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Oxomolybdenum Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and Alkyl- and Aryl-amines

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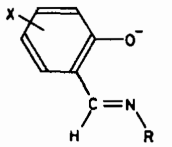
With N-alkyl- and N-aryl-salicylaldiminates (abbreviated as X–Sal–R) as ligands, new molybdenum (V) and molybdenum(VI) complexes of the following three types have been synthesized by reactions of dioxobis(ring-substituted salicylaldehydato)molybdenum(VI) with various alkyl- and aryl-amines: (1) $MoO_2(X\text{–}Sal\text{–}R)_2$, *yellow; (2)* $MoO_2(X\text{–}Sal\text{–}R)$, *red; (3)* $Mo_2O_3(H\text{–}Sal\text{–}R)_4$, *purple. Infrared spectra indicate that the complexes of type (1) are six-coordinate with a cis-*MoO_2 *group. The complexes of type (2) are considered to be multinuclear molybdenum(V) complexes. The complex of type (3), which shows a characteristic UV spectrum, is similar to the acetylacetonato analogue, and is possibly binuclear with one oxygen atom as a bridge.*

Introduction

Although numerous papers have been published about transition metal complexes with N-substituted salicylaldiminates (I),[1,2] relatively little has been reported on their molybdenum complexes. Tris(N-methylsalicylaldiminato)molybdenum(III)[3] and molybdenum(IV) halide complexes with Schiff bases[4] were obtained, and some dioxobis(N-arylsalicylaldiminato)molybdenum(VI) complexes were reported previously.[5] However, more extensive studies about synthesis and characterization of molybdenum(V) and molybdenum(VI) complexes were thought to be very desirable. For example, neither dioxobis(N-alkylsalicylaldiminato)molybdenum(VI) nor related molybdenum(V) complexes have ever been reported in the literature.



(I)

Employing new preparation methods, we have succeeded in obtaining three types of molybdenum(V) and molybdenum(VI) complexes with both N-alkyl- and N-aryl-salicylaldiminates. The present paper deals with their synthesis and some properties.

Experimental

Materials

Dioxobis(ring-substituted salicylaldehydato)-molybdenum(VI), $MoO_2(X\text{–}Sal)_2$

The compound $Mo(H\text{–}Sal)_2$ was reported previously by Rosenheim and Bertheim.[6] Their method was modified to give the following two methods A and B in the present preparation of $MoO_2(X\text{–}Sal)_2$. Method A yielded purer products in a higher yield than method B.

Method A. A solution of ammonium paramolybdate (12.4 g, 0.01 mole) in water (150 ml) and a solution of an excessive amount of an appropriate phenolic aldehyde (about 0.18 mole) in methanol (50 ml) were mixed at room temperature. To the resulting solution was gradually added concentrated hydrochloric acid (10 ml) with vigorous stirring. The reaction was complete in four hours, when the oily substance originally present in the solution was solidified to yield yellow crystals, (about 90% yield). They were filtered off, washed with water–methanol (1:1) mixture and dried *in vacuo.*

Anal. Calcd. for $C_{14}H_{10}MoO_6$, $MoO_2(H\text{–}Sal)_2$: C, 45.42; H, 2.72. Found: C, 45.56; H, 2.67. Calcd. for $C_{16}H_{14}MoO_8$, $MoO_2(3\text{-}CH_3O\text{–}Sal)_2$: C, 44.90; H, 3.28. Found: C, 44.57; H, 3.16.

Method B. A mixture of molybdenum trioxide (0.03 mole) and salicylaldehyde (0.16 mole) was heated under reflux for twenty hours. The solution was filtered off to remove unreacted molybdenum trioxide, and the filtrate was allowed to stand overnight in a refrigerator. Greenish yellow crystals (10% yield based on MoO_3) were collected by filtration, washed with methanol and dried.

Anal. Calcd. for $C_{14}H_{10}MoO_6$: C, 45.42; H, 2.72. Found: C, 44.79; H, 2.52.

These complexes are slightly soluble in common organic solvents. They undergo decomposition in the solutions and also in the solid state, though more gradually, with liberation of the free ligand. They are stable in dimethylformamide.

