Inorganica Chimica Acta, 34 (1979) 57–60

Chemistry of Polydentate Ligands. Part 4 [1]. The Oxidative Denitrogenation of Dichloro-6,6′-dihydrazino-2,2′-bipyridyliron(II)

JACK LEWIS

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.

KEVIN P. WAINWRIGHT

Department of Chemistry, Queen's University of Belfast, Belfast, BT9 5AG, U.K.

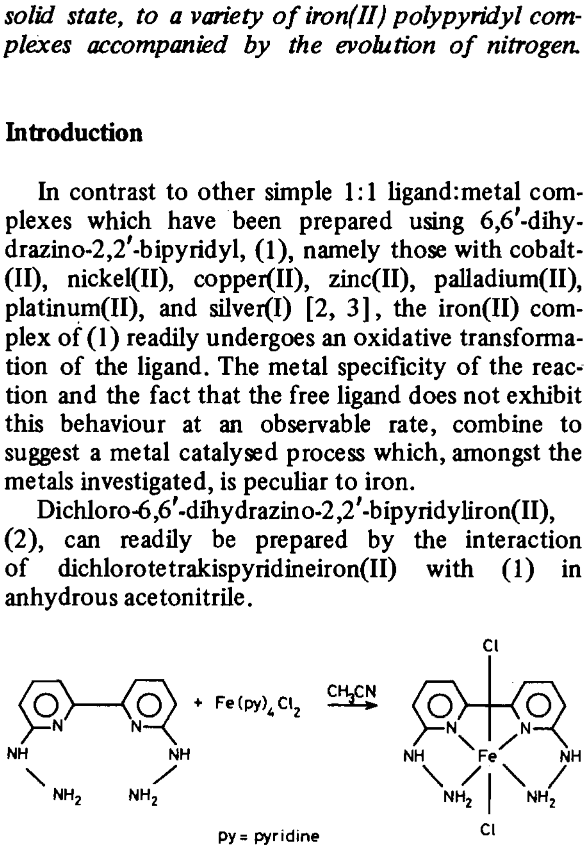
Received August 7, 1978

On exposure to oxygen, crystals of the title compound undergo a quantitative transformation in the solid state, to a variety of iron(II) polypyridyl complexes accompanied by the evolution of nitrogen.

Introduction

In contrast to other simple 1:1 ligand:metal complexes which have been prepared using 6,6′-dihydrazino-2,2′-bipyridyl, (1), namely those with cobalt(II), nickel(II), copper(II), zinc(II), palladium(II), platinum(II), and silver(I) [2, 3], the iron(II) complex of (1) readily undergoes an oxidative transformation of the ligand. The metal specificity of the reaction and the fact that the free ligand does not exhibit this behaviour at an observable rate, combine to suggest a metal catalysed process which, amongst the metals investigated, is peculiar to iron.

Dichloro-6,6′-dihydrazino-2,2′-bipyridyliron(II), (2), can readily be prepared by the interaction of dichlorotetrakispyridineiron(II) with (1) in anhydrous acetonitrile.



py = pyridine

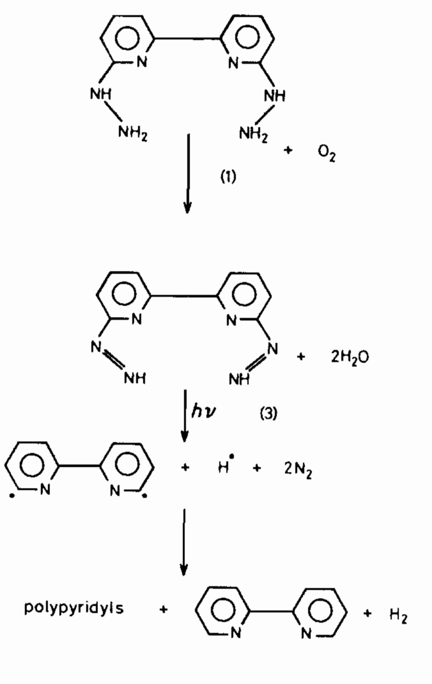
(1) (2)

Provided that the reaction is carried out under anaerobic conditions complex (2) precipitates as analytically pure orange-red crystals, which are indefinitely stable under nitrogen. A comparison of the infrared spectrum of the complexed ligand with that of the free ligand gives no reason to suggest that the ligand has undergone any structural rearrangement during the complexation process. Particularly in this respect it should be noted that the νN–H and δN–H absorptions present in (1) are preserved, with only minor shifts in frequency, in the spectrum of (2).

