

Nuclear Magnetic Resonance Studies of Rates of Electron Exchange between Isonitrile Complexes of Manganese(I) and -(II)

Donald S. Matteson^{1a} and Rodney A. Bailey^{1b}

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. Received September 9, 1968

Abstract: Manganese-isonitrile complex ions $(\text{RNC})_6\text{Mn}^+$ and $(\text{RNC})_6\text{Mn}^{2+}$ are useful for the study of simple electron-transfer reactions since these can occur without ligand transfers or other complications. The rates can be measured by ^{55}Mn nmr line broadening. If R is ethyl the rate constant for electron exchange at 7° is 6.4×10^5 , and if R is *t*-butyl the rate constant is 4.0×10^4 l. mol⁻¹ sec⁻¹. Thus, it appears that the bulky *t*-butyl group has an electrically insulating effect. If R is an electrical conductor such as phenyl or vinyl, more complicated phenomena appear. The Mn^{2+} complex exists as a diamagnetic dimer which is in rapid equilibrium with a paramagnetic species, as shown by paramagnetic contact shifts of the phenyl protons in the 60-MHz proton nmr spectrum. Electron exchange with the Mn^+ complexes was shown to be rapid by the effect on the position of the shifted nmr peaks.

Electron transfer can occur when a suitable donor and an acceptor species approach each other closely enough so that their two wave functions overlap slightly. When the reacting species are metal cations, contact is normally made through intervening ligands. The concept that the electron-conducting ability of an intervening ligand may have a considerable effect on the rate of electron transfer has received considerable recent attention.^{2,3} However, ligand transfer accompanies electron transfer in these reactions, which are consequently not true examples of the idealized simple electron-transfer process.

Simple electron transfer presumably occurs between manganate and permanganate ions, and the rate has been measured by nmr line-broadening techniques.⁴ The cuprous-cupric chloride system provides another possible example of simple electron transfer.⁵ Lower limits but not actual rate constants have been determined for electron exchange between the dipyriddy complexes of osmium(II) and -(III), ferrocene and ferricinium ion, and the phenanthroline complexes of iron(II) and -(III).⁶ These electron transfers are all extremely rapid and probably diffusion controlled, with electrostatic repulsion providing the only substantial energy barrier.

There should be an additional energy barrier to electron transfer if the overlap between the donor and acceptor orbitals is very small at the closest possible approach. We thought that bulky saturated organic ligands might provide such an electrical insulation effect, and that unsaturated ligands would probably act as electron conductors. The manganese-isonitrile com-

plexes first described by Sacco⁷ and Naldini⁸ appeared to be particularly suitable for testing these ideas with kinetic studies. Six isonitrile ligands give the manganese(I) complex a krypton configuration, and the only structural change on going to the strong-field, low-spin manganese(II) complex is the loss of one electron. The alkyl or aryl group of the isocyanide can be chosen almost at will so that effects of structure on reactivity can be determined. Manganese consists of one isotope, ^{55}Mn , which has a nuclear spin of $5/2$ and is suitable for rate measurements based on nmr line broadening.

Results

Synthesis of Complexes. Mn(I) and -(II) complexes were prepared with ethyl, *t*-butyl, vinyl, and phenyl isocyanides with some modification of the published procedures.^{7,8} For some of the reactions of manganous iodide with the isonitriles, *t*-butyl alcohol was found to be a better solvent than ethanol. The previously unknown Mn(II) complexes of alkyl isocyanides are pale yellow or pink, in contrast to the highly colored aromatic isonitrile complexes. The Mn(I) complexes were isolated both as nitrate and as hexafluorophosphate salts, the Mn(II) complexes as hexafluorophosphates when R was saturated alkyl but only as impure tetrabromocadmates when R was phenyl or vinyl. The phenyl and vinyl isocyanide Mn(II) complexes were extremely labile and reverted to Mn(I) on attempted recrystallization of their hexafluorophosphate salts.

Kinetics. The ethyl isocyanide-manganese(I) complex reacts instantaneously with such oxidizing agents as cerium(IV), triphenylmethyl cation, or nitric acid. In order to follow the kinetics of a rapid electron-transfer process, we chose to measure the rate of electron exchange between Mn(I) and Mn(II) by nmr line broadening.

The lifetime T_2 of a nuclear spin state is related to the observed nmr line width by

$$(1/T_2) = \sqrt{3}\gamma\Delta H/2 = \pi\sqrt{3}\Delta\nu \quad (1)$$

(7) A. Sacco, *Gazz. Chim. Ital.*, **86**, 201 (1959); *Ann. Chim.*, **48**, 225 (1958); *Chem. Abstr.*, **53**, 204g (1959).

(8) L. Naldini, *Gazz. Chim. Ital.*, **90**, 971 (1960).

(1) (a) Alfred P. Sloan Foundation Research Fellow, 1966-1968. (b) National Science Foundation Cooperative Fellow, 1965-1967; abstracted from the Ph.D. Thesis of R. A. Bailey; (c) preliminary communication: D. S. Matteson and R. A. Bailey, *J. Am. Chem. Soc.*, **89**, 6389 (1967).

