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Unsymmetrical Tetradentate Ligand Complexes of Copper(II) and Nickel(II) with N_3O Donor Sets and Ethylenediamine Bridges

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Abstract

Novel non-symmetrical tetradentate Schiff base complexes with N_3O donor sites have been obtained using the 'half-unit' 7-amino-4-methyl-5-aza-hept-3-ene-2-one (AEH). Two reaction pathways have been used: (i) preparation of the free ligand which is then reacted with the desired metal salt, and (ii) template synthesis without isolation of the free ligand. The so prepared nickel and copper complexes have been characterized (infrared, visible, EPR and NMR spectroscopies).

Introduction

There has been recent interest in the design, synthesis and study of non-symmetrical Schiff base ligands. This has arisen from the awareness that in many metalloproteins the metal ions are formed in sites of low symmetry and also from an interest in the potential modification of the properties of complexes derived from ligands having present non-symmetrical mixed sets of donor atoms [1, 2]. However a limited number of papers have appeared on the development of synthetic routes to this type of ligand. A general strategy would rely on the possibility of preparing 'half-units' by single condensation of a suitable keto precursor with a diamine and then reacting the half-unit with another keto compound [3, 4]. This process has been successfully applied to the preparation of non-symmetrical tetradentate Schiff bases having present the mixed donor sets N_2O_2, N_3O, N_2OS, [5–12]. Surprisingly the known non-symmetrical (N_2O_2) bases are derived from ethanediamine while most of the (N_3O) ligands involve propanediamine. Due to the influence of the length of the diamine chain upon the properties and even the structure of the related complexes, we have planned to prepare various (N_3O) ligands with an ethanediamine chain. We have recently reported the synthesis of such a base (DH_2, Fig. 1) and of its copper(II) and nickel(II) complexes together with the properties and structures of both complexes [13]. The present paper describes the synthesis and relevant properties of the copper(II) and nickel(II) complexes of three new non-symmetrical (N_3O) Schiff bases ((AH), (BH_2), (CH_2), Fig. 1) obtained upon reacting the (AEH) half-unit with 2-pyridinecarboxaldehyde, 2-aminoacetophenone and 4-aminopent-3-en-2-one, respectively. These ligands are represented in Fig. 1.

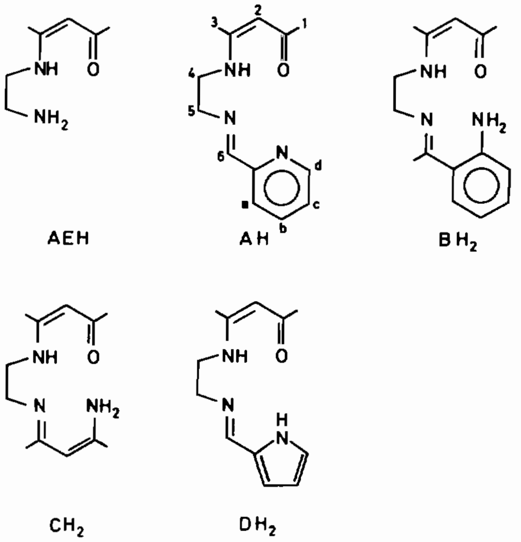

Fig. 1. Ligands with numbering used for the NMR results.

Results and Discussion

The non-symmetric ligands (AH), (BH_2) and (CH_2) were prepared by reaction of the 'half-unit' 7-amino-4-methyl-5-aza-3-heptene-2-one [4] with 2-pyridinecarboxaldehyde, 2-aminoacetophenone and 4-aminopent-3-en-2-one, respectively, in stoichiometric ratio in an appropriate solvent. In one instance the ligand (AH) was recovered as an orange oil and characterized by ^1H NMR. The spectrum, run in $CHCl_3$, gave signals

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TABLE I. ^1H NMR Results (ppm *vs.* TMS)

	CH_3				CH_2		CH			NH	Cycle			
	1	3	6	8	4	5	2	7	6		a	b	c	d
$[NiA]^{+a}$	2.13	2.03			(3.84)		5.34		8.54		(7.8–8.3) m			
NiB^b	1.97	1.90	2.32		3.44t	3.13t	4.90			3.44	7.33d	6.18t	6.84t	6.58d
$[NiCH]^{+c}$	2.19	1.93	2.40 2.42	2.42 2.40	(3.62–3.53)m		5.33	4.38		2.90 8.70				
NiC^b	2.09	2.00	2.12	2.12	(3.34)		5.20	4.50		7.47				

