# Electronic Structure and Photoelectron Spectroscopy of $Al(Me_3CNCHCHNCMe_3)_2$ and $Ga(Me_3CNCHCHNCMe_3)_2$†

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The He I and He II spectra of $M(Me_3CNCHCHNCMe_3)_2$ (M = Al or Ga) have been recorded. A complex band structure arising from ionization of the $\pi_3$ levels of the diazadiene ligands can be understood by reference to the structural distortion from idealized $D_{2d}$ symmetry observed in the ground state. Other higher-lying bands are assigned to $\pi_2$ and $n_+$ and $n_-$ ionizations. The electronic structure of the neutral molecules is discussed and the differences in bond lengths between the rings is attributed to a Jahn–Teller distortion that traps two electrons in the $\pi_3$ orbital of one ring and one in the $\pi_3$ orbital of the other.

Cocondensation of gallium vapour with 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene, $Me_3CNCHCHNCMe_3$, has been shown to give $Ga(Me_3CNCHCHNCMe_3)_2$,[1a] as does the reaction of $LiGaH_4$ and gallium metal with $Me_3CNCHCHNCMe_3$.[1b] Investigation of the molecular structure by X-ray crystallography showed the molecule to possess a distorted-tetrahedral geometry around the central gallium atom. The average C–N and C–C bond lengths (1.326 and 1.389 Å respectively) in one of the $Me_3CNCHCHNCMe_3$ ligands are typical of those found in transition-metal analogues.[2] However the values for the other $Me_3CNCHCHNCMe_3$ ligand show significant deviations; the C–N distance has lengthened to 1.395 Å and C–C shortened to 1.350 Å. These changes are accompanied by a decrease in Ga–N distance from 1.969 to 1.864 Å, and an increase in the bite angle of the ligand from 84.9 to 90.4°. Magnetic data showed the presence of one unpaired electron. Electron spin resonance (ESR) studies at room temperature showed a spectrum exhibiting coupling to Ga and four equivalent nitrogen atoms; the frozen-solution spectrum at 130 K proved more complex.

The analogous aluminium compound, $Al(Me_3CNCHCHNCMe_3)_2$, has been synthesised by reaction of aluminium vapour or $LiAlH_4$–aluminium metal–hexane with 1,4-di-*tert*-butyl-1,4-diazabutadiene.[3] The crystal structure again shows two different ligands with different geometries. The corresponding C–C and C–N distances for the two compounds are within three standard deviations, whereas the M–N distances differ by *ca.* 10 standard deviations with those of the aluminium compound being shorter. X-Ray photoelectron spectroscopy (XPS) on the aluminium compound shows two N 1s signals and an Al 2p region characteristic of $Al^{III}$. The ESR spectrum shows a signal from coupling to four nitrogens; no aluminium coupling is resolved.

In order to investigate further the electronic structure of these interesting molecules we undertook a photoelectron spectroscopy (PES) study using He I and He II radiation.

## Experimental

Gallium vapour, generated from a resistively heated alumina crucible, was cocondensed with an excess of $Me_3CNCHCHNCMe_3$ in toluene at 77 K. The resulting matrix, on warming to room temperature, gave a deep green-brown solution. Removal of the solvent and excess of $Me_3CNCHCHNCMe_3$ by sublimation, followed by low-temperature recrystallization of the residue from toluene–hexane, afforded green-black crystals of $Ga(Me_3CNCHCHNCMe_3)_2$. Yield 20%, 4.0 g based on gallium.

Aluminium vapour (1.3 g, 50 mmol), generated from a resistively heated boron nitride crucible, was cocondensed with an excess of $Me_3CNCHCHNCMe_3$ (30 g, 180 mmol) at −196 °C over a period of 2 h. After warming, the dark green product was extracted from the reactor in toluene (1000 $cm^3$), filtered, and solvent and excess of $Me_3CNCHCHNCMe_3$ removed *in vacuo*. Recrystallization of the residue from toluene–pentane (30 $cm^3$) at −30 °C afforded deep green crystals of $Al(Me_3CNCHCHNCMe_3)_2$. Yield 5 g, 30% based on Al.

