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High Oxidation States

Is Allred's $[Hg(cyclam)]^{3+}$ a True Mercury(III) Complex?**

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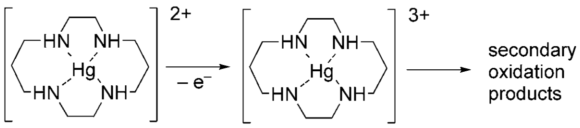
The existence of mercury tetrafluoride (HgF_4) has recently been demonstrated by matrix-isolation IR spectroscopy.[1] An oxidation state of +4 for mercury, which had previously been predicted by quantum-chemical calculations,[2,3] was thus confirmed experimentally for the first time under these low-temperature conditions. Mercury in oxidation states above +2 should be classified as a transition-metal element, as the 5d orbitals must be appreciably involved in bonding. The first claim of a mercury oxidation state of +3 was made more than 30 years ago by Allred and co-workers:[4] electrochemical oxidation of the macrocyclic complex $[Hg(cyclam)](BF_4)_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) in propionitrile provided a short-lived initial oxidation product with a half-life of about five seconds at −78 °C, which was characterized by cyclic voltammetry, EPR spectroscopy, and UV/Vis spectroscopy as a $[Hg(cyclam)]^{3+}$ complex with mercury in its +3 oxidation state (Scheme 1).



Scheme 1. Electrochemical oxidation of $[Hg(cyclam)]^{2+}$.

This experiment was never corroborated independently, however, and apart from some speculation by Jørgensen concerning the existence of HgF_4,[5,6] the study of higher oxidation states in Group 12 lay dormant until the initiation of quantum chemical studies in the 1990s.[2,3] Many questions about this initial experiment have remained open: a) Was the reported short-lived species really $[Hg(cyclam)]^{3+}$? b) If so, is this species really a Hg^{III} complex, or is it at least a true transition-metal complex of mercury in the sense of substantial involvement of the mercury 5d orbitals in metal–ligand bonding? Herein we will answer these questions based on state-of-the-art relativistic density functional (DFT) calculations[7] of its electronic structure, spin-density distribution, EPR spectroscopy parameters (*g* tensor, hyperfine tensors), and excitation energies.

Figure 1 shows DFT-optimized[7] structures for the most important conformers of the dicationic and tricationic complexes $[Hg(cyclam)]^{q+}$ ($q=2,3$). Test calculations (see Table S1 in the Supporting Information) with different functionals on the known structure of $[Au(cyclam)]^{3+}$ gave the shortest, and thus most accurate, Au–N distances with the BHLYP hybrid functional,[8,9] which is consistent with previous results for Hg^{IV} complexes.[10] We therefore decided to focus exclusively on BHLYP-optimized structures. The dication prefers a conformation with an (*R*,*S*,*R*,*S*) configuration at the nitrogen stereocenters and either a distorted (with two longer and two shorter Hg–N bonds, **1′**) or regular square-pyramidal (**1**) arrangement. The latter has been reported to

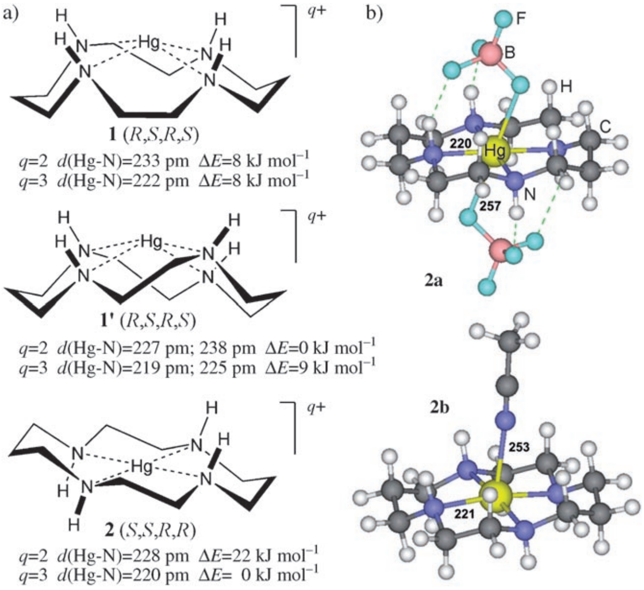


Figure 1. a) Schematic structures, optimized Hg–N bond lengths and relative energies (compared to the most stable one in each case) of the selected minima of $[Hg(cyclam)]^{q+}$ ($q=2,3$) (all other minima are provided in the Supporting Information). b) Complexes of $[Hg(cyclam)]^{3+}$ in square-planar conformation with two BF_4^- anions (**2a**) and an explicit solvent molecule (**2b**). BHLYP/TZVP results with a quasi-relativistic pseudo-potential for Hg and a conductor-like screening (COSMO) solvent model.

