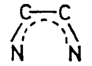
Kinetics of Reactions of Schiff-base Complexes of Iron(II). Part 6.[1] The Preparation and Kinetics of Reactions of Complexes of Multidentate Ligands

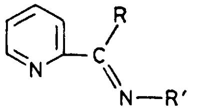
By **Michael J. Blandamer, John Burgess,*** and **Robert I. Haines,** Chemistry Department, University of Leicester, Leicester LE1 7RH
Fikry M. Mekhail, Department of Nuclear Chemistry, Atomic Energy Establishment, Anshas, Cairo, Egypt
Pakinam Askalani, American University in Cairo, Cairo, Egypt

Preparations of iron(II) complexes of bi-, tri-, quadri-, quinque-, and sexi-dentate Schiff bases are reported. The Schiff-base ligands are derived from pyridine-2-carbaldehyde, phenyl 2-pyridyl ketone, pyridine-2,6-dicarbaldehyde, or 2,6-diacetylpyridine, and appropriate amines. All these complexes aquate in acid solution, and react with cyanide to give ternary iron(II)–cyanide–Schiff-base complexes. The kinetics of aquation of several of these Schiff-base complexes, and the kinetics of cyanide attack at all the complexes, are described, and reactivities are compared with those for analogous reactions of other iron(II) di-imine complexes. Solvent effects on the reactivity with cyanide of one of the complexes of the sexidentate Schiff bases in a range of binary aqueous mixtures are discussed.

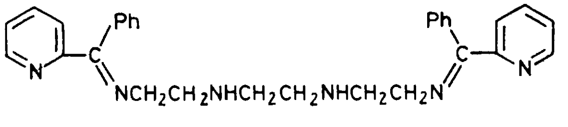
THE existence of stable, low-spin, iron(II) complexes of 2,2′-bipyridyl, $[Fe(bipy)_3]^{2+}$, and of 1,10-phenanthroline, $[Fe(phen)_3]^{2+}$, has been known for nearly a century.[2] The di-imine moiety (1) which is characteristic of these ligands is also present in Schiff bases derived from pyridine-2-carbaldehyde or 2-ketones and amines (2); a wide range of Schiff bases of type (2) also form stable low-spin iron(II) complexes of general formula $[Fe(L\text{–}L)_3]^{2+}$. These Schiff-base complexes aquate in acid solution, and react with hydroxide or cyanide ion relatively slowly (low-spin d^6 Fe^{II} has a high crystal-field activation energy [3]). The kinetics of these reactions have been investigated for a variety of complexes of bidentate Schiff bases of type (2),[4–7] and for an iron(II) complex of the sexidentate Schiff base (3).[1]



(1)



(2)



(3) bpdo

In the present paper we report the preparation of a range of iron(II) complexes of multidentate Schiff bases containing the di-imine moiety (1). These Schiff bases are derived from aldehyde and ketone derivatives of pyridine plus appropriate amines. The complexes contain Schiff bases which are bi-, $[Fe(mbpa)_3]^{2+}$, tri-, $[Fe(btp)_2]^{2+}$, quadri-, $[FeL(OH_2)_2]^{2+}$ (L = ebmp, ebpp, pbmp, or pbpp), quinque-, $[Fe(bpap)(OH_2)]^{2+}$, and sexi-dentate, $[Fe(bpdo)]^{2+}$.† We describe the kinetics of aquation of some of these complexes, and the kinetics of reaction with cyanide for all the complexes. This group contains two different types of complex, those in which the Fe^{II} is co-ordinated to six Schiff-base nitrogen atoms (mbpa, btp, and bpdo complexes) and those in which the Fe^{II} is co-ordinated to water as well as to Schiff-base nitrogen (L and bpap complexes). The reactions with cyanide ion thus involve direct displacement of Schiff base in some cases, but replacement of water in others. We discuss similarities, trends, and differences within the group of Schiff-base complexes, and compare reactivities with those for analogous reactions of other di-imine complexes, particularly the $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ cations.

RESULTS AND DISCUSSION

Bidentate Schiff-base Complexes.—The similarity of tris(Schiff base) complexes containing the di-imine (1) moiety to bipy and phen complexes was demonstrated by the reaction of biacetyl, methylamine [giving the Schiff base (4)], and Fe^{II} in 1953.[8] A semi-aromatic analogue, containing the Schiff base (5), was synthesised from pyridine-2-carbaldehyde, NH_2Me, and Fe^{II} in 1956.[9] The range of products was extended by the use

---

† mbpa = 4-Methyl-*N*-[bis(2-pyridyl)methylene]aniline (6), btp = 2,6-bis(1-*p*-tolylnitriloethyl)pyridine (9), ebmp = 2,2′-ethylenedinitrilobis(methylidynepyridine) (11; R = H), ebpp = 2,2′-ethylenedinitrilobis(phenylmethylidynepyridine) (11; R = Ph), pbmp = 2,2′-*o*-phenylenedinitrilobis(methylidynepyridine) (12; R = H), pbpp = 2,2′-*o*-phenylenedinitrilobis(phenylmethylidynepyridine) (12; R = Ph), bpap = 1,5-bis[phenyl-(2-pyridyl)methyleneamino]-3-azapentane (14), bpdo = 1,8-bis-[phenyl(2-pyridyl)methyleneamino]-3,6-diazaoctane (3), tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine, and bqdo = 1,8-bis[phenyl(2-quinolyl)methyleneamino]-3,6-diazaoctane.

[1] Part 5, E. R. Gardner, F. M. Mekhail, and J. Burgess, *Internat. J. Chem. Kinetics*, 1974, **6**, 133.

[2] F. Blau, *Chem. Ber.*, 1888, **21**, 1077; *Monatsh.*, 1889, **10**, 375; 1898, **19**, 647.

[3] See, for example, F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, ch. 3.

[4] J. Burgess and R. H. Prince, *J. Chem. Soc. (A)*, 1967, 434.

[5] J. Burgess, *J. Chem. Soc. (A)*, 1967, 955.

