Transition Metal Complexes of Cyclic and Open Ozone and Thiozone

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Abstract: Cyclic ozone (O_3) has not been isolated so far, despite its computed kinetic persistence. Possibilities of "trapping" this molecule (or the valence-isoelectronic cyclic thiozone, S_3) in transition metal complexes are investigated in this paper. Candidates were constructed, first using the 18-electron rule as a guide and then optimizing the structures with the DFT-B3LYP method. A variety of structures result: oxo-peroxo species, di-σ- and π-bonded open ozone complexes, some η^1 and η^2 cyclic ozone complexes, and a few bona fide η^3 cyclic O_3 and S_3 complexes. ML_n fragments suitable for complex formation would need to contain very strong π-acceptor ligands. Nitrosyl ligands were chosen to minimize an energy mismatch between the O_3 donor orbitals and the ML_n acceptor orbitals. On this basis, the existence of the complexes $[S_3W(NO)_3]^{3+}$, $[O_3M(NO)_3]^{3+}$ (M = Cr, Mo, W, Fe, Ru, Os), and $[S_3W(NO)_2(CO)]^{2+}$ containing cyclic O_3 and S_3 is suggested. In another approach, facing up to the oxidizing power of O_3, potential systems were built from late transition metals in high oxidation states, and also d^0 early transition metal centers.

Introduction

Ask introductory chemistry students to draw a Lewis structure for O_3 (and do not prejudice the issue by showing them the real structure). The chances are that you will get in a good number of answers the cyclic structure at the top of Scheme 1, and not the resonance-stabilized pair of Lewis structures at the bottom.[1]

And you cannot mark the students' answer as wrong, right?

Interestingly, in the early days of chemistry, once it was established that the molecule contains three oxygen atoms,[2] ozone was also thought to have a cyclic structure. Lothar Meyer, the "other" discoverer of the periodic table, came to this conclusion just on the basis of the then current valence theory. Oxygen was divalent, so Meyer reasoned in 1864 that ozone (discovered by Schönbein in 1840) had to be cyclic.[3] Multiple bonding was a concept just becoming established at that time.

So, cyclic ozone and thiozone (S_3), as well as S_2O and SO_2, belong to the fascinating small set of molecules for which it is possible to draw a perfectly good Lewis structure but which appear not to exist. Yet.

The nonexistence of cyclic S_3 and O_3 is particularly surprising, as we will see. This paper continues a theoretical quest for stabilizing cyclic ozone and thiozone in a transition metal complex, begun by one of the authors and Shen-shu Sung.[4] In the process we discover some potential complexes of normal ozone.

Scheme 1
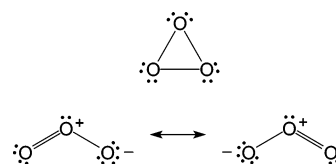
Normal O_3 and S_3, and Their Cyclic Isomers. The structures of O_3 and S_3 are well known. O_3 has an O—O distance of 1.28 Å and an O—O—O angle of 116.8°.[5] For S_3 the structural parameters are 1.92 Å and 117.4°.[6]

In theoretical investigations the D_{3h} ring isomer is found as a locally stable structure with an O—O (S—S) distance of approximately 1.47 Å[7] (2.12 Å).[8] It took a while for calculations of the energy difference between the D_{3h} and the C_{2v} forms of ozone and thiozone to reach some consensus. This is due to the fact that electron correlation plays an important role in these molecules, especially in the open form. An early study that included only two configurations predicted the cyclic form of ozone to be slightly more stable than the bent form.[9] The more recent calculations consistently favor the open form of ozone. A very good calculation, at the CCSD(T) level with a large basis set, yields an energy difference of 29.1 kcal/mol.[10] A more recent elaborate study using a contracted multireference method

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(MRCI) with a CASSCF reference function yields 28.7 kcal/mol.[11] A density functional study, using a B-LYP functional and a DZP basis set, yields 32.5 kcal/mol.[7] For thiozone, the open form is also predicted to be more stable. The energy difference between the two isomers is smaller than for O_3 and found to be 5.6 kcal/mol using CCSD(T),[12] 7.4 kcal/mol using B3LYP/cc-p VDZ,[13] and 9.3 kcal/mol using B3LYP/6-31G(d).[8]

The barriers surrounding the cyclic isomers are quite high. The potential energy surface for ozone was calculated using an all-valence CASSCF method.[14] The barrier for ring opening was determined to be 22.7 kcal/mol, and the barrier for dissociation of the cyclic form into O_2 and O was found to be 46.6 kcal/mol. Thus, the cyclic form of ozone should be kinetically persistent. The lower barrier, the one of the ring-opening reaction, suggests a lifetime for the cyclic species of at least 30 s at 298 K (assuming a relatively high preexponential factor of 10^{15} s^{-1}). For thiozone, the barrier for ring opening of the cyclic form was calculated on the same level of theory to be 27.6 kcal/mol,[15] with B3LYP/6-31G(d) giving 29.4 kcal/mol.[8] The barrier of the dissociation reaction of cyclic S_3 has to our knowledge not been calculated yet. For SO_2 (S_2O) the barrier for the ring-opening reaction is predicted to be 15.6 kcal/mol (23.9 kcal/mol).[15]

Why should there be substantial barriers around the cyclic isomers? The reason is that the decomposition of X_3 to ground states of X_2 + X is an orbital-symmetry-forbidden reaction. Remarkably, also symmetry-forbidden is the simple ring opening of the X−X−X angle, increasing from 60° to the 117° of the stable structure. This is easily seen by counting up σ and π electron pairs in O_3 or S_3: in the cyclic form there are six σ pairs and three π pairs, while in the open form there are seven σ pairs and two π pairs. The mirror plane distinguishing σ from π is preserved in the ring opening; there must be a level crossing.

