

Oxotungsten(VI) Complexes with Schiff Bases Obtained from Salicylaldehyde and Various Amines

K. YAMANOUCHI and S. YAMADA

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka, Japan

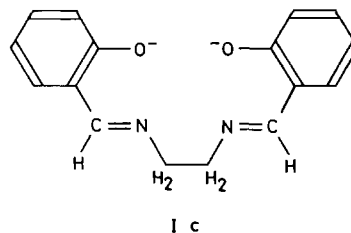
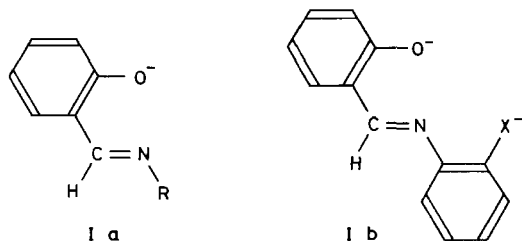
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Oxotungsten(VI) complexes have been synthesized with bi-, ter- and quadri-dentate Schiff bases obtained from salicylaldehyde and various amines. The following types of complexes have been isolated: (1) $WOCl_3$ (bidentate); (2) $WOCl_2$ (terdentate); (3) WO_2 (terdentate); (4) WO_2 (terdentate). L, L being *N,N*-dimethylformamide (DMF) and pyridine (py). With quadridentate *N,N'*-ethylenebis(salicylaldehydeimine), $WOCl_3$ (quadridentate) $_{1/2}$ has been obtained. Results of infrared spectra and electronic spectra are presented and possible structures of these complexes are discussed.

Introduction

Although numerous papers have been published about 3d transition metal complexes with Schiff bases, very little has been studied about their 4d and 5d transition metal complexes. We reported previously synthesis of molybdenum complexes with Schiff bases.¹ In continuation of these studies, tungsten has been taken up as a metal ion.

A few complexes of the series oxodichlorobis(*N*-aryl-5,6-benzosalicylaldehydeimine)tungsten(VI) were reported previously,² but more detailed and systematic studies about these and related compounds are thought to be necessary. The present paper deals with the synthesis and properties of oxotungsten(VI) complexes with Schiff bases (I) obtained from salicylaldehyde and various amines. It is also hoped that studies of this sort may contribute to development of the chemistry of tungsten complexes in general as well as to elucidation of Schiff base tungsten complexes.



Ia: Sal-R; Ib: Sal-phX (X = O, NH); Ic: Salen

Experimental

Materials

All the procedures described below were carried out under nitrogen.

Tungsten(VI) oxytetrachloride

The preparative method of this compound was reported previously, employing the reaction of tungsten trioxide with octachlorocyclopentene.³ In the present work, the previous method was modified, and the compound was prepared in high yield by a method starting from tungsten trioxide and hexachlorocyclopentadiene, which was more readily available to us commercially.

Tungsten trioxide (0.03 mol), which had been dried by heating at 500°C for 3 hr, and hexachlorocyclopentadiene (0.07 mol) were placed in a flask and heated at about 270°C for 2–3 hr. The temperature of the flask was raised to about 300°C and tungsten (VI) oxytetrachloride, which had been formed in the solution, sublimed on the side-tube attached to the flask. The sublimation was over in about 2 hr. Tungsten(VI) oxytetrachloride was obtained as yellow–red needle-like crystals almost quantitatively. For purification, the product was washed with carbon tetrachloride, dried and then sublimed.

The compound is soluble in carbon disulphide, benzene, acetonitrile and dichloromethane to give a red solution. It is moderately soluble in ethyl ether and carbon tetrachloride.

Its infrared spectra and various properties agreed with those reported previously for this compound.^{3–5}

Oxotrichloro(salicylaldehydato)tungsten(VI)

This compound was reported previously by Funk and Mohaupt.⁴ Their method was slightly modified in the present work as follows.

