

CCA-511

546.786:547.442.3.07

Original Scientific Paper

Synthesis of Some Dioxotungsten(VI) Chelates with 1,3-Diketones

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Received May 4, 1968

The preparation of dioxotungsten (VI) chelates of the WO_2L_2 type with acetylacetone and dibenzoylmethane is described and some properties of these chelates are discussed. The chelate with benzoylacetone has a structure apparently different from that of the two other chelates, as evidenced by the differences in the metal to ligand ratio and by the infrared spectra.

In the literature on chelates of various metals with 1,3-diketones, the synthesis and properties of tungsten chelates have received very little attention. To the best of our knowledge, with the exception of some patents¹⁻³ on the use of tungsten(III) and tungsten(IV) acetylacetonates, only Goan *et al.*⁴ have briefly mentioned the compound $[WO_2(OH)acac]_2$ (Hacac = 2,4-pentanedione) which was believed to be formed by the hydrolytic oxidation of tungsten(III) acetylacetonate.

In view of the practical applicability of tungsten chelates and in search for some information about the geometry of the WO_2^{2+} group⁵, we considered it of interest to prepare some dioxotungsten(VI) chelates with 1,3-diketones.

First we attempted to prepare the chelates by heating tungsten(VI) oxide with the corresponding 1,3-diketone in a suitable solvent, a method which has been used to prepare dioxomolybden(VI) acetylacetonate⁶. However, even after 48 hrs. of refluxing, the results were negative.

Good results were obtained when WO_2Cl_2 was refluxed with a benzene solution of the following 1,3-diketones: 2,4-pentanedione (Hacac), 1-phenyl-1,3-butanedione (HBA), and 1,3-diphenyl-1,3-propanedione (HDBM). However, in the case of the chelates with HBA and HDBM, the yield was rather low and the synthesis was time-consuming. An alternative procedure, similar to the one used by Grdenić and Korpar-Čolig⁷ for the preparation of the corresponding dioxomolybden (VI) chelates, gave much better yields and the preparation took less time. The details of this procedure are given in the experimental section.

In order to determine the composition of the prepared chelates, the results of the elemental analysis were correlated with those inferred from the analysis of the infrared spectra.

The spectra of the chelates with Hacac⁸ and HDBM were similar (except, of course, for the bands attributable to vibrations located mainly in the phenyl rings) and could be compared with the spectra of the corresponding dioxomolybden (VI) compounds which are known to have a composition corres-

ponding to the formula MoO_2L_2 . The elemental analysis, giving a WO_2 to ligand ratio of 1:2, further confirmed the same structure of dioxotungsten (VI) acetylacetonate and dibenzoylmethanate.

The situation is more complicated in the case of the chelate with benzoylacetone. The elemental analysis of this compound (prepared by either of the two methods) gave consistently a WO_2 to ligand ratio close to 1:1. On the other hand, the infrared spectrum of this compound differs from the spectrum of the two other chelates and also from that of $\text{MoO}_2(\text{BA})_2$; whereas, in the spectra of the two former chelates the sharp and strong bands around 950 and 905 cm^{-1} could easily be attributed to the $\text{W}=\text{O}$ stretching vibration of the WO_2 group⁵, in the spectrum of the chelate with benzoylacetone there are in the corresponding region fewer strong bands, suggesting that either there are no WO_2 groups or that the structure of the chelate is different from that of the two other chelates. Since, owing to the extremely low solubility of this and the two other chelates, we failed to determine their molecular weight, we are presently unable to determine whether the observed differences are due to the fact that the benzoylacetone is not monomeric (possibly on account of the existence of $\text{W}-\text{W}$ bonds) or to some other reason. Further work on this interesting problem is in progress.

EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer Model 521 Infrared Spectrophotometer in KBr pellets and Nujol mulls. The melting points are uncorrected.

Materials

Tungsten (VI) oxide, 1,3-diphenyl-1,3-propanedione and 1-phenyl-1,3-butanedione were Hopkin and Williams Ltd. (London) products. The solvents, as well as 2,4-pentanedione, were purchased from Merck AG (Darmstadt). WO_2Cl_2 was prepared according to Forcheer⁹ prior to each preparation.

Acetylacetone Chelate

A mixture of dioxotungsten (IV) chloride (2 g.), freshly distilled acetylacetone (10 ml.) and anhydrous benzene (30 ml.) was heated under reflux for 12 hrs., the hot solution filtered, and the solvent partly distilled off. After standing overnight pale yellow crystals were obtained. Addition of petroleum ether increased the yield (2–2.3 g.; 70–80% based on WO_2Cl_2). The crystals were filtered off, washed with petroleum ether and dried. Recrystallization from acetylacetone yielded a pale yellow crystalline substance, m. p. 195–198° C (decomp.). When heated to 170–180° C at 10^{-4} mm. Hg, the product sublimes. It is only very slightly soluble in benzene, chloroform and other common solvents. If left for a long time in a closed test-tube, it decomposes as evidenced by the odor of acetylacetone and the changes in the infrared spectrum.

