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The First End-On Bonded Superoxo Complexes of Ga and In: The Oxygen-Rich Compounds GaO_4 and InO_4

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Dedicated to Prof. Hansgeorg Schnöckel on the occasion of his 65th birthday

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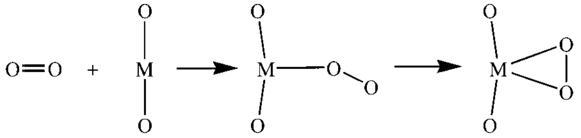
We report the first sighting and characterization of the oxygen-rich molecules GaO_4 and InO_4, being the products of a three-step process taking place in an Ar matrix. This process includes (i) reaction of Ga or In atoms (M) with one dioxygen molecule to give the cyclic superoxo complex MO_2, (ii) photoisomerization into linear OMO by the action of UV light, and (iii) reaction of linear OMO with an additional O_2 molcule. The molecules can be described as end-on bonded superoxo complexes $OMO(O_2)$. On the basis of the observed isotopic data the O–Ga–O angle can be estimated to be ca. 165°. In addition to the experimental studies, quantum chemical calculations were performed to achieve a more complete characterization of these interesting new and unusual molecules, representing the first ever found examples of end-on bonded superoxo complexes of Ga and In.

Introduction

Oxidation of a metal is an important but very complex process. To shed more light on this process, the interaction of O_2 with a number of metals was studied intensively in the past decades.[1] The matrix isolation technique offers the possibility to study in detail the reactivity of metal atoms and small clusters towards dioxygen. E.g. Co atoms react upon photolysis with O_2 to give firstly the linear OCoO molecule with a $^2\Sigma_g^-$ electronic ground state.[2,3] Reaction of this species with a second O_2 molcule leads to an end-on bonded OCoO(OO) complex,[4] which in the matrix slowly undergoes conversion into a side-on bonded complex. According to quantum chemical calculations, the electronic ground state, $^2A_2$, of this complex is indeed the side-on bonded form. The calculations predict a decrease of the OCoO angle from 180° to 116° in the course of complexation. However, a $^4A'$ electronic state with an end-on bonded O_2 unit is only about 35 kJ·mol^{-1} higher in energy. The experimental results show that the excited $^4A'$ state is firstly formed and that the product then relaxes in a spin-forbidden process [Equation (1)] from the end-on bonded complex to the side-on bonded complex. The excited state lifetime amounts to ca. 23 min in Ar and 15 min in Ne. In an Ar matrix, the ν(O–O) mode of the ligated O_2 unit shows at 1286.2 cm^{-1} in the case of the end-on bonded complex and at 950.6 cm^{-1} for the side-on bonded form.



(1)

Very recently it has been shown that Al atoms can bind up to three O_2 units, leading to the oxygen-rich tris-superoxo complex $Al(O_2)_3$.[5] The species $Al(O_2)_2$ was also sighted, being a radical (one unpaired electron) featuring D_{2d} symmetry. It was also shown that photolytically activated AlX (X = F, Cl, Br) molecules react with O_2 to give the peroxo complex $XAlO_2$,[6] or, with an excess of O_2, the bis-superoxo complex $XAl(O_2)_2$.[7] These examples show that group 13 elements and subvalent compounds undergo interesting and complex reactions with O_2.

The reaction of Ga atoms with one O_2 molcule leading to GaO_2 has now been studied in some detail both in inert gas matrices[8–10] and in the gas phase.[11] First the cyclic superoxo complex GaO_2 is formed in the course of a spontaneous reaction in the absence of any significant reaction barrier. The quantum chemical results indicate that the electron is transferred from the Ga atom to the O_2 unit at a distance of ca. 270 pm between Ga and the O_2 centroid. Cyclic GaO_2 in its $^2A_2$ electronic ground state is characterised by an O–Ga–O bond angle of 39° and an O–O bond length of 136 pm. This molecule can be photoconverted

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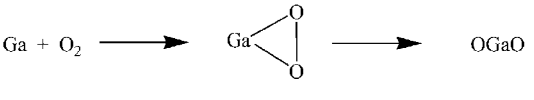
into the linear isomer OGaO [see Equation (2)], which is formally valence isoelectronic to the $[OCO]^+$ cation, by the action of UV light (λ_{max} = 254 nm).[10] Isomerization only by thermal means is opposed to a massive barrier in the order of ca. 300 kJ·mol^{-1}. Quantum chemical calculations on linear OGaO proved to be extremely difficult. Only if highly correlated methods are applied, it can be shown that linear OGaO in its $^2\Pi_g$ electronic ground state is ca. 18 kJ·mol^{-1} more stable than cyclic GaO_2 ($^2A_2$ electronic ground state). As discussed in detail in a previous publication, calculations on the vibrational properties are hampered due to singlet instabilities of the ROHF wavefunction.[10] The analogous reaction between In atoms and O_2 has also been studied.



(2)

Here we will show that the linear OGaO and OInO molecules are capable of binding to an O_2 molcule leading to a species with the overall formula GaO_4 and InO_4, respectively. The vibrational (IR as well as Raman) spectra were used to characterize these interesting species. The results of quantum chemical calculations are also discussed. In the light of the problems with the calculations in the case of OGaO it does not come as surprise that the O_2 complex of this species turned also out to be difficult to calculate.

Results and Discussion

In the following, the results for the reactions of Ga and In atoms with O_2 using IR and Raman spectroscopy will be reported in turn.

