

Coordinative Unsaturation in an Antimony(III)-complex with the 2-Salicylidenaminophenolato Ligand: Synthesis, Crystal Structure, Spectroscopic Analysis, and DFT Studies

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20 **S1 Origin and purity of used chemicals**
Table S1: Used chemicals under specification of the manufacturer, purity and type of purification.

chemical	source	purity	purification
DMSO-d6	Deutero GmbH	99.8 %	-
Cyclopentylmethylether (CPME)	TCI	≥99.5 %	Distillation over Na/Benzophenone
EtOH	Chemsolut	99.7 %	Drying over molecular sieve
2-Aminophenole	Merck	≥99.0 %	Recrystallization from water/EtOH
Salicylaldehyde	Sigma-Aldrich	0,98	Distillation
CaCl ₂	Grüssing GmbH	-	-
SbCl ₃	Merck	≥99 %	Distillation
NEt ₃	Chemsolut	>99%	Distillation over Na/Benzophenone
n-Pentane	VWR Chemicals	≥ 99 %	Drying over molecular sieve
CDCl ₃	Deutero GmbH	99.8 %	Distillation over CaH ₂
Acetonitril			Storing over molecular sieve

S2 ^1H - and ^{13}C -NMR Spectra

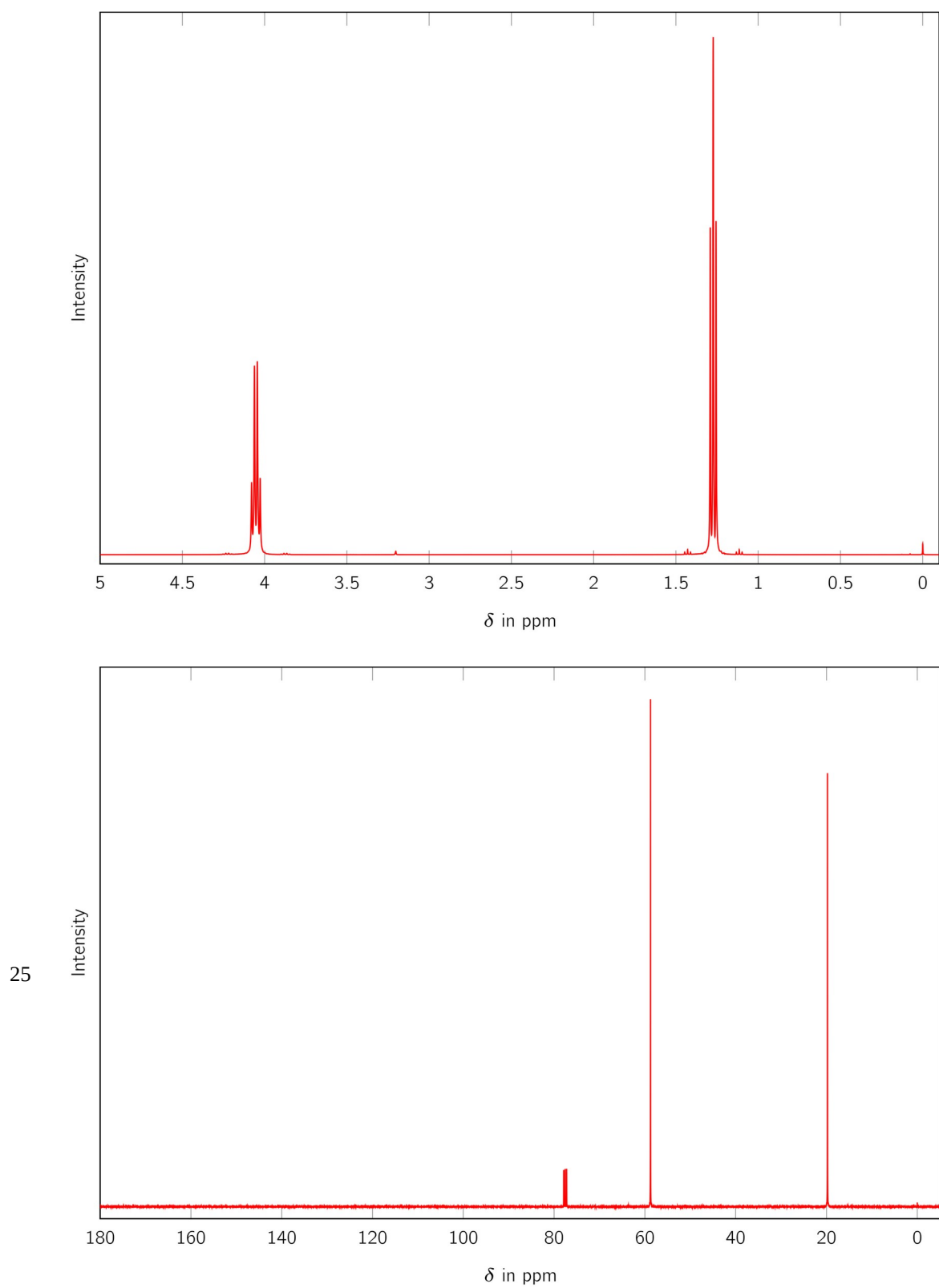


Figure S1: ^1H (top) and ^{13}C (bottom) NMR spectra of the compound $\text{Sb}(\text{OEt})_3$.