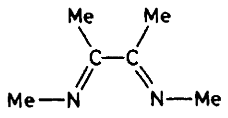
[6] J. Burgess, *J. Chem. Soc. (A)*, 1968, 497.

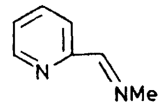
[7] J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc. (A)*, 1971, 44.

[8] P. Krumholz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163.

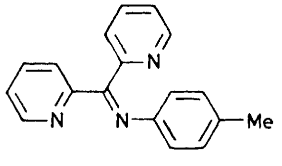
[9] D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, 1956, **78**, 1137.

of a series of amines[10] and by the use of phenyl 2-pyridyl ketone in place of pyridine-2-carbaldehyde.[11] The preparation and properties of such tris(di-imine) complexes of Fe^{II} were reviewed a few years ago;[12] new examples are still being reported.[13] There have been several kinetic studies of reactions of Schiff-base complexes of this type. These have covered aquation,[4,6,10] reactions with nucleophiles such as hydroxide[5,6] and cyanide,[7] and oxidation by peroxodisulphate.[6]


(4)


(5)

We now report the preparation of two new complexes of this type containing bidentate Schiff-base ligands, and the kinetics of reaction of one of these complexes in acid solution and with cyanide ion. The new Schiff-base complexes were prepared from glyoxal and ethylamine (*cf.* biacetyl plus NMe_2H above) and from di-2-pyridyl ketone and *p*-toluidine, plus Fe^{II}. Kinetic studies were carried out on the latter complex, whose method of preparation and analysis are given in the Experimental section.


(6) mbpa

In acid solution the complex $[Fe(mbpa)_3]^{2+}$, containing the bidentate Schiff base (6) derived from di-2-pyridyl ketone and *p*-toluidine, decomposed, following first-order kinetics over at least four half-lives. Observed first-order rate constants as a function of acid concentration and of temperature are reported in Table 1. The dependence of rate on acid concentration for the $[Fe(bipy)_3]^{2+}$ cation is shown in equation (1). We

$$-d[Fe(bipy)_3{}^{2+}]/dt = (k_1 + k_2[H^+])[Fe(bipy)_3{}^{2+}] \quad (1)$$

attempted to fit our results for the very similar $[Fe(mbpa)_3]^{2+}$ cation to an analogous expression. The dependence of $k_{obs.}$ on acid concentration is indeed linear for the Schiff-base complex, but there is no significant intercept of the correlation line. Hence the rate law for aquation of this complex is as shown in equation (2). That there is no k_1 term in this rate law is consistent with our observation that the half-life for dissociation of

$$-d[Fe(mbpa)_3{}^{2+}]/dt = k_2[Fe(mbpa)_3{}^{2+}][H^+] \quad (2)$$

$[Fe(mbpa)_3]^{2+}$ in neutral solution, in the presence of phen to act as scavenger of Fe^{2+}(aq) released, is at least 1 day. Values of k_2 [equation (2)], computed from a least-mean-squares analysis of the dependence of observed first-order rate constants on acid concentration at each temperature, are also included in Table 1. The temperature dependence of these k_2 values indicates an activation enthalpy of 107 kJ mol^{-1} and an activation entropy of 78 J K^{-1} mol^{-1} for this acid-catalysed aquation. These values may be compared with 109—115 kJ mol^{-1} and 62—65 J K^{-1} mol^{-1} for aquation of the $[Fe(bipy)_3]^{2+}$ cation.[14]

TABLE 1

Observed first-order rate constants, $k_{obs.}$, and derived second-order rate constants, k_2, for the aquation of the $[Fe(mbpa)_3]^{2+}$ cation in aqueous sulphuric acid

	T/K				
$[H^+]$/mol dm^{-3}	291.4	294.2	298.2	303.2	309.2
	$10^3k_{obs.}/s^{-1}$				
0.014			0.13		
0.034			0.18		
0.069		0.15	0.23		1.17
0.137	0.10	0.19	0.51	1.03	1.90
0.205	0.18		0.72		2.6
0.27	0.25	0.46	0.90		3.7
0.34				2.1	4.9
0.41	0.31	0.74	1.60	4.1	5.4
0.55	0.40	1.06	2.2	4.6	7.9
0.69	0.55	1.13	2.9		9.6
0.82		1.47		6.3	
0.89	0.77		3.7		
0.96		1.87		7.3	
1.10	1.03	2.3	4.4		
1.23				9.0	
1.37	1.19	2.8	5.5	9.8	
	$10^3k_2/dm^3\ mol^{-1}\ s^{-1}$				
	0.90	2.1	4.1	7.0	14.0

A concentrated aqueous solution containing the $[Fe(mbpa)_3]^{2+}$ cation reacts with cyanide ion to give a dark blue precipitate. This product is sparingly soluble in water, but readily soluble in organic liquids. It has solvatochromic properties[15] similar to those of $[Fe(bipy)_2(CN)_2]$ and $[Fe(phen)_2(CN)_2]$.[16] Its chemical analysis (Experimental section) corresponds to a composition $[Fe(mbpa)_2(CN)_2]\cdot0.5H_2O$. We have been unable to determine whether the $0.5H_2O$ is water of crystallisation or is covalently bonded to a ligand molecule in the manner established by Krumholz for a similar (biacetyl methylimine)iron(II) complex.[17] This uncertainty does not affect the kinetic study of the

---

[10] R. K. Murmann and E. A. Healy, *J. Amer. Chem. Soc.*, 1961, **83**, 2092.

[11] P. Krumholz, *Inorg. Chem.*, 1965, **4**, 609.

[12] P. Krumholz, *Structure and Bonding*, 1971, **9**, 139.

[13] See, for example, F. H. Case, *J. Chem. and Eng. Data*, 1976, **21**, 124; 1977, **22**, 238; H. Li Chum and T. Rabockai, *Inorg. Chim. Acta*, 1976, **19**, 145.

[14] R. Davies, M. Green, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1171; M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 17.

[15] J. Burgess, J. G. Chambers, and R. I. Haines, submitted to *J. Chem. Res.*

[16] J. Burgess, *Spectrochim. Acta*, 1970, **A26**, 1369, 1957.

