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The synthesis and characterization of complexes of zinc(II), cadmium(II), platinum(II) and palladium(II) with potassium 3-dithiocarboxy-3-aza-5-aminopentanoate

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Abstract: Complexes of zinc(II), cadmium(II), platinum(II) and palladium(II) with a new polydentate dithiocarbamate ligand, 3-dithiocarboxy-3-aza-5-aminopentanoate (daap⁻), of the type $M(\text{daap})_2 \cdot n\text{H}_2\text{O}$ ($M = \text{Zn(II)}, \text{Cd(II)}, n = 2$, or $M = \text{Pt(II)}, \text{Pd(II)}, n = 0$), have been prepared and characterized by elemental analysis, IR and UV/VIS spectroscopy, as well as magnetic measurements. The spectra of the complexes suggest a bidentate coordination of the daap⁻ ligand to the metal ions *via* the sulfur atoms of the deprotonated dithiocarbamate group. The fact that under the same experimental conditions its S-methyl ester does not form complexes could be taken as proof of the suggested coordination mode.

Keywords: zinc(II), cadmium(II), platinum(II), palladium(II), complexes, synthesis, dithiocarbamate.

INTRODUCTION

Complexes with dithio ligands are of interest not only theoretically but also from a practical point of view. They have found application as accelerators in vulcanization, as pesticides, fungicides and as bioactive compounds.^{1–5}

Most aliphatic and aromatic dithiocarbamate complexes synthesized up til now have only the dithio group as a ligand, so that they exhibit only uninegative bidentate possibility.^{6–13} On the other hand, dithiocarbamates with up to three ligating residues have rarely been reported in the literature.^{14,15} We have recently synthesized potassium-3-dithiocarboxy-3-aza-5-aminopentanoate-dihydrate ($\text{K-daap} \cdot 2\text{H}_2\text{O}$).¹⁶ This ligand can coordinate bidentately *via* both sulphur atoms (Fig. 1a), or as a tridentate ligand *via* an oxygen atom from the carboxylic group and both nitrogen atoms forming two five-membered che-

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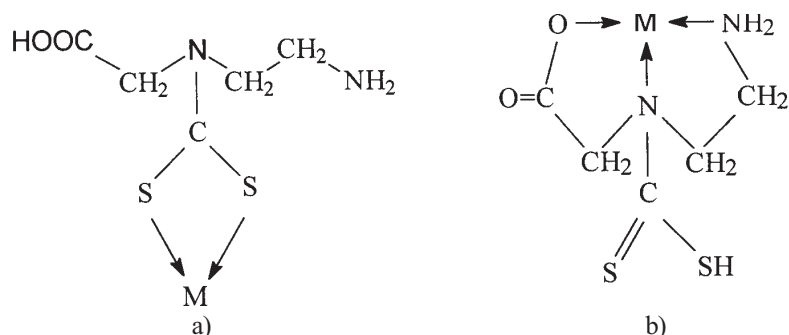


Fig. 1. Possible coordination modes of the daap⁻ ligand.

late rings (Fig. 1b). For example, the low-spin octahedral complex of $K_4[Co(daap)_3]$,¹⁷ as well as $Ni(daap)_2$ and $Cu(daap)_2$ complexes¹⁸ have recently been synthesized showing coordination of the daap⁻ ligand *via* only the sulphur atoms. As a continuation of our investigation of the coordination properties of the daap⁻ ligand, in this paper the synthesis and some of the physical-chemical characteristics of its S-methyl ester and complexes with Zn(II), Cd(II), Pt(II) and Pd(II) ions are reported.

EXPERIMENTAL

Materials

Potassium-3-dithiocarboxy-3-aza-5-aminopentanoate dihydrate was prepared using a previously described procedure.¹⁶ Other reagents were obtained commercially and used without further purification.

Preparation of the S-methyl ester of the daap⁻ ligand

To a warm solution of 10 mmol of ligand ($K\text{-daap} \times 2H_2O$) in 40 ml absolute methanol, 10 mmol CH_3I was slowly added. The obtained mixture was stirred for one hour at room temperature and subsequently refluxed for about 4 hours at 40 °C. After cooling to room temperature, the obtained white precipitate was filtered, washed with methanol and air dried.

Preparation of the complexes

All of the complexes were obtained by a similar procedure. To a solution containing 1 mmol of the required metal salt ($ZnCl_2$, $CdCl_2 \cdot H_2O$, K_2PtCl_4 or K_2PdCl_4), in a small amount of water, 2 mmol (0.536 g) of an aqueous solution of $K\text{-daap} \cdot 2H_2O$ was slowly added at room temperature. The $Zn(daap)_2 \cdot 2H_2O$, $Cd(daap)_2 \cdot 2H_2O$, $Pt(daap)_2$, $Pd(daap)_2$ complexes precipitated immediately. The mixture was stirred for a further half of an hour when the precipitate of the complex was filtered off, washed several times with 1×10^{-3} mol/dm³ HCl, acetone and, finally, air-dried.

