57. *Exchange Studies of Certain Chelate Compounds of the Transitional Metals. Part VIII.*[1] *2,2′,2″-Terpyridine Complexes.**

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The preparation of complexes of 2,2′,2″-terpyridine with bivalent manganese, iron, cobalt, nickel, copper, and zinc is described. The spectra and magnetic susceptibilities of certain of these compounds have been measured. The kinetic lability of the bis-complexes has been examined by [^{3}H]-terpyridine exchange and of the mono-series by metal exchange and from disproportionation rates. The kinetic parameters [including the first results for high-spin iron(II)] are compared with those for bipyridyl complexes, and the energies of activation are discussed in terms of the crystal-field theory of co-ordinate bonding. The preparation of radiochemically pure [^{3}H]terpyridine, by the gas-exposure method and subsequent purification, is described.

We have hitherto studied the metal complexes of the bidentate ligands 2,2′-bipyridyl and 1,10-phenanthroline and also examined the effect of substitution in the aromatic ligand on dissociation rates of nickel(II) complexes. Substitution adjacent to the co-ordinating nitrogen markedly enhances these rates, but if a substituent was chosen which was itself capable of metal co-ordination then the resultant terdentate ligand would form very stable complexes. An example of such a substituent is 2-pyridyl and the ligand, 2,2′,2″-terpyridine (here afterwards abbreviated to terpyridine, terpy), was first described in 1932.[2] Subsequently a number of the reactions with metal salts were investigated.[3] There has since been little systematic work on the complexes formed by this interesting ligand. As a necessary part of the kinetic work, we have therefore investigated the preparation and the spectral and magnetic properties of bis- and mono-terpyridine complexes of bivalent maganese, iron, cobalt, nickel, and copper. We have then examined the lability of the bis-series of complexes by terpyridine exchange studies, and the mono-series by metal exchange and disproportionation rates. Since the direct synthesis of radioactive terpyridine would be difficult, we used generally labelled [^{3}H]-material obtained by exposure of terpyridine to gaseous tritium.[4] We should expect from such treatment, as well as [^{3}H]terpyridine, tritium-containing radiation decomposition products, and several workers using this method of labelling have emphasised the difficulty of purification from such decomposition products. Probably the best method is to carry out a cycle of chemical reactions on the product. A sequence of complex formation and decomposition is likely to be successful here, since other conceivable products will all chelate less strongly than terpyridine and might therefore be removed by this treatment.

EXPERIMENTAL

Materials.—2,2′,2″-Terpyridine was a gift from Dr. A. Jubb of Imperial Chemical Industries Limited. It had m. p. 86—87° (Found: C, 77·1; H, 4·8; N, 18·1. Calc. for $C_{15}H_{11}N_3$: C, 77·2; H, 4·8; N, 18·0%). The ligand is extremely toxic and was handled carefully. The bis-series of complexes were prepared from it as follows:

Bis(terpyridine)manganese(II) *bromide monohydrate.* Manganous chloride tetrahydrate (1·0 mmole), terpyridyl (2·0 mmoles), and water (10 ml.) were boiled and shaken until the base had dissolved. When a saturated solution of potassium bromide was added to the cooled solution, yellow crystals of the complex *bromide* separated. This was recrystallised from

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[1] Part VII, Ellis, Hogg (in part), and Wilkins, *J.*, 1959, 3308.
[2] Morgan and Burstall, *J.*, 1932, 20.
[3] Morgan and Burstall, *J.*, 1937, 1649.
[4] Wilzbach, *J. Amer. Chem. Soc.*, 1957, **79**, 1013.

hot water and air-dried (Found: C, 52·1; H, 3·8. $C_{30}H_{24}Br_2MnN_6O$ requires C, 51·5; H, 3·5%).

Bis(terpyridine)cobalt(II) *chloride pentahydrate.* A solution of cobalt chloride hexahydrate (1·0 mmole) and terpyridine (2·0 mmoles) in water (30 ml.) was evaporated (10 ml.), some green material removed, and the filtrate further evaporated (to 2—3 ml.). Cooling in ice-water caused deep brown crystals to separate (Found: C, 52·8; H, 4·5; N, 12·5. $C_{30}H_{32}Cl_2CoN_6O_5$ requires C, 52·5; H, 4·7; N, 12·3%).

Bis(terpyridine)copper(II) *perchlorate monohydrate.* Copper nitrate trihydrate (0·5 mmole) and terpyridine (1·1 mmoles) were boiled with water (15 ml.) and, when the base had dissolved, the solution was cooled and a small amount of terpyridine which separated was removed. Sodium perchlorate solution precipitated green crystals of the complex *perchlorate.* This was recrystallised from a large amount of hot water and air-dried (Found: C, 47·9; H, 3·5; Terpyridine, 64·5. $C_{30}H_{24}Cl_2CuN_6O_9$ requires C, 48·2; H, 3·2; Terpyridine, 62·2%). The terpyridine in the complex was determined by an isotopic dilution method. The specific activity of [^{3}H]terpyridine was determined before and after mixing (exchanging) with a solution of the complex.

