ACTA CHEMICA SCANDINAVICA 26 (1972) 889–896

The Crystal Structure of Di-triethanolamine-Ni(II)-dinitrate

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Triethanolamine coordinates to the nickel(II) ion with the nitrogen atom and two of the hydroxyl-oxygen atoms in crystalline di-triethanolamine-Ni(II)-dinitrate, $Ni(N(CH_2CH_2OH)_3)_2(NO_3)_2$. The compound is monoclinic, space group $P2_1/c$ with

$a = 7.18 \pm 0.02$, $b = 14.81 \pm 0.03$, $c = 9.35 \pm 0.02$, $\beta = 94.05 \pm 0.2°$

Three-dimensional data were collected using a semiautomatic diffractometer and Mo$K\alpha$-radiation. The structure was refined by the method of least-squares to an R-value of 0.068.

Aminoalcohols, such as 2-hydroxyethylamine and the related 2,2′,2″-trihydroxytriethylamine form numerous complexes with metals. The stereochemistry of these and related aminoalcohols would favour formation of chelate complexes with metal ions. However, most alcohols do not form strong complexes with metal ions and available data on the complexing power of ethanolamines [1,2] do not indicate the existence of a chelate effect. Ethanolamine and triethanolamine appear to be weaker complexing agents than the corresponding monoamines, ethylamine and triethylamine. An exception is some qualitative evidence for formation of complexes between triethanolamine and aluminium and titanium ions. These ions do not have a strong affinity for amine type ligands but do show a strong affinity for oxygen containing ligands. The existence of a number of nickel complexes [3] $NiTEAX_2$, $Ni(TEA)_2X_2$ *etc.* (TEA = triethanolamine, X = halogen, nitrate) gives no clear-cut evidence for or against the existence of chelate compounds of triethanolamine. The Ni^{2+}-ion yields strong complexes with most amines as well as with some oxygen-containing ligands, *e.g.* water and acetylacetonates. In $NiTEA(NO_3)_2$ the TEA may be coordinated as a tetradentate ligand whereas it appeared improbable that both TEA molecules could be bound as tetradentate ligands in $Ni(TEA)_2(NO_3)_2$. The effective magnetic moment of $Ni(TEA)_2(NO_3)_2$ was found to be 3.2 B. M. indicating an octahedral configuration around the nickel ion. An X-ray investigation was carried out in order to answer the question if the nitrate groups or some of the alcohol groups were coordinated to nickel.

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EXPERIMENTAL

Chemistry. 2.9 g $Ni(NO_3)_2.6H_2O$ was dissolved in a mixture of 1 ml H_2O and 5 ml triethanolamine (Ni : TEA = 1 : 4). The mixture was boiled and after cooling needle-shaped crystals were formed. These crystals were re-dissolved in a small amount of water and crystals suitable for X-ray analysis were formed after two days of slow evaporation of water.

Analysis. Nickel was determined by precipitation with dimethylglyoxime after destruction of TEA with H_2O_2. Result: Ni 11.53. Calc. Ni 12.20.

Magnetic measurements were performed using the Gouy method. The magnetic field was measured with a Rawson Gaussmeter.

X-Ray technigue. Lattice type and space group were established from Weissenberg and precession photographs using Cu- and Mo-radiation.

Three-dimensional intensity data were measured using an Arndt-Phillips linear diffractometer. Balanced filters SrO, ZrO_2 in conjunction with a scintillation counter and a pulse height analyser ensured a practically monochromatic Mo$K\alpha$ beam.

The intensities measured were symmetry related in pairs. The diffractometer output was processed by a GIER computer using a program written by Rita Grønbæk Hazell.

CRYSTAL DATA

Crystal system: monoclinic (b unique).

Unit cell: $a = 7.18 \pm 0.02$ Å, $b = 14.81 \pm 0.03$ Å, $c = 9.35 \pm 0.02$ Å, $\beta = 94.05° \pm 0.2°$.

$d_{calc} = 1.61$ g/cm³. 2 mol of $Ni(N(C_2H_4OH)_3)_2(NO_3)_2$ per unit cell. No piezoelectric effect could be detected.

Systematic absences: $h0l$ for l odd, $0k0$ for k odd.

Space group: $P2_1/c$.

