Molecular Orbital Study of the Bridging Dioxygen Ligand in $[Al_2(CH_3)_6(O_2)]^-$ *

Piercarlo Fantucci and Gianfranco Pacchioni
Dipartimento di Chimica Inorganica e Metallorganica, Centro CNR, Università di Milano, Via Venezian 21, 20133 Milano, Italy

A recent *X*-ray structure determination of $[Al_2(CH_3)_6(O_2)]^-$ shows a new bridging co-ordination mode of the dioxygen ligand, with O–O distance and ν(O–O) frequency close to the values observed in solid Na_2O_2. This could suggest classifying the dinuclear aluminium compound as a peroxo complex. On the basis of results obtained from *ab initio* molecular orbital–linear combination of atomic orbital calculations, a different description of the electronic structure of the title compound is proposed. Despite the fact that the co-ordinated O_2 ligand carries a small negative charge (0.41 electrons), the computed O–O bond length and harmonic frequency are close to the theoretical values expected for the gaseous O_2^- species. As a consequence, the classification of the dioxygen complex as a peroxo or superoxo complex is of little help in elucidating the real electronic structure of the dioxygen ligand. The electronic mechanism of bonding of the dioxygen to an *s–p* element like aluminium is markedly different from that occurring in transition-metal compounds, despite some similarities in charge distribution and O–O bond length.

The co-ordination chemistry of the dioxygen ligand in mono- or di-nuclear complexes of transition-metal atoms has been the subject of intensive experimental and theoretical studies for two main reasons: the co-ordination of molecular oxygen is an essential step in reversible oxygenation reactions with proteins [1] and dioxygen–metal complexes are of great interest as possible efficient catalysts in oxidation reactions or as synthetic oxygen carriers.[2–4]

Extensive studies have led to the discovery of a great number of complexes where the dioxygen group is co-ordinated in different ways.[4–9] Several examples are known in which O_2 may act as a uni- or bi-dentate ligand with respect to one or two metal centres, respectively.[7] Different co-ordination geometries of the O_2 ligand correspond to changes in O–O bond length. In order to rationalize the 'nature' of the O–O bond in the dioxygen complexes, Vaska [10] classified as superoxo-like compounds those in which the O–O distance resembles that of the O_2^- ion, and as peroxo systems those having an O–O distance close to that of O_2^{2-}. However, since gas-phase data are not available for O_2^{2-}, the reference bond lengths have been taken from solid-state data.

Qualitative relationships between the electronic and geometrical structure of co-ordinated O_2 and formal oxidation state of the metal atom are widely used [6,11,12] in order to rationalize the structural features and chemical reactivity of this class of complex.

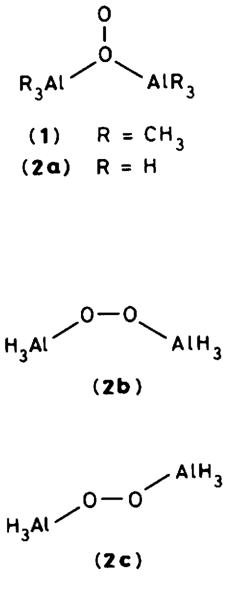
Recently, a new co-ordination mode of the O_2 ligand has been discovered in the complex $[Al_2(CH_3)_6(O_2)]^-$, (**1**):[13] this is a rare example of O_2 co-ordinated to an *s–p* element and the only reported case of a unidentate μ-O_2 co-ordination mode. The *X*-ray structure of complex (**1**) shows that the O_2 molecule is in a bridge position between two $Al(CH_3)_3$ fragments.[13] A similar structure was found for the analogous complex $[Al_2(CH_3)_6(N_3)]^-$.[14]

The O–O bond distance in complex (**1**), 1.47 Å, is substantially elongated with respect to that of the free neutral O_2 molecule (1.207 Å), and closely resembles that of the O_2^{2-} peroxo ion (O–O distance in the ionic compound Na_2O_2 is 1.49 Å). Moreover, an i.r. band attributed to ν(O–O) in (**1**) has been observed at 851 cm^{-1}, a value close to that found for Na_2O_2 (842 cm^{-1}). Both the *R*(O–O) and ν(O–O) observed values seemingly suggest that compound (**1**) is a peroxo-type complex.

