

Unexpected Reaction of 2,2'-Bipyridyl-cycloocta-1,5-diene-nickel(0) with Acetone and Dioxygen

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Dedicated to our Doctoral Supervisor Prof. E. Uhlig on his 70th Birthday

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Abstract. The reaction of (bipy)Ni(cod) (**1**) (bipy = 2,2'-bipyridyl, cod = cycloocta-1,5-diene) with dioxygen and acetone at $-20\text{ }^{\circ}\text{C}$ affords (bipy)Ni(C₉H₁₆O₃) (**2**) (C₉H₁₆O₃)²⁻ = 2,4,6,6-tetramethyl-tetrahydropyran-2,4-diolate), which has been characterized by NMR, MS and an X-ray crystal struc-

ture determination. Acidolysis of compound **2** with two equivalents of acetyl acetone (Hacac) yields (bipy)Ni(acac)₂ and C₉H₁₈O₃ (**3**) (2,4,6,6-tetramethyl-tetrahydropyran-2,4-diol), a cyclic trimer of acetone.

Organometallic compounds are often found to be air sensitive, but the products of the reaction with air remained unidentified in most cases. We observed a "decomposition reaction" of (bipy)Ni(cod) (**1**) (bipy = 2,2'-bipyridyl, cod = cycloocta-1,5-diene) with dioxygen in acetone in 1984 [1]. We have now studied this reaction in more detail.

The typical violet colour of an acetone solution of **1** changes to red when exposed to dioxygen. The yield of the red product **2** is up to 47% when the reaction temperature is below $-20\text{ }^{\circ}\text{C}$, only one equivalent of dioxygen is added slowly, and the crystalline product is separated from the reaction mixture at low temperature. At room temperature the mother liquor becomes jelly-like. In the volatile part the solvent, cod and diacetone alcohol, which is the product of the acetone aldol reaction, could be identified by GC.

In the ¹H NMR spectrum of **2** in addition to unresolved singlets of the bipy-ligand four methyl group singlets are observed. One of it is shifted to unusual low field (2.61 ppm), and thus is bound to a especially electron deficient carbon. The geminal hydrogen atoms of the CH₂-groups are inequivalent. Two methylene hydrogen atoms are strongly coupled (12.8 Hz).

In the ¹³C NMR spectrum there are nine of ten signals resolved for the bipy-ligand the spectrum furthermore displays signals for four methyl groups, two methylene groups, and three quaternary carbon atoms. One of the latter is shifted to unusual low field (94.5 ppm), and this electron deficient carbon is presumably bound to two oxygen atoms. The signals of the other two quaternary carbons (70.8 ppm and 64.2 ppm) indicate that they each are bound to one oxygen atom. It follows from the NMR spectra that complex **2** is chiral.

From a solution of the red nickel complex **2** in THF we obtained well shaped single crystals suitable for a X-ray crystal analysis.

The X-ray crystal structure of complex **2** shows that geometry at the Ni(II) centre is square planar. The compound contains two chelat ligands, 2,2'-bipyridyl and the dianion C₉H₁₆O₃²⁻ (2,4,6,6-tetramethyl-tetrahydropyran-2,4-diolate).

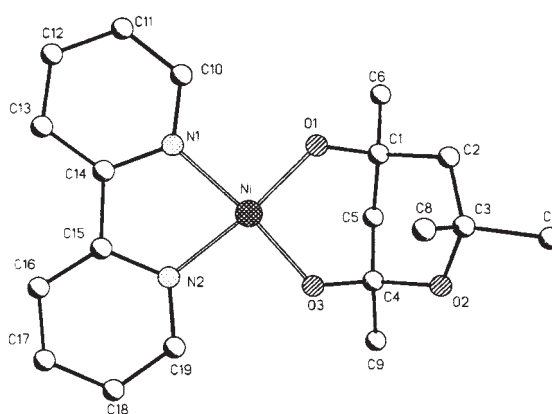
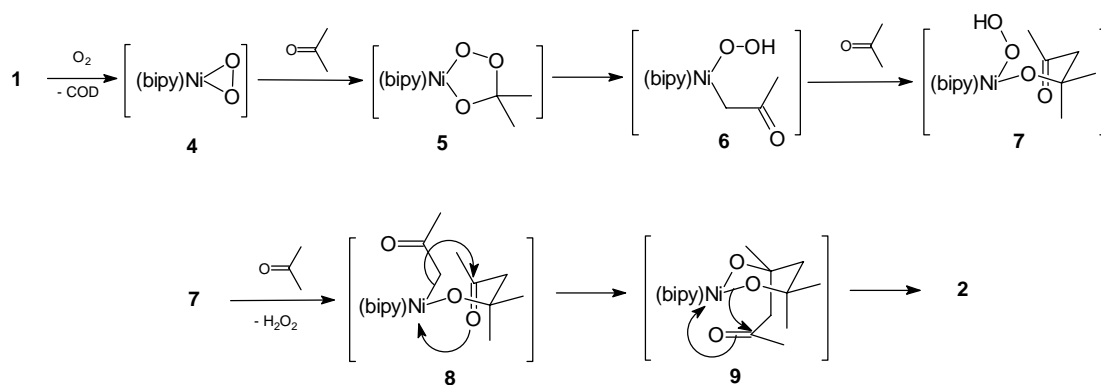