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be present in solution based on ^{13}C NMR spectroscopic studies.[11] However, the energy difference between conformers **1** and **1′** is small. As no inversion of the nitrogen atoms is needed, **1** and **1′** can exist in rapid dynamic equilibrium. For the trication, however, the lowest energy is obtained for a square-planar arrangement (**2**).

For EPR spectroscopy, assignment to an Hg^{III} complex was based on an isotropic *g* value of 2.014, an isotropic mercury hyperfine coupling (HFC) constant of 2124 MHz, and the absence of detectable nitrogen hyperfine coupling.[4] We have used a second-order perturbation method with spin–orbit effective core potentials,[7,12] at the B3LYP-GIAO level,[7] implemented in the ReSpect program,[13] to compute the *g* tensor of the species in question. Comparison with the experimental isotropic *g* value (see Table 1) provides good agreement, that is, a measured value somewhat above the free-electron *g* value is obtained. Any differences between the various conformations of the free cation (**2**) and its complexes with BF_4^- (**2a**) or acetonitrile (**2b**) are minor (see Table S4 in the Supporting Information for more details).

Table 1: Computed EPR spectroscopy parameters and excitation energies for $[Hg(cyclam)]^{3+}$ and its complexes with counterions or solvent molecules.[a]

	^{199}Hg HFC [MHz]		^{14}N HFC [MHz]	g_{iso}	λ_{max}[b] [nm]	
	DKH1	DKH2			1	2
1	−2428	−3094	31	2.017	496	433
1′	−2239	−2860	29	2.016	544	436
2	−2337	−2988	31	2.017	497	418
2a	−2288	−2925	33	2.020	494	422
2b	−2345	−2997	32	2.018	462	431
exptl	±2124		–	2.014	506	428

[a] B3LYP results with extended basis sets (cf. computational details in the Supporting Information), obtained for the BHLYP/TZVP-optimized structures (cf. Figure 1). [b] TDDFT-B3LYP results.

Computation of the HFCs[7] involved the all-electron scalar relativistic Douglas–Kroll–Hess (DKH) approach,[14] augmented by a finite-size Gaussian model for the nuclear charge and nuclear magnetic moment.[15] Calculations on $[Hg(cyclam)]^{3+}$ with the second-order DKH-transformed HFC operator (DKH2) provided a somewhat too negative isotropic HFC, whereas the first-order transformed operator (DKH1) provided better agreement with experiment (Table 1). This behavior is consistent with our previous results for Hg^{I} species and is likely due to neglected higher-order terms in the DKH transformation.[14,15] Coordination of acetonitrile or BF_4^- anion affects the HFC by less than 100 MHz. The same holds for the inclusion of bulk solvent effects by COSMO (see Table S2 in the Supporting Information). The HFCs of other minima (except that of **5**) differ little from those of **2**, therefore it is not possible to determine whether the assumption of Allred and co-workers,[4] namely that the trication is generated in the preferred nonplanar structure of the dication and decomposes before structural relaxation occurs, is correct. The absolute HFCs for $Hg^{I}X$ complexes[14,15] are roughly an order of magnitude larger than the values obtained here, whereas our DKH2 result for a naked Hg^{3+} cation is −1726 MHz, thus somewhat less negative. The computed HFC for the complex and the Hg^{3+} cation is negative, in contrast to the positive HFCs of Hg^{I} complexes. Notably, the computed isotropic ^{14}N HFCs are only about 30 MHz at all levels, which is much less than the experimental line width of 170 MHz and thus explains why no nitrogen HFC was observed.[4] We can therefore conclude that the computed EPR parameters confirm the original assignment of the short-lived initial electrochemical oxidation product as $[Hg(cyclam)]^{3+}$ or a weak aggregate of this cation with solvent molecules or counterions in solution. Time-dependent density functional calculations of the excitation energies of the two lowest excited states are also consistent with the reported UV/Vis spectra of $[Hg(cyclam)]^{3+}$ (Table 1; see also Table S5 in the Supporting Information). No absorbance in the visible region is observed/computed for $[Hg(cyclam)]^{2+}$, therefore we can answer question (a) about the nature of the initial oxidation product affirmatively.

We should now proceed and ask (question (b)) whether this cation represents a true Hg^{III} complex. Table 2 summarizes pertinent electronic-structure data along with those for formally isoelectronic complexes. Strikingly, the bulk of the spin in both the Cd and Hg complexes is found to be located on the cyclam ligand nitrogen atoms, with only a fraction of significantly less than one tenth on the metal. Isosurface plots of the spin density (Figure 2) also clearly show that the spin density is strongly delocalized between metal and ligand, but is predominantly on the ligand nitrogen atoms (the small

Table 2: Comparison of the NPA analyses[16] and Mulliken spin densities for $[Hg(cyclam)]^{3+}$ with formally isoelectronic complexes.[a]