Photoelectron spectra were obtained using a PES Laboratories 0078 spectrometer, fitted with a hollow-cathode helium discharge lamp capable of producing He I and He II radiation. The spectrometer was interfaced with a Research Machines 380Z microprocessor so that spectra were collected by repeated scans and spectral addition. Vertical ionization energies (i.e.s) were obtained by calibrating the spectrum with $N_2$, Xe and He. To obtain sufficient vapour pressure for the gas-phase measurement the samples were held at 90 (Ga) and 100 °C (Al).

## Results and Discussion

The photoelectron spectra of $Al(Me_3CNCHCHNCMe_3)_2$ and $Ga(Me_3CNCHCHNCMe_3)_2$ are presented in Figs. 1 and 2 and vertical i.e. data given in Table 1. The spectrum of the free ligand has been reported[4] as have those of other diazabutadienes and their complexes.[5–7] He I and He II spectra have very similar intensity patterns; any substantial degree of localization of an electron on Al or Ga might be expected to result in a reduction of the relative intensity of the corresponding ionization band in the He II spectrum.

Discussion of the spectra and assignment of bands is best preceded by an examination of the electronic structure of $M(Me_3CNCHCHNCMe_3)_2$.

*Electronic Structure.*—The ligand $Me_3CNCHCHNCMe_3$ has a number of orbitals which may become involved in bonding to a metal. The ones from which we might expect to identify ionizations in a photoelectron spectrum are shown in Fig. 3 and will be referred to as $\pi_2$, $\pi_3$, $n_+$ and $n_-$. The first band in the spectrum of $Me_3CNCHCHNCMe_3$ is assigned to ionization of $\pi_2$, $n_+$ and $n_-$; $\pi_3$ is unoccupied in the free ligand

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† *Non-SI units employed:* G = $10^{-4}$ T, eV ≈ $1.60 \times 10^{-19}$ J.

