Au - Cl

VI 62 I960

ICl_4^-, $AuCl_4^-$, $AuBr_4^-$, $PtCl_4^{2-}$ (U_i силовые постоянные).

Stammreich H., Forneris R.

Spectrochim. acta, I960, I6, N 3, (англ)

Спектры комбинационного рассеяния и силовые постоянные плоских квадратных молекул типа AB_4.

РЖХим.,I96I,4Б80

AuCl4⁻

1964

9 Д291. **Низкочастотные ИК-спектры и колебательные силовые постоянные ионов $AuCl_4^-$, $AuBr_4^-$ и $PtCl_4^{2-}$.** Sabatini A., Sacconi L., Sclettino V. Far-infrared spectra and vibrational force constants of the ions $AuCl_4^-$, $AuBr_4^-$, and $PtCl_4^{2-}$. «Inorgan. Chem.», 1964, 3, № 12, 1775—1776 (англ.)

Изучены ИК-спектры (80—400 $см^{-1}$) комплексов M_2PtCl_4 (M=K, Pb, Cs) и $MAuX_4$ (M=Rb, Cs; X=Cl, Br) (плоские квадратные соединения принадлежат к группе симметрии D_{4h}). Предложено следующее отнесение частот колебаний ионов $AuCl_4^-$, $AuBr_4^-$, $PtCl_4^{2-}$ к типам симметрии: A_{1g} — 347, 212, 335; B_{1g} — 171, 102, 164; B_{2g} — 324, 196, 304; E_u — 356, 252, 316; E_u — 173, 100, 185 $см^{-1}$. Эти частоты использованы для вычисления пяти силовых постоянных в естественных колебательных координатах и трех силовых постоянных в системе Юри — Брэдли каждого иона. М. Ковнер

11-32169

3

ф. 1965. 9Д

1966

VI-4038

Ae (WF_6, FeF_6, OsF_6, IrF_6, PtF_6, AuF_6)

Bartlett N., Beaton S.P., Iha N.K.

Chem.Communs, 1966, N6, 168-69.

Oxiditing trends in the third-transition-geries hexafluorides.

RX. 1966, 18B209. J

$AuCl_4^-$ Jones L. H. (1966

Coord. Chem. Rev., 1(3), 351.

Significance of force constants of a general quadratic valence force field; application to $Au(CN)_2^-$, $PtCl_4^{2-}$, $AuCl_4^-$, $AuBr_4^-$, $Au(CN)_2Cl_2^-$

III [cm. $Au(CN)_2^-$]

$AuCl_4^-$

Вор-4112-Vi

16302u Mean amplitudes of vibration in some square-planar tetrahalo complexes. G. Nagarajan (Univ. of Maryland, College Park). *Acta Phys. Austriaca* 24(1), 20–6(1966)(Eng). The mean amplitudes of vibration for the ions $AuCl_4^-$, $AuBr_4^-$, and $PtCl_4^{--}$ were studied at 298 and 500°K. by utilizing the symmetry coordinates. The secular equations giving the normal frequencies in terms of the mean-sq. amplitude quantities were constructed at 298 and 500°K. with help of the Σ and G matrixes. The symmetrized mean-sq. amplitude matrixes Σ_{11}, Σ_{22}, Σ_{33}, and Σ_{66} were evaluated directly. Since the out-of-plane bending vibration under the symmetry species B_u is inactive in both Raman and ir absorption spectra, the mean-sq. amplitude quantity σ_ϕ was calcd. directly from the symmetrized mean-sq. amplitude matrix Σ_{66}. In general, the mean-sq. amplitude quantity due to the bonded atom pair σ_r is always smaller than that of the non-bonded atom pair σ_d. The mean sq. amplitude quantities due

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C.A. 1967. 67. 4

to the in-plane and out-of-plane bendings σ_θ and σ_ϕ are very much greater than those due to the bonded and nonbonded atom pairs σ_r and σ_d. The situation is reversed in the cases of the corresponding force consts. The mean-sq. amplitude quantity due to the out-of-plane bending σ_ϕ is greater than that of the in-plane bending σ_θ. The mean amplitudes of vibration for the bonded as well as nonbonded atom pairs are in the increasing order from the $AuCl_4^-$ ion to the $AuBr_4^-$ ion at both temps. The values of the mean amplitudes of vibration are reliable at room temp. only when the fundamental frequencies in wave nos. for any mol. or ion are in the range 200–1200 $cm.^{-1}$

