

Cyclopentadienyltris(dimethylamido)molybdenum: photoelectron spectroscopy, electron diffraction and theoretical calculations*

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The synthesis and isolation of $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$ has been performed. Nuclear magnetic resonance and photoelectron spectra and electron diffraction studies are all consistent with a ground-state structure in which one amido group lies with the methyl groups axial to the molybdenum–cyclopentadienyl vector and the other two with the methyl groups equatorial. This conformation is also predicted by density functional calculations.

Tris(amido)molybdenum moieties, $\text{Mo}(\text{NRR}')_3$, have recently been shown to have unusual reactivity in that they can split the bond in dinitrogen forming nitrido derivatives, $\text{MoN}(\text{NRR}')_3$.¹ To exist as an independent molecule the amido groups need to carry sufficiently bulky substituents to prevent aggregation to a triply bonded $\text{Mo}_2(\text{NRR}')_6$ dimer, as is the case when $\text{R} = \text{R}' = \text{Me}$. In the tris(amido)molybdenum fragment the Mo atom is formally a 15-electron centre, hence in the majority of its derivatives it is also bound to another ligand which donates three electrons bringing the complement to 18. The compound $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$ poses an interesting problem in molecular and electronic structure in that if all ligands donate the maximum possible number of electrons to the metal the Mo would have a count of 20.

Amido-functionalized cyclopentadienyl compounds of quadrivalent molybdenum have received little attention so far compared with those of titanium, zirconium and hafnium.^{2–6} Most recently, Herrmann and co-workers^{7,8} extended their work into Group V and Group VI and synthesized analogues of Nb, Ta and Mo. They have reported the preparation of $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$ in diethyl ether solution.⁷

Photoelectron (PE), NMR spectroscopy and electron diffraction (ED) studies have now been carried out in order to elucidate the molecular and electronic structure of $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$. These physical studies have been supported by theoretical studies using density functional theory (DFT).

Experimental

Preparation of $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$

The compound $\text{Mo}(\text{NMe}_2)_4$ (1.86 g, 6.83 mmol), prepared by the literature method,⁹ in benzene (30 cm³) was treated with an excess of cyclopentadiene (2.82 cm³, 34.16 mmol) at 0 °C. After removing the ice-bath, the purple solution was stirred at room temperature for 2 h, turning green. The solvent was removed under reduced pressure. The product was extracted with pentane (3 × 20 cm³), the pentane removed and the product dried under reduced pressure. A green oil was obtained. Yield: 1.90 g (95%). Electron-impact mass spectrum: m/z 295 (M^+), 251 ($M^+ - \text{NMe}_2$) and 207 [$M^+ - 2(\text{NMe}_2)$] [Found: (Calc. for $\text{C}_{11}\text{H}_{23}\text{MoN}_3$): C, 44.12 (45.05); H, 7.42 (7.90); N, 13.29 (14.33)%]. IR (neat): 3090w, 2965s, 2839s, 2797s, 2750s, 1445s, 1406s, 1387m, 1261s, 1222m, 1150s, 1108s, 1015s, 980m, 937s, 863w, 797s and 546s cm⁻¹. ¹H NMR (300 MHz, C_6D_6): δ 5.14

(5 H, s, C_5H_5) and 2.92 (18 H, s, CH_3). ¹³C-{¹H} NMR (75.5 MHz, C_6D_6): δ 97.3 (s, C_5H_5) and 57.5 [s, $\text{N}(\text{CH}_3)_2$].

A number of attempts were made to grow crystals of $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$. The compound has very high solubility in pentane. Solutions were cooled to –20 and –80 °C over a period of 2 months but no crystals formed. Slow sublimation onto a liquid-nitrogen-cooled probe resulted in a non-crystalline waxy solid.

Photoelectron spectroscopy

The photoelectron spectrum was measured using a PES Laboratories 0078 instrument interfaced with an Atari micro-processor which enabled spectrum accumulation with repeated scans. The sample was held at 327 K during spectral measurement and calibrated using He, Xe and N₂.

Computation

Electronic structure calculations were performed using the GAUSSIAN 94 implementation of DFT.¹⁰ Full geometry optimizations were performed on $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$ using first the local spin density approximation (LSDA) (Slater exchange¹¹ and Vosko, Wilk and Nusair correlation functionals¹²) and employing LanL2DZ basis sets,^{13–15} and, subsequently, using the Becke 88 exchange functional¹⁶ with the correlational functional of Lee, Yang and Perdew, which contains both local and non-local terms^{17,18} (BLYP).