STRUCTURE DETERMINATION

The Ni-atoms were placed in the special positions (0,0,0) and $(0,\frac{1}{2},\frac{1}{2})$ and a three dimensional Fourier synthesis was phased from these positions and was calculated using a program written by Lauesen. The false symmetry was resolved by selecting an octahedral arrangement of the light atoms coordinated to Ni and subsequent Fourier maps showed the other light atoms including those of the nitrate group.

The structure was refined using a least squares program written in this laboratory. The program employs anisotropic temperature factors and a block diagonal approximation using 3×3 and 6×6 matrices. Convergence was reached at $R = 6.8$ %.

The standard deviations given by the counting statistics $\sigma(F^2)_c$ were modified for use as weights in the least squares refinement. The weights used were $w = 1/(\mu F)^2$ where $\mu F = \sqrt{\sigma(F^2)_c + kF^2} - F$. The constant k was adjusted to give an average of $w\,|F_o - F_c|^2$ which is nearly independent of the size of F. A best fit was obtained for $k = 1.027$.

A difference Fourier synthesis was calculated after refinement was ended and it showed the hydrogen atoms in the expected positions. No other atoms were discernible. A few additional cycles of least squares refinements were computed with the positional parameters and isotropic temperature factors of the hydrogen atoms included. An agreement factor $R = 6.8$ % was obtained.

Table 1. Final atomic coordinates, and their standard deviations $\times 10^4$. For hydrogen isotropic B-values (Å^2) are given.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	σB
Ni	0.0000	0	0.5000	0	0.5000	0		
N_1	0.6027	6	0.2121	3	0.4875	5		
N_2	0.0861	5	0.4365	2	0.3132	4		
O_1	0.7600	7	0.2223	3	0.5409	6		
O_2	0.5213	6	0.1401	3	0.4795	5		
O_3	0.5356	10	0.2795	4	0.4350	7		
O_4	0.1665	4	0.6003	2	0.4273	3		
O_5	−0.2235	4	0.5396	2	0.3653	3		
O_6	0.2100	5	0.1927	2	0.2757	4		
C_1	0.1847	8	0.2825	3	0.2228	5		
C_2	0.1015	7	0.3384	3	0.3383	5		
C_3	0.2710	7	0.4766	3	0.2902	5		
C_4	−0.0507	7	0.4587	3	0.1929	5		
C_5	0.2636	7	0.5786	4	0.3040	6		
C_6	−0.2397	7	0.4748	3	0.2483	5		
H_{11}	0.1156	55	0.2740	27	0.1359	43	0.6	0.8
H_{12}	0.3168	70	0.3043	33	0.2001	51	2.7	1.2
H_{21}	−0.0187	52	0.3167	27	0.3612	41	0.2	0.8
H_{22}	0.1843	65	0.3210	33	0.4298	49	2.2	1.1
H_{31}	0.3501	61	0.4439	31	0.3675	48	1.5	1.0
H_{32}	0.3018	68	0.4597	32	0.1907	53	2.4	1.1
H_{41}	−0.0584	58	0.4043	28	0.1129	43	0.9	0.9
H_{42}	−0.0224	84	0.5062	32	0.1479	59	3.3	1.3
H_{51}	0.3882	77	0.6016	37	0.3175	59	3.9	1.4
H_{52}	0.2013	74	0.6009	34	0.2083	53	2.8	1.2
H_{61}	−0.3326	66	0.4991	28	0.1615	50	1.5	1.0
H_{62}	−0.2811	56	0.4138	29	0.2855	44	0.9	0.9
H_{04}	0.2020	89	0.6469	33	0.4545	51	2.6	1.2
H_{05}	−0.2049	82	0.5908	37	0.3304	61	3.8	1.4
H_{06}	0.3184	109	0.1861	48	0.3340	76	8.2	2.0

Table 2. Mean square vibration amplitudes, $u_{ij} \times 10^4$. Standard deviations $\times 10^4$.

