obtained from the University of Idaho C, H, & N Analytical Facility and Galbraith Laboratories. The analytical data obtained are available as supplementary material. Other physical properties, including  $^{13}\text{C}$ ,  $^{14}\text{N}$ , and  $^1\text{H}$  NMR, magnetic susceptibility, Raman, infrared, and EPR properties have also been measured and will be presented and discussed in another publication.<sup>16</sup>

Acetonitrile was dried by distillation from  $\text{P}_2\text{O}_5$ . The tetra-*n*-butylammonium tetrafluoroborate was prepared as previously described.<sup>17</sup>

Conductivity studies on  $\text{Mn}(\text{CNCH}_3)_6\text{BF}_4$  were performed and analyzed as previously described.<sup>12</sup> NMR measurements were made<sup>12</sup> with a Nicolet NT200WB instrument operating at 49.52 MHz and using 12-mm sample tubes. The Fourier transformed NMR data were fit to a single Lorentzian using a least-squares program available on the Nicolet instrument. Typically 150 to 200 points above the base line were used in the fit. The NMR measurements involving the  $\text{Mn}(\text{I})$ - $\text{Mn}(\text{II})$  mixtures were performed as rapidly as possible because of the instability of the  $\text{Mn}(\text{II})$  complexes. A sample (5 mL) containing only the  $\text{Mn}(\text{I})$  complex and the  $\text{Bu}_4\text{NBF}_4$  was first allowed to reach temperature equilibrium in the probe, and its spectrum was obtained. The sample was removed, a 1- to 250- $\mu\text{L}$  quantity of a freshly prepared solution of the  $\text{Mn}(\text{II})$  complex was added, and the sample tube was quickly shaken and returned to the probe. Data collection proceeded immediately with five data sets of 1000 pulses each acquired. These data sets were processed independently and the line widths compared. It was found that a constant width was obtained, within 2%, after two data sets were acquired. The last three widths were then averaged. This method resulted in measurements being made on solutions which were less than 15 min old. Decomposition was considered negligible.

Fitting of the rate equations to the line-width data was done using a Cromemco Z80 system running Fortran and weighted least-squares programs, including error in both axes for the concentration-dependence plots.<sup>18,19</sup>

- (1) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441-98.
- (2) *Faraday Discuss. Chem. Soc.* **1982**, *74*.
- (3) Chance, B.; DeVault, D. C.; Frauenfelder, H.; Marcus, R. A.; Schrieffer, J. R.; Sutin, N., Eds. "Tunneling in Biological Systems"; Academic Press: New York, 1979.
- (4) Cannon, R. D. "Electron Transfer Reactions"; Butterworths: London, 1980.
- (5) Kostic, N. M.; Margalit, R.; Che, C.-M.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 7765-67.
- (6) Winkler, J. R.; Nocera, D. G.; Yocum, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798-800.
- (7) Isied, S. S.; Worosila, G.; Atherton, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 7659-61.
- (8) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1-73.
- (9) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670-71.
- (10) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746-56.
- (11) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579-95.
- (12) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 1338-44.
- (13) Matteson, D. S.; Bailey, R. A. *J. Chem. Soc.* **1969**, *91*, 1975-80.

(14) Schuster, R. E.; Scott, J. E.; Casanova, J., Jr. "Organic Syntheses"; Collect Vol V; Wiley: New York, **1973**, pp 772-4.

(15) Appel, R.; Kleinstick, R.; Ziehn, K. D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 132.

(16) Nielson, R. M.; Wherland, S. *Inorg. Chem.*, in press.

(17) Borchardt, D.; Pool, K.; Wherland, S. *Inorg. Chem.* **1982**, *21*, 93-97.