Charles H. Gorski

$AuCl_4^-$ Вф-4112-VI 1966

13 Б160. Средние колебательные амплитуды в некоторых квадратных плоских комплексах тетрагалогенидов. Nagarajan G. Mean amplitudes of vibration in some square-planar tetrahalogeno complexes. «Acta phys. austriaca», 1966, 24, № 1, 20—26 (англ.)

Приводятся частоты колебаний ионов $AuCl_4^-$, $AuBr_4^-$, $PtCl_4^-$, отнесенные к типам симметрии группы D_{4h} и к валентным и деформационным колебаниям. Эти частоты применены для вычисления элементов матриц Σ средних квадратичных амплитуд колебаний в координатах симметрии, средних квадратичных амплитуд колебаний естественных колебательных координат и их взаимодействий и средних амплитуд колебаний расстояний между свя-

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Б812-11

х · 1967 · 13

занными и несвязанными парами атомов. Для всех 3 ионов все указанные амплитуды вычислены при значениях т-ры 298 и 500° К. Из сравнения результатов следует, что средние квадратичные амплитуды плоских и неплоских деформационных колебаний больше соответствующих амплитуд для расстояний между атомами, причем амплитуды колебаний расстояний между несвязанными атомами превосходят амплитуды для пар связанных атомов. Средние амплитуды колебаний расстояний обоих типов возрастают при переходе от $AuCl_4^-$ к $AuBr_4^-$. М. Ковнер

$AuCl_4^-$

$AuBr_4^-$

$PtCl_4^{--}$

Вф-4112-VI

1966

5 Д108. **Средние колебательные амплитуды в некоторых квадратных плоских комплексах тетрагалогенидов.** Nagarajan G. Mean amplitudes of vibration in some square-planar tetrahalogeno complexes. «Acta phys. austriaca», 1966, 24, № 1, 20—26 (англ.)

Приводятся частоты колебаний ионов $AuCl_4^-$, $AuBr_4^-$, $PtCl_4^{--}$, отнесенные к типам симметрии группы D_{4h} и к валентным и деформационным колебаниям. Эти частоты применены для вычисления элементов матриц Σ среднеквадратичных амплитуд колебаний в координатах симметрии, среднеквадратичных амплитуд колебаний естественных колебательных координат и их взаимодействий и средних амплитуд колебаний расстояний между связанными и несвязанными парами атомов. Для

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+3

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всех трех ионов все указанные амплитуды вычислены при значениях т-ры 298 и 500° К. Из сравнения результатов следует, что среднеквадратичные амплитуды плоских и неплоских деформационных колебаний больше соответствующих амплитуд для расстояний между атомами, причем амплитуды колебаний расстояний между несвязанными атомами превосходят амплитуды для пар связанных атомов. Средние амплитуды колебаний расстояний обоих типов возрастают при переходе от $AuCl_4^-$ к $AuBr_4^-$.

М. Ковнер

1967

VI-4041

(XeF_4, ICl_4^-, $PtCl_4^{2-}$, $AuCl_4^-$, $AuBr_4^-$, $/Pt(NH_3)_4/^-$. силовые пост.

Fadini A., Muller A.

Molec.Phys., 1967, 12, N2, 145-48.

Berechnung von Kraftkonstanten des allgemeinen Valenzkrafftfeldes eniniger Molekule und lonen von Typ XY_4 mit D_4h-symmetric nach dem verfahten der nachsten losung.

RF., 1967, 10D156 J

1968

13 Б208. Спектры в дальней ИК-области систем с галоидными мостиками. Часть II. Au_2Cl_6, Al_2B_6, Al_2J_6 и In_2J_6. Adams D. M., Churchill R. G. Vibrational spectra of halogen—bridged systems. Part II. Au_2Cl_6, Al_2Br_6, Al_2J_6, and In_2J_6. «J. Chem. Soc.», 1968, A, № 9, 2141—2144 (англ.)

