# Some Dichloro Schiff Base Complexes of Molybdenum(IV)*

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A series of molybdenum(IV) complexes of the type $[\mathrm{MoCl_2L_2}]$, where HL represents *N*-phenylsalicylideneimine and its derivatives, have been synthesised by reaction of $[\mathrm{MoCl_2(acac)_2}]$ (acac = acetylacetonate) or $[\mathrm{MoCl_4(MeCN)_2}]$ with related Schiff bases. The spectroscopic properties of these six-co-ordinate $d^2$ complexes are discussed.

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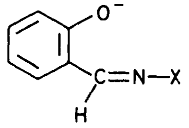
Complexes of Schiff base ligands of the type shown below with transition metals have frequently been studied. However, most of the studies have been concentrated on the first row transition metals,[1,2] whilst complexes of the early heavy transition metals have largely been neglected. Previously reactions of $[\mathrm{Mo(CO)_6}]$ with Schiff bases gave $\mathrm{Mo^{III}}$ [3] and $\mathrm{Mo^{IV}}$ [4] complexes. Complexes of $\mathrm{Mo^{V}}$ [5–7] and $\mathrm{Mo^{VI}}$ [8–11] have been isolated from the molybdenum-oxo-species. Halide derivatives of $\mathrm{Mo^{IV}}$ have also been prepared from $[\mathrm{MoCl_4(MeCN)_2}]$ by Van Den Bergen *et al.*[12]



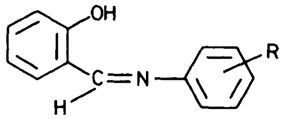
We are presently engaged in the study of $\mathrm{Mo^{IV}}$ Schiff base complexes with the general formula $[\mathrm{MoCl_2L_2}]$, where HL represents an extensive series of *N*-substituted salicylideneimines.

## Experimental

All preparations were carried out under an atmosphere of dinitrogen using standard vacuum line techniques.[13] All solvents were dried and purified by literature methods,[14] under dinitrogen. Schiff bases were prepared by treating the appropriate amines with salicylaldehyde and then recrystallized from ethanol. The compound $\mathrm{MoCl_5}$, obtained from Alfa, was used without further purification and $[\mathrm{MoCl_2(acac)_2}]$ (acac = acetylacetonate) was prepared as reported.[12]

*Dichlorobis(*N*-phenylsalicylideneiminato)molybdenum(*IV*).*— *Method* 1. Methyl cyanide (50 cm$^3$) was added to a mixture of $[\mathrm{MoCl_2(acac)_2}]$ (1.5 g, 4.5 mmol) and *N*-phenylsalicylideneimine (2.1 g, 8.6 mmol). The suspension was heated under reflux in an atmosphere of dinitrogen for *ca.* 5 h. A purple microcrystalline solid came out of solution. After cooling to room temperature, the solid was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield ~80% based on $[\mathrm{MoCl_2(acac)_2}]$.

*Method* 2. Methyl cyanide (50 cm$^3$) was added to a mixture of $[\mathrm{MoCl_4(MeCN)_2}]$ (1.5 g, 4.7 mmol) and *N*-phenylsalicylideneimine (2.3 g, 9.4 mmol). The suspension was heated under reflux in an atmosphere of dinitrogen for *ca.* 1 h. Triethylamine (0.94 g, 9.4 mmol) was added dropwise to the brown suspension. After addition of all the amine, the suspension was heated under reflux for a further 1 h. A purple microcrystalline solid slowly appeared. After cooling to room temperature, the solid was filtered off, washed with ethanol, and diethyl ether, and dried *in vacuo*. Yield ~25% based on $[\mathrm{MoCl_4(MeCN)_2}]$.



HL

| | R | | R |
|---|---|---|---|
| $L^1$, | H | $L^7$, | *m*-Me |
| $L^2$, | *p*-Me | $L^8$, | *m*-OMe |
| $L^3$, | *p*-OMe | $L^9$, | *m*-Cl |
| $L^4$, | *p*-$\mathrm{NO_2}$ | $L^{10}$, | *m*-F |
| $L^5$, | *p*-Cl | $L^{11}$, | *o*-Me |
| $L^6$, | *p*-F | $L^{12}$, | *o*-OMe |
| | | $L^{13}$, | *o*-Cl |

Except for $[\mathrm{MoCl_2(L^{10})_2}]$, which could only be prepared by Method 1, all other analogous complexes could be prepared by both methods with similar yields.

