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Synthesis and Characterization of Spin-Free $[Co_2(N,N'$-Tetra(4-antipyrylmethyl)-1,2-diaminoethane)$Cl_4]$

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Summary. The ligand N,N′-tetra(4-antipyrylmethyl)-1,2-diaminoethane (*TAMEN*) coordinates to two Co(II) ions and forms the tetrahedral homodinuclear complex $[Co_2(TAMEN)Cl_4]$. In methanol, the complex shows a weak absorbtion spectrum with a maximum at 515 ± 0.5 nm and a molar absorbtivity of $40.0 \pm 1.0\ l \cdot mol^{-1} \cdot cm^{-1}$. Variable temperature spectra (282 to 323 K) show no changes of this band and suggest the absence of thermochromicity. The magnetic moments amount to 4.93 to 5.00 μ_B at the temperature range of 232 to 329 K, demonstrating the complex to be spin-free in methanol.

Keywords. N,N′-Tetra(4-antipyrylmethyl)-1,2-diaminoethane (*TAMEN*); Homodinuclear complex; Tetrahedral symmetry; Spin-free state.

Synthese und Charakterisierung von spinfreiem $[Co_2(N,N'$-Tetra(4-antipyrylmethyl)-1,2-diaminoethan)$Cl_4]$

Zusammenfassung. N,N′-Tetra(4-antipyrylmethyl)-1,2-diaminoethan (*TAMEN*) koordiniert mit zwei Co(II)-Ionen zum tetraedrischen homobinuklearen Komplex $[Co_2(TAMEN)Cl_4]$. In Methanol zeigt der Komplex ein schwaches Absorptionsspektrum mit einem Maximum bei 515 ± 0.5 nm und einer molaren Extinktion von $40.0 \pm 1.0\ l \cdot mol^{-1}\ cm^{-1}$. Aufnahmen bei veränderlicher Temperatur (282 bis 323 K) bewirken keine Änderung dieser Bande, woraus auf fehlende Thermochromie geschlossen wird. Die magnetischen Momente im Temperaturbereich von 232 bis 329 K betragen 4.39 bis 5.00 μ_B; daraus resultiert, daß die untersuchte Verbindung keinen Spin hat.

Introduction

Recently, it has been reported that N,N′-tetra(4-antipyrylmethyl)-1,2-diaminoethane (*TAMEN*; antipyryl- = 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one) bridges two metal(II) centers such as Cu, Fe, Co, and Ni as a double-terdentate ligand and forms homodinuclerar complexes of the general formula $[M_2(TAMEN)Cl_4]$ [1]. Complexes of N,N′-*bis*(antipyrylmethyl)piperazine (*AMP*) with these metal ions have been synthesized and investigated in detail [2–4]. Considerable interest results from the fact that the antitumor and antipyretic properties of antipyrine compounds are influenced by interactions with metal ions [1, 5–7]. However, temperature affects the metal-ligand interactions and causes a change in their spin multiplicity [8–10]. In view of this consideration, it was planned to synthesize the complex of Co(II) with N,N′-tetra(4-antipyrylmethyl)-1,2-diaminoethane (*TAMEN*) and to characterize it by UV/Vis and ^{1}H NMR spectroscopy over the temperature range of 230 to 330 K in methanol.

Results and Discussion

The analytical data listed in the experimental section confirm the formation of homodinuclear [Co_2(*TAMEN*)Cl_4]. It has been reported that the blue color is attributable to the formation of tetrahedral 4-coordinated complexes of Co(II) [15]. These are often formed when the Co(II)-ligand bond is rather weak and ionic and when the ligand is bulky (interligand repulsion favors a tetrahedral geometry) [15]. The UV/Vis absorption spectra of [Co_2(*TAMEN*)Cl_2] obtained over the temperature range of 281.9 to 327.6 K in methanol and the spectroscopic data are listed in Table 1. To avoid dissociation of the complex usually observed at high temperature the spectra were run in presence of excess ligand. In fact, the identical spectroscopic data for heating and cooling demonstrate the complex to be quite stable in methanol under the experimental conditions.

