Synthesis, Properties and Crystal Structures of Benzene-1,2-dithiolato Complexes of Antimony-(III) and -(V)†

Joachim Wegener, Kristin Kirschbaum and Dean M. Giolando*
Department of Chemistry, The University of Toledo, Toledo, OH 43606, USA

Anaerobic treatment of $SbCl_3$ with $1,2\text{-}(LiS)_2C_6H_4$ provided a reliable route to $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ which in turn produced $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$ on reaction with $1,2\text{-}(HS)_2C_6H_4$ and O_2 in very good yields ($[NEt_4]^+$ salt, *ca.* 82%). Tetraalkylammonium salts of $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ were isolated after metathesis with either $[NEt_4]Br$ ($[NEt_4]^+$ salt, *ca.* 72%) or $[NBu^n{}_4]I$ ($[NBu^n{}_4]^+$ salt, *ca.* 90%). Slowly cooling hot MeCN solutions of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ gave yellow single crystals. This compound is the first structurally characterized anionic thiolate complex of Sb^{III}. In its structure the stereochemical influence of the lone pair of electrons leads to a distorted Ψ-trigonal-bipyramidal environment [S_{ax}–Sb–S_{ax} 158.95(3), S_{eq}–Sb–S_{eq} 105.08(3)°], however, the degree of distortion is less severe than expected for a complex with a normalized bite (*b*) of 1.31. Dark purple single crystals of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$ were obtained by slowly cooling hot MeCN–MeOH solutions. The co-ordination geometry about Sb is slightly distorted from octahedral with a twist angle of 49.22(3)° and most structural parameters are within 10% of octahedral values.

Complexes of Sb containing sulfur-donor ligands have been known for many years, and have been used in applications ranging from pharmacological activity to technical uses in catalytic processes.[1] Even though several homoleptic thiolate complexes of Sb have been structurally characterized, the number of complexes containing four-co-ordinated Sb^{III} or six-co-ordinated Sb^V is very limited.

Interest in homoleptic thiolate complexes of Sb^{III} is directed towards gaining insights into the stereochemical influence of the lone pair of electrons on the co-ordination geometry. Neutral tris(1,1-dithiolene) complexes, where 1,1-dithiolene is S_2CNR_2, S_2COR, S_2PR_2 or $S_2P(OR)_2$ and R denotes alkyl or aryl groups, dominate structural studies on thiolate complexes of Sb^{III}.[2] Generally, a co-ordination number of at least six is observed which is often increased by intermolecular Sb ··· S or Sb ··· Sb interactions. With some variation, three different descriptions for the SbS_6 core have been used for these complexes: (1) monomeric pentagonal pyramidal, with an apicial lone pair of electrons; (2) dimer of two pentagonal pyramids, wherein cofacial pentagonal planes are joined by Sb ··· S contacts *trans* to the apical position; and (3) as a distorted icosahedron in which a Sb_2 unit is imbedded in a S_{12} shell. Two prominent features of these complexes are the steric requirements of an antimony lone pair of electrons, leading to pentagonal-pyramidal co-ordination, and the tendency of Sb to expand its co-ordination *via* intermolecular interactions. Thiolate complexes with a four-co-ordinated Sb^{III} are lacking which would allow further study of the stereochemical influence on a less-constricted environment. To the best of our knowledge only one such antimony(III) complex has been reported,[3] $[Sb(S_2CNBu_2)_2]^+$.

To our knowledge $[PPh_4][Sb(3,4\text{-}S_2C_6H_3Me)_3]$ is the only fully described[4] thiolate complex of six-co-ordinated Sb^V; in addition $[AsPh_4][Sb(1,2\text{-}S_2C_6H_4)_3]$ has been briefly mentioned[5] with only the twist angle of 48.2° being reported. In $[PPh_4][Sb(3,4\text{-}S_2C_6H_3Me)_3]$ the SbS_6 core is slightly distorted away from octahedral: *cis*-S–Sb–S angles, 83.8(10)–97.3(9); *trans*-S–Sb–S angles, 166.6(12)–172.3(11); twist angle, 48.4°. Structural data for main group [M(dithiolene)$_3$] complexes are limited, however, the co-ordination geometry of each example so far examined being close to the octahedral limit.[4,6] The data are in accord with Kepert's potential-energy calculations, *ca.* 49° twist angle for a normalized bite of *ca.* 1.30,[7] suggesting steric considerations are important in determining the co-ordination geometry of these complexes. In contrast, most transition-metal [M(dithiolene)$_3$] complexes have a geometry closer to the trigonal-prismatic limit where twist angles are between 18 to 0°,[7] although at least one example is unusually close to octahedral.[8] For such complexes electronic factors are considered to determine the structure.

Complexes containing Sb and $S_2C_6H_4$ derivatives have received little attention. Some of the early work[9] employed $3,4\text{-}(HS)_2C_6H_3Me$ for the qualitative analysis of antimony cations, which took advantage of the difference in colour for the complex anions[10] of Sb^{III} {yellow, $[Sb(3,4\text{-}S_2C_6H_3Me)_2]^-$} and Sb^V {red, $[Sb(3,4\text{-}S_2C_6H_3Me)_3]^-$}. Both these complexes were prepared from aqueous solutions of $SbCl_3$ and $3,4\text{-}(HS)_2C_6H_3$-Me–NaOH, however Kisenyi *et al.*[4] later report their inability to isolate $[Sb(3,4\text{-}S_2C_6H_3Me)_2]^-$. Other derivatives of [Sb(dithiolene)$_2$]$^-$, where dithiolene is $1,2\text{-}S_2C_2H_2$, $1,2\text{-}S_2C_6H_2\text{-}Bu^t{}_2\text{-}3,5$ or $1,2\text{-}S_2C_2(CN)_2$, were prepared in non-aqueous media and structural assignments of either square pyramidal or Ψ-trigonal bipyramidal were made based on NMR and IR data.[1d,11,12]

In this paper we report syntheses, molecular structures, electrochemical behaviour and spectroscopic data for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ and $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$.

Experimental

Chemicals and Instrumentation.—All reagents were newly obtained from commercial sources and used without further purification except where noted. Ferrocene, $[NBu^n{}_4][PF_6]$, 1.6 mol dm^{-3} $LiBu^n$ in C_6H_{14}, Na and CaH_2 were obtained from Aldrich, $SbCl_3$ from Strem Chemicals and P_2O_5 and Ph_2CO from Baker Chemical. The compound $1,2\text{-}(HS)_2C_6H_4$ was prepared by literature methods.[13] All solvents were procured from Fisher and distilled: Et_2O and tetrahydrofuran (thf) from sodium–benzophenone; dimethylformamide (dmf), CH_2Cl_2 and $CHCl_3$ from P_2O_5; MeOH and EtOH from Na; and MeCN from CaH_2; dmf was deoxygenated by vacuum distillation. The

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

salt $[NBu^n{}_4][PF_6]$ was recrystallized from hot EtOH. Proton, ^{13}C, and ^{13}C attached proton test NMR spectra were obtained using a Varian VXR-400 FT-NMR spectrometer, UV/VIS spectra on a Varian Cary 5 UV/VIS/NIR spectrophotometer. Cyclic voltammograms were obtained on a BAS CV 1B cyclic voltammograph and thin-layer electrochemical studies employed a BAS CV-27 instrument. Elemental analyses were carried out with a Perkin-Elmer CHN elemental analyzer 2400. All experimental work was done under an inert atmosphere, except where noted.