(2) (a) R. T. M. Fraser, D. K. Sebera, and H. Taube, *ibid.*, **81**, 2906 (1959); (b) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961); (c) F. R. Nordmeyer and H. Taube, *ibid.*, **88**, 4295 (1966); (d) R. Robson and H. Taube, *ibid.*, **89**, 6487 (1967).

(3) E. S. Gould, *ibid.*, **88**, 2983 (1966).

(4) O. E. Myers and J. C. Sheppard, *ibid.*, **83**, 4739 (1961).

(5) H. M. McConnell and H. E. Weaver, Jr., *J. Chem. Phys.*, **25**, 307 (1956).

(6) M. W. Dietrich and A. C. Wahl, *ibid.*, **38**, 1591 (1963).

where $\gamma\Delta H$ is the line width in gauss or $\Delta\nu$ is the width in hertz measured from the minimum to the maximum of the derivative of the Lorentzian absorption curve.⁵ When a small amount of paramagnetic species reacts at a rapid, measurable rate in equilibrium with a large excess of diamagnetic species, the second-order rate constant k is calculated from the difference between the natural line width of the pure diamagnetic species and the line width when a measured amount of paramagnetic species is present by the use of the equation

$$k = (1/[P])[(1/T_2)_{DP} - (1/T_2)_D] \quad (2)$$

where $[P]$ is the concentration of the paramagnetic species, the subscript DP refers to the mixture of diamagnetic and paramagnetic species, and the subscript D to the pure diamagnetic species.⁶ The derivation of eq 2 is based on the assumption that the electron exchange is not nearly as fast as the nuclear spin relaxation of the paramagnetic species.⁶ If this assumption is not correct, the observed line broadenings will set a lower limit for the rate constant that is considerably below the true value. In such cases the amount of line broadening will decrease with increasing temperature instead of increasing in the manner characteristic of true rate constants.

Our measurements were made in acetonitrile, using the nitrate salt of the Mn(I) complex and a small amount of the hexafluorophosphate of the Mn(II) complex. Some representative data for the *t*-butyl isocyanide complexes are shown in Table I. It is readily apparent that the proper dependence of the line width on Mn(II) complex was observed. The concentration of the Mn(I) was not varied over a wide enough range to verify that the line width is independent of this species as required by eq 2. Similar data were obtained with the ethyl isocyanide complexes, except that the Mn(II) concentrations were in the range up to $10^{-3} M$, about one-tenth those required with the *t*-butyl complexes. Both sets of complexes showed the proper Arrhenius temperature dependence of the k 's,⁶ illustrated in Figure 1.

For electron exchange between the ethyl isocyanide complexes, ΔH^* is $1.74 \text{ kcal mol}^{-1}$ and ΔS^* is -26.5 eu . For the *t*-butyl isocyanide complexes, ΔH^* is 4.56 and ΔS^* is -20.7 . The least-squares computer program

Table I. Typical Rate Constants for Electron Exchange between Hexa(*t*-butyl isocyanide)manganese(I) and -(II) in Acetonitrile

Mn(I), M	Mn(II), M	Temp, °C	Line width, Hz	$10^{-4}k_2$, l. mol ⁻¹ sec ⁻¹
0.324	0.0000	-34	81.6	...
0.316	0.0054	-30	90.1	0.85
0.311	0.0089	-31	95.2	0.83
0.306	0.0131	-32	108.5	1.11
0.300	0.0172	-32	117.0	1.12
0.289	0.0249	-32	127.3	1.00
0.391	0.0000	-38	84.1	...
0.372	0.0052	-38	91.8	0.80
0.354	0.0099	-38	102.9	1.03
0.333	0.0155	-38	104.6	0.72
0.391	0.0000	+7	77.3	...
0.354	0.0054	+7	118.3	4.10
0.333	0.0085	+6	157.1	5.10
0.324	0.0000	+10	74.3	...
0.303	0.0114	+8	149.0	3.55
0.285	0.0169	+8	201.0	4.06
0.308	0.0054	+10	106.3	3.62

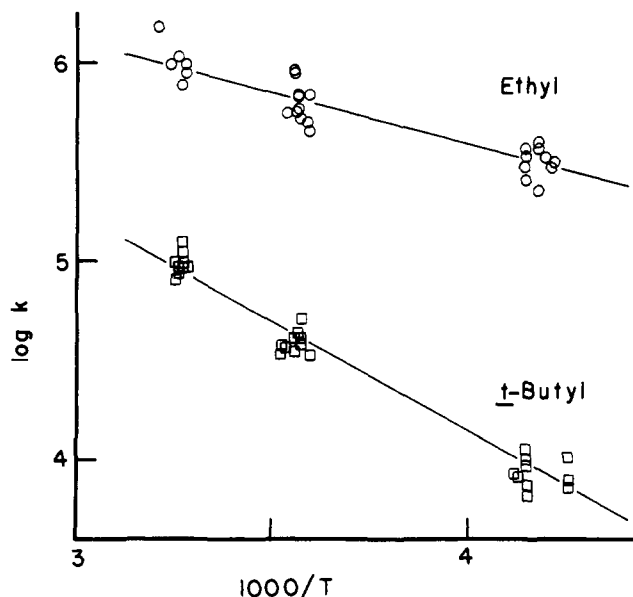


Figure 1. Plot of $\log k$ vs. $1000/T$ for Mn(I)-Mn(II) electron exchange: \circ , ethyl isocyanide complex; \square , *t*-butyl isocyanide complex.

