Monatshefte für Chemie 112, 1113—1121 (1981)

**Monatshefte für Chemie**

# Deprotonated and Non-Deprotonated Cobalt(II) Complexes of the Bis-amide Tetradentate Ligand N,N′-(Dipicolyl)-1,8-naphthylene Diamine. Three Different Modes of Coordination by the Ligand

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*(Received 8 October 1980. Accepted 20 October 1980)*

The preparation and some properties of the cobalt(II) complexes $Co(LH_2)Cl_2 \cdot 2H_2O$, $Co(LH_2)(NCS)_2$ and $CoL \cdot H_2O$ (where $LH_2$ = N,N′-(dipicolyl)-1,8-naphthylenediamine) are reported. On the basis of magnetic moments, visible reflectance and IR data, the structure is proposed to be pseudo-octahedral for $Co(LH_2)Cl_2 \cdot 2H_2O$, pseudo-tetrahedral for $Co(LH_2)(NCS)_2$ and square planar for $CoL \cdot H_2O$.

*[Keywords: Bis-amide tetradentate ligand; Deprotonated complexes; N,N′-(Dipicolyl)-1,8-naphthylenediamine; I.R.]*

### *Deprotonierte und Nicht-deprotonierte Co(II)-Komplexe des vierzähnigen Bis-amid-Liganden N,N′-(Dipicolyl)-1,8-naphthyldiamin. Drei verschiedene Koordinationstypen*

Es werden die Darstellung und einige Eigenschaften der Kobalt(II)-Komplexe $Co(LH_2)Cl_2 \cdot 2H_2O$, $Co(LH_2)(NCS)_2$ und $CoL \cdot H_2O$ [$LH_2$ = N,N′-(dipicolyl)-1,8-naphthylendiamin] diskutiert. Auf der Grundlage von magnetischen Momenten, von Daten der sichtbaren Reflektions- und IR-Spektren wird eine pseudooctaedrische Struktur für $Co(LH_2)Cl_2 \cdot 2H_2O$, eine pseudotetraedrische für $Co(LH_2)(NCS)_2$ und eine planar-quadratische für $CoL \cdot H_2O$ vorgeschlagen.

## Introduction

Many studies have been made on the cationic and non-ionic complexes of several secondary 2-picolinamides[1,2]. It has been shown that deprotonated amide groups coordinate readily to transition metal ions through the amide-N atom forming a very stable delocalized electronic system, while coordination of the neutral 2-picolinamides occurs either through the amide-N or through the amide-O atom.

0026-9247/81/0112/1113/$ 01.80

Most research on metal secondary amide complexes has been limited to those containing one amide group per molecule of ligand; exceptions are Ref.[2,3]. In a previous publication[4] we reported the synthesis of N,N′-(dipicolyl)-1,8-naphthylenediamine ($LH_2$-Fig. 1). $LH_2$ has interesting ligating possibilities because a) it has six donor atoms, hence it is a potential hexadentate ligand and b) the protons on the N-atoms can be removed and deprotonated complexes prepared. We also prepared and studied the complexes Cu$L$ and Ni$L$[4]; the deprotonated ligand acts as a tetradentate, $N_4$, system.

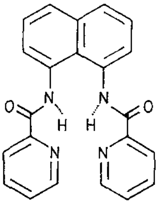

Fig. 1. The ligand N,N′-(dipicolyl)-1,8-naphthylenediamine

Since recently there has been some debate[3,5] over the coordination site of secondary amide groups, it is interesting to study the mode of bonding of the above ligand to cobalt(II).

## Experimental

$LH_2$ was prepared as described previously[4].

### $Co(LH_2)Cl_2 \cdot 2\,H_2O$ *and* $Co(LH_2)(NCS)_2$

To a vigorously stirred, warm solution of 1.0 g $LH_2$ (2.7 mmol) in absolute ethanol (60 ml) was added dropwise 2.7 mmol $CoX_2$ ($X$ = Cl, SCN) dissolved in warm absolute ethanol (30 ml). Precipitates were immediately obtained. After the addition of 50 ml of absolute ethanol, the reaction mixtures were refluxed for 30 min. The precipitates were filtered off after cooling to room temperature, washed with ethanol (3 x 10 ml), acetone (4 x 5 ml) and ether (2 x 5 ml) and finally dried over $P_4O_{10}$ in vacuum to yield 1,16 g of pink $Co(LH_2)Cl_2 \cdot 2\,H_2O$ (81%) and 1.32 g of blue $Co(LH_2)(NCS)_2$ (90%), respectively.

