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Further Examples of Dinuclear Molybdenum(II) Complexes Containing Nitrogen Ligands

D. A. EDWARDS*, G. UDEN
School of Chemistry, University of Bath, Bath BA2 7AY, U.K.

W. S. MIALKI and R. A. WALTON*
Department of Chemistry, Purdue University, West Lafayette, Ind. 47907, U.S.A.

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The reactions of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ *with the potentially bridging nitrogen ligands pyrazine and 2,6-dimethylpyrazine produce polymeric* $[Mo_2Cl_4(pyz)_2]_n$*, in which pyrazine acts as a* Mo_2Cl_4 *intermolecular bridging ligand, and* $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$*, in which the disubstituted pyrazines coordinate in a unidentate manner. The new chelate complexes* $Mo_2Cl_4(L\text{–}L)_2$ *(L–L = 8-aminoquinoline, 2-aminomethylpyridine, di-2-pyridylamine and pyridine-2-carbaldehyde phenylhydrazone) have been prepared by the same method. Although the X-ray photoelectron spectra of all these complexes are in accord with their formulation as quadruple metal–metal bonded molybdenum(II) complexes, that of* $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ *shows some unexpected features in that its Cl 2p and N 1s spectra are time dependent. It is suggested that progressive loss of dimethylpyrazine ligands occurs under the high vacuum conditions within the spectrometer.*

Introduction

Amongst the wide variety of dinuclear molybdenum(II) chloride complexes of general formulae $Mo_2Cl_4L_4$ and $Mo_2Cl_4(L\text{–}L)_2$ (L = unidentate ligand; L–L = bidentate chelating ligand) containing quadruple metal–metal bonds are a number involving nitrogen ligands. Thus, $Mo_2Cl_4(py)_4$ has been produced by direct reaction of the ligand with either $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ [1] or β-$MoCl_2$ [2], by ligand displacement from Mo_2Cl_4(5,8-dithiadodecane)$_2$ [3], and by reduction of the molybdenum(III) complex $Cs_3[Mo_2Cl_8H]$ [4]. Displacement of the pyridine ligands from the above complex by other nitrogen donors then provides a route to the chelate complexes $Mo_2Cl_4(bipy)_2$ and $Mo_2Cl_4(phen)_2$ [1] (bipy = 2,2'-bipyridyl; phen = 1,10-phenanthroline), as well as to $Mo_2Cl_4(NH_3)_4$ [5]. The bipy complex has also been prepared from either $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ or Mo_2Cl_4(4,7-dithiadecane)$_2$ [3]. The nitrile complexes $Mo_2Cl_4(NCR)_4$ (R = Me or Ph), have similarly been prepared by ligand displacement from $Mo_2Cl_4(SMe_2)_4$ [3]. Finally, $Mo_2Cl_4(NHMe_2)_4$ has been found to be a product of the reduction of $MoCl_3$ by anhydrous dimethylamine [6].

We report here on some further nitrogen ligand complexes of these types which are of significance in that they are the first such complexes to involve either potentially bridging nitrogen ligands (pyrazine, pyz; and 2,6-dimethylpyrazine, 2,6-Me_2pyz) or unsymmetrical chelate ligands (8-aminoquinoline, 8-aq; 2-aminomethylpyridine, amp; and pyridine-2-carbaldehyde phenylhydrazone, $C_5H_4NCH{=}NNHPh$, pyph). The symmetrical chelate ligand complex $Mo_2Cl_4(dpa)_2$ (dpa = di-2-pyridylamine) has also been prepared for the first time and characterized.

Experimental

Physical Measurements and Analytical Procedures

Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer using Nujol mulls supported between caesium iodide plates. Far-infrared spectra of samples dispersed in pressed polythene discs were obtained using a Beckman-R.I.I.C. FS 720 interferometer. Diffuse reflectance spectra in the visible region were obtained using a Unicam SP 500 spectrophotometer fitted with the standard reflectance attachment. The reference solid was magnesium oxide. Magnetic susceptibility measurements were made at room temperature only using the Gouy method. Tris(ethylenediamine)nickel(II) thiosulphate was used as calibrant. X-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminium

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*Address correspondence to either of these authors.

TABLE I. Reaction Conditions, Yields and Analyses.

