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First Anhydrous Gold Perchlorato Complex: $ClO_2Au(ClO_4)_4$. Synthesis and Molecular and Crystal Structure Analysis

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Chlorine trioxide, Cl_2O_6, reacts with Au metal, $AuCl_3$, or $HAuCl_4 \cdot nH_2O$ to yield the well-defined chloryl salt, $ClO_2Au(ClO_4)_4$. The crystal and molecular structure of $ClO_2Au(ClO_4)_4$ was solved by a Rietveld analysis of powder X-ray diffraction data. The salt crystallizes in a monoclinic cell, space group $C2/c$, with cell parameters $a = 15.074(5)$, $b = 5.2944(2)$, and $c = 22.2020(2)$ Å and $\beta = 128.325(2)°$. The structure displays discrete ClO_2^+ ions lying in channels formed by $Au(ClO_4)_4^-$ stacks. Au is located in a distorted square planar environment: Au–O = 1.87 and 2.06 Å. $[ClO_4]$ groups are monodentate with $ClO_b = 1.53$ and $ClO_t = 1.39$ Å (mean distances; O_b, oxygen bonded to Au; O_t, free terminal oxygen). A full vibrational study of the $Au(ClO_4)_4^-$ anion is supported by DFT calculations.

Introduction

Over the past 25 years the study of perchlorato complexes has shown the structural richness of this family, with various bonding modes of the $[ClO_4]$ group.[1] Although uses of perchlorato complexes still remain limited owing to their potential hazards, their efficiency as catalysts or electrolytes has been demonstrated.[2,3] In addition, perchlorates are now known as potential sources for nanoceramic materials such as chlorides, oxide chlorides, and oxides.[4] It appears essential to improve the expertise in the synthesis of perchlorato complexes to describe their crystal and molecular structures. This will provide better control of the nature, structure, and morphology of the resulting materials. Precious or rare metals perchlorates remain poorly studied.[1] Data are restricted to rhodium and palladium perchlorato complexes.[5,6] This lack of data results mainly from the difficulties of synthesis, easily explained by Pearson's HSAB principles.[7] The hard base ClO_4^- interacts more easily with hard acids than with soft acids such as gold or platinum. Moreover, the efficient perchlorating reagents involved in the reactions, anhydrous $HClO_4$ or Cl_2O_6, are known to be very strong oxidizers. Therefore, with precious metals in such a highly oxidative medium, O^{2-} competes with ClO_4^- and oxide perchlorates or oxides are expected rather than pure perchlorato complexes.

In this paper, the synthesis of $ClO_2Au(ClO_4)_4$ is described. The compound was obtained by reacting chlorine trioxide with various forms of gold(III) chlorides or on pure gold metal. This salt appeared as the unique gold(III) perchlorato complex which could be isolated and characterized. Prompted by the recent success of structural studies of lanthanide

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perchlorates,[8] the molecular and crystal structure of the gold complex was determined on the basis of powder X-ray diffraction data by ab initio Rietveld analysis. Infrared and Raman vibrational assignments were supported by DFT calculations.

Experimental Section

Caution! Chlorine trioxide and perchlorato complexes are highly reactive compounds. They can explode spontaneously on contact with organic substances or under shock. They must be handled with great care and in small amounts. Efficient protective shielding should be used. Reactions must be continuously monitored.

Materials. The perchlorating reagent Cl_2O_6 and the compounds with which it reacts are very hygroscopic. Perchlorates were prepared by using a vacuum line previously described.[1,9] Starting reactants as well as prepared perchlorates were handled in a glovebox under very dry nitrogen.

The starting salts, $AuCl_3$ (Aldrich 99%), $HAuCl_4 \cdot nH_2O$ (old laboratory stock), and micrometer-sized Au (Goodfellow, 99.95%), were used without purification. Cl_2O_6 was prepared, purified, and stored as previously reported.[1]

Synthesis of $ClO_2Au(ClO_4)_4$. In a typical experiment, small fractional amounts (0.1−0.3 g (0.6−1.8 mmol)) of Cl_2O_6 were successively transferred under vacuum and trapped at −180 °C on ≅0.2 g (≅1 mmol) of gold metal. The mixture was gently warmed to 0 °C, and this temperature was maintained until the Cl_2O_6 fraction was consumed. An excess of Cl_2O_6 was necessary to complete the conversion of the starting material into a perchlorato complex. Unreacted Cl_2O_6 and byproducts were pumped off at 10 °C. The progress of the reaction was followed by weighing and Raman analyses.

