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New MCl_3 (M = Y, Dy, Pr) Salicylato, Maleato, Phtalato, Phenylsufonato and Phosphato Complexes and Adducts: Synthesis and Infrared Study

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Abstract

Nine rare earth complexes have been synthesized from reaction carried in common organic solvent between salicylate, maleate, phtalate, phenylsulfonate or phosphate ammonium salt and MCl3 (M = Y, Dy, Pr). All compounds have been structurally characterized by infrared. Structures involving the complex anions have been proposed. The suggested structures are discrete or of double metallic components type. The oxyanions behave towards metallic centres as monodentate, monochelating or monochelating and monodentate ligands. The coordination number at rare earth metal atoms vary from five (5) for Pr and Dy to twelve (12) for Dy. For compounds containing a protonated amine, when the possible hydrogen bonding interactions are considered supramolecular architectures may be obtained.

Keywords: Discrete; Two Components Structure; Monodentate; Mono chelating; Monodentate; Ligand; Supramolecular Architectures

Introduction

A great variety of transitional and non-transitional metal and non-metal compounds have been synthetized using as starting materials protonated amine salts in general soluble in organic solvents [1-3]. In rare earth halide organometallic compounds, these protonated amine salts can be involved in hydrogen bonds to lead to supramolecular architectures [4-6]. The ability of these cations to form supramolecular structures has been highly noted for numerous complexes with rare earths (lanthanides) [7,8].

In this dynamic salts of salicylic, Phtalic, maleic, phenyl sulfonic and phosphoric acids with dibutylamine, mono cyclohexylamine and diisopropylamino have been prepared and their reactions with trihalides of rare earths, in the purpose of studying the structural arrangements of the obtained complexes and deducing the coordinating ability of oxyanions, have been undertaken. This study has yielded nine new compounds; infrared characterization of which have been carried out then structures suggested on the basis of infrared data.

Materials and Methods

All the chemicals were purchased from Aldrich Company (Germany) and used without any further purification.

$Bu_2NH_2C_6H_4(OH)CO_2$ (L_1), $Bu_2NH_2(C_6H_4(CO_2)_2$ (L_2), $(CyNH_3)_2.O_2C(CH)_2CO_2$ (L_3), $Bu_2NH_2C_6H_5SO_3$ (L_4), $iPr_2NH_2C_6H_5SO_3$ (L_5), and $(CyNH_3)H_2PO_4$ (L_6) have been obtained as powders on allowing to react in methanol:

a) L_1: dibutylamine (Bu_2NH_2) and salicylic acid in a 1:1 ratio

b) L_2: dibutylamine (Bu_2NH_2) and phtalic acid in a 2:1 ratio

c) L_4: dibutylamine (Bu_2NH_2) and phenylsulfonic acid in a 1:1 ratio

d) L_5: diisopropylamine (iPr_2NH) and phenylsulfonic acid in a 1:1 ratio

e) L_6: monocyclohexylamine ($CyNH_2$) and phosphoric acid in a 1:1 ratio

The compounds A, B, C, D, E, F, G, H and I were obtained as white powders after a slow solvent evaporation at room temperature on allowing to react in methanol: L_1 and PrCl3 in a 1:1 ratio (A), L_2 and $Y(CH_3CO_2)_3$ in a 1:1 ratio (B), L_2 and YCl_3 in a 1:1 ratio (C), L_2 and $DyCl_3$ in a 1:1 ratio (D), L_3 and $DyCl_3$ in a 1:1 ratio (E), L_4 and $Y(CH_3CO_2)_3$ in a 1:1 ratio (F), L_4 and Dy Cl_3 in a 1:1 ratio (G), L_5 and $Y(CH_3CO_2)_3$ in a 1:1 ratio (H) and, L_6 and $DyCl_3$ in a 1:1 ratio (I). All 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). The 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 Burgundy, Dijon-France. All chemicals were purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and used without any further purification. Let us consider the main IR data (Tables 2-4) of compounds A-I.

Table 1: Analytical data of compounds A-I.