A solution of salicylaldehyde (0.1 mol) in benzene (150 ml) was added drop by drop to a solution of tungsten(VI) oxytetrachloride (0.02 mol) in benzene (50 ml). Hydrogen chloride evolved immediately, and the solution turned dark red-violet from the original red colour. The solution was allowed to stand for about two days, until the evolution of hydrogen chloride ceased, then filtered, evaporated *in vacuo* to about 100 ml, and again filtered. Carbon tetrachloride (200 ml) was added to the filtrate, and the solution was allowed to stand at room temperature for several hours. Brown-purple plate-like crystals were obtained. *Anal.*: Calcd. for $C_7H_5O_3Cl_3W$, $WOCl_3(\text{Salal})$: C, 19.67; H, 1.18%. Found: C, 19.43; H, 1.10%. The notation Salal represents an anion derived from salicylaldehyde. Infrared bands (cm^{-1}): $\nu(\text{C}=\text{O})$ 1640, 1623; $\nu(\text{W}=\text{O})$ 996.

The compound, which is stable for some hours in the atmosphere, looks red-purple when ground to powder. It is soluble in benzene, acetonitrile, acetone, dichloromethane, chloroform and carbon tetrachloride to give a red-purple solution, which eventually undergoes decomposition slowly, yielding a yellow precipitate. Methanol and ethanol decompose the compound quickly, yielding also a yellow precipitate. It is insoluble in, and inert to, water.

Oxotrichloro(N-arylsalicylaldiminato)tungsten(VI), $WOCl_3(\text{Sal-aryl})$

The complexes of this series were synthesized by the following general method.

A solution of an appropriate N-arylsalicylaldimine (0.03–0.05 mol) in benzene (250 ml) was added to tungsten(VI) oxytetrachloride (0.02 mol) dissolved in benzene (50 ml), and the mixture was heated under reflux. At the beginning, hydrogen chloride evolved and the solution turned dark red-purple. The solution was heated for 4–6 hr, until evolution of hydrogen chloride gas ceased. The solution was filtered, while it was hot, and the filtrate was allowed to stand overnight in a refrigerator. Dark-coloured crystals, mixed with yellow substance, were obtained. Recrystallization was carried out from benzene or carbon tetrachloride to give dark-coloured crystals with metallic lustre.

Carbon tetrachloride and acetonitrile may be used instead of benzene in the synthesis described above.

The compound looks red-purple, when dissolved in organic solvents or when ground to powder. In the solid state, it is very stable to the atmosphere, strong acids and alkalis, and fairly stable in benzene or carbon tetrachloride. It is insoluble in water, but slightly soluble in methanol and ethanol, where decomposition takes place quickly. It is also soluble in acetone, aceto-

TABLE I. Analytical Data of Tungsten(VI) Complexes of the Type $WOCl_3(\text{Sal-R})$.

R	Found, %			Calcd., %		
	C	H	N	C	H	N
ph	30.71	1.95	2.59	31.07	2.01	2.79
<i>o</i> -CH ₃ -ph	32.24	2.28	2.73	32.55	2.34	2.71
<i>m</i> -CH ₃ -ph	32.25	2.22	2.60	32.55	2.34	2.71
<i>p</i> -CH ₃ -ph	32.74	2.30	2.55	32.55	2.34	2.71
<i>p</i> -Cl-ph	29.37	1.66	2.41	29.08	1.69	2.61

nitrile, dichloromethane and chloroform, but extensive decomposition occurs in about 1 hr to give a yellow precipitate.

Analytical data of these complexes are shown in Table I.

Oxodichloro(N-2-oxophenylsalicylaldiminato)tungsten(VI), $WOCl_2(\text{Sal-phO})$

This complex was prepared by a method similar to that described above.

Terdentate N-2-hydroxyphenylsalicylaldimine (0.03 mol) was employed for a Schiff base and heating was continued for about 5 hr. Dark-green crystals obtained were washed with N,N-dimethylformamide and ethyl ether, and dried *in vacuo*. *Anal.*: Calcd. for $C_{13}H_9O_3NCl_2W$: C, 32.39; H, 1.88; N, 2.91; Cl, 14.7%. Found: C, 32.18; H, 1.89; N, 2.61; Cl, 15.14%.

