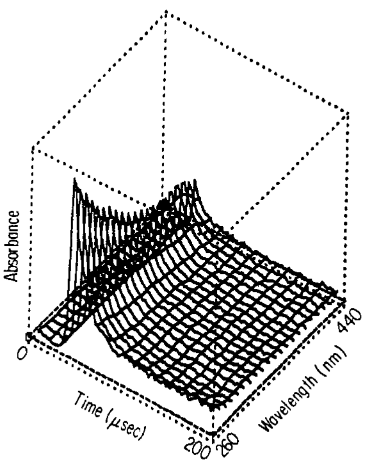

Figure 1. Time-resolved optical absorption signal obtained by pulse irradiating a He-saturated solution of 5 × 10^{-4} M $Cf(ClO_4)_3$ (pH 5.3) containing 0.1 M *tert*-butyl alcohol. Spectrum is interpreted as that of Cf(II).

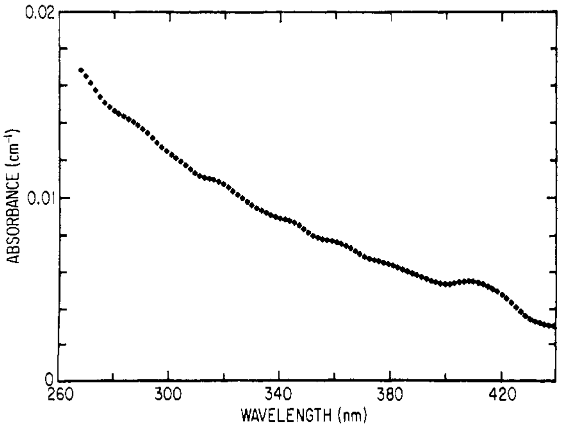

Figure 2. Transient absorption signal of Cf(II) observed 20 μs after the electron pulse (for conditions see Figure 1).

rating and cell-filling device previously described.[6] The time-resolved spectra of the transient species produced by single 13-MeV pulses of electrons in He- or N_2O-saturated solutions were obtained by using the streak camera–TV scanning method described in a previous publication.[7] Transient conductivity measurements were also carried out by a procedure previously described.[8]

Results and Discussion

When a solution of Cf(III) (ca. 5 x 10^{-4} M) in dilute perchloric acid, containing 0.1 M *tert*-butyl alcohol to scavenge OH, adjusted to pH 5.3, is irradiated with a 3-μs electron pulse, a transient absorption is observed that decays with a half-life of approximately 10 μs (Figures 1 and 2). Because of the experimental constraints imposed, the principal reactive radical in the solution is e_{aq}^-. We therefore identify the absorption as due to Cf(II). The estimated rate constant for the reaction of e_{aq}^- with Cf(III) is greater than or equal to 3 × 10^9 M^{-1} s^{-1}. We calculate a value for the absorptivity of $\epsilon \approx 500$ M^{-1} cm^{-1} at λ 270 nm. This is not inconsistent with the calculations of Carnall,[9] who predicts a strong absorption for Cf(II) that extends from ca. 380 nm into the ultraviolet region.

The polarographic reduction of Cf(III) to Cf(II) in acetonitrile solution has been previously reported.[5] Paralleling this experiment were calculations that led to an estimate of the standard aqueous reduction potential for Cf(III)/Cf(II) of ca. 1.6 V.[10] Since the estimate of the potential for the reaction

$$e_{aq}^- + H_3O^+(aq) = {}^1/_2H_2 + H_2O \qquad (1)$$

is −2.86 V,[11] it can be seen that all available evidence is consistent with the identification of the transient absorption as that of Cf(II).

The Cf(II) disappears via an apparent first-order process, with a rate parameters of (7 ± 1) × 10^4 s^{-1}. We should note that this value is similar to that previously determined for the oxidation of Am(II)[4b] (9.7 × 10^4 s^{-1}) despite the $5f^7$ configuration of the latter compared to $5f^{10}$ for Cf(II). We plan to investigate the reactions of Bk(III) with e_{aq}^- to determine if the dynamic stability of the +2 oxidation state is indeed essentially independent of the 5f configuration.