Atom	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
Ni	365	(3)	180	3	265	3	17	3	70	3	−11	2
N_1	614	(26)	510	27	599	29	−69	21	−3	23	−20	22
N_2	406	(17)	277	18	351	20	−28	15	92	16	−47	15
O_1	831	(31)	647	30	1632	50	−41	24	−486	32	118	32
O_2	1049	(34)	720	30	841	34	−476	27	174	28	−154	25
O_3	1461	(51)	741	36	1762	56	−8	35	−687	44	273	37
O_4	589	(18)	301	16	436	18	−148	15	184	16	−27	13
O_5	462	(16)	281	15	414	18	7	13	23	14	21	12
O_6	771	(25)	377	20	778	27	119	18	−170	22	−239	19
C_1	739	(33)	437	29	503	31	107	26	23	28	−145	24
C_2	566	(25)	282	23	428	26	−1	20	103	22	−72	19
C_3	490	(24)	484	30	495	29	−62	24	211	23	−63	25
C_4	586	(27)	410	26	339	25	21	22	54	22	14	19
C_5	642	(29)	493	30	477	29	−184	25	223	26	−47	23
C_6	524	(24)	335	24	496	29	−28	23	−26	23	7	22

Table 3. Interatomic distances and angles. Standard deviations in parentheses.

Bond	Å	Å × 10^{-3}	Bond	Å	Å × 10^{-2}
Ni – N_2	2.115	(3)	C_1 – H_{11}	0.93	(4)
Ni – O_4	2.052	(3)	C_1 – H_{12}	1.04	(5)
Ni – O_5	2.054	(3)	C_2 – H_{21}	0.96	(4)
N_2 – C_2	1.474	(5)	C_2 – H_{22}	1.04	(5)
N_2 – C_3	1.484	(6)	C_3 – H_{31}	1.00	(5)
N_2 – C_4	1.477	(6)	C_3 – H_{32}	1.01	(4)
C_2 – C_1	1.517	(7)	C_4 – H_{41}	1.10	(4)
C_3 – C_5	1.517	(7)	C_4 – H_{42}	0.85	(5)
C_4 – C_6	1.506	(7)	C_5 – H_{51}	0.96	(6)
C_5 – O_4	1.426	(6)	C_5 – H_{52}	1.03	(5)
C_6 – O_5	1.454	(6)	C_6 – H_{61}	1.08	(5)
C_1 – O_6	1.425	(6)	C_6 – H_{62}	1.02	(4)
N_1 – O_1	1.211	(7)	O_4 – H_{04}	0.79	(5)
N_1 – O_2	1.215	(6)	O_5 – H_{05}	0.84	(6)
N_1 – O_3	1.199	(7)	O_6 – H_{06}	0.92	(7)
O_4 – O_1	2.693	(5)	H_{04} – O_1	1.96	(5)
O_5 – O_6	2.629	(5)	H_{05} – O_6	1.81	(6)
O_6 – O_2	2.938	(6)	H_{06} – O_2	2.04	(7)
O_6 – O_3	2.975	(7)	H_{06} – O_3	2.24	(7)

Angle	Degrees	
N_2 – Ni – O_4	80.6	(0.1)
N_2 – Ni – O_5	83.2	(0.1)
O_4 – Ni – O_5	92.2	(0.1)
Ni – N_2 – C_2	109.3	(0.2)
Ni – N_2 – C_3	105.1	(0.2)
Ni – N_2 – C_4	108.3	(0.2)
N_2 – C_2 – C_1	117.0	(0.4)
N_2 – C_3 – C_5	110.4	(0.4)
N_2 – C_4 – C_6	110.2	(0.4)
C_2 – C_1 – O_6	108.0	(0.4)
C_3 – C_5 – O_4	108.6	(0.4)
C_4 – C_6 – O_5	109.9	(0.4)
Ni – O_4 – C_5	116.0	(0.2)
Ni – O_5 – C_6	106.9	(0.2)
O_1 – N_1 – O_2	124.5	(0.5)
O_2 – N_1 – O_3	121.8	(0.5)
O_1 – N_1 – O_3	113.6	(0.5)

The scattering factors used are those of the *International Tables*. They were approximated by Bassi polynomials.[4]

DESCRIPTION OF THE STRUCTURE

Each nickel atom is surrounded by six atoms in an octahedral arrangement made of 2 mol of TEA using the nitrogen and two of the oxygen atoms in the coordination. The third branch of the TEA is not coordinated to Ni. This is

Table 4. Observed and calculated structure factors.

