Inorg. Chem. **2002**, *41*, 4488–4495

Inorganic Chemistry

Article

Characterization of the Side-On Coordinated Bissuperoxo Complexes of Aluminum $FAl(O_2)_2$, $ClAl(O_2)_2$, and $BrAl(O_2)_2$ with Triplet Electronic Ground States: A Combined Matrix IR and Quantum Chemical Study

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Received March 19, 2002

Matrix isolation has been used to study the photolytically induced reaction of AlX (X = F, Cl, or Br) with O_2. The peroxo and bisperoxo compounds $XAlO_2$ and $XAl(O_2)_2$ are found to be the products of these reactions. While the peroxo species $XAlO_2$ were already addressed in a separate work, we concentrate herein on the bissuperoxo complexes $XAl(O_2)_2$, which are to our knowledge the first examples of such complexes with Al centers. Our IR spectroscopic results taking in the effect of isotopic substitution ($^{16}O/^{18}O$) allied with quantum chemical calculations show that the O_2 moieties in these complexes are *side-on* coordinated, leading to an overall C_{2v} symmetry of the complexes and a spin multiplicity of 3. The O–O distance of about 1.366 Å argues for the presence of superoxide units. The force constants are, however, somewhat smaller than expected for a superoxide anion and indicate that the bonding in the complexes cannot be described simply on the basis of an ionic model. Interestingly a photoinduced intramolecular isotopic scrambling process is observed for the compounds resulting in partial conversion of the $XAl(^{16}O_2)(^{18}O)_2$ isotopomer into $XAl(^{16}O^{18}O)(^{16}O^{18}O)$. The properties of the complexes will be compared to those of complexes to transition metal centers.

Introduction

There is an ongoing interest in dioxygen complexes that is mainly stimulated by the role these compounds play as oxygen carrier systems in biology[1] and in preparative chemistry.[2−4] A remarkable variety of different structures are possible and experimentally verified for these complexes. First differentiation has to be made between superoxo and peroxo complexes, depending on whether the dioxygen unit is approximately charged negatively by one or by two e^-. Additionally, the dioxygen unit can be coordinated to either one or two metal centers. Superoxo and peroxo complexes coordinated to one metal center feature either *terminal* or *side-on* coordinated dioxygen units. In the presence of two metal centers *bridged* or *end-on* coordination represent additional possibilities. Transition metal centers with the capability to adapt various oxidation states are especially of interest. Thus, e.g., bisperoxo complexes of vanadium show insulinomimetic properties[2] and bisperoxo complexes of rhenium are involved in olefin epoxidation.[3,4] There is substantial interest in the exploration of new stable peroxo and bisperoxo complexes. The anchoring of dioxygen at metal or other surfaces was also extensively studied in the past, being of importance in the fields of heterogeneous catalysis and corrosion protection. To give just one example, it has been shown recently that the mechanism of dissociation of molecular oxygen at Cu(110) surfaces involves superoxo as well as peroxo complexes.[5]

While formal peroxo compounds of main group elements include prominent and celebrated examples such as the dioxiranes,[6] relatively little information is available about superoxo complexes featuring main group element centers. In fact it turns out that superoxo complexes to main group centers are restricted to a few cases, and almost all of the sparse available information about these species relies on

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10.1021/ic020208g CCC: $22.00

matrix isolation experiments. Thus alkali metals have been shown to form complexes of the form MO_2,[7] and Ca atoms are apparently capable of binding not only to one O_2 moiety but also to two,[8] resulting in a O_2CaO_2 complex with D_{2d} symmetry.

Herein we will show that AlX (X = F, Cl, and Br) forms a bissuperoxo complex with O_2 in an Ar matrix upon photoexcitation.[9] All three products were identified and characterized on the basis of their infrared absorptions [including the effects of isotopic substitution ($^{16}O_2$, $^{18}O_2$, $^{16}O_2/^{18}O_2$, $^{16}O^{18}O$)] and of quantum mechanical calculations [ab initio (UHF) and Density Functional Theory (DFT) calculations]. In agreement with bissuperoxo formulation, the compounds exhibit triplet electronic ground states.

Experimental Section

The subhalogenides AlX (X = F, Cl, and Br) were generated in a Knudsen-cell type graphite oven by passing CHF_3 (Messer, 99.995%), HCl (Messer, 99.98%), or HBr (Messer, 99.98%) over Al (Merck, 99.999%), heated resistively to 900 °C. Hence the AlX vapor produced in this process was co-deposited together with O_2 in an excess of argon onto a copper block kept at 13 K by means of a closed-cycle refrigerator (Leybold LB 510). Other technical details can be found elsewhere.[10] Following deposition the matrices were investigated with IR spectroscopy. Subsequently the deposits were photolyzed with UV radiation and the photolytically induced modifications again monitored with the aid of IR spectroscopy. UV photolysis ($\lambda_{max} = 254$ nm) was achieved with the aid of a low-pressure Hg lamp (Graentzel, Karlsruhe) operating at 200 W.

For IR measurements a Bruker 113v spectrometer was used, equipped with an MCT and a DTGS detector. The spectra were taken with a resolution of 0.5 cm^{-1} for measurements with the MCT detector and 1.0 cm^{-1} for measurements with the DTGS detector.

The chemicals used for the matrix reactions were purchased from the following sources and with the quoted purities: $^{16}O_2$, Messer, 99.9998%; $^{18}O_2$, Prochem, 99.1%; Ar, Messer, 99.9998%.