Ga + O_2

IR. In experiments in which Ga atoms were codeposited together with 1% of $^{16}O_2$ in Ar, bands were observed in the IR spectrum at 1089.3, 380.5/378.9, and 283.2 cm^{-1} which were already sighted previously and shown to belong to the cyclic superoxo complex GaO_2, **1a**. An increase of the O_2 concentration brought about an increase of the band intensities in a way characteristic for a species containing two O atoms. However, even in a pure O_2 matrix the spectra showed no sign of any product of a spontaneous reaction of Ga with more than one O_2 molcule. Thus, under the conditions of our experiments, Ga spontaneously takes up not more than one dioxygen molecule. Subsequently the matrix was subjected to a 15 min period of photolysis with UV light (λ_{max} = 254 nm). The IR spectrum taken after this photolysis treatment (see Figure 1) displayed two families of bands, which both were absent in the spectra taken before photolysis. At the same time, the bands due to the cyclic superoxo complex GaO_2, **1a**, decreased significantly in intensity. The first family showed at 912.6/908.5 and 204.9/204.0 cm^{-1}. The absorber responsible for these bands was already identified to be the linear molecule OGaO, **2a**, formed via photoisomerization of cyclic GaO_2, **1a**.[10] The second group of bands belongs to a different species **3a**, which has not yet been identified. A very intense absorption of **3a** was observed with its maximum of intensity at 568.7 cm^{-1}. Figure 2 shows that this band can be fitted satisfactorily with two pairs of Lorenzian-type curves having their maxima at 568.7/566.2 and 565.9/563.6 cm^{-1}. The relative intensities within each of the pairs amount to 60.1:39.9, reflecting the natural abundances of ^{69}Ga and ^{71}Ga in a species containing only one Ga atom. Thus it is likely that **3a** contains one Ga atom. Convincing support comes from the inspection of the two weaker bands at lower wavenumbers (174.8/174.1 and 165.6/164.9 cm^{-1}), which both clearly show the isotopic pattern ($^{69}Ga/^{71}Ga$) characteristic for a species containing one Ga atom. The bands of **3a** at 1264.2/1261.8 cm^{-1} come in a region in which ν(O–O) modes of end-on coordinated O_2 groups are expected to show [cf. Fe(OO) 1204.5,[12] OCoO(OO) 1286.2 cm^{-1} [4]]. Bands at 1824.7/1820.0, 1816.7/1811.7 cm^{-1} are most likely due to a combination mode between the modes showing near 568 and near 1264 cm^{-1} (the presence of four maxima of absorption is then caused by matrix splitting of the fundamentals).

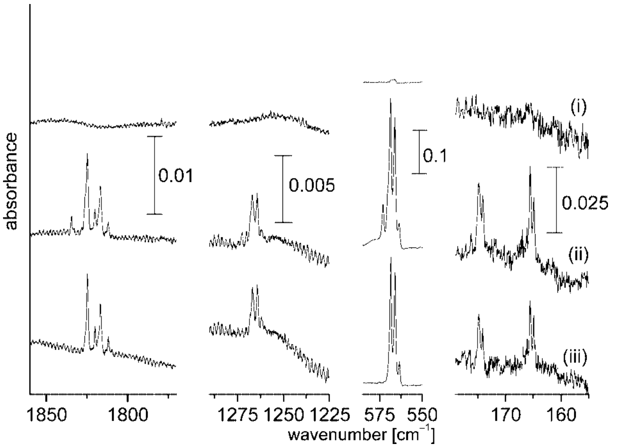


Figure 1. Some regions of the IR spectra recorded for a matrix containing Ga atoms and 0.3% O_2. (i) following deposition, (ii) upon UV photolysis (λ_{max} = 254 nm), and (iii) annealing of the matrix to 30 K.

The experiments were repeated with different concentrations of Ga and O_2 in the matrix. Figure 3 compares two regions of the IR spectra taken for a matrix containing Ga and a) 0.3% and b) 1.0% O_2 in Ar. These two regions show bands characteristic for cyclic GaO_2, **1a**, which appear directly upon deposition and are virtually extinguished upon UV photolysis, and for linear OGaO, **2a**, and species **3a**, which both grow in upon UV photolysis and decrease in intensity upon annealing. For the low concentration of 0.3% of O_2 in the matrix the bands due to linear OGaO are much more intense than the ones due to **3a**. For higher concentrations of O_2 in the matrix (1%), the bands due to **3a** gain in relative intensity. This variation in the relative intensities indicates that two O_2 molcules are involved in the formation of **3a**, arguing for a species with the overall formula GaO_4. Using similar arguments experiments with

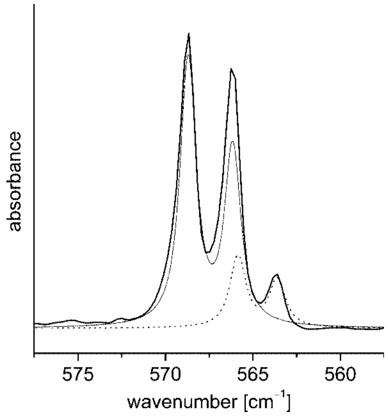


Figure 2. High-resolution IR spectrum showing the structure of the band near 570 cm^{-1}. The band structure can be fitted with two pairs of Lorenzian curves with intensities within each pair in agreement to the natural abundance of the ^{69}Ga and ^{71}Ga isotopomers.

different Ga concentrations are in agreement with the presence of only one Ga atom in **3a**, in line with the observed isotopic pattern.

Subsequently, experiments were carried out in a solid O_2 matrix (see Figure 4). In these experiments, the bands due to cyclic GaO_2, **1a**, were observed in the spectrum recorded immediately after deposition, in analogy to the situation in an O_2-doped Ar matrix. The bands decreased in intensity upon UV photolysis. However, there was no sign of the bands attributable to linear OGaO, **2a**, after photolysis. Instead, the spectra showed massive bands in close energetic proximity to those measured for **3a** in an Ar matrix (at 1853.5/1845.4, 1842.5/1834.3, 1286.0/1283.8, 1279.3/1276.3, 580.5/577.8, 575.9/573.3, 178.2, and 163.3 cm^{-1}). No bands belonging to another product of the reaction between Ga and O_2 were observed. Thus we conclude that GaO_4 can not take up another O_2 molcule. This is in clear difference to Al, which has been shown to form the tris-superoxo complex $Al(O_2)_3$, but in line with the general finding that Ga prefers lower coordination numbers than Al.

