Similar observations have been made by Sargeson et al. for a low-spin Co(II) complex containing a saturated N_3S_3-donor set in an encapsulating caging ligand.[20]

Summary. Electronic spectra, effective magnetic moments, and crystallographic structure determinations of bis(1,4,7-trithiacyclononane)metal(II) complexes (M = Fe, Co, Ni, Cu) have convincingly shown that the small cyclic trithia crown ether is ideally suited to bind these metal centers in an octahedral environment of six sulfur atoms. The ligand exerts a slightly stronger LF than its nitrogen analogue 1,4,7-triazacyclononane, effecting low-spin d^6 and d^7 electronic configurations of Fe(II) and Co(II), respectively.

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Registry No. [Ni([9]aneS$_3$)$_2$](BF$_4$)$_2$, 83650-36-6; [Co([9]aneS$_3$)$_2$](BF$_4$)$_2$, 83650-38-8; [Fe([9]aneS$_3$)$_2$](ClO$_4$)$_2$, 97391-12-3; Fe(ClO$_4$)$_3$·6H$_2$O, 55144-08-6; [Ni([9]aneS$_3$)$_2$](ClO$_4$)$_2$, 97465-53-7; [Co([9]aneS$_3$)$_2$](ClO$_4$)$_2$, 97465-54-8; [Fe([9]aneS$_3$)Cl$_3$], 97391-13-4; [Fe([9]aneS$_3$)$_2$](PF$_6$)$_2$, 97391-14-5; [Co^{I}([9]aneS$_3$)$_2$]$^+$, 97391-15-6; [Co^{III}([9]aneS$_3$)$_2$]$^{3+}$, 97391-16-7; [9]aneS$_3$, 6573-11-1.

Supplementary Material Available: Tables of thermal parameters, coordinates of calculated positions of H atoms, and observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Preparation and Raman Spectra of Thallium(I) Disulfite and Thallium(I) Sulfite

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Thallium(I) disulfite, $Tl_2S_2O_5$, is the product of the reaction of TlOH and liquid sulfur dioxide. Its Raman spectrum closely resembles those of the alkali-metal disulfites. It slowly decomposes at room temperature to thallium(I) sulfite and sulfur dioxide. Comparisons of the vibrational spectra of the thallium(I) sulfite and disulfite with the infrared spectra of the argon-matrix reaction products of Tl_2O and sulfur dioxide indicate that these products are not simply the sulfite and disulfite, as was previously suggested, but that they are probably complex mixtures of several thallium–sulfur–oxygen compounds.

Introduction

Because of the international concern about "acid rain", and because of the diverse and interesting chemistry of sulfur compounds, the reaction chemistry of sulfur dioxide continues to have both practical and theoretical importance.[1] As an acidic oxide, it reacts readily with basic metallic oxides and hydroxides to form three series of salts. Under basic conditions, and with polyvalent cations, only compounds with sulfite (SO_3^{2-}) are produced.[2] With excess SO_2 and/or under acidic conditions, the aqueous solution contains equilibrium mixtures[3] of aquated SO_2, bisulfite with a protonated sulfur atom[3] (HSO_3^-), bisulfite with a protonated oxygen atom[4] (SO_3H^-), and disulfite ($S_2O_5^{2-}$). However, only salts of $S_2O_5^{2-}$ and HSO_3^- are known,[3] and these are formed with monovalent cations such as the alkali metals. From direct reactions of SO_2 with solid alkali-metal hydroxides or their aqueous solutions, one obtains[3] disulfites for Li, Na, or K and bisulfites for Rb or Cs. The Rb and Cs bisulfites can be further dehydrated to the disulfites. Because cation size seems to be a factor in whether a bisulfite or a disulfite will form, we decided to try a reaction between SO_2 and wet TlOH to see whether $TlHSO_3$ or $Tl_2S_2O_5$ is favored. The thallous ion is about the same size[5] as Rb^+, so one would expect the bisulfite. Although thallous sulfite has been known for some time, neither the bisulfite nor the disulfite has been reported in preparative amounts. Recently, David and Ault[6] have interpreted infrared spectra of the reaction products of matrxi-isolated Tl_2O and SO_2 to indicate that Tl_2SO_3 and $Tl_2S_2O_5$ were formed. We report here the preparation and Raman spectra of pure, solid $Tl_2S_2O_5$ and Tl_2SO_3 and compare their properties to those of the corresponding alkali-metal compounds and the data recently published by David and Ault.[6]

Table I. Raman Frequencies (cm^{-1}) of the $S_2O_5^{2-}$ Ion in Various Compounds and Infrared Frequencies Assigned to $Tl_2S_2O_5$ in Matrices

