Inorganica Chimica Acta, *98* (1985) 131–134

Nuclear Magnetic Resonance Study of Pyridine 2-azo-*para*-dimethylaniline and its Nickel(II) and Zinc(II) Complexes

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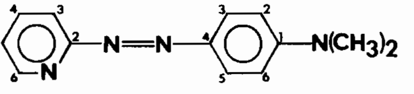
Received July 2, 1984

Abstract

The carbon-13 magnetic resonance spectra of N,N-dimethyl-4-(2-pyridylazo)benzeneamine, (pyridine 2-azo-paradimethylaniline, PADA), and of the 1:1 complex with zinc(II) ions, in the presence and absence of nickel(II) ions, have been obtained. Resonances have been assigned based on established or modified additivity rules. The spectra are interpreted as being consistent with the ligand binding as a *trans* isomer and are compatible with the normal mechanism of binding inferred from kinetic results.

Introduction

The ligand, N,N-dimethyl-4-(2-pyridylazo)benzeneamine (I), frequently named pyridine -2-azo-paradimethylaniline, and abbreviated PAD or PADA, the latter in this communication, has been widely used in a variety of 1:1 transition metal complex formation studies [1]. Its use in a method for titrating sulfhydryl groups has also been reported [2]. Kinetics of metal ion (mostly nickel(II)) binding to PADA have been investigated in neutral aqueous solution [1(a), 1(c)], in some aqueous organic solvent mixtures [3] and in some organic solvents [4, 5]. Early results [1(a)] became part of the compilation of kinetic and thermodynamic data which led to the formulation of the mechanism for metal complex formation [6]. High pressure studies which yield ΔV^{*} for the formation process supported the general features of this mechanism [1(c), 4, 7, 8]. The questions of solvent influence on reactivity [3, 9], and possible effect of variation of the counter ion of the metal [4] were also addressed.



I

The usefulness of PADA lies in part in the magnitude of the equilibrium constants; for example, log K for $\mathrm{Ni(PADA)^{2+}}$ at 298 K and I = 0.15 mol $\mathrm{dm^{-3}}$ (sodium nitrate) is 4.25 [10]. A mixing method, (stopped-flow spectrophotometry [3, 11]), and equilibrium perturbation methods, (temperature-jump with 'joule' heating [1(a), 1(c)] and laser photoinitiated equilibrium shift [4, 12]), may be used for determination of kinetic parameters.

In early kinetic work samples of PADA which were prepared according to the established procedure [13], were used [1(a), 11]. Subsequent studies made use of commercial samples which are available as the *trans* isomer. Where comparisons are possible, in general the agreement between kinetic parameters determined in different investigations is not unreasonable. Among the reactions reported in aqueous solution there are differences in ionic strength and the pH is not always reported. The protonated form of PADA should be only a minor component [10], under the conditions of the experiments, and the reaction thus independent of ionic strength. Examples of the second order rate constants (in $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 298 K) for reaction of PADA with nickel(II) ions in water are 1.35×10^3, I = 0.3 mol $\mathrm{dm^{-3}}$, temperature-jump method, nitrate ion [1(c)]; 1.25×10^3, I = 0, stopped-flow method, nitrate ion [14]; 1.17×10^3, I = 0, laser flash method, perchlorate ion, [4]; 9.0×10^2, from a comprehensive stopped-flow study [3], and from limited stopped-flow results using an assumed value of 0.1 $\mathrm{s^{-1}}$ for the dissociation rate constant [11].

Stability constants are consistent in most cases; for example, for cobalt(II) PADA, the value of log K of 3.32 and 3.36 measured spectrophotometrically [10], and kinetically, respectively [15] with a commercial ligand sample at 298 K and I = 0.3 mol $\mathrm{dm^{-3}}$ (sodium nitrate) and pH 7, compare excellently with 3.32 using a spectrophotometric procedure on an original sample [10], I = 0.15 mol $\mathrm{dm^{-3}}$ (sodium nitrate). The value of log K for $\mathrm{Ni(PADA)^{2+}}$ implied from a kinetics source, 3.95 [3], is reasonably close to those obtained from other

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0020-1693/85/$3.30

kinetics results, 4.1 [1(c)], and with the original spectrophotometrically determined value 4.24 [10]. While it is conceivable that these results are the same when experimental errors are considered, the situation is more uncertain when results in different solvent systems are compared [4, 5, 9].

Little has been said about PADA sample purity except indirectly in terms of the reproducibility of the kinetics and equilibria results. There is a report of use of a purified sample [12], but the procedure and characterization data are not available. The issue of the problem of ligand impurity has been raised [5]. Possible stereochemical variations were noted [13], and metal binding was proposed to occur through the pyridine nitrogen and the azo nitrogen to give a 5-membered chelate ring [10], but the isomeric form of the ligand was not specified, although the implication was a *trans* orientation about the azo linkage. In fact steric restrictions make it difficult to envisage a *cis* isomer if the metal binding occurs with the azo nitrogen further from the pyridine.