h	k	l	Fobs	Fcal
0	0	2	27	23
0	0	4	756	766
0	0	6	409	409
0	0	8	135	131
0	0	10	170	173
0	0	12	87	77
0	1	2	82	90
0	1	3	99	-101
0	1	4	60	-60
0	1	5	246	241
0	1	6	55	46
0	1	7	201	198
0	1	8	90	84
0	1	9	118	121
0	1	11	101	100
0	2	1	91	88
0	2	2	352	-365
0	2	3	249	-243
0	2	4	72	71
0	2	5	186	-185
0	2	6	331	332
0	2	7	57	35
0	2	8	128	125
0	2	10	163	159
0	2	12	71	61
0	3	1	820	818
0	3	2	386	-385
0	3	3	502	510
0	3	4	172	-161
0	3	5	571	577
0	3	6	40	44
0	3	7	254	239
0	3	8	60	13
0	3	9	278	275
0	3	10	44	15
0	3	11	65	64
0	4	0	934	947
0	4	1	72	81
0	4	2	124	128
0	4	3	568	-547
0	4	4	470	487
0	4	5	129	124
0	4	6	226	223
0	4	8	278	279
0	4	9	50	-35
0	4	10	132	124
0	4	11	56	45
0	4	12	45	56
0	5	1	83	75
0	5	2	357	-355
0	5	3	461	438
0	5	4	135	105
0	5	5	68	95
0	5	7	353	367
0	5	8	44	-50
0	5	9	131	134
0	5	11	71	74
0	6	0	276	281
0	6	1	408	382
0	6	2	229	226
0	6	4	381	390
0	6	5	248	233
0	6	6	292	301
0	6	7	91	90
0	6	8	266	265
0	6	9	106	-101
0	6	10	80	72
0	6	12	76	80
0	7	1	301	309
0	7	2	145	143
0	7	3	390	395
0	7	4	68	32
0	7	5	317	326
0	7	6	152	150
0	7	7	207	206
0	7	8	52	-48
0	7	9	182	187
0	7	11	65	59
0	8	0	40	71
0	8	1	203	193
0	8	2	643	641
0	8	3	227	-229
0	8	4	304	304
0	8	5	57	57
0	8	6	131	118
0	8	7	62	45
0	8	8	201	209
0	8	9	67	-71
0	8	10	74	71
0	8	12	81	89
0	9	1	185	191
0	9	2	57	-37
0	9	3	412	401
0	9	4	80	84
0	9	5	109	114
0	9	6	51	66
0	9	7	68	60
0	9	8	30	-18
0	9	9	109	110
0	9	10	38	-20
0	9	11	106	92
0	10	0	350	351
0	10	1	171	182
0	10	2	323	339
0	10	3	151	-151
0	10	4	368	382
0	10	5	171	182
0	10	6	49	41
0	10	8	151	146
0	10	9	56	-36
0	10	10	103	96
0	11	1	387	386
0	11	2	166	-146
0	11	3	374	366
0	11	4	52	35
0	11	5	270	272
0	11	6	31	25
0	11	7	107	99
0	11	9	92	98
0	11	10	64	43
0	11	11	101	93
0	12	1	145	-135
0	12	2	214	213
0	12	4	100	112
0	12	6	154	162
0	12	8	65	57
0	12	9	61	48
0	12	10	77	69
0	13	1	181	183
0	13	2	34	-25
0	13	3	113	101
0	13	4	96	-96
0	13	5	279	284
0	13	6	42	-14
0	13	7	87	73
0	13	9	88	77
0	14	0	203	203
0	14	1	113	99
0	14	2	253	254
0	14	3	43	-53
0	14	4	258	263
0	14	6	183	182
0	14	7	31	-49
0	14	8	82	92
0	14	9	83	63
0	15	1	91	84
0	15	2	72	27
0	15	3	166	155
0	15	5	176	178
0	15	7	92	85
0	15	8	44	40
0	16	1	39	-7
0	16	2	117	126
0	16	4	141	129
0	16	6	135	131
0	16	8	72	68
0	17	1	155	147
0	17	2	83	71
0	17	3	137	141
0	17	5	131	136
0	17	6	55	34
0	17	7	97	92
0	18	0	117	129
0	18	1	38	27
0	18	2	171	168
0	18	3	47	51
0	18	4	80	65
0	18	6	87	114
0	19	1	137	130
0	19	2	77	73
0	19	3	112	93
0	20	0	91	97
0	20	1	83	73
0	21	1	89	96
1	0	-12	64	70
1	0	-10	222	232