Table 1. UV/Vis spectroscopic data of [Co_2(*TAMEN*)Cl_4] ($3.0426.10^{-4}$ *M*) with excess ligand at different temperatures in MeOH

T (K)	λ_{max} (nm)	ε (514 nm) ($l \cdot mol^{-1} \cdot cm^{-1}$)
281.9[1]	514.0	39.25
283.7	514.0	39.33
287.0	514.5	39.48
290.5	514.5	39.64
294.1	515.0	39.48
297.9	515.0	39.99
301.8	514.0	39.85
305.8	515.0	40.38
310.1	514.0	40.93
314.0	515.0	41.13
318.2	515.0	41.34
323.2	515.0	41.94
327.6	515.5	41.84
319.5[2]	514.5	41.75
311.4	515.5	41.33
303.5	514.5	40.93
296.2	514.0	40.24
289.2	514.5	39.91
282.2	513.5	39.26

[1] Start of heating; [2] start of cooling

The spectra of the complex show a weak absorbtion band (absorbtion maximum: 515 ± 0.5 nm; molar absorbtivity: $\varepsilon_{max} = 40.0 \pm 1.0\ l\cdot mol^{-1}\cdot cm^{-1}$) in methanol. Various bands at 680 nm ($625\ l\cdot mol^{-1}\cdot cm^{-1}$), 605 nm ($280\ l\cdot mol^{-1}\cdot cm^{-1}$), and 530 nm ($52\ l\cdot mol^{-1}\cdot cm^{-1}$) visible in *DMF* are assigned to different $^4A \rightarrow {}^4T$ electronic transitions which are characteristic for Co(II) in a C_{2v} *pseudo*-tetrahedral environment [1, 16]. Obviously, the bulkiness of the ligand prevents the formation of a six-fold coordination. An intense broad absorbtion ($\lambda_{max} = 430$ nm, $\varepsilon_{max} = 820\ l\cdot mol^{-1}\cdot cm^{-1}$) of the Cu complex in *DMF* can be attributed to charge transfer ($^4A \rightarrow \pi^*$) [1]. This band is not detected for the Co(II)-analogue. The results suggest that *TAMEN* bridges the two Co(II) centers *via* two groups of donor atoms, each containing two carbonyl oxygens and one amino nitrogen atom. Doing so, *TAMEN* acts as a double-terdentate with respect to coordination to Co(II) and yields a tetrahedrally coordinated homodinuclear complex of $[Co_2(\mathit{TAMEN})Cl_4]$ [1]. However, the tetrahedral *bis*-complex of Co(II) with *L*-histidine shows absorbtion spectra with a maximum at 558 nm ($\varepsilon_{max} = 320\ l\cdot mol^{-1}\cdot cm^{-1}$) in 1 *M* aqueous NaOH [17]. Increase of temperature causes no changes in absorbtion maxima and molar absorbtivities, strongly suggesting the absence of thermochromicity of the complex in methanol [15].

Magnetic moments of $[Co_2(\mathit{TAMEN})Cl_4]$ were measured using *Evans* method [11] at the temperature range of 230 to 330 K in methanol; the results are summarized in Table 2. Magnetic susceptibilities (χ_{exp}) and magnetic moments (μ) per metal ion were calculated from Eqs. (1) and (2) where $\Delta\Delta\nu$ (in ppm) is the paramagnetic shift of a reference compound and [*M*] is the molarity of the paramagnetic ion.

$$\chi_{exp} = (3\Delta\Delta\nu \cdot 0.001/4\pi \cdot [M]) \tag{1}$$

$$\mu_{exp} = 2.84\sqrt{(\chi \cdot T)} \tag{2}$$

All measurements were made in presence of excess ligand to avoid dissociation of the complex. The magnetic moments are found to be 4.93 to 5.00 μ_B at the temperature range of 232 to 329 K (Table 2, Fig. 1) which is characteristic of the

Table 2. Magnetic moments per metal ion of $[Co_2(\mathit{TAMEN})Cl_4]$ ($3.0426\cdot10^{-4}$ *M*) with excess ligand at different temperatures in MeOH

T (K)	μ (μ_B)
231.95	4.933
242.60	4.936
252.83	4.935
263.09	4.939
273.44	4.945
283.86	4.947
294.19	4.958
306.01	4.968
317.77	4.980
329.07	5.001

