Inorg. Chem. **1991**, *30*, 59-62 **59**

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Gas-Phase Structure of Sulfur Cyanate Pentafluoride, SF_5OCN. Electron Diffraction and ab Initio Study

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Received March 15, 1989

The geometric structure of SF_5OCN was determined by gas-phase electron diffraction. The following parameters (r_a values with 3σ uncertainties) were obtained: C≡N = 1.162 (13) Å, O–C = 1.271 (13) Å, $(S–F)_{mean}$ = 1.554 (2) Å, S–O = 1.653 (6) Å, ∠SOC = 120.4 (13)°, ∠OCN = 175.3 (36)°, $\angle F_aSF_e$ = 90.4 (6)°, and tilt = 3.5 (11)° (tilt angle between the C_4 axis of the SF_5 group and the S–O bond, away from OCN group). These results are compared with the gas-phase structure of the analogous isocyanate SF_5NCO. The cyanate and isocyanate group have different substituent effects on the SF_5 moiety. Ab initio calculations (HF/4-31G*) reproduce the experimental geometries of both isomers satisfactorily and predict the energy of the cyanate to be 26 kcal/mol above that of the isocyanate.

Introduction

Remarkably little is known about geometric structures of covalent cyanates and about their stability relative to the corresponding isocyanates. A comprehensive review of the chemical and physical properties of these isomers is given in ref 2. The parent isocyanate, HNCO, has been known for more than 150 years,[3] and its geometry has been characterized extensively by infrared[4] and microwave[5] spectroscopy. The existence of cyanic acid, HOCN, however, has been disputed for many years.[2] It could be proven spectroscopically only by matrix infrared technique, being produced by photolysis of isocyanic acid[6] or fulminic acid, HCNO.[7] Alkyl- and aryl-substituted cyanates exhibit much higher stability and have been characterized by infrared, Raman, and NMR spectroscopy,[8] but no gas-phase structural studies have been reported. An X-ray investigation of (4-chloro-3,5-dimethylphenyl)cyanate resulted in mean bond lengths of C≡N = 1.14 Å and O–C = 1.27 Å.[9] The only cyanate whose gas-phase structure has been determined is SeF_5OCN, which has been studied by electron diffraction.[10] Since C, N, and O make very similar contributions to the scattering intensities, the cyanate and isocyanate structures fit the electron diffraction intensities equally well. The original model was selected on the basis of bond distances, which made the isocyanate structure more likely.[11] Subsequent NMR data, however, proved unambiguously, that this substance was the cyanate.[10]

In the present study we report an electron diffraction investigation of SF_5OCN, whose synthesis has been reported recently.[12] Spectroscopic data[12] unambiguously demonstrate its cyanate structure. Since the geometry of the analogous isocyanate, SF_5NCO, has previously been studied by the same method,[11] these two compounds present the first example where geometric structures of corresponding isomers can be compared. The experimental investigation is supplemented by ab initio calculations, which also give information about their relative stability.

Table I. Experimental and Calculated Geometric Parameters (in Å and deg) for SF_5OCN and SF_5NCO

	SF_5OCN		SF_5NCO	
	ed[a]	ai[b]	ed[c]	ai[b]
C≡N; N=C	1.162 (13)	1.131	1.234 (8)	1.203
O–C; C=O	1.271 (13)	1.289	1.179 (7)	1.136
$(S–F)_{mean}$	1.554 (2)	1.546	1.567 (2)	1.557
$\Delta = r(SF_e) - r(SF_a)$	0[d]	0.005	0[d]	0.002
S–O; S–N	1.653 (6)	1.648	1.668 (6)	1.661
∠SOC; ∠SNC	120.4 (13)	122.2	124.9 (12)	130.4
∠OCN; ∠NCO[e]	175.3 (36)	176.9	173.8 (37)	174.2
$\angle F_aSF_e$	90.4 (6)	90.3	90[d]	88.8
tilt[f]	3.5 (11)	2.0	0[d]	1.3

[a] r_a values from electron diffraction experiment. Estimated uncertainties are 3σ values and include a possible scale error of 0.1%. [b] r_e values from ab initio calculations (HF/4-31G*). [c] r_a values from ref 11. [d] Not refined. [e] Bending of OCN or NCO group in trans direction with respect to sulfur. [f] Tilt angle between C_4 axis of the SF_5 group and SO/SN bond direction. Tilt is away from the OCN or NCO group.