Quantum chemical calculations relied on the GAUSSIAN98 program package.[11] Density Functional Theory (B3LYP) and, where possible, ab initio (UHF) calculations were performed in combination with a 6-311G(d) type basis set. Normal coordinate analyses were carried out with the aid of the ASYM40 program package.[12]

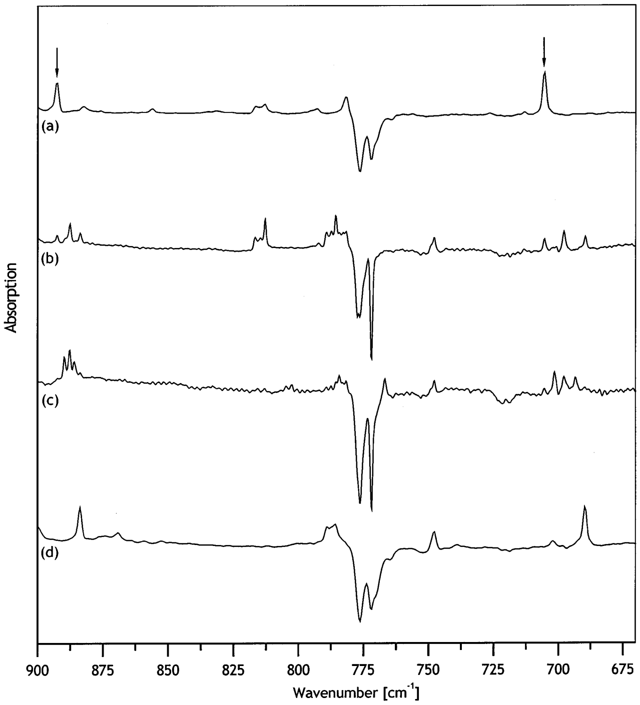

Figure 1. IR difference spectra of a solid argon matrix containing AlF and 5% O_2 after 10 min of photolysis with UV light ($\lambda_{max} = 254$ nm) minus before photolysis: (a) $^{16}O_2$, (b) $^{16}O_2/^{18}O_2$ (1:1 mixture), (c) $^{16}O_2/^{16}O^{18}O/^{18}O_2$ (1:2:1 mixture), and (d) $^{18}O_2$.

Results

The results reported in the following were accumulated in experiments with relatively high concentrations of O_2 (5% in Ar). For lower concentrations of O_2 (1% in Ar) the IR spectra are dominated by signals which were previously assigned to the compound $XAlO_2$,[13] representing formally a peroxo complex to AlX. Experiments with varying concentrations of O_2 showed that increased O_2 concentrations favor the formation of an additional species, which can be assigned, on the basis of the relative intensities of the IR signals, to the product of the reaction of AlX with *two* instead of *one* O_2 moiety. This species is in the focus of this work. The experimental results for the reactions of the AlX subhalides with 5% O_2 in Ar will be reported in turn, first for AlF, then for AlCl, and finally for AlBr.

AlF + O_2. IR spectra taken immediately upon deposition of AlF together with 5% of O_2 in Ar gave no sign of any absorption that can be assigned to a product of the reaction of AlF and O_2. However, UV photolysis brought about the appearance of new absorptions. Figure 1 shows IR spectra taken over a period of 10 min of UV photolysis ($\lambda_{max} = 254$ nm) of a matrix containing AlF and 5% O_2. Besides the signals due to the products of the reaction of AlF and $(AlF)_2$ with *one* O_2 molecule [$FAlO_2$ and $FAl(\mu\text{-}O)_2AlF$, respectively][13] the spectra contained two strong and sharp absorptions, located at 892.4 and 705.3 cm^{-1}, due to a third distinct absorber **A**. The experiments were subsequently repeated with different O_2 isotopomers. Upon $^{16}O/^{18}O$ substitution, the absorptions were shifted to 883.7 and 689.9 cm^{-1},

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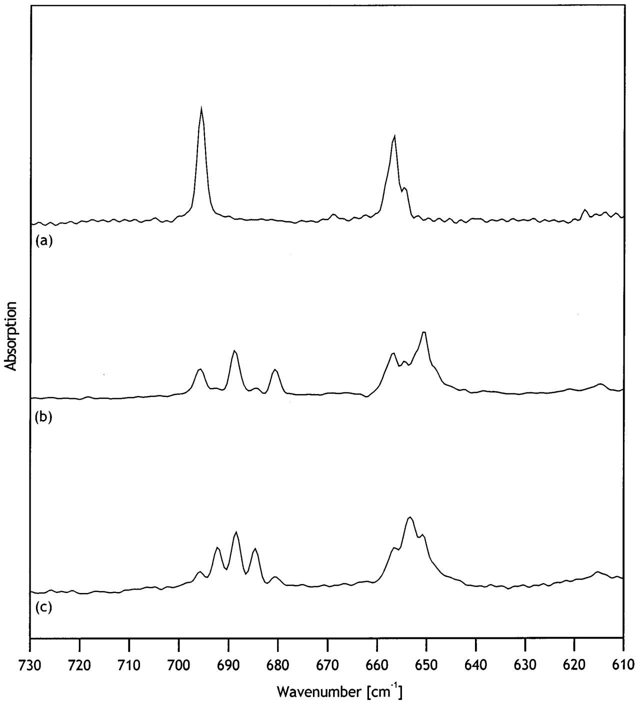

Figure 2. IR difference spectra of a solid argon matrix containing AlCl and 5% O_2 after 10 min of photolysis with UV light ($\lambda_{max} = 254$ nm) minus before photolysis: (a) $^{16}O_2$, (b) $^{16}O_2/^{18}O_2$ (1:1 mixture), and (c) $^{16}O_2/^{16}O^{18}O/^{18}O_2$ (1:2:1 mixture).

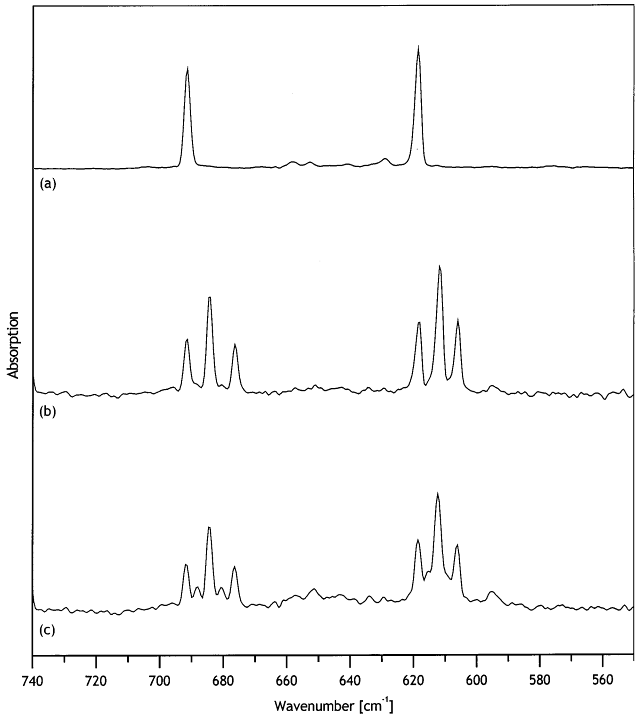

Figure 3. IR difference spectra of a solid argon matrix containing AlBr and 5% O_2 after 10 min of photolysis with UV light ($\lambda_{max} = 254$ nm) minus before photolysis: (a) 15% $^{16}O_2$, (b) 5% $^{16}O_2/^{18}O_2$ (1:1 mixture), 10 min of photolysis, and (c) same matrix as in (b) but now after 1 h of photolysis.