When an N_2O-saturated, aqueous solution of 5 × 10^{-4} M Cf(III), pH 5.1, was subjected to the same irradiation, no transient absorption was observed over the range 240–600 nm. The predominant radical species produced in this environment is the OH radical, a powerful oxidant. Thus, there is no spectrophotometric evidence for the production of Cf(IV) in aqueous perchlorate media. With the same experimental constraints of solution composition, there was no evidence for an oxidation process from transient conductivity measurements.

There has been a previous report of the preparation of Cf(IV) in aqueous solutions of potassium phosphotungstate.[12] The absorption spectrum of the Cf(IV) prepared in this medium has a broad band that extends from ~1000 nm and increases to 390 nm, the limit of the reported observation. This is not consistent with the spectral results we have obtained. In addition, the values for the estimated potentials of OH as an oxidant (2.65 V)[11] and that for the Cf(IV)/Cf(III) couple (3.2 V)[3] are not consistent with the preparation of Cf(IV) via OH oxidation.

Registry No. Cf(III), 22541-43-1; Cf(II), 21112-13-0; perchloric acid, 7601-90-3.

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Structure of (Urea)mercury(II) Chloride and the Effects of Strain on Ligand Properties of Urea

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Received October 6, 1982

Along with the accumulation of the data on the structure of complexes with molecular ligands, there is a growing interest in a search for general features in cation bonding by a particular ligand. The urea molecule, one of the most common multifunctional ligands, coordinates most cations with the carbonyl oxygen.[2] The exceptions are Pt(II) and Pd(II) for which coordination at an amide nitrogen was assigned on the basis of IR absorption data.[3] In the urea complexes with

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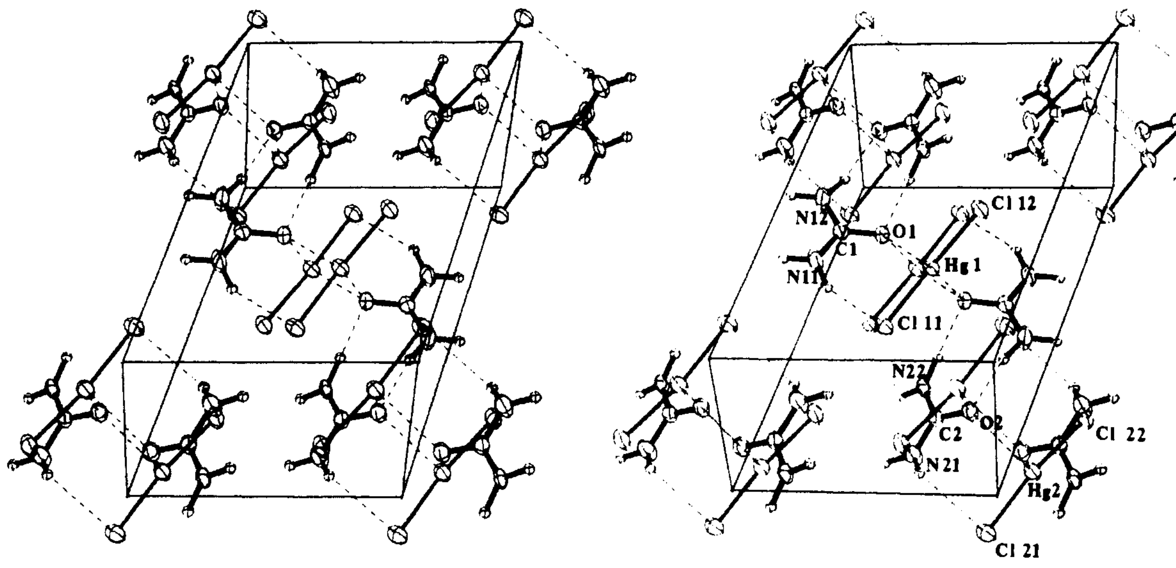

Figure 1. Crystal packing and hydrogen-bond system (ORTEP[18]).

monovalent cations the oxygen atom was found bridging two cations while in the complexes with cations with a higher charge the urea molecule usually serves as a monodentate ligand. Moreover, for divalent cations, there is a preferred geometry of urea–cation bonding such that the cation lies in the plane of the urea molecule and C=O—M angle is about 135°.[2]

Complexes of urea with $HgCl_2$ were particularly interesting as the large radius of the mercury atom should result in a long cation–oxygen distance, thus extending the range of so far observed bond lengths and helping to check correlation between the M^{2+}—O bond length and the C=O—M angle.

