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Preparation of $OMoCl(acac)_2$ by a Novel Oxygen–Chlorine Atom Exchange and its Use as a Reagent for the Synthesis of Monomeric Molybdenum(V) Complexes

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The known monomeric Mo(V) complex $OMoCl(acac)_2$ has been prepared by a unique new reaction involving an overall oxygen–chlorine atom exchange between $MoO_2(acac)_2$ and $MoCl_2(acac)_2$. $OMoCl(acac)_2$ undergoes substitution reactions with the acid forms of a number of bi- and tetradentate ligands to produce the complexes $OMoClL_2$ [L = 8-hydroxyquinolinato, 8-mercaptoquininolato, $S_2P(i\text{-}Pr)_2$] and $OMoClL'$ (L' = salen, salpn, salphen). Spectral (IR, visible, EPR) characterization data for these complexes and for $OMoCl(acac)_2$ itself are presented and in some cases are used to assign the stereochemistry of the species.

Introduction

Because of the recent interest in comparing the reactivity [1, 2] and spectral properties [3, 4] of monomeric molybdenum(V) complexes with those of molybdoenzymes, we are presently attempting to develop general synthetic routes for a variety of these compounds. During the course of our investigations of the reactivity of oxomolybdenum complexes, we have obtained the known [5] species $OMoCl(acac)_2$ (acac = acetylacetonate) via a new reaction. We reasoned that this complex might be a useful reagent for the synthesis of monomeric Mo(V) species since the analogous Mo(VI) compound *cis*-$MoO_2(acac)_2$ has been used [6, 7] to prepare a variety of complexes containing the *cis*-MoO_2^{2+} moiety (eq. 1, 2).

$$MoO_2acac_2 + H_2salen \longrightarrow MoO_2(salen) + 2Hacac \quad (1)$$

$$MoO_2acac_2 + HSC_6H_4NHC_2H_4NHC_6H_4SH \longrightarrow MoO_2(SC_6H_4NHC_2H_4NHC_6H_4S) + 2Hacac \quad (2)$$

Herein, we report the synthesis of $OMoCl(acac)_2$ by a novel oxygen–chlorine exchange reaction and describe its utility for the preparation of both new and previously reported complexes of the form $OMoClL_2$ and $OMoClL'$. Spectral characterization data for these species are presented and, in some cases, are used to determine the stereochemistry of the new complexes.

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Experimental

All reactions were carried out under an inert atmosphere (argon or nitrogen) using standard techniques. All solvents were dried over molecular sieves (with the exception of methanol) and degassed prior to use. 2,4-Pentanedione (Hacac) and 8-quinolinol (Hox) were used as received from Eastman Chemical Co. and $HS_2P(i\text{-}Pr)_2$ and 8-mercaptoquinoline (Htox) were synthesized by literature [8] methods. The complexes [9, 10] $MoO_2(acac)_2$ and $MoCl_2(acac)_2$ and the Schiff base ligands [11] were prepared as previously reported.

Infrared spectra were recorded on a Beckman IR 20A spectrophotometer, uv–visible spectra on a Cary 118C instrument, and EPR spectra on a Varian Associates 4502 spectrometer equipped with a Model V4560 100Kc modulation control unit, an X-band microwave bridge and a Hewlett-Packard X532 G frequency meter. Elemental analysis for CHN were determined in this laboratory using a Perkin-Elmer 240 instrument equipped with a Microjector from Control Equipment Corporation.

Synthesis of Complexes $OMoCl(acac)_2$

Benzene (160 ml) was added to a mixture of $MoCl_2(acac)_2$ (5.00 g, 13.7 mmol) and MoO_2acac_2 (4.48 g, 13.7 mmol) and the solution heated under reflux for 15 min. After cooling to room temperature, the reaction mixture was filtered to remove a small amount of dark impurity and the filtrate was evaporated to dryness under vacuum. Trituration of the residue with diethyl ether gave a greenish yellow solid (8.24 g, 87% yield) which was isolated by filtration, washed with ether and dried *in vacuo*. *Anal.* Calcd for $C_{10}H_{14}ClMoO_5$: C, 34.7; H, 4.05. Found: C, 34.8; H, 4.13%.

$OMoCl[S_2P(i\text{-}Pr)_2]_2$

A solution of $HS_2P(i\text{-}Pr)_2$ (0.55 g) in methanol (20 ml) was added to a solution of $OMoCl(acac)_2$ (0.51 g) in methanol (20 ml). After 20 min at room temperature, the reaction mixture was filtered to yield the product (0.43 g, 57% yield) as an orange-brown solid which was washed with ether and dried *in vacuo*. *Anal.* Calcd for $C_{12}H_{28}ClMoOP_2S_4$: C, 28.3; H, 5.50. Found: C, 28.7; H, 5.74%.