Исследованы низкочастотные ИК-спектры крист. Au_2Cl_6 (I), Al_2Br_6 (II), Al_2J_6 и In_2J_6, а также спектры КР крист. I и р-ра II в циклогексане. Предложено эмпирич. отнесение полос. Проведен анализ нормальных координат для плоских колебаний молекулы I. Найденные силовые постоянные мостиковых и концевых связей Au—Cl соотв. равны: F_b=1,740; F_t=2,384 (*мдин*/А). Величина отношения F_b/F_t в димерах рассматриваемого типа зависит от характера координации металла: для квадратно-плоскостных комплексов она составляет ≈0,75, для тетраэдрич. ≈0,5. Часть I см. РЖХим, 1968, 20Б254.

В. А. Сипачев

Au_2Cl_6

2 6

X. 1969. 13

+3

Au_2Cl_6

Al_2Br_6

Al_2I_6

In_2I_6

(v.)

Raman emiss

+ Bibl

C.A. 1968: 69. 20

V-5903

1968

819578 Vibrational spectra of halogen-bridged systems. II. Au_2Cl_6, Al_2Br_6, Al_2I_6, and In_2I_6. Adams, D. M.; Churchill, R. G. (Univ. Liecester, Liecester, Engl.). *J. Chem. Soc., A* 1968, (9), 2141–4 (Eng). Their partial Raman data are reported and assigned for the title compds. A normal-coordinate anal. has been made for Au_2Cl_6. The most significant result of the calcn. is that the bridge bond stretching force const. in Au_2Cl_6 is 73% that of the terminal bond, whereas it is approx. 50% in Al_2Cl_6; this difference is rationalized and generalized.

RCGF

X

1968

Au_2Cl_6

Beattie I. R.,
Gilson T. R., Ozin G. A.

J. Chem. Soc., A, N 11, 2765

Колеб. спектр

III – Cs

(соед. $Cs_3Tl_2Cl_9$) III

$PdCly_2^-$; $PtCly_2^-$; $PdBry_2^-$; (cun.) 6 1969
$AuCly^-$; $AuBry^-$; $AuIy^-$ (nocm.)

VI 7279

Awiq J.A.; Nagarajan G.,
Monatsh. Chem., 1969, 100(6), 1960-72. (Ge

Potential energy constants and mean amplitudes of vibration in some square planar complexes of palladium, platinum and gold.

10 10

CA 1970 72, N12, 70818h

1970

Vi, cun. noct (I_2Cl_6, Au_2Cl_6)

Fornéris R., Hizaishi Z., 6 11
Miller F.A., Uehara M., VI7317

Spectrochim. acta, 1970, A26, N3, 581-591 (англ.)

Raman and infrared spectra
of I_2Cl_6 and Au_2Cl_6.

Ref Zhur, 1970, 13G154

1973

$AuCl_4$

$PtCl_4$

85018r Green's function formalism and molecular force field ellipses for XY_4 structures. Narayana, K. L.; Sabale, B. P. (Theor. Phys. Group, Shivaji Univ., Kolhapur, India). *Curr. Sci.* 1973, 42(15), 535–6 (Eng). The symmetry force consts. F_{44}, F_{45}, and F_{55} (in mdyne Å), resp., calcd. by the previously described (N. and S., 1972) method for the E_u species of the planar XY_4 mols. are: $AuCl_4$, 1.88, 0, 0.25; $PtCl_4$, +1.406, −0.008516, +0.2861. For both $AuCl_4$ and $PtCl_4$, F_{44} and F_{55} vary as elliptical functions of F_{45}.

Спл. пост.

(+1)

C. A. 1973. 79 N 14

AuCl4

1973

2 Д211. Формализм функций Грина и эллипсы силового поля для молекул типа XY_4. Narayana K. L., Sabale B. P. Green's function formalism and molecular force field ellipses for XY_4 structures. «Curr. Sci.» (Indian), 1973, 42, № 15, 535—536 (англ.)

