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DIVALENT TRANSITION METAL TERNARY COMPLEXES OF N-(2-ACETAMIDO)IMINODIACETIC ACID AND THIOSEMICARBAZIDE AS WELL AS DITHIOCARBAZATE DERIVATIVES

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ABSTRACT

Ternary mixed ligand complexes of the type Na[M(ADA)L] $(H_2O)_x$ where M = Co(II), Ni(II) and Cu(II); ADA = divalent anion of N-(2-acetamido)-iminodiacetic acid, L = S-methyl dithiocarbazate (L^1) and benzalhydrazono methyl dithioformate (L^2), thiosemicarbazide (L^3) and benzalthiosemicarbazone (L^4) have been prepared and characterized by elemental and thermal analyses, IR as well as conductivity measurements.

INTRODUCTION

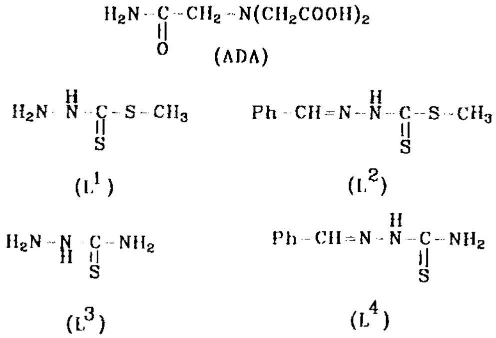
As a part of our program of the synthesis of several ternary complexes, we have recently reported the ternary complexes of divalent transition metal ions with the biologically active[1] N-(2-acetamido)iminodiacetic acid

(H_2ADA)-amino acids[2,3], heterocyclic diimines[4] and aliphatic as well as aromatic acids[5,6]. Further, S-methyl dithiocarbazate (L^1), thiosemicarbazide (L^3) and their derivatives, benzalhydrazono methyl dithioformate (L^2) and benzalthiosemicarbazone (L^4) are versatile compounds which are biologically active[7-11], and have been extensively used in the preparation of several complex systems[12-14]. However, a literature survey reveals that no attention has been paid to mixed ligand complexes of the two biologically important ligands; S-methyl dithiocarbazate or thiosemicarbazide derivatives (L^1-L^4) and H_2ADA (Fig. 1). Accordingly, it is the aim of the present investigation to carry out a systematic study of ternary complexes of divalent transition metal ions with H_2ADA and S-methyl dithiocarbazate as well as thiosemicarbazide derivatives (L^1-L^4). The study involves the synthesis and characterization of these complexes.

EXPERIMENTAL

Materials

The disodium salt of N-(2-acetamido)iminodiacetic acid (Na_2ADA) and thiosemicarbazide were obtained from E. Merck and were used as supplied; S-methyl dithiocarbazate[15] and benzalhydrazono methyl dithioformate[16] as well as benzalthiosemicarbazone[7] were prepared according to the literature methods. Metal salts [$CoCO_3 \cdot Co(OH)_2 \cdot 6H_2O$; $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$; $CuCO_3 \cdot Cu(OH)_2$] of A.R. grade (BDH products) were used.



$H_2N-C(=O)-CH_2-N(CH_2COOH)_2$ (ADA)

$H_2N-NH-C(=S)-S-CH_3$ (L¹)

$Ph-CH=N-NH-C(=S)-S-CH_3$ (L²)

$H_2N-NH-C(=S)-NH_2$ (L³)

$Ph-CH=N-NH-C(=S)-NH_2$ (L⁴)

Fig. 1.

Synthesis of the Metal Ternary Complexes

An EtOH solution (10 mL) containing 5 mmol of each of the ligand (0.61 g, 1.05 g, 0.45 g and 0.89 g for ligands L^1, L^2, L^3 and L^4, respectively) was added to EtOH solution (10 mL) containing 5 mmol of each of the metal salts [$CoCO_3 \cdot Co(OH)_2 \cdot 6H_2O$ (0.79 g); $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (0.57 g); $CuCO_3 \cdot Cu(OH)_2$ (0.55 g)]. To this mixture an EtOH solution (10 mL) containing 5 mmol (1.17 g) of Na_2ADA was added slowly with stirring. In all cases the mixture was refluxed for 3 h, evaporated and cooled. The separated solids were filtered, washed with absolute EtOH, dried at 50°C, crushed to a powder and recrystallized from excess hot methanol and dried under vacuum.

Physical Measurements

Infrared spectra were recorded in the 4000-400 cm^{-1} range on a Shimadzu

470 spectrophotometer. Elemental analyses were performed by the microanalytical unit at Cairo University. All melting points are uncorrected. The molar conductance of DMSO solutions (10^{-4} mol dm^{-3}) of the complexes were measured at 25°C using a YSI conductivity bridge Model 31 with a dip type cell (cell constant = 0.1). Thermogravimetry (TG) curves were recorded automatically using a Dupont 200 thermal analyser. The samples were heated from 50 to 600°C at a 10°C/min. rate in a dynamic air atmoshpere.

