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LIGAND EFFECTS ON THE $\delta \rightarrow \delta^*$ BAND ENERGIES AND INTENSITIES IN A SERIES OF DIIMINE COMPLEXES OF DIMOLYBDENUM

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Abstract—The complexes $Mo_2X_4(\text{diimine})_2$ (X = Cl, Br, I and diimine = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 2,2′-bipyrazine, 3,3′-bipyridazine, 2,2′-bipyrimidine, 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline) have been prepared by reaction of $Mo_2\ (OAc)_4$ with $(CH_3)_3SiX$ in the presence of excess diimine. The product complexes apparently contain non-bridged quadruple molybdenum–molybdenum bonds. Each molybdenum is coordinated to a bidentate diimine and two halogen atoms. Electronic absorption and electrochemical studies have shown that shifts in the energy of the $\delta \rightarrow \delta^*$ band are affected by the mixing of this transition with a metal-to-ligand charge transfer transition, probably a $\delta \rightarrow \pi^*$ transition. It was also found that the compounds $Mo_2X_4(\text{diimine})_2$ react slowly with oxygen to form $Mo_2O_4Cl_4(\text{diimine})_2$ and then $MoO_2Cl_2(\text{diimine})$. The crystal and molecular structure of MoO_2Cl_2 (4,4′-dimethyl-2,2′bipyridine), determined by a three-dimensional X-ray diffraction study, is reported. Copyright © 1996 Elsevier Science Ltd

There has been much discussion in the literature concerning the factors which influence energies and intensities of the $\delta \rightarrow \delta^*$ bands in the electronic spectra of quadruply bonded compounds.[1] In particular, there have been several attempts to correlate characteristics of the $\delta \rightarrow \delta^*$ band with the extent of δ-overlap in the quadruple bond.[2] Recently, however, through a detailed study of Hopkins *et al.*[3] it has become clear that the $\delta \rightarrow \delta^*$ band probably cannot be used as an indicator of the δ-bond strength because of factors independent of δ-bond strength which strongly influence the energies and intensities of those electronic transitions. Further evidence for this notion has been presented by Collman *et al.*,[4] who have been able to measure the energies of rotational barriers for isostructural molybdenum and tungsten quadruply bonded compounds. In that study it was reported that the δ-component in the tungsten–tungsten quadruple bond is stronger than that in the molybdenum–molybdenum quadruple bond, despite the longer M—M distance and a lower energy $\delta \rightarrow \delta^*$ band for the tungsten analogue. Despite the general agreement that ligand effects are important in determining $\delta \rightarrow \delta^*$ band energies and intensities there has been little work reported investigating these effects. In particular, even though the possibility of mixing of $\delta \rightarrow \delta^*$ transitions with metal-to-ligand charge transfer, MLCT, transitions is mentioned in the work of Hopkins *et al.*,[3] this effect has not been documented in the literature, except for our earlier work with dimolybdenum bis(arylimino) isoindoline (BAII) compounds, $Mo_2(OAc)_3(BAII)$.[5]

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These compounds represented the first extensive series of structurally similar dimolybdenum compounds with Mo—N bonds. A detailed electronic absorption study of these compounds suggested that there were metal-to-ligand charge transfer, MLCT, transitions taking place from the occupied δ-orbital to unoccupied π^*-orbitals on the ligand. Indirect evidence for the MLCT transitions in this case was obtained from a study of the trends in the intensities and energies of the $\delta \rightarrow \delta^*$ band in the electronic spectra of the BAII complexes.[6] The unsymmetrical structures of the BAII complexes, which each contain an axial Mo—N bond, shed doubt on the understanding of the electronic structures of these compounds.

As a result we have undertaken a study of a series of dimolybdenum complexes of diimine ligands. These ligands were chosen because their electronic structures and bonding characteristics are well known since they constitute one of the most heavily studied ligand classes for other metal systems. In addition, the α,α-diimines are well known for their π-accepting ability and their dimolybdenum complexes should display MLCT transitions. Finally, it was decided that the halide complexes should be used in this study since this would afford the best comparison with the $Mo_2X_4(PMe_3)_4$ series, for which the most extensive data and discussion exists in the literature. Several diimine complexes have now been synthesized and studies of their electronic absorption spectra and electrochemical behaviour are presented in this paper.

EXPERIMENTAL

Materials and methods

All synthetic procedures were performed under argon using standard Schlenk techniques or a glove box. Methylene chloride was dried by refluxing with calcium hydride. Tetrahydrofuran was refluxed with sodium benzophenone, and methanol was refluxed with calcium sulfate. Acetone was stored over 4 Å molecular sieves. All solvents were distilled under argon just prior to use. Molybdenum acetate was prepared from $Mo(CO)_6$ using a literature method.[7] Trimethylsilyl chloride was vacuum distilled and stored under dry nitrogen until used.

Spectroscopic samples were prepared as CH_2Cl_2 solutions in a glove box using cells equipped with a screw-on cap and spectra were obtained from 900 to 180 nm using a Shimadzu UV-2100 spectrophotometer.

