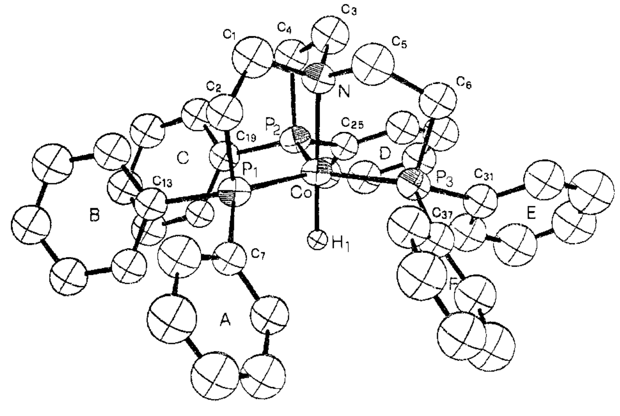

Figure 4. Perspective view of the [CoH(np$_3$)] complex. An artificial factor $B = 1.5$ Å^2 for the hydride atom was used.

tetrahalides of the group VI elements, *e.g.*, SF$_4$, the lone pair is in an equatorial position.[23]

The role of hydride ligands in determining the geometry of metal complexes has been extensively discussed.[24] In this case, however, the geometry of the complex is imposed by the steric requirements of the tripod ligand and is practically unaffected by the presence of the hydride ligand. The influence of the hydrogen atom is so slight that the dimensions of the "cage" formed by the phenylic hydrogens below the metal atom are practically the same in the two complexes. If anything, they are smaller in the hydride cobalt case than in the empty nickel case.

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Registry No. [CoCl(np$_3$)], 29946-09-6; [CoBr(np$_3$)], 54353-69-4; [CoI(np$_3$)], 54353-70-7; [Co(NCS)(np$_3$)], 54382-81-9; [Co(CN)(np$_3$)], 54353-71-8; [CoH(np$_3$)], 53687-39-1; [CoH(CO)(np$_3$)], 54423-75-5; [Co(CO)(np$_3$)]BF$_4$, 54353-73-0; [Co(CO)(np$_3$)]B(C$_6$H$_5$)$_4$, 54353-74-1; [NiCl(np$_3$)], 54423-06-2; [NiBr(np$_3$)], 54382-82-0; [NiI(np$_3$)], 54353-75-2; [Ni(NCS)(np$_3$)], 54382-83-1; [Ni(CN)(np$_3$)], 54353-76-3; [Ni(CO)(np$_3$)]BF$_4$, 54516-86-8; [Ni(CO)(np$_3$)]B(C$_6$H$_5$)$_4$, 54516-85-7; [Ni(np$_3$)], 52633-73-5; [Ni(CO)(np$_3$)], 54423-76-6.

Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40709T.

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Amine–Sulfur Dioxide Complexes.
Structure of *N*,*N*,*N*',*N*'-Tetramethyl-*p*-phenylenediamine–Bis(sulfur dioxide)

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The crystal structure of the 1:2 complex between *N*,*N*,*N*',*N*'-tetramethyl-*p*-phenylenediamine and SO$_2$ has been determined by X-ray diffraction. The crystal is monoclinic, space group $P2_1/c$, with four formula units of the complex in a cell of dimensions a = 6.339 (2) Å, b = 19.163 (4) Å, c = 12.7148 (7) Å, and β = 120.11 (3)°. The intensity data (2765) were collected on an automatic diffractometer. The structure was determined from a Patterson synthesis and refined by full-matrix least-squares methods. The final R was 0.037 for all data. The N–S charge-transfer distances are 2.337 (2) and 2.340 (2) Å. The average S–O bond distance is 1.434 (1) Å and the OSO bond angles are 113.5 (1) and 115.0 (1)°. The phenyl group is planar but the nitrogen geometry is partially tetrahedral, indicating n donation by those atoms. The angles (α) between the N–S charge-transfer bonds and the perpendicular to the SO$_2$ planes are 15.2 (1)° for both SO$_2$ groups.