RESULTS AND DISCUSSION

The analytical data of the complexes synthesized in this work (Table I) are consistent with the general formula $Na[M(ADA)L](H_2O)_x$ where M = cobalt(II), nickel(II) and copper(II), ADA is the divalent anion of Na_2ADA and L is the monovalent anion of the secondary ligand (L^1-L^4). The formation of the complexes can be represented by the following equation:

$$M(II) + Na_2ADA + L \xrightarrow{H_2O} Na\,[M(ADA)\,L\,]\,(H_2O)_x$$

The molar conductance values of the complexes (in DMSO) are in the range 45-100 $ohm^{-1}cm^2\ mol^{-1}$, which is in agreement with the suggested 1:1 electrolytic nature of these chelates.

Infrared Spectra

The following characteristic IR frequencies are seen in the IR spectra of the

Table I. Microchemical Analyses and Physical Properties of the Synthesized Ternary Complexes.

Complex	Empirical formula (MW)	M.p. (°C)	Colour	Yield (%)	Found (Calcd.)(%)				Λ_m Ohm^{-1} cm^{2} mol^{-1}
					C	H	N	S	(DMSO)
Na [Co(ADA)(L^1)](H$_2$O)$_3$	$C_8H_{19}CoN_4NaO_8S_2$ (445.30)	300	Pale violet	51	21.26 (21.58)	4.00 (4.30)	12.73 (12.58)	14.20 (14.40)	47
Na [Co(ADA)(L^2)](H$_2$O)$_2$	$C_{15}H_{21}CoN_4NaO_7S_2$ (515.40)	330	Pink	46	34.49 (34.96)	4.32 (4.11)	10.98 (10.87)	12.00 (12.44)	55
Na [Co(ADA)(L^3)](H$_2$O)$_2$	$C_7H_{16}CoN_5NaO_7S$ (396.22)	320	Pink	49	21.10 (21.22)	3.98 (4.07)	17.63 (17.68)	7.99 (8.09)	62
Na [Co(ADA)(L^4)](H$_2$O)$_2$	$C_{14}H_{20}CoN_4NaO_8S$ (484.32)	335	Pink	55	34.82 (34.72)	4.39 (4.16)	14.68 (14.46)	6.31 (6.62)	66
Na [Ni(ADA)(L^1)] (H$_2$O)$_2$	$C_8H_{17}N_4NaNiO_7S_2$ (427.05)	325	Pall green	54	22.60 (22.50)	3.88 (4.01)	13.00 (13.12)	14.98 (15.01)	100
Na [Ni(ADA)(L^2)] (H$_2$O)$_2$	$C_{15}H_{21}N_4NaNiO_7S_2$ (515.15)	330	Green	66	34.82 (34.97)	3.99 (4.11)	10.77 (10.88)	12.02 (12.45)	47
Na [Ni(ADA)(L^3)](H$_2$O)$_2$	$C_7H_{16}N_5NaNiO_7S$ (395.72)	305	Grey	61	21.26 (21.23)	4.22 (4.07)	18.00 (17.69)	8.21 (8.10)	58
Na [Ni(ADA)(L^4)](H$_2$O)$_3$	$C_{14}H_{22}N_5NaNiO_8S$ (502.10)	310	Pale green	49	33.22 (33.49)	4.05 (4.42)	14.00 (13.95)	6.08 (6.39)	83
Na [Cu(ADA)(L^1)](H$_2$O)	$C_8H_{15}CuN_4NaO_6S_2$ (413.89)	328	Pale blue	47	23.49 (23.22)	4.00 (3.65)	13.11 (13.54)	15.14 (15.49)	90
Na [Cu(ADA)(L^2)](H$_2$O)	$C_{15}H_{19}CuN_4NaO_6S_2$ (501.99)	320	Blue	62	35.92 (35.89)	4.01 (3.81)	10.86 (11.16)	12.53 (12.77)	45
Na [Cu(ADA)(L^3)](H$_2$O)	$C_7H_{14}CuN_5NaO_6S$ (382.81)	300	Blue	54	21.89 (21.96)	3.89 (3.69)	17.99 (18.29)	8.13 (8.37)	95
Na [Cu(ADA)(L^4)] (H$_2$O)	$C_{14}H_{18}CuN_5NaO_6S$ (470.92)	303	Pale blue	59	35.89 (35.71)	3.99 (3.85)	14.59 (14.87)	6.99 (6.81)	66

various synthesized ternary complexes. The complexes display three sharp bands in the high frequency region. The first, at 3545-3300 cm^{-1}, may be attributed to the OH stretching of hydrate water molecules. This is in harmony with the results of both chemical (Table I) and thermal analyses of the complexes as explained below. The second band located in the range 3400-3180 cm^{-1} is assignable to the free NH_2 group stretching vibration of the primary ligand (ADA) and of the secondary ligands (L^3 and L^4). The third band found in the 3195-3180 cm^{-1} range is assignable to the coordinated NH group of the primary and secondary ligands. It is worthwhile to report that in the IR spectra of the complexes [Co-ADA-L^2] and [Cu-ADA-L^1, L^2] the above described three bands overlap with each other and only one broad band is observed.