Вычислены силовые постоянные для трижды вырожденных колебаний молекул $AuCl_4$ и $PtCl_4$, и построены кривые зависимости (эллипсы) диагональных силовых постоянных от недиагональной. М. Р. Алиев

(+1) 18

+ 19792

41011.1926
Ch,TC,MGU,Ph

$PtCl_4$ $AuCl_4^-$ 34469 Д

1974
2512

Thirugnanasambandam P., Mohan S. Molecular constants of some XY_4 square planar type molecules & ions.
"Indian J. Pure and Appl. Phys.", 1974, 12, N 3, 206-209
(англ.) 0709 пик

ВИНИТИ

172 179

$AuCl_2^-$ 1974

Zwanziger Heinz
et. al.

кв. мех.
расчет

Z. Chem 1974, 14(12)
489-90 (Ger).

(см AuF_2^- III)

$AuCl_2^-$ ЖУ-10440 1975

$AuBr_2^-$

AuI_2^-

Ср. квадр. амплит. колеб.

68189n **Mean amplitudes of vibration for some linear gold(I) complexes.** Baran, Enrique J. (Fac. Cienc. Exactas, Univ. Nac. La Plata, La Plata, Argent.). *Spectrosc. Lett.* 1975, 8(2–3), 151–5 (Eng). Mean amplitudes of vibration were calcd. for $AuCl_2^-$, $AuBr_2^-$, and AuI_2^- ions at different temps. between 0 and 500°K; at >300°K, the expected trend of lower values of mean amplitudes of vibration for stronger bonds was obsd. but in the 0–300°K range the so-called low temp. anomaly was evident. Comparisons are made between these results and those previously reported for isoelectronic Hg halides, $AuCl_4^-$ and $AuBr_4^-$ ions and the bonding is discussed. The Bastiansen–Morino shrinkage effect was estd.

(+2) ☒

С.А. 1975. 83. N8

Thirugnanasambandam P., Mohan S. Mean amplitudes of vibration of some square planar XY_4-type molecules and ions. "Indian J. Pure and Appl. Phys.", 1975, 13, N 6, 398–401 (англ.)

$AuCl_4^-$ U-17389 1976

$AuBr_4^-$

86: 35959x **Influence of cation on the harmonic force field and mean vibrational amplitudes of square planar tetrachloroaurate(III) and tetrabromoaurate(III) ions.** Sanyal, Nitish K.; Verma, D. N.; Dixit, Lal J. (Dep. Phys., Univ. Gorakhpur, Gorakhpur, India). *Indian J. Pure Appl. Phys.* 1976, 14(6), 456-60 (Eng). Harmonic force consts. of $AuCl_4^-$ and $AuBr_4^-$ are presented by using general valence force fi... The 3 approx. methods, viz. $L_{12}=0$, $L_{21}=0$ and P. E. D., a... used to solve the 2-degree eigenvalue problem. $L_{12}=0$ Appro... gives better results. The effects of different cations on vari... force consts. are discussed. Esp. f'_{rr} and f_{rr} show anomal... changes with respect to the bending force const. The bond... mean amplitudes show the expected trend of variation whe... nonbonded amplitudes undergo simultaneous changes correspond... to light or heavy cations.

M.M.

C.A. 1987. 86:6 (+1) AJ

70317.1539 Ph, Ch, TC	34469 $AuCl_4^{2-}$	1976 * 4-17395

Sanyal Nitish K., Verma D.N., Dixit L.
Mean vibrational amplitudes and force field of tetrahalogeno-gold(III), -palladium(II), and -platinum(II) anions.
"Indian J. Pure and Appl. Phys.", 1976, 14, N 10, 819-822 (англ.) 0832 ГПНТ

793 793 823 (ссч. $PdCl_4^{2-}$, III) ВИНИТИ

AuCl$_4^{-}$ оттиск 5540 1977

AuBr$_4^{-}$

Di, сим. роет. колеб. (?)

Pandey A. N. et. al.

J. Raman. Spectrosc., 1977, 6, 163-164

Forse constants and Bond palarizability...

$AuCl_4^-$ 1974.

Pandey A. N., et al

сил. кост. J. Mol. Struct., 1977,

42, 171-179.

(сш. $PdCl_4^{2-}$ - III)

$AuCl_2^-$

1981

Husson Elisabeth, et al.