A well-crystallized and very hygroscopic orange compound was obtained in the first step. The Raman spectrum and color were both typical of a chloryl salt as generally observed at this stage.[1]

With 0.186 g of starting Au, 0.619 g of product was obtained, a mass very close to that expected for $ClO_2Au(ClO_4)_4$ (0.625 g). This formula was confirmed later upon solving the crystal structure. Additionally, data from elemental analysis were collected, using a specific perchlorate ion electrode (Orion 93-81) and complexometric analysis for Au. Despite an improved method to solubilize chloryl salts,[10] an excess of ClO_4^- was systematically found. (Calcd: Au, 29.74; ClO_4, 60.07. Found: Au, 29.74; ClO_4, 65.43.) Since, in aqueous media, a precipitated gold compound appeared, an aqua regia solution had to be used for complete dissolution. This strong oxidizing medium could favor oxidation of ClO_3^-, formed from ClO_2^+, into ClO_4^- and could explain the excess of ClO_4^- found.

Similar synthetic results were obtained by using $AuCl_3$ or $HAuCl_4 \cdot nH_2O$ as starting salts. However, only 3 portions of Cl_2O_6 were necessary to get a complete conversion of both salts into the perchlorato complex, while twice as much was needed for an equivalent amount of metallic Au.

Owing to their brittleness, the orange needles that appeared after the first addition of Cl_2O_6 could not be handled and sampled for a single-crystal analysis procedure.

Attempts To Synthesize $Au(ClO_4)_3$. Simple $M(ClO_4)_n$ complexes (M = metal) are usually obtained by a controlled thermal decomposition under dynamic vacuum of the starting corresponding chloryl salt. Unfortunately, $Au(ClO_4)_3$ could not be prepared in such a way at temperatures lower than 80 °C. The thermal decomposition of $ClO_2Au(ClO_4)_4$ is a progressive process that occurs over a large temperature range from 48 to 140 °C. It gives no well-defined $Au(ClO_4)_3$ compound. Although the main lines of $ClO_2Au(ClO_4)_4$ were retained in the Raman spectrum, new lines characteristic of oxo species, appeared above 48 °C. Au−O−Au vibrational modes were identified by broad lines in the 600−800 cm^{-1} range and a sharp line at 300 cm^{-1}. The intensities of these lines increased upon raising the temperature. The compounds became amorphous (XRD control) and darkened. Formation of gold oxides, oxide chlorides, or oxo perchlorato complexes could not therefore be verified by using X-ray analysis.

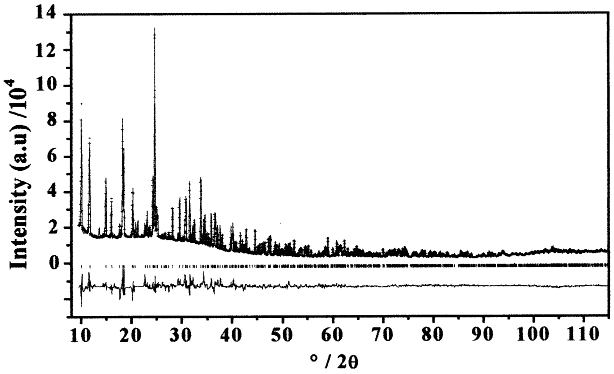

Figure 1. Observed (line) and calculated (crosses) and difference plots and peak markers for $ClO_2Au(ClO_4)_4$ after the final Rietveld refinement.

Attempts to extract Cl_2O_6 from $ClO_2Au(ClO_4)_4$ with anhydrous perchloric acid, an appropriate solvent for Cl_2O_6, were unsuccessful; they also yield oxo species.

