when it cannot be certainly predicted from atomic spectroscopy. Only in the cases for which $e = 1$ are the complexes stable [11] for crystal fields of purely cubic symmetry. For other e values the crystal fields must be somewhat distorted; for $e = 2$, to tetragonal, and for $e = 3$, to rhombic or tetragonal symmetry. Crystal field calculations explain easily [5],[7] the occurrence of tetragonal symmetry in copper(II) or in diamagnetic nickel(II) complexes with no need of dsp^3-hybridization. If complexes are classified according to $e = 1$ and $e = 2$ or 3, it is interesting to compare the absorption spectra as well as the consecutive complexity constants in the various cases. Thus displacements of bands towards lower wavenumbers by increasing symmetry of the crystal field are found only in systems with $e > 1$ (*e. g.* in the cupric ammonia system) and irregularities in the rest effects are found *e. g.* to a higher degree in the cobalt(II) ammonia system than in the nickel(II) system [12],[p.57].

The activation energies are high only when $\varrho(E_1 - E_2)$ is large and $e = 1$. Bjerrum and Poulsen [13] found empirically that half-completed and completed d-shells (with $\varrho = 0$) and nearly complete d-shells (with $e > 1$) give low activation energies, which increase with the oxidation state for purely electrostatic reasons, just as do the complexity constants. In the robust complexes (*e.g.* $\varrho = 6$ and $e = 1$ in chromium (III) and nickel(II)) the activation energy increases with the value of $(E_1 - E_2)$, which [6] is 17 400 cm^{-1} in $[Cr(H_2O)_6]^{+++}$ and 7 600 cm^{-1} in $[Ni(H_2O)_6]^{++}$. If the magnetism is changed during a consecutive complex formation, a sudden change of activation energies and complexity constants are expected, as found in the cyanide and a,a'-dipyridyl complexes of iron(II)[14]. Magnetically anomalous, octahedral complexes should only be possible when $\frac{\varrho}{5}(E_1 - E_2)$ is larger than the energy of the excited states in the free ion with low S, and they are mainly restricted to the electron configurations d^5 and d^6 with the highest value of ϱ. These facts will be discussed in the following papers of the series "Studies of Absorption Spectra"[15].

1. Bethe, H. *Ann. Physik.* [5] **3** (1929) 133.
2. Ilse, F. E. and Hartmann, H. *Z. Naturforschg.* **6a** (1951) 751.
3. van Santen, J. H. and van Wieringen, J. S. *Rec. trav. chim.* **71** (1952) 420.
4. Orgel, L. E. *J. Chem. Soc.* **1952** 4756 and *J. Chem. Phys.* **23** (1955). *(In press).*
5. Ballhausen, C. J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **29** (1954) No. 4.
6. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **8** (1954) 1502.
7. Ballhausen, C. J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **29** (1955) No. 8.
8. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **9** (1955) 116.
9. Pauling, L. *J. Am. Chem. Soc.* **53** (1931) 1367.
10. Fajans, K. *Chem. Eng. News* **27** (1949) 900.
11. van Vleck, J. H. *J. Chem. Phys.* **7** (1939) 61.
12. Bjerrum, J. *Metal Ammine Formation,* Copenhagen 1941.
13. Bjerrum, J. and Poulsen, K. G. *Nature* **169** (1952) 463.
14. Bjerrum, J., Poulsen, K. G. and Poulsen, I. *Symposium on Coordination Chemistry,* Copenhagen 1953, p. 51.
15. Ballhausen, C. J. and Jørgensen, C. Klixbüll *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **29** (1955) No. 14.

Note on the Structure of Dimethoxydihydrofurfural Diacetate

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By the action of bromine in methanol on furfural diacetate Clauson-Kaas and Fakstorp [1] obtained an 81 % yield of an oily dimethoxydihydrofurfural diacetate which by hydrolysis and oxidation with periodic acid gave *cis-β*-formylacrylic acid. Therefore the product must be a derivative of 2-pentene-1,5-dial-4-one (II) and it was assumed to have structure I in analogy with other dimethoxydihydrofurans.

