The observed variations in bond distances, as well as the deviations from planarity, are all consistent with the Hückel molecular orbital picture, which indicates that the highest filled molecular orbital of the dianion makes an antibonding contribution to C(2)–C(3) and to each $C\equiv N$ bond, and bonding contributions to the other C—C bonds.

Acknowledgment. We appreciate the help of Donna Davis, who made the drawings, Bonnie Warn Ehrlich, who collected much of the data, and Sandra Smith, who assisted with computing. We are also grateful to Dr. O. W. Webster for supplying the crystals and to the UCLA Computing Center for cooperation and assistance.

Structural Characterization of a 1-Substituted 5-Tetrazolyl(transition metal) Complex Containing Metal–Carbon Bonding. Stereochemistry of the Tetrakis(1-isopropyltetrazol-5-ato)aurate(III) Anion, $[Au(CN_4R)_4]^-$ ($R = i\text{-}C_3H_7$)

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Abstract: An X-ray crystallographic study of the salt $[As(C_6H_5)_4][Au(CN_4R)_4]$ (where $R = i\text{-}C_3H_7$), obtained from the reaction of $[As(C_6H_5)_4][Au(N_3)_4]$ with isopropylisonitrile, has not only ascertained the existence of a 1-substituted tetrazol-5-ato-metal complex with a metal–carbon σ-bonded covalent linkage but in addition has provided the detailed stereochemistry of a $[Au(CN_4R)_4]^-$ anion. The four tetrazole rings are coordinated in a square-planar arrangement about the central gold(III) with the tetrazole rings oriented such that four rings lie in two mutually perpendicular planes with each pair of trans rings coplanar. The overall symmetry of the entire anion approximately conforms to the S_4-$\bar{4}$ point group with the S_4 improper rotation axis perpendicular to the AuC_4 plane and passing through the gold atom. This sterically most favorable geometry with the isopropyl substituent located at the 1 position of the planar five-membered ring may account for the remarkable stability of the $[Au(CN_4R)_4]^-$ anions to various chemical reagents in that the substituent R groups effectively block to a considerable extent the two vacant octahedral-like coordination sites at the Au(III) against chemical attack. The four Au–C bond lengths range from 1.95 (4) to 2.00 (4) Å with the mean value of 1.98 Å corresponding to a covalent single-bond length. The differences among the equivalent C–N and N–N distances of the four tetrazole rings are not significant, and the average values compare favorably with those in other structurally determined tetrazole derivatives for which electron delocalization has been proposed. The $[As(C_6H_5)_4][Au(CN_4R)_4]$ ($R = i\text{-}C_3H_7$) salt crystallizes with two formula species in a monoclinic unit cell of symmetry $P2_1$ and of dimensions $a = 11.07$, $b = 18.66$, $c = 11.36$ Å, $\beta = 104.5°$. The crystal structure was solved by the heavy-atom method and refined by full-matrix, rigid-body, anisotropic–isotropic least squares to an unweighted R_1 value of 6.0% based on 1426 independent absorption-corrected, diffractometry-obtained intensity maxima.

Although many studies of metal complexation with either neutral or anionic unsubstituted and substituted tetrazoles have been reported,[1–12] detailed stereochemical information concerning the nature of the metal–tetrazole link(s) has only recently become available.

Tetrazolato–metal complexes are formed by the cycloaddition of metal azides with either organic nitriles[8–10] or isonitriles.[8,11] Beck and coworkers[8,9] showed that the former reaction yields 5-substituted tetrazolato–metal complexes in which the metal is nitrogen coordinated.[12] A recently performed X-ray structural investigation of the complex *trans*-$[(C_6H_5)_3P]_2Pd(N_4C(C_6H_5))_2$, which was synthesized by reaction of *trans*-$[(C_6H_5)_3P]_2Pd(N_3)_2$ and benzonitrile,[9] showed the tetrazolato ligand to coordinate to the metal through the nitrogen at position 2.[13] On the other hand, it was suggested that the N(1) nitrogen atom can function as

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the donor site of a tetrazolate anion as well,[11] and for some tetrazolate–metal complexes of platinum(II) the presence in solution of both the N(1)- and N(2)-bonded species has been ascertained by ^1H nmr data.[12a]

The unidentate coordination of 1,5-substituted tetrazole rings through the 4-N position was established from structural determinations by X-ray diffraction of dichlorobis(1-methyltetrazole)zinc(II)[14] and of the iodine monochloride complex of pentamethylenetetrazole (PMT).[15] In both $Zn[N_4(CH_3)C(H)]_2Cl_2$ (which has H and CH_3 substituents at the 5-C and 1-N positions, respectively, of the tetrazole ring)[14] and PMTICl (which has a pentamethylene fragment linked to the 5-C and 1-N atoms of the tetrazole ring),[15] the site and type of coordination of the tetrazole ligand are identical—*viz.*, the nitrogen atom at ring position 4 is covalently attached through a donor σ bond (coplanar with the ring) to the tetrahedrally coordinated Zn(II) in $Zn[N_4(CH_3)C(H)]_2Cl_2$ and to the linearly coordinated iodine atom in PMTICl.

