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Lower Oxidation States of Tellurium. III.[1] Ditellurium(2+) in Chloroaluminate Melts

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The solvated entity Te_2^{2+} is the second species formed (Te^{2+} is the first) by reduction of solutions of $TeCl_4$ with elementary tellurium in $KAlCl_4$ melts buffered with KCl–$ZnCl_2$. Spectrophotometric measurements show that the following equilibrium takes place $3Te^{II} \rightleftharpoons Te_2^{2+} + (1/\bar{n})(Te^{IV})_{\bar{n}}$. At 300° and with $pCl^- = 1.86$, the value of the equilibrium quotient (assuming $\bar{n} = 1$) is estimated as $22 \pm 7\ M^{-1}$. Calculations show that Te_2^{2+}, under the above conditions, has an absorption maximum at *ca.* 29.3 kK with a molar absorptivity of $1500 \pm 150\ M^{-1}\ cm^{-1}$.

Introduction

In a recent publication[3] it was mentioned that in salt melts made from KCl, $AlCl_3$, and $ZnCl_2$ five different tellurium species have been observed spectrophotometrically by varying systematically the composition of the chloroaluminate melt and the concentrations of the dissolved substances, $TeCl_4$ and elementary tellurium. Of these species two have been identified[2-4] with certainty as Te^{2+} and Te_4^{2+}. One species, previously[2] denoted by IV, has been shown to have the charge 2+, and in this paper evidence is presented that it is actually Te_2^{2+}.

It has been known for a long time that tellurium forms colored solutions in sulfuric acid and in oleum.[5,6] Gillespie and coworkers[7] have recently investigated these solutions as well as solutions in other acidic solvents such as HSO_3F by measuring conductivities, freezing point depressions, and absorption spectra. Some of the species found in these acids, for example Te_4^{2+}, are identical with the species found in the chloroaluminate melts.[2-4,8]

An interesting problem is found in connection with monovalent tellurium. The measurements made by Gillespie and coworkers indicate that monovalent tellurium is present as Te_4^{4+}, even if Te_6^{6+} or Te_8^{8+} cannot be completely ruled out. The present experiments show that under certain circumstances (high chloride activity) Te_2^{2+} exists in the melt. The existence of Te_2^{2+} (in disulfuric acid) has also been suggested by Paul, Puri, and Malhotra.[9]

Experimental Section

Materials and Measurements.—KCl and $ZnCl_2$ were reagent grade materials (Baker Analyzed) purified by the standard procedure[10,11] by treatment in the solid and molten states by HCl gas (electronic grade from Matheson, ≥99.99%)—to avoid the formation of OH^-—followed by a treatment with pure N_2 and finally filtration to remove solid particles. The $AlCl_3$ was made from aluminium metal (99.999%) and HCl gas. The $TeCl_4$ was made by reaction between tellurium (99.9995%) and chlorine (Fluka, >99.9%). The reaction between elementary tellurium and solutions containing $TeCl_4$ was followed spectrophotometrically with a Cary 14R spectrophotometer equipped with a furnace, the temperature of which could be kept constant to ±0.1° in the range 100–500° by a Eurotherm regulator, Type LP96/DHS/PID. The optical cells were fused quartz (Ultrasil from Helma) and had fixed path length in the range 10–1 mm. Path lengths around 0.1 mm could be obtained by placing a precision-ground fused-silica insert into a 5-mm cell.

All measurements were performed at 300° in a $KAlCl_4$ melt, buffered with KCl–$ZnCl_2$ to a pCl^- of 1.86 ± 0.03. The measurements of the pCl^-, with $KAlCl_4$ saturated with KCl as a reference, will be the subject of another publication.

The initial amounts of tellurium added to the melt were weighed in air on a microbalance (Cahn) in amounts from 0.5 to 10 mg, while the hygroscopic $AlCl_3$, $ZnCl_2$, and $TeCl_4$ as well as KCl were weighed on another balance in a nitrogen-filled glove box and added to the optical cells.[12]

Since the reaction between tellurium and $TeCl_4$ was rather slow, the spectrophotometric measurements were repeated until they remained constant for at least 1 day.