IR absorption data for (urea)mercury chloride (UMC) indicated that Hg binds to the carbonyl oxygen of urea.[4] On the other hand in bis(ethyleneurea) mercury chloride (BEUMC), the ethyleneurea (imidazolidin-2-one) functions as a bifunctional ligand coordinating one mercury atom with the carbonyl oxygen and the other mercury atom with one of the N atoms.[5] The same bonding situation was found for urea in $[Co(urea)_4](NO_3)_2$.[6] However, this last compound is very hygroscopic and upon H_2O binding turns into $[Co(urea)_4(H_2O)_2](NO_3)_2$ where the urea molecules are monodentate.[7] Thus a comparison of the structures of UMC and BEUMC should prove to be an interesting example of the effect of strain, introduced to the urea molecule by the ethylene bridge on its ligand properties.

Experimental Section

Crystals of the title compound were obtained by slow evaporation of an aqueous solution of mercury chloride and urea in the molar ratio 1:2. They cleaved easily and could not be ground, so a crystal of dimension 0.30 × 0.21 × 0.15 mm was used to collect intensity data on an Enraf-Nonius CAD-4 diffractometer. Variable ω–2θ scans in the θ range 1–28° and graphite monochromatized Mo Kα radiation were used. The intensities of 2 standard reflections were measured every 94 reflections and showed no significant change. The cell parameters a = 8.56 (1) Å, b = 11.335 (5) Å, c = 6.758 (3) Å, α = 103.4 (1)°, β = 97.4 (1)°, and γ = 75.5 (1)° were obtained from a least-squares fit of θ angles for 15 reflections (λ = 0.71069 Å, space group $P\bar{1}$, Z = 4). Lorentz, polarization, and absorption corrections (μ = 248 cm^{-1}) calculated by numerical methods were applied to the intensity data set. The maximum and minimum transmission factors were 0.082 and 0.022, respectively. Of the 2797 measured reflections ($\pm h,\pm k,l$) 2745 had positive net intensity and yielded 2618 unique F values in a sort–merge procedure giving an internal consistency factor of 4.2% for 179 equivalent reflections ($\pm h,\pm k$,0).

Table I. Atomic Positional Coordinates (×10^5 for Hg, ×10^4 for Cl, O, C, and N Atoms) with Esd's in Parentheses

atom	x	y	z
Hg(1)	40887 (5)	61571 (4)	76342 (6)
Cl(11)	4960 (3)	7898 (2)	7425 (4)
Cl(12)	2959 (3)	4692 (2)	8431 (4)
Hg(2)	−13855 (5)	101635 (4)	23450 (6)
Cl(21)	−433 (3)	11776 (2)	1758 (5)
Cl(22)	−2601 (3)	8599 (3)	2507 (5)
O(1)	6751 (7)	4508 (6)	6248 (10)
C(1)	8213 (11)	4625 (9)	6782 (15)
N(11)	8576 (11)	5728 (9)	7152 (17)
N(12)	9395 (10)	3621 (9)	6889 (17)
O(2)	1470 (8)	8878 (6)	3623 (11)
C(2)	2796 (11)	8768 (10)	2818 (15)
N(21)	3185 (11)	9726 (8)	2376 (16)
N(22)	3824 (9)	7632 (8)	2296 (14)

The structure was determined by the heavy-atom method and refined by a full-matrix least-squares procedure using weights $w^{-1} = \sigma^2(F)$ and isotropic secondary extinction corrections calculated as $F_c^* = F_c(1 - (gF_c^2/\sin\theta))$. The refinement converged at $g = 1.53 \times 10^{-7}$ and discrepancy indices R = 0.037 and R_w = 0.035. The maximum extinction correction was for reflection (002) F_c^* = 302, F_c = 388, and F_o = 317 e. The highest peak on the final difference Fourier map was 2.3 e Å^{-3} and located close to the Hg atom; otherwise the map was featureless.