Bis(terpyridine)zinc(II) *perchlorate monohydrate.* Zinc acetate dihydrate (0·5 mmole) and terpyridine (1·0 mmole) were dissolved in boiling water (10 ml.), and the solution was evaporated to 5 ml. Addition of sodium perchlorate solution precipitated the white complex *perchlorate*, which was recrystallised from hot water and air-dried (Found: C, 47·8; H, 3·3. $C_{30}H_{24}Cl_2N_6O_9Zn$ requires C, 48·0; H, 3·2%).

Bis(terpyridine)-iron(II), *-cobalt*(II), *and -nickel*(II) *Bromide Monohydrate.*—These hydrates were prepared as described by Morgan and Burstall.[3]

Bis(terpyridine)nickel(II) *chloride pentahydrate* was prepared by obvious modification of the method used for the corresponding bromide [3] (Found: C, 52·8; H, 4·5. $C_{30}H_{32}Cl_2NiN_6O_5$ requires C, 52·5; H, 4·7%).

The mono(terpyridine) complexes of manganese, iron, cobalt, and nickel were prepared by heating the corresponding bis-compounds (~0·3 g.) *in vacuo.* Hydrate water was removed at lower temperatures (~56°), and at elevated temperatures the theoretical amount of terpyridine sublimed on to the cooler part of the Abderhalden pistol. No loss of terpyridine from the mono-complex occurred, even at higher temperatures. The following new compounds were prepared (reaction time and temperature in parentheses):

Mono(terpyridine)manganese(II) *bromide* (1·5 hr. at 80°), pale yellow solid (Found: C, 40·6; H, 2·7. $C_{15}H_{11}Br_2MnN_3$ requires C, 40·2; H, 2·4%).

Mono(terpyridine)iron(II) *bromide* (6 hr. at 170°), reddish-purple solid giving a cherry-red solution when freshly dissolved in ice-cold water (Found: C, 39·5; H, 2·6; N, 8·9. $C_{15}H_{11}Br_2FeN_3$ requires C, 39·8; H, 2·4; N, 9·4%).

Mono(terpyridine)cobalt(II) *bromide* (3 hr. at 100°), grass-green solid which dissolved in water to a very pale green solution, only slowly changing to deep brown of the bis-complex (Found: C, 39·6; H, 2·6; N, 8·8. $C_{15}H_{11}Br_2CoN_3$ requires C, 39·8; H, 2·4; N, 9·3%).

Mono(terpyridine)cobalt(II) *chloride* (2 hr. at 180°), slightly darker green than corresponding bromide, with signs of very slight decomposition (Found: C, 49·7; H, 3·3; N, 11·8. $C_{15}H_{11}Cl_2CoN_3$ requires C, 49·7; H, 3·1; N, 11·6%).

Mono(terpyridine)nickel(II) *bromide* (9 hr. at 200°), greenish-yellow solid dissolving in water to a green solution (Found: C, 40·0; H, 2·8. $C_{15}H_{11}Br_2NiN_3$ requires C, 39·8; H, 2·4%).

Mono(terpyridine)nickel(II) *chloride* was prepared similarly (Found: C, 50·6; H, 3·4; N, 11·6. $C_{15}H_{11}Cl_2NiN_3$ requires C, 49·7; H, 3·1; N, 11·6%).

Mono(terpyridine)copper(II) *Perchlorate Monohydrate.*—Cupric chloride dihydrate (0·5 mmole), terpyridine (0·5 mmole), and water (50 ml.) were boiled. To the cooled solution, saturated sodium perchlorate solution was added and deep blue plates of the complex *perchlorate* separated. This was fairly soluble in water and recrystallised from a small amount of hot water (Found: C, 35·5; H, 2·6; N, 8·2; Terpyridine, from isotopic dilution, 45·3. $C_{15}H_{13}Cl_2CuN_3O_9$ requires C, 35·0; H, 2·5; N, 8·2; Terpyridine, 45·0%).

Radioactive Metals.—Copper foil (1 g.) was irradiated for 24 hr. at Harwell. The approximate activity of material reaching Sheffield was 30 mc. The foil was partially dissolved in 5M-nitric acid (12 ml.), the final solution that contained $^{64}Cu(NO_3)_2$ having pH ~4. A small aliquot part was used in the exchange experiments. The experimental half-life agreed with the recognised value for ^{64}Cu (12·8 hr.). Radiochemically pure cobalt(II) nitrate solution was prepared from neutron-irradiated metallic cobalt. ^{63}Ni-Containing nickel nitrate solution was as used previously.[5]

