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REACTIONS OF COORDINATED MOLECULES

XI *. THE REACTION OF THE RHENIUM TETRACARBONYL METALLO-ACETYLACETONE COMPLEX WITH HYDRAZINES

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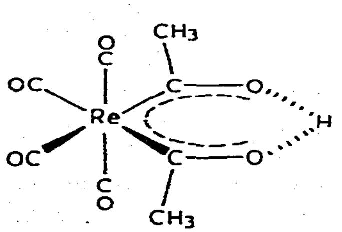
Summary

The reaction of the rhenium tetracarbonyl metallo-acetylacetone molecule, *cis*-$(OC)_4Re[C(CH_3)O\cdots H\cdots O(CH_3)C]$, with hydrazine, methylhydrazine and phenylhydrazine affords the corresponding acetyl-amine complexes, *cis*-$(OC)_4$-$Re(COCH_3)(NH_2R)$, where R = H, CH_3, or C_6H_5, and acetonitrile. The reactions were followed by proton NMR at 36°C. The half-life of the reaction with phenylhydrazine was 8.67 minutes while the other two hydrazines gave complete reaction within 30 seconds. The X-ray molecular structure determination of the acetyl-aniline complex is reported.

Introduction

We reported recently the synthesis and molecular structure of the first example of a metallo-acetylacetone complex (I) where the methine group of the enol tautomer of acetylacetone was replaced formally by a *cis*-$Re(CO)_4$ group [1]. Several other complexes of this type involving diverse substituents on the chelate ring as well as a different metallo group have been prepared [2]. The



(I)

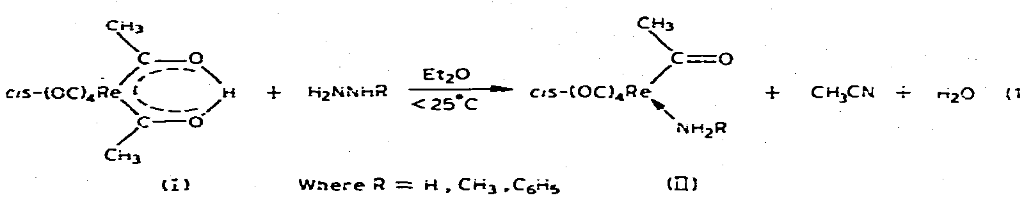
* For Part X see ref. 2.

coordination chemistry of the corresponding metallo-β-diketonate anions is well established, also [2—4].

The intriguing chemical interest in the rhenium-enol complex I is based upon its potential chemical similarity to acetylacetone. Recent results indicate that complex I exhibits an extensive and interesting reaction chemistry. We report here the reaction of complex I with hydrazine, methylhydrazine and phenylhydrazine affording the corresponding *cis*-acetyl(amine)tetracarbonylrhenium complexes along with the elimination of acetonitrile. The X-ray structure determination of the complex, *cis*-$(CH_3CO)(C_6H_5NH_2)Re(CO)_4$ is reported, also.

Results and discussion

When the rhenium-enol complex I is treated with an equimolar amount of several anhydrous hydrazines at below room temperature in ether solution, the corresponding *cis*-acetyl(amine)tetracarbonylrhenium complexes are formed along with the elimination of acetonitrile and, presumably, water as shown in eq. 1.



The amine complexes II were isolated and characterized. In all three cases, the presence of acetonitrile as a reaction product was verified by IR and proton NMR. The yield of acetonitrile was determined by proton NMR integration using a set of standard solutions. The calculated yields of acetonitrile were; 75% with hydrazine, 48% with methylhydrazine, and 53% with phenylhydrazine. No attempt was made to isolate or detect water as a product.

When the reactions were followed by proton NMR in $CDCl_3$, the rate of reaction could be estimated from the disappearance of the resonance of the methyl groups of complex I with time. This resonance disappeared completely within 15 and 30 sec with hydrazine and methylhydrazine, respectively. However, with phenylhydrazine the reaction was sufficiently slow at 36°C that the disappearance of the methyl resonance of complex I could be followed conveniently as well as the concomitant appearance of the acetonitrile resonance. The observed half-life of this reaction, i.e. when 50% of complex I had reacted, was 8.67 min.

