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# Dioxomolybdenum(VI) Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and Polymethylenediamines

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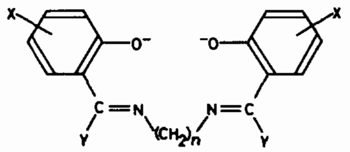
*New dioxomolybdenum(VI) complexes have been synthesized with quadridentate Schiff bases derived from salicylaldehyde derivatives and polymethylenediamines. On the basis of infrared and proton magnetic resonance spectra, it is concluded that the $MoO_2$ group in them has cis structure, in which the quadridentate bis(salicylaldehyde)polymethylenediiminates assume non-planar coordination instead of planar one.*

## Introduction

In a previous paper, we reported on the preparation and properties of molybdenum(V) and molybdenum (VI) complexes with bidentate N-alkyl- and N-aryl-salicylaldiminates.[1] It was concluded therein that the $MoO_2$ group has *cis* structure in these complexes. It seems to be interesting to examine whether the quadridentate ligands obtained from salicylaldehyde derivatives and polymethylenediamines (I) assume planar or non-planar geometry in dioxomolybdenum(VI) complexes. On one hand, bis(salicylaldehyde)ethylenediimine and its ring-substituted derivatives, abbreviated as Salen and X-Salen, respectively, are known to strongly demand planar coordination,[2] and only in expectional cases these ligands may assume non-planar geometry.[3] On the other hand, the non-planar coordination tends to occur, for example, in cobalt(II) and copper(II) complexes, as the polymethylene chain is lengthened.[4]



(I)

For Y = H, n = 2: X-Salen; n = 3: X-Saltn; n = 4: X-Saltetn. For X = H and Y = H, the notations Salen, Saltn and Saltetn, respectively, are employed.

In the present work, the dioxomolybdenum(VI) complexes were prepared with the ligands of type I by a new method and their structure was examined. Although some oxomolybdenum(VI) complexes with 5-Br-Salen and 4-$CH_3$-Salen were described previously in the literature,[5] no detailed examination about their structure has been carried out.

## Experimental

### *Materials*

*Dioxobis(acetylacetonato)molybdenum(VI)*

This complex was prepared, as previously reported.[6]

*Dioxo[bis(salicylaldehyde)polymethylenediiminato]molybdenum(VI)*

These complexes were synthesized as yellow or yellowish orange crystals by the following general method.

To a suspension of dioxobis(acetylacetonato)molybdenum(VI) (0.01 mole) in methanol (150 ml) was added an appropriate Schiff base, and the solution was refluxed; crystals of the desired complex began to appear soon in the solution. After the refluxing was continued for another 1–2 hr, the orangish yellow crystals were filtered, while the solution was hot. They were washed twice with methanol and then with ethyl ether, and dried in a desiccator. Yields were higher than 80%, except for $MoO_2$(Salen), for which the yield was about 60%.

These complexes are almost insoluble in water, carbon tetrachloride, n-hexane, ethyl ether and ethanol, but slightly soluble in N,N-dimethylformamide, methanol, chloroform, acetone and benzene. They are not stable in the solution.

Analytical data are shown in Table I.

*Dioxo[bis(3-methoxysalicylaldehyde)polymethylenediiminato]molybdenum(VI)*

These complexes were synthesized as yellowish orange crystals by the method described above. Analytical data of the complexes are shown in Table I.

TABLE I. Analytical Data of Dioxomolybdenum(VI) Complexes with Bis(ring-substituted-salicylaldehyde) polymethylenediiminates.

| Compound | Melting point[a] | Found, % | | | Calcd., % | | |
|---|---|---|---|---|---|---|---|
| | | C | H | N | C | H | N |
| $MoO_2$(Salen) | 253–254 | 48.34 | 3.67 | 7.02 | 48.74 | 3.58 | 7.11 |
| $MoO_2$(Saltn) | 249–250 | 49.84 | 3.89 | 6.71 | 50.01 | 3.95 | 6.86 |
| $MoO_2$(Saltetn) | 264–265 | 51.33 | 4.38 | 6.59 | 51.19 | 4.30 | 6.64 |
| $MoO_2$(3-$CH_3O$-Salen) | 267–268 | 47.45 | 3.91 | 6.20 | 47.59 | 3.99 | 6.17 |
| $MoO_2$(3-$CH_3O$-Saltn) | 282–284 | 48.52 | 4.28 | 5.96 | 48.73 | 4.30 | 5.98 |
| $MoO_2$(3-$CH_3O$-Saltetn) | 295–296 | 49.64 | 4.49 | 5.77 | 49.80 | 4.60 | 5.81 |

[a] See also the Experimental in the text.