Ab Initio Calculations

In a preceding theoretical study on geometric structures and relative stabilities of cyanates and isocyanates, ab initio calculations with different basis sets and at various levels of theory (HF or MP2) were performed.[13] In the isocyanates polarization functions have a very strong effect on the nitrogen bond angles. Basis sets without polarization functions (3-21G) result in linear XNCO structures, whereas experimental nitrogen bond angles in HNCO and ClNCO are reproduced correctly if polarization functions are included. In the cyanates, XOCN, polarization functions show only minor effects on the oxygen bond angles (decrease of ca. 5°). Bond distances in the NCO group are predicted very well with 3-21G basis sets, whereas 6-31G* basis sets result in bond lengths that are too short. This excessive shortening is compensated if electron correlation effects are taken into account. Obviously, it is not feasible to apply the MP2/6-31G* procedure to the compounds of this study and HF/4-31G* calculations were considered to be an adequate compromise for a structure optimization. The theoretical results are presented in Table I together with the experimental structures. Since the SF_5 groups were constrained to C_{4v} symmetry in the experimental analyses for the cyanate and the isocyanate, the same constraint was applied to the ab initio optimizations. Test calculations[13] for XOCN and XNCO show that basis sets without polarization functions (HF/3-21G) underestimate the energy differences between cyanates and isocyanates compared to basis sets with polarization functions (HF/6-31G*) by about 3 kcal/mol for X = H and by about 19 kcal/mol for X = Cl. Inclusion of electron correlation in the MP2 approximation changes the relative energies only by 1-2 kcal/mol for X = H, CH_3, Cl, or F. These calculations suggest that the HF/4-31G* method gives a realistic estimate of the energy difference between SF_5OCN and SF_5NCO. All calculations were performed with the GAUSSIAN 82 program

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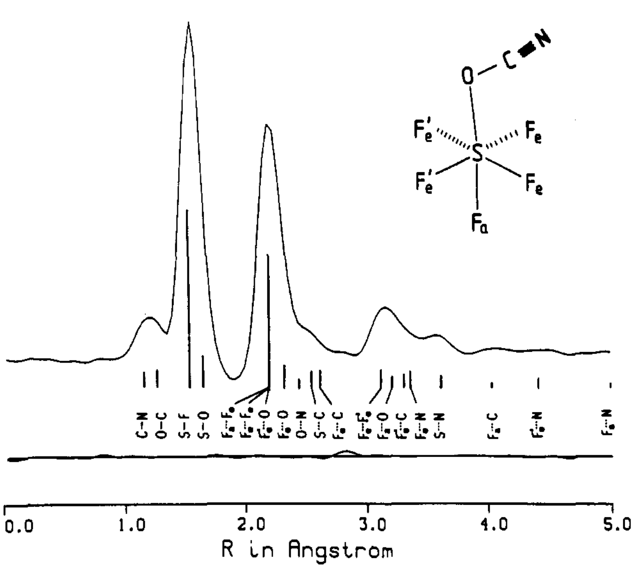

Figure 1. Experimental radial distribution function and difference curve.

Table II. Vibrational Amplitudes (in Å) for SF_5OCN[a]

C≡N	0.046 (23) (l_1)	$F_e\cdot\cdot F_e'$	0.059 (12) (l_5)
O—C	0.043 (24) (l_2)	$F_a\cdot\cdot O$	
S—F	0.045 (3) (l_3)	$S\cdot\cdot C$	0.070 (17) (l_6)
S—O		$S\cdot\cdot N$	0.072 (18) (l_7)
$F_a\cdot\cdot F_e$	0.058 (4) (l_4)	$F_e\cdot\cdot C$	0.22[b]
$F_e\cdot\cdot F_e$		$F_e\cdot\cdot N$	
$F_e'\cdot\cdot O$		$F_e'\cdot\cdot C$	0.20 (7) (l_8)
$F_e\cdot\cdot O$		$F_e'\cdot\cdot N$	
O··N	0.055[b]	$F_a\cdot\cdot C$	0.14 (8) (l_9)
		$F_a\cdot\cdot N$	

[a] Error limits are 3σ values. For atom labeling, see Figure 1. [b] Not refined.

package[14] on a BASF 7/88 computer.