Elemental analyses of the complexes are collected in Table 1.

Nujol-mull i.r. spectra were recorded on a Perkin-Elmer 577 spectrophotometer (200—4 000 cm$^{-1}$). Ultraviolet-visible spectra of freshly prepared *NN*-dimethylformamide (dmf) and/or $\mathrm{CH_2Cl_2}$ solutions were recorded on a Beckman Acta CIII spectrophotometer (200—700 nm).

Magnetic susceptibilities of solid samples were measured by the Gouy method using mercury tetrathiocyanatocobaltate(II) as calibrant.[15] Molecular weights of the complexes in $\mathrm{CH_2Cl_2}$ solution were determined by the method of elevation of boiling point. Cyclic voltammograms of freshly prepared solutions were obtained with Princeton Applied Research (PAR) instruments: model 174 (Universal programmer) and model 173 (Potentiostat/Galvanostat), using a platinum wire working electrode and a saturated calomel reference electrode (s.c.e.), recorded with a Houston model 2000 x—y recorder. Tetrabutylammonium tetrafluoroborate, $[\mathrm{NBu_4}][\mathrm{BF_4}]$, was used as supporting electrolyte. Dissolved oxygen was removed by passing argon gas through the sample solution for 20 min. Elemental analyses of the complexes were determined by the Australian Mineral Development Laboratories.

## Results and Discussion

Complexes of the type $[\mathrm{MoCl_2L_2}]$ (L = $L^1$—$L^{13}$) were obtained by treating $[\mathrm{MoCl_2(acac)_2}]$ with the appropriate Schiff bases in MeCN under reflux conditions in an atmosphere of dinitrogen according to equation (1).

$$[\mathrm{MoCl_2(acac)_2}] + 2\,\mathrm{HL} \xrightarrow[\text{heat}]{\text{MeCN}} [\mathrm{MoCl_2L_2}] + 2\,\mathrm{Hacac} \quad (1)$$

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*Non-S.I. unit employed: 1 B.M. = $0.927 \times 10^{-23}$ A m$^2$.

**Table 1.** Elemental analytical data of [$MoCl_2L_2$] complexes

| | Analysis * (%) | | | | |
|---|---|---|---|---|---|
| Compound | C | H | N | Cl | F |
| [$MoCl_2(L^1)_2$] | 55.3 | 3.8 | 5.4 | 12.3 | |
| | (55.8) | (3.6) | (5.0) | (12.7) | |
| [$MoCl_2(L^2)_2$] | 56.8 | 4.5 | 5.0 | 12.0 | |
| | (57.2) | (4.1) | (4.8) | (12.1) | |
| [$MoCl_2(L^3)_2$] | 54.7 | 3.5 | 4.3 | 11.5 | |
| | (54.3) | (3.9) | (4.5) | (11.5) | |
| [$MoCl_2(L^4)_2$] | 47.7 | 2.9 | 8.4 | 10.8 | |
| | (48.1) | (2.8) | (8.6) | (10.9) | |
| [$MoCl_2(L^5)_2$] | 49.2 | 2.6 | 4.3 | 22.7 | |
| | (49.7) | (2.9) | (4.5) | (22.6) | |
| [$MoCl_2(L^6)_2$] | 52.6 | 3.4 | 4.7 | 11.9 | 6.6 |
| | (52.4) | (3.0) | (4.7) | (11.9) | (6.4) |
| [$MoCl_2(L^7)_2$] | 57.5 | 4.1 | 4.7 | 12.4 | |
| | (57.2) | (4.1) | (4.8) | (12.1) | |
| [$MoCl_2(L^8)_2$] | 54.0 | 3.7 | 4.6 | 11.5 | |
| | (54.3) | (3.9) | (4.5) | (11.5) | |
| [$MoCl_2(L^9)_2$] | 49.7 | 2.9 | 4.4 | 22.8 | |
| | (49.7) | (2.9) | (4.5) | (22.6) | |
| [$MoCl_2(L^{10})_2$] | 52.5 | 3.3 | 4.5 | 12.0 | 6.2 |
| | (52.4) | (3.3) | (4.7) | (11.9) | (6.4) |
| [$MoCl_2(L^{11})_2$] | 57.5 | 3.9 | 4.6 | 12.4 | |
| | (57.2) | (4.1) | (4.8) | (12.1) | |
| [$MoCl_2(L^{12})_2$] | 53.8 | 3.7 | 4.4 | 11.8 | |
| | (54.3) | (3.9) | (4.5) | (11.5) | |
| [$MoCl_2(L^{13})_2$] | 49.7 | 2.8 | 4.4 | 22.7 | |
| | (49.7) | (2.9) | (4.5) | (22.6) | |

* Calculated values in parentheses.

