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Dioxotungsten(VI) Complexes with Neutral Schiff Bases as Ligands

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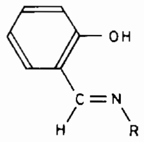
The reaction of WO_2Cl_2 with various N-arylsalicylaldimines (abbreviated as (Sal-R)H) has yielded tungsten(VI) complexes of the type $WO_2Cl_2[(Sal\text{-}R)H]_2$. It is very likely that these complexes involve the neutral Schiff bases, which are coordinated as unidentate ligands to tungsten(VI) ion. Infrared spectra indicate that the tungstenyl group WO_2^{2+} in these complexes has a cis-configuration.

Introduction

In a previous paper[1] we reported the synthesis and characterization of oxotungsten(VI) complexes with N-substituted salicylaldiminates, which are abbreviated as Sal-R. In these complexes, the Schiff bases in their anionic form are coordinated with tungsten(VI) ion, as has also been found to be the case with most transition metal complexes with the same ligands.

We have recently found that the reaction of tungsten(VI) dioxodichloride with N-aryl-substituted salicylaldimines (I, abbreviated as (Sal-R)H) yields a series of dioxotungsten(VI) complexes, which are believed to have the neutral Schiff bases coordinated to tungsten(VI) ion. The present paper describes accounts of the synthesis and properties of these complexes.



I

Abbreviated as (Sal·R)H

Experimental

Materials

Tungsten(VI) dioxodichloride

This compound was prepared as described previously,[2] except that the molar ratio 1:2 of tungsten(VI) hexachloride to tungsten(VI) trioxide was employed in our preparation.

Dioxodichlorobis(triphenylphosphine oxide)tungsten(VI)

This complex was reported previously.[3,4,5] The preparation method originally reported by Brisdon and Feil[3,5] was slightly modified in the present work, as follows.

Acetone (250 ml) was gently added to tungsten(VI) hexachloride (0.085 mol), which was placed in a round-bottomed flask furnished with a calcium chloride tube and a refluxing condenser. The solution started to evolve hydrogen chloride gas at once and the initial orange red solution turned dark blue with continuous generation of heat. After cooling to room temperature, oxygen was bubbled through the solution with stirring. To the yellow green solution obtained was added dropwise a solution of triphenylphosphine oxide (0.2 mol) in acetone (350 ml) to give a white precipitate immediately. The precipitate was filtered off, washed with acetone, and dried *in vacuo.* Recrystallization of the product from dichloromethane or dichloromethane–acetone yielded white crystals of the desired complex (yield about 80%). *Anal.* Found: C, 51.07; H, 3.68%. Calcd. for $C_{36}H_{30}O_4P_2Cl_2W$: C, 51.26; H, 3.59%.

Infrared bands (cm^{-1}): $\nu(W{=}O)$ 914, 960; $\nu(P{-}O)$ 1148, 1177.

Dioxodichlorobis(N-arylsalicylaldimine)tungsten(VI)

These complexes were obtained as yellow microcrystals by either of the following two methods A and B.

Method A. A suspension of tungsten(VI) dioxodichloride (0.01 mol) and an appropriate Schiff base (0.025 mol) in acetonitrile (100 ml) was heated under reflux for about 20–30 hr. Yellow microcrystals were filtered off, washed with ethyl ether, and dried *in vacuo.* The yield was almost quantitative.

When benzene or dichloromethane was employed as a solvent instead of acetonitrile, the reaction did not proceed smoothly; no complex of significant composition was isolated.

Method B. A solution of dioxodichlorobis(triphenylphosphine oxide)tungsten(VI) (0.01 mol) and an appropriate Schiff base (0.025 mol) in dichloromethane

(70 ml) was heated with stirring under reflux for 2–3 hr. Yellow microcrystals were filtered off, washed with dichloromethane, and dried *in vacuo;* yield 70–80%.

A similar successful result was obtained, when benzene or acetonitrile was employed for a solvent instead of dichloromethane.

Recrystallization was not possible due to spontaneous decomposition in appropriate solvents, but they were found to be pure without recrystallization. Analytical data are shown in Table I.

The complexes of this series in the solid state are fairly stable in the atmosphere at room temperature, but they are decomposed gradually with liberation of the free Schiff base molecules, when heated above 100° C. They are insoluble in water and common organic solvents, but slightly soluble in dimethylformamide and dimethylsulphoxide, although decomposed quickly in the solutions.