The aim of the present paper is to analyse the electronic structure of the dioxygen complex on the basis of theoretical molecular orbital–linear combination of atomic orbital (m.o.–l.c.a.o.) calculations in order to clarify whether the O–O distance observed in the dioxygen adducts may be in general taken as an indication of the electron density on the O_2 moiety. The relationship between electronic charge and electron spin distribution in paramagnetic dioxygen adducts is also worthy of careful examination, in order to avoid improper conclusions about the mechanism of charge shifts and spin polarization occurring during the oxygenation reaction.

Experimental

Computational Method.—Theoretical m.o.–l.c.a.o. calculations on the neutral and anionic forms of complexes (**1**) and (**2a**)—(**2c**) have been carried out at the *ab initio* level using



Scheme.

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* *Non-S.I. units employed:* cal = 4.184 J; a.u. = 2 622 kJ mol^{-1}.

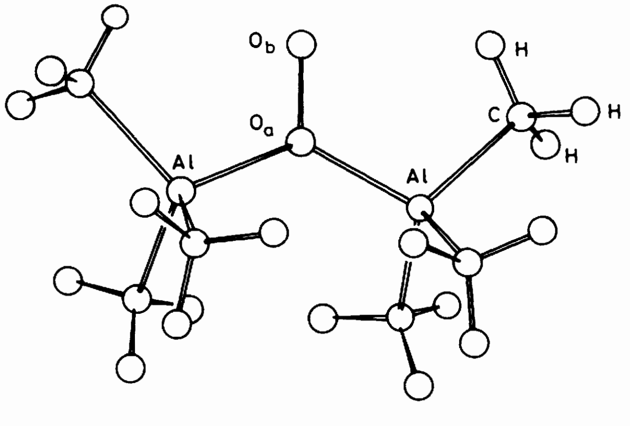

Figure 1. Molecular structure of the complex studied. The following values have been used in the calculations: Al–O = 1.86, Al–C = 2.0, C–H = 1.09 Å, Al–O–Al = 128°

Table 1. Electronic properties of O_2, O_2^-, and O_2^{2-} molecules (E_T = total energy, ω_e = harmonic frequency)

System	Ground state	E_T/a.u.	R(O–O)/Å		ω_e/cm^{-1}	
			Calc.	Found	Calc.	Found
O_2	$^3\Sigma_g^-$	−147.6354	1.226	1.207[a]	2 231	1 555[b]
O_2	$^1\Delta_g$	−147.5530	1.230	1.216[c]	2 236	1 484[d]
O_2^-	$^2\Pi_g$	−147.3854	1.312	1.34[e]	1 983	1 146[f]
O_2^{2-}	$^1\Sigma_g$	−147.6228	1.470	1.49[g]	1 304	842[h]

[a] J. C. Abrahms, *Q. Rev. Chem. Soc.*, 1956, **10**, 407. [b] G. Herzberg, 'Molecular Spectra and Molecular Structure,' 2nd edn., Van Nostrand, New York, 1950. [c] M. Kasha and A. U. Kahn, *Ann. N. Y. Acad. Sci.*, 1970, **5**, 171. [d] L. Herzberg and G. Herzberg, *Astrophys. J.*, 1947, **105**, 353. [e] O_2^-(g), R. J. Celotta, R. A. Bennett, J. L. Hall, M. W. Siegel, and J. Levine, *Phys. Rev. A*, 1972, **6**, 631. [f] KO_2, F. J. Blunt, P. J. Hendra, and J. R. MacKenzie, *Chem. Commun.*, 1969, 278. [g] Na_2O_2, R. Tallman, J. L. Margrave, and S. W. Bailey, *J. Am. Chem. Soc.*, 1957, **79**, 2979. [h] Na_2O_2, J. C. Evans, *Chem. Commun.*, 1969, 682.

the standard STO-3G minimal basis.[15] The quantitative predicting capability of such a minimal basis is certainly low and in particular the computed binding energies may be seriously overestimated because of basis set superposition errors (b.s.s.e.). However, we believe that the STO-3G basis is reliable in providing correct qualitative results especially in studying trends of the values of physical quantities in a series of similar molecules. Moreover, the b.s.s.e. does not significantly affect the trend of the computed stabilities where the molecular systems investigated are all characterized by similar spatial compactness and when the molecular stability is considered as a function of total charge and spin multiplicity. We have chosen to carry out unrestricted Hartree-Fock calculations[16] on the open-shell systems because this is the easiest computational way to evaluate the spin density distribution taking into account both delocalization and polarization mechanisms. Besides complex (**1**), the simpler hypothetical molecule $Al_2H_6(O_2)$ and its anionic forms have been studied in three different geometrical arrangements (Scheme) in order to investigate how variation of the electronic properties of the AlR_3 fragment and the co-ordination mode of the dioxygen can influence the charge distribution on the co-ordinated O_2.