[^{3}H]*Terpyridine*.—Terpyridine (0·1 g.) and gaseous tritium (2 c; obtained from The Radiochemical Centre, Amersham) were left together for 7 days (about 20 cm. pressure). The solid was occasionally shaken to expose fresh surface.[6] The tritium was manipulated by using a Toepler pump in a somewhat simpler arrangement than that described by Rydberg and Hanngren.[6] At the end of the contact period, the material was dissolved in acid (pale yellow solution) and terpyridine was reprecipitated with alkali. Any adsorbed gas was removed by this means. The active material was then diluted with terpyridine (0·9 g.) *via* ligroin solution and the dried terpyridine radioassayed as an " infinitely " thick 1 : 1 graphite mixture [7] (with standard conditions, 3·7 × 10^4 counts/min.). Zinc ions and the radiochemically impure terpyridine (mol. ratio 1 : 1·05, so that radioactive decomposition products must compete with terpyridine for zinc) were heated and the aqueous solution shaken with chloroform and then benzene to extract any free organic compounds. Mono(terpyridine)zinc perchlorate was precipitated from the solution, washed with absolute alcohol, and recrystallised from aqueous alcohol. [^{3}H]Terpyridine was regenerated by dissolving the zinc complex in acid, decomposing it with 2M-sodium hydroxide, and extracting the base with benzene. The base was extracted from the benzene by acid and precipitated with alkali. It was recrystallised from ligroin (b. p. 40—60°) (1·9 × 10^4 counts/min.). Repetition of this cycle afforded [^{3}H]terpyridine (1·1 × 10^4 counts/min.) and the specific activity was not lowered further with another " zinc cycle," or by a similar cycle *via* mono(terpyridine)copper(II) perchlorate (complex decomposed by hydrogen sulphide in acid solution). The material (0·7 g.) was considered radiochemically pure. This was reasonably justified as follows:

[^{3}H]Terpyridine (5 mg.) in aqueous solution was added to a solution (430 ml.) containing $[\mathrm{Ni\ terpy_2}]^{2+}$ (0·23 mmole/l.) and terpyridine (0·6 mmole/l.). The mixture was divided into two: from one portion radioactive terpyridine was extracted with benzene, the complex remaining precipitated, dried, and radioassayed as the perchlorate (~20 counts/min.), and the terpyridine recovered from the benzene (1060 counts/min., as 1 : 1 graphite mixture). The second portion was refluxed for an hour to complete exchange, and terpyridine was extracted and radioassayed (640, 632; theor., 600 counts/min.).

[^{3}H]Bipyridyl was also prepared by the gas-exposure method and purified (to constant specific activity) similarly to terpyridine by forming and decomposing (with EDTA) the tris(bipyridyl)nickel complex. The material gave the same exchange rate for the $[\mathrm{Ni\ bipy_3}]^{2+}$–bipyridyl system as was obtained by using [^{14}C]bipyridyl synthesised from [1-^{14}C]glycerol.[8] Purification of terpyridine *via* the nickel complex was not feasible because of its extreme stability to decomposition.

Spectral Measurements.—These were important in confirming the species present in the exchange studies, since no quantitative stability data are available. Spectra were determined with a Unicam S.P. 600 in the range 400—1000 mμ, where metal ion and ligand absorption is negligible. The spectrum (bis) remained sensibly constant when two or more equivalents of ligand to metal ion were used. The spectrum of the mono-species was obtained by dissolving the solid complexes of iron, cobalt, and nickel in water and (especially with iron at 0°) quickly measuring the spectrum, before disproportionation became important. In the cases of manganese and copper, the mono-species is sufficiently stable for a mixture of ligand with an excess of metal ions to provide the required spectrum. The results are shown in the Figure and in Table 1 for the important wavelength regions.

Susceptibility Measurements.—The Gouy method, involving the normal arrangements, was used and measurements were carried out at room temperature (20°) and at liquid-nitrogen temperature. For intermediate temperatures " slush " baths were used. The apparatus was calibrated by means of ferrous ammonium sulphate. The results are shown in Table 2.

Kinetic Experiments.—(a) *Ligand exchange*. A solution of the bis-complex (~1 mM) and terpyridine (~1 mM) was prepared by heating the metal salt with terpyridine in aqueous solution until the base had dissolved. The solution was then left overnight at the temperature of the exchange experiment. A small amount of [^{3}H]terpyridine (~2% of the total terpyridine; in

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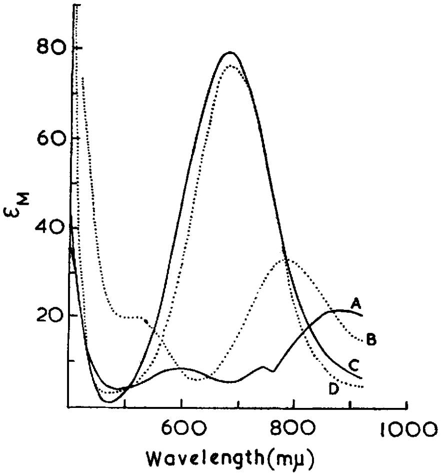
[5] Wilkins and Williams, *J.*, 1957, 4514.
[6] Rydberg and Hanngren, *Acta Chem. Scand.*, 1958, **12**, 332.
[7] Ahmed and Wilkins, *J.*, 1959, 3700.
[8] Ellis, Ph.D. Thesis, Sheffield, 1958.

aqueous solution) was added to initiate exchange. The complex was separated as the perchlorate by means of concentrated sodium perchlorate solution. The precipitate was washed with water and dried, washed with ethyl acetate (to remove any remaining sodium perchlorate), and finally dried in a vacuum desiccator. The material was radioassayed in a gas-flow proportional counter as described previously.[7] " Zero-time " exchange was small, ~5% with iron and nickel and 15% with cobalt system. Excellent first-order exchange plots were obtained, with 5—7 points per run. Boiled-out conductivity water was used and an inert atmosphere maintained for the cobalt complex (although omission of these precautions did not markedly alter the exchange rate). The pH of most experiments was 5·5—6·3. Detailed work on the ferrous complex shows the rate is independent of acidity in this region. Results are shown in Table 3.