The compound in the solid state is very stable to the atmosphere. It is soluble in acetonitrile, acetone, dichloromethane, chloroform and benzene to give a green solution, where decomposition occurs gradually. It is slightly soluble in carbon tetrachloride and ethyl ether and insoluble in water. It is highly soluble, with decomposition, in N,N-dimethylformamide.

Reaction of tungsten(VI) oxytetrachloride with N,N'-o-phenylenebis(salicylaldimine)

A method similar to that described above was followed, except that N,N'-*o*-phenylenebis(salicylaldimine) (0.02 mol) for a Schiff base and acetonitrile (300 ml) as a solvent were employed. The desired complex was obtained in dark green crystals. Purification was carried out by dissolving the crude product in a small amount of N,N-dimethylformamide at room temperature, filtering the solution and adding a large amount of water to the filtrate. Green microcrystals obtained were dried *in vacuo*. *Anal.*: Calcd. for $C_{13}H_{10}O_2N_2Cl_2W$, $WOCl_2(\text{Sal-phNH})$: C, 32.46; H, 2.10; N, 5.82; Cl, 14.74%. Found: C, 32.35; H, 2.06; N, 5.74; Cl, 14.48%. Infrared bands (cm^{-1}): $\nu(\text{N-H})$ 3250; $\nu(\text{C}=\text{N})$ 1618; $\nu(\text{W}=\text{O})$ 960.

From elemental analysis and infrared spectra, the compound isolated was identified to be oxodichloro(N-2-aminophenylsalicylaldiminato)tungsten(VI).

The compound is stable to the atmosphere. Its solubility is similar to, but slightly lower than, that of oxodichloro(N-2-oxophenylsalicylaldiminato)tungsten(VI). When dissolved, a green solution is formed at first, but is decomposed gradually.

Reaction of tungsten(VI) oxytetrachloride with N, N'-ethylenebis(salicylaldimine)

A method similar to that described above was followed. Quadridentate N,N'-ethylenebis(salicylaldimine) (0.02 mol) was employed for a Schiff base with benzene (300 ml) as a solvent. The reaction proceeded slowly, and the solution turned dark-red in 2 hr, beginning to evolve hydrogen chloride. The reaction was complete in 6 hr. After the solution was filtered while it was hot, the filtrate was evaporated under reduced pressure to 50 ml, and carbon tetrachloride (100 ml) was added to the solution to yield red-purple crystals. *Anal.*: Calcd. for $C_{16}H_{14}O_4N_2Cl_6W_2$, $WOCl_3(Salen)_{1/2}$: C, 21.86; H, 1.61; N, 3.19; Cl, 24.20%. Found: C, 23.95; H, 1.57; N, 3.19; Cl, 24.12%. Infrared bands (cm^{-1}): $\nu(C=N)$ 1620; $\nu(W=O)$ 980.

This complex is stable to the atmosphere. Its solubility is similar to, but slightly lower than, that of oxotrichloro(N-arylsalicylaldiminato)tungsten(VI). When dissolved, a red solution is formed at first, but is decomposed quickly.

Reaction of tungsten(VI) oxytetrachloride with bidentate N-alkyl-salicylaldimines

A method similar to that described above was followed, employing N-alkylsalicylaldimines in various solvents. The solution turned dark-red, but the reaction did not proceed smoothly, no hydrogen chloride gas being evolved. No stable compounds corresponding to definite composition could be isolated.

Dioxo(N-2-oxophenylsalicylaldiminato)(N,N-dimethylformamide)tungsten(VI)

Oxodichloro(N-2-oxophenylsalicylaldiminato)tungsten(VI) (*vide supra*) (0.01 mol) was dissolved at room temperature in N,N-dimethylformamide (100 ml) and filtered. The filtrate was allowed to stand at room temperature for 1 hr; the solution, which had been green at first, turned yellow. Addition of ethyl ether (200 ml) to the solution yielded yellow needle-like crystals of the N,N-dimethylformamide adduct. *Anal.*: Calcd. for $C_{16}H_{16}O_5N_2W$, $WO_2(Sal-phO) \cdot DMF$: C, 38.41; H, 3.22; N, 5.60%. Found: C, 38.24; H, 3.35; N, 5.43%. Infrared bands (cm^{-1}): $\nu(C=O)$ 1650; $\nu(C=N)$ 1615; $\nu(W=O)$ 903, 942.