When repeating the synthesis of dimethoxydihydrofurfural diacetate a somewhat lower yield (about 65 %) was regularly obtained while the reaction product at the same time contained about 15 % of unreacted furfural diacetate. Since the methoxylation of furfural diacetate is a slower reaction than the usual furan methoxylation reactions, the discrepancy may be due to a catalytic effect.

$$\text{I} \quad \xrightarrow{\text{H}_2\text{O}} \quad \left[\begin{array}{c}\text{CH}=\!=\!\text{CH} \\ | \quad\quad | \\ \text{CHO} \quad \text{CO}-\text{CHO}\end{array}\right]_{\text{II}} \quad \xrightarrow[70\%]{\text{H}_5\text{JO}_6} \quad \begin{array}{c}\text{CH}=\!=\!\text{CH} \\ | \quad\quad | \\ \text{CHO} \quad \text{COOH}\end{array} + \text{HCOOH}$$

On standig, a crystalline isomer was precipitated from the oily dimethoxydihydrofurfural diacetate (yield 14 %). Treatment of this crystalline dimethoxydihydrofurfural diacetate with sodium methoxide in methanol gave a liquid with the formula $C_5H_4O_2(OMe)_2$. Catalytic hydrogenation gave a liquid $C_5H_6O(OMe)_2(OAc)_2$, which with sodium methoxide gave a third liquid $C_5H_6O_2(OMe)_2$. We think that these reactions are best explained as shown below, where structure I (either the *cis* or the *trans* form) is assigned to the crystalline dimethoxydihydrofurfural diacetate, while the three liquids are proposed to be the new 2,5-dimethoxy-2,5-dihydrofurfural (III), 2,5-dimethoxytetrahydrofurfural diacetate (IV) and 2,5-dimethoxytetrahydrofurfural (V), all having the same steric configuration as I at the α-carbons.

The mother liquor from the crystalline dimethoxydihydrofurfural diacetate (I) gave, with sodium methoxide, a dark red solution, from which 9 % of the liquid $C_5H_4O_2(OMe)_2$ (2,5-dimethoxy-2,5-dihydrofurfural (III)) was isolated. The main part of the reaction product remained as a red mass. Very probably III is formed from a certain amount (about 11 %) of I, which has remained in the mother liquor, the total yield of I thus being about 22 %. The major component of the mother liquor can, on the other hand, not be one of the two stereoisomeric forms of I, but must be another derivative of 2-pentene-1,5-dial-4-one (II). So far we have not been able to elucidate its structure.

Experimental. (Microanalyses by E. Boss and K. Glens). *Isolation of crystalline dimeth-oxydihydrofurfural diacetate (I).* Furfural diacetate (39.6 g) was methoxylated as described by Clauson-Kaas and Fakstorp [1]. The yield of the reaction product (slightly yellow oil, b.p.$_2$ 119—125°, n_D^2 1.4494) was 31.1 g (60 %, three other preparations gave 61, 63 and 67 %) (Found: C 50.8; H 6.4; OCH_3 20.4; $COCH_3$ 34.6. Calc. for $C_5H_4O_2(OCH_3)_2(COCH_3)_2$ (260.2) containing 15 % of $C_5H_4O_2(COCH_3)_2$ (198.2): C 51.3; H 6.0; OCH_3 20.4; $COCH_3$ 34.7).

30.0 g of the reaction product was left standing at room temperature for five weeks, a precipitate of white crystals of I removed by filtration (4.26 g = 14 %) and the filtrate (n_D 1.4498) analysed (Found: C 50.8; H 6.4; OCH_3 19.0; $COCH_3$ 34.8. Calc. for $C_5H_4O_2$ $(OCH_3)_2(COCH_3)_2$ (260.2) containing 18 % of $C_5H_4O_2(COCH_3)_2$ (198.2): C 51.5; H 6.0; OCH_3 19.6; $COCH_3$ 34.9).

The crystals were crystallized from methanol (4.5 ml) and washed twice with methanol (4 ml in all). Hereby 3.04 g of a product melting at 110—111° (Hershberg apparatus corr.) was obtained. Further crystallization did not change the m.p. (Found: C 50.8; H 6.3; OCH_3 23.6; $COCH_3$ 33.5. Calc. for $C_5H_4O_2$ $(OCH_3)_2(COCH_3)_2$ (260.2): C 50.8; H 6.2; OCH_3 23.9; $COCH_3$ 33.1).

The acetyl determinations were carried out by acidimetric titration at room temperature (phenolphthalein indicator). In the usual determinations (distillation of acetic acid from a 48 % sulfuric acid solution) acetyl values about 30 % higher than the calculated amount were obtained. We believe this to be due to hydrolytic cleavage of 2-pentene-1,5-dial-4-one (II) with the formation of formic acid.

$$\text{I} \quad \xrightarrow[77\%]{\text{NaOMe}} \quad \text{III}$$

$$81\% \downarrow \text{PtO}_2,\text{H}_2$$

$$\text{IV} \quad \xrightarrow[77\%]{\text{NaOMe}} \quad \text{V}$$

2,5-Dimethoxy-2,5-dihydrofurfural (III). I
(3.01 g, 0.116 mole) was dissolved in methanol
(10 ml) and the solution added to a solution of
sodium methoxide (from 0.266 g of sodium;
0.0116 mole) in methanol (15 ml). After stand-
ing at room temperature for 15 minutes the
methanol and the methyl acetate formed by
the reaction were distilled in a vacuum. Ether
(50 ml) was added to the colorless residue, a
precipitate of sodium acetate (0.88 g = 93 %)
removed by filtration and the ether solution
distilled. The yield was 1.40 g (77 %) of III
(colorless liquid, b.p.$_{10}$ 88°, n_D^{25} 1.4430) (Found:
C 53.3; H 6.8; OCH$_3$ 39.6. Calc. for C$_5$H$_4$O$_2$
(OCH$_3$)$_2$ (158.2): C 53.2; H 6.4; OCH$_3$ 39.3).