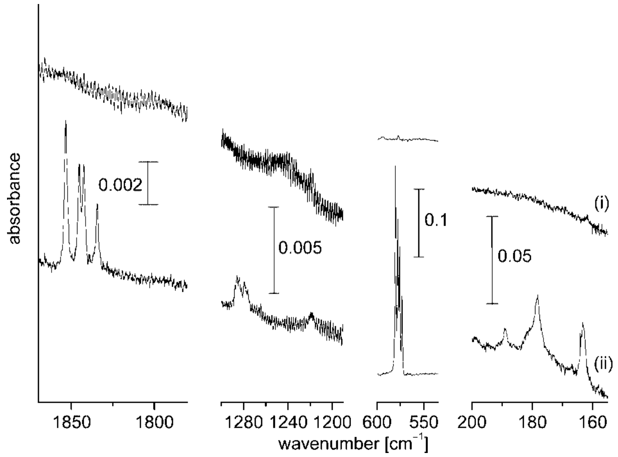


Figure 4. IR spectrum taken for an O_2 matrix containing Ga atoms. (i) upon deposition. (ii) upon UV radiation (λ_{max} = 254 nm).

Finally, the experiments were repeated with different O_2 isotopomers. Figure 5 shows the regions of the IR spectra which contain bands due to **3a** for $^{16}O_2$, $^{18}O_2$, equimolar mixtures of $^{16}O_2$ and $^{18}O_2$ and 1:2:1 mixtures of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$. Note that the spectra in the low (600–30 cm^{-1}) and high (2000–600 cm^{-1}) wavenumber region had to be recorded for different matrices using a Bolometer for the low and an MCT detector for the high wavenumber region (since we had to change the material of the windows of our high-vacuum apparatus from CsI for measurements with the MCT detector to polyethylene for measurements with the bolometer). It can be seen that all bands due to **3a** are red-shifted if $^{16}O_2$ is replaced by $^{18}O_2$. The IR spectra taken in the case of equimolar mixtures of $^{16}O_2$ and $^{18}O_2$ in the matrix virtually are the superposition of the IR spectra taken for $^{16}O_2$ and $^{18}O_2$ alone. The only difference is a

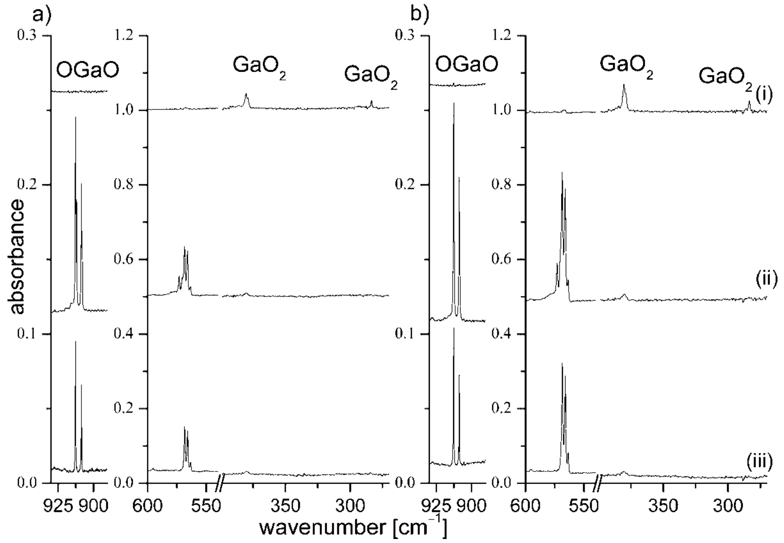


Figure 3. IR spectra taken for an Ar matrix containing Ga atoms (emitted from an oven kept at 1000 °C) and a) 0.3% and b) 1% O_2. (i) after deposition at 10 K, (ii) after UV photolysis (λ_{max} = 254 nm), and (iii) after annealing to 30 K.

slight but nevertheless significant (see Discussion) broadening of the bands, especially those around 1266 and 1824 cm^{-1} and the corresponding bands observed for the ^{18}O counterpart. This broadening is significant and will be shown to be consistent with the formulation of **3a** as an end-on bonded OGaO(OO) complex. The spectra taken with 1:2:1 mixtures of $^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$ give evidence for extra bands with wavenumbers between those measured for $^{16}O_2$ and $^{18}O_2$. The wavenumbers of all bands are included in Table 1.

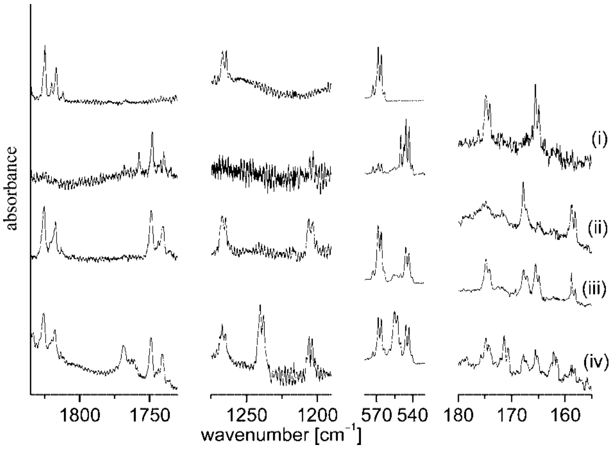


Figure 5. IR spectra taken after UV photolysis (λ_{max} = 254 nm) of Ar matrices containing Ga atoms and (i) $^{16}O_2$, (ii) $^{18}O_2$, (iii) an equimolar mixture of $^{16}O_2$ and $^{18}O_2$, and (iv) a 1:2:1 mixture of $^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$.

