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# XPS as Sensor for the Bonding Nature in Metal Acetates

O. Pérez[1], O. F. Odio[2,*], E. Reguera[1,*]

1) *Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Unidad Legaria, Ciudad México, México.*

2) CONACyT- *Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Unidad Legaria, Ciudad México, México.*

## A) XPS data for the measured metal acetates

**Table S1.** Binding energy values for the $–CH_3$ group for the measured metal acetates.

| **Metal acetate** | **$E_B[C\ 1s]_{-CH3}$ (eV)** |
|---|---|
| Li | 285.23 |
| Na | 285.30 |
| Mg | 285.21 |
| K | 285.18 |
| Mn | 285.17 |
| Fe | 285.28 |
| Co | 285.37 |
| Ni | 285.43 |
| Cu | 285.35 |
| Zn | 285.17 |
| Ag | 285.20 |
| Cd | 285.27 |
| Hg | 285.29 |
| Pb | 285.29 |

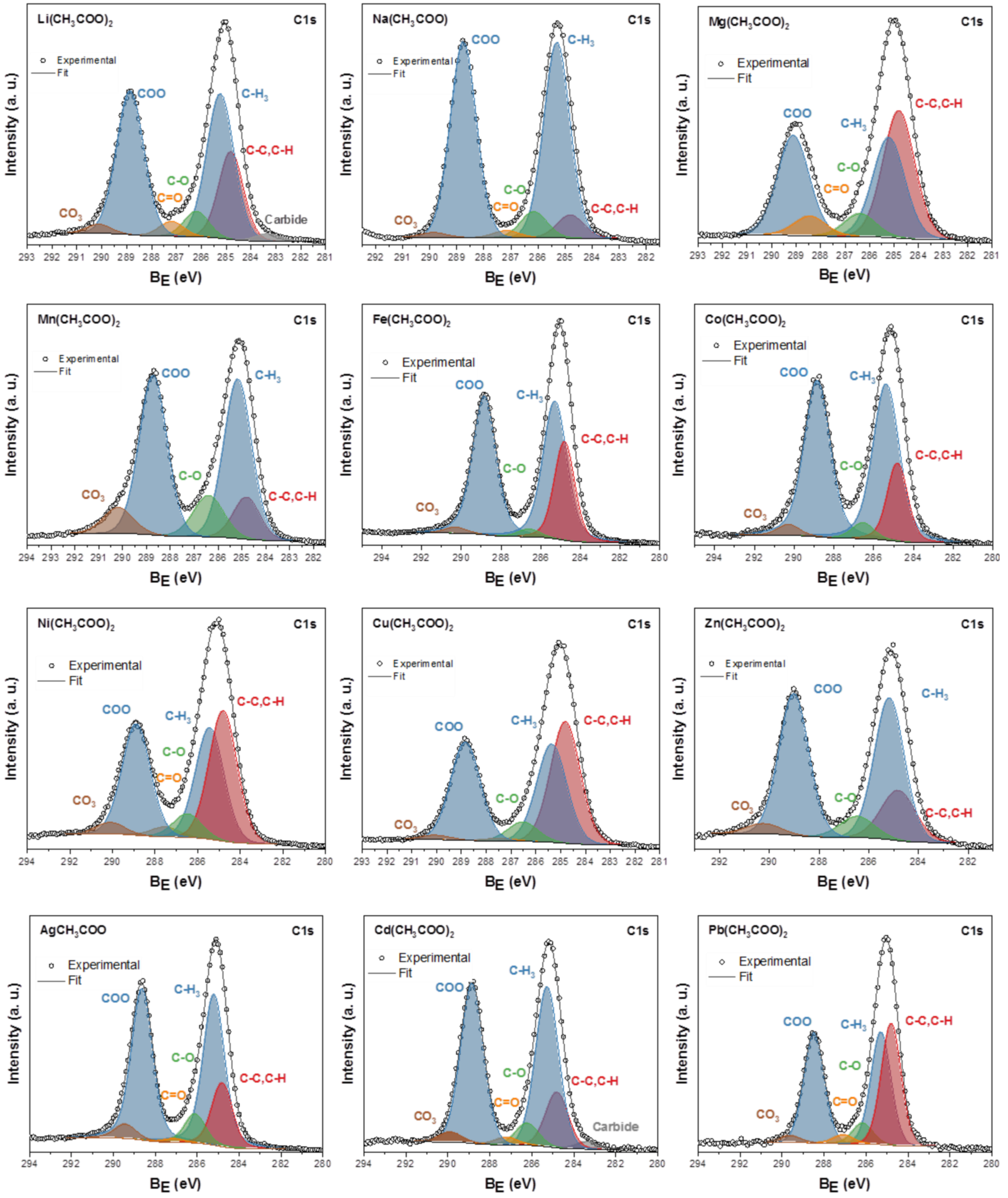

**Figure S1.** Curve fitting for C 1s spectra of the studied metal acetates. Signals pertaining to model compounds are shown in blue while those related to adventitious contamination are shown in other colors

