

Articles

Synthesis and Structure of WNCl_3 and Evidence for Structural Modifications with Bound Chlorocarbon Solvents

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A convenient synthesis of WNCl_3 resulted from the reaction between WCl_6 and Me_3SiN_3 in 1:1 molar ratio in refluxing 1,2-dichloroethane (DCE) at 84 °C. The isolated material was shown by elemental analysis, IR, and NMR to be $\text{WNCl}_3 \cdot 1.1\text{DCE}$. Heating *in vacuo* at 160 °C was required to remove the DCE and give unsolvated $[\text{WNCl}_3]_4$. Crystals of the latter were grown by sublimation in a sealed tube under a temperature gradient of 290/300 °C. WNCl_3 is isostructural with MoNCl_3 ; triclinic $P\bar{1}$, $a = 7.752(2)$ Å, $b = 8.143(2)$ Å, $c = 9.114(2)$ Å, $\alpha = 98.71(3)^\circ$, $\beta = 107.52(3)^\circ$, $\gamma = 110.40(3)^\circ$, $Z = 4$, $R = 0.0431$, $R_w = 0.0554$. The structure is composed of $[\text{WNCl}_3]_4$ molecules interconnected through W—Cl—W bridge bonding. The tetramers consist of planar W_4N_4 rings with alternating short and long W—N bonds, with average distances of 1.696(7) and 2.082(7) Å, respectively, similar to several complexes $[\text{WNCl}_3 \cdot \text{L}]_4$ known previously.

WNCl_3 was prepared initially by Dehnicke et al. in 1965 by the reaction of WCl_6 and chlorine azide (ClN_3) in carbon tetrachloride at 30 °C.¹ More recent studies utilized trimethylsilyl azide² and tris(trimethylsilyl)amine³ as the nitriding reactants for the formation of MNCl_3 from molybdenum and tungsten halides, respectively. However, the reaction of $\text{W}(\text{CO})_6$ with NCl_3 in CCl_4 also provides a very efficient synthesis of WNCl_3 .⁴ MNCl_3 ($M = \text{Mo}, \text{W}$)¹ were characterized initially by infrared spectroscopy, X-ray powder diffraction, and elemental analyses. Since that time, related compounds such as $[\text{MoNCl}_3]_4$,⁵ $[\text{MoNCl}_3 \cdot \text{OPCl}_3]_4$,⁶ $[\text{WNCl}_3 \cdot \text{OPCl}_3]_4 \cdot 2\text{OPCl}_3$,⁷ $[\text{WNCl}_3 \cdot 0.5\text{HN}_3]_4$,⁸ and $[\text{WNCl}_3 \cdot \text{NCPH}]_4 \cdot 3\text{CH}_2\text{Cl}_2$ ⁹ have been characterized structurally by single-crystal X-ray diffraction methods. WNCl_3 was formulated as a polymer $[\text{WNCl}_3]_\infty$ in a 1981 review of metal nitride multiple bonding.¹⁰ On the basis of W—N—W interactions, two possibilities for polymeric WNCl_3 are readily apparent. One would possess an infinite zigzag chain geometry which has yet to be observed, and the other would contain a linear chain similar to those found in ReNCl_4 ¹¹ and $\text{WN}(\text{t-BuO})_3$.¹² However, the crystal structure of WNCl_3 as a compound uncoordinated by other ligands has been conspicuously absent from the literature.¹³

In order to increase the utility of WNCl_3 as a starting material for subsequent research, a new method for production of WNCl_3 has been developed which yields relatively pure WNCl_3 in high yields. Through the metathesis reaction between trimethylsilyl azide and hexachlorotungsten(VI), two modifications of $[\text{WNCl}_3]_4$ can be produced. The structure of $[\text{WNCl}_3]_4$ has been determined by single-crystal X-ray methods. Three different compounds of WNCl_3 have been identified by single-crystal and powder X-ray diffraction, and the differences in structure have been attributed to the interactions of solvent molecules with the $[\text{WNCl}_3]_4$ units and possibly variation of their mode of interconnection. In one crystallographic variation, solvent appears to coordinate to the tungsten, trans to the W—N multiple bond, thus disrupting the packing and inter-chloride linking of adjacent tetrameric $[\text{WNCl}_3]_4$ units.