Definitions.—The formal absorptivity is defined by A/c' where A is the absorptivity (absorbance divided by the path length), corrected for the absorbance of cell and solvent, and c' (the formality) is the initial molar amount of one of the added substances (in the present work either Te or $TeCl_4$) dissolved in 1 l. of the melt. The density of the buffered $KAlCl_4$ solutions was calculated assuming ideal mixtures of KCl, $ZnCl_2$, $TeCl_4$, and $KAlCl_4$. This assumption is reasonable, as the amounts of KCl, $ZnCl_2$, and $TeCl_4$ added were small compared to the amounts of $KAlCl_4$ present. The density of the $KAlCl_4$ was obtained from the work of Morrey and Carter.[13]

Results and Discussion

Species Formed in Buffered $KAlCl_4$.—A previous study[3] has shown that the first reaction product when tetravalent tellurium is reduced with elementary tellurium in a $KAlCl_4$ melt buffered to a fairly high chloride activity ($pCl^- = 1.86$) with $ZnCl_2$–KCl is divalent tellurium. If the formality of the dissolved tellurium is increased to higher values, a new species, previously denoted by IV and shown[2] to have the formal charge 2+, will appear. The formality at which it begins to appear depends on the concentration of the tetravalent tellurium. A high concentration of tetravalent tellurium will depress the formation of species IV, and the formality of Te must be increased to maintain the IV concentration.

The change in the spectra from pure Te^{2+} to a mixture of Te^{2+} and species IV is illustrated in Figure 1. Beyond 18.2 kK, a correction has been made for the absorbance due to Te^{IV} but the high absorbance of

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(1) With previous works[2,3] numbered I and II, respectively.

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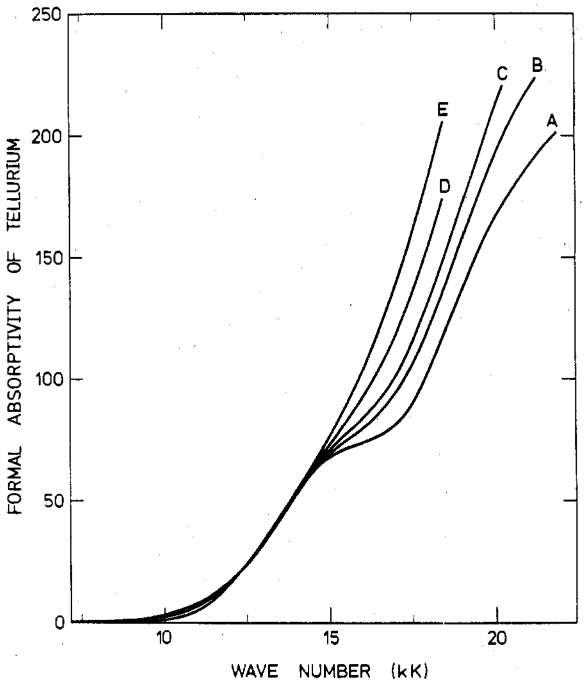

Figure 1.—Series of spectra of reaction products measured at 300° in $KAlCl_4$ buffered with KCl–$ZnCl_2$–$TeCl_4$. The concentration of KCl was 0.482 *F*, of $ZnCl_2$ 0.318 *F*, and of $TeCl_4$ 0.161 *F*. Concentrations of added tellurium: A, 0.0056 *F*; B, 0.0101 *F*; C, 0.0149 *F*; D, 0.0211 *F*; E, 0.0285 *F*.

Te^{IV} (as chloro complexes) makes it difficult to extend the measurements of the corrected spectra much beyond 21 kK.