The distinct band appearing in the range 1720-1670 cm^{-1} is attributable to the free CO group of the ADA moiety. The absence of any bands in the 1750-1700 cm^{-1} range reveals the contribution of the two carboxylate groups of ADA in the coordination to the metal ion. Accordingly, the two bands located in the 1610-1570 and 1420-1385 cm^{-1} ranges can likely be ascribed to asymmetric and symmetric stretching vibrations of the coordinated carboxylates[17]. Further, there is the disappearance of the band due to the vibration of the C=S bond of the secondary ligands which usually appears at 1190 cm^{-1} and the simultaneous appearance of a new band at 775-740 cm^{-1} assignable to ν_{C-S}. This indicates the presence of the secondary ligands (L^1-L^4) in their thiol form. In addition, the IR spectra of the mixed ligand complexes [M-ADA-L^1 or L^2] exhibit two new bands around 1000 cm^{-1} which may be due to the asymmetric and symmetric stretching modes of the S=C-S- group[18]. On the other hand, the two bands at 1480-1470 cm^{-1} and 1620-1600 cm^{-1} are due to C=N and azomethine (-CH=N) groups, respectively.

Thermogravimetric Analyses

In order to confirm the number of water molecules existing in the various ternary complexes in Table I, thermogravimetric analyses of the synthesized complexes were carried out (Fig. 2). The recorded TG curves of [Co-ADA-L^1 or L^3] display an initial weight loss amounting to 12.30 and 9.00%, over the temperature range 50-150 and 70-150°C, respectively. The weight loss could be ascribed to the removal of three and two water molecules from these complexes (Table I), the calculated weight loss is 12.13 and 9.09%, respectively.

The recorded TG curves for the Ni(II) ternary complexes, [Ni-ADA-L^1, L^3 or L^4] display an initial weight loss amounting to 8.93, 9.98 and 10.76%, over the temperature ranges 75-125, 75-115 and 50-150°C, respectively. This weight loss corresponds to the loss of two water