Experimental Section

Materials. All the materials are extremely reactive with oxygen and water. Manipulations of oxygen- and water-sensitive compounds were performed under inert-atmosphere conditions using standard drybox, vacuum, and Schlenk techniques.

Dichloromethane and 1,2-dichloroethane (DCE) were dried by standard methods. Tungsten hexachloride was obtained from Pressure Chemical Co. and sublimed under conditions for removal of the more volatile WOCl_4 . Trimethylsilyl azide (TMSA) was obtained from Petrarch Chemical Co. and used as received.

Synthesis. In a typical preparation, a solution of DCE (15 mL) and TMSA (2.34 mL, 17.6 mmol, 2.03 g) was added dropwise (approximately 3 drops/s) to a refluxing solution of WCl_6 (6.975 g, 17.6 mmol) in DCE (80 mL). During the reaction, the color of the solution remained purple but the color of the particulate solid changed from purple to orange-brown after 2 days. The reaction solution was allowed to continue at refluxing temperature for 3 days. Solid orange-brown WNCl_3 was isolated by filtration and purified by a 2 day extraction with DCE to remove soluble silane compounds or WCl_6 . The solid was then dried under vacuum for a period not less than 12 h and isolated in a drybox. A typical yield was 4.20 g (78.5%). The WNCl_3 was then heated under dynamic vacuum at 160 °C for 12 h to eliminate DCE and WCl_6 . Anal. Calcd for WNCl_3 : W, 60.43; Cl, 34.96; W:Cl, 1:3.00. Found (before heating): W, 55.18; Cl, 32.53; W:Cl, 1:3.06.

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Table 1. Crystallographic Data for WNCl_3

chem formula	WNCl_3	$V, \text{Å}^3$	492.6(4)
fw	304.21	Z	4
space group	$P\bar{1}$	$T, ^\circ\text{C}$	22
$a, \text{Å}$	7.752(2)	$\lambda(\text{Mo K}\alpha), \text{Å}$	0.710 73
$b, \text{Å}$	8.143(2)	$\rho_{\text{calcd}}, \text{g/cm}^3$	4.102
$c, \text{Å}$	9.114(2)	μ, cm^{-1}	2.4891
α, deg	98.71(3)	R^a	0.0431
β, deg	107.52(3)	R_w^b	0.0554
γ, deg	110.40(3)		

$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Found (after heating): W, 60.32; Cl, 34.60; W:Cl, 1:2.98. IR (Nujol, cm^{-1})¹⁴ of WNCl_3 (before heating): 1082–1080 s, ca. 1086 sh ($\nu(\text{W}\equiv\text{N})$); 685 s ($\nu(\text{C}-\text{Cl})$); 400 s, 384 s, 371 s, 365 s, 358 s, 349 s, 343 s, 315 s ($\nu(\text{W}-\text{Cl})$). IR of WNCl_3 (after heating): 1082–1078 s, ca. 1086 sh ($\nu(\text{W}\equiv\text{N})$); 399 s, 389 sh, 378 s, 361 s, 356 sh, 331 s, 309 s ($\nu(\text{W}-\text{Cl})$).

Physical Measurements. Infrared spectra were obtained on an IBM IR/90 or a Bomem MB-Series Fourier transform infrared spectrometer. The samples were prepared as Nujol mulls and pressed between CsI plates. The spectra were recorded separately for the mid-IR (4000–600 cm^{-1}) and far-IR (600–200 cm^{-1}) in the case of the IBM spectrometer and from 4000 to 185 cm^{-1} with the Bomem spectrometer.

