Inorganica Chimica Acta, 45 (1980) L115–L116

Tetrachloromolybdenum(IV) Complexes Containing Neutral Schiff Base Ligands

CHARLES A. McAULIFFE, ARLYN C. RICE

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 IQD, U.K.

and WILLIAM E. HILL

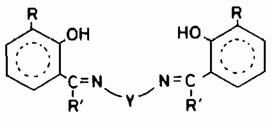
Department of Chemistry, Auburn University, Auburn, Ala., 36830, U.S.A.

Received April 29, 1980

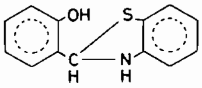
We are currently involved in an investigation of high-valent molybdenum and tungsten complexes of potentially bidentate, tridentate and tetradentate Schiff base ligands [1–3]. Although a number of molybdenum(IV) complexes of anionic Schiff base ligands $MoCl_2(Sal\text{-}NR)_2$, have been prepared [4], no study of molybdenum(IV) with neutral Schiff bases has been reported; though Fowles and Walton [4] did observe this type of complex as a contaminant in their $MoCl_2(Sal\text{-}NR)_2$ compounds, this could be avoided by addition of the base triethylamine to the reaction mixture. We here wish to report the isolation of a series of new complexes of neutral Schiff base ligands L (Table I 1a–fH_2, 2·H and 3·H) with molybdenum(IV).

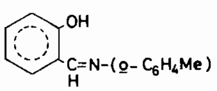
These complexes were prepared by a general procedure. This is exemplified by the preparation of $[Mo(1a\cdot H_2)Cl_4]\cdot C_7H_7$. Bis(salicylaldehyde)ethylenediimine (1.07 g, 0.004 mol) was dissolved in freshly distilled toluene (40 cm^3) and tetrachlorobis(butyronitrile)molybdenum(IV) (1.5 g 0.004 mol) in toluene (20 cm^3) was added and stirred under N_2. After 30 min. the resultant precipitate was filtered in a Schlenk apparatus, washed with n-pentane (10 cm^3) and dried *in vacuo*. Yields, 80–90%.

TABLE I. Complexes of Neutral Schiff Base Ligands.



	R	R′	Y
1a·H_2	H	H	$(CH_2)_2$
1b·H_2	H	H	$(CH_2)_3$
1c·H_2	H	H	o-C_6H_4
1d·H_2	H	H	m-MeC_6H_3
1e·H_2	H	CH_3	$(CH_2)_2$
1f·H_2	H	CH_3	CH_3CHCH_2
1g·H_2	OMe	H	$(CH_2)_2$
1j·H_2	OMe	H	o-C_6H_4





Most of the complexes, Table II, were obtained as toluene adducts and drying under vacuum for days did not remove this solvate. These green or purple complexes appear to be indefinitely stable once isolated and ampouled. After five months we observed no sign of the reactions:

$$Mo(L\cdot H_2)Cl_4 \rightarrow Mo(L)Cl_2 + 2HCl$$

or

TABLE II. Analytical Data for the Molybdenum(IV) Complexes.

Complex	Colour	%C[a]	%H[a]	%N[a]	%Mo[a]	%Cl[a]
$[Mo(1a\cdot H_2)Cl_4]\cdot C_7H_7$	purple			5.1(4.7)	16.0(16.1)	22.9(23.7)
$[Mo(1b\cdot H_2)Cl_4]\cdot \frac{1}{2}C_7H_7$	purple			5.1(4.9)	17.3(17.3)	24.6(25.0)
$[Mo(1c\cdot H_2)Cl_4]\cdot \frac{1}{4}C_7H_7$	green			4.9(4.5)	15.7(15.3)	21.8(21.9)
$[Mo(1d\cdot H_2)Cl_4]\cdot \frac{1}{2}C_7H_7$	green			4.8(4.7)	15.1(15.6)	23.0(23.1)
$[Mo(1e\cdot H_2)Cl_4]\cdot C_7H_7$	purple	47.7(47.9)	5.0(4.5)	4.7(4.5)	14.8(15.3)	21.9(23.6)
$[Mo(1f\cdot H_2)Cl_4]\cdot C_7H_7$	purple			5.0(4.4)	14.8(15.0)	21.5(22.0)
$[Mo(1g\cdot H_2)Cl_4]\cdot C_7H_7$	green			4.6(4.3)	14.8(14.5)	21.3(21.5)
$[Mo(1h\cdot H_2)Cl_4]\cdot C_7H_7$	green	46.5(47.3)	4.3(4.4)	4.6(4.1)	13.4(13.9)	20.0(20.7)
$[Mo(2\cdot H)_2Cl_4]\cdot C_7H_7$	purple	47.2(47.7)	3.3(3.5)	4.2(3.8)	13.0(13.0)	20.3(19.1)
$[Mo(3\cdot H)_2Cl_4]$	purple	51.2(50.9)	4.0(3.4)	4.2(4.2)	14.1(14.5)	20.9(21.5)

