Inorganica Chimica Acta, 207 (1993) 255–258

Short Communication

1:1 Metal complexes of 2-(2′-pyridyl)quinoxaline, a ligand unexpectedly formed by the reaction between 2-acetylpyridine and 1,2-phenylenediamine

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(Received June 11, 1992; revised December 28, 1992)

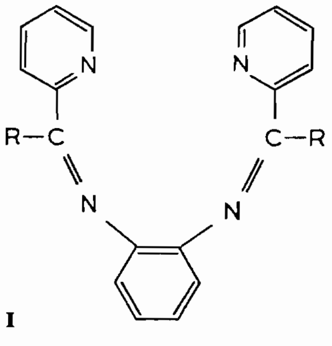
Abstract

The complexes [$MLCl_2$] (M = Co, Ni, Cu, Zn), where L is the new ligand 2-(2′-pyridyl)quinoxaline derived unexpectedly from 2-acetylpyridine and 1,2-phenylenediamine, were isolated. The ligand and its complexes have been characterized by a variety of physical and spectroscopic techniques. L behaves as a bidentate chelating ligand in the monomeric pseudotetrahedral Zn^{II} compound; all three nitrogen atoms of L are involved in coordination in the polymeric Co^{II}, Ni^{II} and Cu^{II} complexes giving five-coordinate (Co^{II}) or six-coordinate (Ni^{II}, Cu^{II}) structures.

Introduction

We are currently involved [1] in the preparation and study of monomeric complexes with acyclic N_4 Schiff base ligands as potential precursors to shish-kebab, transition metal-containing, polymers [2]. Recently, we have employed **Ia** as a ligand and have prepared complexes with interesting properties [1a]. **Ia** was prepared by Schiff base condensation of 2-pyridinecarboxaldehyde and 1,2-phenylenediamine. In an attempt to prepare compound **Ib**, the aldehyde starting material was replaced by the related ketone (2-acetylpyridine). However, in addition to forming the desired Schiff base ligand [3], the compound 2-(2′-pyridyl)quinoxaline (**II**, L) formed via an unusual cyclization reaction.

Compound L, which may combine the chelating properties of 2,2′-bipyridine [4] with the bridging properties of quinoxaline [5], belongs to a class of aromatic nitrogen heterocycles whose coordination chemistry is currently a subject of intense research [6]. The study of complexes of such ligands is important in developing our understanding of the theory of electron transfer processes, of mixed-valence compounds, of excited-state acid–base properties of inorganic compounds and of magnetic coupling interactions. Such compounds are also used to model important bioinorganic systems and are finding applications as photosensitizers, catalysts and in low dimensional conducting coordination polymers. For the above reasons we decided to study the coordination chemistry of the new, potentially binucleating, ligand L in detail and herein report the first results of this study. It is worth noting that the coordination chemistry of the parent pyrazine ligand 2-(2′-pyridyl)pyrazine is also completely unexplored [6a], in contrast to 2,3-bis(2′-pyridyl)pyrazine [7, 8] and 2,3-bis(2′-pyridyl)-quinoxaline [8] which have been well studied as binucleating ligands.



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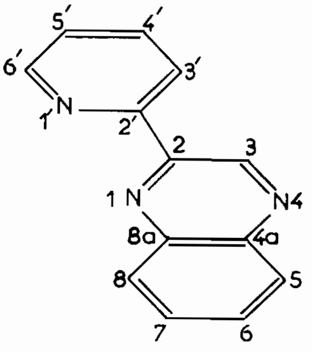

II, L

(Ia: R = H; Ib: R = CH_3)

Experimental

Elemental analyses, physicochemical measurements and spectroscopic techniques were carried out by published methods [9].

2-(2′-Pyridyl)quinoxaline was unexpectedly prepared according to the following procedure. 2-Acetylpyridine (4.5 ml, 40.1 mmol) was added to a solution of 1,2-

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0020-1693/93/$6.00

phenylenediamine (2,16 g, 20.0 mmol) and methyl chloroformate (0.4 ml, 5.2 mmol) in 2-propanol (30 ml). The resultant solution was heated at 50 °C for 48 h. The flask was stored at −5 °C overnight and the resulting cream crystals were collected by filtration, washed with Et_2O and dried in air. The yield was *c.* 60%. Recrystallyzation can be effected from 2-propanol. Melting point: 114–116 °C. *Anal.* Calc. for $C_{13}H_9N_3$: C, 75.33; H, 4.39; N, 20.28. Found C, 75.90; H, 4.57; N, 20.02%. Electron ionization (EI) mass spectrum: *m/z* of the molecular ion was 207 (85.6%) (calc. formula weight 207.25). The most abundant ion in the chemical ionization (CI) mass spectrum of L is at 208, i.e. $(L+1)^+$.