used to determine the line slopes in Figure 1 indicated that the standard deviation in ΔH^* is $\pm 0.18 \text{ kcal/mol}$ and in ΔS^* is $\pm 0.5 \text{ eu}$. A more conservative intuitive estimate of error would be ± 0.8 for ΔH^* and ± 2 for ΔS^* . Average deviations in the rate constants are about $\pm 10\%$. Averaged numerical values of the rate constant k_2 for the ethyl isocyanide complex are 3.3×10^5 at -33° , 6.4×10^5 at 7° , and 9.9×10^5 at 34° , and for the *t*-butyl isocyanide complex, 0.9×10^4 at -35° , 4.0×10^4 at 7° , and 10.2×10^4 at 34° .

Varying the solvent had little effect on the observed reaction rates, as shown in Table II. Addition of $0.18 M$ lithium chloride also had no measurable effect on the rate. At low temperatures viscosity line-broadening effects were observed in dimethyl sulfoxide and in ethanol, but when this was corrected for, the rate constants showed Arrhenius behavior.

Table II. Solvent Effects on the Second-Order Rate Constants for the Electron Exchange between Some Mn(I) and Mn(II) Isocyanide Complexes

Solvent	Ligand	Mn(II) salt	Temp, °C	k_2 , l. mol ⁻¹ sec ⁻¹
CH ₃ CN	<i>t</i> -BuNC	PF ₆ ⁻	7	4.0×10^4
CH ₃ COCH ₃	<i>t</i> -BuNC	PF ₆ ⁻	8	2.8×10^4 ^a
CH ₃ CN	EtNC	PF ₆ ⁻	7	6.4×10^5
EtOH	EtNC	PF ₆ ⁻	7	5.5×10^5
CH ₃ SOCH ₃	EtNC	PF ₆ ⁻	7	$16. \times 10^5$
CH ₃ SOCH ₃	EtNC	CdBr ₄ ²⁻	11	8.2×10^5

^a The Mn(II) complexes appear to decompose partially in acetone, and consequently this result may be somewhat low.

The instability of the phenyl isocyanide-manganese(II) complex made it difficult to obtain rate measurements for electron exchange, which in this case is probably a complicated process (see Discussion). A very brief study yielded $k = 5.2 \times 10^4 \text{ l. mol}^{-1} \text{ sec}^{-1}$ at -20° , $k = 3.5 \times 10^4$ at -28° . These measurements were made with the Mn(I) complex concentration at $0.04 M$

and the Mn(II) at 0.015 *M*. Thus, it appears that these rate constants are showing the proper Arrhenius behavior and are in the measurable range, though the probable error is much larger than with the aliphatic isocyanide complexes.

Physical Properties. Magnetic moments of the Mn(II) complexes were determined by nmr. The peak due to the solvent sealed in an inner capillary tube is upfield from that of the solvent containing the paramagnetic substance, and the magnetic susceptibility can be measured by comparison with known standards.⁹ Magnetic susceptibilities determined in this way include hexa(ethyl isocyanide)manganese(II) hexafluorophosphate, 2.12 BM, tetrabromocadmate, 1.95 BM, and hexa(*t*-butyl isocyanide)manganese(II) hexafluorophosphate, 1.95 BM, corresponding to one unpaired electron in each case. Hexa(phenyl isocyanide)manganese(II) tetrabromocadmate showed no detectable magnetic moment in freshly prepared acetonitrile solution.

The infrared spectra of the isonitriles and their complexes with Mn(I) and Mn(II) are summarized in Table III.

Table III. Infrared Data for Some Mn(I) and Mn(II) Isocyanide Complexes

Isocyanide	Solvent	Infrared, μ		
		Uncomplexed	Mn(I)	Mn(II)
CH ₃ CH ₂ NC	CH ₂ Cl ₂	4.63	4.77	4.53
<i>t</i> -BuNC	CH ₂ Cl ₂	4.70	4.78, 4.85	4.60
PhNC	CH ₃ CN			4.61, 4.80 ^a
	CH ₂ Cl ₂		4.80	
CH ₂ =CHNC	KBr			4.61, 4.85 ^a
	CH ₃ CN			4.60, 4.78 ^a
	CH ₂ Cl ₂	4.70	4.79	
	KBr			4.62, 4.86 ^a

^a Second peak believed due to contamination by Mn(I) complex.

