Coordination compounds of a potentially polydentate ligand

Michaela Dina Stanescu,*[a] Cornelia Guran[b] and Ioana Jitaru[b]

[a] *"Aurel Vlaicu" University, Bd. Revolutiei No 81, 2900 Arad, Romania*
[b] *"Politehnica" University, Str. Polizu No 1, Bucharest, Romania*

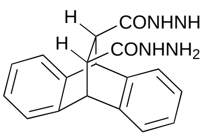
A series of complexes of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dihydrazide (**1**) has been prepared. Ligand **1** presents multiple potential coordination sites. The structures of the new complexes have been proposed based on the experimental data and molecular model calculations (MOPAC).

Complexes d'un ligand à plusieurs centres de coordination. Nous avons synthetisé une serie de complexes coordinatives en partant de l'hydrazide de l'acid *cis*-9,10-dihydro-9,10-éthanoanthracene-11,12-dicarboxylique (**1**). Le ligand **1** presente une multitude de centres potentiels de coordination. Les structures des complexes preparés ont été proposées en tenant compte des données obtenues et des calculs MOPAC.

The interest in the synthesis and study of the *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dihydrazide **1** metal complexes originates in the presence in such compounds of two units with potential biological activity: the dibenzobicyclo[2.2.2]-octane skeleton and the hydrazide functional group. Compounds with a dibenzobicyclo[2.2.2]octane skeleton, such as **2** and **3** have been recently mentioned as cholecystokinin inhibitors[1] or immunomodulators.[2] Antimicrobial, antialgal, cytostatic, as well as pesticide activity, have been evidenced for some coordination complexes of hydrazides.[3]

The $-CONHNH_2$ group has revealed interesting properties as a ligand. It contains three possible coordination sites (the three heteroatoms) and has a number of possible structures (**I**–**III**), due to conjugation or an enol transformation.[4] Thus, many controversial views have been expressed concerning the structure of hydrazide coordination complexes. Structures such as **IV**, **V** or **VI** have been suggested,[5] with the hydrazide group acting as a mono- or bidentate ligand.

All these reasons explain the interest for preparing a number of complexes having as a ligand the dihydrazine **1**.



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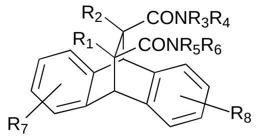

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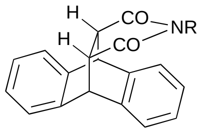

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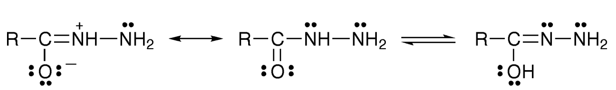
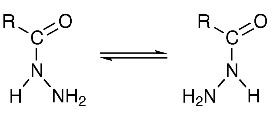


$$\mathrm{R{-}\underset{\underset{:\ddot{O}:^{-}}{|}}{C}{=}\overset{+}{N}H{-}\ddot{N}H_2 \longleftrightarrow R{-}\underset{\underset{:O:}{\|}}{C}{-}\ddot{N}H{-}\ddot{N}H_2 \rightleftharpoons R{-}\underset{\underset{:\ddot{O}H}{|}}{C}{=}\ddot{N}{-}\ddot{N}H_2}$$

I **II** **III**



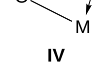
IIA(*Z*) **IIA(*E*)**

The ligand was synthesized from the corresponding ester by the previously described procedure.[6]

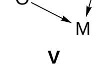
According to the IR (KBr) and ^1H NMR (DMSO) spectral data, compound **1** seems to have the conjugated amide structure **I**. The carbonyl stretching vibration occurs at 16400 cm^{-1}, in agreement with a conjugated carbonyl group[7] (for nonconjugated carbonyls the average value is 1715 cm^{-1}). The values for the NH vibrations: 1580 cm^{-1} (bending) and 3320 and 3340 cm^{-1} (stretching) confirm the proposed structure and reveal the hydrogen bond presence.[7] No enolic absorption[7] (2700–3000 cm^{-1}) was observed. The ^1H NMR spectrum (see Experimental section) agreed with the proposed structure. Quantum mechanical calculations[8] (MOPAC) of the interatomic distances evidenced a partial CO—NH conjugation. Thus, the C=O bond length of 1.23 Å is longer than the average value of 1.21 Å[9] and the C—N bond length of 1.44 Å is shorter than the usual 1.47 Å value.[9] The shorter value (1.38 Å *versus* 1.41 Å[9]) of the N—N bond is due to the decrease of the lone electron pair repulsion, generated by the electron attracting effect of the neighbouring aryl group. Besides this, these calculations provide evidence for the higher stability of a semi-enol structure **4**, which seems to be less sterically crowded; the calculated values of the formation enthalpy are 44.4 and 49.5 kcal mol^{-1} for compounds **4** and **1**, respectively.