Table 1. Wavenumbers observed for the reaction between Ga atoms and O_2 in Ar and pure solid O_2 matrices following photolysis at λ_{max} = 254 nm.

	Ga/O_2/Ar			Ga/O_2	
	$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$	$^{16}O_2$	$^{18}O_2$
GaO_2, **1a**	1089.3	1059.0	1027.9	1087.4	1026.0
	380.5/378.9	373.6/372.2	365.9/364.5	380.2	364.9
	283.2	275.3	268.1	288.8	273.1
OGaO, **2a**	912.6/908.5	897.4/893.4	877.6/873.4	–	–
	204.9/204.0	201.1/200.1	197.3/196.3	–	–
GaO_4, **3a**	1824.7	1769.1	1748.0	1853.5	1775.4
	1820.0		1743.3	1845.4	–
	1816.7	1761.4	1739.8	1842.5	1765.5
	1811.7		1735.2	1834.3	–
	1266.9	1240.4	1205.1	1286.0	–
	1264.2	1238.1	1202.5	1279.3	–
	716.2[a]	676.0[a]	697.6[a]		
	568.7	555.2	545.5	580.5	556.8
	565.9	552.5	543.1	577.8	553.9
	563.6	550.1	540.7	575.9	552.7
				573.3	549.9
	174.8/174.1	171.4/170.6	167.8/167.1	178.2	–
	165.6/164.9	162.2/161.5	158.8/158.1	163.3	–

[a] Observed in the Raman experiments.

Raman. The Raman spectrum of a matrix containing Ga and $^{16}O_2$ showed an intense signal at 716.2 cm^{-1} (Figure 6, i). This signal is already present directly after deposition, and shows no significant alterations in intensity upon radiation with UV light. On the basis of experiments in which the concentration of O_2 and Ga in the matrix was varied, it is likely that species **3a** is the author of this signal. Since the experiments have shown that photolysis is necessary to generate **3a**, the only reasonable explanation for the appearance of the band directly upon deposition is that **3a** is generated by the laser light used to excite the Raman spectra. In Figure 6, the Raman spectra taken for $^{16}O_2$, $^{18}O_2$, 1:1 mixtures of $^{16}O_2$ and $^{18}O_2$, and 1:2:1 mixtures of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ are compared. Again, the spectrum measured for a 1:1 mixture of $^{16}O_2$ and $^{18}O_2$ is not significantly different to the superposition of the spectra taken for $^{16}O_2$ and $^{18}O_2$ alone, thus showing two signals at 716.2 and 676.0 cm^{-1}. An extra signal at 697.6 cm^{-1} appeared in the spectra taken for a 1:2:1 mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$. The wavenumbers are included in Table 1. Experiments were also carried out with Ga isolated in a solid O_2 matrix. These experiments give evidence for a signal at 723.0 cm^{-1}, slightly blue shifted with respect to the signal detected in an Ar matrix.

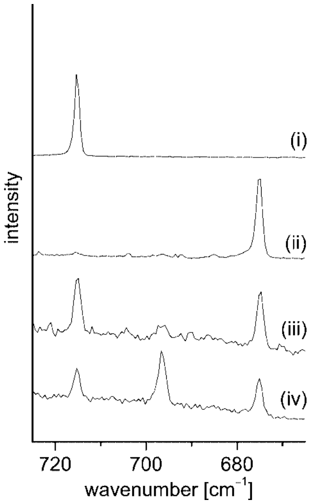


Figure 6. Raman spectra upon deposition for an Ar matrix containing Ga atoms and (i) $^{16}O_2$, (ii) $^{18}O_2$, (iii) an equimolar mixture of $^{16}O_2$ and $^{18}O_2$, and (iv) a 1:2:1 mixture of $^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$.

In + O_2

IR. The IR spectra taken for an Ar matrix containing In atoms and $^{16}O_2$ are displayed in Figure 7. The spectrum taken immediately upon deposition contains sharp absorptions at 1084.2, 331.7 and 276.5 cm^{-1} which were already previously assigned to cyclic InO_2, **1b**.[9,10] The effect of photolysis of the matrix with UV radiation (λ_{max} = 254 nm) is the decrease of the bands due to **1b**. At the same time, two families of absorptions grow in. One family shows at 754.6 and 159.7 cm^{-1} and belongs to linear OInO, **2b**.[10] The other family shows at 1498.8/1493.4, 1067.6/1063.8, 462.1/459.2, 151.3, and 146.5 cm^{-1} and can be assigned to a new species **3b**. The conditions of its appearance indicate that **3b** is the In analogue to **3a**. In analogy to the experiments with Ga, the response of the bands due to **3b** to different concentrations of In and O_2 in the matrix are in agreement with the presence of one In atom and four O

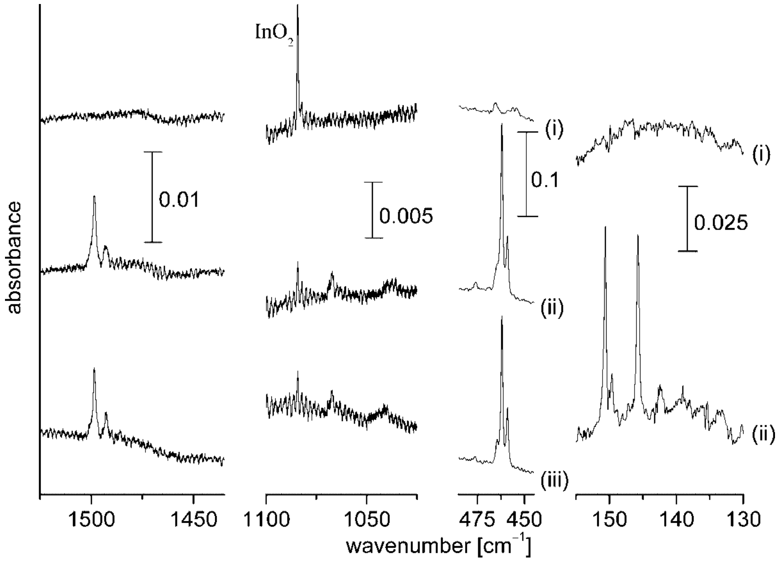


Figure 7. IR spectra of an Ar matrix containing Ga atoms and $^{16}O_2$. (i) upon deposition, (ii) upon UV photolysis (λ_{max} = 254 nm), (iii) upon annealing to 30 K.