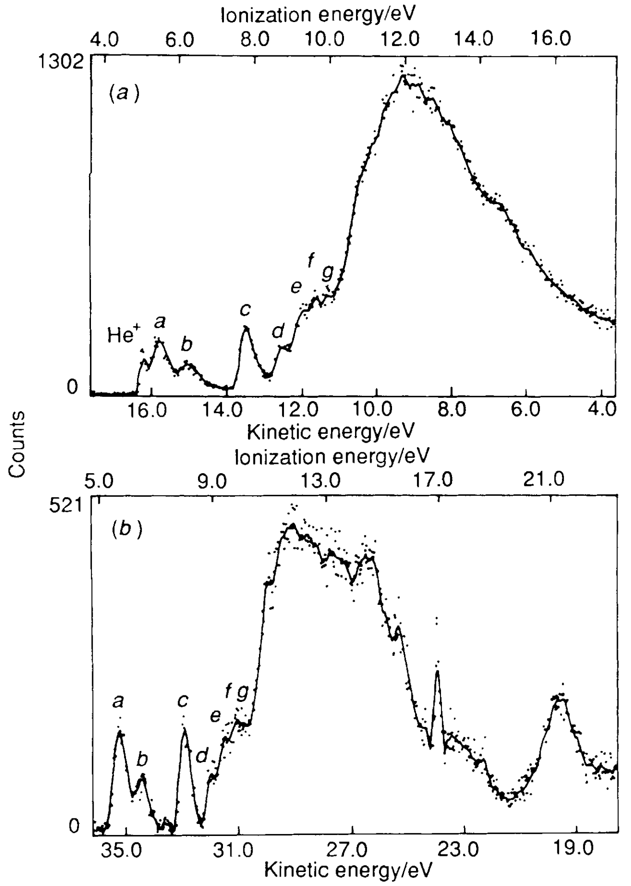

**Fig. 1** Full range (*a*) He I and (*b*) He II spectra of Ga(Me$_3$CNCHCHNCMe$_3$)$_2$

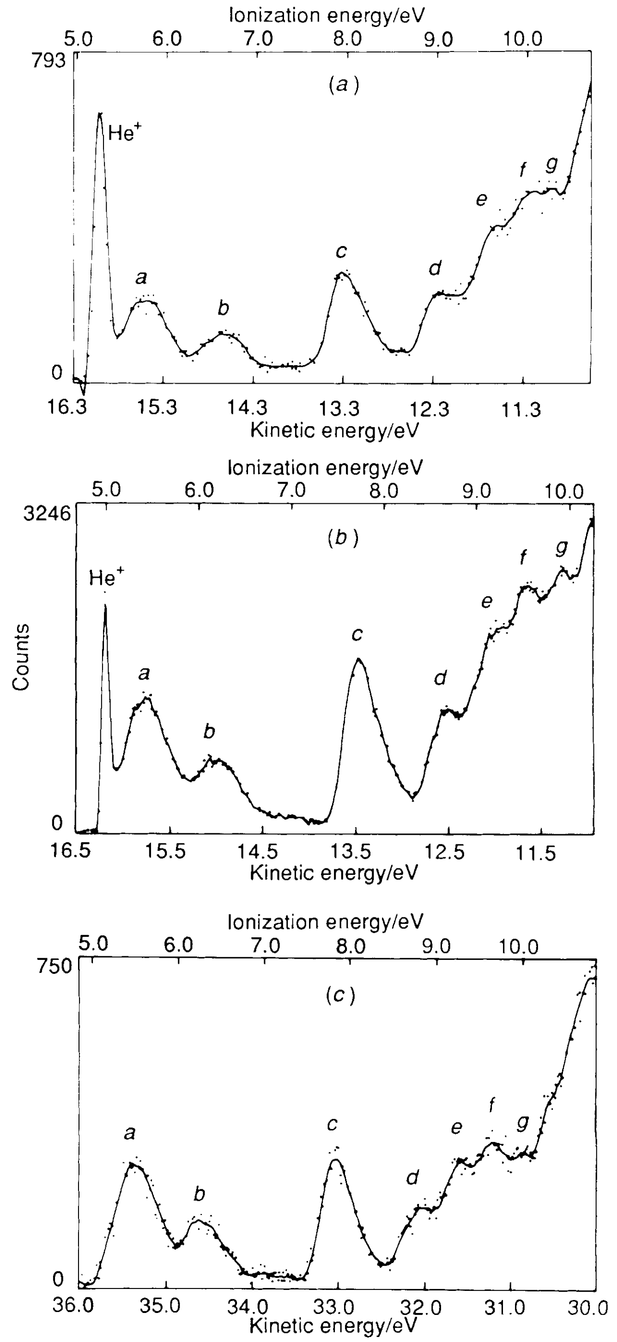

**Fig. 2** Low i.e. range photoelectron spectra: (*a*) He I of Al(Me$_3$CNCHCHNCMe$_3$)$_2$, (*b*) He I of Ga(Me$_3$CNCHCHNCMe$_3$)$_2$ and (*c*) He II of Ga(Me$_3$CNCHCHNCMe$_3$)$_2$

and is generally considered to be the lowest unoccupied molecular orbital (LUMO) of Me$_3$CNCHCHNCMe$_3$.

Initially we chose to consider Ga(Me$_3$CNCHCHNCMe$_3$)$_2$ as having idealized $D_{2d}$ symmetry. The molecular axes are shown in Fig. 4 and the transformation properties of the orbitals given in Table 2.