The use of isonitrile reagents to give metal–carbon bonded 1-substituted tetrazol-5-ato–metal complexes was first demonstrated by Beck and Fehlhammer,[8] who, from the reaction of the tetraphenylarsonium tetraazidoaurate(III) salt, $[As(C_6H_5)_4][Au(N_3)_4]$, with cyclohexylisonitrile in dichloromethane under mild conditions, isolated and identified the salt $[As(C_6H_5)_4]$-$[Au(CN_4R)_4]$ (where R = C_6H_{11}). Interpretations of the infrared, proton nmr, and mass spectra of this salt and other similarly produced 1-substituted gold(III) derivatives (R = CH_3, i-C_3H_7, $CH_2C_6H_5$, C_6H_5, and p-$C_6H_4OCH_3$)[11] as well as 1-substituted tetrazol-5-ato–metal complexes of gold(I), platinum(II), and mercury(II)[11] were made on the basis that these compounds contain covalent metal–carbon bonds.[16,17] A similar proposal of a distinct metal–carbon bond for bis(1-methyl-5-tetrazolyl)nickel(II), $Ni(CN_4R)_2$ (where R = CH_3), was previously made by Garber and Brubaker,[6] who prepared this complex and subsequently the 1-cyclohexyl analog[7] from the reaction of 1-R-5-tetrazolyllithium·0.5THF (where R = CH_3 or C_6H_{11}) with $[(C_2H_5)_3P]_2NiCl_2$.[18] Prior to this present investigation, no structural data were available for any metal–tetrazolato complexes. The results of an X-ray structural determination of $[As(C_6H_5)_4][Au(CN_4R)_4]$ (where R = i-C_3H_7) reported here not only provide substantiation for a 1-substituted tetrazol-5-ato–metal complex with a metal–carbon σ-bonded covalent linkage, but in addition furnish the detailed stereochemistry of an $[Au(CN_4R)_4]^-$ anion.

Experimental Section

Preparation and Crystal Data. Tetraphenylarsonium tetrakis(1-isopropyltetrazol-5-ato)aurate(III), $[As(C_6H_5)_4][Au(CN_4R)_4]$ (where R = i-C_3H_7), was prepared by reaction of the corresponding azide complex $[As(C_6H_5)_4][Au(N_3)_4]$ with isopropylisonitrile in dichloromethane at room temperature.[11] Single crystals suitable for X-ray diffraction studies were obtained by slow recrystallization of the surprisingly stable compound from an acetone–water mixture. They form colorless platelike parallelepipeds belonging to the monoclinic system. Examination of the $hk0$–$hk3$ Weissenberg, and $0kl$, $1kl$, $h0l$, and $h1l$ precession photographs of two crystals (each one mounted on its monoclinic c axis) revealed systematic absences only for $\{0k0\}$ with k odd, characteristic for both space groups $P2_1$ (C_2^2; no. 4) and $P2_1/m$ (C_{2h}^2; no. 11). The successful solution of the crystal structure (*vide infra*) was found to conform to the noncentrosymmetric one, $P2_1$. A parallelepiped-shaped crystal of dimensions 0.28 × 0.20 × 0.10 mm (referred to the [001], [120], and [210] directions which are normal to the major crystal faces) was transferred to a General Electric full-circle Datex-controlled diffractometer with the c axis (coincident with the crystal direction of elongation) parallel with ϕ. Unit cell dimensions (23 ± 2°) of a = 11.067 (6), b = 18.657 (12), c = 11.358 (9) Å, and β = 104.54 (3)° were obtained by use of Mo Kα radiation from a least-squares fit[19] of the setting angles for 31 carefully centered,[20] mostly high-angle reflections; a multiplication factor of 3 was applied to the estimated standard deviations from the least-squares calculation to give the reported uncertainties in precision. The cell volume equals 2270.2 Å^3. The calculated density of 1.50 g cm^{-3} for two formula units of $AuAsN_{16}C_{40}H_{48}$ in the cell ($Z = 2$) is in good agreement with the observed density of 1.49 ± 0.02 g cm^{-3} obtained by the flotation method (1-bromonaphthalene).

Collection and Reduction of X-Ray Data. The refined lattice constants were used to generate the angle settings for all data reflections with a local version of the Argonne National Laboratory orientation and angle setting program.[21] Intensities were measured at a takeoff angle of 2.0° by the θ–2θ scan technique with symmetric 2θ scans at a 2.0°/min rate over a range of 2.2°. Stationary crystal–stationary counter background counts of 15 sec were taken at the beginning and end of each scan. A counter aperture of 2 mm diameter was placed 31 mm from the crystal. Zr-filtered Mo Kα radiation was employed with a scintillation detector equipped with a pulse-height analyzer set to pass the central 90% of the Mo Kα peak. Intensity data for $2\theta \leq 35°$ were collected for two asymmetric units—*viz.*, octants hkl, $\bar{h}kl$ and $\bar{h}k\bar{l}$, $hk\bar{l}$. A set of four reflections—*viz.* (101), (042), ($\bar{3}$43), and (060)—was measured every 50 reflections throughout the data collection as a check on crystal and instrument stability. The intensities of each of the four standard reflections decreased by approximately 9% at the termination of the first independent unit and by almost 25% at the end of the second one. A correction curve was derived by an averaging of the decrease in intensities of the four standards and then fitting the resulting data points to a curve composed of several straight-line sections. Scale factors were assigned to the beginning and end of each block of data. An individual correction factor, found by linear interpolation within the block, was applied for each reflection to restore the intensities to their values at the beginning of the data collection.[22] Since the alignment of the crystal was found not to have changed within experimental error at the end of the data collection, the decrease was attributed to a largely isotropic crystal decomposition, which was also evident from a slight change in color to pale yellow.