Dioxobis(N-alkyl- and Dioxobis(N-aryl-ring-substituted salicylaldiminato)molybdenum (VI), $MoO_2(X–Sal–R)_2$

These complexes were prepared by either of the following two methods A and B. In general, method A was employed in the first place, and when this proved to be unsuccessful, method B was then made use of. As far as possible, recrystallization of the products was carried out from methanol.

Method A. To a suspension of $MoO_2(X–Sal)_2$ (0.01 mole) in methanol (100 ml) was added an appropriate amine (0.02 mole), and the mixture was heated under reflux for about half an hour. After allowed to stand overnight at room temperature, the crystals formed in the solution were collected by filtration, washed with methanol and dried.

Method B. A solution of an amine (0.02 mole) in methanol (100 ml) was stirred into a suspension of $MoO_2(X–Sal)_2$ (0.01 mole) in methanol (150 ml) at 0°, and the mixture was placed in a refrigerator. After about a week, the solution was filtered, and the filtrate was again left in a refrigerator for several days, until yellow crystals appeared in the solution. The crystals were filtered off, washed with methanol, and dried.

Analytical data of these complexes are shown in Table I. They are yellow to orange, stable for a considerably long time in the atmosphere at room temperature and slightly soluble in alcohols, dichloromethane and chloroform but insoluble in benzene, ether and carbon tetrachloride.

$MoO_2(X–Sal–R)$

A mixture of $MoO_2(X–Sal)_2$ (0.01 mole) and an appropriate amine (0.02 mole) was heated at 150°, using iso-butyl alcohol or n-amyl alcohol (100 ml) as a solvent. When heated, the solution changed its colour from orange first to blue and finally to dark red. After about an hour, insoluble materials were filtered off. The resulting solution was again heated at 150°, and the reaction was complete in about six hours. Red microcrystals were filtered from the hot solution, washed with methanol and dried. They are insoluble in common organic solvents and stable toward strong acids and bases. Analytical data of these complexes are shown in Table II.

μ-Oxo-dioxotetrakis(N-methylsalicylaldiminato)dimolybdenum(V), $Mo_2O_3(H–Sal–CH_3)_4$

A similar method to that described above was employed, using n-amyl alcohol as a solvent and methylamine as an amine. By heating the reaction mixture at 160° for five hours, dark green crystals were obtained in 70% yield. The green crystals appear purple when ground to powder, and they are stable in the atmosphere for a fairly long time. They are soluble in common organic solvents, giving a purple solution, which slowly undergoes decomposition, accompanied by colour change.

Anal. Calcd. for $C_{32}H_{32}Mo_2N_4O_7$: C, 49.49; H, 4.15; N, 7.22. Found: C, 48.98; H, 4.17; N, 7.14.

TABLE I. Analytical Data of Molybdenum(VI) Complexes of the $MoO_2(X–SAL–R)_2$ Type.

X	R	Calcd. %			Found. %			Prep. Method
		C	H	N	C	H	N	
H	CH_3	49.11	4.12	7.16	48.54	4.05	7.02	A
	C_2H_5	50.95	4.75	6.60	51.19	4.65	6.67	B
	n-C_3H_7	53.10	5.35	6.19	53.49	5.38	6.08	B
	n-C_4H_9	55.00	5.87	5.83	54.24	5.86	5.71	B
	CH_2Ph	61.32	4.41	5.11	61.81	4.47	5.10	B
	Ph	60.00	3.87	5.38	60.16	3.87	5.26	A
	p-CH_3-Ph	61.32	4.41	5.11	61.56	4.26	4.93	A
	p-Cl-Ph	52.99	3.08	4.75	52.90	3.06	4.38	A
	p-Br-Ph	46.04	2.67	4.13	45.80	2.58	3.89	A
3-OCH_3	CH_2Ph	59.21	4.64	4.60	58.76	4.58	4.52	A
	m-CH_3-Ph	59.21	4.64	4.60	58.62	4.54	4.58	A
	p-Cl-Ph	51.79	3.42	4.31	51.68	3.32	4.28	A
	p-Br-Ph	45.55	3.00	3.79	45.23	2.84	3.67	A
	p-Ph-Ph	65.57	4.40	3.82	65.35	4.26	3.75	A

TABLE II. Analytical Data of Molybdenum(V) Complexes of the MoO_2(X–SAL–R) Type.