Fig. 1 Molecular structure of (2,2'-bipyridyl)(2,4,6,6-tetramethyl-tetrahydropyran-2,4-diolato)nickel(+2) (**2**). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni–N(1) 1.920(3), Ni–N(2) 1.916(4), Ni–O(1) 1.813(3), Ni–O(3) 1.827(3), O(1)–C(1) 1.426(5), O(2)–C(3) 1.461(6), O(2)–C(4) 1.470(5), O(3)–C(4) 1.395(6) N(1)–Ni–N(2) 82.76(18), N(1)–Ni–O(1) 90.68(17), O(1)–Ni–O(3) 95.94(15), O(3)–Ni–N(2) 90.60(16)

The two donor atoms of the dianion are the alcoholate and the semiketalic oxygen atom. The bond distances in the semiketalic moiety C(4)–O(2) and C(4)–O(3) are significantly different. The six-membered chelate ring has boat conformation, whereas the pyran ring has chair conformation. The chelate ring and the pyran ring share two asymmetric carbon atoms. There are only two ways to coordinate the chelate ligand with the anionic oxygen donor atoms to nickel, thereby forming a pair of enantiomers. In the X-ray crystal structure we found both in a 1 : 1 ratio.

The new ligand is composed from three molecules of acetone, and the synthesis is thought to include a dioxygen attack and two deprotonation steps as shown in Scheme 1.

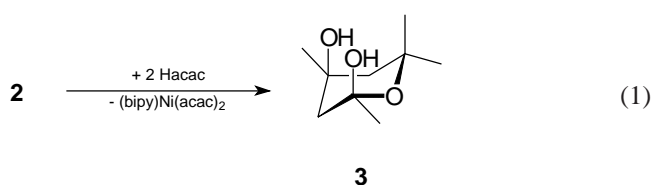


Scheme 1 Proposed reaction course of (bipy)Ni(cod) (**1**) with dioxygen in acetone

(Bipy)Ni(cod) does not react with acetone [2], and the bipy-ligand is hard to oxidize [3]. So the initial step should be attack of dioxygen at the nickel center of **1** forming intermediate (bipy)NiO₂ (**4**). Addition of an acetone solvent molecule to **4** affords the nickelperoxoacetone (bipy)Ni(O₂C(CH₃)₂O) (**5**). The platinum and palladium derivatives of **5** have been isolated [4]. The peroxy group of **5** undergoes hydrogen abstraction from a methyl group, followed by rearrangement to intermediate **6**. In the next step acetone insertion in the Ni–C-bond of **6** gives intermediate **7**. The perhydroxo ligand in **7** deprotonates another solvent acetone molecule. The resulting intermediate **8** also features a reactive Ni–C-bond where an intramolecular carbonyl bond insertion is possible. In the last step an alcoholate oxygen in the six-membered chelate complex **9** intramolecularly attacks the ketone carbon to give the semiketalic moiety of the final compound **2**. Hydrogen peroxide is the second reaction product. It oxidizes a part of nickel to a brown yellow product. This unidentified product contains the remaining half of nickel.

Acidolysis of complex **2** with two equivalents of acetyl acetone yields (bipy)Ni(acac)₂ and liberates the new compound C₉H₁₈O₃ (**3**) (2,4,6,6-tetramethyl-tetrahydro-pyran-2,4-diol). **3** exhibits in the IR spectrum a broad ν(OH) at 3170 cm⁻¹. In the EI mass spectrum no mole peak could be obtained. The highest observed mass was 159 *m/e*, which corresponds to a fragment where the molecular ion has lost a methyl group to form a highly stable 2,4,6-substituted pyrylium ion. Applying softer CI-technics, with water vapour ionisation [M–H]⁺ was dedicated at 175 *m/e* and with ammonia ionisation [M–NH₄]⁺ at 192 *m/e*. If D₂O is used for chemical ionisation, a H–D exchange of both hydroxyl groups of **3** takes place in the injector, and the pseudo molecule ion is shifted to 178 *m/e*. In the high-resolution-MS (electro spray ionisation with sodium) the mole peak was observed at 197.11510 *m/e* (calc. 197.11536).