X-ray powder diffraction data were obtained from an Enraf-Nonius Delft triple-focusing Guinier camera using copper $\text{K}\alpha_1$ radiation ($\lambda = 1.540 56 \text{Å}$) or a Philips ADP3520 X-ray powder diffractometer or a Scintag $\theta-\theta$ diffractometer using $\text{Cu K}\alpha_1, \text{K}\alpha_2$ averaged radiation. An airtight cylindrical sample chamber for X-ray powder diffraction was designed and built to accommodate the air-reactive materials¹⁵ on the Philips diffractometer.

Crystal Growth. Crystals suitable for X-ray studies were obtained by sublimation in a controlled thermal gradient. Specifically, small samples of heated WNCl_3 (15 mg) were sealed under vacuum in 15 cm \times 1 cm (outer diameter) Pyrex tubes and placed in a two-zone furnace under a thermal gradient of 10 $^\circ\text{C}$ at several temperatures ranging from a 160/170 $^\circ\text{C}$ gradient to a 290/300 $^\circ\text{C}$ gradient. It was thus found that crystallites of sufficient size (3–400 μm) for single-crystal X-ray diffraction could be obtained by using a thermal gradient of 290/300 $^\circ\text{C}$ for 3 days.

Data Collection and Structural Determination. Data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer. Lattice parameters were determined from 15 reflections with $18.5 < 2\theta < 32.4^\circ$. Graphite-monochromated Mo $\text{K}\alpha$ radiation was used to collect the data with a 2θ range of 4–60 $^\circ$. The $\theta-2\theta$ scan technique was used. The data were corrected for Lorentz and polarization effects. The transmission factors, based on ψ scans, varied from 1.00 to 0.25. An empirical absorption correction based on the ψ scans was made. The intensities of three standard reflections were constant throughout the data collection; therefore a standard correction was not applied. A total of 5964 reflections were collected, of which 2581 were unique with $F_o/\sigma(F_o) > 4$. The structure was solved by direct methods and refined by full-matrix least-squares techniques to $R = 0.043$ and $R_w = 0.055$ using SHELXTL PLUS (PC version) software developed for the Siemens Corp. by G. Sheldrick. All atoms were located and refined anisotropically. The largest difference Fourier peaks were located at distances less than 0.90 Å from tungsten.

Details of the data collection are given in Table 1, and final atomic positional parameters and selected bond distances and angles are given in Tables 2 and 3, respectively.

Results and Discussion

Synthesis of $[\text{WNCl}_3]_4$. The following reactions, conducted in DCE at 84 $^\circ\text{C}$, illustrate the formation of WNCl_3 :

(14) Designations for IR peak intensities: s = strong, m = medium, w = weak, sh = shoulder.

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$) for $[\text{WNCl}_3]_4$

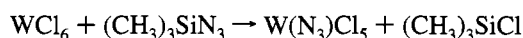
atom	x	y	z	$U(\text{eq})^a$
W(1)	−0.0136(1)	−0.0544(1)	0.7743(1)	15(1)
W(2)	0.1338(1)	0.3623(1)	0.6272(1)	15(1)
Cl(1)	−0.3145(3)	−0.0402(4)	0.7057(3)	32(1)
Cl(2)	−0.0756(3)	0.2310(3)	0.9465(2)	27(1)
Cl(3)	0.3234(3)	0.0477(3)	0.8865(3)	30(1)
Cl(4)	−0.1921(3)	0.3515(3)	0.5156(3)	24(1)
Cl(5)	0.2194(4)	0.5803(3)	0.8533(3)	33(1)
Cl(6)	0.4500(3)	0.4066(4)	0.6611(3)	33(1)
N(1)	−0.0645(10)	−0.2155(8)	0.6055(8)	20(3)
N(2)	0.0610(9)	0.1737(9)	0.6889(7)	1.6(1)

