Title

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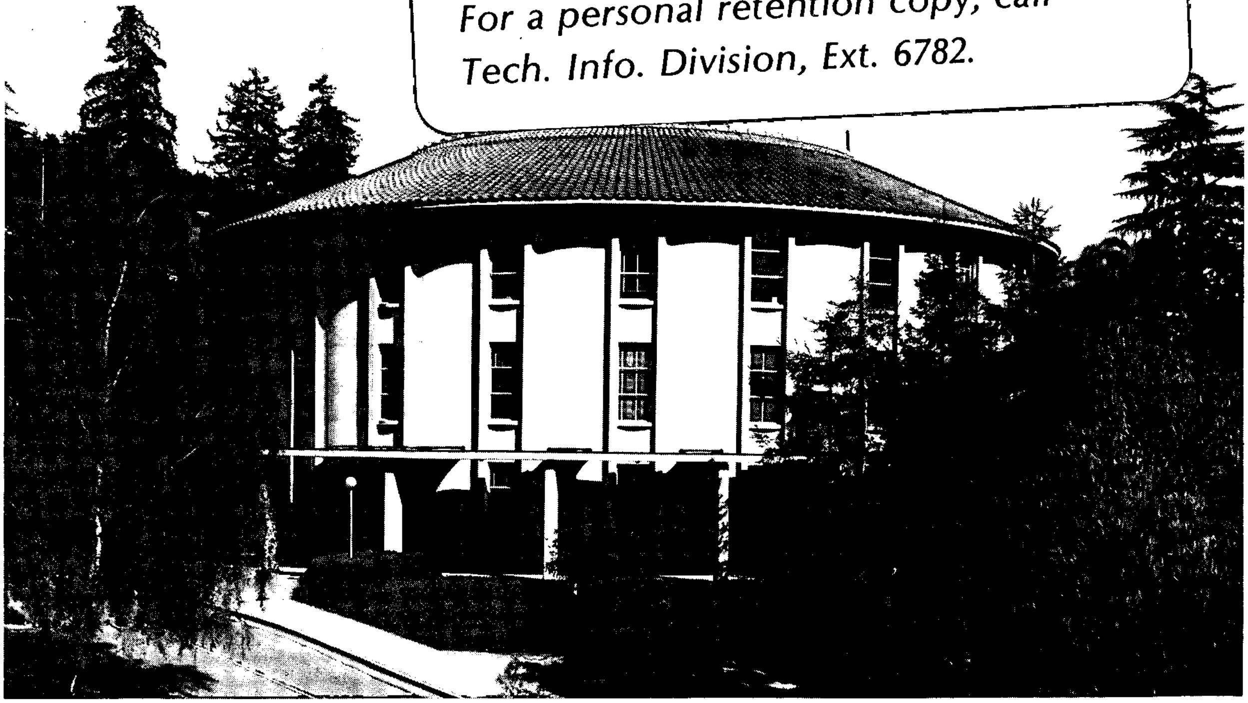
May 1983



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Crystal and Molecular Structure of Chloro-[bis-(N-butyl-3-fluorosalicylaldimato)] Manganese(III)

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X-ray analysis of single crystals of the title compound yielded space group $P\bar{1}$ with $a = 8.4994$ (9) Å, $b = 11.8262$ (11) Å and $c = 11.9721$ (9) Å. $\alpha = 77.335^{o}$ (7), $\beta = 75.415^{o}$ (7), $\gamma = 77.892^{o}$ (8), $V = 1120.9$ (2) $Å^3$ and $Z = 2$. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques to $R = 0.044$. The structure consists of a five-coordinated manganese with the two bidentate ligands slightly out of plane in a trans configuration, and one axial chloro ligand.

