

Thionylimido Complexes

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Dedication with warmest wishes to Prof. H. W. Roesky on the Occasion of his 85th Birthday

Abstract. An improved route to d-block and main group NSO complexes is presented including the synthesis of the first antimony(V) complexes, $(\text{Ar}_3\text{Sb}(\text{NSO})_2)$, and copper examples $[\text{CuBipy}(\text{PPh}_3)\text{NSO}]$. The structures of eight complexes are reported.

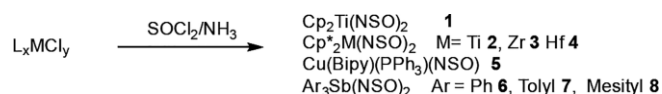
The observed variation in M–N–S bond angles is due to the combination of orbital overlap (ligand-to-metal bonding) and the degree of ionicity of the bonding.

Thionylimide gas (HNSO) was first synthesized by the reaction of thionyl chloride and ammonia gas in 1911.^[1] It is a colorless gas which condenses as a colorless liquid which freezes at $-85\text{ }^\circ\text{C}$ and rapidly polymerizes to the dark brown solid, polythionylimide $(\text{HNSO})_n$.^[2] There is one published example of an HNSO complex,^[3] although there is minimal supporting characterization data, the synthesis has not been reproduced and the crystal structure in question, which contains a number of unusual features, must be treated with some scepticism. Although the $[\text{NSO}]^-$ anion can be isolated in simple salts these can be quite difficult to handle (often explosive and/or air sensitive) and progress in developing its coordination chemistry has been limited by lack of straightforward syntheses. A few transition metal complexes of the thionylimido (or as it could be called, thiazate) ligand have been reported,^[5–12] from reactions such as that of metal halides with Me_3SiNSO , or KNSO, or of thionyl chloride in liquid ammonia.^[5–12] There is one example^[13] of a coordinated NSO ligand stabilized by a BF_3 group in $\text{Cp}(\text{NO})_2\text{Cr}(\text{NSO})\cdot\text{BF}_3$, and recently there has been renewed interest in the area with the isolation of the iminosulfonium ion $[\text{Me}_3\text{Si}-\text{N}=\text{S}-\text{O}-\text{SiMe}_3]^+$, a potential source of $[\text{NSO}]^+$, as well as other adducts of RNSO (R = H and Me_3Si) with Lewis acids.^[14]

Herein we describe a simplified route to M-NSO complexes including the first examples of antimony(V), and copper com-

plexes of the thionylimido ligand (compounds **5**, and **6**, **7** and **8** respectively).

The direct addition of thionyl chloride to liquid ammonia is very exothermic and hazardous; we developed a considerably less challenging synthetic route than previously used, by adding a THF solution of thionyl chloride to liquid ammonia to generate the $[\text{NSO}]^-$ anion which was then treated with appropriate metal systems (Scheme 1). The well-known $\text{Cp}_2\text{Ti}(\text{NSO})_2$ **1** was obtained in 79% yield (cf. 48%^[12] [neat SOCl_2 in liquid ammonia] and 80%^[6] [using KNSO]) whilst $\text{Cp}^*\text{M}(\text{NSO})_2$ [M = Ti, Zr, Hf (**2–4**)] were isolated in 10, 71, and 76% yield respectively (**2** was difficult to isolate and was purified by column chromatography). We suggest the relatively low yield of complex **2** is due to the larger Cp^* and hence the more sterically crowded nature of the **2** compared to Cp. Complexes **2**, **3**, and **4** appear to be particularly insensitive to air and moisture.



Scheme 1. Synthesis of thionylimido complexes.

To test the generality of our procedure we reacted $\text{Cu}(\text{Bipy})(\text{PPh}_3)\text{Cl}$ under similar conditions to give $\text{Cu}(\text{Bipy})(\text{PPh}_3)(\text{NSO})$ **5** in excellent yield (88%).

Furthermore the antimony compounds $\text{Ph}_3\text{Sb}(\text{NSO})_2$ (**6**), $\text{To}_3\text{Sb}(\text{NSO})_2$ (**7**), and $\text{Mes}_3\text{Sb}(\text{NSO})_2$ (**8**) were prepared in 58–78% yields; these are the first examples of copper and antimony thionylimide complexes. We did note that **5** hydrolyses to $(\text{bipy})\text{CuCl}(\text{N}(\text{SO}_3)_2)\text{Cu}(\text{bipy})_2$ which was characterized crystallographically as the first example of a complex containing the $[\text{N}(\text{SO}_3)_2]^-$ anion (see Supporting Information).