implying $^{16}O/^{18}O$ ratios of 1.0102 and 1.0232, respectively. In a third experiment, a 1:1 mixture of $^{16}O_2$ and $^{18}O_2$ was used. Following UV photolysis two groups of absorptions were observed to grow in, with three signals in each group. The signals of the first group were located at 892.4/887.6/883.7 cm^{-1}, those of the second group at 705.3/697.9/689.8 cm^{-1}. From this pattern it follows that two O_2 moieties are present in the absorber **A**, in agreement with the results of experiments with varying concentrations of O_2 in the matrix. Finally, the experiment was repeated with 1:2:1 mixtures of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$. Again, two groups of signals appeared, but this time with as much as five signals in each group. Hence one group consisted of signals at 892.4/889.7/887.6/885.9/883.7 cm^{-1} and the second group of signals at 705.6/701.5/697.9/693.5/689.8 cm^{-1}. This pattern indicates the presence of two pairs of equivalent O atoms in **A**.

AlCl + O$_2$. In the same way, experiments with AlCl in place of AlF gave evidence for the generation of a species **B** as the product of the photolytically induced matrix reaction of AlCl with two O_2 molecules. The IR spectra for this reaction are displayed in Figure 2. The experiments were again repeated with different isotopomers [$^{16}O_2$, $^{18}O_2$, $^{16}O_2/^{18}O_2$ mixtures (1:1), and $^{16}O_2/^{16}O^{18}O/^{18}O_2$ mixtures (1:2:1)]. Two strong signals due to **B** at 695.8 and 656.6 cm^{-1} were observed in the experiments with $^{16}O_2$. The wavelengths of the absorptions and the conditions of their appearance indicate that **B** is the Cl equivalent of product **A**. The two absorptions of **B** shifted to 680.5 and 650.4 cm^{-1} in the experiments with $^{18}O_2$, according to $^{16}O/^{18}O$ ratios of 1.0225 and 1.0095, respectively. In the experiments with $^{16}O_2/^{18}O_2$ mixtures, two triplets were observed, located at 695.8/688.8/680.5 and 656.6/654.6/650.4 cm^{-1}.[14] The observation of a triplet pattern again shows the presence of more than two oxygen atoms in the molecule. Finally, the experiment was repeated but with a 1:2:1 mixture of $^{16}O_2/^{1618}O/^{18}O_2$, and in this experiment again two groups of signals were observed, the positions of the signals being 695.8/692.2/688.3/684.6/680.5 cm^{-1} for one group and 656.6/653.6/652.7/650.5 cm^{-1} for the other group. Both groups should consist of five signals. However, the signals of the group near 650 cm^{-1} are so close together that it proved impossible to see all but only four of the signals with certainty. Nevertheless, the sum of all results obtained for the different isotopomers of **B** argues strongly for the presence of two equivalent dioxygen pairs in the molecule.

AlBr + O$_2$. The photoinduced matrix reaction of AlBr with two molecules of dioxygen followed a similar pattern as observed before in the experiments with AlF and AlCl. The spectra are reproduced in Figure 3 and indicate the formation of a species **C** upon UV photolysis. Two strong absorptions at 691.6 and 618.3 cm^{-1} in the experiments with $^{16}O_2$ can be assigned to this species, which represents in all certainty the Br equivalent of **A** and **B**. In the $^{18}O_2$ experiments, these two absorptions appeared at 676.2 and 605.7 cm^{-1}, bearing thus $^{16}O/^{18}O$ ratios of 1.0228 and 1.0208. The experiment with $^{16}O_2/^{18}O_2$ mixtures again points to the presence of more than two oxygen atoms in the molecule. In this experiment, two triplet features at 691.6/683.9/676.2 and 618.3/611.3/605.7 cm^{-1} were observed. Finally, there

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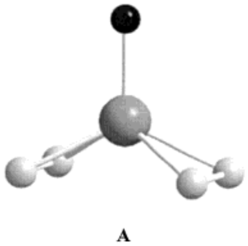
(14) The signal at 654.6 cm^{-1} is close to one of the absorptions of $HAlCl_2$, which is also formed in smaller yields in the course of the reaction (see ref 16).

were, as anticipated, two groups attributable to the molecule in the experiments with 1:2:1 mixtures of $^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$. These were located at 691.6/688.2/683.9/680.6/676.2 and 618.3/615.7/611.3/605.7 cm^{-1} and give support to the presence of two pairs of equivalent oxygen atoms in the molecule.

Interestingly, the $^{16}O^{18}O$ equivalent of product **C** can also be formed when a matrix containing AlBr and a mixture of $^{16}O_2$ and $^{18}O_2$ is exposed to a prolonged period of UV photolysis (1 h). On the other hand, control experiments of a matrix containing only dioxygen in the absence of any AlBr gave no sign of any photolytically induced production of O_3. Thus it is unlikely that the effect of photolysis is to produce ^{16}O and ^{18}O atoms which then recombine to give $^{16}O^{18}O$. The experiments in fact clearly show that product **C** in its ($^{16}O_2$)($^{18}O_2$) form is the precursor to the ($^{16}O^{18}O$)($^{16}O^{18}O$) isotopomer. The IR signals due to **C** in its ($^{16}O_2$)($^{18}O_2$) form are developed completely after 10 min of photolysis (see Figure 3b). Further photolysis leads to the decrease of the absorptions attributable to the ($^{16}O_2$)($^{18}O_2$) guise of **C** and the simultaneous appearance of the signals due to its ($^{16}O^{18}O$)($^{16}O^{18}O$) version. All this argues for the intramolecular nature of the observed isotopic scrambling process.

