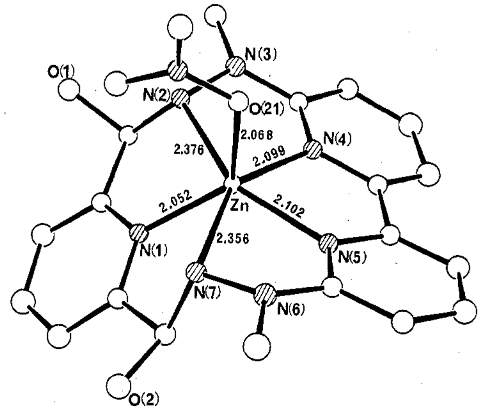

Figure 1. Structure of the monocation of **2**. The mean esd for the bond lengths shown is 0.004 Å. Bond angles (deg) in the coordination sphere (mean esd 0.2°) defined by pairs of donor atoms are N(1),N(2) = 74.3, N(1),N(4) = 123.4, N(1),N(5) = 121.4, N(1),N(7) = 76.0, N(1),O(21) = 126.5, N(2),N(4) = 71.5, N(2),N(5) = 146.6, N(2),N(7) = 141.1, N(2),O(21) = 88.1, N(4),N(5) = 76.1, N(4),N(7) = 147.7, N(4),O(21) = 95.5, N(5),N(7) = 71.6, N(5),O(21) = 101.1, and N(7),O(21) = 89.9°.

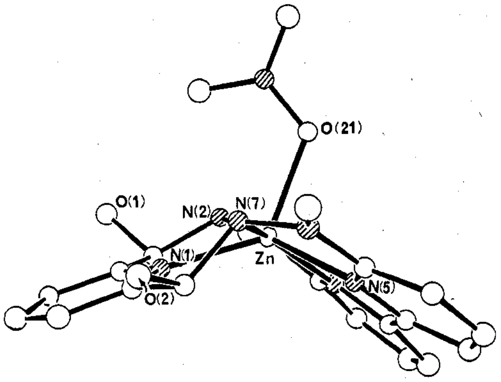

Figure 2. The "folding" of the macrocycle about a line through the carbinolamine nitrogen atoms N(2) and N(7).

The structure determination confirmed the presence of a quinquedenate macrocyclic ligand, in which the expected nitrogen atoms are coordinated to the zinc(II) ion (Figure 1), and showed that the carbinolamine C–O and N–H bonds are all displaced to the same side of the macrocycle. Such a meso arrangement allows the macrocycle to fold about a line through the carbinolamine nitrogen atoms so that the N(1), N(2), N(7) plane is inclined at 64° to the coordination plane defined by the bipyridyl unit (Figure 2).

The isolation of **2** suggests that the formation of **1a–c** (and possibly other complexes of planar conjugated macrocycles) may proceed by formation of a dicarbinolamine before any elimination of water occurs. This might be expected when the ligand precursors are both relatively rigid, because the cyclization step becomes less favorable once one imine bond has formed, since the approach of the second amine nitrogen atom on a line perpendicular to the carbonyl group becomes less probable. Molecular models show that such an effect will be particularly significant when the macrocyclic product has an unstrained planar inner great ring.

In only one case previously[7] has an X-ray structure been reported for a metal complex of a carbinolamine ligand, although such complexes are implicated[8] in a number of metal-catalyzed and enzymatic reactions. Closely related compounds which contain α-amino ether groups are more common.[9] The stability of **2** can be ascribed partly to the extensive inter- and intramolecular H bonding between hydroxyl groups and nitrate ions and partly to the ability of zinc(II) ions to form strong bonds to nitrogen and oxygen donors even in very irregular coordination polyhedra (see Figure 1). Such properties are assumed to be important in a number of other reactions[10] which are promoted by zinc(II) ions.

Acknowledgment. We thank the S.R.C. for grants for diffractometer equipment, computing facilities, and support (to Z.P.H.).

Registry No. **2**, 71171-43-2.

Supplementary Material Available: A listing of structure factor amplitudes for **2** (19 pages). Ordering information is given on any current masthead page.

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(5) Compounds **1a** and **2** have the same molecular formula $ZnC_{19}H_{21}N_9O_8$. Satisfactory C, H, N, and Zn analyses were obtained.
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Contribution from the Department of Chemistry,
University of New Brunswick,
Fredericton, N.B., Canada E3B 5A3

A Convenient Synthesis and Vibrational Spectrum of Tellurium Bromide Pentafluoride

Lawrence Lawlor and Jack Passmore*

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Tellurium pentafluoride ($TeBrF_5$) was first prepared in low yield by Fraser, Peacock, and Watkins[1] by the reaction of fluorine and tellurium tetrabromide. Large amounts of tellurium hexafluoride and bromine were also produced from which the product was not separated. We wish to report a convenient synthesis of $TeBrF_5$ in good yield, by the reaction of bromine, fluorine, and tellurium tetrafluoride. The vibrational spectrum was obtained and assigned by comparison with related molecules.