[a]In DMSO. [b]In chloroform. [c]In acetone.

at 1.98 (s, 3H, $CH_3{}^1$)*, 1.96 (s, 3H, $CH_3{}^3$), 3.82 (q, 2H, $CH_2{}^4$), 3.65 (t, 2H, $CH_2{}^5$), 4.95 (s, H, CH^2), 8.40 (s, H, CH^6), 11.0 (s, H, NH), 8.02 (d, H, CH^a), 7.74 (t, H, CH^b), 7.32 (t, H, CH^c), and 8.63 p.p.m. (d, H, CH^d). These features clearly indicated that the ligand was non-symmetrical and existed essentially as the keto-tautomer. The orange oil was then used, without further purification, to prepare the metal complexes. In the other cases, the complexes were obtained by an *in situ* reaction in which sodium hydroxide and the required metal salt were added to the reaction mixture. It is noteworthy that in the case of ligand (C), two nickel(II) complexes, *i.e.* (NiC) and $(NiCH)^+$ were obtained depending on the experimental conditions.

The complexes were first characterized by elemental analyses. From the data reported in the experimental part, the following formulations were suggested $(NiA)ClO_4$, $(CuA)ClO_4$, (NiB), (CuB), (NiC) and $(NiCH)BF_4$. They were further supported by spectroscopic arguments.

Moreover, molar conductances in methanolic solutions indicate that the $(NiA)^+$, $(CuA)^+$, and $(NiCH)^+$ complexes are 1:1 electrolytes with $\Lambda_M = 85–90$ Ω^{-1} cm^2 mol^{-1} which requires that the Schiff bases coordinate as uninegative ligands.

^1H NMR Spectroscopy

Due to their diamagnetic behaviour (*vide infra*), the nickel complexes may be characterized by ^1H NMR spectroscopy. The values of the chemical shifts are reported in Table I. In all cases the spectra show the simultaneous occurrence of two sets of signals, which are attributable on the one hand to the (AE) entity and, on the other hand, to the second moiety of the non-symmetrical ligand. No signals attributable to symmetrical species have been observed.

Particular attention has been paid to the N*H* signals which allow a clear distinction to be made between the complexes in connection with their protonation state. The N*H* resonance which appears at 11.0 ppm in the (AH) spectrum is no longer observed in the $(NiA)ClO_4$ spectrum as a result of deprotonation. The absence of this signal can also be noticed in the spectra of (NiB) and (NiC) which, moreover, show a single N*H* signal at 3.44 and 7.47 ppm, respectively, in agreement with the ligands being twice deprotonated. As expected on the basis of the formulation deduced from microanalytical data, two N*H* resonances (2.90 and 8.70 ppm) are observed for $(NiCH)^+$ suggesting that one nitrogen of the ethylenediamine bridge is still protonated. Indeed, the existence of a NH_2 form instead of two NH functions is not supported by infrared data (*vide infra*).

Mass Spectroscopy

The mass spectra data characterizing the neutral complexes are summarized in Table II. They show parent peaks corresponding to the molecular weight of the complexes (315 amu (Ni) and 320 amu (Cu) for (MB) complexes and 279 amu for (NiC)). The fragmentation patterns are characteristic [14] of such types of molecules. Thus, the main fragments result from a symmetrical cleavage of the ethylenediamine chain and it is possible, for the (MB) complexes, to detect peaks corresponding to the acetylacetone half plus metal (169 (Ni) and 174 amu (Cu)), the other half moiety appearing with a loss of 1 amu (Ni and Cu)). In the case of (NiC), one may observe both half moieties linked to the nickel (169 and 168 amu) but

TABLE II. Mass Spectra

	NiB	CuB	NiC
M^{+a}	315(100)[b]	320(100)	279(100)
$[M-Q]^{+c}$	169(55)	174(30)	
$[Q-H]^+$	145(75)	145(90)	
$[M-Q']^{+d}$			169(22)
$[M-Q'']^{+e}$			168(65)
$[Q'-H]^+$			109(70)

[a]Molecular ion. [b]Relative intensities. [c]$Q = CH_3C(NCH_2)$-$C_6H_4NH)$. [d]$Q' = CH_3C(NH)CHC(NCH_2)CH_3$. [e]$Q'' = CH_3C(O)CHC(NCH_2)CH_3$.