An analysis (*vide infra*) of the spectra shown in Figure 1 suggests that only two species are present. As mentioned above, an increase of the concentration of tetravalent tellurium, other things being equal, will cause a decrease in the amount of species IV present. What will be observed is a change opposite the change shown in Figure 1. Such a behavior implies that, in a description of the equilibrium considered, we must have divalent tellurium on one side and species IV and tetravalent tellurium on the other side of the equation. This can be expressed as

$$\alpha Te^{2+} \rightleftharpoons Te_{(\alpha+1)/2}{}^{2+} + ((\alpha - 1)/2\bar{n})(Te^{IV})_{\bar{n}} \qquad (1)$$

As noted above the charge on IV is 2+. Since the number of atoms in species IV has to be an integer and since $(\alpha - 1)/2\bar{n}$ is positive, α is restricted to the values 3, 5, 7, . . . , corresponding to the formulas $Te_2{}^{2+}$, $Te_3{}^{2+}$, $Te_4{}^{2+}$, ... The tetravalent tellurium has been formulated as $(Te^{IV})_{\bar{n}}$ to include the possibility of chloride bridging. The reason for considering chloride bridging is the following. Spectrophotometric measurements show that at high chloride activity, which can be obtained by saturating $KAlCl_4$ with solid KCl (the pCl^- of such a melt is 0.28 at 300°), a well-defined band is found for tetravalent tellurium at 26.7 kK with a molar absorptivity of 1.28×10^3 l./mol cm. This band is caused by $TeCl_6{}^{2-}$.[2,14] At the present pCl^- (1.86) the absorptivity is still high in the ultraviolet part of the spectrum, but no bands are present at 26.7 kK. Therefore there are reasons to believe that we are dealing with an average coordination number lower than 6 but higher than 4, since an uncharged molecule would not be very soluble in an ionic melt. The complex could be $TeCl_5{}^-$, but when the average coordination number is lower than 6, dimerization is known to occur, as in the case of bismuth and antimony with the formation of $Bi_2Cl_8{}^{2-}$ and $Sb_2F_{11}{}^-$.[15,16]

Determination of α, g_I, and g_{II}.—The mass action relation for eq 1 can be formulated as

$$\frac{(Te_{(\alpha+1)/2}{}^{2+})((Te^{IV})_{\bar{n}})^{(\alpha-1)/2\bar{n}}}{(Te^{2+})^{\alpha}} = K_1 \qquad (2)$$

If the concentration of the tetravalent tellurium is much higher than the concentration of divalent tellurium and of species IV, then as a first approximation it can be considered constant, when the formality of tellurium, and hence the concentration of Te^{2+} and IV, is changed within a limited range. In this case the mass action relation (2) can be reduced to

$$\frac{(Te_{(\alpha+1)/2}{}^{2+})}{(Te^{2+})^{\alpha}} = K_2 \qquad (3)$$

The value of α can now be determined solely from the absorption spectra of the mixture containing Te^{II}, IV, and $(Te^{IV})_{\bar{n}}$, as has been shown for a similar equilibrium among Bi^+, $Bi_5{}^{3+}$, and Bi^{III}.[12]

Consider two wave numbers ν_1' and ν_2' at which Te^{II} and IV absorb but $(Te^{IV})_{\bar{n}}$ does not. It can be shown that

$$M_I = \frac{A(\nu_1') - g_{II}A(\nu_2')}{(1 - g_I g_{II})MA_I(\nu_1')} \qquad (4)$$

and

$$M_{II} = \frac{A(\nu_2') - g_I A(\nu_1')}{(1 - g_I g_{II})MA_{II}(\nu_2')} \qquad (5)$$

where M_I and M_{II} are the concentrations of Te^{2+} and IV, respectively. $A(\nu_1')$ and $A(\nu_2')$ are the total absorptivities at ν_1' and at ν_2'. The constants $MA_I(\nu_1')$ and $MA_{II}(\nu_2')$ are the molar absorptivities of Te^{2+} and IV at ν_1' and at ν_2', respectively. g_I and g_{II} are also constants defined by

$$g_I = A_I(\nu_2')/A_I(\nu_1') \qquad (6)$$

$$g_{II} = A_{II}(\nu_1')/A_{II}(\nu_2') \qquad (7)$$

where generally $A_i(\nu_j)$ is the absorptivity of species i and the j wave number. Substituting eq 4 and 5 into eq 3 and taking the logarithm give

$$\log[A(\nu_2') - g_I A(\nu_1')] - \alpha \log [A(\nu_1') - g_{II}A(\nu_2')] = \log K_1' \qquad (8)$$