The continuing interest in model compounds for the catalytic site of the oxygen-evolving enzyme in plants has produced different types of manganese complexes, since the general consensus is that manganese is directly involved in photosynthetic oxygen evolution.[1)] Among the major classes of manganese complexes investigated are the manganese porphyrins,[2-7)] manganese phthalocyanins,[8)] manganese bipyridyls[9-10)] or polyimine-complexes[10-12)], manganese quinones[13)], -gluconates[14)], -polyhydroxy-[15)] and Schiff base complexes[16-19)]. Such Schiff base complexes derived from salicylaldehyde have been proposed as being able to produce oxygen from water, when the manganese is oxidized to the +IV state.[17)] Despite this very interesting perspective, only little structural work has been done in the area of manganese complexes with salicylaldehyde Schiff bases.[20-24)] We have, therefore, decided to determine the exact structure of the compound in its most stable form, i.e., manganese in the oxidation state +III. The synthesis and characterization of this compound will be described elsewhere.[25)]

EXPERIMENTAL

Pale green platelike and columnar crystals of the compound were obtained by slow recrystallization from 1,2-dichloroethane. Fragments cleaved from the columnar crystals were mounted on glass fibers in air, using polycyanoacrylate cement. Preliminary precision photographs yielded rough cell dimensions and revealed no symmetry higher than triclinic.

The crystal was then transferred to the Enraf-Nonius CAD4 diffractometer[26)] and centered in the beam. Automatic peak search and indexing procedures revealed a reduced primitive triclinic cell, and inspection of the Niggli values[27)] revealed no conventional cells of symmetry higher than triclinic. The final cell parameters and details of the data collection procedure are given in Table I.

The 3780 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background and Lorentz and polarization effects.[28-30)] Inspection of the azimuthal scan data[31)] showed an average variation of only ± 3% in intensity. No absorption or decay corrections were applied.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The assumption that the space group was centric was confirmed by the successful refinement of the structure.

On a difference Fourier map calculated after all atoms had been refined with anisotropic thermal parameters, the two largest peaks were interpreted as disordered carbon positions for the n-butyl group of the second ligand, and the other peaks were easily assignable as hydrogen atoms on the ring of the second ligand and on both ring and butyl group of the first ligand. The disordered carbons were assigned occupancies of 0.2 based on comparison with a difference Fourier calculated with the whole second n-butyl group removed. Hydrogens were included in their theoretical positions but not refined in least-squares. The disordered carbon atoms were allowed to refine with isotropic thermal parameters. A subsequent difference Fourier showed the position of a third disorder component for C29 and this was included at 0.2 occupancy, and the occupancies of C28 anc C29 and their hydrogen atoms were adjusted. No peaks interpretable as hydrogens were seen near C31, so no prediction was made of these hydrogen positions. The final residuals from 283 variables refined against the 3070 data for which $F^2 > 3\sigma\ (F^2)$ were R = 4.39%, wR = 6.94% and GOF = 3.181. The R value for all 3780 data was 5.82%.

The quantity minimized by the least squares program was $\Sigma W\ (|Fo| - |Fo|)^2$, where W is the weight of a given observation. The p-factor$^{30)}$ used to reduce the weight of intense reflections was set to 0.03 throughout the refinement. The analytical forms for the scattering factor tables for the neutral atoms were used$^{32)}$ and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.$^{33)}$

Inspection of the residuals ordered in ranges of sin θ/λ, $|Fo|$ and parity and value of the individual indexes showed no unusual features or trends. There was no evidence of secondary extinction in the low-angle, high-intensity data.

The largest peak in the final difference Fourier map had an electron density of 0.42 $e^-/Å^3$ near C8, C9 and C10 (see Fig. 1). The other top peaks were near the disordered n-butyl group.

The positional and thermal parameters of the non-hydrogen atoms are given in Table II. The positions of the hydrogen atoms and a listing of the values of F_o and F_c are available as supplementary material.

RESULTS AND DISCUSSION

The labeling of atoms in the molecular structure is shown in Fig. 1. The pentacoordination of the manganese is rather unusual34) and only recently has there been derived a general theory of substituent effects and geometrical preferences.37) Since the ligands in our case show both σ- and π-bonding effects, the prediction of the substitutional preference is not straightforward and will also depend on the geometry. Hoffmann and Rossi37) calculated energy levels of a square-pyramidal ML_5 as a function of the pyramidality angle θ between L(apical), M and L(basal) which suggest for a d^4 system $\theta > 90^0$. This is indeed the case here as can be seen from the N-Mn-N angle of 169.1 degrees and the O-Mn-O angle of 159.4 degrees. The difference between these two angles as well as the difference between the two Cl-Mn-O angles clearly indicates the distortion introduced into the structure by the non-identical ligand sites. Previously, it was assumed on the basis of X-ray powder diffraction experiments that these complexes should possess a binuclear or linear chain structure.[35] Figure 2 shows clearly that the structure consists of monomeric units. A similar five-coordinate structure has, however, been found in a chloro-bis(N-n-propylsalicylaldimato) iron(III) which also consists of monomeric units.[36]

