Inorganica Chimica Acta, 19 (1976) 159–163

Transition Metal Complexes of N-Substituted Derivatives of 2-[(N-acetyl)amino]pyridine

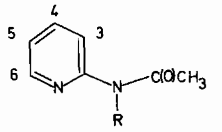
J. BOULD and B. J. BRISDON
School of Chemistry, University of Bath, Bath BA2 7AY, U.K.
Received, January 12, 1976

The stereochemistries of complexes formed between the dichlorides of cobalt, nickel, copper and zinc and the tertiary amides 2-[(N-acetyl-N-methyl)amino]pyridine (amp) and 2-[(N-acetyl-N-phenyl)amino]pyridine (app) have been investigated by infrared, electronic and nmr spectroscopies. Both ligands chelate via the pyridine-N and amide-O atoms in the pseudotetrahedral $M(amp)Cl_2$ (M = Co and Zn) and $M(app)Cl_2$ (M = Co, Ni, Cu and Zn) complexes. The effects of the bulky N-substituents on complex formation and the conformation of the free ligand are discussed in comparison with the parent amide, 2-[(N-acetyl)amino] pyridine (aapH).

Introduction

Pyridine derivatives with a suitable donor atom in an *ortho*-substituent can be very useful chelating agents. Ligands of this type in which the side-chain contains the amide group have been shown to coordinate to metal ions via the pyridine-N atom and either the nitrogen or oxygen of the amide group[1–4]. In complexes of primary or secondary amides the nitrogen atom may deprotonate when the ligand coordinates, depending upon a variety of electronic and experimental factors[4].

This paper reports upon the stereochemical and complexing properties of some secondary and tertiary amides (I) derived from 2-aminopyridine.



(I)

R = H, Me or Ph

Experimental

Preparation of Ligands

2-[(N-acetyl)amino]pyridine (aapH)

2-Aminopyridine (0.04 mol) was heated with acetic anhydride (0.06 mol) on a steam bath for one hour. Water (100 ml) was then added and the mixture heated for a further 15 minutes to hydrolyse unreacted acetic anhydride. The resultant solution was neutralised with Na_2CO_3, and then extracted four times with ether (25 ml). The combined extract was evaporated to dryness and the crude product recrystallised twice from ether to give large colourless crystals (m.p. 66–67° C) in a 75% yield. Found: C, 61.6; H, 5.7; N, 20.6%. Calcd. for $C_7H_8N_2O$: C, 61.8; H, 5.9; N, 20.7%.

2-[(N-acetyl-N-methyl)amino]pyridine (amp)

2-[(N-methyl)amino]pyridine was prepared in 70% yield from methylamine and 2-bromopyridine by the method of Anderson and Seeger[5]. The secondary amine was acetylated by literature methods[6] and isolated in 80% yield (b.p. 108° C at 1 mm Hg pressure). Found: C, 61.9; H, 6.5; N, 18.7%. Calcd. for $C_8H_{10}N_2O$: C, 62.0; H, 6.7; N, 18.7%.

2-[(N-acetyl-N-phenyl)amino]pyridine (app)

The parent secondary amine was prepared by standard procedures[7] and then acetylated as outlined above for 2-aminopyridine. The acetyl compound was obtained as colourless crystals (m.p. 51–52° C) from ether solution in a yield of 90%. Found: C, 72.2; H, 5.9; N, 13.8%. Calcd. for $C_{12}H_{12}N_2O$: C, 72.0; H, 6.1; N, 14.0%.

Preparation of Complexes

All complexes were prepared by the same basic method. Solutions of the anhydrous transition metal chlorides and ligands were mixed together at room temperature in a 1:3 mol ratio using the solvents listed in Table I. The products, which formed on standing, were washed with ether and stored *in vacuo*. Elemental analyses are given in Table I.

The secondary amide complexes were soluble without reaction in polar solvents such as acetone, acetonitrile and methanol, whereas the tertiary amide complexes were more susceptible to decomposition. The cobalt–, copper– and zinc–tertiary amide complexes were soluble in acetone without major spectral changes, but the nickel complex appeared to decompose in all solvents in which it dissolved.

TABLE I. Preparative and Analytical Data for the Complexes.