Complex[a]	Weight of ligand used (g)	Reaction time (h)	Yield (%)	Analysis Found (Calc.)			
				C	H	N	Mo
$[Mo_2Cl_4(pyz)_2]_n$	0.11	2.0	95	19.7	1.73	11.6	38.2
				(19.5)	(1.63)	(11.4)	(38.9)
$Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$	0.16	1.0	75	37.8	4.46	14.7	24.0
				(37.6)	(4.21)	(14.6)	(25.0)
$Mo_2Cl_4(pyph)_2$	0.22	1.0	89	34.8	2.89	10.5	25.8
				(39.5)	(3.04)	(11.5)	(26.3)
$Mo_2Cl_4(8\text{-}aq)_2$	0.14	1.0	82	34.4	2.72	8.87	29.2
				(34.8)	(2.59)	(9.01)	(30.8)
$Mo_2Cl_4(amp)_2$	0.12	1.0	59	26.4	3.15	10.0	
				(26.2)	(2.93)	(10.2)	
$Mo_2Cl_4(dpa)_2$	0.17	1.0	52	35.8	2.89	12.2	26.8
				(35.5)	(2.68)	(12.4)	(28.3)

[a] For ligand abbreviations see Introduction.

$K\alpha_{1,2}$ line (1486.6 eV) was used as the excitation source. An X-ray beam power of 1000 W was routinely used, but in many instances the spectra were also recorded at 600 W to confirm the absence of any X-ray induced decomposition of the samples. Sample preparation for the XPS measurements and full details of the experimental procedure are described elsewhere [7, 8].

Carbon, hydrogen and nitrogen were estimated by microanalysis. Molybdenum was determined by initially treating the samples with a nitric–sulphuric acid mixture, followed by ignition at 500 °C and weighing as MoO_3. Higher ignition temperatures were not used since volatilization of the oxide may occur.

Starting Materials

The dinuclear molybdenum(II) compounds $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ [9] and $K_4Mo_2Cl_8$ [10] were prepared by established procedures. Pyridine-2-carbaldehyde phenylhydrazone [11] was prepared as before. Other solid ligands were commercial products and were purified by vacuum sublimation and drying before use.

Synthetic Procedure

The following general procedure was followed. $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ (0.3 g) and ligand were allowed to react under nitrogen at room temperature in anhydrous, degassed, methanol (20 cm^3). The solid products were collected by suction filtration, washed with further methanol and dried *in vacuo*. Weights of ligands and reaction times employed, as well as yields and analyses of the products are given in Table I. Identical products could be prepared using $K_4Mo_2Cl_8$ in place of the ammonium salt but reaction rates were found to be considerably slower.

Results and Discussion

The nitrogen ligand complexes $Mo_2Cl_4L_4$ (L = 2,6-dimethylpyrazine) and $Mo_2Cl_4(L\text{–}L)_2$ (L–L = pyrazine, 8-aminoquinoline, 2-aminomethylpyridine, di-2-pyridylamine and pyridine-2-carbaldehyde phenylhydrazone) have been prepared by reaction of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ with the appropriate ligand in methanol at room temperature, a method previously employed by San Filippo and co-workers [3] to prepare a variety of such complexes where L = unidentate nitrogen, oxygen, phosphorus and sulphur donors, and L–L = bidentate nitrogen, phosphorus and sulphur donors. We have also prepared the above complexes starting from $K_4Mo_2Cl_8$ but the reactions took place at a considerably slower rate. For example, by monitoring the reduction in intensity of the infrared ν(Mo–Cl) bands of either $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ or $K_4Mo_2Cl_8$ and the concomitant growth of the infrared ν(Mo–Cl) bands of the product $[Mo_2Cl_4(pyz)_2]_n$ it was possible to show that formation of the pyrazine complex from the ammonium salt was complete after two hours whereas a reaction time of approximately 100 hours was necessary when using the potassium salt. Interestingly, it has been found [2] that $K_4Mo_2Cl_8$ is as effective a starting material as $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ for the synthesis of phosphine complexes of the type $Mo_2Cl_4L_4$ (L = PEt_3, PEt_2Ph, $PEtPh_2$, or $PMePh_2$).