OMoCl(salen)

$OMoCl(acac)_2$ (0.59 g) and H_2salen (0.37 g) were dissolved in MeOH (30 ml) and the reaction mixture stirred at room temperature for 20 min. After evaporation to dryness under vacuum and trituration of the residue with diethyl ether, the crude product was isolated by filtration, washed with ether and dried *in vacuo*. Recrystallization of this solid from CH_2Cl_2/diethylether yielded the product (0.38 g, 63% yield). *Anal.* Calcd for $C_{16}H_{14}N_2ClMoO_3$: C, 46.4; H, 3.39; N, 6.77. Found: C, 46.2; H, 3.65; N, 6.15%.

OMoCl(salpn)

This complex was prepared similarly to OMoCl(salen). The yield was 66%. *Anal.* Calcd for $C_{17}H_{16}N_2ClMoO_3$: C, 47.7; H, 3.74; N, 6.55. Found: C, 48.1; H, 4.19; N, 5.91%.

OMoCl(salphen)

This complex was prepared similarly to OMoCl(salen) but using H_2salphen. The yield was 73%. *Anal.* Calcd for $C_{20}H_{14}N_2O_3ClMo$: C, 52.0; H, 3.03; N, 6.07. Found: C, 51.9; H, 3.05; N, 6.02%.

$OMoCl(ox)_2$

Methanol (50 ml) was added to a mixture of $OMoCl(acac)_2$ (0.50 g) and 8-quinolinol (0.43 g). After stirring at room temperature for 2 hr, the reaction mixture was filtered to yield the product as a green solid which was washed with methanol and dried *in vacuo*. *Anal.* Calcd for $C_{18}H_{12}N_2ClMoO_3$: C, 49.6; H, 2.76; N, 6.43. Found: C, 49.9; H, 3.06; N, 6.43%.

$OMoCl(tox)_2$

This compound was prepared similarly to $OMoCl(ox)_2$ but using 8-mercaptoquinoline. The yield was 72%. *Anal.* Calcd for $C_{18}H_{12}N_2ClMoOS_2$: C, 46.2; H, 2.57; N, 5.99. Found: C, 44.5; H, 2.57; N, 5.64%.

Results and Discussion

Synthesis and Characterization of $OMoCl(acac)_2$

Previously, we reported [12] the reactions between the complexes $Mo(CO)_2L_2$ and MoO_2L_2 [L = S_2CNR_2, $S_2P(i\text{-}Pr)_2$] to yield two mol of the Mo(IV) species $OMoL_2$. We were also able to utilize [12] this type of intermetal oxygen atom transfer reaction to prepare the first tungsten(VI) dithiocarbamate complexes, $WO_2(S_2CNR_2)_2$ (R = Me, Et, n-Pr) as shown in eq 3. Because of our general interest in this type of reactivity,

$$W(CO)_2(PPh_3)(S_2CNR_2)_2 + 2MoO_2[S_2P(OEt)_2]_2 \longrightarrow WO_2(S_2CNR_2)_2 + 2CO + PPh_3 + 2OMo[S_2P(OEt)_2]_2 \quad (3)$$

we have investigated the interaction between the known compounds $MoO_2(acac)_2$ and $MoCl_2(acac)_2$. Instead of the products expected from simple oxygen atom transfer [$OMo(acac)_2$ and $OMoCl_2(acac)_2$], two moles of the monomeric Mo(V) complex $OMoCl(acac)_2$ were obtained as shown in eq 4. Previously [5], this complex had been prepared by the reaction of $OMoCl_3$ with acetylacetone in benzene solution.

$$MoO_2acac_2 + MoCl_2acac_2 \longrightarrow 2OMoClacac_2 \quad (4)$$

The reaction shown in eq 4 is unique in that it represents the first reported oxygen–chlorine *exchange* between two different complexes. The most likely mechanism for the overall reaction is either (a) a two-step process initiated by oxygen atom transfer to form $OMo(acac)_2$ and $OMoCl_2(acac)_2$ followed by chlorine atom transfer between these two species (eq 5, 6) or (b) a concerted atom transfer

$$MoO_2(acac)_2 + MoCl_2(acac)_2 \longrightarrow OMo(acac)_2 + OMoCl_2(acac)_2 \quad (5)$$

$$OMo(acac)_2 + OMoCl_2(acac)_2 \longrightarrow 2OMoCl(acac)_2 \quad (6)$$

step involving no intermediates. Mechanism (a) gains support from our demonstration [13] of chlorine atom transfer between the dithiocarbamate complexes $OMo(S_2CNEt_2)_2$ and $OMoCl_2(S_2CNEt_2)_2$ to yield $OMoCl(S_2CNEt_2)_2$. However, additional insight into the interaction of $MoO_2(acac)_2$ and $MoCl_2(acac)_2$ should be provided by kinetic studies.