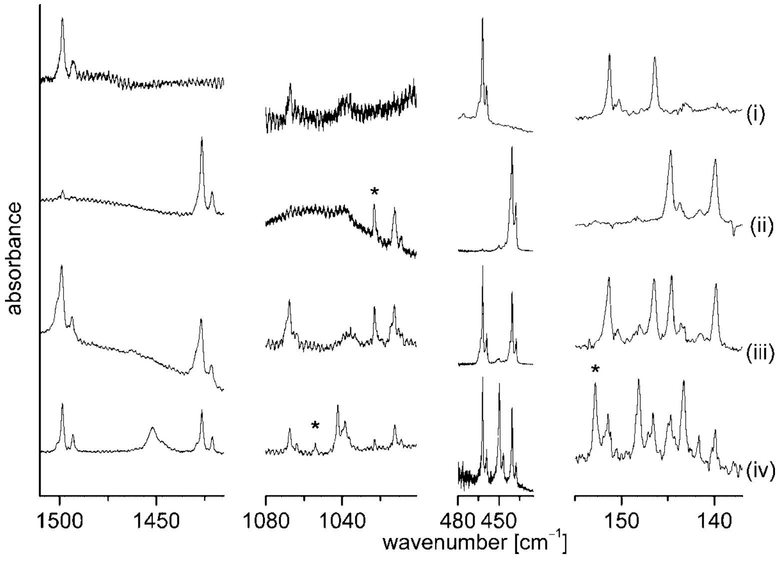


Figure 8. IR spectra taken after UV photolyis (λ_{max} = 254 nm) of an Ar matrices containing Ga atoms and (i) $^{16}O_2$, (ii) $^{18}O_2$, (iii) an equimolar mixture of $^{16}O_2$ and $^{18}O_2$, and (iv) a 1:2:1 mixture of $^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$. Bands marked by an asteriks are due to InO_2.

atoms in the molecule. Figure 8 compares the spectra measured in experiments using different O_2 isotopomers ($^{16}O_2$, $^{18}O_2$, equimolar mixtures of $^{16}O_2$ and $^{18}O_2$, and 1:2:1 mixtures of $^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$). The band at 1498.8/1493.4 cm^{-1} in the experiments with $^{16}O_2$ shifts to 1426.8/1421.5 cm^{-1} with $^{18}O_2$. The band at 1067.6/1063.8 cm^{-1} experienced a red-shift to 1012.6/1009.1 cm^{-1} [$\nu(^{16}O):\nu(^{18}O)$ = 1.054]. The intense absorption at 462.1/459.2 cm^{-1} shifts to 440.5/437.7 cm^{-1} [$\nu(^{16}O):\nu(^{18}O)$ = 1.049]. The two bands which occur at 151.3 and 146.5 cm^{-1} in the experiments with $^{16}O_2$ show at 144.6 and 139.8 cm^{-1} with $^{18}O_2$. All bands are included in Table 2.

Raman. In difference to the reaction with Ga, the Raman spectra taken immediately upon deposition of In with O_2 shows the signals characteristic of cyclic InO_2, **1b** (see Figure 9). These signals decrease in intensity if the matrix is subjected to UV photolysis (λ_{max} = 254 nm). At the same time a new intense signal appears at 621.0 cm^{-1}. Its response to photolysis and annealing and to variations in the concentrations of In and O_2 in the matrix indicates that this signal belongs to species **3b**. In experiments in which $^{16}O_2$ was replaced by $^{18}O_2$, the signal shifts to 586.6 cm^{-1}.

Identification and Characterization

The identification of **3a** and **3b** can be made on the basis of (i) the $^{69}Ga/^{71}Ga$ isotopic shifts and the effects observed in experiments in which $^{16}O^{18}O$ and $^{18}O_2$ were used in place for $^{16}O_2$, (ii) the effects of varying the concentration of Ga or In and O_2 in the matrix and of annealing on the IR

Table 2. Wavenumbers observed for the reaction between In atoms and O_2 in Ar and pure solid O_2 matrices following photolysis at λ_{max} = 254 nm.

	In/O_2/Ar			In/O_2
	$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$	$^{16}O_2$
InO_2, **1a**	1084.2	1054.0	1022.9	1082.8
	331.7	325.2	317.2	331.7
	276.5	267.8	261.3	283.5
OInO, **2a**	754.6	741.4	721.7	–
	159.7	156.3	152.8	–
InO_4, **3a**	1498.8	1452.0	1426.8	1522.1
	1493.4	1447.1	1421.5	–
	1067.6	1042.2	1012.6	–
	1063.8	1038.4	1009.1	–
	621.0[a]	–	586.6[a]	–
	462.1	449.8	440.5	471.8
	459.2	447.0	437.7	468.4
	151.3	148.2	144.6	–
	146.5	143.3	139.8	–

[a] Observed in the Raman experiments.

and Raman intensities, (iv) the conditions of formation and consumption of the bands due to **3a** and **3b**, and (v) the IR and Raman intensities. It will be shown that **3a** and **3b** can be described as dioxygen complexes to OGaO and OInO, respectively. The discussion in this work will predominantly concentrate on the Ga reaction, because that of In atoms follows a similar pattern.