Introduction

Although reports of structural, spectral and thermodynamic investigations of the molecular complexes formed between amines and halogens are numerous,[1] little attention has been given to the corresponding complexes involving sulfur dioxide. In spite of this lack of information some structural generalizations based on crystallographic data for the SO$_2$ adducts of trimethylamine[2] and certain organometallic complexes[3–6] in which the SO$_2$ ligand functions as an electron acceptor are possible. (1) The complexes appear to be stabilized by the

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Table I. Crystallographic Data

Formula	$C_{10}H_{16}N_2S_2O_4$	μ(Mo Kα)	3.96 cm^{-1}
Fw	292.36	*a*	6.339 (2) Å[b]
F(000)	616	*b*	19.163 (4) Å
Space group	$P2_1/c$	*c*	12.7148 (7) Å
d_m[a]	1.4 (1) g/cm³	β	120.11 (3)°
d_c	1.44 g/cm³	Intensity data	2765 unique reflections measured twice (Mo Kα)
Z	4		

[a] Measured by flotation in *n*-heptane–CCl_4 mixtures at 25°.
[b] Measured from +2θ and −2θ values of 28 reflections using Cu Kα_1 (λ 1.54051 Å).

formation of a charge-transfer bond involving primarily the nitrogen of the amine and the sulfur of SO_2. The length of this N–S bond is intermediate between the van der Waals N–S distance and a normal single bond. (2) The orientation of the nitrogen atom and the SO_2 molecule is not planar but rather can be characterized by an angle α defined by the N–S bond and the normal to the SO_2 plane; α is usually in the range of 21–32°. Also, the N–SO_2 group has approximate C_m symmetry. (3) The O–S–O angle definitely appears to contract several degrees upon formation of the complex; however, changes in the S–O distances are uncertain due to the large thermal motions usually encountered in these complexes.

In order to obtain a better understanding of the interactions and geometries involved in complexes of this type, the structure of the complex between *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and SO_2 has been determined by X-ray diffraction techniques.

Experimental Section

Preparation SO_2–$N(CH_3)_2(C_6H_4)(CH_3)_2N$–$SO_2$. A solution of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in *n*-heptane was treated with anhydrous SO_2 by bubbling the gas directly into the heptane mixture at 25°. The orange precipitate which formed immediately was collected into weighing bottles under nitrogen atmosphere and stored at 25° for several months. During this period, well defined red-orange crystals, similar in appearance and properties to those described earlier by Byrd,[7] formed on the walls of the container. The crystals lose their color slowly when exposed to the atmosphere leaving a white residue and consequently were loaded at reduced temperature into lithium glass capillaries under nitrogen atmosphere prior to X-ray examination. An interesting property of these crystals, which was not investigated, was the visible thermochromic shift which occurred as the temperature was lowered from room temperature to that of liquid nitrogen.

X-Ray Diffraction. A preliminary survey of the crystals on a General Electric XRD-5 diffractometer was performed by the construction of reciprocal lattice plots which indicated the crystal system to be monoclinic with systematic absences 0*k*0 and *h*0*l* of *k* = 2*n* + 1 and *l* = 2*n* + 1, respectively. The only space group consistent with these absences is $P2_1/c$. The lattice constants were determined at 25° by least-squares refinement of ±2θ values for 24 higher order reflections which were centered on a Nonius CAD-4 automatic diffractometer using Cu Kα_1 radiation. The refined cell constants, as well as other pertinent crystallographic data, are given in Table I.

A small prismatic crystal bounded by the faces (010), (0$\bar{1}$0), (10$\bar{1}$), ($\bar{1}$01), (01$\bar{1}$), and (0$\bar{1}$1) was selected for data collection; the perpendicular distances for the geometric center of the crystal to the faces were 0.129, 0.129, 0.319, 0.319, 0.147, and 0.147 mm, respectively. Measurement of the mosaicity of the crystal by a narrow-source (1° takeoff angle), ω-scan technique gave total widths in the range 0.3–0.4° at the base of randomly selected strong reflections. The crystal was mounted in a lithium glass capillary with the (10$\bar{1}$) reciprocal lattice vector approximately coincident with the spindle axis. The intensities were measured on a Nonius CAD-4 automatic diffractometer using Zr-filtered Mo Kα ($\bar{\lambda}$ 0.71069 Å) radiation and a θ–2θ scan technique with scan widths adjusted according to dispersion by the formula ($A + B \tan \theta$) where A = 0.6 and B = 0.06. The intensities of 2765 reflections out to a 2θ limit of 53° were measured twice at a takeoff angle of 4°; only the unique reflections were recorded. A horizontal receiving aperture with a variable width (width (mm) = 4 + 0.4 tan θ) and a height of 6 mm was located 17.3 cm from the crystal. In each data set, a reflection was scanned twice (once through the peak in the +2θ direction and once through in the −2θ direction) for a maximum time of 180 sec/total scan; the final result represents the average of the two scans. Of the total time spent on a reflection, two-thirds was spent in the 2θ scans and one-sixth on the left and right backgrounds with stationary crystal and counter. A 2θ scan speed of 1.36°/min was employed for reflections with count rates less than 833 counts/min. This count rate was maintained for the stronger reflections by the use of increased scan speeds. The intensities of reflections with count rates in excess of 50,000 counts/sec were automatically attenuated by the insertion of a Zr filter (filter factor 8.27 ± 0.07) in the diffracted beam. The intensity of one standard reflection recorded every 30 min to monitor crystal and instrument alignment and stability showed no significant changes in intensity during the data collection process.