Syntheses.—$[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$. A solution of $LiBu^n$ (2.5 cm^3, 4.0 mmol, 1.6 mol dm^{-3} in C_6H_{14}) was added dropwise to a solution of $1,2\text{-}(HS)_2C_6H_4$ (0.30 g, 2.1 mmol) in degassed MeOH (10 cm^3), which was cooled to −78 °C in an EtOH–solid CO_2 bath. After slowly warming to room temperature a solution of $SbCl_3$ (0.23 g, 1.0 mmol) dissolved in MeOH (10 cm^3) was added dropwise. The resultant yellow-orange mixture was stirred for 24 h and then treated with $[NEt_4]Br$ (0.24 g, 1.2 mmol) dissolved in MeOH (10 cm^3). A yellow solid precipitated which was filtered off and dried *in vacuo*. Recrystallization from hot MeCN provided pale yellow single crystals (0.385 g, 0.72 mmol, 72% based on $SbCl_3$), m.p. 158–159 °C (from MeCN) (Found: C, 45.3; H, 5.5; N, 2.9. $C_{20}H_{28}NS_4Sb$ requires C, 45.1; H, 5.3; N, 2.6%). λ_{max}/nm (0.08 mmol dm^{-3}, in MeCN): 246, 308 (8800) and 384 (ε/dm^3 mol^{-1} cm^{-1} 1600). ν_{max}(KBr) 3037, 2981, 1543, 1481, 1437, 1435, 1412, 1393, 1261, 1238, 1173, 1097, 999, 787, 752, 652, 470 and 432 cm^{-1}. δ_H(400 MHz, CD_3CN, 21 °C) 7.18 (4 H, m, $S_2C_6H_4$), 6.71 (4 H, m, $S_2C_6H_4$), 3.12 (8 H, q, NCH_2CH_3) and 1.17 (12 H, tt, NCH_2CH_3). $\delta_C\{^1H\}$(101 MHz, CD_3CN, 21 °C) 144.61 ($S_2C_6H_4$), 130.18 ($S_2C_6H_4$), 123.31 ($S_2C_6H_4$), 52.98 (NCH_2CH_3) and 7.64 (NCH_2CH_3).

$[NBu^n{}_4][Sb(1,2\text{-}S_2C_6H_4)_2]$. The synthetic procedure was identical to that described above except that in the metathesis step $[NBu^n{}_4]I$ (0.44 g, 1.2 mmol) was used. The product was recrystallized from hot MeCN to give yellow crystals in *ca.* 90% isolated yield, m.p. 126–128 °C (from MeCN) (Found: C, 51.1; H, 6.9; N, 2.2. $C_{28}H_{44}NS_4Sb$ requires C, 52.2; H, 6.9; N, 2.2%). δ_H(200 MHz, $CDCl_3$, 21 °C) 7.22 (4 H, m, $S_2C_6H_4$), 6.67 (4 H, m, $S_2C_6H_4$), 2.97 (8 H, t, $NCH_2CH_2CH_2CH_3$), 1.32 (16 H, m, $NCH_2CH_2CH_2CH_3$) and 0.90 (12 H, m, $NCH_2CH_2CH_2CH_3$); (CD_2Cl_2) 7.22 (4 H, m, $S_2C_6H_4$), 6.72 (4 H, m, $S_2C_6H_4$), 2.98 (8 H, t, $NCH_2CH_2CH_2CH_3$), 1.40 (16 H, m, $NCH_2CH_2CH_2CH_3$) and 1.00 (12 H, m, $NCH_2CH_2CH_2CH_3$); (400 MHz, CD_3CN) 7.18 (4 H, m, $S_2C_6H_4$), 6.71 (4 H, m, $S_2C_6H_4$), 3.04 (8 H, t, $NCH_2CH_2CH_2CH_3$), 1.54 (8 H, m, $NCH_2CH_2CH_2CH_3$), 1.32 (8 H, m, $NCH_2CH_2CH_2CH_3$) and 0.94 (12 H, m, $NCH_2CH_2CH_2CH_3$). $\delta_C\{^1H\}$(50 MHz, CD_2Cl_2, 21 °C) 143.69 ($S_2C_6H_4$), 129.74 ($S_2C_6H_4$), 122.88 ($S_2C_6H_4$), 59.13 ($NCH_2CH_2CH_2CH_3$), 24.29 ($NCH_2CH_2CH_2CH_3$), 20.09 ($NCH_2CH_2CH_2CH_3$) and 13.84 ($NCH_2CH_2CH_2CH_3$); (101 MHz, CD_3CN) 144.57 ($S_2C_6H_4$), 130.14 ($S_2C_6H_4$), 123.27 ($S_2C_6H_4$), 59.20 ($NCH_2CH_2CH_2CH_3$), 24.25 ($NCH_2CH_2CH_2CH_3$), 20.25 ($NCH_2CH_2CH_2CH_3$) and 13.78 ($NCH_2CH_2CH_2CH_3$).

$[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$. (*a*) 2:1 *Ratio of* $1,2\text{-}(HS)_2C_6H_4$ *to* $SbCl_3$ *in air.* In a typical experiment, $1,2\text{-}(HS)_2C_6H_4$ (0.27 g, 1.9 mmol) dissolved in MeOH (10 cm^3) was added dropwise to a solution of NaOMe (20 cm^3, 11 mmol, 0.53 mol dm^{-3} in MeOH). Afterwards $SbCl_3$ (0.23 g, 1.0 mmol) dissolved in MeOH (10 cm^3) was added dropwise. The colourless solution turned yellow, then orange and finally became a deep red to purple. The reaction mixture was stirred overnight and then treated with $[NEt_4]Br$ (0.36 g, 1.8 mmol) dissolved in MeOH (10 cm^3). The slowly formed fine precipitate was filtered off and dried *in vacuo*. The filtrate was cooled to −20 °C for 24 h whereupon purple single crystals deposited in low yields (10–20% based on $SbCl_3$).