The epr spectrum of the ethyl isocyanide-Mn(II) complex shows the expected sextet resulting from splitting by the ⁵⁵Mn nucleus. However, freshly prepared solutions of the phenyl isocyanide-Mn(II) complex in acetonitrile yield no epr signal. This does not necessarily mean that no paramagnetic species is present, since other complexes are known which fail to yield the expected epr signal, perhaps because of extremely broadened lines resulting from rapid electron exchange.⁶

Solutions of the phenyl isocyanide-Mn(II) complex in acetonitrile in a capped (not sealed) nmr tube lose their color within a day or two at 25°, starting from the upper surface. The fading is accompanied by the development of a strong epr signal and paramagnetic susceptibility. Decomposition is almost instantaneous in dimethyl sulfoxide or ethanol. Since the Mn(I) complex can be recovered from ethanol, and since the magnetic susceptibility of dimethyl sulfoxide solutions eventually rises far beyond the theoretical value for low-spin Mn(II), it seems probable that the decomposed solutions contain ordinary solvated high-spin Mn(II) and complexed Mn(I), the liberated isocyanide being a potential reducing agent for complexed Mn(II).

We suspect but have not proved that the paramagnetism of solid aryl isocyanide complexes reported by Naldini,⁸ corresponding to one unpaired electron, might

be due to contamination by high-spin Mn(II) impurities. We observed 2.4 BM with a sample of the vinyl isocyanide complex in an early phase of our work, but the sample was probably grossly impure and we have not re-investigated.

In spite of the lack of other evidence for paramagnetism in the phenyl and vinyl isocyanide complexes of manganese(II), both showed large contact shifts in the proton nmr spectra. Because of its greater stability, the phenyl isocyanide complex was chosen for detailed study. At -20°, a freshly prepared solution of hexa(phenyl isocyanide)manganese(II) in acetonitrile had a slightly broadened nmr absorption about 270 Hz downfield from the phenyl peak of the Mn(I) complex. The line broadening amounted to about a sixfold increase over that of the manganese(I) complex. The addition of Mn(I) complex to the solution moved the position of the absorption toward the normal position for phenyl protons. An upfield peak, often masked by the solvent, also appears, its position being 157 Hz upfield when the other peak is 75 Hz downfield. This mixture shows no peak in the normal position for the Mn(I) complex. The downfield shift is a result of decreased spin density on the *meta* carbon atom of the phenyl ring and the upfield results from increased spin density on the *ortho* and *para* atoms.¹⁰ When the Mn(I) concentration exceeds the Mn(II) concentration, the downfield peak is resolved into a triplet and the upfield peak into a doublet with the relative ratios 2:3 and a coupling constant *J* = 7.0 Hz.

The diamagnetic Mn(II) species has to be a dimer. The structure is considered in the Discussion section. The simplest paramagnetic Mn(II) species would be the dissociated monomer. Equilibration would then yield a linear relationship between the nmr contact shift and the quantity [Mn(II)]^{1/2}/([Mn(I)] + [Mn(II)]). There is considerable deviation from this relationship, shown by the circular symbols in Figure 2. Each set of points was obtained by adding aliquots of Mn(I) solution to the Mn(II) solution, and the failure of the line to pass through the origin may be attributed to progressive partial decomposition of the Mn(II) complex. The deviant set of points obtained from a run at higher dilution might have a similar cause.

If the monomer ions are short lived and exist mainly as solvent-caged pairs, or if the paramagnetism results from some other type of triplet state of the dimer, then the nmr shift will be proportional to [Mn(II)]/([Mn(I)] + [Mn(II)]). This relationship, illustrated by the square symbols in Figure 2, fits all the runs onto one line, though the slope is still affected by decomposition of the Mn(II) complex. The instability of the complex and the solubility limit of its tetrabromocadmate salt appeared to preclude any hope of getting truly quantitative data.

Unless the paramagnetic state is the state of lowest enthalpy, which is incompatible with our dissociation hypothesis, the nmr contact shift should increase with increasing temperature.¹⁰ The shift actually decreases somewhat with increasing temperature and increases a few per cent on recooling, though not all the way back to the original value, as if slight decomposition occurs.

(10) (a) W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960); (b) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *ibid.*, **37**, 347 (1962); (c) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962); (d) D. R. Eaton, W. D. Phillips, and D. S. Caldwell, *ibid.*, **85**, 397 (1963).

(9) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

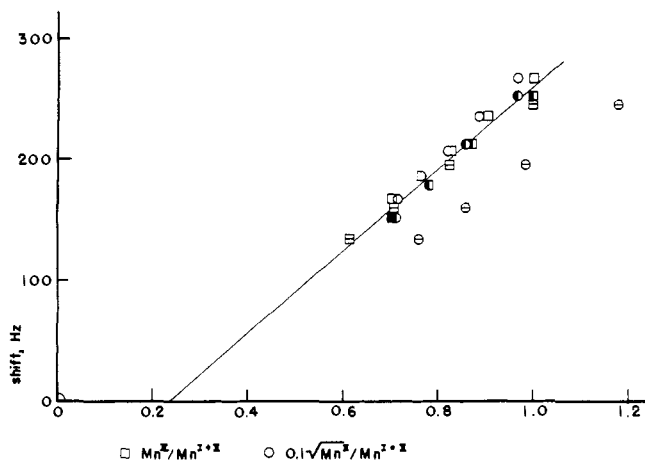


Figure 2. Plots of contact shift vs. $[\text{Mn(II)}]/([\text{Mn(I)}] + [\text{Mn(II)}])$ (squares) and $[\text{Mn(II)}]^{1/2}/([\text{Mn(I)}] + [\text{Mn(II)}])$ (circles), the latter adjusted to fit the same scale, for the phenyl isocyanide-manganese complexes at -20° . Three different runs are identified by different markings in the symbols.