The final atomic coordinates and their standard deviations are given in Table I.

Some of the H atoms were identified on difference Fourier maps, but the refinement of their parameters resulted in unrealistic temperature factors. In the final least-squares cycle, the positional parameters of the H atoms, calculated from the geometry of the urea molecule, and their thermal parameters were fixed; neutral-atom scattering factors were used.[8]

Results and Discussion

In UMC there are two crystallographically independent centrosymmetric dimers $[HgCl_2(urea)]_2$ with basically the same structure as shown in Figure 1. Each Hg atom is essentially in the form of a discrete $HgCl_2$ molecule. The average length of a Hg–Cl bond is 2.308 Å and the average Cl–H–Cl angle is 169.6°. A similar distortion of the linear

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Table II. Distances (Å) and Angles (deg) with Esd's in Parentheses

Hg(1)–Cl(11)	2.315 (3)		
Hg(1)–Cl(12)	2.301 (3)	Cl(11)–Hg(1)–Cl(12)	168.0 (1)
Hg(2)–Cl(21)	2.310 (3)		
Hg(2)–Cl(22)	2.299 (3)	Cl(21)–Hg(2)–Cl(22)	171.3 (1)
Hg(1)–Cl(21)	3.415 (3)	O(1)–Hg(1)–O(1′)	77.5 (4)
Hg(1)–Cl(12′)	3.553 (3)	Hg(1)–O(1)–Hg(1′)	102.5 (5)
Hg(2)–Cl(11)	3.288 (3)	O(2)–Hg(2)–O(2′)	80.9 (4)
Hg(2)–Cl(21′)	3.394 (3)	Hg(2)–O(2)–Hg(2′)	99.1 (5)
Hg(1)–O(1)	2.678 (6)	C(1)–O(1)–Hg(1)	125.2 (6)
Hg(1)–O(1′)	2.615 (6)	C(1)–O(1)–Hg(1′)	118.5 (6)
Hg(2)–O(2)	2.666 (6)	C(2)–O(2)–Hg(2)	123.2 (7)
Hg(2)–O(2′)	2.692 (6)	C(2)–O(2)–Hg(2′)	117.1 (6)
Cl(11)–Hg(1)–O(1)	95.4 (4)	Cl(21)–Hg(2)–O(2)	92.8 (4)
Cl(12)–Hg(1)–O(1)	94.6 (4)	Cl(22)–Hg(2)–O(2)	93.2 (4)
Cl(11)–Hg(1)–O(1′)	96.7 (4)	Cl(21)–Hg(2)–O(2′)	96.1 (4)
Cl(12)–Hg(1)–O(1′)	91.7 (4)	Cl(22)–Hg(2)–O(2′)	90.9 (4)
O(1)–C(1)	1.288 (12)	O(1)–C(1)–N(11)	121.0 (9)
C(1)–N(11)	1.324 (15)	O(1)–C(1)–N(12)	119.9 (10)
C(1)–N(12)	1.329 (13)	N(11)–C(1)–N(12)	119.0 (9)
O(2)–C(2)	1.288 (13)	O(2)–C(2)–N(21)	122.0 (9)
C(2)–N(21)	1.318 (16)	O(2)–C(2)–N(22)	120.7 (10)
C(2)–N(22)	1.363 (12)	N(21)–C(2)–N(22)	117.2 (9)
urea 1 plane–Hg(1)	1.222 (1)	urea 2 plane–Hg(2)	1.646 (1)
urea 1 plane–Hg(1′)	−2.295 (2)	urea 2 plane–Hg(2′)	−2.307 (2)