Analytical methods

Analyses for C, H and N were carried out by conventional methods. The content of Zn and Cd was determined by atomic absorption spectrometry using a Perkin-Elmer spectrophotometer, Model 1100-B.

Infrared spectra (KBr technique) in the 4000–400 cm⁻¹ region were measured on a Perkin-Elmer FTIR 317 25X spectrophotometer. Far IR spectra (Nujol mull supported between CsI sheets) were measured on a Perkin-Elmer spectrophotometer, Model 983.

Magnetic susceptibilities were determined at room temperature using a magnetic susceptibility balance MSB-MK1. The data were corrected for diamagnetism.

The diffusion-reflection spectra were measured on a monochromator SPM-2 (Zeiss-Jena) using a reflection cell (type R-45/0) in the 10 000–45 000 cm⁻¹ range. The spectra of the ligand and the Zn(II) and Pt(II) complexes were obtained using pure samples, but the spectra of the Cd(II) and Pd(II) complexes were measured using diluted (MgO) samples.

RESULTS AND DISCUSSION

Synthesis and general physical characterization

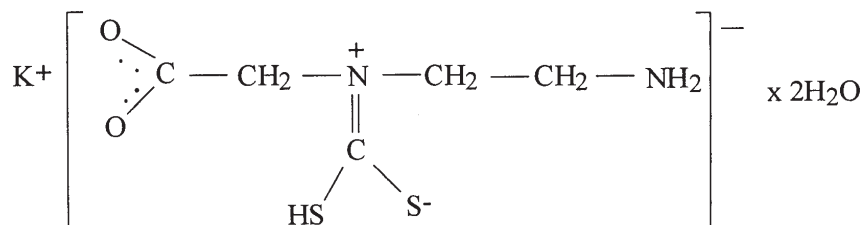
The complexes $M(\text{daap})_2 \cdot n\text{H}_2\text{O}$ ($M = \text{Zn(II)}, \text{Cd(II)}, n = 2$ and $M = \text{Pt(II)}, \text{Pd(II)}, n = 0$) (Table I) were prepared in high yields (65–95 %) upon mixing aqueous solutions of $M\text{Cl}_2 \times n\text{H}_2\text{O}$ ($M = \text{Zn(II)}, \text{Cd(II)}$ or K_2MCl_4 ($M = \text{Pt(II)}, \text{Pd(II)}$) and potassium 3-dithiocarboxy-3-aza-5-aminopentanoate (K-daap), in a 1:2 mole ratio at room temperature.

The analytical data are in good agreement with the proposed composition of the complexes (Table I). The spectral data of the complexes suggest that both daap^- ligands are coordinated as monoanions. The formation of the monoanion can result *via* deprotonation not only of the carboxylic group, but by also of the dithio group. X-Ray data for the free ligand¹⁶ show a deprotonated carboxylic, but not dithio group (Fig. 2). The IR data indicate that this ligand coordinates *via* the deprotonated dithio moiety in the complexes. Considering the composition of the prepared complexes, *i.e.*, from their non-ionic nature, it can be deduced that besides deprotonation of the dithio group, also protonation of the NH_2 group occurs. Thus, the ligand appears as a zwitter ion. The protonation is obviously assisted by the acidity of the aqueous solutions of the metal salts. In contrast with these complexes, in the $\text{K}_4[\text{Co}(\text{daap})_3]$ ¹⁷ complex, the daap^- ligand behaves as a dianion bidentate S,S' ligand.

TABLE I. Analytical and physical data of the ligand, S-methyl ester and the investigated complexes

Empirical formula	Formula weight	Colour	Found (Calcd.)/%			Yield/%	M.P./°C
			C	H	N		
K-daap·2H ₂ O (K ₂ C ₅ H ₁₃ N ₂ O ₄ S ₂)	268.40	White	21.86 (22.38)	4.88 (4.85)	9.86 (10.45)	65	158
CH ₃ -daap·0.5 H ₂ O (C ₆ H ₁₂ N ₂ S ₂ O ₂)	217.00	White	33.95 (33.20)	5.77 (5.99)	12.88 (12.90)	69	–
Zn(daap) ₂ ·2H ₂ O (ZnC ₁₀ H ₂₂ O ₆ N ₄ S ₄)	487.92	White	24.77 (24.61)	4.83 (4.54)	11.05 (11.49)	63	179
Cd(daap) ₂ ·2H ₂ O (CdC ₁₀ H ₂₂ O ₆ N ₄ S ₄)	534.95	White	22.10 (22.45)	4.52 (4.15)	10.07 (10.48)	81	183
Pt(daap) ₂ (PtC ₁₀ H ₁₈ N ₄ O ₄ S ₄)	581.10	Yellow brown	21.07 (20.65)	3.46 (3.09)	9.58 (9.64)	95	>300
Pd(daap) ₂ (PdC ₁₀ H ₁₈ N ₄ O ₄ S ₄)	492.40	Dark yellow	24.79 (24.37)	4.04 (3.66)	10.95 (11.37)	33	>300

All complexes are insoluble in water and most common organic solvents. They were obtained as powders and are stable at room temperature (Table I). All the complexes are diamagnetic.