Results and Discussion

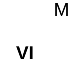
Nine complexes have been prepared starting from ligand **1** and Cu^{2+}, Co^{2+} and Ni^{2+} salts (see Experimental section). Some properties of these substances are presented in Table 1. The general formulae of these compounds have been sup-



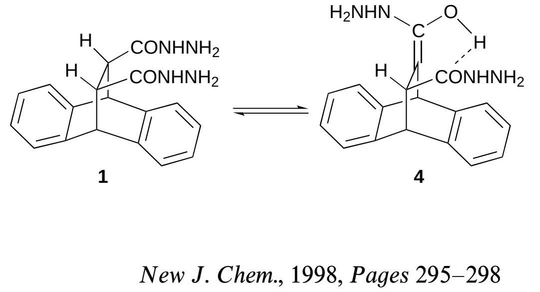
IV



V



VI



1 **4**

Table 1 Characteristics of the coordination compounds of dihydrazide **1** (L)

Compound	Colour	Elemental analysis calcd/found (%) C	H	N	Cl	M	Molar cond.[a]/S cm^2 mol^{-1}
$[CuLCl_2]\cdot 2H_2O$ **5a**	green	43.87/ 44.15	4.50/ 4.70	11.37/ 11.66	14.39/ 14.27	12.90/ 13.20	18.6
$[CuL(NO_3)_2]\cdot 2H_2O$ **5b**	dark green	39.60/ 39.80	4.05/ 3.90	15.39/ 15.55	—	11.60/ 11.40	15.1
$[CuL(OAc)_2]\cdot 2H_2O$ **5c**	yellow-green	48.93/ 49.22	5.23/ 4.95	10.37/ 10.25	—	11.77/ 11.52	5.58
$[CoLCl_2]$ **6a**	green-gray	47.81/ 48.02	4.01/ 4.18	12.39/ 12.20	15.68/ 15.88	13.03/ 13.22	13.64
$[CoL(NO_3)_2(H_2O)_2]$ **6b**	pink	39.94/ 39.70	4.10/ 4.09	15.52/ 15.28	—	10.88/ 10.66	12.52
$[CoL(OAc)_2]\cdot 2H_2O$ **6c**	pink	49.35/ 49.60	5.27/ 5.31	10.46/ 10.08	—	11.01/ 10.65	14.28
$[NiLCl_2]$ **7a**	blue-green	47.84/ 47.63	4.01/ 4.37	12.40/ 11.88	15.69/ 15.20	12.03/ 12.79	19.20
$[NiL(NO_3)_2(H_2O)_2]$ **7b**	green	39.96/ 39.73	4.10/ 4.23	15.53/ 14.98	—	10.85/ 10.50	15.75
$[NiL(OAc)_2]\cdot 2H_2O$ **7c**	light blue	49.37/ 49.41	5.27/ 5.08	10.47/ 10.88	—	10.97/ 10.68	16.72

[a] Measurements performed on 10^{-3} M solutions at a temperature of 25 °C, using DMF as solvent.

ported by the elemental analysis. The compounds are nonelectrolytes as suggested by the measurements of their molar electric conductivity. A 1 : 1 ratio (metal : ligand **1**) is confirmed by these experimental data. The other coordination sites of the metal are occupied by the anions of the salts used in the syntheses (Cl^-, NO_3^-, CH_3COO^-) and sometimes H_2O.

The IR, UV/VIS and EPR spectral data as well as the magnetic moments, presented in Tables 2 and 3, have been used for establishing the probable structures of the prepared coordination compounds. The N—N stretching (νNN) vibration has a bathocromic shift compared with the value corresponding to the dihydrazide **1**. On the other hand, hypsochromic shifts, in comparison with the ligand, have been observed for the NH_2 bending (δNH_2) and N—H stretching (νNH) vibrations in all the complexes. Such behaviour points to a metal–nitrogen interaction in all the prepared complexes.[10] No noticeable shift was observed for the carbonyl group stretching vibration (νCO) of the coordinated dihydrazide **1**. The presence of the coordinated NO_3^- ion in compounds **5b**–**7b** was evidenced by the existence of both stretching (νNO) vibrations, characteristic of this anion,[11] at 870–880 cm^{-1} and 1380 cm^{-1}. According to the IR spectra of **5c**–**7c**, the acetate ion presents a strong interaction with the metal. The 1430 and 1600 cm^{-1} values for the carbonyl absorptions of the acetate group (ν_s/ν_{as}OCO) suggest a bidentate coordination.[12]

The electronic spectra of **5a** and **5b** showed a large asymmetrical band in the 615–625 nm range, probably assigned to d–d transitions of a Cu^{2+} cation in a distorted T_d geometry. The μ_{eff} values and EPR spectral data for **5a** (1.80 μ_B; $g_x = 2.243$, $g_y = 2.141$, $g_z = 2.040$) and **5b** (1.85 μ_B; $g_{iso} = 2.149$) provide evidence that these compounds are paramagnetic with a strong rhombic anisotropy (axially compressed geometry). Such a geometry implies a dimer structure in which the hydrazide **1** most probably has a bridge position (see structure **a**); the spin compensation is forbidden by the bulky structure of this ligand.