The two independently measured sets of *hkl* data were corrected for absorption effects using a gaussian procedure (6 × 6 × 6 grid) as described by Coppens, Leiserowitz, and Rabinovich;[8] the absorption coefficients varied between 0.87 and 0.96. The intensities were merged into one unique data set; data reproducibility ($\sum|\Delta I|/\sum I$) of 0.014 was taken as a further indication of crystal and instrument stability. Structure factors were obtained following application of Lorentz and polarization factors. For the purposes of refinement, a total of 342 reflections were considered unobserved based on the fact that the net count was less than 1.4$\sigma(I)$; unobserved intensities were assigned values of 0.7$\sigma(I)$. The method of calculating $\sigma(I)$, $\sigma(F)$, and the weight ($w_F = 1/\sigma(F)^2$) assigned to each structure amplitude has been described previously.[9]

Structure Refinement and Solution. The positions of the two independent sulfur atoms were located from a sharpened Patterson synthesis. A Fourier synthesis based on the contributions of the sulfur atoms revealed the positions of the remaining nonhydrogen atoms. The atomic positions, isotropic temperature factors, and scale factor, *K*, were refined with the full-matrix structure factor least-squares program ORFLS of Busing, Martin, and Levy[10] which minimizes the quantity of $\sum w_F(F_o - KF_c)^2$. All calculations used in the refinement were performed on an IBM 360/50 computer using the atomic scattering factors for C, O, N, and S as listed in ref 11. The hydrogen atom scattering factors were those of Stewart, Davidson, and Simpson.[12]

After three cycles, the refinement converged to a conventional *R* factor ($R_c = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.12 and a weighted *R* factor ($R_w = (\sum w_F(|F_o| - |F_c|)^2/\sum w_F|F_o|^2)^{1/2}$ of 0.15. All of the hydrogen atoms were located in a subsequent difference-Fourier synthesis; hydrogen atom peak heights ranged from 0.5 to 0.6 e/Å³. Three further refinement cycles in which the nonhydrogen atoms were refined anisotropically and the hydrogen atoms isotropically resulted in the final *R* values of R_c = 0.037 and R_w = 0.039 for all intensity data and R_c = 0.031 and R_w = 0.039 for the data with unobserved intensities excluded. For all atoms the shifts were less than 0.02σ in the final least-squares cycle. The mean values of $w_F(|F_o| - |F_c|)^2$ calculated for various ranges of $|F_o|$ increased only slightly with increasing $|F_o|$ and were considered an indication of the validity of the weighting scheme. The observed and calculated structure factors are available.[13]

A difference Fourier calculated from the final atomic parameters (Tables II and III) showed only minor (−0.2 to +0.2 e/Å³) peaks located mainly around the atomic positions. These residuals are a further indication of the validity of the structure and were not considered further.

Discussion of the Structure

The structure consists of discrete molecular complexes containing one TMPD molecule and two SO_2 molecules (Figure 1). The attachment is through two N–S bonds of experimentally equal lengths (2.340 (2) and 2.337 (2) Å). These lengths are intermediate between the normal van der Waals contact (3.25 Å) and the predicted N–S single-bond distance (1.73 Å) as expected for complexes of the charge-transfer type. The distances are longer than that observed in the trimethylamine (TMA)–sulfur dioxide complex.[2] Although this lengthening is not predicted on the basis of the ionization potentials of the two donor molecules