(*b*) 3:1 *Ratio of* $1,2\text{-}(HS)_2C_6H_4$ *to* $SbCl_3$ *in air.* In a typical experiment, $1,2\text{-}(HS)_2C_6H_4$ (0.43 g, 3.0 mmol) dissolved in MeOH (10 cm^3) was added portionwise to a solution of NaOMe (6.0 cm^3, 3.2 mmol, 0.53 mol dm^{-3} in MeOH) and then stirred for 0.5 h. Upon adding $SbCl_3$ (0.23 g, 1.0 mmol) dissolved in MeOH (10 cm^3), the former colourless solution turned yellow to orange, then purple and finally a fine precipitation was formed. After stirring for 24 h the precipitate could be redissolved by adding 0.53 mol dm^{-3} NaOMe–MeOH solution (*ca.* 1.5 cm^3). Dropwise addition of $[NEt_4]Br$ (0.22 g, 1.1 mmol) in MeOH (10 cm^3) was accompanied by the formation of a purple solid. After stirring overnight the purple precipitate was filtered off and dried *in vacuo*. This procedure led to the crude product (0.56 g, 0.83 mmol). Recrystallization from MeCN–MeOH (1:1) gave almost black platelets suitable for X-ray crystallography (0.20 g, 0.30 mmol, 30% based on $SbCl_3$), m.p. 175–176 °C [from MeCN–MeOH (1:1)] (Found: C, 46.5; H, 4.8; N, 2.1. $C_{26}H_{32}NS_6Sb$ requires C, 46.4; H, 4.8; N, 2.1%). λ_{max}/nm (0.23 mmol dm^{-3} in MeCN): 252 (17 900), 312 (5000) and 488 (ε/dm^3 mol^{-1} cm^{-1} 2700). ν_{max}(KBr) 3040, 2971, 1547, 1481, 1439, 1393, 1258, 1242, 1169, 1096, 1038, 999, 941, 783, 752, 741, 656, 470 and 432 cm^{-1}. δ_H(400 MHz, CD_3CN, 21 °C) 7.31 (6 H, m, $S_2C_6H_4$), 6.89 (6 H, m, $S_2C_6H_4$), 3.12 (8 H, q, NCH_2CH_3) and 1.18 (12 H, tt, NCH_2CH_3). $\delta_C\{^1H\}$(101 MHz, CD_3CN, 21 °C) 141.32 ($S_2C_6H_4$), 128.54 ($S_2C_6H_4$), 124.52 ($S_2C_6H_4$), 52.93 (NCH_2CH_3) and 7.57 (NCH_2CH_3).

(*c*) 1:1 *Ratio of* $1,2\text{-}(HS)_2C_6H_4$ *to* $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ *excluding moisture.* In a typical experiment, $1,2\text{-}(HS)_2C_6H_4$ (0.058 g, 0.41 mmol) and $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ (0.18 g, 0.34 mmol) were dissolved in degassed MeCN (15 cm^3). A slow stream of O_2 was passed through the pale yellow solution which turned purple within 3 h and finally after 24 h became almost black. The reaction mixture was stored at −20 °C for 24 h and the deep purple microcrystalline solid filtered off and dried *in vacuo* {0.19 g, 0.28 mmol, 82% based on $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$}, m.p. 175–177 °C (from MeCN).

Crystallography.—*Crystal data.* $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$, $C_{20}H_{28}NS_4Sb$, M_r = 532.46, monoclinic, space group $P2_1/c$, a = 10.600(2), b = 14.222(2), c = 15.913(3) Å, β = 106.35(1)°, U = 2302(1) Å^3, D_m = 1.50 g cm^{-3}, F(000) = 1080, Z = 4, D_c = 1.54 g cm^{-3}, μ = 15.6 cm^{-1}.

$[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$, $C_{26}H_{32}NS_6Sb$, M_r = 672.69, monoclinic, space group $P2_1/c$, a = 12.363(2), b = 11.332(1), c = 20.772(3) Å, β = 92.18(1)°, U = 2908(1) Å^3, D_m = 1.48 g cm^{-3}, F(000) = 1368, Z = 4, D_c = 1.54 g cm^{-3}, μ = 13.8 cm^{-1}.

Single crystals of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ ($[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$) selected for data collection were mounted with 'super glue' on a glass fibre. X-Ray diffraction data were collected with an Enraf-Nonius CAD-4 diffractometer [graphite monochromated, λ(Mo-Kα) = 0.710 73 Å] in the ω–2θ mode, to a maximum 2θ of 52°. The unit-cell dimensions and their standard deviations were derived from a least-squares fit of the setting angles of 25 centred reflections in the range $11 < \theta < 14°$ ($9 < \theta < 14°$). The intensities of three standard reflections were measured every 50 (42) min, indicating a total loss of intensity of 1.3 (1.9%). Anisotropic decay corrections were applied with correction factors on I ranging from 0.993 to 1.041 (0.968 to 1.038). The raw intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (ψ scan) was applied to the data set. A total of 4971 (6290) reflections were measured, of which 3682 (4558) with $F_o{}^2 > 3.0\sigma(F_o)^2$ were used in the calculations.

Solution and refinement. All calculations were performed on a VAX 3100 computer using MolEN.[14] In each case the observed systematic absences were consistent with the monoclinic space group $P2_1/c$. Starting models for both structures were provided by the heavy-atom method (Patterson function). In both cases they were further developed to final structure models with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Refinement included a secondary extinction coefficient, 5×10^{-7} (2×10^{-7}). The final full-matrix least-squares refinement cycles included 348 (436) variable parameters and converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.024$ (0.024) and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.031$ (0.035). The function minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o)^2$. Atomic scattering factors for spherical neutral free (non-H atoms) or bonded (H) atoms as well as anomalous scattering contributions were taken from ref. 15. Tables 1 and 2 show the final positional parameters and selected bond distances and angles for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$, Tables 3 and 4 for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$.

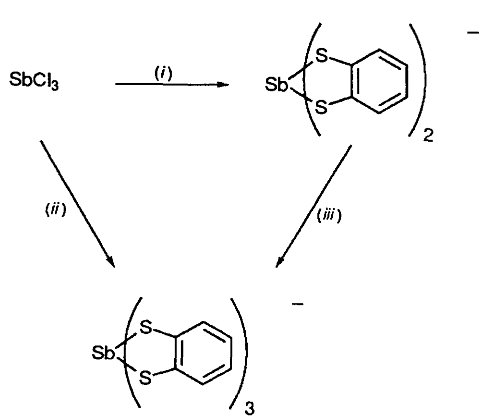
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Cyclic Voltammetry.—The cyclic voltammetry apparatus consisted of a potentiostat with potential-scan capability, a voltameter and an electrochemical cell. A three-electrode system was used[16] comprising a platinum disc working electrode, platinum wire auxiliary electrode, Ag–AgCl reference electrode, and 1.0 mol dm^{-3} solutions of $[NBu^n{}_4][PF_6]$ as electrolyte in MeCN or dmf. The electrochemical cell was constructed in a dry-box. In a typical experiment: 14 mg (18 mg) of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ ($[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$) was dissolved in electrolyte solution (25 cm^3) providing a sample concentration of 10^{-3} mol dm^{-3}. Test solutions (10 cm^3) were transferred to the electrochemical cell and a slow constant stream of argon was blown above the solution during the measurement. Scans started at +1.0 (+0.3 V) with a scan rate of 50 (50 mV s^{-1}) to −1.5 (−1.3 V). Background scans with electrolyte were carried out in these regions.