The corrected intensities (*i.e.*, $I = S - [0.5(t_S/t_B)(B_1 + B_2)]$ and $\sigma^2(I) = S + 0.25(t_S/t_B)^2(B_1 + B_2) + \mathrm{ISK}I^2$, where S = the count associated with total scan in scan time t_S, B_1 = initial background count, B_2 = final background count, t_B = time taken for each background count, and ISK = instrument instability or "ignorance" factor empirically assigned a value of 0.0025) were used to calculate[23] structure factor amplitudes, $|F_o| = (I/Lp)^{1/2}$, where Lp is the

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(16) Beck, *et al.*,[11] postulated that the reaction path in the ring formation of the metal–carbon bonded tetrazole proceeds by initial attachment of the isonitrile reagent with the metal atom, followed by cycloaddition and cleavage of the metal–(azide nitrogen) bond. This proposal is in accord with the recent findings of Treichel, Knebel, and Hess,[17] who produced the platinum–CN_4CH_3 complexes, $[(C_6H_5)_3P]_2Pt(CNCH_3)$-$(CN_4CH_3)^+$ and (diphos)$Pt(CN_4CH_3)_2$, by reactions of the azide ion with the platinum–(methyl isocyanide) complexes, $[(C_6H_5)_3P]_2Pt$-$(CNCH_3)_2{}^{2+}$ and (diphos)$Pt(CNCH_3)_2{}^{2+}$, respectively.

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(18) Garber and Brubaker[6,7] speculated from solid-state electronic and infrared spectra and from magnetic susceptibility measurements that these two insoluble 1-substituted (5-tetrazolato)nickel(II) compounds possess polymeric geometries in which each tetrazole ring is coordinated with Ni(II) atoms by one Ni–C and two Ni–N bonds to give a localized octahedral-like environment about each Ni(II) which contains two unpaired electrons.

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Table I. Final Parameters for $[As(C_6H_5)_4][Au(CN_4\text{-}i\text{-}C_3H_7)_4]$[a]

Atom	*x*	*y*	*z*	*B*
Au	0.3507 (1)	0.25	0.1949 (1)	*b*
As	−0.0499 (3)	0.3817 (2)	0.5917 (3)	*b*
CN_4(1) N(1)[c]	0.5487 (31)	0.1965 (15)	0.4175 (29)	6.6 (7)
N(2)	0.6743 (33)	0.2018 (16)	0.4633 (30)	7.4 (8)
N(3)	0.7177 (32)	0.2430 (32)	0.3870 (33)	10.5 (10)
N(4)	0.6208 (32)	0.2605 (35)	0.2942 (28)	9.0 (8)
C(5)	0.5148 (33)	0.2341 (19)	0.3143 (30)	5.3 (10)
i-C_3H_7(1) C(6)[d]	0.4596	0.1633	0.4662	9.6 (13)
C(7)	0.4471	0.0835	0.4302	10.1 (12)
C(8)	0.5040	0.1699	0.6055	12.0 (15)
CN_4(2) N(1)	0.3043 (23)	0.3943 (14)	0.3056 (24)	5.0 (6)
N(2)	0.2767 (27)	0.4263 (16)	0.4030 (29)	7.0 (8)
N(3)	0.2673 (28)	0.3718 (20)	0.4673 (28)	7.9 (8)
N(4)	0.2849 (28)	0.3079 (17)	0.4152 (30)	7.6 (8)
C(5)	0.3082 (32)	0.3201 (19)	0.3047 (34)	5.9 (9)
i-C_3H_7(2) C(6)	0.3323	0.4339	0.2015	7.7 (10)
C(7)	0.4704	0.4568	0.2349	9.1 (12)
C(8)	0.2486	0.5010	0.1803	11.3 (14)
CN_4(3) N(1)	0.0875 (33)	0.2237 (14)	0.0716 (29)	6.7 (9)
N(2)	−0.0163 (27)	0.2540 (33)	−0.0137 (26)	9.3 (8)
N(3)	0.0173 (33)	0.3110 (18)	−0.0441 (30)	7.4 (9)
N(4)	0.1411 (29)	0.3208 (15)	0.0152 (26)	5.6 (7)
C(5)	0.1882 (28)	0.2701 (19)	0.0841 (25)	4.8 (8)
i-C_3H_7(3) C(6)	0.0846	0.1499	0.1270	9.2 (12)
C(7)	0.0350	0.1654	0.2395	14.0 (18)
C(8)	−0.0087	0.1016	0.0382	10.1 (13)
CN_4(4) N(1)	0.4623 (26)	0.1877 (15)	−0.0027 (28)	5.2 (7)
N(2)	0.4763 (29)	0.1276 (18)	−0.0595 (26)	7.1 (8)
N(3)	0.4065 (38)	0.0831 (22)	−0.0237 (39)	10.9 (12)
N(4)	0.3568 (34)	0.1100 (20)	0.0669 (32)	9.4 (10)
C(5)	0.3927 (33)	0.1811 (18)	0.0761 (33)	5.0 (9)
i-C_3H_7(4) C(6)	0.4734	0.7508	0.0140	10.0 (10)
C(7)	0.3477	0.7361	0.0445	11.4 (15)
C(8)	0.5559	0.7973	0.1148	12.1 (15)
C_6H_5(1) C(1)[d]	0.8062	0.4035	0.6518	7.6 (5)[e]
C(2)	0.6891	0.3807	0.5862	
H(2)	0.6794	0.3516	0.5022	
C(3)	0.5844	0.3954	0.6287	
H(3)	0.4934	0.3777	0.5778	
C(4)	0.5968	0.4329	0.7369	
H(4)	0.5155	0.4443	0.7700	
C(5)	0.7140	0.4557	0.8025	
H(5)	0.7236	0.4848	0.8866	
C(6)	0.8187	0.4410	0.7600	
H(6)	0.9097	0.4587	0.8110	
C_6H_5(2) C(1)	1.0825	0.4462	0.6603	6.8 (5)
C(2)	1.1584	0.4358	0.7766	
H(2)	1.1424	0.3908	0.8305	
C(3)	1.2550	0.4835	0.8237	
H(3)	1.3140	0.4755	0.9141	
C(4)	1.2756	0.5415	0.7544	
H(4)	1.3506	0.5786	0.7910	
C(5)	1.1996	0.5519	0.6381	
H(5)	1.2156	0.5969	0.5843	
C(6)	1.1031	0.5042	0.5910	
H(6)	1.0441	0.5122	0.5006	
C_6H_5(3) C(1)	0.9044	0.3953	0.4215	9.7 (6)
C(2)	0.9596	0.3508	0.3518	
H(2)	1.0227	0.3089	0.3949	
C(3)	0.9334	0.3601	0.2265	
H(3)	0.9763	0.3255	0.1723	
C(4)	0.8521	0.4140	0.1709	
H(4)	0.8318	0.4212	0.0736	
C(5)	0.7970	0.4585	0.2406	
H(5)	0.7339	0.5003	0.1975	
C(6)	0.8232	0.4492	0.3659	
H(6)	0.7803	0.4838	0.4201	
C_6H_5(4) C(1)	1.0022	0.2880	0.6364	9.6 (6)
C(2)	1.1217	0.2646	0.6374	
H(2)	1.1872	0.3010	0.6127	
C(3)	1.1569	0.1945	0.6702	
H(3)	1.2497	0.1763	0.6709	
C(4)	1.0726	0.1477	0.7019	
H(4)	1.1000	0.0931	0.7274	