Absorption spectra of nickel– and copper–terpyridine complexes; A, [Ni terpy]$^{2+}$; B, [Ni terpy$_2$]$^{2+}$; C, [Cu terpy]$^{2+}$; D, [Cu terpy$_2$]$^{2+}$.

TABLE 1.

Spectral data of terpyridine complexes.

Wavelength (mμ)	[Mn terpy$_2$]$^{2+}$ (ε_M)	[Mn terpy]$^{2+}$ (ε_M)	[Fe terpy$_2$]$^{2+}$ ($10^{-3}\varepsilon_M$)	[Fe terpy]$^{2+}$ ($10^{-2}\varepsilon_M$)	[Co terpy$_2$]$^{2+}$ ($10^{-3}\varepsilon_M$)	[Co terpy]$^{2+}$ (ε_M)
400	214	30		1·5	1·4	53
410	152	20				40
420	103	14			1·5	30
430	81	10				23
440	56	6·7			1·6	21
450	37	4·4		2·7	1·62	19
460	28	3·3			1·5	18
470	21	2·5			1·4	18
480	15	2·0			1·3	18
490	11	1·6			1·3	19
500	8·3	1·4	6·2	6·4	1·4	20
510	6·1	1·2	6·7		1·42	21
520	4·4		7·1	7·2	1·1	15
530	2·0		7·8		0·7	
540			9·1		0·58	
550			11·3	8·6	0·6	
560			9·1	7·8		12
570			5·4			
580			3·5		0·25	
590			2·7			
600			2·4	1·2		

(b) *Metal exchange.* A solution of the cobalt or nickel bis- or copper mono-complex and metal ion was equilibrated at the exchange temperature. A small amount of the respective radioactive metal nitrate solution was added, and the complex separated as perchlorate and washed as described above. A standard amount of the cobalt or copper complex was radioassayed with an end-window counter, and an " infinite " thickness of the nickel complex with

TABLE 2.

Magnetic susceptibilities of terpyridine complexes.

Compound	Temp.	$10^6\psi_M$	$10^6\psi_M$ [a] (corr.)	μ (B.M.)
Terpyridyl	20°	−148		
[Mn terpy$_2$]Br$_2$	20	13,620	13,985	5·9
[Fe terpy$_2$]Br$_2$,H$_2$O	20	0	380	0·0
[Fe terpy Br$_2$]	20	11,045	11,263	5·1
[Co terpy$_2$]Br$_2$,H$_2$O	78	2995	3375	3·1
	20	2716	3096	2·7
	−85	2638	3018	2·1
	−196	4991	5371	1·9
	20 [b]	1625	2005	2·2
[Co terpy$_2$]Cl$_2$,H$_2$O	20	1425	1782	2·1
[Co terpy$_2$](ClO$_4$)$_2$	20	7540	7900	4·3
[Co terpy Br$_2$]	20	10,100	10,318	4·9
	−196	34,900	35,118	4·7
[Ni terpy$_2$]Br$_2$	22	3770	4135	3·1
	−196	14,927	15,292	3·1
[Ni terpy Br$_2$]	24	4068	4286	3·2

[a] Corrected value; diamagnetic corrections from Figgis and Lewis in "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, Chapter 6. [b] 0·06M-Aqueous solution.

TABLE 3.

Exchange of [M terpy$_2$]$^{2+}$ with terpyridine.

Complex	Temp.	Complex (mmole l.$^{-1}$)	Terpyridine (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ (min.)	10^3k_2 (min.$^{-1}$)
M = Fe	35·4°	0·79	0·98	8400	0·06
	45·8	0·83	1·30	2730	0·22
	60·5	0·83	1·30	438	1·4
	66·0	0·84	1·28	164	3·65
	70·8	0·84	1·30	95	6·4
	70·8	0·69	1·66	110	6·9
M = Co	0·1	0·97	1·05	50	9·8
	0·1 [a]	0·27	1·23	95	10·1
	6·0	0·76	0·86	30	17·0
	10·5	0·77	0·84	19	25·8
	10·5	0·27	1·22	36	26·7
M = Ni	44·8	0·45	0·47	610 [b]	0·78
	44·8	1·22	1·28	540	0·88
	44·8	1·13	1·27	570	0·87
	59·0	1·13	1·26	138	3·6
	70·2	1·13	1·26	51	9·8
	70·2	1·13	1·90	61	10·1
M = Mn, Cu, and Zn	0·1	1·4 [c]	1·3	<0·1	

[a] pH = 6·9. [b] Similar half-life from examining specific activity of terpyridine. [c] On basis that formation of the bis-complex is complete.