[17] P. Krumholz, O. A. Sera, and M. A. de Paoli, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1820.

$[Fe(mbpa)_3]^{2+}$ cations with cyanide which is detailed in the following paragraph. Interestingly, there is no evidence for any water in salts of the $[Fe(mbpa)_3]^{2+}$ cation itself (*cf.* analysis in Experimental section).

The complex $[Fe(mbpa)_3]^{2+}$ reacts with cyanide in solution according to first-order kinetics under conditions where the complex concentration is appropriate to spectrophotometric monitoring (*ca.* 10^{-4} mol dm^{-3}) and cyanide ion is present in large excess. Observed first-order rate constants are shown in Table 2. The dependence of rate on cyanide concentration is given in equation (3); k_2 values defined by this equation are also shown in Table 2. The variation of k_2 with temperature

$$-d[Fe(mbpa)_3{}^{2+}]/dt = k_2[Fe(mbpa)_3{}^{2+}][CN^-] \quad (3)$$

indicates activation parameters $\Delta H^\ddagger = 71$ kJ mol^{-1} and $\Delta S^\ddagger = -32$ J K^{-1} mol^{-1}. These values are compared with those for analogous reactions of some other tris(di-imine)iron(II) complexes in Table 3. Presumably, the mechanism of reaction with cyanide here involves initial attack of the cyanide at the co-ordinated Schiff base, with subsequent transfer of the cyanide to the iron atom.[18]

TABLE 2

Observed first-order rate constants, $k_{obs.}$, and derived second-order rate constants, k_2, for the reaction of the $[Fe(mbpa)_3]^{2+}$ cation with cyanide ion in 30% v/v methanol–water; $I = 0.20$ mol dm^{-3} ($K[NO_3]$)

	T/K			
[KCN]/mol dm^{-3}	294.3	298.6	302.8	307.5
	$10^3k_{obs.}/s^{-1}$			
0.010				1.18
0.020				1.81
0.025	0.65	0.92	1.83	
0.030				2.8
0.040				3.2
0.050	1.41	1.65	2.5	4.6
0.060				5.1
0.075	2.1	2.7	5.4	
0.080				7.9
0.100	2.7	3.8	6.7	9.0
0.125	3.3	4.5	8.5	
0.150	4.0	5.5	9.8	
0.175	4.6	6.7	11.4	
0.200	5.5	7.0	13.4	
	$10^2k_2/dm^3$ mol^{-1} s^{-1}			
	2.7	3.7	6.6	9.3

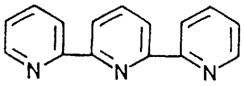
Tridentate Schiff-base Complexes.—Just as it is a straightforward matter to generate bidentate Schiff bases analogous to bipy, and their iron(II) complexes, so tridentate Schiff bases analogous to 2,2′:6′,2″-terpyridyl (terpy) (7) and their iron(II) complexes can also readily be prepared. The first such report of a terpyridyl-like ligand and its bis(ligand)iron(II) complex dealt with the Schiff base (8) derived from pyridine-2-carbaldehyde and 8-aminoquinoline.[19] Five similar ligands derived, for example, from pyridine-2,6-dicarbaldehyde and primary amines were described later.[20] The generation of such ligands has been reviewed;[21] a recent example is the Schiff base derived from pyridine-2,6-dicarbaldehyde and *o*-aminophenol.[22] The last-named Schiff base is reported to form complexes with numerous metal ions; surprisingly, Fe^{II} is not mentioned in this report! There appear to have been no detailed kinetic studies on such $[Fe(L-L-L)_2]^{2+}$ cations, which is hardly surprising in view of the complicated kinetics for aquation[23-25] and for base hydrolysis[23] of the $[Fe(terpy)_2]^{2+}$ cation.

TABLE 3

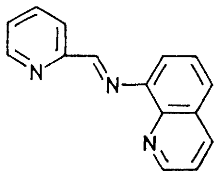
Comparison of rate constants and activation parameters for the reaction of tris(di-imine)iron(II) complexes with cyanide ion[a] at 308.2 K

Ligand	Conditions[b]	k_2 / dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K mol^{-1}	Ref.
bipy	$I = 2.0$	0.028	96	−4	*c*
phen	$I = 2.0$	0.025	86	−42	*d*
5Me-phen	$I = 0.33$	0.016	83	0	*e*
ppsa[f]	$I = 0.33$	0.003 4	105	−50	*g*
mbpa	30% MeOH, $I = 0.2$	0.093	71	−32	*h*
pma[i]	95% MeOH, $I = 0.004$	5.6	73	−8	7

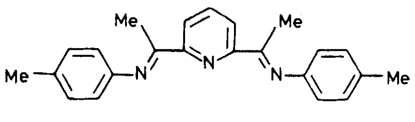
[a] The analogous reactions of sexidentate Schiff-base complexes have much smaller k_2 and higher $\Delta H^\ddagger$ values, see below. [b] In aqueous solution except where stated otherwise. [c] J. Burgess, *J.C.S. Dalton*, 1972, 1061. [d] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706. [e] J. G. Chambers, unpublished work. [f] ppsa = 5,6-Bis(phenylsulphonyl)-3-(2-pyridyl)-1,2,4-triazine, known as ferrozine. [g] E. R. Gardner, F. M. Mekhail, J. Burgess, and J. M. Rankin, *J.C.S. Dalton*, 1973, 1340. [h] This work. [i] pma = *N*-(2-Pyridylmethylene)aniline.



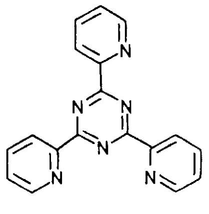
(7) terpy



(8)



(9) btp



(10) tptz

We have prepared the complex $[Fe(btp)_2]^{2+}$, where btp = the tridentate Schiff base (9) from 2,6-diacetylpyridine and *p*-toluidine. This complex undergoes

---

[18] R. D. Gillard, *Co-ordination Chem. Rev.*, 1975, **16**, 67; J. Burgess and R. I. Haines, *J.C.S. Dalton*, 1978, in the press.

