Four-coordinate Nickel(II) and Copper(II) Complexes of 7-Amino-4-methyl-5-aza-3-heptene-2-one

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Summary

The condensation of acetylacetone with ethylenediamine yields 7-amino-4-methyl-5-aza-3-heptene-2-one (AEH). This terdentate (N$_2$O) Schiff base forms various types of ternary complexes, depending on the nature of the second ligand. Examples of five- and six-coordination have been previously reported. The present paper points to the possibility of preparing a less common type of complex, *i.e.* [M^{II}(AE)Py]$^+$ (M = Ni or Cu) in which the use of a monodentate ligand (pyridine) favours a square planar geometry.

Introduction

Most of the terdentate (N$_2$O) Schiff bases reported in the literature result from the condensation of a diketo-precursor with a non-symmetrical diamine which has one non-reactive end such as H$_2$N-(CH$_2$)$_n$-NRR′ (R = H, R′ = Me or R = R′ = Me)[1, 2]. Generally speaking, these ligands (L) yield complexes [ML$_2$]. However, complexes [MLX] (X = Cl, Br or NCS) have been obtained using the 1 : 1 condensation product of 2-acetyldimedone with N-substituted ethylenediamine[3]. All attempts to prepare similar complexes substituting acetylacetone for dimedone have failed[3].

We have recently reported a terdentate (N$_2$O) Schiff base from non-substituted ethylenediamine[4]. This ligand (abbreviated as AEH below and represented in Figure 1) has yet been used to obtain [M(AE)$_2$]$^+$X$^{(4)}$ (X = Br) and [{M(AE)X}$_2$]$^{(5, 6)}$ complexes (X = Br or AcO$^-$) in which the metal is hexa- and penta-coordinate, respectively. The present paper is devoted to a less common type of complex involving four-coordinate metal ions, *i.e.* [M^{II}(AE)Py]$^+$ with M = Ni^{2+}, or Cu^{2+} and Py = C$_5$H$_5$N *(1)*.
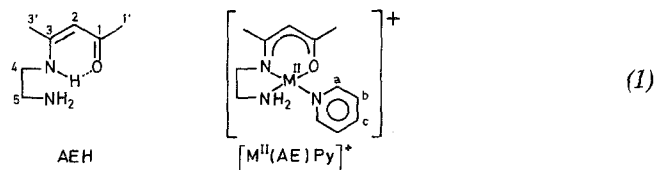
Experimental

Microanalyses were performed by the Service Central de Microanalyse du CNRS, Lyon. Infrared spectra (KBr discs) were recorded using a Perkin-Elmer 577 spectrometer, and visible spectra using a Cary 14 spectrophotometer. Proton and ^{13}C n.m.r. spectra were run on a Bruker WH 90 using TMS (^{1}H spectra) and CDCl$_3$ (^{13}C spectra) as internal references. All chemical shifts (^{1}H and ^{13}C) are given in ppm *versus* TMS using CDCl$_3$ as solvent. E.p.r. spectra were obtained on a Bruker 200 TT spectrometer. Measurements of electrolytic conductance were made with 10^{-3} M solutions in methanol and acetone.

7-Amino-4-methyl-5-aza-3-heptene-2-one (AEH)

This compound was prepared according to the literature[4].

[7-Amino-4-methyl-5-aza-3-heptene-2-onato(1-)nickel(II)-pyridine]perchlorate, [Ni(AE)Py]ClO$_4$

The compound may be obtained by either of the following methods:

a) To a solution of AEH (7 × 10^{-3}M) in *n*-butanol (50 cm^3) was added with stirring the equivalent amount of a MeOH solution of NaOMe and pyridine (1 cm^3). A methanolic solution of Ni(ClO$_4$)$_2$ · 6H$_2$O (2.57 g in 20 cm^3 of MeOH) was added after 10 min. The solution turned orange and a bulky precipitate appeared a few min later. The precipitate was collected by filtration and recrystallized from Me$_2$CO to give thin orange needles. Yield: 70%. (Found: C, 38.0; H, 4.7; N, 11.1; Cl, 9.1, Ni, 15.4. C$_{12}$H$_{18}$ClN$_3$NiO$_5$ calcd.: C, 38.1; H, 4.8; N, 11.1; Cl, 9,4; Ni, 15.4%.)