Table I (*Continued*)

Atom	x	y	z	B
C(5)	0.9531	0.1710	0.7010	
H(5)	0.8876	0.1347	0.7257	
C(6)	0.9179	0.2412	0.6682	
H(6)	0.8250	0.2594	0.6674	

[a] Estimated standard deviations of the last significant figures are enclosed in parentheses. [b] Anisotropic thermal parameters, used for the gold and arsenic atoms, are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The resulting thermal coefficients are given as follows

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au	0.0101 (1)	0.0034 (1)	0.0100 (1)	0.0001 (2)	0.0025 (1)	−0.0004 (2)
As	0.0143 (6)	0.0039 (2)	0.0125 (5)	−0.0001 (3)	0.0047 (5)	0.0005 (3)

[c] The notation $CN_4(i)$ N(j) designates the jth nitrogen atom of the ith tetrazole ring. The same notation is applicable to the isopropyl group atoms, i-$C_3H_7(k)$ C(l) (where k = 1–4, l = 6–8) and to phenyl ring atoms, $C_6H_5(m)$ C(n) and $C_6H_5(m)$ H(n) (where m = 1–4, n = 1–6). [d] These individual atomic parameters are based on the refined rigid-body crystallographic coordinates. [e] An overall isotropic temperature factor was varied for each phenyl group; an additional B term of 1.0 Å^2 for C(2) and C(6), 2.0 Å^2 for C(3) and C(5), and 3.0 Å^2 for C(4) was given to each carbon atom and held constant throughout the refinement in order to allow for the expected changes in atomic thermal motion occurring for each $C_6H_5(i)$ phenyl ring (i = 1, 2, 3, 4) attached to the arsenic atom through C(1).

Table II. Final Rigid-Body Parameters[a]

Group	x	y	z	ϕ	θ	ρ
i-$C_3H_7(1)$	0.4702 (24)	0.1385 (15)	0.5006 (29)	0.219 (30)	1.838 (31)	1.337 (19)
i-$C_3H_7(2)$	0.3504 (26)	0.4635 (14)	0.2056 (21)	−2.871 (28)	−3.065 (57)	−0.241 (41)
i-$C_3H_7(3)$	0.0370 (26)	0.1386 (14)	0.1349 (28)	−0.927 (55)	−2.743 (36)	−1.059 (38)
i-$C_3H_7(4)$	0.4590 (27)	0.7610 (16)	0.0578 (22)	2.973 (57)	2.144 (62)	−2.729 (84)
$C_6H_5(1)$	0.7015 (17)	0.4178 (8)	0.6944 (16)	−0.696 (26)	−2.225 (15)	−0.586 (25)
$C_6H_5(2)$	1.1790 (15)	0.4935 (9)	0.7074 (17)	0.065 (29)	2.130 (15)	−2.364 (29)
$C_6H_5(3)$	0.8783 (17)	0.4043 (11)	0.2962 (20)	0.701 (16)	−3.077 (23)	1.689 (17)
$C_6H_5(4)$	1.0262 (43)	0.3115 (11)	0.6219 (27)	1.755 (23)	−3.000 (15)	−0.265 (16)

[a] All phenyl group refinements were based on the following model. Each ring was presumed to have D_{6h} symmetry with a C–C bond length of 1.39 Å. The hydrogen atoms are located on the lines defined by diagonally opposite carbons, with a C–H bond length of 1.08 Å. The orthonormal set (x', y', z') has x' along C(4)–C(1), y' along C(5)–C(3), and z' along x' cross y'. The origin is at the center of the carbon framework. For the isopropyl group, the $+x'$ direction was chosen parallel to the C(6)–C(7) bond, with the origin coinciding with the center of gravity of the isopropyl carbon framework, z' is normal to the C_3 plane, and y' is the vector product of x' and z'. The angles ϕ, θ, and ρ (in radians) define the orientation of the internal rigid-group axial system with respect to an external orthogonal system by rotations about x', y', and z', respectively.

