in taking spectra. Some metal complex syntheses were performed by P. B. Bowman. Elemental analyses were done by C. S. Yeh.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
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The Kinetics of Replacement Reactions of Complexes of the Transition Metals with 2,2′,2′′-Terpyridine

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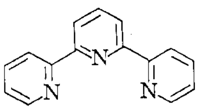
The kinetics of formation and dissociation of complexes of Mn–Zn and Cd with 2,6-bis(2′-pyridyl)pyridine (2,2′,2′′-terpyridine) have been measured by the stopped-flow method. Stability constants have been calculated from these results and the thermodynamic and kinetic data are compared with those for bipyridine and phenanthroline complexes.

Introduction

The kinetics of reactions of metal–phenanthroline and bipyridine complexes have been investigated extensively recently.[2] Many of the labile complexes of the transition metal ions were included in the study and a number of conclusions were reached regarding the mechanism of their formation and dissociation. The present work is an extension to similar complexes of the terdentate ligand 2,6-bis(2′-pyridyl)pyridine (2,2′,2′′-terpyridine, terpy, I). These have been previously much less studied than their bidentate analogs.[3,4] For our purposes, however, terpyridine is a very suitable ligand. It has the desirable properties[2] of high extinction coefficients (bands shifted in the metal complex), weak basicity (pK_1 = 4.7, pK_2 = 3.3),[5] strong chelation, and sufficient solubility in water ($\sim 10^{-3}$ M) for study in micromolar concentration. Furthermore, it has the decided advantage that it forms only two metal complex species in solution, namely, mono and bis, and this simplifies somewhat the unravelling of consecutive associative reactions. (These complexes can exist in only one stereoisomeric form because of the planarity of the ligand.) Finally, the solid complexes M(terpy)Br$_2$, M = Fe, Co, and Ni, can be prepared,[4] and dissolution of these generates M(terpy)(H$_2$O)$_n^{2+}$ ions, which only slowly disproportionate and can thus be allowed to react with ligand to allow unequivocal study of the formation of the bis species. A combination of formation rate data with dissociative rate constants (some obtained previously by conventional exchange methods[4]) allows the estimation of stability constants of the complexes, an added bonus from this work, since thermodynamic data for the terpyridine complexes are virtually nonexistent. A few experiments with another strongly chelating terdentate ligand 4-(2-pyridylazo)resorcinol (PAR, II) have also been performed for comparative purposes. This forms strongly colored complexes of analytical value.[6]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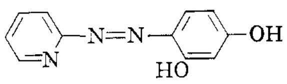
II

Experimental Section

Materials.—Terpyridine, purchased from B. Newton Maine and G. F. Smith, was purified by heating *in vacuo* at 130° for several hours. The white sublimate had mp 86°. M(terpy)Br$_2$, M = Fe, Co, and Ni, was prepared as described previously.[4] PAR and the other reagents were AR grade. Standard solutions were prepared by shaking weighed amounts of terpyridine with hot conductivity water and analyzing the cooled solutions colorimetrically with ferrous ion before runs.

Spectra.—In general two peaks between 310 and 340 mμ are observed for the metal complexes, well separated from the maximum of the free ligand base at 285 mμ.[7] For example the maxima for the bis(terpyridine) complexes in this region are (Ni) ϵ_{334} 3.2×10^4, ϵ_{320} 3.6×10^4; (Cu) ϵ_{323} 3.8×10^4; (Zn) ϵ_{333} 4.1×10^4, ϵ_{320} 3.9×10^4; and for the mono (Co) ϵ_{325} 1.9×10^4, ϵ_{315} 1.8×10^4; (Ni) ϵ_{331} 2.0×10^4, ϵ_{318} 1.8×10^4; (Cu) ϵ_{340} 1.4×10^4, ϵ_{326} 1.4×10^4; (Zn) ϵ_{330} 2.3×10^4, ϵ_{317} 2.2×10^4. For free terpyridine, maxima are at 290 mμ (ϵ 1.6×10^4) and 228 mμ (ϵ 2.0×10^4).

The bulk of the formation studies were observed at wavelengths of 320–335 mμ. The decomposition studies used the visible and near-infrared absorption characteristics of the iron(II), cobalt(II), and copper(II) complexes.[4] The experiments with PAR were observed around 500 mμ where the metal complexes have high absorption.