The reaction with phenylhydrazine was examined in more detail. When treating complex I with aniline, the acetyl-aniline complex was not formed. However, this aniline complex was obtained by independent synthesis when acetylpentacarbonylrhenium was photolyzed in hexane solution in the presence of aniline. This product gave IR and proton NMR spectra identical to those of the product isolated from the phenylhydrazine reaction.

Single crystals of *cis*-acetyl(aniline)tetracarbonylrhenium were examined via X-ray crystallography by Molecular Structure Corporation as a technical service.

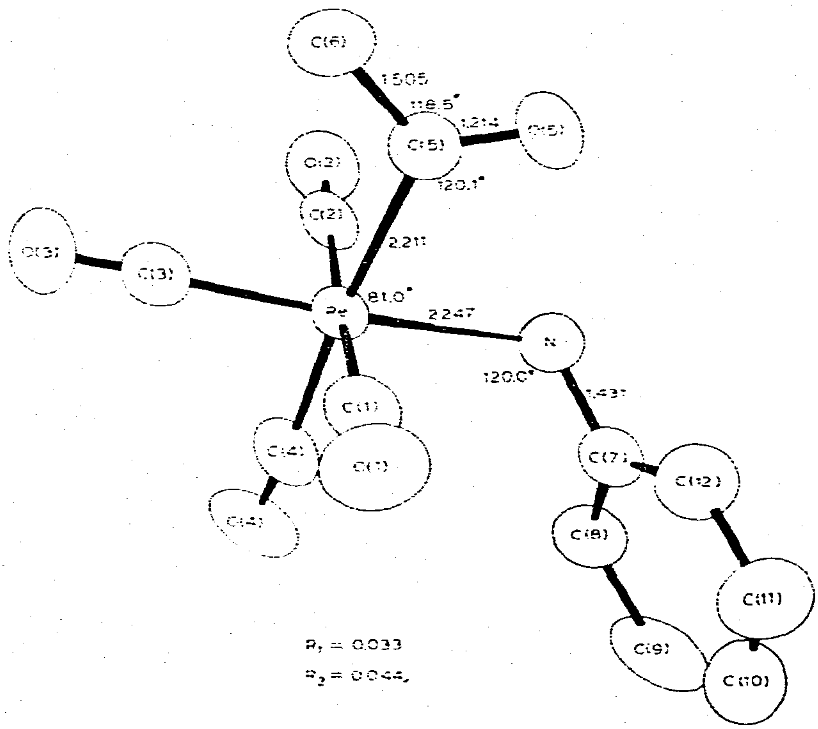


Fig. 1. An ORTEP view of *cis*-$(OC)_4Re(COCH_3)(NH_2C_6H_5)$ showing the atomic numbering scheme. The sizes and shapes of the atoms are determined by their final thermal parameters and their perspective view.

The ORTEP diagram of the molecule is shown in Fig. 1. The atomic positional and thermal parameters are given in Table 1. The bond angles and distances are provided in Table 2.

The molecular structure shows the nearly octahedral coordination geometry about the rhenium atom. The three coordination axes are essentially linear (average angle is 174.5°) and the angles centered at rhenium between adjacent ligands are near 90° (average angle is 90.8°) except for the C(5)—Re—N angle which is 81.0°. The acetyl and aniline ligands are on adjacent coordination sites and the atoms O(5) and N are in a *syn* orientation relative to the C(5)—Re bond. The atoms Re, C(3), C(4), C(5) and N are essentially coplanar (maximum atomic deviation from this plane is 0.029 Å), and the atoms C(6) and O(5) lie close to this plane having atomic deviations from this plane of 0.065 Å and −0.032 Å, respectively, while atom C(7) lies 0.951 Å below this plane. The six atoms of the phenyl ring are essentially coplanar (maximum atomic deviation is 0.008 Å), and the dihedral angle between this plane and the plane defined by the atoms Re, C(3), C(4), C(5) and N is 62.6°. The possibility of a hydrogen bonding interaction between the protons of the aniline ligand and the acetyl oxygen atom is only speculative since the hydrogen atoms were not located.