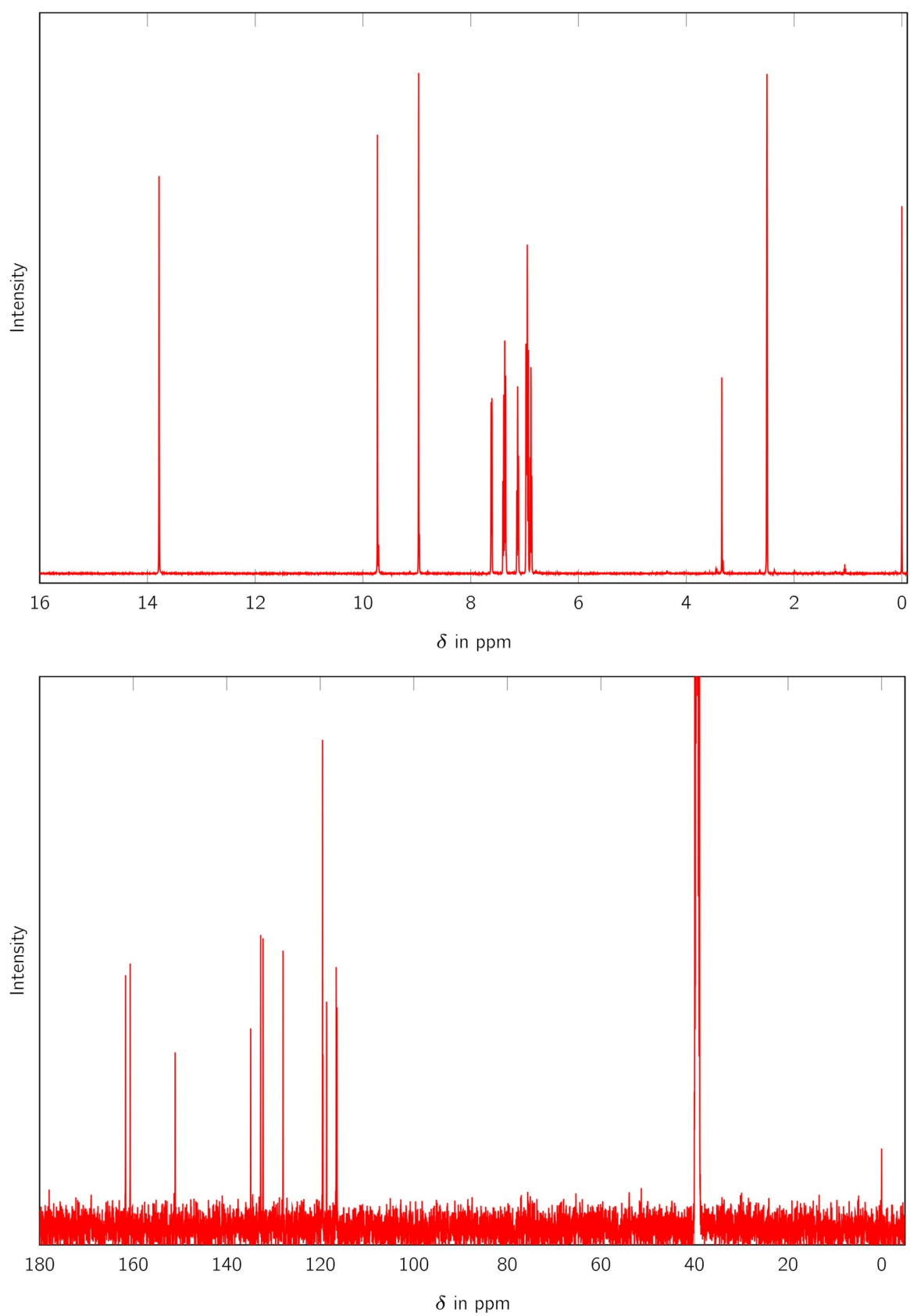


Figure S2: ¹H (top) and ¹³C (bottom) NMR spectra of the compound **H₂L**.