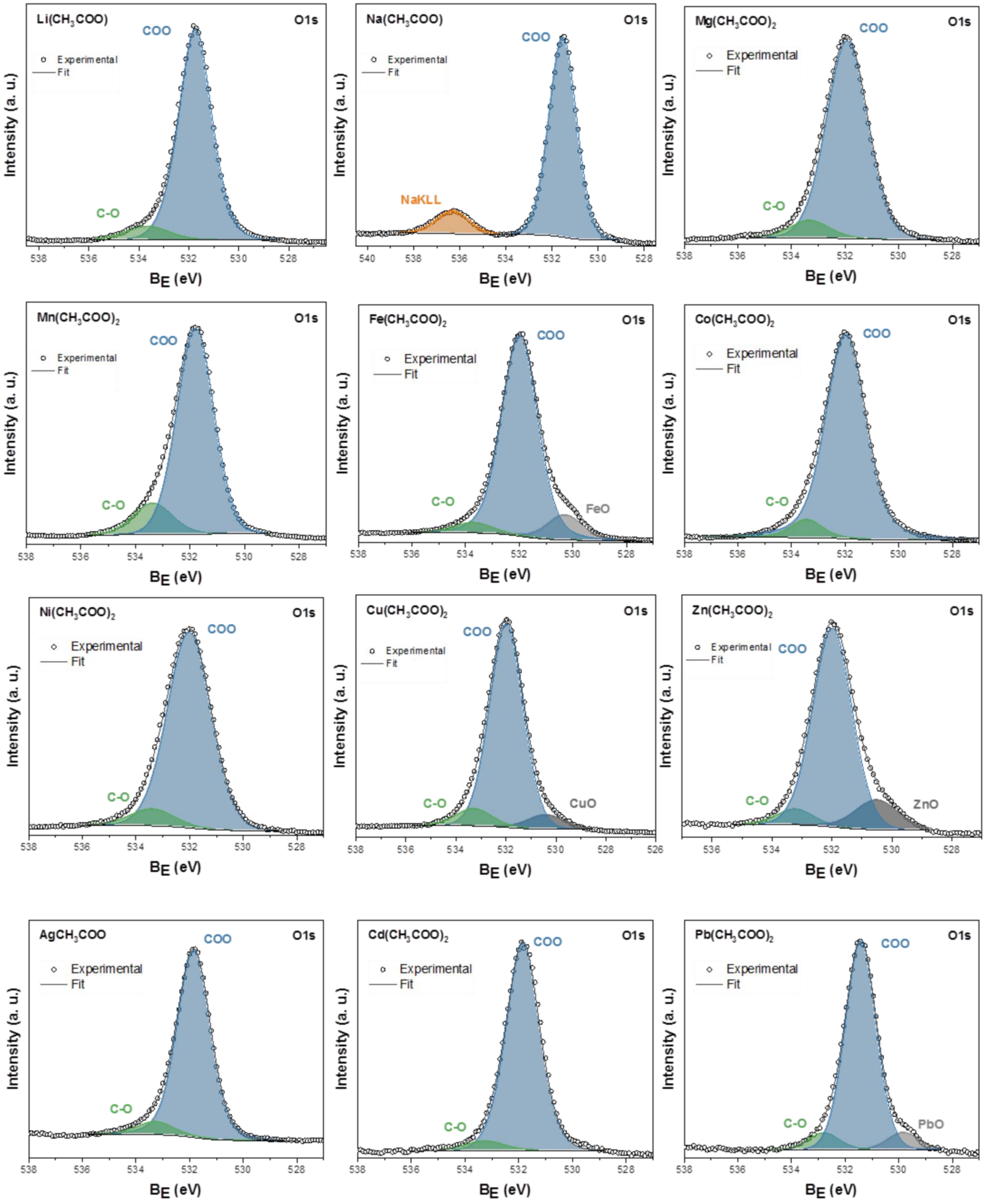

**Figure S2.** Curve fitting for O 1s spectra of the studied metal acetates. Signals pertaining to model compounds are shown in blue while those related to adventitious contamination or acetate decomposition are shown in other colors