Experimental Structure Analysis

A preliminary structural model for SF_5OCN was derived from the radial distribution function (Figure 1) and was then refined by a least-squares analysis of the molecular intensities. The impurity that was observed in the liquid phase (<3% ClCN) could not be detected in the diffraction pattern of the vapor. In the least-squares procedure a diagonal weight matrix was applied to the intensities and scattering amplitudes and phases of Haase were used.[15] The SF_5 group was constrained to C_{4v} symmetry with equal axial and equatorial bond lengths. Ab initio calculations predict the difference between S–F bond lengths to be very small (see Table I). The OCN group was fixed at the staggered position with respect to the equatorial fluorines, and a tilt angle between the C_{4v} axis and the S–O bond was introduced. The bond lengths in the cyanate group are not well determined in the electron diffraction experiment, because (i) their contributions to the molecular intensities or radial distribution function (peak at 1.22 Å in Figure 1) are small compared to those of the S–F bonds and (ii) these bond lengths are highly correlated with their vibrational amplitudes (see below). Although these amplitudes are determined with large uncertainties (see Table II), they were not fixed in the least-squares analysis, and their refinement results in "realistic" values for the standard deviations of the bond lengths. Vibrational amplitudes were grouped according to their distances and/or type. Constraints are evident from Table II. With the above assumptions eight geometric parameters and nine amplitudes were refined simultaneously and the following correlation coefficients had values larger than |0.6|: $\angle F_aSF_e$/tilt = 0.88, CN/l_1 = 0.71, OC/l_2 = −0.70, SO/l_3 = −0.69, and l_1/l_2 = 0.83. The results are presented in Table I (geometric parameters) and Table II (vibrational amplitudes). Estimated uncertainties are 3σ values and include a possible scale error of 0.1% for bond lengths. Test calculations demonstrate that introducing small differences between amplitudes that have been grouped together or distorting the SF_5 group slightly from the C_{4v} symmetry affects skeletal parameters only within their estimated uncertainties.

In the electron diffraction analysis for SF_5NCO, which was performed eight years ago,[11] two additional geometric constraints were applied: all FSF angles were set to 90°, and the S–N bond was assumed to be colinear with the C_4 axis of the SF_5 group (tilt = 0°). To allow strict comparison between the cyanate and isocyanate structures, the analysis for the isocyanate was repeated by applying the same constraints as used for the cyanate (see above). Thereby, the F_aSF_e angle decreases to 89.0 (6)° and the refined tilt angle is 0.2 (26)°. Since all other geometric parameters change by less than their experimental uncertainties, the values of the original analysis[11] are used for comparison.

Results and Discussion

Table I compares experimental and calculated structures of SF_5OCN with those of the corresponding isocyanate. As expected, the formal C≡N triple bond in the cyanate is shorter than the N=C double bond in the isocyanate. On the other hand, the O–C single bond in the cyanate is longer by about 0.1 Å than the C=O double bond in the isocyanate. This experimental single bond is much shorter than the Schomaker–Stevenson rule predicts for such an O–C(sp) bond (1.34–1.39 Å).[16] This discrepancy can possibly be explained by two effects: (i) the oxygen covalent radius used in the above estimate applies to sp^3 hybridization, whereas the oxygen bond angle is ca. 120° in SF_5OCN, and (ii) the above rule underestimates the polarity of this bond. The ab initio calculations predict all multiple bonds too short,[17] and the calculated O–C single bond is slightly longer than the experimental value. The experimental bond lengths of the cyanate group agree with those in the corresponding selenium compound, SeF_5OCN[10] (C≡N = 1.181 (10) Å, and O–C = 1.257 (10) Å) within their combined error limits.