X	R	Calcd. %			Found. %		
		C	H	N	C	H	N
H	C_2H_5	39.14	3.65	5.07	38.53	3.66	5.01
	n-C_3H_7	41.39	4.17	4.83	41.32	4.22	4.65
	n-C_4H_9	43.43	4.64	4.61	43.01	4.66	4.39
	CH_2Ph	49.72	3.58	4.14	49.43	3.58	3.99
3-OCH_3	CH_3	37.00	3.45	4.75	36.32	3.48	4.65

Measurements

Visible and ultraviolet absorption spectra of the complexes in solution and in nujols were measured on a Shimadzu MPS–50L spectrophotometer.

Infrared spectra were obtained from nujol mulls using a Hitachi EPI–S2 infrared spectrophotometer.

Magnetic measurements were carried out by the Gouy method at room temperature.

Results and Discussion

Molybdenum(V) and molybdenum(VI) complexes of the following three types have been synthesized in the present work: (1) $Mo^{VI}O_2$(X–Sal–R)$_2$, yellow; (2) $Mo^{V}O_2$(X–Sal–R), red; (3) $Mo^{V}{}_2O_3$(X–Sal–R)$_4$, purple. All the molybdenum complexes described in the Experimental are new compounds, with the exception of MoO_2(H–Sal–Ph)$_2$, which was synthesized previously by the reaction of dioxomolybdenum (VI) dichloride with N-phenylsalicylaldimine.[5]

Some complexes of type (1) were reported previously to be prepared by reactions of dioxomolybdenum(VI) dichloride with N-arylsalicylaldimines, but the N-alkylsalicylaldiminato complexes were not obtained by this method. In the present work, many N-alkylsalicylaldiminato complexes as well as some new N-arylsalicylaldiminato complexes were synthesized by methods starting from complexes of the type MoO_2 (X–Sal)$_2$, which were prepared by the acidification techniques from molybdenum trioxide or ammonium paramolybdate.

The complexes of the type MoO_2(X–Sal–R)$_2$ show two or three infrared absorption bands due to the $MoO_2{}^{2+}$ group in the region from 890 to 940 cm^{-1}. Some of the representative data are shown in Table III. The corresponding bands of MoO_2(H–Sal)$_2$ were observed at 908 and 935 cm^{-1}, respectively, in addition to a C–O band at 1545 cm^{-1} and a C=O band at 1621 cm^{-1}. According to the criterion proposed previously,[7,8] it may be presumed that the two oxygen atoms of the molybdenyl group are *cis* to each other in these complexes. This presumption is corroborated by the result of an X-ray crystal structure analysis, which has revealed that MoO_2(H–Sal–n-C_3H_7)$_2$ consists of six-coordinate molybdenum(VI) complexes containing a *cis*-MoO_2 group.[9]

TABLE III. Mo–O Stretching Frequencies (ν) of MoO_2(X–Sal–R)$_2$.

X	R	ν, cm^{-1}
H	CH_3	900, 925
	CH_2Ph	909, 931
	Ph	904, 922
	p-Cl-Ph	898, 917
3-CH_3O	CH_2Ph	899, 921
	p-Cl-Ph	904, 921

The electronic spectrum of MoO_2(H–Sal–CH_3)$_2$ is similar to those of the other alkyl analogues, implying that their structure is similar to each other. These alkyl analogues of type (1) show absorption bands of considerably high intensity at about 25.8 and 32.4 kK, a typical curve being shown in Figure 1. Taking into consideration previous studies on electronic spectra of molybdenyl complexes,[10,11] these two absorption bands may be assigned to ligand-to-metal charge trans-

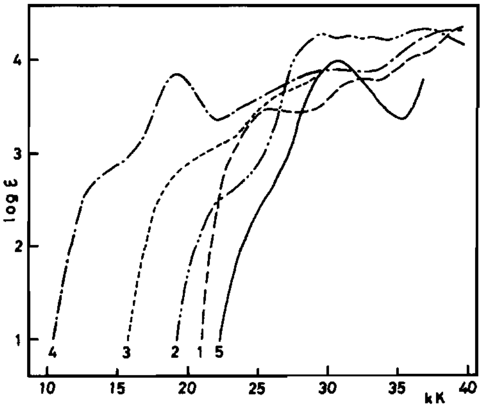


Figure 1. Electronic absorption spectra of molybdenum compounds. 1, MoO_2(H–Sal–CH_3)$_2$, in methanol; 2, MoO_2 (H–Sal–Ph)$_2$, in methanol; 3, MoO_2(H–Sal–C_2H_5), in nujol; 4, Mo_2O_3(H–Sal–CH_3)$_4$, in dichloromethane; 5, MoO_2(H–Sal)$_2$, in dimethylformamide. The abscissa for the curve 3 is in arbitrary scale.