The experiments indicate that product **3a** contains one Ga atom and four O atoms. They also suggest that it is formed by reaction of linear OGaO and O_2. As already mentioned, the band at 1266.9/1264.2 cm^{-1} can be assigned to the ν(O–O) mode of an O_2 unit, which is weakened by coordination. The wavenumber of the ν(O–O) mode can be compared e.g. with that observed for the end-on bonded complexes FeOO (1204.5 cm^{-1})[13] or $O_2Co(O_2)$ (1286.2 cm^{-1}).[4] Of course, the electronic situation in these transition metal dioxygen complexes is different, but the coupling between the O–O coordinate and the other coordinates in the molecule is in all cases fairly weak. This gets also evident when the isotopic data are considered. The ν(O–O) mode of the coordinated O_2 unit of $^{18}O_2Co(^{16}O_2)$ occurs virtually at the same wavenumber as that of $^{16}O_2Co(^{16}O_2)$. Similarly, the O–O coordinate of the ligated O_2 unit in **3a** (and **3b**) is not significantly coupled to the other Ga–O coordinates. The only sign of weak coupling is a slight increase of the halfwidth of some of the bands in the experiments with $^{16}O_2/^{18}O_2$ mixtures with respect to those with $^{16}O_2$ or $^{18}O_2$ alone (see the bands around 1266 and 1824 cm^{-1}). In the case of the end-on bonded complex FeOO, the wavenumber measured for the ν(O–O) band is almost identical for the two versions $Fe^{16}O^{18}O$ and $Fe^{18}O^{16}O$ (1173.0 and 1170.4 cm^{-1}). The same is the case for $O_2Co(O_2)$ and also for **3a** and **3b**. The mode at 568.7/565.9/563.6 cm^{-1} exhibits a smaller isotopic shift than the one at 1266.9/1264.2 cm^{-1} when $^{16}O_2$ is replaced by $^{18}O_2$ (about –23 cm^{-1}). The obvious inference is that it belongs to a ν(Ga–O) mode, this time involving motion of the other O atoms in **3a**. The observed Ga isotopic splitting is in agreement with this assignment. From these considerations we conclude that **3a** is a complex between OGaO and O_2. The mode at 568.7/565.9/563.6 cm^{-1} is then the antisymmetric Ga–O stretch, ν_{as}(Ga–O), of the OGaO unit. This mode is IR-active, but virtually Raman silent. The corresponding symmetric Ga–O stretch, ν_s(Ga–O), on the other hand, is visible at 716.2 cm^{-1} in the Raman spectra, but more or less IR silent. Because the Ga atom is not involved in the motion, this signal exhibits no observable Ga isotopic splitting. The fact that no detectable band appears at 716.2 cm^{-1} in the IR spectra indicates that the O–Ga–O bond angle of the OGaO unit is still close to 180° after coordination of O_2. The isotopic pattern observed for the antisymmetric stretch is in good agreement to this assumption. Thus the

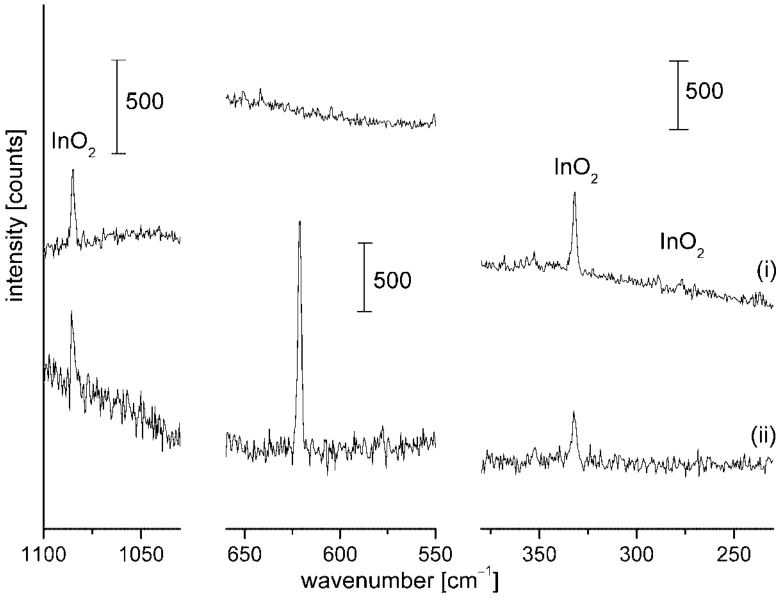
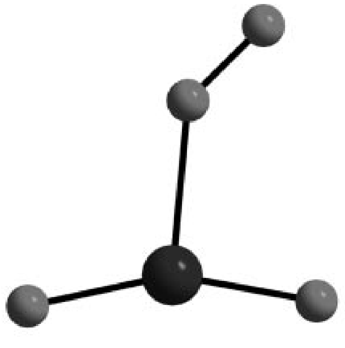


Figure 9. Raman spectra of an Ar matrix containing In atoms and $^{16}O_2$. (i) upon deposition. (ii) upon UV photolysis (λ_{max} = 254 nm).

mode occurs at 568.7 cm^{-1} for the O^{69}GaO unit and at 566.2 cm^{-1} for the O^{71}GaO unit. From this isotopic shift the O–Ga–O angle can be estimated to be 165°. Strong support for this assignment comes also from the wavenumbers as measured for the ν_{as}(Ga–O) and ν_s(Ga–O) modes of the ^{16}OGa^{18}O(O$_2$) version of **3a**. The band due to the ν_{as}(Ga–O) mode is slightly red shifted with respect to the center of the bands measured for the $^{16}O_2$ and $^{18}O_2$ isotopomers. On the other hand, the band due to the ν_s(Ga–O) mode is slightly blue shifted with respect to the corresponding center. This shift is a consequence of the coupling of the symmetric and antisymmetric stretch in the ^{16}OGa^{18}O(O$_2$) isotopomer. The bands at 1824.7, 1820.0, 1816.7, and 1811.7 cm^{-1} can be assigned to the combination ν(O–O) + ν_{as}(Ga–O). The sum of the wavenumbers measured for the two modes is between 1835.6 and 1827.8 cm^{-1}. The bands at 174.8/174.1 and 165.6/164.9 cm^{-1} most likely belong to deformation modes involving some degree of motion of the Ga atoms as evidenced by the isotopic pattern. Thus our experiments hit on five fundamentals and one combinational mode of GaO$_4$.

