

NEW MX_2 AND $\text{M}'\text{Cl}_3$ ($\text{M} = \text{Cu}, \text{Zn}$; $\text{M}' = \text{Y}, \text{Dy}, \text{Pr}$; $\text{X} = \text{Cl}, \text{Br}$) MALEATO COMPLEXES AND TETRAPHENYLANTIMONY FORMIATE ADDUCT: SYNTHESIS AND INFRARED STUDY

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Abstract: Eleven complexes and adduct have been synthesized and studied by infrared. The suggested structures are discrete with tetrahedral, trigonal bipyramidal, square planar or octahedral environments around Zn, Ni, Hg and Cu centres – the coordination number is eight in the yttrium compound and ten in the dysprosium one-. The maleate anion behaves as a bidentate, a monochelating, a bichelating or a tetradentate ligand while the formiate anion behaves as a monodentate ligand. For compounds containing a protonated amine or a methanol molecule, when hydrogen bonds are considered a supramolecular architecture may be obtained.

Keywords: bidentate, bichelating, discrete structure, supramolecular architecture

1. INTRODUCTION

Maleic ammonium salts led to the formation of many complexes with metals such as, platine, copper, silver [1-4]. Organometallic compounds arouse a great interest because of the numerous applications found in various fields [5-10]. In the dynamic of our seeking new maleato organometallic compounds, we have initiated the interactions between $(\text{CyNH}_3)_2\text{O}_2\text{C}(\text{CH})_2\text{CO}_2$ or $(\text{iPr}_2\text{NH}_2)_2\text{O}_2\text{C}(\text{CH})_2\text{CO}_2$ and MX_2 or $\text{M}'\text{X}_3$ ($\text{M} = \text{Cu}, \text{Zn}, \text{Hg}, \text{Ni}$; $\text{M}' = \text{Dy}, \text{Y}$; $\text{X} = \text{Cl}, \text{Br}$). This has yielded eleven new compounds which infrared study are carried out then structures suggested on the basis of infrared data.

2. EXPERIMENTAL SETUP

$(\text{CyNH}_3)_2\text{O}_2\text{C}(\text{CH})_2\text{CO}_2$ (**L**₁) and $(\text{iPr}_2\text{NH}_2)_2\text{O}_2\text{C}(\text{CH})_2\text{CO}_2$ (**L**₂) have been obtained as white powders on allowing monocyclohexylamine (CyNH_2) and diisopropylamine (iPr_2NH) to react in water with maleic acid in 1:1 ratio respectively. Compounds **A**, **B**, **D**, **F**, **G** and **J** were obtained as white powders after a slow solvent evaporation at room temperature, on allowing **L**₁ to react in methanol with, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a 1:2 ratio (**A**) or in a 1:2 ratio (**F**), ZnCl_2 in a 1:2 ratio (**B**), CuBr_2 in a 1:2 ratio (**D**), HgCl_2 in a 1:2 ratio (**G**) and DyCl_3 in a 1:1 ratio (**J**). Compounds **C**, **E**, **H**, **I** and **K** were obtained on allowing **L**₂ to react in methanol with NiCl_2 in a 1:2 ratio (**C**), ZnCl_2 in a 1:2 ratio (**E**), HgCl_2 in a 1:2 ratio (**H**), YCl_3 in a 1:1 ratio (**I**), and SbPh_3 in a 1:1 ratio (**K**). All the solutions were stirred around two hours before being submitted to a slow solvent evaporation.

The analytical data [% calculated (% found)], have allowed to suggest the following formulae (Table 1).

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Table 1. Results of the elemental analyses of compounds A-H.