**Table 2.** Selected characteristic strong i.r. absorption bands and magnetic moments of [$MoCl_2L_2$] complexes *

| | I.r./cm$^{-1}$ | | | |
|---|---|---|---|---|
| Compound | ν(C=N) | ν(C-O) | ν(Mo-Cl) | $\mu_{eff.}$/B.M. |
| [$MoCl_2(L^1)_2$] | 1 600, | 1 530 | 315, | 2.58 |
| | 1 610 | | 313 (sh) | |
| [$MoCl_2(L^2)_2$] | 1 600, | 1 535 | 312, | 2.64 |
| | 1 610 | | 310 (sh) | |
| [$MoCl_2(L^3)_2$] | 1 600, | 1 540 | 310, | 2.65 |
| | 1 615 | | 312 (sh) | |
| [$MoCl_2(L^4)_2$] | 1 595, | 1 525 | 315, | 2.80 |
| | 1 605 | | 312 (sh) | |
| [$MoCl_2(L^5)_2$] | 1 600, | 1 535 | 315, | 2.60 |
| | 1 610 | | 313 (sh) | |
| [$MoCl_2(L^6)_2$] | 1 585, | 1 540 | 320, | 2.58 |
| | 1 600 | | 322 (sh) | |
| [$MoCl_2(L^7)_2$] | 1 585, | 1 545 | 325, | 2.64 |
| | 1 600 | | 323 (sh) | |
| [$MoCl_2(L^8)_2$] | 1 585, | 1 545 | 325, | 2.70 |
| | 1 600 | | 323 (sh) | |
| [$MoCl_2(L^9)_2$] | 1 590, | 1 560 | 320, | 2.65 |
| | 1 600 | | 317 (sh) | |
| [$MoCl_2(L^{10})_2$] | 1 595, | 1 550 | 320, | 2.60 |
| | 1 605 | | 318 (sh) | |
| [$MoCl_2(L^{11})_2$] | 1 590, | 1 540 | 325, | 2.60 |
| | 1 600 | | 323 (sh) | |
| [$MoCl_2(L^{12})_2$] | 1 590, | 1 545 | 328, | 2.61 |
| | 1 600 | | 326 (sh) | |
| [$MoCl_2(L^{13})_2$] | 1 580, | 1 535 | 325, | 2.69 |
| | 1 590 | | 323 (sh) | |

* sh = Shoulder.

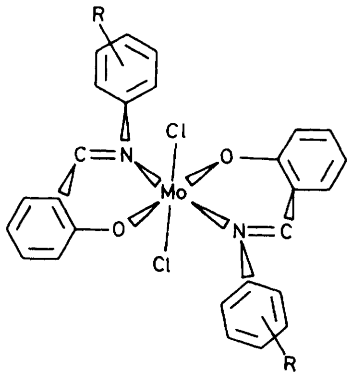
All these complexes, with the exception of [$MoCl_2(L^{10})_2$], could also be prepared by using Van Den Bergen's method [12] from the reaction of [$MoCl_4(MeCN)_2$] with the appropriate ligands in MeCN in the presence of triethylamine according to equation (2).

$$[MoCl_4(MeCN)_2] + 2\,HL + 2\,NEt_3 \xrightarrow[\text{heat}]{\text{MeCN}} [MoCl_2L_2] + 2\,NEt_3HCl + 2\,MeCN \quad (2)$$

The latter method is less convenient because the starting material, [$MoCl_4(MeCN)_2$], is less stable compared to [$MoCl_2(acac)_2$] and the yield is therefore lower.

All the complexes are microcrystalline purple solids and appear indefinitely stable in the solid state. They are insoluble in most organic solvents but slightly soluble in dichloromethane and *NN*-dimethylformamide (dmf). In $CH_2Cl_2$, the complexes are stable for several days but the dmf solution gradually turns green within 1 d. Molecular weight determinations of the complexes indicate that they are monomeric. Magnetic moment measurements of the complexes confirm the presence of two unpaired electrons per molecule.

