INTERACTIONS BETWEEN $C_6H_4(CH_2NH_3)_2[PhCO_2]_2$, $Et_2NH_2[Ph(OH)CO_2]$ AND $CuCl_2$, $ErCl_3$ or $SnPh_3OH$: AN INFRARED STUDY

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Abstract: The interactions of benzoic or salycilic acids salts with di-, trihalides or $SnPh_3OH$ have yielded four new complexes and adducts studied by infrared.The suggested structures are discrete or of infinite chain type, the anion behaving as monodentate and hydrogen bonding involved, or bidentate, the environments around the metallic centres being tetrahedral, octahedral or trigonal bipyramidal. When N-H groups are involved in extra hydrogen bonding, a supramolecular architecture may be obtained.

Keywords: complexes and adduct, discrete structures, mono- and bidentate benzoate, monochelating and monodentate, monochelating benzoate, monochelating or only hydrogen bonding involved salycilate

1. INTRODUCTION

Most of substituted ammonium salts with carboxylic acids being soluble in organic solvents, trying to synthesize the complexes of these salts with transitional or no transitional metallic halides, acetates or nitrates may be a specific way to study the coordinating ability of the carboxylate anions obtained from the protonation of substituted amines. To complete the data on the coordination ability of oxyanions summarized by Hathaway [1], our group and others worldwide have reported many new complexes obtained from protonated amine salts [2-4]. We initiate here the study of the interactions between the salts of Et_2NH or $C_6H_4(CH_2NH_2)_2$ and benzoic or salicylic acids with some metallic halides and $SnPh_3OH$ which has yielded the studied complexes and adduct, infrared study of which has been carried out then structures suggested.

2. MATERIAL AND METHODS

On mixing in ethanol $C_6H_4(CH_2NH_2)_2$, PhCOOH and $CuCl_2.2H_2O$ in 1-2-2 ratio a solution is obtained and a green powder collected after a slow solvent evaporation. Its analytical data -%Calculated(%Found)- **% C** = 33.71(33.52), **% H** = 3.09(3.06), **% N** = 3.57(3.61) have allowed to suggest $C_6H_4(CH_2NH_3)_2$ $[PhCO_2]_2.3CuCl_2$ as formula -[**A**]-. On mixing in ethanol $C_6H_4(CH_2NH_2)_2$, PhCOOHand $HgCl_2$.1-2-2 ratio a white precipitate is obtained stirred and collected. Its analytical data [% Calculated (% Found)] **% C** = 30.58 (30.31), **% H** = 2.98(3.04), **% N** = 2.97(3.03) have allowed to suggest $C_6H_4(CH_2NH_3)_2[PhCO_2]_2.2[HgCl (HCO_2)]$ as formula -[**B**]-. On allowing $C_6H_4(CH_2NH_2)_2$, Ph(OH)COOH and $SnPh_3OH$ to react in ethanol in 1-2-2 ratio a solution is obtained. After a slow solvent evaporation a white powder is obtained. Its analytical data [% Calculated(%Found)] **% C** = 61.64(61.65), **% H** = 5.17(5.12), **% N** = 3.59(3.50) have allowed to suggest $C_6H_4(CH_2NH_2)_2[Ph(OH)CO_2.SnPh_3]_2.2H_2O$ or $C_6H_4(CH_2NH_3)_2[Ph(OH)CO_2]_2.2SnPh_3OH$ as formula -[**C**]-. On

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allowing Et_2NH, Ph(OH)(COOH) and $ErCl_3.6H_2O$ to react in ethanol in 1-1-1 ratio a solution is obtained. After a slow solvent evaporation a purple powder is obtained. Its analytical data [%Calculated(%Found)] **% C** = 32.77(33.62), **% H** = 5.66(5.62), **% N** = 2.25(2.29) have allowed to suggest $Et_2NH_2[Ph(OH)CO_2].ErCl_3.3EtOH$ as formula -[**D**]-.

IR abbreviations: br(broad), vs(very strong). The elemental analyses have been obtained from the Microanalyses Laboratory-University of Burgundy-Dijon-France, the infrared spectra from University of Burgundy-France using a FTIR spectrometer. The chemicals were purchased from Aldrich Company-Germany-and used without any further purification.

3. RESULTS AND DISCUSSION

The data relative to the carboxylate group of the studied adducts and complexes are very strong bands in the region 1600-1300 cm^{-1}:

- [**A**]: νCO21594, 1376, νNH 3000;
- [**B**]: νCO2 1675, 1600, 1274, νNH 3010
- the last band at 1274 is wide with shoulders), this multiplicity of bands is due to the presence of two different anions.