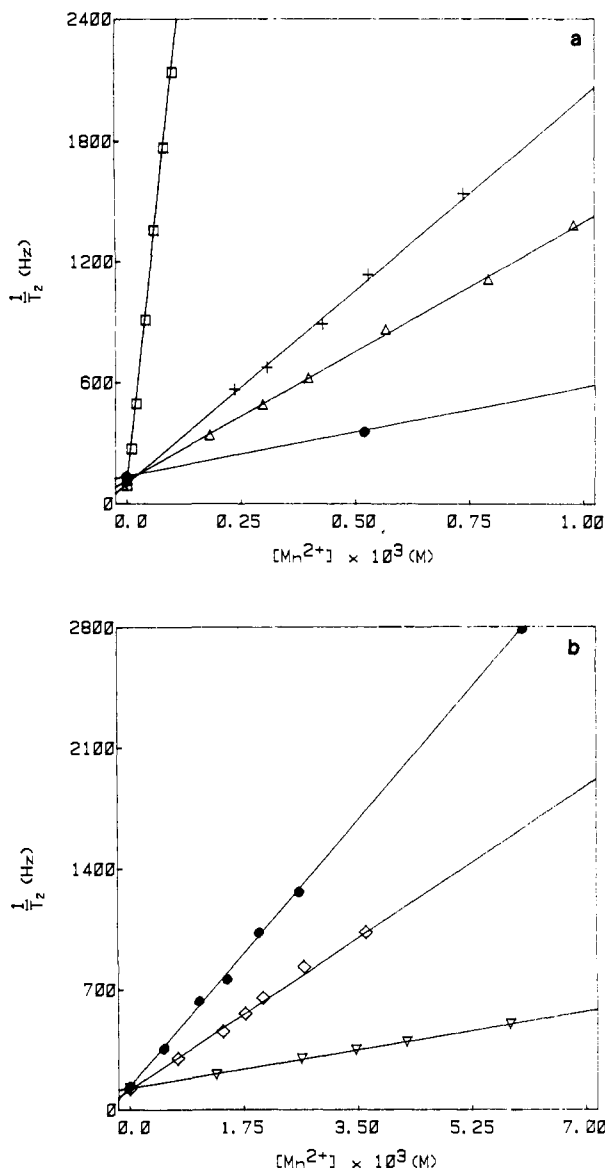


Figure 1. (a, b) Dependence of  $1/T_2$  on the concentration of  $\text{Mn}(\text{CNR})_6(\text{BF}_4)_2$  at 26 °C, 0.10 M  $\text{Bu}_4\text{NBF}_4$ , in  $\text{CH}_3\text{CN}$ : ( $\square$ ) R = methyl, (+) ethyl, (O) isopropyl, ( $\nabla$ ) *tert*-butyl, ( $\bullet$ ) cyclohexyl (ref 12), ( $\Delta$ ) benzyl.

### Results and Calculations

The rate of the electron-exchange process, eq 1, was obtained



from <sup>55</sup>Mn NMR line widths, using eq 2a and 2b, as previously

$$k = (1/[\text{MnL}_6^{2+}])(1/T_{2P} - 1/T_{2D}) \quad (2a)$$

$$1/T_2 = \pi\Delta\nu \quad (2b)$$

described.<sup>12</sup>  $T_{2P}$  is the apparent spin-spin relaxation time of a mixture of the diamagnetic  $\text{MnL}_6^+$  and the low-spin paramagnetic  $\text{MnL}_6^{2+}$ ,  $T_{2D}$  is for the  $\text{MnL}_6^+$  complex alone, and  $\Delta\nu$  is the full width at half-height of the fit Lorentzian line.

Supplementary tables give the experimental conditions and line widths for all measurements.

Adherence to eq 2 is shown in the concentration dependences plotted in Figure 1. Table I includes the second-order rate constants derived from these plots. The Eyring plots of the temperature dependence data are shown in Figure 2, and the  $\Delta H^\ddagger$