In the ' double bond ' region, 1 700—1 200 cm$^{-1}$, of the i.r. spectra for [$MoCl_2L_2$], a doublet shows at ~1 600 cm$^{-1}$. The pattern is typical of chelation [16] of the ligand in salicylaldimine form, *i.e.* the bands at ~1 620 cm$^{-1}$ of $-C=N-$ for the free ligands are generally moved to lower frequency by *ca.* 20 cm$^{-1}$. Assignments of the $-C=N-$ and Mo-Cl stretching frequencies are listed in Table 2. The Mo-Cl stretching frequencies appear in the region ~315 cm$^{-1}$ with a shoulder appearing either on the left or right of the band. It is rather difficult to conclude here the relative arrangement of the two chloride ligands by i.r. spectroscopy alone. Since the spectroscopic properties of [$MoCl_2L_2$] are closely related to their *N*-methyl analogue which was found to have the *trans*-dichloro configuration,[17] the complexes are believed to have a similar configuration, as shown above.



Electronic absorption spectra of [$MoCl_2L_2$] in $CH_2Cl_2$ and/or dmf solutions are listed in Table 3. The spectra of these complexes are characterized by a well defined band at ~560 nm and an ill defined shoulder at ~450 nm which appears before the intense bands in the u.v. regions. These bands could not be assigned with certainty. Van Den Bergen has tentatively assigned these bands as the *d*—*d* transitions $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g} \rightarrow {}^3T_{1g}(P)$ respectively. However, this assignment is questionable in view of the high intensities of these transitions. The lower energy band is very intense compared with that of [$MoCl_4(bipy)$] (bipy = 2,2′-bipyridyl) [18] and is therefore likely to be a charge-transfer transition. Ligand-field transitions may be obscured by these intense bands.

Table 4 contains the relevant electrochemical data for the [$MoCl_2L_2$] complexes in dmf which contains [$NBu_4$][$BF_4$]

**Table 3**. Electronic absorption spectra of $[MoCl_2L_2]$ complexes

| Compound | Solvent | $\nu_{max.}$/nm ($\varepsilon$ /dm$^3$ mol$^{-1}$ cm$^{-1}$) * |
|---|---|---|
| $[MoCl_2(L^1)_2]$ | $CH_2Cl_2$ | 565 (4 200), 446 (sh) (~3 500), 356 (14 000), 280 (sh) (~17 000), 255 (35 000) |
| $[MoCl_2(L^2)_2]$ | dmf | 575 (4 100), 450 (sh) (~3 200), 368 (9 700), 310 (sh) (~15 000), 290 (17 000) |
| $[MoCl_2(L^3)_2]$ | $CH_2Cl_2$ | 568 (2 100), 408 (3 800), 360 (sh) (~7 800), 321 (8 000), 258 (11 000), 240 (13 000) |
| | dmf | 565 (3 500), 405 (6 400), 350 (sh) (~10 000), 315 (13 000), 271 (12 000) |
| $[MoCl_2(L^4)_2]$ | $CH_2Cl_2$ | 571 (4 000), 450 (sh) (~3 000), 360 (17 300), 320 (sh) (~22 000), 280 (30 000), 236 (23 000) |
| | dmf | 562 (5 600), 420 (sh) (~5 500), 361 (30 000), 314 (36 000), 278 (35 000) |
| $[MoCl_2(L^5)_2]$ | $CH_2Cl_2$ | 562 (2 600), 435 (sh) (~2 000), 352 (11 000), 305 (15 000), 254 (20 000), 237 (23 000) |
| $[MoCl_2(L^6)_2]$ | $CH_2Cl_2$ | 562 (2 600), 435 (sh) (~2 000), 352 (6 300), 300 (sh) (~8 000), 260 (11 000), 236 (13 000) |
| $[MoCl_2(L^7)_2]$ | $CH_2Cl_2$ | 560 (3 800), 442 (sh) (~3 100), 352 (8 800), 302 (12 000), 270 (14 000), 257 (16 000), 238 (16 000) |
| $[MoCl_2(L^8)_2]$ | dmf | 560 (6 300), 430 (sh) (~4 600), 355 (15 000), 298 (18 000), 286 (18 000) |
| | $CH_2Cl_2$ | 560 (2 400), 420 (sh) (~2 500), 355 (6 200), 310 (7 200), 262 (12 000), 236 (13 000) |
| $[MoCl_2(L^9)_2]$ | dmf | 562 (4 800), 456 (sh) (~4 000), 353 (12 000), 311 (15 000), 270 (22 000) |
| | $CH_2Cl_2$ | 568 (3 800), 450 (3 100), 366 (9 210), 270 (18 000), 244 (18 000) |
| $[MoCl_2(L^{10})_2]$ | $CH_2Cl_2$ | 564 (6 300), 440 (5 600), 360 (15 000), 268 (31 000), 238 (29 000) |
| $[MoCl_2(L^{11})_2]$ | $CH_2Cl_2$ | 555 (4 800), 418 (sh) (~4 500), 356 (11 500), 300 (13 000), 256 (21 000), 240 (19 000) |
| | dmf | 550 (2 900), 430 (sh) (~2 700), 354 (6 800), 295 (9 100), 271 (9 700) |
| $[MoCl_2(L^{12})_2]$ | $CH_2Cl_2$ | 555 (2 600), 405 (sh) (~3 400), 360 (7 300), 315 (8 300), 268 (13 500), 240 (12 500) |
| | dmf | 555 (4 800), 405 (6 900), 352 (13 500), 309 (13 000), 278 (19 000) |
| $[MoCl_2(L^{13})_2]$ | $CH_2Cl_2$ | 558 (3 400), 450 (3 000), 360 (7 800), 305 (sh) (~11 000), 260 (16 000), 240 (16 500) |
| | dmf | 562 (4 700), 438 (sh) (~4 000), 360 (11 500), 278 (20 000) |