The ¹³C NMR spectra of **3** in d₄-methanol reveals the expected nine signals for the compound. The spectrum in d₁-chloroform is more complicated. In addition to three signals of quaternary carbon atoms two sets of signals appear for the methylene and methyl groups. It is reasonable to assume that in chloroform solution strong hydrogen bridges exist between the molecules of **3**. The hydrogen bridges are broken in methanolic solution. The results are summarized in equation 1.



Diacetone alcohol is the first product of the aldol reaction of acetone. This compound usually undergoes aldol condensation with a third acetone molecule to give the open-chain compound triacetone alcohol [5]. Compound **3** is a cyclic isomer of triacetone alcohol which was not prepared until now. It is sensitive to air, acids and room temperature.

Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were distilled under argon before use acetone from P₂O₅, THF, ether, and toluene from Na/benzophenone. NMR spectra were taken on a Bruker AC 200 spectrometer (200 and 50.3 MHz for ¹H and ¹³C, respectively). The EI and CI mass spectra were recorded on a spectrometer SSQ 710 (Finnigan MAT). The electron impact energy was 70 eV and the source pressure in CI was about 200 Pa. For high mass experiments a MAT 95 XL with electrospray-interface (Finnigan MAT) was used. The compound **3** (0.001%) was injected in methanolic solution containing polyethylene glycol as internal standard. IR spectra were obtained in nujol mull on a Perkin-Elmer system 2000 spectrometer. Elemental analysis were carried out at the Institute of Organic Chemistry and Macromolecular Chemistry (Friedrich Schiller University Jena). 2,2'-Bipyridyl was purchased from POCh (Poland), cycloocta-1,5-diene from MERCK, and triethyl aluminium from Witko GmbH, Bergkamen. Dioxygen was used in purity of 99,5%. (Bipy)Ni(cod) was prepared according to a literature method [6].

Crystal Structure Determination

Intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo–K_α radiation.

Data were corrected for Lorentz and polarization effects, but not for absorption [7]. The structures were solved by direct methods (SHELXS [8]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [9]). The hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All nonhydrogen atoms were refined anisotropically [9]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for (2,2'-Bipyridyl)(2,4,6,6-tetramethyl-tetrahydropyran-2,4-diolato)nickel(+2) 2 [10]

$C_{19}H_{24}N_2NiO_3$, Mr = 387.11 g mol⁻¹, red prism, size 0.22 × 0.18 × 0.12 mm³, monoclinic, space group C2/c, a = 21.092(2), b = 11.986(2), c = 16.029(2) Å, β = 115.717(6)°, V = 3650.9(8) Å³, T = -90 °C, Z = 8, ρ_{calcd} = 1.409 g cm⁻³, μ (Mo-Kα) = 10.83 cm⁻¹, F(000) = 1632, 6123 reflections in h(-27/27), k(-15/12), l(-20/20), measured in the range 3.36° ≤ Θ ≤ 27.48°, completeness Θ_{max} = 95%, 3984 independent reflections, R_{int} = 0.101, 2254 reflections with F_o > 4σ(F_o), 320 parameters, R¹_{obs} = 0.079, wR²_{obs} = 0.114, R¹_{all} = 0.118, wR²_{all} = 0.137, GOOF = 1.027, largest difference peak and hole: 0.352/-0.399 e Å⁻³.