Lorentz–polarization factor, and their estimated standard deviations $\sigma^2(F) = \sigma^2(I)(4ILp)^{-1}$. A given reflection was considered "unobserved" if I was less than $2.5\sigma(I)$. Subsequently, the corrected data of the two equivalent forms were merged by a least-squares procedure to give a single set of data on one scale.[24] A total of 1426 observed and 576 unobserved independent reflections originated from this procedure. The linear absorption coefficient of $[As(C_6H_5)_4][Au(CN_4R)_4]$ (where R = i-C_3H_7) is 41.5 cm^{-1} for Mo Kα radiation,[25] and hence a general absorption correction was made[26] with transmission coefficients for the chosen crystal ranging from 0.496 to 0.723.

Solution and Refinement of the Structure. An interpretation of a three-dimensional Patterson function, computed from the $|F_o|^2$, yielded initial coordinates for the Au and As atoms. The fact that the independent gold atom had a y coordinate different from that of the independent arsenic atom showed unambiguously that for two tetraphenylarsonium cations and two gold–tetrazole anions per cell (*i.e.*, $Z = 2$) the true space group is $P2_1$ rather than the centrosymmetric $P2_1/m$. The noncentrosymmetric space group $P2_1$ does not impose any crystallographic site symmetry; thus all 106 independent atoms (comprised of 58 nonhydrogen and 48 hydrogen atoms) of the one independent cation and anion occupy the following twofold sets of general positions $x, y, z;\ \bar{x}, \frac{1}{2} + y, \bar{z}$. The fractional y coordinate of the gold atom was fixed at $^1/_4$ in order to define the origin of the unit cell. Of the two possible As positions (related to each other by reflection across a pseudo mirror plane at $y = {}^1/_4$) obtained from the solution of the Patterson function, one position was arbitrarily chosen at this point in the solution of the structure. A three-dimensional Fourier map phased on the gold and arsenic atoms revealed plausible locations for most of the nonhydrogen atoms of the phenyl and tetrazole rings. However, of the 12 carbon atoms contained in the four isopropyl substituents of the tetrazole rings, only two were located at this stage. Several cycles of full-matrix isotropic least-squares refinement of these atoms with each of the four phenyl rings treated as a rigid body (for which one overall isotropic thermal parameter was varied)[27] resulted in an unweighted reliability index of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]100 = 13.7\%$ and a weighted one of $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2}100 = 18.9\%$. This refinement was based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ in which the weights were assigned according to the usual relationship $w_i = 1/\sigma_i^2(F_o)$. Subsequent difference Fourier maps, interspersed with anisotropic–isotropic least-squares refinements, led to the positions of all remaining nonhydrogen atoms (R_1 = 9.8%, R_2 = 10.1%), but at the same time a considerable inconsistency in bond lengths (including a distinct asymmetry in the four Au–C bond lengths which ranged from 1.82 to 2.27 Å), along with large temperature factors and large esd's, was observed. At this point there were two possible structures to consider: enantiomorph I, the structure heretofore assumed, and enantiomorph II, the mirror image of I as reflected across a plane at $y = {}^1/_4$. A structure factor calculation on 283 selected reflections with $(\bar{h}\bar{k}\bar{l})$ assumed in the place of (hkl) gave R_1 and R_2 values of 19.8 and 20.7%, respectively, compared to 14.9 and 15.4%, thereby indicating that the correct enantiomer (the one generating a right-handed screw in moving in the $+y$ direction from As to Au to As and so forth) was accidentally chosen from the beginning.

A further drop in the R values was finally achieved by geometrically constraining as rigid bodies[27] not only the phenyl rings (includ-

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(24) SORTMERGE, a Fortran program for sorting and merging crystallographic intensity data: J. Calabrese, Ph.D. Thesis, University of Wisconsin (Madison), 1971.

(25) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 157.

(26) J. F. Blount, DEAR, an absorption correction program based on the method of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 10, 180 (1957).

(27) A description of the rigid-body refinement is outlined in Table

Table III. Intramolecular Distances (Å) and Angles (deg) for [As(C$_6$H$_5$)$_4$][Au(CN$_4$-*i*-C$_3$H$_7$)$_4$][a]

