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Complexes of N,N′-bis-(aceto-glucose)-ethylenediamine with Cu(II), Ni(II) and Co(II)

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Introduction

In an earlier paper [1] we reported the preparation of N,N′-bis-(aminobenzyl)-ethylenediamine and its complexes with Cu(II) and Ni(II). These complexes are very important for the control of various pathogenic fungi. Following these investigations we have tried to react bromo-acetoglucose with ethylene diamine in order to prepare and investigate the Cu(II), Ni(II) and Co(II) complexes of the resulting compound. The investigation was carried out using IR, ESR, and electron spectroscopy. Magnetic measurements and elemental analysis completed the experimental data. The results suggest that the amido group, as well as the oxygen atom of the six-membered ring of acetoglucose, are coordinated with the metal.

Experimental

The starting substances were purchased by Fluka and Merck companies and their purity was of 'puriss' and 'pro analisi' grade. IR spectra of the prepared compounds were taken on KBr tablets with a Perkin-Elmer Mod. 521 instrument and the UV spectra with a Zeiss Ikon model RP 020A apparatus. For ESR-spectra a Varian E-4 instrument was used. The decomposition point was not corrected.

N,N′-bis-(acetoglucose)-ethylenediamine (AGAD). (1)

0.02 mol (8.22 g) of acetobromoglucose were dissolved in 100 ml of absolute chloroform and 0.03 mol (1.83 g) of ethylenediamine were added dropwise with vigorous stirring and exclusion of moisture. During the addition the solution was cooled with ice-water mixture. After completion of ethylenediamine addition the reaction mixture was heated for an hour at the boiling temperature, under a reflux condenser. A white precipitate was gradually formed, which was identified by means of thin layer chromatography as the ethylenediamine hydrochloride.

The whole mixture was allowed to cool overnight and was then filtered. The chloroform was vacuum evaporated and an oily residue remained which was then treated with ethanol and acetone. By this action white crystals were separated, which were suitable for elemental analysis. The solid substance was vacuum-dried for two days at 50 °C. M.P.: 67–68 °C. Yield: 4.744 g. (80% of the theoretical). The molecular weight of the compound, measured by routine processes, was found to be 752.

Anal. Calc.: C, 47.8, N, 3.8; O, 4.2; H, 5.8.
Found.: C, 47.1; N, 3.2; O, 4.5; H, 5.5%.

(N,N′-bis-(aceto-glucose)-ethylenediaminato)-Cu(II) chloride (2)

5.9 g (0.01 mol) of (1) were dissolved in 50 ml of absolute chloroform and 1.5 g (0.01 mol) of anhydrous $CuCl_2$ were suspended in the same solvent. The whole mixture was vigorous stirred for 2 days at room temperature. A blue green precipitate was formed which was well washed with warm absolute ethanol. The precipitate obtained was dried at 80 °C. Decomposition point: 165–168 °C. Yield: 7.17 g (98% of the theoretical).

Anal. Calc.: C, 40.6; N, 3.1; Cu, 7.2; H, 4.9.
Found.: C, 40.0; N, 2.9; Cu, 7.0; H, 4.7%.

(N,N′-bis-(aceto-glucose)-ethylenediaminato)-Ni(II) chloride (3)

11.2 g (0.01 mol) of (1) were dissolved in 50 ml of absolute chloroform and 1.4 g of anhydrous $NiCl_2$ were suspended in the same solvent. The whole mixture was vigorously stirred for 1 hour at room temperature. A light violet precipitate was formed, which was treated with absolute ethanol–acetone (1:1). The precipitate was dried at 80 °C. Decomposition point: 142–146 °C. Yield: 13.03 g (98% of the theoretical)

Anal. Calc.: C, 33.0; N, 3.4; Ni, 3.4; H, 5.4.
Found.: C, 33.1; N, 3.1; Ni, 3.4; H, 5.1%.

(N,N′-bis-(acetoglucose)-ethylenediaminato)-Co(II) chloride (4)

2.4 g (0.01 mol) of $CoCl_2 \cdot 6H_2O$ were dissolved in 50 ml ethanol and 11.9 g (0.02 mol) of (1) were added under stirring. The whole mixture was vigorously stirred for 72 hours. A pink red precipitate was formed, which was washed well with chloroform. This precipitate was vacuum dried for 24 hours. Decomposition point: 132–134 °C. Yield: 7.27 g (55% of the theoretical).