Table II. Final Positional and Thermal Isotropic Parameters[a]

	x	y	z	B, Å^2
S(1)	0.01167 (7)	0.26674 (2)	0.35908 (3)	
O(11)	−0.2041 (2)	0.22512 (7)	0.29236 (11)	
O(12)	0.2333 (2)	0.22774 (7)	0.40438 (11)	
N(1)	0.0037 (2)	0.27643 (6)	0.54052 (11)	
C(11)	−0.2296 (3)	0.31219 (9)	0.50131 (18)	
C(12)	0.2145 (3)	0.32133 (9)	0.61690 (16)	
C(1)	0.0217 (2)	0.20624 (7)	0.58245 (12)	
C(2)	−0.1840 (3)	0.16744 (8)	0.55586 (14)	
C(3)	−0.1626 (3)	0.09849 (8)	0.59400 (13)	
C(4)	0.0626 (3)	0.06593 (7)	0.65744 (12)	
C(5)	0.2684 (3)	0.10492 (8)	0.68400 (13)	
C(6)	0.2482 (3)	0.17373 (8)	0.64670 (13)	
N(2)	0.0839 (2)	−0.00377 (6)	0.70206 (11)	
C(21)	0.3084 (4)	−0.04612 (9)	0.73053 (19)	
C(22)	−0.1332 (4)	−0.04805 (9)	0.63742 (17)	
S(2)	0.12800 (8)	0.01191 (2)	0.89437 (4)	
O(21)	0.3083 (2)	0.06603 (7)	0.93614 (11)	
O(22)	−0.1146 (2)	0.03497 (8)	0.85696 (13)	
H(C11)	−0.221 (3)	0.3577 (9)	0.4723 (15)	3.9 (4)
H(C11)	−0.260 (3)	0.3173 (10)	0.5718 (18)	5.5 (5)
H(C11)	−0.367 (3)	0.2873 (9)	0.4337 (16)	3.8 (4)
H(C12)	0.365 (3)	0.3051 (9)	0.6162 (15)	4.1 (4)
H(C12)	0.241 (3)	0.3219 (10)	0.7022 (19)	5.8 (5)
H(C12)	0.183 (3)	0.3658 (10)	0.5807 (17)	5.2 (4)
H(C2)	−0.337 (3)	0.1851 (8)	0.5125 (15)	3.5 (3)
H(C3)	−0.305 (3)	0.0756 (8)	0.5755 (14)	3.6 (3)
H(C5)	0.435 (3)	0.0866 (8)	0.7316 (14)	3.2 (3)
H(C6)	0.388 (3)	0.1953 (8)	0.6663 (14)	3.0 (3)
H(C21)	0.305 (3)	−0.0864 (11)	0.7635 (18)	5.9 (5)
H(C21)	0.326 (4)	−0.0485 (11)	0.6560 (20)	6.6 (5)
H(C21)	0.450 (4)	−0.0180 (10)	0.7954 (19)	5.2 (5)
H(C22)	−0.178 (4)	−0.0550 (12)	0.5529 (21)	6.9 (5)
H(C22)	−0.090 (3)	−0.0952 (11)	0.6776 (18)	5.5 (4)
H(C22)	−0.272 (3)	−0.0273 (10)	0.6435 (17)	4.9 (4)

[a] Standard deviations for last digits are in parentheses.

Table III. Anisotropic Thermal Parameters[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	3.54 (2)	2.88 (2)	2.80 (2)	−0.02 (1)	1.57 (1)	0.15 (1)
O(11)	3.67 (5)	5.96 (7)	3.73 (5)	−0.69 (5)	1.01 (4)	−1.23 (5)
O(12)	3.48 (5)	6.22 (7)	4.84 (6)	0.61 (5)	2.38 (5)	−0.17 (5)
N(1)	2.70 (5)	2.35 (5)	2.85 (5)	−0.00 (4)	1.26 (4)	0.31 (4)
C(11)	3.94 (8)	2.93 (7)	4.78 (8)	0.83 (6)	2.52 (7)	0.87 (6)
C(12)	4.31 (8)	2.59 (6)	3.46 (7)	−0.81 (6)	1.44 (6)	−0.03 (5)
C(1)	2.68 (6)	2.37 (5)	2.28 (5)	−0.07 (4)	1.22 (4)	0.17 (4)
C(2)	2.35 (6)	2.94 (6)	3.28 (6)	0.17 (5)	1.12 (5)	0.39 (5)
C(3)	2.48 (6)	2.87 (6)	3.41 (6)	−0.55 (5)	1.29 (5)	0.13 (5)
C(4)	3.06 (6)	2.34 (5)	2.19 (5)	−0.20 (5)	1.34 (4)	0.02 (4)
C(5)	2.43 (6)	2.93 (6)	2.95 (6)	0.19 (5)	1.06 (5)	0.46 (5)
C(6)	2.28 (6)	2.86 (6)	3.21 (6)	−0.34 (5)	1.15 (5)	0.34 (5)
N(2)	3.43 (5)	2.20 (5)	2.92 (5)	−0.15 (4)	1.67 (4)	0.02 (4)
C(21)	4.94 (9)	2.77 (7)	5.02 (9)	0.92 (7)	3.04 (8)	0.57 (6)
C(22)	5.04 (9)	2.87 (7)	3.91 (8)	−1.14 (7)	1.96 (7)	−0.32 (6)
S(2)	4.60 (2)	3.27 (2)	2.94 (2)	0.46 (1)	2.16 (2)	0.42 (1)
O(21)	5.05 (6)	4.72 (6)	3.78 (5)	−0.51 (5)	1.78 (5)	−1.02 (5)
O(22)	4.58 (6)	7.57 (8)	5.17 (6)	0.39 (6)	3.24 (5)	−0.46 (6)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-{}^1/_4(B_{11}\cdot h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

