Complex Formation Between Polymers containing the 2,2′-Bipyridyl Group and Iron(II)

J. David Miller * and David S. Morton
Department of Chemistry, University of Aston, Birmingham B4 7ET

Condensation polymers derived from the reaction of butane-1,4-diol and either the 4,4′- or 5,5′-di-acid derivatives of 2,2′-bipyridyl have been prepared. The formation of strongly coloured complexes between iron(II) and soluble portions of the products has been investigated. In the case of the polymer derived from the 5,5′-disubstituted bipyridyl the polymeric ligand appears to behave as a collection of independent ligand groups, but approximately one half of these groups are prevented from taking part in the formation of a ' tris ' complex. The polymer derived from the 4,4′-disubstituted ligand behaves differently. The polymer chain develops *meta* to the ring–ring bond of the bipyridyl group. The difficulty of rotation of this bond produces two different types of bipyridyl repeat unit. One behaves as a ligand in the same way as the monomeric ligand, the other does not. Presumably these are fixed *cis* and *trans* configurations. The inflexibility of the polymer chain prevents the majority of the potential ligand groups from participating in the formation of a ' tris ' complex, which formation involves only two polymer chains. Data are quoted for the stability constants relating to both polymers.

The ligand 2,2′-bipyridyl (bipy), and its substituted derivatives and relatives such as 1,10-phenanthroline, constitute one of the most widely studied groups of ligands,[1,2] partly as a result of photochemical interest.[3] Several recent reports in the literature open up completely new aspects of the co-ordination behaviour of bipy-like ligands. Thus there is considerable interest in monolayer assemblies of bipy complexes,[4] their behaviour in micellar systems,[5] the attachment of such ligand groups to organic polymers [6-10] and to electrode surfaces.[11] The results reported in this paper have some relevance to these topics. The behaviour of two polymers, containing the 2,2′-bipyridyl group as an integral part of the polymeric chain, has been examined and some data on stability constants calculated. We have examined polyesters, obtained by condensation of either 2,2′-bipyridyl-4,4′-dicarboxylic acid or the analogous 5,5′-di-acid with diols, $HO(CH_2)_nOH$. For convenience we identify these polyesters by a numerical code. Thus the polyester obtained from the 4,4′-di-acid and the diol with $n = 10$ is identified as the 4,10-polymer. A diagram showing the repeat units is given, see Figure 1.

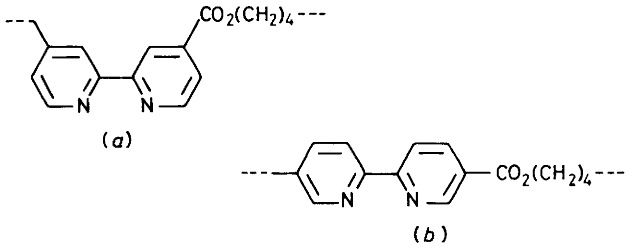

Figure 1. The repeat units of the 4,4- (*a*) and 5,4-polymers (*b*)

Results and Discussion

We experienced considerable difficulty in preparing polymeric ligands with sufficient solubility to enable us to study their interaction with salts. However, during the condensation polymerisation in dry tetrahydrofuran (thf) of systems with $n = 4$ we were able to separate a thf-soluble fraction. The majority of the product was insoluble. The addition of a concentrated thf solution of such a fraction to a larger volume of water gave homogeneous solutions. We have used these predominantly aqueous solutions as stock solutions in our study of stability constants. Thus the data discussed below refer to H_2O–thf mixtures containing less than 7% thf by volume.

As the data given below clearly show, we are dealing with a ligand whose behaviour is fundamentally different from that of bipyridyl. This requires a modified mathematical approach to the determination of stability constants. The basis of our chosen approach is now described.