where K_1' is a constant independent of the concentration, and $A(\nu_1')$ and $A(\nu_2')$ are directly obtainable from the measurements. g_I can be obtained from a series of spectra at low formalities of tellurium, where only Te^{2+} and $(Te^{IV})_{\bar{n}}$ are present. A plot to determine g_I is shown in Figure 2 where ν_1' is 15.0 kK and ν_2' is 18.2 kK. Te^{II} has a band at 15.0 kK, but IV has no bands in the visible range. At the wave number chosen, 18.2 kK, the absorptivity of IV is reasonably

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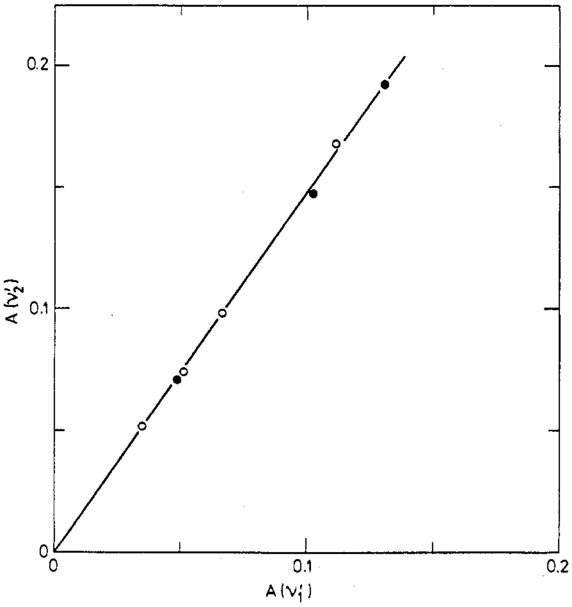

Figure 2.—Relations between the absorptivity at ν_1' (15.0 kK) and the absorptivity at ν_2' (18.2 kK) at low concentrations of tellurium (less than 0.0028 *F*). The concentrations of $TeCl_4$ were 0.161 *F* (filled circles) and 0.162 *F* (open circles).

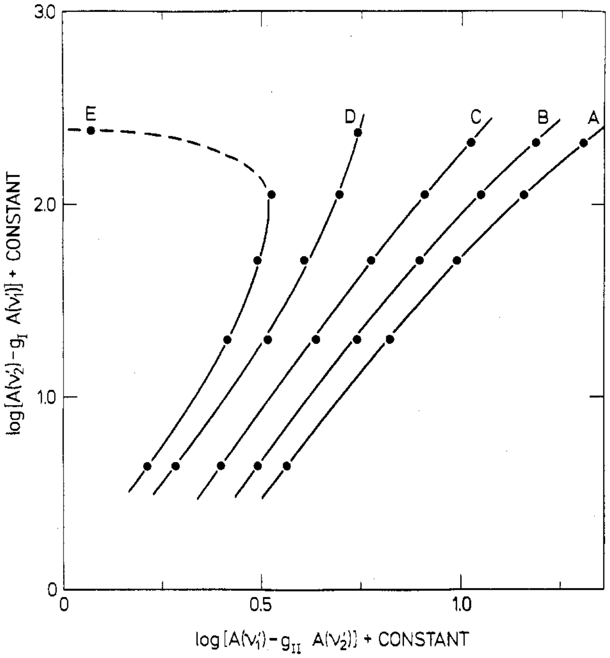

Figure 3.—Plots used to deduce the formula of species IV. The interpretations of the quantities plotted are given in the text. The concentration of KCl was 0.482 *F*, of $ZnCl_2$ 0.318 *F*, and of $TeCl_4$ 0.161 *F*. The concentrations of added tellurium were 0.0056, 0.0101, 0.0149, 0.0211, and 0.0285 *F*. g_I had the fixed value 1.47 whereas g_{II} had the following values: A, 0.0; B, 0.10; C, 0.20; D, 0.30; E, 0.35.

high, and the absorptivity due to the tetravalent tellurium is still negligible. The value of g_I was found to be 1.47 ± 0.02 at a tellurium concentration of about 0.161 *F*. The value of g_{II} however cannot be obtained directly.

