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Molybdenum (VI) dioxidedihalide Complexes

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A series of molybdenum (VI) dioxidedichloride and dioxidedibromide complexes with monodentate nitrogen ligands (alkyl cyanides, pyridine, and trimethylamine), bidentate chelating nitrogen ligands (2,2′-bipyridyl and 1,10-phenanthroline) and potentially bidentate nitrogen ligands (4,4′-bipyridyl, quinoxaline, and pyrazine) have been prepared. Reactions of the halides with some oxygen ligands (tetrahydrofuran, pentamethyleneoxide, dioxan, ethyleneglycoldimethyether, triphenylphosphine oxide, and triphenylarsine oxide) are also reported. Complexes isolated have been characterised by magnetic, spectroscopic, and conductivity measurements.

Introduction

Over the past five years a number of complexes of general formula $MoO_2X_2 . 2L$ or $MoO_2X_2 . B$ ($X = Cl$ or Br, $L =$ monodentate ligand, $B =$ bidentate ligand) have been prepared,[1-7] but few have been adequately characterised.

We have now prepared a much wider range of complexes with nitrogen-donor ligands, repeated the preparation of some oxygen-donor complexes, and prepared several new oxygen-donor adducts. We have characterised these complexes by a variety of physical measurements, including conductance, and ultraviolet, and infrared spectra. Much of this work had been completed before the publication of references 3-7.

Experimental Section

Materials. Molybdenum(VI) dioxidedichloride and dioxidedibromide were prepared by passing an oxygen-halogen mixture over heated molybdenum.[8] Purification was effected by sublimation. Liquid ligands were dried by repeated distillation in vacuo from suitable desiccants (P_2O_5 for NMe_3 and RCN, CaH_2 for py, CaH_2 followed by Na and K for oxygen-donor ligands). Solid ligands were recrystallised and dried by pumping in vacuo, together with vacuum sublimation where possible.

Analyses. Molybdenum was determined as the «oxinate» and chloride or bromide by potentiometric titration with silver nitrate. Phosphorus was estimated as quinoline phosphomolybdate and arsenic by the iodometric method of Ingram[9] after peroxide fusion of the complexes. Carbon, hydrogen, and nitrogen analyses were carried out by a professional analyst; these analyses are less reliable than the remainder for those complexes which are particularly susceptible to hydrolysis, because the handling of the compounds was not under our control.

Physical measurements. Ultraviolet and visible spectra were examined for solutions in 1 cm. sealed silica cells, using Unicam SP 800 and 700 C and Perkin-Elmer 137 spectrophotometers. The cells were filled and sealed while attached to the vacuum line, in order to eliminate hydrolysis. Diffuse reflectance spectra were measured by means of the SP 700 C fitted with a 735 attachment, the samples being prepared in a drybox. Infrared spectra were measured for Nujol mulls on Unicam SP 200, Perkin-Elmer 237 and 337, and Grubb-Parsons DM 4 spectrophotometers, the specimens being again prepared in a drybox. Oxidation state determinations were carried out by oxidation of a weighed sample with a known excess of cerium(IV) sulphate solution, the excess of the latter being titrated with standard iron(II) solution. Conductance measurements were made at 25° on nitrobenzene or methyl cyanide solutions in sealed cells by means of a Wayne-Kerr Autobalance universal bridge.

Reactions. These were all carried out by means of a vacuum line, but several methods (differing in detail) were used; these (A-H) are detailed below. (i) *Method A.* Excess of anhydrous ligand was distilled on to the oxyhalide in vacuo and the solution obtained filtered, if necessary. Excess of ligand was distilled from the filtrate and the residue pumped for several hours at room temperature. (ii) *Method B.* The oxyhalide and at least a five-molar excess of the solid ligand were mixed in a tube attached to the vacuum line; after the tube and its contents had been evacuated the tube was sealed and heated for at least a day at 130° (200° for Ph_3PO). The tube was cooled, opened under nitrogen and attached to the vacuum line; excess of ligand was removed by extraction of the reaction mixture with benzene and dichloromethane, and the product pumped for several hours. (iii) *Method C.* An excess of

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Table I.