ав. иос. Spectrochim. Acta, Part A 1981, 37A (12), 1087 - 1092.

(см. AuCl; III)

Au-Cl соединения. 1981

Tossell J. A., et al.

Энергии связи

Inorg. Chem. 1981, 20, N10, 3333-3340.

(см. Cu-Cl соед. I III)

$AuCl_2^-$ | От. 17404 | 1983

Колебат. анализ. сил. пост.

Srinivasan B. M., Ramasamy R., et al., Indian J. Pure and Appl. Phys., 1983, 21, N1, 16-18.

$AuCl_2^-$

ОМ. 23053

1985

Bowmaker G. A., Boyd P. D. W., Sorrenson R. J.,

Расчет электрон. структ., спектр. прост.

J. Chem. Soc. Faraday Trans., 1985, Pt 2, N 11, 1627–1641.

$AuCl_2$ 1985

Bowmaker Graham A.

Boyd Peter D.W., et al.

el. n. J. Chem. Soc. Faraday Trans.,
1985, PT2, 81, N 11, 1627-1641.

(сл. $CuCl_2^-$; III)

$AuCl_2^-$ (Dm·27876) 1987

Chowdhury A. Kasem,
Wilkins Ch. L.

Do J. Amer. Chem. Soc.,
1987, 109, N 18, 5336-
5343.

(see. $Ar^+ - CH_2$; III)

Au-Cl (OM. 27876) 1987

Chowdhury A.K., Wilkins Ch.L.,

Do J. Amer. Chem. Soc., 1987, 109, N 18, 5336-5343.

$AuCl_2^-$ ОМ 31248 1988

10 Б1045. Электронная структура противоионов в органических солях AuX_2^-, X=Cl, Br, I / Гуцев Г. Л. // Изв. АН СССР. Сер. хим.— 1988.— № 12.— С. 2777—2779.— Рус.

Установлено, что первые Пт ионизации анионов дигалогенидов золота имеют довольно высокие значения, что объясняет образование солей с их участием. Высокие значения ПИ анионов дигалогенидов золота связаны со структурой ВЗМО. По данным расчета ДВМ-X_α-методом, образование солей с участием анионов дигалогенидов золота объяснено высокими значениями их первых Пт ионизации, связанными со структурой верхней занятой МО, имеющей π-тип и локализованной преимущественно на атомах галогенов. Из резюме

М.П.

(12) IX

$AuBr_2^-$, AuJ_2^-

Х. 1989, N 10

Au_2Cl_6

1992

117: 241821h Raman spectra and molecular vibrations of digold hexachloride and gold aluminum hexachloride. Nalbandian, L.; Papatheodorou, G. N. (Inst. Chem. Eng. High Temp. Chem. Processes, Univ. Patras, Patras, Greece GR-26110). *Vib. Spectrosc.* 1992, 4(1), 25–34 (Eng). Raman spectra of gold(III) chloride in the solid and vapor ($Au_2Cl_6(g)$) phases and of the vapor complex $AuAlCl_6(g)$ were measured at temps. up to 570 K. The distribution of vibrational modes in $AuCl_3(s)$ were derived and six low frequency Raman bands were assigned to librational modes of the solid. Fifteen internal modes of the $AuCl_3(s)$ were measured in the Raman and IR spectra and were assigned to the Au_2Cl_6 mol. in the crystal. Normal coordinate anal. was performed and a complete force field was derived for the Au_2Cl_6 in the crystal. Expt. difficulties arising from laser induced decompn. of the colored vapors Au_2Cl_6 and $AuAlCl_6$ were overcome by using a rotating Raman cell inside the optical furnace. Four polarized bands at 386, 324, 157 and 93 cm^{-1} and their combinations and overtones were measured in the resonance Raman spectra of $Au_2Cl_6(g)$. The Raman intensities of the $AuAlCl_6(g)$ were also resonance enhanced and seven polarized fundamentals were measured at 435, 386, 330, 300, 183, 156 and 98 cm^{-1}. A tentative normal coordinate anal. was performed for $Au_2Cl_6(g)$ and $AuAlCl_6(g)$. The force field calcns. of $AuClCl_6(g)$ with a C_{2v} symmetry were based on a procedure of mixing the force consts. of the $Al_2Cl_6(g)$ and $Au_2Cl_6(g)$.