Results and Discussion

Synthesis and General Consideration.—Antimony(III) chloride reacts with solutions of $1,2\text{-}(MS)_2C_6H_4$ to afford $M[Sb(1,2\text{-}S_2C_6H_4)_x]$ (x = 2 or 3; M = Li or Na). The outcome of these reactions (see Scheme 1) is strongly influenced by the presence of moisture and oxygen. When reaction of $1,2\text{-}(MS)_2C_6H_4$ (M = Li or Na) and $SbCl_3$, in either a 1:2 or 1:3 ratio, is conducted aerobically $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$ is the only isolated product. Even under optimum conditions the isolated yield is under 30%. In addition, sparging the reaction mixture with air, to maintain a higher oxygen concentration, proved to be detrimental because the isolated yield dropped to 10%. Furthermore, aerobic purification is hampered by the presence of several impurities, most notably an insoluble amorphous orange material. This orange material is probably Sb_2S_3 which, in addition to Sb_2O_3, has been suggested as a decomposition product for thiolate complexes of Sb.[2c,17,18]

Under anaerobic conditions, the reaction of $SbCl_3$ with 2 molar equivalents of $1,2\text{-}(LiS)_2C_6H_4$ followed by metathesis with either $[NEt_4]Br$ or $[NBu^n{}_4]I$ yields a yellow precipitate of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ (*ca.* 72% yield) or $[NBu^n{}_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ (*ca.* 90% yield), respectively. These tetraalkylammonium salts are soluble in dmf and MeCN, exhibit modest solubility in $CHCl_3$ and Me_2CO, and are insoluble in water, MeOH, Et_2O and thf. While solid samples of $[NR_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ (R = Et or Bu^n) are stable to air, solutions are modestly air sensitive. When heated to *ca.* 156 °C crystals of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ change from yellow to red. As this occurs very close to the melting point (158–159 °C) we have not been able to determine whether it is caused by a phase change, a decomposition or is just a melting feature. The $[NBu^n{}_4]^+$ salt exhibits the same behaviour at its melting point of 126–128 °C. The UV/VIS spectrum of $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ (MeCN) showed three maxima at 246, 308 and 384 nm due to charge-transfer interactions between Sb and sulfur. The analogous red complex $[Bi(1,2\text{-}S_2C_6H_4)_2]^-$ exhibits similar maxima at 246, 314, 366 and 448 nm.[19] Cyclic voltametry on $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ (MeCN) revealed an irreversible oxidation wave with a peak potential of *ca.* 0.45 V (*vs.* Ag–AgCl). Two reduction waves of much lower intensity could be observed at *ca.* −1.0 and *ca.* −0.65 V, which are coupled to the former oxidation wave. Changing the solvent from MeCN to dmf provided an oxidation wave at a peak potential of *ca.* 0.47 V coupled to a single reduction wave at *ca.* −0.69 V of almost the same intensity.



Scheme 1 (*i*) $1,2\text{-}(LiS)_2C_6H_4$, anaerobic, yield 72–90%; (*ii*) $1,2\text{-}(LiS)_2C_6H_4$, aerobic, <30%; (*iii*) $1,2\text{-}(HS)_2C_6H_4$, O_2, 82%

With the synthesis of $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ improved we redirected our attention to improving the preparation of $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$. Bearing in mind that in the presence of traces of air a solution of the former slowly converts into a solution of the latter, we examined the reaction of $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ and $1,2\text{-}(HS)_2C_6H_4$ in the presence of dry O_2. Using this procedure a dark purple precipitate of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$ can be isolated in 82% yield. The physical properties of $[NR_4][Sb(1,2\text{-}S_2C_6H_4)_3]$ are very similar to those of $[NR_4][Sb(1,2\text{-}S_2C_6H_4)_2]$. The electronic spectrum (MeCN) contains maxima at 224, 252, 312 and 488 nm. It is interesting that the absorption coefficient at 488 nm is significantly smaller than the corresponding value[4] of $[Sb(3,4\text{-}S_2C_6H_3Me)_3]^-$. In comparison to transition metal $[M(1,2\text{-}S_2C_6H_4)_3]$ complexes[5a] the absorption coefficient is also much lower. Although the solid-state structure of $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$ is close to octahedral, the UV/VIS spectrum showed an intense absorption in the visible region, which according to Schrauzer's studies[20] is indicative of trigonal-prismatic co-ordination geometry. Cyclovoltammograms (MeCN) contain an irreversible reduction wave at a peak potential of *ca.* −1.0 V (*vs.* Ag–AgCl) coupled to an oxidation wave of low intensity at *ca.* +0.16 V.

Crystal Structures.—Structural analyses of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ and $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$ by X-ray crystallography reveal the presence of discrete $[Sb(1,2\text{-}S_2C_6H_4)_x]^-$ (x = 2 or 3) anions and $[NEt_4]^+$ cations; shortest intermolecular Sb···S interactions are greater than 5.4 Å. Both monomeric anions consist of an Sb atom solely co-ordinated by the sulfur atoms of $1,2\text{-}S_2C_6H_4$ ligands. Bond distances within the latter are very similar to those found in $[M(1,2\text{-}S_2C_6H_4)_3]^{2-}$ (M = Ti, Zr or Ta) and are interpreted as indicating dithiolato, rather than dithioketonic,[21] character. In the present cases the $S_2C_6H_4$ fragments are almost planar (±0.1 Å) while the SbS_2C_6 moieties are bent about the S···S vectors: $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$, 7.3(1), 15.2(1); $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$, 12.4(1), 15.1(1), 22.0(1)°.

$[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$. Recrystallization of the complex from hot MeCN provides pale yellow crystals suitable for X-ray crystallography. Fig. 1 shows the molecular structure of the anion along with the numbering scheme. The Sb^{III} is chelated by two $1,2\text{-}S_2C_6H_4$ ligands thereby providing the only example of an anionic complex containing an SbS_4 core.