The deviation of the atoms from the 2N-2O plane is ± 0.077 Å with the manganese displaced 0.27 Å from the plane. The large difference in bond length between Mn-O and Mn-N is probably due to Coulombic effects, as the negative charge on the ligand seems to be concentrated on the oxygen (based on the C-O bond length which is close to a single bond).

Each of the ligands is very nearly planar. The deviations of the ring atoms are up to ± 0.027 and of the attached atoms up to 0.040 Å. The planes are tilted 5.3 and 8.0 degrees with respect to the 2N-2O plane. These angles are a combination of tilt away from the Cl and a twist of the plane about the two Mn-"ligand"-vectors.

The bond distances and angles in the complex are given in Table II. The agreement between the two ligands is good, but not excellent. The bond distances in the n-butyl groups are especially affected by thermal motion and disorder.

The difference between the two n-butyl groups must be attributed to packing forces in the crystal. It is clear from Fig. 2 that the ordered n-butyl group is "sandwiched" between ring planes in the crystal while the n-butyl group of ligand 2 has more room to move. It is obvious from the fact that the disorder exists that there is little or no internal constraint on the orientation of the butyl groups.

In summary, the structure consists of well separated molecules of the monomeric complex. The closest contacts between molecules are between the fluorine atoms of molecules related by translation in the *b*-direction (F....F = 3.202(2)). No contacts are abnormally short. The closest intermolecular contact to the manganese atom is 4.62 Å to one of the oxygen atoms of the molecule related by the center of inversion at the origin. The nearest Mn-Mn contact is 5.88 Å to the manganese related by that same center of inversion. These contacts can be clearly seen in Fig. 2. The packing is dominated by aromatic interactions between the ligands of molecules stacking on the $\underset{\sim}{c}$ axis.

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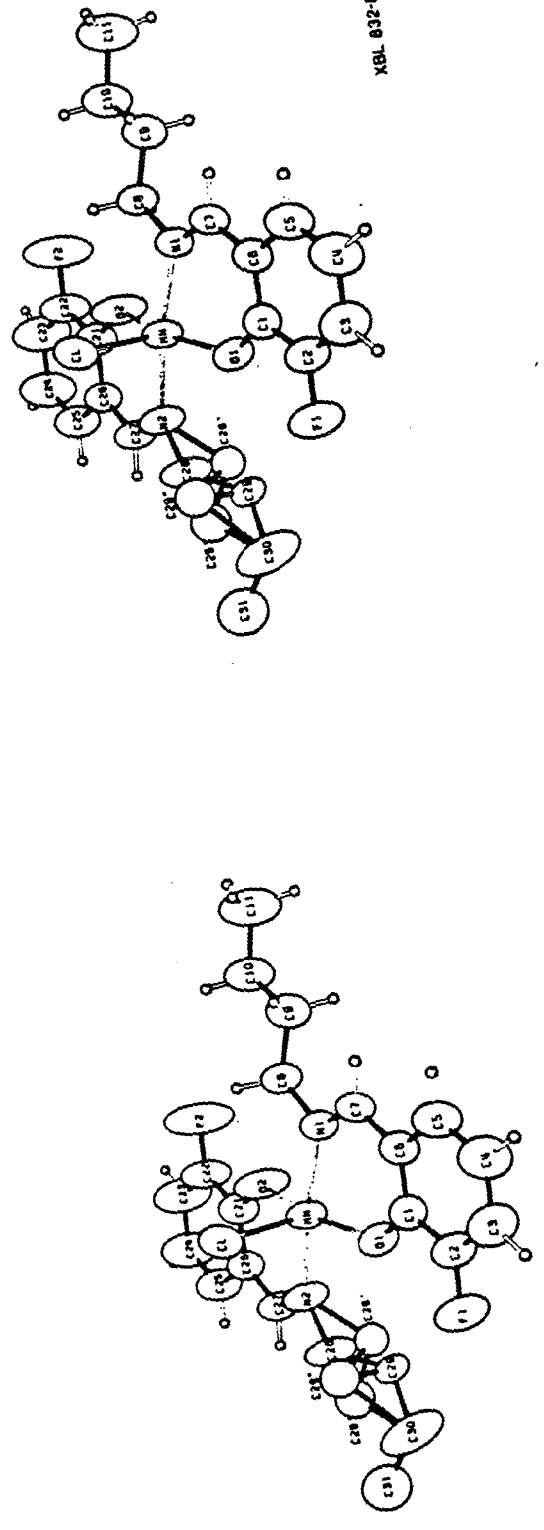
FIGURE CAPTIONS