As will be shown later, substitution of the methyl groups in $Al(CH_3)_3$ with hydrogen atoms does not significantly change the bonding mechanism and electron distribution on the O_2 molecule. Therefore, some useful information about the aluminium–dioxygen complexes can be deduced by also considering the simple $Al_2H_6(O_2)$ species, which requires a much smaller computational effort.

The geometrical parameters (Figure 1) have been taken from *X*-ray crystallographic data[13,14] (Al–O = 1.86, Al–C = 2.0, Al–H = 1.65, C–H = 1.09 Å, Al–O–Al = 128°). As expected, the charge distribution on the co-ordinated O_2 depends on the assumed O–O distance. Since the experimental measurement[13] is affected by quite a large error, we decided to optimize the R(O–O) distance in both the neutral and anionic forms of (**1**) and (**2a**).

A full discussion of the electronic structure of the co-ordinated dioxygen is possible only on the basis of a comparison among electronic distributions within the complexes and the isolated fragments $Al(CH_3)_3$, AlH_3, O_2, O_2^-, and O_2^{2-}.

Results and Discussion

First, we report the results for O_2, O_2^-, and O_2^{2-} free molecules and for different geometrical forms of the $Al(CH_3)_3$ and AlH_3 fragments in order to set some reference points to be used in the following discussion. The optimization of the O–O distance has been performed for the $^3\Sigma_g^-$, $^2\Pi_g$, and $^1\Sigma_g$ ground states of O_2, O_2^-, and O_2^{2-}, respectively. The computed O–O equilibrium bond lengths are in good agreement with the available experimental data (Table 1), which, however, in some cases are taken from solid-state compounds. In the solid state the O_2^- and O_2^{2-} anions are certainly perturbed by lattice effects so that the O–O distances observed in the bulk solid may be different from those of the gas phase. This would suggest that a cautious estimate of the accuracy of the presently computed O–O distances is *ca.* ±0.05 Å. The theoretical vibrational frequencies (ω_e) are largely overestimated (Table 1), an expected result due to the limited flexibility of the STO-3G basis set and to the limitations of the one-electron picture. In fact, in order accurately to predict the vibrational frequencies, much larger basis sets and highly correlated wavefunctions are required.[17] However, the trend in the series O_2, O_2^-, and O_2^{2-} is qualitatively correct: a reduction of the O–O bond order is accompanied by an elongation of the equilibrium O–O distance and by a decrease of the vibrational frequency.

The $Al(CH_3)_3$ molecule has been studied in its neutral and anionic forms and in two geometrical structures. The first ('planar') has the AlC_3 sub-group of atoms in a planar arrangement, with the Al atom in sp^2 hybridization. The second form is a pyramidal distortion in which the hybridization of the aluminium atom is of the sp^3 type. The fourth empty sp^3 hybrid may be considered the 'acid' site on the Al atom. The data reported in Table 2 show that the pyramidal distortion requires an energy of *ca.* 19 kcal mol^{-1} but does not induce any appreciable modification of the atomic electron density. The electron attachment process leading to $[Al(CH_3)_3]^-$ is an energy-demanding process for both the planar and pyramidal forms. About half an electron is localized on the Al centre, which in the anionic species still carries a net positive charge.

The neutral form of (**1**) has an even number of electrons. In principle, the complex may be considered to be formed by reaction of two closed-shell AlR_3 fragments with a $^3\Sigma_g^-$ oxygen molecule. Thus, both singlet and triplet states are possible for the resulting complex. The data of Table 2 show that the $^1A_1$ and $^3A_2$ states are both unstable (by at least 30 kcal mol^{-1}) with respect to the dissociation into $2AlR_3 + O_2$. However, the triplet state is favoured, since its formation occurs with conservation of the total spin. The O–O distance in neutral complexes (**1**) and (**2a**) has been optimized. In both singlet and triplet states the minimum correlates with a O–O bond length elongation of *ca.* 0.06 Å with respect to the free O_2 molecule. The total energy of the complex is *ca.* 30 kcal mol^{-1} higher than