Fig. 2. Schematic presentation of a K-daap \cdot 2H $_2$ O molecule.*Infrared spectra*

The most important IR data for K-daap and the corresponding Zn(II), Cd(II), Pt(II) and Pd(II) complexes have been collected in Table II.

The absence of asymmetric stretching frequencies of the COOH group (1700 – 1750 cm^{-1})¹⁹ suggests the presence of carboxylate ions (Table II) in the free ligand as well as in the complexes. This fact confirms that the daap $^-$ ligand exists as the potassium carboxylate salt and not as potassium dithiocarbamate. Also, in all complexes, as well as in methyl ester of the ligand, there are no bands assignable to the stretching vibration of the NH $_2$ group (3100 – 3500 cm^{-1}). However, from the band at *ca.* 2950 cm^{-1} , the presence of the zwitter ion can be concluded.

TABLE II. The most important bands in the IR spectra of the ligand, S-methyl ester and the investigated M(II)-(daap) $_2$ complexes

Compound	NH $_3^+$		COO $^-$		CSS $^-$		S-H	N-C	M-C
	ν	ν_{as}	ν_{s}	ν_{as}	ν_{s}	ν	ν	ν	
K-daap \cdot 2H $_2$ O (ligand)	2920	1597	1414	963	635	2631	1453	–	
CH $_3$ -daap \cdot 0.5 H $_2$ O	3050	1632	1399	987 ^d		–	1381	–	
				637					
Zn(daap) $_2$ \cdot 2H $_2$ O	3025	1587	1408	1004		–	1464	389	
Cd(daap) $_2$ \cdot 2H $_2$ O	2920	1570	1410	990		–	1481	390	
Pt(daap) $_2$	2950	1623	1385	949		–	1510	353	
Pd(daap) $_2$	2950	1625	1398	950		–	1499	360	

The intense bands at 1460 – 1510 cm^{-1} indicate a partial double bond in the S $_2$ C \cdots N moiety.^{8,9,19} The position of this band is affected by the central atom. The band was shifted to lower frequencies in the sequence: Pt(daap) $_2$ > Pd(daap) $_2$ > Cd(daap) $_2$ > Zn(daap) $_2$, which is in agreement with the order of decreasing electron acceptor abilities from Pt to Zn.³

The bands in the region of 940 – 1010 cm^{-1} were attributed to the stretching mode of the C–S bond. The position of this band has been used by several authors^{2,3,21} as a criterion for symmetric or asymmetric coordination of the dithiocarbamate group. The singlet in the IR spectrum of the daap $^-$ ligand confirms the equivalence of the S-atoms, but the doubled

at 987 cm^{-1} in the IR spectrum of the methyl-ester of ligand indicates non-equivalence of the S-atoms in this compound. The bands in the IR spectra of the platinum and palladium complexes are strong and suggest isobidentate binding of the dithiocarbamate group. In the case the zinc and cadmium complexes, this band is split. This may be due to the uniequivalent bonding of dithiocarbamate group, and/or to the interactions between the metal atom and a sulfur atom of a neighboring molecule in the crystal. This phenomenon is common among zinc dithiocarbamate complexes.²¹

The absence of $\nu(\text{S-H})$ band, as well as the presence of $\nu(\text{M-S})$ band in the complexes in the $300\text{--}400\text{ cm}^{-1}$ region (Table II), confirms the coordination of the daap⁻ ligand to Zn(II), Cd(II), Pt(II) and Pd(II) ions *via* sulphur atoms.