In a previous publication, the band at 568.7 cm^{-1} has been assigned to the [OGaO]$^-$ anion.[9] However, on the basis of our new experiments it can be immediately concluded that this identification cannot be correct, since it is impossible to produce a charged species in our experimental setup. Of course, **3a** cannot be this species also because the number of fundamentals detected for **3a** in our experiments exeeds the number of fundamentals a threeatomic molecule exhibits. Nevertheless, we have performed quantum chemical calculations on this species. The linear [OGaO]$^-$ molecule exhibits a $^1\Sigma_g^+$ electronic state. Applying CASSCF/TZVPPext, the following vibrational modes were calculated (in cm^{-1}, with IR intensities in km mol^{-1} given in parenthesis): 752.5 (0, σ_g), 224.0 (114, π_u), 909.4 (145, σ_u). Thus no mode should be visible in the region around 570 cm^{-1}. A cyclic form [OGaO]$^-$, exhibiting a $^1A_1$ electronic state, is 131 kJ·mol^{-1} higher in energy (including vibrational zero-point energy corrections). It is characterized by Ga–O and O–O bond lengths of 189.9 and 160.9 pm, respectively, and an O–Ga–O bond angle of 50.1°. The vibrational properties (in cm^{-1}, with IR intensities in km mol^{-1} given in parenthesis) were calculated to be: 743.8(33), 513.0(74), and 461.9(22). We also performed calculations on the cationic species GaO$_2^+$. If the OGaO(O$_2$) complex can be regarded as a superoxo complex, the OGaO unit should carry a formal charge of +1. As anticipated and in difference to the situation with GaO$_2^-$, a bent structure ($^3A_2$) is more stable in the case of the cation. Cyclic [GaO$_2$]$^+$ is by ca. 73 kJ·mol^{-1} (according to CASSCF/TZVPPext) more stable than linear [OGaO]$^+$. Its vibrational fundamentals are calculated to show at the following wavenumbers (in cm^{-1}, with IR intensities in km·mol^{-1} given in parenthesis): 998.6(2), 573.4(47), and 420.2(0). Thus there is indeed a strong fundamental in the region around 570 cm^{-1}. The calculated isotopic shifts –22.4 cm^{-1} for Ga(^{18}O)$_2$ and –10.5 cm^{-1} for Ga(^{16}O^{18}O) are also close to those observed in the experiments. According to the calculations, the Ga–O and O–O bond lengths are 190.4 and 141.3 pm and the O–Ga–O bond angle is 43.5°.

Because of the fact that the electronic situation in linear OGaO is already very complicated and extremely difficult to calculate,[10] it might not come as surprise that GaO(O$_2$) turned out to be difficult to calculate. Nevertheless, using the BP86 method and an SVP basis set, we succeeded in finding an energy minimum which should be close to the correct structure.[14] According to these calculations, the coordination of the O$_2$ molcule to the OGaO unit results in a decrease of the O–Ga–O angle to a value of 157.8°. This value is not too far away from the 168° estimated from the experimental results. The coordinating O$_2$ molcule features an O–O distance of 125.6 pm and is thus significantly elongated with respect to the distance in free O$_2$ (121.6 pm as calculated using the same method and basis set). In line with this elongation the ν(O–O) mode (a′ symmetry) is calculated to occur at 1304.7 cm^{-1}. This wavenumber compares with an experimental one of 1264.2/1261.8 cm^{-1}. Two vibrations at very low wavenumbers and with sufficient IR intensity are calculated to show at 189.9 (a′) and 151.0 (a′′) cm^{-1}. In the experiments, two bands show at 174.8/174.1 and 165.6/164.9 cm^{-1}. As already experienced in the case of linear OGaO, calculations on the symmetric and antisymmetric GaO$_2$ stretches of the OGaO unit are not very reliable. While the calculated 662.7 cm^{-1} for the symmetric GaO$_2$ stretch (a′) is in fair agreement with the observed 716.2 cm^{-1}, the calculated 732.3 cm^{-1} for the antisymmetric stretch (also a′) is not in good agreement with the observed 568.7 cm^{-1}. Other calculated wavenumbers are 705.5 (a′′), 258.7 (a′), 108.6 (a′), and 81.7 (a′); however, all these bands are predicted to have only very small IR intensities. In summary the calculations, although there are inconsistencies, are in line with the description of GaO$_4$ as an end-on bonded O$_2$ complex to OGaO. Using the observed wavenumbers the valence force constant *f*(Ga–O) of the OGaO unit in GaO$_4$ can be estimated to be 350 N·m^{-1}. Thus the force constant is significantly smaller than that of OGaO prior to O$_2$ complexation (586 N·m^{-1}). This decrease is not surprising since the donation of electron density from the OGaO unit into the ligated O$_2$ leads to a partial depopulation of one of the bonding π_g orbitals.