Compound	Chemical formula	Elemental analysis [%]					
		C		H		N	
		calc.	found	calc.	Found	calc.	Found
A	(CyNH ₃) ₂ O ₂ C(CH) ₂ CO ₂ CuCl	38.34	38.32	5.15	5.33	4.47	4.44
B	(CyNH ₃) ₂ O ₂ C(CH) ₂ CO ₂ ZnCl	38.12	38.53	5.12	5.16	4.45	4.65
C	(iPr ₂ NH ₂) ₂ O ₂ C(CH) ₂ CO ₂ NiCl	38.69	38.11	5.85	5.40	4.51	4.80
D	(CyNH ₃) ₂ O ₂ C(CH) ₂ CO ₂ CuBr	33.58	34.04	4.51	5.36	3.92	4.06
E	(iPr ₂ NH ₂) ₂ O ₂ C(CH) ₂ CO ₂ ZnCl	37.88	38.03	5.72	6.33	4.42	5.38
F	(iPr ₂ NH ₂ Cl)CuC ₂ H ₂ (CO ₂) ₂ H ₂ O	36.04	37.62	6.05	6.52	4.20	4.46
G	(CyNH ₃) ₂ O ₂ C(CH) ₂ CO ₂ .HgO ₂ C(CH) ₂ CO ₂	38.31	37.37	4.82	5.19	4.47	4.78
H	(iPrNH ₂) ₂ O ₂ C(CH) ₂ CO ₂ .HgO ₂ C(CH) ₂ CO ₂	37.94	38.34	5.73	6.20	4.44	5.13
I	[Y ₂ (O ₂ C(CH) ₂ CO ₂) ₃].4MeOH	28.79	29.04	2.42	3.56	0	0
J	[(CyNH ₃) ₂ O ₂ C(CH) ₂ CO ₂] ₃ [Dy(O ₂ C(CH) ₂ CO ₂)Cl.DyCl ₃] ₂	37.05	37.80	4.89	4.68	4.63	4.78
K	SbPh ₄ CO ₃ H	61.13	60.90	4.60	4.56	0	0

Infrared spectra were recorded on a Bruker Vector 22 spectrometer equipped with a Specac Golden Gate™ ATR device. Infrared data are given in cm⁻¹ [IR abbreviations: (vs) very strong, (s) strong, (m) medium]. Elemental analyses were performed at the “Institut de Chimie Moléculaire”, University of Bourgundy, Dijon-France. All chemicals were purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and used without any further purification.

3. RESULTS AND DISCUSSION

3.1. Compounds obtained with MCl₂ moiety

Let us consider the main IR data in cm⁻¹ of the studied compounds (Table 2).

Table 2. Main IR data of compounds A-K.

Complexes	vasCOO ⁻	vsCOO ⁻	δCOO ⁻	v(NH ₂)	vas(NH ₂)
A	1548(m) 1576(m)	1318(m)	835(m)	3251(m) 3385(m)	1619(s) 1648(m)
B	1543(m) 1583(m)	1375(m)	795(m)	2937(m) 2860(m)	1628(s) 1660(s)
C	1440(m) 1531(m)	1325(m)	685(s)	3218(m)	1602(m) 1620(m)
D	1543(m) 1516(m)	1398(m)	767(s)	2934(m)	1625(m) 1684(m)
E	1537(m)	1221(m)	863(s)	3029(m)	1630(s) 1689(m)
F	1572(m)	1425(m)	878(s)	2861(m) 2939(m)	1639(m)
G	1566(m)	1382(m)	785(s)	2985(m)	--
H	1474(m) 1584(m)	1381(m)	872(m)	2782(m) 2867(m) 2947(m)	--
I	1520(m)	1316(m)	864(s)	3239(m)	1615(m) 1620(s)
J	1569(m) 1457(m)	1391(m)	778(s)	2897 (m)	1612(s) 1618(m)
	<i>v(OH)</i>		<i>v(COH)</i>		<i>v(CO₃)</i>
K	2900 (m)		1063 (m)		1427 (m) 1500 (m)

From these infrared data we have suggested:

- For A, B, C, D and E, while considering the complex-anion, a dimeric structure with two external maleato anions behaving as monochelating ligands and two bridging halogen atoms, the environment

around the metallic centre being square planar in the cases of Cu and Ni (Figure 1a) or tetrahedral in the case of Zn (Figure 1b).

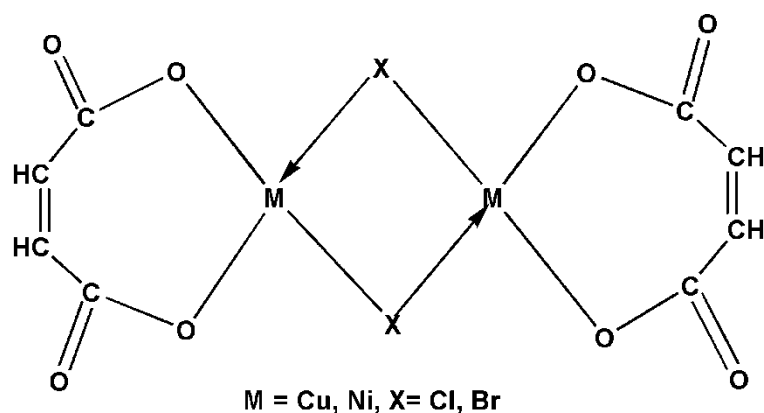


Fig. 1a. Proposed structure for compounds **A**, **C** and **D**.