Complex	Solvent	Colour	C% (Calcd.)	H% (calcd.)	N% (calcd.)
$Co(aapH)_2Cl_2$	EtOH	Purple	41.6(41.8)	4.0(4.0)	13.7(13.9)
$Ni(aapH)_2Cl_2$	EtOH	Green	41.7(41.8)	4.2(4.0)	13.8(13.9)
$Cu(aapH)_2Cl_2$	EtOH	Blue	41.0(41.3)	4.0(4.0)	13.5(13.8)
$Zn(aapH)_2Cl_2$	EtOH	White	41.1(41.2)	3.9(4.2)	13.4(13.4)
$Co(amp)Cl_2$	Et_2O–Me_2CO[a]	Blue	34.3(34.3)	3.7(3.6)	9.8(10.0)
$Zn(amp)Cl_2$	Et_2O–Me_2CO[a]	White	33.5(33.7)	3.5(3.7)	9.8(9.7)
$Co(app)Cl_2$	Et_2O–Me_2CO[a]	Blue	45.3(45.6)	3.7(3.5)	8.1(8.2)
$Ni(app)Cl_2$	EtOH	Green	45.5(45.6)	3.8(3.5)	8.2(8.2)
$Cu(app)Cl_2$	EtOH	Brown	45.2(45.1)	3.7(3.5)	8.1(8.1)
$Zn(app)Cl_2$	Et_2O–Me_2CO[a]	White	45.1(44.8)	3.5(3.4)	8.1(8.0)

[a] Contained 2% 2,2′-dimethoxypropane to remove traces of water.

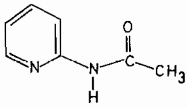
Physical Measurements

Infrared spectra in the region 4000–200 cm^{-1} were measured on Nujol mulls of the complexes using a Perkin Elmer Model 577 Spectrophotometer. Diffuse reflectance spectra in the visible region were recorded on powdered samples diluted with magnesium oxide on a Unicam SP 700 C Spectrophotometer. ^1H nmr spectra were recorded on a JEOL-PS100 instrument equipped with a variable temperature probe, with tetramethylsilane as internal or external standard. Bulk susceptibility measurements were made at room temperature on a Gouy balance calibrated with $HgCo(NCS)_4$.

Results and Discussion

Free Ligand Configurations

^1H nmr spectral results on the free ligands are summarised in Table II. The data on the secondary amide aapH are in good agreement with published data[8,9], which have been interpreted in terms of a planar structure (II) for aapH, with the aromatic ring *trans* to the methyl group (Z-form).



(II)

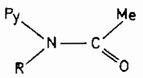
TABLE II. ^1H Nmr Data on the Free Ligands.

Ligand	Chemical Shifts (ppm, δ value) in $CDCl_3$ at 30° C					
	Pyridine Protons				C(O)Me	NMe
	3	4	5	6		
aapH	8.24	7.82	7.12	8.36	2.16	
amp	7.46	7.82	7.26	8.52	2.14	2.42
app	7.4[a]	7.72	7.15	8.44	2.11	

[a] Partially obscured by signals from phenyl protons.

Although this configuration usually predominates for monosubstituted amides in both the solid state and in solution at room temperature[10], the rotational energy barrier about the C(O)–N bond is often small enough for these compounds to show temperature dependent isomerism effects in their nmr spectra at, or just above, room temperature[10–12]. However, the strong dipole–dipole interactions between the pyridine ring and the acetamido group in the same plane, are expected to stabilize the Z-configuration (II) for aapH[8], and also hinder rotation about the C(ring)–N bond. In agreement with this, no new features were observed in the nmr spectrum of this compound over the range 180 to –95° C.

The conformation of the unsymmetrical N,N-disubstituted amides amp and app will depend upon steric as well as electronic and dipole interactions. Steric requirements will force the plane of the ring substituents well out of the amide plane, as found for the structurally related compounds N,N-diphenylacetamide[13] and N-methylacetanilide[14]. Under these circumstances structure (III), in which the pyridine ring is *trans* to oxygen (a conformation similar to that adopted by most N-alkylacetanilides[10]), would minimise steric and dipolar interactions for both amp and app.



(III)

R = Me or Ph

The 3-protons of the pyridine rings in this or the alternative rotameric form are no longer deshielded by the carbonyl group, and consequently appear at considerably higher fields in their nmr spectra compared with aapH.