For comparative purposes a number of restricted geometry optimizations were also carried out at the local level. In these the local symmetry of the $\text{Mo}(\text{C}_5\text{H}_5)$ fragment was constrained to be C_{5v} , to ensure an η^5 co-ordination mode for the cyclopentadienyl ring. The dimethylamido groups were fixed either equatorially or axially. In the two cases of all three groups axial, **I** and all three groups equatorial, **II**, local C_{3v} symmetry was fixed for the $\text{Mo}(\text{NMe}_2)_3$ fragment. In these restricted cases the MoNC_2 unit of the dimethylamido groups was taken as planar and the geometry of the methyl groups was fixed, though the C–N bonds were allowed to vary within the symmetry constraints.

The molecular force field was calculated at the BLYP level and scaled through multiplication with the constant 0.90. Root-mean-square vibrational amplitudes, l , at the temperature of the GED experiment were then calculated with the program ASYM 40.¹⁹

Gas electron diffraction

The GED data were recorded on the Balzers KDG2 unit at

* This paper is dedicated to Professor Sir Geoffrey Wilkinson, a much valued friend and colleague.

Oslo^{20,21} with a conventional metal inlet system at about 80 °C. Exposures were made at nozzle-to-plate distances of ca. 50 (2 × 6 plates) and 25 cm (6 plates). The plates were scanned on an Agfa Arcus II scanner and the data processed by standard procedures.²² Atomic scattering factors were taken from Bonham and Schäffer.²³ Backgrounds were drawn as least-squares-adjusted polynomials to the difference between total experimental and calculated molecular scattering intensities. Structure refinements by least-squares calculations on the intensity data were carried out with the program KCED 26.²⁴

Initial structure refinements were carried out on a molecular model consisting of coaxial Mo(C₅H₅) and Mo(NMe₂)₃ fragments of C_{5v} and C₃ symmetry respectively. Such a model was, however, found to be incompatible with the GED data. The final refinements were based on a molecular model of C_s symmetry as indicated by the DFT calculations (Fig. 3). The molecule is so large, and the symmetry of the model so low, that a complete structure determination by gas electron diffraction is impossible: the determination of the skeletal geometry alone would require the successful refinement of 22 parameters; hydrogen atom positions and vibrational amplitudes would add even more. The number of independent structure parameters was therefore reduced to fifteen through imposition of local symmetries and other constraints: (i) the cyclopentadienyl ring was assumed to have D_{5h} symmetry; (ii) the difference between the Mo–N(1) and Mo–N(2) bond distances was fixed at the DFT BLYP value; (iii) the differences between symmetry-inequivalent N–C bond distances were fixed at the DFT BLYP values; all C–N–C valence angles were assumed equal; (iv) all NCH₃ fragments were assumed to have C_{3v} symmetry, the difference between the C–H bond distance in the methyl group and in the C₅H₅ ligand was fixed at the calculated value and the methyl group orientations were fixed such that one dihedral angle, τ(CNCH), equalled 180°.

The fifteen independent structure parameters are listed in Table 3. The average valence angles C–N–C and N–C–H could not be refined and were fixed at the calculated values. The remaining thirteen structure parameters were refined by least-squares calculations on the intensity data along with four average root-mean-square (r.m.s.) vibrational amplitudes of the bond distances. See Table 2 for details. The vibrational amplitudes of the non-bonded Mo···C (Me) distances were fixed at 0.120 Å; all other amplitudes between non-bonded atom pairs were fixed at the calculated values. Vibrational correction terms were not included.

Results

Synthesis

Purple tetrakis(dimethylamido)molybdenum Mo(NMe₂)₄ was first prepared by Bradley and Chisholm⁹ in 1971 using the reaction of MoCl₅ with 5 equivalents of LiNMe₂. Stirring a solution of Mo(NMe₂)₄ in benzene with an excess of cyclopentadiene results in a change to green within 2.5 h. After removal of the solvent, extraction into pentane, followed by filtration and removal of the pentane, cyclopentadienyltris(dimethylamido)molybdenum Mo(C₅H₅)(NMe₂)₃ **1** can be isolated in almost quantitative yield. The mass and NMR spectral results agree with those previously reported.⁷ Although essentially pure as shown by ¹H NMR spectroscopy, **1** is a very air-sensitive, volatile, sticky oil which can be distilled at 25 °C (10^{–2} Torr; 1 Torr ≈ 133 Pa).