[19] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem. Soc.*, 1953, **75**, 3834.

[20] P. Krumholz, *Inorg. Chem.*, 1965, **4**, 612.

[21] E. C. Alyea and P. H. Merrell, *Synth. React. Inorg. Met.-Org. Chem.*, 1974, **4**, 535.

[22] S. K. Thabet, S. M. Adrouni, and H. A. Tayim, *Analyt. Chem.*, 1975, **47**, 1870.

[23] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 6061.

[24] R. Farina, R. Hogg, and R. G. Wilkins, *Inorg. Chem.*, 1968, **7**, 170.

[25] J. Burgess and M. V. Twigg, *J.C.S. Dalton*, 1974, 2032.

rapid hydrolysis in acidic and in basic aqueous media, in contrast to $[Fe(terpy)_2]^{2+}$ (ref. 25) and $[Fe(tptz)_2]^{2+}$ [tptz = (10)].[26] It also reacts with cyanide to give, initially, the $[Fe(btp)(CN)_3]^-$ anion, a reaction analogous to that of the $[Fe(terpy)_2]^{2+}$ cation.[25] Observed first-order rate constants for this reaction, in the presence of a considerable excess of cyanide, are reported in Table 4. These results indicate a rate law as shown in equation (4), which suggests parallel rate-determining dissociation (k_1 term) and cyanide attack (k_2 term). At 298.2 K in aqueous solution, values of k_1 and k_2 are 1.5×10^{-3} s^{-1} and 5.4 dm^3 mol^{-1} s^{-1} respectively. The latter value is very much greater than the analogous rate constant, *ca.* 7×10^{-4} dm^3 mol^{-1} s^{-1} at 298 K,[25] for cyanide attack at the $[Fe(terpy)_2]^{2+}$ cation. The rate constant for rate-determining dissociation of $[Fe(btp)_2]^{2+}$, k_1 of equation (4), is also very much larger than that for $[Fe(terpy)_2]^{2+}$.[25] These greater rates for the tridentate Schiff-base complex must be a reflection of considerably weaker iron–nitrogen bonding in this complex than in the $[Fe(terpy)_2]^{2+}$ cation.

TABLE 4

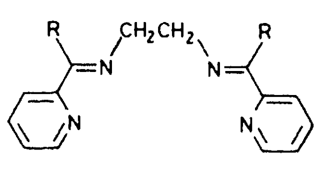
Observed first-order rate constants for the reaction of the $[Fe(btp)_2]^{2+}$ cation with cyanide ion in aqueous solution at 298.2 K and I = 0.40 mol dm^{-3} ($K[NO_3]$)

[KCN]/mol dm^{-3}	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18
$10^3k_{obs.}$/s^{-1}	2.7	3.5	4.9	5.5	7.1	7.9	8.9	10.9	11.4

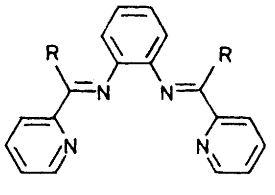
$$-d[Fe(btp)_2{}^{2+}]/dt = (k_1 + k_2[CN^-])[Fe(btp)_2{}^{2+}] \quad (4)$$

Quadridentate Schiff-base Complexes.—Quadridentate (four nitrogen donor atoms) Schiff bases can readily be prepared, for example by condensation of pyridine-2-carbaldehyde or quinoline-2-carbaldehyde with ethylenediamine.[27] However, such linear quadridentate Schiff bases do not form stable low-spin complexes with Fe^{II}.[3,*] It has been claimed that such Schiff bases form bis(ligand) complexes with Fe^{II} in which the quadridentate Schiff-base molecules lose one molecule of heteroaromatic aldehyde to give tridentate ligands during complex formation. The condensation of pyridine-2-carbaldehyde with *o*-phenylenediamine gives a potentially quadridentate Schiff base which is said to act as a bidentate ligand towards Fe^{II}.[29] On the other hand, a number of cyclic quadridentate (four nitrogen donor atoms) ligands do give low-spin iron(II) complexes, for example iron(II) phthalocyanines. Most such cyclic ligands are unsaturated compounds,[30] in some cases containing di-imine moieties,[31] although the saturated ligand 1,4,8,11-tetra-azacyclotetradecane (cyclam) gives a low-spin complex $Fe(cyclam)(NCS)_2$.[32]

We have prepared iron(II) complexes of the four quadridentate Schiff-base ligands, (11) and (12), derived



(11) R = H (ebmp)
R = Ph (ebpp)



(12) R = H (pbmp)
R = Ph (pbpp)

from all the combinations of pyridine-2-carbaldehyde or phenyl 2-pyridyl ketone, and ethylenediamine or *o*-phenylenediamine. The reaction of Fe^{II} with glyoxal plus naphthalene-1,8-diamine does not give a Schiff-base complex (nor does the reaction of Fe^{II} with phenyl 2-pyridyl ketone or pyridine-2-carbaldehyde with naphthalene-1,8-diamine), but Fe^{II} plus glyoxal and propane-1,3-diamine does give a product having a visible absorption spectrum characteristic of a low-spin iron–Schiff base complex. Analyses of the four complexes containing the Schiff bases (11) and (12) (see Experimental section) indicate that these are the perchlorate salts of the cations $[FeL(OH_2)_2]^{2+}$. Presumably, the water molecules are co-ordinated to the iron atom rather than bonded to the ligand, in contrast to the proposed ligand-bonded alcohol molecules in similar copper(II) complexes.[33]

All the four complexes $[FeL(OH_2)_2]^{2+}$ dissociate rapidly in acidic aqueous solution. A preliminary study of the kinetics of aquation showed complicated dependences of rates on acid concentration (*cf.* the tridentate Schiff-base complex above and the $[Fe(terpy)_2]^{2+}$ cation [25]); a full kinetic investigation was not conducted.