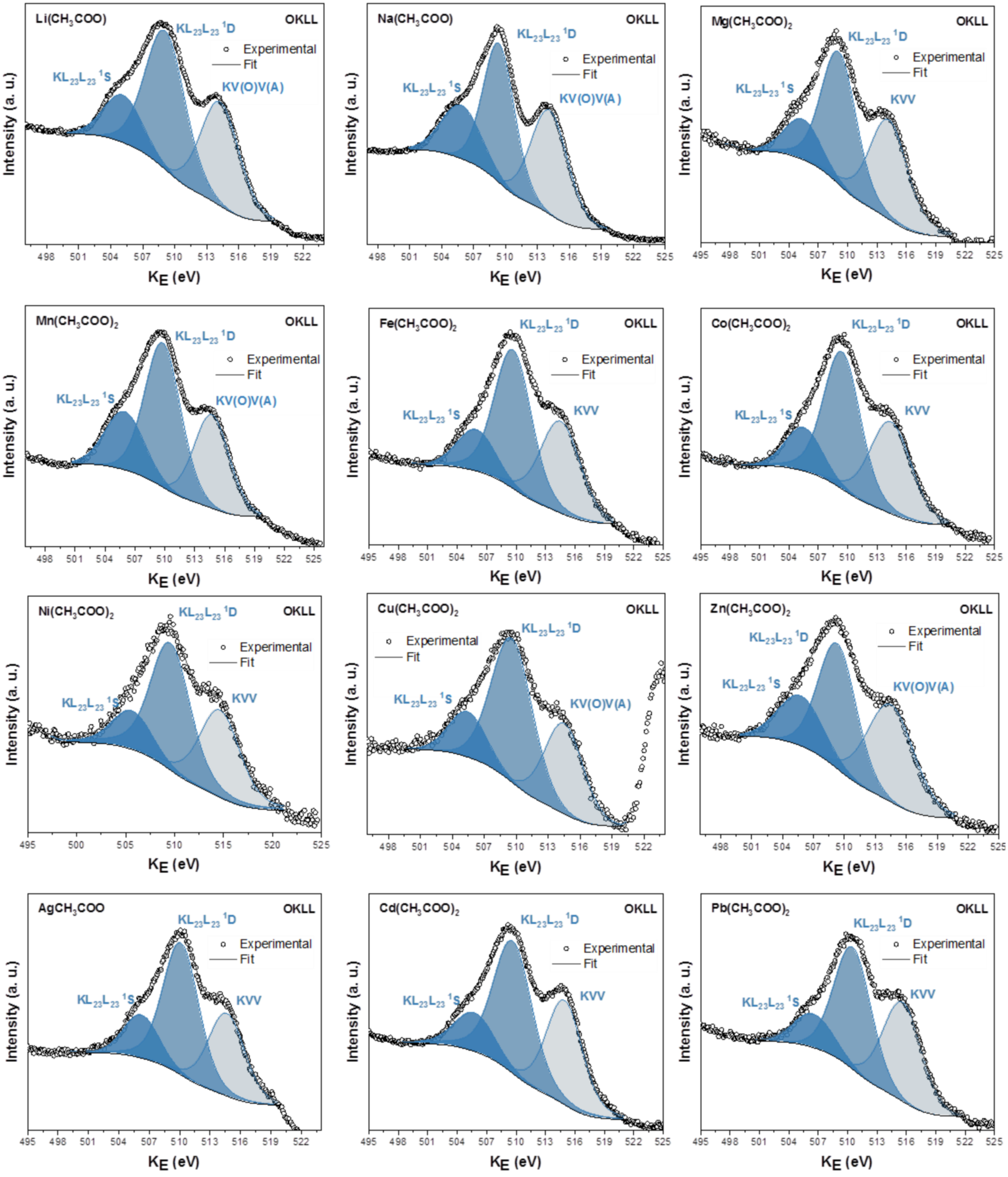

**Figure S3.** Curve fitting for the O KLL Auger region of the studied metal acetates

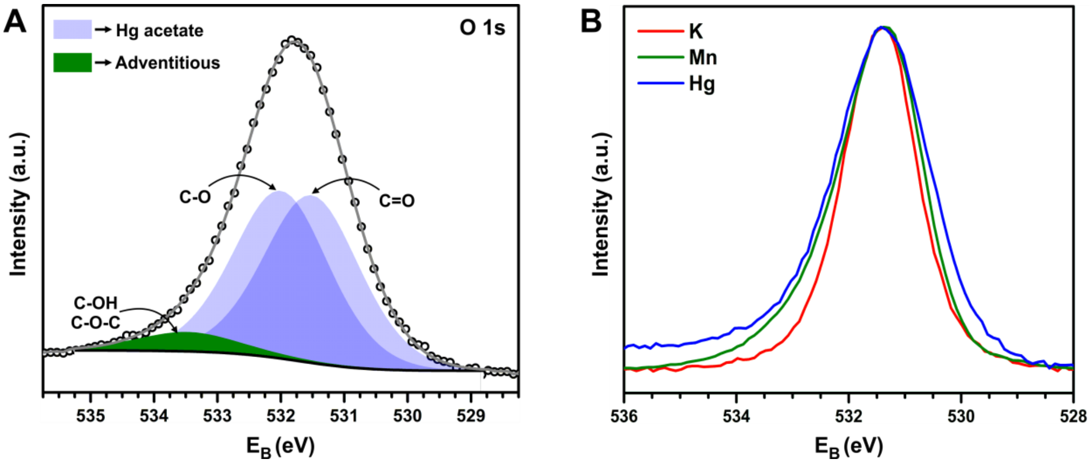

**Figure S4. A)** Curve fitting of the high-resolution O 1s spectrum for the Hg acetate considering two contributions from the acetate group; the energy difference is 0.5 eV and the FWHM are 1.8-1.9 eV. **B)** Comparison of the line-shape profiles for K, Mn, and Hg acetates; note the absence of distinct features in the Hg spectrum.