Complex*	Prep. Method	Found %					Required %					Oxidation state
		Mo	Hal	C	H	N,P,or As	Mo	Hal	C	H	N,P,or As	
MoO_2Br_2,THF	A	26.5	44.7	13.8	2.7	—	26.7	44.4	13.4	2.3	—	—
MoO_2Br_2,2THF	A	23.4	39.9	20.5	3.7	—	22.2	37.0	22.2	3.7	—	5.9
MoO_2Br_2,PMO	A	25.5	42.5	14.2	3.1	—	25.7	42.8	16.1	2.7	—	6.0
MoO_2Br_2,dioxan	A	25.1	42.8	14.5	2.8	—	25.5	42.5	12.8	2.2	—	5.9
MoO_2Br_2,EGDE	A	25.6	42.7	12.9	3.0	—	25.4	42.3	12.7	2.7	—	—
MoO_2Br_2,2Ph_3PO	B	11.3	19.6	49.8	3.8	7.3	11.4	19.0	51.2	3.6	7.3	5.7
MoO_2Br_2,2Ph_3AsO	D	10.1	17.0	48.6	3.4	16.0	10.3	17.1	46.4	3.3	16.1	—
MoO_2Cl_2,2Ph_3PO	C	12.9	9.6	56.9	3.4	8.3	12.7	9.4	57.2	4.0	8.2	—
MoO_2Cl_2,2Ph_3AsO	F	11.1	8.6	51.5	3.3	17.6	11.4	8.4	51.3	3.6	17.8	—
MoO_2Br_2,MeCN	A	29.0	47.9	7.5	0.96	3.8	29.2	48.6	7.3	0.80	4.3	—
MoO_2Br_2,2MeCN	A	26.1	43.4	11.1	1.2	6.8	25.9	43.2	13.0	1.6	7.6	—
MoO_2Br_2,EtCN	A	28.6	47.0	9.9	1.5	4.1	28.0	46.6	10.5	1.5	4.0	—
MoO_2Br_2,2EtCN	A	24.4	40.1	—	—	—	24.1	40.1	—	—	—	—
MoO_2Br_2,Pr^{n}CN	A	27.3	44.8	13.5	2.0	3.9	26.9	44.7	13.7	2.1	3.6	—
MoO_2Br_2,2Pr^{n}CN	A	23.2	39.5	—	—	—	22.5	37.5	—	—	—	—
MoO_2Cl_2,EtCN	A	38.0	27.8	—	—	—	37.8	27.9	—	—	—	—
MoO_2Cl_2,Pr^{n}CN	A	35.4	26.2	—	—	—	35.8	26.5	—	—	—	—
MoO_2Br_2,2py	A	21.7	37.6	26.6	2.2	6.2	21.5	35.8	26.9	2.3	6.3	—
MoO_2Cl_2,bipy	C	26.6	19.0	35.0	2.6	8.1	27.0	20.0	33.8	2.3	7.9	—
MoO_2Br_2,bipy	B or C	21.2	34.6	27.6	1.8	6.4	21.6	36.0	27.0	1.8	6.3	—
MoO_2Cl_2,phen	C	25.0	18.2	38.4	2.2	7.6	25.3	18.7	38.0	2.1	7.4	—
MoO_2Br_2,phen	B or C	20.5	34.5	30.8	1.9	5.6	20.5	34.2	30.8	1.7	6.0	—
MoO_2Cl_2,2NMe_3	H	30.0	22.9	21.6	5.2	8.2	30.3	22.4	22.7	5.7	8.8	—
MoO_2Cl_2,2pyz	D	27.0	19.9	24.2	2.6	14.1	26.7	19.7	26.8	2.2	15.6	—
MoO_2Br_2,2pyz	F	21.3	36.1	21.2	2.3	12.3	21.4	35.7	21.4	1.8	12.5	—
MoO_2Cl_2,1 . 5BP	G	21.4	15.5	42.1	4.2	9.9	22.1	16.4	41.6	2.8	9.7	—
MoO_2Br_2,2BP	E	17.0	29.0	—	—	—	16.0	26.6	—	—	—	—
MoO_2Cl_2,1 . 5qox	D	24.5	17.8	—	—	—	24.3	18.0	—	—	—	—
MoO_2Br_2,2qox	D	17.4	28.9	34.8	2.8	10.2	17.5	29.2	35.1	2.2	10.2	—

* Abbreviations: THF = tetrahydrofuran; PMO = pentamethyleneoxide; EGDE = ethyleneglycol dimethylether; py = pyridine; bipy = 2,2′-bipyridyl; phen = 1,10-phenanthroline; pyz = pyrazine; BP = 4.4′-dipyridyl; qox = quinoxaline.

