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SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION OF NEW DITHIOCARABAMATO LIGAND AND ITS COMPLEXES WITH COPPER(II), NICKEL(II) AND PALLADIUM(II)

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Triammonium-N-dithiocarboxyiminodiacetate, $(NH_4)_3L$, a new dithiocarbamato derivative of iminodiacetate, has been synthesized. The coordination properties of the ligand were tested in reactions with copper(II), nickel(II) and palladium(II) salts in acidic solutions. Complexes with a general formula $M(H_2L)_2$ were obtained, with the coordination taking place through the sulfur atoms of the dithiocarbamate moiety. The new compounds were characterized by elemental analysis, UV/VIS and IR spectroscopy, thermal analysis and magnetic measurements. In addition, the ligand was characterized by ^{1}H- and ^{13}C-NMR spectroscopy and molar conductivity measurements. The copper(II) complex is paramagnetic, while the nickel(II) and palladium(II) compounds are diamagnetic. The thermal decomposition of all compounds is continuous and the thermal stability of the complexes is higher than that of the ligand, as expected.

Keywords: *copper(II) complexes, IR, nickel(II) complexes, palladium(II) complexes, thermal analysis, triammonium-N-dithiocarboxyiminodiacetate, UV/VIS-spectrometry*

Introduction

Dithiocarbamates are of great research interest owing to their diverse applications. They are used as vulcanization accelerators, high-pressure lubricants, as active ingredients of fungicides, pesticides and pharmaceutical products [1–4]. This kind of compounds show detoxicant and immunopharmacological properties [5] and react readily with Pt(II), providing an interesting route to withdraw from the organism the excess of Pt(II) as a consequence of antitumoral therapy with *cis*-DDP, *cis*-dichlorodiamminplatinum(II), and its derivatives.

Most of aliphatic and aromatic dithiocarbamates synthesized until now may coordinate only through the dithio-group, behaving as uninegative bidentate ligands in reactions with metal ions [6–9]. However, dithiocarbamates with three or more donor atoms are seldom reported in literature [10–12].

Coordination compounds with dithiocarbamates have attracted attention because of their potential biological activity [13–19]. As the applicability of these products often depends on their thermal stability, the determination of thermal properties of this kind of compounds is a routine procedure in their characterization [20–24].

As a continuation of our research on synthesis of dithiocarbamates with more donor atoms [25] and their complexes [26–28], we have prepared a new dithiocarbamato ligand, triammonium-N-dithiocarboxyiminodiacetate. This compound may coordinate either as a bidentate or as a tridentate ligand through the two sulfur atoms or the nitrogen and oxygen atoms of the iminodiacetate group. Investigating its coordination properties, we have prepared complexes with Cu(II), Ni(II) and Pd(II) ions in order to determine the coordination mode of the ligand and to test the thermal stability of the obtained compounds.

Experimental

Analytical methods

Elemental analyses (C, H, N) were performed using Vario III CHNOS Elemental Analyzer, Elemental Analysensysteme GmbH.

Infrared spectra in the 4000–400 cm^{-1} were measured on a Perkin-Elmer FTIR 317 25X spectrophotometer using KBr pellets. Far IR spectra were obtained on a Perkin-Elmer 983 spectrophotometer, using Nujol mull between CsI sheets.

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The diffusion-reflection spectra were recorded on a SPM-2 monochromator, Karl Zeiss, Jena using a reflection cell type R-45/0 within the range of 10,000–45,000 cm^{-1}. Samples were prepared in accordance with the procedure of Kubelka–Munk [29]. The spectra of the ligand and the complexes were obtained with solid samples.

^1H- and ^{13}C-NMR spectroscopy was performed using a Varian-Gemini 2000 spectrometer in D_2O solution. The chemical shifts were determined relative to TMS.

Magnetic susceptibilities were measured at room temperature using a magnetic susceptibility balance MSB-MKI.

Molar conductivity of freshly-prepared $1\cdot10^{-3}$ mol dm^{-3} aqueous solution of ligand was determined using a Jenway 4010 conductivity meter.