The 1:1 metal complexes of the type $[MLCl_2]$ (M = Co, Ni, Cu, Zn) were all prepared similarly. To a solution containing 1.0 mmol of the required anhydrous metal chloride (for the preparation of the Ni^{II} compound the starting material was $NiCl_2 \cdot 6H_2O$) in EtOH (5 ml) was added dropwise an ethanol solution (5 ml) of L (1.0 mmol). The resulting solutions were stirred at ambient temperature for 2 h. Solid products were deposited during this time, which were collected by filtration, washed with cold ethanol and ether and dried *in vacuo* over P_4O_{10}. Yields were *c.* 40% for the Zn^{II} complex and in the 60–70% range for the Co^{II}, Ni^{II} and Cu^{II} compounds. All complexes gave excellent analytical results for metal, chloride, C, H and N.

Results and discussion

The synthesis of L from 2-acetylpyridine and 1,2-phenylenediamine, in the presence of small amounts of methyl chloroformate (this reagent was added to 'activate' the amino groups of the diamine) was totally unpredictable and its mechanism of formation unclear and difficult to ascertain. The identity of L was unambiguously established by microanalyses, mass, ^1H NMR (Table 1) and IR spectra. The ^1H NMR study was based on comparisons with a number of related molecules [7, 10]. It was possible to assign al the peaks by using two-dimensional COSY NMR as well, as illustrated in Fig. 1. For example, on the basis of assignment of 8.94 ppm to $H_{6'}$ [7], the cross-peak to this resonance leads to the assignment of $H_{5'}$ at 7.74 ppm. The cross-peak at the chemical shift coordinates 7.74 and 8.19 ppm identifies the $H_{4'}$ proton at 8.19 ppm, etc. The minor cross-peak at the coordinates 7.74 and 8.69 ppm is attributed to long-range coupling between $H_{5'}$ and $H_{3'}$.

TABLE 1. 200 MHz ^1H NMR[a] chemical shifts δ (ppm/TMS) for L protons in DMSO-d_6

Proton	δ
H_3	10.00s
H_5, H_8	8.29mt
H_6, H_7	8.04mt
$H_{3'}$	8.69d
$H_{4'}$	8.19mt
$H_{5'}$	7.74mt
$H_{6'}$	8.94d

[a]The integrations of the signals are consistent with the assignments. d = doublet; s = singlet; mt = multiplet.

Physical properties and diagnostic spectral data for the prepared 1:1 metal complexes are given in Table 2. The complexes are microcrystalline or powder-like, stable in atmospheric conditions and soluble in DMF and DMSO; the Zn^{II} compound is, however, soluble in methanol, nitromethane and acetonitrile. The Λ_M values of **2**, **3** and **4** in DMF are in accord with these complexes being formulated as non-electrolytes; complex **1** is partially ionized in this solvent. X-ray powder patterns indicate that the Ni^{II} and Cu^{II} compounds are nearly isomorphous; the complexes **1** and **4** have different patterns. The small number of diffraction lines observed for **1**–**3** may suggest polymeric structures [11].

The room temperature μ_{eff} values, d–d frequencies and calculated ligand field parameters of **2** are all characteristic of pseudo-octahedral high-spin stereochemistry [12, 13]. The 10 *Dq* value (8530 cm^{-1}) is reasonable for the proposed $Ni^{II}N_3Cl_3$ chromophore [13]. The electronic spectrum of **3** is fairly typical of a tetragonally distorted octahedral structure [13]. The X-band room temperature ESR spectrum of a neat powdered sample of this complex shows only a broad featureless resonance at $g = 2.067$. Such signals are observed in Cu^{II} complexes displaying weak intermolecular coupling [14]. The ligand field spectrum of **1** is quite rich and typical for high-spin five-coordinate cobalt(II) complexes with a distorted trigonal bipyramidal structure [13, 15]. In D_{3h} symmetry the bands at 12.24, 17.30 and 19.23 kK are assigned to the $^4A'_2 \rightarrow {}^4E'$, $^4A'_2 \rightarrow {}^4A'_2(P)$ and $^4A'_2 \rightarrow {}^4E''(P)$ transitions, respectively [13]. The μ_{eff} value of the five-coordinate Co^{II} complex **1** is smaller than the values of the six-coordinate Co^{II} complexes in agreement with reported values [15].