Complex	NPA charges and populations			Mulliken spin densities[b]	
	Q(M)	*Q*(N)	pop. (M)	M	N
$[Zn(cyclam)]^{3+}$	1.57	−0.63	$4s^{0.46}\ 4d^{9.92}$	0.007	0.186
$[Cd(cyclam)]^{3+}$	1.59	−0.62	$5s^{0.48}\ 4d^{9.89}$	0.011	0.195
$[Hg(cyclam)]^{3+}$	1.55	−0.61	$6s^{0.62}\ 5d^{9.80}$	0.067	0.199
$[Au(cyclam)]^{2+}$	0.93	−0.59	$6s^{0.68}\ 5d^{9.45}$	0.356	0.155

[a] B3YP//BHLYP results for square-planar structures. M: metal, N: nitrogen. [b] Total spin density on metal and ligand add to 1.000, with the bulk being on the four nitrogen atoms.

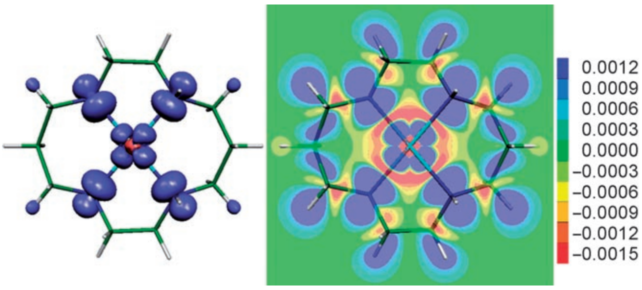

Figure 2. Spin-density distribution in $[Hg(cyclam)]^{3+}$. Left: isosurface plot ±0.005 a.u. (blue indicates positive spin density and red indicates negative spin density); right: cut-plane ±0.0015 a.u.

nitrogen HFCs may be understood from nodes of the SOMO at the nitrogen positions, which give rise to only a small spin density at the nuclei by spin polarization). Aggregation with counterions or solvent molecules affects this picture very little, therefore we refrain from giving these additional data. Natural population analysis (NPA, Table 2; cf. Table S8 in the Supporting Information for the dication) confirm that upon one-electron oxidation of $[Hg(cyclam)]^{2+}$ only a small fraction of the removed electron comes from the mercury 5d orbitals, with a much larger part coming from the ligand. While the spin density on the metal and the depletion of the metal d orbitals is significantly larger than for the Cd analogue, the presumably more genuine d^9 Au^{II} complex exhibits a strikingly larger metal spin density and d-orbital involvement (cf. Figure S3 in the Supporting Information). Our analysis thus contradicts the assumption of redox-innocence generally made for cyclam ligands as, in the present case, cyclam is clearly a redox-active ligand.[4,6]

In this case, formal oxidation states become useless, and physical or spectroscopic oxidation states[17] have to be invoked (see, for example, reference [18]). We thus have to ask whether a description with a genuine Hg^{III} center and a neutral ligand or one with an Hg^{II} center and a radical cation cyclam ligand is more realistic. The spin densities (Table 2) clearly support the latter assignment as, in this case, the mercury d-orbital participation in bonding should be small. The delocalized nature of bonding in the title complex prohibits a detailed hybridization analysis of the individual Hg–N bonds. However, the metal d-orbital populations below 10.0 (Table 2) may be traced mainly to depletion of the d_{xy} orbital due to its involvement in σ bonding to the ligand. These d_{xy} NPA populations are 1.996 for $[Hg(cyclam)]^{2+}$, 1.860 for $[Hg(cyclam)]^{3+}$, 1.989 for $[Au(cyclam)]^{+}$, and 1.599 for $[Au(cyclam)]^{2+}$. The d-orbital participation in bonding for the title complex is thus significantly higher than in its reduced precursor but far lower than in the d^9 Au^{II} complex (and significantly lower than for $Hg^{IV}F_4$, where the Hg–F σ-bonding d natural atomic orbial exhibits a population of 1.423). The relatively large 6s population in Table 2, which marks the predominant covalent contribution to the Hg–cyclam bonding in the title complex, should also be noted.

In conclusion, our calculations confirm that the short-lived species detected in the experiments of Allred and coworkers in 1976[4] is $[Hg(cyclam)]^{3+}$, possibly weakly aggregated with solvent molecules and/or counterions. However, electronic-structure analyses indicate predominant oxidation of the cyclam ligand, which had been presumed to be redox-inactive.[4,6] The trication is therefore best described as an Hg^{II} complex with a cyclam radical cation ligand. The answer to the title question (and to question (b)) is thus negative, even though the d-orbital involvement in bonding is clearly somewhat larger than for $[Hg(cyclam)]^{2+}$. A true Hg^{III} species therefore still remains a challenge for synthetic chemists,[19] and the recent spectroscopic detection of HgF_4 in Ne and Ar matrices at low temperatures[1] marks the first experimental observation of a genuine mercury oxidation state beyond +2.

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