Initially we assume that polymer chains behave in the same fashion irrespective of their length and that both nitrogen atoms of each group must be attached to the same metal centre, *i.e.* each repeat unit behaves as a bidentate ligand. We term this as one linkage. For a metal exhibiting a maximum co-ordination number of six, three such linkages are possible. These linkages could be made to varying numbers of polymer chains. The various metal species present in solution can be represented by terms of the general form M_{il}, where i represents the number of polymer chains linked to the particular metal ion, and l the total number of linkages, *i.e.*, $0 \leqslant l \leqslant 3$ and $i < l$. Some potentially ligating sites on a polymer may be blocked off by the co-ordination of a nearby site. Thus we must define a term Z_{il}, the average number of ligand groups blocked per complex M_{il}. We can now write expressions for the total concentration of all metal ions, [A], and bipy groups, [B], in solution as given by equations (i) and (ii), where [S]

$$[A] = \sum_{i=0}^{l} \sum_{l=0}^{3} [M_{il}] \qquad \text{(i)}$$

$$[B] = [S] + \sum_{l=0} \sum_{i=0}^{3} Z_{il}[M_{il}] \qquad \text{(ii)}$$

represents the concentration of bipy repeat groups still available for co-ordination. For convenience of representation, all terms $[M_{0l}]$ other than $[M_{00}]$ are equated to zero. The concentration of free-metal ions in solution is represented by $[M_{00}]$.

The defining equation for the stability constant of a complex involving one n-dentate ligand contains the ligand concentration to the power i rather than n. By analogy the overall stability constants for polymeric ligands, β_{il}, should be defined according to equation (iii), that is, free-ligand sites are

$$[M_{il}] = \beta_{il}[M_{00}][S]^l \qquad \text{(iii)}$$

involved to the power i and not l. One result of this equation is that the ratios of the concentrations of all species having the same value of i depend only on the values of β_{il}. This enables equations (i) and (ii) to be substantially simplified. We can usefully define $[N_i]$ as the concentration of all metal ions to which i chains are attached [equation (iv)], and β_i as a composite overall stability constant for such centres [equation (v)].

$$[N_i] = \sum_{l=i}^{3} [M_{il}] \qquad \text{(iv)}$$

$$[N_i] = \beta_i[M_{00}][S]^i \qquad \text{(v)}$$

$$Y_i[N_i] = \sum_{l=i}^{3} Z_{il}[M_{il}] \qquad \text{(vi)}$$

Correspondingly, Y_i is the average number of ligand sites blocked per centre with i chains attached [equation (vi)]. Therefore equations (vii) and (viii) hold. These equations

$$[A] = [M_{00}](1 + \sum_{i=1}^{3} \beta_i[S]^i) \qquad \text{(vii)}$$

$$[B] = [S] + [M_{00}] \sum_{i=1}^{3} Y_i\beta_i[S]^i \qquad \text{(viii)}$$

should be of general applicability. However, since they each contain several terms, their use would be very awkward.

We chose to examine complex formation with iron(II) for reasons of measurement and simplification. The addition of iron(II) to our polymeric bipyridyl materials, even the insoluble ones, produces colours similar in wavelength and intensity to that of $[Fe(bipy)_3]^{2+}$. We assume that the appearance of these absorption bands is due to the formation of this same colour centre within the polymeric framework. Thus we can define the total concentration of such colour centres as [C] [equation (ix)]. If f_i is the fraction of all species involving i chains which have $l = 3$, then equation (x) applies. This

$$[C] = \sum_{i=1}^{3} [M_{i3}] \qquad \text{(ix)}$$

$$[C] = [M_{00}] \sum_{i=1}^{3} f_i\beta_i[S]^i \qquad \text{(x)}$$

equation can be used with equations (vii) and (viii) to eliminate the unknown $[M_{00}]$ giving equations (xi) and (xii); two intractable equations.

$$[A] = [C](1 + \sum_{i=1}^{3} \beta_i[S]^i)/\sum_{i=1}^{3} f_i\beta_i[S]^i \qquad \text{(xi)}$$

$$[B] = [S] + [C]\sum_{i=1}^{3} Y_i\beta_i[S]^i/\sum_{i=1}^{3} f_i\beta_i[S]^i \qquad \text{(xii)}$$

Fortunately, a further simplification can be made for the particular polymers we studied. Of the various complexes, $[Fe(bipy)_x]^{2+}$, possible for the 2,2′-bipyridyl monomer only those with $x = 0$ or 3 are normally found to be present in significant concentrations. By analogy, we assume that species with $l = 1$ and 2 can be ignored in the present case. If this is so, then all values of f_i can be taken to be unity.