In contrast with these two compounds, **5c** was characterized by a μ_{eff} of only 1.05 μ_B and the absence of an EPR signal. This behaviour attests most probably to a strong interaction between two copper atoms in a dimeric structure having two bidentate acetate anions as bridges (see structure **b**).

For the coordination compounds of Co^{2+} and Ni^{2+} two geometries have been observed: T_d for **6a** and **7a** and O_h for the other complexes (**6b**, **6c** and **7b**, **7c**). Table 3 presents the

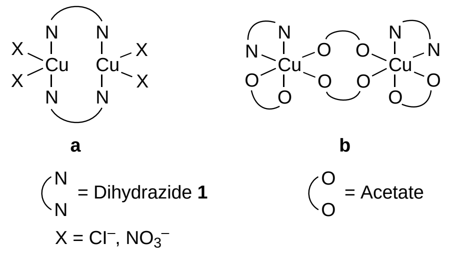


Table 2 IR frequencies (cm^{-1}) and their assignments

Compound	δNH_2	νNH	νNN	νNO	ν_{as}OCO	ν_sOCO	νCO
1	1640	3320; 3340	890	—	—	—	1640
5a	1550	3100	935	—	—	—	1640
5b	1560	3150	930	870; 1380	—	—	1635
5c	1555	3100	930	—	1600	1430	1640
6a	1550	3100	935	—	—	—	1640
6b	1550	3050	930	875; 1380	—	—	1645
6c	1555	3050	935	—	1600	1430	1645
7a	1550	3070	935	—	—	—	1640
7b	1540	3100	930	880; 1380	—	—	1635
7c	1550	3080	930	—	1600	1430	1640

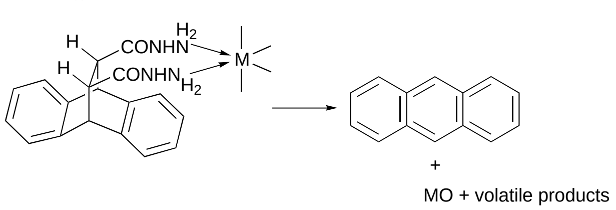
Table 3 Electronic spectral parameters and magnetic moments of the complexes

Compound	ν/kK	10 D_q/kK	B/kK	β	μ_{eff}/μ_B[c]
6a	$8.33[^4A_2 \rightarrow {}^4T_1(F)]$ $15.62[^4A_2 \rightarrow {}^4T_1(P)]$	4.95	0.606	0.624[a]	4.60
6b	$9.52[^4T_{1g} \rightarrow {}^4T_{2g}]$ $19.23[^4T_{1g} \rightarrow {}^4T_{1g}(P)]$	10.46	0.710	0.731[a]	5.15
6c	$8.33[^4T_{1g} \rightarrow {}^4T_{2g}]$ $19.05[^4T_{1g} \rightarrow {}^4T_{1g}(P)]$	9.43	0.788	0.811[a]	5.10
7a	$9.52[^3T_1 \rightarrow {}^3A_2]$ $16.0[^3T_1 \rightarrow {}^3T_1(P)]$	4.94	0.785	0.762[b]	3.75
7b	$9.61[^3A_{2g} \rightarrow {}^3T_{2g}]$ $15.51[^3A_{2g} \rightarrow {}^3T_{1g}(F)]$ $26.80[^3A_{2g} \rightarrow {}^3T_{1g}(P)]$	9.61	0.874	0.848[b]	3.35
7c	$9.17[^3A_{2g} \rightarrow {}^3T_{2g}]$ $14.6[^3A_{2g} \rightarrow {}^3T_{1g}(F)]$ $26.31[^3A_{2g} \rightarrow {}^3T_{1g}(P)]$	9.17	0.893	0.866[b]	3.30

[a] $B_0 = 0.971$ kK. [b] $B_0 = 1.030$ kK. [c] Measured at 300 K.

values of the d–d transitions, their assignments, the values of the Racah parameter and of the nephelauxetic ratio β for the studied complexes.[13]

The thermal behaviour of the dihydrazide **1** complexes is similar to other previously described compounds having a ligand with a dibenzobicyclo[2.2.2]octane skeleton.[14] When heating these complexes in a sublimation apparatus at temperatures over 200 °C, decomposition was observed with sublimation of anthracene, isolated and identified by its specific UV/VIS spectrum.[7] The polycyclic ligand **1** gave the thermally allowed cycloreversion reaction characteristic of compounds with this skeleton.[15]



A DTG analysis on some of these compounds revealed the proposed metal : ligand ratio of 1 : 1 as was expected from the elemental analysis. Beside anthracene, a number of volatile products and a solid metal-oxide residue were obtained. Thus, for **6b** a 26% weight loss at around 230 °C indicated the release of anthracene; the total experimental weight loss at 570 °C is 87.3%, corresponding to formation of CoO (as the final product).