All the four complexes react with cyanide in solution, but there are differences in behaviour between the complexes of the flexible ligands (11) and those of the rigid ligands (12). The former undergo a two-stage reaction, the latter one stage. The product of the reaction of the complex of pbpp with cyanide analyses as $[Fe(pbpp)(CN)_2]\cdot H_2O$ even after prolonged desiccation *in vacuo* over P_4O_{10}. Presumably here, as for the complex $[Fe(mbpa)_2(CN)_2]\cdot 0.5H_2O$ mentioned above, there is some water covalently bonded to the co-ordinated Schiff base. The solvatochromic behaviour of the $[FeL(CN)_2]$ products is just what would be expected.[15,16] The complexes of the flexible ligands (11) give $[FeL(CN)_2]$ in the first stage, and then react with more cyanide to give $[FeL(CN)_4]^{2-}$, in which the Schiff base

---

* Interestingly, the reaction of Fe^{II} with quinoline-2-carbaldehyde, ethylenediamine, or *o*-phenylenediamine, and cyanide appears to give a low-spin complex whose properties suggest a composition $[Fe(L–L–L–L)(CN)_2]$.[28]

[26] G. K. Pagenkopf and D. W. Margerum, *Inorg. Chem.*, 1968, 1968, **7**, 2514.

[27] J. Reihsig and H. W. Krause, *J. prakt. Chem.*, 1966, **31**, 167 and refs. therein.

[28] J. Burgess and P. G. Wellings, preliminary experiments.

[29] E. Hoyer and B. Lorenz, *Z. anorg. Chem.*, 1967, **350**, 160.

[30] See, for example, D. P. Riley, J. A. Stone, and D. H. Busch, *J. Amer. Chem. Soc.*, 1976, **98**, 1752; 1977, **99**, 767.

[31] See, for example, V. L. Goedken, J. J. Pluth, Shie-Ming Peng, and B. Bursten, *J. Amer. Chem. Soc.*, 1976, **98**, 8014.

[32] D. D. Watkins, D. P. Riley, J. A. Stone, and D. H. Busch, *Inorg. Chem.*, 1976, **15**, 387.

[33] C. M. Harris and E. D. McKenzie, *J. Chem. Soc. (A)*, 1969, 746.

acts as a bidentate ligand. Such a sequence parallels that described for the reactions of complexes of the $[Fe(bipy)_3]^{2+}$ type with cyanide.[34] Approximate analyses * and solvatochromic behaviour [15,16] of the intermediates and products are consistent with the suggested reaction sequence; the products of the second stage certainly still contain Schiff base co-ordinated to the iron and are not simply $[Fe(CN)_6]^{4-}$. The difference in behaviour between the complexes of the rigid and flexible ligands is readily understandable in the light of the difficulty of removing four nitrogen donor atoms at once from the metal in the case of the former. This situation may be compared with the known difficulty of removing metal ions from phthalocyanine complexes.

For the complexes containing the flexible ligands (11) the second stage is sufficiently slower than the first for the two stages to be treated as kinetically independent. For both stages of the reactions of these complexes, and for the one-stage reactions of the complexes of the rigid ligands (12), the kinetic pattern is, in the presence of a large excess of cyanide ion, first-order up to at least three half-lives [two half-lives at least for the first stage of the reactions of the complexes of ligands (11)]. Observed first-order rate constants are reported in Table 5. For all these reactions, plots of observed first-order rate constants ($k_{obs.}$) against cyanide concentration are linear and pass through the origin, implying a rate law of the type shown in equation (5). Values for the derived

$$-d[FeL(OH_2)_2{}^{2+}]/dt = k_2[FeL(OH_2)_2{}^{2+}][CN^-] \qquad (5)$$

second-order constants k_2, computed using a standard unweighted least-mean-squares program, are also given in Table 5.

TABLE 5

Observed first-order rate constants, $k_{obs.}$, and derived second-order rate constants, k_2 [*cf.* text, equation (5)], for the reactions of quadridentate Schiff-base complexes $[FeL(OH_2)_2]^{2+}$ with cyanide ion in aqueous methanol (30% v/v methanol) at 298.2 K and $I = 1.33$ mol dm^{-3} (K[NO$_3$])

	[KCN]/mol dm^{-3}					
Ligand	0.083	0.167	0.333	0.500	0.667	
First stage	$10^2k_{obs.}$/s^{-1}					10^2k_2/ dm^3 mol^{-1} s^{-1}
ebmp	0.65	1.33	2.4	4.1		7.8
dbpp	0.33	0.75	1.40	2.1	2.6	4.1
pbmp	0.61	1.22	2.5	3.7		7.4
pbpp	0.55	1.10	2.2	3.6	4.7	6.8
Second stage	$10^3k_{obs.}$/s^{-1}					10^4k_2/ dm^3 mol^{-1} s^{-1}
ebmp	10	19	27	55	74	107
ebpp	0.017	0.036	0.075	0.113	0.149	2.2

The most striking feature of the results in Table 5 is the close similarity of the k_2 values for all the four complexes (first stage). Since the reaction in each case involves the replacement of water, and the other ligands are very similar, this strongly suggests that it involves direct displacement of water by cyanide. If the reaction first involved attack of cyanide at the co-ordinated ligand, as proposed for $[Fe(phen)_3]^{2+}$ and related complexes,[18] then a greater range of rates would be expected. Indeed, a wide range of k_2 values has been found for a range of ligands in iron(II) complexes of variously substituted 1,10-phenanthrolines,[35] and for various sexidentate Schiff-base complexes (see below). Moreover, the k_2 values for the second stage of the reaction of the complexes of ligands (11) do differ markedly. Here cyanide is displacing co-ordinated nitrogen, not relatively weakly co-ordinated water, and attack initially at the co-ordinated ligand is more likely. It is impossible to compare the k_2 values for cyanide attack at $[FeL(CN)_2]$ directly with analogous k_2 values for, for example, $[Fe(phen)_2(CN)_2]$,[36] since experimental conditions differ. However, there is a difference in reactivity of a factor of *ca.* 10^3, with the quadridentate Schiff base much more rapidly displaced than phen or bipy.

