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Five-Coordinate Nickel(II) and Copper(II) Complexes of Quinquedentate Acid Amides

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Five-coordinate nickel(II) and copper(II) complexes of novel linear quinquedentate acid amides have been prepared and their magnetic moments, infrared and electronic spectra were measured. The amide groups of these quinquedentate ligands are coordinated to metals with deprotonated nitrogen atoms. The copper complexes show unique electronic spectra with a high intensity. Nickel forms five-coordinate complexes more easily with deprotonated amide-nitrogen atoms than with azomethine-nitrogen atoms of the ligands having a similar skeleton. These five-coordinate nickel complexes of the acid amides are paramagnetic which have never been reported before.

Introduction

Numerous five-coordinate nickel(II) complexes are known,[1] but there has been no example reported for a five-coordinate nickel(II) complex coordinated with acid amides. In this paper the first examples of five-coordinate nickel(II) and copper(II) complexes of the following acid amides will be described (*cf.* Fig. 1):

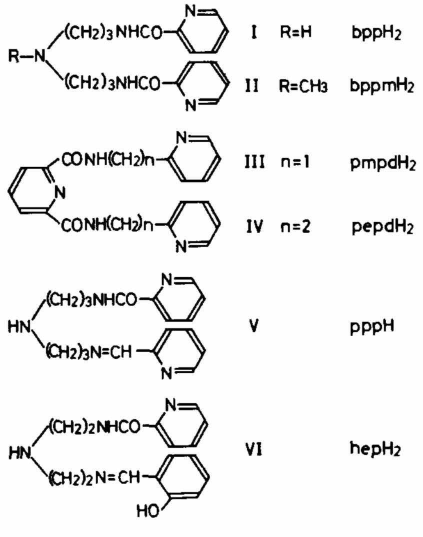

Figure 1. Ligands and their abbreviations.

I Bis[3-(2-pyridinecarboxamido)propyl]amine (abbreviated as $bppH_2$),
II Bis[3-(2-pyridinecarboxamido)propyl]methylamine ($bppmH_2$),
III N,N′-bis(2-pyridylmethyl)-2,6-pyridinedicarboxamide ($pmpdH_2$),
IV N,N′-bis[2-(2-pyridyl)ethyl]-2,6-pyridinedicarboxamide ($pepdH_2$),
V N-3-[3-(2-pyridylmethyleneamino)propylamino] propyl-2-pyridinecarboxamide (pppH),
VI N-2-[2-(2-hydroxybenzylideneamino)ethylamino]ethyl-2-pyridinecarboxamide ($hepH_2$).

These nickel complexes are rather exceptional because most nickel(II) complexes coordinated with deprotonated acid amide-nitrogen atoms are diamagnetic and square-planar.[2–5]

Experimental Section

Preparation of Ligands

Four ligands, $bppH_2$, $bppmH_2$, $pmpdH_2$, and $pepdH_2$ were obtained by refluxing for five hours a mixture of the ethyl ester of pyridine-2-carboxylic acid (for the former two) or pyridine-2,6-dicarboxylic acid (for the latter two) and a calculated amount of the appropriate amine. The reaction product was used to prepare complexes without isolation of the respective ligand except $pmpdH_2$ which was recrystallized from ethanol (Table I). The other three ligands hardly crystallized and could not be distilled without decomposition because of a high molecular weight.

The ligand pppH was prepared by condensation of pyridine-2-carbaldehyde with N-3-(3-aminopropylamino)propyl-2-pyridinecarboxamide at 130° C. The amide had been obtained by refluxing ethyl pyridine-2-carboxylate with excess bis(3-aminopropyl)amine and by removing unreacted bis(3-aminopropyl)amine. The ligand $hepH_2$ was synthesized under similar conditions using 2-hydroxybenzaldehyde and N-2-(2-aminoethyl-amino)ethyl-2-pyridinecarboxamide. These two ligands were also used without purification for preparing complexes.