The Re—C(5) distance of 2.211(6) Å and the C(5)—O(5) distance of 1.214(7) Å indicate normal bond distances for acylrhenium complexes. The correspond-

TABLE 1

ATOMIC COORDINATES [a] FOR cis-$(OC)_4Re(COCH_3)(NH_2C_6H_5)$ WITH ESTIMATED STANDARD DEVIATIONS OF THE LEAST SIGNIFICANT DIGIT IN PARENTHESES

	x	y	z
Re	0.50623(2)	0.33065(4)	0.30830(1)
O(1)	0.4934(6)	0.7356(9)	0.3750(4)
O(2)	0.5293(5)	−0.0497(8)	0.2236(3)
O(3)	0.2431(5)	0.3622(10)	0.2438(4)
O(4)	0.4175(6)	0.1367(9)	0.4503(3)
O(5)	0.6922(5)	0.4846(8)	0.2097(3)
N	0.7035(5)	0.3177(8)	0.3470(3)
C(1)	0.4986(6)	0.5886(11)	0.3525(4)
C(2)	0.5210(6)	0.0862(10)	0.2555(4)
C(3)	0.3420(7)	0.3510(10)	0.2674(4)
C(4)	0.4529(7)	0.2085(11)	0.3994(4)
C(5)	0.5838(6)	0.4581(9)	0.2099(4)
C(6)	0.5043(8)	0.5176(14)	0.1428(4)
C(7)	0.7432(6)	0.3867(11)	0.4193(4)
C(8)	0.7353(8)	0.2716(14)	0.4804(4)
C(9)	0.7804(9)	0.3625(20)	0.5534(5)
C(10)	0.8267(9)	0.5442(18)	0.5558(6)
C(11)	0.8304(10)	0.6436(16)	0.4946(6)
C(12)	0.7895(8)	0.5718(13)	0.4258(5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.00561(2)	0.01357(5)	0.00265(1)	0.00079(5)	0.00174(2)	0.00036(3)
O(1)	0.0148(7)	0.023(1)	0.0051(2)	0.008(2)	0.0007(7)	−0.0070(10)
O(2)	0.0104(5)	0.020(1)	0.0052(2)	0.000(1)	0.0028(6)	−0.0061(8)
O(3)	0.0067(4)	0.041(2)	0.0054(2)	0.006(2)	−0.0008(6)	−0.0009(12)
O(4)	0.0152(7)	0.034(2)	0.0048(2)	0.007(2)	0.0087(6)	0.0083(10)
O(5)	0.0079(4)	0.027(1)	0.0041(2)	−0.005(1)	0.0017(4)	0.0060(9)
N	0.0068(4)	0.018(1)	0.0028(2)	0.001(1)	0.0002(5)	−0.0010(8)
C(1)	0.0075(6)	0.019(1)	0.0033(2)	0.006(2)	0.0013(6)	−0.0015(10)
C(2)	0.0062(5)	0.018(1)	0.0032(2)	−0.002(2)	0.0026(6)	0.0016(10)
C(3)	0.0084(6)	0.019(2)	0.0034(2)	−0.001(2)	0.0022(7)	−0.0017(10)
C(4)	0.0076(6)	0.018(1)	0.0040(3)	0.007(2)	0.0026(7)	0.0026(11)
C(5)	0.0083(6)	0.014(1)	0.0029(2)	−0.003(1)	0.0008(6)	0.0004(9)
C(6)	0.0109(7)	0.031(2)	0.0031(2)	−0.007(2)	−0.0005(7)	0.0070(13)
C(7)	0.0058(5)	0.025(2)	0.0029(2)	0.004(2)	0.0012(6)	−0.0021(11)
C(8)	0.0097(7)	0.038(2)	0.0027(2)	0.011(2)	0.0007(7)	0.0063(13)
C(9)	0.0102(8)	0.082(4)	0.0030(3)	0.026(3)	0.0021(8)	0.0126(17)
C(10)	0.0108(9)	0.050(4)	0.0058(4)	0.001(3)	0.0007(10)	−0.0091(21)
C(11)	0.0117(9)	0.050(3)	0.0049(4)	0.006(3)	−0.0006(10)	−0.0118(18)
C(12)	0.0103(8)	0.026(2)	0.0049(3)	−0.001(2)	0.0024(8)	−0.0082(13)