NMR studies

The ¹H NMR spectrum of compound **1** in C₆D₆ at room temperature has two resonances, one peak of relative intensity 5 at δ 5.14 corresponding to the cyclopentadienyl protons and another of relative intensity 18 at δ 2.92 assigned to the methyl protons of the NMe₂ groups. Cooling a solution of **1** in [²H₈]tol-

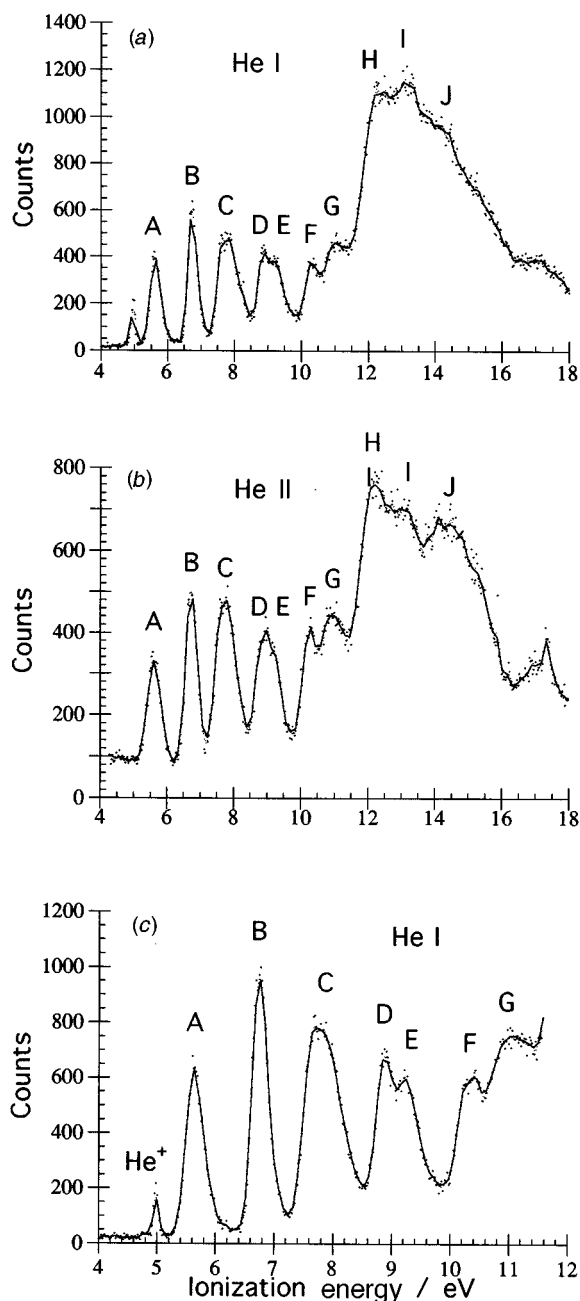


Fig. 1 The He I (a) and (c) and He II (b) PE spectra of Mo(C₅H₅)(NMe₂)₃

uene to –80 °C produced no change in the ¹H NMR spectrum. The ¹³C NMR spectrum of a pentane solution with two drops of CD₂Cl₂ enabling measurement down to –125 °C again showed only two resonances, one at δ 97.3 assigned to the ring carbons and one at δ 57.5 due to the methyl carbons. At –110 °C the methyl carbon resonance broadened but did not split. The C₅H₅ peak, however, remained sharp over the whole temperature range.

PE studies

The PE spectrum of Mo(C₅H₅)(NMe₂)₃ is shown in Fig. 1 and vertical ionization energies (*E*_v) are given in Table 1.