Kinetics Runs.—The general procedure resembled that reported previously.[2] Both the Sheffield and the Buffalo stopped-flow apparatus were used in this work. Pseudo-first-order kinetics were usually obtained in the formation studies by using rela-

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tively high concentrations of ligand. In some systems with high rate constants, a low ligand : metal ion ratio had to be used to ensure a measurable rate. At the end of the reaction pseudo-first-order conditions still hold, however, and this part was used for measurement. Errors in the rate constants are about ±8% for reactions with first-order rate constant $k \sim 5$ sec^{-1}, ±10–15% for $k \sim 50$ sec^{-1}, and ±20% for $k \sim 150$ sec^{-1}. Half-lives below 5 msec are qualitative only. The formation of the mono species is the rate-limiting step in the reaction of metal ion with excess terpyridine. This could be shown from spectral and kinetic considerations. The formation of the bis species could therefore be measured only with the Fe, Co, and Ni systems since only with these could mono be obtained in solution, by dissolving the solid mono complex. Disproportionation occurs particularly rapidly with iron(II) so that in these experiments fresh solutions of the mono complex were used quickly. In order to ensure complete formation of the manganese–terpyridine complex, relatively high concentrations of ligand had to be used and experiments at lowered temperatures only were feasible. A solution containing nickel nitrate (1×10^{-2} M) and terpyridine (3.9×10^{-3} M) was left for several days at elevated temperature. It was then cooled, diluted 200-fold, left for some time, and then allowed to react with excess PAR (1×10^{-4} M) at pH 6.8 at 500 mμ. Two stages were observed, a fast one ($t_{1/2}$ = 280 msec at 25°) and a much slower one which could be eliminated by the prior addition of EDTA. From the optical density changes [Ni(terpy)$^{2+}$] in the original solution was estimated at 1.6×10^{-3} M (calcd 1.6×10^{-3} M).

Decomposition of the metal complexes was effected by addition of much higher concentrations of an appropriate metal ion. The first-order decomposition rate constant was found to be independent of the concentration of metal ion as in ref 2, thus ensuring the measurement of the dissociation rate. Furthermore, the value for Co(terpy)$_2^{2+}$ → Co(terpy)$^{2+}$ agreed well with that obtained from [^{3}H]-terpyridine exchange studies.[4] It was not found possible to decompose Cu(terpy)$^{2+}$. Little effect on formation or dissociation rates was observed of changes of pH 5.8–6.8, ionic strength, or anion, in low concentrations. A constant ionic strength or buffer was, therefore, not employed. Temperature control of the reactions was ±0.2°. The results are collected in Tables I and II. Several runs were performed with each condition shown, and the results are the mean values.

Results and Discussion

Kinetic Data.—Rate constants and activation parameters are collected in Table III, which also includes previous results for phenanthroline and bipyridine complexes. Energies of activation are approximately ±0.5 kcal/mole^{-1}. The similarity in second-order formation rate constants for a particular metal ion is striking and strongly supports the idea that the addition of any of these ligands to the metal ion is controlled by the first attachment and that this is followed by rapid completion of the chelate. We have previously[2] fully discussed this for the bipyridine complexes and believe similar considerations hold for terpyridine coordination. Further it is clear that the rate of the first step mainly depends upon the water-exchange rate of the metal ion.[8] To us, the most striking evidence for this considering also our previous arguments[2] is the extremely similar rate constants for reaction of nickel ion with pyridine, bipyridine, and terpyridine (Table III). The order of formation rate constants of the mono complex, $Ni^{2+} < Co^{2+} < Fe^{2+} \sim Mn^{2+} < Zn^{2+} <$