We have no explanation for this anomalous temperature dependence.

Contact shifts were also detected for the methyl groups of the ethyl isocyanide-Mn(II) complex. The interaction is relatively small, amounting to only about 20–30 Hz downfield in the pure Mn(II) complex. The methyl peak is broadened by about a factor of 2. However, the methylene protons of the ethyl isocyanide group are broadened or shifted so extensively that they cannot be detected. Spectra of mixtures with the Mn(I) complex indicate rapid equilibration, as expected.

Discussion

Mechanism of Electron Exchange. Our kinetic data are consistent with a simple electron-transfer mechanism for the reaction of ethyl or *t*-butyl isocyanide-Mn(I) with the corresponding Mn(II) complex. The rate constants in the 10^4 – 10^6 l. mol $^{-1}$ sec $^{-1}$ range and the ΔS^\ddagger values of -20 to -25 eu are comparable to those of previously studied simple electron-transfer processes.^{4,5}

The molecular orbitals involved in the electron exchange are composed of the t_{2g} set of d orbitals of the manganese and the π^* orbitals of the surrounding isocyanide groups. In the collision of two *t*-butyl isocyanide complexes there can be no direct contact between the central Mn(CN) $_6$ units because of steric hindrance by the surrounding *t*-butyl groups. The electron must therefore pass through the *t*-butyl groups in the transfer process. The overlap between the donor and acceptor orbitals must thus be small, though not zero, and there is a considerable potential barrier imposed by the *t*-butyl groups. (This might be construed loosely as electrical insulation on a molecular scale.) The potential barrier should be smaller in the ethyl isocyanide complex, but models indicate that direct contact between the central Mn(CN) $_6$ units is still unlikely.

If the potential barrier is high enough, electron tunnelling will be the rate-limiting process. A lower barrier and higher orbital overlap will allow repeated electron exchange during each collision. If the electron exchange is fast enough, the colliding pair of ions can be described

adequately by a "time-independent" Schrödinger equation, there will be an appreciable exchange integral, and chemical bonding can be said to exist between the colliding species. If this bonding is more than offset by electrostatic repulsion, the point of closest approach is the transition state; if bonding exceeds repulsions, it is an intermediate.

The manganese complexes presumably exist largely as ion pairs in acetonitrile solution. The associated anions undoubtedly facilitate close approach of the cations, and might even form a bridge for conduction of the electron from one cation to the other. There is no way to decide whether the very low activation energies observed actually represent the barrier to electron transfer or a combination of electrostatic repulsion partially offset by weak chemical bonding. Whatever the details may be, the finding that the activation energy for the *t*-butyl is 3 kcal mol $^{-1}$ higher than for the ethyl isocyanide complex is certainly in the expected direction.

We cannot rigorously exclude the possibility that the Mn(I) or Mn(II) complex can lose one isocyanide ligand reversibly and that pentacoordinate manganese is involved in the electron transfer. However, such complicated mechanisms should be several orders of magnitude slower than simple electron exchange, as are most of the reported oxidation-reduction reactions which involve ligand transfer.^{2,3} The Mn(I) complex clearly does not dissociate to any strongly reducing free Mn(I) ion, and dissociation of the Mn(II) complex to manganese ion is irreversible when it occurs.

Dimerization of Hexa(phenyl isocyanide)manganese(II).

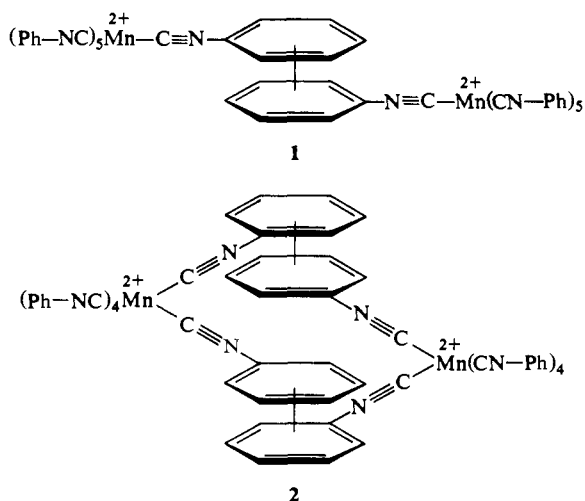
We had hoped to find extremely rapid electron exchange through phenyl or vinyl isocyanide ligands, which should be good π -electron conductors. Very rapid electron exchange has been observed previously with other aromatic complexes.⁶ However, it is difficult to imagine a much lower enthalpy of activation than the 1.7 kcal found with the ethyl isocyanide complex.