As is usually observed, anhydrous $HClO_4$ behaved as a soft perchlorating reagent and was unable to react with either the starting products to yield $Au(ClO_4)_3$ or with any gold perchlorato complexes.

Structural Studies

Vibrational Analysis. Raman spectra were recorded at room temperature on a Labram Dilor spectrometer equipped with a BX40-(50LFx) Olympus microscope. Samples sealed in 0.3−0.5 mm thin-walled Pyrex capillaries were illuminated with a He−Ne laser (632.8 nm, 20 mW). IR data were collected on a Bomen DA8 FTIR spectrometer. Samples were pressed between well polished AgCl plates and placed in a very tight holder.

Molecular and Crystal Structure Determination. X-ray diffraction patterns were collected at the IMN (Nantes, France) on a INEL PSD DCS 120 diffractometer equipped with a curved detector. The Cu Kα_1 radiation, 1.540 59 Å, was used. $Na_2Ca_3Al_2F_{14}$ was the external standard (a = 10.250 12 Å). Carefully and finely ground samples were sieved and sealed in 0.3 mm thin-walled Lindemann capillary tubes.

The diffraction powder pattern (Figure 1) was indexed on the basis of 20 well-defined lines by running the TREOR90 program.[11] Figures of merit were quite low: $M(20) = 18(0.000\,040\,8)$, $F(20) = 25(0.011\,647\,70)$.[12] The solution was retained since a good fit was observed between the characteristic lines. A rough monoclinic cell was found: $a = 11.943$, $b = 5.2972$, $c = 11.108$ Å; $\beta = 98.51(3)°$; $V = 695.0$ Å^3.

A complete analysis of the observed lines with the DTETA program and selection of the extinction rules led to the determination

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of the space group.[13] Extinction conditions, $h + k = 2n$ for $hk0$, $h + l = 2n$ for $h0l$, $l = 2n$ for $00l$, and $k = 2n$ for $0k0$, are consistent with the $P2_1/n$ space group. However, an additional condition was observed, $h + k + l = 2n$, corresponding to an $\bar{I}$-centered cell. The primitive lattice was transformed to a doubled centered one by doubling the c parameter. New parameters were calculated as follows for a $C2/c$ symmetry: $a = 15.032$, $b = 5.297$, $c = 22.216$ Å; $\beta = 128.24°$.

The lack of compounds in the literature that show an isostructural relationship to $ClO_2Au(ClO_4)_4$ required that ab initio methods be used to build a structural model.

By consideration of the Le Bail method[14] first, integrated intensities were extracted from the powder pattern with the program suite EXTRA and SIRPOW (EXPO program).[15] A total of 947 lines were extracted in the angular range 9.57−114.72° (2θ). The semi-invariant profile method (direct method) adapted to powder patterns converged to a rough solution giving a set of atoms that describe a complete $ClO_2Au(ClO_4)_4$ crystallographic unit cell. A set of 13 atomic positions was found (1 Au, 3 Cl, 9 O) and chosen as the starting point for Rietveld refinements with the FULLPROF program.[16] The background was then extracted by linear interpolation over 24 points. A pseudo-Voigt function was used for the peak shape profile, and the asymmetry at low angles was corrected.[17] At this step, data obtained from vibrational data were considered (see below for a complete analysis). A previously established correlation function[1] showed that, from observed stretching frequencies in the complex, ClO_4 is monodentate with $ClO_b \approx 1.59$ Å and $ClO_t \approx 1.40$ Å (O_b = bridged oxygen to Au; O_t = free terminal oxygen). In another consideration, the Au−O distance, deduced from Brown and Shannon effective ionic radii for Au in a square planar environment, is expected at about 2.02 Å.[18] These relationships allowed us to constrain the values of 10 distances and 12 angles. In the final refinement, 47 parameters were varied simultaneously. Conditions and details for the refinement are summarized in Table 1. Plots of experimental and calculated X-ray diffraction patterns as well as their difference after the final Rietveld refinement are shown in Figure 1. Final atomic positions and isotropic thermal parameters are given in Table 2. Selected distances and angles appear in Table 3.