The low temperature ^1H nmr spectra of app and amp showed additional features (Figure 1). Below 196 K, a new band was resolved on the low field side of the methyl resonance of app, while amp showed additional

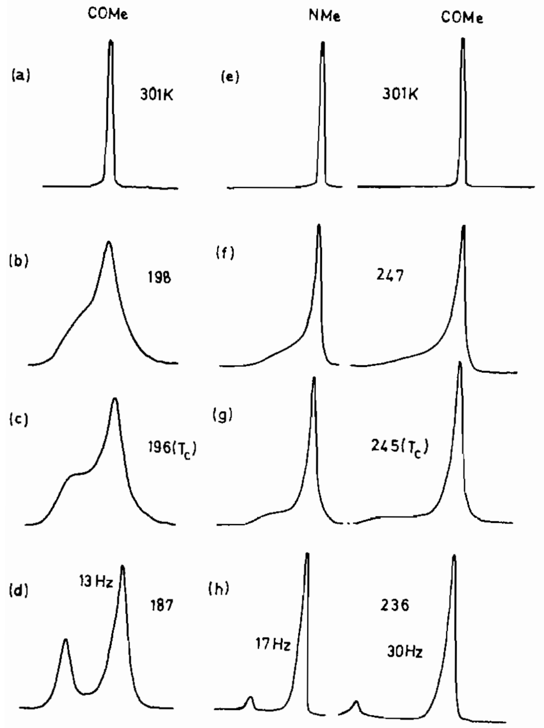


Figure 1. Expanded low temperature nmr spectra of app (a–d) and amp (e–h) in $CDCl_3$.

signals adjacent to both the acetyl and N-methyl resonances. Calculations based on the Shanan–Atidi and Ber–Eli procedure for uncoupled two-site exchanges with unequal populations[15], led to activation energies of 54 and 43 kJ mol^{-1} for the exchange processes occurring in amp and app respectively. These values may reflect relatively low energy barriers to rotation about the C(O)–N bonds in both compounds, each of which would then exist as a rapidly interchanging mixture of rotamers at room temperature, or be ascribed to restricted rotation about the C(pyridine)–N bond of one rotamer. Further investigations are being carried out in an attempt to positively identify the low temperature processes occurring in these and related pyridinamine derivatives.

Metal Halide Complexes

It was found that the preparation of complexes using alcohol as solvent led to partial or complete deacetylation of the ligands under certain conditions. With aapH this only occurred to a limited extent at the boiling point of the solvent, so that 2 : 1 complexes were readily obtained at room temperature. However, amp, and to a much lesser extent app, were partially deacetylated by all four metal chlorides on standing at room temperature. In aprotic solvents no such reaction occurred and pure 1 : 1 adducts were obtained with the exception of nickel and copper chloride – amp complexes.

During the course of these investigations a report on the stereochemistries of aapH complex of some Pd(II), Co(II), Ni(II) and Cu(II) salts was published[4]. Our results and conclusions on the Co, Ni and Cu halide complexes are in good agreement with this work, which concluded that all three metal ions form *trans*-octahedral complexes in which the bidentate aapH ligand is chelated through the pyridine -N and amide-O atoms. Consequently further discussion will be confined

TABLE III. Infrared Data on Metal Chloride Complexes.

Complex	Ligand Bands (cm^{-1})							M–Cl Stretching Frequencies (cm^{-1})
	Pyridine Ring Vibrations					Amide Bands		
	A_1 νCC,CN	B_1 νCC,CN	A_1 νCC,CN	A_2 δCH	B_1 δCH	I	VI	
aapH	1600m	1580s	1465s	1000m	775s	1695s	556m	
$Co(aapH)_2Cl_2$	1624s	1614w	1480m	1015m	788m	1668s	570m	~200s
$Ni(aapH)_2Cl_2$	1622s	1615w	1480m	1012m	800s 790s	1675s	581m	208s
$Cu(aapH)_2Cl_2$	1620s	1614w	1480m	1015m	773s	1650s	598m	
$Zn(aapH)_2Cl_2$	1623s	1616w	1480m	1016m	795m	1669s	580m	~200s
amp	1590s	1578sh	1475m	990w	785m	1670s	555m	
$Co(amp)Cl_2$	1592m	1580sh	1490m	–	780s	1640s	575m	300br
$Zn(amp)Cl_2$	1608s	1565m	1478m	1026m	794s	1632s	570m	325s, 300sh
app	1590s	1578sh	1495m	985m	775s	1676s	509m	
$Co(app)Cl_2$	1610s	1593sh	1492m	1025m	784s	1640s	520m	300br
$Ni(app)Cl_2$	1606s	1578m	1483m	1023m	780br	1635s	517m	315s, 296sh
$Cu(app)Cl_2$	1618s	1590m	1480m	1027m	765s	1640s	522m	285br
$Zn(app)Cl_2$	1610s	1593sh	1488m	1025m	780s 763s	1630s	575m	330s, 290s