The procedure for obtaining the values of α and g_{II} is as follows. In a series of measurements (where the concentration of (Te^{IV}) as a first approximation could be considered constant) a series of values for g_{II} are assumed, and log $[A(\nu_2') - g_I A(\nu_1')]$ are plotted against log $[A(\nu_1') - g_{II} A(\nu_2')]$ with the formality of tellurium as a parametric variable. The resultant curves are shown in Figure 3. If eq 8 is valid, a correct value of g_{II} should produce a straight line with the slope α. From Figure 3 it is clear that such a straight line can be obtained. A numerical analysis (least-squares method) made by means of a digital computer gave the results shown in Table Ia. The value of g_I is here varied within the standard deviation of ±0.02. The numbers in parentheses show the value obtained when a correction for the decrease in the concentration of $(Te^{IV})_{\bar{n}}$ due to reduction by tellurium has been made assuming that $\bar{n}$ has its lowest value which is unity. Higher values of $\bar{n}$ will give smaller correction. Since α is restricted to the values 3, 5, 7, . . . , it is safe to assume, on the basis of the results shown in Table Ia, that α is equal to 3. This corresponds to Te_2^{2+} being the formula for species IV.

TABLE I

DETERMINATION OF g_{II} AND α

$[TeCl_4]$, *F*	g_I	g_{II}	α
		Part a	
0.161	1.45	0.21 (0.22)	2.7 (2.6)
0.161	1.47	0.23 (0.24)	2.9 (2.9)
0.161	1.49	0.24 (0.25)	3.1 (3.1)
		Part b	
0.0640	1.32	0.26 (0.27)	3.0 (2.9)
0.0640	1.35	0.27 (0.28)	3.2 (3.2)
0.0640	1.38	0.28 (0.29)	3.6 (3.7)

Table Ib shows the results for another run with a lower $TeCl_4$ formality. The values obtained here also show that α is 3. However, the value of g_{II} seems not too well determined. An interesting phenomenon is that g_I is not independent of the formality of $(Te^{IV})_{\bar{n}}$. At the low formality (0.0640 *F*) a g_I value of 1.35 ± 0.03 was found, compared with a g_I value of 1.47 ± 0.02 at high formality. This is probably due to an intervalence-transfer absorption effect.[15] This phenomenon is found to a smaller or larger extent when ions of different oxidation states are present together. Many examples are known from aqueous chemistry,[17] and the phenomenon is also known in molten salts.[12,18] The values from which the low g_I value has been found are shown in Table II (the first four measurements). The last four measurements in Table II have been used to calculate the value of α (Table Ib).

TABLE II

FORMALITIES AND ABSORPTIVITIES FOR A $Te{-}TeCl_4$ SYSTEM (SOLVENT $KAlCl_4{-}ZnCl_2{-}KCl$)

Formality		Absorptivity	
$TeCl_4$	Te	15.0 kK	18.2 kK
0.0640	0.00049	0.024	0.036
0.0640	0.00121	0.072	0.094
0.0640	0.00157	0.090	0.122
0.0640	0.00193	0.114	0.156
0.0640	0.00401	0.262	0.384
0.0640	0.00870	0.572	1.012
0.0640	0.01563	1.102	2.412
0.0640	*Ca.* 0.0258[a]	2.68	7.36

[a] Melt saturated.