1	0	-8	144	162
1	0	-6	52	-29
1	0	-4	211	202
1	0	-2	773	-777
1	0	2	43	36
1	0	6	560	558
1	0	10	78	50
1	0	12	91	98
1	1	-12	43	13
1	1	-11	101	98
1	1	-10	66	53
1	1	-9	276	277
1	1	-8	46	-44
1	1	-7	135	144
1	1	-6	99	92
1	1	-5	275	275
1	1	-4	379	378
1	1	-3	524	515
1	1	-2	886	929
1	1	2	624	618
1	1	3	551	542
1	1	4	287	-273
1	1	5	419	411
1	1	6	78	-85
1	1	7	413	412
1	1	11	118	124
1	2	-12	76	61
1	2	-10	190	194
1	2	-8	240	238
1	2	-7	315	-320
1	2	-6	162	164
1	2	-5	70	77
1	2	-4	591	607
1	2	-3	105	102
1	2	-2	710	719
1	2	-1	342	-345
1	2	1	233	214
1	2	2	695	679
1	2	3	95	-98
1	2	4	270	264
1	2	5	101	-103
1	2	6	507	500
1	2	7	84	-52
1	2	8	57	62
1	2	9	47	18
1	2	10	139	146
1	2	12	94	97
1	3	-9	244	251
1	3	-8	81	-83
1	3	-7	132	145
1	3	-6	224	-230
1	3	-5	112	114
1	3	-4	275	261
1	3	-3	505	498
1	3	-2	456	-452
1	3	-1	269	261
1	3	0	137	130
1	3	1	35	28
1	3	2	339	-346
1	3	3	176	165
1	3	4	128	124
1	3	5	270	279
1	3	6	145	-142
1	3	7	196	191
1	3	8	50	-30
1	3	9	103	97
1	3	11	108	110
1	3	12	67	22
1	4	-10	125	128
1	4	-8	228	234
1	4	-7	41	-29
1	4	-6	265	268
1	4	-5	64	-61
1	4	-4	534	527
1	4	-3	574	586
1	4	-2	564	563
1	4	-1	50	-45
1	4	0	380	377
1	4	1	234	241
1	4	2	111	100
1	4	3	258	261
1	4	4	406	422
1	4	5	66	-71
1	4	6	358	358
1	4	7	61	62
1	4	8	186	191
1	4	9	119	-138
1	4	10	132	138
1	4	12	79	72
1	5	-11	57	63
1	5	-9	142	141
1	5	-8	44	-48
1	5	-7	310	313
1	5	-6	61	-62
1	5	-5	411	414
1	5	-4	79	84
1	5	-3	501	505
1	5	-2	236	232
1	5	-1	644	629
1	5	0	29	34
1	5	1	115	-111
1	5	2	87	-91
1	5	3	283	299
1	5	4	217	219
1	5	5	159	157
1	5	7	315	325
1	5	9	156	158
1	5	10	45	-1
1	5	11	112	114
1	6	-12	111	102
1	6	-10	75	52
1	6	-9	77	75
1	6	-8	215	207
1	6	-7	103	-107
1	6	-6	277	284
1	6	-5	65	68
1	6	-4	372	390
1	6	-3	100	99
1	6	-2	386	386
1	6	-1	477	-494
1	6	0	363	347
1	6	1	246	-261
1	6	2	264	255
1	6	3	139	-147
1	6	4	117	107
1	6	6	238	240
1	6	8	177	184
1	6	10	123	130
1	6	12	66	59
1	7	-11	83	84
1	7	-9	108	106
1	7	-8	51	43
1	7	-7	218	228
1	7	-5	249	258
1	7	-4	69	60
1	7	-3	287	290
1	7	-2	82	-81
1	7	-1	568	580
1	7	0	617	-597
1	7	1	454	453
1	7	2	158	140
1	7	3	471	464
1	7	4	183	179
1	7	5	257	255
1	7	7	154	159
1	7	8	46	46
1	7	9	154	158
1	8	-12	108	96
1	8	-11	44	40
1	8	-10	73	74
1	8	-8	161	182
1	8	-7	40	30
1	8	-6	223	219
1	8	-5	46	-48
1	8	-4	122	125
1	8	-3	208	225
1	8	-2	436	438
1	8	-1	277	-255
1	8	0	79	122
1	8	1	78	7
1	8	2	373	387
1	8	3	417	422
1	8	4	370	382
1	8	5	48	32
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3	9	-3	122	141
3	9	-1	273	280
3	9	0	77	72
3	9	1	60	66