In the IR spectra of the four complexes studied, the characteristic in-plane and out-of-plane deformation bands of the 2-substituted pyridine ring (observed at 620 and 401 cm^{-1}, respectively, in free L) shift to higher frequencies to indicate coordination of N(1′) [15a]. The 900–1000 cm^{-1} region is viewed as the key to differentiate between monodentate and bidentate bridging coordination of the quinoxaline system [16b, 16c]. The splitting of the strong L band at *c.* 950 cm^{-1} into a triplet in the spectra of **1**, **2** and **3** is indicative of participation of both N(1) and N(4) in coordination [16b]; the appearance of a very sharp single band at

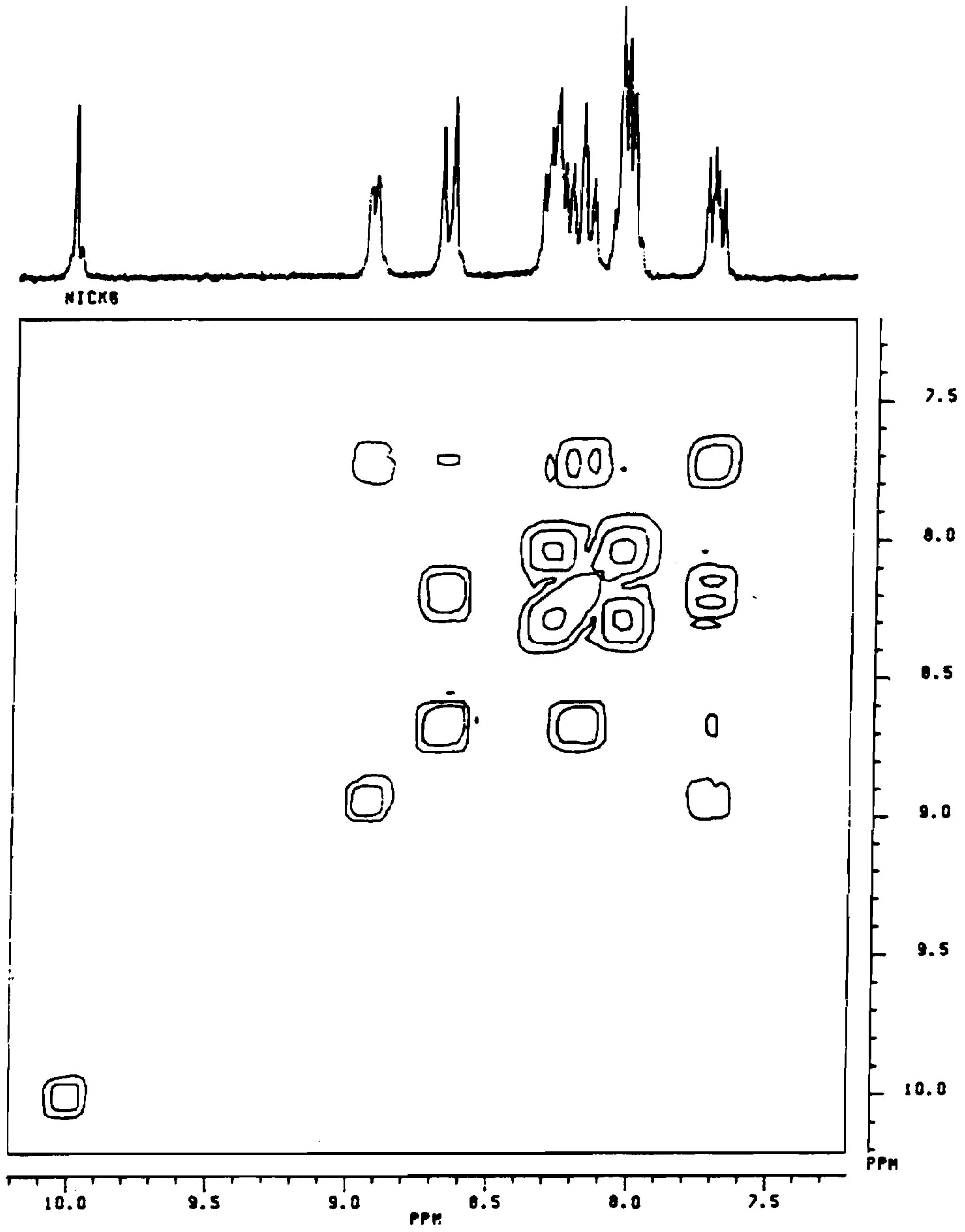

Fig. 1. COSY ^1H NMR spectrum of L in DMSO-d_6 at 200 MHz.

930 cm^{-1} in **4** characterizes a monodentate quinoxaline coordination [16c]. The far-IR spectrum of **4** shows the two $\nu(Zn{-}Cl)_t$ modes (antisymmetric and symmetric) in the region expected for pseudotetrahedral C_{2v} stereochemistry [17]. The far-IR spectra of **2** and **3** are indicative of the existence of both terminal and bridging M–Cl bonds [17, 18], while the terminal Co–Cl stretching frequencies in **1** are in accord [17] with the proposed five-coordinate structure.

In summary, the data collected here lead to the conclusion that L behaves as a chelating N(1),N(1′) ligand in the monomeric tetrahedral Zn complex **4**. In polymers **1–3**, the ligand bridges in a mixed bidentate chelating N(1),N(1′)-monodentate N(4) coordination mode forming the five-coordinate (with exclusively terminal chlorides) compound **1** and six-coordinate complexes **2** and **3**. The variation in structural types observed is believed to be a consequence of the stereochemical adaptability of the ligand to the electronic demands of the metal ions. Work in progress on this intriguing ligand reveals that monomeric and dimeric/polymeric (both homonuclear and heteronuclear) complexes, with