Usually, molecules find a way to escape symmetry-forbidden least motion reaction paths. Cyclic ozone just does not have that option, ergo the substantial walls surrounding it. The existence of these walls, and their orbital origin, make it appropriate to term the open and cyclic X_3 forms isomers.

The theoretical consensus is that the total energy of the cyclic form is slightly above the experimentally well-known dissociation energy of open O_3 into O_2 and O.[16,17] In the case of cyclic ozone the difference is 1−2 kcal/mol, if the zero-point vibrational energy is taken into account.[18] Therefore, attempts to reach the cyclic isomer from normal ozone by simple heating are bound to fail. And the simple experiment for detecting even the fleeting existence of a cyclic isomer, by heating $^{16}O^{18}O^{18}O$ or an isotopomer and looking for isotope scrambling, will not work. More promising seems a specific approach of excited O atoms toward the middle of aligned O_2 molecules.[19]

Despite the largely negative findings (one suspects that there has been much work here, but as often is the case with negative results, they go largely unreported), there have been some hints of finding cyclic ozone. Cyclo-O_3 is proposed as a short-lived precursor with a lifetime of 5 μs during the formation of O_3 from the recombination of O_2 and O generated in a radiolysis of oxygen.[20] An unassigned UV signal at 315 nm[21] for one precursor species, O_3^α, and its single IR signal at 6.6 μm[22] were thought to be indicative of the existence of the D_{3h}-symmetric isomer. There is another experimental report of cyclic O_3, now observed by means of transmission electron diffraction on a reconstructed MgO surface after annealing it under oxygen.[23] The measurement has apparently been repeated by the same research group.[24] It would be interesting to see a computational confirmation of this finding or other experimental evidence for cyclic ozone formed at reconstructed oxide surfaces.

Stabilizing Cyclic Ozone. The instability of cyclic ozone (isoelectronic to cyclopropane) is understood chemically as the consequence of the repulsion between the oxygen lone pairs (whether viewed as σ, π, or as hybrids) in the three-membered ring. More specifically, in the π system of the molecule one is cramming six electrons into a small space. The avoidance of eclipsed lone pairs is responsible for the nonplanar conformations of molecules such as H_2O_2 and hydrazine. In line with this very qualitative reasoning is the fact that the relative instability of cyclic thiozone is less pronounced than for ozone and that even the reverse (cyclic form more stable) is predicted in calculations for Te$_3$.[8] As the distance between the atoms gets larger for the higher homologues, the repulsive interaction of the lone pairs gets weaker.

Perhaps if these lone pairs could be engaged in coordinative covalent bonding, electron density could be transferred to a metal atom and the cyclic isomer stabilized as a complex or an adsorbate. There are also numerous examples of species that are unstable or metastable in the gas phase, but exist as complexes. The vinylidene fragment ($H_2C=C$) is such an example. It is found in many complexes,[25] and is an important intermediate in surface reactions,[26] but may not even be a local minimum on its own.

Let us distinguish the chemistry we propose from ozone chemistry known so far. Familiar species are the so-called primary ozonides that are formed as intermediates in the reactions of ozone with unsaturated organic compounds. The assignment of formal oxidation states in the primary ozonides would lead to an ozonide with a formal charge of −2 and an increased oxidation number of the carbon atoms involved in the reaction. The phosphite ozonides $O_3P(OR)_3$ [27] allow two choices for the oxidation state assignment, corresponding to ozone or ozonide, depending on the formal oxidation state assigned to the phosphorus atom (3+ or 5+). Salt-like, ionic ozonides contain the radical anion O_3^-, for example in $Cs_2Ba(O_3)_4$.[28] Complexes with ozone in its cyclic form or in

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Table 1. Extended Hückel Parameters

atom	orbital	H_{ii} (eV)	ζ_1	c_1	ζ_2	c_2
W	6s	−8.26	2.341			
	6p	−5.17	2.309			
	5d	−10.37	4.982	0.6940	2.068	0.5631
C	2s	−21.4	1.625			
	2p	−11.4	1.625			
O	2s	−32.3	2.275			
	2p	−14.8	2.275			
S	3s	−20.0	2.122			
	3p	−11.0	1.827			

its bent form (as ozone or ozonide) acting as a ligand toward transition metals are not known so far. There is unconfirmed evidence (from stoichiometric considerations) of a rhodium complex of ozone whose structure is still not determined.[29]

This paper is the second approach toward designing transition metal complexes containing ML_n fragments that are capable of binding cyclic or bent ozone and thiozone, respectively. In a previous study[4] some guidelines for stabilization could be derived, but reliable geometry optimizations were not available at the time to test the predictions made. This time we can do better.

Computational Details

Density functional calculations (DFT) were carried out with Gaussian 03[30] using the B3LYP functional[31] with the basis set 6-31G(d) for the main group atoms. For the transition metals, the Los Alamos effective core potentials LANL2 with the corresponding valence electron basis sets were used.[32] The type of the chosen pseudopotential basis set accounts for the ns, np, nd, $(n + 1)$s, and $(n + 1)$p electrons. For a Ni atom, for example, 18 electrons ($3s^2$, $3p^6$, $3d^8$, $4s^2$, $4p^0$) are explicitly considered in the calculations.

That all complexes reported as minima on their respective potential energy surface were such was verified by a frequency analysis in each case. All DFT geometry optimizations were carried out in C_1 symmetry, starting in all cases from significantly unsymmetrical structures.

The bonding of hypothetical complexes was analyzed using an extended-Hückel fragment molecular orbital analysis (eH-FMO), as made available in the program package YAeHMOP.[33] For the visualization of molecular orbitals the package CACAO[34] was used. Extended Hückel parameters[35−37] were used as implemented in the eH program and shown in Table 1.