When allowed to stand in the atmosphere, the complex is decomposed gradually. It is slightly soluble in acetonitrile and acetone.

Dioxo(N-2-oxophenylsalicylaldiminato)pyridine-tungsten(VI)

This complex was obtained in yellow crystals by recrystallizing the corresponding N,N-dimethylform-

amide (*loc. cit.*) from pyridine. *Anal.*: Calcd. for $C_{18}H_{14}O_4N_2W$, $WO_2(Sal-phO) \cdot py$: C, 42.70; H, 2.79; N, 5.54%. Found: C, 42.93; H, 2.78; N, 5.47%. Infrared bands (cm^{-1}): $\nu(C=N)$ 1618; $\nu(W=O)$ 900, 940.

When allowed to stand in the atmosphere, the complex is decomposed slowly, liberating pyridine. It is slightly soluble in acetonitrile and acetone.

Dioxo(N-2-oxophenylsalicylaldiminato)tungsten(VI)

The complex was obtained in orange-red crystals, when the corresponding adducts with dimethylformamide and pyridine were allowed to stand for some days in the atmosphere or their methanol solutions were heated. *Anal.*: Calcd. for $C_{13}H_9O_4NW$, $WO_2(Sal-phO)$: C, 36.55; H, 2.12; N, 3.28%. Found: C, 36.44; H, 2.19; N, 3.24%. Infrared bands (cm^{-1}): $\nu(C=N)$ 1620; $\nu(W=O)$ 943; $\nu(W-O-W)$ 760; $\nu(O-H)$, none.

This complex in the solid state is very stable to the atmosphere. It is almost insoluble in many organic solvents. However, it is soluble in pyridine and N,N-dimethylformamide to form the corresponding adducts.

Measurements

Electronic absorption spectra of the complexes were measured on a Shimadzu MPS-50L spectrophotometer. Infrared absorption spectra were obtained from nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer.

Since many of the complexes underwent decomposition in solution, spectral measurements were carried out as quickly as possible. Moreover, for all the solution spectra reported in the present paper, measurements were repeated after the spectra had once been determined, to see if any spectral change due to decomposition during the measurements occurred or not.

Results and Discussion

Oxotungsten(VI) Complexes with Bidentate N-Arylsalicylaldimines

The scheme showing preparative routes of these complexes is shown in Figure 1. Complexes of the type $WOCl_3(Sal-aryl)$ were obtained by reactions of tungsten(VI) oxytetrachloride with various N-arylsalicylaldimines. Further substitution of the salicylaldiminate for the chloride ions in $WOCl_3(Sal-aryl)$, however, has not been successfully accomplished so far by treatment of $WOCl_3(Sal-aryl)$ with the salicylaldimines.

The corresponding N-alkyl-complexes of the type $WOCl_3(Sal-alkyl)$ could not be isolated by reactions of $WOCl_4$ with N-alkylsalicylaldimines. Even reactions of $WOCl_3(salal)$ or $WOCl_3(Sal-aryl)$ with N-alkylsalicylaldimines did not yield successful results.