Experimental Section

Techniques and apparatus are described in ref 2. Sodium fluoride, TeO_2, and SF_4 were used without further purification. Fluorine (Matheson) was stored over NaF to remove HF. Bromine (McArthur Chemical Co.) was dried over P_2O_5. Tellurium tetrafluoride was prepared by the reaction of TeO_2 with SF_4 and resublimed before use.[3]

Infrared spectra were recorded on a Perkin-Elmer 467 spectrometer in the range of 4000–250 cm^{-1}. Stainless steel cells of 10-cm path length fitted with AgCl windows and a glass cell fitted with polyethylene windows were used as sample containers. Samples of liquid $TeBrF_5$ for Raman spectroscopy were prepared by condensing $TeBrF_5$ into glass capillary tubes which were then vacuum sealed. Raman spectra were recorded by using a Spex Ramalab spectrometer and a 5145-Å line light source from a 2-W Ar/Kr ion laser. Polarization measurements were carried out by means of an Ednalite polarization rotator. ^{19}F NMR spectra were recorded by using a Varian Associates HA 60 spectrometer operating at 56.4 MHz. Vapor pressure measurements were made by using a Helicoid Monel Bourdon type gauge.

Preparation of Tellurium Bromide Pentafluoride. In a typical reaction bromine (11.6 mmol) was condensed into a Monel can containing tellurium tetrafluoride (28.7 mmol). A slight excess of fluorine (14.0 mmol) was added in small aliquots (~3 mmol) with the vessel held at −196 °C. After each addition the can was placed in a −22 °C bath for 1.5 h and an ice bath for 1.5 h and finally left to stand at room temperature for 4 h or overnight, before the next addition. Excess fluorine was removed by pumping at −196 °C. The slightly reddish brown liquid product consisted of a mixture of TeBrF$_5$, TeF$_6$, and traces of SiF$_4$ and Br$_2$. Pure material (14.4 mmol) was obtained by condensing out a portion of the product until the infrared spectrum indicated the absence of TeF$_6$ and SiF$_4$ and that only TeBrF$_5$ remained. TeBrF$_5$ was then separated from the more volatile fraction by pumping on the mixure at −78 °C. The product (4.96 mmol) was retained in the −78 °C vessel, giving a total of 19.4 (14.4 + 4.96) mmol of colorless TeBrF$_5$ or an 83% yield based on the amount of bromine used. Reactions which were carried out with the same stoichiometry as above but over a shorter time interval resulted in the product containing greatly increased amounts of TeF$_6$ and Br$_2$.

The identity of the material was established by comparison of its ^{19}F NMR spectrum with that reported in the literature.[1] A ^{125}Te to ^{19}F (equatorial fluorine) coupling constant of 3600 ± 2 Hz was observed (3613 Hz in TeClF$_5$[4]). TeBrF$_5$ is a colorless liquid with a melting point of −32 ± 1 °C (−28 ± 1 °C for TeClF$_5$)[5]. The vapor pressure of TeBrF$_5$ at 20 and −23 °C is 290 and 64 mm, respectively. The vapor pressure data between 0 and 20 °C were fit by the equation $\log P_{\text{torr}} = 7.36 - 1438/(T\ (\text{K}))$. The molar heat of vaporization is 6.6 kcal and the Trouton constant 20.5 eu. Bromine was formed during the course of the vapor pressure measurements and thus caused some uncertainty in the data.

TeBrF$_5$ has been stored without noticeable decomposition in dry Teflon apparatus at −78 °C for 15 weeks; however, at room temperature, bromine was observed after 4 days. A solution of SO$_2$ and TeBrF$_5$ was allowed to stand at room temperature for 10 days. The volatile material was removed from the reaction vessel at room temperature and shown by infrared spectroscopy to contain SO$_2$, TeF$_6$, and traces of TeBrF$_5$ and SO$_2$BrF. The physical properties of the volatiles indicated the presence of Br$_2$. A white solid remaining in the reaction vessel was shown to be TeF$_4$ by its Raman spectrum. In glass, traces of SiF$_4$ and bromine were detectable after 1 day. Bromine was observed on transfer of the product in the Monel vacuum line. The crude product mixture was shaken with mercury at 0 °C for 2–3 h to remove bromine; however, TeBrF$_5$ was also consumed. After 1 h at room temperature the crude product was found to react with tetrabutylammonium bromide with consumption of TeBrF$_5$ and formation of bromine. For this reason it is important that the synthesis be carried out with a deficit of bromine and thus remove the necessity of its separation from TeBrF$_5$.