Our observations suggest that the phenyl and vinyl groups conduct electrons too well for our purpose, and that electron exchange becomes so facile that a substantial exchange integral and net chemical bonding between two ions results. The only disappointment is that this bonding links a pair of Mn(II) complexes instead of a Mn(II) and a Mn(I) complex. We postulate that the dimers consist of π complexes linked through the phenyl (or vinyl) groups (**1** or **2**). Itoh and Kosower have postulated similar π complex structures for radical dimers in the substituted-pyridine series.¹¹

Our postulated dimer structures **1** and **2** require that the Mn(II) atoms undergo a partial internal reduction to Mn(I) and thus remove sufficient electron density from the benzene rings to allow bonding interactions of the π -complex type. Expressed another way, overlapping the π systems of two benzene rings must lead to a bonding and an antibonding molecular orbital, and the Mn(II) atoms pull the antibonding electron pair out of the way to yield a net bonding interaction. These structures are analogous to conventional donor-acceptor π complexes, except that both groups share equally in the electron exchange and electron spin pairing is required in making the linkage.

The intense purple color of the phenyl isocyanide

(11) M. Itoh and E. M. Kosower, *J. Am. Chem. Soc.*, **89**, 3655 (1967).



complex and the orange-red color of the vinyl isocyanide complex are consistent with the postulated π -complex structures. The saturated isonitrile-Mn(II) complexes are very pale yellow or pink, in accord with the forbidden character of the t_{2g} to e_g transition of the manganese. Simple conjugation seems inadequate as an explanation for the intense colors of the unsaturated or aromatic isonitrile complexes.

The magnitude of the proton nmr contact shifts in the phenyl isocyanide-Mn(II) complex suggests the presence of a few per cent of paramagnetic species, based on previously observed values of such shifts.¹⁰ As noted in the Results section, the evidence regarding whether the paramagnetic species is dissociated monomer is ambiguous. Since mixtures of Mn(I) and Mn(II) complex show a single, narrow *meta*-proton peak shifted by more than 250 Hz, the electron exchange must be complete in considerably less than $1/250$ sec.¹⁰

The very limited ⁵⁵Mn nmr data on the rate of electron exchange between the phenyl isocyanide-Mn(I) and -Mn(II) complexes also confirm that the reaction is very fast. The observed k_2 value of 5×10^4 l. mol⁻¹ sec⁻¹ at -20° must be regarded as a minimum. If our observation of Arrhenius temperature dependence was erroneous or if the Mn(II) complex was grossly impure, the actual rate constant would be larger. In any event, this is not the rate constant for direct reaction of the Mn(I) and monomeric Mn(II) complexes, since the latter can be present to the extent of a few per cent at most. The direct reaction of Mn(I) with monomeric Mn(II) complex may be an order of magnitude or more faster, with the rate-determining step the dissociation of the Mn(II) dimer, or the electron-exchange mechanism might involve attack of an Mn(I) complex on the Mn(II) dimer to displace a different Mn(I) unit.

Experimental Section

Hexa(vinyl isocyanide)manganese(I) Iodide. Manganese(II) iodide monohydrate was prepared by passing anhydrous hydrogen iodide into an ether-ethanol suspension of manganese carbonate, followed by concentration of the solution under vacuum. Addition of 5 ml of vinyl isocyanide to a solution of 2.0 g of manganese(II) iodide in 10 ml of *t*-butyl alcohol and 5 ml of 2,2-dimethoxypropane yielded a brown precipitate. This was collected, dissolved in methylene chloride, and filtered to remove insoluble impurities. The filtrate was shaken with 10 ml of cold saturated aqueous sodium thiosulfate, and the methylene chloride solution of the isocyanide-manganese complex was concentrated, leaving the

iodide salt as a crystalline residue in 30–50% yield, recrystallized from ethanol-water, mp 213.5–214.5° dec.

Anal. Calcd for C₁₈H₁₈IMnN₆: C, 43.22; H, 3.63; I, 25.37; Mn, 10.98; N, 16.80. Found: C, 43.30; H, 3.79; I, 25.46; Mn, 10.71; N, 16.70.

Hexa(vinyl isocyanide)manganese(I) Nitrate. The iodide salt was dissolved in a mixture of methylene chloride, ethanol, and water and passed through a column of ion-exchange resin which had been converted to the nitrate form. The solution was concentrated under vacuum and the residue was recrystallized from aqueous ethanol, mp 210° dec.

Anal. Calcd for C₁₈H₁₈MnN₇O₃: C, 49.67; H, 4.17; Mn, 12.62; N, 22.53. Found: C, 49.90; H, 4.32; Mn, 12.59; N, 22.30.

Hexa(ethyl isocyanide)manganese(I) nitrate was prepared by a similar sequence, except that absolute ethanol sufficed for the reaction of the isocyanide with manganese(II) iodide, as described by Sacco,⁷ mp 183–187° dec.

Anal. Calcd for C₁₈H₃₀MnN₇O₃: C, 48.33; H, 6.76; Mn, 12.28; N, 21.92. Found: C, 48.16; H, 6.58; Mn, 12.07; N, 21.68.

Hexa(*t*-butyl isocyanide)manganese(I) nitrate was similarly prepared, except that the iodide salt did not precipitate from ethanol and was obtained in crude form by concentration of the solution under vacuum. The over-all yield of the nitrate was 19%, mp 227–229°.