b) To an EtOH solution (50 cm^3) of the ligand AEH (7 × 10^{-3}M) was added a stoichiometric amount of Et$_3$N and pyridine. The resulting mixture was stirred and nickel perchlorate hexahydrate (2.57 g in 20 cm^3 of EtOH) was added in one portion. The product precipitated a few min later and was isolated as above.

[7-Amino-4-methyl-5-aza-3-heptene-2-onato(1-)copper(II)-pyridine]perchlorate, [Cu(AE)Py]ClO$_4$

To a MeOH solution (50 cm^3) of the ligand AEH (7 × 10^{-3}M) containing the equivalent amount of NaOMe was added a MeOH solution (50 cm^3) of copper perchlorate hexahydrate (2.6 g) and twice the amount of pyridine. 30 Min later, the solution was filtered to leave a blue precipitate. The filtrate was then evaporated to dryness. Me$_2$CO was added and the solution filtered again. Evaporation of Me$_2$CO left the desired mauve product. The yield (20%) is quite low compared to the nickel compound. (Found: C, 36.6; H, 4.6; N, 10.6; Cl, 9.0; Cu, 16.2. C$_{12}$H$_{18}$ClCuN$_3$O$_5$ calcd.: C, 37.6; H, 4.7; N, 11.0; Cl, 9.3; Cu, 16.6%.)

Results and Discussion

As expected, ternary complexes of copper(II) and nickel(II) may be obtained by reacting the "half-unit" AEH with copper and nickel ions in the presence of pyridine. Surprisingly, the yield of the reaction depends on the metal centre. In the case of copper, a low yield of *ca.* 20% results from an unexpected precipitate at an early stage of the reaction. This precipitate has not yet been identified but analytical and spectroscopic data point to the absence of pyridine.

The [M(AE)Py]$^+$ formulation suggested by microanalytical data is further supported by the spectroscopic results obtained for solid state and solution samples.

Compounds in the solid state

Static susceptibility measurements show the nickel complex to be diamagnetic. The copper complex is paramagnetic with a moment of 1.77 μ_B per copper atom. The reflectance spectra (Table 1) are consistent with a square planar geometry for both complexes.

The infrared spectra of the copper and nickel complexes are almost identical in the 4000–600 cm^{-1} range and very indicative of their nature since a comparison with the spectra of the free ligands (AEH and Py) and related complexes ([{Cu(AE)Br}$_2$][5], [{Cu(AE)AcO}$_2$][6] and [CuCl$_2$py$_2$][7]) allows a straight forward assignment of all the relevant absorptions.

Regarding the AE moiety, two bands at *ca.* 3298 and 3242 cm^{-1} are attributed to the NH$_2$. Two bands at *ca.* 1590 and 1517 cm^{-1} may be assigned to the "double-bonds" C=O, C=C and C=N. The band at 1590 cm^{-1} which is lacking in the spectrum of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotet-radeca-4,6,11,12-tetraenato(2-)nickel(II)[8] can be confidently attributed to ν(C=O). The positions of these absorptions are consistent with an extensive electronic delocalization over the acetylacetone framework. The out-of-plane deformation of the C–H bond is observed at 762 cm^{-1} in both complexes. With reference to the spectrum of [CuCl$_2$py$_2$], the pyridine bands are easily identified at 1610, 1450, 1218 and 696 cm^{-1}. A broad band at 1090 cm^{-1} and s sharper one st 625 cm^{-1} are attributed to the perchlorate (ν_3 and ν_4), respectively[9]. The lack of any splitting would be consistent with a non coordinated, tetrahedral ClO$_4^-$ [10].