A schematic MO diagram is given in Fig. 4. Occupancy of these orbitals by 15 electrons results in placing three electrons in the 2e level, thus giving a $^2$E ground state. Such a state would be expected to be Jahn–Teller active and lead to a lowering of symmetry. As mentioned above a gross distortion from $D_{2d}$ symmetry is shown in the crystal structure where differing bond lengths for the two chelate rings are found. The distances for the gallium and aluminium compounds are summarized in Table 3. When these distortions are examined alongside the bonding properties of $\pi_3$, which is C–C bonding and C–N antibonding (see Fig. 3), it is evident that occupancy of $\pi_3$ is higher on one ligand than the other. We therefore propose that the structural 'distortion' is such that two electrons are trapped in the $\pi_3$ orbital on one of the Me$_3$CNCHCHNCMe$_3$ ligands and one electron on the other. The C–C and C–N distances found (see Table 3) strongly suggest that one ligand is effectively doubly reduced and the other singly reduced. (We shall refer to them as ring A and B respectively.) The room-temperature ESR spectrum, which shows the unpaired electron coupling equally to all four nitrogens, suggests that on such a time-scale the Jahn–Teller distortion is dynamic and an electron is hopping from one ligand to another.

Magnetic measurements on the aluminium complex[8] over the temperature range 0–300 K give linear plots of $\chi_M^{-1}$ *vs.* $T$ with $\mu_{eff} = 1.649 \pm 0.003$ and $\theta = 0.44$ K at 5 kG magnetic field and $\mu_{eff} = 1.613 \pm 0.003$ and $\theta = -0.46$ K at 40 kG magnetic field. Such values rule out a model where the Al is in the II oxidation state and both ligands are singly reduced, and is consistent with one of the ligands being doubly reduced and an unpaired electron being localized on the other ligand or on the Al. Absence of strong $^{27}$Al hyperfine coupling in the ESR spectrum would support the picture of the unpaired electron being mainly ligand localized.

We carried out simple extended-Hückel calculations on Ga(HNCHCHNH)$_2$ both with a distorted structure with the crystallographic bond lengths and an undistorted structure with averaged bond lengths. The former was found to have a lesser sum of one-electron energies by 0.16 eV. The largest energy changes are for the two $\pi_3$ orbitals which split by 0.42 eV.

The calculations show the 2e orbitals to have very little gallium content. The principal mixing in the e symmetry set is between the p$_x$ and p$_y$ orbitals on the Ga and the ligand n$_-$ orbitals, presumably because the latter are better directed for overlap. (The 1e set together with the a$_1$ and b$_2$ orbitals, which are all bonding, provide the MO equivalent of the nitrogen lone

**Table 1** Vertical ionization energies and assignments of the photoelectron spectra of $M(Me_3CNCHCHNCMe_3)_2$

| Band | M = Ga | M = Al | Assignment |
|---|---|---|---|
| *a* | 5.47 | 5.52 | $A\pi_3{}^1B\pi_3{}^1$ |
| *b* | 6.21 | 6.41 | $A\pi_3{}^2$ |
| *c* | 7.80 | 7.74 | $\pi_2$ |
| *d* | 8.84 | 8.85 | $n_+$ |
| *e* | 9.33 | 9.51 | $n_-$ |
| *f* | 9.64 | 9.84 | $n_-$ |
| *g* | 10.08 | 10.12 | $n_+$ |
|  | 12.33 | 12.20 |  |