A. Bond Lengths		
Gold to Tetrazole Carbon		
	Au–C(CN$_4$(1))	2.00 (3)
	Au–C(CN$_4$(2))	1.95 (4)
	Au–C(CN$_4$(3))	1.96 (3)
	Au–C(CN$_4$(4))	2.00 (4)
		1.98 (av)
Within the Tetrazole Rings		
CN$_4$(1)	C(5)–N(1)	1.34 (4)
	N(1)–N(2)	1.36 (4)
	N(2)–N(3)	1.34 (5)
	N(3)–N(4)	1.34 (4)
	N(4)–C(5)	1.34 (4)
CN$_4$(2)	C(5)–N(1)	1.39 (4)
	N(1)–N(2)	1.36 (3)
	N(2)–N(3)	1.27 (4)
	N(3)–N(4)	1.37 (4)
	N(4)–C(5)	1.36 (4)
CN$_4$(3)	C(5)–N(1)	1.39 (3)
	N(1)–N(2)	1.42 (4)
	N(2)–N(3)	1.21 (6)
	N(3)–N(4)	1.38 (4)
	N(4)–C(5)	1.25 (3)
CN$_4$(4)	C(5)–N(1)	1.33 (4)
	N(1)–N(2)	1.32 (3)
	N(2)–N(3)	1.27 (4)
	N(3)–N(4)	1.38 (4)
	N(4)–C(5)	1.37 (4)
Tetrazole Nitrogen to Isopropyl Carbon		
CN$_4$(1)	N(1)–C(6)	1.39 (4)
CN$_4$(2)	N(1)–C(6)	1.49 (4)
CN$_4$(3)	N(1)–C(6)	1.51 (4)
CN$_4$(4)	N(1)–C(6)	1.40 (3)
		1.45 (av)
Arsenic to Phenyl Carbon		
	As–C(C$_6$H$_5$(1))	1.93 (3)
	As–C(C$_6$H$_5$(2))	1.90 (3)
	As–C(C$_6$H$_5$(3))	1.89 (3)
	As–C(C$_6$H$_5$(4))	1.87 (3)
		1.90 (av)
B. Bond Angles		
Carbon—Gold—Carbon		
	C(CN$_4$(1))–Au–C(CN$_4$(2))	89.4 (14)
	C(CN$_4$(1))–Au–C(CN$_4$(4))	92.1 (14)
	C(CN$_4$(2))–Au–C(CN$_4$(3))	87.3 (14)
	C(CN$_4$(3))–Au–C(CN$_4$(4))	91.2 (13)
		90.0 (av)
CN$_4$(1)	Au–C(5)–N(1)	133 (2)
	Au–C(5)–N(4)	121 (3)
	N(4)–C(5)–N(1)	106 (3)
	C(5)–N(1)–N(2)	109 (3)
	C(5)–N(1)–C(6)	121 (3)
	N(2)–N(1)–C(6)	130 (3)
	N(1)–N(2)–N(3)	107 (2)
	N(2)–N(3)–N(4)	108 (2)
	N(3)–N(4)–C(5)	110 (3)
CN$_4$(2)	Au–C(5)–N(1)	134 (3)
	Au–C(5)–N(4)	128 (3)
	N(4)–C(5)–N(1)	98 (3)
	C(5)–N(1)–N(2)	117 (3)
	C(5)–N(1)–C(6)	118 (3)
	N(2)–N(1)–C(6)	124 (3)
	N(1)–N(2)–N(3)	101 (2)
	N(2)–N(3)–N(4)	114 (2)
	N(3)–N(4)–C(5)	109 (3)
CN$_4$(3)	Au–C(5)–N(1)	122 (3)
	Au–C(5)–N(4)	136 (3)
	N(4)–C(5)–N(1)	102 (3)
	C(5)–N(1)–N(2)	108 (3)
	C(5)–N(1)–C(6)	128 (3)
	N(2)–N(1)–C(6)	123 (3)
	N(1)–N(2)–N(3)	107 (3)
	N(2)–N(3)–N(4)	108 (3)
	N(3)–N(4)–C(5)	114 (3)
CN$_4$(4)	Au–C(5)–N(1)	132 (2)
	Au–C(5)–N(4)	124 (3)
	N(4)–C(5)–N(1)	104 (3)
	C(5)–N(1)–N(2)	114 (3)
	C(5)–N(1)–C(6)	122 (3)
	N(2)–N(1)–C(6)	123 (3)
	N(1)–N(2)–N(3)	104 (2)
	N(2)–N(3)–N(4)	113 (3)
	N(3)–N(4)–C(5)	104 (3)
About C(6)		
i-C$_3$H$_7$(1)	N(1)–C(6)–C(7)	110 (3)
	N(1)–C(6)–C(8)	107 (2)
i-C$_3$H$_7$(2)	N(1)–C(6)–C(7)	110 (3)
	N(1)–C(6)–C(8)	107 (2)
i-C$_3$H$_7$(3)	N(1)–C(6)–C(7)	103 (3)
	N(1)–C(6)–C(8)	110 (3)
i-C$_3$H$_7$(4)	N(1)–C(6)–C(7)	112 (2)
	N(1)–C(6)–C(8)	109 (2)
Carbon—Arsenic—Carbon		
	C(C$_6$H$_5$(1))–As–C(C$_6$H$_5$(2))	110 (2)
	C(C$_6$H$_5$(1))–As–C(C$_6$H$_5$(3))	108 (2)
	C(C$_6$H$_5$(1))–As–C(C$_6$H$_5$(4))	109 (2)
	C(C$_6$H$_5$(2))–As–C(C$_6$H$_5$(3))	108 (2)
	C(C$_6$H$_5$(2))–As–C(C$_6$H$_5$(4))	109 (2)
	C(C$_6$H$_5$(3))–As–C(C$_6$H$_5$(4))	113 (2)
		109.5 (av)

[a] Estimated standard deviation in the last digit is given in parentheses.