Voltammograms were obtained employing a BAS CV-27 Electrochemical Analyzer and a Hewlett–Packard 7015 **B** *X–Y* Recorder. Methylene chloride, containing 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAH) as supporting electrolyte, was used as solvent. The cell included a platinum disc working electrode, platinum wire auxiliary electrode and isolated saturated calomel reference electrode. The electrolyte solution was prepared by dissolving about 0.1 g of each different $Mo_2X_4L_2$ sample in 20 cm^3 of solvent inside the glove box. Once outside the glove box, the solution was bubbled with methylene chloride-saturated argon for 5 min. The sample was then blanketed with argon during scanning. The potentials were scanned from 0.0 to +1.5 V; the scan rate was varied from 20 to 500 mV s^{-1}.

Mo_2Cl_4(2,2′-*bipyridine*)$_2$

A mixture of $Mo_2(OAc)_4$ (0.21 g, 0.49 mmol), 2,2′bipyridine (0.15 g, 0.96 mmol) and dry, degassed THF (25 cm^3) was treated with excess $(CH_3)_3SiCl$ (0.25 cm^3). The solution quickly developed a blue–green colour which turned purple after 30 s. The mixture was stirred for 1 h under argon. The resulting purple precipitate was filtered, washed with hexane and dried *in vacuo*. Yield was essentially quantitative. Found: C, 37.7; H, 2.9; N, 8.6. Calc. for $Mo_2Cl_4N_4C_{20}H_{16}$: C, 37.2; H, 2.5; N, 8.7%.

Mo_2Cl_4(1,10-*phenanthroline*)$_2$

A mixture of Mo_2 $(OAc)_4$ (0.69 g, 1.6 mmol), 1,10-phenanthroline (0.72, 4.0 mmol) and dry, degassed THF (25 cm^3) was treated with excess $(CH_3)_3SiCl$ (0.2 cm^3). The solution quickly developed a blue–green colour which turned purple after 5 s. The mixture was stirred for 5 h under argon. The resulting purple precipitate was filtered, washed with hexane and dried *in vacuo*. Yield was essentially quantitative. Found: C, 40.7; H, 2.8; N, 7.5; Cl, 19.0. Calc. for $Mo_2Cl_4N_4C_{24}H_{16}$: C, 41.5; H, 2.3; N, 8.1; Cl, 20.5%.

Mo_2Cl_4(4,7-*diphenyl*-1,10-*phenanthroline*)$_2$

Mo_2 $(OAc)_4$ (0.142 g, 0.33 mmol) was treated with 0.198 g (0.59 mmol) of 4,7-diphenyl-1,10-phenanthroline in 25 cm^3 dry, degassed THF. After a few minutes, 0.2 cm^3 of $(CH_3)_3SiCl$ was added via syringe. An emerald green solution resulted which, after 1.5 h, yielded a green precipitate. The solid was filtered and dried *in vacuo*. This solid was reasonably soluble in chloroform and methylene chloride but the solutions in these solvents are purple in colour. ^1H NMR (DMF-d_7): δ 10.18 (d), 8.20 (d), 8.20 (s), 7.71 (m, phenyl).

General syntheses of other diimine complexes

The procedure used for synthesis of the other Mo_2X_4(diimine)$_2$ complexes was identical to that used for the preparation of the 1,10-phenanthroline complex. Typically, a mixture of $Mo_2(OAc)_4$ (about 1.6 mmol), the appropriate diimine (about 4.0 mmol) and dry, degassed THF (25 cm^3) was treated with excess $(CH_3)_3SiX$ (about 7.9 mmol). In each case, the mixture was stirred for 5 h under argon. The resulting purple–black precipitate was filtered, washed with hexane and dried *in vacuo*. Yields were greater than 90% in each case.

MoO_2Cl_2(*4,4′-dimethyl-2,2′-bipyridine*)

A long narrow tube was charged with a solution of Mo_2Cl_4(4,4′-dimethyl-2,2′-bipyridine)$_2$ dissolved in CH_2Cl_2. A layer of hexane was floated on top of this solution in an attempt to produce crystals. After 2 weeks, colourless crystals were collected from the tube by filtration. These crystals proved to be MoO_2Cl_2(4,4′-dimethyl-2,2′-bipyridine) as shown by an X-ray crystallographic study.

Crystallographic data collection and refinement of the structure of MoO_2Cl_2(*4,4′-dimethyl-2,2′-bipyridine*)

A pale rhombohedral crystal of $C_{12}H_{12}MoO_2Cl_2N_2$ having approximate dimensions of $0.10 \times 0.10 \times 0.10$ mm^3 was mounted on a glass fibre. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo-K_α radiation and a 2 kW sealed tube generator. Based on the systematic absences of:

$$h01 : h+1 \neq 2n \quad 0k0 : k \neq 2n$$

and the successful solution and refinement of the structure the space group was determined to be $P2^1/n$ (no. 14).