TABLE I. Colours and Analytical Data for the Complexes.

No.	Complex	Colour	M % (Calcd.)	C % (Calcd.)	H % (Calcd.)	N % (Calcd.)	H_2O % (Calcd.)
1	Ni(bpp) · $5H_2O$	Yellow	12.28 (12.03)	44.25 (44.29)	4.92 (4.97)	14.20 (14.35)	17.79 (18.45)
2	Ni(bppm) · $5H_2O$	Yellow	11.68 (11.69)	45.99 (45.44)	5.27 (5.09)	13.92 (13.99)	17.70 (17.93)
3	Cu(bppm)	Blue	15.20 (15.24)	54.36 (54.73)	5.72 (5.56)	16.53 (16.81)	
4	Cu(pmpd) · $2H_2O$	Green	14.18 (14.28)	a		15.57 (15.74)	8.15 (8.10)
5	Cu(pepd) · H_2O	Blue	14.13 (13.97)	55.36 (55.44)	4.73 (4.65)	15.39 (15.49)	4.07 (3.96)
6	Ni(ppp)ClO_4 · $3/2H_2O$	Brown	11.62 (11.52)	42.48 (42.49)	5.03 (4.94)	13.63 (13.73)	1.85[b] (1.77)
7	Ni(hep) · $7/2H_2O$	Yellowish green	13.57 (13.59)	47.42 (47.25)	6.17 (5.84)	12.65 (12.97)	14.49 (14.59)
8	Cu(hep) · $5H_2O$	Bluish green	13.77 (13.70)	44.27 (44.01)	5.88 (6.08)	11.85 (12.07)	18.36 (19.41)
9	Ni(bpa)$(ClO_4)_2$ · H_2O	Brown	9.93 (10.01)	37.37 (36.96)	4.59 (4.31)	12.25 (11.97)	c
10	Cu(bpa)$(ClO_4)_2$ · $1/2H_2O$	Bluish green	11.13 (10.94)			11.92 (12.09)	1.76 (1.55)

[a] Elemental analysis for pmpdH_2: C, 65.74(65.70); H, 4.90(4.93); N, 20.06(20.16%). Its m.p. is 151.5–152.5° C.
[b] Only a half mol of H_2O can be dehydrated before decomposition occurs and so this value is calculated for a half mol of H_2O. [c] Water of crystallization is not dehydrated without decomposition.

The presence of acid amide groups in the ligands (Fig. 1) is confirmed by the infrared spectra of the crude products, which show characteristic bands[6] of a secondary acid amide group: ν(N–H) at *ca.* 3370, the amide I at *ca.* 1660, the amide II at *ca.* 1525, and the amide III at *ca.* 1250 cm^{-1}.

A Schiff base ligand, bis[3-(2-pyridylmethyleneamino)propyl]amine (abbreviated as bpa) having a similar skeleton as that of bppH_2 and its nickel(II) and copper(II) complexes were prepared for comparison. Its nickel(II) complexes have been reported,[7] but the preparation in this paper was carried out prior to the report.

Preparation of Complexes

The complexes listed in Table I were prepared by mixing a metal salt, the ligand, and a required amount of potassium hydroxide in a mixture of water and ethanol. The precipitated complexes were recrystallized from water or a mixture of water and ethanol. The yield based on the crude ligand was 30–70%. The complexes were dehydrated at 110° C under vacuum for a few hours as occasion demands.

Measurements

Magnetic susceptibilities were measured by the Gouy method at 25° C by using $Hg[Co(NCS)_4]$ as a calibrant. Electronic spectra were recorded on Zeiß PMQ II, Hitachi EPU–2A, and Hitachi 323 spectrophotometers at 25° C. For diffuse reflectance spectra MgO was used as a reference standard. Infrared spectra were recorded on a JASCO DS–402G infrared spectrophotometer by means of Nujol and hexachlorobutadiene mull methods.

Results and Discussion

The complexes prepared are listed in Table I together with their analytical data and in Table II with their magnetic moments which are normal for the high-spin complexes.