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*s, d, t, m = singlet, doublet, triplet, multiplet. The numbering refers to Fig. 1.

TABLE III. Infrared Spectra

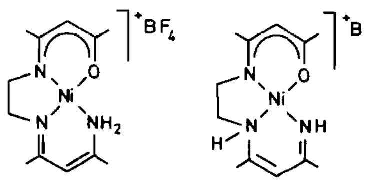
	$[NiA]ClO_4$	$[CuA]ClO_4$	NiB	CuB	$[NiCH]BF_4$
νNH			3340	3335	3391
					3276
νCO +	1595	1600	1605	1600	1593
νCN + νCC	1570	1585	1595	1592	1590
	1505	1505	1560	1565	
			1510	1510	1516
ν anion	1090	1090			1054
	620	620			
δCH	780	780	760	760	793
	765	770	740	740	

only one of the free forms, the aminopentenone moiety at 109 amu. These compounds verify the nitrogen rule (parent peak with an odd amu for an odd number of nitrogen atoms and an even mass number of the metallic atom (nickel case) or conversely an odd mass number (copper case)). Finally, there is no evidence for any of the two symmetrical tetradentate species (N_2O_2 and N_4 donor sets) which could arise through rearrangement reactions. Unfortunately, we could not obtain the parent peaks for the $(NiA)^+$ and $(CuA)^+$ complexes.

Infrared Spectroscopy

The infrared spectra, quoted in Table III, show that in all the complexes the (AE) moiety was present. Two or three bands around 1600 cm^{-1} were attributed to ν(C=O), ν(C=N), ν(C=C) whereas a band near 770 cm^{-1} was related to the out-of-plane deformation of the C–H bond.

For $(NiA)^+$ and $(CuA)^+$, bands characteristic of the pyridine ring were found at 1597 and 780 cm^{-1}. Deprotonation of the aminoacetophenone moiety in the (B) complexes was indicated by the observation of a single sharp absorption at 3340 (NiB) and 3335 (CuB) cm^{-1}. The $(NiCH)^+$ spectrum displayed two absorptions, a sharp band at 3276 cm^{-1} and a broader band at 3391 cm^{-1}. This feature is not consistent with a NH_2 form (2a, Fig. 2) and therefore suggests that two NH groups are actually present in the complex in accordance with the NMR results. Taking into consideration that previous works [15, 16] have established that, in non-symmetrical Schiff base complexes, the N*H* group close to the acetylacetone moiety deprotonated first, we considered that the isomer (2b) represented in Fig. 2 is the most likely.



(a) (b)

Fig. 2. $[NiCH]BF_4$: possible structures.

In the $(NiA)^+$ and $(CuA)^+$ spectra, bands attributable to ionic perchlorates are observed at 1090 (ν_3) and 615 (ν_4) cm^{-1}.

Electronic Spectroscopy

These spectra (Table IV) are consistent with a square planar coordination of the metal centre. For the nickel complexes, the d–d transitions are clearly located at 480 $(NiA)^+$, 580 (NiB), 555 (NiC) and 510 $(NiCH)^+$ nm. Comparing the (NiC) complex with *N,N'*-ethylene-bis(acetylacetoneiminato)nickel(II) (NiBAE) shows a shift of the d–d transition from 555 to 562 nm in agreement with a change in the environment of the nickel from N_3O to N_2O_2. Another shift of the d–d transitions between the neutral complexes and the unipositive ones is quite noteworthy. Other unipositive complexes with a N_3O donor set show the same trend [16]. We also noticed that the d–d transition is clearly observed in NiB while this band is hidden beneath a charge transfer

TABLE IV. Absorption Bands (in nm) with Absorption Coefficients given in Parentheses