Table 2. Total energies and atomic populations of the $[Al_2(CH_3)_6(O_2)]^-$ complex and related compounds

				Gross atomic populations				
Compound	Ground state	R(O–O)/Å	E_T/a.u.	O_a	O_b	Al	C	H
$AlCH_3$	$^1A_1$		−278.1098			12.53	6.47	1.00
$Al(CH_3)_3$ (planar)	$^1A_1$		−356.5112			12.01	6.41	0.97
$[Al(CH_3)_3]^-$ (planar)	$^2A_1$		−356.2145			12.57	6.40	1.03
$Al(CH_3)_3$ (trigonal)	$^1A_1$		−356.4808			12.01	6.40	0.98
$[Al(CH_3)_3]^-$ (trigonal)	$^2A_1$		−356.2954			12.43	6.42	1.04
AlH_3 (planar)	$^1A_1'$		−240.6922			12.17		1.28
$[AlH_3]^-$ (trigonal)	$^1A_1$		−240.6546			12.17		1.28
(**1**) $Al_2(CH_3)_6(O_2)$	$^1A_1$	1.289	−860.5462	8.15	7.73	12.07	6.40	0.97
(**1**) $Al_2(CH_3)_6(O_2)$	$^3A_2$	1.281	−860.6136	8.09	7.71	12.08	6.41	0.98
(**1**) $[Al_2(CH_3)_6(O_2)]^-$	$^2B_2$	1.364	−860.7366	8.39	8.02	12.00	6.42	1.00
(**2a**) $Al_2H_6(O_2)$	$^1A_1$	1.287	−628.8524	8.21	7.70	12.21		1.27
(**2a**) $Al_2H_6(O_2)$	$^3A_2$	1.284	−628.9755	8.08	7.76	12.24		1.27
(**2a**) $[Al_2H_6(O_2)]^-$	$^2B_2$	1.385	−629.0754	8.39	8.04	12.19		1.37
(**2a**) $[Al_2H_6(O_2)]^{2-}$	$^1A_1$	1.483	−628.7195	8.53	8.49	12.20		1.43
(**2b**) $Al_2H_6(O_2)$	$^1A_1$	1.30*	−628.8633	7.99	7.99	12.20		1.27
(**2b**) $Al_2H_6(O_2)$	$^3A_2$		−628.9440	7.94	7.94	12.21		1.28
(**2b**) $[Al_2H_6(O_2)]^-$	$^2B_2$		−629.0025	8.27	8.27	12.15		1.36
(**2b**) $[Al_2H_6(O_2)]^{2-}$	$^1A_1$		−628.6752	8.52	8.52	12.19		1.43
(**2b**) $[Al_2H_6(O_2)]^{2-}$	$^3A_1$		−628.5113	8.35	8.35	12.32		1.44
(**2c**) $Al_2H_6(O_2)$	^1A_g		−628.8676	7.99	7.99	12.20		1.27
(**2c**) $Al_2H_6(O_2)$	$^3B_{2g}$		−628.9441	7.94	7.94	12.21		1.28
(**2c**) $[Al_2H_6(O_2)]^-$	$^2B_{3g}$		−629.0083	8.26	8.26	12.15		1.36
(**2c**) $[Al_2H_6(O_2)]^{2-}$	^1A_g		−628.6674	8.54	8.54	12.17		1.43
(**2c**) $[Al_2H_6(O_2)]^{2-}$	$^3B_{1u}$		−628.5290	8.33	8.33	12.34		1.44

* Distance not optimized.

the sum of the energies of the separated AlR_3 (R = H or CH_3) and O_2 molecules. Therefore, on the basis of the present calculation it is possible to conclude that the formation of the neutral species is an unlikely process.

The addition of one electron to the neutral complexes (**1**) and (**2a**) is accompanied by an energy lowering of 77 and 63 kcal mol^{-1} respectively. The most relevant consequence is that the anionic form of (**1**) is stable towards dissociation into $2Al(CH_3)_3$ (planar) fragments and O_2 by 49 kcal mol^{-1} and with respect to $2Al(CH_3)_3$ and O_2^- by 206 kcal mol^{-1}. In a similar way complex (**2a**) is 35 (192) kcal mol^{-1} more stable than the separate systems $2AlH_3$ (planar) and O_2 (O_2^-).