to these aspects of the aapH investigations not reported previously, and to comparative results for app and amp complexes.

Infrared Data

Infrared data on the metal chloride complexes are summarised in Table III. Assignments of the substituted pyridine bands are based on Katritsky's data for uncomplexed aapH and amp[16], and other work on monosubstituted pyridines[17, 18]. There is, as is usual in such complexes, a slight shift of most ring bands to higher wavenumber on coordination. Of the amide bands, the CO stretching (amide I) and out-of-plane bending (amide VI) modes can be used to diagnose O or N coordination. The decrease in frequency of band I and the increase in frequency of band VI on complex formation confirm that the amide group is O-bonded in all complexes.

In the far infrared region, one broad or two separate metal–chlorine stretching frequencies were observed near 300 cm^{-1} for each of the app and amp complexes. This is compatible with a pseudotetrahedral stereochemistry for these 1:1 adducts, but does not exclude other formulations such as $[ML_2]^{2+}[MCl_4]^{2-}$. A single strong band at approximately 200 cm^{-1} was found for $Zn(aapH)_2Cl_2$, $Co(aapH)_2Cl_2$ and $Ni(aapH)_2Cl_2$, in agreement with the *trans*-octahedral stereochemistry suggested for several aapH complexes of this stoichiometry[4].

Visible Spectra

In the solid state the app and amp complexes of cobalt and nickel have visible spectra characteristic of pseudotetrahedral complexes (Table IV). The two intense bands centred at approximately 15,000 and 5,000 cm^{-1} for both the app and amp complexes of Co(II) are assigned to the $^4A_2 \rightarrow {}^4T_1$ (P and F) transitions, while for $Ni(app)Cl_2$, the $^4T_1(F) \rightarrow {}^4T_1(P)$ and $^4T_1(F) \rightarrow {}^4A_2$ transitions were observed at 13,600 and 8,000 cm^{-1}. On dissolution in acetone the spectra of the cobalt and copper complexes changed very little, whereas significant changes occurred for $Ni(app)Cl_2$. Consequently for this complex extinction coefficients could not be measured to substantiate assignments. However, the solid state spectra of the cobalt and nickel complexes do not contain bands characteristic of MCl_4^{2-} species, consequently a pseudotetrahedral non-ionic formulation seems probable. No firm conclusions can be drawn about the stereochemistry of $Cu(app)Cl_2$ from its visible spectrum, but the broad band at 10,500 cm^{-1} is within the range typical of flattened tetrahedral copper complexes[19].

TABLE IV. Spectra of Tertiary Amide Complexes.

Complex	μ_{eff}(B.M.)	Absorption Maxima in 10^3 cm^{-1}
$Co(amp)Cl_2$	4.48	5.0br; 15.0s; 16.2sh; 18.2sh; 21.4sh [a] 5.0(40); 5.2sh; 14.8(420); 15.2(450); 16.0sh; 21.3sh
$Co(app)Cl_2$	4.51	5.0br; 14.5s; 15.5sh; 18.4sh; 25.9sh [a]4.9sh; 5.2(35); 14.7(400); 15.0sh; 25.6sh
$Ni(app)Cl_2$	3.31	8.0s; 13.6s; 23.4sh
$Cu(app)Cl_2$	1.88	10.5br; 21.0sh [a]9.8(85); 21.0sh

[a] Solution data in acetone.