structure of $HgCl_2$ was found in (benzylammoniumyl)bis(dichloromercury(II)) chloride. Urea molecules are coordinated by the oxygen atom of carbonyl group to two Hg atoms in a bridging mode. The coordination with the carbonyl group confirms the IR spectra analysis by Antonenko and Nuger.[4] Two centrosymmetric O atoms coordinate Hg atoms with an average Hg–O distance of 2.66 Å, while two Cl atoms from neighboring molecules complete the coordination of Hg to octahedral (Table II). These latter interactions have to be considered marginal as their average Hg–Cl distance of 3.41 Å is close to the sum of the atomic radii (1.7 + 1.8 Å).[11] Nevertheless, the angles between the stronger bonds at the Hg atoms are relatively close to 90°. Octahedral coordinations were also found in other complexes of $HgCl_2$ and Lewis bases containing an oxygen atom as the donor.[9,12]

The described urea coordination is similar to that found for biuret in the structure of bis(biuret)mercury(II) chloride where the carbonyl oxygens also serve as bridging ligands and amine groups are not bonded to Hg.[13] Hoever, this bonding situation is quite different than in BEUMC where ethyleneurea molecules bridge two Hg atoms, as in UMC, but UMC is bidentate and one atom is coordinated with a N-atom while the other with the O atom.

An explanation of this different function of the ligands can be the strain forced by the ethylene bridge in the cyclic ethyleneurea molecule (imidazolidin-2-one). In hexakis(ethyleneurea)cadmium(II) perchlorate (HEUCP) the ethyleneurea molecules are coordinated to Cd^{2+} with the oxygen atoms.[14] Cation binding in this mode does not change significantly the geometry of urea ligands.[2] The ethyleneurea molecule is planar, with average bonds lengths C–O = 1.257, C–N = 1.345 and C–C = 1.564 Å, which compare to those found for the urea molecule, C–O = 1.246 (2) and C–N = 1.333 (1) Å.[17] The ethylene bridge forces the bonding angles, N–C–N = 110.9°, C–N–C = 111.9°, and N–C–C = 102.3°, to deviate from those in the urea molecule which are 116.2 (1)° for N–C–N and very close to 120° for C–N–H and H–N–H as found by neutron diffraction.[17] It can be expected that this stressing of the bonding angles affects π-electron delocalization. Unfortunately the relatively low precision of the HEUCP structure determination does not allow quantitative discussion of the C–N bond length (esd of the average of six observations is 0.005 Å).

Table III. Distances (Å) in the Hydrogen-Bonding System

D–H···A	acceptor position	D···A
N(11)–H(112)···Cl(11)	$1-x, 1-y, 1-z$	3.432
N(21)–H(212)···Cl(21)	$-x, 2-y, 1-z$	3.416
N(12)–H(122)···O(2)	$1-x, 1-y, 1-z$	3.036
N(22)–H(222)···O(1)	$1-x, 1-y, 1-z$	2.987

In the structure of BEUMC[5] the linear $HgCl_2$ molecule occupies a centrosymmetric site and forms in the equatorial plane two secondary bonds Hg–O (2.673 (9) Å) and two Hg–N (2.953 (11) Å) resulting in an approximately octahedral coordination. The ethyleneurea ligand shows significant loss of the symmetry of the amide C–N bonds whose lengths are 1.380 (16) Å at the Hg site and 1.322 (17) Å at the nonbonded side and C–N–C angles that are 108.2 (10)° at the Hg site and 112.5 (11)°. Also, the ethylenic C atom closer to Hg deviates 0.33 Å from the molecular plane. The other relevant angles are Hg–N–C(amide) = 114.1 (10)° and Hg–N–C(ethylenic) = 106.6 (6)°. This bonding geometry shows that binding to the electrophilic Hg(II) decreases π-electron delocalization in the ethyleneurea molecule and induced more sp^3 character at the N atom.