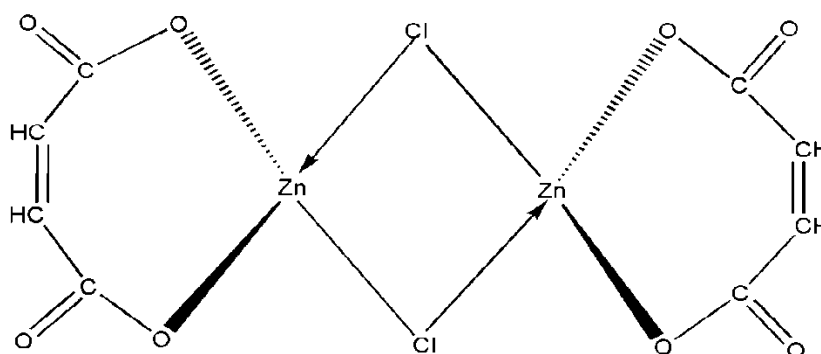


Fig. 1b. Proposed structure for compounds **B** and **E**.

- For **F**, a dimer similar to the one suggested in the previous zinc compound by replacing the bridging chlorides by bridging water molecules (Figure 2).

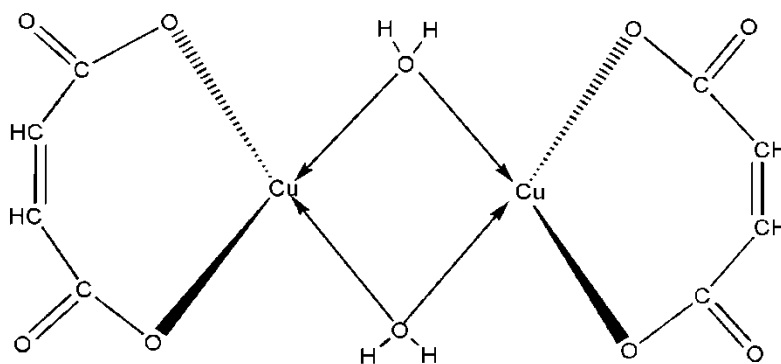
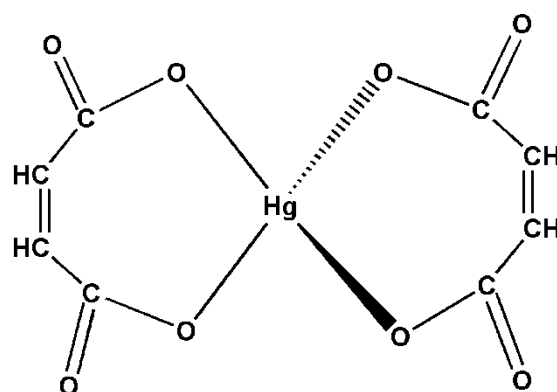
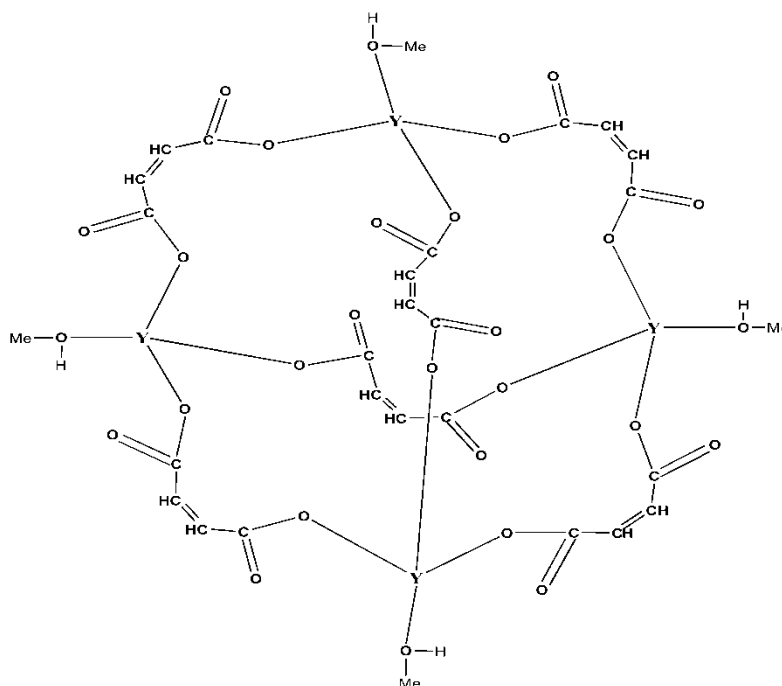


Fig. 2. Proposed structure for the compound **F**.