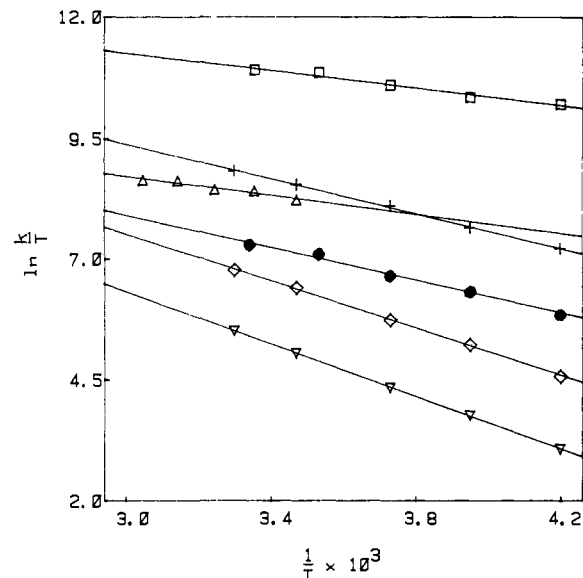


Figure 2. Eyring plots of the temperature dependences in  $\text{CH}_3\text{CN}$  and 0.10 M  $\text{Bu}_4\text{NBF}_4$ : ( $\square$ ) methyl, (+) ethyl, ( $\diamond$ ) isopropyl, ( $\Delta$ ) *tert*-butyl, ( $\bullet$ ) cyclohexyl (ref 12), ( $\Delta$ ) benzyl.

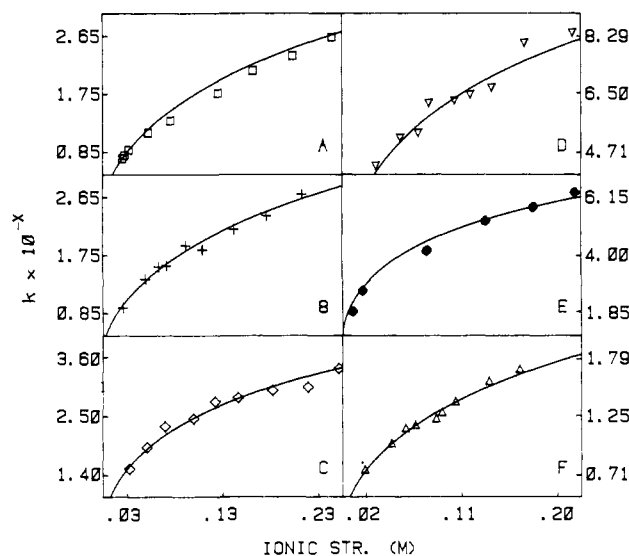


Figure 3. Dependence of the observed rate,  $k$ , on the ionic strength of the medium. The solid lines are the fits to eq 3: (A) methyl,  $x = 7$ ; (B) ethyl,  $x = 6$ ; (C) isopropyl,  $x = 5$ ; (D) *tert*-butyl,  $x = 4$ ; (E) cyclohexyl (ref 12),  $x = 5$ ; (F) benzyl,  $x = 6$ .

and  $\Delta S^\ddagger$  derived are given in Table I. The concentration and temperature-dependence data are for the condition of 0.10 M added  $\text{Bu}_4\text{NBF}_4$ . Figure 3 shows the dependence of the rate on the ionic strength of the medium.

These results can be compared with the earlier work of Matteson and Bailey<sup>13</sup> on the ethyl and *tert*-butyl isocyanide complexes. They obtained second-order rate constants, at 7 °C ( $\text{M}^{-1}\text{s}^{-1}$ ), enthalpy (kcal/mol), and entropy of activation (cal/mol-deg) of  $6.4 \times 10^5$ , 1.7, and  $-21$ , respectively, for the ethyl isocyanide complex, and  $4.0 \times 10^4$ , 4.6,  $-21$ , respectively, for the *tert*-butyl isocyanide complex. These experiments were performed using acetonitrile as the solvent, and with no added salt but higher concentrations of the manganese complexes. The rate constants and activation parameters are in quite reasonable agreement especially considering the instability of the  $\text{Mn}(\text{CNCH}_2\text{CH}_3)_6^{2+}$  complex and the longer time the Matteson and Bailey experiments required.

Conductivity measurements on  $\text{Mn}(\text{CNCH}_3)_6\text{BF}_4$  were performed to establish the extent of ion pairing in acetonitrile. The derived association constant is  $8.1 \times 10^{-4} \text{ M}^{-1}$ . The conductivity data are available in the supplementary material.

(18) Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969.