### $CoL \cdot H_2O$

A warm ethanolic solution (70 ml) of 1.0 g of $LH_2$ (2.7 mmol) was mixed with a warm aqueous solution (50 ml) of 0.35 g of $CoCl_2$ (2.7 mmol). To the solution obtained an aqueous solution (20 ml) of 0.21 g of NaOH (5.3 mmol) was added dropwise, under vigorous stirring. A brown precipitate was immediately obtained. The precipitate was filtered off after 5 h, washed and dried as described above to yield 0.50 g of the desired product (42%).

Magnetic susceptibilities in the solid state were measured at room temperature by the *Faraday* method, using a Cahn-Ventron balance, model RM-2. Mercuric tetrathiocyanato-cobaltate(II) was used as the magnetic susceptibility standard. Diamagnetic corrections were effected using *Pascal's* constants. The visible diffuse reflectance spectra (750–400 nm) of the finely powdered solids were recorded on a Bausch Lomb-Shimadzu Spectronic 210 UV spectrophotometer, fitted with a standard reflectance attachment and spectroscopic grade MgO in the reference beam, at room temperature.

The other physical measurements were carried out as previously reported[6]. The conductivity of the solutions was measured within 10 min of dissolution.

## Results and Discussion

The prepared complexes (Table 1), which gave satisfactory elemental analyses, are crystalline and stable in the normal laboratory atmosphere. They are insoluble in nonpolar solvents, alcohols and $C_6H_5NO_2$, slightly soluble in $H_2O$ and $CH_3NO_2$, and soluble in *DMF* and *DMSO*; they decompose in dilute mineral acids.

From the $\Lambda_M$ values obtained, we can conclude that $CoL \cdot H_2O$ is a non-ionic complex. For the chloride or thiocyanate ions in $Co(LH_2)X_2$ to be not coordinated, the non-deprotonated complexes would have abnormally low $\Lambda_M$ values in both solvents[7]. On the other hand, a non-ionic formulation cannot be ruled out because *DMF* and *DMSO* have strong donor capabilities, which frequently lead to displacement of anionic ligands and change of the electrolyte type[8].

Both the magnetic[9,10] and visible reflectance[10,11] data indicate that $Co(LH_2)Cl_2 \cdot 2\,H_2O$ has a pseudo-octahedral high-spin configuration, while $Co(LH_2)(NCS)_2$ has a pseudo-tetrahedral structure. The deprotonated complex has $\mu_{eff} = 2.89$ B.M. consistent with a square planar stereochemistry on cobalt[9,10]. Planar cobalt(II) complexes normally have magnetic moments in the range of 2.4–2.9 B.M.[9], as a result of the large orbital contribution[12]. Square planar low-spin cobalt(II) complexes can be classified into complexes of the $(d_{z^2})^1$ ground state and those of the $(d_{yz})^1$ ground state[13]. An absorption maximum at 470 nm is attributed to a transition from low-lying filled d-orbitals to the empty $d_{x^2-y^2}$ $\sigma$ antibonding orbital[13]. However, this band could also be attributed to a transition from the ligand $\pi$-orbitals to the metal $d_{yz}$ orbital[14].

Table 2 gives some characteristic and diagnostic IR bands of the complexes. In general, the spectra are very complex, but a careful study can lead to fairly important structural conclusions.