TABLE I

KINETIC DATA FOR METAL COMPLEX FORMATION

[metal ion], mM	[ligand], mM	Temp, °C	k_f, M^{-1} sec^{-1}
Mn^{2+} + terpy			
0.025	0.20	9.0	5.8×10^4
		18.0	8.1×10^4
		25.0	1.1×10^5
Fe^{2+} + terpy			
0.005	0.10	0.2	1.4×10^4
0.003	0.05	7.5	2.5×10^4
0.005	0.10	15.0	3.8×10^4
0.003	0.05	20.0	5.2×10^4
0.005	0.10	25.0	5.6×10^4
Fe(terpy)$^{2+}$ + terpy			
0.002	0.005	5.0	1.1×10^7
Co^{2+} + terpy			
0.01	0.096	0.2	5.4×10^3
0.01	0.096	14.4	1.3×10^4
0.005	0.120	15.0	1.5×10^4
0.005	0.120	25.0	2.4×10^4
Co(terpy)$^{2+}$ + terpy			
0.005	0.02	5.0	5×10^6
Co(terpy)$^{2+}$ + PAR			
0.001	0.005	5.0	6.7×10^6
0.001	0.005	12.0	1.1×10^7
Ni^{2+} + terpy			
0.005	0.07	6.8[a]	2.4×10^2
0.005	0.14	6.8[a]	2.7×10^2
100	0.05	7.0	4.6×10^2
0.005	0.07	16.2[a]	5.4×10^2
0.005	0.14	16.2[a]	5.8×10^2
0.005	0.08	25.0[a]	1.4×10^3
Ni^{2+} + PAR			
1.0	0.01	25.0	1.4×10^3 [b] 3.2×10^3 [c]
Ni(terpy)$^{2+}$ + terpy			
0.01	0.10	10.0	7.6×10^4
0.01	0.10	18.0	1.3×10^5
0.01	0.10	25.0	2.2×10^5
0.10	0.01	25.0	2.2×10^5
0.01	0.10	32.0	3.3×10^5
0.01	0.10	40.0	6.9×10^5
Ni(terpy)$^{2+}$ + PAR			
0.01	0.05	25.0	6.8×10^4
0.10	0.01	25.0	6.3×10^4
Ni(bipy)$_2$ + bipy			
0.01	0.07	25.0	4.7×10^3
Ni(bipy)$_2$ + terpy			
0.01	0.04	25.0	5×10^3 [d]
Ni(bipy)$_2$ + PAR			
0.01	0.06	25.0	8.3×10^3 [c,d]
Cu^{2+} + terpy			
0.01	0.04	6.5	2×10^7
Zn^{2+} + terpy			
0.0025	0.03	0.2	3.9×10^5
0.002	0.05	7.5	6.3×10^5
0.002	0.05	15.0	8.0×10^5
0.002	0.05	25.0	1.1×10^6
Cd^{2+} + terpy			
0.002	0.01	0.2	1.1×10^6
0.002	0.01	5.0	1.4×10^6
0.002	0.01	15.0	2.0×10^6
0.002	0.01	25.0	3.2×10^6

[a] Using a commercial spectrophotometer. [b] pH 5.0, the PAR reactant is II. [c] pH 6.7, the PAR reactant is partly 3-O$^-$ form of II.[6] [d] These reactions are followed by slower ones as bipyridine is released.

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(8) M. Eigen and R. G. Wilkins, "The Kinetics and Mechanism of Formation of Metal Complexes," Advances in Chemistry Series, No. 29, American Chemical Society, Washington, D. C., contains an account and full tabulation of kinetics and mechanism of formation of metal complexes.

TABLE II

KINETIC DATA FOR DISSOCIATION OF METAL–TERPYRIDINE COMPLEXES

[metal ion], mM	[decomposing metal ion], mM	Temp, °C	k_1, sec^{-1}
$Mn(terpy)^{2+}$	Co^{2+}		
0.2	2.6	11.0	1.4
		19.0	2.5
		25.0	3.8
		32.0	6.3
		40.0	10.7
$Co(terpy)_2^{2+}$	Fe^{2+}		
0.03	10.0	25.5	1.1×10^{-3} [a]
$Zn(terpy)^{2+}$	Cu^{2+}		
5.0	20.0	10.0	0.25
		18.0	0.58
		25.0	1.2
		32.0	2.5
		40.0	5.7
$Cd(terpy)^{2+}$	Cu^{2+}		
5.0	20.0	10.0	8.2
		19.0	16
		25.0	26
		32.0	39
		40.0	69

[a] From exchange studies,[4] $k_1 = 1.4 \times 10^{-3}$.