By the process of trial and error we have found that for the cases reported here, one term for one particular value of i is dominant. That is, i can be taken as a single constant in equations (xiii) and (xiv). These equations can be combined, eliminating the unknown [S], and expressing [C] in terms of

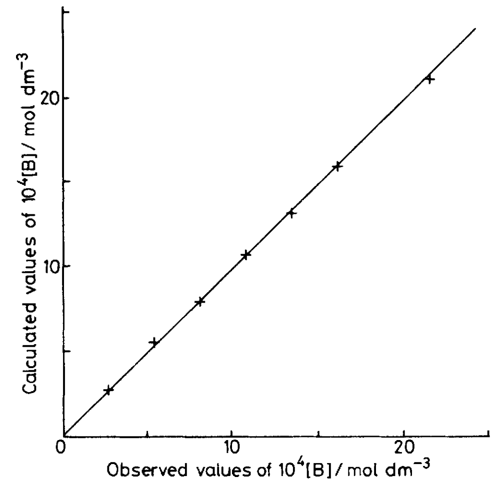

Figure 2. Plot of calculated against observed values of [B] for the 4,4-polymer at 25.0 °C. The ranges of individual values, calculated according to equation (xv) are shown by a vertical spread of points

$$[A] = [C](1 + 1/\beta_i[S]^i) \qquad \text{(xiii)}$$

$$[B] = [S] + Y_i[C] \qquad \text{(xiv)}$$

the optical density D at an appropriate wavelength. Thus for a cell of pathlength x, equation (xv) is formed. We emphasise

$$\sqrt[i]{D/\beta_i(\varepsilon x[A] - D)} = [B] - Y_iD/\varepsilon x \qquad \text{(xv)}$$

that while equations up to and including (xii) should be of general applicability, equation (xv) is a special, simple case. To be more exact it represents two special cases since $i = 2$ applies to one polymer while $i = 3$ applies to the other, a point which is brought out and discussed below.

The three constants, β_i, ε, and Y_i are independent. Best values of all three at a particular temperature can be obtained from equation (xv). We prefer a slightly different approach. We have applied this equation separately to each set of data with a constant value of [B] and T. Thence we have obtained a mean value of ε for each polymer. We have then adopted this value in order to obtain β_i and Y_i as functions of temperature, T. The values of the absorption coefficients thus obtained are similar to those for non-polymeric ligands; just as are the positions of absorption maxima.

Figure 2 shows the good degree of fitting of equation (xv) to the experimental data by comparing the observed and calculated data for all experiments using the 4,4-polymer at 25.0 °C. Values of the constants, Y_2 *etc.*, were however computed by the method of least squares and not graphically.

Complex Formation between Iron(II) *and the* 5,4-*Polymer*.— By a process of trial and error we found that our data for the attachment of iron(II) ions to the 5,4-polymer can be described by equation (xv) with $i = 3$. Computations involving equations (xi) and (xii) in less simplified forms result in terms which, except for that with $i = l = 3$, are insignificant. Further, such additional constants vary in a random manner as the experimental parameters are changed. Thus we were led to this simple equation. When the ratio [A] : [B] is very much greater than 1 : Y_3 a slight divergence between observed and

Table 1. Overall data for the formation of complex centres of the $[Fe(bipy)_3]^{2+}$ type

Ligand	ΔH/ kJ mol^{-1}	ΔS/ J K^{-1} mol^{-1}	log β	Y	Ref.
2,2′-Bipyridyl	−117	−58	17.5	3	1
5,4-Polymer	−7.7 ± 1.2	+186 ± 5	11.1	6	This work
4,4-Polymer *	−43 ± 3	0 ± 9	7.6	20	This work

* In the case of the 4,4-polymer these data refer to co-ordination to only two polymer chains and only to the ligationally active bipy sites (see text).