Yellow Ni(bpp) · $5H_2O$ and Ni(bppm) · $5H_2O$ turn orange–brown when dehydrated at 110° C under vacuum, and yellowish green Ni(hep) · $7/2H_2O$ turns yellow. The original hydrated complexes are recovered upon recrystallization from water or a mixture of water and ethanol. When heated, Ni(ppp)ClO_4 · $3/2H_2O$ loses only a half mol of water of crystallization without colour change, and the remaining water is dehydrated only with decomposition. The hydrated copper complexes retain original colours even after dehydration. These facts show that in the nickel complexes water is coordinated, while in the copper complexes it is not.

Infrared Spectra

The infrared spectra of all the complexes show the characteristic bands of N-coordinated amide groups at

TABLE II. Magnetic Moments and Electronic Spectra of the Complexes.

No.	Complex	μ_{eff} B.M.	Electronic Spectrum State[a]	Absorption Maximum in 10^3 cm^{-1}(logε[b])
1	Ni(bpp)·$5H_2O$	3.11	Solid	10.0sh[c] 12.3 16.0sh
			Solid[d]	6.9 10.0sh 14.0sh 18.0sh
			$CHCl_3$	7.7(1.43) 10.1(1.05) 11.5(0.94) 15.0sh 18.5sh 22.5sh
2	Ni(bppm)·$5H_2O$	3.06	Solid	10.6 12.5sh 16.0sh
			Solid[d]	6.9 9.8 14.0sh 18.5sh
			$CHCl_3$	7.7(1.48) 10.2(1.11) 11.4(0.99) 14.5(1.16) 18.8(1.56) 22.7sh
3	Cu(bppm)	1.83	Solid	12.5sh 17.2br
			$CHCl_3$	13.2sh 15.5(2.35) 17.0(2.40)
4	Cu(pmpd)·$2H_2O$	1.86	Solid	9.7 13.1 15.2sh
			$CHCl_3$	9.6(1.84) 12.3(1.95) 13.1sh 15.4(1.91) 19.0sh
5	Cu(pepd)·H_2O	1.82	Solid	11.5sh 16.2br
			$CHCl_3$	14.0(2.34) 16.5(2.38)
6	Ni(ppp)ClO_4·$3/2H_2O$	3.14	Solid	10.1 13.0 17.0sh
			CH_3NO_2	10.5(0.90) 12.6(0.68) 13.9sh 20.5sh
7	Ni(hep)·$7/2H_2O$	3.19	Solid	11.1 17.0sh
			DMF[e]	11.3(1.10) 17.0sh
8	Cu(hep)·$5H_2O$	1.86	Solid	11.5sh 14.0 17.5sh 24.0sh
			$CHCl_3$	12.0sh 15.5(1.17) 16.7sh 17.9sh
9	Ni(bpa)$(ClO_4)_2$·H_2O	3.11	Solid	10.7 12.2sh 23.0sh
			CH_3NO_2	11.0(0.94) 17.8sh 19.1(1.26)
10	Cu(bpa)$(ClO_4)_2$·$1/2H_2O$	1.86	Solid	12.5sh 15.5
			CH_3CN	12.8sh 15.2(2.30)

[a] Solid = diffuse reflectance spectrum and «solvent» indicates an absorption spectrum. [b] ε = molar extinction coefficient. [c] sh = shoulder and br = broad. [d] The spectrum of the dehydrated complex. [e] DMF = N,N-dimethylformamide.

ca. 1600 and 1400 cm^{-1}, except for those of the complexes of bpa. No band of O-coordinated amide groups was observed.[5] The medium band at *ca.* 1645 cm^{-1} observed for Ni(ppp)ClO_4·$3/2H_2O$, Ni(hep)·$7/2H_2O$, Ni(bpa)$(ClO_4)_2$·H_2O, Cu(hep)·$5H_2O$, and Cu(bpa)$(ClO_4)_2$·$1/2H_2O$, which is not observed for the other complexes, is assigned to ν(C=N) of the azomethine group,[7] since these five complexes have azomethine groups. A very strong broad band at *ca.* 1100 cm^{-1} of the complex perchlorates (Nos. 6, 9, and 10 in Tables I and II) is characteristic of free ClO_4.