The estimated binding energy, even considering possible corrections due to effects of basis set extension and electron correlation, is indicative of formation of quite a strong bond in the dioxygen adduct. This prediction agrees with the experimental evidence that the anionic form of complex (**1**) is thermally stable even at relatively high temperature (refluxing toluene).[13]

The optimization of the dioxygen bond length in the anionic forms of (**1**) and (**2a**) yields two values, 1.364 and 1.385 Å respectively, which are much closer to the optimum distance computed for the O_2^- superoxo ion rather than to that of the O_2^{2-} peroxo species (Table 1). Moreover, the computed harmonic frequency (ω_e) in (**1**), 1 957 cm^{-1}, compares well with that computed for the free O_2^- ion (1 983 cm^{-1}). A slightly larger ν(O–O) was estimated for complex (**2a**) (2 063 cm^{-1}). As discussed above, accepting that the computed distances in the present approach are in error by ±0.05 Å, it is possible to estimate as an upper limit of the O–O distance in the aluminium adducts the values 1.41 and 1.43 Å for the monoanionic complexes (**1**) and (**2a**), respectively. These values are smaller than that observed experimentally.[13] However, considering that this latter value is affected by large uncertainty due to thermal motion, the predicted theoretical value seems to be quite acceptable.

The further addition of one electron to $[Al_2H_6(O_2)]^-$ (**2a**) results in a decrease of stability of the complex which, however, is still considerably stable when the dissociation into O_2^{2-} and AlH_3 is considered. The optimized O–O bond length in $[Al_2H_6(O_2)]^{2-}$ (**2a**), 1.483 Å (Table 2), is very close to the value found for the gas-phase O_2^{2-} molecule, despite the fact that only one negative charge is shared by the two O atoms, the second one being delocalized over the AlH_3 groups (Table 2). This further indicates that no direct and simple correlation can be established between the equilibrium bond length and the electron distribution of free and co-ordinated O_2^{n-} systems.

Two other possible co-ordination modes [(**2b**) and (**2c**)] of O_2 to Al_2H_6 have been considered, as shown in the Scheme. In these systems the O–O distance was fixed at 1.30 Å. Similarly as in complexes (**1**) and (**2a**), the ground state of the neutral form is a triplet. However, the total energy of neutral (**2b**) and (**2c**) is *ca.* 20 kcal mol^{-1} higher than that of (**2a**). Both neutral (**2b**) and (**2c**) are stabilized by the addition of one electron (Table 2), but the resulting complexes are *ca.* 40 kcal mol^{-1} less stable than the monoanionic form of complex (**2a**). Therefore, the theory confirms the preference for the bonding mode observed in complex (**1**). Of course the optimization of the O–O distance in (**2b**) and (**2c**) will improve the total energy, but this energy gain is expected to be much smaller than the energy difference between forms (**2a**) and (**2b**) or (**2a**) and (**2c**).

The mechanism of bond formation between O_2 and AlR_3 groups in complex (**1**) can be understood by analyzing the composition of the valence m.o.s. In Figure 2 a qualitative picture of the only m.o.s contributing to stabilization of the dioxygen adduct is shown. The most important one-electron levels are $1b_1$, $5a_1$, and $4b_1$. The electron density associated with the lowest m.o. ($1b_1$) corresponds to a donation from the filled π_{ux} orbital of O_2 to the empty sp^3 hybrid orbital of Al. However, since $1b_1$ has a large π_u contribution, only a small fraction of electronic charge is transferred to the AlR_3 group through this mechanism. More important in this respect is the $5a_1$ m.o. which represents the σ interaction between a lone pair on the O_a atom and the empty sp^3 hybrids of the AlR_3 fragments. The flow of