The co-ordination geometry about Sb is distorted Ψ-trigonal bipyramidal[22] with an equatorial position occupied by the lone pair of electrons of the Sb^{III}. Approximately, the SbS_4 core has

Table 1 Positional parameters for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$

Atom	*x*	*y*	*z*
Sb	0.783 75(2)	0.222 89(1)	0.044 44(1)
S(1)	0.893 22(7)	0.059 63(5)	0.091 44(4)
S(2)	0.827 88(7)	0.242 40(5)	0.202 43(4)
S(3)	0.618 89(8)	0.363 66(5)	0.031 28(5)
S(4)	0.580 05(6)	0.131 94(4)	−0.000 70(4)
N	0.626 6(2)	−0.084 0(1)	−0.231 6(1)
C(1)	0.869 1(2)	0.130 2(2)	0.248 3(2)
C(2)	0.875 5(3)	0.120 1(2)	0.336 9(2)
C(3)	0.905 4(3)	0.035 0(2)	0.378 9(2)
C(4)	0.929 0(3)	−0.041 8(2)	0.332 9(2)
C(5)	0.921 7(3)	−0.034 0(2)	0.245 1(2)
C(6)	0.893 4(2)	0.052 1(2)	0.201 2(2)
C(7)	0.449 5(2)	0.211 1(2)	−0.008 4(1)
C(8)	0.323 5(3)	0.172 2(2)	−0.032 1(2)
C(9)	0.215 4(3)	0.226 1(3)	−0.030 8(2)
C(10)	0.233 2(3)	0.319 7(3)	−0.006 7(2)
C(11)	0.355 9(3)	0.360 0(2)	0.014 2(2)
C(12)	0.467 6(3)	0.306 8(2)	0.012 3(2)
C(13)	0.708 0(2)	−0.035 3(2)	−0.149 0(1)
C(14)	0.777 3(3)	0.052 1(2)	−0.162 6(2)
C(15)	0.554 1(2)	−0.164 1(2)	−0.203 0(2)
C(16)	0.471 7(3)	−0.222 7(2)	−0.276 0(2)
C(17)	0.531 1(3)	−0.016 2(2)	−0.290 3(2)
C(18)	0.432 4(3)	0.026 7(2)	−0.246 9(2)
C(19)	0.714 3(3)	−0.121 6(2)	−0.284 6(2)
C(20)	0.807 3(3)	−0.197 7(3)	−0.240 5(3)

Table 2 Selected distances (Å) and angles (°) for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$

Sb–S(1)	2.6093(7)	S(1)–C(6)	1.749(3)
Sb–S(2)	2.4400(7)	S(2)–C(1)	1.758(3)
Sb–S(3)	2.6266(8)	S(3)–C(12)	1.745(3)
Sb–S(4)	2.4450(7)	S(4)–C(7)	1.761(3)
S(1)–Sb–S(2)	82.24(2)	S(1)–C(6)–C(1)	122.4(2)
S(1)–Sb–S(3)	158.95(3)	S(1)–C(6)–C(5)	119.4(2)
S(1)–Sb–S(4)	84.15(2)	S(2)–C(1)–C(2)	116.6(2)
S(2)–Sb–S(3)	85.74(2)	S(2)–C(1)–C(6)	123.9(2)
S(2)–Sb–S(4)	105.08(3)	S(3)–C(12)–C(7)	123.4(2)
S(3)–Sb–S(4)	82.36(2)	S(3)–C(12)–C(11)	118.9(2)
Sb–S(1)–C(6)	102.46(9)	S(4)–C(7)–C(8)	116.1(2)
Sb–S(2)–C(1)	106.11(9)	S(4)–C(7)–C(12)	123.5(2)
Sb–S(3)–C(12)	102.64(9)		
Sb–S(4)–C(7)	107.11(8)		

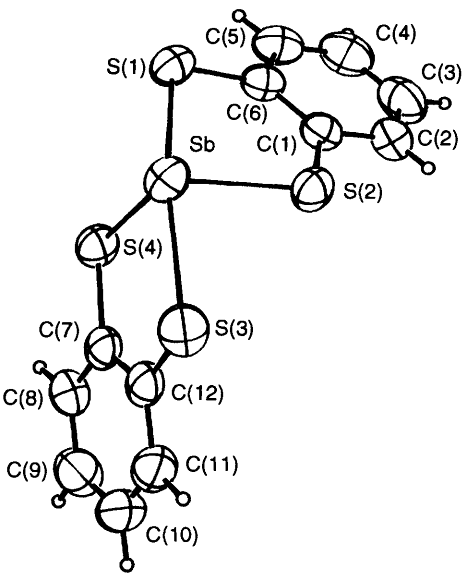


Fig. 1 Structure and numbering scheme for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ with 50% probability ellipsoids

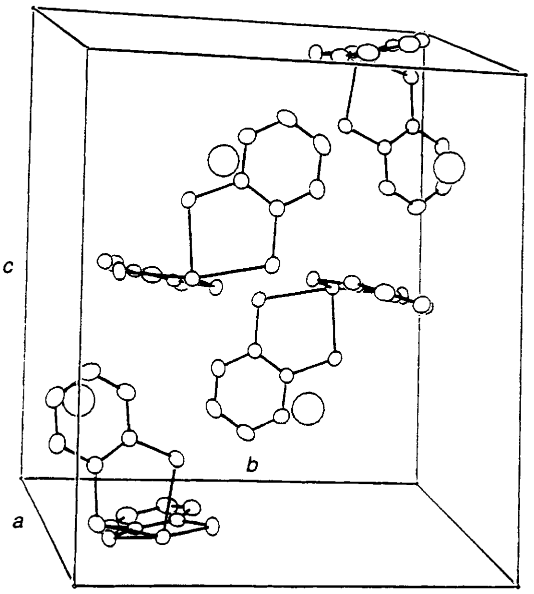


Fig. 2 Unit cell for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$; for clarity the H atoms are not shown and the cation, $[NEt_4]^+$, is represented by a sphere

C_{2v} point-group symmetry. Distortion from ideality is manifested by a significant reduction of S–Sb–S angles [S_{ax}–Sb–S_{ax} 158.95(3), S_{eq}–Sb–S_{eq} 105.08(3)° compared to 180 and 120° in the ideal polyhedron] attributable to the stereoactivity of the antimony lone electron pair. In contrast to expectations, the degree of distortion is small when compared to that in $[Sb(S_2CNBu_2)_2]^+$ and other [M(symmetric bidentate ligand)$_2$(lone pair)] complexes,[23] where M = Te, Sn or Pb, which have normalized bites (*b*) from 1.00 to 1.30, φ_A from 103 to 113° and φ_B from 130 to 137°.[7] For example, in $[Sb(S_2CNBu_2)_2]^+$ a stronger distortion is revealed by a more pronounced lowering of S–Sb–S angles [S_{ax}–Sb–S_{ax} 145.1(2), S_{eq}–Sb–S_{eq} 94.6(2)°], giving rise to $\varphi_A = 107.5°$ and $\varphi_B = 132.7°$. Contrary to this, in $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ ($b = 1.31$) the smaller distortion leads to $\varphi_A = 100.5°$ and $\varphi_B = 127.5°$, values characteristic of the [M(unsymmetric bidentate ligand)$_2$(lone pair)] class of complexes which have *b* from 1.32 to 1.40, φ_A from 91 to 100° and φ_B from 126 to 129°. Lastly, it is interesting that the asymmetry in the Sb–S bond lengths in $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ ($\Delta_{av} = 0.175$ Å) is comparable to that in $[Sb(S_2CNBu_2)_2]^+$, where anisobidentate 1,1-dithiocarbamate ligands are bonded to the Sb atom, and the ratio of Sb–S_{ax} to Sb–S_{eq} of *ca.* 1.07 : 1 is in agreement with expectations for ψ-trigonal-bipyramidal co-ordination.