TABLE 4.

Dissociation of [M terpy]$^{2+}$.

Metal	Temp.	10^3k_1 (min.$^{-1}$)	Metal	Temp.	[Complex] (mmole l.$^{-1}$)	[Metal] (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ (exch) (min.)	10^3k_1 (min.$^{-1}$)
Mn (D)	1·5°	>7000	Co (D)	1·7°				0·36
Fe (D)	1·4	30	(D)	25·2				6·4
(D)	1·7	32	(E)	25·0	6·45	1·60	17	6·8
(D)	22·3	320	(D)	33·3				15·9
(D)	22·3	320	Ni (D)	79·0				1·8
			(E)	80·7	11·05	3·7	102	1·7
			(E)	94·6	11·05	3·7	27·5	6·3
			Cu (E)	0·1	6·2	20·0	<0·1	>7000

a gas-flow proportional counter. With the conditions of exchange for cobalt and nickel systems (see Table 4) only small amounts (6—10%) of the mono-species were present; the expression ln (1 − fraction exchange) = − R_1 [total metal] . t/[complexed metal][free metal] was used.[9] A high ratio for $[Cu^{2+}]/[Cu\ terpy^{2+}]$ was used to obtain as slow an exchange rate as possible. The results are indicated E in Table 4.

(c) *Disproportionation studies.* A sample of solid mono(terpyridine)-manganese, -iron, -cobalt, or -nickel halide complex was dissolved quickly by shaking it vigorously with water from a thermostat, and the solution was transferred to a thermostatted cell in a Unicam S.P. 600 spectrophotometer. The wavelength was chosen to reflect the greatest possible change in optical density during the disproportionation (see Figure and Table 1): Mn 450 mμ, Fe 550 mμ, Co 440 mμ, Ni 780, 850, and 890 mμ. The concentration of the complex was estimated from the optical density of the final solution, in which an excess of terpyridine had been dissolved to ensure formation of the bis-complex. For the disproportionation $2[M\ terpy]^{2+} \longrightarrow [M\ terpy_2]^{2+} + M^{2+}$, the optical density of the reaction solution in a 1 cm. cell at time t is

$$O_t = O_{\text{mono}} + O_{\text{bis}} = \varepsilon_{\text{mono}}[\text{mono}]_t + \varepsilon_{\text{bis}}([\text{mono}]_0 - [\text{mono}]_t)/2.$$

Thus

$$[\text{mono}]_t = (2O_t - \varepsilon_{\text{bis}}[\text{mono}]_0)/(2\varepsilon_{\text{mono}} - \varepsilon_{\text{bis}}).$$

From a plot of log $(2O_t - \varepsilon_{\text{bis}}[\text{mono}]_0)$ against time, compiled from very early values, the disproportionation rate constant can be estimated (D in Table 4).

RESULTS AND DISCUSSION

Preparation of Complexes.—The bis-complexes of manganese, copper, and zinc have not been described previously. Although Morgan and Burstall[3] found that the solubility of mono(terpyridine)copper(II) chloride and mono(terpyridine)zinc(II) chloride in water was enhanced by terpyridine, they were unable to isolate higher complexes. We found that addition of perchlorate to a solution containing a 2 : 1 molar ratio of ligand to metal precipitates the solid bisperchlorate; this was used as a separation method for ligand exchange.

The mono-complexes of manganese, iron, cobalt, and nickel were prepared by heating the corresponding bis-compounds *in vacuo*, a treatment resembling that for obtaining the lower bipyridyl and phenanthroline complexes.[10,11] They are paler than the bis-complexes. For a particular anion (bromide) the ease of removal of terpyridine decreases in the sequence Mn > Co > Fe > Ni and for a particular metal (cobalt) decreases in the order Br > Cl > NO_3. Metal terpyridine perchlorates explode violently when heated.

Spectral and Magnetic Characteristics.—This section will be concerned mostly with a comparison between the terpyridine and bipyridyl complexes.

There is no maximum in the visible spectra of the manganese–terpyridine complexes and this resembles the situation with bipyridyl and phenanthroline complexes[12] (see Table 1). All the complexes are of high-spin type, the magnetic moment of $[Mn\ bipy_3]Br_2$ (6·0 B.M.)[13] being similar to the value for the corresponding terpyridine compound (see Table 2).