Compound	Chemical formula	Elemental analyses [%]							
		C		H		N		S	
		calc.	Found	calc.	Found	calc	Found	calc.	Found
A	$Bu_2NH_2[C_6H_4(OH)CO_2Y(CH_3CO_2)_3]$	56.74	57.16	7.71	7.6	3.15	3.12	-	-
B	$(4Bu_2NH_2)2[(C_6H_4(CO_2)_2)2.3PrCl_3]$	36.28	36.16	5.54	5.69	3.02	3.07	-	-
C	$(4Bu_2NH_2)2[(C_6H_4(CO_2)_2)2.3YCl_3]$	40.69	40.41	5.51	5.32	2.96	2.85	-	-
D	$(4Bu_2NH_2)2[(C_6H_4(CO_2)_2)2.3DyCl_3]$	34.71	34.45	5.3	5.27	3.37	3.31	-	-
E	$3((CyNH_3)_2.O_2C(CH)_2CO_2)[Dy(O_2C(CH)_2CO^2)ClDyCl_3]2$	30.81	31.06	5.75	5.68	1.79	1.76	-	-
F	$(Bu_2NH_2)[C_6H_5SO_3Y(CH_3CO_2)_3]$	47.64	47.7	8.1	8.08	3.35	3.4	7.09	7.11
G	$3(iPr_2NH_2C_6H_5SO_3)$ $[Dy(C_6H_5SO_3)2.Cl.$ $DyCl_3]2$	30.81	31.06	5.75	5.68	1.79	1.76	9.08	8.9
H	$(CyNH_3)[H_2PO_4Y(CH_3CO_2)2$ $H_2PO_4.H_2O]$	4.49	4.34	1.86	1.88	0.96	0.92	-	-
I	$3(CyNH_3PO_4H_2)[DyHPO4ClDyCl_3]2$	31.12	31.06	4.13	4.45	0.6	0.65	-	-

Table 2: Main IR data of compounds A-E.

Compound	νasCOO-	νsCOO-	δCOO-	ν(NH_2)	δ(NH_2)
A	1548 (m)	1255(s)	757(s)	2936(w)	1548(m)
B	1520(vs)	1316(m)	864(s)	3239(m)	1615(m) 1620(s)
C	1422(m)	1355(m)	752(s)	2950 (vs)	1625(m)
D	1478(m)	1275(m)	785(s)	2898(vs)	1617(m)
E	1455(m)	1357(m)	762(s)	2997(vs)	1612(s)

Table 3: Main IR data of compounds F and G.

Compound	νSO_3	νasSO_3	ν(NH_2)	δ(NH_2)
F	1034(m)	610(m) 568(m)	2962(s) 2870(s)	1618(m)
G	1072(m)	602(m) 546(m)	2915(s) 2989(s)	1627(m)

Table 4: Main IR data of compounds H and I.

Compound	ν(PO_4)	ν(NH_3)	δ(NH_2)
H	1118(m)	2942(m) 2855(m)	1559(m)
I	1198(m)	2996(F) 2865(F)	1655(m)

Results and Discussion

From these infrared data we have suggested while considering the complex anion of the studied complexes and adducts: For A, a discrete structure with an Y^{3+} ion chelated by three acetate and the salicylate anions conferring a coordination number of eight (8) to the Y^{3+} ion (Figure 1). For B, C and D which have the same formula

$(Bu_2NH_2)_4[(C_6H_4(CO_2)_2)_2.3MCl_3]$ and M = Dy, Y or Pr, we will consider one of them as the relative molecule. As structure, we can consider a central $PrCl_3$ molecule monocoordinated to each of the phtalate ions providing a coordination number of five (5) to the Pr^{3+} center. The external PrCl3 are each one mono chelated by the carboxylate group not involved in the coordination of the central PrCl3 molecule. Thus, all metal centers have a coordination number of five (5) (Figure 2).

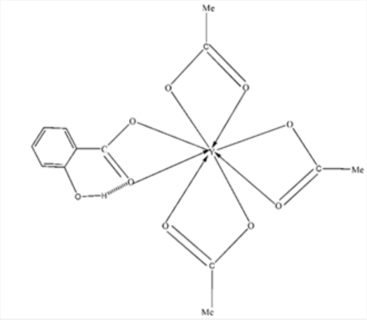

Figure 1: Proposed structure for the compound A

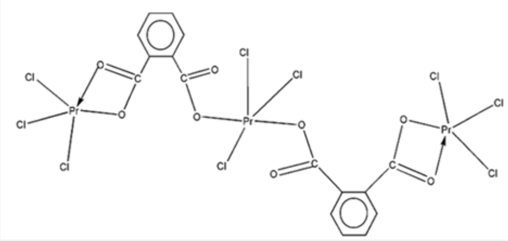

Figure 2: Proposed structure for the compound B.