(CKP zaja)

(42)

C.A. 1992, 117, IV 24

$2AuCl_3(к) = Au_2Cl_6(г)$ 1992

116: 222358a Vaporization and vapor complexation in the gold(III) chloride-aluminum(III) chloride system. Nalbandian, L.; Boghosian, S.; Papatheodorou, G. N. (Inst. Chem. Eng. High Temp. Chem. Processes, Univ. Patras, Patras, Greece 26110). *Inorg. Chem.* 1992, 31(10), 1769–73 (Eng). The vapors over solid gold(III) chloride and the vapor–phase equil. of the gold(III) chloride–aluminum(III) chloride binary system were investigated spectrophotometrically. The thermodn. functions of the sublimation $2AuCl_3(s) = Au_2Cl_6(g)$ were detd.: ΔH_s° = 114.2 + 1.8 J/mol. and ΔS_s° = 160.5 ± 3.3 J/mol.K (480 < T < 580 K). One predominant vapor complex found in the binary system formed according to the reaction $AuCl_3(s) + 1/2Al_2Cl_6(g) = AuAlCl_6(g)$ with ΔH_R° = 59.9 ± 0.8 kJ/mol ΔS_R° = 91.5 ± 1.6 J/mol.K (470 ≤ T ≤ 550 K). At 470 K and 1 atm $Al_2Cl_6(g)$ pressure the volatility enhancement of $AuCl_3$ is ~300. The electronic absorption spectra of the $Au_2Cl_6(g)$ and $AuAlCl_6(g)$ mols. were interpreted in terms of a distorted square planar geometry of Au(III). "Bridged" and "terminal" ligand-to-metal charge-transfer bands were indentified in the spectra.

$\Delta S_{sub.}, \Delta H^\circ_{sub.}$

(+2) IX

$Au_2Cl_6(2)$ (электрон. спектр поглощ. спектра)

$AuAlCl_6(2)$

C. A. 1992, 116, N 22

F: Ar-AuCl
P: 3
2000
133:96171 Noble Gas-Metal Chemical Bonds. Microwave Spectra, Geometries, and Nuclear Quadrupole Coupling Constants of Ar-AuCl and Kr-AuCl. Evans, Corey J.; Lesarri, Alberto; Gerry, Michael C. L. Department of Chemistry, The University of British Columbia Vancouver, BC V6T 1Z1, Can. J. Am. Chem. Soc., 122(25), 6100-6105 (English) 2000. The pure rotational spectra of Ar-AuCl and Kr-AuCl were measured using a pulsed-jet cavity Fourier transform microwave spectrometer. Both complexes are linear and are relatively rigid in their ground vibrational states. The noble gas-Au stretching frequencies are 198 and 161 cm-1 for Ar-AuCl and Kr-AuCl, resp. From the isotopic data obtained, r0 structures were calcd. for both Ar-AuCl and Kr-AuCl, while a partial substitution (rs) structure was obtained for Kr-AuCl. The Ar-Au distance is 2.47 A, while the Kr-Au distance is 2.52 A. Ab

initio calcns. were performed at the MP2 level of theory on both complexes to obtain geometries, vibrational frequencies, and dissocn. energies. The dissocn. energies for Ar-AuCl and Kr-AuCl are 47 and 71 kJ mol-1, resp. The nuclear quadrupole coupling const. of Au was found to change significantly on complex formation (to -259.8 MHz in Ar-AuCl, and -349.9 MHz in Kr-AuCl) from its value in the monomer unit (+9.6 MHz in AuCl), which is consistent with extensive charge rearrangement on formation of the complexes. This, in conjunction with the sizable dissocn. energies, indicates that the Ar-Au and Kr-Au bonds are weakly covalent.

Aull

Om. 40897

2000

Corey J. Evans and
Michael C.L. Gerry,

шестний
вращат.
спектр,
м.п.