A rough assignment of PE bands may be made on the basis of characteristic ionization energy regions and comparison with PE spectra of other metallocenes²⁵ and dimethylamido complexes.^{26,27} Bands lying above 11.5 eV (1 eV ≈ 1.60 × 10^{–19} J), H–J, are characteristic of ionizations from C–H, C–C and C–N bonds and will not be discussed further. Metal-nitrogen σ ionizations are found to occur around 10 eV for other dimethylamido compounds^{26,27} which suggests assign-

Table 1 Vertical ionization energies E_i for $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$ and principal orbital character

Band	E_i/eV	Assignment
A	5.67	Mo d
B	6.79	N π
C	7.82	N π
D	8.92	C_5H_5 e_1
E	9.27	C_5H_5 e_1
F	10.28	Mo–N σ
G	11.03	Mo–N σ
H	12.35	
I	13.14	
J	14.20	

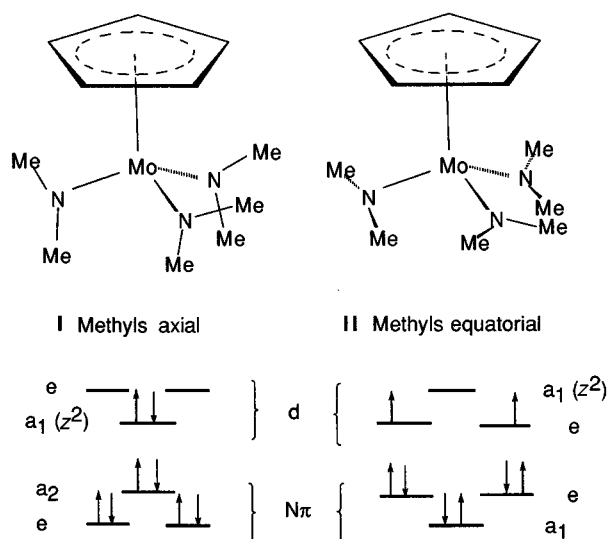


Fig. 2 Possible structures for $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$ with dimethylamido groups axially, **I**, and equatorially, **II**, arranged, together with the likely ordering of the frontier orbitals

ment of bands F and G to the three Mo–N σ bonds. Amido p_π electrons are found to ionize between 6 and 9 eV^{26,27} whereas cyclopentadienyl e_1 bands are generally found to lie between 8 and 10 eV. Thus the ranges for these two types of ionization overlap, but we can infer that bands B and C are likely to be principally N p_π in character whereas D and E probably originate mainly from the cyclopentadienyl ring. Band C has about double the intensity of band B which suggests that it accounts for two N p_π ionizations. Band A is assigned to the two molybdenum d electrons in this molybdenum(IV) compound.

Though bands A–G generally increase in intensity with respect to H–J as the radiation is changed from He I to He II, there are no marked changes in relative intensity among the set A–G.

Further band assignment requires assumptions about the molecular structure and computation of an energy-level scheme.

Discussion

The two simplest symmetrical structures which can be envisaged for compound **1** have the cyclopentadienyl ring coordinated in an η^5 fashion and the dimethylamido groups lying either all axial, **I**, or all equatorial, **II** (see Fig. 2).

Structure **II** fits the ^1H NMR results in that all cyclopentadienyl hydrogens and all methyl hydrogens are equivalent, given normal assumptions of ring and methyl group rotation. For structure **I** to be compatible with the proton NMR spectrum the up and down methyl groups would have to exchange on an NMR time-scale. The low-temperature ^{13}C NMR spectrum shows a broadening of the methyl ^{13}C resonance and suggests that such a fluxional process may well be occurring.

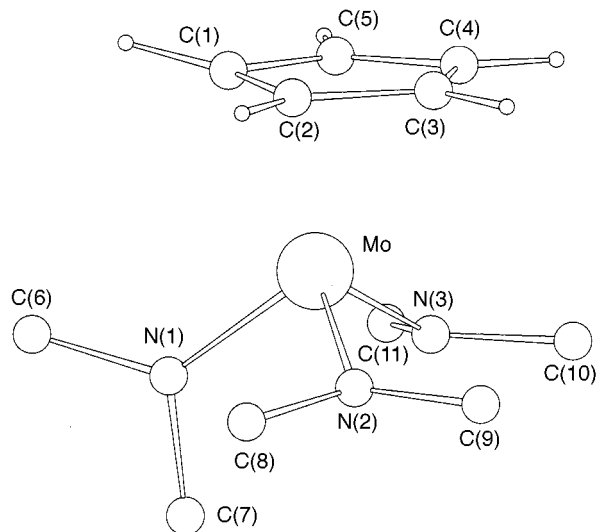


Fig. 3 Optimum structure for $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$ predicted by theoretical calculations