Fig. 1 ORTEP[38] stereopair drawing of the $Mn(C_{11}H_{14}NOF)_2Cl$ molecule. The ellipsoids are scaled to represent the 50% probability surface. Hydrogen atoms are given as arbitrary small spheres for clarity.

Fig. 2 Stereoview of the crystal packing diagram (ellipsoids scaled to represent the 20% probability surface) showing the overlap of the planar portions of the ligands on adjacent molecules.



XBL 832-8031

Figure 1

Figure 2

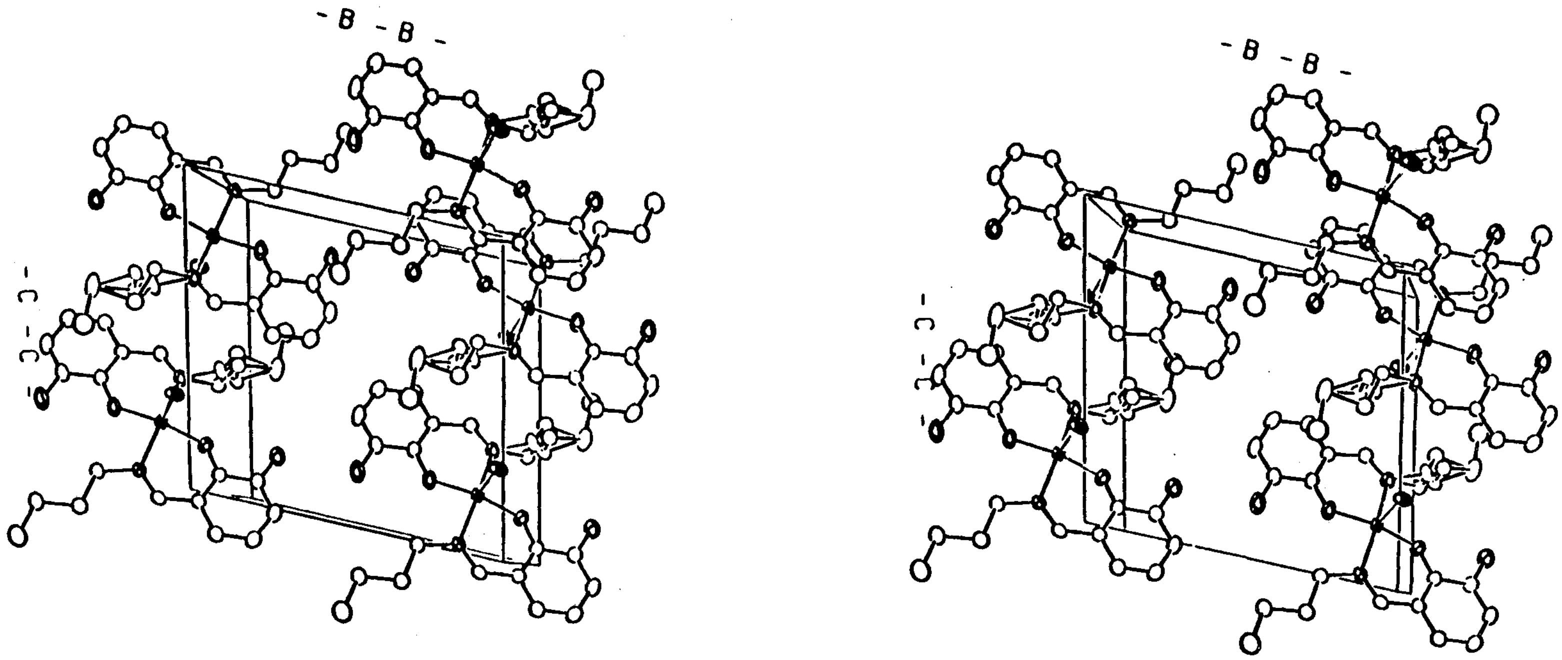


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TABLE I - Crystal and Data Collection Parameters

Compound: Mn Cl $(C_{11}H_{14}NOF)_2$

A) Crystal Parameters @ 25 °C a)b)

a = 8.4994(9)
b = 11.8262(11)
c = 11.9721(9)
α = 77.335(7)
β = 75.415(7)
γ = 77.892(8)
V = 1120.9(2)

Space Group: $P\bar{1}$
Formula weight: 478.85 amn
Z = 2
d (calc.) = 1.419 g cm^{-3}
d (obs.) = 1.425 g cm^{-3}
μ (calc.) = 7.209 cm^{-1}
Size: 0.17 x 0.25 x 0.34 nm

B) Data Measurement Parameters

Diffractometer : Enraf-Nonius CAD-4 8)
Radiation: Mo Kα ($\bar{\lambda}$ = 0.71073 Å)
Monochromator: Highly-oriented graphite ($2\theta_m$ = 12.2)
Perpendicular mode, assumed 50% perfect.
Detector: Crystal scintillation counter, with PHA.
Aperture → crystal = 173 mm. Vertical aperture = .0 mm.
Horizontal Aperture = 2 + 1 tan(θ) mm (variable).
Reflections measured: +H ±K ±L
2θ Range: 3-50 Scan type: θ-2θ
Scan speed: 0.6-6.7 (θ, deg./min)
Scan width: $\Delta\theta$ = 0.5 + 0.317 tan(θ)