a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{WNCl}_3]_4^a$

W(1)–Cl(1)	2.276(3)	W(2)–Cl(4)	2.387(2)
W(1)–Cl(2)	2.328(3)	W(2)–Cl(5)	2.255(2)
W(1)–Cl(3)	2.276(2)	W(2)–Cl(6)	2.264(3)
W(1)–N(1)	1.705(7)	W(2)–N(1')	2.077(7)
W(1)–N(2)	2.085(7)	W(2)–N(2)	1.686(7)
W(1)–Cl(2a)	2.895(3)	W(2)–Cl(4a)	2.805(3)
Cl(1)–W(1)–Cl(3)	157.8(1)	Cl(4)–W(2)–Cl(6)	160.7(1)
Cl(1)–W(1)–Cl(2)	93.6(1)	Cl(4)–W(2)–Cl(5)	92.9(1)
Cl(1)–W(1)–N(1)	98.5(3)	Cl(4)–W(2)–N(1)	83.5(2)
Cl(1)–W(1)–N(2)	82.8(2)	Cl(4)–W(2)–N(2)	95.1(2)
Cl(2)–W(1)–Cl(3)	95.0(1)	Cl(5)–W(2)–Cl(6)	95.3(1)
Cl(2)–W(1)–N(1)	101.8(3)	Cl(5)–W(2)–N(1)	165.8(2)
Cl(2)–W(1)–N(2)	160.2(2)	Cl(5)–W(2)–N(2)	100.2(2)
Cl(3)–W(1)–N(1)	99.8(3)	Cl(6)–W(2)–N(1)	84.2(2)
Cl(3)–W(1)–N(2)	82.2(2)	Cl(6)–W(2)–N(2)	100.6(3)
N(1)–W(1)–N(2)	98.0(3)	N(1)–W(2)–N(2)	93.3(3)
W(1)–N(1)–W(2')	165.8(5)	W(1)–N(2)–W(2)	176.9(4)

a Numbers in parentheses are estimated standard deviations in the least significant digits.



The intermediate, $\text{W}(\text{N}_3)\text{Cl}_5$, is relatively stable in solution. When the reaction is conducted in refluxing dichloromethane (DCM) at 40 $^\circ\text{C}$, decomposition of the azide intermediate does not occur after 6 days, whereas in refluxing DCE at 84 $^\circ\text{C}$, complete decomposition of the azide occurs within 2 days. It was noted by Dehnicke and co-workers³ that at lower temperatures an insoluble μ -nitrido compound, $[\text{Cl}_4\text{WNWCl}_3]$, can be formed by reaction between WNCl_3 and WCl_6 . The formation of such a compound in this work was indicated in early reactions where high chloride analyses were obtained for the products. In order to avoid formation of the adduct, a TMSA/DCE solution was added directly to a refluxing solution of WCl_6 in DCE. The adduct was not observed, and relatively pure WNCl_3 was produced in yields above 75%. The IR spectrum of the product isolated from DCE always contained an unexpected band at 685 cm^{-1} , which was assigned to a C–Cl mode of bound DCE. Heating the WNCl_3 to 160 $^\circ\text{C}$ under dynamic vacuum was required to remove all of the DCE. The DCE was identified by ^1H NMR as the sole volatile component evolved under these conditions. On the basis of analytical data, the unheated compound has the composition $[\text{WNCl}_3]_4 \cdot 1.1\text{DCE}$.

Structure of $[\text{WNCl}_3]_4$. The crystals of sublimed WNCl_3 were shown to be composed of the tetramer, analogous to $[\text{MoNCl}_3]_4$, in which the four tungsten and four nitrogen atoms define a planar ring as shown in Figure 1. In the ring there are

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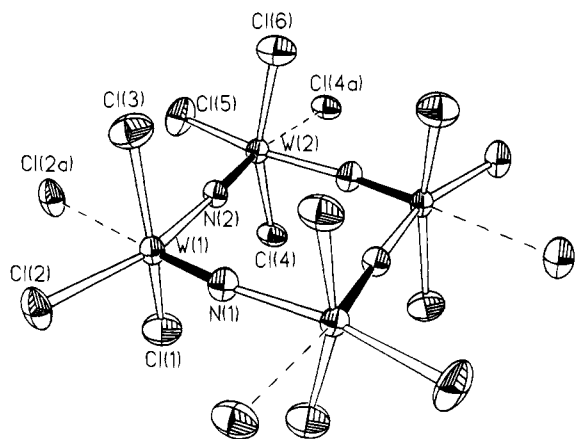


Figure 1. Structure of the molecular units $[\text{WNC1}_3]_4$ as represented by 80% thermal ellipsoids. Cl(2a) and Cl(4a) are atoms from adjacent molecules. An inversion center is located at the center of the W_4N_4 ring.