Results and Discussion

Preparation of TeBrF5. Tellurium bromide pentafluoride has been prepared in good yield by the reaction of excess tellurium tetrafluoride and a mixture of bromine and fluorine. Presumably the addition of fluorine to bromine leads to the formation[6] of BrF which reacts with TeF$_4$ to give TeBrF$_5$.

TeBrF$_5$ has properties similar to those of TeClF$_5$; however, it is more reactive toward mercury and glass and is less thermally stable than the chloride. SBrF$_5$ has been noted to have greater reactivity than SClF$_5$ toward halo olefins, and it decomposes photochemically more readily.[7-9] The products of the decomposition of TeBrF$_5$ in the presence of SO$_2$ at room temperature were TeF$_6$, TeF$_4$, Br$_2$, and traces of SO$_2$BrF, indicating the following mode of decomposition: $2\text{TeBrF}_5 \rightarrow \text{TeF}_4 + \text{TeF}_6 + \text{Br}_2$.

Vibration Spectrum of TeBrF$_5$. Figure 1 shows the infrared spectrum of gaseous TeBrF$_5$ in the region 1600–250 cm^{-1}, and Figure 2 the Raman spectrum of liquid TeBrF$_5$. Table I lists the observed frequencies and assignments.

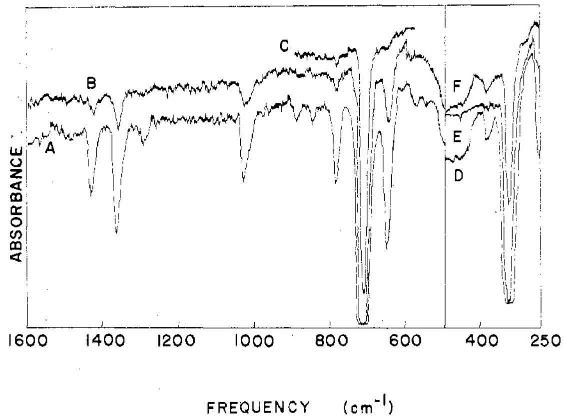

Figure 1. Infrared spectrum of gaseous TeBrF$_5$: (A) 200, (B) 50, and (C) ~1 torr pressure in a 10-cm cell with AgCl windows; (D) 100, (E) 15, and (F) ~1 torr pressure in a 10-cm cell with polyethylene windows.

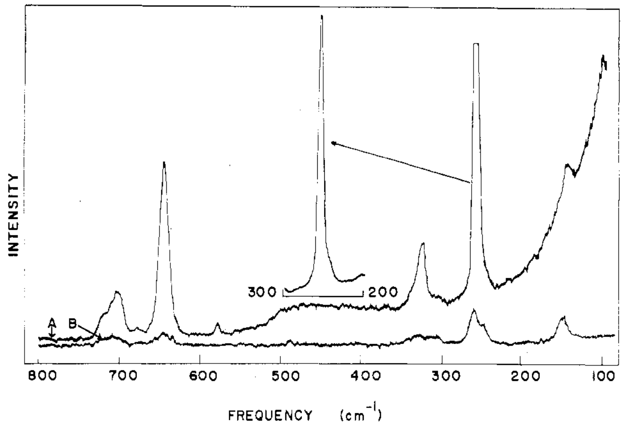

Figure 2. Raman spectrum of liquid TeBrF$_5$ at room temperature slit width 4 cm^{-1} and exciting line 5145 Å: (A) incident polarization parallel; (B) incident polarization perpendicular.