- For **G** and **H**, while considering the complex-anion $[\text{Hg}(\text{O}_2\text{C}(\text{CH})_2\text{CO}_2)_2]^{2-}$, a discrete structure in which the maleate dianion behaves as a monochelating ligand, the environment around the mercury centre being tetrahedral (Figure 3).

Fig. 3. Proposed structure for compounds **G** and **H**.

- For **I**, by dimerizing, a discrete structure containing four metallic centres distributed in a tetrahedron manner, the metallic centres being linked by bidentate maleate anions leading to a P_4O_6 structure type. Each yttrium centre is then coordinated by a methanol molecule giving finally a P_4O_{10} structure type, the remaining methanol molecules being lattice (Figure 4).

Fig. 4. Proposed structure for the compound **I**.

- For **J**, while considering the complex-anion, after a dimerization followed by a rearrangement, two structures:
 - ✓ A first discrete one in which the four metal centres distributed in a square manner are connected to each other *via* bidentate maleate anions, each dysprosium centre being then bonded to two chlorine atoms (Figure 5a). The coordination number of each metal centre is seven (7), very common in rare earths chemistry.
 - ✓ A second two components one, the first component being a dysprosium centre monochelated by the five maleates, the second component consisting of three $[DyCl_2]^+$ moieties linked by pair through a bridging chlorine atom, and two chloride ions both coordinating the three dysprosium centres (Figure 5b).

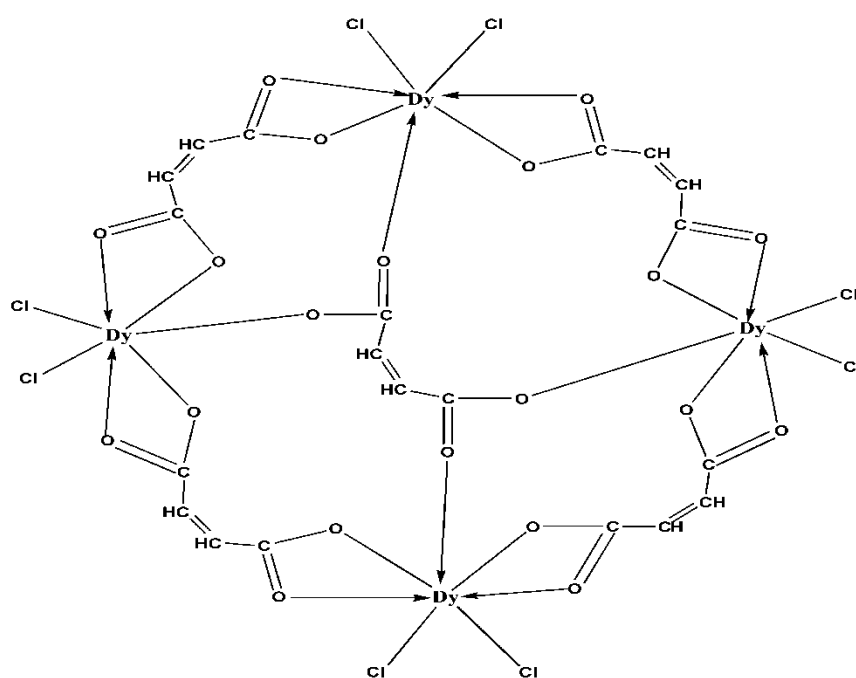


Fig. 5a. Proposed structure for the compound J.