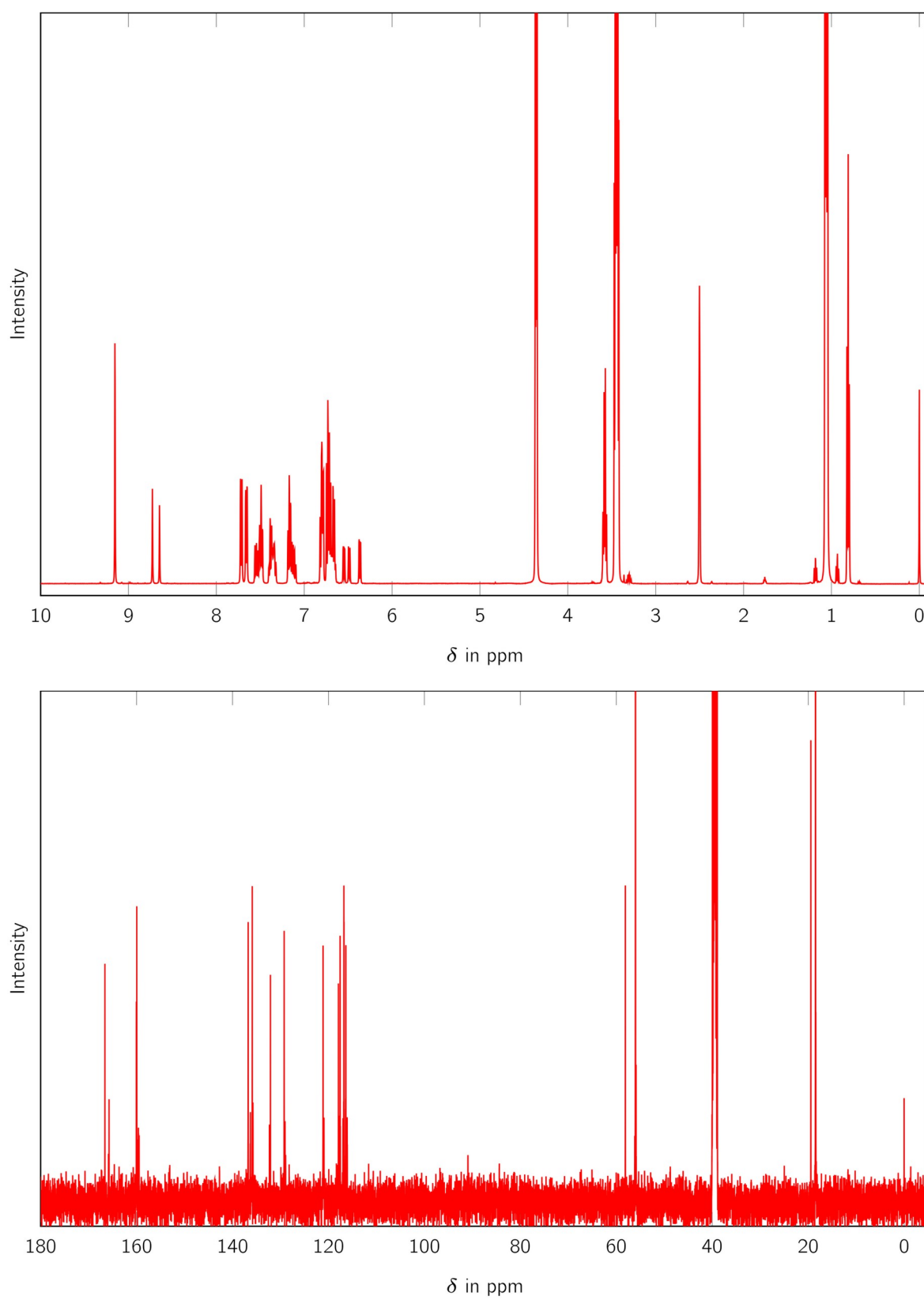


Figure S3: ^1H (top) and ^{13}C (bottom) NMR spectra of the compound **LSb**.