As a calibration of the theoretical methodology, the geometries of ozone and thiozone in their open and closed form were optimized with

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Scheme 2. Correlation Diagram Relating the Orbitals of Cyclic (D_{3h}) and Open (C_{2v}) O_3; Three Levels at Lower Energy (Mainly O 2s) Are Not Shown
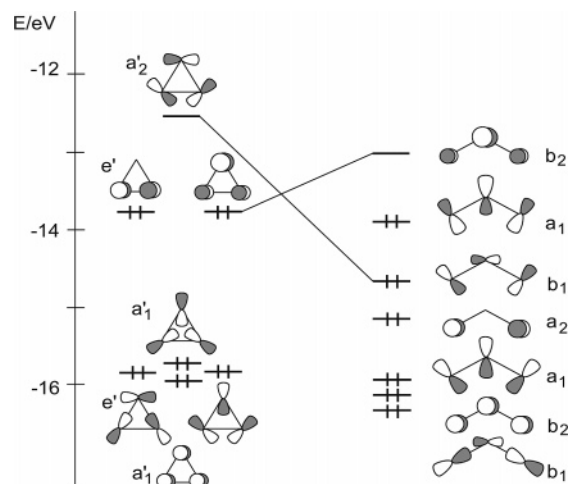
DFT, and the energy differences between the two isomers were determined. For ozone in the C_{2v} geometry an O−O bond length of 1.26 Å and an O−O−O angle of 118° were found. The D_{3h} isomer was found to be 27.4 kcal/mol higher in energy, with an O−O bond length of 1.44 Å. For C_{2v} thiozone a S−S bond length of 1.95 Å and an angle of 118° were calculated. For the ring form of S_3 a S−S bond length of 2.11 Å was obtained; the isomer is calculated to lie 9.3 kcal/mol above the open minimum. (The energy differences are given without the zero-point correction.) These results are in good agreement with the available experimental and theoretical data.[8]

Results

The Frontier Orbitals of Cyclic and Open X_3. The electronic structure of the open and closed isomers of ozone has been described in a number of places in the literature. For details we refer the reader to the references cited,[7, 9−11, 14] but especially to a detailed study by Peyerimhoff and Buenker,[38] who nicely correlated the orbital occupation scheme with the energetic preference for the X−X−X angle. Scheme 2 shows the result of an eH calculation for cyclic and open ozone and a level correlation diagram. It can be seen that the ring-opening/closing reaction is a symmetry-forbidden reaction. As anticipated, three π orbitals are occupied in the ring, compared to only two in the open form. To compensate, one more σ-type orbital is occupied in the open form.

As a consequence of the different orbital occupation in the cyclic and the open forms, the two isomers are expected to have different bonding properties. Cyclic O_3 could act as 6π-electron donor in η^3-coordination, while the open form of O_3 could donate a maximum of four electrons in π-type coordination. The highest occupied MOs of C_{2v} ozone of a_1 and b_1 symmetry can be thought of as in-phase and out-of-phase lone pair combinations, which could act as σ-donors in a bidentate binding mode. An analogous orbital picture would be obtained for thiozone.

Interaction of Cyclic Ozone with an ML_n Fragment. Let's begin by ignoring the (extraordinary) oxidizing capability of ozone and think simply of the molecule as a ligand in an organometallic compound. If we assume that a cyclic O_3 acts as an η^3-ligand, ML_n fragments with 12 valence electrons would

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Figure 1. Complexes with open O_3 and S_3 ligands: (a) $O_3W(CO)_4$, (b) $O_3Fe(CO)_3$ (the same structure type was obtained for $O_3Ru(CO)_3$, $S_3Fe(CO)_3$, $S_3Ru(CO)_3$, and $S_3Os(CO)_3$), and (c) $O_3Os(CO)_3$.

Scheme 3. Hypothetical 18-Electron Complex $O_3W(L)_3$
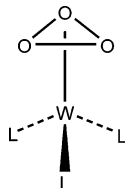
Scheme 4. Interaction Diagram for $O_3W(CO)_3$ in C_{3v} Symmetry
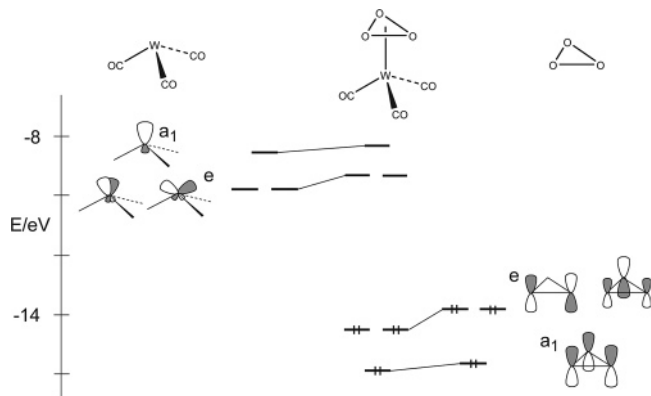
allow the resulting complexes to obtain an 18-electron count. A candidate system that comes to mind consists of a d^6 metal center with three, two-electron ligands attached, for example $W(CO)_3$. The bonding of this fragment to O_3 would provide a quasi-octahedral coordination environment for the metal in $O_3W(CO)_3$, as shown in Scheme 3.

A fragment molecular orbital (FMO) analysis is used to analyze the bonding in this hypothetical complex. As the interaction diagram in Scheme 4 shows, there is a substantial energy mismatch between the donor orbitals of the O_3 ligand (at around -14 eV in this eH calculation) and the acceptor orbitals of the $W(CO)_3$ fragment (at around -9 eV). As a result (and perhaps because of a disparity in the size of the orbitals interacting) there is little interaction; significant bonding for this system cannot be expected.

If O_3 is replaced by S_3, this situation improves somewhat, as the donor orbitals of S_3 move up in energy by about 2 eV. There is still a considerable energy mismatch between S_3 donor levels and acceptor levels of the $M(CO)_3$ fragment.