DFT Calculations. All calculations on the $Au(ClO_4)_4^-$ anion were carried out with the GAUSSIAN98 set of programs.[19] Gold was described with the Los Alamos relativistic core potential (ECP) for the 47 innermost electrons and its associated double-ζ basis set.[20] The chlorine atoms were also described with the Los Alamos ECPs and their associated double-ζ basis set [21] augmented by polarization d functions.[22] A 6-31G* basis set was used for the oxygen atoms.[23] For calculations at the higher level of theory, chlorine and oxygen atoms were described with the double- or triple-ζ correlation consistent basis set of Dunning and coworkers.[24]

Table 1. Details of Rietveld Refinements for $ClO_2Au(ClO_4)_4$

composn	$AuCl_5O_{18}$
M_r	662.22
symmetry	monoclinic
space group	$C2/c$
lattice params (Å, deg)	$a = 15.0474(5)$ $b = 5.2944(2)$ $c = 22.2020(2)$ $\beta = 128.325(2)$
Z	4
lattice vol (Å^3)	1387.62(8)
d(calcd) (g cm^{-3})	3.18
X-ray wavelength (Å)	1.540 60
2θ range (deg)	9.57−114.72
step incr (2θ)	0.03
no. of reflcns	948
no. of struct params	47
no. of restraint lengths	10
no. of restraint angles	12
no. of atoms	13
R_F	0.133
R_B	0.109
R_p	0.0705
R_{wp}	0.0943

Table 2. Atomic Coordinates and Isotropic Displacement Parameters (Å^2) for $ClO_2Au(ClO_4)_4$

atom	x	y	z	B_{iso}
Au	0.00000(0)	0.00000(0)	0.50000(0)	0.8(2)
Cl1	0.1010(7)	0.0274(19)	0.6705(5)	1.3(3)
Cl2	0.00000(0)	0.5090(5)	0.75000(0)	2.9(3)
Cl3	−0.1884(9)	0.3714(18)	0.4547(6)	1.9(2)
O1	−0.1350(10)	0.5280(4)	0.4362(7)	4.1(9)
O2	0.0790(13)	−0.0927(19)	0.7132(10)	6.0(2)
O3	0.2072(9)	0.0144(17)	0.6943(9)	3.7(2)
O4	−0.3099(7)	0.3913(18)	0.3917(6)	4.3(3)
O5	−0.1639(16)	0.092(2)	0.4527(11)	4.0(4)
O6	−0.1676(11)	0.4358(17)	0.5207(5)	3.8(2)
O7	0.0234(16)	−0.0891(16)	0.5902(8)	5.3(8)
O8	0.0641(13)	0.2828(19)	0.6579(11)	4.7(2)
O9	0.1029(19)	0.616(5)	0.8123(14)	4.9(6)

Table 3. Selected Bonds (Å) and Angles (deg)

bond dists	bond angles[a]
$Au(ClO_4)_4^-$	
2 × Au−O5 = 2.06(2)	O5−Au−O7 = 90.0(8)
2 × Au−O7 = 1.87(1)	
2 × Cl3−O1 = 1.41(2)	Au−O_b−Cl = 123.1(1)
2 × Cl3−O4 = 1.47(4)	O_b−Cl−O_t = 107(1)
2 × Cl3−O5 = 1.53(2)	O_t−Cl−O_t = 112(3)
2 × Cl3−O6 = 1.35(1)	
2 × Cl1−O2 = 1.35(2)	
2 × Cl1−O3 = 1.33(1)	
2 × Cl1−O7 = 1.53(2)	
2 × Cl1−O8 = 1.43(2)	
ClO_2^+	
2 × Cl2−O9 = 1.40(3)	O9−Cl2−O9 = 132(3)

[a] Mean values for $ClO_2Au(ClO_4)_4$. b: bridged. t: terminal.

Calculations were performed within the framework of density functional theory. The exchange potential was the one proposed by Becke[25] and included in part the exact Hartree−Fock exchange.[26] The correlation potential of Perdew and Wang (B3PW91) was used.[27]

Vibrational modes were displayed with the MOLDEN program.[28]

Results and Discussion

Synthesis. The main chemical abilities of Cl_2O_6, oxidation, perchloratation, and dehydration, were encountered during this work. Au(0) was oxidized to Au(III), [ClO_4] was allowed to bind to Au, and from a hydrated acidic chloride, this led to an anhydrous complex, as was the case from Au or $AuCl_3$.