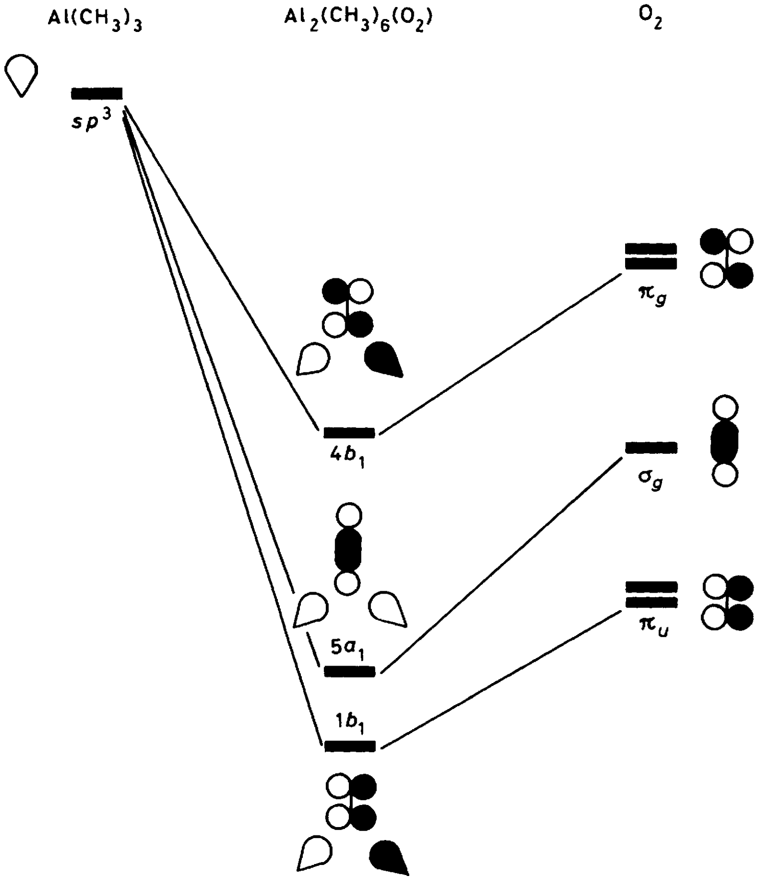

Figure 2. Qualitative character of bonding and antibonding m.o.s in $Al_2(CH_3)_6(O_2)$ (see also Figure 1)

charge from these bonding O_2 orbitals towards AlR_3 groups reduces the formal bond order within the O_2 fragment and, in consequence, produces a lengthening of the O–O distance (see Tables 1 and 2). Also, the antibonding π_g m.o. of O_2 can interact with the sp^3 hybrid of Al to form the $4b_1$ m.o. (Figure 2). This m.o. plays an important role in the anionic form since it allows delocalization of the excess of negative charge formally associated with the O_2 moiety over the other atomic centres.

This simple representation of the bond formation easily accounts for the results of the Mulliken population analysis (Table 2). In all the cases examined (singlet or triplet states of neutral and doublet state of anionic forms) the AlR_3 groups act as strong electron-accepting groups, so that the bond with the dioxygen ligand is essentially due to a donation mechanism $O_2 \longrightarrow AlR_3$. Due to the geometry of the complex, both the σ and π m.o.s of the O_2 moiety are involved in the donation mechanism. In particular, in the neutral form 0.12 and 0.20 electrons are transferred from O_2 to AlR_3 groups, in $^1A_1$ and $^3A_2$ states, respectively. An important reorganization of the electron density within the O_2 ligand is observed: both the σ and π electron clouds are strongly polarized from O_b towards O_a, so that the net charges of the complex show the sign alternation: $Al^{\delta+}$–$O_a{}^{\delta-}$–$O_b{}^{\delta+}$.

Larger $O_2 \longrightarrow AlR_3$ charge transfer occurs in the anionic form, for both σ and π donation mechanisms. In particular, according to the population analysis (Table 2), 0.59 electrons are transferred from the O_2^- group to the AlR_3 fragments, 0.18 of σ type and 0.41 of π type. The negative charge is largely delocalized over the methyl groups, but no important difference in net atomic charge on the Al atoms is observed on going from the neutral to the anionic form. A net charge of −0.41 is associated with the O_2 moiety. As previously mentioned, due to the charge shift from O_b to O_a, the negative charge is mainly localized on O_a, while the O_b atom is almost neutral.

This result is also confirmed by analysis of the electron-density difference map, obtained as the difference between the density of the anionic complex (**1**) in its equilibrium geometry and the electron densities of non-interacting neutral $Al(CH_3)_3$ and O_2 fragments. The resulting density, which integrates to one electron, is displayed in Figure 3, which shows that the negative charge is mainly localized around the O_a atom while the region around O_b is characterized by a charge depletion process.