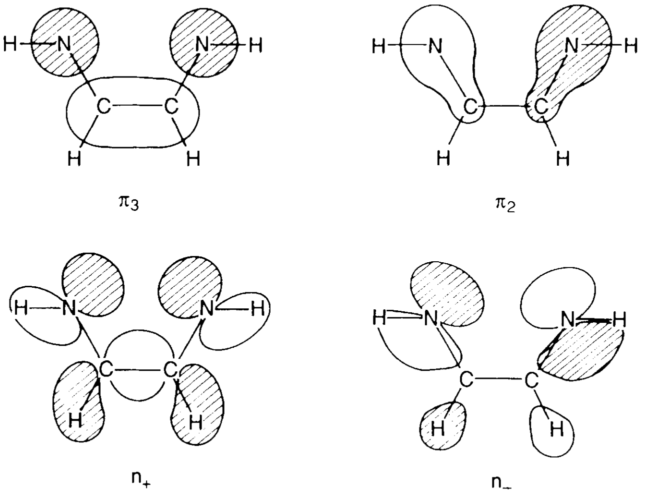

**Fig. 3** Selected molecular orbitals of RNCHCHNR. The orbitals $\pi_2$ and $\pi_3$ have a node in the plane of the molecule and are represented by a projection onto that plane, $n_+$ and $n_-$ lie in the molecular plane, and $\pi_3$ is unoccupied in the free ligand

pairs donating into gallium $sp^3$ hybrids.) One might therefore expect the Jahn–Teller distortion to be principally concerned with changes on the ligand itself and there to be little change in Ga–N distances. However, once one ligand is doubly reduced and the other singly reduced, we can expect a consequent effect on metal–ligand distance; the shorter Ga–N distances are found in conjunction with the longer C–N and shorter C–C distances so rehybridization at nitrogen is a possible cause.

*Spectral Assignment.*—The photoelectron spectra of $Al(Me_3CNCHCHNCMe_3)_2$ and $Ga(Me_3CNCHCHNCMe_3)_2$ are very similar and, given the structural similarities described above, we assume that their electronic structures are also very similar. For clarity, we will discuss the ionization bands in terms of the $D_{2d}$ symmetry labels for the undistorted structure, while recognizing that the actual molecular symmetry is lower than this.

Comparison of the spectrum of the complex and the free ligand suggests that ionization features above 7 but below 10.5 eV are associated with 1e, $a_1$, $b_1$, $a_2$ and $b_2$ ionizations: these all originate from ligand $n_+$, $n_-$ and $\pi_2$ ligand orbitals. Those above 10.5 eV consist of ionization from $\pi_1$ and other ligand-based $\sigma$ orbitals and will not be discussed further. The ionization band below 7 eV which is absent in the spectrum of the free ligand is assigned to ionization from the $\pi_3$ (2e) orbitals.

Ionization of a molecule in a doublet ground state can give rise to both singlet and triplet ion states. However, for the assignment of most bands exchange splitting is not evident.

The band in the complex spectrum which has the lowest i.e. out of the set originating from occupied ligand orbitals is band *c* at *ca.* 7.8 eV. We assign this to the $\pi_2$ ionizations ($a_2$ and $b_1$) as these have no involvement with metal–ligand bonding. The $\pi_2$ ionizations occur at a lower energy than that of the free ligand presumably as a result of accumulation of negative charge on the ligand on complexing. The four bands, *d*–*g*, which lie at higher i.e. are from the relatively stabilized $n_+$ and $n_-$ orbitals (1e, $b_1$ and $a_1$). That four are observed suggests that one $n_-$ orbital is more strongly bound to the metal than the other, again consistent with the very different M–N distances observed. The calculation would suggest the following assignment; *d* to $n_+$ ($b_2$), *e* and *f* to the $n_-$ orbitals (e), and *g* to $n_+(a_1)$.