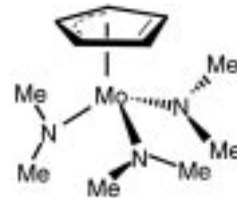
Simple consideration of the frontier orbitals of the two structures suggests that they might have different spin states. Both structures are considered as effectively having C_{3v} symmetry. In **I** the nitrogen p_π electron pairs transform as a_2 and e , the a_2 combination finding no symmetry match among the metal d orbitals. In **II** the nitrogen p_π electrons transform as a_1 and e ; in this case the a_1 combination can donate into the metal d_z orbital. Predicted orbital schemes are shown in Fig. 2. These simple considerations suggest **I** to be diamagnetic with the two metal d electrons occupying the d_z orbital, and **II** to be paramagnetic with the d electrons in a degenerate pair of e orbitals giving rise to a triplet ground state.

The diamagnetism of the compound, inferred from the NMR spectrum, favours structure **I**.

Theoretical calculations

A full geometry optimization was carried out for compound **1** using DFT at the local level (LSDA). No constraints were applied. The starting geometry was that of structure **I** with an η^5 - C_5H_5 ring and all three amido ligands with the metal groups axially disposed. The optimum structure found is shown in Fig. 3 and key predicted bond lengths and angles are given in Table 2. It may be seen that the predicted structure is very close to possessing a plane of symmetry.

The optimized structure has one amido group with the methyl groups axially disposed while the other two amido groups have the methyls arranged equatorially. The unique amido group has a shorter Mo–N distance. The sum of angles around this N is 360° , while the other two nitrogens are very slightly pyramidal having an angle sum of 355° . The cyclopentadienyl group is shifted away from the axial amido group, so that three of its carbon atoms are closer to the Mo than the other two. A variation of C–C distances is found; that between the two remoter carbon atoms is significantly shorter. Thus the predicted co-ordination mode of the cyclopentadienyl ligand may be regarded as η^3 and the structure represented as **III**.



This result was then confirmed at the non-local level (BLYP) using the optimized structure at the local level as the starting geometry. The results are shown in Table 2. Though the actual

Table 2 Predicted and experimental bond lengths (Å) and angles (°) for compound **1**

	DFT			GED	
	LSDA	BLYP	l_{calc}	r_a	l_{exptl}
Mo–N(1)	1.931	1.977	0.051	1.971(4) ^a	0.090(5) ^e
Mo–N(2)	1.961	2.007	0.055	2.001(4) ^a	0.093(5) ^e
Mo–N(3)	1.964	2.007	0.055	2.001(4) ^a	0.093(5) ^e
Mo–C(1)	2.224	2.324		2.341(30)	0.102(13) ^f
Mo–C(2)	2.288	2.435		2.387(9)	0.120(13) ^f
Mo–C(3)	2.536	2.730	0.098	2.460(29)	0.121(13) ^f
Mo–C(4)	2.554	2.730		2.460(29)	0.121(13) ^f
Mo–C(5)	2.323	2.435		2.387(9)	0.120(13) ^f
C(1)–C(2)	1.454	1.462		1.434(8) ^b	0.058(5) ^g
C(2)–C(3)	1.446	1.458		1.434(8) ^b	0.058(5) ^g
C(3)–C(4)	1.406	1.420	0.051	1.434(8) ^b	0.058(5) ^g
C(4)–C(5)	1.440	1.458		1.434(8) ^b	0.058(5) ^g
C(5)–C(1)	1.452	1.462		1.434(8) ^b	0.058(5) ^g
N–C average	1.454	1.494	0.055	1.476(7)	0.063(5) ^g
C–H methyl average	1.111	1.109	0.080	1.104(4) ^c	0.092(5) ^h
C–H ring average	1.093	1.091	0.077	1.094(4) ^c	0.089(5) ^h
Important non-bonded distances					
Mo...C (Me) average				3.042	0.120 ⁱ
N...N average				3.026	0.115 ^{ij}
C (C ₅ H ₅)...C (C ₅ H ₅)				2.320	0.056 ⁱ
C (Me)...C (Me) average				2.424	0.077 ⁱ
Valence angles					
	DFT		GED		
	LSDA	BLYP	r_a		
N(1)–Mo–N(2)	94.5	95.0	97(2)		
N(1)–Mo–N(3)	92.3	95.0	97(2)		
N(2)–Mo–N(3)	104.1	106.5	104(2)		
Mo–N(1)–C(6)	126.8	127.0	115(3)		
Mo–N(1)–C(7)	120.6	122.7	135(3)		
C(6)–N(1)–C(7)	112.3	110.3	110.2 ^d		
Mo–N(2)–C(8)	117.6	120.8	125(4)		
Mo–N(2)–C(9)	126.6	125.3	117(4)		
C(8)–N(2)–C(9)	111.4	110.2	110.2 ^d		
Mo–N(3)–C(10)	124.9	125.4	117(4)		
Mo–N(3)–C(11)	118.8	120.7	125(4)		
C(10)–N(3)–C(11)	111.4	110.2	110.2 ^d		
Dihedral angles					
			GED		
N(1)–Mo–N(2)–C(8)			41(9)		
N(1)–Mo–N(2)–C(9)			–105(6)		