Table 2. Stability constant data for complex formation between Fe^{II} and the 4,4-polymer (data obtained at 550 nm, using $i = 2$)

T/°C	$10^{-5}(\beta_2)_{obs.}$/ dm^6 mol^{-2}	$(Y_2)_{obs.}$	$10^{-5}(\beta_2)_{true}$/ dm^6 mol^{-2}	K_0
25.0	85.0	43.0	375	1.1
35.0	27.5	48.2	158	1.4
41.0	19.0	53.4	128	1.6
45.0	9.33	55.2	73.1	1.8
50.0	7.92	59.6	71.3	2.0
60.0	3.87	68.9	44.7	2.4
70.0	2.10	78.3	31.9	2.9
75.0	1.43	85.3	25.2	3.2

The full range of reagent concentrations used for each set of conditions is given in the text.

calculated optical densities begins to appear, the observed value being the lower. At high total metal-ion concentrations the optical density begins to decrease very slightly. Thus the simplifying approximations are not completely valid under these conditions. The disparity between observed and calculated values is too small for a quantitative treatment. Presumably $l = 1$ or $l = 2$ is beginning to intrude.

When the simple equation with $i = 3$ was applied to our data we found that Y_3 was independent of temperature, within experimental error. We computed a value of 6.1 ± 0.2. The overall stability constant has log $\beta_3 = 11.1$ at 25 °C, while its temperature variation yields values of $\Delta H_3 = -7.7 \pm 1.2$ kJ mol^{-1} and $\Delta S_3 = 186 \pm 5$ J K^{-1} mol^{-1}. Roughly one half of the polymeric repeat units are not used in co-ordination even though ring–ring rotation in a 5,5′-disubstituted 2,2′-bipyridyl should be easy. Presumably the sheer bulk of the solvated $[Fe(bipy)_3]^{2+}$ group makes it difficult to form such groups closely adjacent to each other in a polymeric framework cross-linked by the complex centres.

The computed values of ΔH and ΔS, which are close to the relevant standard terms, are very different for the complexes formed by 2,2′-bipyridyl itself and by the 5,4-polymer, see Table 1. These differences are probably a reflection of the markedly different solvation changes necessary in the two processes of complex formation. The polymeric ligand is not as good a ligand as the non-polymeric parent, as shown by a difference of 6 in log β_3. This difference resides mainly in the enthalpy terms and must relate to the problems of cross-linking the polymer chains and altering their shapes in order to make this cross-linking possible.

Complex Formation between Iron(II) *and the* 4,4-*Polymer*.—When solutions containing iron(II) ions were mixed with solutions containing the 4,4-polymer the expected colour developed, but slowly. In all our experiments we allowed at least twenty minutes for equilibration. We found this period to be adequate but not markedly excessive. The spectrophotometric data obtained were then fitted to equation (xv). The fit is again very good until a large excess of metal ion is present; but a value of $i = 2$ must be used. This feature was unexpected. However, the concentration of chains in solution is directly proportional to the concentration of repeat units. Therefore values of i of less than 3 are permissible if more than one bipy group can co-ordinate to the same metal centre.

We interpret the observed value of i as demonstrating the balance of two opposing factors. The chelate effect [12] will operate in favour of low values of i. Opposition to this will arise because of the position of the chain linkage. Relative to the ring–ring bond the polymer chain is in a *meta* position. Therefore twisting the chain to a particular spatial arrangement and getting the relevant bipyridyl groups into a *cis* configuration may be difficult. This factor will favour higher values of i. It will also render γ bigger, see below. The use of the soluble fraction of the total polymeric product will have substantially reduced or even removed high-molecular-weight polymers. These are the individual chains which would be most likely to give $i = 1$ products, further favouring the compromise value found for i.