DSC and thermogravimetric curves were recorded on DuPont 2000 TA system with a thermobalance DuPont 951 TGA analyzer in an air atmosphere with a heating rate of 10 K min^{-1}. TA curves for $Cu(H_2L)_2$ were carried out in both air and nitrogen.

Reagents

All chemicals were commercial products of analytical reagent grade and were used as received.

Synthesis of the ligand

To the solution of 2 mmol (2.66 g) of iminodiacetate acid in 100 cm^3 methanol 0.10 mol (14 cm^3, 25%) NH_3(aq) and 4 mmol (2.4 cm^3) CS_2 were added. The mixture was continuously stirred at room temperature. After 2 h the white precipitate of $(NH_4)_3L$ was filtered off, washed with MeOH and air-dried. Yield: 4.1 g (78.9%). Elemental analysis data, $C_5H_{16}N_4O_4S_4$ (found, (calc.)%): C 23.55 (23.07), H 6.51 (6.15); N 21.95 (21.50).

Synthesis of the complexes

To 10 cm^3 of aqueous solution containing 1 mmol of metal salts ($Cu(NO_3)_2\cdot3H_2O$, $NiCl_2\cdot6H_2O$ and K_2PdCl_4) 2 mmol (0.52 g) of (solid) ligand was added. The reaction was carried out in an acidic solution, in the presence of 4 mmol (2 cm^3, 2 mol dm^{-3}) HCl, under constant stirring for about 20 min at room temperature. A brown, green and yellow complexes of $Cu(H_2L)_2$, $Ni(H_2L)_2$ and $Pd(H_2L)_2$, respectively, were precipitated immediately. The precipitate was filtered off, washed several times with water and air-dried. Yields: 0.20 g (42%), 0.90 g (95%), 0.42 g (80%), respectively. Elemental analyses data (found (calc.), %), $CuC_{10}H_{12}N_2O_8S_4$: C 25.22 (25.02), H 2.70 (2.50); N 5.31 (5.84), Cu 13.03 (13.26), μ_{eff}=1.44 μ_B; $NiC_{10}H_{12}N_2O_8S_4$: C 25.55 (25.28), H 2.51 (2.53); N 5.98 (5.90); $PdC_{10}H_{12}N_2O_8S_4$: C 22.69 (22.97), H 2.89 (2.29); N 6.09 (5.36).

Results and discussion

Triammonium-N-dithiocarboxyiminodiacetate, $(NH_4)_3L$

Related dithiocarbamato derivatives of iminodiacetic acid to our knowledge are not known, although some hydrohalide derivatives have been reported in the literature [30–33]. We have obtained N-dithiocarboxyiminodiacetate in a form of its ammonium salt, $(NH_4)_3L$, which is a white crystalline substance stable in air at room temperature and well soluble in water. Its molar conductivity value in water (348 S cm^2 mol^{-1}) refers to a 1:3 electrolyte [34].

In the IR spectrum of $(NH_4)_3L$ the $\nu_{as(C=O)}$ and $\nu_{s(C=O)}$ carboxylate group vibrations appear at 1577 and 1446 cm^{-1}, respectively. The absence of the ν_{SH} band around 2550 cm^{-1} confirms the deprotonation of the dithiocarbamate group [35]. To $\nu_{C\text{–}S}$ vibrations usually two bands at ca. 1000 and 660 cm^{-1} are ascribed [12, 15, 36]. We observed only one band at 991 cm^{-1} and assigned it to $\nu_{as(CSS)}$ [12], which indicates that both sulfur atoms are equivalent. The vibration at 1577 cm^{-1} is due to $\nu_{C\text{–}N}$ of the NCS_2 group, while the other one at 1215 cm^{-1} corresponds to $\nu_{C\text{–}N}$ of $NCCO_2$ moiety. In the ^1H NMR spectrum of $(NH_4)_3L$ the two signals at δ=3.63 and 4.64 ppm in an intensity ratio of 1:3 are assigned to $-CH_2$ and NH_4^+ protons, respectively. The ^{13}C spectrum shows only three signals at δ=124.99, 179.33 and 61.97 ppm corresponding to –CSS; –COO and $-CH_2$ carbons, respectively. The low signal number suggests a symmetrical molecule which is presented in Fig. 1.