Discussion

In the following it will be shown on the basis of the experimental results as well as quantum chemical calculations that species **A**, **B**, and **C** can be identified as the first known examples of bissuperoxo complexes of aluminum, namely $FAl(O_2)_2$, $ClAl(O_2)_2$, and $BrAl(O_2)_2$, all exhibiting triplet electronic ground states.



A

Table 1. Comparison between the IR Spectra Observed and Calculated [Wavenumber in cm^{-1}, with Intensities (in km mol^{-1}) Given in Parentheses] for $FAl(^{16}O_2)_2$/$FAl(^{18}O_2)_2$/$FAl(^{16}O^{18}O)_2$

$FAl^{16}O_4$		$FAl^{18}O_4$		$FAl^{16}O_2{}^{18}O_2$		
obsd	calcd[a]	obsd	calcd[a]	obsd	calcd[a]	assign
c	1138.6 (2)	c	1074.0 (3)	c	1136.8 (5)	$\nu_1(a_1)$
892.4	900.6 (151)	883.7	898.9 (149)	887.6	899.8	$\nu_2(a_1)$
c	506.9 (9)	c	486.0 (10)	c	496.2 (10)	$\nu_3(a_1)$
b	186.1 (20)	b	178.9 (18)	b	182.5 (19)	$\nu_4(a_1)$
c	404.7 (0)	c	380.6 (0)	c	390.8 (0)	$\nu_5(a_2)$
b	69.9 (0)	b	65.9 (0)	b	67.8 (0)	$\nu_6(a_2)$
c	490.6 (1)	c	467.2 (2)	c	479.9 (1)	$\nu_7(b_1)$
c	242.5 (50)	c	238.3 (38)	c	240.2 (49)	$\nu_8(b_1)$
b	176.0 (0.01)	b	166.9 (0.03)	b	171.4 (0.03)	$\nu_9(b_1)$
c	1135.1 (12)	c	1071.0 (9)	c	1072.5 (6)	$\nu_{10}(b_2)$
705.3	714.3 (179)	689.9	694.2 (175)	697.9	701.5 (177)	$\nu_{11}(b_2)$
c	205.3 (26)	c	199.6 (24)	c	201.8 (24)	$\nu_{12}(b_2)$

[a] C_{2v} symmetry. Geometry (bond lengths in Å, angles in deg): Al−F 1.6552; Al−O 1.8562; O−O 1.3673; O−Al−O 43.2. [b] Out of range of detection. [c] Too weak to be detected or IR silent.

$FAl(O_2)_2$, A. As already mentioned, species **A** can be assigned to the product of the reaction of AlF with two O_2 moieties and therefore most likely exhibits the sum formula $FAlO_4$. Our DFT calculations led to a global minimum structure with C_{2v} symmetry and a triplet electronic ground state for such a molecule. The Al−F distance amounts to 1.6552 Å, a typical value for Al−F bonds of Al(III) species (e.g. OAlF 1.623 Å,[15,16] $FAlO_2$ 1.6430 Å[13]). The 1.3673 Å O−O bond length is significantly shorter than that found in $FAlO_2$ (1.6637 Å),[13] but is in good agreement with the distance expected for the free superoxide anion O_2^- (1.3519 Å according to calculations relying on the B3LYP method). The O−Al−O angle (with the two O atoms being of the same O_2 unit) exhibits a value of 43° and is thus smaller than the value found in $FAlO_2$ (58.4°).[13] As a consequence, the Al−O distance increases from 1.7006 Å in $FAlO_2$[13] to 1.8562 Å in $FAl(O_2)_2$. The calculated wavenumbers for the three isotopomers $FAl(^{16}O_2)_2$, $FAl(^{18}O_2)_2$, and $FAl(^{16}O_2)(^{18}O_2)$ are given in Table 1, together with the observed values. The calculations predict two of the 12 modes to carry sufficient intensity to guarantee their detection subject to the molecule being formed in sufficient yields. This is in agreement with the experiments which give clear evidence of two strong absorptions and the observed wavenumbers are in pleasing agreement with the calculated ones for these two modes. However, the calculations predict an ^{16}O/^{18}O isotopic shift of only 1.7 cm^{-1} for the $\nu_2(a_1)$ mode, while the experimentally observed shift amounts to 8.7 cm^{-1}. It will be shown below that the calculated shifts for $ClAl(O_2)_2$ and $BrAl(O_2)_2$ are in much better agreement with the experimentally observed values. One possible explanation for this deviation in the case of $FAl(O_2)_2$ is the interaction between the $\nu_2(a_1)$ mode and the [$\nu_1(a_1)-\nu_4(a_1)$] combination mode. For the ^{16}O isotopomer, this combination mode has a wavenumber of 952.5 cm^{-1}, being therefore more than 50 cm^{-1} higher than the wavenumber calculated and observed for the $\nu_2(a_1)$ mode. However, in the case of the ^{18}O isotopomer, the waveumber of the combination mode lies very close (at 895.1 cm^{-1}) to that of the $\nu_2(a_1)$ mode (difference of only 3.8 cm^{-1}) and therefore the interaction between the two modes should be substantial leading to an increase of the observed wavenumber for one mode and a decrease for the other mode. The combination mode has to occur at a slightly higher wavenumber than the $\nu_2(a_1)$ mode to give a shift in the right direction. With due allowance to the usual amount of computational inaccuracy (5−10 cm^{-1} for wavenumbers in the considered range) it is likely that the combination mode has in reality a wavenumber slightly higher than that of the $\nu_2(a_1)$ mode.

Unfortunately, the vibrational analysis of the molecule with ab initio MP2 methods failed.[17] It was, however, possible to calculate the geometry and the vibrational properties of $FAl(O_2)_2$ on the HF level of theory (applying a 6-311G* type basis). These calculations again found a triplet electronic

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ground state, but now slightly distorted from C_{2v} symmetry, resulting in only C_2 symmetry. Thus one of the O atoms of each O_2 moiety exhibited an Al−O distance of 1.8798 Å, while the other one exhibited a smaller distance of 1.7849 Å. Other geometrical parameters (bond lengths in Å, angles in deg) are the following: Al−F 1.6327, O−O 1.3030, F−Al−O 112.7/120.4, O−Al−O 40.6 (with the O atoms being from the same O_2 unit). As expected, the frequency calculation from the HF method resulted in wavenumbers higher than those calculated with DFT methods. Thus the following frequencies were calculated for $FAl(^{16}O_2)_2$ [in cm^{-1}, with symmetry assignment and intensity (in km mol^{-1}) in parentheses]: 1329.3 (*b*, 101), 1320.0 (*a*, 9), 954.1 (*a*, 185), 797.1 (*b*, 273), 569.8 (*a*, 6), 388.2 (*b*, 51), 300.9 (*a*, 7), 220.0 (*b*, 33), 211.8 (*b*, 22), 199.8 (*a*, 24), 175.2 (*b*, 2), 124.2 (*a*, 0.09). Unfortunately all attempts to calculate the structure and frequencies with the MP2 method failed.