Table I. Vibrational Spectra of TeBrF$_5$ (cm^{-1})

infrared (gas)[a]	Raman (liq)[b]	assignt	approx description of mode[d]
1428[c] mw		$2\nu_1(a_1)$	
1362 m		$\nu_1 + \nu_2$	
1293 w		$2\nu_2$	
1026 mw		imp SiF$_4$?	
888 w			
845 w			
785 mw		$\nu_2 + \nu_{11}$	
715 vvs	720 (5) dp	$\nu_8(e)$	$\nu_{as}(\text{TeF}_4)$
	707 (32) p	$\nu_1(a_1)$	$\nu(\text{TeF}')$
	682 (1) p	imp?	
648[c] ms	646 (68) p	$\nu_2(a_1)$	$\nu_{sym}(\text{TeF}_4)$
	580 (2) p	imp?	
330 vs	326 (30) p	$\nu_3(a_1)$	$\delta_{sym}(\text{TeF}_4)$
302 sh	306 (14) dp	$\nu_9(e)$	$\delta(\text{F}'\text{TeF}_4)$
248 m[e]	257 (100) p	$\nu_4(a_1)$	$\nu(\text{TeBr})$
	244 (5) dp	$\nu_{10}(e)$	$\delta_{as}(\text{TeF}_4)$
	144 (20) dp	$\nu_{11}(e)$	$\delta(\text{BrTeF}_4)$

[a] Frequencies have an accuracy of ca. 2 cm^{-1}. [b] Relative intensities are given in parentheses. [c] PQR branches observed. The listed frequency is for the Q branch. [d] Correspond to those given by Christe et al.[13] [e] Obtained with a Beckman IR 12 spectrometer.

Tellurium bromide pentafluoride is expected to have C_{4v} symmetry and on the basis should exhibit 11 fundamental vibrational modes: 4 a$_1$ (R, p; IR) + 2 b$_1$ (R, dp) + b$_2$ (R, dp) + 4 e (R, dp; IR).

Four Raman-polarized bands appeared at 707, 646, 326, and 257 cm^{-1} and are therefore a_1 modes and are assigned by comparison with related molecules ($SBrF_5$,[10,11] $MClF_5$[12,13] (M = S, Se, Te)) as $\nu_1(a_1)$, $\nu_2(a_1)$, $\nu_3(a_1)$, and $\nu_4(a_1)$. Three corresponding infrared bands occur at 648, 330, and 248 cm^{-1} with the 707-cm^{-1} band presumably hidden under the intense 715-cm^{-1} band. The depolarized band at 720 cm^{-1} in the Raman with a strong counterpart in the infrared at 715 cm^{-1} is readily assigned as $\nu_8(e)$. The low-frequency depolarized bands at 244 and 144 cm^{-1} are assigned as $\nu_{10}(e)$ and $\nu_{11}(e)$, respectively, by comparison with related molecules. The Raman band at 306 cm^{-1} appears to have a counterpart in the infrared at 302 cm^{-1} (sh) and can be assigned as $\nu_9(e)$. One of the b_1 modes, ν_6, is too low in intensity to be observed in similar molecules,[12,13] and $\nu_5(b_2)$ is probably hidden under the strong 646-cm^{-1} band.

Those vibrations involving motions of the TeF_5 part of the molecule are rather similar in frequency to those reported for $TeClF_5$.[12] The TeBr stretching frequency of the 257-cm^{-1} (ν_4) band is similar to the highest TeBr stretch in $TeBr_4$[14] (250 cm^{-1}).

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Registry No. $TeBrF_5$, 21975-45-1; bromine, 7726-95-6; fluorine, 7782-41-4.

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Contribution from the Department of Chemistry,
University of New Brunswick,
Fredericton, N.B., Canada E3B 5A3

Existence of Cesium Salts of CO_2F^-, $CO_2F_2^{2-}$, and $NO_2F_2^-$

Lawrence Lawlor and Jack Passmore*

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The reported synthesis of the salts of $CO_2F_2^{2-}$[1] and NO_4^{3-}[2] anions extends the series of known isoelectronic, 32-valence-electron species BF_4^-, CF_4, NF_4^+,[3] ONF_3,[4,5] and OCF_3^-.[6] The formation of salts of CO_2F^-, a member of the series BF_3, CO_3^{2-}, NO_3^-, FNO_2, OCF_2, and ONF_2^+, has been reported[1] but not characterized. There have been conflicting reports[7] of the synthesis of $CsNO_2F_2$. While attempting to prepare derivatives of $NO_2F_2^-$ (a 32-valence-electron species), we repeated the syntheses of $CO_2F_2^{2-}$- and CO_2F^--containing species without success. We wish to report the results of a careful reexamination of the reported reactions of carbon dioxide and nitrosyl fluoride with cesium fluoride and the reaction of dicesium oxide with carbonyl fluoride.

Experimental Section

Techniques and apparatus are described in ref 8. Purity of starting materials was routinely established by X-ray powder photography or infrared spectroscopy. Cesium fluoride (Ozark Mahoning) was dried by heating at 150 °C in vacuo for 12 h and then finely ground before use. Molecular sieve, 3 Å (Davidson Chemical), was heated at 350–400 °C in vacuo for 24 h before use.