Consequently, DFT geometry optimizations of complexes with group 6 metals starting out from this initial geometry (an η^3-X_3 ring, X = O, S) lead to very different minimum structures (not shown here). For Cr as the central atom, a major transformation of the system occurs, accompanied by loss of a CO ligand, into an oxo-peroxo complex $(O)(O_2)Cr(CO)_2$. Oxo-

peroxo complexes are known for group 5 and group 6 metals with a d^0 metal center and a valence electron count of 16.[39,40] For Mo and W the cyclic O_3 ligand opens up into its bent isomer and adopts an orientation that allows partial π- and partial σ-interaction. For S_3 as well the ligand binds in its open form in an orientation that allows partial σ and π donation, for Cr and Mo. In the case of W, the thiozone splits into a thio and an S_2 ligand. All these systems have an electron count below 18.

Complexes of the same structure type as our candidate system with a valence electron count of 18 do indeed exist. These contain cyclo-triphosphorus, which can be considered as P_3^{3-}, i.e., valence-isoelectronic to O_3 and S_3. The three-membered ring is η^3-coordinated to a metal d^6 center. The role of the three two-electron donors L is taken by triphos, a tridentate organophosphorus ligand. Examples of these 18-valence-electron systems are $[(triphos)M(P_3)]^+$ (M = Pd, Pt) with Pd(IV) and Pt(IV)[41] and $[(triphos)CoP_3]$ with Co(III).[42,43]

Systems with Open Ozone and Thiozone. On paper, the X_3 molecules can be "directed" to bind in their open form if only four electrons are needed by the central atom to reach a total of 18 valence electrons. Starting from our initial ML_n fragment $W(CO)_3$, this situation can be created by adding an additional CO ligand, or by using a central metal with two more electrons. Indeed, complexes with open O_3 and S_3 ligands as σ-only or π-only ligands were obtained with the $W(CO)_4$ fragment and with group 8 metal tricarbonyls.

The assignment of the formal oxidation states for the X_3 ligand and the central metal in these complexes can be done in two ways. The ligand could be regarded as neutral, corresponding to oxidation state zero for the metal. Or one could think of the ligand as an ozonide or thiozonide, respectively, corresponding to a metal oxidation state $2+$. The Mulliken population analysis for the resulting complexes, which might be a rough guideline here, gives a charge of the X_3 ligands in the various complexes around -0.7 for X = O and around ±0.0 for X = S. This indicates the presence of some ozonide character in the O_3 ligand.

Figure 1 shows the optimized structures for selected complexes with open X_3 molecules; all of them are 18-valence-electron systems. Important structural parameters are given in Table 2. It is interesting to see that the open form of ozone acts

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Table 2. Selected Structural Parameters for Complexes with Open Ozone and Thiozone, X$_3$M(CO)$_3$, and for O$_3$W(CO)$_4$

| | | O$_3$M(CO)$_3$ | | | S$_3$M(CO)$_3$ | | |
	O$_3$W(CO)$_4$	M = Fe	M = Ru	M = Os	M = Fe	M = Ru	M = Os
X−X, Å	1.50	1.43	1.44	1.42	2.13	2.15	2.17
X−X−X, deg	98	101	101	101	98	97	96
M−X, Å	1.99	1.90	2.06	1.98	2.35	2.47	2.49
M−C, Å	2.05	1.84	1.93	1.94	1.81	1.94	1.92

Table 3. Selected Structural Parameters for the Complex Cations [X$_3$M(NO)$_3$]$^{3+}$ and [S$_3$W(NO)$_2$CO]$^{2+}$

| | [O$_3$M(NO)$_3$]$^{3+}$ | | | [S$_3$M(NO)$_3$]$^{3+}$ | | | |
	M = Cr	M = Mo	M = W	M = Cr	M = Mo	M = W	[S$_3$W(NO)$_2$CO]$^{2+}$
X−X, Å	1.45	1.45	1.46	2.16	2.18	2.20	2.19
M−X, Å	2.20	2.41	2.39	2.46	2.67	2.66	2.69
X−M−X, deg	39	33	36	52	48	49	48
M−N (M−C), Å	1.87	1.96	1.93	1.81	1.96	1.93	1.86 (2.07)
M−N−O, deg	176	176	176	180	178	178	178
N−O (C−O), Å	1.11	1.11	1.12	1.11	1.12	1.12	1.14 (1.13)

as a π- or a σ-ligand, depending on the size of the group 8 central atom. In contrast, the open thiozone is a π-donor in all complexes with group 8 metals, Fe to Os. The bonding angle of the isolated molecule decreases noticeably (from 118° to ~100°) in the complexes, independent of the coordination of the molecule as a bidentate σ-ligand or an η^3-π-ligand. The general picture of a choice being made between di-σ and π bonding is reminiscent of similar options available for a butadiene ligand.[44]

Potential Cyclic X$_3$ Complexes with NO$^+$ Ligands. We did not give up on stabilizing the cyclic form. It seemed that the energy mismatch between the acceptor levels of the W(CO)$_3$ fragment and the donor levels of the cyclic molecule was for both O$_3$ and S$_3$ too big to lead to bound complexes of the cyclic form. This mismatch was noted in our earlier study, and formed the basis of an alternative stabilization strategy there.[4] To manipulate the fragment acceptor levels, we chose to replace the CO ligand with the even stronger π-acceptor nitrosyl (NO$^+$).