TABLE 2. Diagnostic physical and spectroscopic properties for the metal complexes of L

No.	Complex	Colour	Λ_M[a] (S cm^2 mol^{-1})	μ_{eff}[b] (BM)	Electronic spectral[c, d] data (10^3 cm^{-1})	Far-IR	
						ν(M–Cl)$_t$	ν(MCl)$_b$
1	[CoLCl$_2$]	green	28	4.38	12.24, 16.31sh, 17.30, 19.23, 24.45[e]	308sh, 298vs	
2[g]	[NiLCl$_2$]	green	7	3.15	13.60, 19.53sh[f], 22.22, 27.78[e]	239s	197m
3	[CuLCl$_2$]	yellow	14	1.88	11.90, 17.86, 26.31[e]	317s	177m
4	[ZnLCl$_2$]	white	5	dia		342vs, 326s	

[a] Values of molar conductance for *c*. 10^{-3} M solutions in DMF at 25 °C. [b] Per metal ion at room temperature. [c] Solid state (diffuse reflectance) spectra in the 11.10–29.40 kK region. [d] Mainly d–d ligand field bands. [e] Maxima due to a charge-transfer transition. [f] The $^3A_{2g} \rightarrow {}^1T_{2g}$ spin-forbidden band frequently observed in octahedral (O_h) Ni^{II} complexes. [g] Assuming O_h symmetry, the $^3A_{2g} \rightarrow {}^3T_{1g}$(P) (22.22 kK) and $^3A_{2g} \rightarrow {}^3T_{1g}$(F) (13.60 kK) transitions give $10Dq = 8530$ cm^{-1}, $B = 699$ cm^{-1} and $\beta = 0.67$. dia = diamagnetic; M = metal; m = medium; s = strong; sh = shoulder; vs = very strong; ν(M–Cl)$_t$ = the stretching vibration of the terminal M–Cl bond; ν(MCl)$_b$ = the stretching vibration of the M–Cl bond in the bridging MClM group.

various stoichiometries and interestic electronic, magnetic and photophysical properties, can be prepared. This work will be the subject of a future publication.

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