To obtain a better understanding of the bonding in the peroxo complex and to get estimates for the force constants a normal coordinate analysis was performed. The following nonnormalized symmetry coordinates were used in this analysis for all the species of the type $XAl(O_2)_2$: S_1, $r(O^1-O^2) + r(O^3-O^4)$; S_2, $r(Al-F)$; S_3, $r(Al-O^1) + r(Al-O^2) + r(Al-O^3) + r(Al-O^4)$; S_4, $r(O^1-O^3) + r(O^2-O^4)$; S_5, $r(Al-O^1) + r(Al-O^2) - r(Al-O^3) - r(Al-O^4)$; S_6, $\delta(F-Al-O^1) + \delta(F-Al-O^2) - \delta(F-Al-O^3) - \delta(F-Al-O^4)$; S_7, $r(Al-O^1) + r(Al-O^4) - r(Al-O^2) - r(Al-O^3)$; S_8, $\delta(F-Al-O^1) + \delta(F-Al-O^4) - \delta(F-Al-O^2) - \delta(F-Al-O^3)$; S_9, $r(O^1-O^3) - r(O^2-O^4)$; S_{10}, $r(O^1-O^2) - r(O^3-O^4)$; S_{11}, $r(Al-O^1) + r(Al-O^3) - r(Al-O^2) - r(Al-O^4)$; S_{12}, $\delta(F-Al-O^1) + \delta(F-Al-O^3) - \delta(F-Al-O^2) - \delta(F-Al-O^4)$ (with O^1, O^2 and O^3, O^4 belonging to the same O_2 unit). Where available, experimental data were used for the analysis. For the not-observed modes calculated wavenumbers were used. A force constant $f(O-O)$ of 585 N m^{-1} was derived. Thus the force constant $f(O-O)$ is significantly smaller than that for KO_2[18] (680 N m^{-1}) and of the hypothetical free O_2^- anion (660 N m^{-1}). This argues against a simple ionic description of the molecule that appears to be adequate if only the O−O distances are taken into consideration. A possible explanation is that the O−Al−O angle potential weakens the $f(O-O)$ force constant. The O−Al−O angle potential certainly has its energy minimum at much higher values of the O−Al−O angle than the 43.2° found in the $XAl(O_2)_2$ complex. The force constants $f(Al-F)$ and $f(Al-O)$ of $FAl(O_2)_2$ amount to 493 [cf. $f(Al-F) = 500$ N m^{-1} in AlF_3[19]] and 193 N m^{-1}. Thus the $f(Al-O)$ force constant in $FAl(O_2)_2$ is significantly smaller that that derived for $FAlO_2$ (506.7 N m^{-1}), in line with the different electronic structures anticipated for these two species. The normal coordinate analysis also provides an estimate for the force constant for O^1-Al-O^3 bending, now with the two O atoms stemming from different O_2 moieties. With 54 N m^{-1} this force constant turns out to be rather small.

Table 2. Comparison between the IR Spectra Observed and Calculated [Wavenumbers in cm^{-1}, with Intensities (in km mol^{-1}) Given in Parentheses] for $ClAl(^{16}O_2)_2/ClAl(^{18}O_2)_2/ClAl(^{16}O^{18}O)_2$

$ClAl^{16}O_4$		$ClAl^{18}O_4$		$ClAl^{16}O_2{}^{18}O_2$		
obsd	calcd[a]	obsd	calcd[a]	obsd	calcd[a]	assign
c	1140.3 (1)	*c*	1075.2 (2)	*c*	1138.3 (4)	$\nu_1(a_1)$
656.6	656.8 (204)	650.4	649.2 (204)	653.6	652.2 (202)	$\nu_2(a_1)$
c	427.0 (3)	*c*	412.1 (2)	*c*	499.5 (2)	$\nu_3(a_1)$
b	177.3 (19)	*b*	170.3 (18)	*b*	173.9 (19)	$\nu_4(a_1)$
c	397.3 (0)	*c*	373.7 (0)	*c*	383.7 (0.1)	$\nu_5(a_2)$
b	66.1 (0)	*b*	62.3 (0)	*b*	64.1 (0.002)	$\nu_6(a_2)$
c	483.4 (1)	*c*	460.8 (1)	*c*	473.2 (1)	$\nu_7(b_1)$
c	211.7 (29)	*c*	205.9 (28)	*c*	208.3 (28)	$\nu_8(b_1)$
b	162.6 (2)	*b*	154.5 (2)	*b*	158.6 (2)	$\nu_9(b_1)$
c	1136.4 (7)	*c*	1072.1 (7)	*c*	1073.6 (5)	$\nu_{10}(b_2)$
695.8	700.5 (146)	680.5	681.8 (141)	688.8	689.8 (144)	$\nu_{11}(b_2)$
b	149.7 (10)	*b*	144.9 (10)	*b*	147.2 (10)	$\nu_{11}(b_2)$

[a] C_{2v} symmetry. Geometry (bond lengths in Å, angles in deg): Al−Cl 2.0786; Al−O 1.8614; O−O 1.3657; O−Al−O 43.0. [b] Out of range of detection. [c] Too weak to be detected or IR silent.

The analysis of the vibrational modes shows that the degree of mode coupling is substantial. Therefore it proved impossible to describe the vibrational modes adequately. The mode coupling also indicates that the species cannot be simply described as an ionic species of the form $FAl^{2+}(O_2^-)_2$.