The data were collected at a temperature of -100 ± 1°C using the ω–2θ scan technique to a maximum 2θ value of 47.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.27° with a take-off angle of 6.0°. Scans of $(1.00+0.30 \tan \theta)$° were made at a speed of 4.0° min^{-1} (in omega). The weak reflections $[I < 10.0\sigma(I)]$ were rescanned (maximum of three rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1. The diameter of the incident beam collimator was 1.0 mm and the crystal-to-detector distance was 285.0 mm.

Of the 2351 reflections which were collected, 2232 were unique ($R_{int} = 0.041$). The intensities of three representative reflections which were measured after every 150 remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo-K_α is 12.8 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.77 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[8] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement* was based on 1676 observed reflections $[I > 3.00\alpha(I)]$ and 172 variable parameters, and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o| = 0.036$$

$$R_w = [(\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2} = 0.049.$$

The standard deviation of an observation of unit weight† was 1.97. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $(\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.74 and -0.43 e $Å^{-3}$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[9] Anomalous dispersion effects were included in F_c;[10] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[11] All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure corporation.[12] A summary of the crystal and other data is given in Table 1. Atomic coordinates are plated in the supplementary Materials and have been deposited with the Cambridge Crystallographic Centre.

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* Least-squares Function minimized: $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$, S = Scan rate, C = Total integrated peak count, R = Ratio of scan time to background counting time, B = Total background count, Lp = Lorentz–polarization factor and p = p-factor.

† Standard deviation of an observation of unit weight: $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

Table 1. Crystallographic data for MoO_2Cl_2(4,4′-dimethyl-2,2′-bipyridine)$_2$

Parameter	Data
Formula	$C_{12}H_{12}MoO_2Cl_2N_2$
Formula weight	383.08
Crystal system	monoclinic
Space group	$P2_1/n$
Temp. (°C)	−100
a (Å)	11.746(2)
b (Å)	10.369(2)
c (Å)	11.956(2)
β (°)	103.57(2)
V (Å^3)	1415.5(5)
D_{calc} (g cm^{-3})	1.798
Z	4
Cryst. dimensions (mm^3)	0.1 × 0.1 × 0.1
Radiation (Å)	0.71069
Abs. coeff (cm^{-1})	12.83
Unique data	2232
Averaging R	0.041
R (%)[a]	3.6
R_w (%)[b]	4.9

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.

[b] $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{1/2}$.

RESULTS

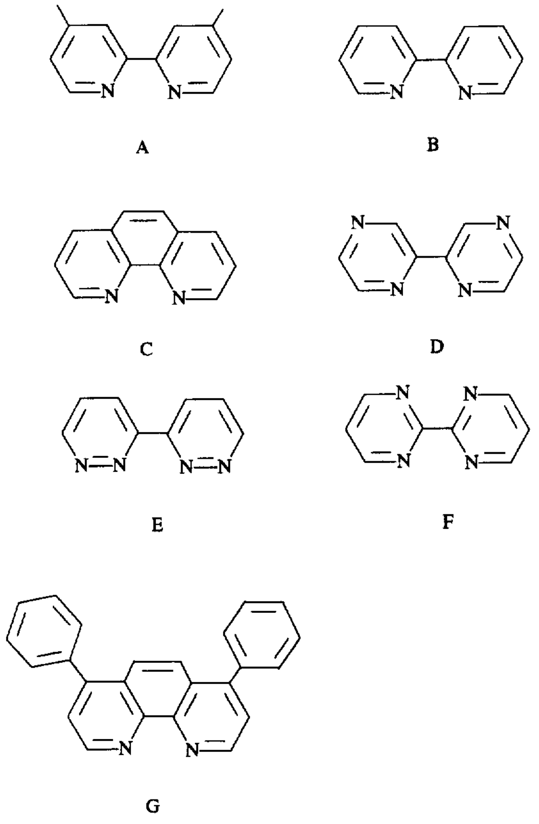
Synthesis and characterization of the compounds

There have been several reports of complexes with the formula Mo_2X_4(2,2′-bipyridine)$_2$. The results of these reports indicate at least one thing about the class of compounds with diimines and halogens bonded to dimolybdenum. That is, that they are only slightly soluble and do not yield crystals suitable for X-ray analysis. Bowen and Taube[13] reported the synthesis of Mo_2Cl_4(2,2′-bipyridine)$_2$ from $K_4Mo_2Cl_8$ as a purple precipitate that was insoluble in most solvents, but slightly soluble in acetone. San Filippo *et al.*[14] reported the synthesis of the same compound along with its bromide analogue. In this case Mo_2Cl_4(2,2′-bipyridine)$_2$ was synthesized from both $(NH_4)_5Mo_2Cl_9$ and Mo_2Cl_4 (dithiooctane)$_2$. Here, the product is reported as being an insoluble grey compound. In addition, Mo_2Br_4(2,2′-bipyridine)$_2$ was synthesized from Mo_2Br_4 (pyridine)$_4$ and was reported to be an insoluble blue–grey material. Finally, Nocera and coworkers[15] reported the synthesis of Mo_2Cl_4(4,4′-dimethyl-2,2′-bipyridine)$_2$ using San Filippo's method. The colour and other properties of this compound were not mentioned in this report. However, it was reported that Mo_2Cl_4(4,4′-dimethyl-2,2′-bipyridine)$_2$ reacted with oxygen to form $Mo_2O_4Cl_4$(4,4′-dimethyl-2,2′-bipyridine)$_2$.