The spectroscopic properties of **2–8** are as expected with appropriate NMR signals and ($\nu_{\text{asym}} \text{NSO}$) at ca. 1270 cm^{-1} , ($\nu_{\text{sym}} \text{NSO}$) ca. 1090 cm^{-1} , except in the case of **5** where the ($\nu_{\text{sym}} \text{NSO}$) was significantly lower in frequency at 1021 cm^{-1} . The X-ray structures of **2–4** and **6–8** (examples in Figure 1) confirm the formulations.

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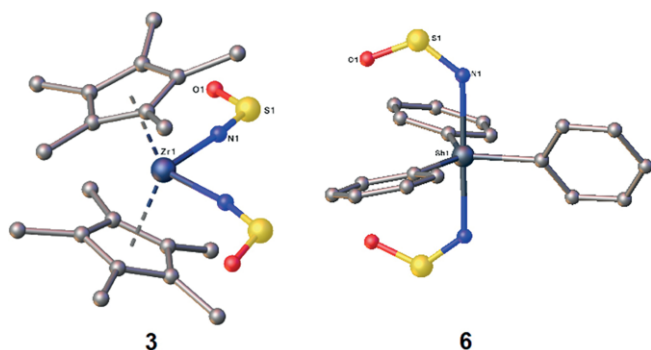


Figure 1. The single-crystal X-ray structures of **3** and **6**. Selected bond lengths /Å and angles /°: M–N 2.116(4), 2.185(4), N–S 1.469(5) 1.487(4), S–O 1.453(5) 1.461(4), M–N–S 170.3(3) 127.2(1), N–S–O 119.4(2) 119.9(2), N–M–N 99.8(3) 179.4(2).

General features of the structures are normal N=S [1.466(5)–1.487(4) Å] and S=O bond lengths [1.452(3)–1.473(5) Å] with N–S–O angles of ca 120° and M–N–S angles having quite a large range [127.1(2)–170.3(3)°]. The most notable variability of the M–N–S bond angle is between **1** and **2** which one would naively assume to be very similar. **1** has a Ti–N–S bond angle of 150.8(2)°,^[6] where **2** has an angle of 170.0(1)° this striking difference is most probably due to the larger Cp* ligands versus Cp. However, we noted the unexpected contraction of the Ti–N bond from 2.055(1) Å in **1** to 1.992(2) Å in **2**. While this contraction is relatively minor in a more sterically crowded system it is at first counter intuitive. Our hypothesis was that while the steric bulk of the Cp* led to an increase in overlap of the nitrogen centered lone pair with empty d orbitals on the titanium, this was further investigated with DFT calculations.

According to DFT calculations (RI-BP86 level, see Supporting Information for details), the observed variation in M–N–S bond angles is due to a combination of factors, namely the extent of orbital overlap (ligand-to-metal bonding) and the degree of ionicity. For early d-block metals, orbital overlap between lone pairs on N and empty d-orbitals on the metal (see Figure S2, Supporting Information) leads to an increased bond angle, which can be further increased through ionic contributions to the bonding (e.g. in **2**). Late d-block metals (as in **5**) with no empty d-orbitals prefer smaller bond angles.

In the antimony examples the Sb–N–S angle range is 127.1(2)–143.0(3)° as a consequence of the relative steric bulk of the other substituents, phenyl giving the smallest angle and mesityl the largest, this also causes a change in arrangement of the aryl substituents (Figure 2). As the antimony has no partially filled d orbitals it shows less preference for any particular Sb–N–S bond angle and the *ortho*-methyl groups of the mesityl groups (**8**) prevent the aryl substituents adopting the same arrangement as in **6**. There is no significant change in Sb–N bond length in compounds **6–8** again, this is likely due to the lack of partially filled d-orbitals.