Table II.

Complex	χ_A $\times 10^6$ c.g.s.u.	Λ_M (ohm^{-1} cm^2 mole^{-1})	Concn. $\times 10^4$M	$\nu_{(M=O)}$ (cm^{-1})	ν_{Mo-X} (cm^{-1})	$\nu_{E=O}$ (E=P, As) (cm^{-1})	ν_{COC} (cm^{-1})		$\nu_{C\equiv N}$ (cm^{-1})
							Sym	Asym	
MoO_2Br_2,THF	66	—	—	924, 966	—	—	839	1010	—
MoO_2Br_2,2THF	53	—	—	931, 961	—	—	861	1015	—
MoO_2Br_2,PMO	49	—	—	923, 965	260	—	855	1075, 1083	—
MoO_2Br_2,dioxan	29	—	—	930, 969	265, 254	—	855, 869	1090, 1110	—
MoO_2Br_2,EGDE	54	—	—	917, 957	258	—	—	1074, 1104	—
MoO_2Br_2,2Ph_3PO [a]	240	7.2 [c]	2.4	903, 947	245	1173, 1150	—	—	—
MoO_2Br_2,2Ph_3AsO	92	14.0 [c]	3.3	920, 955	—	885, 862	—	—	—
MoO_2Cl_2,2Ph_3PO [b]	136	4.0 [c]	5.3	905, 947	—	1165, 1147	—	—	—
MoO_2Cl_2,2Ph_3AsO [b]	—	6.0 [c]	3.0	925, 960	—	890, 865	—	—	—
MoO_2Br_2,MeCN	- 10	—	—	960, 923	—	—	—	—	2300
MoO_2Br_2,2MeCN	30	2.0 [c]	1.8	953, 918	—	—	—	—	2310
MoO_2Br_2,EtCN	36	—	—	962, 922	—	—	—	—	2305
MoO_2Br_2,2EtCN	—	0.8 [d]	3.7	958, 918	—	—	—	—	2284
MoO_2Br_2,Pr^{n}CN	50	—	—	967, 925	—	—	—	—	2315
MoO_2Br_2,2Pr^{n}CN	37	1.4 [d]	1.6	957, 920	—	—	—	—	2288
MoO_2Cl_2,EtCN	—	0.3 [d]	9.9	965, 922	—	—	—	—	2280
MoO_2Cl_2,Pr^{n}CN	28	0.7	3.0	962, 922	—	—	—	—	2288
MoO_2Br_2,2py	56	—	—	942, 909	243	—	—	—	—
MoO_2Cl_2,bipy [e]	100	4.0 [c]	0.45	933, 903	—	—	—	—	—
MoO_2Br_2,bipy [e]	22	7.0 [c]	0.70	930, 902	253	—	—	—	—
MoO_2Cl_2,phen	32	2.0 [c]	1.3	935, 902	—	—	—	—	—
MoO_2Br_2,phen	42	7.0 [c]	0.56	933, 900	244	—	—	—	—
MoO_2Cl_2,2NMe_3	480	8.0 [d]	1.5	965, 920	—	—	—	—	—
MoO_2Cl_2,2pyz	35	44.0 [c]	0.9	948, 910	—	—	—	—	—
MoO_2Br_2,2pyz	54	51.5 [c]	1.6	945, 907	—	—	—	—	—
MoO_2Cl_2,1 . 5BP	490	insol. [c,d]	—	940, 908	—	—	—	—	—
MoO_2Br_2,2BP	—	insol. [c,d]	—	940, 908	—	—	—	—	—
MoO_2Cl_2,1 . qox	270	31.0 [c]	2.5	950, 915	—	—	—	—	—
MoO_2Br_2,2qox	—	35.0 [c]	0.9	950, 910	—	—	—	—	—

[a] Ref. 5. [b] Ref. 2. [c] In MeCN. [d] In $PhNO_2$. [e] Ref. 7.