Geometry optimizations starting out from a cyclic X$_3$ geometry lead to minimum structures that are indeed cyclic ozone complexes. The three X−X bonds are identical within numerical limits (the calculation was carried out in C_1 symmetry). Thus, the cyclic ligand in these complexes represents an equilateral triangle. All three group 6 transition metals with cyclic ozone and cyclic thiozone lead to complexes with the same structure type, as shown in Figure 2. The structural parameters are listed in Table 3. The formal electron count for these systems with linear coordinated NO$^+$ would be d^6 + 3·2(NO$^+$) + 3·2(X$_3$) = 18 valence electrons (X = O, S). The orientation of the X$_3$ ligand with respect to the three NO$^+$ ligands is staggered (i.e., pseudooctahedral at the metal).

A qualitative analysis of the bonding between the two fragments, X$_3$ and M(NO)$_3$$^{3+}$, using the optimized structures of the complexes, shows that the three bonding MOs are of the character anticipated earlier. In C_{3v} symmetry these are a set of e MOs and an a$_1$ MO, as shown in Scheme 5.

The e symmetry MOs turn out to be more important in X$_3$-to-ML$_3$ bonding. Note that the ring fragment π-orbitals mix to some extent with the corresponding σ-orbitals on complexation, so that (in the e orbitals) the resulting orbital lobes at the ring
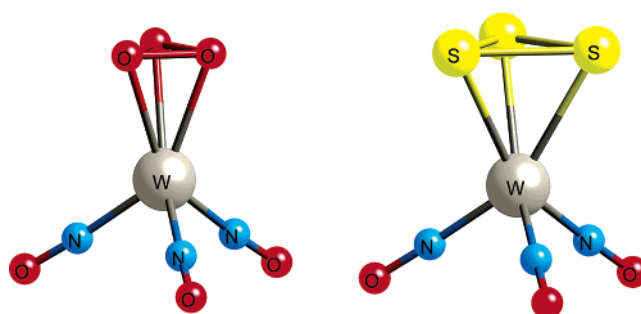
Figure 2. Optimized structures of [O$_3$W(NO)$_3$]$^{3+}$ and [S$_3$W(NO)$_3$]$^{3+}$. The same structure type was obtained for Cr and Mo as central atoms, respectively, and for [S$_3$W(NO)$_2$CO]$^{2+}$.

Scheme 5. Bonding MOs between the Fragments X$_3$ and [M(NO)$_3$]$^{3+}$
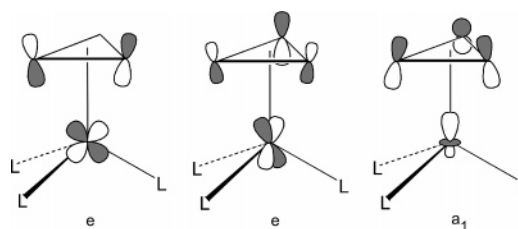
atoms point slightly toward the metal atom core. Such s−p mixing facilitates a better overlap between the metal and the ring orbitals and has been studied earlier, for π-complexes of cyclic hydrocarbons.[45] For a given metal, the larger ring (S$_3$) mixes in more σ-character than the smaller ring (O$_3$). (For O$_3$ there is almost no σ-contribution.) By varying the size of the X$_3$ ring (for X = O, S) and looking at the effect on the calculated overlap between corresponding fragment MOs, this reasoning can be tested. The overlap between the π-type-only ring fragment orbital and its metal-centered counterpart decreases with longer S−S bonds and increases with shorter S−S bonds until it reaches an asymptote at a certain short bond length. For O$_3$ the corresponding overlap decreases at very large O−O distances and remains unchanged at medium and small O−O distances.

It is therefore somewhat surprising that the bonding lobes of the ligand in the a$_1$ MO point slightly away from the metal atom

(44) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105−119.

(45) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148−1155.
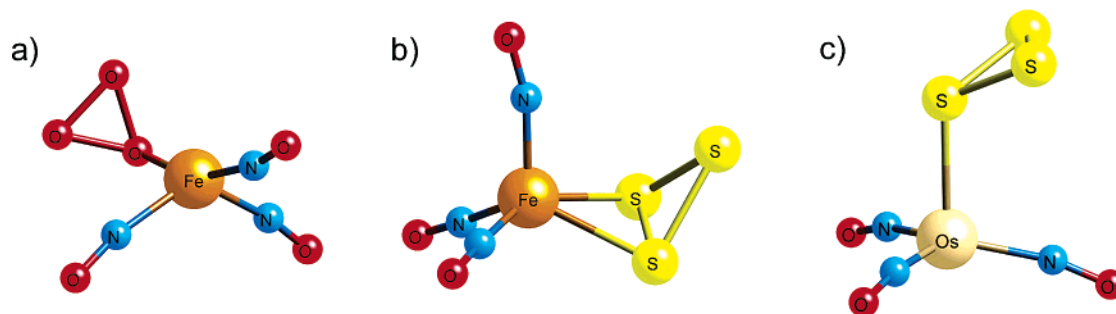
Figure 3. Optimized geometry of the complexes $[X_3M(NO)_3]^{3+}$ with group 8 metals: (a) $[O_3Fe(NO)_3]^{3+}$ (the same structure type was obtained for $[O_3Ru(NO)_3]^{3+}$ and $[O_3Os(NO)_3]^{3+}$), (b) $[S_3Fe(NO)_3]^{3+}$, and (c) $[S_3Os(NO)_3]^{3+}$ (the same structure type was found for $[S_3Ru(NO)_3]^{3+}$).

core. A better overlap would be provided with lobes pointing toward the atom center, as seen for the e MOs and anticipated for this axially symmetric MO. This expectation can again be tested by means of the corresponding fragment orbital overlaps. The smaller the S–S or O–O distance in the ring, the higher is the overlap between the pure π a_1 fragment orbitals of X_3 and ML_3. Therefore, this pointing away from the atom center in the a_1 complex MO cannot be productive for ring-to-metal bonding. Interestingly, it is observed for the O_3 ligand to a larger extent, less so for the S_3 ligand.