In UMC the open secondary coordination sites in the equatorial plane of the $HgCl_2$ molecule are filled by marginally interacting Cl atoms from neighboring molecules and not by the apparently available N atoms of urea molecules. The probable explanation is that the amide N atoms in the strained ethyleneurea, with one angle already close to tetrahedral, are prone to redistribute electron density and form coordination bonds to a cation. This is not the case in the urea molecule where the geometry of bonds corresponds to sp^2 hybridization. Interestingly, in protein cyrstallography, where mercurials are used for obtaining heavy–atom derivatives, it was been found that $HgCl_2$ usually produces multiple binding sites. It is conceivable that $HgCl_2$ binds to prolines in which bonds at peptide nitrogens are also strained.

An analysis of divalent cation–urea interactions suggested that for monodentate urea ligands there may be a correlation between the M^{2+}–O distance and the M^{2+}—O═C angle.[2] Our initial aim was to extend the range of observations beyond the M^{2+}–O distance of 2.4 Å. However, it turned out that in this compound the urea molecules serve as bridging ligands. Such a situation is usually met in monovalent cation complexes[2] with urea, while it is exceptional in divalent cation complexes. So far it has been found only in $CuSO_4\cdot 3(H_2N)_2CO$[15] where the weakly bound axial urea ligand with a Cu^{2+}–O distance of 2.61 Å is shared by two Cu^{2+} cations. Also when the Hg^{2+} cation forms essentially covalent bonds with other ligands, it is unable to provide sufficient matching for the Lewis base strength[16] of the urea molecule and urea functions as a shared ligand.

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The oxygen atoms are the acceptors in H bonds formed by the amine groups of urea molecules belonging to the neighboring dimers (Table III). Distances between the N and Cl atoms suggest H bonds within the dimers and between them. However, the calculated positions of H atoms indicate that there are only the intracomplex N–H···Cl bonds.

Acknowledgment. We thank SLAFiBS, Krakow, for letting us use the diffractometer. We are also grateful to the Polish Academy of Sciences for partially supporting this work (MR-I.9.).

Registry No. UMC, 86064-71-3; urea, 57-13-6.

Supplementary Material Available: Tables of anisotropic atomic thermal motion parameters, calculated atomic positional coordinates for hydrogen atoms, nonessential angles, equations of planes, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische Chemie der Universität Göttingen, Göttingen, Federal Republic of Germany, and Institut für Kristallographie und Mineralogie der Universität Frankfurt am Main, Frankfurt am Main, Federal Republic of Germany

Preparation and Crystal Structure of $\{Zn[S(NSO)_2]_2\}(AsF_6)_2 \cdot 2SO_2$: A Compound with a Two-Dimensional Network through Oxygen Atoms

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Received August 10, 1982

Bis(sulfinylamino) sulfide, $S(NSO)_2$, was first prepared by Goehring and Heinke.[1] X-ray analysis showed a noncyclic arrangement of the atoms.[2] Reactions of $S(NSO)_2$ are only known with nonmetallic elements or compounds. It was shown that $S(NSO)_2$ reacts with silicon–nitrogen compounds with cleavage of the Si–N bond and formation of compounds containing the sulfoximide group.[3] Herein we report the first example where $S(NSO)_2$ functions as a ligand in metal complexes.

Experimental Section

The compound $S(NSO)_2$ may be prepared from ammonia and thionyl chloride[1] or by the reaction of $(CH_3)_3SiNSO$ and sulfur dichloride.[4]

Preparation of Bis[bis(sulfinylamino)sulfido]zinc(II) Bis[hexafluoroarsenate(V)]-Bis(sulfur dioxide). A 3.2-g amount (5 mmol) of $[Zn(SO_2)_2](AsF_6)_2$[7] and 1.74 g (11 mmol) of $S(NSO)_2$[4] were placed in a pressure flask and cooled to −78 °C. Twenty milliliters of SO_2 was added. The solution was allowed to warm to room temperature and was stirred for 12 h. After removal of SO_2, the bright yellow residue was washed with dry methylene chloride several times and recrystallized from liquid SO_2: dec pt 170–185 °C; yield 4.19 g (95%). Anal. Calcd for $\{Zn[S(NSO)_2]_2\}(AsF_6)_2 \cdot 2SO_2$: F, 25.8; S, 28.9; N, 6.3. Found: F, 27.1; S, 27.9; N, 6.7.