In addition to using the structural data associated with the SbS_4 core, the co-ordination geometry also can be described by the non-bonding S···S distances and the dihedral angle between adjacent S_3 planes (denoted as δ).[24] In a Ψ-trigonal bipyramid three different sets of S···S distances should exist ($S_{ax}\cdots S_{ax}$, $S_{eq}\cdots S_{eq}$ and $S_{ax}\cdots S_{eq}$ listed in the order of decreasing length) and δ is 53.1°.[24] In $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ the S···S distances can be divided into three sets [5.148(1), 3.878(1) and average 3.376 Å] and δ is 42.78(3)°.

One consequence of the Ψ-trigonal-bipyramidal co-ordination geometry is an orthogonal positioning of the two phenyl groups, dihedral angle 87.31(9)°. This aspect of the structure of $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ becomes even more interesting when the packing of the anions in the unit cell is examined. The phenyl groups of each anion are oriented such that one lies almost perpendicular to the *a* axis and the other one almost perpendicular to the *c* axis. Parallel to the *c*-axis alignment of one of the C_6 fragments of the benzene rings leads to a 'pipeline'

Table 3 Positional parameters for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$

Atom	x	y	z
Sb	−0.208 51(1)	0.071 01(1)	−0.134 78(1)
S(1)	−0.348 13(6)	−0.085 92(6)	−0.154 23(4)
S(2)	−0.294 30(6)	0.171 25(6)	−0.228 52(3)
S(3)	−0.100 39(5)	0.255 46(7)	−0.121 71(3)
S(4)	−0.322 15(5)	0.155 72(7)	−0.050 20(4)
S(5)	−0.115 38(6)	−0.039 32(8)	−0.047 34(3)
S(6)	−0.067 73(5)	−0.011 98(6)	−0.203 53(3)
N	0.279 7(2)	0.110 5(2)	0.856 3(1)
C(1)	−0.404 5(2)	−0.043 9(2)	−0.230 3(1)
C(2)	−0.380 6(2)	0.061 7(2)	−0.261 4(1)
C(3)	−0.428 0(2)	0.084 5(3)	−0.321 8(1)
C(4)	−0.500 9(3)	0.006 5(3)	−0.350 9(1)
C(5)	−0.526 0(2)	−0.096 0(3)	−0.320 3(2)
C(6)	−0.476 9(2)	−0.122 6(2)	−0.260 6(1)
C(7)	−0.187 1(2)	0.345 0(2)	−0.077 8(1)
C(8)	−0.277 4(2)	0.302 4(2)	−0.046 0(1)
C(9)	−0.336 5(2)	0.381 1(3)	−0.009 5(1)
C(10)	−0.309 1(3)	0.497 9(3)	−0.003 9(2)
C(11)	−0.221 9(3)	0.540 7(3)	−0.036 3(2)
C(12)	−0.161 5(3)	0.464 7(3)	−0.072 5(2)
C(13)	−0.041 2(2)	−0.143 5(2)	−0.090 2(1)
C(14)	−0.023 8(2)	−0.133 2(2)	−0.156 7(1)
C(15)	0.035 0(2)	−0.222 0(3)	−0.186 3(1)
C(16)	0.078 3(3)	−0.314 8(3)	−0.151 7(2)
C(17)	0.063 6(2)	−0.322 5(3)	−0.086 2(1)
C(18)	0.003 3(2)	−0.238 6(3)	−0.056 3(1)
C(19)	0.185 9(2)	0.194 3(3)	0.866 6(2)
C(20)	0.204 9(3)	0.320 2(3)	0.848 1(2)
C(21)	0.381 4(2)	0.150 2(3)	0.893 0(1)
C(22)	0.372 8(3)	0.156 7(3)	0.965 1(2)
C(23)	0.242 9(2)	−0.009 4(3)	0.879 5(1)
C(24)	0.322 6(3)	−0.108 6(3)	0.872 4(2)
C(25)	0.307 0(2)	0.107 4(3)	0.785 7(1)
C(26)	0.217 3(3)	0.064 2(4)	0.739 7(2)

Table 4 Selected distances (Å) and angles (°) for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$

Sb–S(1)	2.5004(7)	S(1)–C(1)	1.769(2)
Sb–S(2)	2.4597(7)	S(2)–C(2)	1.758(2)
Sb–S(3)	2.4903(8)	S(3)–C(7)	1.757(3)
Sb–S(4)	2.4837(7)	S(4)–C(8)	1.753(3)
Sb–S(5)	2.4553(7)	S(5)–C(13)	1.758(3)
Sb–S(6)	2.4784(7)	S(6)–C(14)	1.758(3)
S(1)–Sb–S(2)	85.77(2)	Sb–S(3)–C(7)	101.86(9)
S(1)–Sb–S(3)	168.22(2)	Sb–S(4)–C(8)	102.43(9)
S(1)–Sb–S(4)	89.06(2)	Sb–S(5)–C(13)	101.89(8)
S(1)–Sb–S(5)	93.37(3)	Sb–S(6)–C(14)	100.75(8)
S(1)–Sb–S(6)	97.62(2)	S(1)–C(1)–C(2)	124.1(2)
S(2)–Sb–S(3)	84.96(2)	S(1)–C(1)–C(6)	117.1(2)
S(2)–Sb–S(4)	98.23(2)	S(2)–C(2)–C(1)	124.1(2)
S(2)–Sb–S(5)	175.37(2)	S(2)–C(2)–C(3)	116.7(2)
S(2)–Sb–S(6)	90.58(2)	S(3)–C(7)–C(8)	123.9(2)
S(3)–Sb–S(4)	85.08(2)	S(3)–C(7)–C(12)	117.4(2)
S(3)–Sb–S(5)	96.43(3)	S(4)–C(8)–C(7)	123.9(2)
S(3)–Sb–S(6)	89.74(2)	S(4)–C(8)–C(9)	117.4(2)
S(4)–Sb–S(5)	86.30(2)	S(5)–C(13)–C(14)	122.9(2)
S(4)–Sb–S(6)	169.34(2)	S(5)–C(13)–C(18)	117.9(2)
S(5)–Sb–S(6)	85.02(2)	S(6)–C(14)–C(13)	123.4(2)
Sb–S(1)–C(1)	101.50(8)	S(6)–C(14)–C(15)	118.3(2)
Sb–S(2)–C(2)	102.64(8)		

structure, whereas parallel to the *a* axis no such pipeline can be observed as these phenyl groups lie in an alternating orientation. Fig. 2 shows a packing diagram of the unit cell.