Consistent results have now been obtained by reacting Mo_2 $(OAc)_4$ with $(CH_3)_3SiX$ in the presence of a slight excess of the diimine ligands shown in Scheme 1.

In many cases an initial blue–green solution forms which converts rapidly to a purple solution followed by precipitation of a purple–black solid. In the case of Mo_2Cl_4(4,7-diphenyl-1,10-phenanthroline)$_2$ the solid product is green. The compounds Mo_2X_4(diimine)$_2$ are somewhat soluble in CH_2Cl_2 and acetone but are relatively insoluble in most other solvents. The complexes dissolve in DMF but the solutions quickly decolorize, apparently due to formation of MoO_2Cl_2(diimine) as a result of even the smallest amount of oxygen or water in the solvent. An example of that product type, MoO_2Cl_2(2,2′-dimethyl-4,4′-bipyridine), has been isolated as colourless crystals from a solution intended to grow crystals of Mo_2Cl_4(4,4′-dimethyl-2,2′-bipyridine)$_2$. The structure of this compound has been determined through a three-dimensional X-ray diffraction study (see below).

As in the previously reported cases, production of crystals of the dimolybdenum complexes synthesized here which are suitable for X-ray analysis



Scheme 1.

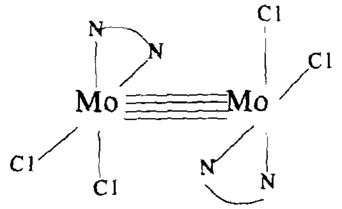


Fig. 1. Proposed structure of $Mo_2X_4(diimine)_2$ compounds.

has been unsuccessful. Therefore, characterization of the compounds was accomplished by comparison with the spectroscopic properties of other dimolybdenum compounds whose structures are known and whose physical properties have been reported.

Each of the $Mo_2X_4(diimine)_2$ compounds apparently contains a non-bridged molybdenum–molybdenum quadruple bond, with each molybdenum atom bonded to two halogens and one diimine, as shown in Fig. 1. Some support for this structural assignment has recently been presented by Dunbar and co-workers,[16] who have shown the purple compound $Mo_2(CF_3CO_2)_4(bpy)_2$ to possess this structure by X-ray crystallography. The structure of a closely related complex, Mo_2(1,10-phenanthroline)$_4$ $(CH_3CN)_4$, has also been determined by X-ray analysis and is similar.[17] To our knowledge these are the only crystal structures of diimine dimolybdenum complexes in the literature that have no ligands bridging the two metals.

Additional evidence for the structural assignment can be obtained from the electronic absorption spectra of the diimine complexes, which agree with those reported for $Mo_2Cl_4(bpy)_2$ in previous reports[13–15] (see Fig. 2). In addition, the spectra are remarkably similar in appearance to those reported by other workers for the well studied $Mo_2X_4(PMe_3)_4$ series.[1,18] In particular, the energy of the $\delta \rightarrow \delta^*$ band for the diimine compounds red shifts as the halogen is changed from chlorine to bromine to iodine in cases where the diimine is the same (see Table 2). This trend is as expected for dimolybdenum complexes and is in agreement with the trend reported for the $Mo_2X_4(bpy)_2$ series (X = Cl, Br, I) by other workers.[19] In addition, this trend is in agreement with that observed for the trimethylphosphine series as the halogen atoms are altered.[1,18] The source of this red shift has been attributed to the mixing of the $\delta \rightarrow \delta^*$ transition with a $\pi_{(ligand)} \rightarrow \delta^*$ ligand-to-metal charge transfer (LMCT) transition. Thus, as the energy of the LMCT transition decreases in energy according to Cl > Br > I there is a concomitant decrease in the energy of the $\delta \rightarrow \delta^*$ band.

Finally, a ^1H NMR spectrum has been obtained for the 4,7-diphenyl-1,10-phenanthroline complex where X = Cl. This was the only complex prepared which is soluble enough to be analysed by NMR spectroscopy. There are upfield shifts of the resonance lines of the phenathroline molecule, which are consistent with metal coordination by the ligand. Only one set of ligand resonance lines appears in the spectrum, confirming that the two diimine ligands are magnetically equivalent. In addition, the spectrum does not change over the temperature range of 30–70°C. The comparison of NMR shifts of the free 4,7-diphenyl-1,10-phenanthroline ligand and its dimolybdenum complex are presented in Table 3.