It is of interest to compare the reactivities of the above ternary aquairon(II) complexes with that of the $[Fe(CN)_5(OH_2)]^{3-}$ anion. For the pentacyano-anion, as for most complexes of the type $[Fe(CN)_5L]^{n-}$, ligand replacement, *e.g.* by cyanide, takes place by a limiting dissociative (*D*) mechanism.[37] The difference between the first stage of the reaction of a $[FeL(OH_2)_2]^{2+}$ cation (L = quadridentate ligand) and of $[Fe(CN)_5(OH_2)]^{3-}$ is that in the former the leaving water is *trans* to another water ligand, but in the latter it is *trans* to cyanide. It may well be that in the detailed reaction sequence [equations (6) and (7)] which corresponds to the first stage of the reaction of one of these quadridentate Schiff-base complexes with cyanide the first and rate-determining step [equation (6)] is associative as we propose, but that the subsequent reaction [equation (7)] is fast and *D* in mechanism now that water is leaving from a position *trans* to cyanide.

$$[FeL(OH_2)_2]^{2+} + [CN]^- \longrightarrow [FeL(CN)(OH_2)]^+ + H_2O \qquad (6)$$

$$[FeL(CN)(OH_2)]^+ + [CN]^- \longrightarrow [FeL(CN)_2] + H_2O \qquad (7)$$

Quinquedentate Schiff-base Complexes.—Few examples of these have been prepared.[38] We have carried out a preliminary examination of two quinquedentate Schiff-base ligands. The reaction of 2,6-diacetylpyridine with 3,6-diazaoctane-1,8-diamine (3,6NH-od) and Fe^{II} in aqueous solution gives an iron(III) complex (*cf.* Fe^{II} plus

---

* Products of neither stage could be obtained pure. First-stage products were contaminated with material which had reacted further with cyanide, while the products of the second stage had solubility properties too close to those of potassium cyanide for us to be able to achive a complete separation.

[34] A. A. Schilt, *J. Amer. Chem. Soc.*, 1960, **82**, 3000.

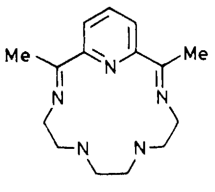
[35] J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.

[36] J. Burgess and R. I. Haines, unpublished work.

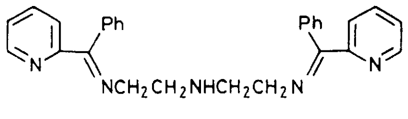
[37] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 2080.

[38] See, for example, N. W. Alcock, D. C. Liles, M. McPartlin, and P. A. Tasker, *J.C.S. Chem. Comm.*, 1974, 727; M. G. B. Drew, J. Grimshaw, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1976, 1388 and refs. therein.

glyoxal and methylamine[39]). Presumably, the cyclic Schiff base (13) is formed first, and then undergoes redox reactions involving the Fe^{2+} ion.[40] The reaction of phenyl 2-pyridyl ketone with 3-azapentane-1,5-diamine and Fe^{II} gives a complex of the garland Schiff base (14) in which the iron is still in oxidation state II. Solutions of the iodide and perchlorate salts of this complex give the same kinetic behaviour and rates of reaction with cyanide and in acidic aqueous solution {first order in cyanide and acid concentration, respectively, as in the case of $[Fe(mbpa)_3]^{2+}$ above}. These observations suggest the complex to be $[Fe(bpap)(OH_2)]^{2+}$; presumably the reactions with cyanide involve rapid replacement of water, perhaps by a *D* process (*cf.* above), followed by a slower reaction in which part of the quinquedentate Schiff base is displaced from the iron.



(13)



(14) bpap

Sexidentate Schiff-base Complexes.—The reaction of pyridine-2-carbaldehyde with 2-aminomethylpropane-1,3-diamine gives a sexidentate ligand, incorporating three di-imine units (1), which forms a low-spin iron(II) complex.[41] Kinetics of several reactions of iron(II) complexes of garland sexidentate Schiff bases derived from pyridine-2-carbaldehyde[42] or phenyl 2-pyridyl ketone[1] and 3,6NH-od have been described. We have now prepared a similar complex from quinoline-2-carbaldehyde, 3,6NH-od, and Fe^{II} (see Experimental section) and here report on its kinetics of reaction in acid solution and with cyanide. We also report and discuss the variation of reactivity with solvent for the reaction with cyanide in binary aqueous mixtures of the complex prepared from phenyl 2-pyridyl ketone.

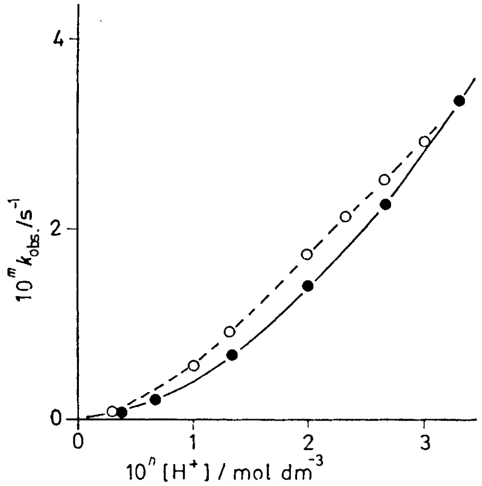
The decomposition of the complex derived from quinoline-2-carbaldehyde, 3,6NH-od, and Fe^{II}, $[Fe(bqdo)]^{2+}$, in acid solution follows first-order kinetics. First-order rate constants for this dissociation in various strengths of acid are reported in Table 6. The dependence of the rate constant on acid concentration is compared with that for the analogous complex derived from phenyl 2-pyridyl ketone in the Figure. This shows a very similar curvature for the two plots, which indeed are similar to that reported for the $[Fe(terpy)_2]^{2+}$ cation,[25] and the expected greater reactivity of the bqdo complex.