In this study an attempt was made to determine the conformation of the ligand and the complex using carbon-13 magnetic resonance measurements on a commonly employed commercial sample. By comparing the initial and product structures the binding process may be inferred and related to the expectations of the Eigen-Wilkins' mechanism, and to reasonable molecular models.

Experimental

Materials

PADA was a Sigma Chemical Company sample, Lot 30C-5270, and was donated by Dr. J. Burgess. Metal salts used were nickel(II) perchlorate and zinc(II) nitrate. Deionized water was used for making solutions for UV-visible spectrophotometry and kinetics purposes. Dimethylsulfoxide, gold label grade, and deuterium oxide were from Aldrich Chemical Company. Deuterated dimethylsulfoxide was acquired from Stohler Isotopes.

Methods

The kinetic viability of the PADA sample was checked by stopped-flow measurements using a Durrum-Gibson spectrophotometer with a Kel-F flow path and a 0.020 m path length. Spectra in the visible region were taken on a Cary 219 spectrophotometer. Nuclear magnetic resonance spectra were obtained on a JEOL FX90Q spectrometer using a 90° pulse and a 2 second cycle time. All solutions for the NMR experiments were made in 3 volumes d-6 dimethylsulfoxide to 1 volume deuterium oxide mixed solvent. Chemical shifts were referenced internally to the dimethylsulfoxide and corrected to TMS.

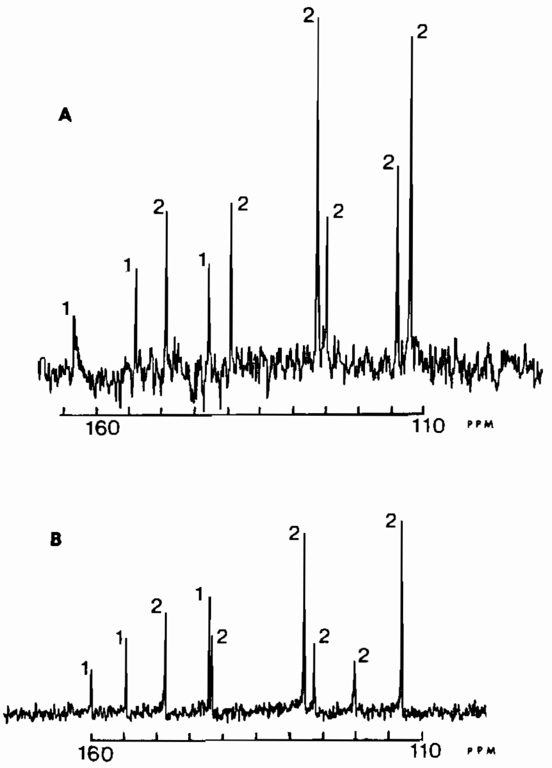

Fig. 1. ^{13}C FTNMR Spectra, Aromatic Region (a) Free ligand in DMSO/D_2O solution. (b) Zinc complex in DMSO/D_2O solution.

Results and Discussion

The sample of PADA was checked for kinetics efficacy by measuring the rate constants for the formation of $Ni(PADA)^{2+}$ and for loss of PADA absorbance in both water and a 3:1 dimethylsulfoxide/water mixture. The latter solvent system was used because it was found to be suitable for the NMR experiments. In water using $[Ni^{2+}] = 2.5 \times 10^{-3}$ mol dm^{-3} and $[PADA] = 1.25 \times 10^{-4}$ mol dm^{-3}, k for $-(d/dt)[PADA]$ (470 nm) is 3.4 s^{-1} and for $(d/dt)[Ni(PADA)^{2+}]$ (550 nm) is 3.5 s^{-1} at 298 K, pH 6.6 and $I = 0$. The corresponding values in the solvent mixture are 6.2 s^{-1} and 6.9 s^{-1}. By assuming a value for k_d of 0.1 s^{-1}, in pure water the formation rate constant is estimated as 1.3×10^3 dm^3 mol^{-1} s^{-1}, consistent with some of the previous results. In aqueous dimethylsulfoxide the observed reaction is accelerated by a factor of two, but in the absence of measurement of the dissociation rate constant or the stability constant, the second order forward rate constant as such is not obtainable. However, the observed reaction is first

TABLE I. ^{13}C NMR Data for PADA and Zn(PADA)$^{2+}$.