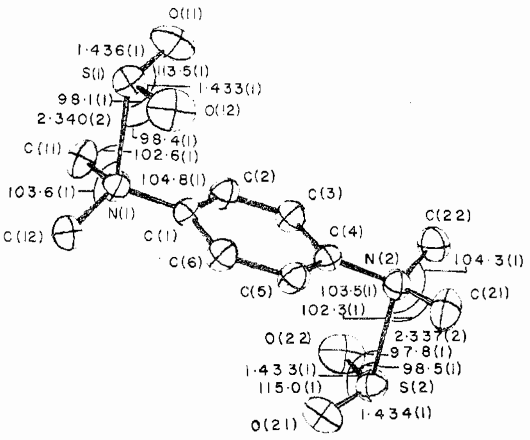

Figure 1. An ORTEP[25] plot of the complex.

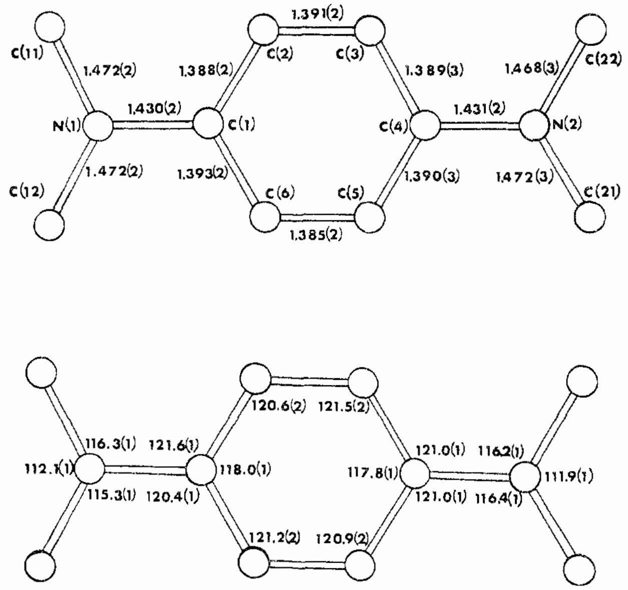

Figure 2. Bond distances and bond angles in the tetramethylphenylenediamine group.

(6.7 eV for TMPD[14] and 7.82 eV for TMA[15]), such factors as the formation of a 1:2 complex instead of a 1:1 complex and nonbonded intramolecular interactions may affect the geometry of the complexes.

The S–O distances (average 1.434 Å) are essentially the same as those found in solid[16] (1.430 (15) Å) and gaseous[17] (1.431 (1) Å) SO_2. The O–S–O angles on the other hand are considerably contracted (113.5 and 115.0°) from those found in solid and gaseous SO_2 (119.5 (1.5) and 119.0 (5)°) in agreement with previous observations on complexes and adducts of SO_2.[2–6] The difference in the two bond angles is significant. No explanation can be given for this observation although the environment of the two SO_2 groups is dissimilar (vide infra). The changes found in the SO_2 molecule on complex formation imply that the lowest unoccupied molecular orbital of the acceptor is probably only slightly antibonding with respect to the S–O bonds and slightly bonding with respect to the oxygen atoms. The detailed molecular orbital treatment of SO_2[18] is in essential agreement[19] with these observations.