The S–O bond in the cyanate (1.653 (6) Å) is longer by about 0.07 Å than this bond in the oxide $(SF_5)_2O$[22] (1.586 (11) Å). This difference is even larger in the analogous selenium derivatives (Se–O = 1.794 (6) Å in SeF_5OCN[10] and 1.697 (13) Å in $(SeF_5)_2O$[20]). This large variation of S–O and Se–O bond lengths is partly due to the increased oxygen bond angles in the oxides (about 142°), which lead to higher s character in these bonds, and possible also due to higher polar effects in the oxides relative to the cyanates. The S–N bond in the isocyanate is only slightly shorter than such bonds in amines with three-coordinate nitrogen (e.g. 1.679 (7) Å in $(SF_5)_2NH$[21] or 1.685 (5) Å in $(SF_5)_2NF$[21]). The oxygen bond angle in the cyanate (120.4 (13)°) is smaller than the nitrogen bond angle in the isocyanate (124.9 (12)°), but it is considerably larger than expected for a formally sp^3-hybridized oxygen. For cyanates with small substituents (H, CH_3, Cl, F) ab initio calculations[13] predict oxygen angles between 104.2 and 113.5°, and for SeF_5OCN the electron diffraction experiment results in an SeOC angle of 116.8 (8)°. Thus, we conclude that the larger value in the SF_5 derivative is a consequence of steric interactions. The nonbonded $F_e\cdot\cdot C$ distances are only 2.60 Å.

The comparison in Table I reveals that cyanate and isocyanate groups have different structural effects on the SF_5 moiety. In SF_5NCO the mean S–F bonds are slightly longer relative to SF_6[22]

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(1.5623 (4) Å). This trend is in agreement with that in all other monosubstituted SF_6 derivatives, whose structures have been determined in the gas phase. In XSF_5 compounds with X = Cl,[23] Br,[24] CF_3,[25] $CH{=}CH_2$,[26] $C{\equiv}CH$,[27,28] and CH_3,[29] the S–F bonds lengthen with decreasing electronegativity of the substituents, suggesting that this variation is due to electrostatic effects. Decreasing electron-withdrawing ability of the substituent decreases the positive sulfur net charge and thus lowers the attractive $S^{\delta+}$–$F^{\delta-}$ interaction. The cyanate is an exception, insofar as the S–F bonds (1.554 (2) Å) are shorter than those in SF_6. The same trend is observed for the analogous selenium compounds, where Se–F = 1.677 (2) Å in the cyanate[10] and 1.684 (2) Å in SeF_6.[30] If the electrostatic model described above is applied to the cyanates, this would imply a higher electron-withdrawing ability of the OCN group relative to that of fluorine. Mulliken population analyses for the sulfur derivatives indicate that the cyanate group is a stronger electron-withdrawing ligand than the isocyanate group (net charges of −0.50 and −0.30 au for OCN and NCO, respectively), but the OCN net charge is only marginally higher than that of the fluorine atoms (−0.48 au). Thus, electrostatic contributions explain trends in S–F bonds correctly but not the actual size of the effects.

In SF_5OCN the equatorial fluorines are bent slightly toward oxygen (F_aSF_e = 90.4 (6)°). In the analysis for SF_5NCO this angle was constrained to 90°, but refinement of this parameter (see above) results in a slight bend away from nitrogen (F_aSF_e = 89.0 (6)°). Although these deviations from the 90° angles in SF_6 are smaller or only marginally larger than the respective error limits, they appear to be real as demonstrated by the ab initio results. In the VSEPR picture these angles indicate a higher polarity of the S–O bond and a lower polarity of the S–N bond relative to S–F_a and are consistent with the variations of the S–F bond lengths.

Our experimental data do not allow any conclusion about the stability of the cyanate relative to the isocyanate. The calculated energy difference, *E*(cyanate) − *E*(isocyanate), of 26 kcal/mol is close to that predicted[13] for cyanic acid (24 kcal/mol) and for the methyl derivative (27 kcal/mol), but it is smaller than the relative energies of the chlorine (36 kcal/mol) or fluorine cyanates (44 kcal/mol).

Experimental Section

Materials. Freon 12 was dried over P_2O_5 (Merck). The compounds SF_5OCl[31] and $Cl_2C{=}NCl$[32] were prepared by using the literature methods. SF_5OCl was stored over CsF (Ventron) at −78 °C in a 100-mL steel autoclave.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass or metal vacuum apparatus. Volatile starting materials were measured quantitatively by weight. IR spectra were recorded on a Perkin-Elmer 983 spectrometer with a 10-cm gas cell fitted with KCl windows. Raman spectra were obtained with a Cary 82 instrument equipped with a Spectraphysics argon laser using the 488-nm exciting line. The ^{19}F and ^{14}N NMR spectra were recorded on a JOEL FX 90Q instrument with $CFCl_3$ and NH_4NO_3 as external reference standards at 84.24 and 6.43 MHz. Mass spectra were obtained on a Varian MAT 711 instrument at 80 eV. Gas chromatographic separations were carried out with an ERBA Science Fractovap equipped with a gas inlet. For the ultrasound reaction an ultrasound bath with 2-L contents from SONOREX was used.