Attempts to isolate $Mo_2Cl_4(pyz)_4$, in which the pyrazine ligands would be unidentate, by using a large excess of pyrazine, were unsuccessful. Con-

TABLE II. Infrared ν(Mo–Cl) Frequencies and Visible Spectra.

Complex	ν(Mo–Cl) cm^{-1} Nujol Mulls	λ_{max}, nm[a]
$[Mo_2Cl_4(pyz)_2]_n$	374 s, 282 m	562, 440
$Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$	365 s, 291 m	560, 451
$Mo_2Cl_4(py)_4$[b]	343 s, 283 mw	560, 405[c]
$Mo_2Cl_4(NHMe_2)_4$[d]		555, 472
$Mo_2Cl_4(amp)_2$	304 s, 290 s	542, 407
$Mo_2Cl_4(8\text{-}aq)_2$	295 s, 275 m	555
$Mo_2Cl_4(dpa)_2$	293 s, 280 s	541
$Mo_2Cl_4(pyph)_2$	304 s	~540 br
$Mo_2Cl_4(bipy)_2$[e]	304 s	530[f]

[a] Diffuse reflectance unless otherwise noted. [b] Ref. 2. [c] Nujol mull. [d] Ref. 6. [e] Ref. 3. [f] $CHCl_3$ solution.

versely, $[Mo_2Cl_4(2,6\text{-}Me_2pyz)_2]_n$ in which the dimethylpyrazine ligands would be acting in a bridging mode, could not be isolated by using a deficiency of the ligand, the products always being a mixture of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ and $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$. Attempts to utilise the same method to prepare analogous complexes containing the potentially bridging ligands piperazine, 1,4-dicyanobenzene and 4,4′-bipyridyl were unsuccessful. Although quite rapid reactions occurred in each case, pure dinuclear molybdenum(II) products were not obtained, so these reactions were not studied further.

The complexes were obtained in good yields (Table I), as powders displaying very poor solubility in a range of organic solvents such as ethanol, ether, chloroform and dichloromethane. As any very dilute solutions that could be produced were rapidly air-oxidised, as shown by the detection of infrared ν(Mo–O) bands between 1000 and 900 cm^{-1}, characterization was confined to solid state infrared, visible and X-ray photoelectron spectroscopic and magnetic susceptibility measurements. Good analytical results could not be obtained for $Mo_2Cl_4(pyph)_2$ (see Table I), so although spectroscopic evidence clearly showed that this complex had been prepared its purity must be suspect. The evidence acquired clearly points to the fact that all six new complexes prepared are indeed dinuclear molybdenum(II) complexes containing quadruple metal-metal bonds. Each of the complexes are essentially diamagnetic and their reflectance visible spectra (Table II) are characteristic [3] of such a formulation, with a major peak maximum at 540–560 nm that is responsible for the colours of the complexes. This band has been assigned [12] to the $\delta \rightarrow \delta^*$ transition.

The infrared bands assignable to ν(Mo–Cl) modes are also listed in Table II and merit some discussion.

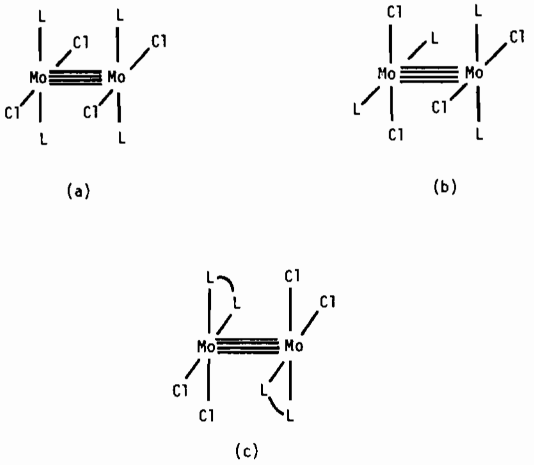

Fig. 1. Structural alternatives for $Mo_2Cl_4L_4$ complexes and the suggested structure for $Mo_2Cl_4(L\text{–}L)_2$ complexes.