We think that this seemingly inconsistent picture of σ and π mixing in the cyclic ligand is the result of a compromise between two opposing trends: optimal metal-to-ligand bonding (mixing of X_3 σ and π so as to create combinations pointing toward the metal atom core) and maximum avoidance of the overlap (ergo repulsion) of the π electrons in these small ring systems (pointing away from the metal atom core). For the a_1 MO, which is not as important for X_3-to-ML_3 bonding as the e MOs, the latter effect dominates.

Mixed Carbonyl/Nitrosyl Complexes, and Changing the Electron Count at the Metal. Known nitrosyl complexes usually contain one or two nitrosyl ligands.[46] This fact, and the relatively high positive charge of the systems as a whole, will make it somewhat challenging (to put it mildly) to obtain such compounds experimentally.

Therefore, we also looked at the analogous systems with one and two nitrosyl ligands and the corresponding number of carbonyl ligands for one of the central metals, tungsten. A closed-ring minimum structure was found for $[S_3W(NO)_2CO]^{2+}$ (Table 3). The corresponding systems with one NO^+ ligand resulted in structures with X_3 (X = S, O) bound in the open form as a partial σ- and π-ligand, as described above in the first optimization attempts with d^6 metal tricarbonyls.

Note that in the computed structures where the O_3 or S_3 ligand remains intact, the O–O bond is stretched a little (1 pm) and the S–S bond quite a lot (5–9 pm), relative to the computed geometries of isolated X_3. Such lengthening is consistent with what we know happens to π-systems on coordination in organometallics.

For a complex with a group 8 transition metal, the 18 valence electron count would be reached for cyclic X_3 binding in a dihapto mode. Calculations starting from the same η^3 starting geometry as before in fact lead to the respective monohapto systems, formally 16-electron complexes (see Figure 3 and Table 4). In one case, for an S_3 ligand and an Fe central atom, η^2

Table 4. Selected Structural Parameters for Complexes $[X_3M(NO)_3]^{3+}$ with Group 8 Transition Metals

	$[O_3M(NO)_3]^{3+}$			$[S_3M(NO)_3]^{3+}$		
	M = Fe	M = Ru	M = Os	M = Fe	M = Ru	M = Os
X–X, Å	1.45^a	1.45^a	1.46^a	2.18^b	2.16^c	2.16^c
M–X, Å	1.97	2.13	2.13	2.44	2.54	2.55
M–N, Å	1.87	1.99	1.91	1.78	1.96	1.91
X–M–N, deg	158	168	168	102	100	98
M–N–O, deg	168	170	173	166	161	168

^{a} No noticeable difference between the three O–O bonds. ^{b} Averaged value for S–S; the bond between the two donor atoms (see Figure 3b) is 0.1 Å shorter than the two bonds to the uncoordinated atom. ^{c} Averaged value for S–S; the bond between the two uncoordinated atoms (see Figure 3c) is 0.2 Å longer than the two bonds to the donor atom.

coordination was found, indicating a formal 18 electron system. The η^1 O_3 complexes (16-electron complexes) shown in Figure 3 are reminiscent of the angular structure found in other d^8 ML_4 systems, in $Fe(CO)_4$ for example.[47]

For the complexes with η^1 and η^2 coordination, a distortion of the X_3 ring is likely, due to lowering of the symmetry. A noticeable distortion is found for the systems with a group 8 central metal and S_3 as a ligand. The pattern of the ring distortion should mainly be governed by the shape of the main donor orbitals, the e MOs. Indeed, the η^2 complex exhibits a shortening of the bond between the two donor S atoms corresponding to a partial depopulation of the e MO, with the nodal plane through one apex of the triangle and antibonding character between the two remaining apexes (see also Scheme 5). The η^1 complex undergoes a shortening of the two bonds connected to the one donor S atom and a lengthening of the remaining bond in the triangle. This corresponds to a partial depopulation of the other e MO, the one with the nodal plane through the sides of the triangle.

In general, it appears that even if the transition metal is formally electron deficient, the additional electrons the O_3 ligand carries are just not good enough bases to satisfy that electron deficiency.

Systems with the Metal in a Higher Oxidation State. It is time to face the great oxidizing power of ozone. The complexes constructed so far had central metal atoms in formal oxidation state zero. Although these are minima on their potential energy surfaces, they might be inaccessible, as the central metal might be relatively easily oxidized by ozone. We turned therefore to systems that involve the metal in a higher or maximal oxidation state.

(46) Hoffmann, R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666–2675.

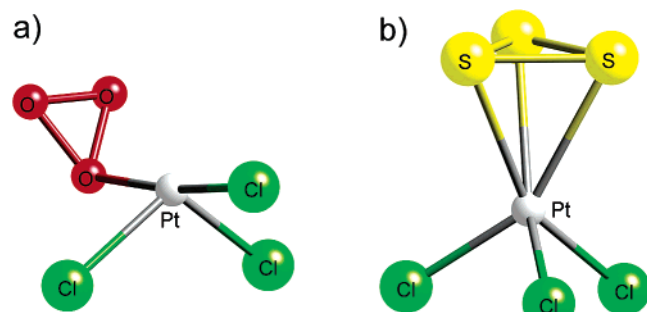(47) Hoffmann, R.; Minot, C.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 2001–2005.

a)

b)

Figure 4. (a) Optimized geometry of the complex $[O_3Pt(Cl)_3]^+$. The same structure type was obtained for $[O_3Ni(Cl)_3]^+$ and $[O_3Pd(Cl)_3]^+$. (b) Optimized geometry of the complex $[S_3Pt(Cl)_3]^+$. The same structure type was obtained for $[S_3Ni(Cl)_3]^+$ and $[S_3Pd(Cl)_3]^+$.