The structure indicates that TMPD functions as an n-type rather than π-type donor in the complex. This is indicated by a lengthening of the N(1)–C(1) and N(2)–C(4) bonds (Figure 2) to 1.430 and 1.431 Å from an estimated 1.39 Å in the free TMPD molecule.[20] Evidently, the sp^2 hybridization of the nitrogen atoms found in free TMPD has become partially tetrahedral in character upon complex formation. This is reflected by the bond angles around the nitrogen atoms which add up to 343.7° for N(1) and 344.5° for N(2) instead of 360°. The tetrahedral character of the nitrogen atoms is definitely larger than that found in the TMPD,[21] *N*,*N*-dimethyl-*p*-phenylenediamine[20] and phenylenediamine[22] complexes with tetracyanobenzene, in which the donor molecules also clearly show n donation, and probably results from the stronger charge-transfer interaction in the SO_2 complex.

The main interaction with the SO_2 molecule appears to occur at the sulfur atom since the N–S distances are considerably shorter than the corresponding intramolecular N–O distances (Table IV) and since projections of the nitrogen atoms onto the SO_2 planes fall on the bisectors of the *obtuse* O–S–O

Table IV. Nonbonded Intra- and Intermolecular Distances (Å)[a]

Intramolecular Distances			
S(1)–C(11)	3.024	S(2)–C(21)	3.015
S(1)–C(12)	3.044	S(2)–C(22)	3.051
S(1)–C(1)	3.039	S(2)–C(4)	3.011
O(11)–N(1)	2.913	O(21)–N(2)	2.902
O(11)–C(1)	3.238	O(21)–C(4)	3.073
O(11)–C(2)	3.469	O(21)–C(5)	3.175
O(12)–N(1)	2.918	O(22)–N(2)	2.915
O(12)–C(1)	3.185	O(22)–C(4)	3.303
O(12)–C(6)	3.206	O(22)–C(3)	3.425

All Intermolecular Distances Less Than 3.5 Å			
O(11)–C(12) (45404)[b]	3.332	S(2)–O(21) (65702)	3.452
O(12)–C(11) (65501)	3.394	O(21)–O(21) (65702)	3.315
O(12)–C(2) (65501)	3.399	O(21)–C(12) (55504)	3.416
O(12)–C(22) (55602)	3.493	O(22)–O(22) (55702)	3.440
S(2)–O(22) (55702)	3.329	O(22)–C(21) (45501)	3.495

[a] Symmetry relations are indicated by the atom designator code used in ORTEP.[25] Symmetry relations are with respect to the coordinates listed in Table II. [b] (01) x, y, z; (02) $-x, -y, -z$; (03) $-x, {}^1/_2 + y, {}^1/_2 - z$; (04) $x, {}^1/_2 - y, {}^1/_2 + z$.

angles, about 0.61 Å from the respective sulfur atoms. In theoretical considerations, Walsh[23] concluded that the lowest unoccupied molecular orbital (LUMO) of SO_2 was localized mainly on the sulfur and composed of contributions from the p atomic orbitals of each atom. However, Dunitz[24] has emphasized the importance of including some sulfur d-orbital contribution in the LUMO of SO_2 and a recent more quantitative orbital scheme[18] includes significant oxygen participation. In each of these treatments, the LUMO of SO_2 is described as a π-antibonding type orbital and, in this sense, SO_2 might be considered a π acceptor. In the complex, the interaction at the sulfur rather than the oxygens of SO_2 probably results from the decreased electron density on that atom.[18]

The angle (α) between the N–S bonds and the perpendicular of the SO_2 plane is 15.2° for both charge-transfer bonds. This value is definitely smaller than the 22° found in the trimethylamine complex[2] and is the smallest angle observed so far. In four organometallic complexes[3–6] of SO_2, α varies between 21 and 32°. Considering the lowest unoccupied molecular orbital of sulfur dioxide,[18] it has been shown that maximum overlap between the donor and acceptor molecules occurs when α is 35°.[2,19] The discrepancies between the theoretical and observed values are probably the result of inaccuracies in the molecular orbital expression and changes in the molecular orbitals of SO_2 on complex formation.