Both $[Mo_2Cl_4(pyz)_2]_n$ and $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ show two such bands quite widely separated in frequency at *ca.* 350 cm^{-1} and *ca.* 285 cm^{-1}, a feature previously reported for other unidentate ligand $Mo_2Cl_4L_4$ complexes [2, 3, 13] (L = pyridine, RCN, R_3P, $(RO)_3P$ and R_2S), as well as for $Mo_2Cl_4(Ph_2PCH_2PPh_2)_2$ and the β-isomer of $Mo_2Cl_4(Ph_2PCH_2CH_2PPh_2)_2$ [14]. Each of these complexes are held to involve a *trans*-$MoCl_2$ arrangement within each $MoCl_2L_2$ unit. With the exception of β-$Mo_2Cl_4(Ph_2PCH_2CH_2PPh_2)_2$†, these complexes may be represented by structures (a) or (b) of Fig. 1. We therefore believe both $[Mo_2Cl_4(pyz)_2]_n$ and $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ have analogous structures. Unfortunately two infrared-active ν(Mo–Cl) modes are predicted for both structural types (a) and (b), so we have no direct evidence favouring one of these two possible structures. However, $Re_2Cl_4(PEt_3)_4$ is known [15] to be of type (b), presumably this structure being preferred over that of (a) because of the importance of minimising steric crowding of the bulky phosphine ligands. For a similar reason, (b) is likely to be preferred for the molybdenum(II) complexes, particularly since the metal–metal distances in the molybdenum complexes will be somewhat shorter than that in the rhenium(II) complex.

The differing metal:ligand ratios in $[Mo_2Cl_4(pyz)_2]_n$ and $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ deserves comment. Since it is impossible for pyrazine to chelate, it must be acting as a bridging ligand between indivi-

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† This complex has a staggered geometry as shown by a crystal structure determination of the isostructural $Mo_2Br_4(Ph_2PCH_2CH_2AsPh_2)_2$ (see, F. A. Cotton, P. E. Fanwick, J. W. Fitch, H. D. Glicksman and R. A. Walton, *J. Am. Chem. Soc.*, *101*, 1752 (1979).

TABLE III. X-Ray Photoelectron Spectra.^{a}

Complex	Mo 3d$_{5/2}$^{b}	Cl 2p$_{3/2}$^{b}	N 1s^c	C 1s
[Mo$_2$Cl$_4$(pyz)$_2$]$_n$	228.7 (1.5)	198.2 (1.9)	399.9	285.5
Mo$_2$Cl$_4$(2,6-Me$_2$pyz)$_4$	228.8 (1.8)	d	399.3	285.0
Mo$_2$Cl$_4$(dpa)$_2$	228.7 (1.9)	197.9 (1.8)	399.7	284.8
Mo$_2$Cl$_4$(amp)$_2$	228.7 (1.9)	198.2 (2.0)	399.8	284.8
Mo$_2$Cl$_4$(8-aq)$_2$	228.7 (1.9)	198.1 (2.0)	399.7	285.2

^{a}Full-width half-maximum values (fwhm) are given in parentheses for the Mo 3d$_{5/2}$ and Cl 2p$_{3/2}$ peaks. ^{b}The spin–orbit components Mo 3d$_{3/2}$ and Cl 2p$_{1/2}$ are located at ~3.0 eV and ~1.5 eV, respectively, to the high binding energy side of the Mo 3d$_{5/2}$ and Cl 2p$_{3/2}$ levels. ^{c}A broad peak located to the low binding energy side (~395 eV) of the N 1s level is due to Mo 3p$_{3/2}$ emission. This latter peak can prove to be useful for intensity comparisons. ^{d}See text.

dual Mo$_2$Cl$_4$ moieties producing a polymeric chain structure for [Mo$_2$Cl$_4$(pyz)$_2$]$_n$. Each nitrogen of the pyrazine ligands can thus be regarded as coordinating to a Mo$_2$Cl$_4$ unit in much the same way as pyridine does in forming Mo$_2$Cl$_4$(py)$_4$. It is not surprising therefore that the visible spectra and the numbers and frequencies of the infrared ν(Mo–Cl) bands of the two complexes are similar (see Table II). The only other dinuclear molybdenum(II) chloro-complex previously reported [3] which contains a bridging ligand is [Mo$_2$Cl$_4$(1,4-dithiane)$_2$]$_n$. Although pyrazine may be quaternised or protonated at only one nitrogen site, several complexes are known *e.g.* [MoOCl$_3$(pyz)]$_n$ [16] in which the ligand is bridging and thus in a situation where both nitrogens are sufficiently basic to donate to metal atoms. Crystallographic evidence is also available to confirm the bridging mode of coordination of this ligand in [AgNO$_3$(pyz)]$_n$ [17].