### *Dioxo[bis(2-hydroxyacetophenone)ethylenediiminato]molybdenum(VI)*

This complex, abbreviated as $MoO_2$(hapen), was synthesized as yellow crystals by the method described above. *Anal.* Calcd. for $C_{18}H_{18}MoN_2O_4$: C, 51.19; H, 4.30; N, 6.64%. Found: C, 51.18; H, 4.35; N, 6.69%. When heated, the compound began to be decomposed at about 210°, turning into a black substance finally at 300°. The solubility, which was lower than that of the other complexes reported in this paper, was not high enough for precise measurement of the proton magnetic resonance (PMR) spectra.

Similar procedures using the corresponding trimethylene- or tetramethylene-diimine have not yielded the desired complexes so far.

The melting point of all these complexes varied rather widely, depending upon the heating rate. The complexes were often decomposed, while temperature was raised. Precaution was, therefore, exercised, so that the decomposition might not occur during the measurements. The best data, which are given in Table I and are reasonably reproducible, were obtained, when temperature was raised comparatively fast from the room temperature to about 20° below the melting point and then the specimen was heated very slowly, until they finally melted. With most complexes, the colour turned slightly darker, without melting, at several to thirty degrees below the melting point.

### *Measurements*

Electronic absorption spectra of the complexes in solution were measured on a Shimadzu MPS–50L spectrophotometer. 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.

Since many of the complexes underwent decomposition fairly fast on dissolution, utmost care was exercised in the spectral measurements. For instance, the 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 been once obtained, to see if any spectral change due to decomposition occurred or not, and Beer's law was confirmed to hold.

## Results and Discussion

It was reported previously that the reaction of dioxobis(salicylaldehydato)molybdenum(VI) with alkyl- and aryl-amines yielded bis(N-alkyl- or bis (N-aryl-salicylaldiminato) complexes of dioxomolybdenum (VI),[1] but this method was not successful for the synthesis of the present complexes. Accordingly we made use of a new method starting from dioxobis(acetylacetonato)molybdenum(VI), which was allowed to react with the Schiff bases (I, X = H and 3-$CH_3O$) to yield the bis(salicylaldehyde)polymethylenediiminato complexes. With 5-chloro- or 5-bromo-analogue as a Schiff base (I, X = 5-Cl or 5-Br), the same procedures yielded different products, which had more complicated composition and were not further characterized in the present work. The reason for this difference in the synthesis is not clarified at the moment.

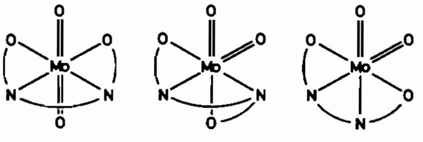
The complexes $MoO_2$(X-Salen), $MoO_2$(X-Saltn) and $MoO_2$(X-Saltetn) show two infrared absorption bands due to the $MoO_2$ group in the region from 880 to 920 $cm^{-1}$, as shown in Table II. According to the criterion proposed previously,[1,7] it may be presumed that the two oxygen atoms of the molybdenyl group are *cis* to each other in these complexes. In consequence, the structure I in Figure 1 may be excluded.

For the *cis* structure, the two configurations are possible, as shown in Figure 1. The PMR spectra of all these complexes have two signals each for the methine, phenyl and polymethylene protons, as may be seen from Table III. It is also seen from Table III that the

TABLE II. IR Spectra in Nujol and UV Spectra in Solution of Dioxomolybdenum(VI) Complexes with the Schiff Bases.[a]

| Compound | IR[b] | | UV |
|---|---|---|---|
| | $\nu$(C=N)[c] | $\nu$(Mo=O) | $\nu$(log$\varepsilon$) |
| $MoO_2$(Salen) | 1640 | 920<br>885 | 24.2<br>(3.46)[d]<br>24.2<br>(3.46) |
| $MoO_2$(Saltn) | 1633 | 910<br>870 | 24.3<br>(3.44) |
| $MoO_2$(Saltetn) | 1625 | 907<br>885 | 24.8<br>(3.38) |
| $MoO_2$(3-$CH_3$O-Salen) | 1640 | 903<br>875 | 23.5<br>(3.2)[e] |
| $MoO_2$(3-$CH_3$O-Saltn) | 1630 | 914<br>882 | 23.5<br>(3.2)[e] |
| $MoO_2$(3-$CH_3$O-Saltetn) | 1627 | 918<br>890 | 23.5<br>(3.1)[e] |
| $MoO_2$(hapen) | 1605 | 910<br>885 | 25.0<br>(3.46) |

[a] Only the maxima in the lowest frequency region are listed, as the spectra do not show well defined maxima in the higher frequency region. The solvent used is N,N-dimethylformamide, unless otherwise stated. [b] The assignments are based on the previous papers: P. Teyssie and J.J. Charette, *Spectrochim. Acta 19,* 1407 (1963); J.E. Kovacic, *ibid., 23A,* 183 (1967). [c] $\nu$: $cm^{-1}$. [d] In dichloromethane. [e] Not well defined.