The spectral characterization data (Table I) for $OMoCl(acac)_2$ is relatively straightforward. The infrared spectrum of the complex contains single bands at 960 cm^{-1} and 330 cm^{-1} assigned to ν(Mo=O) (in agreement with the previous [5] value) and ν(Mo–Cl) respectively. The room temperature EPR spectrum of the complex (Fig. 1) exhibits a single strong signal at g = 1.939 with ^{95}Mo satellites (A = 53 gauss) and with no observable chlorine hyperfine structure. Although *cis* and *trans* isomers are possible for $OMoCl(acac)_2$, the above spectral data indicate that only one of these species is present both in solution and in the solid state. The visible spectral data for the complex in benzene is somewhat different

TABLE I. Infrared and Visible Spectral Data for the Complexes $OMoClL_2$ and $OMoClL'$.

Complex	Infrared[a]		Visible[b]
	ν(Mo=O)	ν(Mo–Cl)	
$OMoClacac_2$	960	330	710(47), 453(480), 383(2940), 327(7250)[c]
$OMoCl(ox)_2$	935	324	625(578), 560(593), 395(4650)[d]
$OMoCl(tox)_2$	955	[f]	600(2360), 536(3130), 425(5780)[d]
$OMoCl[S_2P(i\text{-}Pr)_2]_2$	925	313	439(1300), 365(1880)[e]
OMoCl(salen)	938, 945	277	430(2310)[d]
OMoCl(salpn)	935	[f]	492(1970)[d]
OMoCl(salphen)	943	[f]	430(~4000)[d,g]

[a]KBr pellets with values in cm^{-1}. [b]Peak positions in nm with molar absorbitivities in parentheses. [c]Benzene solution. [d]CH_2Cl_2 solution. [e]Acetone solution. [f]No definitive assignment could be made. [g]Complete dissolution of the compound could not be attained.

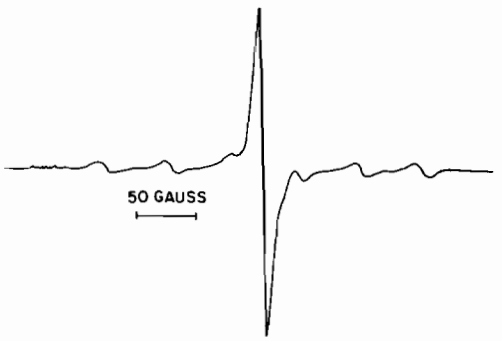


Fig. 1. EPR spectrum of $OMoCl(acac)_2$.

from that previously reported (λ_{max} = 379 nm with shoulders at 594 and 740 nm) [5] in that we also observed bands at 435 and 327 nm.

Reactivity of $OMoCl(acac)_2$

cis-$MoO_2(acac)_2$ has been shown [6, 7] to be a useful species for the synthesis of a number of Mo(VI) complexes by the generalized reaction shown in eq 7. We felt that $OMoCl(acac)_2$ might exhibit

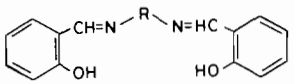
$$MoO_2acac_2 + 2HL \longrightarrow MoO_2L_2 + 2Hacac \quad (7)$$

analogous utility as a synthetic reagent for the preparation of monomeric Mo(V) compounds and have therefore studied its reactivity with the acid forms of several common bidentate and tetradentate ligands. Reaction of the complex with the bidentate ligands 8-quinolinol (Hox) and $HS_2P(i\text{-}Pr)_2$ in methanol solution at room temperature proceeded smoothly to yield new complexes of the form $OMoClL_2$ as in eq 8, confirming the similar reactivity patterns of the Mo(V) and Mo(VI) acetylacetonate

$$OMoCl(acac)_2 + 2HL \longrightarrow OMoClL_2 + 2Hacac \quad (8)$$

species. Reaction of $OMoCl(acac)_2$ with 8-mercaptoquinoline (Htox) yielded a product whose spectral data were consistent with $OMoCl(tox)_2$, but whose elemental analytical data indicated the presence of a small amount of impurity (see Experimental Section).