Background: Measured over an additional 0.25($\Delta\theta$) added to each end of the scan.

No. of unique reflections: 3780

Intensity standards: 500 , 082 , 108 ; measured every 2 hours of x-ray exposure time. Over the period of data collection No decay in intensity was observed.

Orientation: 3 reflections were checked after every 250 measurements. Crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1 °. Major Reorientation was necessary once during data collection.

Table I (cont.)

a) Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo $K\bar{\alpha}$ components of 24 reflections with 2θ between 25^0 and 31^0.

b) In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) given.

Table II. a) INTRAMOLECULAR DISTANCES

Mn Cl (C11 H14 N O F)2
Intramolecular distances

ATOM 1	ATOM 2	DISTANCE
MN	O2	1.841(1)
MN	N2	2.045(2)
C21	O2	1.317(2)
C21	C26	1.383(2)
C21	C22	1.403(3)
C22	F2	1.352(2)
C22	C23	1.352(3)
C23	C24	1.382(3)
C24	C25	1.361(3)
C25	C26	1.401(3)
C26	C27	1.423(2)
C27	N2	1.279(2)
N2	C28	1.495(3)
C28	C29	1.460(5)
C29	C30	1.581(4)
C30	C31	1.442(4)
N2	C28'	1.705(12)
C28'	C29	1.361(15)
C28'	C29"	1.369(16)
C29'	C30	1.598(12)
C29"	C30	1.936(13)

Mn Cl (C11 H14 N O F)2
Intramolecular distances

ATOM 1	ATOM 2	DISTANCE
MN	CL	2.391(1)
MN	O1	1.850(1)
MN	N1	2.039(1)
C1	O1	1.321(2)
C1	C6	1.390(2)
C1	C2	1.410(3)
C2	F1	1.356(2)
C2	C3	1.369(3)
C3	C4	1.377(3)
C4	C5	1.378(3)
C5	C6	1.407(3)
C6	C7	1.444(2)
C7	N1	1.288(2)
N1	C8	1.497(2)
C8	C9	1.495(3)
C9	C10	1.537(3)
C10	C11	1.499(3)