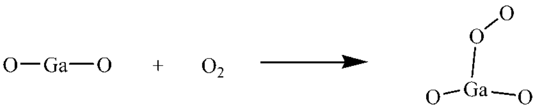
Model of the GaO$_4$ molecule, **3a**

Thus the geometry of GaO$_4$ is very different to that reported for the AlO$_4$ molcule.[5] AlO$_4$ in its energy minimum form exhibits D_{2d} symmetry and is characterized by O–O and Al–O distances of 148 and 175 pm, respectively. The distances of the O_2 groups are both equal and the unpaired electron is located in parts on both groups. This means that the O_2 groups can be described as being in between superoxo- and peroxo groups. In the case of GaO_4, the D_{2d} symmetric structure defines not an energy minimum on the potential energy hypersurface. For the doublet electronic state we calculated O–O and Ga–O bond lengths of 148 and 184 pm, respectively. According to B3LYP/TZVPP calculations, its energy is 89 kJ·mol^{-1} higher than that of separated OGaO and O_2.

There are all indications that InO_4, **3b**, has a structure similar to that of GaO_4. The ν(O–O) mode of the ligated O_2 unit shows now at 1067.6/1063.8 cm^{-1}. This wavenumber is close to that adopted e.g. in the end-on bonded superoxo complex CuOO (1089.6 cm^{-1}).[15] In line with this assignment, the $\nu(^{16}O)/\nu(^{18}O)$ ratio is relatively large (1.054). The ν_{as}(In–O) mode and the ν_s(In–O) mode of the OInO unit in InO_4 show at 462.1/459.2 and 621.0 cm^{-1}.[16] The fact that one is IR active and the other Raman active indicates that the O–In–O angle is, in similarity with the Ga homologue, close to 180°. DFT (BP86) calculations yielded a structure for this complex with In–O and O–O bond lengths of 192.3 and 127.7 pm, respectively, and O–In–O and In–O–O bond angles of 147.8° and 137.8°, respectively. The ν(O–O) mode of the ligated O_2 unit was calculated to show at 1220.8 cm^{-1}. Thus, the calculations predict the wavenumber to be lower than the corresponding one of the Ga homologue. This trend is in agreement with the experimental results (1264.2/1261.8 cm^{-1} for GaO_4 and 1067.6/1063.8 cm^{-1} for InO_4), although the deviation between experiment and calculation is quite high. The ν_{as}(In–O) mode of the OInO unit is calculated to show at 578.0 cm^{-1}. This value compares with an observed one of 462.1/459.2 cm^{-1}. Like in the case of GaO_4, the calculations predict a too low wavenumber for the ν_s(In–O) mode of the O–In–O unit (calculated: 551.9 cm^{-1}, measured: 621.0 cm^{-1}). Two modes calculated at 204.9 cm^{-1} (a′′) and 175.3 cm^{-1} (a′) can be assigned to observed ones at 151.3 and 146.5 cm^{-1}. Other weak modes, which were not detected in our experiments, were calculated to show at 303.5 (a′), 113.9 (a′′), 91.9 (a′), and 77.5 (a′) cm^{-1}.

Conclusions

The reactions of Ga and In atoms in Ar matrices with O_2 lead spontaneously to the cyclic GaO_2 and InO_2 molcules, respectively. These species can be photoconverted into linear OGaO and OInO. Reaction of linear OGaO and OInO with a second O_2 molcule leads to the new end-on bonded superoxo complexes $OGaO(O_2)$ [see Equation (3)] and $OInO(O_2)$. These molecules represent the first ever experimentally verified end-on bonded superoxo complexes of Ga and In. Our experimental findings show that the group 13 elements Ga and In are capable to bind up to four O atoms. The experimental results indicate that the O–Ga–O angle in this complex is ca. 165°. Quantum chemical calculations provide further details of the structure of the new molecules, which differs remarkably from that of the D_{2d} symmetric $Al(O_2)_2$ complex. The characterization of these oxidation processes is of relevance to the mechanism of metal oxidation in general and thus contributes to a more detailed understanding of this very important but complex class of reactions.



(3)

Experimental Section and Calculational Details

In a vacuum apparatus, thermally evaporated gallium or gallium metal was deposited together with dioxygen in an excess of Ar onto a freshly polished Cu block kept at 12 K with the aid of a closed-cycle refrigerator (Leybold LB115). The experiment was repeated with different dioxygen isotopomers. $^{16}O_2$ was used as delivered from Messer (purity 99.9998%). $^{18}O_2$ was purchased from Linde (isotopic purity 99.0%). For experiments with a 1:2:1 mixture of $^{16}O_2/^{16}O^{18}O/^{18}O_2$, an equimolar mixture of $^{16}O_2$ and $^{18}O_2$ in a glass bulb was subjected for several hours to an electric discharge. The resulting O_3 molcules were trapped in a cold finger at 77 K. Subsequently the cold finger was warmed up again to room temperature and decomposition of the O_3 molcules results in the statistical 1:2:1 mixture of $^{16}O_2/^{1}O^{18}O/^{18}O_2$. Experiments in solid O_2 matrices were also carried out. Further details of the matrix isolation technique can be found elsewhere.[17]

IR spectra were recorded on a Bruker 113v FT-IR spectrometer equipped with a DTGS and an MCT detector for measurements in the spectral regions 4000–200 cm^{-1}, respectively, and a bolometer for measurements between 700 and 30 cm^{-1}.

Raman spectra were measured on a XY800 spectrometer from Jobin Yvon Horiba, equipped with a CCD camera (Wright Instruments). The spectra were excited with an Ar^+ ion laser. Both the 488.0 nm and 514.5 nm lines were used.

Quantum chemical (DFT) calculations using the B3LYP[18] and the BP86[19] functionals were performed with the aid of the TURBOMOLE[20] programme and using either an SVP[21] or a TZVPPext[22] basis set. The Dalton programme code[23] was used for CASSCF calculations. All valence orbitals were included into the active space.

Acknowledgments

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