^{a–c} Denote sets of distances refined with constant difference, ^d angles assumed equal, ^{e–h} sets of amplitudes refined with constant difference, ⁱ fixed values and ^j average value.

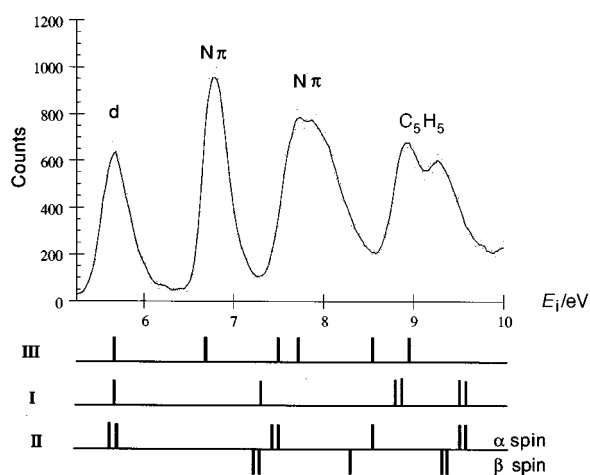


Fig. 4 Comparison of Kohn-Sham one-electron energies for structures **I**, **II** and **III** with the low E_1 bands of the PE spectrum of $\text{Mo}(\text{C}_5\text{H}_5)(\text{NMe}_2)_3$

distances and angles predicted differed, the essence of the structural prediction was the same.

Calculations were also carried out on structures **I** and **II**. In these cases the geometry was optimized with certain constraints, namely the $\text{Mo}(\text{C}_5\text{H}_5)$ unit had local C_{5v} symmetry and the $\text{Mo}(\text{NMe}_2)_3$ had local C_{3v} symmetry. Structure **II** was found to have a triplet ground state. The optimized bond lengths and angles for these structures are given in Table 3.

Though Kohn-Sham one-electron energies bear no formal relation to ionization energies, it is generally found that their ordering and energy pattern are closer to those of photoelectron bands than are self-consistent field (SCF) orbital energies. In Fig. 4 we compare the one-electron energies found for structures **I–III** with the low E_1 PE spectrum (values are given in Table 4). The one-electron energies are aligned so that the highest occupied orbital (HOMO) is coincident with the first ionization band.

The separations of orbitals found for structure **III** fit the spectrum much better than either for **I** or **II**. Both **I** and **III** reproduce the nitrogen p_π ionization ordering correctly with the band of intensity 1 having a lower E_1 than that of intensity 2. In the predicted pattern for **II** the order is reversed. For both **I** and

Table 3 Optimized bond lengths (Å) and angles (°) for structures **I** and **II**

	Structure I	Structure II
Mo–C	2.462	2.415
C–C	1.428	1.433
Mo–N	1.968	2.005
N–C	1.455 (down) 1.477 (up)	1.454
C–H (methyl)	1.109	1.110
C–H (ring)	1.091	1.091
N–Mo–N	97.1	103.7
Mo–N–C	130.2 (down) 121.7 (up)	127.1

Table 4 Kohn-Sham one-electron energies (eV) for the nine highest occupied orbitals for structures **I–III**