Anal. $\text{C}_{10}\text{H}_{14}\text{O}_6\text{W}$ (414.08) calc'd.: C 29.00; H 3.41; W 44.40%
found: C 29.15; H 3.48; W 44.21%

Infrared spectrum. 3115 (vw), 2965 (vw), 2915 (w), 1584 (vs), 1495 (vs), 1430 (sh), 1412 (m), 1358 (vs), 1302 (vw), 1270 (vs), 1264 (vs), 1171 (m), 1036 (sh), 1023 (s), 954 (vs), 940 (sh), 935 (vs), 908 (vs), 805 (s), 684 (s), 674 (s), 652 (w), 578 (m), 551 (w), 464 (s), 455 (s), 412 (m), 401 (sh), 363 (m), 351 (sh).

Dibenzoylmethane Chelate

Dioxotungsten (VI) acetylacetonate (2 g.), dibenzoylmethane (6 g.) and anhydrous xylene (40 ml.) were heated under reflux for 1 hr, the excess of xylene and the liberated acetylacetone distilled off, a new portion of xylene added and the procedure

repeated until there was no acetylacetone in the distilled xylene. Approximately 10 ml. of benzene was added to the residue, the insoluble part filtered off and petroleum ether added to the filtrate. Upon standing, this solution yielded 2.6–2.9 g. (80–90% based on $\text{WO}_2(\text{acac})_2$ of crystallized canary yellow product. The crude product was recrystallized from benzene to which HDBM (1 g. to 20 ml. benzene) was added, filtered, washed with petroleum ether and dried in air. The pure product does not melt until approximately 300°C, although above 230° it is partly sintered and its color changed to orange. It is very slightly soluble in benzene and chloroform, and still less in other common solvents. It is stable for a much longer time than the corresponding acetylacetone derivative.

Anal. $\text{C}_{30}\text{H}_{22}\text{O}_6\text{W}$ (662.37) calc'd.: C 54.40; H 3.25; W 27.76%
found: C 54.12; H 3.19; W 27.49%

Infrared spectrum. 3143 (vw), 3095 (vw), 3065 (w), 1595 (vs), 1564 (vs), 1550 (vs), 1510 (vs), 1478 (vs), 1436 (s), 1355 (s), 1314 (vs), 1295 (vs), 1230 (s), 1185 (m), 1155 (w), 1122 (m), 1095 (w), 1062 (s), 1020 (s), 998 (m), 951 (vs), 938 (vs), 905 (vs), 870 (w), 845 (w), 820 (m), 790 (m), 762 (s), 695 (s), 678 (s), 628 (s), 589 (s), 577 (s), 530 (m), 460 (w), 385 (w), 368 (w).

Benzoylacetone Chelate

A reaction mixture consisting of $\text{WO}_2(\text{acac})_2$ (2 g.), HBA (6 g.) and anhydrous benzene (40 ml.), was heated under reflux for 1 hr. The excess of benzene containing the liberated acetylacetone, was partly distilled off and the procedure repeated several times until there was no detectable acetylacetone in the distillate. To the remaining oily liquid, 20 ml. of anhydrous benzene was added and the insoluble material filtered off. A pale yellowish, finely crystalline substance precipitated when petroleum ether was added to the filtrate. The crystals were filtered, washed with petroleum ether and dried in air to give approximately 1.5 g. (80% based on $\text{WO}_2(\text{acac})_2$). The crude product was recrystallized from 20 ml. benzene to which 0.5 g. HBA was added. Larger crystals resulted and were filtered, washed with a small amount of benzene followed by petroleum ether and dried in air.

The yellowish substance (m. p. 220–223°C decomp.) is slightly soluble in benzene and chloroform.

Anal. $\text{C}_{10}\text{H}_9\text{O}_4\text{W}$ (377.04) calc'd.: C 31.85; H 2.41; W 48.72%
found: C 31.42; H 2.41; W 48.55%

Infrared spectrum. 3115 (vw), 3100 (vw), 3060 (w), 2915 (w), 1590 (vs), 1550 (vs), 1520 (vs), 1486 (vs), 1450 (m), 1432 (m), 1355 (s), 1318 (m), 1295 (m), 1205 (w), 1180 (w), 1155 (vw), 1105 (m), 1070 (w), 1025 (m), 1020 (m), 998 (w), 962 (s), 875 (vs), 770 (s), 710 (m), 688 (s), 620 (vw), 565 (m), 445 (m), 365 (w, br), 350 (w, br).

Acknowledgments. Many sincere thanks are due to Professor Drago Grdenić of the Faculty of Science at the University of Zagreb who introduced me to the present problem. The help and discussions with Dr. Branka Korpar-Čolig of the same faculty and my colleague Bojan Šoptrajanov are greatly appreciated.

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ИЗВОД**Синтеза на некои диоксволфрам(VI) хелати со 1,3-дикетони***А. Николовски*

Опишана е синтезата и дадени се некои својства на диоксволфрам(VI) хелати од типот WO_2L_2 со ацетилацетон и дибензоилметан. Хелатот со бензоилацетон, што беше аналогно приготвен, очигледно има структура различна од онаа на другите два хелати, како што се гледа од разликите во односот метал-лиганд и во инфрацрвените спектри.

ХЕМИСКИ ИНСТИТУТ
ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
СКОПЈЕ

Примено на 4. мај 1968.