The first impression of the complex is that it contains a center of symmetry. There are however small but significant distortions from this symmetry. Table V lists a number of conformational angles. They show that there is no rotation around the N(2)–C(4) bond, but a significant rotation around the N(1)–C(1) bond (6.5°). It is interesting to note that S(1) follows the rotation of the N(1) atom and the nonbonding electrons of the atom. This can be seen from the fact that the angle between the plane through the S(1), N(1), and C(1) atoms and the phenyl group is 83.7° (Table VI), while the angle of the S(2)–N(2)–C(4) plane with the phenyl group is 89.0°. There are also rotations around the N–S bonds, a small one of 3° around the N(1)–S(1) bond and a large one of 11.5° around N(2)–S(2) bond. The latter can be understood from intermolecular contacts of the S(2)–O(21)–O(22) groups across a crystallographic center of symmetry. The rotations around the C–N and N–S bonds can also be seen in the intramolecular nonbonded distances (Table IV) and the distances of various atoms from the least-squares plane through the phenyl group (Table VI). The phenyl group is perfectly planar; also the hydrogen atoms bonded to C(2), C(3), C(5), and C(6) are located in this plane (Table VI). The nitrogen atoms are significantly displaced from this plane in the direction of the respective sulfur atoms with which they interact. The displacements, however, are different: 0.055 Å for N(1) and 0.079 Å for N(2). We are not able to find a reasonable explanation for this difference.

Table V. Conformational Angles (deg)[a]

C(11)–N(1)–C(1)–C(2)	18	C(22)–N(2)–C(4)–C(3)	25
C(12)–N(1)–C(1)–C(2)	152	C(21)–N(2)–C(4)–C(3)	160
C(11)–N(1)–C(1)–C(6)	−165	C(22)–N(2)–C(4)–C(5)	−160
C(12)–N(1)–C(1)–C(6)	−31	C(21)–N(2)–C(4)–C(5)	−25
O(11)–S(1)–N(1)–C(12)	182	O(21)–S(2)–N(2)–C(22)	191
O(12)–S(1)–N(1)–C(12)	67	O(22)–S(2)–N(2)–C(22)	−52
O(11)–S(1)–N(1)–C(11)	−61	O(21)–S(2)–N(2)–C(21)	75
O(12)–S(1)–N(1)–C(11)	184	O(22)–S(2)–N(2)–C(21)	192
O(11)–S(1)–N(1)–C(1)	61	O(21)–S(2)–N(2)–C(4)	−47
O(12)–S(1)–N(1)–C(1)	−54	O(22)–S(2)–N(2)–C(4)	70

[a] The angles listed are the ones necessary to obtain the observed conformations from the cis conformation. Only relative values are important because the space group is centrosymmetric.

Table VI. Least-Squares Planes[a]

	A	*B*	*C*	*D*
Plane 1: S(1), O(11), O(12)	−3.1785	−3.5506	12.4941	3.5022
Plane 2: S(2), O(21), O(22)	−2.1456	−2.4333	12.4143	10.7994
Plane 3: C(1), C(2), C(3), C(4), C(5), C(6)	2.6183	−5.7433	−12.0938	−8.1699

Distances from Plane, Δ(3), Å					
C(1)	−0.002	N(1)	0.055	H(C2)	0.03
C(2)	0.004	C(11)	−0.287	H(C3)	−0.02
C(3)	−0.005	C(12)	−0.575	H(C5)	−0.04
C(4)	0.004	S(1)	2.326	H(C6)	0.01
C(5)	−0.002	N(2)	−0.079		
C(6)	0.001	C(21)	0.382		
		C(22)	0.388		
		S(2)	−2.380		

Angles between Planes (Bonds), Deg			
Plane 1–plane 2	11.1	Plane 1–[N(1)–S(1)] (α)	15.2
Plane 1–plane 3	28.5	Plane 2–[N(2)–S(2)] (α)	15.2
Plane 2–plane 3	25.4		
Plane S(1), N(1), C(1)–plane 3	83.7		
Plane S(2), N(2), C(4)–plane 3	89.0		

[a] The planes are described with the expression $Ax + By + Cz = D$, in which x, y, and z are fractional coordinates and D is the distance of the plane from the origin.

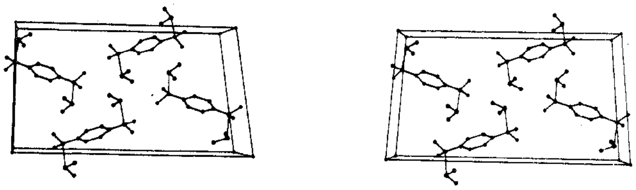

Figure 3. An ORTEP[25] plot of the molecular packing.