TABLE II. b) INTRAMOLECULAR ANGLES

Mn Cl (C11 H14 N O F)2
Intramolecular Angles (ligand 2)

ATOM 1	ATOM 2	ATOM 3	ANGLE
O2	C21	C22	118.00(17)
O2	C21	C26	124.26(17)
C26	C21	C22	117.74(18)
F2	C22	C21	117.34(19)
F2	C22	C23	120.46(19)
C21	C22	C23	122.17(20)
C22	C23	C24	119.81(21)
C23	C24	C25	119.67(21)
C24	C25	C26	121.01(19)
C25	C26	C21	119.57(17)
C25	C26	C27	118.62(17)
C21	C26	C27	121.74(17)
C26	C27	N2	126.83(17)
C27	N2	C28	115.95(18)
N2	C28	C29	111.6(3)
C28	C29	C30	108.0(3)
C29	C30	C31	119.1(3)
C27	N2	C28'	111.4(4)
N2	C28'	C29'	109.2(9)
N2	C28'	C29"	38.7(10)
C28'	C29'	C30	101.6(9)
C28'	C29"	C30	56.3(8)
C29'	C30	C31	85.6(5)
C29"	C30	C31	106.3(4)

Mn Cl (C11 H14 N O F)2
Intramolecular Angles with Mn

ATOM 1	ATOM 2	ATOM 3	ANGLE
CL	MN	O1	96.89(5)
CL	MN	O2	102.70(6)
CL	MN	N1	95.93(5)
CL	MN	N2	94.38(6)
O1	MN	O2	158.40(8)
O1	MN	N1	90.39(6)
O1	MN	N2	89.16(6)
O2	MN	N1	86.86(6)
O2	MN	N2	89.57(6)
N1	MN	N2	169.12(7)
MN	O1	C1	129.02(12)
MN	O2	C21	132.46(12)
MN	N1	C7	123.54(12)
MN	N1	C8	117.12(12)
MN	N2	C27	124.95(13)
MN	N2	C28	118.25(15)
MN	N2	C28'	116.5(4)

Mn Cl (C11 H14 N O F)2
Intramolecular Angles (ligand 1)

ATOM 1	ATOM 2	ATOM 3	ANGLE
O1	C1	C2	118.65(16)
O1	C1	C6	124.66(16)
C6	C1	C2	116.68(17)
F1	C2	C1	116.81(18)
F1	C2	C3	120.16(18)
C1	C2	C3	123.00(19)
C2	C3	C4	119.51(19)
C3	C4	C5	119.59(20)
C4	C5	C6	120.96(19)
C5	C6	C1	120.21(17)
C5	C6	C7	118.13(17)
C1	C6	C7	121.57(17)
C6	C7	N1	126.05(16)
C7	N1	C8	119.17(15)
N1	C8	C9	118.65(17)
C8	C9	C10	109.22(18)
C9	C10	C11	109.62(21)

TABLE II. c) TORSIONAL ANGLES

Table of Torsional Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C6	C1	O1	MN	-19.5
C26	C21	O2	MN	-5.0
C6	C7	N1	MN	6.7
C26	C27	N2	MN	1.4
C1	O1	MN	CL	-72.4
C21	O2	MN	CL	-89.9
C7	N1	MN	CL	81.9
C27	N2	MN	CL	99.6
C6	C7	N1	C8	-176.1
C26	C27	N2	C28	170.6
C7	N1	C8	C9	3.6
C27	N2	C28	C29	83.6
N1	C8	C9	C10	176.6
N2	C28	C29	C30	-173.8
C8	C9	C10	C11	174.3
C28	C29	C30	C31	63.7
C26	C27	N2	C28'	-147.7
C27	N2	C28'	C29'	-58.4
C27	N2	C28'	C29"	-103.0
N2	C28'	C29'	C30	-153.8
N2	C28'	C29"	C30	171.1
C28'	C29'	C30	C31	-158.1
C28'	C29"	C30	C31	-119.2

Footnotes for Table II a),b),c)

(1) The esd's, given in parentheses right-adjusted to the least significant digit(s) shown, are calculated including the correlation terms derived from the inverted least-squares matrix.

(2) Distances and angles are uncorrected for thermal motion.

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