Electronic spectra

The solid state electronic spectra of the ligand and the complexes display the absorption bands listed in Table III. The ligand shows five bands; the three most intense bands can be assigned to the chromophore group NCS_2 .^{3,22} Thus, the band at 40000 cm^{-1} is due to intraligand $\pi \rightarrow \pi^*$ transitions located on the $\text{N}\equiv\text{C}\equiv\text{S}$.^{23,24} The next band located at 32200 cm^{-1} also arises from $\pi \rightarrow \pi^*$ transitions, but within the $\text{S}\equiv\text{C}\equiv\text{S}$ group.²⁵ The band at 27200 cm^{-1} is attributed to $n \rightarrow \pi^*$ electronic transitions located on the sulphur atoms.^{26,27}

TABLE III. Electronic spectral data of the ligand and the investigated complexes

Compound	Tansitions/($\text{cm}^{-1} \times 10^3$)		
	d-d	CT	IL
K-daap · 2H ₂ O (ligand)	–	–	10.8; 20.2; 27.2; 32.2; 40.0
Zn(daap) ₂ · 2H ₂ O	–	17.4(M-L)	10.2; 23.0; 28.0; 32.4; 40.8
Cd(daap) ₂ · 2H ₂ O	–	18.0(M-L) > 44.0(L-M)	11.0; 24.4; 28.6; 34.4; 40.5
Pd(daap) ₂	14.0*; 16.6; 23.8; 25.0	>44.0(L-M)	<10.0; 21.5; 28.0; 32.0; 40.8
Pt(daap) ₂	12.8; 15.5; 25.0*	>45.0(L-M)	<10.0; 20.0; 28.6; 32.8; 41.0

*Superposed with CT

The spectra of all complexes, in addition to intraligand bands, contain bands which are attributed to charge transfer (CT) transitions of the types M→L. The Pt and Pd complexes also show a transition, assigned as d→d transitions. So, M→L charge transfer (CT) transitions result in bands at 17400 cm^{-1} and 18000 cm^{-1} for the Zn and Cd complexes, respectively. The band at the highest energy ($> 44000\text{ cm}^{-1}$) in the spectra of the Cd, Pt and Pd complexes is probably due to CT transitions of the type L→M. The remaining bands in the spectra of the Pd and Pt complexes are designated as d→d transitions. Some of them are superposed by CT transitions. Hence, in the spectra of Pd(daap)₂, the bands at 16600 , 23800 and 25000 cm^{-1} are assigned as $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$, $^1\text{E}_g$ and $^1\text{B}_{1g}$, respectively.²⁸ The band at 14000 cm^{-1} could arise from spin forbidden $^1\text{A}_{1g} \rightarrow ^3\text{A}_{2g}$ transitions. Since the in-

tensity of the band is very high, the $^1A_{1g} \rightarrow ^3A_{2g}$ transitions are probably superposed by CT transitions of the M \rightarrow L type.

Two weak bands at 12800 cm^{-1} and 15500 cm^{-1} could be attributed to spin forbidden transitions: $^1A_{1g} \rightarrow ^3A_{2g}$ and $^3B_{1g}$ in the spectrum of the Pt complex. The most intensive band in this spectrum is that at 25000 cm^{-1} . It is possible that this band arises from the superposition of CT and d \rightarrow d transitions $^1A_{1g} \rightarrow ^1E_g$ and $^1B_{1g}$.²⁸

These observations suggest a square-planar geometry of the Pt(II)- and Pd(II)-daap complexes.

The corresponding Zn(II) and Cd(II) complexes loose water molecules at 160 °C. Since the electronic spectra of the hydrous and anhydrous complexes are identical, it could be concluded that H₂O does not enter into coordination. The relative high dehydration temperature is probably caused by strong hydrogen bonding of the water molecules in the crystal. A tetrahedral geometry may be supposed for the Zn(II)- and Cd(II)-daap complexes.

In all the complexes, the daap⁻ ligand is coordinated through both sulphur atoms of the deprotonated dithio group. As an additional chemical proof of the suggested coordination may be taken. The fact that under same experimental conditions the monothioester derivative of daap⁻ does not form complexes with the investigated metals may be taken as additional chemical proof of the suggested coordination.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА КОМПЛЕКСА ЦИНК(II), КАДМИЈУМ(II),
ПЛАТИНА(II), И ПАЛАДИЈУМ(II) СА
КАЛИЈУМ-3-ДИТИОКАРБОКСИ-3-АЗА-5-АМИНОПЕНТАНОАТОМ
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СКУБАН⁴ И СРЕЋКО ТРИФУНОВИЋ²

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Реакцијом између цинк(II), кадмијум(II), платина(II) и паладијум(II)-соли и калијум-3-дитиокарбокси-3-аза-5-аминопентаноата добијени су договарајући комплекси типа M(daap)₂·nH₂O. Изоловани комплекси су окарактерисани елементарном анализом, IR и UV/VIS спектроскопијом као и мерењем магнетних суцептибилитета. Спектри комплекса сугеришу бидентатну координацију даар⁻ лиганда са наведеним металним јонима преко атома сумпора депротонване дитиокарбамато групе. Као доказ наведеног начина координације може послужити чињеница да при истим експерименталним условима S-метил естар лиганда не даје комплексе.

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