In the electronic spectrum of the solid $(NH_4)_3L$, from the observed three bands, that of the highest energy at 39,400 cm^{-1} is assigned to the intraligand (IL) band of the NCS_2 chromophore as a consequence of a $\pi\to\pi^*$ transition of the N⎓C⎓S group [37]. The next IL band at 31,800 cm^{-1} is due to a $\pi\to\pi^*$ transition, too, but within the S⎓C⎓S group. The band at 27,200 cm^{-1} is attributed to an $n\to\pi^*$ transition located on the sulfur atoms [15, 37].

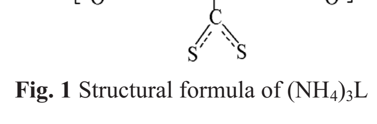
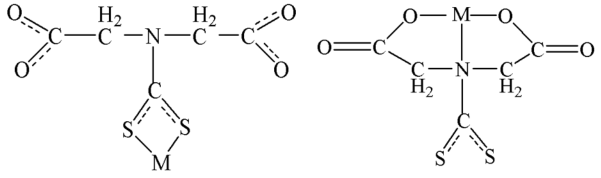


Fig. 1 Structural formula of $(NH_4)_3L$

Complexes of Cu(II), Ni(II) and Pd(II)

$(NH_4)_3L$ (Fig. 1) has five potential donor atoms: the two sulfurs of the dithiocarbamate group, two carboxyl oxygens and that of the imino nitrogen. $(NH_4)_3L$ may take part either in a bidentate coordination through both of its sulfur atoms (Fig. 2a) forming thus a four-membered chelate ring or act as tridentate through an oxygen atom on each carboxyl group and imino nitrogen atom forming two five-membered chelate rings (Fig. 2b). Also, a pentadentate coordination mode is not excluded, by simultaneous coordination though both of the previously mentioned coordination centers, resulting in binuclear complexes.



a b

Fig. 2 Possible coordination modes of $(NH_4)_3L$

In reaction with Cu(II), Ni(II) and Pd(II) salts in an acidic solution bis(ligand) complexes, $M(H_2L)_2$, of nonelectrolytic character were obtained. The solubility of the compounds according to their structure in common solvents (H_2O, MeOH, EtOH, $CHCl_3$) is low.

Instead of two carboxyl group stretching vibration appearing in the IR spectrum of $(NH_4)_3L$, in the spectra of the Cu(II), Ni(II) and Pd(II) complexes only one band is observed at 1725, 1732 and 1710 cm^{-1}, respectively, which corresponds to protonated carboxyl group vibration. This indicates that the coordination takes place through sulfur atoms of the ligand [12, 35]. The position of the $\nu_{M\text{–}S}$ bands in the 300–400 cm^{-1} IR region (345 cm^{-1} for $Cu(H_2L)_2$ [13], 399 cm^{-1} for $Ni(H_2L)_2$ [11, 13] while that for $Pd(H_2L)_2$ at 397 cm^{-1} appears at somewhat higher frequency than found in literature [28, 38]) supports the supposition of coordination via sulfur atoms.

In electronic spectrum of the complexes, beside the intraligand bands, present also in the free ligand spectrum, charge transfer (CT) and $d\to d$ bands have been identified. Bands in the spectrum of $Cu(H_2L)_2$ at 15,600 and 22,400 cm^{-1} are due to $d_{xy}\to d_z2$ and $d_{xy}\to d_{xz}$ transitions which is consistent with D_{2h} symmetry of the compound [6, 39]. The band at 34,400 cm^{-1} suggests an anisobidentate coordination of the dithiocarbamato group [15, 37]. These data refer to a distorted tetrahedral surrounding around copper(II). The lower magnetic susceptibility ($1.44\mu_B$) of the complex according to the spin-only value suggests a possible intra- or intermolecular magnetic exchange in the solid compound [40]. In the case of $Ni(H_2L)_2$ nine transition bands were observed. The bands at the highest energies are probably due to IL transitions, as well as that at 11,000 cm^{-1} which is characteristic for the ligand. Bands at 25,600 and 24,000 cm^{-1} are attributed to CT transitions of the type M→L [10, 13, 15]. The low intensities of the two bands at 15,600 and 22,000 cm^{-1} indicate $d\to d$ Laporte and spinforbidden transitions [11], respectively. The absence of the band at around 34,000 cm^{-1} supports a square-planar geometry with isobidentate coordination of the dithiocarbamate group [13, 37]. The intensive and sharp band at 21,600 cm^{-1} in the spectrum of $Pd(H_2L)_2$ indicates a possibility of superposition of IL transitions with $d\to d$ ($^1A_g\to{}^1B_{1g}$) transition [38]. The band at 16,000 cm^{-1} could be interpreted as a $d\to d$ ($^1A_g\to{}^1A_{2g}$) transition.

