671. *Exchange Studies of Certain Chelate Compounds of the Transitional Metals. Part VII.* Substituent Effects on the Dissociation Rates of Nickel*(II)*–Phenanthroline and –Bipyridyl Complexes.*

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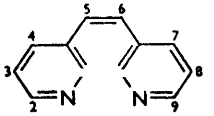
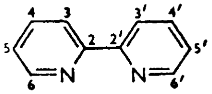
From ^{63}Ni exchange experiments, the rates of dissociation of nine different ions of the type $[NiA]^{2+}$ † have been investigated, where A represents various phenanthrolines or bipyridyls substituted in the 2-, 4-, or 5-position in the aromatic nucleus. The results are discussed with particular reference to changes in the pre-exponential and energy of activation values.

There have been several studies of the effect of ring substitution in 1,10-phenanthroline (phen) (I) and 2,2′-bipyridyl (bipy) (II) in modifying the properties of transition-metal complexes with these ligands. These include spectral,[1,2] redox,[1,3] and thermodynamic stability [4,5] characteristics, but, so far, no systematic investigation of substituent effects on reaction rates has been reported.



(I)



(II)

It is apparent from our earlier work [6] that we might examine for this purpose the rate of exchange of nickel-63 between Ni^{2+} and the monocomplex $[NiA]^{2+}$ † where A represents the phenanthroline or bipyridyl derivative. There are several reasons for this choice. First, of all the elements in the first transition period, probably only nickel gives monocomplexes which exhibit easily measurable dissociation rates, with the *whole* range of

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* Part VI, *J.*, 1959, 299.

† Probable co-ordinated water will be ignored in this paper.

[1] Brandt and Smith, *Analyt. Chem.*, 1949, **21**, 1313.

[2] Williams, *J.*, 1955, 137.

[3] Tomkinson and Williams, *J.*, 1958, 2010.

[4] Brandt and Gullstrom, *J. Amer. Chem. Soc.*, 1952, **74**, 3532.

[5] Irving, Cabell, and Mellor, *J.*, 1953, 3417.

[6] Wilkins and Williams, *J.*, 1957, 4514.

ligands studied. Secondly, there is no apparent difficulty in obtaining the mono- as the *predominant* complex species *in solution* even with the sterically hindered ligands, and this might not be the situation with the higher complexes (cf. ref. 5). In addition, with unsymmetrical ligands there is no complication with the formation of *cis*- and *trans*-isomers, as is the case, for example, with the tris-derivative,[7] $[Ni(5\text{-methylphen})_3]^{2+}$. Finally, interpretation of the exchange data is straightforward and these measure the rate constant for overall dissociation.[8] We have accordingly investigated, at different temperatures, the exchange rates of nine different nickel complexes containing ligands substituted in various positions in the aromatic nucleus.

EXPERIMENTAL

Materials.—Radiochemically pure $^{63}Ni(NO_3)_2$ was obtained as described previously.[6] Bipyridyl and phenanthroline were of " AnalaR " quality. 4,4′-Dimethylbipyridyl and 5-methyl-, 5-chloro-, and 4,7-dimethyl-phenanthroline were purchased from G. Frederick Smith Chemical Co., U.S.A., and 5-nitrophenanthroline from L. Light and Co., Ltd. 2-Methylphenanthroline dihydrate and 2-chlorophenanthroline were prepared by recognised methods.[5,9] The materials were either recrystallised from the appropriate solvent (*e.g.*, with 5-chloro- and 5-nitro-phenanthroline when the commercial product was strongly coloured) or it was checked that the original material gave the same kinetic result as a recrystallised portion. This was necessary since some earlier work with 5-methylphenanthroline gave obviously spurious results. The m. p. in the literature and/or the correct analysis was found for each ligand. The following complex compounds were prepared:

$[Ni\ bipy(H_2O)_4](NO_3)_2$.—Bipyridyl (1 mmole) and nickel nitrate (5 mmoles) were heated in aqueous solution. A pale blue material separated when the concentrated solution was cooled, and it was washed with a *small* amount of ice-cold water (Found: C, 30·0; H, 3·8; Ni, 14·3. $C_{10}H_{16}O_{10}N_4Ni$ requires C, 29·2; H, 3·9; Ni 14·3%). The *complex* labelled with ^{63}Ni was prepared similarly.