TABLE III

KINETIC PARAMETERS FOR FORMATION AND DISSOCIATION OF METAL COMPLEXES WITH BIDENTATE AND TERDENTATE LIGANDS AT 25.0°

Ion	Ligand	Log k_f[a]	Log A_f	E_f	Log k_d[b]	Log A_d	E_d
Mn^{2+}	phen	5.1[c]			1.5[c]	9.6	10.4
	terpy	5.0	9.8	6.6	0.6	9.7	12.3
Fe^{2+}	bipy	5.2	13.5	11.3			
	terpy	4.9	12.2	10.0	−2.2	11.0	18.0
$Fe(bipy)_2^{2+}$	bipy	5.1					
$Fe(terpy)^{2+}$	terpy	~7.0[d]			−6.8	14.3	28.7
Co^{2+}	phen	5.5	13.7	11.2	−1.8	12.4	19.4
	bipy	4.8	12.5	10.4			
	terpy	4.4	11.4	9.5	−4.0	10.8	20.2
$Co(terpy)^{2+}$	terpy	~6.7[d]			−3.2	7.7	14.8
	PAR	6.9[d]					
Ni^{2+}	phen	3.5	13.6	13.7	−5.0	13.0	24.5
	py	~3.6		~12	1.6	13.6	16.0
	bipy	3.2	13.3	13.8	−4.3	13.2	23.7
	terpy	3.1	13.9	14.7	−7.6	10.2	24.2
	PAR	3.5					
$Ni(bipy)_2^{2+}$	bipy	3.7			−2.5	13.8	22.2
	terpy	~3.7					
	PAR	3.9					
$Ni(terpy)^{2+}$	terpy	5.3	14.2	12.1	−5.8	9.5	20.8
	PAR	4.8					
Cu^{2+}	bipy	⩾7.0					
	terpy	~7.3[d]					
Zn^{2+}	phen	~6.3			0.6	9.7	12.3
	bipy	6.0	11.1	6.9	1.2	10.1	12.1
	terpy	6.1	12.3	8.4	0.1	13.5	18.3
Cd^{2+}	phen	~7.0			1.6	12.2	14.4
	terpy	6.5	11.6	7.0	1.4	10.6	12.5

[a] Formation rate constant, M^{-1} sec^{-1}. [b] Dissociation rate constant, sec^{-1}. [c] 11.0°. [d] 5.0°.

$Cd^{2+} < Cu^{2+}$, previously observed with the bidentate ligands, is maintained. The most unexpected result, however, which emerges from this study concerns the rate constants for the formation of the bis from the mono species for the iron, cobalt, and nickel ions. Although it might be expected, from statistical and stereochemical considerations, that the values would be significantly smaller than the corresponding values for the formation of mono, in fact they are some 200 times greater. Margerum and Eigen[9] have studied the effect of coordinated ligands (of polyamine and amino carboxylate types) on the subsequent rates of water substitution but observed (at the most) a tenfold enhancement compared with the aquated nickel ion itself. Since our observed effect is such a large one we have also measured the reaction rate of $Ni(terpy)^{2+} \rightarrow Ni(terpy)_2^{2+}$ in another manner. In the event that the solid mono complexes do not dissolve in aqueous solution to produce the $M(terpy)(H_2O)_n^{2+}$ species, we have allowed an equilibrated mixture of Ni^{2+}, $Ni(terpy)^{2+}$, and $Ni(terpy)_2^{2+}$ to react with excess terpyridine in the stopped-flow apparatus. Two rate processes were observed, a fast and a slow reaction, which could be quantitatively assigned to the terpyridine reaction with mono species and the nickel ion, respectively. The slow reaction could be suppressed by the addition of EDTA to the equilibrated mixture just prior to the kinetic experiment. Further, the amount of mono species could be assessed from the (fast) optical density change on the addition of terpyridine, and this agreed well with that calculated from the kinetically-determined stability constants. The enhanced reactivity of the $M(terpy)^{2+}$ species (toward terpy or PAR) contrasts sharply with the much slower reactions of $Ni(bipy)_2^{2+}$ with bipy, terpy, or PAR, all of which have a rate constant around 5×10^3 M^{-1} sec^{-1} at 25°. The current ideas[8] on complex formation with these metal ions equates the formation rate constant (k_f) with an outer-sphere or collision complex association constant (K_0) and the first-order rate constant for water exchange of the outer-sphere complexes (k_1); *i.e.*, $k_f = K_0k_1$. A high value for k_1 cannot be the explanation for the reactivity of $Ni(terpy)^{2+}$ since the water exchange rate of the latter is similar to that of Ni^{2+} by nmr measurements.[10] We conclude than that the terpyridine either takes part in an S_N2 attack on the complex ion or is able to form a strong adduct ($K_0 \gg 1$) prior to formation of the inner-sphere complex. The *modus operandi* of the effect remains unknown to us to us, however.