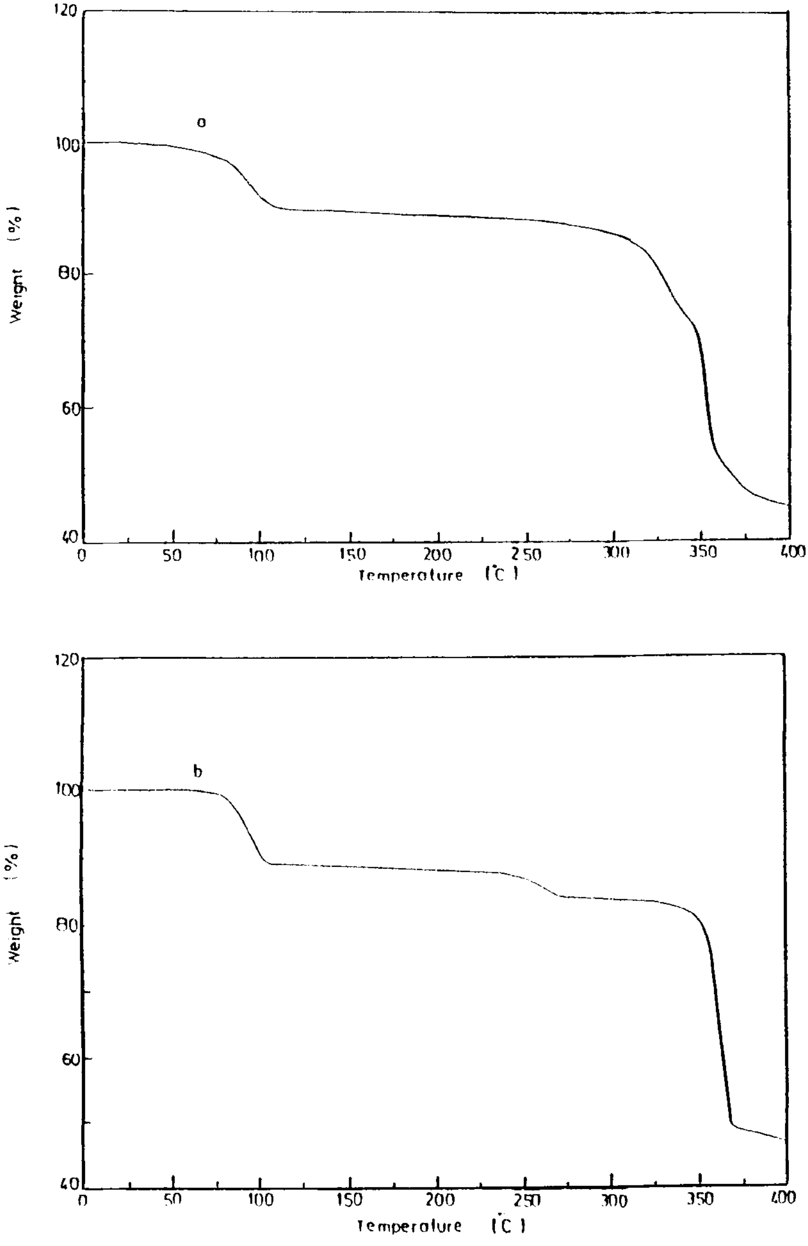
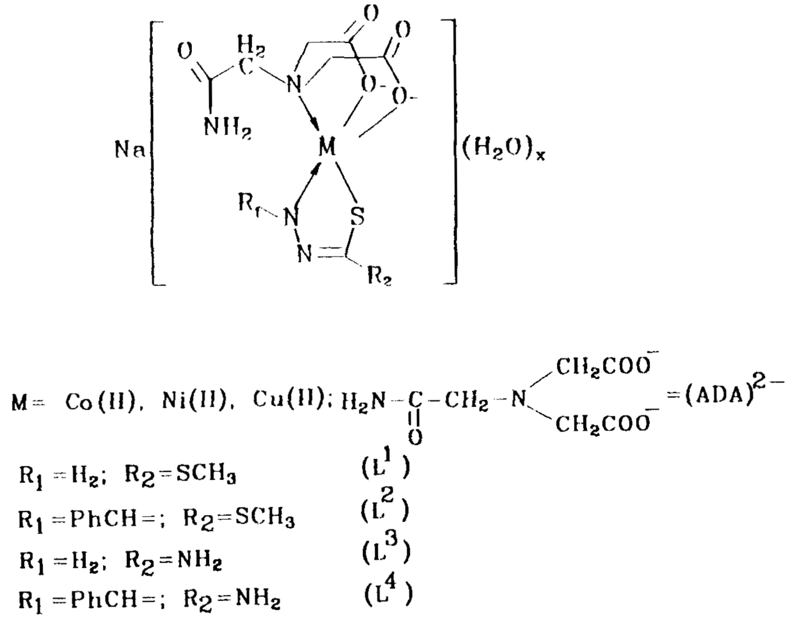


Fig. 2. TG-Curves of the Co(II), Ni(II)-ADA-L^3 Ternary Complexes.

a: Co(ADA) L^3, b: Ni(ADA) L^3.



M = Co(II), Ni(II), Cu(II); $H_2N-\underset{\underset{O}{\|}}{C}-CH_2-N\begin{smallmatrix}CH_2COO^-\\CH_2COO^-\end{smallmatrix} = (ADA)^{2-}$

$R_1 = H_2$; $R_2 = SCH_3$ (L^1)

$R_1 = PhCH=$; $R_2 = SCH_3$ (L^2)

$R_1 = H_2$; $R_2 = NH_2$ (L^3)

$R_1 = PhCH=$; $R_2 = NH_2$ (L^4)

Fig. 3. Suggested Structures of the Complexes.

molecules in the former two complexes and three water molecules in the latter one (Table I). The calculated weight loss is 8.43, 9.09 and 10.75%, respectively.

TG curves of the synthesized Cu(II) complexes, [Cu-ADA-L^1, L^2, L^3 or L^4], display a smooth weight loss over the temperature ranges 50-125, 75-150, 75-125 and 50-220°C, respectively. The magnitude of the weight loss over these temperature ranges amounts to 4.20, 4.00, 4.50 and 3.40%, respectively. This weight loss, which is in accordance with the loss of one water molecule, is calculated to be 4.35, 3.59, 4.70 and 3.82, respectively.

At high temperature, all the recorded TG curves are characterized by successive weight loss steps. This is due to the rapid decomposition of the complexes where both organic ligands are removed.

Conclusions

(i) The divalent anions of the primary ligand N-(2-acetamido)imino-diacetic acid (ADA^{-2}) are coordinated to the central metal ion as a tridentate N,O,O ligand, where two five-membered rings are formed.

(ii) The monovalent anions of the secondary ligands (L^1-L^4) are coordinated to the central metal ion as bidentate N,S ligands forming a five-membered chelate ring. Based on these conclusions, the following structure is proposed for the various isolated ternary complexes (Fig. 3).

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