$[NiA]ClO_4$ [a]	480(sh), 430(4000)
$[CuA]ClO_4$ [a]	540(160), 368(1100)
$[NiCH]BF_4$ [a]	510(80), 344(3600), 330(3400)
NiBAE [b, e]	562(80), 357(5070), 352(5330), 305(4100)
NiB [c]	580(330), 486(2500), 418(2600), 390(3300), 300(13200)
Ni aben [d, f]	480(6500), 365(8800), 318(25000)
CuBAE [b, e]	540(180), 335(5900), 306(23300)
CuB [c]	656(110), 520(180), 446(4020), 424(4700), 335(7600)
Cu aben [d, f]	680(330), 529(400), 461(4000), 416(13000), 395(6700), 298(11000)

[a] In acetone. [b] In methanol. [c] In dichloromethane. [d] In chloroform. [e] Ref. 17. [f] Ref. 18.

band for *N,N'*-ethylene-bis(*o*-aminobenzylideneiminato)nickel(II) (Ni aben).

As expected for a square planar coordination, the $(CuA)^+$ complex exhibits a band at 540 nm. In the case of (CuB) two bands at 656 and 520 nm may be attributed to d–d transitions. Furthermore the band at 656 nm falls outside the range where the d–d absorptions are expected for square planar coordination. This may be related either to a distortion of the square planar geometry or to the occurrence of interactions between monomeric units or to the addition of a solvent molecule on the copper atom to increase its coordination number from four to five.

It is noteworthy that two d–d transitions (680, 530 nm) have also been observed in the spectrum of *N,N'*-ethylene-bis(*o*-aminobenzylideneiminato)-copper(II) (Cu aben) [18] where the copper has an N_4 environment. In view of the molecular structure of this complex, the 'abnormal' absorption at 680 nm may be due to a tetrahedral distortion of the coordination polyhedron [19].

Magnetic Behaviour and EPR Spectroscopy

Static susceptibility measurements show the nickel complexes to be diamagnetic, as expected for a square planar geometry. The copper complexes are paramagnetic with moments of 1.79 μB per copper atom for $(CuA)^+$ and (CuB).

Very similar EPR spectra have been obtained for $(CuA)^+$, (CuB) and also for the previously studied (CuD) complex [18]. This suggests that the three complexes may not differ widely in their structure.

The main features of frozen solution spectra are attributable to mononuclear copper(II) species. However, at low temperature and using high instrument gain 'half-field' (*ca.* 1500 G) lines are detected. In the case of (CuB), the seven lines expected for coupling of the free electron with two copper nuclei are clearly observed. The proportions of dinuclear species remain low even at 110 K so that observation of the related $\Delta M_S = \pm 1$ transitions proved difficult.

The parameters characterizing the mononuclear forms are reported in Table V. They are consistent with a tetragonal coordination. In the case of (CuB), the perpendicular component displays a superhyperfine structure of seven lines with a spacing of *ca.* 14.5 G. This feature arises from the presence of three nitrogen atoms around the paramagnetic centre.

Conclusions

The new non-symmetrical ligands give neutral complexes and examples of unipositive complexes which are quite unusual in the chemistry of the tetradentate Schiff bases. It is noteworthy that ligand **A** allows the preparation and isolation of complexes where the metal-to-ligand ratio is 1:1 whereas such compounds could not be obtained with the symmetrical Schiff base derived from ethylenediamine and 2-pyridinecarboxaldehyde. In the latter case, the azomethine linkages are not retained: a methanol molecule [20] or two water molecules [21] have been added across one or two azomethine linkages. This hydrolytic instability, generally attributed to the steric strain induced in the ligand accompanying planar chelation, does not exist in the case of ligand **A** which has only one azomethine linkage. Another interest in these non-symmetrical ligands originates in the fact that they allow a subtle modulation in the redox potentials of metal complexes. This study will be the subject of a later publication.

Experimental

Microanalyses were performed by the Service Central de Microanalyses du CNRS, Lyon. Infrared spectra of KBr discs were recorded using a Perkin-Elmer 577 spectrometer, visible spectra using a Cary 14 spectrophotometer. Mass spectra were obtained using a VG Micromass 7070F spectrometer. Proton NMR spectra were run on a Bruker WH90 using TMS as internal reference. All chemical shifts are given in ppm *versus* TMS. EPR spectra were obtained on a Bruker 200 TT spectrometer.