fer transitions, possibly superposed by other intraligand transitions. The band at about 30.8 kK (logε 4.0) of $MoO_2(H{-}Sal)_2$ apparently corresponds to the low energy band at 29.9 kK (logε 3.58) of the free ligand in n-hexane. It seems reasonable to assume that a characteristic molybdenyl band does not occur in this region.[11]

As may also be seen in Figure 1, the aryl analogues of type (1) show a slight shoulder at about 23 kK. The intensity of this band seems to be much lower than ordinary charge transfer bands, and may probably be due to intraligand transitions of semi-forbidden character.

The molybdenum(V) complexes of type (2) possibly have a binuclear or multinuclear structure, judging from their composition and the normal coordination number of molybdenum(V). They show two Mo–O infrared bands at about 900 and 960 cm^{-1}, but no absorption was observed in the region from 3000 to 3500 cm^{-1}, in agreement with the proposed formula containing no hydroxyl group. They are nearly diamagnetic, implying the presence of Mo–Mo interaction. Although the normal d^1 system would be expected to be paramagnetic with a magnetic moment of about 1.7 B.M., there have been known some number of molybdenum(V) complexes showing diamagnetism or very slight paramagnetism which is independent of temperature.[12]

The electronic absorption spectra of the complexes of type (2) are similar to each other, suggesting that their structure is also similar. They show an absorption band of moderate intensity at about 20 kK. It is very likely that this absorption band, which occurs at a much lower frequency than the lowest energy band of $MoO_2(X{-}Sal{-}R)_2$, arises mainly from d–d transitions. However, there seems to remain another possibility that this band might be due to the charge transfer transitions, and the definitive discussion on the assignment is deferred until more data are accumulated.[13]

All these findings combined seem to indicate that the complexes of type (2) may be binuclear or multinuclear with strong interaction between molybdenum (V) ions. Unfortunately, the solubility of the complexes of types (2) and (3) is too low for molecular weight determination.

For X = H and R = CH_3, a compound of type (3) was isolated, in addition to the compound of type (1). This compound shows two Mo–O bands at 910 and 931 cm^{-1} and a C–O band at 1550 cm^{-1}. The electronic absorption spectrum of $Mo_2O_3(H{-}Sal{-}CH_3)_4$, which is shown in Figure 1, has characteristic bands at about 14.5 and 19.3 kK. These bands are remarkably similar to those of the molybdenum(V) compounds containing the Mo_2O_3 grouping,[7,14,15] and particularly to those of the corresponding acetylacetonato complex $Mo_2O_3(acac)_4$, acac being an acetylacetonate anion.[16] The two bands cited above of $Mo_2O_3(H{-}Sal{-}CH_3)_4$ most probably correspond to the bands at 13.3 and 20.6 kK, respectively, of $Mo_2O_3(acac)_4$. Assignment of these bands was discussed previously,[15] and it is very likely that the band at about 13–15 kK may be originated from d–d transitions in the d^1 system. The d–d band at 14.5 kK for $Mo_2O_3(H{-}Sal{-}CH_3)_4$ is found at a slightly higher energy than for the related acetylacetonato complex, in agreement with the expected ligand field order. On the contrary, the band at 20.6 kK may be assigned to O-to-Mo charge transfer rather than d–d transition, judging from its high intensity.

The compound $Mo_2O_3(H{-}Sal{-}CH_3)_4$ is nearly diamagnetic, most probably due to intense spin-pairing between molybdenum(V) ions, as has also been reported to be the case with the diamagnetic Mo_2O_3 $(acac)_4$ and related complexes. A binuclear structure with an oxygen atom as a bridge was concluded for these compounds, and a similar structure may be assigned to the N-methylsalicylaldiminato molybdenum (V) complex.

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