Table III. Ultraviolet Spectra (in kK)

Complex	Method*	Peak positions (ε_{max} in parentheses)
MoO_2Br_2,THF	THF soln.	29.4; 33.3$^+$
MoO_2Br_2,PMO	PMO soln.	28.6; 34.5; 37.5; 41.7; 44.6
»	D.R.	37.4; 45.6
MoO_2Br_2,dioxan	dioxan soln.	34.5$^+$
»	D.R.	37.5; 45.2
MoO_2Br_2,EGDE	EGDE soln.	32.3; 38.2
»	D.R.	28.3; 30.2; 37.7; 45.0
MoO_2Br_2,2Ph_3PO	MeCN soln.	33.0 (~4000); 43.1 (34000) phenyl bands at 36.6; 37.6; 38.5; 39.2 (ε for band envelope 13000)
	D.R.$^{\neq}$	27.8
$_2Br_2$,2Ph_3AsO	MeCN soln.	33.0 (~1800); 45.1 (35000) phenyl bands at 37.1; 37.9; 38.7; 39.9 (ε for band envelope 8100)
	D.R.$^{\neq}$	28.0
oO_2Cl_2,2Ph_3PO	MeCN soln.	32.7 (~4000); 44.8 (37000) phenyl bands at 36.8; 37.7; 38.2; 38.7
	D.R.	38.9; 39.6; 40.0 and 40.7 (ε for band envelope 7300)
MoO_2Cl_2,2Ph_3AsO	MeCN soln.	32.8 (~1300); 45.1 (38000) phenyl bands at 37.0; 38.0; 38.8; 39.0; 39.7; 40.7 (ε for band envelope 7000)
	D.R.$^{\neq}$	29.2
MoO_2Br_2,MeCN	MeCN soln.	33.7; 37.7
MoO_2Br_2,2MeCN	MeCN soln.	33.1sh (2300); 37.8 (4000); 38.6 (3900); 39.5 (3400); 40.4 (2900); 41.2 (2600); 45.7 (3700)
MoO_2Br_2,EtCN	EtCN soln.	33.1; 37.5
MoO_2Br_2,Pr^nCN	Pr^nCN soln.	37.0
MoO_2Br_2,2py	D.R.	21.5; 24.3; 30.2; 37.9; 44.8
MoO_2Br_2,bipy	D.R.	20.4; 23.6; 30.1; 36.5; 37.6; 44.8
	MeCN soln.	31.1 (10000); 37.3 (12000); 38.0 (12500); 38.8 (13000); 39.7 (12000); 40.6 (11000); 44.6 (13000); 45.9 (15000)
MoO_2Cl_2,bipy	MeCN soln.	31.4 (7800); 36.0 (8200); 39.3 (9300); 40.2 (10000); 41.3 (11000); 41.8 (12000); 43.1 (12000); 45.8 (15000)
MoO_2Br_2,phen	D.R.	20.9; 25.8; 38.6; 47.4
	MeCN soln.	28.8sh (~2000); 33.6sh (~8000); 38.2 (22000); 38.8 (22000); 39.6 (16000); 40.7 (13000); 45.9 (28000)
MoO_2Cl_2,phen	MeCN soln.	29.0 (960); 33.9 (6000); 35.6 (9600); 36.2 (1000); 38.2 (11000); 38.8 (11000); 39.1 (11000); 39.7 (9000); 45.7 (17000)
MoO_2Cl_2,2NMe_3	MeCN soln.	31.6 (1500); 38.2 (2000); 39.1 (2200); 40.0 (2300); 41.4 (2400); 45.7 (3600)
MoO_2Cl_2,2pyz	MeCN soln.	31.6sh (~ 1700); 32.3 (1900); ~ 36.8sh (4500); 37.5 (8200); 38.2 (9600); 38.6 (9400); 38.9 (9000); 39.5 (8000); 39.8 (7300); 40.3 (6200); 43.5 (5200)
MoO_2Br_2,2pyz	MeCN soln.	31.6sh (~3000); 32.7 (3600); 36.9 (11000); 37.6 (16000); 38.2 (16000); 38.6 (15000); 38.9 (14000); 39.5 (12000); 40.5 (9000)
MoO_2Cl_2,1 . 5BP	MeCN soln.	~30.8sh (1400); 33.7 (5300); 38.2 (27000); 39.0 (27000); 39.9 (27000); 40.7 (25000); 46.1 (11000)
MoO_2Br_2,2BP	MeCN soln.	25.8 (340); 33.0 (6700); 38.1 (34000); 38.8 (35000); 39.7 (33000); 40.7 (28000)
MoO_2Cl_2,1 . 5qox	MeCN soln.	30.5sh (3500); 31.8 (8300); 33.0 (7400); 34.5 (5500); 39.5 (6200)
MoO_2Br_2,2qox	MeCN soln.	28.1 (1030); 30.7 (9300); 31.8 (9300); 32.3 (8300); 32.8 (8000); 34.5 (6200); 37.7 (6000); 41.2 (12000); 42.6 (20000); 43.1 (21000)