Upon dehydration of all the hydrated complexes only the bands of water disappear and no remarkable change of other bands is observed, indicating the retention of the coordination modes of the ligands.

Electronic Spectra and Structure of the Complexes

The magnetic moments of the copper complexes are all normal (Table II) showing no copper–copper interaction. The same diffuse reflectance spectra observed for both the hydrated and the dehydrated copper complexes (Figure 2) suggest the non-coordination of water of crystallization in the solid. The absorption spectra of the copper complexes in chloroform (Figure 3) are identical for the hydrated and dehydrated forms, indicating non-coordination of water molecules in chloroform solution, either.

The molar extinction coefficient (ε) of the ligand field bands of these copper complexes are much larger than those of the six-coordinate copper complexes which are usually less than 100 (Table II). Larger molar extinction coefficients[8] may suggest the five-coordination of the copper complexes studied here, because the ligands used have five donor atoms. The splitting of the intense ligand field bands indicates the lower symmetry and supports also the five-coordination.

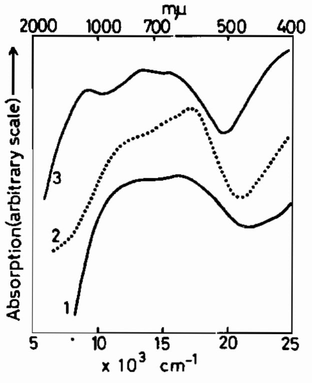

Figure 2. Diffuse reflectance spectra of 1: Cu(pepd)·H_2O, 2: Cu(bppm), and 3: Cu(pmpd)·$2H_2O$.

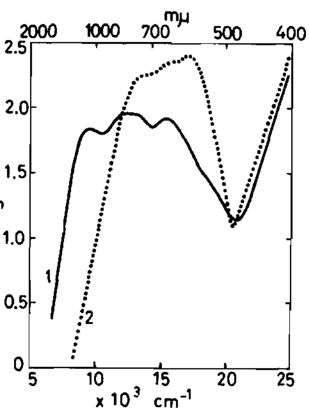

Figure 3. Absorption spectra of chloroform solutions of 1: Cu (pmpd)·$2H_2O$ and 2: Cu(bppm).

It has been shown that an amide group prefers coplanar coordination of the amide-N atom and two donor atoms adjacent to it, namely, meridional coordination of the three donor atoms.[5] If the molecular models are built, there is a fairly larger strain around the amide-N atom (Figure 4B, 2-N) for a square-pyramid than for a trigonal bipyramid. Consequently a trigonal bipyramidal structure seems to be favourable for the ligands studied here, although it is difficult to determine the structure only from the spectral data.[9]

The diffuse reflectance spectra of the hydrated nickel complexes (Figure 5 and Table II) are indicative of six-coordination. The spectra of both Ni(hep)·$7/2H_2O$ and Ni(ppp)ClO_4·$3/2H_2O$ in the solid state, and in N,N-dimethyl-formamide and nitromethane solutions, respectively, are interpreted as those of pseudo-octahedral complexes. The spectra of these two complexes do not appreciably change when dried at 110° C under vacuum.

The diffuse reflectance spectra of Ni(bpp)·$5H_2O$ and Ni(bppm)·$5H_2O$ show a peak and a shoulder in the region of $^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1) (Figure 5). The splitting of ν_1 is indicative of a tetragonal ligand field which may arise from coordination of a weaker field water molecule at the axial site (Figure 4B).[10] Upon dehydration, their spectra change remarkably (Figure 5 and Table II) and they are similar to those in chloroform (Figure 6), indicating similar structures in both states. Non-co-ordination of water molecules in chloroform is confirmed by the identical spectra of the hydrated and dehydrated forms.