Table 5. Selected Structural Parameters for Complexes $[X_3MCl_3]^+$ with Group 10 Transition Metals in the Oxidation State IV

|	$[O_3MCl_3]^+$			$[S_3MCl_3]^+$		
	M = Ni	M = Pd	M = Pt	M = Ni	M = Pd	M = Pt
X−X, Å	1.44	1.45	1.44	2.17	2.18	2.18
M−X, Å	2.06	2.27	2.28	2.53	2.69	2.68
M−Cl, Å	2.12	2.26	2.27	2.15	2.29	2.30
O−M−Cl$_{axial}$, deg	167	173	174			

Two main approaches were pursued to construct such systems. In the first approach, as in the original idea, a d^6 central atom was used, but now realized as a group 10 metal in oxidation state IV. To avoid a high positive charge of the whole system, chloride ligands were introduced. We come to $[X_3MCl_3]^+$ (M = Ni, Pd, Pt; X = O, S). These were optimized starting from a geometry as shown in Scheme 3 with X_3 in the cyclic form as an η^3 ligand.

The calculations lead to η^1 complexes, formally 14-electron systems, with ozone bound in its cyclic form, and to η^3 complexes with thiozone as a ligand, formally 18-electron systems, as shown in Figure 4 and Table 5. The systems optimized to have C_{3v} symmetry show, as expected, no distortion of the ring. The η^1-bound complexes with O_3 show no noticeable differences between the three O−O bonds in the ring.

In the second approach, hypothetical complexes were constructed from existing molecules that contain at least three oxo ligands and the metal in its maximal oxidation state, corresponding to a d^0 system. One example of such a system is the well-known complex ReO_3Cl, a formal 14-electron system, which is valence-isoelectronic to the permanganate ion. Further examples are the octahedral complexes $[ReO_3Cl_3]^{2-}$ [48] and $[ReO_6]^{5-}$,[49] formal 18-electron systems, with rhenium in oxidation state 7+. Suppose one imagined oxidizing the system further. The oxidation would have to take place at the formal oxide ligands, forming O−O bonds. By a six-electron oxidation one could reach a cyclic ozone complex, in, for instance, $[O_3ReO_3]^+$, as shown schematically in Scheme 6.

This approach proved less productive than we hoped: bound complexes were obtained only for metals coordinated with oxo ligands alone. The favored geometries contain cyclic ozone and thiozone as η^1 ligands, as shown in Figure 5a,b and Table 6. These are formal 14-electron systems, as the original ReO_3Cl.

(48) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1980; p 885.
(49) Baran, E. J.; Müller, A. Z. *Anorg. Allg. Chem.* **1969**, *368*, 168−173.

Scheme 6. Formal Oxidation of Three Oxo Ligands in $[ReO_6]^{5-}$ by Two Electrons Each to One Ozone Ligand
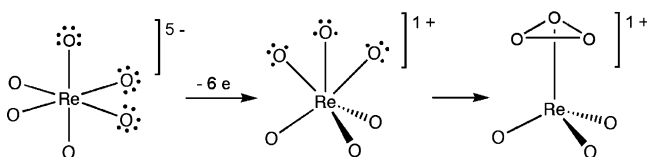
Scheme 7. Schematic Four-Electron Oxidation of $[ReO_6]^{5-}$
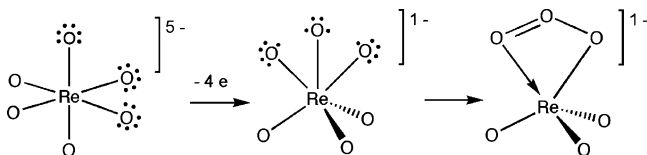
One could ask the question, what would happen if the formal oxidation of the oxo ligands in $[ReO_6]^{5-}$ were "incomplete", for example a four-electron oxidation instead of a six-electron oxidation? In this case one oxo ligand could lose two electrons and two other oxo ligands could lose one electron each (Scheme 7).

As a result, one of the three O−O bonds needed for cyclic ozone could not be formed and a complex $[O_3ReO_3]^-$ with coordinated open O_3 could be expected. The O_3 could be viewed as either an ozonide (assuming Re^{VII}) or ozone (corresponding to a formal Re^V). Indeed, geometry optimization of one representative system of this group of complexes, $[O_3ReO_3]^-$, leads to the corresponding structure with open ozone, as shown in Figure 5c and Table 6.

Other Isomers of the Complexes. To obtain the complexes shown above, all geometry optimizations started from a complex with a cyclic η^3 ligand of the type shown in Scheme 3. The search for ozone complexes thus was biased toward the cyclic form of the ligand. The question should be addressed whether other isomers of the complexes exist, especially those with O_3 and S_3 bound in the open form, and where these are in energy.

We studied one representative system, $[CrO_3(NO)_3]^{3+}$, in detail. The following alternatives to an η^3-ozone ligand come to mind: three oxo ligands, one peroxo and one oxo ligand, and open ozone as a ligand. Starting from corresponding initial geometries, the calculations lead only in the case of open ozone to a minimum structure with the molecule as a bidentate σ-ligand.

The possible loss of an O_2 molecule from the ozone complex was also investigated, by a calculation of the complex with one oxo ligand and an isolated O_2 molecule. This did not result in a stable structure for the mono-oxo complex. The results indicate (at least in this case) that dissociation of complexed O_3 into O_2 and O may not be a path we need to worry about.

The isomeric complex $[CrO_3(NO)_3]^{3+}$ with bound open ozone is significantly lower in energy (37.9 kcal/mol) than its isomer with cyclic O_3, despite the fact that the electron count for the central atom in this case is only 16 valence electrons. In fact, this complex is set up to bind another NO^+ ligand to become an 18-electron complex, presumably with the same structure type as $O_3W(CO)_4$ described earlier.