* D.R. = Diffuse Reflectance. $^+$ Solutions too concentrated for more intense higher energy bands to be measured. $^{\neq}$ Measured on SP 500 only, so limited to ~31 kK.

anhydrous methyl cyanide was distilled on to the oxyhalide in vacuo and warmed gently to yield a solution; the latter was added to a methyl cyanide solution containing excess of ligand, and the precipitate formed was filtered, and washed successively with benzene (or dichloromethane) and diethylether before being pumped for several hours. (iv) *Method D.* Methyl cyanide solutions were prepared and mixed as in Method C, but as no solid precipitated the solvent was distilled off in vacuo and the residue washed with benzene, dichloromethane, or 60-80° petroleum spirit before pumping. (v) *Method E.* Methyl cyanide solutions were mixed as in Method C, but because only a small amount of precipitate formed (and added benzene caused no further precipitation) the solvents were partly distilled off so that further precipitate deposited. This precipitate was treated as in D. (vi) *Method F.* As method D except that dichloromethane was used as solvent. (vii) *Method G.* As Method C but dichloromethane was used as solvent. (viii) *Method H.* Excess of anhydrous ligand was distilled (in vacuo) on to the oxyhalide contained in an ampoule attached to the vacuum line. After it had been sealed, the ampoule was placed on a mechanical shaker for two weeks, during which time a solid product formed. The ampoule was opened, attached to the vacuum line, and excess of ligand removed by the pump. Table I gives the analytical data for the complexes prepared.

Results and Discussion

Table II summarises the complexes prepared and their susceptibilities, conductances and significant infrared data. The susceptibilities and oxidation state titrations generally confirm the complexes as being of molybdenum(VI), although the slight paramagnetism of one or two complexes indicates a small measure of reduction.

The complexes were not sufficiently soluble in suitable solvents for molecular weight measurements to be made, although soluble enough in most cases for conductance measurements. The latter show the compounds to be non-ionic, except possibly the pyrazine and quinoxaline ones where some dissociation is indicated.

The infrared spectra are consistent with six-coordinate molybdenum. Thus the Mo-Cl and Mo-Br stretching modes are in the expected region, and there is no indication of higher co-ordination through Mo-O-Mo linkages; all compounds show very strong terminal Mo=O frequencies. The significant ligand peaks are modified on co-ordination as would be expected, with COC (sym. and asym.), P=O, and As=O frequencies noteably lower and $^{\nu}C{\equiv}N$ modes higher. The spectrum of the dioxan complex shows both oxygen atoms to be co-ordinated, but the pyrazine complexes would appear to contain monodentate ligands in view of the band at 965 cm.$^{-1}$.[10] Both of these observations support the postulate of six-coordinated molybdenum.

The unusual stoichiometry of the complexes formed by the oxychloride with 4,4′-bipyridyl and quinoxaline ($MoO_2Cl_2 . 1.5L$) is completely reproducible, and is best explained either by the bridging of two molybdenum atoms by one ligand molecule or by an ionic arrangement, e.g., $[MoO_2ClL_2][MoO_2Cl_3L]$; the latter suggestion is in line with proposals[11] for $MoBr_3$,1.5bipyr and supported by the conductance of the quinoxaline complex in methyl cyanide.

Ultraviolet spectra are summarised in Table III; additional peaks of very low intensity were observed for some of the complexes in the visible region (10,000-23,000 cm.$^{-1}$), probably as a result of traces of molybdenum(V) compounds. Because the complexes are generally of low symmetry the complicated nature of the spectra is not unexpected, and detailed assignments cannot be made at this point.

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