The values of β_2 and Y_2 computed using the method of least squares are quoted in Table 2. Note the smooth variation of both parameters with temperature and the large values of Y_2. All data quoted were derived using a range of total iron(II) concentrations from 2.89×10^{-5} to 2.89×10^{-4} mol dm^{-3}. At 25, 35, and 45 °C a range of repeat group concentrations from 2.68×10^{-4} to 2.15×10^{-3} mol dm^{-3} was used. At other temperatures this concentration was held at 1.61×10^{-3} mol dm^{-3}.

The parent ligand, 2,2′-bipyridyl, exists in the *trans* or *transoidal* configuration in solution. Rotation about the ring–ring bond is necessary before complex formation can be completed. Within a polymer chain in which the polymer forming linkage is *meta* to this bond, such rotation could be very difficult since it would require the movement of a large section of the polymeric structure. By comparison, the 5,4-polymer can be regarded as analogous to a string of threaded beads which are free to rotate about the thread. This rotation problem will lead to a large value of Y_2 through a series of complementary effects. For example, when part of a polymer chain is anchored by complex formation, ring–ring rotation in neighbouring repeat units will be even more difficult. Also the bipy groups actually used in ligation in a tetradentate chain may be widely separated along that chain, making the intervening groups unusable.

Not only is Y_2 large, but it varies with temperature. We believe this variation to be a genuine feature rather than an artifact of the application of an inappropriate equation. The following interpretation is consistent with all the available information and with the use of an equation of the form applied.

Suppose that two forms of the repeat unit of the polymer exist in solution, P_a being active with respect to complex formation and P_{in} being inactive. If these forms are at equilibrium then we can write equation (xvi). The ratios of metal

$$P_a \overset{K_0}{\rightleftharpoons} P_{in} \qquad \text{(xvi)}$$

ions to bipy groups at which the optical densities are observed to reach a maximum show that there are always at least 40 unco-ordinated bipy groups for each colour centre produced in our experiments. Therefore it is reasonable to make the approximation that the position of equilibrium (xvi) is essentially unaltered by the addition of iron(II) under the conditions we used. If that assumption is correct then the term [B] in equations (xii) onwards should be replaced by the term $[B]/(1 + K_0)$. Thus the determined constants can be written by equations (xvii) and (xviii). These equations pose

$$(\beta_2)_{obs.} = (\beta_2)_{true}/(1 + K_0) \qquad \text{(xvii)}$$

$$(Y_2)_{obs.} = (Y_2)_{true}\,(1 + K_0) \qquad \text{(xviii)}$$

the problem of separating three constants from the data of two observed parameters. The temperature variation of $(\beta_2)_{obs.}$ and $(Y_2)_{obs.}$ as calculated using equation (xv) offers the best opportunity, but will lead to a greater degree of uncertainty than would be the case for two unknowns. The temperature variation demanded by equation (xviii) can be written by equation (xix). Values of the constants in this

$$\log[(Y_2)_{obs.}/(Y_2)_{true} - 1] = \Delta S_0/R - \Delta H_0/RT \qquad \text{(xix)}$$

equation can be found which will minimise the sum of squared differences. We obtained values of $(Y_2)_{true} = 20$, $\Delta S_0 = 62 \pm 2$ J K^{-1} mol^{-1} and $\Delta H_0 = 18 \pm 0.6$ kJ mol^{-1} in this way. Hence we could obtain the values of K_0 and $(\beta_2)_{true}$ as quoted in the final columns of Table 1. To these data may be added $\Delta S_2 = 0 \pm 9$ J K^{-1} mol^{-1} and $\Delta H_2 = -43 \pm 3$ kJ mol^{-1}. Again, these determined thermodynamic parameters should be close to the standard terms.

Clearly there exists the possibility that we have over- or wrongly-interpreted our data. The only possible response is that we have sought alternative ways of handling the data but have not found any other process to provide a reasonable fit. We are therefore led to accept the correctness of this approach. That is, we believe that the polyester containing the 4,4′-disubstituted 2,2′-bipyridyl group is very inflexible, even in solution. When a solution of the polymer has equilibrated at a particular temperature, at least half the potential ligand groups are unavailable for co-ordination. The most likely reason is that ring–ring rotation is this bipy group is not easy; therefore those groups present in the *transoid* form when metal ions are added remain in that form, unusable. Additionally, complex formation locks large numbers of repeat groups into inaccessible positions.