Kudryavtsev and Savich² reported oxodichlorobis(N-aryl-5,6-benzosalicylaldiminato)tungsten(VI) com-

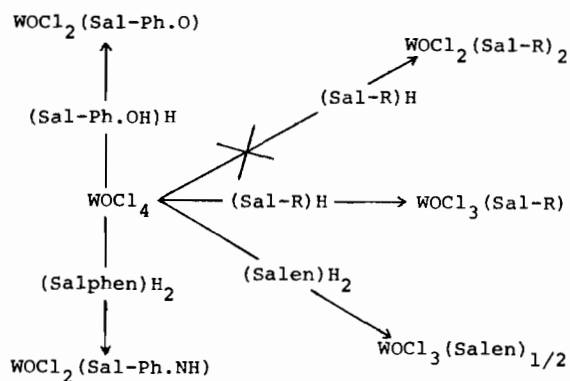


Figure 1. Reaction scheme starting from tungsten(VI)oxytetrachloride.

plexes. However, any attempt to prepare the corresponding $\text{WOCl}_2(\text{Sal-aryl})_2$ by reactions of WOCl_4 with the Schiff bases has not been successful in the present work; such attempts always yielded $\text{WOCl}_3(\text{Sal-aryl})$.

The tungsten(VI) complexes of the type $\text{WOCl}_3(\text{Sal-aryl})$ and $\text{WOCl}_3(\text{salal})$ all appear to be straightforward six-coordinate. Their infrared spectra have one band at about 970 cm^{-1} that may be ascribed to a $\text{W}=\text{O}$ stretching mode, as shown in Table II. The bridging $\text{W}-\text{O}-\text{W}$ structure would produce peaks at lower frequencies,⁶ where these complexes show no such bands.

Data of electronic absorption spectra are given in Table III. Their spectra are similar to each other, suggesting that these complexes all have a similar structure. Since the tungsten(VI) ion has no 5d electron, these complexes are expected to exhibit no absorption bands of pure d-d origins. The two bands at 21 kK and 29 kK are, therefore, regarded as due to charge transfer transitions. The charge transfer bands of oxohalogeno-tungsten(VI) complexes with neutral ligands were previously discussed by Fowles and Frost⁶ on the basis of interpretation proposed by Kon and Sharpless.⁷ They assigned the first charge transfer band of WOCl_4 and $\text{WOCl}_4 \cdot \text{CH}_3\text{CN}$ at 22.4 kK to a halogen b_1 to

TABLE II. Main Infrared Absorption Maxima of Tungsten(VI) Complexes of the Type $\text{WOCl}_3(\text{Sal-R})$ (cm^{-1}).

R	$\nu(\text{C}=\text{N})$	$\nu(\text{W}=\text{O})$
ph	1615	972
<i>o</i> - CH_3 -ph	1615	975
<i>m</i> - CH_3 -ph	1610	970
<i>p</i> - CH_3 -ph	1615	972
<i>p</i> -Cl-ph	1615	972

metal $b_2(d_{xy}, d_{yz})$ transition and the second one at 27.9 kK to a halogen e_g to metal b_2 transition. In a similar way, we may tentatively assign the band of $\text{WOCl}_3(\text{Sal-aryl})$ at about 21 kK to the former transition. The second charge transfer band at about 29 kK may similarly be assigned to the halogen e_g to metal b_2 transition. It is also likely that the intraligand transitions of the Schiff bases are overlapped with the charge transfer bands mentioned above.

Oxotungsten(VI) Complexes with Terdentate *N*-Substituted Salicylaldiminates

Complexes of the following types were obtained in the present work with terdentate Schiff bases: (1) $\text{WOCl}_2(\text{Sal-phX})$ for $\text{X} = \text{O}, \text{NH}$; (2) $\text{WO}_2(\text{Sal-phO}) \cdot \text{L}$ for $\text{L} = \text{DMF}, \text{py}$; (3) $\text{WO}_2(\text{Sal-phO})$. The reaction scheme of these tungsten(VI) complexes is summarized in Figure 2.

Treatment of WOCl_4 with *N,N'*-*o*-phenylenebis(salicylaldimine) has not yielded tungsten(VI) complex with the quadridentate ligand, but oxodichloro-*N*-2-aminophenylsalicylaldiminato-tungsten(VI) was

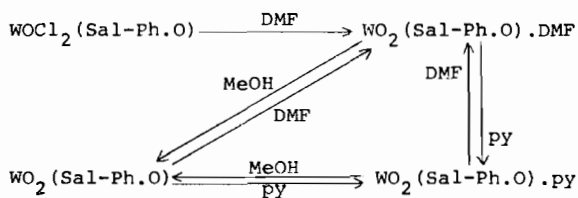


Figure 2. Reaction scheme starting from $\text{WOCl}_2(\text{Sal-phO})$.