Thermodynamic Data.—Our kinetic results give the free energy and heat of reaction for the terpyridine complexes and are shown in Table IV together with bipyridine data.[11,12] The usual sequence of stability $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} > Zn^{2+} > Cd^{2+}$ pertains for the mono complex. This order is very much dictated by the dissociative rate constants, which also accounts for the enhanced stability of the terpyridine compared to the corresponding bipyridine complex. The free energies of formation of the mono(terpyridine) complexes of Mn, Fe, Co, and Ni are 1.5–1.7 times those of the corresponding bipyridine analogs; the total free energies of formation of the bis(terpyridine) complexes of Fe, Co, and Ni are, however, only slightly greater than those of $M(bipy)_3^{2+}$. This behavior resembles closely that of ethylenediamine compared with

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TABLE IV
THERMODYNAMIC PARAMETERS FOR METAL–BIPYRIDINE[a] AND –TERPYRIDINE[b] COMPLEXES AT 25°

Metal ion	Ligand	Log K_1	$-\Delta H_1$	Log β_n[c]
Mn^{2+}	bipy	2.6	3.5	
	terpy	4.4	5.7	
Fe^{2+}	bipy	4.3	(6.0)[d]	17.5
	terpy	7.1	8.0	20.9
Co^{2+}	bipy	5.7	8.2	16.1
	terpy	8.4	10.7	18.3
Ni^{2+}	bipy	7.1	9.6	20.1
	terpy	10.7	9.5	21.8
Zn^{2+}	bipy	5.2	7.1	
	terpy	6.0	10.1	
Cd^{2+}	bipy	4.3	5.1	
	terpy	5.1	5.5	

[a] Data from ref 11 and 12. [b] $K = k_f/k_d$; $\Delta H = E_f - E_d$. [c] $\beta_n = K_1K_2K_3$ for bipy and K_1K_2 for terpy. [d] Estimated.[12]

diethylenetriamine complexes. The corresponding ratio for the zinc and cadmium complexes is only 1.2, suggesting that terpyridine chelates comparatively more weakly with these metal ions. It is unlikely, however, that they are acting as bidentate ligands only, since the structure of Zn(terpy)Cl_2 shows that all three nitrogens coordinate with only minor strain.[13]

Although there are puzzling features which certainly require further examination, nevertheless a good deal of understanding now exists in this particular area. We are turning our attention to solvents other than water as well as metal ions such as chromium(II) and vanadium(II), for which there is a paucity of data.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS, AND THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The Synthesis, Structures, and Solution Equilibria of Bis(pyrrole-2-aldimino)metal(II) Complexes

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Synthesis of an extensive series of bis(pyrrole-2-aldimino)metal(II) complexes with M(II) = Co, Ni, Pd, Cu, and Zn and various alkyl groups (R) appended to the azomethine nitrogen has been effected by a nonaqueous chelation reaction in tetrahydrofuran. Preliminary single crystal X-ray results for complexes with R = *t*-butyl reveal that cobalt, nickel, and zinc complexes are isomorphous, but appreciable differences in the cell constants of the nickel complex indicate that it is not truly isostructural with the tetrahedral cobalt and zinc complexes. The copper complex exists in two crystalline modifications, neither of which is isomorphous with the Co–Ni–Zn series. Spectral and magnetic studies in solution show that the *t*-butyl cobalt complex is tetrahedral whereas the corresponding copper complex is distorted from planarity to an unknown extent. Copper complexes with less bulky R groups are planar. The *t*-butyl nickel complex is pseudo-tetrahedral; complexes with *sec*-alkyl groups such as isopropyl are involved in a configurational equilibrium between planar and pseudo-tetrahedral forms. The paramagnetic nickel complexes show large isotropic proton hyperfine contact shifts. Spin density calculations for the coordinated ligand system are used as the basis of proton resonance assignments. It is concluded that in the pseudo-tetrahedral form spin imbalance exists in the highest filled ligand π-MO and that in addition there is an underlying spin imbalance in the highest filled σ-MO, the result of which is observable in the proton resonance spectra. Thermodynamic parameters characterizing the structural change have been obtained for the nickel complexes from the temperature dependence of the proton contact shifts. A quantitative comparison of the stabilization of tetrahedral Ni(II) by pyrrole-2-aldimine, salicylaldimine, and β-ketoamine ligand systems is presented.

Introduction

During the past several years efforts in these laboratories have been directed toward an examination of the occurrence of conformational equilibria of metal complexes in solutions of noncoordinating solvents and evaluation of the relative stabilities of the stereoisomers involved. Particular emphasis has been placed on the planar $\rightleftharpoons$ tetrahedral equilibrium of four-coordinate nickel(II) complexes. It is now well established that this equilibrium, while still rare, does persist in four general groups of bis-bidentate nickel(II) complexes, *viz.*, salicylaldimines,[2-4] naphthaldimines,[5] β-ketoamines,[6] and aminotroponeiminates,[7] and is frequently measurably altered in position by changes in solvent, temperature, and substituents appended to the basic ligand structure. In addition to our studies, those of

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