The intense purple colour of the ferrous complexes with this type of ligand is well known. Our values for the peak position and intensity of $[Fe\ terpy_2]^{2+}$ absorption agree well with those of Martin and Lissfelt[14] who obtained $\varepsilon_{\text{max.}}$ at 552 mμ = $1{\cdot}16 \times 10^4$, showing an increased absorption and a shift to longer wavelengths compared with $[Fe\ bipy_3]^{2+}$ ($\varepsilon_{\text{max.}}$ at 523 mμ = $0{\cdot}85 \times 10^4$). Evidence for a lower ferrous complex with bipyridyl and phenanthroline is afforded by the appearance of a transient yellow colour when a small amount of the ligand in acid solution is added to a large excess of ferrous ion.[15,16] The spectral characteristics of $[Fe\ bipy]^{2+}$ have been carefully

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[9] Wilkins and Williams, *J. Inorg. Nuclear Chem.*, 1958, **6**, 52.
[10] Pfeiffer and Tappermann, *Z. anorg. Chem.*, 1933, **215**, 273.
[11] Basolo and Dwyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1454.
[12] Miller and Brandt, *J. Amer. Chem. Soc.*, 1955, **77**, 1384.
[13] Burstall and Nyholm, *J.*, 1952, 3571.
[14] Martin and Lissfelt, *J. Amer. Chem. Soc.*, 1956, **78**, 938.
[15] Krumholz, *J. Amer. Chem. Soc.*, 1949, **71**, 3654.
[16] Lee, Kolthoff, and Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 3596.

measured.[15] The peak is at 435 mμ and is about 25 times less intense (ε $3{\cdot}1 \times 10^2$) than for the tris-complex. With [Fe terpy]$^{2+}$ we note also a reduction in the intensity of the peak but no displacement of its position from that in the bis-complex ($\varepsilon_{\text{max.}}$ at 555 mμ = $8{\cdot}6 \times 10^2$). This absorption spectrum has been measured directly on a freshly prepared solution of [Fe terpy Br_2] in water. The solid mono-complex must contain a negligible amount of the more intensely absorbing bis-complex (from the details of its preparation and from the optical density of the solution after disproportionation has become complete). The existence of *some* [Fe terpy]$^{2+}$ in solution has been deduced previously from an observation of 50% reduction in optical density when a solution containing [Fe $terpy_2$]$^{2+}$ was treated with a thousand-fold excess of ferrous ion.[14] When the diamagnetic tris(bipyridyl)iron(II) complexes lose bipyridyl on heating, lower paramagnetic complexes are formed.[11] The first product, [Fe $bipy_2$ Cl_2], has a moment (5·2 B.M.) corresponding to a high-spin complex; the final product, [Fe bipy Cl_2], has an anomalous moment of 1·8 B.M. which is ascribed to possible metal–metal interaction in the solid. With terpyridine also, a high-spin lower complex is obtained (μ 5·1 B.M.).

The bis(terpyridine)cobalt(II) ion has intense charge-transfer bands at 445 and 505 mμ and a weaker band at 553 mμ, and because of these the use of terpyridine for colorimetric estimation of cobalt has been proposed.[17,18] The peak positions and intensities are confirmed in this study and we have shown that the spectrum of the mono-species is much less intense, with a broad shallow band at 470 mμ. The magnetic moments of the cobalt–terpyridine complexes are difficult to understand. The values for the bis-series have a very unusual dependence on the anion present, ranging from 4·3 B.M. for perchlorate to 2·1 B.M., which is only slightly higher than that for a low-spin complex, for chloride (both at room temperature). The bromide was studied at various temperatures and it was tempting to explain the results in terms of a low-spin–high-spin equilibrium, present in the solid. Mr. G. Webb and Dr. J. Lewis (University College, London) kindly measured the magnetic susceptibility of the bromide at a larger number of temperatures and their results (a maximum value for $1/\psi$ of $3{\cdot}02 \times 10^{-4}$ at −57·6°) show that if such an equilibrium is the explanation then it cannot be simple, and the magnetic moment of the low-spin and/or the high-spin form must be temperature-dependent. The magnetic moment of the mono-complex is the normal high-spin value {cf. [Co $bipy_3$]$(ClO_4)_2$, 4·85 B.M.[13]}.

The larger crystal-field strength of terpyridine than of bipyridyl is most clearly seen from the spectra of the nickel complexes, where the usual *d–d* transitions arise, unattended by charge-transfer bands. Thus, [Ni $terpy_2$]$^{2+}$ shows bands ($\varepsilon_{\text{max.}}$ at 785 mμ = 32·3; $\varepsilon_{\text{infl.}}$ at 500 mμ = 20) at higher wave-numbers than [Ni $bipy_3$]$^{2+}$, which has absorption bands at 521 (ε 11·6), 790 (ε 7·1), and 868 mμ (ε 5·7).[19,20] Similarly [Ni bipy]$^{2+}$ has peaks at 610 (ε 3·6) and 960 (ε 5·4) [8] while [Ni terpy]$^{2+}$ bands are at 590 (ε 7·5), 742 (ε 9·5), and 890 mμ (ε 20·7). As usual, the terpyridine complexes have the higher absorption. Both nickel–terpyridine complexes have the normal magnetic moment associated with two unpaired electrons.

Although the copper(II) ion does not readily co-ordinate more than two molecules of ethylenediamine, it takes on three molecules of bipyridyl or phenanthroline. A solution containing blue [Cu terpy]$^{2+}$ ion will dissolve a further equivalent of terpyridine (far in excess of its normal solubility), forming a green solution with slight but significant spectral changes (see Figure). Benzene extracts only a small proportion (~7%) of total terpyridine from the green solution and, less significantly, a solid bisperchlorate can be precipitated from it. From recent studies of redox potentials, James and Williams [21] were unable to detect a higher than 1 : 1 complex within the conditions of their experiments. The copper–

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[17] Moss and Mellon, *Ind. Chem. Eng., Analyt.*, 1943, **15**, 74.