**Table 2** Transformation properties of the metal and ligand basis-set orbitals of $M(Me_3CNCHCHNCMe_3)_2$ in the point group $D_{2d}$

| Symmetry | Metal orbital | Ligand orbital |
|---|---|---|
| $a_1$ | 4s | $n_+(A) + n_+(B)$ |
| $b_2$ | $4p_z$ | $n_+(A) - n_+(B)$ |
| e | $4p_x$, $4p_y$ | $n_-(A), n_-(B)$<br>$\pi_3(A), \pi_3(B)$ |
| $b_1$ |  | $\pi_2(A) + \pi_2(B)$ |
| $a_2$ |  | $\pi_2(A) - \pi_2(B)$ |

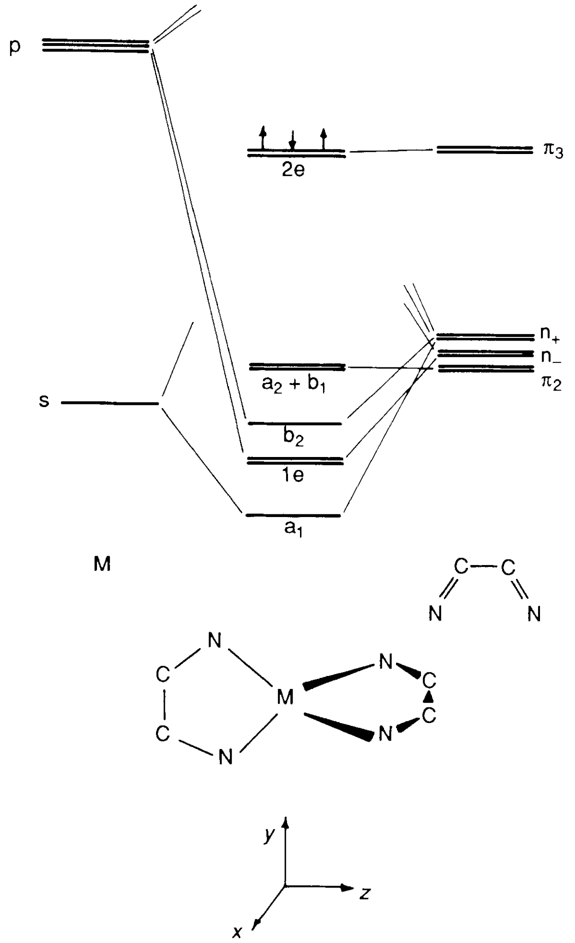

**Fig. 4** Schematic MO diagram for $M(Me_3CNCHCHNCMe_3)_2$ assuming $D_{2d}$ symmetry

In assigning bands *a* and *b*, which appear to have relative intensity of 2:1, we must consider electron–electron repulsion terms carefully. In a delocalized description of ionization from a $^2E$ state of a $e^3$ configuration the accessible ion states are $^3A_2$, $^1A_1$, $^1B_1$ and $^1B_2$, with the expected intensity of the transitions being $\frac{3}{2}:\frac{1}{2}:\frac{1}{2}:\frac{1}{2}$ respectively. In both the $^3A_2$ and $^1B_1$ states the two remaining electrons are on different ligands; in the $^1A_1$ and $^1B_2$ states the two electrons are on the same ligand. The observed intensity pattern of 2:1 is best understood by assigning band *a* to $^3A_2$ and $^1B_1$ and band *b* to $^1A_1$ and $^1B_2$, on the grounds that the energy of the former

**Table 3** Selected distances (Å) in the crystal structures of $M(Me_3CNCHCHNCMe_3)_2$[1,3]

| | M = Al | M = Ga |
|---|---|---|
| Ring A | | |
| C–C | 1.343(5) | 1.350(7) |
| C–N | 1.415(3) | 1.395(6) |
| M–N | 1.823(2) | 1.864(4) |
| Ring B | | |
| C–C | 1.395(6) | 1.389(10) |
| C–N | 1.346(5) | 1.331(9) |
| | 1.331(5) | 1.321(9) |
| M–N | 1.916(3) | 1.972(6) |
| | 1.924(3) | 1.966(5) |

Electron diffraction on $Me_3CNCHCHNCMe_3$ shows for the majority of molecules a *gauche* conformation with respect to the central C–C bond with a torsion of about 65° from the *s-cis* form. The C–C bond length is found to be 1.496(20) Å and the C–N bond length 1.283(6) Å.