- *On the importance of shake-up satellites in the studied metal acetates*

Spectra from Figures S1 and S2 do not show any shake-up satellite structure from the acetate –COO group, mainly because the weak signals are obscured by the inelastic background. However, shake-up satellites can be detected indirectly as an imbalance in the stoichiometry of the compounds; in our case, such imbalance is reflected in an intensity ratio between the carbon atoms –COO/CH3 < 1, typically between 1 and 0.8.[1] In order to estimate the signal intensity reduction in –COO relative to $–CH_3$, we analyzed the K acetate, which is expected to be the compound where the charge in the acetate ion is the most delocalized. For this endeavor, the high-resolution C 1s spectrum was fitted by fixing the area ratio $–COO/CH_3$ in the range of 0.8 – 1.0; for each curve fit, the binding energies of the acetate peaks and the corresponding $\chi^2$ values were recorded. The results are presented in Figure S4. First, the –COO binding energy (not shown), which is the most relevant C 1s signal for our work, suffered no variation as a function of the area ratio $–COO/CH_3$, but it remained constant at 288.34 eV. Second, note in the figure that the $CH_3$ binding energy decreases only 0.07 eV as the stoichiometry departs from 1. Third, the goodness of the fit is practically constant from 1 to 0.9, but for stoichiometry less than 0.9 it rapidly falls off (increasing values of $\chi^2$). By combining these result, we conclude that, as far as our primary goals are concerned, the intensity decay of the –COO group by shake up satellite is of minor importance and can be safely disregarded.

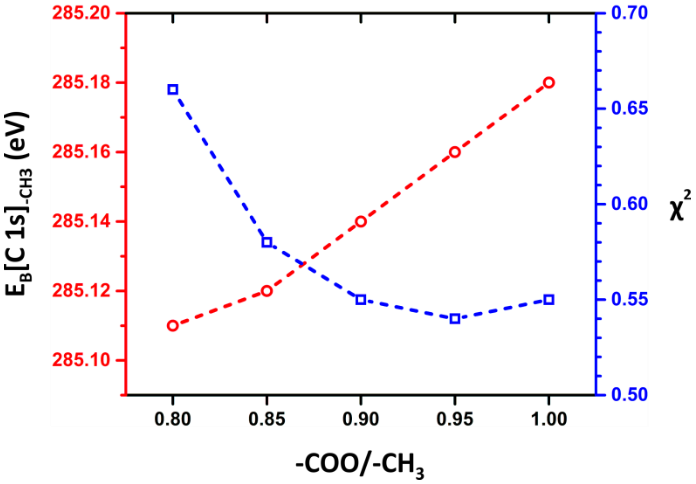

**Figure S5**. Variation of the binding energy for the C 1s of the K acetate methyl group and the goodness of the curve fitting process as a function of the area ratio $-COO/CH_3$.

## B) Synthesis and characterization of $Co(CH_3COO)_2(C_3N_2H_4)_2$ and $Zn(CH_3COO)_2(C_3N_2H_4)_2$

These compounds were prepared by a synthetic rout described by Chen *et al.*[2]

**$Co(CH_3COO)_2(C_3N_2H_4)_2$.** 136 mg of imidazole ($C_3H_4N_2$) were dissolved in 5 ml of methanol under stirring. In the same manner, 249 mg of cobalt(II) acetate tetrahydrate ($Co(CH_3CO_2)_2\cdot 4\ H_2O$) were dissolved in 10 ml of methanol. Then, the imidazole solution was added dropwise to the cobalt acetate solution under stirring. A purple precipitate is formed after methanol evaporation.

**$Zn(CH_3COO)_2(C_3N_2H_4)_2$.** 220 mg of zinc acetate dihydrate ($Zn(CH_3CO_2)_2\cdot 2H_2O$) were dissolved in 15 ml of an aqueous ethanol solution in a 1:2 (v:v) ratio. Then, 136 mg of imidazole ($C_3H_4N_2$) were added to the zinc acetate solution. Under stirring, a crystalline colorless precipitate was formed after solvent evaporation.