The suggested structure for [**A**] is discrete with $PhCO_2^-$ acting as a monochelating and monocoordinating ligand, the environnement around the Cu centres being tetrahedral (Figure 1).

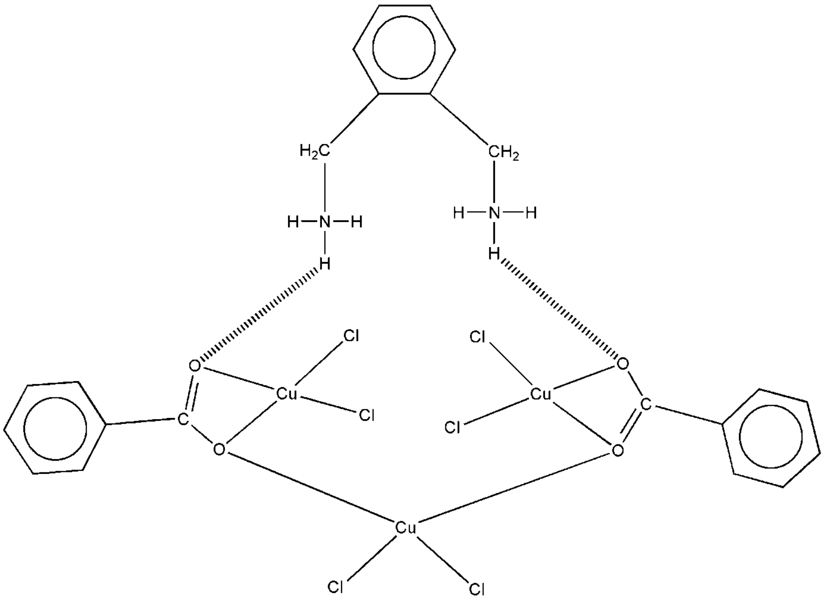


Fig. 1. Proposed structure for compound **A.**

In this compound some dephenylation of the benzoate into formiate occurs. The suggested structure for [**B**] is discrete with $PhCO_2^-$ acting as a monochelating ligand and the formiate anion as a monocoordinating one, the environment around the Hg centers being tetrahedral (Figure 2).

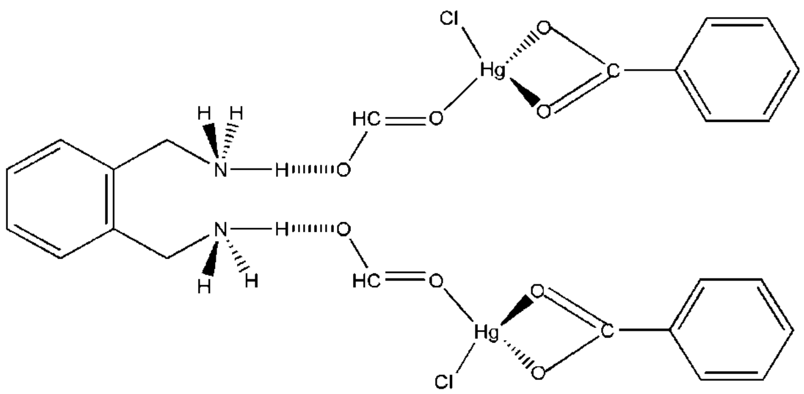
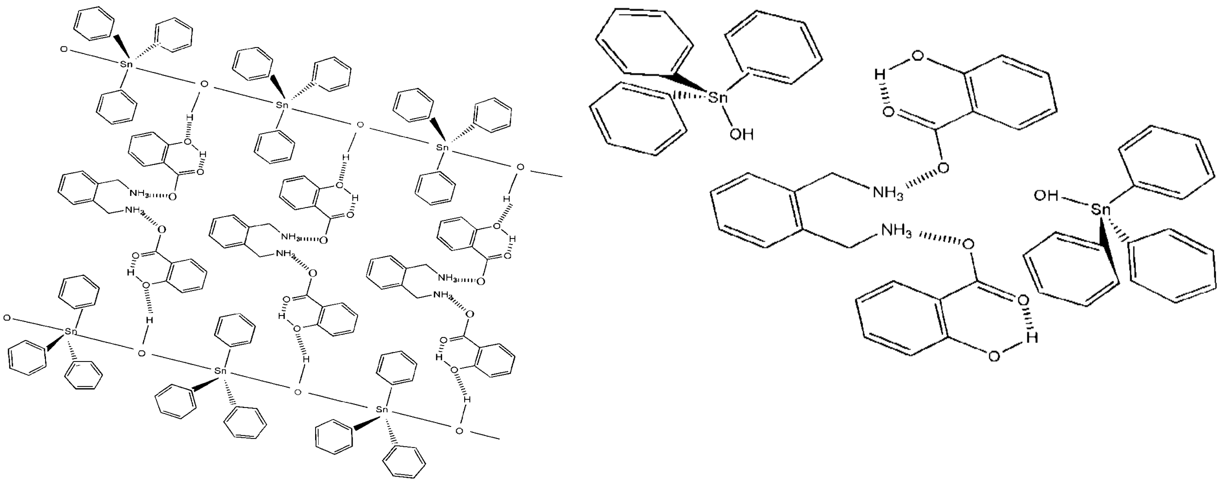


Fig. 2. Proposed structure for compound **B.**

- **C**]:ν CO2 1590, 1392, νNH 3010, νOH 3300.