As usually observed when using Cl_2O_6 as perchlorating reagent, a chloryl salt was obtained in a first step. Upon

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warming or washing with anhydrous $HClO_4$, $ClO_2Au(ClO_4)_4$ did not lead to the expected neutral complex $Au(ClO_4)_3$. Such a result has already been encountered with $(ClO_2)_2Ge(ClO_4)_6$; so far, $Ge(ClO_4)_4$ has never been obtained.[29]

For $Au(ClO_4)_3$, two structural hypothesis can be brought forward:

(1) A monomeric unit is formed in which $[ClO_4]$ should be either a monodentate or a chelating bidentate ligand. In both cases Au(III) should be in a trigonal or octahedral configuration never or rarely found at this oxidation state.[30]

(2) A polymeric unit is formed which is impossible to build starting from monomeric $ClO_2Au(ClO_4)_4$ species.

These hypothesis are supported by recent results on Pd perchlorato complexes[6] and main results in the perchlorato complex family.[1] Monomeric $(ClO_2)_2Pd(ClO_4)_4$ in which Pd is in a square planar configuration led to the monomeric $Pd(ClO_4)_2$ with Pd remaining in a square plane surrounded with chelating bidentate $[ClO_4]$ groups. Chloryl salts generally show polymeric structures, and their configurations are retained in the neutral complex formed by their decomposition.[1] However, we have to emphasize that with SO_3F^-, whose Pearson hardness is close to that of ClO_4^-, Aubke et al. characterized polymeric $Au(SO_3F)_3$ with Au in a square planar environment.[31]

Molecular Structure Analysis. The molecular structure shows individual ClO_2^+ and $Au(ClO_4)_4^-$ ions. Au is bonded to 4 oxygen atoms in a distorted square planar environment with two long and two short Au−O bonds, respectively: 2.06 and 1.87 Å (Figure 2). A similar environment was previously observed in a gold fluorosulfato complex by Aubke et al.[31] The mean Au−O distance (1.96 Å) is substantially lower than expected (2.03 Å) but very close to that found in

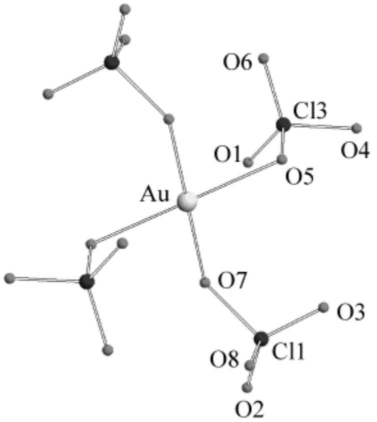

Figure 2. Anion $Au(ClO_4)_4^-$.

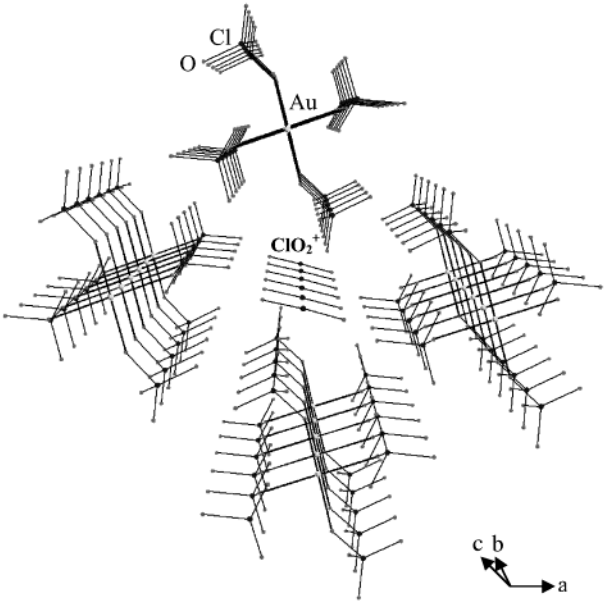

Figure 3. Perspective view of the stacking of ClO_2^+ and $Au(ClO_4)_4^-$ along the *b* axis.