(19) Irvin, J. A.; Quickenden, T. I. *J. Chem. Educ.* 1983, 60, 711-12.

**Table II.** Symmetrical Stretching Frequencies and Derived  $\Delta G_{in}$ 

R	$Mn(CNR)_6BF_4$		$Mn(CNR)_6(BF_4)_2$		$\Delta G_{in}$ (kcal/mol)
	$\bar{\nu} \pm 2$ cm <sup>-1</sup>	$f_r$ (mdyn/Å)	$\bar{\nu} \pm 2$ cm <sup>-1</sup>	$f_o$ (mdyn/Å)	
CH <sub>3</sub>	292	2.06	270	1.76	0.56
CH <sub>2</sub> CH <sub>3</sub>	267	2.31	231	1.73	0.59
CH(CH <sub>3</sub> ) <sub>2</sub>	225	2.06	200	1.63	0.54
C(CH <sub>3</sub> ) <sub>3</sub>	196	1.88	170	1.42	0.48
C <sub>6</sub> H <sub>11</sub>	173	1.93	183	2.15	0.60
CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	190	2.49	1,1	2.26	0.70

### Discussion

The observed rate constants vary by more than a factor of 300 decreasing with increasing bulk in the order methyl > ethyl > isopropyl > *tert*-butyl. The cyclohexyl isocyanide complex has a rate constant between isopropyl and *tert*-butyl, indicating a greater sensitivity to substitution at the carbon nearest the C≡N group than at carbons further removed. The benzyl isocyanide complexes exchange electrons even more rapidly than the ethyl isocyanide complexes; thus the phenyl group enhances the rate slightly compared with a methyl substituent. This last observation is counter to a simple steric argument.

The qualitative observation of a decrease in electron-transfer rate constant with increasing ligand size can be compared to several other studies. The most complete series has been studied by Brown and Sutin<sup>20</sup> and includes Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup>, Ru(NH<sub>3</sub>)<sub>4</sub>(bpy)<sup>3+/2+</sup>, Ru(NH<sub>3</sub>)<sub>2</sub>(bpy)<sub>2</sub><sup>3+/2+</sup>, and Ru(bpy)<sub>3</sub><sup>3+/2+</sup> (bpy = bipyridyl). In this series the logarithm of the carefully estimated self-exchange rate constant decreases linearly with 1/*r*, where *r* is the mean distance of closest approach, by five orders of magnitude. This is the pattern expected if the solvent reorganization and the electrostatic work to form the precursor complex are rate controlling (vide infra). No contribution from decreased adiabaticity or electron-transfer efficiency with distance was required. An important point in this study is that the increased size was accomplished by replacing ammonia with the conjugated bipyridyl ligands which may facilitate electron transfer of the  $\pi$  symmetry electrons involved. The reduction of Co(ethanediamine)<sub>3</sub><sup>3+</sup> by a variety of reagents occurred at virtually the same rate as the reduction of the similar complex with the cyclohexanediamine ligand.<sup>21</sup> The substitution of cyclohexanedione dioxime for dimethylglyoxime increases the rate of reduction by ferrocene of the cobalt clathrochelate made from this ligand.<sup>22</sup> The measured self-exchange rate constants for a series Fe(phenanthroline)<sub>3</sub><sup>3+/2+</sup> complexes show little correlation with size. The addition of methyl groups to the periphery of the ring increases the rate constant, but the addition of a cyclohexyl group significantly decreases the rate, and substitution by a phenyl makes no difference.<sup>23</sup> There may be a delicate balance here of the effects of increasing size on the electrostatic work and outer-sphere reorganization terms and the orbital overlap. Alternatively, it may be that substitution out on the far edge of the large phenanthroline ligand makes little difference to electron transfer because the interligand spaces are still available and allow close enough approach to attain quite adequate orbital overlap. The measured self-exchange rate constants for various ferrocenes<sup>24</sup> and chromium arene<sup>25</sup> complexes show little dependence on the size of the ring, but here, as in the ethanediamine-cyclohexanediamine comparison mentioned above, the substitution makes one dimension increase but leaves an axial approach unaffected.