Thermal decomposition of the compounds

The thermogravimetrical and DSC curves of the ligand and the complexes were recorded in air atmosphere with a sample mass of about 5 mg. The thermal decomposition of $Cu(H_2L)_2$ was followed also in argon.

In air the decomposition of the ligand is endothermic through the recorded temperature range (Fig. 3) while the DSC curves of the complexes begin with an endothermic effect followed by combustion of $Ni(H_2L)_2$ and $Pd(H_2L)_2$. The heat effects during the

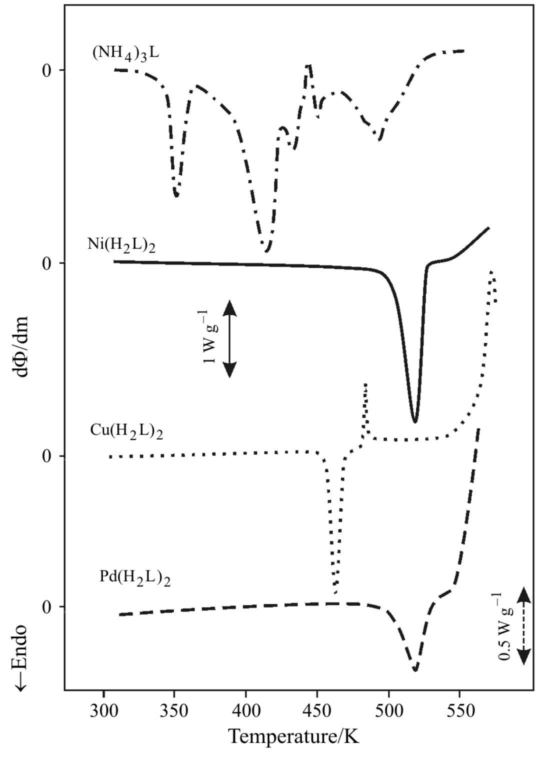


Fig. 3 DSC curves of $(NH_4)_3L$, $Cu(H_2L)_2$, $Ni(H_2L)_2$ and $Pd(H_2L)_2$

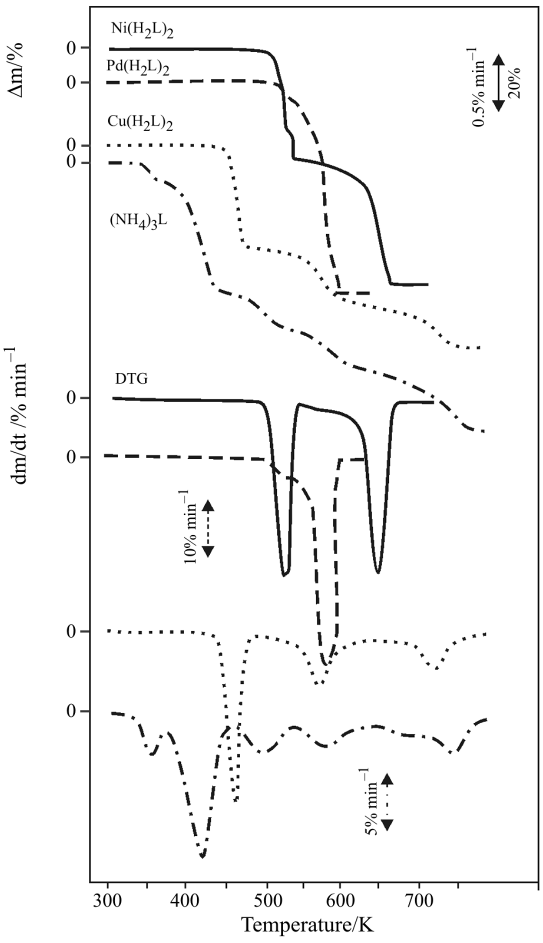


Fig. 4 TG and DTG curves of the compounds in air

decomposition of Cu(H$_2$L)$_2$ are endothermic in argon, including the melting of the sample, except the sharp exothermic peak at 470 K which is probably due to a structural rearrangement. In air, above 500 K, exothermic oxidation processes are taking place, but without combustion of the sample.

The thermal stability of (NH$_4$)$_3$L is rather low (Fig. 4). Its stepwise continuous decomposition begins at 330 K. The first mass loss corresponds probably to the elimination of one ammonia molecule (exp. 6.4%, calc. 6.50%). From the TG data the second decomposition step seems to be a decarboxylation, as was observed in other dithiocarbamato compounds [12]. The decomposition of the ligand is completed at about 800 K with a coke residue or C$_3$N$_4$ which appears in the decomposition of some organic molecules [41].

The decomposition of Cu(H$_2$L)$_2$ begins at 450 K (Fig. 3) and takes place in three clearly distinguishable steps. At the first step, in a temperature range of only 25 K the mass loss (36%) corresponds to superposed elimination of three acetyl groups (36.90%) or its fragments. In the next step the remaining acetyl group probably together with a sulfur containing fragment are departing (found: 21%, calc. 19.40%, for H$_2$S). The decomposition is seemingly finished at about 750 K. However, the residue of the supposed final product (30%) in air does not correspond neither to an oxide (16.57%) nor a sulfide (19.92%). As the decomposition is accompanied with melting, it probable prevents the free departure of the evolved gases, and as a consequence, the decomposition