$M(OClO_3)_n$ complexes.[1] Au−O−Au angles are close to 90° (88.3 and 91.7°).

$Au(ClO_4)_4^-$ ions are stacked along the *b* axis (Figure 3). Au atoms are $\bar{1}$ centered, and therefore the Au---Au distance corresponds to the *b* parameter value: 5.294 Å. Four $Au(ClO_4)_4^-$ stackings form a channel in which ClO_2^+ ions are located. $[ClO_4]$ groups are monodentate, and mean ClO_b and ClO_t distances (respectively 1.53 and 1.39 Å) are close to those observed for other complexes that show monodentate $[ClO_4]$ groups.[1] However, ClO_b distances are shorter than those expected from vibrational data (1.59 Å). Some disorder gives a poor accuracy and a spreading of ClO_t distances values; such a phenomenon has previously been observed in $(ClO_2)_2Sn(ClO_4)_6$[32] and often arises in compounds containing $[ClO_4]$.[1]

ClO distances in ClO_2^+ (1.40 Å) are similar to those found in chloryl salts such as ClO_2ClO_4,[33] $ClO_2Sb_2F_{11}$,[34] ClO_2GeF_5,[35] ClO_2BF_4,[36] and $(ClO_2)_2Sn(ClO_4)_6$.[32] However, the

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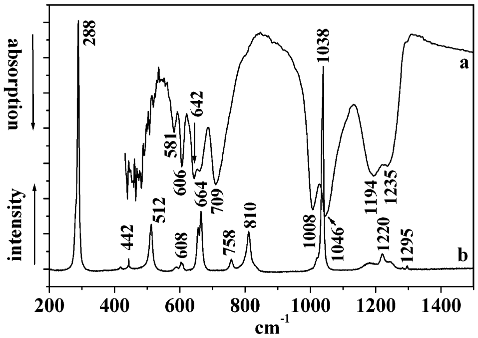

Figure 4. IR (a) and Raman (b) spectra of $ClO_2Au(ClO_4)_4$.

Table 4. DFT Optimization of the $Au(ClO_4)_4^-$ Geometrical Data (Bonds (Å); Angles (deg)) at the B3PW91 Level of Theory and Given Basis Sets (Au, LANL2DZ; Cl, O, cc-pVTZ) Compared to Values Obtained from Relationships Established Elsewhere[1] (REE) and Crystal Data

bonds/angles	DFT data	REE data	cryst data
Au−O	2.020	2.035[a]	2.06
	2.016	2.035[a]	1.87
$Cl-O_t$	1.437	1.405[b]	1.40
$Cl-O_b$	1.602	1.586[b]	1.53
$Au-O_p-Cl$	117.8		123.1
O_p-Cl-O_t	105.4		107
O_t-Cl-O_t	113.2		112
O−Au−O	87.7		88.3
	92.3		91.7
E (ua)	−317.617 331 91		

[a] $d(MO) = f(eir)$ (eir: effective ionic radii from Brown an Shannon[17]). [b] $\nu = f(d(ClO))$.

OClO angle is larger than those previously observed (132° compared to 120°). Distances between the Cl atom in ClO_2^+ and a terminal oxygen atom of one of two monodentate ClO_4 group lie between 2.78 and 3.00 Å, which are shorter than the sum of Cl and O van de Waals radii: 3.2 Å. A similar anion−cation interaction has previously been observed in perchlorato chloryl salts.[1] The shorter Au−O distance is that of the monodentate $[ClO_4]$ group interacting with the ClO_2^+ cation. Steric as well as electronic considerations could explain the unusual distorted square planar surrounding for the 16 electron $Au(ClO_4)_4^-$ anion.

Vibrational Analysis. IR and Raman spectra are shown Figure 4. A first assigment was done on the basis of well-established previous results.[1]

The ClO_2^+ cation is unambiguously characterized by the strong Raman line at 1038 cm^{-1}. This symmetric stretching mode appears at 1046 cm^{-1} in the IR spectrum. The other characteristic lines are the bending mode at 512 cm^{-1} and the antisymmetric stretching mode, split by a $^{35}Cl-^{37}Cl$ isotopic shift at 1282 and 1295 cm^{-1}. These modes are poorly observed in the IR spectrum; they are hidden by $[ClO_4]$ vibrational modes.