The diimine complexes exhibit electrochemical behaviour characteristic of many other dimolybdenum compounds.[20] In methylene chloride containing 0.1 M TBAH, there is a reversible one-electron oxidation process between 0.4 and 0.65 V which has i_c/i_a values very close to 1.0 at scan rates from 20 to 500 mV s^{-1} and $E_{p,c}$–$E_{p,a}$ separations very

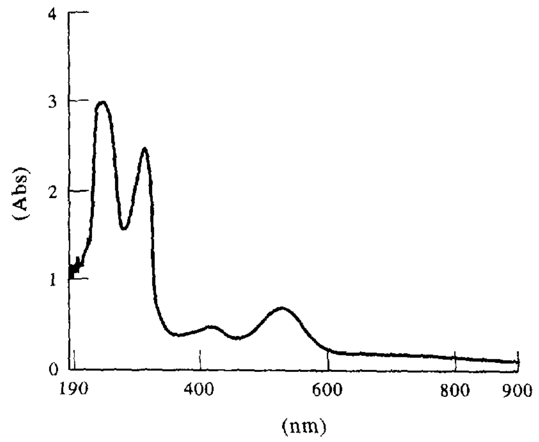


Fig. 2. Electronic absorption spectrum of Mo_2Cl_2(2,2′-bipyridine)$_2$ taken in CH_2Cl_2.

Table 2. Electronic absorption data for $Mo_2X_4(diimine)_2$: energies and intensities of $\delta \rightarrow \delta^*$ band

Compound[a]	Wavelength (nm)	Energy (cm^{-1})	f
$Mo_2Cl_4(bipy)_2$	531	18,830	0.013
$Mo_2Br_4(bipy)_2$	538	18,590	0.034
$Mo_2I_4(bipy)_2$	564	17,730	0.049
$Mo_2Cl_4(phen)_2$	532	18,800	0.018
$Mo_2Br_4(phen)_2$	540	18,520	0.020
$Mo_2I_4(phen)_2$	564	17,730	0.038

[a] bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline.

Table 3. ^1H NMR comparison for 4,7-diphenyl-1,10-phenanthroline and Mo_2Cl_4(4,7-diphenyl-1,10-phenanthroline)$_2$[a]

	2	3	Bridge	Phenyl
Ph_2—Phen	9.25 (d)	7.58 (d)	7.84 (s)	7.50 (m)
$Mo_2Cl_4(Ph_2$—Phen$)_2$	10.28 (d)	8.20 (d)	8.20 (s)	7.71 (m)

[a] All values in units of δ.

close to 59 mV. At potentials higher than 0.95 V, an irreversible oxidation process is observed.

Oxidation of Mo_2Cl_4*(4,4′-dimethyl-2,2′-bipyridine)*$_2$

Numerous attempts were made to grow X-ray quality crystals of the dimolybdenum complexes. In each case three types of crystals were obtained: small purple blocks, red–orange diamonds and pale orthorhombic crystals. In each case the purple blocks were too small and did not adequately diffract X-rays.

The red–orange crystals did diffract. Unit cell parameters for the compound derived from Mo_2X_4(4,4′-dimethyl-2,2′-bipyridine)$_2$ agreed with those of the previously reported $Mo_2O_4Cl_4$(4,4′-dimethyl-2,2′-bipyridine)$_2$.[15,21] As a result, it was assumed that the red–orange crystals had this identity as well.

The pale crystals from the same solution were also subjected to X-ray analysis and proved to be MoO_2Cl_2(4,4′-dimethyl-2,2′-bipyridine).

Structure of MoO_2Cl_2*(4,4′-dimethyl-2,2′-bipyridine)*

The structure of this complex is shown in Fig. 3 and selected bond distances and angles are shown in Table 4. The complex has a distorted octahedral arrangement about the molybdenum atom with the two oxygen atoms having a *cis* and the two chlorine atoms having a *trans* arrangement. The structure of this complex has been compared to those reported for the related complexes MoO_2F_2(2,2′-bipyridine)[22] and MoO_2Cl_2(1,10-phenanthroline).[23] Selected bond distances and angles of the three complexes are reported in Table 5 for comparison. It might be anticipated that changing the identity of the halogen, particularly to fluorine, and adding electron-releasing methyl groups to the bypridine might have an impact on the structure of the compounds. In fact, the O—Mo—O angles in all three compounds are remarkably similar. There is some small change observed in the X—Mo—X angle on going from the dimethyl-bipyridine derivative to the 1,10-phenanthroline derivative, even though the halogen atoms are the same. Despite this change, the Mo—Cl bond distances are the same in both complexes. As has been found in other MoO_2^{2+} complexes, the Mo=O bonds are insensitive to changes in the ligand environment around the metal atoms. The Mo=O bond distances in all three complexes are essentially the same.