Similarly, reaction of $OMoCl(acac)_2$ with the tetradentate Schiff base ligands H_2salen (I), H_2salpn (II), and H_2salphen (III) gave complexes of the form OMoClL which were previously [11] synthesized



I R = CH_2CH_2, H_2salen
II R = $CH_2CH_2CH_2$, H_2salpn
III R = *o*-C_6H_4, H_2salphen

from mixtures of $OMoCl_3(THF)_2$ and the deprotonated ligand in ethanol or CH_3CN. $OMoCl(acac)_2$ may prove to be more convenient than $OMoCl_3(THF)_2$ as a starting material for these reactions since its use precludes the need to initially neutralize the ligand and since in general it is more easily handled. However, the synthetic technique described herein does not represent a major improvement over the techniques described previously for the preparation of the Schiff base complexes and should be viewed as an complementary synthetic method. It is important to note that the similar lability of acetylacetonate in these Mo(V) and Mo(VI) compounds suggests that other complexes of the ligand, *e.g.*, $MoCl_2(acac)_2$ and $Mo_2O_3(acac)_4$, may also be useful as synthetic reagents.

Infrared Spectra

Assignments of Mo=O and Mo–Cl stretching frequencies are summarized in Table I. The solid state spectra of all complexes, with the exception of OMoCl(salen), contain single bands in the 900–1000 cm^{-1} region due to ν(Mo=O). As previously reported [11], the spectrum of OMoCl(salen) contains two Mo=O stretching frequencies. We were concerned that this splitting might arise from solid state effects but have found that these two bands persist in CH_2Cl_2 solution. The previous [11] suggestion that these two bands are due to the presence of the isomers of OMoCl(salen), therefore, seems to be correct. However, because the relative intensities of these ν(Mo=O) bands in the ir (10:8) are very different to the relative intensities of the two EPR signals (~10:1, *vide infra*), which are assigned [11] to the same two isomers, this interpretation must remain tentative.

Because of ligand bands in the 250–350 cm^{-1} region, the assignments of ν(Mo–Cl) are equivocal, except in the case of $OMoCl(acac)_2$ where a strong band at 330 cm^{-1} (not present in the spectrum of $MoO_2(acac)_2$) is observed. We suggest that the previous correlation of ν(Mo–Cl) at 322 cm^{-1} to the *trans*-oxochloro configuration and ν(Mo–Cl) at 278 cm^{-1} to the *cis* isomer for OMoCl(salen) is open to question. We were able to observe bands at 278 and 337 cm^{-1} in the KBr pellet spectrum of this complex. A band at 337 cm^{-1} also occurred in the spectrum of *cis*-MoO_2(salen), however, suggesting that it is not due to a Mo–Cl vibration. We observed no band at 322 cm^{-1}. We prefer to assign the 278 cm^{-1} band to ν(Mo–Cl) of the predominant isomer which, by virtue of the constraints imposed by the salen ligand, is more likely to be the *trans* configuration.

Visible Spectra

Peak positions and molar absorptivities for the new and previously reported complexes are given in Table I. The data are provided only as an aid to future characterization and no attempt has been made to assign the various transitions.

EPR Spectra

The EPR spectra of the complexes OMoClL (L = salen, salpn, salphen) are identical within experimental error to those reported previously [11]. The spectrum of OMoCl(salen) shows two signals (g = 1.939 and 1.949) with an intensity ratio of about 10 to 1 which were assigned to isomers of the complex. The spectra of the salpn and salphen derivatives show single signals at g = 1.943 and g = 1.939 respectively. All of the above signals exhibit ^{95,97}Mo hyperfine as reported [11].

The room temperature EPR spectrum of the complex $OMoCl(ox)_2$ (Fig. 2) exhibits two signals (g = 1.952 and 1.943), both with ^{95,97}Mo hyperfine

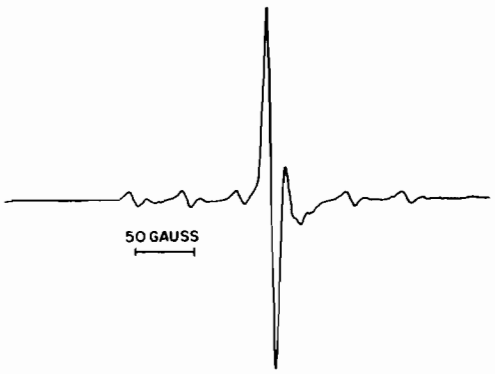


Fig. 2. EPR spectrum of $OMoCl(ox)_2$.