TABLE III. Main Electronic Absorption Maxima of Tungsten(VI) Complexes of the Type $\text{WOCl}_3(\text{Sal-R})$.

Sal-R	Solvent	$\nu(\log \epsilon)$
Sal-ph	CH_2Cl_2	21.2(3.74), 29.4(3.85), 35.6(4.11), 42.9(4.27)
Sal- <i>o</i> - CH_3 -ph	CH_2Cl_2	20.8(3.77), 28.9(3.88), 35.3(4.13), 42.8(4.30)
Sal- <i>m</i> - CH_3 -ph	CH_2Cl_2	21.1(3.81), 29.0(3.93), 35.0(4.18), 42.7(4.34)
Sal- <i>p</i> - CH_3 -ph	CH_2Cl_2	21.2(3.77), 29.0(3.88), 35.4(4.10), 42.9(4.30)
	CH_3CN	21.2(3.73), 29.4(3.85), 35.0(4.10)
	C_6H_6	21.3(3.78), 29.1(3.92), 35.5(4.15)
Sal- <i>p</i> -Cl-ph	CH_2Cl_2	21.1(3.81), 29.6(3.91), 35.8(4.19), 42.5(4.34)
	C_6H_6	21.3(3.73), 30.2(3.90)sh, 35.6(4.15)
$(\text{Salen})_{1/2}$	CH_2Cl_2	20.5(3.78), 28.6(3.82), 34.8(4.08), 43.0(4.32)

$\nu: 10^3\text{ cm}^{-1}$.

isolated, as shown in Figure 2, the original quadridentate ligand being hydrolyzed during the reaction to give the terdentate ligand. A small amount of water contained in the solvent or moisture in the atmosphere may probably play a role in this hydrolysis reaction.

Complexes of the type (2) readily lose a unidentate ligand, L, being transformed into $\text{WO}_2(\text{Sal-phO})$. The corresponding methanol adduct was not obtained, in contrast to molybdenum,⁸ which forms the methanol adduct.

Main infrared bands of complexes of the types (1), (2) and (3) are given in the section of Experimental. Complexes of the type (1) show one infrared band at about 970 cm^{-1} , which may be ascribed to $\text{W}=\text{O}$ vibration. No absorption band is observed at lower frequencies, where absorption due to a bridging $\text{W}-\text{O}-\text{W}$ grouping is known to occur. In addition to the infrared band discussed above, $\text{WOC}_2(\text{Sal-phNH})$ shows a band at 3250 cm^{-1} , which may be assigned to $\text{N}-\text{H}$ vibration.

The adducts of the type (2) exhibit two bands at about 900 cm^{-1} and 940 cm^{-1} , which may be assigned to $\text{W}=\text{O}$ vibrations. According to the criterion proposed previously,^{9,10} it is most likely that the WO_2 group may assume a *cis*-configuration. It is expected that the corresponding *trans*-complex would show one unsplit sharp band in this region. The tendency of WO_2^{2+} to assume a *cis*-configuration may be explained as due to double π -bonding between tungsten and two oxygen atoms.^{5,11}

Since terdentate Sal-phO strongly demands planar geometry, a possible structure for these adducts may be such that a unidentate ligand L occupies a coordination site *trans* to one of the oxygen atoms of the WO_2^{2+} group.

The infrared spectrum of $\text{WO}_2(\text{Sal-phO})$ is essentially similar to that of $\text{MoO}_2(\text{Sal-phO})$,⁸ showing a band at 760 cm^{-1} assigned to a $\text{W}-\text{O}-\text{W}$ grouping,¹¹ in addition to two $\text{W}=\text{O}$ bands at about 900 cm^{-1} and 943 cm^{-1} . Judging from this result and the high tendency of Sal-phO to act as a planar terdentate ligand, it is very likely that this tungsten complex has a bi-

nuclear or multinuclear structure, in which one oxygen atom of the WO_2^{2+} group acts as a bridging atom, the ligand Sal-phO being a planar terdentate ligand.