2,6-Dimethylpyrazine, on the other hand, obviously acts as a unidentate ligand in Mo$_2$Cl$_4$(2,6-Me$_2$pyz)$_4$, presumably because steric crowding of the nitrogen adjacent to the methyl groups renders it unavailable for coordination to the metal. This ligand is known to be similarly unidentate in, for example, MoCl$_4$(2,6-Me$_2$pyz)$_2$ [18].

The infrared bands assigned to the ν(Mo–Cl) vibrations of Mo$_2$Cl$_4$(L–L)$_2$ (L–L = amp, 8-aq, dpa) exhibit a different pattern to that mentioned above. Two bands are still observed but both fall in the narrow range 275–305 cm^{-1}, a feature previously observed [14] for the chelate complex α-Mo$_2$Cl$_4$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$. However Mo$_2$Cl$_4$(bipy)$_2$ [3], Mo$_2$Cl$_4$(phen)$_2$ [1] and Mo$_2$Cl$_4$(pyph)$_2$ merely display a broad unresolved single ν(Mo–Cl) band at *ca.* 300 cm^{-1}. Since the ligands listed above are known to behave as chelate ligands we suggest that the observation of two *closely spaced* ν(Mo–Cl) bands is indicative of an arrangement in which the chlorines of an individual MoCl$_2$L$_2$ unit are mutually *cis*. It has previously been pointed out [3] that there are three alternative structures for such *cis*-Mo$_2$Cl$_4$(L–L)$_2$ complexes. However the only one for which two infrared-active ν(Mo–Cl) modes are predicted is that shown in Fig. 1 (c). Adoption of this structure may be preferred as it provides the least steric interaction between chelate ligands coordinated to adjacent metal centres.

Finally XPS measurements on the new molybdenum(II) complexes isolated in this work show that their Mo 3d binding energies are characteristic of species of the type Mo$_2$Cl$_4$L$_4$ [14, 19]. It has previously been demonstrated [19, 20] that the Mo 3d binding energies of molybdenum chloride complexes of the types MoCl$_4$L$_2$, Mo$_2$Cl$_9^{3-}$, MoCl$_6^{3-}$, MoCl$_3$L$_3$, Mo$_2$Cl$_8^{4-}$ and Mo$_2$Cl$_4$L$_4$, where L represents an amine or phosphine donor, decrease in the sequence Mo(IV) > Mo(III) > Mo(II). The new data are presented in Table III, along with the related Cl 2p, N 1s and C 1s binding energies.

For all complexes except Mo$_2$Cl$_4$(2,6-Me$_2$pyz)$_4$ there is a close similarity in the appearance of the spectra and in the values of the Mo 3d, Cl 2p and N 1s binding energies. While the Cl 2p$_{1/2,3/2}$ spin–orbit doublets were not that well resolved, (the Cl 2p spectrum of [Mo$_2$Cl$_4$(pyz)$_2$]$_n$ is shown in Fig. 2), nonetheless, there is no evidence that these complexes contain chlorine environments in other than terminal Mo–Cl bonds [7, 21, 22]. In fact, the values of the sets of Mo 3d and Cl 2p binding energies match with those of other complexes of the type Mo$_2$Cl$_4$L$_4$ which we have investigated previously [14, 19] and which are structurally well characterized.

The one complex whose XPS did not conform to this pattern was Mo$_2$Cl$_4$(2,6-Me$_2$pyz)$_4$. While its Mo 3d spectrum closely resembled that of the other complexes, its Cl 2p and N 1s spectra were time-dependent. Although details of the time dependence did vary from sample to sample to some extent, several general features were common to all samples of this complex.