$[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$. Almost black platelets suitable for X-ray crystallography were obtained by recrystallization of the complex from MeCN–MeOH (1:1). Fig. 3 shows the molecular structure along with the numbering scheme.

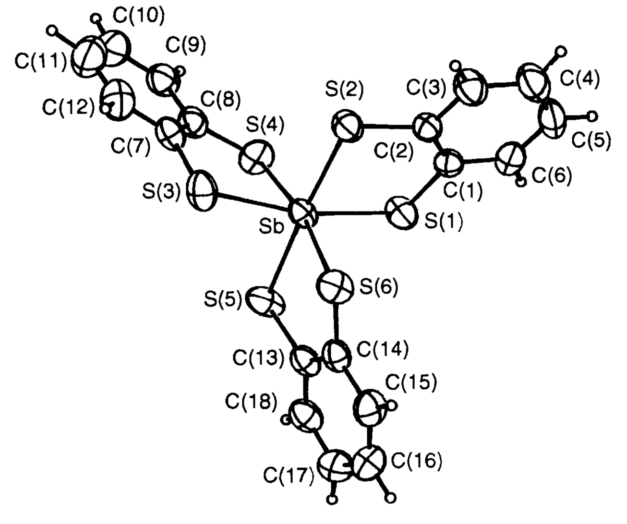


Fig. 3 Structure and numbering scheme for $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_3]$ with 50% probability ellipsoids

Monomeric $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$ consists of a central Sb^V surrounded by the six sulfur atoms of three $1,2\text{-}S_2C_6H_4$ ligands. Normally six-co-ordinated metal centres are found to be close to the octahedral limit, rather than to the trigonal-prismatic limit.[25] Notable exceptions are the transition-metal [M(dithiolene)$_3$] and $[M(1,2\text{-}S_2C_6H_4)_3]$ complexes, the majority of which adopt a geometry close to the trigonal-prismatic limit.[26] Data for analogous main-group element complexes are rather limited,[4,6] however, in contrast to transition-metal complexes, the co-ordination geometry of the s^0p^0 metal centres is slightly distorted from the octahedral limit. The SbS_6 core in $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$ is best described as having D_3 symmetry which is close to the octahedral limit. Much of the structural data is within 10% of expectations for octahedral geometry: (1) the *cis*-S–Sb–S angles range from 85.02(2) to 98.23(2)° and *trans*-S–Sb–S angles from 168.22(2) to 175.37(2)°; (2) the SbS(1)S(2)S(3)S(5), SbS(1)S(3)S(4)S(6) or SbS(2)S(4)S(5)S(6) planes (± 0.2 Å) are nearly orthogonal, dihedral angles from 89.11(1) to 91.07(1)°; and (3) the non-bonding S···S distances range from 3.334(1) to 3.747(1) Å for adjacent sulfur atoms and 4.911(1) to 4.964(1) Å for opposing S atoms thereby providing an average ratio of 0.710:1 which is the same as for an ideal O_h polyhedron. Distortion from an octahedral geometry becomes more evident upon examination of the following data: (1) the dihedral angle formed by planes of opposing S_3 faces ranges from 2.8(4) to 13.2(1)° where only one set of opposing S_3 faces [S(2)S(3)S(6)/S(1)S(4)S(5) 2.8(4)°] is almost parallel; (2) the average twist[27] angle was computed to be 49.22(3)° in good agreement with the value given by Martin and Takats;[5] and (3) dihedral angles between adjacent S_3 faces (δ)[24] vary from 57.66(3) to 79.84(2)° with b_1 of 60.79(3) and b_2 of 78.67(3)°. The overall co-ordination geometry is probably determined by a combination of steric factors and ligand bite as evidenced by the observed δ values being in good agreement with expectations for compounds with *ca.* 49° twist angles: b_1 of *ca.* 60 and b_2 of *ca.* 80°.[24]

NMR Spectroscopy.—The ^{13}C and ^1H NMR spectra (CD_3CN) of $[NEt_4][Sb(1,2\text{-}S_2C_6H_4)_2]$ are interpreted as a AA′BB′ spin system: ^{13}C, δ 144.61, 130.18 and 123.31; ^1H, multiplets at δ 6.71 and 7.18. Chemical shift assignments were made with the aid of selective decoupling experiments: δ 144.61, carbon atom bonded to sulfur; 130.18 [^1J(C–H) = 156 Hz], *m*-carbon; and 123.31 [^1J(C–H) = 159 Hz], *o*-carbon. Those H atoms closest to sulfur atoms resonate at δ 6.71, whereas those further from sulfur resonate at δ 7.18. In addition to the aromatic region it is interesting that the $[NEt_4]^+$ cation generates an expected quartet for the CH_2 protons, but a triplet of triplets for the CH_3 protons, which is caused by coupling of the latter to the nitrogen.[10]

The observed AA′BB′ pattern of the aromatic resonances disagrees with the solid-state structure which lacks the required symmetry elements. Kepert's potential-energy calculations indicate that the movement from a trigonal-bipyramidal conformation over a square-pyramidal intermediate to the inverse trigonal bipyramid, usually described as the Berry pseudo-rotation,[28] has an extremely low energy barrier.[7] In Kepert's analysis, for the [M(bidentate ligand)$_2$(unidentate ligand)] complexes, the potential-energy surface shows a strong dependence on the normalized bite *b*. With *b* of 1.2 a single minimum on the potential-energy surface occurs for the square-pyramidal conformation, characterized by equal values for S_{eq}–M–S_{ax} and S_{eq}–M–S_{eq} angles, which undergoes a symmetric split at *ca.* *b* of 1.28 into two minima corresponding to two equivalent trigonal bipyramids. We calculate *b* of 1.31 for $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$, suggesting that conformational flipping according to the Berry pathway is very possible. Thermal energy at room temperature is sufficient to cause facile conformational changes such that the two *o*-protons and the two *m*-protons, respectively, are equivalent. Variable-temperature NMR studies at 20, −11, −68 and −89 °C did not show any noticeable variations in the patterns of the aromatic resonances, indicating that at −89 °C the thermal energy [*ca.* 5 kcal mol^{-1} (*ca.* 20.92 kJ mol^{-1})][29] is still higher than the activation energy for the Berry pseudo-rotation.