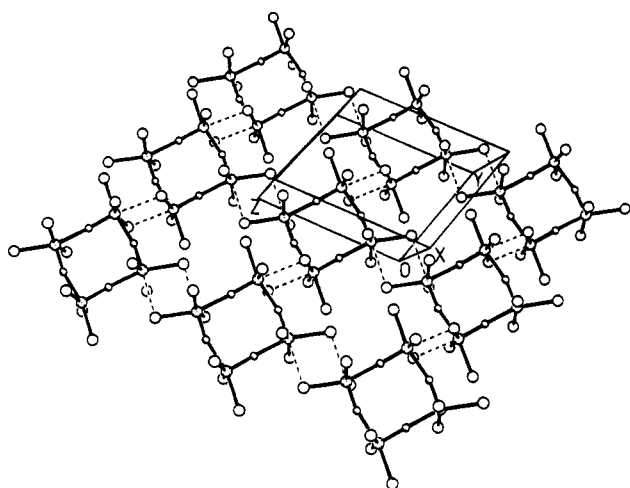


Figure 2. ORTEP drawing of the extended interactions of the WNC1_3 tetramers and outline of the unit cell.

essentially two significantly different tungsten–nitrogen bond lengths resulting from an alternated multiple bond/single bond W_4N_4 ring system. The multiple bond (formally a triple bond) was assigned a bond order of 2.4 by Goubeau¹⁶ on the basis of the IR stretching frequency and has a bond length of 1.696 Å (average), whereas 2.081 Å (average) is the length of the W–N single bond. Each tungsten in the discrete tetramer is coordinated by five atoms, resulting in a distorted square pyramid formed by the multiply bonded N at the apex and three chlorides and one nitrogen atom in the basal plane. An atom from an

adjacent tetramer is weakly bonded, $d(\text{W}–\text{Cl}) = 2.850$ Å (average) in the sixth site, trans to the W–N multiple bond, to complete a distorted octahedral coordination around tungsten. It is this sixth site that is potentially occupied by chlorine from DCE and probably accounts for the tenacious retention of DCE in the unheated material. Coordination of WNC1_3 by basic ligands occurs in this trans position as verified by several recent papers^{10,13} and should be the site of initial coordination of reactive molecules such as ammonia or trimethylsilyl azide. Because of the strong tungsten–nitrogen multiple bond, any coordinated ligand in the sixth position should be weakly bound, due to the trans influence.

The extended interactions of $[\text{WNC1}_3]_4$ in the solid state are of two types (Figure 2). Along the *c* axis the inter-ring chloride bridges lie in the plane of the tungsten–nitrogen heterocycles, whereas the chloride bridges along the *b* axis are essentially normal to the plane of the ring. This leads to W–Cl bonds of different lengths in the positions trans to the short W–N bonds. In turn, one might expect that the W–N short distances would also differ, depending on the trans W–Cl bond distance. However, the tungsten heterocycle does not show a significant difference in the W–N multiple bond distances, $d(\text{W}(1)–\text{N}(1)) = 1.705(7)$ and $d(\text{W}(2)–\text{N}(2)) = 1.686(7)$ Å, which could result from the difference in the dative Cl–W bond distances ($d(\text{W}(1)–\text{Cl}(X')) = 2.805(3)$, $d(\text{W}(2)–\text{Cl}(X'')) = 2.895(3)$ Å). The Mo–N multiple bond distances of the molybdenum analog⁵ show the indicated trend (Table 4), but again, these distances are not statistically different; therefore a meaningful conclusion cannot be determined.