The Synthesis of A

To a solution of 7-amino-4-methyl-5-aza-hept-3-en-2-one [4] (4 g, 2.8×10^{-2} mol) in ethanol (50 cm^3) was added 2-pyridinecarboxaldehyde (3 g, 2.8×10^{-2} mol). The solution was refluxed for 15 min. After cooling, the solvent was removed to leave a yellow oil which was characterized by ^1H NMR and used without further purification.

The Synthesis of [NiA]ClO₄ and [CuA]ClO₄

The mixture of the ligand **A** (1 g, 4.3×10^{-3} mol) in methanol (30 cm^3) with a methanolic solution

TABLE V. EPR Data

	g_{iso} [a]	A_{iso} [a] (10^{-4} cm^{-1})	$g_{\parallel}$ [b]	$A_{\parallel}$ [b] (10^{-4} cm^{-1})	$g_{\perp}$ [b]
$[CuA]ClO_4$ [c]	2.090	88	2.201	190	2.033
CuB [d]	2.087	67	2.199	186	2.032

[a] 293 K spectra. [b] 113 K spectra. [c] In acetone. [d] In $CH_2Cl_2/CH_3C_6H_5$ (4/1).

(20 cm^3) of the desired metal perchlorate salt brought about the fast precipitation of an orange (nickel) or brown (copper) product. Recrystallization from acetone (nickel) or methanol (copper) yielded pure products. *Anal.* Calc. for $C_{13}H_{16}ClN_3NiO_5$: C, 40.26; H, 4.13; Cl, 9.16; N, 10.84; Ni, 14.97. Found: C, 39.56; H, 4.01; Cl, 8.91; N, 10.65; Ni, 14.36%. Calc. for $C_{13}H_{16}ClCuN_3O_5$: C, 39.69; H, 4.07; Cl, 9.03; Cu, 16.16; N, 10.69. Found: C, 39.39; H, 3.98; Cl, 9.10; Cu, 15.58; N, 10.51%.

The Synthesis of NiB and CuB

To a solution of 7-amino-4-methyl-5-aza-hept-3-en-2-one (1.4 g, 1×10^{-2} mol) and 2-aminoacetophenone (1.35 g, 1×10^{-2} mol) in methanol (50 cm^3) was first added, with stirring, NaOH (0.8 g, 2×10^{-2} mol) dissolved in the minimum amount of water and then a methanolic solution (40 cm^3) of the metal salt ($NiCl_2 \cdot 6H_2O$ or $CuCl_2$). This mixture was refluxed and concentrated to half-volume. Adding water to the hot solution brought about the precipitation of a red (nickel) or yellow–green (copper) product. *Anal.* Calc. for $C_{15}H_{19}N_3NiO$: C, 57.14; H, 6.03; N, 13.33; Ni, 18.41. Found: C, 56.50; H, 5.85; N, 13.30; Ni, 18.00%. Calc. for $C_{15}H_{19}CuN_3O$: C, 56.16; H, 5.93; Cu, 19.81; N, 13.10. Found: C, 55.75; H, 5.95; Cu, 19.05; N, 13.08%.

The Synthesis of [NiCH]BF$_4$ and NiC

To a solution of 4-aminopent-3-en-2-one (0.7 g, 7×10^{-3} mol) [22] in dry dichloromethane (20 cm^3) was added triethyloxonium tetrafluoroborate (1.4 g, 7×10^{-3} mol) dissolved in dry dichloromethane (10 cm^3). The solution was stirred for 15 min at room temperature under argon atmosphere. A solution of 7-amino-4-methyl-5-aza-hept-3-en-2-one (1 g) in dichloromethane (10 cm^3) was added dropwise. One hour later, dichloromethane was removed under reduced pressure and replaced with absolute methanol (20 cm^3). $NiCl_2 \cdot 6H_2O$ (1.6 g, 7×10^{-3} mol) dissolved in methanol was added at once and then NaOH (0.3 g). The solution was refluxed for 30 min and concentrated. After cooling, an orange–brown precipitate appeared. Recrystallization from acetone gave the desired product. *Anal.* Calc. for $C_{12}H_{20}BF_4N_3NiO$: C, 39.23; H, 5.44; N, 11.44; Ni, 15.80. Found: C, 39.13; H, 5.42; N, 11.18; Ni, 15.17%. After adding NaOH to a water solution of (NiCH)BF_4, the NiC neutral complex was easily isolated by phase transfer from water to dichloromethane.

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