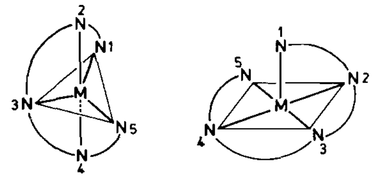

Figure 4. Two possible structures of five-coordination.

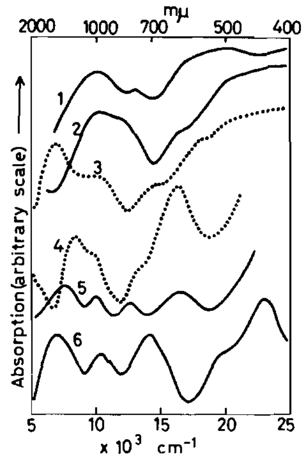

Figure 5. Diffuse reflectance spectra of 1: Ni(ppp)ClO_4·$3/2H_2O$, 2: Ni(bppm)·$5H_2O$, 3: the anhydride of 2, 4: Ni(H-Sal-MeDPT), 5: Ni(5-Cl-Sal-en-NEt_2)$_2$, and 6: [Ni (Me_6tren)Br]Br.

For comparison some typical spectra of five-coordinate nickel(II) complexes reported[1] are shown in Figure 5, where H-Sal-MeDPT is bis 3-(2-hydroxybenzylideneamino)propylmethylamine[11], 5-Cl-Sal-en-N$(Et)_2$ is 2-(2-hydroxy-5-chlorobenzylideneamino)-ethyldiethylamine[12], and Me_6tren is tris(2-dimethylaminoethyl)amine.[13] The spectra of the two acid amide complexes (Nos. 1 and 2 in Table II) in the anhydrous state and in chloroform are similar to that of Ni(H-Sal-MeDPT) studied by Sacconi *et al.*[14], which has an intermediate structure between a trigonal bipyramid and a square pyramid. The similarity of the spectra supports the five-coordination of the nickel

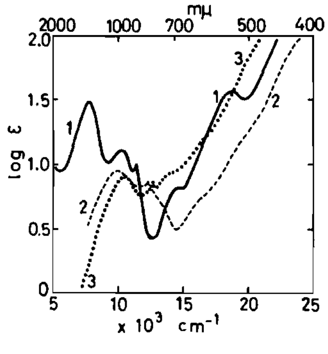

Figure 6. Absorption spectra of 1: Ni(bppm)·$5H_2O$ in chloroform, 2: Ni(bpp)·$5H_2O$ in water, and 3: Ni(ppp)ClO_4·$3/2H_2O$ in nitromethane.

complexes of $bppH_2$ and $bppmH_2$ in chloroform solution and in the anhydrous solid state. The band shifts found may be due to the difference in the ligand field strengths and structures of the acid amide and the Schiff base ligands.

It is interesting that no five-coordinate nickel complexes are obtained with pppH which has a similar skeletal structure to that of $bppH_2$. The former ligand has one amide group and one azomethine group instead of the two amide groups of the latter. The ligand pppH formed an octahedral complex $Ni(ppp)ClO_4 \cdot 3/2H_2O$. The Schiff base, bpa, with a similar skeleton to that of $bppH_2$ forms only octahedral complexes, $Ni(bpa)X_2 \cdot H_2O$ ($X = ClO_4$ or PF_6).[7] In these complexes, the water molecule at the sixth site of the octahedron can not be removed without decomposition, whereas water of crystallization of $Ni(bpp) \cdot 5H_2O$ and $Ni(bppm) \cdot 5H_2O$ is easily released. These facts show that six-coordination of nickel(II) is destabilized by the coordination of the deprotonated amide-N atoms. The reason may be the strong planarity and ligand field of an acid amide group[5] which favour the trigonal bipyramidal arrangement.

Acknowledgement

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