An analysis of the hypothetical unimolecular isomerization using the respective optimized structures shows that this transformation is (as in the case of the isolated molecule) a symmetry-forbidden reaction. During this transformation one mirror plane is preserved. The essential part of the level
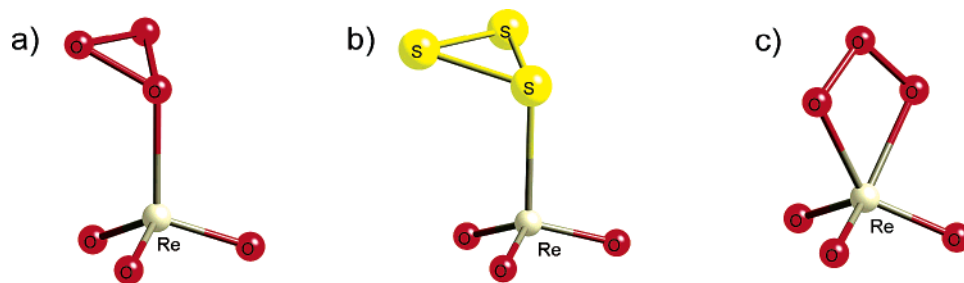
Figure 5. Optimized structure of complexes with d^0 metals: (a) $[O_3ReO_3]^+$, (b) $[S_3ReO_3]^+$ (the same structure type was obtained for $[X_3MnO_3]^+$), and (c) $[O_3ReO_3]^-$.

Table 6. Selected Structural Parameters (in Å) for Complexes $[X_3MO_3]^+$ and $[O_3ReO_3]^-$

	$[O_3MO_3]^+$		$[S_3MO_3]^+$		
	M = Mn	M = Re	M = Mn	M = Re	$[O_3ReO_3]^-$
X−X	1.45^a	1.44^a	2.16^b	2.17^b	1.43
M−X	2.00	2.22	2.39	2.55	2.02
M−O	1.55	1.71	1.56	1.70	1.73

^{a} No noticeable difference between the three O−O bonds. ^{b} Averaged value for S−S; the bond between the two uncoordinated atoms (see Figure 5b) is 0.1 Å longer than the two bonds to the donor atom.

Scheme 8. Correlation Diagram for the Transformation of Complexed Cyclic Ozone to Complexed Open Ozone
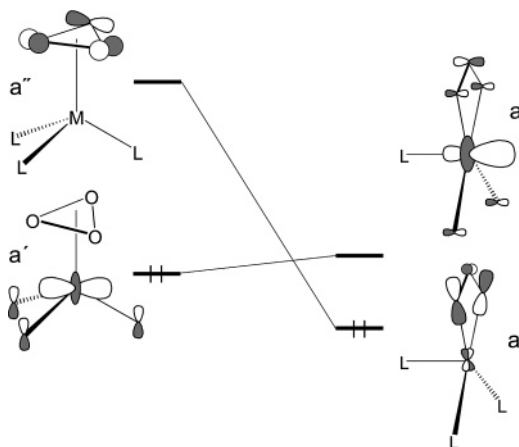
correlation diagram (illustrated in Scheme 8) shows a level crossing involving two MOs of different symmetry with respect to the remaining mirror plane. One of the MOs, of a″ symmetry (σ-antibonding and empty for the cyclic ligand, one of the in-plane lone pairs for the open ligand), corresponds exactly to the one that crossed for the isolated molecule.

The nature of the other MO involved in the crossing differs from the isolated ligand case, because of metal−ligand bonding. It is an MO of a′ symmetry that is centered at the ML_n fragment. This MO is metal−NO bonding for the complex with cyclic X_3 and a three-fold coordination by NO ligands. In the complex with open ozone with a slightly different optimized coordination environment, it is mainly an empty z^2 orbital, a distorted version of the nonbonding z^2 MO of a square pyramidal complex.

The isomer studies suggest that a synthesis of a complex with bound cyclic ozone (or thiozone) probably will not lead to just oxidation of the central chromium atom, resulting in the corresponding d^0 complex with oxo ligands. More likely, the complex with open ozone would be obtained.

We have not examined the isomerization possibilities for the other complex structures with cyclic ozone. To estimate transition barriers between these isomers is not going to be easy; highly correlated methods would definitely be required to obtain such barriers.

Conclusions

In this paper we investigated the possibilities of stabilizing cyclic ozone or its homologue thiozone as ligands in transition metal complexes, as well as so far unknown complexes with these molecules in the open form.

ML_3 d^6 fragments represent possible bonding partners to cyclic ozone and thiozone, formally 6π-electron donors. Stable minimum structures were obtained for strong π-accepting ligands L involving nitrosyl (and some carbonyl ligands) at the metal fragment, such as $[\eta^3-X_3M(NO)_3]^{3+}$ (X = O, S; M = Cr, Mo, W). For d^8 central metals, a cyclic X_3 coordinates mono-hapto; in one case, $[S_3Fe(NO)_3]^{3+}$, a di-hapto coordination of cyclic thiozone was found. Complexes with open ozone and thiozone, four-electron π- or σ-donors, were obtained for the d^8 ML_3 systems $X_3M(CO)_3$ (X = S, O; M = Fe, Ru, Os).

Further complexes containing ML_n fragments with the metal in a higher oxidation state were constructed in two ways: following an "18-electron strategy" using a group 10 metal in oxidation state IV, and following a "ligand oxidation strategy" using group 7 oxo complexes with the metal in oxidation state VII. Monohapto complexes $[O_3M(Cl)_3]^+$ and trihapto complexes $[S_3M(Cl)_3]^+$ (M = Ni, Pd, Pt) with cyclic ozone and thiozone were found for group 10 central atoms and chloro ligands. The metastable d^0 systems investigated include the monohapto systems $[X_3MO_3]^+$ (X = O, S; M = Mn, Re).

Cyclic ozone (and thiozone) has been an elusive species. We offer some suggestions for stabilizing the ring as a transition metal complex.