The distribution and frequencies of bands and lines in the 400−1300 cm^{-1} range demonstrate a monodentate $[ClO_4]$ group. Stretching modes (symmetric and antisymmetric modes) of the ClO_t bonds are located respectively at 1008 (IR), 1020−1038 (Raman) and 1194−1235 (IR), and 1180−1243 (Raman) cm^{-1}.

The anion−cation interaction above, characterized in the molecular structure of $ClO_2Au(ClO_4)_4$, obviously appears in the Raman spectrum. ClO_4 interacting with ClO_2^+ shows that it behaves as a pseudobidentate ligand, and the stretching ClO_b frequency shifts to higher energy: 810 cm^{-1}. In contrast, for the noninteracting ClO_4, $\nu(ClO_b)$ appears at 758 cm^{-1} very close to that usually observed.[1] The deformation modes are located as expected between 400 and 700 cm^{-1}. The very strong line at 288 cm^{-1} is the Au−O stretching mode.

DFT Calculations. To improve the assigments of vibrational modes and to evidence couplings, a DFT calculation was carried out. Calculations were run only for the individual anion $Au(ClO_4)_4^-$. The negative charge can be considered to be delocalized over the 21 atoms of the $Au(ClO_4)_4^-$ anion so that the calculational problems usually encountered for anions are minimized. The geometry was optimized starting from a model based on crystallographic data. Anion−cation interactions were neglected. Calculations were repeated at three different levels of theory (LANL2DZ/6-31G*, LANL2DZ/ccpVDZ, LANL2DZ/ccpVTZ). They all converged to the same calculated geometry with Au in a distorted square planar environment and monodentate ClO_4 groups. Geometrical data from the higher level of calculation (B3PW91/LANL2DZ/ccpVTZ) are compared to values obtained from relationships established elsewhere[1] and crystal data in Table 4.

Regardless of the level of theory and basis set used, the same classifications of vibrational energy levels and couplings were obtained. The best agreement between experimental and calculated data were obtained with the higher level of calculation (B3PW91/LANL2DZ/ccpVTZ). Calculated and experimental vibrational frequencies as well as their assignments are given Table 5. Shifts between experimental and calculated data are reasonable although anion−cation interactions are not taken into account. Shifts are also consistent with those observed in several solids for which a similar procedure was carried out.[37]

The main energy levels of vibrational modes are identical to rough assignments obtained from literature data on complexes, including monodentate $[ClO_4]$. They are also consistent with previous calculations on a distorted $[ClO_4]$ group model without any interactions with a metallic cation[1] and results on anhydrous $HClO_4$.[38] The main striking feature concerns a complete description of couplings between ClO vibrations themselves as well as those involving the ClO vibrations and the MO_n skeleton vibrations. As expected, strong couplings appear between the $[ClO_4]$ group deformation modes and the AuO_4 stretching and deformation modes in the 350−700 cm^{-1} range. This is the first time that a such description has been given for a whole perchlorato complex including a metallic core and monodentate $[ClO_4]$ groups.

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Table 5. Experimental and Unscaled Calculated Frequencies, Assignments, and Mode Descriptions for $ClO_2Au(ClO_4)_4$[a]