In summary, we have presented an improved method for the synthesis of NSO complexes. We have demonstrated the generality of this route with the synthesis of the first examples

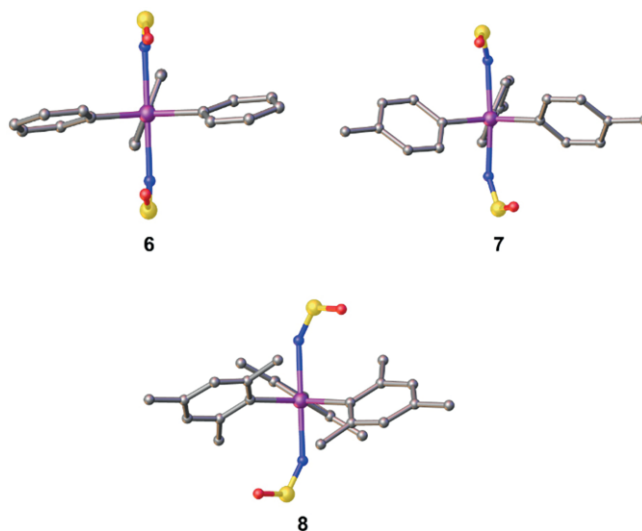


Figure 2. Comparison of antimony compounds **6**, **7**, and **8** showing the change in orientation of aryl groups and the thionylimido groups with increase steric bulk.

of copper and antimony(V) complexes and we report 8 new crystal structures of NSO complexes.

Experimental Section

General: Unless otherwise noted all manipulations were carried out under a moisture and oxygen free nitrogen atmosphere using standard Schlenk techniques and glassware or under a moisture and oxygen free argon atmosphere in a glovebox. IR spectra were collected on a Perkin–Elmer 2000 NIR Fourier Transform spectrometer. ¹H and ¹³C NMR spectra were obtained on either a Bruker Avance III 500 spectrometer or a JEOL GSX Delta 270 with δ_{H} and δ_{C} relative to TMS, ³¹P NMR spectra are reported with respect to an external standard of 85% H₃PO₄ in D₂O. All measurements were performed at 25 °C with shifts reported in ppm.

Cp₂Ti(NSO)₂ (1): Ammonia (30 mL) was condensed at –78 °C under nitrogen into a pre-dried 2-neck Schlenk flask. Thionyl chloride (0.13 mL, 1.8 mmol) in THF (10 mL) was cooled to –78 °C and added dropwise, the reaction mixture was stirred for 10 min turning pale yellow. Titanocene dichloride (0.18 g, 0.75 mmol) was added as a solution in dichloromethane (10 mL) and the reaction stirred at –78 °C for 30 min the color quickly turned yellow. The reaction mixture was allowed to slowly warm to room temperature and the ammonia was allowed to evaporate under a stream of nitrogen. The reaction mixture was filtered and the solvent removed in vacuo. The residue was dissolved in dry acetonitrile (5 mL) and cooled to –30 °C overnight, yielding the product as yellow-orange crystals (0.18 g, 79%). Crystals suitable for single-crystal X-ray diffraction were grown by slow cooling of a saturated toluene solution of **1**. ¹H NMR (CDCl₃): δ_{H} = 6.38 (s, 10 H, C–H). ¹H NMR ([D₆]acetone): δ_{H} = 6.49 (s, 10 H, CH) ¹H NMR (CDCl₃): δ_{C} = 114.6 (s, CH) ppm. IR (KBr): $\tilde{\nu}$ = 3111m (ν Ar C–H), 1439m, 1436s, 1233vs. (ν_{asym} NSO), 1073s (ν_{sym} NSO), 1017m, 834s, and 523m (δ NSO) cm^{–1}.

Cp₂*Ti(NSO)₂ (2): Ammonia (30 mL) was condensed at –78 °C under nitrogen into a pre-dried 2-neck Schlenk flask. Thionyl chloride (0.2 mL, 2.8 mmol) in THF (10 mL) was cooled to –78 °C and added dropwise, the reaction mixture was stirred for 10 min turning pale