$K_2S_2O_5$	$Rb_2S_2O_5$	$Cs_2S_2O_5$	$Tl_2S_2O_5$	$Tl_2S_2O_5$ (IR) matrix[b]
217 m[a]	220 m	224 m	212 m	
244 vs	242 vs	240 vs	225 vs	
318 m	315 m	315 m	307 m	
434 s	432 s	435 s	423 s	435
515 w	519 w	519 w	504 w	495
557 w	545 w	545 w	533 w	595
	558 vw	558 vw	546 vw	657
643 vw	643 vw	643 vw		776
653 s	654 s	654 s	641 s	882
970 w	950 w	952 w	959 w	956, 973
1060 s	1047 s	1047 s	1033 s	1040
1088 m	1068 w	1071 w		1050
1178 m	1154 w	1155 w	1120 w	1089
1178 m	1188 w	1181 w	1157 w	1102

[a] Key (relative intensities): vw = very weak, w = weak, m = medium, s = strong, vs = very strong. [b] Reference 6.

Experimental Section

A few drops of water were added to wet some solid TlOH in a tube, which was fitted for a vacuum line. The slurry was degassed and SO_2 condensed onto it at 77 K. The system was allowed to warm to room temperature in a sealed pressure container, so that the SO_2 remained liquid. After several minutes, the excess SO_2 and water were evaporated on the vacuum line. The white residue was collected, and its Raman spectrum was recorded. The sample was stored in a vacuum for 24 h,

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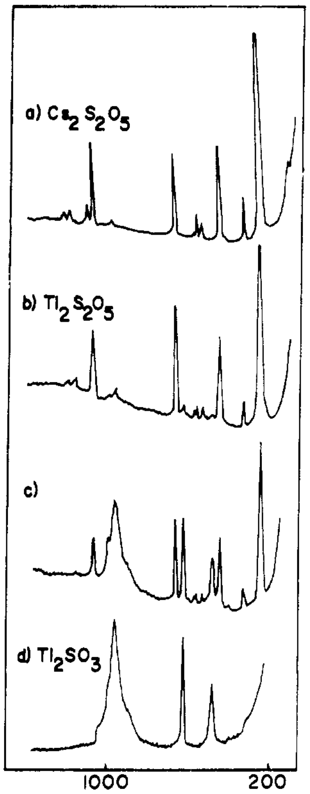

Figure 1. Raman spectra: (a) solid $Cs_2S_2O_5$; (b) TlOH–SO_2 reaction product after initial drying; (c) TlOH–SO_2 reaction product after 24 h in vacuo; (d) TlOH–SO_2 reaction product after final drying.

and the Raman spectrum was again measured. Finally, the sample was gently warmed with a hot-air blower in vacuo for 15 min, and the Raman spectrum was again recorded. All spectra were measured by using the 488.0-nm Ar^+ line of a Coherent Radiation Model 52MG laser and a Spex 1401 double monochromator.

Results and Discussion

The Raman spectrum of the freshly dried residue closely resembled that of the alkali metal disulfites, as can be seen in Table I and Figure 1a,b. We have therefore concluded that the primary substance in the white reaction product is $Tl_2S_2O_5$. Table I compares the Raman frequencies of $Tl_2S_2O_5$ with those of some alkali-metal disulfites, and Figure 1a,b is a visual comparison of the $Cs_2S_2O_5$ and $Tl_2S_2O_5$ spectra. All the alkal-metal disulfites have Raman spectra of similar appearance.[3] The thallous disulfite spectrum shows weak impurity bands at 457, 600, and 928 cm^{-1}, which grew dramatically at the expense of the disulfite bands upon storing the product in a vacuum for 24 h. Figure 1c shows this Raman spectrum. The vacuum trap smelled strongly of SO_2. After gentle warming in vacuo, the disulfite bands totally disappeared in favor of the three "impurity" bands, with additional SO_2 release. Figure 1d shows the Raman spectrum of this final product. This final product, which was the impurity in the initial product, is Tl_2SO_3. Table II compares the Raman spectrum of thallous sulfite with those of the alkali-metal sulfites and the aqueous solution sulfite spectrum.[7] The thallium(I) sulfite gives a spectrum that differs from the general features of the alkali-metal sulfite spectra in three ways: (1) all the Tl compound frequencies are slightly lower; (2) the ν_2 band is relatively more intense; (3) ν_1 and ν_3 appear as a broad singlet rather than a closely spaced doublet. However, this last feature resembles that of the aqueous solution, in which the upper two bands can only be resolved with difficulty. The differences are probably due to the much greater polarizing ability of Tl.