$ClAl(O_2)_2$, B. Like **A**, species **B** is the product of the reaction of AlCl with two O_2 molecules and should thus exhibit the sum formula $ClAlO_4$. With Al−O and O−O distances of 1.8611 and 1.3657 Å the energy minimum geometry of $ClAlO_4$ as calculated with DFT methods resembles that of $FAl(O_2)_2$. The molecule again prefers a triplet electronic ground state. The Al−Cl distance (2.0785 Å) is in agreement with the distances adapted in other Al(III) species (e.g. $HAlCl_2$ 2.096[20,21]). Table 2 includes a comparison between the wavenumbers observed and calculated for such a molecule in various isotopic forms. This comparison leaves little doubt that **B** indeed is the bissuperoxo complex $ClAl(O_2)_2$. Again the experiments succeeded in detecting the two most intense absorptions. Our normal coordinate analysis yielded the following force constants (values in N m^{-1}): $f(Al-Cl)$ 368; $f(O-O)$ 439; and $f(Al-O)$ 274. The force constant $f(Al-Cl)$ in $ClAl(O_2)_2$ is somewhat larger than that of $ClAlO_2$ (272 N m^{-1})[13] and $AlCl_3$ (274 N m^{-1})[22] and the $f(Al-O)$ force constant is somewhat larger than that of the F-derivative $FAl(O_2)_2$. On the other hand the $f(O-O)$ force constant comes out to be smaller than that of $FAl(O_2)_2$. A detailed evaluation of the electronic structure of the compound is necessary to give a satisfying explanation for these alterations. However, more sophisti-

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(17) The geometry optimization using the MP2 method in combination with a SVP type basis set resulted in the following bond distances (in Å): Al−F 1.6484, Al−O 1.8644/1.8646, O−O 1.4312 for $FAl(O_2)_2$, Al−Cl 2.0691, Al−O 1.8696/1.8718, O−O 1.3924 for $ClAl(O_2)_2$, and Al−Br 2.2166, Al−O 1.8731/1.8732, O−O 1.4318 for $BrAl(O_2)_2$. Thus the O−O bond distance is almost 0.1 Å longer than with DFT according to MP2. The MP2 calculations failed to predict reasonable wavenumbers of the vibrational modes. Thus one of the vibrational modes was calculated to occur above 2000 cm^{-1} with an intensity of some 10 000 km mol^{-1}. Calculations with MP3 caused similar problems. One reason for the problems of the calculations might be the difficulty in treating the ionic and covalent contributions to the bonding adequately. Ab initio methods tend to overestimate ionic contributions.

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Table 3. Comparison between the IR Spectra Observed and Calculated [Wavenumbers in cm^{-1}, with Intensities (in km mol^{-1}) Given in Parentheses] for $BrAl(^{16}O_2)_2$/$BrAl(^{18}O_2)_2$/$BrAl(^{16}O^{18}O)_2$

$BrAl^{16}O_4$		$BrAl^{18}O_4$		$BrAl^{16}O_2{}^{18}O_2$		
obsd	calcd[a]	obsd	calcd.[a]	obsd	calcd[a]	assign
c	1139.9 (1)	*c*	1074.8 (2)	*c*	1137.7 (4)	$\nu_1(a_1)$
618.3	616.5 (185)	605.7	604.9 (128)	611.3	610.1 (186)	$\nu_2(a_1)$
c	353.0 (17)	*c*	341.2 (13)	*c*	347.1 (15)	$\nu_3(a_1)$
b	163.0 (15)	*b*	156.1 (14)	*b*	159.7 (14)	$\nu_4(a_1)$
c	391.7 (0)	*c*	368.5 (0)	*c*	378.3 (0.1)	$\nu_5(a_2)$
b	67.0 (0)	*b*	63.2 (0)	*b*	65.0 (0.0001)	$\nu_6(a_2)$
c	478.0 (1)	*c*	455.8 (1)	*c*	468.1 (1)	$\nu_7(b_1)$
c	206.8 (21)	*c*	200.6 (21)	*c*	203.4 (21)	$\nu_8(b_1)$
b	155.3 (3)	*b*	147.6 (2)	*b*	151.5 (3)	$\nu_9(b_1)$
c	1135.4 (7)	*c*	1071.3 (7)	*c*	1071.9 (5)	$\nu_{10}(b_2)$
691.6	691.3 (133)	676.2	674.2 (128)	683.9	682.0 (131)	$\nu_{11}(b_2)$
b	129.8 (6)	*b*	124.8 (6)	*b*	127.2 (6)	$\nu_{12}(b_2)$

[a] C_{2v} symmetry. Geometry (bond lengths in Å, angles in deg): Al−Br 2.2333; Al−O 1.8650; O−O 1.3655; O−Al−O 43.0. [b] Out of range of detection. [c] Too weak to be detected or IR silent.

cated theoretical methods should be used for such a study, which is certainly beyond the scope of this work. It is well-known that bonding in the subhalides AlF and AlCl differs to a large extend [23] and therefore it is not surprising that differences are also monitored for their bissuperoxo complexes.

$BrAl(O_2)_2$, C. On the basis of the experiments **C** can be assigned to the Br equivalent $BrAl(O_2)_2$ of $FAl(O_2)_2$ and $ClAl(O_2)_2$. Table 3 includes the calculated and observed wavenumbers for $BrAl(O_2)_2$ in various isotopic versions. The agreement between experimental and calculated results is extremely pleasing. According to our calculations, the molecule again exhibits C_{2v} symmetry. The following bond lengths (in Å) and angles (in deg) were obtained: Al−Br 2.0786, Al−O 1.8614, O−O 1.3657, and O−Al−O 43.0. Thus the Al−Br bond length is in agreement with the values obtained for other Al(III) species (e.g. $HAlBr_2$ 2.260 Å) and the O−O distance is close to the value calculated for O_2^- (1.352 Å). With the help of normal coordinate analysis the following force constants were obtained for $BrAl(O_2)_2$ (values given in N m^{-1}): *f*(Al−Br) 429, *f*(O−O) 521, and *f*(Al−O) 195. Thus the *f*(O−O) and *f*(Al−O) force constants for $BrAl(O_2)_2$ are in good agreement with the values deduced for $FAl(O_2)_2$.