yellow. Bis(pentamethylcyclopentadienyl)titanium dichloride (0.389 g, 1.0 mmol) was added as a solution in dichloromethane (10 mL) and the reaction stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction mixture was allowed to slowly warm to room temperature and the ammonia was allowed to evaporate under a stream of nitrogen. The reaction mixture was filtered and the solvent removed in vacuo to give the crude product as a brown solid. The compound was purified by column chromatography (silica, 50/50 v/v ethyl acetate/hexanes) to give **2** as an orange solid (0.04 g, 10%). Crystals of **2** suitable for single-crystal X-ray diffraction were grown from acetonitrile solution by cooling to $-30\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$ (CDCl_3): $\delta_{\text{H}} = 1.92$ (30 H, CH_3). $^{13}\text{C NMR}$ (CDCl_3): $\delta_{\text{C}} = 124.0$ (qC) and 12.7 (CH_3) ppm. **IR** (KBr): $\tilde{\nu} = 2963\text{m}$ (v Alkyl C-H), 1491m , 1434m , 1377m , 1229vs . (ν_{ASym} NSO), 1098m , 1062s (ν_{Sym} NSO), 802 and 516m (δ NSO) cm^{-1} . **EI-MS**: m/z 442.1 (10%, [M]⁺). $\text{C}_{20}\text{H}_{30}\text{TiN}_2\text{S}_2\text{O}_2$: calcd. C 54.29; H 6.83; N 6.33%; found: C 54.16; H 6.62; N 6.34%.

Cp₂*Zr(NSO)₂ (3): Ammonia (30 mL) was condensed at $-78\text{ }^{\circ}\text{C}$ under nitrogen into a pre-dried 2-neck Schlenk flask. Thionyl chloride (0.09 mL, 1.2 mmol) in THF (10 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and added dropwise, the reaction mixture was stirred for 10 min turning pale yellow. Bis(pentamethylcyclopentadienyl)zirconium dichloride (0.22 g, 0.5 mmol) was added as a solution in dichloromethane (10 mL) and the reaction stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction mixture was allowed to slowly warm to room temperature and the ammonia was allowed to evaporate under a stream of nitrogen. The reaction mixture was filtered and the solvent removed in vacuo to give **3** as an orange solid (0.18 g, 71%). Crystals of **3** suitable for single-crystal X-ray diffraction were grown from acetonitrile solution by cooling to $-30\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$ (C_6D_6): $\delta_{\text{H}} = 1.68$ (s, 30 H, CH). $^{13}\text{C NMR}$ (C_6D_6): $\delta_{\text{C}} = 121.4$ (qC) and 11.8 (CH_3) ppm. **Raman** (glass capillary): $\tilde{\nu} = 2926\text{w}$ (v C-H), 1423w , 1286m , 1260s (ν_{ASym} NSO), 1084vs . (ν_{Sym} NSO), 599w and 550vw cm^{-1} . **EI-MS**: m/z 422.11 (85%, [M-NSO]⁺). $\text{C}_{20}\text{H}_{30}\text{ZrN}_2\text{S}_2\text{O}_2$: calcd. C 49.45; H 6.22; N 5.77% Found: C 49.71; H 6.64; N 6.08%.

Cp₂*Hf(NSO)₂ (4): Ammonia (30 mL) was condensed at $-78\text{ }^{\circ}\text{C}$ under nitrogen into a pre-dried 2-neck Schlenk flask. Thionyl chloride (0.09 mL, 1.2 mmol) in THF (10 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and added dropwise, the reaction mixture was stirred for 10 min turning pale yellow. Bis(pentamethylcyclopentadienyl)hafnium dichloride (0.27 g, 0.5 mmol) was added as a solution in dichloromethane (10 mL) and the reaction stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction mixture was allowed to slowly warm to room temperature and the ammonia was allowed to evaporate under a stream of nitrogen. The reaction mixture was filtered and the solvent removed in vacuo to give **4** as an orange solid (0.226 g, 76%). Crystals suitable for single-crystal X-ray diffraction were grown from acetonitrile solution by cooling to $-30\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$ (C_6D_6): $\delta_{\text{H}} = 1.72$ (CH_3). $^{13}\text{C NMR}$ (C_6D_6): $\delta_{\text{C}} = 119.6$ (qC) and 11.7 (CH_3) ppm. **Raman** (glass capillary): $\tilde{\nu} = 2916.4\text{w}$ (v Ar C-H), 1296m , 1268s (ν_{asym} NSO), 1086m (ν_{sym} NSO), and 599w (δ NSO) cm^{-1} . **EI-MS**: m/z 574.1 (10%, [M]⁺). $\text{C}_{20}\text{H}_{30}\text{HfN}_2\text{S}_2\text{O}_2$: calcd. C 41.92, H 5.28, N 4.89%; found: C 42.33, H 5.45, N 5.17%.