Further interpretation must rely on comparisons with theoretical predictions. Within current electron-transfer theory,<sup>1-4</sup> the rate

**Table III.** Estimated Radii and Electron-Transfer Theory Parameters

R	$r_{min}$ (Å)	$r_{max}$ (Å)	$\Delta G_{out}^a$ (kcal/mol)	$P^b$	$A$
CH <sub>3</sub>	2.8	5.6	1.36	0.05	$5.1 \times 10^{10}$
CH <sub>2</sub> CH <sub>3</sub>	3.1	6.8	1.00	0.06	$2.3 \times 10^9$
CH(CH <sub>3</sub> ) <sub>2</sub>	3.5	6.8	1.16	0.07	$1.9 \times 10^8$
C(CH <sub>3</sub> ) <sub>3</sub>	4.0	6.8	1.35	0.10	$4.7 \times 10^7$
C <sub>6</sub> H <sub>11</sub>	3.8	8.3	0.82	0.09	$1.7 \times 10^8$
CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3.5	7.6	0.91	0.07	$1.1 \times 10^9$

<sup>a</sup> Calculated from eq 11:  $a = r_{max} + r_{min}$ ;  $b = r_{max}$ ;  $r = 2r_{min}$ .  
<sup>b</sup> Taking  $\delta r$  as 0.8 Å (Rosseinsky, D. R. *Comments Inorg. Chem.* **1984**, *3*, 153-170).

of a bimolecular electron-transfer process is treated as a three-step mechanism: formation of a precursor complex, electron transfer to give the successor complex, and separation of the successor complex into products. We will assume that the formation of the precursor complex can be represented as a pre-equilibrium; thus<sup>26</sup>

$$k = K_a k_{et} \quad (3)$$

This discussion is concerned with estimating contributions to  $K_a$  and  $k_{et}$  in order to investigate the origin of the rate variation observed. Note that in this treatment,  $k_{et}$  is a unimolecular rate constant.

The formation of the precursor complex involves the assembly of the reactants in the geometry appropriate for electron transfer. The value of  $K_a$  can be estimated from:

$$K_a = P e^{-w/RT} \quad (4)$$

$$P = 4\pi N r^2 \delta r / 1000 \quad (5)$$

$$w = \frac{Z_1 Z_2 e^2}{\epsilon r (1 + \beta r_\mu)} \quad (6)$$

$$\beta = (8\pi N e^2 / 1000 \epsilon RT)^{1/2} \mu^{1/2} \quad (7)$$

The value of the Mn-Mn distance in the precursor complex (*r*) was estimated using CPK space-filling models and fitting them tightly together in a face-to-face geometry with the ligands in an optimal conformation and staggered. Table III lists half of the Mn-Mn distance so obtained as  $r_{min}$ , and the values of *P* calculated.

The contributions from the electrostatic work terms were estimated by fitting the ionic strength dependence data using eq 3-7. The ionic strength ( $\mu$ ) was calculated assuming partial dissociation of the electrolyte Bu<sub>4</sub>NBF<sub>4</sub>,<sup>12</sup> and the manganese complexes were assumed not to be ion paired, as indicated by the conductivity results. In the fitting procedure,  $r_\mu$  and  $k_\infty$  were variable parameters. The  $k_\infty$  value is the rate extrapolated to infinite ionic strength where there is no electrostatic work. We choose to estimate the contribution from the electrostatic work in this way since the extrapolation is not large and it does not rely too heavily on the precision of the equations, which are based on Debye-Hückel theory and thus probably are not especially accurate at the ionic strengths and the dielectric constant of the experiments. The fit values of  $r_\mu$  and  $k_\infty$  are given in Table I and the ionic-strength-dependence data and fit lines are shown in Figure 3. The fit is not especially sensitive to  $r_\mu$ , which should be approximately the anion-cation distance, but the trend in these values is consistent with the complexes increasing in effective size with increased ligand bulk.

The effect of correcting for electrostatic work is to increase all of the rate constants by a factor of from 3 to 5. Thus in the absence of electrostatic work, the range of rate constants is virtually

(20) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883-92.