$[Ni(5\text{-Mephen})Cl_2]$ —5-Methylphenanthroline (1 mmole) and nickel chloride (6 mmoles) were evaporated in aqueous solution to crystallisation. The yellow-green *complex* was dried (P_2O_5) at 80° *in vacuo* for 12 hr. (Found: C, 47·6; H, 3·4; N, 8·8. $C_{13}H_{10}N_2Cl_2Ni$ requires C, 47·9; H, 3·1; N, 8·7%).

Exchange Runs.—The procedure used was very much as described previously for the $[Ni\ phen]^{2+}$–Ni^{2+} exchanges.[6] Chemical and thermal equilibrium were established with the ligand dissolved in nickel nitrate solution (metal/complex $\simeq$ 5/1), and exchange was initiated by the addition of a small amount of ^{63}Ni nitrate. For the separation from nickel ion, the complex was precipitated with naphthalene-1,5-disulphonate ion except with the bipyridyl and phenanthroline complexes for which thiocyanate was used. With the 2-methyl and the 2-chloro-derivative vigorous scratching was necessary for precipitation. The washed solid was decomposed with hot concentrated aqueous ammonia, and radioassayed as nickel dimethylglyoxime.[6] In some cases it was better to preheat the mixture with perchloric acid for about an hour to decompose the separated complex before precipitation with dimethylglyoxime. For runs between 0° and room temperature, the thermostat was placed in a refrigerated room.

The results are shown in Table 1. Several of the runs represent the mean of duplicate experiments. The previous investigation of the phenanthroline system indicated that $R_{(\text{exch})} = k_{(\text{exch})}[\text{mono}]$ with the rate independent of acidity in the pH range studied. This behaviour was assumed also for the ligands examined here and, indeed, indicated in several experiments (runs 2—5, 22, and 23). Unless otherwise stated, the pH was 4·8—5·5 and a nitrate medium was used, with no attempt made to maintain a constant ionic strength because of the unimportance of this on the rate. The existence of the mono-species as the predominant complex ion, with excess of nickel ion present, was demonstrated with the bipyridyl compound, since apart from the 2-substituted phenanthrolines, this nickel complex is likely to be the least stable of the series. A small quantity of $^{63}Ni^{2+}$ was added to an equilibrated mixture prepared from nickel ion (193 mmolar) and bipyridyl (35·2 mmolar). A deficiency of dimethylglyoxime was added (*a*) just after mixing, and (*b*) at isotopic equilibrium, and the specific activities of the

[7] Basolo, personal communication.

[8] Wilkins and Williams, *J. Inorg. Nuclear Chem.*, 1958, **6**, 52.

[9] Halcrow and Kermack, *J.*, 1946, 155.

TABLE 1. *Exchange of* $[NiA]^{2+}$ *with* Ni^{2+}.