Comparison with Related Systems. Superoxo complexes to transition metal centers have been investigated extensively in the past, major methods of interrogation being IR and UV/Vis spectroscopy and, where possible, X-ray diffraction. The structures of these complexes show a distinct mutuality, and the O_2^- unit can be coordinated either by one or by two metal centers. *Side-on* coordination was observed e.g. in the complexes $Tp'Co(O_2)$[24] and $(Tp')_2Sm(O_2)$[25] [Tp′ = hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borate]. The compound {(*meso*-Me_6-[14]aneN_4)($CH_3CNRhOO$}{CF_3SO_3}$_2$ features a superoxo ligand with terminal coordination to the Rh center.[26] An example of a O_2^- unit bridging two metal centers is provided by the complex $Co_2(\mu\text{-}OH)(\mu\text{-}O_2)(\mu\text{-}NH_2)(NH_3)_6(NO_3)_3\cdot 1.25H_2O$, the structure of which has recently been reinvestigated with X-ray diffraction.[27] Finally, quantum chemical calculations suggest the presence of an *end-on* coordinated O_2^- unit in the mixed valence Fe(II)/Fe(III) complex $(H_2O)_2(NH_2)Fe(\eta^2\text{-}HCOO)_2Fe(NH_2)(H_2O)(O_2)$,[28] just to name a few examples reported recently.

Table 4. Geometric Parameters (O−O and M−O Distances, Values in Å) of Some Complexes to O_2

compd	O−O distance	M−O distance	coord	ref
NaO_2	1.3599	2.1506	side-on	7, *b*
$Ca(O_2)_2$	1.344	2.226	side-on	8
AlO_2	1.6393	1.7296	side-on	30, *b*
$FAl(O_2)_2$	1.3673	1.8562	side-on	*b*
$ClAl(O_2)_2$	1.3657	1.8614	side-on	*b*
$BrAl(O_2)_2$	1.3655	1.8650	side-on	*b*
O_2^-	1.3519			*b*
$(H_2O)_2(NH_2)Fe(\eta^2\text{-}HCOO)_2$ $Fe(NH_2)(H_2O)(O_2)$	1.390	2.247	end-on	27
{(*meso*-Me_6-[14]aneN_4) (CH_3CN)RhOO}{CF_3SO_3}$_2$	1.306	2.005	terminal	25
$Co_2(\mu\text{-}O_2)(\mu\text{-}NH_2)$- $(NH_3)_6(NO_3)_3\cdot 1.25H_2O$	1.340	1.872/1.887	bridged	26
$Tp'Cp(O_2)$[a]	1.262	1.816/1.799	side-on	23
$(Tp')_2Sm(O_2)$	1.319	2.329/2.321	side-on	24

[a] Tp′ = hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borate. [b] Calculated in this work.

As already mentioned, superoxo complexes to main group centers are restricted to a few cases. Alkali metals form complexes of the form MO_2[29] for which quantum chemical calculations predict an O−O distance of 1.36 Å. Matrix experiments indicate that alkali earth atoms are capable of forming a 1:2 complex with O_2,[30] resulting in a O_2MO_2 species with D_{2d} symmetry. For O_2CaO_2, quantum chemical calculations predict O−O and Ca−O distances of 1.344 and 2.226 Å, respectively. Like $XAl(O_2)_2$, this species exhibits a triplet electronic ground state.

Al atoms, when isolated together with O_2 in an inert-gas matrix, form an AlO_2 complex.[31] However, the experimental and theoretical results accumulated for this species show that it contains a long O−O distance of 1.64 Å and a short Al−O distance of 1.73 Å. These values are almost identical with those found in $XAlO_2$ (X = F, Cl, or Br) (e.g., 1.64 and 1.71 Å, respectively, in $FAlO_2$). Thus the unpaired electron of AlO_2 appears to be located near the Al atom rather than near the dioxygen unit.

Table 4 includes the O−O and M−O distances for several studied superoxo complexes to transition and main group

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(23) For an evaluation of the AlF bond properties, see for example: Schnöckel, H.; Mehner, T.; Plitt, H. S.; Schunck, S. *J. Am. Chem. Soc.* **1989**, *111*, 4578.

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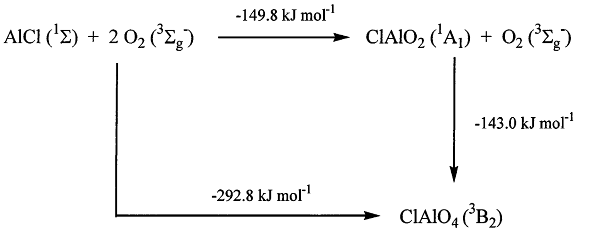
Table 5. Calculated Energies (Values Given in kJ mol^{-1}) for Several Possible Reaction Steps Leading to the Bissperoxo Complexes $FAl(O_2)_2$, $ClAl(O_2)_2$, and $BrAl(O_2)_2$ in Their $^3B_2$ Electronic Ground States

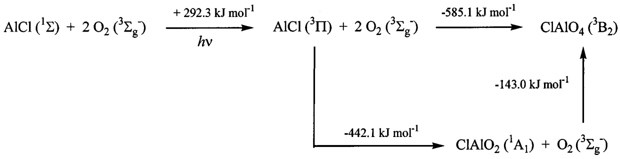
reactants	product	reaction energy	product	reaction energy
AlF ($^1\Sigma$) + $2O_2$ ($^3\Sigma_g{}^-$)	$FAlO_2$ ($^1A_1$) + O_2 ($^3\Sigma_g{}^-$)	−140.3	$FAl(O_2)_2$ ($^3B_2$)	−292.7
AlCl ($^1\Sigma$) + $2O_2$ ($^3\Sigma_g{}^-$)	$ClAlO_2$ ($^1A_1$) + O_2 ($^3\Sigma_g{}^-$)	−149.8	$ClAl(O_2)_2$ ($^3B_2$)	−292.8
AlBr ($^1\Sigma$) + $2O_2$ ($^3\Sigma_g{}^-$)	$BrAlO_2$ ($^1A_1$) + O_2 ($^3\Sigma_g{}^-$)	−153.4	$BrAl(O_2)_2$ ($^3B_2$)	−291.7
AlF ($^3\Pi$) + $2O_2$ ($^3\Sigma_g{}^-$)	$FAlO_2$ ($^1A_1$) + O_2 ($^3\Sigma_g{}^-$)	−474.3	$FAl(O_2)_2$ ($^3B_2$)	−626.6
AlCl ($^3\Pi$) + $2O_2$ ($^3\Sigma_g{}^-$)	$ClAlO_2$ ($^1A_1$) + O_2 ($^3\Sigma_g{}^-$)	−442.1	$ClAl(O_2)_2$ ($^3B_2$)	−585.1
AlBr ($^3\Pi$) + $2O_2$ ($^3\Sigma_g{}^-$)	$BrAlO_2$ ($^1A_1$) + O_2 ($^3\Sigma_g{}^-$)	−436.0	$BrAl(O_2)_2$ ($^3B_2$)	−495.6