The Mössbauer spectrum and the magnetic properties of (2) both independently characterises it as a spin free iron(II) species. The Mössbauer shows a quadrupole doublet (δ = 0.84 mm sec^{-1} with respect to natural iron, ΔE_q = 3.06 mm sec^{-1}) with the large splitting uniquely characteristic of high spin iron(II) [4], and the magnetic moment was found to be 5.33 B.M. at 295 K and temperature dependent, also fully in accordance with that expected for a species having a $^5T_{2g}$ ground state [5].

On exposure to air, however, it was found that during the course of *ca.* one week crystals of (2) (and also the analogous diisothiocyanato, dibromo and diiodo complexes) gradually crumbled to a deep red powder whose elemental analysis corresponded to that of (2), but with the loss of two molecules of nitrogen and the incorporation of 1.33 molecules of water (Found: C, 39.2, 38.9; H, 2.97, 3.30; N, 9.07, 9.23; Cl, 23.5, 23.3. $C_{10}H_{10.66}Cl_2FeN_2O_{1.33}$ requires: C, 39.1; H, 3.50; N, 9.13; Cl, 23.1%). Additionally the infrared spectrum of the product showed a total loss of all νN–H and δN–H absorptions. Measurements during the decomposition showed the uptake of one mol of oxygen and the evolution of two mol of nitrogen. The gas evolution was markedly more rapid when the sample was exposed to direct sunlight.

It seems likely that the process involves oxidation of the ligand to 2,2′-bipyridyl (hereafter bipy). Hydrazines are known to decompose by a mechanism which initially involves oxidation to an azene followed by free radical breakdown resulting in the evolution of nitrogen [6, 7]. This mechanism as applied to 6,6′-dihydrazino-2,2′-bipyridyl, (1), is shown in Scheme One. However, the process is more complex than this since it would be expected to produce a single species having the stoichiometry



SCHEME ONE

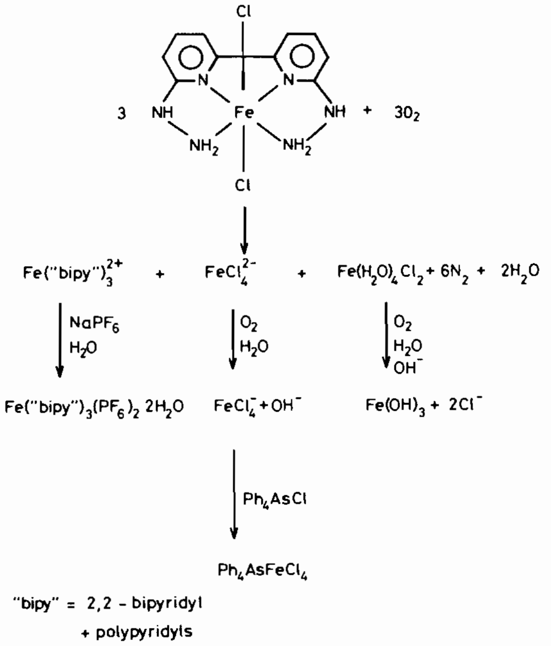
Fe(bipy)Cl$_2$. This species, however, is ferromagnetically ordered [8] with a room temperature magnetic moment of *ca.* 5.4 B.M. and the Mössbauer parameters are in accordance with the magnetic data, the compound showing a simple quadrupole doublet at room temperature which splits into a well resolved six line Zeeman spectrum at 4.2 K. Neither the Mössbauer spectrum nor the magnetic properties of the denitrogenation product are compatible with this, but rather both suggest the presence of more than one iron-containing species. The Mössbauer shows a broad envelope of peaks at room temperature and at 77 K, and a plot of reciprocal magnetic susceptibility *versus* temperature shows essentially Curie–Weiss behaviour corresponding to a magnetic moment of 3.85 B.M. and a θ values of −20 K.