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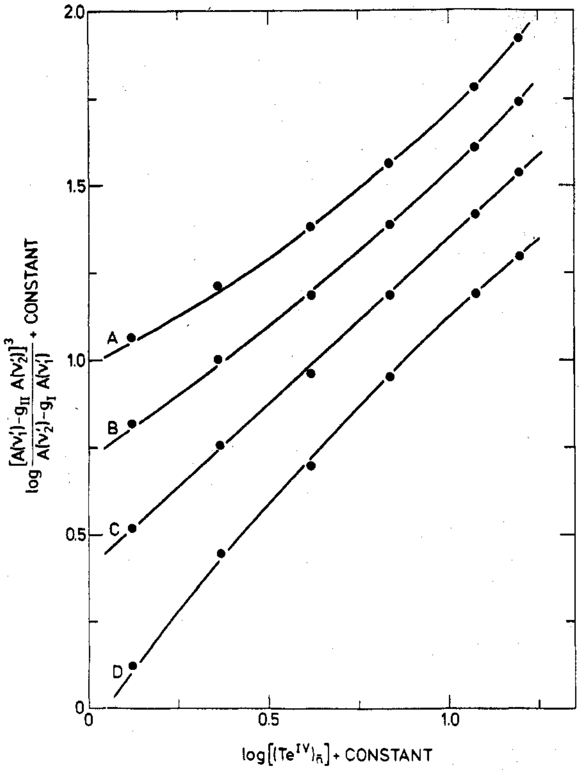

Figure 4.—Plots used to deduce the value of $\bar{n}$. The interpretations of the quantities plotted are given in the text. The concentrations of $TeCl_4$ were 0.0246, 0.0369, 0.0593, 0.0906, 0.1397, and 0.203 *F*. The concentration of tellurium was not known accurately. It varied between 0.0096 and *ca.* 0.011 *F*. g_I had the following values (given in the same order as the formalities of $TeCl_4$): 1.29, 1.31, 1.33, 1.37, 1.43, 1.51. g_{II} had the following values: A, 0.20; B, 0.25; C, 0.30; D, 0.35.

Determination of $\bar{n}$.—An α value of 3 will give the mass action relation (2) the form

$$\frac{(Te_2^{2+})((Te^{IV})_{\bar{n}})^{1/\bar{n}}}{(Te^{2+})^3} = K_1 \qquad (9)$$

The value of $\bar{n}$ is here restricted to be equal to or larger than unity. To obtain the value of $\bar{n}$, a series of experiments in which the formality of $TeCl_4$ was varied, while the formality of tellurium was kept constant, was conducted. Substituting eq 4 and 5 into eq 2 followed by taking the logarithm will give us

$$\log \frac{[A(\nu_1') - g_{II}A(\nu_2')]^{\alpha}}{A(\nu_2') - g_I A(\nu_1')} - \frac{1}{\bar{n}} \log ((Te^{IV})_{\bar{n}}) = \log K_2' \qquad (10)$$

where K_2' is a constant, independent of concentration. The only unknowns in this equation are $\bar{n}$ and $(Te^{IV})_{\bar{n}}$. Since we are dealing with logarithmic functions, substituting $(Te^{IV})_{\bar{n}}$ with $\bar{n}(Te^{IV})_{\bar{n}}$ (which we know fairly accurately) will not change the slope of $\log [A(\nu_1') - g_{II}A(\nu_2')]^{\alpha}/[A(\nu_2') - g_I A(\nu_1')]$ *vs.* $\log ((Te^{IV})_{\bar{n}})$, which should give us the value of $1/\bar{n}$. Such a plot is shown in Figure 4. Since the value of g_{II} is not known accurately (see Table I), some different values of g_{II} in the range 0.20–0.35 has been plotted. If our assumptions concerning eq 10 are correct, a straight line should be obtained for the correct g_{II} factor. From the plot it seems to be possible to get such a straight line. A numerical analysis gave as a result that the slope of the best straight line had the value 1.03, corresponding to an $\bar{n}$ value of 0.97. The corresponding g_{II} value was found to be 0.31. Apart from the high g_{II} value, this seems to indicate clearly that we are dealing with a monomeric unit. The result however is based on several assumptions which make it less obvious. First, a g_{II} value of 0.24 which was found at the high formality of $TeCl_4$ will give us an $\bar{n}$ value of 0.84 but this is still a reasonable value. Another assumption which has been made is that g_I varies linearly with the formality of $TeCl_4$ at low formalities of $TeCl_4$. This is a reasonable guess, since it is known to be true for almost all valence interaction in aqueous solutions.[17] A more serious assumption is that the formal absorptivity at 15.0 kK for divalent tellurium is considered independent of the formality of $TeCl_4$. If for example the formal absorptivity is allowed to increase linearly with the formality of $TeCl_4$ based on a formal absorptivity of 66 and 70 at 0.064 and 0.161 *F* $TeCl_4$, respectively, then the best straight line is obtained for an $\bar{n}$ value of 0.76 and a g_{II} value of 0.26. Increase of the formal absorptivity with increasing formality of $TeCl_4$ seems to agree with the measured absorptivities but disagrees with the stoichiometry regarding the added tellurium.