(21) Beattie, J. K.; Bunstead, R. A.; Broccardo, M. *Inorg. Chem.* **1978**, *17*, 1822-26.

(22) Borchardt, D.; Wherland, S. *Inorg. Chem.*, submitted.

(23) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542-9.

(24) Yang, E. S.; Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094-9.

(25) Toni, T. T. L.; Weaver, M. J.; Brubaker, C. H., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2381-6.

(26) The symbols are: *R*, gas constant; *T*, absolute temperature; *Z*<sub>1</sub> and *Z*<sub>2</sub>, reactant charges; *e*, charge on the electron; *N*, Avogadro's number;  $\epsilon$ , solvent dielectric constant; *n*<sub>l</sub>, number of ligands; *f*<sub>o</sub> and *f*<sub>r</sub>, force constants for the totally symmetric mode of the oxidized and reduced complexes; *c*, speed of light; *a* and *b*, major and minor radii of the elliptical transition state; *n*, solvent index of refraction; *P*<sub>1</sub> and *Q*<sub>1</sub>, Legendre polynomials of the first and second kind.

unchanged. Similarly the calculated values of  $P$  cover a range of about a factor of 2 and are not the source of the large variation in  $k$ . However, this treatment only considers the electrostatic work and relies on the radius estimates. If there is significant non-electrostatic work, and especially if the precursor complexes formed from the bulkier ligands have significant steric strain caused by distorting the ligands in order to attain short Mn–Mn distances, the precursor complex formation constant could be much smaller for the bulkier complexes. This possibility could explain the entire effect on  $k$ , and is discussed further below in comparison with another interpretation.

Using a semiclassical electron-transfer theory in the high-temperature limit,<sup>1</sup> the electron-transfer rate constant can be expressed by eq 8, and the activation energies  $\Delta G_{in}$  and  $\Delta G_{out}$  by eq 9–13.

$$k_{et} = Ae^{-(\Delta G_{in} + \Delta G_{out})/RT} \quad (8)$$

$$\Delta G_{in} = \frac{1}{2} \left( \frac{n_L}{2} \left( \frac{f_{of}}{f_o + f_r} \right) \right) \Delta d^2 \quad (9)$$

$$f = 4\pi^2 \bar{\nu}^2 c^2 m / N \quad (10)$$

$$\Delta G_{out} = \left( \frac{e^2 r^2}{2a^2 b} \right) \left( \frac{1}{n^2} - \frac{1}{\epsilon} \right) T(\lambda) \quad (11)$$

$$T(\lambda) = \sum_{l=1,3,5,\dots}^{\infty} (2l+1)(\lambda)(\lambda^2-1) \frac{Q_l(\lambda)}{P_l(\lambda)} \quad (12)$$

$$\lambda^2 = a^2 / (a^2 - b^2) \quad (13)$$

The inner-sphere reorganization energy,  $\Delta G_{in}$ , is the energy required to distort the coordination spheres to a common energy state. It is calculated based on the measured symmetrical breathing mode frequencies in Table II, converted to force constants using eq 10 and the assumption that  $m$  is the ligand mass. The difference in metal ligand bond length ( $\Delta d$ ) between the oxidized and reduced forms of the complex is not known, but it can be estimated as 0.037 Å from the isoelectronic system CrL<sub>6</sub><sup>+</sup>/CrL<sub>6</sub><sup>0</sup> where L is phenyl isocyanide.<sup>27</sup> The inner-sphere reorganization energies so calculated vary little, as shown in Table II.

The outer-sphere reorganization energy involves solvent reorientation prior to electron transfer. Equations 11–13 are for an elliptical transition state and are due to Cannon.<sup>28</sup> The radii used are described in Table III. The value of  $r_{max}$  was estimated from the molecular model as the distance from the Mn to the ligand periphery. The variation of  $\Delta G_{out}$  is greater than in the inner-sphere reorganization, but it is still small and does not parallel the trend in  $k$ ; thus it is not the principal origin of the variation in  $k$ .