is not completed up to 770 K. Ni(H$_2$L)$_2$ and Pd(H$_2$L)$_2$ have about the same thermal stability which is somewhat higher compared to copper(II) compound (ca. 500 K). The first decomposition step involves the departure of the carboxylate groups, too. At the beginning of the decomposition of Pd(H$_2$L)$_2$ fragments of two carboxyl groups, probably H$_2$CO$_2$ and CO$_2$, depart in two slightly distinguishable steps (found 19%, calc. 19.71%) followed by the combustion of the sample. The decomposition is finished at 600 K. Ni(H$_2$L)$_2$ decomposes somewhat slower and takes place in two clearly divided steps involving the evolution of carboxylate group fragments followed by the departure of oxidation products of the heteroatoms. The final product of the decomposition of the last two complexes may correspond to formation of oxides or sulfides. Found residue for Ni(H$_2$L)$_2$ 17.7%, (calc. for NiO 15.72% and NiS 19.10%); for Pd(H$_2$L)$_2$ 25.2% (calc. 23.41% for PdO and 26.48% for PdS). The relatively low temperature of the completed decomposition suggests that the residue is a sulfide, according to some analogous square-planar d^8 dithiocarbamato complexes [42], but most probable it is a mixture of sulfide and oxide.

Conclusions

The ligand has five potential donor atoms (two S atoms of the –CSS group, two O atoms of the –COO group and the imino N atom). In its complexes with Cu(II), Ni(II) and Pd(II), *L* acts as a bidentate ligand and the coordination takes place through the dithiocarbamato sulfur atoms, resulting in square-planar diamagnetic Ni(H$_2$L)$_2$ and Pd(H$_2$L)$_2$ complexes and the paramagnetic Cu(H$_2$L)$_2$ complex, with Cu most likely in a distorted tetrahedral environment.

Thermal stability of (NH$_4$)$_3$L is low and its decomposition, which starts with evaporation of an ammonia molecule, is endothermic in the measured temperature range. Of the three complexes, Cu(H$_2$L)$_2$ is the least thermally stable. Thermal decomposition of the complexes most likely begins with decarboxylation. It is endothermic up to 500 K, but exothermic oxidation processes are observed above this temperature. Thermal decomposition of Cu(H$_2$L)$_2$ is accompanied by its melting and with an exothermic structural rearrangement.

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