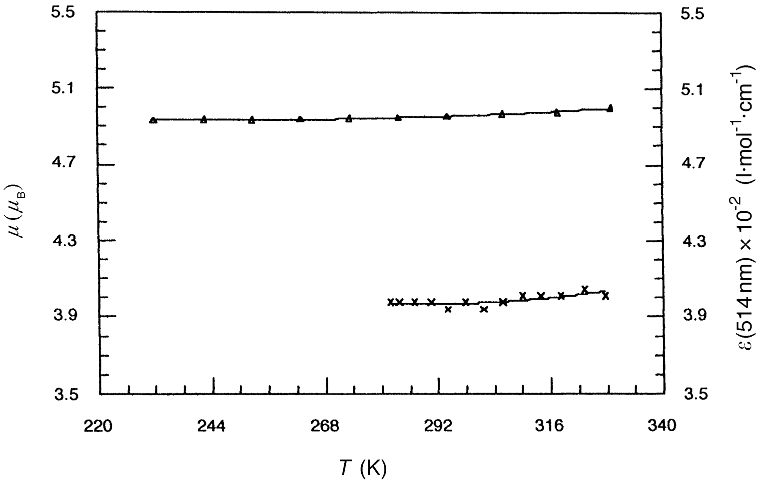

Fig. 1. Magnetic moments (Δ) and molar absorbtivities ($\times$) *Vs.* temperature for [Co_2(*TAMEN*)Cl_4] ($3.0426.10^{-4}$ *M*) in presence of excess ligand in MeOH

spin-free state of Co(II)-complexes [10]. Hence, [Co_2(*TAMEN*)Cl_4] is spin-free in methanol. In fact, the solid complex has been reported to be spin-free with a magnetic moment of 4.41 μ_B. The ligand leads to a weak ligand field (10 Dq) when coordinated to the Co(II) ion [1]. Metal ions with d^7 electronic configuration afford only spin-free complexes in tetrahedral symmetry [18]. The constant magnetic moment over the temperature range of 232 to 329 K indicates that no change takes place the spin-state of the complex. These results are a strong indication in favour of tetrahedral spin-free [Co_2(*TAMEN*)Cl_4] being present in methanol.

Experimental

Chemicals

Chemicals were used as received from Riedel, Fluka, and Merck. Commercial grade methanol was refluxed over CaO for 24 hours and fractionated.

Synthesis

N,N′-Tetra(4-antipyrylmethyl)-1,2-diaminoethane (*TAMEN*; antipyryl- = 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one) was synthesized by *Mannich* reaction of antipyrine with ethylenediamine in aqueous formaldehyde solution [3]. [Co_2(*TAMEN*)Cl_4] was synthesized according to the literature [1, 2–4]. 6 mmol of $CoCl_2 \cdot 6H_2O$ in 50% (v/v) H_2O:EtOH were combined with 3 mmol of *TAMEN* dissolved in 20 cm^3 of EtOH with continuous stirring to give a blue solution. A blue precipitate was formed after 10 to 15 minutes which was filtered off, purified by recrystallization from ethanol, and dried in air over P_2O_5. Finally, a blue microcrystalline powder was obtained. $Co_2C_{50}H_{56}N_{10}O_4Cl_4$; calcd.: H 5.04, C 53.59, N 12.50, Cl 12.65; found: H 5.15, C 53.20, N 12.75, Cl 12.50.

Physical measurements

^{1}H NMR spectra were run on a Bruker AC 250 FT spectrometer operating at 250 MHz. High precision NMR sample tubes of type 528-PP (Wilmad Glass Co., New Jersey) with sealed Wilmad coaxial inserts (WGS-5BL) containing 5% *TMS* in acetone-d_6 were used as external standard and as instrument lock. Solution magnetic moments (μ) were measured by *Evans*' method [11] using the solvent methanol for temperature calibration [12]. The measurements were corrected for sample concentration, solvent density, and changes with temperature [13–14]. Dioxane (0.5% v/v) was used as an internal reference.

UV/Vis spectra were recorded on a Shimadzu UV-1601 PC spectrophotometer equipped with a thermoelectrically temperature controlled cell holder (Shimadzu TCC-240A) for the range of $7-60(\pm 0.5)$°C. The actual temperature within the sample cell was measured with a Copper-Constantan thermocouple. Below room temperature (≤ 20°C), dry nitrogen gas was blown into the cell compartment. The observed molar absorbtivities $(\varepsilon, 1 \cdot mol^{-1} \cdot cm^{-1})$ were corrected for changes in the solvent's density, changing the concentration of solute, with temperature variation [13–14].

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