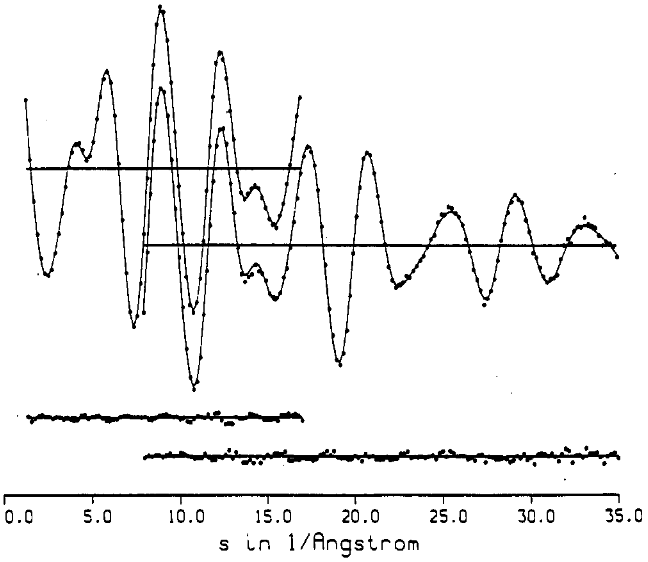

Figure 2. Experimental (dots) and calculated (full line) molecular intensities and differences.

Preparation of Dichloro((pentafluorothio)oxy)-*N*,*N*-dichloromethanamine, $SF_5O{-}CCl_2{-}NCl_2$. The preparation was modified compared to ref 12. SF_5OCl (63 mmol) was purified by fractional condensation through traps kept at −115 and −196 °C to remove traces of SOF_4 and ClF. The pure SF_5OCl was collected in the −115 °C trap. A 40-g amount of CF_2Cl_2 (Freon 12) and $Cl_2C{=}NCl$ (183 mmol) were condensed at −196 °C into this trap. The mixture was shaken occasionally and allowed to warm slowly from −110 to −90 °C. Complete disappearance of the colorless intermediate precipitate indicates the termination of the reaction. Fractional condensation through traps at −20, −78, and −196 °C yielded $SF_5O{-}CCl_2{-}NCl_2$ (9.8 g, 55%) in the trap at −20 °C. The trap at −78 °C contained small amounts of $SF_5O{-}CCl{=}NCl$ and $CFCl_2NCl_2$ and the trap at −196 °C contained SOF_4 and Cl–CN, as determined by ^{19}F NMR and IR spectroscopy. $SF_5O{-}CCl_2{-}NCl_2$ is a colorless liquid, mp −39 °C, and must be stored at −78 °C. The compound undergoes chlorine elimination and decomposes at room temperature. The ^{19}F NMR spectrum exhibits an ab_4 pattern with δ_a = 64.2, δ_b = 71.1, and J_{ab} = 159 Hz. The IR spectrum (gas, 7 mbar) shows absorption bands at 1120 (m), 990 (s), 885 (s), and 800 (m) cm^{-1}. The mass spectrum exhibits *m*/*e* peaks consistent with the presence of the following ions: $(M - Cl_2)^+$, 29; CCl_2NCl^+, 60; SF_5^+, 67; $CClNCl^+$, 100; smaller fragment ions.