Tetramethylammonium dioxotetrachlorotungstate(VI)

This complex was prepared by a method modifying a previously reported one.[6]

Tungsten(VI) hexachloride (0.085 mol) was added to a solution of tetramethylammonium chloride in conc. hydrochloric acid and the mixture was stirred at room temperature. The reaction proceeded slowly and was complete in two days to yield a withe crystalline precipitate of the desired complex in quantitative yield. The precipitate was filtered off, washed with thionyl chloride, and dried *in vacuo.*

Infrared bands (cm^{-1}): $\nu(W{=}O)$ 943, 895.

Tetramethylammonium dioxodichloromono(acetylacetonato)tungstate(VI)

Acetylacetone (30 ml) was added to tetramethylammonium dioxotetrachlorotungstate(VI) (0.01 mol), which was prepared as reported previously,[6] and the mixture was heated at about 110° C with stirring, hydrogen chloride gas being thereby evolved. The heating was continued for about 5 hr, until evolution of hydrogen chloride gas ceased. A yellow precipitate was filtered off, washed with acetonitrile and ethyl ether, and dried *in vacuo.* Recrystallization of the crude product from acetylacetone yielded pale-yellow crystals. The yield was almost quantitative. *Anal.* Found: C, 23.49; H, 4.14; N, 3.12%. Calcd. for $C_9H_{19}O_4NCl_2W$: C, 23.49; H, 4.14; N, 3.05%.

Infrared bands (cm^{-1}): $\nu(C{=}O)$ 1570; $\nu(C{=}C)$ 1530; $\nu(W{=}O)$ 940, 895. Proton magnetic resonance spectra (ppm): δ(C–H) 5.70; $\delta(CH_3$, acetylacetonate) 2.02 in d_6-dimethylsulphoxide.

This complex, which is stable in the atmosphere, is soluble in dimethylformamide and dimethylsulphoxide with gradual decomposition. It is slightly soluble in acetylacetone but insoluble in other common organic solvents and water.

TABLE I. Analytical Data of Dioxodichlorobis(N-arylsalicylaldimine)tungsten(VI), $WO_2Cl_2[(Sal\text{-}R)H]_2$.

R	Calcd., %			Found, %		
	C	H	N	C	H	N
ph[a]	45.83	3.26	4.11	45.46	3.11	4.08
p-CH_3-ph	47.41	3.69	3.95	47.25	3.69	3.93
p-Cl-ph	41.62	2.69	3.74	41.27	2.66	3.74

[a] ph: phenyl.

Measurements

Infrared spectra were obtained from nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer. Proton magnetic resonance spectra in d_6-dimethylsulphoxide were measured on a Varian Model A-60 spectrometer using tetramethylsilane as an internal reference.

The diamagnetism of the tungsten(VI) complexes was detected by the Gouy method.

Results and Discussion

In a previous paper, it was reported that the reaction of tungsten(VI) oxytetrachloride with N-arylsalicylaldimines yielded oxotrichloromono(N-arylsalicylaldiminato)tungsten(VI) and not the bis(N-arylsalicylaldiminato)-complexes, in contrast to the case of molybdenum(VI), which forms dioxobis(N-arylsalicylaldiminato)-complexes.[7]

On the contrary, the present work has shown that the reaction of tungsten(VI) dioxodichloride with N-arylsalicylaldimines yields only dioxodichlorobis(N-arylsalicylaldimine)tungsten(VI) complexes with the neutral Schiff bases coordinated. It is thus found that there are such cases where the structure of the starting material greatly affects the reaction product as well as the reaction routes. Complexes of a similar type $WO_2Cl_2(L)_2$, L being neutral ligands, such as dimethylsulphoxide, dimethylformamide, methyl cyanide, triphenylphosphine oxide, and so on, were previously reported.[5]

It should be noted that in the method A acetonitrile may be used as a solvent for obtaining dioxodichlorobis(N-aryl-salicylaldimine)tungsten(VI), whereas other solvents, such as benzene and dichloromethane, yield no successful results. It is likely that the reaction proceeds via intermediate complexes with acetonitrile coordinated to the tungsten(VI) ion. In fact, dioxodichlorobis(acetonitrile)tungsten(VI) was isolated as crystals previously.[5]

Although the reaction of acetylacetone with tetramethylammonium dioxotetrachlorotungstate(VI) yielded tetramethylammonium dioxodichloromono(acetylacetonato)tungstate(VI), the corresponding reaction

TABLE II. Main Infrared Bands of Oxotungsten(VI) Complexes.[a]

Compounds	ν(O–H–N)	ν(C=N) or ν(C–O)	ν (W=O)
(Sal-ph)H	2800–2900	1622	–
$WOCl_3$(Sal-ph)	–	1615	972
$WO_2Cl_2[(Sal\text{-}ph)H]_2$	3050	1640	950, 908
$WO_2Cl_2[O\text{-}P(ph)_3]_2$	–	–	960, 915
$[N(CH_3)_4][WO_2Cl_2(acac)]$	–	1570	940, 895

[a] ν: cm^{-1}.

of N-substituted salicylaldimines or salicylaldehyde did not give any dioxotungsten(VI) complex of a similar composition.