S3 Raman Spectra

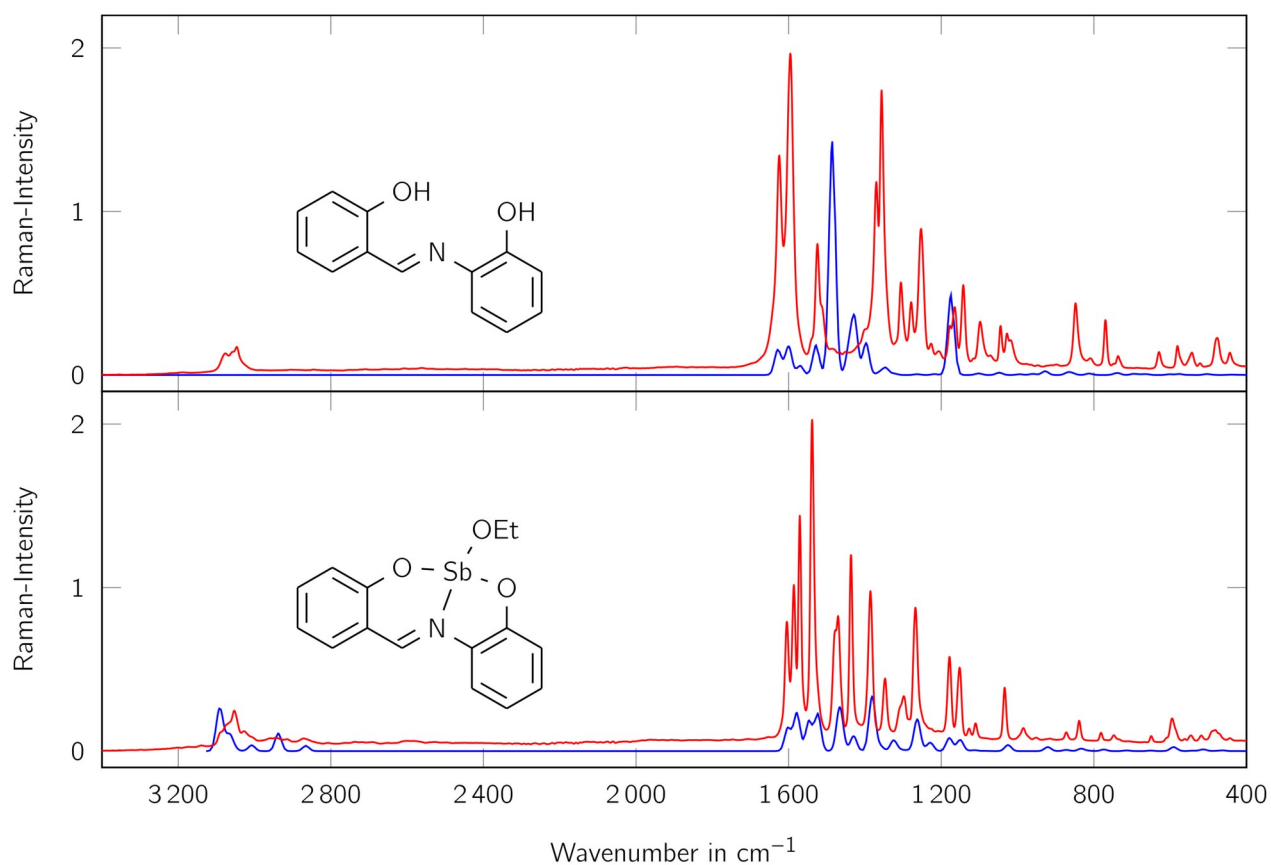


Figure S4: Raman spectra of the ligand H_2L (top) and the complex LSb (bottom). Red lines show the measured spectra, blue lines the calculated ones. Wavelength of the calculated spectra are scaled according to Katsyuba et. al. [51]. The values at the y axis apply to the experimental data.