Preparation of Chloro((pentafluorothio)oxy)-*N*-chloromethanimine, $SF_5O{-}CCl{=}NCl$. A 250-mL Pyrex glass flask with vacuum glass valve equipped with a magnetic stirring bar was charged with 200 g of Hg. $SF_5O{-}CCl_2{-}NCl_2$ (10 mmol) was condensed under vacuum to the mercury. The mixture was stirred for 4 h at −20 °C. The crude product (2.4 g) was condensed slowly in a dynamic vacuum of 10^{-2} mbar into a trap at −196 °C and purified by fractional condensation through traps at −78 and −196 °C. The trap at −78 °C contained 2.1 g of $SF_5O{-}CCl{=}NCl$, both *E* and *Z* isomers (*E*:*Z* ratio = 60:40, as determined by NMR integration). The isomers can be separated by gas chromatography on a 2-m halocarbon chromosorb column. $SF_5O{-}CCl{=}NCl$ is a colorless liquid, bp 85.8 °C, mp −77.5 °C (*E* isomer), −87.0 °C (*Z* isomer). In the ^{19}F NMR spectrum both isomers exhibit an ab_4 pattern with δ_a = 63.1, δ_b = 67.6, and J_{ab} = 158.7 Hz (*E* isomer) and δ_a = 62.5, δ_b = 70.2, and J_{ab} = 158.7 Hz (*Z* isomer). The IR spectrum (gas, 10 mbar) shows absorption bands at 1600 (m), 1158 (m), 1120 (m), 940 (vs), 900 (s), 845 (s), and 610 (s) cm^{-1}. Bands in the Raman spectrum (liquid) appear at 1587 (w), 1562 (w), 1140 (w, b), 952 (w), 832 (w), 737 (vs), 704 (w), 668 (m), 640 (m), and 615 (s) cm^{-1}. The mass spectrum exhibits *m*/*e* peaks consistent with the presence of the following ions: M^+, 2; $(M - Cl)^+$, 0.5; SF_5^+, 100; $CClNCl^+$, 61.

Preparation of Sulfur Cyanate Pentafluoride, $SF_5{-}O{-}C{\equiv}N$. With 30 g of Hg in a 60-mL Pyrex glass ampule, $SF_5O{-}CCl{=}NCl$ (11 mmol) was condensed at −196 °C and sealed under vacuum. The sealed ampule was exposed to ultrasound for 2 h at 20 °C. Every 15 min the ampule was shaken to renew the surface of the Hg metal. The reaction is finished when the ampule contains a light gray powder and no more liquid components. The ampule was opened, and the volatile products were condensed in a trap at −196 °C. The crude product was fractionally condensated through traps at −78, −125, and −196 °C, yielding 1.1 g of $SF_5{-}OCN$ contaminated with Cl–CN (Cl–CN:$SF_5{-}OCN$ molar ratio = 60:40, as determined by integration of the ^{14}N NMR signals) as colorless

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crystals in the trap at −125 °C. SF_5–OCN can be separated by gas chromatography on a 4-m squalan chromosorb column at 45 °C, yielding 0.2 g of SF_5–OCN (10%). The purified SF_5–OCN contains less than 3% of Cl–CN and melts at −82 °C. The ^{19}F NMR spectrum exhibits an ab_4 pattern with $\delta_a = 51.7$, $\delta_b = 66.5$, and $J_{ab} = 147$ Hz. The ^{14}N NMR spectrum consist of one signal at $\delta = -194$ with $\upsilon_{1/2} = 57$ Hz. The IR spectrum (gas, 10 mbar) shows absorption bands at 2283 (m), 1111 (m), 944 (vs), 879 (vs), 736 (w), and 607 (s) cm^{-1}. Bands in the Raman spectrum (liquid) appear at 2284 (vs, p), 1118 (w, dp), 945 (w, p), 875 (w, p), 736 (vs, p), 643 (m, p), and 605 (w, p) cm^{-1}. The mass spectrum (*m/e*) indicates the presence of the following ions: $(M - F)^+$, 6.3; SF_5^+, 89.6; SF_4^+, 15.6; SF_3^+, 100; $CNOF^+$, 59.4.

Electron Diffraction. A sample of SF_5–OCN was transported to Tübingen, West Germany, in liquid nitrogen. The scattering intensities were recorded with a Balzers gas diffractograph[33] at two camera distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The electron wavelength was calibrated with ZnO diffraction patterns. The sample reservoir was kept at −50 °C and inlet system and nozzle were at room temperature. The camera pressure did not exceed 2×10^{-5} mbar during the experiment. Two photographic plates for each camera distance were analyzed by the usual procedures,[34] and the averaged molecular intensities for the scattering ranges 1.4–17 and 8–35 $Å^{-1}$ in steps of $\Delta s = 0.2$ $Å^{-1}$ are presented in Figure 2.[35]

Acknowledgment. We are grateful for financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supplementary Material Available: Tables of electron diffraction scattering intensities (2 pages). Ordering information is given on any current masthead page.