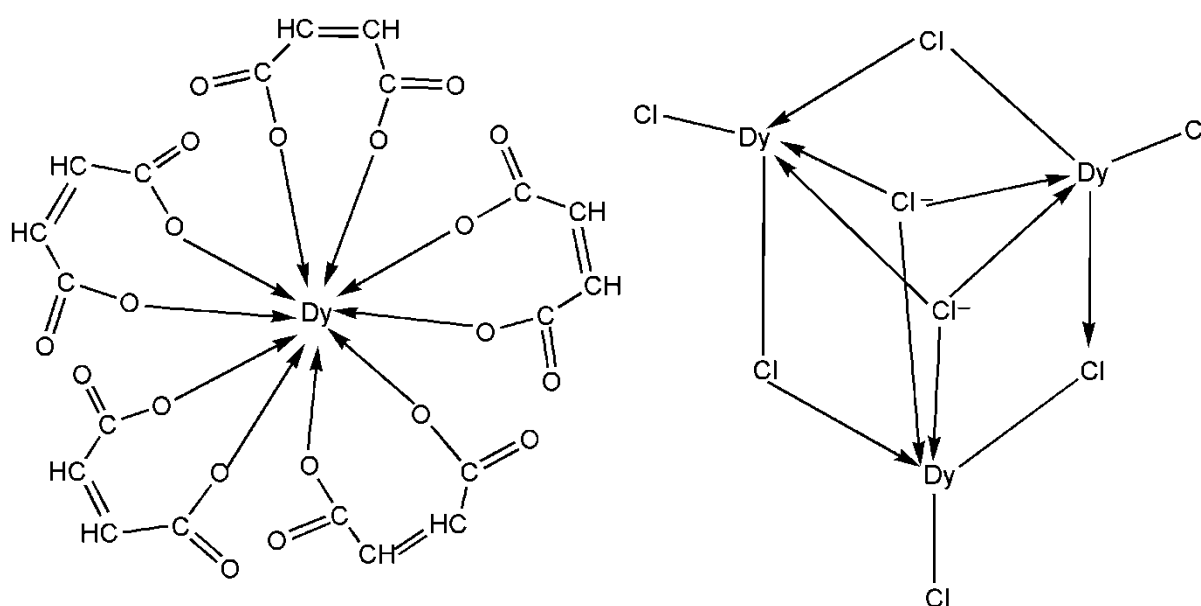
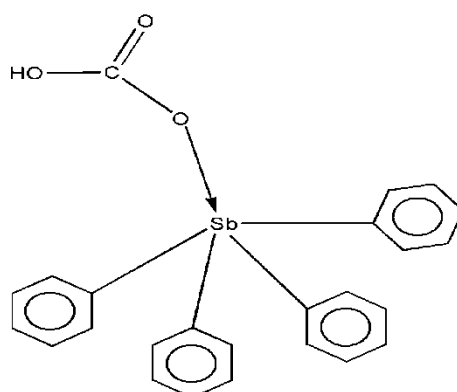
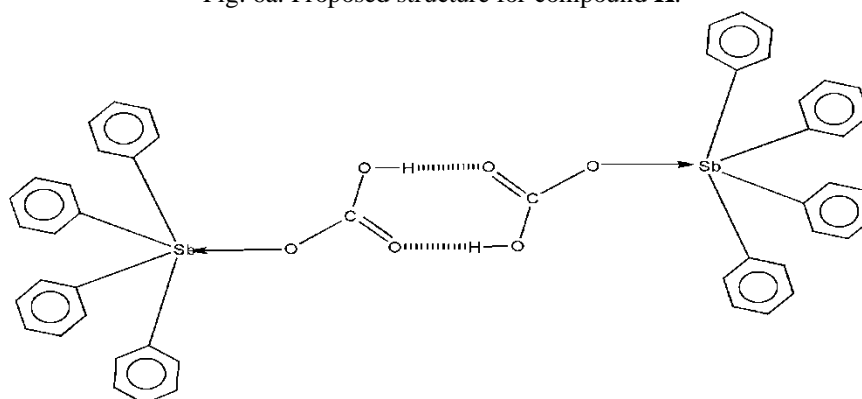


Fig. 5b. Proposed structure for the compound J.

- For **K**, a first discrete structure with a monodentate formate coordinating the SbPh_4 residue, the environment around the Sb centre being pentagonal (Figure 6a) and a second dimer one, the dimerization being ensured by O-H...O hydrogen bonds (Figure 6b).

In all the structures except for **F** and **K**, the cations interact with complex-anions *via* hydrogen bonds. While considering intermolecular hydrogen bonds supramolecular architectures may be obtained in all the suggested structures.

Fig. 6a. Proposed structure for compound **K**.Fig. 6b. Proposed structure for the compound **K**.

4. CONCLUSION

The studied complexes and adduct have discrete structures, the maleate behaving as a monochelating, a bichelating, a bidentate or a tetradentate ligand whereas the formiate behaves as a monodentate ligand. The environment around the transitional metal centres is tetrahedral or square planar. The rare earth yttrium centre is four coordinated while the dysprosium centre is five, seven and ten coordinated. In all the proposed structures, while considering extra hydrogen bonding interactions, supramolecular architectures may be obtained.

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