element centers. While transition metal complexes show a remarkable variation of coordinational modes (*side-on*, *end-on*, *terminal*, and *bridging* coordination), the few known main group element superoxo complexes are generally *side-on* coordinated in their energy minimum structures. The O−O distances deduced for the $XAl(O_2)_2$ compounds described herein are in good agreement to those found for other superoxo complexes. However, the force constants derived from our normal coordinate analysis show that arguments which are simply based on bond distances have to be treated with caution.

Reaction Pathway. The quantum chemical calculations clearly show that the $XAl(O_2)_2$ bissuperoxo complexes exhibit triplet electronic ground states. The formation of $XAl(O_2)_2$ can proceed either in a one-step process starting with AlX and two O_2 moieties or in a two-step process leading first to $XAlO_2$ which then reacts with a second O_2 molecule to give $XAl(O_2)_2$ (reaction sequence 1). The one-step mechanism and the first step (reaction of AlX with O_2) of the two-step pathway should both be spin-forbidden for the molecules in their electronic ground states. However, they become spin-allowed upon photolysis. It has been shown previously that UV -photolysis (λ_{max} = 254 nm) brings about excitation of AlCl into its lowest energy triplet electronic state, $^3\Pi$. Thus AlCl reacts e.g. with HCl upon activation with UV light.[16] According to our calculations, the $^3\Pi$ electronic states of AlF, AlCl, and AlBr have energies 334.0, 292.3, and 282.6 kJ mol^{-1} higher than those of their $^1\Sigma$ electronic ground states (see sequence 2). Experiments with O_2 isolated in the absence of any other reactants in an Ar matrix showed that our selected UV photolysis at λ_{max} = 254 nm does not cause excitation of the O_2 molecule leading to bond cleavage. The IR spectra gave no sign of O_3 which should be formed from reaction of O atoms with O_2 in the case of photolytical production of O atoms. Table 5 summarizes the energies calculated for the possible steps of the reaction pathways.



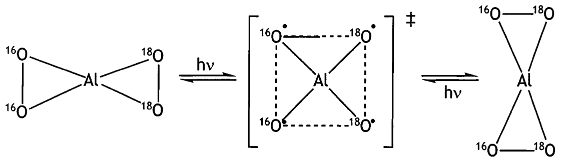
(1)



(2)

Mechanism of the Isotopic Scrambling of $BrAl(O_2)_2$. One of the striking results is the isotopic scrambling observed for the $XAl(^{16}O_2)(^{18}O_2)$ species upon photolysis, which leads to the formation of $XAl(^{16}O^{18}O)(^{16}O^{18}O)$ on increased photolysis times. Since the total quantity of $XAl(O_2)_2$ molecules in all possible isotopic forms does not increase between 10 min and 1 h of photolysis (see Figure 3b,c), the isotopic scrambling most likely represents an intramolecular process. On the other hand, an intermolecular scrambling process in the course of the reaction of $XAlO_2$ with O_2 can be ruled out.

A possible geometry for the transition state is illustrated in eq 3. The halogen atoms are omitted for the sake of clarity of presentation. We have also thought of calculating possible structures for the transition state. Using simple hybrid DFT (B3LYP) methods, we obtained for the Br compound a structure with O−O, Al−O, and Al−Br distances of 2.4738, 1.7923, and 2.3556 Å, respectively, and a Br−Al−O angle of 130.0°, in calculations in which the overall symmetry was restricted to C_{4v} and with a spin multiplicity of 3. Calculations were also performed for a singlet electronic state and here the O−O, Al−O, and Al−Br distances and Br−Al−O angle at the energy minimum geometry were calculated to be 1.9903, 1.8369, and 2.2270 Å and 102.6°, respectively. The singlet electronic state has an energy about 50 kJ mol^{-1} higher than that of the triplet state. However, the energy gap between the C_{2v} triplet ground state of $BrAl(O_2)_2$ and the calculated possible transition state with C_{4v} symmetry in its triplet electronic state amounts to about 700 kJ mol^{-1}, a value too high to be accessible with the UV photolysis used in these studies. Certainly the level of theory in our calculations is not adequate to describe the electronic properties of this transition state, which should be treated with multireference methods and for which singlet, triplet, and pentet multiplicities have to be taken into consideration. Nevertheless, the prediction of such a transition state seems reasonable on the basis of our calculations.



(3)

Conclusions

AlF, AlCl, and AlBr are shown to react on photoactivation in a solid Ar matrix at temperatures of 12 K with O_2 to give the bissuperoxo complexes $FAl(O_2)_2$,$ClAl(O_2)_2$, and $BrAl(O_2)_2$, respectively, representing the first examples of superoxo-like coordiated O_2 units to an aluminum center. The complexes are characterized experimentally by their IR spectra (including various isotopomers) and theoretically by quantum chemical calculations. The results show that the compounds exhibit triplet electronic ground states with a C_{2v} symmetric global minimum structure, in which the O_2 units are *side-on* coordinated to the Al center. The O−O distances of about 1.37 Å are in good agreement with the distances found in other known superoxo complexes. Normal coordinate analysis of the vibrational modes indicates, however, that the bonding cannot be described by a purely ionic model. Strikingly, the $XAl(^{16}O_2)(^{18}O_2)$ isopomer (X = F, Cl, or Br) can be photolytically converted in an intramolecular process into the $XAl(^{16}O^{18}O)(^{16}O^{18}O)$ isotopomer. A transition state with C_{4v} symmetry is predicted for this process.

Acknowledgment. The authors thank Professor Ahlrichs for fruitful discussions and the Deutsche Forschungsgemeinschaft for the award of an Habilitation grant to H.-J.H.

IC020208G