The M_4N_4 ring is slightly more distorted in $[\text{WNC1}_3]_4$ relative to $[\text{MoNC1}_3]_4$. The deviations of W(1), W(2), N(1), and N(2) from a least-squares plane through the W_4N_4 ring were found to be 0.021, 0.045, 0.057, and 0.030 Å, respectively. The corresponding Mo_4N_4 deviations of 0.003, 0.010, 0.079, and 0.015 Å were reported for $[\text{MoNC1}_3]_4$.⁵ The bond lengths and angles of $[\text{WNC1}_3]_4$ are similar to those in previously prepared tungsten and molybdenum nitride tetramers (Table 4), within statistical deviation. The exception is found in the length of the M–N single and triple bonds, which are shorter and longer, respectively, in WNC1_3 relative to MoNC1_3 . This difference in bond lengths reflects a slightly stronger $\text{M}=\text{N}$ bond for MoNC1_3 compared to WNC1_3 .

WNC1_3 was initially investigated by X-ray powder diffraction.¹ In this study, powders of WNC1_3 were characterized by X-ray diffraction using the special environment cell for the Philips diffractometer described previously.¹⁵ A comparison between the X-ray powder data reported by Dehnicke¹ for WNC1_3 , that of the unheated WNC1_3 prepared in this investiga-

Table 4. Comparison of Bond Lengths (Å) in Selected $[\text{MNC1}_3]$ Tetramers

bond	$[\text{WNC1}_3]_4$ (1)	$[\text{MoNC1}_3]_4$ (2)	$[\text{WNC1}_3 \cdot 0.5\text{HN}_3]_4$ (3)	$[\text{WNC1}_3 \cdot \text{NCPH}]_4$ (4)	$[\text{WNC1}_3 \cdot \text{OPCl}_3]_4 \cdot 2\text{OPCl}_3$ (5) ^b
M(1)–N(1)	1.705(7)	1.638(10)	1.69(3)	1.65(2)	1.671(2)
M(1)–N(2)	2.085(7)	2.143(10)	2.11(3)	2.08(2)	2.169(3)
M(1)–Cl(1)	2.276(2)	2.278(9)	2.30(1)	2.280(6)	2.287(3)
M(1)–Cl(2)	2.328(3)	2.316(6)	2.27(1)	2.270(6)	2.336(3)
M(1)–Cl(3)	2.276(2)	2.276(5)	2.28(1)	2.291(6)	2.318(3)
M(1)–X' ^a	2.895(3)	2.937(7)	2.44(2)	2.49(2)	2.379(2)
M(2)–N(1)	2.077(7)	2.198(11)	2.08(3)	2.11(2)	2.163(2)
M(2)–N(2)	1.686(7)	1.672(10)	1.68(3)	1.70(2)	1.648(3)
M(2)–Cl(4)	2.387(2)	2.379(7)	2.26(1)	2.283(6)	2.318(2)
M(2)–Cl(5)	2.255(2)	2.241(10)	2.30(1)	2.315(6)	2.323(3)
M(2)–Cl(6)	2.265(2)	2.270(5)	2.38(1)	2.324(6)	2.359(3)
M(2)–X'' ^a	2.805(3)	2.822(7)	2.80(2)	2.28(2)	2.316(3)

^a Both X' and X'' represent Cl, N, or O atoms weakly bonded trans to the metal–nitrogen multiple bond. For molecules 1 and 2, X', X'' = Cl, for molecules 3 and 4, X', X'' = N, and for molecules 5a and 5b, X', X'' = O. ^b Contains two independent molecules in the unit cell. In the second molecule, corresponding distances are W(3)–N(3) = 1.556(2), W(3)–N(4) = 2.119(4), W(4)–N(4) = 1.691(2), and W(4)–N(3) = 2.420(3) Å.