The internal charge shift for the O_2 ligand cannot occur in complexes (**2b**) and (**2c**) for symmetry reasons and probably this is the cause of the lower stability of these two forms with respect to the co-ordination mode of (**2a**).

It is important to stress that the positive spin density in both $[Al_2(CH_3)_6(O_2)]^-$ (**1**) and $[Al_2H_6(O_2)]^-$ (**2a**) is mainly concentrated on the O_b atom (Table 3). The O_a atom carries only a small fraction of negative spin density (−0.002), due to polarization effects. The same applies to the other atoms which carry a spin density never exceeding the value ±0.002. The expected value of 0.7553 for the S^2 spin operator shows that the wavefunction is close to a pure doublet state.

The electron and spin distribution computed for the anionic form of (**2a**) are very similar to those of the corresponding methyl derivative (Table 3). This confirms that a variation in electron withdrawing properties of the R groups in AlR_3 does not significantly alter the charge and spin distribution on the co-ordinated dioxygen.

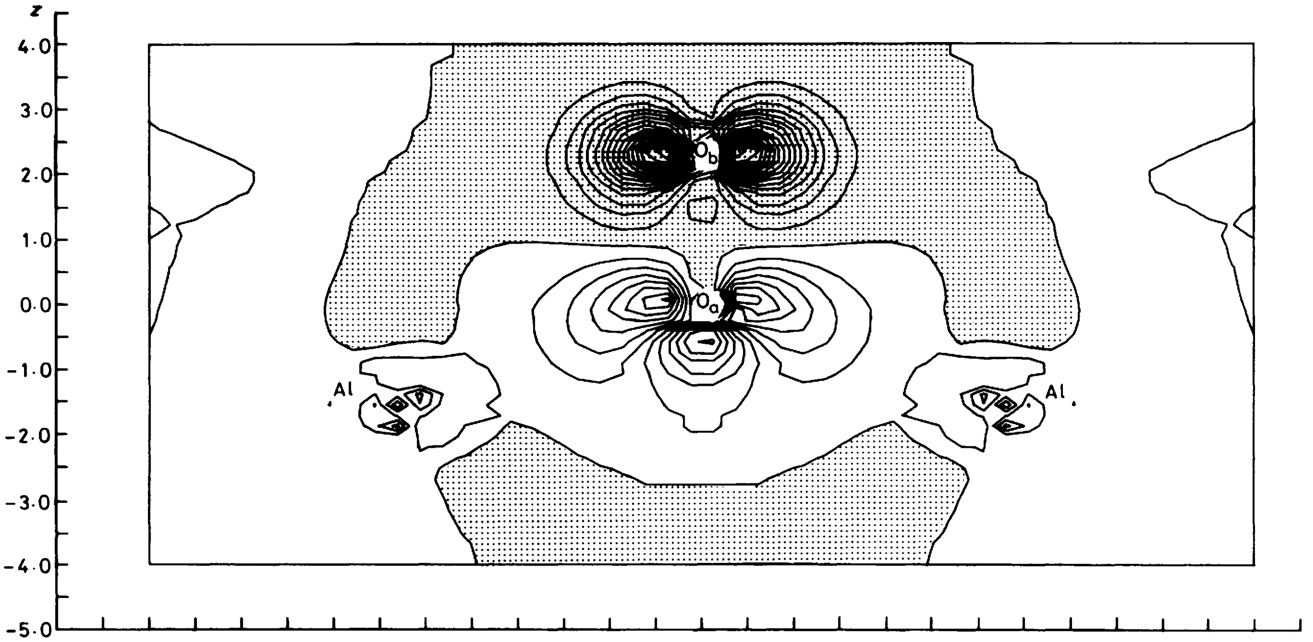

Figure 3. Electron-density difference map of $[Al_2(CH_3)_6(O_2)]^-$ determined in the Al–O–Al plane (see text). Accumulation and depletion of negative charge are represented by unfilled and filled regions, respectively; co-ordinates are in a.u.