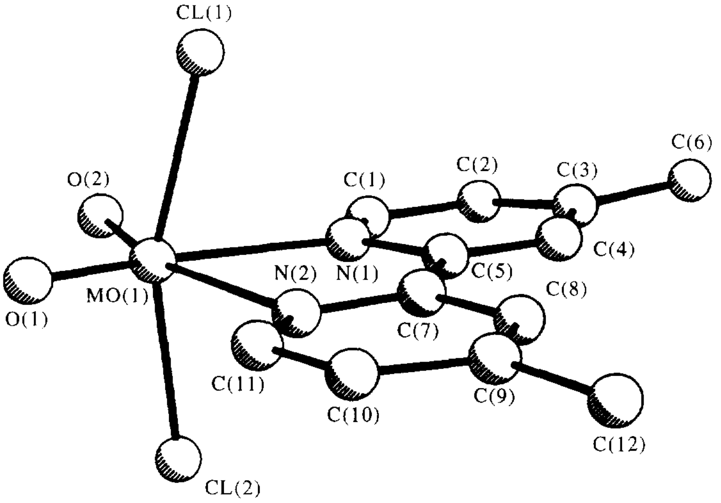


Fig. 3. View of the molecular structure of MoO_2Cl_2(4,4′-dimethyl-2,2′-bipyridine). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% level.

Table 4. Bond distances (Å) and angles (°) for MoO_2Cl_4(4,4′-dimethyl-2,2′-bipyridine)$_2$

Mo(1)—Cl(1)	2.375(2)	C(2)—C(2)	1.386(9)
Mo(1)—Cl(2)	2.370(2)	C(3)—C(4)	1.390(8)
Mo(1)—O(1)	1.696(4)	C(3)—C(6)	1.522(8)
Mo(1)—O(2)	1.695(4)	C(4)—C(5)	1.397(8)
Mo(1)—N(1)	2.310(5)	C(5)—C(7)	1.477(8)
Mo(1)—N(2)	2.304(5)	C(7)—C(8)	1.393(8)
N(1)—C(1)	1.343(7)	C(8)—C(9)	1.403(8)
N(1)—C(5)	1.357(7)	C(9)—C(10)	1.401(9)
N(2)—C(7)	1.362(7)	C(9)—C(12)	1.518(9)
N(2)—C(11)	1.348(8)	C(10)—C(11)	1.392(9)
C(1)—C(2)	1.480(8)		

Cl(1)—Mo(1)—Cl(2)	159.35(6)	C(7)—N(2)—C(11)	118.9(5)
Cl(1)—Mo(1)—O(1)	98.8(2)	N(1)—C(1)—C(2)	121.9(6)
Cl(1)—Mo(1)—O(2)	96.4(2)	C(1)—C(2)—C(3)	118.6(6)
Cl(1)—Mo(1)—N(1)	80.6(1)	C(2)—C(3)—C(4)	119.3(5)
Cl(1)—Mo(1)—N(2)	81.5(1)	C(2)—C(3)—C(6)	121.7(6)
Cl(2)—Mo(1)—O(1)	96.4(2)	C(4)—C(3)—C(6)	119.0(6)
Cl(2)—Mo(1)—O(2)	94.9(2)	C(3)—C(4)—C(5)	119.5(6)
Cl(2)—Mo(1)—N(1)	81.6(1)	N(1)—C(5)—C(4)	121.2(5)
Cl(2)—Mo(1)—N(2)	82.7(1)	N(1)—C(5)—C(7)	116.0(5)
O(1)—Mo(1)—O(2)	106.6(2)	C(4)—C(5)—C(7)	122.9(5)
O(1)—Mo(1)—N(1)	160.4(2)	N(2)—C(7)—C(5)	115.0(5)
O(1)—Mo(1)—N(2)	90.3(2)	N(2)—C(7)—C(8)	122.1(5)
O(2)—Mo(1)—N(1)	93.0(2)	C(5)—C(7)—C(8)	122.9(5)
O(2)—Mo(1)—N(2)	163.0(2)	C(7)—C(8)—C(9)	119.1(6)
N(1)—Mo(1)—N(2)	70.0(2)	C(8)—C(9)—C(10)	118.2(6)
Mo(1)—N(1)—C(1)	121.3(4)	C(8)—C(9)—C(12)	120.7(6)
Mo(1)—N(1)—C(5)	118.9(4)	C(10)—C(9)—C(12)	121.1(6)
C(1)—N(1)—C(5)	119.5(5)	C(9)—C(10)—C(11)	119.7(6)
Mo(1)—N(2)—C(7)	119.5(4)	N(2)—C(11)—C(10)	121.9(6)
Mo(1)—N(2)—C(11)	121.4(4)		

Estimated standard deviations in the least significant figure are given in parentheses.

Table 5. Comparison of selected bond distances (Å) and angles (°) for MoO_2Cl_2(4,4′-dimethyl-2,2′-bipyridine) (**I**), MoO_2F_2(2,2′-bipyridine)[22] (**II**) and MoO_2Cl_2(1,10-phenanthroline)[23] (**III**)

	I	II	III
X—Mo—X	159.35	154.4	157.71
O—Mo—O	106.6	106.8	106.2
N—Mo—N	70.0	70.7	69.5
Mo=O	1.69	1.69	1.68
Mo—X	2.37	2.36	1.90

Electronic absorption studies

Each of the complexes displays an electronic absorption spectrum which has the $\delta \rightarrow \delta^*$ band as the lowest energy absorption. A typical spectrum is shown in Fig. 2. The energies and intensities of the $\delta \rightarrow \delta^*$ bands for the diimine complexes in which halogen is constant and the diimine ligand is varied are reported in Table 6.