Anal. Calc.: C, 33.0; N, 3.4; Co, 3.4; H, 5.4.
Found.: C, 32.8; N, 3.2; Co, 3.3; H, 5.3%.

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TABLE I. Characteristic IR Frequencies of the Complexes.

AGAD·$CuCl_2$	$(AGAD)_2NiCl_2$	$(AGAD)_2CoCl_2$	Assignment	
3240	3232	3240	ν-NH-	s
2115	2100	2110	ν-$\overset{+}{N}$H-	s
1620	1650	1630	ν-C=O	s
1570	1610	1610	δ-NH-	s
529	520	460	ν(M–O) + ν(C–C)	s
475	490	498	ν(M–N)	m
370	–	364	ν(M–O)	m
310	315	322	ν(M–Cl)	m

The IR spectra of compound (1) to (4) are listed in Table I.

Results and Discussion

Compound (2) shows the stretching vibrations of complexed aliphatic amido group at 3240 cm^{-1}. A widening of this band, a simultaneous shift to lower frequencies and a reduction of intensity were observed. The same changes were observed in the IR-spectrum of N,N′-bis-(*o*-aminobenzyl)-ethylenediamine after complexation with $CuCl_2$ and $NiCl_2$ [1]. A δ_{NH} vibration likewise appears at about 1570 cm^{-1} as an intense band, suggesting a coordination with Cu(II). In the range between 500 cm^{-1} and 350 cm^{-1} where the N–Cu stretching vibrations probably occur, a very intensive absorption is found at 475 cm^{-1}. A band at *ca.* 370 cm^{-1} can be probably attributed to O–Cu vibration. On the basis of elemental analysis, as well as the ESR spectra and magnetic measurements, we can consider the possible coordination of Cu(II) with the two nitrogen atoms of ethylenediamine and with the two oxygen atoms of two opposite standing acetate groups of aceto-glucose, so that the complex shows the structure of a distorted octahedron.

For the compound (3) the absorption at *ca.* 3232 cm^{-1} leads us to conclude that it belongs to the coordinated amido groups. The δ_{NH} vibration is shifted to 1610 cm^{-1}. In the range 500–350 cm^{-1}, the N–Ni stretching vibration of the compound (3) probably appears, specifically at 490 cm^{-} [2]. No O–Ni vibration was observed and this, along with the analytical data, leads us to conclude that Ni(II) is coordinated with two organic ligands through the two nitrogen atoms of ethylenediamine and that the complex has a planar structure with the two chlorine atoms in ionic form. The same is true for compound (4), in which the 3240 cm^{-1} vibration belongs to the coordinated amido group [3] as well as for the 498 cm^{-1} vibration, where the probable stretching vibration of Co–N appears.

From the ESR spectra we conclude that the Cu-complex has a distorted octahedral structure (Fig. 1).

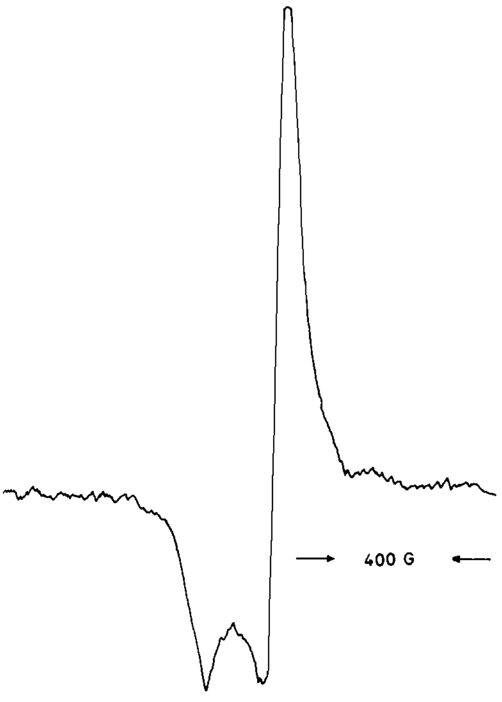

Fig. 1. ESR of Cu complexes.

Its λ_{max} for the d–d transition corresponds to the value of 520 nm. Its ESR parameters are $g// = 2.221$ and $g\perp = 2.051$. These values correspond to a d^9 electron configuration.

The bands of Cu(II)-complex in the electronic spectrum lead to the conclusion that the complex shows a smaller tetragonal distortion from the octahedral symmetry. We must suppose that the bands cited in Table II, on the basis of Tanabe–Sugano diagram, belongs to the $^2A_{1g} \leftarrow {}^2B_{1g}$, $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_{1g} \leftarrow {}^2B_{1g}$ electron transitions.