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A ^{183}W NMR Study of Mononuclear Tungsten(VI) Methyl Complexes Containing Terminal Oxo, Sulfido, and Imido Ligands

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Received May 25, 1990

The ^{183}W chemical shifts of a number of organometallic oxo–, sulfido–, and imido–tungsten(VI) complexes have been measured by indirect detection using $^1H\{^{183}W\}$ double-resonance and $^1H\{^1H,^{183}W\}$ triple-resonance techniques. The shielding trends within a series of ligands, including O^{2-}, S^{2-}, PhN^{2-}, Cl^-, Br^-, η^2-O_2^{2-}, and η^2-S_2^{2-}, are discussed with respect to ligand polarizability and bond multiplicity. The tungsten(VI) nuclei become more deshielded with increasing ligand polarizability and bond multiplicity. The ^{183}W chemical shifts of $Cp^*W({=}O)X_2Me$ complexes show an inverse halogen dependence, as expected from relative polarizability arguments.

Introduction

In our exploration of the chemistry of high oxidation state tungsten and molybdenum organometallics, ^1H NMR spectroscopy proved to be of limited value in some situations. Examination of compounds such as $Cp^*W({=}O)(\eta^2\text{-}O_2)Me$ and its sulfur analogues by ^1H NMR provides only two singlets, which are indicative, but not unequivocally characteristic, of a particular set of ligands. We anticipated that NMR data on the metal nuclei would provide better characterization of new complexes. In order to evaluate the diagnostic utility of ^{183}W chemical shifts for structural determination in these systems, we have compiled the data for a selected group of complexes. We have examined the relative importance of factors contributing to the magnetic shielding of tungsten nuclei in these complexes so as to provide some useful criteria for predicting chemical shifts for a given set of ligands.

Owing to the extremely low sensitivity of ^{183}W, the ^{183}W chemical shifts reported have been limited to a very small number.[1] In the past, the low NMR sensitivity of ^{183}W to detection had been overcome by employing double-resonance and triple-resonance techniques provided that resolvable coupling existed between ^{183}W and other relatively more sensitive nuclei such as ^1H, ^{19}F, and ^{31}P.[2-6] Although detection has been made easier in recent years with the introduction of more sensitive spectrometers and modern FT pulse experiments,[7] the more traditional techniques still remain useful, particularly for small quantities. In our preparation and characterization of high oxidation state organometallic tungsten(VI) complexes, we have noted that W(VI) complexes with alkyl ligands have fairly large couplings between ^{183}W and the α-H on the alkyl groups; values of $^2J_{W-H}$ vary from 4 to 11 Hz.[8] These relatively large $^2J_{W-H}$ have afforded ready access to the ^{183}W chemical shifts in these complexes upon application of double-resonance techniques. The variations in ^{183}W chemical shifts effected by ligand substitution will be presented in the context of providing some guidelines for interpretation of the observed shifts.

Experimental Section

Preparations of all the complexes used in this work except for $Cp^*W({=}O)({=}NPh)Me$ and $Cp^*W({=}O)Br_2Me$ have been described elsewhere.[8,9] The NMR sample of the complex $Cp^*W({=}O)({=}NPh)Me$ was prepared in situ by mixing $Cp^*W({=}O)Cl_2Me$ and a slight excess of aniline. The compound is extremely moisture sensitive, as is the case with most of the known imido complexes. As a result, no attempt at isolation was made. The presence of the imido complex was verified by mass spectroscopy of the sample mixture, which contained both the product $Cp^*W({=}O)({=}NPh)Me$ and $Cp^*W({=}O)_2Me$, the latter resulting from partial hydrolysis. The $Cp^*W({=}O)Br_2Me$ complex was prepared by stirring a diethyl ether solution of $Cp^*W({=}O)_2Me$ with an excess of Me_3SiBr overnight, which resulted in a yellow crystalline precipitate. The procedure is essentially similar to the preparation of the chloride analogue described in the literature.[9]

The ^{183}W resonance frequencies were obtained on a Bruker WM-500 spectrometer using $^1H\{^{183}W\}$ double resonance for most compounds and triple resonance in the case of $CpW({=}O)Me_3$, where ^1H decoupling of

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0020-1669/91/1330-0062$02.50/0 © 1991 American Chemical Society