(Bpy)(Ph₃P)Cu(NSO) (5): Ammonia (30 mL) was condensed at $-78\text{ }^{\circ}\text{C}$ under nitrogen into a pre-dried 2-neck Schlenk flask. Thionyl chloride (0.17 mL, 2.4 mmol) in THF (10 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and added dropwise, the reaction mixture was stirred for 10 min turning pale yellow. BpyPh₃PCuCl (1 g, 1.9 mmol) was added as a suspension in THF (10 mL) and the reaction stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, the color gradually darkening. The reaction mixture was allowed to slowly warm to room temperature and the ammonia was allowed to evaporate under a stream of nitrogen. The reaction mixture was filtered through celite and the solvent removed in vacuo to afford **5** as an orange solid

(0.91 g, 88%). $^1\text{H NMR}$ (CDCl_3): $\delta_{\text{H}} = 8.2\text{--}7.2$ (m). $^{13}\text{C NMR}$ (CDCl_3): $\delta_{\text{C}} = 133.64$ (d, $J = 13.7$ Hz, Ph *o*C), 132.37 (d, $J = 10.7$ Hz, Ph *m*C), 131.69 (d, $J = 2.8$ Hz, Ph *p*C), 129.7 (s, bipy), and $128.7\text{--}128.6$ (m, bipy). $^{31}\text{P NMR}$ (CDCl_3): $\delta_{\text{P}} = -1.3$ (Br s) ppm. **IR** (KBr): $\tilde{\nu} = 3065\text{m}$ (v Ar C-H), 1596m , 1436s , 1283s (ν_{ASym} NSO), 1094m , 1021s (ν_{Sym} NSO), 768s , 745s and 698s cm^{-1} . **Raman** (glass capillary): $\tilde{\nu} = 3051\text{s}$ (v Ar C-H), 1596s , 1485s , 1281s (ν_{ASym} NSO), 1095m and 1014s (ν_{Sym} NSO) cm^{-1} . M.p. $158\text{ }^{\circ}\text{C}$. **ESI-MS**: m/z 481.09 [(BpyPh₃PCu)⁺]

Ph₃Sb(NSO)₂ (6): Ammonia (30 mL) was condensed at $-78\text{ }^{\circ}\text{C}$ under nitrogen into a pre-dried 2-neck Schlenk flask. Thionyl chloride (0.15 mL, 22 mmol) in THF (10 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and added dropwise, the reaction mixture was stirred for 10 min turning pale yellow. Ph₃SbBr₂ (0.50 g, 1.0 mmol) was added as a solid and the reaction stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction mixture was allowed too slowly warm to room temperature and the ammonia was allowed to evaporate under a stream of nitrogen. The reaction mixture was filtered and the solvent removed in vacuo to give **6** as a pale yellow solid (0.288 g, 62%). Crystals suitable for single-crystal X-ray diffraction were grown by slow cooling of a saturated acetonitrile solution of **6**. $^1\text{H NMR}$ (CDCl_3): $\delta_{\text{H}} = 8.28\text{--}8.07$ (m, 6 H, *m*CH) and $7.63\text{--}7.52$ (m, 9 H, *o/p*CH). $^{13}\text{C NMR}$ (CDCl_3): $\delta_{\text{C}} = 142.4$ (s, qC, Sb-C), 133.7 (s, qC, *p*C), 128.5 (s, *o*C), 130.7 (s, *m*C) ppm. **IR** (KBr): $\tilde{\nu} = 3031\text{w}$ (vArC-H), 1591w (ArC=C), 1490s , 1396m , 1251vs . ($\nu_{\text{AS}}\text{NSO}$), 1084s ($\nu_{\text{S}}\text{NSO}$), 808s , 590w , 553m (δNSO) cm^{-1} . **MS**: 414.0 (10% [M-NSO]⁺), 352.0 (15% [M-2(NSO)]⁺), 197.9 (100% [PhSb]⁺), 77.0 (25% [Ph]⁺). $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_2\text{S}_2\text{Sb}$: calcd. C 45.30; H 3.17, N 5.87%; found: C 45.81, H 3.64, N 5.42%.