J. Mol. Spectrosc.,
2000, 203, 105-117.

2000

F: Kr-AuCl
P: 3
133:96171 Noble Gas-Metal Chemical Bonds. Microwave Spectra, Geometries, and Nuclear Quadrupole Coupling Constants of Ar-AuCl and Kr- AuCl. Evans, Corey J.; Lesarri, Alberto; Gerry, Michael C. L. Department of Chemistry, The University of British Columbia Vancouver, BC V6T 1Z1, Can. J. Am. Chem. Soc., 122(25), 6100-6105 (English) 2000. The pure rotational spectra of Ar-AuCl and Kr-AuCl were measured using a pulsed-jet cavity Fourier transform microwave spectrometer. Both complexes are linear and are relatively rigid in their ground vibrational states. The noble gas-Au stretching frequencies are 198 and 161 cm-1 for Ar-AuCl and Kr-AuCl, resp. From the isotopic

data obtained, r0 structures were calcd. for both Ar-AuCl and Kr-AuCl, while a partial substitution (rs) structure was obtained for Kr-AuCl. The Ar-Au distance is 2.47 A, while the Kr-Au distance is 2.52 A. Ab initio calcns. were performed at the MP2 level of theory on both complexes to obtain geometries, vibrational frequencies, and dissocn. energies. The dissocn. energies for Ar-AuCl and Kr-AuCl are 47 and 71 kJ mol-1, resp. The nuclear quadrupole coupling const. of Au was found to change significantly on complex formation (to -259.8 MHz in Ar-AuCl, and -349.9 MHz in Kr-AuCl) from its value in the monomer unit (+9.6 MHz in AuCl), which is consistent with extensive charge rearrangement on formation of the complexes. This, in conjunction with the sizable dissocn. energies, indicates that the Ar-Au and Kr-Au bonds are weakly covalent.

F: AuCl3
P: 3

2001

134:271514 **Molecular Structure, Bonding, and Jahn-Teller Effect in Gold Chlorides: Quantum Chemical Study of AuCl3, Au2Cl6, AuCl4-, AuCl, and Au2Cl2 and Electron Diffraction Study of Au2Cl6.** Hargittai, Magdolna; Schulz, Axel; Reffy, Balazs; Kolonits, Maria. Structural Chemistry Research Group, Hungarian Academy of Sciences Eoetvoes University, Budapest, Hung. J. Am. Chem. Soc. (2001), 123(7), 1449-1458. in English.

The mol. geometry of dimeric gold trichloride has been detd. by gas-phase electron diffraction and high-level quantum chem. calcns. The mol. has a planar, D2h-symmetry halogen-bridged geometry, with the gold atom in an almost square-planar coordination. The geometrical parameters from electron diffraction (rg and ∠α) are: Au-Clt, 2.236 ± 0.013 .ANG.; Au-Clb, 2.355 ± 0.013 .ANG.; ∠Clt-Au-Clt, 92.7 ± 2.5°; and ∠Clb-Au-Clb, 86.8 ± 1.8° (t, terminal; b, bridging chlorine). Quantum chem. calcns. have also

been carried out on the ground-state and transition-state structures of monomeric AuCl3; both have C2v-symmetry structures due to Jahn-Teller distortion. CASSCF calcns. show that the triplet D3h-symmetry structure lies .apprx.29 kcal/mol above the 1A1 symmetry ground state. The Mexican-hat-type potential energy surface of the monomer has three equal min.-energy positions around the brim of the hat, sepd. by three transition-state structures, apprx.6 kcal/mol higher in energy, at the CASSCF level. The distortion of AuCl3 is smaller than that of AuF3, and the possible reasons are discussed. The structure of the AuCl4- ion has also been calcd., the latter both in planar, D4h, and tetrahedral, Td, arrangements. The tetrahedral configuration of AuCl4- is subject to Jahn-Teller effect, which leads to a complicated potential energy surface. The factors leading to the planar geometry of AuCl4- and Au2Cl6 are discussed. The frequently suggested dsp2 hybridization as a possible cause for planarity is not supported by this study. The geometries of AuCl and Au2Cl2 have also been calcd. The very short Au··Au distance in the latter, similarly to Au2F2, is indicative of the aurophilic interaction.

F: Au2Cl2
P: 3

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2001

F: AuCl4-
P: 3

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F: Au2Cl6
P: 3

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