Inspection of the data reveals that the energy of the $\delta \rightarrow \delta^*$ band shows a considerable dependence on the nature of the diimine ligand. There appears to be some correlation between the energy of the $\delta \rightarrow \delta^*$ band and the π-accepting ability of the diimine ligands. This comment is based on a study conducted by Ernst and Kaim,[24] who have found, using theoretical methods, that in the region of the Coulomb integral parameter $h_N = 0.5$–1.0 that the lowest unoccupied molecular orbital (LUMO) of the diimines used in this study follows the order 2,2′-bipyrazine < 2,2′-bipyrimidine < 3,3′-bipyridazine < 2,2′-bipyridine in order of increasing LUMO energy. Except for the bipyrazine case,

Table 6. Electronic absorption data taken in CH_2Cl_2 for $Mo_2Cl_4(diimine)_2$: energies and intensities of band I, the $\delta \rightarrow \delta^*$ band

Diimine[a]	Wavelength (nm)	Energy (cm^{-1})	f
A 4,4′-$(CH_3)_2$-bipy	518	19,300	0.008
B 2,2′-bipy	531	18,830	0.013
C 1,10-phen	532	18,800	0.018
D 2,2′-bipyrazine	583	17,150	0.036
E 3,3′-bipyridazine	693	14,430	0.053
F 2,2′-bipyrimidine	763	13,100	0.063

[a] bipy = bipyridine; phen = phenanthroline.

this is the same as the order of increase of the $\delta \rightarrow \delta^*$ band energy. In addition, the same authors found that the order of the ligand reduction potentials is the same as the order of the relative energies of the LUMOs on the free diimine ligands and can thus be approximated by their first reduction potentials.[11] Except for the bipyrazine case again, the $\delta \rightarrow \delta^*$ band energy correlates fairly well with the reduction potentials of the free ligands, as shown in Fig. 4.

It should be noted here that the energy of the $\delta \rightarrow \delta^*$ band is also influenced by the substituents attached to the parent diimine ring system. Comparison of the energy of the $\delta \rightarrow \delta^*$ band for $Mo_2Cl_4(diimine)_2$ for diimine = bipyridine and 4,4′-dimethylbipyridine shows that addition of electron-releasing substituents to the heterocyclic ring causes an increase in the energy of this band. While these data are limited, they agree with the trend found in the $Mo_2(OAc)_3(BAII)$ series, where the data were more extensive,[6] and with the results of Ewing and Shupack,[25] who studied a series of pyridine, picoline and lutidene complexes of dimolybdenum.

It has also been found that as the energy of the $\delta \rightarrow \delta^*$ band increases, its intensity dramatically increases across the series of diimine ligands. In fact, a plot of $\delta \rightarrow \delta^*$ band energy versus intensity gives a straight line, as shown in Fig. 5, indicating that these two properties are affected in the same way by ligand changes. The situation of increasing intensity with decreasing energy also occurs in the well studied $Mo_2X_4(PMe_3)_4$ series.[1]

Electrochemical studies

In order to further characterize the effect of ligand substitution on the electronic structures of dimolybdenum compounds, a cyclic voltammetric study of the complexes was undertaken. A typical voltammogram is shown in Fig. 6 and the potentials of both the reversible and irreversible processes for each of the compounds studied are presented in Table 7. Inspection of the data reveals a dependence of both the reversible and irreversible redox processes on the identity of the diimine. Presuming that lower π^*-orbitals on a diimine make it a better electron acceptor then the order of $E_{1/2}$ makes sense.

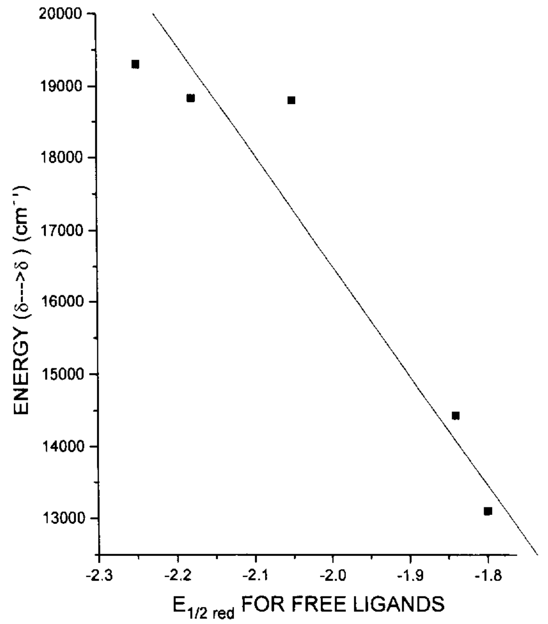


Fig. 4. Plot of energy of the $\delta \rightarrow \delta^*$ band *vs* $E_{1/2}$ for the reversible one electron reduction process.