exptl (cm^{-1})			
IR	Raman	DFT results (cm^{-1})	assignts
	1295 (2)		$\nu_s(ClO_2^+)$
	1282 (2)		
1235 (m)	1243 (4) br	1240 (0)	$\nu_{as}(ClO_{3t})$
	1220 (7)	1233 (27)	
		1231 (40)	
1194 (m)	1180 (4) br	1229 (0)	
		1227 (65)	
		1221 (0)	
		1217 (15)	
		1214 (0)	
1046 (s)	1038 (82)		$\nu_s(ClO_2^+)$
	1035 sh		
		1029 (0)	$\nu_s(ClO_{3t}) + \nu(ClO_b) + \delta_s(ClO_{3t})$
1008 (s)	1020 sh	1013 (0)	
		1013 (36)	
		1007 (26)	
807 (sh)	810 (16)	764 (0)	$\nu(ClO_b) + \delta_s(ClO_{3t})$
		732 (0)	
	758 (5)	706 (100)	$\nu(ClO_b) + \delta_s(ClO_{3t}) + \Pi(AuO_4)$ (a) (b)
709 (s)		696 (92)	
	664 (24)	669 (62)	$\delta_{as}(ClO_{3t}) + \delta(AuOCl) + \nu_d(AuO)$
660 (m)		662 (0.6)	
	655 (18)	640 (0)	$\delta_{as}(ClO_{3t}) + \delta(AuOCl) + \nu_s(AuO)$
642 (m)		630 (0)	$\delta_{as}(ClO_{3t}) + \delta(AuOCl) + \nu_a(AuO)$
606 (m)	608 (3)	597 (0.8)	$\delta_s(ClO_{3t}) + \Pi(AuO_4)$ (a)
	603 (4)	594 (1)	
581 (w)	589 sh br	587 (0)	$\delta_s(ClO_{3t}) + \delta(AuOCl)$
		582 (0)	
		568 (0)	$\rho(ClO_4) + \delta_s(AuO_4)$
		567 (3)	$\rho(ClO_4) + \delta_d(AuO_4)$
	544 (<1)	562 (3)	
		559 (0)	$\delta_s(ClO_{3t}) + \rho$ (c)
	512 (19)		$\delta(ClO_2^+)$
		505 (3)	$\delta_s(ClO_{3t}) + \Pi(AuO_4)$ (a)
		504 (1)	$\delta_s(ClO_{3t}) + \Pi(AuO_4)$ (b)
		491 (0)	$\delta_s(ClO_{3t}) + \delta(AuOCl)$
	442 (3)	486 (0)	
	440 (5)	416 (ϵ)	$\rho(ClO_4) + \delta_d(AuO_4)$
	417 (2)	411 (0)	$\rho(ClO_4) + \delta(AuO_4)$
	371 (<1)	396 (ϵ)	$\rho(ClO_4) + \delta_d(AuO_4)$
		388 (0)	ρ (c)
	288 (100)	285 (4)	$\nu_a(AuO)$
		283 (5)	
		257 (0)	$\nu_s(AuO)$
		251 (0)	

[a] Level of theory and basis sets are specified in the text and in the title of Table 4. Experimental and calculated IR intensities are given in parentheses. Key: s = strong; m = medium; w = weak; sh = shoulder; br = broad. a: ν_3 (D_{4h}). b: ν_5 (D_{4h}). c: overall motion.

Conclusions

Since the pioneering works of Schmeisser et al.[39] and Hathaway[40] on perchlorato complexes, the family has greatly expanded. A recent review on the subject displayed a large variety of complexes among the elements of the periodic table.[1] Despite this extensive information, knowledge on this versatile and fascinating family increases again. Notwithstanding unfavorable conditions, perchlorato complexes of gold (this work), palladium,[6] platinum,[41] and rhenium[42] could be prepared and characterized. While perchlorato complexes are generally polymeric, they were found to be monomeric for Pd, Pt, and Au. ClO_4 did not act in these cases as a building block as is usually found. According to the HSAB principles, with these soft acids, in a strong oxidizing medium, O^{2-}, as a hard base, should be a better building block than ClO_4^-. Therefore, perchlorato complexes with two- or three-dimensional networks would be expected to be in the form of oxo complexes with $M-O_n-M$ bridges.

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Note Added after Print Publication: Due to a production error, the superscript + of ClO_2^+ in Figure 3 appeared too distant from ClO_2 in the version of this article published on the Web on 07/10/2002 (ASAP) and in the August 12, 2002, issue (Vol. 41, No. 16, 4173−4178); the correct electronic version of Figure 3 was published on 09/20/2002, and an Addition and Correction appears in the October 21, 2002, issue (Vol. 41, No. 21).

Supporting Information Available: Tables of structural and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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