Behaviour in solution

According to the conductivity values observed in methanol ($\Lambda_M = 89 \pm 1\ \Omega^{-1}\,m^2\,eq^{-1}$) and acetone ($\Lambda_M = 115 \pm 2\ \Omega^{-1}\,m^2\,eq^{-1}$), both complexes are 1:1 electrolytes[11]. The data reported in Table 1 reveal that the electronic spectra are solvent-dependent. As expected, the spectra of CH$_2$Cl$_2$ solutions look very much like the reflectance spectra but in potentially coordinating solvents such as methanol and pyridine, the overall appearance is modified. In pyridine the spectrum of the nickel complex is consistent with an octahedral geometry which would result from coordination of two moles of the solvent in axial positions. In methanol the simultaneous occurrence of absorptions characteristic for the planar (446 nm) and octahedral species (835 nm) suggests that these two forms exist in an equilibrium. This is further substantiated by magnetic measurements[12] since, in both solvents, a paramagnetic behaviour is observed. However, the magnetic moment is equal to 3.1 μ_B in pyridine and 2.0 μ_B in methanol. The percentages of the paramagnetic species estimated from

Table 1. Electronic spectra.

Complexes	Reflectance	CH$_2$Cl$_2$	MeOH	Pyridine
[Ni(AE)py]ClO$_4$	450	448 (490)	446	
	535	540(sh)	535(sh)	546(49)
				776(34)
			835	826(49)
[Cu(AE)py]ClO$_4$		*ca.* 400(sh)		420(sh)
	540	545(90)		
	640	640(sh)		600(120)
				810(30)

Wavelengths in nm, extinction coefficients in parentheses.

Table 2. E.p.r. data for [Cu(AE)py]ClO$_4$ in different solvents.

Solvent			
Pyridine	g_{iso} = 2.110[a]	$g_\parallel$ = 2.221	$g_\perp$ = 2.054
	A_{iso} = 76.5	$A_\parallel$ = 179	
CH$_2$Cl$_2$/PhMe (4/1)	g_{iso} = 2.099	$g_\parallel$ = 2.203	$g_\perp$ = 2.046
	A_{iso} = 88	$A_\parallel$ = 198	
THF	g_{iso} = 2.106	$g_\parallel$ = 2.214	$g_\perp$ = 2.051
	A_{iso} = 82	$A_\parallel$ = 192	

[a] g_{iso} and A_{iso} from spectra at ambient temperature; $g_\parallel$ and $A_\parallel$ from spectra at 100 K; $g_\perp$ from $g_\perp = (3\,g_{iso} - g_\parallel)/2$. A_{iso} and $A_\parallel$ in cm^{-1} × 10^4.

both magnetic and spectroscopic properties are *ca.* 100% (py) and 50% (MeOH) at room temperature[1]. The electronic spectrum of the copper complex is less affected by changing the solvent than the spectrum of its nickel analogue. Still, the red shift of the main absorption (from 545 to 600 nm) and the appearance of a band at 810 nm in pyridine may be associated with a structural change of the coordination polyhedron from square planar to square pyramidal or trigonal bipyramidal[13].

This conclusion is further supported by e.s.r. data. For the three solvents used in the present investigation (Table 2) the room-temperature spectra show the four-line pattern characteristic of monomeric copper(II) complexes. However, the values of the related parameters (g_{iso} and A_{iso}) depend on the solvent. The decrease of $|A_{iso}|$ from 90 G (CH$_2$Cl$_2$/MePh) to 76 G (py) is consistent with an increase of coordination number from four to five[14]. Furthermore the frozen spectra (100 K) are anisotropic with $g_\parallel > g_\perp$ in accordance with a square planar geometry for the coordinate species and a square pyramidal geometry for the fivecoordinate complex.