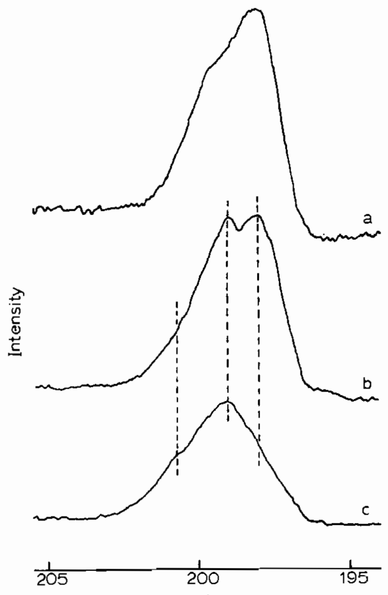

Fig. 2. Chlorine 2p binding energy spectra of (a) $[Mo_2Cl_4(pyz)_2]_n$, (b) a sample of $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ after *ca.* 30 min in the spectrometer and (c) the same sample as (b) but after *ca.* 210 min. For spectra (a), (b) and (c) the times for data collection were 26.0, 19.6 and 39.5 min, respectively.

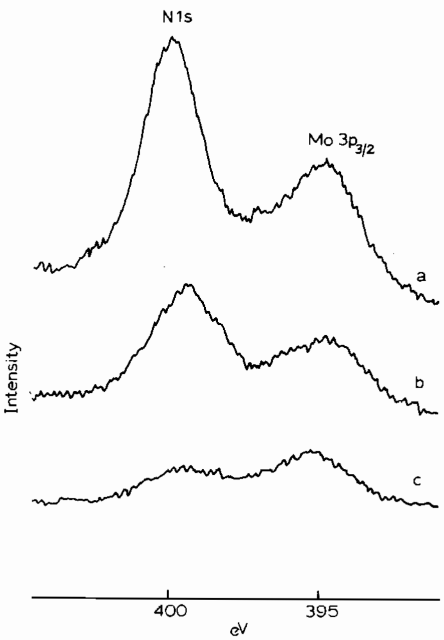

Fig. 3. Nitrogen 1s and molybdenum $3p_{3/2}$ binding energy spectra of (a) $[Mo_2Cl_4(pyz)_2]_n$, (b) a sample of $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ after *ca.* 30 min in the spectrometer and (c) the same sample as (b) but after *ca.* 210 min. For spectra (a), (b) and (c) the times for data collection were 57.5, 13.5 and 6.0 min, respectively.

First, the intensity of the N 1s peak at 399.3 eV decreased relative to that of the Mo $3p_{3/2}$ peak at ~395 eV with increase in time. This is clearly demonstrated by a comparison with the related spectrum of $[Mo_2Cl_4(pyz)_2]_n$ in Fig. 3. The intensity ratio I(N 1s)/I(Mo $3p_{3/2}$) for the pyrazine complex was 1.5 ± 0.1, a value which was at all times significantly greater than that observed for $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$, a complex with a higher N:Mo stoichiometric ratio (4:1 *versus* 2:1) [23]. The decrease in the value of I(N 1s)/I(Mo $3p_{3/2}$) for $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ with increase in the time that the sample was kept in the spectrometer implies that there is progressive loss of the dimethylpyrazine ligands under the high vacuum conditions (*ca.* 10^{-8} torr) maintained in the spectrometer.

The second common feature for all samples of this complex is the change in the Cl 2p spectrum with time (Fig. 2). The decrease in intensity of the Cl $2p_{1/2,3/2}$ doublet (Cl $2p_{3/2}$ at 198.1 eV) which is typical of chlorine in terminal Mo–Cl bonds, is accompanied by the concomitant growth of a higher energy doublet whose Cl $2p_{3/2}$ component at 199.2 eV overlaps the Cl $2p_{1/2}$ component (located at *ca.* 199.6 eV) of the low energy doublet. We believe that the higher energy Cl $2p_{1/2,3/2}$ doublet arises from the formation of β-$MoCl_2$ through loss of the 2,6-dimethylpyrazine ligands from $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$. This conclusion is supported by literature data for β-$MoCl_2$ [7] and dimers of the type $Mo_2Cl_4L_4$ [14] (see also the data in Table III) which show that the energy differences ΔE(Mo $3d_{5/2}$ – Cl $2p_{3/2}$) differ by *ca.* 0.8 eV (values are 29.8 eV for β-$MoCl_2$ and *ca.* 30.6 eV for $Mo_2Cl_4L_4$). Since only a single Mo $3d_{3/2,5/2}$ doublet is observed in the XPS of $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$, this must mean that the Mo 3d energies of $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ and β-$MoCl_2$ are coincident. Thus the energy difference of 0.9 eV between the two sets of Cl 2p binding energies in the XPS of $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ (Fig. 2) is in accord with its conversion to β-$MoCl_2$.