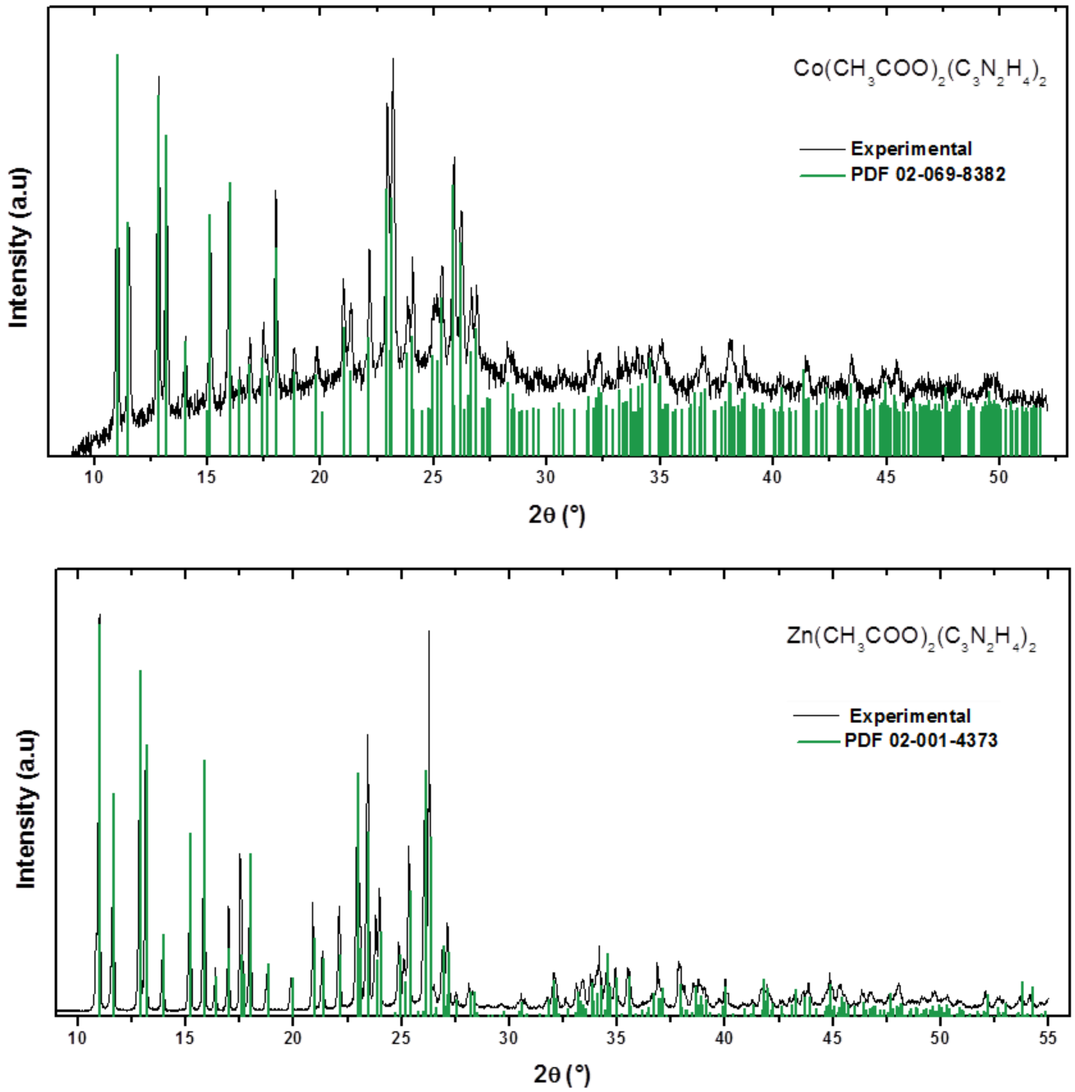

**Figure S6.** XRD powder patterns of Co(CH$_3$COO)$_2$(C$_3$N$_2$H$_4$)$_2$ (*top*) an Zn(CH$_3$COO)$_2$(C$_3$N$_2$H$_4$)$_2$ (*bottom*). The correspondent crystalline phase was identified through PDF-2 database.