TABLE 6

Observed first-order rate constants, $k_{obs.}$, for aquation of $[Fe(bqdo)]^{2+}$ in aqueous solution in the presence of sulphuric acid at 298.2 K

$10^4[H_2SO_4]$/ mol dm^{-3}	1.7	3.3	6.7	10.0	13.3	16.7
$10^4k_{obs.}$/s^{-1}	4	21	67	142	226	357

The bqdo complex reacts with cyanide ion in aqueous solution according to first-order kinetics; repeat-scan monitoring shows clear isosbestic points at 557 and 598 nm. Satisfactory analyses could not be obtained for the product,* but its solubility and solvatochromic properties indicate a composition $[Fe(bqdo)(CN)_3]^-$, in which the ligand is tridentate. First-order rate constants for the reaction with cyanide, perforce at the relatively low temperature of 281.2 K since the reaction is fast for conventional monitoring techniques, are reported in Table 7. The relative reactivities of these iron(II)–sexidentate Schiff-base complexes towards cyanide are shown in Table 8. The order of increasing rapidity of reaction parallels the expected order of stability of the complexes.



Dependence of the rate constant for aquation of sexidentate Schiff-base complexes of Fe^{II} in aqueous acid: (●) $[Fe(bqdo)]^{2+}$ at 298.2 K, $n = 3$, and $m = 2$; (○) $[Fe(bpdo)]^{2+}$ at 308.2 K, $n = 1$, and $m = 5$

TABLE 7

Observed first-order rate constants, $k_{obs.}$, for the reaction of $[Fe(bqdo)]^{2+}$ with cyanide in aqueous solution at 281.2 K

10^2[KCN]/mol dm^{-3}	2.0	5.0	10.0	20.0	30.0
$10^2k_{obs.}$/s^{-1}	0.34	1.03	1.69	3.3	5.1

We have recently demonstrated the importance of the variation of the chemical potential of cyanide ion in determining the variation of second-order rate constants for the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide

---

* The reaction product could not be satisfactorily separated from potassium cyanide; when tetraethylammonium cyanide was used for the preparation only tarry products were obtained.

[39] H. L. Chum, T. Rabockai, J. Phillips, and R. A. Osteryoung, *Inorg. Chem.*, 1977, **16**, 812.

[40] See, for example, P. Krumholz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163; G. G. Christoph and V. L. Goedken, *ibid.*, 1973, **95**, 3869; A. M. G. da Costa Ferreira, P. Krumholz, and J. M. Riveros, *J.C.S. Dalton*, 1977, 896.

[41] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, 1954, **54**, 959 (see p. 980).

[42] J. Burgess and G. M. Burton, accepted for publication in *Rev. Latinoamer. Quim.*

in binary aqueous solvent mixtures.[43,44] We were therefore interested to see whether the reactivity patterns for other low-spin iron(II) complexes with cyanide are similar. Observed first-order rate constants ($k_{obs.}$) for the reaction of the $[Fe(bpdo)]^{2+}$ cation (bpdo = the sexidentate Schiff base derived from phenyl 2-pyridyl ketone and 3,6NH-od) with cyanide ion (in large excess) in various binary aqueous mixtures are reported in Table 9.

TABLE 8

Values of k_2 for the reaction of sexidentate Schiff bases of Fe^{II} derived from 3,6NH-od and the stated keto-compound with cyanide, in aqueous solution at I = 0.3—0.33 mol dm^{-3}

Schiff-base keto-component	T/K	k_2/dm^3 mol^{-1} s^{-1}	Ref.
Quinoline-2-carbaldehyde	281.2	1.6	This work
Pyridine-2-carbaldehyde	288.7	0.6×10^{-3}	42
	298.3	2.1×10^{-3}	
Phenyl 2-pyridyl ketone	298.5	0.94×10^{-5}	1

TABLE 9

Observed first-order rate constants ($k_{obs.}$) and derived second-order rate constants (k_2) for the reaction of the $[Fe(bpdo)]^{2+}$ cation with cyanide ion in binary aqueous solvent mixtures at I = 0.333 mol dm^{-3} (KCl)

Co-solvent [a]		[KCN]/mol dm^{-3} 0.133	0.199	0.267	0.333	10^5k_2/dm^3 mol^{-1} s^{-1}
		$10^5k_{obs.}$/s^{-1}				
None [b]		0.103	0.153	0.225	0.292	0.87
Methanol [b]:	30	0.20	0.38	0.45	0.69	1.8
	50	0.44	0.69	0.96	1.29	3.7
	75	0.61	1.74	2.05	2.92	8.1
Ethanol [b]:	30	0.29	0.42	0.59	0.66	2.2
	50	1.30	1.92	2.6	3.4	9.9
	75	3.8	5.5	6.5	8.4	25.5
t-Butyl alcohol [c]:	10	0.70	0.97	1.65	1.89	5.7
	15	1.07	1.3	2.1	2.7	7.8
	20	1.1	1.7	2.8	3.2	9.6
	30	3.1	4.1	5.5	7.4	21
	40	5.1	6.7	9.2	12.2	35
Dioxan [b]:	30	0.41	0.61	0.80	1.00	3.0
	50	2.7	3.3	5.0	6.2	18.3

[a] Solvent compositions are in percentages by volume before mixing. [b] At 298.6 K. [c] At 308.9 K.

Plots of $k_{obs.}$ against cyanide concentration for the reaction in the binary aqueous mixtures are, within experimental uncertainty, linear with zero intercepts, as demonstrated and explained earlier for aqueous solution.[1] This simple linear dependence is in contrast to the curved dependence of the observed first-order rate constant on nucleophile concentration for the reaction with hydroxide.[45] The different kinetic behaviour with cyanide and hydroxide may arise from the latter being a better nucleophile for attacking the co-ordinated ligand,[18] so that two hydroxide ions per molecule of complex may be involved at high hydroxide concentration.