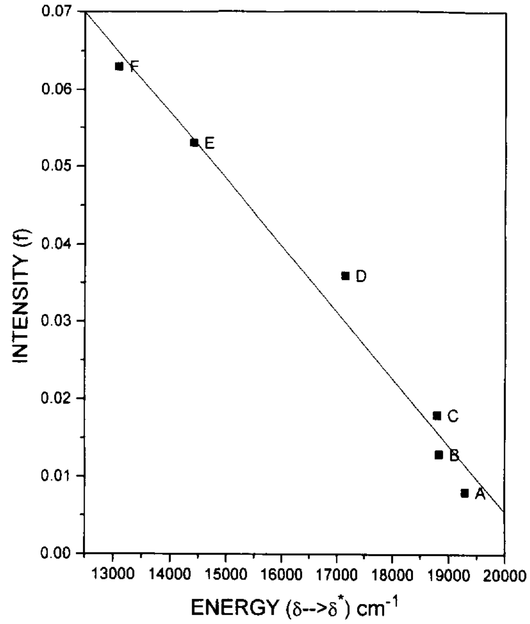


Fig. 5. Plot of $\delta \rightarrow \delta^*$ band energy *vs* corresponding intensity. Labels refer to Table 3.

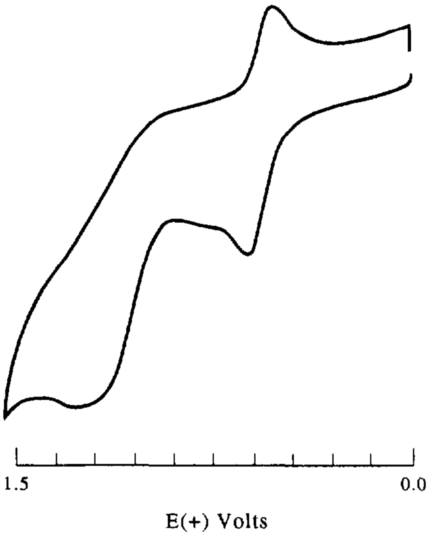


Fig. 6. Typical cyclic voltammogram for Mo_2X_4(diimine)$_2$ complexes as demonstrated by the voltammogram of Mo_2Cl_4(bipy)$_2$ taken in CH_2Cl_2 at a scan rate of 50 mV s^{-1}.

Table 7. Cyclic voltammetric data for Mo_2Cl_4(diimine)$_2$

Diimine[a]	$E_{1/2(ox)}$(V) reversible	$E_{1/2(ox)}$(V) irreversible
A 4,4′-$(CH_3)_2$-bipy	0.43	0.96
B 2,2′-bipy	0.50	1.07
C 1,10-phen	0.51	1.12
E 3,3′-bipyridazine	0.59	1.20
F 2,2′-bipyrimidine	0.64	1.27

[a] bipy = bipyridine; phen = phenanthroline.

As more electron density is removed from the metals, the complex becomes harder to oxidize.

DISCUSSION

The purpose of this work was to characterize ligand effects on the energies and intensities of the $\delta \rightarrow \delta^*$ band in the electronic spectra of dimolybdenum compounds, particularly in the cases in which the complexes contain diimines and halogens. Several observations help with this characterization. The energies of the bands are dependent on two aspects of the diimine ligands. As the energy of the ligand LUMO decreases (as measured by the ligand reduction potentials), the energy of the $\delta \rightarrow \delta^*$ band also decreases. In addition, the presence of electron-releasing groups on the diimines causes an increase in the energy of the $\delta \rightarrow \delta^*$ band. These two observations, taken together, seem to point to the mixing of the $\delta \rightarrow \delta^*$ transition with a MLCT transition (probably $\delta \rightarrow \pi^*_L$) which is nearby in energy. This statement is based on the notion that as the energy of the π^* LUMO on the diimine is increased, a concomitant increase in the MLCT transition should take place. In turn, mixing of this higher energy MLCT transition with the $\delta \rightarrow \delta^*$ transition should lead to a higher energy $\delta \rightarrow \delta^*$ band in the electronic spectrum. The observed group effect supports this proposal. Electron-releasing groups are observed to raise the energy of the MLCT band by increasing the electron density on the diimine, thus making charge transfer to the ligand more difficult.

The above proposal is further supported by the observation that the intensity of the $\delta \rightarrow \delta^*$ band increases as its energy decreases. This effect has also been observed in the series of complexes $Mo_2X_4(PMe_3)_4$.[1] In that case this trend was proposed to result from the mixing of the $\delta \rightarrow \delta^*$ band with an LMCT nearby in energy. The energy of the band is thus accompanied by an increase in intensity due to more efficient mixing as the LMCT band gets lower in energy.

The observation of increasing intensity with decreasing energy for the $\delta \rightarrow \delta^*$ band in the complexes Mo_2X_4(diimine)$_2$ may be interpreted in the same way. However, in this case a MLCT transition is apparently involved.

Actually, in the series $Mo_2X_4(PP)_2$, where PP = bidentate bridging phosphorus ligand, in which the overlap of the *d*-orbitals forming the δ-bond decreases because of twisting about the metal–metal bond, a decrease in the $\delta \rightarrow \delta^*$ band energy is accompanied by a decrease in intensity.[26]

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