In the $\nu$ O—H region the spectrum of $Co(LH_2)Cl_2 \cdot 2\,H_2O$ exhibits medium, relatively sharp maxima at 3 535 and 3 440 cm$^{-1}$, attributable to the presence of coordinated water molecules[15]. In the spectrum of

Table 1. $\Lambda_M$ *values, effects of heat, magnetic moments and visible reflectance spectral properties of the complexes*

| Complex | $\Lambda_M^a$/S cm$^2$ mol$^{-1}$ |  | Effect of Heat/°C | $\mu_{eff}$/B.M. | $\lambda_{max}$/nm | Assignments[b] | Comments |
|---|---|---|---|---|---|---|---|
|  | *DMF* | *DMSO* |  |  |  |  |  |
| $Co(LH_2)Cl_2 \cdot 2\,H_2O$ | 28 | 42 | no visible change till 295, decomposes between 300–320 | 4.75 | 559<br>491 sh | $^4T_{1g}(F) \rightarrow {}^4A_{2g}$<br>$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ | pseudo-octahedral |
| $Co(LH_2)(NCS)_2$ | 51 | 47 | no visible change till 200, decomposes above 205 | 4.19 | 623, 586, 568 sh<br>512, 474 | $^4A_2 \rightarrow {}^4T_1(P)$<br>spin-forbidden and charge-transfer | pseudo-tetrahedral |
| $CoL \cdot H_2O$ | 2 | 3 | darkens above 80, decomposes above 295 | 2.89 | 470 v.b. |  | square planar |

[a] Values of molar conductance for ca. $10^{-3} M$ solutions at 25 °C (the compounds were assumed to be monomeric).

[b] The spectra are interpreted and assigned on the basis of simple ligand field considerations for a $d^7$ ion in octahedral and tetrahedral fields. sh = shoulder, v.b. = very broad.

Table 2. *IR Spectral assignments*[a, b] *of bands* (*cm*$^{-1}$) *of diagnostic value for the complexes*

| Compound | ν N—H | Amide Bands I | II | III | V | δ(*Py*)[e] | δ(*Py*)[f] |
|---|---|---|---|---|---|---|---|
| $LH_2$ | 3285 s | 1669 vs | 1519 m | 1278 m, 1238 m | 658 s, b | 622 m | 410 m |
| $Co(LH_2)Cl_2 \cdot 2\,H_2O$ | 3160 m, b | 1630 vs | 1539 s | 1310 s, 1272 s | 663 m | 642 m, 629 w | 421 m |
| $Co(LH_2)(NCS)_2$[g] | 3330 m, b | 1673 s | 1550 m | 1308 m | 662 s | 644 w | |
| | 3225 m, b | 1635 vs | 1525 m | 1270 m, 1237 w | | 623 m | 411 m, b |
| $CoL \cdot H_2O$ | [c] | 1622 m | [d] | [c] | [c] | 639 w | 415 w |

[a] Tentative assignments.

[b] From Refs.[1–3,5,16,18].

[c] Absent.

[d] Not assigned.

[e] In-plane ring deformation.

[f] Out-of-plane ring deformation.

[g] The spectrum of this complex exhibits ν C—N at 2075 (vs), δ (NCS) at 482 (m) and ν Co—NCS at 308 (m) and 282 (w) cm$^{-1}$; the ν C—S mode is obscured by the ligand bands. vs = very strong, s = strong, m = medium, w = weak, b = broad.

Co$L \cdot H_2O$ a very broad continuous absorption, covering the whole 3 550-3 150 cm$^{-1}$ region, indicates that lattice water is present[15].

The spectrum of $LH_2$ shows (Table 2) the characteristic bands of a secondary hydrogen-bonded acid amide[16].

As would be expected, the N—H stretching band is absent in the deprotonated complex. The ν N—H bands, which are present in the spectra of Co($LH_2$)$Cl_2 \cdot 2\,H_2O$ and Co($LH_2$) $(NCS)_2$, suggest coordination of the ligand without deprotonation of the amidic hydrogens. The shift of this band to lower frequencies may indicate coordination of theeaide-N atoms; however, this decrease in ν N—H could also be due to stronger hydrogen bonding to the anions or O-atoms by the amidic hydrogens, when compared to the hydrogen bonding in the pure ligand. The band at 3 330 cm$^{-1}$ in the spectrum of Co($LH_2$) $(NCS)_2$ probably indicates the presence of an uncoordinated amide group.

The data reveal that the amide I, II, and III bands of Co($LH_2$)$Cl_2 \cdot 2\,H_2O$ shift towards the region expected for the amide O-coordination[1,5]*. Co($LH_2$) $(NCS)_2$ shows absorption bands indicative of both coordinated and uncoordinated amide groups[3].