[a] Found (calculated).

TABLE III. Spectroscopic Data for the Molybdenum(IV) Complexes.

	ν(OH)	ν(CN)	ν(Mo–Cl) (cm^{-1})	$E_{max} \times 10^3$ cm^{-1}
$[Mo(1a \cdot H_2)Cl_4] \cdot C_7H_7$	3050	1650, 1620	350–290	22.7, 16.9
$[Mo(1b \cdot H_2)Cl_4] \cdot ½C_7H_7$	3040	1650, 1598	340, 330, 320, 310	22.7, 17.0
$[Mo(1c \cdot H_2)Cl_4] \cdot ¼C_7H_7$	3040	1640, 1605	335, 325, 312, 305	22.2, 17.3
$[Mo(1d \cdot H_2)Cl_4] \cdot ½C_7H_7$	3060	1640, 1610	335, 328, 315, 310	23.3, 17.3
$[Mo(1e \cdot H_2)Cl_4] \cdot C_7H_7$	3030	1635, 1600	330, 315, 310, 303	23.5
$[Mo(1f \cdot H_2)Cl_4] \cdot C_7H_7$	3060	1630, 1600	330, 315, 310, 300	23.5, 17.9
$[Mo(1g \cdot H_2)Cl_4] \cdot C_7H_7$	3080	1660, 1610	345, 335, 330, 310	21.3, 17.9
$[Mo(1h \cdot H_2)Cl_4] \cdot C_7H_7$	3080	1640, 1605	330, 318, 313, 306	23.8, 14.7
$[Mo(2 \cdot H)_2Cl_4] \cdot C_7H_7$	3060		335, 330, 325, 311	23.3, 17.3
$[Mo(3 \cdot H)_2Cl_4]$	3080	1644, 1603 1600, 1590	330, 314, 304, 295	21.5, 16.7

$$Mo(L \cdot H)_2Cl_4 \rightarrow MO(L)_2Cl + 2HCl$$

However, in moist air or in polar solvents the presence of HCl was soon detected.

The magnetic moments are all *ca.* 2.6 BM, quite typical of d^2 molybdenum(IV) with some orbital contribution [5]. The electronic reflectance spectra are characterised by two absorption bands at *ca.* 17,000 and 23,000 cm^{-1} tentatively assigned to $^3T_1 \rightarrow {}^3T_2$ and $^3T_1 \rightarrow {}^3T_1(P)$ respectively. The infrared spectra do not exhibit bands between 900–1000 cm^{-1} which could be assigned to ν(Mo=O); nor do the complexes exhibit e.p.r. signals. Thus, no oxidation to oxomolybdenum(V) has occurred. The infrared spectra all shown ν(CN) absorptions, Table III, shifted to higher frequency by approximately 20 cm^{-1}. The free ligands exhibit weak absorptions centered at 2700 cm^{-1} assignable to H-bonded OH groups; on coordination this H-bonding system breaks and a broad ν(OH) appears in the spectra of the complexes at 3080–3040 cm^{-1}. Thus, for the complexes $[Mo(L \cdot H_2)Cl_4]$ and $[Mo(L \cdot H)_2Cl_4]$ the infrared spectra are consistent with coordination through the azomethine nitrogen [5, 6]. It is not clear to us how ligand 2·H binds to molybdenum. The C–S bond does not break, as we have observed earlier [1], but a N–H proton is observed at 8.05 ppm in d^6-DMSO solutions of $[Mo(2 \cdot H)_2Cl_4]$, shifted from 7.0 ppm in the free ligand. This may indicate coordination *via* the nitrogen.

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