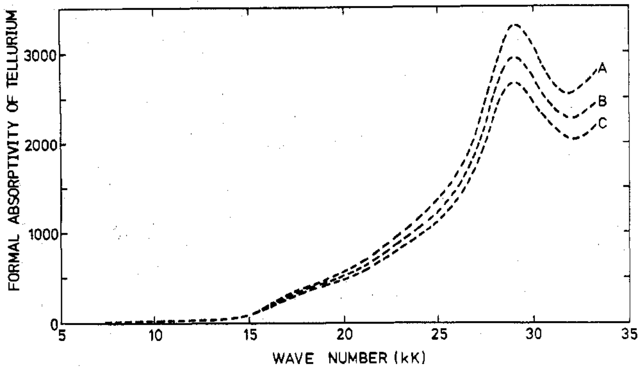

Figure 5.—Calculated spectra of Te_2^{2+}. The solvent was buffered $KAlCl_4$ at 300°. The spectra were calculated from the spectra of three different solutions. For all solutions the concentration of $TeCl_4$ was 0.0640 *F*. The concentrations of tellurium were 0.0000, 0.0087, and 0.0156 *F*. The path length of the cell was 0.00836 cm. The values of g_I and g_{II} were 1.35 and 0.25 (A), 0.26 (B), and 0.27 (C), respectively.

Finally it is assumed, that the reaction is not affected by changes in the pCl^- caused by the addition of $TeCl_4$ (up to a formality of 0.203 *F*). The concentration of $ZnCl_2$, which is added as a buffer, is only 0.318 *F*. Addition of KCl (0.103 *F*) to the solution with the high $TeCl_4$ content did not change the absorbance significantly. Addition of KCl to the solution to a concentration of 0.212 *F* changed the spectrum slightly, but a calculation showed that it had little influence on the value of $\bar{n}$. On the basis of this it was assumed that the change in pCl^- was unimportant in the present case. The conclusion is that it is a good guess to believe that tetravalent tellurium is present in a monomeric unit, probably as $TeCl_5^-$. That such a pentahalogeno complex can exist is verified by the structure of $KTeF_5$,[19] but a more direct approach is needed before the existence of monomeric Te^{IV} in the melt can be shown convincingly.

If a monomeric Te^{IV} is present, an approximate value for the equilibrium quotient (K_1 in (9) with $\bar{n}$ = 1) can be calculated. The value was found to be 20 ± 5

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[19] S. H. Mastin, R. R. Ryan, and L. B. Asprey, *Inorg. Chem.*, **9**, 2100 (1970).

l./mol for the high $TeCl_4$ formality (0.161 *F*) using the best g_{II} value (0.24) and 24 ± 5 l./mol for the low $TeCl_4$ formality (0.064 *F*) using the best g_{II} value of 0.28.

Spectrum of Te_2^{2+}.—From three spectra of mixtures containing Te^{IV}, Te^{II}, and Te_2^{2+}, from the obtained values of g_I and g_{II}, and from the formalities of the tellurium and $TeCl_4$ added originally it is possible to calculate a spectrum of Te_2^{2+}. Such calculated spectra are shown in Figure 5. To obtain the ultraviolet part of the spectra a small path length (0.00836 cm) was used. Since the value of g_{II} is not well determined, three different g_{II} values, 0.25, 0.26, and 0.27, were used. A g_{II} value of 0.25 gives an α value close to 3, but a g_{II} value of 0.27 agrees better (as Table Ib shows) with the criteria of the best straight line. As the figure shows the formal absorptivity is not well defined, but at least an idea of the features of the spectrum can be obtained. Apparently only one broad band is present, located at *ca.* 29.3 kK. In order to obtain the molar absorptivity of Te_2^{2+} in Figure 5 the formal absorptivity should be multiplied by $^3/_2$, as is seen from the reaction $3Te^0 + Te^{IV} \rightarrow 2Te_2^{2+}$.