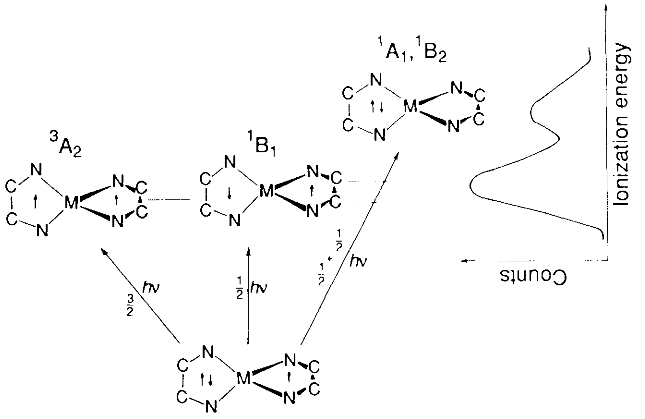

**Fig. 5** Representation of ionization from the $\pi_3$ orbitals. Ring A is the doubly reduced ligand and ring B the singly reduced ligand. The electrons in the $\pi_3$ orbitals are represented by arrows, the direction of the arrow indicating the spin of the electron. The symmetry of the corresponding state in $D_{2d}$ symmetry is also given.

states is lower as the electron–electron repulsion is least when the two electrons are on different ligands. If the exchange splitting were to be dominant we would expect two bands of equal intensity ($\frac{3}{2}:\frac{3}{2}$).

If the symmetry is broken and lowered to $C_{2v}$, as is the case if the ligand planes are perpendicular to one another, a localized approach gives a similar result. Let us assume $A\pi_3$ is the $\pi_3$ orbital on the ligand with the shorter C–C bond (*i.e.* the more reduced ligand) and $B\pi_3$ is the $\pi_3$ orbital on the ring with the longer C–C bond. The orbital ordering is $A\pi_3 < B\pi_3$ and the ground-state configuration is therefore $A\pi_3^2B\pi_3^1$. A naive application of Koopmans' theorem with neglect of any electron-repulsion considerations would assign the first band *a* to the configuration $A\pi_3^2$ and band *b* to the configuration $A\pi_3^1B\pi_3^1$ and expect the intensity ratio to be 1:2. This is clearly not in accord with the experimental observation of a 2:1 intensity ratio. Furthermore, the splitting of *ca.* 1 eV is around twice as great as that calculated for the difference in the two orbital energies. If we again assume that electron–electron repulsion is much greater when both electrons occupy the same $\pi_3$ orbital, we make the reverse assignment with band *a* correlating with the configuration $A\pi_3^1B\pi_3^1$, and band *b* being due to the ions with configuration $A\pi_3^2$. This is indicated diagrammatically in Fig. 5 where the correlations between the localized and delocalized interpretations is also given.

## Conclusion

In the compounds $Ga(Me_3CNCHCHNCMe_3)_2$ and $Al(Me_3CNCHCHNCMe_3)_2$ one of the $Me_3CNCHCHNCMe_3$ ligands is singly reduced while the other is doubly reduced, the additional electrons occupying the $\pi_3$ orbitals. The distances found for the molecules by X-ray diffraction are entirely consistent with this picture of the electronic structure, as are photoelectron spectra. Formally, the distortion from idealized $D_{2d}$ symmetry may be thought to arise as a result of a Jahn–Teller distortion of the $^2E$ ground state, which traps one electron on one ligand and two on the other. That the ESR spectra show coupling to four equivalent nitrogens suggests that an electron is hopping from one ligand to another on a time-scale comparable to that of the ESR experiment. XPS on the aluminium compound, where the time-scale is faster, shows inequivalent nitrogens on the two ligands.

Interpretation of the photoelectron spectra predicts that oxidation of the complexes should result in a cation where both ligands are singly reduced with a triplet ground state.

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