The  $A$  term of eq 8 remains to be discussed. As shown in eq 14, this term is rather complex. Combining the previous estimates

$$A = \nu_{n,eff} \kappa_{el} S(r,\theta) \quad (14)$$

for  $P$ ,  $k$ ,  $\Delta G_{in}$ , and  $\Delta G_{out}$ , the apparent value of  $A$  can be calculated and is given in Table III. The value of the effective nuclear frequency,  $\nu_{n,eff}$ , is essentially constant. The steric factor,  $S(r,\theta)$ , has a value of 1 for spherical reactants and decreases if specific orientation is required to form the precursor complex. It is thus a correction to the spherical reactant assumption used in the formula for the  $P$  term. From inspection of the space-filling models, it is clear that, by selecting specific orientations and conformations, the ligands of the two complexes can be fit together and provide a relatively short electron-transfer distance without inducing significant steric interaction. Thus  $P(r,\theta)$  is certainly less than 1 and greater than 0.01. This value is not expected to vary a great deal between complexes since all have similar structures. This leaves  $\kappa_{el}$ , the electronic transmission coefficient,

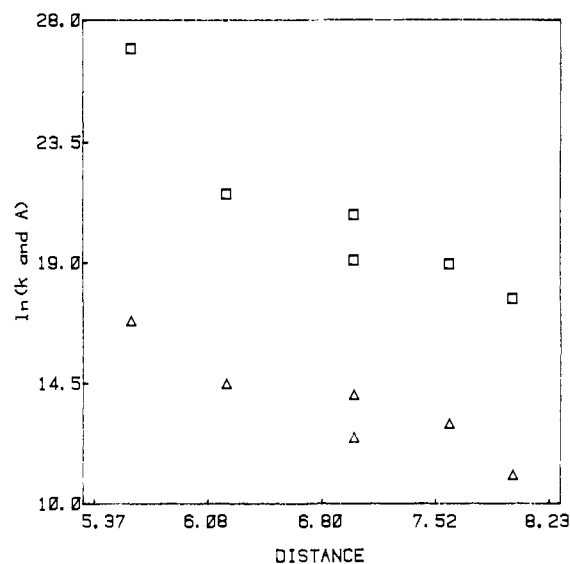


Figure 4. Plot of  $\log k$  ( $\Delta$ ) and  $\log A$  ( $\square$ ) vs. the electron-transfer distance in Ångströms ( $r$ ). Data are from Tables I and III.

as the factor which is primarily associated with the variation in electron-transfer efficiency, under the assumptions of the calculations. This transmission coefficient varies from 1 for purely adiabatic reactions to small values for nonadiabatic reactions. The equations for  $\kappa_{el}$ , which have been evaluated, are presented by Sutin.<sup>1</sup> Its distance dependence can be crudely approximated as an exponential due to donor–acceptor orbital overlap, and this is adequate for the current discussion. Figure 4 shows that the observed rate constants as well as the calculated value of  $A$  decrease roughly exponentially with  $r$ . The variation is similar to that predicted and observed in several systems with known electron-transfer distance.<sup>9–11,28–31</sup> Thus, this treatment of the data indicates that the rate variation is due to an electron-transfer distance effect. In considering the actual distance involved, it should be emphasized that the donor and acceptor orbitals are delocalized onto the C≡N atoms by back bonding, and thus the Mn–Mn distance is an overestimate of the distance actually involved.

The activation parameters remain to be discussed. They show an essentially constant  $\Delta S^\ddagger$  and a significant variation in  $\Delta H^\ddagger$ . These parameters cannot be factored into the various contributions, as was done for the overall activation energy, with any confidence. The theory used above has been much more successful in correlating overall rate constants than the activation parameters.<sup>32</sup> This is probably because of the difficulty in estimating the enthalpy and entropy of precursor complex formation. However, the general trend in the activation parameters is consistent with the rate variation being due to a progressive increase in the enthalpy of precursor complex formation for the bulkier complexes. This would be due to increased distortion of the ligands required to attain a minimum electron-transfer distance. If the variation in the  $A$  term were the only change, then the activation entropy should have become more negative for the bulkier complexes.