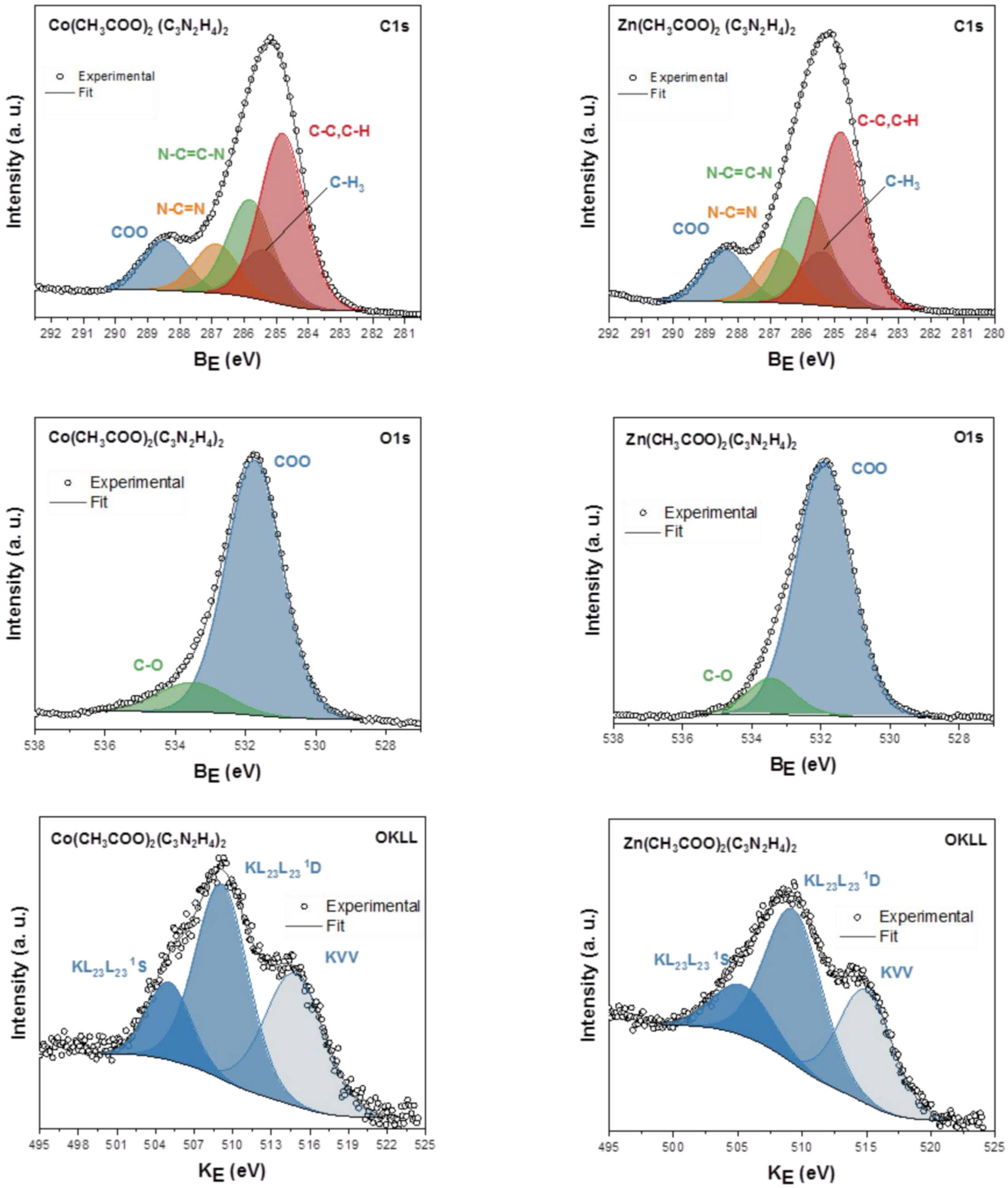

**Figure S7.** Curve fitting of the C 1s, O 1s and Auger O KLL spectra for Co(CH$_3$COO)$_2$(C$_3$N$_2$H$_4$)$_2$ and Zn(CH$_3$COO)$_2$(C$_3$N$_2$H$_4$)$_2$