Values of the second-order rate constants for cyanide attack at the $[Fe(bpdo)]^{2+}$ cation, computed using an unweighted least-mean-squares analysis of the dependence of $k_{obs.}$ on cyanide concentration, are included in Table 9. In Table 10 we compare reactivity trends for the $[Fe(bpdo)]^{2+}$ and $[Fe(bipy)_3]^{2+}$ cations, in terms of the ratios of rate constants in binary aqueous mixtures to those in water. The change in reactivity of the bpdo complex is somewhat less than that of the bipy complex in practically all the situations where direct or almost direct comparison can be made. In our earlier analysis of the variation in rate constant with solvent composition for the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide, we found that this could be attributed primarily to the variation in chemical potential of the cyanide. The chemical potentials of this anion in binary aqueous mixtures were estimated *via* published values of the chemical potentials of chloride ion.[43,44,46] The ratios of rate constants (aqueous mixture : water) for the $[Fe(bpdo)]^{2+}$ cation reacting with cyanide are considerably less than the values forecast from the changes in chemical potential of the cyanide in those few cases where values of $\delta_m\mu^{\ominus}(CN^-)$ can be estimated. (Estimates in solvent mixtures containing higher proportions of organic co-solvents are precluded by the lack of published data for chloride ion.) Therefore it seems that solvation differences in going from the initial to the transition state

TABLE 10

Ratios ($k_2 : k_0$) of rate constants for cyanide attack at the $[Fe(bpdo)]^{2+}$ and $[Fe(bipy)_3]^{2+}$ cations in binary aqueous mixtures, k_2, to those in water, k_0, as determined experimentally and as calculated from estimated values for Gibbs free energies of transfer of cyanide ion from water into binary aqueous mixtures [$\delta_m\mu^{\ominus}(CN^-)$, molar scale]. Values are at 298.2 K except where indicated otherwise

Co-solvent [a]		$\delta_m\mu^{\ominus}(CN^-)$/kJ mol^{-1}	$k_2 : k_0$ calc.	$[Fe(bpdo)]^{2+}$	$[Fe(bipy)_3]^{2+}$
Methanol:	10	0.85	1.4		1.6 [b]
	20	2.10	2.3		2.1 [b]
	30	3.55	4.0	2.1	3.2 [b]
	50			4.2	
	75			9.3	
Ethanol:	30			2.5	2.9 [b]
	50			11.4	
	75			29.3	
t-Butyl alcohol:	10	1.8	2.0	1.5 [c]	1.4
	15			2.0 [c]	
	20			2.5 [c]	
	28.4	3.3	8.3		7.0
	30			5.4 [c]	
	40			8.9 [c]	
	48.2	9.0	38		16
Dioxan:	30			3.4	4.5 [b]
	50			21.0	

[a] Composition in % v/v. [b] At 308.2 K. [c] At 308.9 K.

---

[43] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1976, 606.

[44] M. J. Blandamer, J. Burgess, J. G. Chambers, R. I. Haines, and H. E. Marshall, *J.C.S. Dalton*, 1977, 165.

[45] M. J. Blandamer, J. Burgess, P. Cookson, D. L. Roberts, P. G. Wellings, M. Mekhail, and P. Askalani, *J.C.S. Dalton*, 1978, preceding paper.

[46] See, for example, C. F. Wells, *J.C.S. Faraday I*, 1973, 984 and refs. cited in refs. 43 and 44.

are more important in the case of the $[Fe(bipy)_3]^{2+}$ cation.

EXPERIMENTAL

Preparations.—The iron(II) complexes of the various Schiff bases were all made by the same general method.[47] Stoicheiometric proportions of methanolic solutions of the appropriate precursors of the required Schiff-base ligand were mixed at room temperature. To this '*in situ*' Schiff-base solution was added the stoicheiometric amount of iron(II) chloride tetrahydrate dissolved in methanol containing a few drops of acetic acid [this inhibits oxidation of the Fe^{II} (ref. 46)]. The reaction solution was allowed to stand at room temperature until full development of the blue colour due to the product (15—60 min). The resulting solution was filtered (Celite) and rotary evaporated to dryness. The crude product was washed with toluene, then diethyl ether, dissolved in water, and filtered (Celite). The complex cation was precipitated as its perchlorate salt, which was filtered, washed with water, then ethanol, then diethyl ether, and dried *in vacuo* over P_4O_{10}. The mixed Schiff base–cyanide complexes were precipitated by adding a large excess of potassium cyanide to a strong aqueous solution of the iron(II) Schiff-base complex.

Analyses are reported, for the cationic complexes prepared as described above and for reaction products of two of these Schiff-base complexes with cyanide, in Table 11. They were carried out by the Butterworth Microanalytical Company, Teddington, Middlesex.

Kinetics.—All the runs were conducted in 10-mm silica cells in the thermostatted cell compartment of a Unicam SP 800 or Beckman DK2 recording spectrophotometer; optical densities were monitored at the respective wavelengths of maximum absorption of the complexes.

TABLE 11

Analysis results, with calculated figures given in parentheses

Complex	Analysis (%) C	H	N
$[Fe(mbpa)_3][ClO_4]_2$	59.7	4.10	12.0
	(60.3)	(4.20)	(11.7)
$[FeL(OH_2)_2][ClO_4]$ L = ebmp	31.3	3.20	9.6
	(30.8)	(3.35)	(10.3)
= ebpp	45.9	4.05	8.2
	(45.8)	(3.85)	(8.2)
= pbmp	36.1	2.90	8.6
	(35.3)	(2.95)	(9.1)
= pbpp	49.8	3.60	8.1
	(49.4)	(3.60)	(7.7)
$[Fe(bqdo)][ClO_4]_2$	45.9	4.20	11.9
	(45.9)	(4.30)	(12.3)
$[Fe(mbpa)_2(CN)_2]\cdot 0.5H_2O$	68.0	4.80	16.4
	(68.8)	(4.70)	(16.9)
$[Fe(pbpp)(CN)_2]\cdot 0.5H_2O$ *	68.5	3.80	14.2
	(69.2)	(4.15)	(15.1)

* Fe = 8.8% by atomic-absorption spectroscopy.

We thank the Royal Society for the award of a Grant-in-aid for the purchase of the Unicam SP 800 spectrophotometer.

[7/1984 *Received*, 10*th November*, 1977]

---

[47] L. F. Lindoy. *Quart. Rev.*, 1971, **25**, 379.