Run no.	Temp.	[mono] (mmole l.$^{-1}$)	[Ni^{2+}] (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ (min.)	10^5R (min.$^{-1}$ mole l.$^{-1}$)	$10^3k_{(exch)}$ (min.$^{-1}$)
A = Bipyridyl						
1	13·8°	35·2	159·6	840	2·4	0·68
2[a]	25·0	35·2	159·6	174	11·5	3·3
3[b]	25·0	35·2	159·6	168	11·9	3·4
4[c]	25·0	33·9	334·5	198	10·8	3·2
5[a]	25·0	70·5	180·6	168	20·9	3·0
6[d]	25·0	35·2	159·6	171	11·7	3·3
7	30·0	35·2	159·6	84	23·8	6·8
8	30·0	35·2	159·6	90	22·2	6·3
9	35·0	35·2	159·6	46·5	43·0	12·2
10	35·0	35·2	159·6	46	43·5	12·4
A = 4,4′-Dimethylbipyridyl						
11	24·9	39·4	155·8	500	4·4	1·1
12	40·0	39·4	155·8	70	31·1	7·9
A = Phenanthroline						
13	25·0	3·6	15·9	910	0·22	0·62
14	25·0	3·6	15·9	910	0·22	0·62
15	30·2	3·6	15·9	402	0·51	1·4
16	40·0	3·6	15·9	134	1·52	4·2
A = 5-Methylphenanthroline						
17	25·0	34·8	160·3	1305	1·5	0·44
18	34·8	34·7	160·3	345	5·7	1·65
19	40·0	34·8	160·3	180	11·0	3·2
20[e]	45·0	36·8	193·2	95	22·5	6·1
21	45·0	34·7	160·3	97	20·4	5·9
22[a]	45·0	34·5	159·0	90	21·8	6·3
23[c]	45·0	34·7	160·3	92	21·5	6·2
24	49·8	34·7	160·3	58	34·1	9·8
A = 5-Nitrophenanthroline						
25	0·0	42·7	152·9	5790	0·4	0·09
26	20·1	42·7	152·9	295	7·8	1·8
27	30·2	42·7	152·9	79	29·3	6·9
28	30·2	42·7	152·9	76	30·5	7·1
A = 5-Chlorophenanthroline						
29	25·0	17·5	79·7	378	2·6	1·5
30	25·1	17·5	79·7	380	2·6	1·5
31	34·9	17·5	79·7	105	9·5	5·4
32	39·9	17·5	79·7	54	18·4	10·5
A = 4,7-Dimethylphenanthroline						
33[f]	39·9	19·7	79·5	618	1·8	0·9
34[f]	40·0	19·6	79·6	648	1·7	0·85
35[f]	59·5	19·6	79·6	60	18·2	9·3
36	59·5	19·6	79·6	54	20·2	10·3
37	59·5	15·8	64·0	55	15·8	10·0
A = 2-Methylphenanthroline						
38	0·1	63·5	291·0	438	8·25	1·3
39	7·8	52·0	238·0	145	20·4	3·9
40	15·8	52·0	238·0	58·0	51·0	9·8
41	25·0	63·5	466·0	20·5	189	29·8
42	25·0	63·5	291·0	20	181	28·4
A = 2-Chlorophenanthroline						
43	0·1	68·0	287·0	12	318	46·7
44	0·1	68·0	287·0	12	318	46·7
45	5·2	68·0	287·0	6·5	586	86·2
46	5·2	68·0	287·0	7	544	80·1

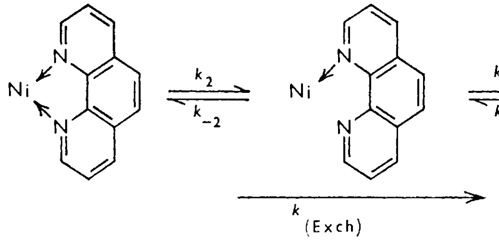
[a] pH = 6·2. [b] pH = 4·2. [c] pH = 3·8. [d] Exchange followed by decrease in specific activity of complex by using $[^{63}Ni\ bipy(H_2O)_4](NO_3)_2$. [e] Solid $Ni(5\text{-}Mephen)Cl_2$ added to Ni^{2+}. [f] Chloride medium, since complex nitrate is precipitated below 50°.