(I) (II) (III)

Figure 1. *Cis* and *trans* structures for Dioxo[bis(salicylaldehyde polymethylenediiminato]molybdenum(VI).

methoxy protons in $MoO_2$(3-$CH_3$O-Salen) and $MoO_2$ (3-$CH_3$O-Saltn) exhibit two signals, in addition to those mentioned above.

As also shown in Table III, the PMR spectrum of *trans*-[Co(Salen)$(NH_3)_2$]$ClO_4$, in which the ligand Salen assumes planar coordination,[8] exhibits a singlet each for the N=CH and N–$CH_2$ protons. A similar result was reported for other complexes, which contain bis(salicylaldehyde)ethylenediiminate with planar geometry.[9] On the contrary, the PMR spectrum for [Co (acac)(Salen)], in which Salen assumes non-planar geometry, shows two sharp singlets for the N=CH protons,[3] *acac* being acetylacetonate anion.

A detailed discussion has been presented so far to show that the PMR spectra are useful for deducing reliable conclusions on the overall structure of this type of complex.[3,9] The structure III is more symmetrical than the structure II, having a $C_2$ symmetry axis, which bisects the N–$CH_2$–$CH_2$–N chain. The two methine hydrogen atoms of the Salen ligand are not equivalent in II, whereas they are so in III as well as in I.

Consequently, comparison of the present data with the previously reported ones indicates that the PMR spectra of the dioxomolybdenum(VI) complexes prepared in the present work are in contradiction with the structure III in Figure 1 but consistent with the structure II. The complexes with the structure III would exhibit only one singlet for the N=CH protons, as discussed above.[3,9]

It is thus concluded that the quadridentate ligands in the present complexes assume non-planar geometry, independently of the polymethylene chain length. It is interesting to note that even the ligands X-Salen, which normally demand planar geometry, assume twisted geometry in these complexes. This configuration may be regarded to be caused by the high tendency

TABLE III. Chemical Shifts in Proton Magnetic Resonance Spectra of Metal Complexes with Bis(ring-substituted-salicylaldehyde)polymethylenediiminates in $(CD_3)_2SO$.[a]

| Compound | N=CH | Ph[b] | N–$CH_2$ | $OCH_3$ |
|---|---|---|---|---|
| SalenH$_2$ | 8.62 | 6.75–7.57 | 3.95 | |
| Co(Salen)$(NH_3)_2^+$[c] | 8.13 | 6.33–7.40 | 3.86 | |
| Co(acac)(Salen)[d] | 8.01, 7.80 | 6.39–7.34 | 3.73, 3.94<br>3.64, 4.06 | |
| $MoO_2$(Salen) | 8.91, 8.74 | 6.62–7.73 | 4.35, 4.23[b] | |
| SaltnH$_2$ | 8.56 | 6.73–7.52 | 3.71[e] | |
| $MoO_2$(Saltn) | 8.75, 8.47 | 6.40–7.65 | 3.65–4.43[f] | |
| 3-$CH_3$O-SalenH$_2$ | 8.55 | 6.63–7.13 | 3.93 | 3.76 |
| $MoO_2$(3-$CH_3$O-Salen) | 8.91, 8.74 | 6.50–7.33 | 4.30, 4.20[b] | 3.84, 3.66 |
| 3-$CH_3$O-SaltnH$_2$ | 8.53 | 6.63–7.12 | 3.68[e] | 3.80 |
| $MoO_2$(3-$CH_3$O-Saltn) | 8.77, 8.50 | 6.4–7.5[g] | | 3.82, 3.50 |

[a] $\delta$ in ppm downfield from TMS. [b] Broad. [c] Prepared by the method of ref. 8 in the text. [d] Data taken from ref. 3 in the text. [e] Triplet. [f] Multiplet, unresolved because of the low solubility. [g] Obscured, because of the low solubility.

of the molybdenyl group to assume *cis* structure. It should also be noted that these complexes provide the first examples of six-coordinate complexes, which contain the non-planar X-Salcn ligands and the other two unidentate ligands.

Brief mention is finally given of their electronic absorption spectra, the maxima being tabulated in Table II. The absorption bands at about 23.5 to 25 kK most probably correspond to the bands at about 25 kK for dioxobis(N-alkylsalicylaldiminato)molybdenum (VI),[1] and may be interpreted in a similar way; these bands may tentatively be assigned as ligand to metal charge transfer, as discussed previously.

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