## C) Supplementary data for the non-linear surface regression of Equation (6) [see Manuscript]

Table S2. Cation data used for the non-linear surface regression of Equation (6)

| **Metal ion** | **$r_{\mathrm{M}}$ (Å)$^{a)}$** | **$\chi_{\mathrm{M}}$$^{b)}$** | **$\sigma_{\mathrm{M}}$$^{c)}$** |
|---|---|---|---|
| $K^+$ | 1.51 | 0.91 | 0.92 |
| $Na^+$ | 0.99 | 0.98 | 0.93 |
| $Li^+$ | 0.59 | 1.02 | 0.36 |
| $Mg^{2+}$ | 0.89 | 1.12 | 0.87 |
| $Mn^{2+}$ | 0.66 | 1.44 | 3.03 |
| $Fe^{2+}$ | 0.63 | 1.63 | 3.09 |
| $Co^{2+}$ | 0.58 | 1.58 | 2.96 |
| $Ni^{2+}$ | 0.55 | 1.5 | 2.82 |
| $Cu^{2+}$ | 0.57 | 1.78 | 2.89 |
| $Zn^{2+}$ | 0.6 | 1.62 | 2.34 |
| $Cd^{2+}$ | 0.78 | 1.44 | 3.04 |
| $Ag^+$ | 0.67 | 1.52 | 3.99 |
| $Hg^{2+}$ | 0.96 | 1.61 | 4.25 |
| $Pb^{2+}$ | 1.19 | 1.25 | 3.58 |

a) From the reference of Shannon[3]

b) From reference of Matar *et al.*[4]

c) From reference of Misono *et al.*[5]

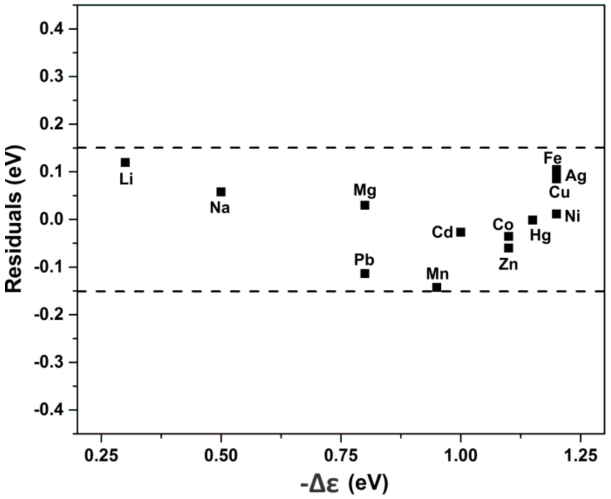

**Figure S8.** Residuals plot for the non-linear surface regression of Equation (6)

## References

1. G. Beamson and D. Briggs, *Journal of Chemical Education*, 1993, **70**, A25.
2. X.-M. Chen, B.-H. Ye, X.-C. Huang and Z.-T. Xu, *Journal of the Chemical Society, Dalton Transactions*, 1996, DOI: 10.1039/DT9960003465, 3465-3468.
3. R. D. Shannon, *Acta crystallographica section A: crystal physics, diffraction, theoretical and general crystallography*, 1976, **32**, 751-767.
4. S. F. Matar, G. Campet and M. A. Subramanian, *Progress in Solid State Chemistry*, 2011, **39**, 70-95.
5. M. Misono, E. i. Ochiai, Y. Saito and Y. Yoneda, *Journal of Inorganic and Nuclear Chemistry*, 1967, **29**, 2685-2691.