[a] The anisotropic temperature factors are of the form $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$

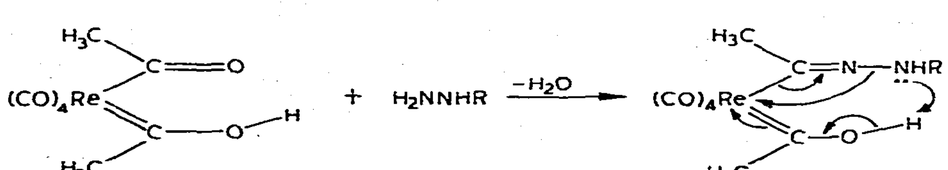
ing bond distances in p-chlorobenzoylpentacarbonylrhenium are 2.22(1) and 1.16(2) Å, respectively [5]. The analogous distances found in complex I of 2.16(2) and 1.27(2) Å, respectively, indicate the loss of the delocalization present in complex I when forming the acetyl-aniline complex. The Re—N distance of 2.247(5) Å is presumably a normal Re—N (sp^3) bond distance. Using the Re—Cl distance of 2.521(4) Å found in $trans$-$(Me_2PhP)_4Re(N_2)Cl$ [6] to define a Re^I—Cl single bond distance and the covalent radius of Cl as 0.994 Å [7], the covalent radius of Re^I may be estimated as 1.53 Å. Adding the covalent radius of a N (sp^3) atom of 0.70 Å [7] to this value provides an estimate of a Re^I—N (sp^3) bond distance of 2.23 Å.

TABLE 2

BOND DISTANCES AND ANGLES IN *cis*-$(OC)_4Re(COCH_3)(NH_2C_6H_5)$

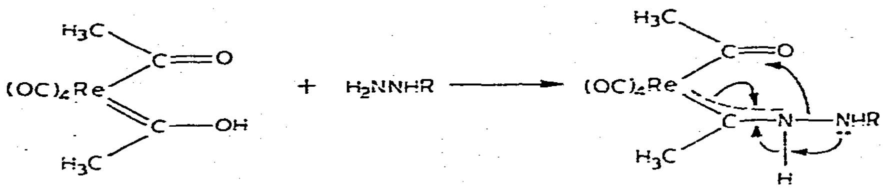
Distances (Å)		Angles (°)	
Re—N	2.247(5)	N—Re—C(1)	88.9(2)
Re—C(1)	1.999(7)	N—Re—C(2)	90.2(2)
Re—C(2)	1.989(6)	N—Re—C(3)	175.0(2)
Re—C(3)	1.918(7)	N—Re—C(4)	93.6(2)
Re—C(4)	1.979(7)	N—Re—C(5)	81.0(2)
Re—C(5)	2.211(6)	C(1)—Re—C(2)	174.2(2)
O(1)—C(1)	1.121(8)	C(1)—Re—C(3)	91.1(3)
O(2)—C(2)	1.129(7)	C(1)—Re—C(4)	92.8(3)
O(3)—C(3)	1.148(8)	C(1)—Re—C(5)	88.5(2)
O(4)—C(4)	1.139(8)	C(2)—Re—C(3)	89.3(3)
O(5)—C(5)	1.214(7)	C(2)—Re—C(4)	93.0(3)
N—C(7)	1.431(8)	C(2)—Re—C(5)	85.7(2)
C(5)—C(6)	1.505(8)	C(3)—Re—C(4)	91.4(3)
C(7)—C(8)	1.376(10)	C(3)—Re—C(5)	94.0(3)
C(7)—C(12)	1.411(10)	C(4)—Re—C(5)	174.5(2)
C(8)—C(9)	1.516(14)	Re—N—C(7)	120.0(4)
C(9)—C(10)	1.387(15)	Re—C(1)—O(1)	177.7(6)
C(10)—C(11)	1.310(14)	Re—C(2)—O(2)	177.9(6)
C(11)—C(12)	1.386(11)	Re—C(3)—O(3)	179.0(6)
		Re—C(4)—O(4)	177.1(6)
		Re—C(5)—O(5)	120.1(4)
		Re—C(5)—C(6)	121.3(4)
		O(5)—C(5)—C(6)	118.5(5)
		N—C(7)—C(8)	119.4(6)
		N—C(7)—C(12)	118.7(6)
		C(8)—C(7)—C(12)	121.9(7)
		C(7)—C(8)—C(9)	113.8(8)
		C(8)—C(9)—C(10)	121.4(9)
		C(9)—C(10)—C(11)	120(1)
		C(10)—C(11)—C(12)	122(1)
		C(7)—C(12)—C(11)	120.6(9)