precipitated nickel dimethylglyoxime (*a*) and (*b*) determined. The values, (*a*) 682, (*b*) 565 counts/min., showed the predominance of the mono-species [theor. (*b*) 558] and the virtual absence of the bis-species [theor. (*b*) 620]. Further evidence is indicated by the independence of the rate constant of nickel-ion concentration (runs 3 and 4) and by the spectra of the mixture which (against a nickel ion blank) corresponds closely to that of $[\text{Ni bipy}(H_2O)_4](NO_3)_2$ in solution with maxima at 610 and 960—970 mμ. With the 2-substituted phenanthrolines, the spectra of the exchange mixtures measured against free nickel ion of the appropriate concentration as " blank " indicated the predominance of the mono-complex with a characteristic peak at 625—635 mμ and ε_M value ~3·5. The spectra and exchange rate (runs 41 and 42) remained unchanged by further addition of nickel. This could be predicted, at least for the 2-methylphenanthroline case, from the estimated dissociation constant for the mono-complex, which would be expected to be smaller than for the bis-complex, and to lie between about 2×10^{-9} ($[\text{Ni phen}]^{2+}$) [10] and 6×10^{-5} ($[\text{Fe(2-Mephen)}]^{2+}$)[5] since nickel(II) forms a stronger complex with phenanthroline than does iron(II).[10a] The estimated constant of the nickel mono-complex with 2,9-dimethylphenanthroline is 4×10^{-2}.[11]

Earlier results for the phenanthroline compound [6] have been modified. It was apparent from the present study that the energy of activation value of 26·2 kcal. mole^{-1} and the *PZ* value of 10^{16} obtained previously were too high. The values depended greatly on one determination at 25·0° and a duplicate at this temperature showed this result to be in error. In fact the revised value ($0{\cdot}62 \times 10^{-3}$ min.$^{-1}$) accords well with that obtained indirectly in the previous study ($0{\cdot}60 \times 10^{-3}$ min.$^{-1}$) in $[\text{Ni phen}_2]^{2+}$–$[\text{Ni phen}]^{2+}$–Ni^{2+} exchanges. The present values for *E* and *PZ* are obtained from the rate constants shown in Table 1, in addition to the value at 45·1° ($8{\cdot}4 \times 10^{-3}$ min.$^{-1}$) obtained previously [6] as a mean of five separate runs.

DISCUSSION

The results are collected in Table 2. The estimated errors in the *E* and $\log_{10}PZ$ terms are about ±0·3 unit except for the 2-substituted phenanthrolines where the errors are greater, because of the faster rates. The kinetic parameters refer to the overall dissociation process (rate constant $k_{(\text{exch})}$): *



It has been suggested [13] that, because of the geometry of the rigid phenanthroline molecule, the intermediate step involving " one-ended " attachment will not be important, and applied to our case, $k_{(\text{exch})} = k_2$. Margerum, Bystroff, and Banks [10] have, however, studied the dissociation of $[\text{Ni phen}]^{2+}$ at different acidities and explained their results in terms of intermediate species. At low acidity, $k_{(\text{exch})}$ will equal $k_2k_1/(k_1 + k_{-2})$,[13] and our rate constant is thus a composite one. Even in the latter eventuality, it is reasonable to suppose that structural changes which affect k_2 will be reflected in parallel changes in $k_{(\text{exch})}$. One indication that this view is correct insofar as activation energies are concerned is shown by a consideration of the compounds $[\text{M bipy}_3]^{2+}$ (M = Ni or Fe). With these, where such a mechanism as pictured above can operate (cf. ref. 13), the activation energies

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* In this scheme, charge and co-ordinated water will be ignored.

[10] (*a*) Margerum, Bystroff, and Banks, *J. Amer. Chem. Soc.*, 1956, **78**, 4211; (*b*) Anderegg, *Helv. Chim. Acta*, 1959, **42**, 344.

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

[12] Yasada, Sone, and Yamasaki, *J. Phys. Chem.*, 1956, **60**, 1667.

[13] Basolo, Hayes, and Neumann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807.