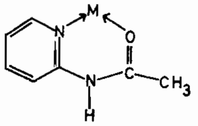
^1H Nmr Spectra

On complex formation with $ZnCl_2$, the ^1H nmr spectra of all three ligands altered significantly (Table V). The signals of the acetyl group are shifted to lower field in all cases due to the increased delocalisation of electrons in the carbonyl group on chelate formation. The large chemical shift change of the N-Me group of amp is also caused by chelation which brings the N-Me group within range of the anisotropic deshielding effect of the pyridine ring. However, the most significant change occurs in the chemical shift of the 3-H atom in the pyridine ring of $Zn(aapH)_2Cl_2$. On chelating aapH must change its configuration from (II) to (IV). The 3-H in the complexed ligand is no longer deshielded by the carbonyl group, and consequently appears at a much higher field.

TABLE V. ^1H Nmr Data on $ZnCl_2$ Complexes of aapH, amp and app in $(CD_3)_2CO$.

Complex	Chemical Shifts of Pyridine Protons and Their Change from Free Ligand Values					
	3	4	5	6	COMe	NMe
$Zn(aapH)_2Cl_2$	7.84 (–0.40)	8.34 (0.52)	7.70 (0.58)	8.72 (0.36)	2.70 (0.54)	
$Zn(amp)Cl_2$	7.94[a] (0.48)	8.48 (0.66)	7.88[a] (0.62)	8.94 (0.42)	2.46 (0.32)	3.75 (1.23)
$Zn(app)Cl_2$	7.60[a] (0.20)	8.12 (0.40)	7.26 (0.11)	8.61 (0.17)	2.21 (0.10)	

[a] Partially obscured by other bands.



(IV)

Conclusions

This work confirms that aapH forms *trans*-octahedral complexes $M(aapH)_2Cl_2$, whereas app forms pseudo-tetrahedral 1:1 complexes with dichlorides of Co, Ni, Zn and possibly Cu. The two amp complexes isolated also have a tetrahedral structure. This may be explained in terms of the greatly increased steric effects of the N-methyl and N-phenyl groups in the tertiary amides compared with the amide H-atom in aapH. Although aapH can retain a planar chelate ring structure in the ligand configuration (IV) adopted on complex formation, the bulky N-alkyl and aryl substituents in amp and app must cause distortion of the ligand such that the pyridine ring –N–C(O) group is no longer planar. As a consequence the formation of octahedral ML_2X_2 complexes is sterically hindered, and only pseudo-tetrahedral complexes are isolated.

References

1 M. Sekizaki, *Acta Cryst., B29,* 327 (1973) and references therein.

2 M. Sekizaki and K. Yamasaki, *Inorg. Chim. Acta, 4,* 296 (1970).

3 M. Nonoyama and K. Yamasaki, *Inorg. Chim. Acta, 3,* 585 (1969).

4 M. Nonoyama, S. Tomita and K. Yamasaki, *Inorg. Chim. Acta, 12,* 33 (1975).

5 L.C. Anderson and N.V. Seeger, *J. Am. Chem. Soc., 71,* 340 (1949).

6 R.A. Jones and A.R. Katritsky, *J. Chem. Soc.,* 1317 (1959).

7 J.P. Wibaut and G. Tilman, *Rec. Trav. Chim., 52,* 987 (1933).

8 R.F.C. Brown, L. Radon, S. Sternhill and I.D. Rae, *Can. J. Chem., 46,* 2577 (1968).

9 N. Watanabe and M. Kando, *Ann. Sankyo Res. Lab., 23,* 62 (1971).

10 W.E. Stewart and T.H. Siddall (III), *Chem. Rev., 70,* 517 (1970).

11 H. Kessler, *Angew. Chem. Int. Ed. Engl., 9,* 219 (1970).

12 L. Isbrandt, W.C.T. Tung and M.T. Rogers, *J. Magn. Resonance, 9,* 461 (1973).

13 W.R. Kingbaum, R.J. Roe and J.D. Woods, *Acta Cryst., B24,* 1304 (1968).

14 B.F. Pedersen and B. Pedersen, *Tetr. Lett., 34,* 2995 (1965).

15 H. Shanan–Atidi and K.H. Ber–Eli, *J. Phys. Chem., 74,* 961 (1970).

16 A.R. Katritsky, *J. Chem. Soc.,* 2202 (1958).

17 J.H.S. Green, W. Kynaston and H.M. Paisley, *Spec. Acta, 19,* 549 (1963).

18 R.E. Yingst and B.E. Douglas, *Inorg. Chem., 3,* 1177 (1964).

19 W.E. Hatfield and R. Whyman, *Transition Metal Chem., 5,* 47 (1969).