The ^1H NMR spectrum (CD_3CN) of $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$ also shows two multiplets in the aromatic region at δ 7.31 and 6.89 with an AA′BB′ pattern, which is in agreement with the nearly D_3 solid-state structure. Compared to $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$, the aromatic resonances are shifted to lower field, so that the signals of both compounds appear separately and do not interfere with one another. Therefore when anaerobically prepared samples of $[Sb(1,2\text{-}S_2C_6H_4)_2]^-$ were exposed to air we could observe the conversion into $[Sb(1,2\text{-}S_2C_6H_4)_3]^-$. The aromatic carbons of the latter resonate at δ 141.32, 128.54 and 124.52. Gated decoupling experiments revealed that the first signal is related to the sulfur-bound carbon, the second [^1J(C–H) = 161 Hz] to the *m*-carbons and the third [^1J(C–H) = 162 Hz] to the *o*-carbons. Interestingly, the ^1J(C–H) coupling constants of the two anions differ by approximately 4 Hz.

Acknowledgements

We are indebted to the State of Ohio Academic Challenge Program for funds for a high-field NMR spectrometer and for support of this research, and to the College of Arts and Sciences for support of the X-ray crystallographic facilities. Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

1 (*a*) C. A. McAuliffe, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3; (*b*) G. Alonzo, N. Bertazzi and M. Consiglio, *Inorg. Chim. Acta*, 1984, **85**, L35; (*c*) G. H. Dale and D. L. McKay, *Hydrocarbon Processing*, September 1977, 97; (*d*) S. O. Wandiga, *J. Chem. Soc., Dalton Trans.*, 1975, 1894.

2 (*a*) D. L. Kepert, C. L. Raston, A. H. White and G. Winter, *Aust. J. Chem.*, 1978, **31**, 757; (*b*) R. Mattes and D. Rühl, *Inorg. Chim. Acta*, 1984, **84**, 125; (*c*) D. B. Sowerby, I. Haiduc, A. Barbul-Rusu and M. Salajan, *Inorg. Chim. Acta*, 1983, **68**, 87; (*d*) R. O. Day, M. M. Chauvin and W. E. McEwen, *Phosphorus Sulfur*, 1980, **8**, 121; (*e*) M. J. Begley, D. B. Sowerby and I. Haiduc, *J. Chem. Soc., Dalton Trans.*, 1987, 145; (*f*) M. J. Begley, D. B. Sowerby and I. Haiduc, *J. Chem. Soc., Chem. Commun.*, 1980, 64; (*g*) C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 791; (*h*) J. A. Howard, D. R. Russell and W. Scutcher, *Acta Crystallogr., Sect. A*, 1975, **31**, S141; (*i*) C. A. Kavounis, S. C. Kokkou, P. J. Rentzeperis and P. Karagiannidis, *Acta Crystallogr., Sect. B*, 1982, **38**, 2686; (*j*) C. A. Kavounis, S. C. Kokkou, P. J. Rentzeperis and P. Karagiannidis, *Acta Crystallogr., Sect. B*, 1980, **36**, 2954; (*k*) M. R. Snow and E. R. T. Tiekink, *Aust. J. Chem.*, 1987, **40**, 743; (*l*) G. Gottardi, *Z. Kristallogr.*, 1961, **115**, 451; (*m*) B. F. Hoskins, E. R. T. Tiekink and G. Winter, *Inorg. Chim. Acta*, 1985, **99**, 177.

3 P. J. H. A. M. van de Leemput, J. A. Cras and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, 1977, **96**, 288.

4 J. M. Kisenyi, G. R. Willey, M. G. B. Drew and S. O. Wandiga, *J. Chem. Soc., Dalton Trans.*, 1985, 69.

5 J. L. Martin and J. Takats (*a*) *Inorg. Chem.*, 1975, **14**, 73; (*b*) *Abstract of the 172nd American Chemical Society Meeting, Inorganic Section*, 1976, no. 181.

6 F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc. A*, 1971, 2762; R. O. Day, J. M. Holmes, S. Shafieezad, V. Chandrasekhar and R. R. Holmes, *J. Am. Chem. Soc.*, 1988, **110**, 5377; A. Foecker, K. Kirschbaum, B. Krebs and D. M. Giolando, unpublished work.

7 D. L. Kepert, *Inorg. Chem. Concepts*, 1982, **6**, 1.

8 A. Sequeira and I. Bernal, *J. Cryst. Mol. Struct.*, 1973, **3**, 157.

9 R. E. D. Clark, *Analyst* (*London*), 1957, **82**, 177; R. E. D. Clark and R. G. Neville, *J. Chem. Educ.*, 1959, **36**, 390.

10 E. Gagliardi and A. Durst, *Monatsh. Chemie*, 1972, **103**, 292.

11 D. Sellmann, G. Freyberger and M. Moll, *Z. Naturforsch., Teil B*, 1989, **44**, 1015.

12 G. Hunter, *J. Chem. Soc., Dalton Trans.*, 1972, 1496; E. Hoyer, W. Dietzsch, H. Hennig and W. Schroth, *Chem. Ber.*, 1969, **102**, 603.

13 D. M. Giolando and K. Kirschbaum, *J. Synth. Org. Chem.*, 1992, **5**, 451.

14 C. K. Fair, MolEN, An Interactive Intelligent System for Crystal Structure Analysis, User Manual, Enraf-Nonius, Delft, 1990.

15 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

16 K. M. Kissinger and W. R. Heinemann, *J. Chem. Educ.*, 1983, **60**, 702.

17 M. Hall and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1980, 1292.

18 R. A. Howie, D. W. Grant and J. L. Wardell, *Inorg. Chim. Acta*, 1978, **30**, 233.

19 M. Eisenhawer, D. M. Giolando and K. Kirschbaum, unpublished work.

20 G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1966, **88**, 3235.

21 M. Könemann, W. Stüer, K. Kirschbaum and D. M. Giolando, *Polyhedron*, in the press; M. Cowie and M. J. Bennett, *Inorg. Chem.*, 1976, **15**, 1595; J. L. Martin and J. Takats, *Inorg. Chem.*, 1975, **14**, 1358.

22 R. J. Gillespie, *Can. J. Chem.*, 1960, **38**, 818.

23 Ref. 7, p. 64.

24 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748.

25 J. E. Huheey, *Inorganic Chemistry*, Harper & Row, New York, 3rd edn., 1983, ch. 10, p. 464.

26 J. L. Martin and J. Takats, *Can. J. Chem.*, 1989, **67**, 1914 and refs. therein; D. L. Kepert, *Prog. Inorg. Chem.*, 1977, **23**, 1.

27 K. R. Dymock and G. J. Palenik, *Inorg. Chem.*, 1975, **14**, 1220.

28 R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

29 G. Binsch, *Top. Stereochem.*, 1968, **3**, 97; A. Steigel, in *NMR Basic Principles and Progress: Dynamic NMR Spectroscopy*, eds. P. Diehl, E. Fluck and R. Kosfeld, Springer, Berlin, 1978, vol. 15.

Received 23*rd November* 1993; *Paper* 3/06972I