Contrary to the Cu(II)-complex, the Ni(II)-complex gives no ESR spectrum. Magnetic measurements prove a low-spin configuration, so that the structure of the complex is probably planar and we must identify it as $(Ni(AGAD)_2)\cdot Cl_2$.

From the electronic spectra we can deduce that there are three spin-permitted transitions; thus, we

TABLE II. Electronic Spectra and Magnetic Moments of Complexes (2), (3) and (4).

Complex	Frequency (cm^{-1})	Magnetic Moments (B.M. 20 °C) Calc.	Found
(2)	10282, 15580, 25500	1.82	1.73
(3)	11100, 18540, 30000	2.86	2.83
(4)	8400, 14520, –	1.71	1.73

can attribute the bands observed in the spectrum to the following transitions [5]:

${}^3A^2{}_g \to {}^3T_{2g}$, ${}^3A_{2g} \to {}^3T_{1g}(F)$, ${}^3A_{2g} \to {}^3T_{1g}(P)$

In the case of Co(II)-complex, since the $t_{2g}^6e_g^1$ configuration implies a high Jahn-Teller distortion, we must not expect a strict octahedral structure. Strictly speaking, the situation is rather complicated and not completely clear.

From the electronic spectra, which are fairly weak and lie in the blue region of the spectrum, we conclude that there are three spin-permitted d–d transitions to suggest, specifically the

${}^4T_{1g}(F) \to {}^4T_{2g}$, ${}^4T_{1g}(F) \to {}^4A_{2g}$, ${}^4T_{1g}(F) \to {}^4T_{1g}(P)$

Nevertheless, since the ${}^4A_{2g}$ term is derived from a $t_{2g}^3e_g^4$ configuration, while the ${}^4T_{1g}(F)$ term is derived principally from the $t_{2g}^5e_g^2$ configuration, the ${}^4T_{1g}(F) \to {}^4A_{2g}$ transition implies a two-electron process and must be less intensive (by 10^{-2}) than other transitions. This smaller intensity, along with the close neighborhood of the ${}^4T_{1g}(F) \to {}^4T_{1g}(P)$ bands, is the reason why the ${}^4T_{1g}(F) \to {}^4A_{2g}$ transition fails to appear [6]. According to these results we can ascribe as possible the structure

$(Co(AGAD)_2 \cdot (H_2O)_4)Cl_2$

The ESR spectrum of Co(II)-complex shows an anisotropy, which is the cause of an hyperfine structure. No anisotropy of g-factor was observed at room temperature. The g-Factor was experimentally calculated to 2.1414 (Fig. 2).

The observed magnetic moments were obtained with the Guy balance; Table II shows the values for some complexes.

The magnetic moment that has been found for compound (2) is increased, through spin-spin coupling, in comparison with the true spin value and is typical for Cu(II)-complexes.

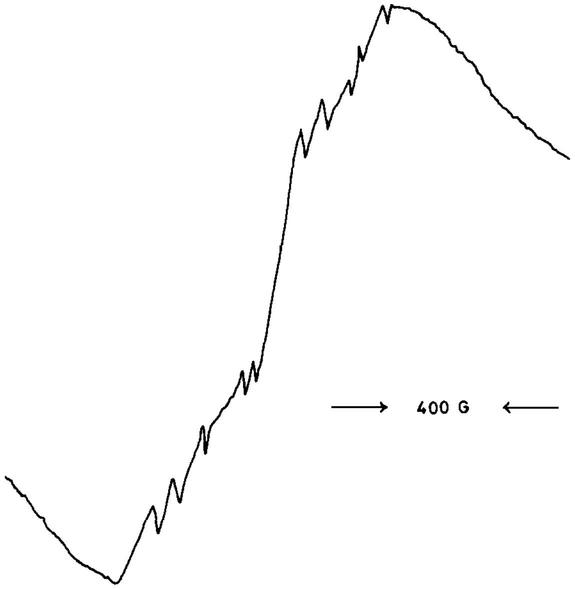

Fig. 2. ESR of Co complexes.

The magnetic moment being found for Ni-complexes agrees with the value expected for 'low-spin' in the planar Ni(II)-compounds [7]. A certain increase is observed, because of spin–spin coupling.

In the case of the Co(II)-compound the magnetic moment matches with the value expected for 'low-spin.'

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