Tol₃Sb(NSO)₂ (7): Ammonia (30 mL) was condensed at $-78\text{ }^{\circ}\text{C}$ under nitrogen into a pre-dried 2-neck Schlenk flask. Thionyl chloride (0.17 mL, 2.4 mmol) in THF (10 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and added dropwise, the reaction mixture was stirred for 10 min turning pale yellow. Tol₃SbCl₂ (0.466 g, 1.0 mmol) was added as a solid and the reaction stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction mixture was allowed too slowly warm to room temperature and the ammonia was allowed to evaporate under a stream of nitrogen. The reaction mixture was filtered and the solvent removed in vacuo to give **7** as a pale yellow solid (0.300 g, 58%). Crystals suitable for single-crystal X-ray diffraction were grown by slow cooling of a saturated acetonitrile solution of **7**. $^1\text{H NMR}$ (CDCl_3): $\delta_{\text{H}} = 8.08$ (d, 6 H, $J = 8.2$ Hz, *o*CH), 7.38 (d, 6 H, $J = 7.8$ Hz, *m*CH), 2.43 (s, 9 H, CH_3). $^{13}\text{C NMR}$ (CDCl_3): $\delta_{\text{C}} = 142.4$ (s, qC, Sb-C), 133.9 (s, qC, C- CH_3), 133.6 (s, *o*CH), 130.7 (s, *m*CH), and 21.6 (s, CH_3) ppm. **IR** (KBr): $\tilde{\nu} = 3032\text{w}$ (vArC-H), 2920w (vAlkylC-H), 1591w (ArC=C), 1493s , 1396m , 1253vs , ($\nu_{\text{AS}}\text{NSO}$), 1085s ($\nu_{\text{S}}\text{NSO}$), 803s , 585w , 535s (δNSO), 486s cm^{-1} . **MS**: 456.0 (5% [M-NSO]⁺), 394.1 (15% [M-2(NSO)]⁺), 212.0 (100% [TolSb]⁺), 91.0 (30% [Tol]⁺). M.p. $134\text{--}136\text{ }^{\circ}\text{C}$. $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_2\text{S}_2\text{Sb}$: calcd. C 48.57, H 4.08, N 5.39%; found: C 48.62, H 4.04, N 5.19%

Mes₃Sb(NSO)₂ (8): Ammonia (30 mL) was condensed at $-78\text{ }^{\circ}\text{C}$ under nitrogen into a pre-dried 2-neck Schlenk flask. Thionyl chloride (0.1 mL cm^3 , 2.4 mmol) in THF (10 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and added dropwise, the reaction mixture was stirred for 10 min turning pale yellow. Mes₃SbCl₂ (0.550 g, 1.0 mmol) was added as a solid and the reaction stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction mixture was allowed too slowly warm to room temperature and the ammonia was allowed to evaporate under a stream of nitrogen. The reaction mixture was filtered and the solvent removed in vacuo to give **8** as a pale yellow solid (0.472 g, 78%). Crystals suitable for single crystal X-ray diffraction were grown by slow cooling of a saturated solution in acetonitrile. $^1\text{H NMR}$ (CDCl_3): $\delta_{\text{H}} = 7.03$ (s, 6 H, *m*CH), 2.61 (s, 18 H, *o*CH₃), 2.32 (s, 9 H, *p*CH₃). $^{13}\text{C NMR}$ (CDCl_3): $\delta_{\text{C}} = 142.8$ (s,

qC, oC), 140.9 (s, qC, pC), 140.3 (s, qC, Sb-C), 130.9 (s, mCH), 25.3 (s, oCH₃), and 21.0 (s, pCH₃) ppm. IR (KBr): $\tilde{\nu}$ = 3010w (v Ar C–H), 2855w (v Alkyl C–H), 1598, 1562, 1453m, 1260s (v_{asym} NSO), 1083m (v_{sym} NSO), 1023w, 852w, 544w (δ NSO), 521w cm⁻¹. MS: 540.2 (30% [M-NSO]⁺), 478.2 (75% [M-2(NSO)]⁺), 119.0 (100% [Mes]⁺). C₂₇H₃₃N₂O₂S₂Sb: calcd. C 53.74, H 5.51, N 4.64%; found: C 53.41 H 5.07 N 4.93%.

Supporting Information (see footnote on the first page of this article): contains details of the X-ray crystallography and computational studies.

Keywords: Thionylimide; Thiazate; Antimony complex; Antimony; X-ray diffraction

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