Ring	Carbon	Calc.	PADA Shift (ppm)		ZnPADA	
			Assign.	A_{ik} (azo)	Assign.	Complxn. Shift
Pyr.	2	173.8	163.8	+14.5	160.3	−3.5
	3	117.8	114.5	−8.6	120.1	+5.6
	4	136.0	139.9	+4.7	141.3	+1.4
	5	125.8	125.2	+2.2	126.2	+1.0
	6	150.1	149.7	+0.4	148.9	−0.8
Anil	1	153.1	154.3		155.0	+0.7
	2, 6	113.1	112.5		112.7	+0.2
	3, 5	123.5	126.7		127.7	+1.0
	4	140.7	143.2		142.3	−0.9
	$N(CH_3)$		40.2		40.2	0.0

order for over three half lives and the observed rate constant is within reasonable expectations.

The ^{13}C NMR spectrum of the free ligand in the mixed solvent system is shown in Fig. 1(a). The spectrum of the sample showed no evidence of impurities which would be detectable; minor impurities would not be observed by the NMR method. The multiplicities of the proton coupled spectrum are noted at the top of each peak, for identification of the substituted C and CH of the aromatic rings. The two CH resonances of highest intensity are attributed to the dimethylaniline half of the molecule since free rotation about the C–N(azo) bond allows only two different CH shifts. This would also be consistent with a *trans* arrangement across the azo linkage. The resonances of this half of the molecule can be assigned using the established additivity rule [16]:

$$\delta C(k) = 128.5 + \sum_i A_i(R) \qquad (1)$$

where $\delta C(k)$ is the position of the resonance of the kth carbon and A_i is the shift caused by the substituent R on the ith carbon. Both the calculated shifts and the assigned peaks are given in Table I, showing that the agreement is satisfactory. The A_i values for $R = N(CH_3)_2$ are tabulated [16] and those for the azo group were obtained from the published spectrum of azobenzene [17].

The pyridyl half of the molecule can be assigned from the known shifts for pyridine, $\delta C_{(R)}$ using the modified additivity rule [18];

$$\delta C(k) = C_{(k)} + \sum_i A_{ik}(R) \qquad (2)$$

where A_{ik} refers to the correction for the kth carbon due to a substituent R on the ith carbon (numbered from the heteroatom). The A_{ik} values for the azo group were not available, so the A_i values used above were employed instead. It may be noted from the published tables [18] that for a substituent in the 2-position of pyridine, the A_{22} value is generally less downfield than the corresponding A_2 value. Similarly the A_{23} shift is generally more upfield than a corresponding A_3 shift. The estimated 2-azopyridyl shifts and the assignments made are shown in Table I. Also shown are the estimated A_{ik} values for the 2-azo substituent for future reference.

The ^{13}C NMR spectrum of the zinc complex is shown in Fig. 1(b), together with the proton coupled multiplicities. The complexation shifts are not very pronounced, the largest being for the 3 and 2 positions of the pyridyl ring, followed by smaller shifts for the other pyridyl carbon atoms. None of the dimethylaniline ring peaks are shifted to any great degree, and there is no evidence that complexation introduces any asymmetry to the environment of this moiety. This could imply free rotation but if the ring were frozen perpendicular to the azo-pyridyl plane the symmetry would also be preserved, and this may be the case for the metal complex.

The large downfield shift at the pyridyl 3-position can be attributed to the enforced planarity of the pyridyl-azo moiety due to metal binding. In this position the 3-carbon is constantly in a strongly deshielding part of N=N bond magnetic anisotropy, whereas in the free ligand rotation will cause the deshielding to be averaged out to a lower value.

The corresponding nickel complex of the ligand gave no NMR spectrum, the resonances being relaxed by the paramagnetic nature of the system. A solution of the free ligand was systematically dosed with nickel ion up to a 0.5:1 ratio of metal to ligand. With each addition the observed NMR peaks decreased in intensity without any appreciable broadening.

This is consistent with the low dissociation rate for the nickel complex which would be the rate determining step in ligand exchange. Similarly, mixtures of zinc and nickel PADA solutions showed only NMR spectra for the zinc complex, neither shifted or broadened to any significant degree.

Thus in summary, the NMR spectra are consistent with a coplanar pyridyl-azo system, with the aniline moiety either free to rotate, or frozen in a plane perpendicular to the pyridyl-azo plane. The rate of exchange between the zinc and nickel derivatives is shown to be slow. These results are compatible with PADA binding to transition metal ions as a *trans* isomer, and operating as a normal ligand within the context of the Eigen-Wilkins' mechanism.

Acknowledgement

The National Science Foundation supported this research by providing funds to purchase the spectrometer, (Grant No. CHE-778983) and the spectrophotometer (Grant No. CHE-7908399).

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