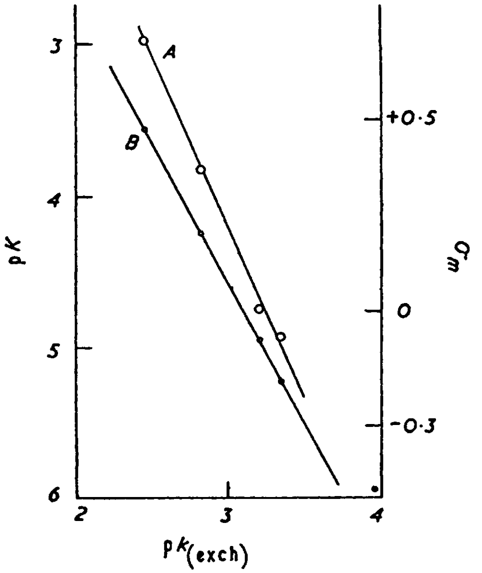
TABLE 2. *Rates of dissociation of* $[\mathrm{NiA(H_2O)_4}]^{2+}$ *from* $^{63}\mathrm{Ni}^{2+}$ *exchange studies.*

Species A	$10^3k_{(\mathrm{exch})}$ (min.$^{-1}$; 25°)	p*K*	*E* (kcal./mole)	$\log_{10} PZ$ (min.$^{-1}$)
2,2′-Bipyridyl	3·2	4·44 [b]	23·7	15·0
4,4′-Dimethylbipyridyl	1·1	5·32 [b]	24·0	14·7
1,10-Phenanthroline	0·6	4·96 [a]	24·5	14·8
5-Methylphenanthroline	0·45	5·23 [a]	24·4	14·6
5-Nitrophenanthroline	3·55	3·57 [a]	23·5	14·9
5-Chlorophenanthroline	1·5	4·26 [a]	23·9	14·9
4,7-Dimethylphenanthroline	0·11	5·94 [b]	25·7	14·9
2-Methylphenanthroline	29·0	5·42 [b]	20·1	13·2
2-Chlorophenanthroline	~700	—	17·0	12·3

[a] See ref. 4. [b] See ref. 12.

of the dissociation process in strong acid (regarded as measuring k_2) are 27·4 (Fe) [13] and 21·8 (Ni),[14] while the values from [^{14}C]bipyridyl exchanges [15] in *neutral* solution are 28 (Fe) and 22·2 (Ni) kcal. mole^{-1}.

5-*Substitution*.—Here we are concerned with substituents well removed from the reaction site. The effect of substitution parallels closely the observed behaviour of ring substitution on aromatic reactivity. Compared with the parent compound, the methyl group has an opposite (and smaller) effect than the chloro- or the nitro-group. There is an excellent linear relation between $\mathrm{p}k_{(\mathrm{exch})}$ and the p*K* of the base for this admittedly limited series (see Figure, Curve *B*). Brandt and Gullstrom [4] have measured the thermodynamic stability of the ferroin-type compounds $[\mathrm{FeA_3}]^{2+}$ where A are various 5-substituted phenanthrolines, by direct methods, and also from the ratio of formation and dissociation rate constants. Examination of their results shows that the decrease in thermodynamic stability observed, phen ~ 5-phenyl > 5-chloro > 5-nitro, is a result of a *combination* of a decreased formation and an increased dissociation rate constant. A linear relation of our type for $\mathrm{p}k_{(\mathrm{diss})}$-p*K* holds with their results also, although the slopes of the lines differ somewhat. The change in rate observed in the present work results mainly from changes in activation energy, small variations in the entropy factors being scattered in a non-systematic fashion. Substitution of small groups in the large phenanthroline molecule away from the reaction site might be expected only to have an electronic effect without influence on the entropy factor, leaving the form of the transition state unchanged and simply weakening or strengthening the metal–nitrogen bond. With the helpful, although not essential, situation of constant *PZ*,[16,17] one can attempt a quantitative correlation of the Hammett type [16] of dissociation rates and substituents. There are two difficulties. The 5-substituent effect may be transmitted to the reaction site by two paths and it is therefore difficult to decide whether such substitution is equivalent to *meta* or *para*. Secondly, it is uncertain which σ-type [16,18] should be used for such a reaction as studied



Dependence of $\mathrm{p}k_{(\mathrm{exch.})}$ *on* p*K* (*curve B*) *and* σm (*curve A*).