Table 3. Spin distribution in $[Al_2(CH_3)_6(O_2)]^-$ and related compounds

Complex	Ground state	Atomic spin densities		
		O_a	O_b	Al
(1) $Al_2(CH_3)_6(O_2)$	$^3A_2$	0.65	1.22	−0.09
(1) $[Al_2(CH_3)_6(O_2)]^-$	$^2B_2$	0.00	1.01	0.00
(2a) $Al_2H_6(O_2)$	$^3A_2$	0.67	1.19	−0.10
(2a) $[Al_2H_6(O_2)]^-$	$^2B_2$	0.00	0.98	0.01
(2b) $Al_2H_6(O_2)$	$^3A_2$	0.96	0.96	−0.11
(2b) $[Al_2H_6(O_2)]^-$	$^2B_2$	0.49	0.49	−0.01
(2b) $[Al_2H_6(O_2)]^{2-}$	$^3A_1$	0.62	0.62	0.33
(2c) $Al_2H_6(O_2)$	$^3B_{2g}$	0.95	0.95	−0.11
(2c) $[Al_2H_6(O_2)]^-$	$^2B_{3g}$	0.49	0.49	−0.01
(2c) $[Al_2H_6(O_2)]^{2-}$	$^3B_{1u}$	0.62	0.62	0.33

Conclusions

It is apparent that in the $[Al_2(CH_3)_6(O_2)]^-$ complex [and in the related complexes **(2a)**—**(2c)**] the bonding mechanism is dominated by σ and π charge transfer from the co-ordinated dioxygen to the AlR_3 groups. Back-bonding donation from the AlR_3 groups to the O_2 moiety is impossible because the only suitable Al orbitals to combine with the O_2 π_g orbitals are empty in the free AlR_3 fragments. The situation is completely different from that occurring in transition-metal dioxygen adducts in which a small, but significant, metal-to-dioxygen charge transfer occurs, even in neutral systems. In this case, the back donation originates from occupied *d* orbitals of proper symmetry. Therefore, for transition elements the co-ordination of O_2 to a metal centre leads to a real activation (*i.e.* a partial reduction) of the dioxygen group.[18,19] Furthermore, the transition metal–dioxygen interaction may be interpreted as a typical spin-coupling process occurring between the two open-shell systems. Usually, the unpaired *d* electron of the metal atom pairs off with an unpaired π_g electron of O_2 to form the bond.[20] In contrast, the reaction $2Al(CH_3)_3$ $(^1A_1)$ + O_2 $(^3\Sigma_g^-)$ ⟶ $Al_2(CH_3)_6(O_2)$ $(^3A_2)$ proceeds with retention of the spin multiplicity.

In the dinuclear aluminium complex, the only evident electronic effect is that the O_2^- and O_2^{2-} species (energetically unfavoured in the free state) are stabilized through interaction with acidic aluminium centres which allow delocalization of the excess of negative charge over the rest of the molecule. On the other hand, the delocalization process acts in such a way that the co-ordinated O_2 moiety assumes an electronic situation different from that characteristic of a superoxide or peroxide species. Despite this, the theoretical values of the O–O bond length and ν(O–O) frequency of the co-ordinated O_2 ligand in complex (**1**) are very similar to those of the free O_2^- species. This only proves that no direct relation exists between these latter observables and the net charge on the O_2 ligand and suggests that care is required in deriving chemical information from the comparison of bond distances of fragments in different molecular environments.

Finally, the present results have shown that the process of electronic charge accumulation may be completely distinct and independent of the process of spin localization. In the anionic form of (**1**), the total charge on the co-ordinated O_2 amounts to 0.41, while the spin density is almost exactly equal to +1. Moreover, the negative charge is essentially localized on the O_a atom which carries no spin density, while the maximum spin density is associated with the almost neutral O_b atom. The situation closely parallels that occurring in the mononuclear transition-metal dioxygen complexes (*e.g.* Co^{II} complexes[20]) where the distribution of spin density seems to be independent of the total charge distribution. This is a very important point because a non-clear-cut distinction between the two processes (charge and spin transfer) is the main source of erroneous interpretation of the electronic mechanism of the formation of dioxygen adducts. In fact, attempts to derive information about the net charge on the co-ordinated dioxygen from e.s.r. data (obviously related only with the spin distribution) are not uncommon in the literature, while other approaches seem to be based on better theoretical grounds by making use of a definition (albeit simplified) of the m.o.s mainly involved in metal–dioxygen bonds and spin transfer processes.[9]

The present theoretical investigation further confirms that the presence of an unpaired electron does not necessarily imply the presence of a large negative charge on the co-ordinated dioxygen, and that the assignment of a formal charge to the O_2 moiety on the basis of O–O bond lengths and stretching frequencies may be seriously questionable.

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