The perpendicular component of the frozen spectrum obtained with the CH$_2$Cl$_2$/MePh mixture shows superhyperfine structure which indicates interaction of the unpaired spin with three ^{14}N nuclei. This structure is lost when coordinating solvents (THF, py) are used. A similar behaviour has been previously observed[15, 16].

Returning to the nickel complex, its diamagnetism in noncoordinating solvents allows the use of ^{1}H and ^{13}C spectroscopy for further characterization[17]. The data are reported in Table 3. The ^{1}H resonances of the CH$_2$ groups are of particular interest. In the free ligand AEH, the C(4)H$_2$ resonance is a quadruplet due to coupling with the adjacent C(5)H$_2$ and NH protons, the related constants being almost identical (J *ca.* 5 Hz). The C(5)H$_2$ resonance is a triplet. These features indicate that the free ligand is well represented by the tautomeric form depicted in Figure 1. The large downfield shift of NH supports the occurrence of strong hydrogen bonding. In the complex, the NH signal is absent and the C(4)H$_2$ resonance reduces to a triplet. However, C(5)H$_2$ appears as an asymmetrical multiplet. This is due (i) to coupling with the adjacent C(4)H$_2$ and NH$_2$ protons and (ii) to an overlap with the NH$_2$ resonance. These assignments are firmly established by double-irradiation experiments and by the spectra of deuteriated samples. The pyridine signals are deshielded upon complexation (from 8.5, 7.1 and 7.5 ppm to 8.72, 7.43 and 7.83 ppm, respectively). The ^{13}C spectra show that the two CH$_2$ are affected unequally in changing from the free ligand to the complex. They are both deshielded but C(4) suffers a more important shift (*ca.* 8.5 ppm) than C(5) (*ca.* 3.0 ppm). The difference is attributable to deprotonation effects. Interestingly all the ^{13}C nuclei but C(1) and, to a lesser extent, C(1')

Table 3. ^{1}H and ^{13}C n.m.r. data (ppm *vs*. TMS).

	CH$_3$ 1'	3'	CH$_2$ 4	5	CH 2	C 1	3	NH$_2$	NH	Pyridine a	b	c
^{1}H n.m.r.												
AEH	1.94(s)	1.90(s)	3.27(q)	2.87(t)	4.94(s)	–	–	1.27	10.80	–	–	–
[Ni(AE)py]ClO$_4$	1.95(s)	1.72(s)	3.17(t)	2.61(m)	5.06(s)	–	–	2.61	–	8.71	7.43	7.83
py	–	–	–	–	–	–	–	–	–	8.50	7.10	7.50
^{13}C n.m.r.												
AEH	27.4	17.5	45.5	40.8	94.0	193.1	162.1	–	–	–	–	–
[Ni(AE)py]ClO$_4$	24.0	21.6	54.1	43.9	100.7	176.0	166.5	–	–	151.0	125.5	138.6
py	–	–	–	–	–	–	–	–	–	150.6	124.5	136.4

CDCl$_3$ as solvent. Numbering as in *(1)*.

are deshielded upon complexation. For instance, the pyridine signals move from 150.6, 124.5 and 136.4 ppm to 151.0, 125.5 and 138.6 ppm, respectively.

Finally, it is clear that the "half-unit" AEH may be involved in very different types of complexes, according to the second ligand. This second ligand may be AEH itself, leading to octahedral species (4). Potentially bridging ligands (such as Cl$^-$, Br$^-$, AcO$^-$ ...) give dinuclear species in which the metal is five-coordinate[5, 6]. In the present paper, we have shown that a monodentate ligand like pyridine favours a squarebased geometry. It is inferred that bidentate ligands (ethylenediamine, *ortho*-phenylenediamine...) offer the possibility of obtaining dinuclear species of the type [(AE)MBM(AE)]. This possibility is being studied.

Acknowledgements

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