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Three-Dimensional Macrocyclic Encapsulation Reactions. III.[1,2] Geometrical and Electronic Features of Tris(diimine) Complexes of Trigonal-Prismatic, Antiprismatic, and Intermediate Stereochemistry

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The electronic properties of the generalized tris chelate $M(L-L)_3$, whose structure may be described in part by a twist angle ϕ, have been investigated over the trigonal-prismatic (TP, $\phi = 0°$) to trigonal-antiprismatic (TAP, $\phi = 60°$) range by the angular overlap method. One-electron d-orbital energies have been calculated as a function of angular parameters and energy-level schemes for TP $d^{7,8}$ and TP-TAP d^8 computed. Certain relationships between the twist angle and structural parameters of the coordination sphere have been derived. These considerations have been applied to the series of complexes $[M(PccBF)]^+$ (**1**), $[M((py)_3tach)]^{2+}$ (**2**), $[M((py)_3tame)]^{2+}$ (**3**), $[M((py)_3tren)]^{2+}$ (**4**), $[M(P(py)_3)_2]^{2+}$ (**7**), and $[M(bipy)_3]^{2+}$. X-Ray structural results have shown that these series encompass the TP and TAP structural extremes and include cases of intermediate stereochemistry. For the Fe(II), Co(II), Ni(II), and Zn(II) clathro chelates **1**, whose synthesis was reported in earlier parts of this series, the rigid ligand structure imposes smaller twist angles than for other complexes of these ions. The observed structural trends within the series **1–4** having constant ligand structure and variant metal ion may be rationalized in terms of destabilization of d^{6-8} configuration in TP compared to TAP geometry, with low-spin Fe(II) the most unstable (in agreement with earlier ligand-field calculations), and displacement toward the TAP geometry with decreasing ionic radius, other structural factors being approximately constant. Electronic spectra [Co(II), Ni(II)], pmr spectra [Ni(II)], polarographic redox potentials [Co(II), Fe(II)], and Mössbauer spectra [Fe(II)] of the above series of complexes have been found to undergo progressive, although not necessarily monotonic, changes with twist angle. Proton line widths of Ni(II) complexes have been observed to be particularly sensitive to stereochemistry and a qualitative model has been proposed. These results have been applied to the new sexadentate complexes of unknown stereochemistry $[M(P(CH_3pox)_3)]^{2+}$ (**5**) and $[M(P(bipy)_3)]^{2+}$ (**6**) [M = Fe(II), Co(II), Ni(II)], similar properties of which have been measured. The Ni(II) and Co(II) complexes are proposed to have intermediate solution stereochemistry, with that of the latter nearer the TP limit. The Fe(II) complexes are estimated to approach or perhaps achieve TAP geometry in solution and in the solid state.

Introduction

A rapidly accumulating body of evidence reveals that six-coordinate chelate complexes of the transition elements can adopt stable structures in which the $M-L_6$ coordination unit is significantly distorted from the usual octahedral or trigonal-antiprismatic (TAP, D_{3d}) microsymmetry while retaining a true or "pseudo" threefold rotation axis. Such structures may be partially described (*vide infra*) by a torsional or "twist" angle ϕ of the two L_3 donor atom triangles whose planes are normal to the threefold axis. Limiting values of ϕ are 60 and 0° for TAP and trigonal prismatic (TP) structures, respectively. X-Ray structural studies on complexes containing bidentate ligands have established TP coordination for certain oxidized metal tris(dithiolenes)[4] and tris(selenetenes),[5] $Er(dpm)_3$,[6a] and for the $Co-O_6$ unit in one diastereomer of $[Co(Co(OCH_2CH_2NH_2)_3)_2]^{2+}$.[6b] Intermediate geometries have been demonstrated recently for a number of tris-chelate species derived from anionic ligands such as tropolo-

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