For E, while considering a dimerization followed by a rearrangement, a two components structure is suggested. The first component is a dysprosium center mono chelated by the five maleates, the second component $[Dy_3Cl_8]^+$ being trinuclear consisting of three $[DyCl_2]^+$ moieties linked through bridging chlorine atoms, the three centers being hold together through two trico ordinating chloride ions (Figure 3). The two Trico ordinating chlorine atoms are located on the C_3 axis of the Cy_3 triangle.

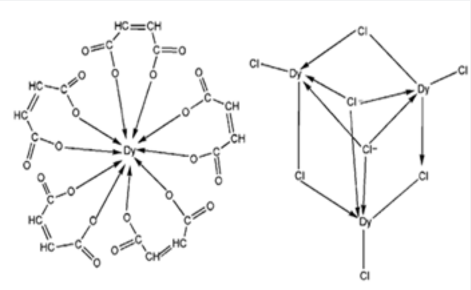

Figure 3: Proposed structure for the compound E.

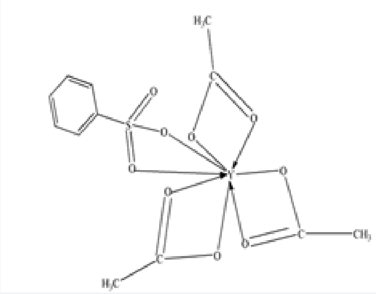

Figure 4: Proposed structure for the compound F.

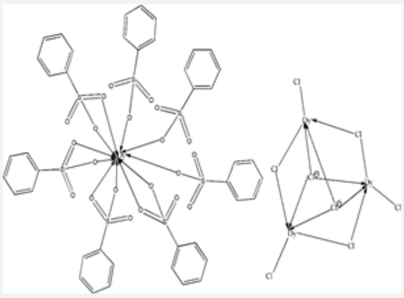

Figure 5: Proposed structure for the compound G.

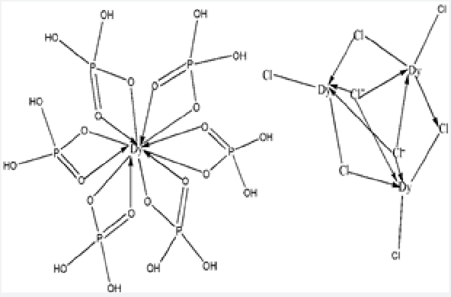

Figure 6: Proposed structure for the compound H.

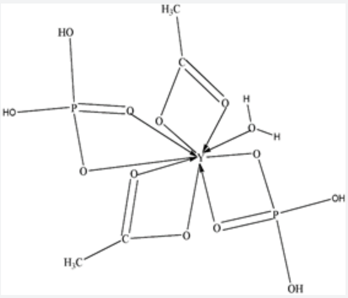

Figure 7: Proposed structure for the compound I.

For F, the suggested structure is discrete with a metal center mono chelated by acetate and sulfonate anions, the coordination number around yttrium being eight (8) (Figure 4). For G or H, the proposed structure is like that suggested for E by replacing maleates with phenyl sulfonates (Figure 5) or dihydrogen phosphates (Figure 6). For I, the structure consists of a Y^{3+} coordinated to a water molecule and mono chelated by the H_2PO_4- and the acetate anions giving to the yttrium a coordination number of nine (9) (Figure 7). NB: in all these studied compounds while considering the involvement of the cation through hydrogen bonds a supramolecular architecture may be obtained.

Conclusion

We have synthesized and studied nine new complexes and adducts of rare earth metals containing carboxylate, phosphate and phenyl sulfonate anions. The studied compounds have allowed proposing monomeric and double metallic components structures. The presence of the complex-ion [M3Cl8]- in several compounds and a double metal component is noteworthy. The coordination number of the metal center of the second metal component may exceed ten (10).

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