Orbital	I	II		III
		α	β	
Mo d	-2.51	-3.21	-3.22	-3.59
N p _{π}	-4.13	-4.89	-4.66	-4.64
N p _{π}	-5.64	-4.89	-4.67	-5.44
N p _{π}	-5.65	-6.01	-5.77	-5.67
C ₅ H ₅ –Mo	-6.41	-6.98	-6.76	-6.46
C ₅ H ₅ –Mo	-6.41	-7.03	-6.82	-6.84
N σ –Mo	-7.82	-7.94	-7.92	-7.61
N σ –Mo	-8.05	-8.22	-8.05	-8.20
N σ –Mo	-8.06	-8.24	-8.08	-8.57

Table 5 The independent structure parameters of compound **1** refined by least-squares calculations to the GED data. Estimated standard deviations in parentheses in units of the last digit. Distances in Å, angles in °

1. Average C–H bond distance	1.102(4)
2. Average C–C bond distance in the C ₅ H ₅ ring	1.434(8)
3. Perpendicular metal to ring distance	2.072(8)
4. Slip = distance from the projection of the metal atom onto the C ₅ H ₅ ring plane to the ring centre (Z)	0.13(6)
5. Average Mo–N bond distance	1.991(4)
6. Average N–C bond distance	1.478(7)
7. Valence angle Z–Mo–N(1)	144(6)
8. Valence angle N(1)–Mo–N(2)	97(2)
9. Valence angle N(2)–Mo–N(3)	104(2)
10. Valence angle Mo–N(1)–C(6)	115(4)
11. Valence angle Mo–N(2)–C(8)	117(4)
12. Valence angle Mo–N(2)–C(9)	125(4)
13. Dihedral angle N(1)–Mo–N(2)–C(8)	41(9)
14. Valence angle C–N–C	110.2*
15. Valence angle N–C–H	110.0*

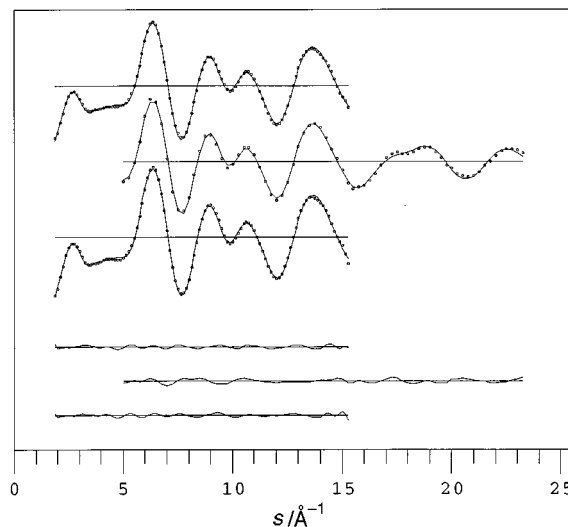
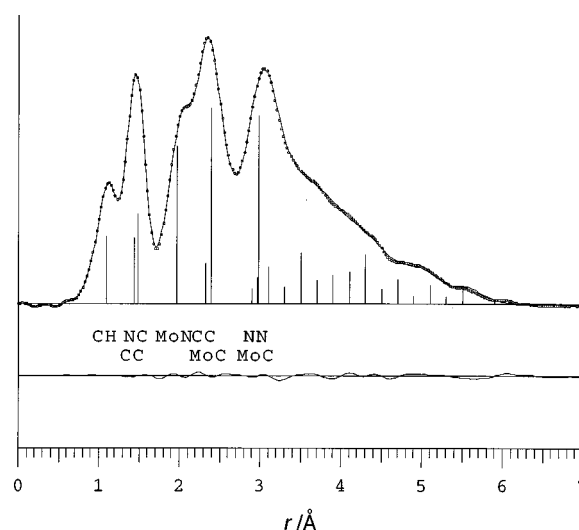
* Not refined.

II the two cyclopentadienyl bands are expected to be coincident due to the η^5 nature of the ring. In **III** the energies are separated by 0.38 eV which agrees well with the 0.35 eV separation between bands D and E.

The HOMO is found to be mainly molybdenum 3d in character. The next highest orbital consists of an out-of-phase combination of the 2p _{π} orbitals on the equatorial nitrogens. The nodal properties of this combination is such that there is very little overlap with molybdenum 4d orbitals and the resultant orbital is non-bonding. The subsequent two orbitals all show Mo–N π -bonding character. All three nitrogens are thus involved in π bonding but the equatorial nitrogens less so than the axial nitrogen, hence the latter has a shorter Mo–N bond.