When considering the resonance structures of complex I, two plausible mechanisms for these reactions may be proposed. The first mechanism is analogous to the condensation reaction of acetylacetone where the acetyl ligand undergoes a Schiff base condensation forming a hydrazone intermediate [8] which rearranges to the observed products (eq. 2).



(2)

The second mechanism utilizes the hydroxy-carbenoid ligand. This ligand could undergo an "aminolysis" reaction with the elimination of water followed by the rearrangement of the aminocarbenoid ligand affording the observed products (eq. 3). A similar mechanism was proposed by Fischer to explain the



(3)

formation of $(OC)_5Cr(NCCH_3)$ and free dimethylamine when treating the carbenoid complex, $(OC)_5CrC(OCH_3)(CH_3)$, with *N,N*-dimethylhydrazine [9]. Further synthetic studies are being pursued to resolve this question.

Experimental

All reactions were performed under dry, prepurified nitrogen. The rhenium-enol I was prepared by a literature method [1]. The anhydrous hydrazines were purchased commercially and were dissolved in either ethanol or methylene chloride as stock solutions. All solvents were dried before use.

Infrared spectra were recorded on a Perkin—Elmer 727 spectrometer as ether solutions in 0.10 mm sodium chloride cavity cells using the solvent as a reference and a polystyrene film as a calibration standard. Peak frequencies are reported in cm^{-1}. Proton NMR spectra were obtained on a Jeol MH-100 spectrometer using TMS as a reference.

Microanalysis were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. The single crystal X-ray structure determination of the complex, *cis*-$(OC)_4Re(NH_2C_6H_5)(COCH_3)$, was performed as a technical service by Molecular Structure Corporation of College Station, Texas.

Preparation of cis-acetylamminotetracarbonylrhenium

To a stirred solution of 0.30 g (0.78 mmol) of complex I in 15 ml of distilled ether at —40°C was added 0.025 g (0.78 mmol) of hydrazine as a methylene chloride solution. After stirring for 10 min at 25°C, the solvent was removed at reduced pressure affording 0.12 g (43%) of the product as a yellow solid which was recrystallized from ether at —20°C for 20 h: m.p. 70—72°C; IR: ν(CO) 2075m, 1970vs(br), 1922s, ν(acyl) 1590m; ^{1}H NMR ($CDCl_3$): τ (ppm) 7.49 (singlet, 3, CH_3), 4.32 (broad singlet, 3, NH_3). Analysis Found: C, 20.80; H, 1.60; N, 3.88. $C_6H_6O_5NRe$ calcd.: C, 20.11; H, 1.68; N, 3.91%.

Preparation of cis-acetyl(methylamine)tetracarbonylrhenium

To a stirred solution of 0.30 g (0.78 mmol) of complex I in 10 ml of ether at 0°C was added 0.04 g (0.86 mmol) of methylhydrazine as an ethanol solution. After stirring for 1 h at 0°C the solvent was removed at reduced pressure. The yellow, oily residue was dissolved in a minimum volume of 10% ether/pentane solution and was stored at —20°C for 20 h affording 4.2 mg (1.4%) of the product as yellow crystals: m.p. 75—78°C; IR: ν(CO) 2070m, 1965vs(br), 1927s, ν(acyl) 1588m; ^{1}H NMR ($CDCl_3$); τ(ppm) 7.43 (singlet, 3, CH_3); 7.26

(singlet, 3, N—CH_3); 4.30 (singlet, 2, NH_2). Analysis Found: C; 22.38; H, 2.10. $C_7H_8O_5NRe$ calcd.: C, 22.58; H, 2.17%.