Acetonitrile (Matheson Coleman and Bell) was purified by method B of Walter and Ramaley.[9] In addition, the acetonitrile was vacuum distilled through a 60-cm column containing dehydrated molecular sieve and collected in a glass vessel also containing molecular sieve. The acetonitrile was then distilled twice into similarly prepared vessels. For a further check on the purity of starting materials, cesium fluoride pretreated as above was reacted with OCF_2 in acetonitrile according to ref 6 and was shown to readily give $CsOCF_3$.[6,10]

FNO_2 was prepared by the reaction of excess F_2 (Matheson) with NO_2 (Matheson) in a Monel can. Excess F_2 was removed by pumping on the reaction vessel held at −196 °C. FNO_2 (bp −72.5 °C) was distilled as needed from the reaction vessel held at −78 °C. Tetraethylammonium fluoride dihydrate ($Et_4NF{\cdot}2H_2O$, Eastman Organic Chemicals) was dehydrated by the method of Miller, Freid, and Goldwhite[11] and finely ground before use. CO_2 (Matheson, Bone Dry), Cs_2O (Alfa-Ventron), OCF_2 (Pierce Chemical Co.), SF_4 (Columbia Organic Chemicals), and $CsNO_3$ (PCR Research Chemicals) were used without further purification.

Reaction of CsF and CO_2. In a typical experiment, acetonitrile (12.2 mmol) was condensed into a 50-cm^3 Parr bomb containing CsF (13.5 mmol). CO_2 (71.6 mmol) was condensed into the bomb which was allowed to stand at room temperature, with continuous stirring, for 7 days. The excess CO_2 was removed by pumping on the reaction vessel held at −78 °C. The acetonitrile was distilled from the reaction vessel held at −22 °C. The weight of solid product was identical with the weight of starting CsF. The product was identified as unreacted CsF by its X-ray powder diffraction photograph. Various experiments were done with pressures of CO_2 up to 110 atm.

Reaction of CO_2 and $Et_4NF{\cdot}2H_2O$. CH_3CN (43.2 mmol) was condensed into a glass vessel containing $Et_4NF{\cdot}2H_2O$ (2.32 mmol) with partial dissolution. The reaction vessel was opened to the vacuum line, and CO_2 was expanded into the line to a pressure of 1000 torr. Some CO_2 was taken up immediately, and the insoluble $Et_4NF{\cdot}2H_2O$ was taken into solution. The CO_2 pressure was increased to 1500 torr, and the reaction vessel was closed and held at room temperature for 1 day with occasional shaking. The volatiles were condensed from the reaction vessel held at room temperature, leaving behind a pasty white solid (0.48 g).

Reaction of CO_2 and Et_4NF. Acetonitrile (56.1 mmol) was condensed into a glass vessel containing Et_4NF (1.76 mmol). The reaction vessel was opened to the vacuum line, and CO_2 was expanded into the line to a pressure of 760 torr. The pressure remained constant over several hours, indicating no uptake of CO_2. The vessel was closed and held at room temperature overnight. The volatiles were quickly condensed out from the reaction vessel held at room temperature. The weight of product was identical with the weight of starting Et_4NF.

Reaction of Cs_2O and OCF_2 in CH_3CN. CH_3CN (40.7 mmol) was condensed into a Monel can containing Cs_2O (4.40 mmol). COF_2 (7.12 mmol) was also condensed into the can which was held at room temperature for 6 days with continuous stirring. The infrared spectrum of the volatiles showed CO_2 and a trace of CF_4 (an impurity in COF_2) to be present. The presence of a noncondensable gas was also observed. The CO_2 was pumped from the reaction vessel held at −78 °C, and the CH_3CN (1.74 g) was condensed out at room temperature. The infrared spectrum of the volatiles above the CH_3CN showed CO_2 to be present. The product remaining in the reaction vessel was a tan-brown solid (1.43 g). The infrared spectrum of the solid showed $CsOCF_3$, possibly Cs_2CO_3, and traces of $CsHF_2$. Cs_2CO_3 is difficult to identify in the presence of the other two anions since their spectra overlap. The solid product was heated to 100 °C for 1 h, and the volatiles given off were shown to be CO_2 and OCF_2 by infrared spectroscopy.

Reaction of $CsNO_3$ and SF_4. CH_3CN (68.5 mmol) was condensed into a Monel can containing $CsNO_3$ (5.85 mmol). SF_4 (18.0 mmol) was condensed into the can which was allowed to react at room temperature for 10 days with continuous stirring. The infrared