Electron diffraction

The gas-phase electron diffraction data were found to be incompatible with structures **I**, **II** or any other model in which the Mo(NMe₂)₃ fragment is constrained to C₃ symmetry.

**Fig. 5** Experimental (dots) and calculated (full line) modified molecular GED intensity of Mo(C₅H₅)(NMe₂)₃. Below: difference curves**Fig. 6** Experimental (dots) and calculated (full line) radial distribution curves of Mo(C₅H₅)(NMe₂)₃. Major interatomic distances are indicated by bars of height approximately equal to the area under the corresponding peak (see comment in text). Artificial damping constant $k = 0.0025 \text{ \AA}^2$. Below: difference curve

Refinement of a C₅ model with a conformation of the Mo(NMe₂)₃ fragment similar to that indicated by the DFT calculations (Fig. 3) proceeded without difficulty to yield the independent structure parameters listed in Table 5 and the bond distances and valence angles in Table 2. Since the parameter values obtained depend on the geometrical constraints and on the calculated vibrational amplitudes, it is difficult to assess their accuracy. The estimated standard deviations (e.s.d.s) listed for the bond distances and their vibrational amplitudes have been obtained from those calculated by the program through multiplication by a factor of 3.0. The e.s.d.s listed for angles have been multiplied by a factor of 6.0, but may still be too small.

Experimental and calculated intensity curves are compared in Fig. 5. We find the agreement satisfactory. Experimental and calculated radial distribution functions are compared in Fig. 6. Major interatomic distances are indicated by bars of height approximately equal to the area under the corresponding peak. The bars corresponding to the mean bond distances and to the predominant non-bonded distances listed in Table 2 are identified by atomic symbols. Forty-two non-bonded C···C distances and 27 non-bonded N···C distances are not listed in

Table 2. Some of these distances are unique while others occur in symmetry-related pairs. The heights of the unmarked bars in Fig. 6 correspond to the sum of the areas under the peaks centred within each 0.20 Å interval from 2.80 to 6.00 Å.

The DFT calculations indicate that the cyclopentadienyl ring is slipped sideways into an unsymmetric, polyhaptic bonding mode as indicated in Fig. 3. The magnitude of the slip is larger at the BLYP level than at the LSDA level, and there is no certainty that the slip would not be changed at a higher computational level. The GED data contain little information about the asymmetry of the Mo(C₅H₅) fragment: the value obtained for the slip parameter (see Table 5 for definition) is 0.13(6) Å. Refinements of models with slip > 0.32 Å fail to yield satisfactory agreement between calculated and experimental intensities. The GED investigation thus indicates that the slip is smaller than calculated.

The mean Mo–C bond distance obtained by GED, 2.41 Å, is considerably shorter than the average bond distance obtained by the DFT BLYP calculations, 2.53 Å. Both are significantly longer than the Mo–C distance in the 18-electron complex Mo(η⁵-C₅H₅)₂H₂, 2.29 Å,²⁸ and indicate significantly weaker bonding in the 20-electron molecule.

The Mo–N–C valence angles in the Mo(NMe₂)₃ fragment obtained by GED are rather different from those obtained by the calculations. All attempts to find another least-squared minimum in closer agreement with calculations were unsuccessful. We suspect that the discrepancy is due to inadequate r.m.s. vibrational amplitudes. The mean Mo–N distance, 1.991(4) Å, is in excellent agreement with the mean bond distance obtained by the DFT calculations, 1.997 Å. Both are significantly longer than in the diamagnetic 18-electron complex Mo(NMe₂)₄, 1.93 Å,²⁹ again indicating somewhat weaker metal-to-ligand bonding in the 20-electron complex.

Conclusion

The weight of the evidence from the physical and theoretical investigations is that the dimethylamido groups in Mo(C₅H₅)(NMe₂)₃ lack C₃ symmetry and are arranged so that one amido group has the methyls axial and the other two have their methyl groups equatorial. From the splitting of the PE bands and the DFT calculations it also seems possible that the cyclopentadienyl ring is slipped and has an η³ co-ordination mode. The slip is away from the axially bound amido group which is more fully π bonded to the metal than the other two. The GED results, however, suggest that the slip is smaller than calculated.

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