ing the hydrogen atoms) of the As(C$_6$H$_5$)$_4^+$ cation but also the whole of each isopropyl group and each tetrazole ring. The isopropyl group was idealized by the use of C–C bond distances of 1.54 Å and C–C–C bond angles of 109.5°.[27] A reasonable rigid-body model for each tetrazole ring was constructed by an averaging of corresponding bond lengths and angles of the four tetrazole groups followed by a superposition of the "averaged" tetrazole ring and isopropyl substituent by means of MIRAGE[28] in a mean orientation of each previously refined individual –CN$_4$(*i*-C$_3$H$_7$) ligand. After further least-squares refinement with these three kinds of rigid groups, the constraints of the four tetrazole rings (but not of the phenyl and isopropyl groups) were removed. In these latter refinements anisotropic thermal parameters were utilized for the gold and arsenic atoms, while isotropic ones were varied for the isopropyl carbon atoms along with an overall isotropic one for each phenyl ring. This above refinement procedure converged with a marked decrease in R_1 and R_2 values to 6.0 and 5.8%, respectively; in the final cycle all parameter shifts were less than 50% of their individual esd's.

A difference Fourier map calculated from the final data set (also including unobserved reflections) showed evidence of some light-atom thermal anisotropy, but otherwise indicated a reasonably complete refinement with no residual peak heights greater than +0.9 e/Å^3 or less than −0.65 e/Å^3. No convincing positions for the iso-

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II. See also S. F. Watkins, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1967, and references cited therein.

(28) MIRAGE, a general vector program for obtaining atomic coordinates: J. Calabrese, Ph.D. Thesis, University of Wisconsin (Madison), 1971.

propyl hydrogen atoms were found on this map. The relatively high individual isotropic temperature factors for the light nonhydrogen atoms in the $[Au(CN_4(i\text{-}C_3H_7))_4]^-$ anion, especially those of the isopropyl substituents, undoubtedly are a consequence of the inadequacy of the isotropic thermal model in representing the presumed high anisotropic thermal motion of these atoms. Nevertheless, the contemplated expenses involving an anisotropic least-squares treatment of the 32 carbon and nitrogen atoms in the anion did not justify such further refinement from the viewpoint that the scientific gain from a somewhat better refined structure was not worth the large estimated financial cost.

All Patterson and Fourier maps were calculated with the Blount program.[29] Neutral scattering factors were used for both nonhydrogen[30] and hydrogen[31] atoms, with those of gold and arsenic being corrected for real and imaginary anomalous dispersion.[32,33] Least-squares refinements were carried out with a local modification of the Busing–Martin–Levy ORFLS program.[34] Interatomic distances and angles and their esd's were calculated with the Busing–Martin–Levy ORFFE program[35] from the full inverse matrix (which included the estimated errors in lattice parameters). Atomic and rigid-body parameters from the output of the last least-squares cycle[36] are presented in Tables I and II, while Table III lists the interatomic bond lengths and angles. Best least-squares planes formed by certain atoms, and the distances of these and other atoms from the planes were calculated.[37,38]

Results and Discussion

The crystal structure of tetraphenylarsonium tetrakis(1-isopropyltetrazol-5-ato)aurate(III) is comprised of discrete $As(C_6H_5)_4^+$ cations and $[Au(CN_4(i\text{-}C_3H_7))_4]^-$ anions. In this crystal structure the distances between the cations and anions are all normal, with N(tetrazole)$\cdots$C(phenyl) closest distances of 3.2–3.3 Å except for one unusually short distance of 2.64 Å between the $N(3)(CN_4(3))$ tetrazole atom and the $C(3)(C_6H_5(3))$ phenyl atom (*i.e.*, see footnote *c* of Table I for atom designation); the associated short distance of 1.65 Å between the $N(3)(CN_4(3))$ and $H(3)(C_6H_5(3))$ atoms suggests that the crystal is partially stabilized by this CH$\cdots$N hydrogen-bonding interaction.

The configuration of the anion (Figure 1) consists of a square-planar arrangement of the four tetrazole ligands about the central gold atom. The four tetrazole rings are oriented such that the geometry of the entire anion approximately conforms to the S_4-$\bar{4}$ point group with the S_4 improper rotation axis perpendicular to the AuC_4 plane[39] and passing through the gold atom. This geometry with the isopropyl substituent located at the 1 position of the five-membered ring (adjacent to the metal-attached ring atom) is in agreement with that sterically expected for a four-coordinated Au(III) covalently linked through the carbon ring atoms of the four 1-substituted tetrazole ligands. Each planar tetrazole ring was found to be approximately coplanar with its nitrogen-attached carbon atom of the isopropyl side chain as well as with the gold atom. The maximum perpendicular deviations of the five ring atoms from the "best" least-squares plane calculated through each of the four tetrazole ligands range from only 0.01 to 0.02 Å. The perpendicular deviations of the Au(III) from the four tetrazole "best" planes vary between 0.01 and 0.10 Å, while the nitrogen-attached isopropyl carbon atoms range from 0.06 to 0.10 Å. Hence, each of the five atoms in a tetrazole ligand may be considered to be trigonal with each tetrazole ring thereby having six pπ electrons available for electron delocalization over the entire ring to give it possible aromatic character. The four Au–C σ-bonded tetrazole rings are in an almost perpendicular alignment with respect to the central AuC_4 plane, as evidenced by the four dihedral angles deviating from 90° by only 14–19°. This sterically most favorable geometry provides sufficient space above and below the AuC_4 coordination plane for the bulky isopropyl side chain located in the ortho ring position with respect to the gold–carbon bond. In order to minimize mutual repulsions, the $i\text{-}C_3H_7$ groups attached to adjacent (cisoid) tetrazole ligands are oriented in opposite directions (anti to each other) to give the S_4 isomer in which the transoid isopropyl substituents are syn related. Therefore, the remarkable stability of the $[Au(CN_4R)_4]^-$ anions to various chemical reagents[11b] may be attributed at least partly to the substituent R groups (in particular to the "tertiary" hydrogen atoms thereof) effectively blocking to a considerable extent the two vacant octahedral-like coordination sites at the Au(III) against chemical attack.