The reactivity of the benzyl isocyanide complex deserves special consideration. Molecular orbital calculations and physical measurements on the complexes indicates that, despite the methylene group, there is some interaction between the M–C≡N orbitals and the phenyl ring.<sup>16</sup> The higher reactivity, considered as  $k$ ,  $k_{obs}$ , or  $A$ , relative to its rather large size, could be due to enhanced overlap arising from the delocalized donor/acceptor orbitals. It could also be due to enhanced precursor complex stability due to stacking interactions or intertwining of the benzyl ligands. Again, the activation parameters indicate the latter since

(27) Bohling, D. A.; Mann, K. R. *Inorg. Chem.*, in press.  
 (28) Cannon, R. D. *Chem. Phys. Lett.* **1977**, *49*, 299–304.

(29) Anderes, B.; Lavallee, D. K. *Inorg. Chem.* **1983**, *22*, 2665–66.  
 (30) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640–4.  
 (31) Jortner, J. J. *J. Chem. Phys.* **1976**, *64*, 4860–7.  
 (32) Weaver, M. T.; Yee, E. L. *Inorg. Chem.* **1980**, *19*, 1936–45.

$\Delta H^*$  and  $\Delta S^*$  are both decreased compared with the other complexes of similar size.

In conclusion, the series of  $\text{Mn}(\text{CNR})_6^{+/2+}$  complexes considered shows a significant variation in electron self-exchange rate constant which correlates with the steric bulk of the complexes. There are two likely explanations for this. Dissection of the activation energy into contributions for precursor complex stability based on an electrostatic model and free volume considerations, inner and outer-sphere reorganization energy, and electron-transfer probability indicates that it is primarily a change in electron-transfer probability due to increased electron-transfer distance that is the cause. The theory used has been rather successful at predicting rate constants for electron-transfer processes, and the rate variation is large, so the result seems sound. The second explanation attributes the variation to changes in precursor complex stability. In this model, the reaction path includes extensive distortion of the coordination spheres at a high enthalpic price in order to attain a shorter electron-transfer distance. The activation parameters are consistent with this interpretation. Both factors are necessarily involved, but we tentatively favor the explanation based on electron-transfer distance as being most influential. Electron transfer, especially from delocalized systems, can take place at distances larger than those involved here, as has been amply demonstrated.<sup>33-35</sup> Furthermore, the activation pa-

rameters for electron-transfer reactions are poorly understood and seem to typically involve a great deal of enthalpy/entropy compensation; thus the apparent support for the precursor complex variation argument from the activation parameters is not so solid as it might seem.

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**Registry No.** Mn, 7439-96-5;  $\text{Mn}(\text{CNCH}_3)_6^+$ , 45228-39-5;  $\text{Mn}(\text{CNCH}_3)_6^{2+}$ , 45228-38-4;  $\text{Mn}(\text{CNCH}_2\text{CH}_3)_6^+$ , 18972-31-1;  $\text{Mn}(\text{CNCH}_2\text{CH}_3)_6^{2+}$ , 18972-32-2;  $\text{Mn}(\text{CNCH}(\text{CH}_3)_2)_6^+$ , 91281-20-8;  $\text{Mn}(\text{CNCH}(\text{CH}_3)_2)_6^{2+}$ , 94645-20-2;  $\text{Mn}(\text{CNC}(\text{CH}_3)_3)_6^+$ , 18972-33-3;  $\text{Mn}(\text{CNC}(\text{CH}_3)_3)_6^{2+}$ , 19154-91-7;  $\text{Mn}(\text{CNCH}_2\text{C}_6\text{H}_5)_6^+$ , 48243-32-9;  $\text{Mn}(\text{CNCH}_2\text{C}_6\text{H}_5)_6^{2+}$ , 52394-11-3.

**Supplementary Material Available:** Tables of kinetic and conductivity data (6 pages). Ordering information is given on any current masthead page.

(33) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047-9.

(34) Isied, S. S.; Kuehn, C.; Worosila, G.; *J. Am. Chem. Soc.* **1984**, *106*, 1722-6.

(35) Winkler, J.; Nocera, D.; Yocum, K.; Bodignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798-800.