The internal bond angles of the phenyl group (Figure 2) fall in two groups: the bond angles for C(1) and C(4) are significantly smaller than those for C(2), C(3), C(5), and C(6). The same observation has been made in the tetracyanobenzene complexes with phenylenediamine and its di- and tetramethyl derivatives.[20–22] This difference is not clearly reflected in the bond distances, because, although the average of the distances associated with the C(1) and C(4) atoms is longer than the average of the C(2)–C(3) and C(5)–C(6) bonds, the difference is not significant: 0.002 Å.

The molecular packing is shown in Figure 3. The environment of the two SO_2 groups is dissimilar. The S(2)–O(21)–O(22) group is primarily in contact with other SO_2 groups, while the S(1)–O(11)–O(12) group has fewer intermolecular contacts less than 3.5 Å, and those only with carbon atoms. Although dipolar interactions should be important in the packing of the molecules, we cannot recognize a simple or predominant arrangement of dipoles.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 per photocopy or \$2.50 for microfiche, referring to code number AIC40729V.

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Preparation, Crystal Structure, and Properties of $NH_4ReO_{1.5}F_3 \cdot H_2O$

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Single crystals of $NH_4ReO_{1.5}F_3 \cdot H_2O$ have been prepared and characterized. The material is synthesized by allowing ammonium perrhenate, rhenium metal, and ammonium hydrogen fluoride to react under a hydrostatic pressure of 20,000 psi at 400°. The product crystallizes in the cubic system, space group $Fm3m$, with $a_0 = 16.563\ (6)$ Å; $\rho_{\text{exptl}} = 3.57\ (2)$ g cm^{-3}, and $\rho_{\text{calcd}} = 3.55$ g cm^{-3} for $Z = 32$. The structure consists of isolated $Re_8O_{12}F_{24}$ units bridged by ammonium ions and body-centered rhombic dodecahedra of water molecules. The material has unpaired electrons, as shown by its temperature-dependent paramagnetism, and is an insulator because of the isolation of the $Re_8O_{12}F_{24}$ units.

Introduction

The substitution of fluorine for oxygen in transition metal oxides changes the transport properties of these materials.[1-5] The preparation and properties of members of the series $MO_{3-x}F_x$ (M = W, Mo) have been studied by a number of investigators.[1,3,5] As fluorine is substituted for oxygen into MoO_3 and WO_3, the resulting oxyfluorides $MoO_{3-x}F_x$ and $WO_{3-x}F_x$ become metallic.[3,5]

ReO_3 crystallizes with the perovskite (ABO_3) structure with the A sites vacant. Goodenough[6] has proposed a conduction mechanism for the ReO_3-type compounds involving a strong covalent mixing between the metal t_{2g} and the oxygen p_π orbitals. When the resulting band is partially occupied, as in ReO_3, metallic behavior is observed. Whereas the substitution of oxygen by fluorine increases the electron concentration in this band, it may also decrease the degree of delocalization of the electrons, since fluorine is more electronegative than oxygen. It would, therefore, be of interest to study the effect of the substitution of oxygen by fluorine in metallic ReO_3.

The existence of several unstable, hygroscopic rhenium oxyfluorides such as $ReOF_4$, $ReOF_3$, ReO_3F, and ReO_2F_2 has been described by various investigators,[7-9] but the system $ReO_{3-x}F_x$ has not been reported. An attempt was made to prepare members of this system by hydrothermal synthesis similar to the procedures described for the preparation of $MoO_{3-x}F_x$; however, no appreciable fluorine substitution was observed when aqueous solvents were employed. It was, therefore, necessary to develop a new technique which involves the application of hydrostatic pressure to molten salts. Ammonium hydrogen fluoride was chosen as the molten salt because it is a low-melting solid (125°), a strong fluorinating agent, and a nonaqueous solvent. The reaction of ammonium perrhenate and rhenium metal in the presence of this compound yielded a new phase with the composition $NH_4ReO_{1.5}F_3 \cdot H_2O$. Lustrous black octahedral crystals (0.05–0.50 mm on edge) of this compound were obtained.

This paper describes the preparation of this compound and the characterization of the material by chemical analysis, density measurements, X-ray structure determination, and nuclear magnetic resonance techniques.

Experimental Section

Preparation of Materials. $NH_4ReO_{1.5}F_3 \cdot H_2O$ single crystals were synthesized with the hydrothermal apparatus described previously.[3] A mixture of spectroscopically pure ammonium perrhenate (J. Matthey and Co.), high-purity rhenium metal (Atomergic Chemicals Co.), and recrystallized ammonium hydrogen fluoride in the mole