The experimental data suggest a metal–dihydrazide coordination through the terminal nitrogen atom of the $CONHNH_2$ groups. The molecular model calculations for the ligand[8] confirm this suggestion. Thus, the N—O (2.97 Å) and O—O′ (3.37 Å) distances are too small for metal insertion in comparison with the N—N′ distance (5.37 Å). Literature X-ray data for copper sustain this assertion; the Cu—O coordination bond is evaluated at 1.92–2.6 Å and the Cu—N one at 1.96–2.14 Å.[16]

In conclusion, from the experimental and theoretical data a bidentate coordination through the terminal nitrogen atoms of ligand **1** seems plausible for all the newly synthesized compounds. A future investigation by X-ray spectroscopy will be appropriate to confirm the proposed structures.

Experimental

All the solvents and metal salts were commercial products and were used without further purification. The IR spectra were recorded with a double-beam K. Zeiss Jena UR 20 spectrophotometer and the electronic spectra with a K. Zeiss Jena VSU-2G spectrophotometer (MgO as the reference material). A Varian A60 was used for the ^{1}H NMR analyses.

Synthesis of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dihydrazide (1)

The diester of the *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid[17] was treated with 85% hydrazide hydrate in a 1 : 8 molar ratio in ethanol for 7 h at reflux. The solvent was evaporated in part and the solid product filtered after cooling (yields of 75–80%). The dihydrazide **1** is a white solid; m.p. 290–291 °C (recrystallized from DMF), lit. 292–3.[18] Anal. calcd for $C_{18}H_{18}N_4O_2$: C 67.05; H 5.63; N 17.38%. Found: C 67.02; H 5.74; N 17.02%. IR spectrum (KBr, cm^{-1}): 580m, 740m, 765w, 890w, 1020w, 1160w, 1215w, 1245w, 1460w, 1515w, 1580s 1640vs, 2930–3050m, 3320vs, 3340s. ^{1}H NMR spectrum (DMSO, δ): 3.25 (br s, 2H, $H_{11,12}$); 4.66 (br s, 2H, $H_{9,10}$); 7.08–7.68 (m, 8H, H_{arom}).

Preparation of the coordination compounds of dihydrazide 1

For the synthesis of the chloro complexes **5a**–**7a**, a mixture of 1 g (3.1 mmol) dihydrazide **1** and 0.51 g $CuCl_2 \cdot 2H_2O$ (0.74 g $CoCl_2 \cdot 6H_2O$ or 0.73 g $NiCl_2 \cdot 6H_2O$), in 25 mL ethanol was refluxed on a hot water bath (70–80 °C) for 2–3 h. After solvent evaporation, crystalline coloured compounds were obtained. The nitrate (**5b**–**7b**) and acetate (**5c**–**7c**) complexes were prepared by the same procedure, in ethanol at reflux, using a dihydrazide : metal salt [$Cu(NO_3)_2 \cdot 3H_2O$; $Co(NO_3)_2 \cdot 6H_2O$: $Ni(NO_3)_2 \cdot 6H_2O$: and $Cu(OAc)_2 \cdot H_2O$; $Co(OAc)_2 \cdot 4H_2O$; $Ni(OAc)_2 \cdot 4H_2O$] molar ratio of 1 : 1. All the newly synthesized compounds were purified by recrystallization from a 7 : 3 ethanol : water mixture (global yields 70–80%).

Thermal behaviour of some coordination compounds of dihydrazide 1

In a sublimation apparatus (efficiently cooled) at a vacuum of 200 mm Hg, compound **5c** (0.0914 g, 0.17 mmol) was heated over a temperature range of 200–600 °C. Decomposition with elimination of the volatile products was observed. A solid product was isolated on the cold finger of the apparatus and collected with CH_2Cl_2. The usual work-up gave anthracene (0.025 g; 0.14 mmol), identified by its UV/VIS spectrum. The brown-black residue was calcinated in an oven for 0.5 h, giving a black solid that is CuO (0.0155 g; 0.19 mmol). Similarly, from **6b** (0.0869; 0.16 mmol), anthracene (0.0249 g; 0.14 mmol) and CoO (0.0128 g; 0.17 mmol) and from **7c** (0.1960 g; 0.36 mmol), anthracene (0.0534 g; 0.30 mmol) and NiO (0.027 g; 0.36 mmol), were obtained.

Acknowledgements

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