The in-plane and out-of-plane deformation bands of the pyridine ring occur at 622 and 410 cm$^{-1}$, respectively, for free $LH_2$. For our three complexes they shift to higher frequencies, indicative of coordination to cobalt(II)[18]. The bands at 623 and 411 cm$^{-1}$ in the spectrum of Co($LH_2$) $(NCS)_2$ indicate that one of the two pyridine rings is not coordinated[19]; this is also supported by the splitting of the mid-IR spectral bands due to the pyridine groups[20]. Bands due to Co—N (*Py*) stretching vibrations appear below 250 cm$^{-1}$ (the low frequency limit of the instrument used)[21].

The NCS groups in Co($LH_2$) $(NCS)_2$ seem to be coordinated via the N-atom, since ν C—N and δ(NCS) are observed in the regions expected for N-coordination[6]. ν C—N at 2 075 cm$^{-1}$ indicates the absence of bridged —SCN— groups or free thiocyanate ions.

The bands at 308 and 282 cm$^{-1}$ are assigned to ν Co—NCS. These frequencies are consistent with a tetrahedral environment around cobalt(II)[22]. The complex probably belongs to the symmetry group $C_{2v}$, which requires two ν Co—NCS to be IR active. No strong bands, which would be assigned to Co—Cl stretching modes are observed above 250 cm$^{-1}$ in the spectrum of the chloro complex.

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* However, *Farona* et al.[17] have shown that the positions of the ν N—H, amide I, II and III bands do not provide unequivocal evidence for the nature of the metal-amide bond and the observed shifts in frequency constitute only very tenuous evidence on which to base a clear structural conclusion.

## Conclusions

A square planar geometry is most likely for the deprotonated complex (Fig. 2*a*). Deprotonation would lead to a planar system having a considerable degree of electron delocalization. This mode of coordination is similar to that found by other workers[3,23].

For complexes of neutral amides, several structural possibilities exist. Some authors believe that O-coordination is more favoured than N-coordination[1,5,19,24]. Examples of neutral N-coordinated amide complexes have been reported[3,24,25]. Most of those workers have proposed an "iminol" form, with the proton bonded to the O-atom; this form of some acid amides may be stabilized on coordination to certain metal ions. The "iminol" form coordination of an amide group seems to be an intermediate for deprotonated N-coordination[26].

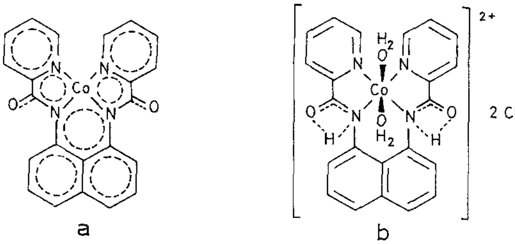

Fig. 2. The most probable structural arrangements for *a* $CoL \cdot H_2O$ and *b* $Co(LH_2)Cl_2 \cdot 2\,H_2O$

In the case of our ligand, cobalt(II) does not promote amide deprotonation on coordination. In $Co(LH_2)Cl_2 \cdot 2\,H_2O$, $LH_2$ acts as a tetradentate ligand. In $Co(LH_2)(NCS)_2$, $LH_2$ shows a bidentate behaviour, being coordinated through one amide group and one ring-N atom. A coordination behaviour employing the two amide-O atoms would involve a decrease in the potential chelating ability of $LH_2$[3]. Hence, in the octahedral chloro complex a $N_4$ function would be expected (Fig. 2*b*). However, on the basis of the IR evidences alone, a $N_2O_2$ function of $LH_2$ cannot be ruled out. It is feasible[3] that the amidic hydrogen is involved in hydrogen bonding between both amide-N and amide-O atoms, but chloride ions or water molecules may also be involved.

The iminol form of coordination is ruled out in our non-deprotonated complexes, because of the non-appearance of the $\nu\,C = N$ and $\nu\,C—O$ bands[24].

## Acknowledgements

Financial support from the Foundation "Alexandros Onasis" is gratefully acknowledged. We thank Dr. *J. Mantzos* of the National Hellenic Research Foundation for the microanalyses.

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