(2,2'-Bipyridyl)(2,4,6,6-tetramethyl-tetrahydropyran-2,4-diolato)nickel(+2) (2)

A slurry of 8.0 g (24.8 mmol) (bipy)Ni(cod) in 150 ml acetone was placed in a three-necked flask. The mixture was mechanically stirred while cooled to -20 °C. The flask was fitted with an adapter with a Schlenk-tube containing 555 ml (24.8 mmol) dioxygen. During the reaction time of 20 h the colour changed from dark violet to red. Then the reaction mixture was kept over night at -78 °C. The red crystalline precipitate was collected on a cooled frit and washed with ether. The product was recrystallized from THF and dried *in vacuo*. Yield: 4.5 g (46.9%) magnetic susceptibility: χ_g = 0.76 10⁻⁶ cm³ g⁻¹, 19.2 °C). - UV/Vis (THF): 28 400 cm⁻¹ (ε = 1 500 l mol⁻¹ cm⁻¹), 19 900 cm⁻¹ (ε = 1500 l mol⁻¹ cm⁻¹) with a shoulder at 22 200 cm⁻¹. - ¹H NMR (d₈-THF): δ/ppm = 8.84 (2H, s, CH), 7.94 (4H, s, CH), 7.46 (2H, s, CH), 2.61 (3H, s, CH₃), 2.05 (1H, s, CH₂), 1.62 (1H, s, CH₂), 1.50 (1H, d, J = 12.8 Hz, CH₂), 1.26 (3H, s, CH₃), 1.20 (1H, d, J = 12.8 Hz, CH₂), 1.10 (3H, s, CH₃), 0.94 (3H, s, CH₃). - ¹³C NMR (d₈-THF): δ/ppm = 154.2 (C), 148.7 (CH), 148.6 (CH), 138.2 (CH), 138.1 (CH), 125.2 (CH), 125.0 (CH), 120.5 (CH), 120.4 (CH), 94.5 (O-C-O), 70.8 (O-C), 64.2 (O-C), 58.1 (CH₂), 51.0 (CH₂), 36.5 (CH₃), 33.6 (CH₃), 31.9 (CH₃), 31.7 (CH₃). - IR (Nujol mull): ν/cm⁻¹ = (bipy) 1605.

$C_{19}H_{24}N_2NiO_3$ Calcd.: C 58.95 H 6.25 N 7.24 (387.10) Found: C 58.67 H 6.38 N 7.16.

2,4,6,6-Tetramethyl-tetrahydropyran-2,4-diol (3)

A slurry of 3.9 g (10.1 mmol) **2** in 50 ml diethylether was stirred at 0 °C in a Schlenk tube. A solution of 2.0 g (20.0 mmol) acetyl acetone in 50 ml diethylether was added dropwise to the suspension. The colour of the precipitate changed from red to light green. The insoluble (bipy)Ni(acac)₂ was collected on a frit and washed with ether. The colourless filtrate was evaporated to dryness *in vacuo*. Yield: 1.6 g

(91.8%); The white crystalline residue is sensitive to air and acids and is unstable at ambient temperature. It has to be stored below 0 °C. *m.p.* 72–74 °C. - IR (Nujol mull): ν/cm⁻¹ = ν(OH) 3170. - ¹H NMR (d₄-methanol): δ/ppm = 2.76 (1H, m; CH₂), 1.70 (1H, m, CH₂), 1.46 (5H, m, CH₂, CH₃), 1.32 (3H, s, CH₃), 1.20 (3H, s, CH₃), 1.16 (3H, s, CH₃). - ¹³C NMR (d₄-methanol): δ/ppm = 98.3 (O-C-O), 73.3 (O-C), 70.5 (O-C), 47.9 (CH₂), 45.9 (CH), 34.8 (CH₃), 31.7 (CH₃), 30.7 (CH₃), 30.1 (CH₃). - ¹³C NMR (CDCl₃): δ/ppm = 97.1 (O-C-O), 72.0 (O-C), 69.3 (O-C), 54.2 (CH₂), 50.9 (CH₂), 47.0 (CH₂), 44.7 (CH₂), 34.1 (CH₃), 31.8 (CH₃), 31.6 (CH₃), 31.5 (CH₃), 31.4 (CH₃), 30.7 (CH₃), 29.5 (CH₃), 29.1 (CH₃). - MS: (EI, 70eV, [m/e]): 43.1 (48%), 56.1 (14.8%), 58.1 (66.9%), 59.1 (22.8%), 83.0 (8.48%), 96.1 (34.1%), 98.0 (21.6%), 99.1 (33.8%), 101.1 (100.0%), 103.1 (8.9%), 118.1 (11.2%), 123.1 (8.8%), 141.0 (33.8%), 156.0 (11.6%), 159.0 (18.4%). - High-resolution-MS (ESI, Na-adduct): found: 197.11510 m/e calcd. for C₉H₃₈O₃Na: 197.115364 m/e.

$C_9H_{18}O_3$ Calcd.: C 62.04 H 10.41 (174.23 g/mol) Found: C 61.86 H 10.70.

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