The polyester containing the 5,5′-disubstituted group behaves differently. The chain linkage *para* to the ring–ring bond offers no bar to ring–ring rotation and so the polymer remains flexible. This results in a much lower value of Y and a higher value of i. Probably the ligand groups are behaving as though they are independent of each other.

Experimental

The polymeric ligands were prepared using the well documented sequence of reactions required to convert a picoline to the appropriate symmetrical bipyridyl diester, the only modifications being those necessary for the formation of a polymer rather than a monomer. These minor changes can be illustrated by the preparation of the 4,4-polymer. In this instance the di-acid chloride (0.89 g) obtained from 2,2′-bipyridyl-4,4′-dicarboxylic acid was dissolved in dry thf (30 cm^3). The solution was heated and stirred; butane-1,4-diol (0.28 g) dissolved in dry thf (5 cm^3) was added. The reaction mixture was then brought to the boil, when a precipitate began to form, sometimes as a powder and sometimes as a coating on the inside of the flask. In this latter case the coating can be subsequently loosened by boiling with chloroform. After allowing the mixture to boil for a few minutes, the solid product was filtered from the hot mother-liquor. The solid was then quickly washed with methanol and air dried. Typically this solid represents 60% of the total theoretical yield. A further quantity of a polymeric product can be obtained by concentrating the filtrate and then cooling it in ice. This second portion may represent a 20% yield and is the portion we used in subsequent solution experiments. Data for elemental analyses obtained at all stages of the preparative sequence for this and for the other polymers we prepared are in agreement with the expected values. We were unable to carry out a thorough characterisation of these polymers prior to their use. We will report in a later paper what information we have concerning these ligands, the preparation of complexes from them, and the properties of such complexes.

The observations used to compute stability constant data were made as follows. A known weight of the second, thf-soluble, portion of polymer was dissolved in the minimum volume of thf necessary to achieve solution. Water was then added to make up the solution to a measured volume. Suitable volumes of this solution were then added to freshly prepared aqueous solutions containing known concentrations of AnalaR iron(II) sulphate and the mixture allowed to equilibrate in a thermostat-bath for at least half an hour. As mentioned earlier, the presence of metal ions renders the ligand more soluble in aqueous solutions, while in some cases the development of the characteristic iron(II) complex colour is slow. Therefore we always used ligand solutions as soon as possible after their preparation, certainly within 2 h. For all uses, the thf was dried, redistilled and freed from peroxide. Optical density measurements were made using a Pye-Unicam SP8-100 or an SP6 spectrophotometer.

Acknowledgements

One of us (D. S. M.) wishes to thank the S.R.C. for a research studentship.

References

1 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Radiochem.*, 1969, **12**, 135.
2 M. Gratzel, *Acc. Chem. Res.*, 1981, **14**, 376.
3 D. G. Whitten, *Angew. Chem.*, 1979, **18**, 440.
4 G. and H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947.
5 N. J. Turro, M. Gratzel, and A. M. Braun, *Angew. Chem.*, 1980, **19**, 675.
6 R. J. Card and D. C. Neckers, *J. Am. Chem. Soc.*, 1977, **99**, 7733.
7 M. Kaneko, S. Nemoto, A. Yamada, and Y. Kurimura, *Inorg. Chim. Acta*, 1980, **45**, L73.
8 I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, 1980, **102**, 6441.
9 J. M. Clar, J. M. Kelly, C. M. O'Connell, and J. G. Vos, *J. Chem. Res. (S)*, 1981, 260.
10 J. M. Calvert and T. J. Meyer, *Inorg. Chem.*, 1981, **20**, 27.
11 R. W. Murray, *Acc. Chem. Res.*, 1980, **13**, 135.
12 S. J. Ashcroft and C. T. Mortimer, 'Thermochemistry of Transition Metal Complexes,' Academic Press, London, 1970.

Received 28*th September* 1982; *Paper* 2/1662