There are also some interesting features with respect to the formation, decomposition, and Raman spectrum of $Tl_2S_2O_5$. Although the sulfite has been known for a long time, the disulfite has only now been prepared and identified.[3] This is probably due to the fact that it readily decomposes, releasing SO_2. In this respect it closely resembles $Li_2S_2O_5$, which also readily decomposes, but it is different than the other alkali-metal disulfites, which are indefinitely stable at ordinary temperatures.[3] If cation size alone was important, one would expect the thallium(I) disulfite to be more stable. Indeed, considering its size similarity[5] to rubidium, one would expect the initial formation of $TlHSO_3$, which could be converted to a stable disulfite.[3] Finally, the Raman bands of the disulfite ion in $Tl_2S_2O_5$ occur at consistantly lower frequencies than the corresponding ones in the alkali-metal disulfite spectra.[3]

Table II. Raman Frequencies (cm^{-1}) and Band Assignments for the Sulfite Ion in Solution and Ionic Compounds and Infrared Frequencies Assigned to Tl_2SO_3 in Matrices

species	ν_1 (A_1)	ν_3 (E)	ν_2 (A_1)	ν_4 (E)
SO_3^{2-}(aq)	966	933	620	470
Na_2SO_3	990	950	639	499
K_2SO_3	978	952	628	478
Rb_2SO_3	963	952	628	479
Cs_2SO_3	951	936	620	470
Tl_2SO_3	928	928	600	457
Tl_2SO_3 (IR) matrix[a]	958, 974	1064, 1086	588	442, 548

[a] Reference 6.

The only other report of the existance of $Tl_2S_2O_5$ is a recent interpretation of complex infrared spectra of the reaction of Tl_2O and SO_2 in an argon or N_2 matrix.[6] The spectra were found to be temperature and concentration dependent. The authors, David and Ault, interpreted their spectra to mean that both Tl_2SO_3 and $Tl_2S_2O_5$ were formed. The relative amount of each is strongly influenced by the matrix-deposition conditions. Although their choice of products is intuitively reasonable, their infrared band assignments are questionable in light of this and previous work.

A symmetric sulfite ion has C_{3v} point symmetry, giving rise to four vibrational normal modes, 2 A_1 and 2 E, all of which should be both Raman and infrared active. These modes can be unambiguously assigned to the four bands observed in the aqueous sulfite Raman spectrum by depolarization ratio measurements.[7] Sulfur-34 isotope work[8] on solid K_2SO_3 would indicate that there is a direct correspondence of the relative position of the Raman bands between the aqueous solution spectrum and the spectra of the alkali-metal sulfites. Table II lists the sulfite Raman frequencies and their assignments. The symmetric and asymmetric S–O stretching frequencies are quite close together, and, somewhat unusually, the symmetric mode has the higher energy vibration.[7]

The vibrational frequencies and assignments chosen for Tl_2SO_3 in the matrices[6] are also in Table II for comparison. The four normal modes for sulfite were assigned as follows.[6] ν_1, (958, 974); ν_2, 588; ν_3, (1061, 1067) and 1086; ν_4, 442 and 548. (All values are in cm^{-1}.) The multiple frequencies for ν_3 and ν_4 were rationalized as the removal of the degeneracy of the E modes due to reduced SO_3^{2-} symmetry in the matrix caused by ion pairing. Three features of their data and interpretation are incompatable with our work and previous work. First, the matrix oxygen-18 experiments showed no shift in the bands assigned by the authors to ν_4. It is our experience[3] with similar compounds that there should have been a shift in the 15–25-cm^{-1} range, as did occur[6] with their parent SO_2. Second, Raman depolarization ratios indicate[7] that the highest frequency band is the A_1 mode in the S–O stretching region (Table II), just opposite the matrix assignment. Third, the bands above 1060 cm^{-1} are far too high for sulfite. In fact, these frequencies correspond to the symmetric S–O stretching frequencies in the polythionates and sulfonates, where the sulfur atom is singly bonded to a fourth ligand. There is a theoretical basis[9,10] for S–O bond strengthening if the polarizing and polarizable Tl^+ ion interacts with the sulfur atom in a covalent manner. But this would increase the frequencies

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of both stretching vibrations, which is not the case in the matrix data. If the Tl^+ covalently interacts instead with a sulfite oxygen, the S–O bond would be weakened, lowering the vibrational frequencies. Electrostatically, the Tl–O interaction would be more likely and is apparently what occurs in crystalline Tl_2SO_3, judging from the relatively low vibrational frequencies.