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[14] Basolo, Hayes, and Neamann, *J. Amer. Chem. Soc.*, 1953, **75**, 5102.
[15] Ellis and Wilkins, unpublished observations.
[16] Jaffe, *Chem. Rev.*, 1953, **53**, 191.
[17] Leffler, *J. Org. Chem.*, 1955, **20**, 1202.
[18] Okamoto and Brown, *ibid.*, 1957, **22**, 493.

here. Notwithstanding this, it is found that a good linear plot of σ_m against $pk_{(\text{exch})}$ is obtained (Figure, Curve *A*) with ρ positive, the reaction being facilitated by low electron density at the reaction site. It does appear then that the substituent effects on free-energy differences, which are predictable for so many organic reactions, apply also to reactivity of metal complexes.

4-*Substitution*.—We only examined one substituted bipyridyl, 4,4′-dimethylbipyridyl, and observed a marked decrease in rate compared with the parent compound. Even when allowance is made for the presence of two methyl groups, the rate for the 4,7-dimethylphenanthroline compound is slower than that for the 5-derivative. This accords with the known higher sensitivity (compared with the 5-compound) of this position to methyl substitution with regard to stability,[12] redox,[1,3] and spectral [1] effects, as well as to relative charge distribution in the phenanthroline molecule from quantum-mechanical calculations.[19] It should be noted, however, that the data for this compound (bottom, right) are removed from the linear plot of the Figure, so that the relation displayed by the 5-substituted series is a very limited one. All three compounds have *PZ* values similar to those in the 5-substituted series.

2-*Substitution*.—We were interested in 2-substituted derivatives because it is known that 2-chloro- and 2-methyl-substitution in phenanthroline markedly modify the properties of its iron(II) complexes. The strong absorption, characteristic of the diamagnetic ferroin type of complex, is absent,[2,5] and $[\text{Fe(2-Mephen)}_3]^{2+}$ is paramagnetic.[20] Indeed the $[\text{Fe(2-Mephen)}_3]^{2+}/^{3+}$ couple is the only case of an iron phenanthroline couple with a redox potential less positive than that of the $\text{Fe}^{2+}/^{3+}$ aquo system.[3]

The effect of 2-substitution on the dissociation rates is drastic. The $[\text{Ni(2-Mephen)}]^{2+}$ ion dissociates almost 50 times and the $[\text{Ni(2-Clphen)}]^{2+}$ ion over 1000 times faster than the unsubstituted compound at the same temperature. The rates are just measurable with the chloro-compound and since the separation procedure is not rapid it must be emphasised that the kinetic data, and more especially the Arrhenius parameters, are less accurate than with the other ligands. The increased rates are produced by a decrease of the activation energy, partly offset by a lower frequency factor. This type of "compensating" behaviour has been well recognised for some time.[17,21] The consequence in this case is that the 2-chlorophenanthroline compound has (for this type of ligand) the remarkably low activation energy of 17 kcal. mole^{-1}. The substituents, being now adjacent to the co-ordinating nitrogen, are in a position to alter the relative shapes of the reactants and the transition state, and probably, in particular, the vibrational, rotational, or translational energy levels, thus producing entropy changes and concomitant potential-energy differences also, the latter reflected in activation energy changes. The steric interaction between the 2-substituent and the reaction centre must be less in the transition state than in the reactant state although it is not immediately obvious why the chlorine should have such a larger effect than the sterically similar methyl group. However, we must remember that superimposed on this steric effect will be the usual electronic one, and it might very well be that the chloro-group will have a relatively much larger rate-accelerating effect than is the case with the 5-substituents, since the 2-position is a sensitive one, judging from π-electron distribution calculations.[19]

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[19] Longuet-Higgins and Coulson, *J.*, 1949, 971.

[20] Irving, quoted in ref. 3.

[21] For recent discussion and previous literature see Blackadder and Hinshelwood, *J.*, 1958, 2728.