Table 4. Continued.

in accordance with the finding that the temperature factors of the outer atoms of this branch are larger than those of the corresponding atoms in the coordinated branches. The $Ni(TEA)_2$ group is depicted in Fig. 1.

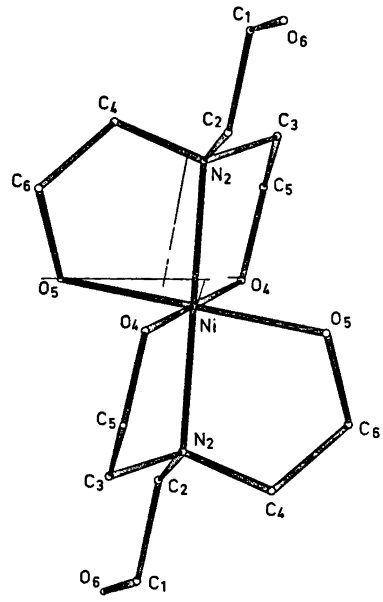

Fig. 1. Perspective drawing of $Ni(TEA)_2$ ion.

A hydrogen bond (2.69 Å) is found from one of the oxygen atoms coordinated to Ni to a nitrate oxygen atom, and the other ligand oxygen atom forms a hydrogen bond of 2.63 Å to the free alcohol oxygen atom of another molecule. This OH group in turn forms weak hydrogen bonds (2.94 Å and 2.97 Å) with the remaining two nitrate oxygen atoms.

The temperature movements of the nitrate group are large but there is no evidence that the group should be rotating. It appears to be planar with threefold rotation symmetry within experimental error.

DISCUSSION

Triethanolamine is related in structure to 2,2′,2″-triaminotriethylamine, tren, and to nitrilo-triacetic acid. The two latter compounds act as tetradentate ligands in all structurally investigated complexes, whereas TEA acts as only a tridentate ligand in $Ni(TEA)_2(NO_3)_2$. If the protons are dissociated from the alcohol groups the resulting alcoholate ion is a much stronger complexing agent than the corresponding neutral molecule. The compound 1-ethyl-germatrane, $C_2H_5Ge(OCH_2CH_2)_3N$, may formally be considered composed from $C_2H_5Ge^{3+}$ and $N(CH_2CH_2O)_3^{3-}$ groups. In this compound [5] all three oxygen atoms are bound to germanium. The Ge – O distances are 1.75 Å, the

same value as found in a number of germanium-oxide compounds.[6] The Ge – N distance is 2.24 Å indicating a weak bond. Thus the $N(CH_2CH_2O)_3^{3-}$ ion is a tetradentate ligand. A similar structure is found in $C_6H_5-Si-(OCH_2CH_2)_3N$.[7] In the $Ni(TEA)_2^{2+}$ group, the Ni – N distance, 2.115 Å, is the same as that reported for the corresponding distance in Ni-tren$(NCS)_2$.[8,9] The Ni – O distance of 2.05 Å is approximately 0.04 Å shorter than nickel-oxygen distances in some nickel-aqua complexes.[10] We are not aware of published data on complexity constants of the Ni^{2+} – TEA system. The structural data indicate, however, that $Ni(TEA)_2^{+}$ must have a fairly high complexity constant in aqueous solution. The N – C distances with an average of 1.478 Å are equal to the corresponding N – C distances in tren,[11] 1.474 Å, within one standard deviation. The average of the C – C distances, 1.513 Å, appears to be slightly larger than the corresponding C – C distances in tren, 1.495 Å. As the estimated standard deviation of these bond lengths is 0.005 Å, the difference is of doubtful significance. The average C – O distance of 1.435 Å is in agreement with accepted values[12] for paraffinic single carbon-oxygen bonds.

Acknowledgement. We are indebted to the *Carlsberg Foundation* for the linear diffractometer.

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Received June 16, 1971.