Crystal Structure Determination. A yellow crystal was sealed in a glass capillary to prevent it from decomposing in the air. The cell constants were determined on an Enraf-Nonius CAD4 diffractometer from 25 well-centered reflections. The systematic extinctions correspond to space group $P2_1/n$; the cell volume corresponds to two formula units. Reflections were collected with an ω-scan and Mo $K\alpha$ radiation (graphite monochromator) at 298 K in two quadrants of reciprocal space up to 2θ = 50 and 55°, respectively. Data were rescaled with respect to an intensity decrease of about 4% of the standard reflections. An empirical absorption correction based on ψ-scans of four reflections gave maximum differences in transmission of 18%.[5] Equivalent reflections were averaged ($R(I)_{\text{internal}} = 0.018$), and all observations with $I > 0.3\sigma(I)$ were used in the analysis. For further details see Table I.

Table I. Crystal Data and Structure Analysis

space group	$P2_1/n$
a, Å	8.442 (1)
b, Å	13.106 (2)
c, Å	10.997 (1)
β, deg	101.47 (1)
V, Å^3	1192.3 (5)
cryst dimens, mm	0.30 × 0.35 × 0.55
D_{calcd}, g cm^{-3}	2.461
total no. of reflctns	5665
no. of indep reflctns	2731
$I > 0.3\sigma(I)$	2600
$[(\sin\theta)/\lambda]_{\max}$	0.65
$R(F)$	0.051
$R_w(F)$	0.059

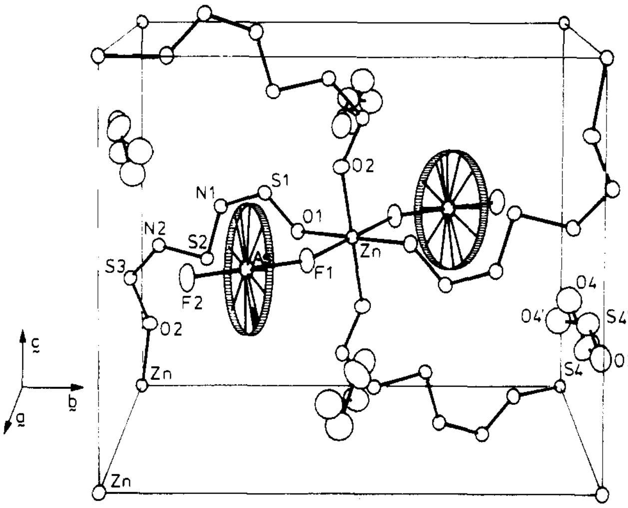

Figure 1. View of the crystal structure of the title compound. The positions of the 14 fragments of the four fluorine atoms are represented by a wheel. The two positions of the split atoms of the SO_2 group are included.

The structure was determined by Patterson and Fourier techniques. In the course of the structure determination it was found that the $[AsF_6]^-$ and SO_2 groups were disordered. For the $[AsF_6]^-$ group only two fluorine atoms are well localized (the axial atoms F(1) and F(2)), while a smeared ring of electron density ranging between 2.5 and 4.5 e/Å^3 was observed about the F(1)–As–F(2) axis. Consequently the group was supposed to be considerably disordered or to rotate about this axis. The problem was overcome by describing the ring of F atoms by a large number of partly occupied atoms (14 fragments). The positions of these fragments are represented in Figure 1 in the form of a wheel. Their positional parameters, occupation numbers, and isotropic temperature factors are included in the supplementary material. The structure analysis does not allow us to distinguish between rotational or static disorder of this group. For the SO_2 group only the O(3) atom was well localized, while two positions were found for both S(4) and O(4). These atoms were described with a split-atom model. Both positions for the disordered atoms are included in Figure 1; they are labeled S(4), S(4′), O(4), and O(4′). Atomic scattering factors and anomalous dispersion factors were taken from ref 6. The

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0020-1669/83/1322-2342$01.50/0 © 1983 American Chemical Society