The dioxotungsten(VI) complexes synthesized in the present work are all diamagnetic. As shown in Table II, they exhibit infrared absorption bands at about 895–915 cm^{-1} and 940–960 cm^{-1}, which may be assigned to W=O stretching. According to the criterion proposed previously,[8,9] it may be presumed that the two oxygen atoms of the tungstenyl group are *cis* to each other in these complexes. The *trans*-dioxo-complex would show one unsplit W=O band in this region. The tungsten(VI) complexes obtained in the present work show no band to be assigned to a bridging W–O–W structure in the region 700–900 cm^{-1}. It is thus considered that these dioxotungsten(VI) complexes have a *cis*- tungstenyl (O=W=O) structure, with no bridging W–O–W structure.

The high tendency of the tungstenyl group, WO_2^{2+}, to assume a *cis*-configuration is explained in terms of the multiple π-bonding between the oxygen and tungsten atoms, as was also proposed for the molybdenyl ion.[10] It may be assumed that maximum overlap of dative π-bonding between the oxygen and the metal ion with a small number of *d*-electrons is attained for the *cis*-MO_2 rather than for the *trans*-MO_2 configuration.

The complexes $WO_2Cl_2[(Sal\text{-}R)H]_2$ also show a band at about 1640 cm^{-1}, which is assigned to ν(C=N) of the Schiff bases. There are known those complexes, in which neutral molecules of N-substituted salicylaldimines are bound with a metal ion. As such examples may be cited $CoCl_2[(Sal\text{-}R)H]_2$,[11] $FeCl_3[(Sal\text{-}R)H]_2$[12] and $SnCl_4[(Sal\text{-}p\text{-}CH_3\cdot ph)H]_2$.[13,14,15] These complexes show an infrared band at about 1640 cm^{-1}, which was regarded as characteristic of a keto-amine form of the neutral salicylaldimine coordinated to a metal ion, while the bidentate N-substituted salicylaldiminate bound with a metal ion and the free schiff base exhibit the corresponding band at lower frequencies, that is, about 1610–1620 cm^{-1} and 1620 cm^{-1}, respectively.[16] It is thus likely that the neutral Schiff base molecules in $WO_2Cl_2[(Sal\text{-}R)H]_2$ may be in a similar electronic state to that in the complexes mentioned above.

In agreement with the formulation involving the neutral Schiff bases, the complexes $WO_2Cl_2[(Sal\text{-}R)H]_2$ show a band at about 3050 cm^{-1}, which may be ascribed to a strongly hydrogen-bonded NH or OH group. The Schiff bases in the unionized neutral form are known to show the corresponding band at about 2800–2900 cm^{-1} and in the anionic form they exhibit no absorption of this sort in this region.

Unfortunately, insolubility and instability of these complexes in proper solvents did not allow measurements of proton magnetic resonance spectra, molecular weight or conductivity.

Based on the informations available, various structures may be proposed for $WO_2Cl_2[(Sal\text{-}R)H]_2$. For instance, the tungsten(VI) ion in these complexes can achieve six-co-ordination either with two oxygen atoms, unidentate Schiff bases, and coordinated chloride ions, or with two oxygen atoms, bidentate Schiff bases, and non-bonded chloride ions. Judging from comparatively strong bond often observed between chlorine atom and tungsten(VI) ion, it seems very likely that they may have a similar structure to that of the type $WO_2Cl_2(L)_2$.[5]

Recently Randaccio[17] determined the structure of a bis(salicylaldehyde)ethylenediimine adduct with dimethyldichlorotin(IV), abbreviated as $Me_2SnCl_2\cdot SalenH_2$. In this adduct, the $SalenH_2$ molecules are coordinated to the tin atoms through their oxygen atoms and bridge the Me_2SnCl_2 units. Taking this conclusion into consideration and based on the informations obtained in the present work, we are inclined to assume that the complexes $WO_2Cl_2[(Sal\text{-}R)H]_2$ may be six-co-ordinate with the two oxygen atoms, two chloride ions and two neutral Schiff bases as unidentate ligands, the neutral Schiff bases being bound to the tungsten(VI) ion through their oxygen atoms. The definitive conclusions about the structure of these complexes, however, must await further studies including X-ray structural work.

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