Anal. Calcd for C₃₀H₅₄MnN₇O₃: C, 58.52; H, 8.84; Mn, 8.92; N, 15.93. Found: C, 58.62; H, 8.85; Mn, 9.10; N, 15.77.

Hexa(phenyl isocyanide)manganese(I) nitrate was similarly prepared, yield 46%, mp 193–196° dec.

Anal. Calcd for C₄₂H₃₀MnN₇O₃: C, 68.56; H, 4.11; Mn, 7.47; N, 13.33. Found: C, 68.70; H, 4.34; Mn, 7.66; N, 13.16.

Hexa(ethyl isocyanide)manganese(II) Hexafluorophosphate. At 25°, 3 μ l of 70% nitric acid was added to a solution of 0.22 g of hexa(ethyl isocyanide)manganese(I) nitrate in 2.0 ml of glacial acetic acid and stirred for 30–45 min. The yellow solution was added to an aqueous solution of 0.2 g of sodium hexafluorophosphate. The light pink precipitate was filtered and was recrystallized from a minimum amount of acetone without heating, adding water to cause crystallization, then dried under vacuum, yield 0.15 g (43%), mp 140–150° dec.

Anal. Calcd for C₁₈H₃₀F₁₂MnN₆P₂: C, 32.01; H, 4.48; F, 33.75; Mn, 8.13; N, 12.45; P, 9.17. Found: C, 32.27; H, 4.69; F, 33.57; Mn, 8.30; N, 12.67; P, 9.04.

Hexa(*t*-butyl isocyanide)manganese(II) hexafluorophosphate was similarly prepared in 47% yield, mp 130–131° dec.

Anal. Calcd for C₃₀H₅₄F₁₂MnN₆P₂: C, 42.71; H, 6.45; Mn, 6.51; N, 9.96; P, 7.34. Found: C, 42.48; H, 6.44; Mn, 6.70; N, 9.85; P, 7.50.

Hexa(vinyl isocyanide)manganese(II) Tetrabromocadmiate. At 25°, a solution of 0.51 g of cadmium bromide in the minimum amount of ethanol was added to a stirred solution of 0.33 g of hexa(vinyl isocyanide)manganese(I) nitrate in 6 ml of ethanol-chloroform-acetic acid (3:3:1 by volume). To this was added 0.50 ml of 70% nitric acid. The dark red precipitate was filtered, rinsed with methanol, and stored at -8°, yield 0.3 g (52%), mp 109° dec, λ_{\max} 450 nm.

Anal. Calcd for C₁₈H₁₈Br₄CdMnN₆·0.82CdBr₂: C, 21.03; H, 1.76; Br, 44.35; Cd, 19.92; Mn, 5.35; N, 8.17. Found: C, 20.46–20.67; H, 1.72–1.64; Br, 43.87–43.68; Mn, 5.38–5.25; N, 8.28–8.23.

Hexa(phenyl isocyanide)manganese(II) tetrabromocadmiate was similarly prepared, mp 135° dec, λ_{\max} 490 nm.

Anal. Calcd for C₄₂H₃₀Br₄CdMnN₆·0.25CdBr₂: C, 42.97; H, 2.58; Br, 30.64; Cd, 11.97; Mn, 4.68; N, 7.16. Found: C, 42.85–42.63; H, 2.51–2.60; Br, 29.72–29.68; Cd, 11.79–11.98; Mn, 4.79; N, 7.37.

Hexa(ethyl isocyanide)manganese(II) tetrabromocadmiate was similarly prepared in 34% yield, mp 140° dec.

Anal. Calcd for C₁₈H₃₀Br₄CdMnN₆·0.80 CdBr₂: C, 20.88; H, 2.92; Br, 43.22; Cd, 19.54; Mn, 5.13; N, 8.12. Found: C, 20.79–20.58; H, 2.77–2.92; Br, 44.57–44.41; Mn, 5.38–5.20; N, 7.96–7.90.

Kinetics. The Mn(I) isocyanide complexes were recrystallized in a glove box under an argon atmosphere and stored in a vacuum desiccator. Tightly stopped solutions of the Mn(I) isocyanide complexes were stable for kinetic purposes for 1–2 weeks at -15°. The acetonitrile used as a solvent was Eastman Spectro

Grade, and other solvents were reagent grade without further purification. The Mn(II) isocyanide complexes were stored at -78° , where they were stable for prolonged periods as indicated by infrared spectra. Solutions of the Mn(II) complexes showed signs of decomposition within 1–2 days at -15 or -78° , depending on the complex, and were generally prepared just prior to a series of kinetic runs.