Preparation of cis-acetyl(aniline)tetracarbonylrhenium

To a stirred solution of 0.30 g (0.78 mmol) of complex I in 10 ml of ether at 0°C was added dropwise 0.084 g (0.78 mmol) of phenylhydrazine as an ethanol solution. After stirring at 25°C for 45 min the solvent was removed at reduced pressure. The yellow reaction residue was dissolved in 3 ml of ether and was stored at −20°C for 18 h affording 0.070 g (21%) of white needles: m.p. 147–148°C; IR: ν(CO) 2080m, 1972vs(br), 1927s, ν(acyl) 1578m; ^{1}H NMR (C_6D_6): τ(ppm) 7.37 (singlet, 3, CH_3), 4.76 (broad singlet, 2, NH_2), 3.16 (complex multiplet, 5, C_6H_5). Analysis Found: C, 33.48; H, 2.25; N, 3.27. $C_{12}H_{10}O_5NRe$ calcd.: C, 33.17; H, 2.32; N, 3.22%.

Preparation of cis-acetyl(aniline)tetracarbonylrhenium by photolysis

A stirred solution of 0.30 g (0.81 mmol) of acetylpentacarbonylrhenium and 0.075 ml (0.82 mmol) of aniline in 50 ml of hexane was irradiated for 2 h by a Blak-Ray UV lamp model B-100A at a distance of 30 cm. The solvent was removed at reduced pressure and the residue was dissolved in 5 ml of ether and stored at −20°C for 20 h affording 0.017 (6%) of white needles. The product gave identical IR and ^{1}H NMR spectra to the product obtained from the phenylhydrazine reaction. Analysis Found: C, 33.45; H, 2.69; N, 3.25. $C_{12}H_{10}O_5NRe$ calcd.: C, 33.17; H, 2.32; N, 3.22%.

X-ray crystallographic study of cis-$(OC)_4Re(COCH_3)(NH_2Ph)$

An equidimensional single crystal having 0.11 mm on an edge was attached to a glass fiber and mounted directly on an Enraf-Nonius CAD4 diffractometer. The automatic centering and angle refinement of 25 reflections (Mo-K_α, λ 0.71073 Å) yielded the cell data; *a* 11.057 (1), *b* 7.094 (3), *c* 17.988 (2) Å, β 93.87(2)°, *d* (calcd.) 2.040 g/cm^3, *V* 1407.6(9) Å^3 at 23°C with $Z = 4$ for the monoclinic space group $P2_1/n$.

Intensity data were collected with Mo-K_α radiation which was filtered by a graphite-crystal incident-beam monochromator. The data were collected with a take-off angle of 5.8° using a $\theta - 2\theta$ scan of variable scan rate (4° to 24°/min) for the range of data of $0° < 2\theta$ (Mo-K_α) $< 50°$ with a scan range of from 2θ (Mo-$K_{\alpha1}$) − 1.1° to 2θ(Mo-$K_{\alpha2}$) + 1.1°. Three standard reflections were measured periodically and no significant change was observed. Intensities and standard deviations on intensities were calculated using the formulae:

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count and p is a factor introduced to downweight intense reflections and was set at 0.05. Lorentz and polarization corrections were applied to the data. An extinction correction was not necessary and an absorption correction (linear absorption coefficient 91.36 cm^{-1}) was not necessary due to the uniform shape of the crystal. Of the 2826 data measured, 2059 had $F_0^2 > 3\sigma(F_0^2)$ and were used in the solution and refinement of the structure.

The structure was solved using the Patterson method yielding the location of the rhenium atom. Subsequent difference Fourier syntheses yielded the location of the remaining non-hydrogen atoms. The hydrogen atoms could not be located. Anisotropic full-matrix least-squares refinement of all non-hydrogen atoms including anomalous scattering contributions for the rhenium atom resulted in final agreement factors of $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.033$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2} = 0.044$. The calculated and observed structure factors have been deposited *.

Acknowledgements

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* The table of structure factors has been deposited as NAPS Document No. 03073 (9 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.