S4 Intrinsic Bond Orbitals

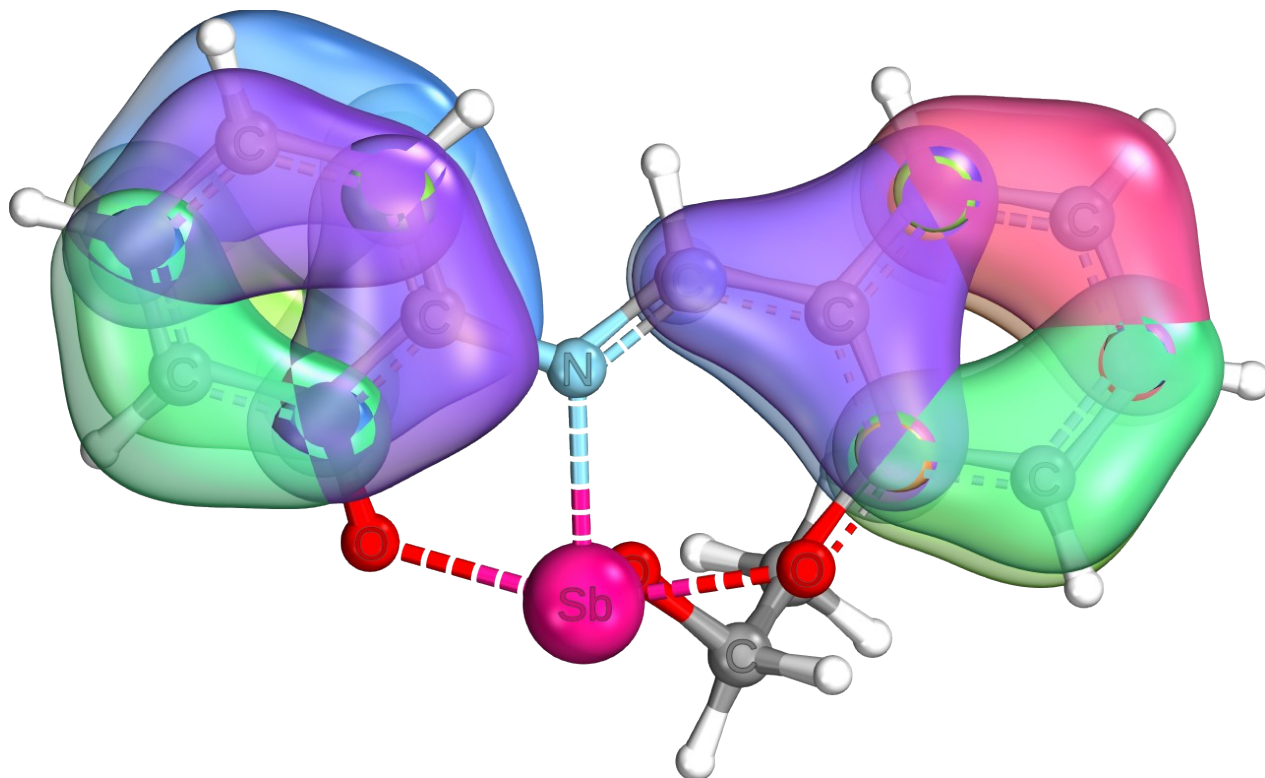


Figure S5: Intrinsic bond orbitals of the aromatic orbitals of the compound **LSb**.

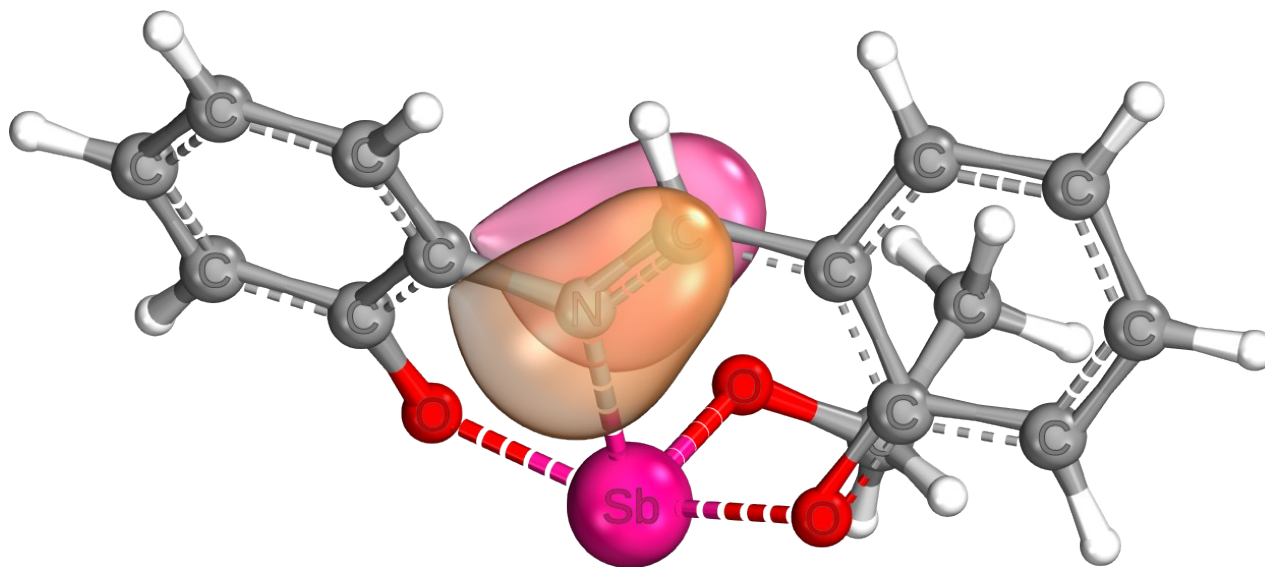


Figure S6: Intrinsic bond orbital of the C=N π -bond of the compound **LSb**.

S5 Thin Layer Chromatography

For the TLC was used Merck TLC Silica gel 60 RP-18 F_{254S} as stationary phase and acetonitrile as eluent.