Main electronic absorption bands of these complexes are shown in Table IV. The complexes of the type (1) show similar electronic spectra, suggesting that they have essentially similar structure. Since tungsten(VI) ion has no 5d electron, absorption bands of pure d-d origins are not expected to appear. As discussed in the preceding part of the present paper, the band at about 17 kK of these complexes may possibly be assigned as charge transfer transition from a non-bonding chlorine orbital to a metal d orbital. Many other bands appear in the higher energy region, but assignment of these bands is very difficult at the moment and will not be attempted in the present paper.

Oxohalogenotungsten(VI) Complexes with Quadridentate *N,N'*-Ethylenebis(salicylaldehyde)

Treatment of WOC_4 with *N,N'*-ethylenebis(salicylaldehyde) did not yield a simple uninuclear complex with this quadridentate ligand, but instead a compound of the composition $\text{WOC}_3(\text{Salen})_{1/2}$ was isolated as crystals. In the infrared region, the complex shows a $\text{W}=\text{O}$ infrared band at about 970 cm^{-1} . No $\text{W}-\text{O}-\text{W}$ structure is presumed to be present in this complex, since in the region there appears no band, which may be ascribed to the $\text{W}-\text{O}-\text{W}$ structure.

Its electronic absorption spectrum, as shown in Table III, is very similar to those of complexes of the type $\text{WOC}_3(\text{Sal-R})$, suggesting that the structure of $\text{WOC}_3(\text{Salen})_{1/2}$ is also similar to that of $\text{WOC}_3(\text{Sal-R})$, as far as the geometry around the tungsten(VI) ion is concerned.

All these results combined, together with the composition of the complex and the normal coordination number of tungsten(VI), seem to indicate that a possible structure of this complex may be such that the quadridentate ligand Salen bridges two tungsten(VI) ions, occupying two coordination sites of each tungsten(VI) ion. It may thus be likely that each of the tungsten(VI) ions is coordinated with the other four

TABLE IV. Main Electronic Absorption Maxima of Tungsten(VI) Complexes with Terdentate Schiff Bases.

Complexes	Solvent	ν (log ϵ)
$\text{WOC}_2(\text{Sal-phO})$	CH_2Cl_2	17.3(2.75), 24(ca. 3.2)sh, 27.7(4.04)sh, 30.6(4.26), 38.6(3.93)sh, 43.3(4.04)
	nujol	16.8, 24.3, 29.0
$\text{WOC}_2(\text{Sal-phNH})$	DMF	17.2(2.85), 25.3(3.85)sh, 30.2(4.31)
	nujol	17.1, 23.8, 29.2
$\text{WOC}_2(\text{Sal-phO})\text{DMF}$	DMF	24.6(3.93), 27.4(3.77), 31(3.75)sh, 35.7(4.17)
	py	24.3(3.94), 27.4(3.76), 31(3.78)sh, 32.8(3.99)
$\text{WO}_2(\text{Sal-phO})\text{py}$	py	24.3(3.94), 27.4(3.76), 31(3.78)sh, 32.8(3.99)
$\text{WO}_2(\text{Sal-phO})$	nujol	22.2, 26.8sh

ν : 10^3 cm^{-1} .

ligands, namely three chlorine and one oxygen atoms. A similar structure containing a related quadridentate ligand was previously reported in a binuclear complex $\text{Co}_2(3\text{-CH}_3\text{O-Salen})_3$,¹² where 3-CH₃O-Salen represents N,N'-ethylenebis(3-methoxysalicylaldiminate). However, the suggested structure of $\text{WOCl}_3(\text{Salen})_{1/2}$ is by no means conclusive, but the definitive conclusion about it must await X-ray studies.

Acknowledgement

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