On standing the product changes into a
more viscous liquid with a higher refractive
index. Probably polymerization takes place.
Redistillation of 1.20 g after 10 days gave 0.74
g of the original product (b.p.$_{20}$ 98°, n_D^{25} 1.4431).

2,5-Dimethoxytetrahydrofurfural　diacetate
(IV). I (2.34 g) was dissolved in dioxan
(50 ml) and the solution shaken (3 hr) with
Adams platinum oxide catalyst (100 mg) under
hydrogen (70 atm). The product was isolated
by distillation. The yield was 1.92 g (81 %)
of IV (colorless liquid, b.p.$_{0.3}$ 97—99°, n_D^2
1.4398) (Found: C 50.7; H 7.2; OCH$_3$ 23.5;
COCH$_3$ 31.8. Calc. for C$_5$H$_6$O$_3$(OCH$_3$)$_2$(COCH$_3$)$_2$
(262.3): C 50.4; H 6.9; OCH$_3$ 23.7; COCH$_3$
32.8).

2,5-Dimethoxytetrahydrofurfural　(V). IV
(3.00 g) was treated with sodium methoxide
as described above for the preparation of III.
The yield was 1.40 g (77 %) of V (slightly
yellow liquid, b.p.$_{14}$ 82—84°, n_D^{25} 1.4307)
(Found: C 52.9; H 7.9; OCH$_3$ 38.9. Calc. for
C$_5$H$_6$O$_2$(OCH$_3$)$_2$ (160.2): C 52.5; H 7.6; OCH$_3$
38.7).

The following day the refractive index of the
product had risen to 1.4323. Redistillation of
1.23 g gave 1.02 g of the original product
(colorless liquid, b.p.$_{14}$ 82—83°, n_D^{25} 1.4306).
Apparently V, like the corresponding dihydro-
furan III, polymerizes on standing.

Reaction of liquid dimethoxydihydrofurfural
diacetate with sodium methoxide. A portion
(15.0 g) of the mother liquor from the isolation
of I was treated with sodium methoxide in
methanol and the red reaction mixture worked
up as described for the preparation of III.
The yield was 0.82 g (9 %) of III (b.p$_{11}$ 93—
94°, n_D^{25} 1.4450) (Found: C 53.0; H 6.6;
OCH$_3$ 39.2).

1. Clauson-Kaas, N., and Fakstorp, J. *Acta*
Chem. Scand. **1** (1947) 415.

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Fixation of Nitrogen by Nodules Excised from Illuminated and Darkened Pea Plants

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In the symbiotic nitrogen fixing system
of leguminous plant and root nodule
bacteria, the photosynthesizing plant must
translocate substrates to the nodule to
support its general respiration and growth,
to supply energy for nitrogen fixation, and
to accept the fixed nitrogen. There is little
information to indicate how rapidly these
substrates are exhausted after photosyn-
thesis ceases. Lindstrom, Newton and
Wilson [1] have demonstrated a progressive
and marked decrease in nitrogen fixation
by red clover plants when they are darken-
ed. Virtanen [2] has reported the conver-
sion of leghaemoglobin to a green pigment
in the nodules of plants kept in the dark,
and found that such a conversion is con-
nected with the inactivation of the nitro-
gen fixing system. The present experi-
ments show that there is a striking and
rapid decay in the nitrogen fixing capacity
of nodules on darkened plants.

Torstai peas were planted in a sand
substrate on June 30, were inoculated with
Rhizobium leguminosarum strain H-43, and
were furnished a nitrogen-free nutrient
solution during their period of growth in a
greenhouse. The plants, in early flower,
were approximately 6 weeks old at the
time of the experiments, and they were
green, vigorous, and well nodulated. The
nodules had red centers indicative of the
presence of abundant leghaemoglobin.

At harvest the sand was rinsed from the
roots, and the nodules were removed from
the roots and placed immediately in a small
respirometer vessel. The vessel on a War-
burg manometer was evacuated [3], flushed
twice with O$_2$ and reevacuated; a mixture