A Varian DP-60 wide-line nmr instrument was used to measure the ^{55}Mn absorption, which appears as a single signal ≥ 70 Hz wide at 15.8 MHz, 15,000 G. The instrument was calibrated (in Hz/mm of chart) by means of the two ^{14}N peaks of ammonium nitrate. Signals were obtained as derivative curves, and care was taken to avoid saturation. The sample cell was constructed so that a constant temperature ($\pm 2^\circ$) could be obtained by passing a heated or cooled gas through a coiled glass tube in the cell. The outside had an unsilvered vacuum jacket, and a thermocouple well and an opening for introducing the sample were also provided. About 2.2–3.0 ml of 0.3 M Mn(I) isocyanide complex solution was introduced into the sample cell and the opening was stoppered with a rubber septum. Five traces of the nmr signal were recorded. Then a small sample of the Mn(II) isocyanide complex

solution (generally 5–50 μl) was introduced by syringe through the rubber septum, resulting in a concentration of 10^{-6} – 10^{-3} M, and the nmr signal was again recorded five times. This was continued until four to five points had been obtained. A new Mn(I) sample was generally used for each different temperature. Rates were calculated as indicated in the Results section.

Contact Shifts. A freshly prepared solution of the Mn(II) isocyanide complex (about 0.3–0.4 ml, 10^{-2} M) was placed in an nmr tube and the proton spectrum recorded on a Varian A-60. The solution was kept stoppered at -78° except when in the instrument, and the spectra were recorded below 0° with the solvent acting as an internal reference. Measured amounts of the corresponding Mn(I) solution were added up to a concentration of about 10^{-3} M and the spectrum was rerecorded until four to five points had been measured.

Acknowledgment. We thank Professors J. P. Hunt and H. W. Dodgen and Drs. Stephen Marks and William Gary for helpful discussions and information.

The Dimeric Nature of Hemin Hydroxides

Irwin A. Cohen

Contribution from the Department of Chemistry, The Polytechnic Institute of Brooklyn, Brooklyn, New York 11201. Received October 14, 1968

Abstract: The hematins derived from tetraphenylporphine and deuteroporphyrin IX dimethyl ester have been found to be dimeric in methylene chloride by molecular weight measurements. Infrared studies indicate the presence of iron–oxo–iron bridges in both systems. The room-temperature magnetic moment of one, the μ -oxo-bis(tetraphenylporphineaquiron(III)), was found to be 1.74 BM per iron. The results of previous magnetic studies for hematins are interpreted as due to mixtures of high-spin hydroxo monomers and low-spin oxo dimers. The difference between the Mössbauer spectra of hemins and hematins is discussed.

Dimerization and polymerization of hemins (porphyrin Fe(III)X, X = OH) and hematins (X \neq OH) in aqueous solutions are well known.¹ A recent polarographic study of the reduction of hemin chloride in 0.1 M aqueous base indicated, under very specific conditions, a two-electron step was operative, consistent with the hemin dimer being the reducible species.² But in view of the low solubility of hemins in water and the hydrophobic nature of the porphyrin ring, it is not necessary to invoke inter-iron bridging groups in these dimers to explain their formation. There have been no direct observations of hematin dimerization in nonaqueous solvents prior to this work.

A crystallographic study³ has shown that a Mn(III) model of hematin, μ -oxo-bis(phthalacyanopyridine-manganese(III)), is a dimer with a linear Mn–O–Mn bridge. But crystal structures of methoxyiron(III) mesoporphyrin IX dimethyl ester⁴ and hemin chloride⁵ have shown them to be monomeric. The reported monomeric

crystallographic structure of tetraphenylporphineiron(III) hydroxide⁶ has subsequently been shown in error,⁷ but no conclusions could have been drawn as to its true structure.

Oxo-bridged dimers of ferrihemes have recently been postulated twice, by Schugar, *et al.*,⁸ on the basis of magnetic studies of aqueous model systems and by Alben, *et al.*,⁹ after an analytical study of the solid product from the autoxidation of a ferroporphyrin in benzene.

Experimental Section

μ -Oxo-bis(tetraphenylporphineaquiron(III)). The method of Dorough, Miller, and Huennekens¹⁰ for the preparation of tetraphenylporphineiron(III) hydroxide was used to obtain a crude product. This was followed by chromatography on alumina with chloroform. The eluent was evaporated to dryness and the residue was exposed to air and then dried *in vacuo*.

Anal. Calcd for $\text{C}_{88}\text{H}_{60}\text{N}_8\text{O}_3\text{Fe}_2$: C, 76.08; H, 4.32; N, 8.08. Found: C, 76.37; H, 4.45; N, 8.03.

Deuteroporphyrin IX dimethyl ester iron(III) methoxide was pre-

(1) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., Amsterdam, 1964, p 45, and references therein.

(2) J. Jordan and T. M. Bednarski, *J. Amer. Chem. Soc.*, **86**, 5690 (1964).

(3) L. H. Vogt, A. Zalkin, and D. H. Templeton, *Science*, **151**, 569 (1966).

(4) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, **87**, 2312 (1965).

(5) D. F. Konig, *Acta Cryst.*, **18**, 663 (1965).

(6) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, **86**, 2342 (1964).

(7) J. L. Hoard, G. H. Cohen, and M. D. Glick, *ibid.*, **89**, 1992 (1967).

(8) H. Schugar, C. Walling, R. B. Jones, and H. B. Gray, *ibid.*, **89**, 3712 (1967).

(9) J. O. Alben, W. H. Fuchsman, C. A. Beaudreau, and W. S. Caughey, *Biochemistry*, **7**, 624 (1968).

(10) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Amer. Soc. Chem.*, **73**, 4315 (1951).