Conductivity measurements indicated that the denitrogenation product is an electrolyte. Addition of sodium hexafluorophosphate to a methanolic solution of the denitrogenation product resulted in the precipitation of a red crystalline substance, (4), whose analysis corresponded to Fe(bipy)$_3$(PF$_6$)$_2\cdot$2H$_2$O (Found: C, 42.5; H, 3.00; N, 9.66; P, 7.36. $C_{30}H_{28}F_{12}FeN_6O_2P_2$ requires: C, 42.4; H, 3.32; N, 9.88; P, 7.28%). The magnetic moment of (4), however, was not in accordance with this formulation; it was found to be 2.4 B.M. at 295 K, and a plot of inverse susceptibility *versus* temperature gave a θ value of −100 K. Tris-2,2′-bipyridyliron(II) species are generally low spin and exhibit a magnetic moment of between 0 and 1 B.M. arising from temperature independent paramagnetism [5]. A sample of Fe(bipy)$_3$(PF$_6$)$_2$ was prepared using the method employed by Burstall and Nyholm [9], and it showed a moment of 0.84 B.M. at 295 K. Thus the cationic species present in the denitrogenation product is not simply Fe(bipy)$_3^{2+}$.

This anomaly was clarified by hydrolysis of (4) with aqueous 2 *M* NaOH, which resulted in liberation of the ligand. Mass spectroscopic studies of the free ligand revealed that it consisted not only of bipy, but that *ca.* 20% of the bipy had undergone oligomerization to form polypyridyl chains of up to four bipy residues in length. This observation is consistent with the free radical mechanism proposed for the decomposition of the diazene, (3), wherein bipyridyl free radicals can couple together to form the polypyridyl species. The presence of polypyridyls in the bulk ligand also explains the anomalous magnetic properties of the hexafluorophosphate salt, (4). It is well established that minor perturbations from the idealised bond distances and angles in low spin tris(bipy)iron(II) compounds are sufficient to result in a decrease in the ligand field strength below the threshold value necessary for spin pairing [10]. If the polypyridyl entity is involved in bridging it will have the efficiency of its ligand field constrained by the impositions of the lattice, and if bound to one centre alone, it has been shown by previous work [11] that this results in extreme distortions due to internal geometrical constraints. Thus the hexafluorophosphate salt, (4), consists of a mixture of high and low spin species. The resultant magnetic moment of 2.4 B.M. is arrived at by a 20% abundance of the high spin species and this correlates well with the percentage of bipyridyl residues known to have undergone coupling to form polypyridyls. Additionally the linking together of adjacent iron centres by bridging polypyridyls may well be sufficient to render the sample magnetically non-dilute and to thus account for the high value of θ which is indicative of antiferromagnetic interaction.

A physical mixture of high and low spin species is further indicated by the Mössbauer spectrum of (4) which shows two superimposed quadrupole doublets. The principal of these (δ = 0.30 mm sec^{-1} with respect to natural iron, ΔE_q = 0.44 mm sec^{-1}) has spectral parameters very close to those reported for tris(bipy)iron(II) perchlorate [12] (δ = 0.32 mm sec^{-1} with respect to natural iron, ΔE_q = 0.39 mm sec^{-1}) and corresponds to the low spin species. The weaker of the two (δ = 0.85 mm sec^{-1} with respect to natural iron, ΔE_q = 2.30 mm sec^{-1}) corresponds to the high spin component of the mixture.

Precipitation of the anionic component of the denitrogenation product with tetraphenylarsonium chloride resulted in the formation of the known compound tetraphenylarsonium tetrachloroferrate(III) [13], the species FeCl$_4^-$ probably arising from the secondary oxidation of FeCl$_4^{2-}$. The balance of the stoichiometry from the starting material is then made up by the addition of hydrated ferrous chloride to the right hand side of the decomposition equation (Scheme Two). Under the basic conditions created by the oxidation of $FeCl_4^{2-}$ this is largely converted to ferric hydroxide whose presence in the denitrogenation product was indicated by variable amounts of highly insoluble material which exhibited pronounced νO–H bands in the infrared spectrum.



SCHEME TWO

The denitrogenation reaction also proceeds at a considerably faster rate in solution in solvents that are not strongly electron donating. In pyridine, however, the reaction does not occur. The consequence of dissolving (2) in pyridine could be the irreversible blocking of an additional co-ordination site otherwise utilised by oxygen for the initiation of the reaction, but attempts to isolate pyridine-containing adducts of (2) were unsuccessful.