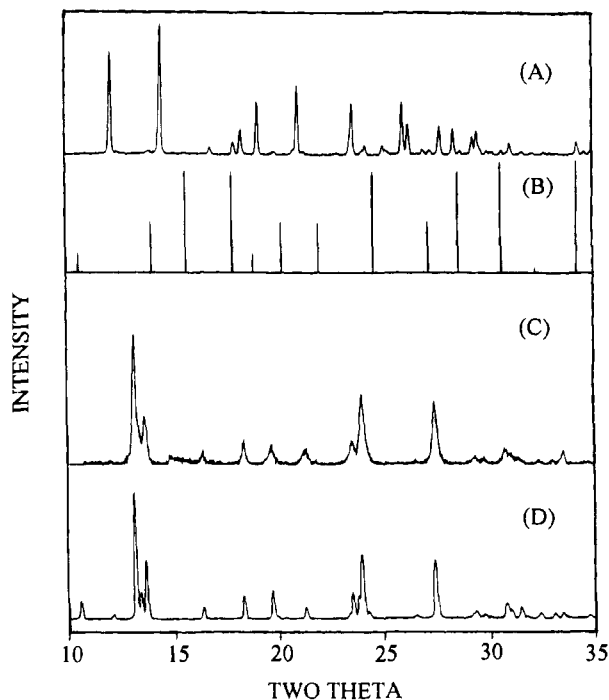


Figure 3. Comparison of X-ray powder diffraction data: (A) data for unheated sample of $[\text{WNCl}_3]_4 \cdot 1.1\text{DCE}$; (B) simulation pattern for WNCl_3 as reported by Dehnicke;¹ (C) data for sample of WNCl_3 after heating at 160°C *in vacuo* for 3 h; (D) calculated powder pattern based upon single-crystal data and structure refinement.

tion, that of WNCl_3 heated to 160°C under dynamic vacuum, and the calculated powder pattern, based on the unit cell information obtained from the $[\text{WNCl}_3]_4$ structural solution, indicates that there are at least three separate crystallographic modifications for WNCl_3 (Figure 3). The particular modification depends on the method of preparation. Many reflections were observed for each form of WNCl_3 , which indicates that each crystallizes in a lower symmetry group, probably triclinic. The diffraction pattern of the heated WNCl_3 and the simulated pattern are essentially the same. Because it is known that extraneous solvent molecules, even very weak donors, when coordinated trans to the multiply bonded nitrogen may cause a

disruption of the inter-tetramer $\text{W}-\text{Cl}$ linkage, it is likely that the structural variations are due to solvent molecules coordinating in these trans positions. The composition of the unheated material, $[\text{WNCl}_3]_4 \cdot 1.1\text{DCE}$, confirms this. On the basis of analytical data given by Dehnicke and Strähle, it is likely that their preparation of WNCl_3 contains some CCl_4 , either bound or incorporated in the lattice. Thus three variations of the WNCl_3 extended lattice have been found, but it is likely that other modifications can form if different solvents are used in the preparation.

Physical Measurements. Infrared spectroscopy has been used extensively to characterize these molybdenum and tungsten tetramers. The utility of IR is based on the strong stretching mode of the metal–nitrogen multiple bond and the sensitivity of the $\text{W}-\text{Cl}$ stretching frequencies. The $\text{W}-\text{N}$ multiple bond IR stretching frequency was reported¹ at 1068 and 1084 cm^{-1} . The IR spectra for every sample of WNCl_3 synthesized in this work have shown strong bands at 1076 – 1086 cm^{-1} with weak shoulders at lower energy. The IR spectrum for a sample prepared from single crystals of sublimed $[\text{WNCl}_3]_4$ shows a single peak at 1086 cm^{-1} corresponding to the $\text{W}-\text{N}$ multiple bond stretch, while the unheated heated and unheated WNCl_3 exhibit a major peak at 1076 – 1082 cm^{-1} and a shoulder at ca. 1086 cm^{-1} . On the basis of the $\text{W}-\text{N}$ stretching modes, a distinction cannot be made between the heated and unheated WNCl_3 , but the variation in $\text{W}-\text{Cl}$ vibrational modes between these two modifications presents additional evidence for crystallographic differences between the two compounds. It is reasonable that the number and frequencies of the bands should depend upon the crystal modification, solvent coordination, and mode of connection between cluster units.

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Supplementary Material Available: Full details of the crystallographic data (Table I-S) and anisotropic thermal parameters (Table II-S) (2 pages). Ordering information is given on any current masthead page.