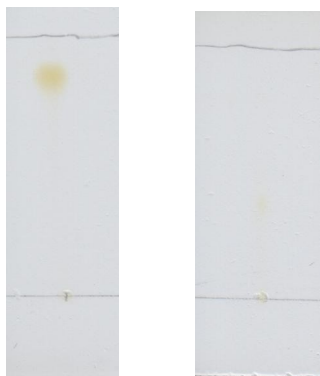


Figure S7: TLC plates. Left with the complex **LSb** and right with the complex after hydrolysis in acetonitrile (with drops of water). The complex is pure and as can be seen on the left TLC plate ($R_F=0.82$). No migration of the hydrolysis product occurs, as can be seen on the right TLC plate.

S6 Powder XRD analysis

A Bruker D2 Phaser was used to collect the diffractograms.

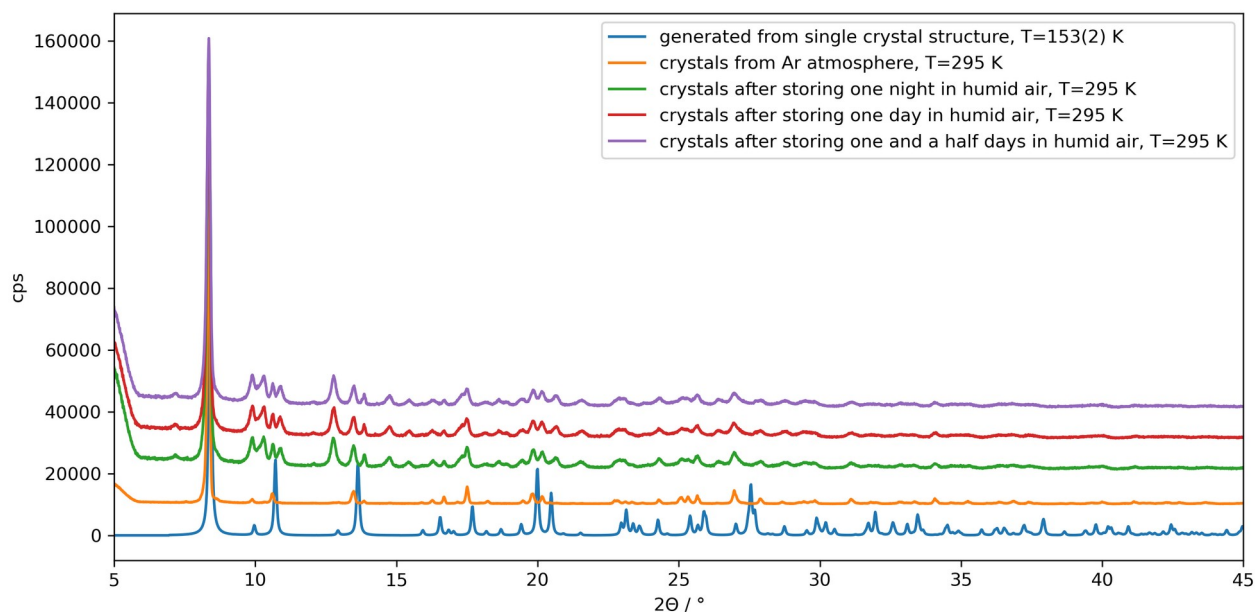


Figure S8: XRD analysis of the pure complex **LSb** from storing under Ar atmosphere, the diffractogramm generated from single crystal structure and the powder of **LSb** after one night in humid air. Differences between the pure **LSb** and the calculated diffractogram originates from temperature differences.

S7 Synthesis of Sb(OEt)₃ and H₂L

Triethoxystibate (Sb(OEt)₃) (based on Böhme^[53])

In a 500 mL three necked flask with a 100 mL dropping funnel 132.53 g (0.571 mol) SbCl₃ were solved in 108 mL ethanol to give a yellow solution. Afterwards, 251 mL triethylamine was added.