Experimental

Magnetic susceptibilities were determined on a Newport Gouy balance and are corrected for ligand and inner core diamagnetism using Pascal's constants [14]. ^{57}Fe Mössbauer spectra were recorded at 77 K using a ^{57}Co in Pd source in conjunction with a spectrometer that has been described in the literature [15]. Infrared spectra were measured as nujol mulls using a Perkin Elmer 237 spectrometer. Microanalyses were by the University Chemical Laboratory Microanalytical Department.

6,6′-Dihydrazino-2,2′-bipyridyl and dichlorotetrakis-pyridineiron(II) were prepared by published procedures [2, 16]. Acetonitrile was obtained commercially and was purified in recommended manner [17].

Dichloro-6,6′-dihydrazino-2,2′-bipyridyliron(II), (2)

Dichlorotetrakispyridineiron(II) (0.5 g) was added to dry degassed acetonitrile (40 cm^3) which had been heated to 50 °C in a stream of nitrogen. The suspension was stirred for ten minutes before adding 6,6′-dihydrazino-2,2′-bipyridyl (0.25 g), the resulting slurry was then stirred for one hour. The fine orange-red precipitate which had completely formed by this time was collected by filtration under nitrogen and washed with degassed acetonitrile (2 X 5 cm^3) yielding the pure product (0.35 g, 89%). Found: C, 34.9; H, 3.54; N, 24.3. $C_{10}H_{12}Cl_2FeN_6$ requires: C, 35.0; H, 3.53; N, 24.5%. I.R. (nujol): 3315s, 3235s, 3175s, 1628m, 1597m, 1571m, 1560m, 1415m, 1312w, 1270m, 1186m, 1075m, 1023m, 994s, 791s.

Tris-2,2′-bipyridyliron(II) Hexafluorophosphate

2,2′-Bipyridyl (2.0 g) was dissolved in hot distilled water (300 cm^3) and was treated with an excess of ferrous ammonium sulphate (2.0 g) and ammonium hexafluorophosphate (2.1 g). The red suspension was heated on a water bath for one hour and left to cool. The red crystalline precipitate (3.4 g, 97%) which separated was filtered off, washed with distilled water and dried *in vacuo*. Found: C, 44.3; H, 3.05; N, 10.3. $C_{30}H_{24}F_{12}FeN_6P_2$ requires: C, 44.3; H, 2.97; N, 10.3%.

References

1 Part III: J. Lewis and K. P. Wainwright, *J. Chem. Soc. Dalton*, 440 (1978).
2 J. Lewis and K. P. Wainwright, *J. Chem. Soc. Dalton*, 734 (1977).
3 J. Lewis and K. P. Wainwright, unpublished work.
4 N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy', Chapman and Hall, London (1971).
5 B. N. Figgis, 'Introduction to Ligand Fields', Interscience, New York (1966).
6 E. M. Kosower, *Accounts Chem Res.*, 191 (1971).
7 M. N. Ackermann, M. R. Hallmark, S. K. Hammond and A. N. Roe, *Inorg. Chem.*, *11*, 3076 (1972).
8 W. M. Reif and S. Foner, *J. Am. Chem. Soc.*, *95*, 260 (1973).
9 F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).
10 R. L. Martin and A. H. White, 'Transition Metal Chemistry', Vol. 4, Ed. R. L. Carlin, Arnold, London (1968) p. 127.
11 E. N. Maslen, C. L. Raston and A. H. White, *J. Chem. Soc. Dalton*, 323 (1975).

12 R. L. Collins, R. Pettit and W. A. Baker, *J. Inorg. Nuclear Chem.*, *28*, 1001 (1966).
13 N. S. Gill, *J. Chem. Soc.*, 3512 (1961).
14 B. N. Figgis and J. Lewis, 'Modern Co-ordination Chemistry', eds. J. Lewis and R. G. Wilkins, Interscience, New York (1960) p. 400.
15 G. M. Bancroft, A. G. Maddock and J. Ward, *Chem. and Ind.*, 423 (1966).
16 O. Baudisch and W. H. Hartung, *Inorg. Synth.*, *1*, 184 (1939).
17 J. F. Coetzee, *Pure and Applied Chem.*, *13*, 429 (1966).