The observation of ligand loss for $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$ may explain some results we had earlier observed in our XPS studies on the complexes $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(py)_4$ [14, 19]. At the time, we were puzzled by the fact that while the Mo 3d spectra of these two molybdenum(II) complexes were quite normal, the corresponding Cl 2p spectra usually exhibited the type of three peak pattern which is displayed by $Mo_2Cl_4(2,6\text{-}Me_2pyz)_4$; the relative intensities of the peaks varied somewhat from sample to sample. Clearly, one obvious explanation is that these complexes are subject to various degrees of ligand loss under the high vacuum conditions which exist in the spectrometer.

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References

1 J. V. Brencic, D. Dobcnik and P. Segedin, *Monatshefte, 105*, 142 (1974).
2 H. D. Glicksman, A. D. Hamer, T. J. Smith and R. A. Walton, *Inorg. Chem., 15*, 2205 (1976).
3 J. San Filippo, Jr., H. J. Sniadoch and R. L. Grayson, *Inorg. Chem., 13*, 2121 (1974).
4 J. San Filippo, Jr., and M. A. S. King, *Inorg. Chem., 15*, 1228 (1976).
5 J. V. Brencic, D. Dobcnik and P. Segedin, *Monatshefte, 105*, 944 (1974).
6 J. E. Armstrong, D. A. Edwards, J. J. Maguire and R. A. Walton, *Inorg. Chem., 18*, 1172 (1979).
7 A. D. Hamer and R. A. Walton, *Inorg. Chem., 13*, 1446 (1974).
8 A. D. Hamer, D. G. Tisley and R. A. Walton, *J. Inorg. Nuclear Chem., 36*, 1771 (1974).
9 J. V.Brencic and F. A. Cotton, *Inorg. Chem., 9*, 346 (1970).
10 J. V. Brencic and F. A. Cotton, *Inorg. Chem., 9*, 351 (1970).
11 J. G. Dunn and D. A. Edwards, *J. Chem. Soc. A*, 988 (1971).
12 F. A. Cotton, D. S. Martin, P. A. Fanwick, T. E. Peters and T. R. Webb, *J. Am. Chem. Soc., 98*, 4681 (1976).
13 J. San Filippo, Jr., *Inorg. Chem., 11*, 3140 (1972).
14 S. A. Best, T. J. Smith and R. A. Walton, *Inorg. Chem., 17*, 99 (1978).
15 F. A. Cotton, B. A. Frenz, J. R. Ebner and R. A. Walton *Chem. Commun.*, 4 (1974); *Inorg. Chem., 15*, 1630 (1976).
16 W. M. Carmichael and D. A. Edwards, *J. Inorg. Nucl. Chem., 32*, 1199 (1970).
17 R. G. Vranka and E. L. Amma, *Inorg. Chem., 5*, 1020 (1966).
18 E. A. Allen, K. Feenan and G. W. A. Fowles, *J. Chem. Soc.*, 1636 (1965).
19 R. A. Walton, 'Proceedings of the Climax Second International Conference on the Chemistry and Uses of Molybdenum', P. C. H. Mitchell, Ed., Climax Molybdenum Co. Ltd. (1976) p. 35; see also, *J. Less-Common Met., 54*, 71 (1977).
20 J. Chatt, C. M. Elson, G. J. Leigh and J. A. Connor, *J. Chem. Soc. Dalton*, 1351 (1976).
21 R. A. Walton, *Coord. Chem. Rev., 21*, 63 (1976).
22 S. A. Best and R. A. Walton, *Inorg. Chem., 18*, 484 (1979).
23 The use of the I(N 1s)/I(Mo $3p_{3/2}$) ratio as a means of monitoring the structural integrity of samples while in the spectrometer has been used previously by other workers (see P. Brant and R. D. Feltham, *J. Electron Spectrosc. Related Phenom., 9*, 77 (1976)).