This compound can be written in two ways: considering the presence of water molecules or not. The presence of the doublet at 895 and 910 cm^{-1} on the spectrum confirm the presence of $SnPh_3OH$ and the absence of water molecules.

The suggested structure is an inclusion structure consisting of $C_6H_4(CH_2NH_3)_2[Ph(OH)CO_2]_2$ molecules interacting or not through hydrogen bonds with $SnPh_3OH$ ones (Figure 3a and 3b).



a) b)

Fig. 3. *Proposed structure for compound* **C.**

- [**D**]: νCO2 1655, 1325,νNH3010 , νOH 3340.

The rare earth metals are known to bear up to 10 bonds [5]. The suggested structure discrete with a monochelating salycilate and monocoordinating ethanol molecules, is reported in Figure 4.

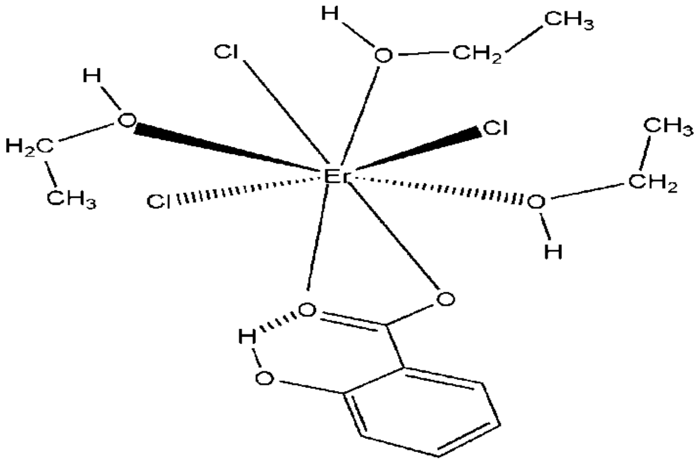


Fig. 4. Proposed structure for compound **D.**

For all the compounds the CO_2 bands are very strong while OH and NH are broad. The cation may be involved in hydrogen bonds leading to a supramolecular architecture.

4. CONCLUSION

The studied adducts have discrete or infinite chain structures, the anion behaving a monochelating ligand and monocoordinating (or involved in hydrogen bonding), or as a monodentate ligand. The environments around the metallic centres are tetrahedral or trigonal bipyramidal. The metal is eight coordinated in the rare earth complex. When extra molecular hydrogen bonds are possible supramolecular architectures maybe obtained; partial dearylation occurs in one compound leading to the presence of two anions.

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REFERENCES

[1] Hathaway, B.J., Comprehensive coordination chemistry, Ed.Wilkinson, G., Gillard, R.D., McCleverty, J.A. Pergamon Press, Oxford, 1st edition, Vol. 5, 1987.
[2] Ibrahim, A.A., Khaledi, H., Ali, H.M., A multiprotic indole-based thiocarbohydrazone in the formationof mono-, di- and hexa-nuclear metal complexes, Polyhedron, vol. 81, 2014, p. 457–464.
[3] Dessapt, R., Kervern, D., Bujoli-Doeuff, M., Deniard, P., Evain, M., Jobic, S., How does the synthesis temperature impact hybrid organic-inorganic molybdate material design?, Inorganic chemistry, vol. 49, no. 24, 2010, p. 11309-11316.
[4] Gueye, N., Diop, L., Stoeckli-Evans, H., Tetrakis(dipropylammonium) tetrakis(oxalato-κ 2O1,O2)stannate (IV) monohydrate: a complex with an eight-coordinate Sn IV atom, Acta crystallographica, vol. E70, no. 2, 2014, m 49 – m 50.
[5] Sokolov, M.N., Gushchin, A.L., Kovalenko, K.A., Peresypkina, E.V., Virovets, A.V., Sanchiz, J., Fedin, V.P., Triangular oxalate clusters [W-3(mu(3)-S)(mu(2)-S-2)(3)(C2O4)(3)](2-) as building blocks for coordination polymers and nanosized complexes, Inorganic chemistry, vol. 46, no. 6, 2007, p. 2115-2123.