[18] Miller and Brandt, *Analyt. Chem.*, 1954, **26**, 1968.

[19] Sone and Kato, *Naturwiss.*, 1958, **45**, 10.

[20] Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

[21] James and Williams, *J.*, 1961, 2007.

terpyridine species absorb at slightly lower wavelengths than the corresponding bipyridyl complexes.[20]

Jørgensen [20] has suggested that the tetragonal character of copper(II) complexes may be assessed from the value for ν_{Cu}/ν_{Ni}, by using, for example, the first-band maximum. A low value (~1·1) is obtained when the copper complex approximates to cubic symmetry (*e.g.*, [Cu bipy$_3$]$^{2+}$) and a higher value (~1·7) when there is strong tetragonality (*e.g.*, [Cu en$_2$(H$_2$O)$_2$]$^{2+}$). For the bisterpyridine complexes, $\nu_{Cu}/\nu_{Ni} = 1{\cdot}13$ and for the mono $\nu_{Cu}/\nu_{Ni} = 1{\cdot}31$, reasonable values in view of the above arguments.

Disproportionation and Metal Exchange.—The disproportionation of the mono-complex can be easily followed spectrally. Dissolution of [Mn terpy Br$_2$] in cold water leads to very rapid production of the bis-compound, but the corresponding iron complex is sufficiently stable for its spectrum and rate of disproportionation to be measured. These are the first data for a high-spin iron(II) complex. The cobalt and nickel mono-complexes disproportionate very slowly but, unlike the iron analogue, not completely. The rate of production of the bis-complex by this process is a measure of the dissociation rate of the mono provided that k_{-2}[M terpy^{2+}][terpy] $\gg k_{-1}$[M^{2+}][terpy], where the rate constants have the significance indicated below. This condition is likely to obtain, since at the beginning of the reaction, [M terpy^{2+}] > [M^{2+}]. Another possible method for determining (and checking) dissociation rates for the mono-complex is from [M terpy$_2$]$^{2+}$–M^{2+} exchange studies. The equilibria involved can be represented:

$$[\text{M terpy}_2]^{2+} \rightleftharpoons [\text{M terpy}]^{2+} + \text{terpy} \quad . \quad . \quad . \quad k_2,\ k_{-2}\ (R_2)$$
$$[\text{M terpy}]^{2+} \rightleftharpoons \text{M}^{2+} + \text{terpy} \quad . \quad . \quad . \quad . \quad . \quad . \quad k_1,\ k_{-1}\ (R_1)$$

We know that for the cobalt and nickel complexes $R_1 \ll R_2$ and, since [bis],[metal] > [mono], $R_{exch} = R_1 = k_1$[mono].[9] The agreement in the values from the two methods (Table 4) is reassuring.* Because the spectral changes involved with the nickel complexes are small, the exchange results were used for the estimation of kinetic parameters. For the iron system it is difficult to assess the relative values of R_1 and R_2 and, since there are large spectral changes involved, the spectral data were used to estimate the lability of the mono-species. The conditions specified above are shown to hold by the fact that the solid mono-complex, on dissolving in 1M-hydrochloric acid, or in M-hydrochloric acid containing a small amount of terpyridine, immediately gives the deep bis-colour, which then fades slowly. In similar concentrations, ferrous ion and terpyridine in M-hydrochloric acid do not react.

The [Cu terpy]$^{2+}$–Cu^{2+} exchange is complete at 0·1° within the separation time. The lability of [Zn terpy]$^{2+}$ is shown indirectly. Addition of cupric ions to the zinc complex rapidly produces the characteristic blue of the copper complex. Ferrous ions produce [Fe terpy$_2$]$^{2+}$ only slowly, because of relatively slow formation rates with the iron complexes.

Ligand Exchange.—The lability of the bis-complex is examined most simply by exchange studies with labelled terpyridine. The spectra indicate that in the presence of an excess of terpyridine the bis-species is completely formed, except perhaps with the copper although even here at least 90% of the complexed copper is in the bis-form (from other evidence). Unfortunately, the exchange of the manganese, copper, and zinc complexes is rapid, so that even with this stabilising terdentate ligand we have been unsuccessful in obtaining kinetic data for these metals. For cobalt and nickel, $R_2 \gg R_1$, and the expression $R_{exch} = R_2 = k_2$[bis] is indicated by the constancy of k_2 with a variety of concentration conditions (Table 3). The situation is less clear in the iron case but ligand exchange is probably only operative through the first dissociative stage since the concentration of the mono-complex

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* West [22] found that the exchange half-life between [Co terpy$_2$]$^{2+}$ and cobalt sulphate was 2·8 hr. at 15°, in reasonable agreement with our measurements.

[22] West, *J.*, 1954, 578.

in the ligand exchange is extremely small, more than compensating for the large rate constant.