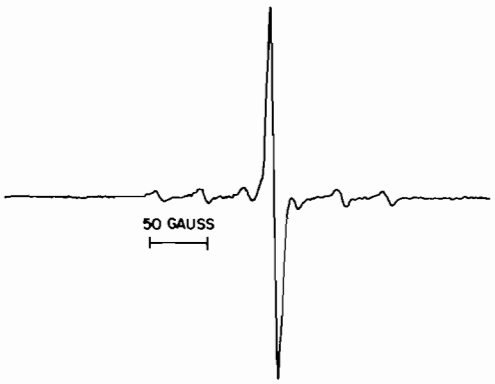


Fig. 3. EPR spectrum of $OMoCl(tox)_2$.

splitting of 47 gauss. The spectrum suggests the presence of both *cis* and *trans* isomers (as was suggested for OMoCl(salen)), with the relative signal intensities (~10:1) indicating that one isomer is predominant. Only one isomer is present for $OMoCl(tox)_2$, however, as evidenced by the fact that the EPR spectrum of this complex contains a single signal [g = 1.966, A(^{95,97}Mo) = 41 gauss] (Fig. 3).

For the new complex $OMoCl[S_2P(i\text{-}Pr)_2]_2$, the EPR spectral data can be used to assign the stereochemistry. The room temperature spectra of the complex (Fig. 4) shows a two-line pattern (A = 26

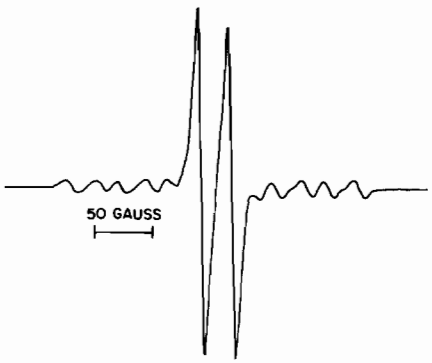
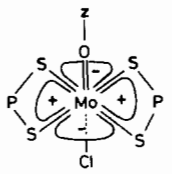
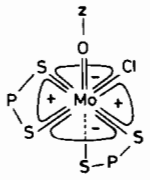


Fig. 4. EPR spectrum of $OMoCl[S_2P(i\text{-}Pr)_2]_2$.

gauss) arising from ^{31}P hyperfine coupling. $^{95,97}Mo$ hyperfine structure is also observed. The two-line pattern indicates that the molybdenum unpaired electron (predicted to be in the d_{xy} orbital) interacts with *only one* of the phosphorus nuclei. This effect is indicative of *cis* stereochemistry for the compounds (V) since in this configuration, only the phosphorus atom of the equatorial ligand is in the proper orientation for overlap. The phosphorus of the ligand which bridges axial and equatorial positions is located on (or is in close proximity to) a node of the d_{xy} orbital and this location would thus be expected to result in a minimal hyperfine interaction. In the alternative *trans* structure (IV), both phosphorus atoms should be located properly for overlap with the d_{xy} orbital, resulting in a three-line pattern. This assignment of stereochemistry is also supported by a simpler argument. If the configuration were *trans*, the



IV



V

phosphorus nuclei must be magnetically equivalent and produce either *no* splitting or a *three-line* pattern, while only the *cis* structure results in the ^{31}P non-equivalence necessary to produce a two-line pattern.

Summary and Conclusions

The previously reported monomeric Mo(V) complex $OMoCl(acac)_2$ has been prepared by a unique new reaction involving an overall oxygen–chlorine atom exchange between dioxomolybdenum(VI) and dichloromolybdenum(IV) compounds. Previously, the ability of oxomolybdenum complexes to carry out atom transfer redox reactions with both organic compounds [9, 14, 15] and other molybdenum and tungsten complexes [12] has been demonstrated. The above synthesis of $OMoCl(acac)_2$ further illustrates the generality of this type of reactivity which may well prove useful in future synthetic studies. The complex $OMoCl(acac)_2$ has also been shown to be a useful reagent for the synthesis of a number of monomeric Mo(V) complexes. The key to the utility of this compound (and to that of the molybdenum(VI) species $MoO_2(acac)_2$ is the substitution lability of the acetylacetonate ligand which may be due in part to the stability of the released acetylacetone. Studies are in progress to further explore both the synthetic utility of Mo–acac complexes and the atom transfer reactions of molybdenum and tungsten species.

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