* sh = Shoulder.

**Table 4**. Oxidation potentials (*versus* s.c.e.) of some Schiff base molybdenum(IV) complexes in dmf *

| Compound | $E_p^{red}$/V | $E_p^{ox}$/V | $E_p^{ox} - E_p^{red}$/ mV | $i_p^{red}/i_p^{ox}$ | $E_{\frac{1}{2}}^{ox}$/V |
|---|---|---|---|---|---|
| $[MoCl_2(L^1)_2]$ | −0.32 | −0.24 | 80 | 1.01 | −0.28 |
| $[MoCl_2(L^2)_2]$ | −0.28 | −0.20 | 80 | 1.10 | −0.24 |
| $[MoCl_2(L^3)_2]$ | −0.33 | −0.27 | 60 | 1.05 | −0.30 |
| $[MoCl_2(L^4)_2]$ | −0.19 | −0.11 | 80 | 1.02 | −0.15 |
| $[MoCl_2(L^5)_2]$ | −0.25 | −0.17 | 80 | 1.05 | −0.21 |
| $[MoCl_2(L^6)_2]$ | −0.28 | −0.23 | 60 | 1.06 | −0.25 |
| $[MoCl_2(L^7)_2]$ | −0.34 | −0.26 | 80 | 1.00 | −0.30 |
| $[MoCl_2(L^8)_2]$ | −0.32 | −0.22 | 80 | 1.01 | −0.28 |
| $[MoCl_2(L^9)_2]$ | −0.22 | −0.16 | 60 | 1.03 | −0.19 |
| $[MoCl_2(L^{10})_2]$ | −0.24 | −0.16 | 80 | 1.10 | −0.20 |
| $[MoCl_2(L^{11})_2]$ | −0.34 | −0.28 | 60 | 1.10 | −0.31 |
| $[MoCl_2(L^{12})_2]$ | −0.39 | −0.31 | 80 | 1.01 | −0.35 |
| $[MoCl_2(L^{13})_2]$ | −0.31 | −0.23 | 80 | 1.04 | −0.27 |

* Complexes ~0.5 × $10^{-3}$ mol dm$^{-3}$; supporting electrolyte $[NBu_4][BF_4]$ (0.2 mol dm$^{-3}$).

(0.2 mol dm$^{-3}$) as supporting electrolyte. The reversible oxidation potential is quoted as $E_{\frac{1}{2}}^{ox} = \frac{1}{2}(E_p^{ox} + E_p^{red})$ *versus* s.c.e. They are typical of one-electron reversible processes for $Mo^{IV}$–$Mo^{V}$ couples.[19] No further oxidation to $Mo^{VI}$ was observed in the voltage range used. It is quite clear that the $E_{\frac{1}{2}}^{ox}$ values of the complexes depended on the nature of the Schiff base ligands. The potentials increase with electron-withdrawing substituents, such as *p*-$NO_2$, but decrease with electron-donating substituents, such as *p*-OMe and *m*-OMe.

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