Kinetic Data.—These are collected with similar data for bipyridyl complexes in Table 5. As expected, the complexes of the terdentate ligand react much more slowly than the corresponding ones of the bidentate ligand and this results mainly in a decreased entropy of activation. Basolo and Pearson [23a] have stimulated a good deal of interest in the effect of the electronic configuration of the metal on the rate of reaction of its complexes. The difference, ΔE, in the crystal-field stabilisation energy (C.F.S.E.) has been calculated for the octahedral and square-pyramid configurations for various d^n systems. These configurations are considered to approximate to the reactant and transition state, respectively. Naturally, then, for a series of metal complexes with a similar ligand it is reasonable to suppose that the greater the loss of this energy in the change, the higher might the energy of activation be expected for the reaction. Some results for phenanthroline complexes have been used to support this idea [24,25] and the present results with terpyridine offer further evidence. For the bis(terpyridine)metal complexes there are increasing energies of activation in the sequence, cobalt, nickel, and iron. The increments are about 6—8 kcal. mole^{-1} and this is in good agreement with the estimated increasing C.F.S.E. losses ($\Delta E \sim 2Dq \sim 6$ kcal. mole^{-1}) (see Table 5). The rate sequence is cobalt > nickel > iron, but the effect of the large differences in energy of activation is largely offset by compensating A factors. The same sequence obtains with the tris(phenanthroline) complexes,[25] with similar increments for the energies of activation, which are however some 5 kcal. mole^{-1} higher than the values for terpyridine: cobalt 20·6, nickel 25·2, and iron 32·1. For the monoterpyridine series, the energies of activation are much closer, in agreement with the calculated C.F.S.E. ΔE changes of 0 (Fe), 0(Co), and 2 (Ni). Since the A factor is sensibly constant, the rate is governed by the energy of activation and decreases in the order iron > cobalt > nickel.

TABLE 5.

Kinetic data for the dissociation of polypyridine complexes at pH ~7 and 25°.

Complex ion (all bivalent)	10^3k (min.$^{-1}$)	log A	E (kcal. mole^{-1})	Electronic system	$\Delta E(Dq)$ [23a]
Mn terpy	Fast			d^5	0
Fe terpy$_2$	0·01	16·1	28·7	$d_\epsilon^6 d_\gamma^0$	4
Fe terpy	398	12·8	18·0	$d_\epsilon^4 d_\gamma^2$	0
Fe bipy$_3$ [a]	8·0	18·8	28·4	$d_\epsilon^6 d_\gamma^0$	4
Co terpy$_2$	40·0	9·5	14·8	d^7	0
Co terpy	6·3	12·6	20·2	d^7	0
Ni terpy$_2$	0·1	11·3	20·8	d^8	2
Ni terpy	0·0016	12·0	24·2	d^8	2
Ni bipy$_3$ [a]	18·6	15·6	22·2	d^8	2
Ni bipy [b]	3·7	15·0	23·7	d^8	2
Cu terpy	Fast			d^9	0
Zn terpy	Fast			d^{10}	0

[a] See ref. 8. [b] See ref. 1.

The lower nickel species has an energy of activation some 1—3 kcal. mole^{-1} larger than the value for the corresponding higher complex (see Table 5). A small difference also exists between the mono- and tris-phenanthroline complexes of cobalt(II),[25] and the appreciable difference of 5 kcal. mole^{-1} between the mono- and the bis-terpyridinecobalt(II) complex is unusual. The very much larger energy of activation for the low-spin [Fe terpy$_2$]$^{2+}$ than for the high-spin [Fe terpy]$^{2+}$ is thus striking. The 11 kcal. mole^{-1} difference (or the modified 13—15 kcal. mole^{-1} value, after consideration of the difference of activation energy operating in the opposite direction mentioned above for the cobalt

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[23] Basolo and Pearson, " Mechanisms of Inorganic Reactions," Wiley, New York, 1958, (*a*) pp. 96 *et seq.*, (*b*) p. 269.

[24] Pearson, *J. Phys. Chem.*, 1959, **63**, 321.

[25] Ellis and Wilkins, *J.*, 1959, 299.

and nickel *) is in good agreement with the value of $4Dq$ predicted. On either a displacement or a dissociation mechanism for reaction, a much larger C.S.F.E. loss would be expected for the diamagnetic than for the paramagnetic iron complex.[23a] The entropies of activation for the two iron–terpyridine complexes are also interesting. The positive value for the bis-species can be explained in terms of a " loosening " of structure in the transition state of the diamagnetic ⟶ paramagnetic change, much like the argument [23b] used for $[\text{Fe bipy}_3]^{2+}$. This view is given support by the highly negative value of the entropy of activation for the mono- and for the other terpyridine complexes.

These results relate to neutral exchange, where the rate constant is composite. However, the discussion of crystal field effects concerns the energy of activation, and from a detailed study of $[\text{Fe terpy}_2]^{2+}$ ion, we know that this value is similar in neutral and in acid solution (where the results probably refer to the more appropriate and simple single-bond breakage process).

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* We thank the Referees for drawing our attention to this point.