30 Further 60 mL of *n*-pentane were added and the suspension stirred overnight. The reaction mixture was filtrated and washed several times with *n*-pentane. This gave a white solid and a yellow filtrate. The solvent was removed from the filtrate under reduced pressure. Distillation of the liquid residue under reduced pressure ($7 \cdot 10^{-2}$ mbar) and a temperature of 50 to 52 °C gave the pure colorless product. The IUPAC name of this compound is triethyl stiborite.

35 **¹H NMR (400 MHz, CDCl₃):** δ (ppm) = 1,27 (t, ³J(H) = 7,0 Hz, 9 H, CH₃), 4,05 (q, ³J(H) = 7,0 Hz, 6 H, CH₂)

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 58,7 (CH₂), 19,8 (CH₃)

IR (ATR): ν (cm⁻¹) = 600 (m), 631 (m), 888 (m), 1033 (s), 1092 (m), 1378 (m), 1443 (w), 1477 (w), 2863 (m), 2919 (w), 2963 (m)

40 **Raman:** ν (cm⁻¹) = 115 (m), 325 (m), 597 (m), 1063 (w), 1098 (w), 1285 (w), 1451 (m), 1476 (w), 2705 (w), 2747 (w), 2866 (s), 2922 (s), 2967 (s)

2-Salicylideneaminophenol (H₂L) (based on Schwetlick^[66]):

45 In a 100 mL flask with magnetic stirrer, 12.271 g (0.112 mol) of 2-aminophenol were suspended in 50 mL ethanol. Afterwards, 13.230 g (0.118 mol) of salicylaldehyde were slowly added via a septum. Thereby, an orange solid precipitated. The suspension was stirred under reflux for 2 hours and filtered as hot solution. To the remaining solid, 20 mL of ethanol were added three times, heated to boiling, and filtered hot. The collected filtrates were cooled to room temperature and orange-red needles precipitated. The supernatant solution was removed by suction filtration and the filter cake
50 was washed with ethanol. The solid was dried for 7 days in a desiccator under vacuum over CaCl₂ to give 20.949 g (0.098 mol, 85.5%) H₂L. The IUPAC name of this compound is 2-[(2-hydroxyphenyl)imino]methylphenol.

¹H NMR (500 MHz, DMSO): δ (ppm) = 13.79 (s, 1 H, OH), 9.73 (s, 1 H, OH), 8.97 (s, 1 H, H-7), 7.61 (dd, ³J(H) = 7.67 Hz, ⁴J(H) = 1.60 Hz, 1 H, H-12), 7.34-7.41 (m, 2 H, H-2. H-10), 7.13 (td, ³J(H) = 7.65 Hz, ⁴J(H) = 1.61 Hz, 1 H, H-4), 6.926-6.99 (m, 3 H, H-5. H-9. H-11), 6.88 (td, 3 J(H) = 7.66 Hz, ⁴J(H) = 1.44 Hz, 1 H, H-3)

¹³C NMR (125 MHz, DMSO): δ (ppm) = 161.6 (C-1), 160.6 (C-13), 151.0 (C-7), 134.9 (C-8), 132.7 (C-11), 132.2 (C-9), 127.9 (C-4), 119.5 (C-3. C-2), 119.4 (C-6), 118.6 (C-10), 116.6 (C-5), 116.4 (C-12)

60 **MS (Acetonitrile, ACPI):** m/z = 213.946 ([M + H]⁺)

IR (KBr): ν (cm⁻¹) = 1118 (m), 1141 (s), 1224 (m), 1243 (m), 1276 (s), 1307 (m), 1464 (s), 1487 (m), 1530 (m), 1593 (m), 1632 (s), 2360 (w)

UV/Vis: λ (nm) = 198 (ϵ = 24843 cm² mmol⁻¹), 267 (ϵ = 10077 cm² mmol⁻¹), 347 (ϵ = 10556 cm² mmol⁻¹)