David and Ault[6] also propose the symmetrical structure, $^-O_2SOSO_2^-$, for the disulfite ions in their matrices. The vibrational frequencies that they assign to this structure are listed in Table I. What is most surprising about this report is the unexpected stability of this oxygen-bridged species, which apparently exceeds that of sulfite. The structure[11] and vibrational spectrum of the disulfite ion in crystalline solids[3,12] and solution[4a,12] is well established. Our room-temperature spectrum of $Tl_2S_2O_5$ closely matches the spectra of the other disulfites (Table I). The disulfite spectrum is also known in low-temperature matrices.[13] Normally, disulfite has an unsymmetrical structure, which can be described as a sulfonate group and a sulfinate group connected by a somewhat long[11] sulfur–sulfur bond. There is no evidence in solution[4] or otherwise for the symmetrical structure with an oxygen atom bridging two SO_2^- groups. A substantial part of the argument for the symmetric disulfite structure in the matrices[6] rests on the assignment to a bridging oxygen stretching mode an infrared band at 776 cm^{-1}. However, the dithionate ion ($S_2O_6^{2-}$) also has a band in this region,[14] but has no bridging oxygen, and Connick and co-workers have convincingly shown that a Raman band with a similar frequency in the bisulfite–disulfite aqueous solution spectrum[4a] belongs to an S–(OH) stretching vibration of the SO_3H^- isomer of bisulfite.[4b] There is theoretical support for this latter assignment.[10] Finally, in the low-temperature matrix experiments,[6] only three of the eleven infrared bands, which were assigned the symmetric disulfite, shifted when oxygen-18 was used in place of normal oxygen. Theoretically, all of the bands should have shifted measurably, which is our ^{18}O experience with the unsymmetric disulfite,[3] with the bands in the S–O stretching region shifting in the 30–50-cm^{-1} range. This indicates that secondary reaction products are probably being formed. Both thallium and sulfur can occur in more than one common oxidation state. Either the hot molecular beams of Tl_2O monomers and dimers, which converge with the SO_2 just before deposition, or traces of water or hydroxide, which are notoriously difficult to totally eliminate in matrix work with metal oxides, are fully capable of initiating the complex autoredox reactions, which oxysulfur compounds of intermediate oxidation state are known to undergo.[15] The infrared spectra of the matrix reaction products are not inconsistent with the existence of polythionates, polysulfides, and/or other oxysulfur species.

In conclusion, the primary reaction product of the room-temperature reaction of wet, solid TlOH and excess liquid SO_2 is thallium(I) disulfite. It readily decomposes to Tl_2SO_3 and SO_2, and its Raman spectrum indicates that the disulfite ion has the common unsymmetric structure. In contrast, the complex infrared spectra of the reaction products of converging molecular beams of hot Tl_2O vapor and SO_2, trapped in argon matrices at cryogenic temperatures, are not consistent with simple $Tl_2S_2O_5$ and Tl_2SO_3 formation but may suggest the formation of polythionates and/or complex mixtures of other oxysulfur species.

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Notes

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Structures of Bis(1-thia-4,7-diazacyclononane)copper(II) Nitrate and Bis(1,7-diaza-4-thiaheptane)copper(II) Nitrate. A Different Conformation for the Coordinated Macrocycle

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Recently we reported the crystal structures of the bis complexes of daes[1b] and (9-ane-N_2S)[2] with nickel(II), but because the bis(1,7-diaza-4-thiaheptane) complex has the sulfur atoms cis to each other, while in the macrocyclic complex they are trans, the complexes were not exactly comparable. Crystal structures of transition-metal complexes $[M(daes)_2]^{n+}$ have been determined for M = Ni(II)[1] and Co(III).[3] In both structures the unsymmetrical facial geometric isomer is found to occur.

Examination of the literature shows that when bonds to copper(II) are distorted, first-row donor atoms will occupy the equatorial positions in preference to second- or third-row donors, which will occupy the axial sites (pseudo-Jahn–Teller distortion). Thus, the tendency of the two sulfurs to occupy the axial sites should lead to the *s-fac* rather than the *u-fac* structure. This would then allow for a direct comparison between the bis(1,7-diaza-4-thiaheptane) copper complex and the bis(1-thia-4,7-diazacyclononane)copper complex. The role of compression[4] around the metal center or distortions[5] of any nature in contributing to the high ligand field strength could therefore be evaluated.

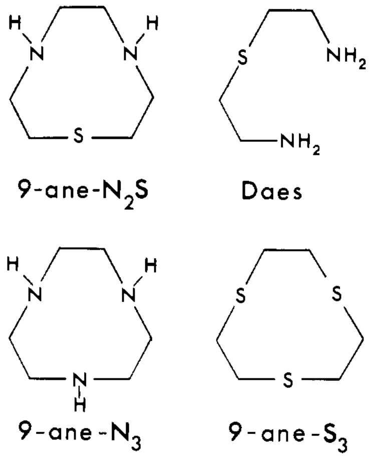

Figure 1. Ligands discussed in this paper.

We report here an improved synthesis of the ligand 9-ane-N_2S (see Figure 1), the electronic spectra of the bis(1-thia-4,7-dia-

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