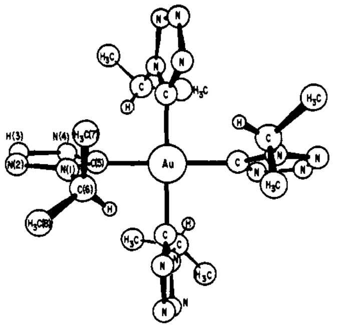

Figure 1. Structure of the tetrakis(1-isopropyltetrazol-5-ato)aurate(III) anion, $[Au(CN_4R)_4]^-$ (where R = $i\text{-}C_3H_7$), which approximately conforms to S_4-$\bar{4}$ symmetry.

The four Au(III)–C bond lengths range from 1.95 (4) to 2.00 (4) Å, with a mean of 1.98 Å. This average value is analogous to a calculated one of 2.00 Å obtained from assumed covalent radii of 1.25 Å for square-planar gold(III)[40] and 0.745 Å for trigonal car-

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[29] J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program," Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1965.

[30] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

[31] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[32] For Mo Kα radiation, the real and imaginary dispersion corrections to the atomic scattering factors are $\Delta f' = -5$, $\Delta f'' = 15$ for gold; $\Delta f' = -0.7$, $\Delta f'' = 2.2$ for arsenic.[33] These dispersion corrections are especially sensitive for polar space groups such as $P2_1$.

[33] D. H. Templeton in ref 25, p 215.

[34] ORFLSD, a local modification of the program by W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[35] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[36] Calculated and observed structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-3370. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche.

[37] D. L. Smith, Ph.D. Thesis (Appendix IV), University of Wisconsin (Madison), 1962.

[38] LSQPL, a local version of the least-squares planes program of V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, 12, 600 (1959), Max Planck Institut für Eiweiss und Lederforschung, Munich.

[39] Its closeness to exact planarity within experimental error is revealed from a calculated "best" least-squares plane through the AuC_4 fragment showing the perpendicular displacements of all five atoms to be less than 0.02 Å.

[40] Estimated from the X-ray structural determination of Au_2Cl_6:

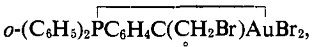
Table IV. Comparison of Bond Distances (Å) and Angles (deg) in Various Tetrazole Derivatives

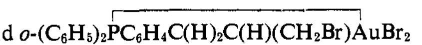
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
C(5)–N(1)	1.36 (2)	1.30 (2)	1.34 (4)	1.329 (15)	1.329 (3)	1.318 (6)	1.32 (2)	1.38
N(1)–N(2)	1.36 (2)	1.34 (2)	1.38 (5)	1.381 (15)	1.348 (2)	1.356 (8)	1.34 (2)	1.35
N(2)–N(3)	1.26 (2)	1.29 (2)	1.28 (5)	1.255 (15)	1.310 (2)	1.295 (7)	1.29 (2)	1.30
N(3)–N(4)	1.37 (2)	1.33 (2)	1.39 (4)	1.373 (15)	1.348 (2)	1.346 (6)	1.32 (2)	1.31
N(4)–C(5)	1.33 (2)	1.30 (2)	1.33 (5)	1.321 (15)	1.329 (3)	1.302 (8)	1.35 (2)	1.36
N(1)–C(6)	1.45 (3)	1.47 (2)	1.44 (5)					1.45
N(4)–C(5)–N(1)	103 (1.5)	109 (2)	109 (6)	109.8 (7)	112.5 (2)	113.2	112	106
C(5)–N(1)–N(2)	112 (1.5)	109 (2)	108 (6)	106.4 (7)	104.3 (2)	103.4	101	110
N(1)–N(2)–N(3)	105 (1.5)	106 (2)	107 (6)	107.6 (7)	109.5 (2)	109.6	114	103
N(2)–N(3)–N(4)	109 (2)	111 (2)	109 (6)	111.1 (7)	109.5 (2)	109.0	107	117
N(3)–N(4)–C(5)	109 (2)	106 (1)	108 (6)	105.0 (7)	104.3 (2)	104.8	106	104
C(5)–N(1)–C(6)	122 (2)	130 (3)	129 (6)					131
N(2)–N(1)–C(6)	125 (2)	121 (2)	123 (6)					119

[a] This work. Tabulated are the average values of bond lengths and angles of the four independent tetrazolyl ligands; $\sigma(\bar{x})$ was estimated as $\sigma_{av}/\sqrt{n}$, where σ_{av} refers to the average of the standard deviation and n the number of values averaged. [b] Dichlorobis(1-methyltetrazole)-zinc(II). Coordination site of the neutral tetrazole molecule is the nitrogen atom in position 4: N. C. Baenziger and R. J. Schultz, *Inorg. Chem.*, **10**, 661 (1971). [c] Pentamethylentetrazole·ICl. Coordination site is N(4): N. C. Baenziger, A. D. Nelson, A. Tulinsky, J. H. Bloor, and A. I. Popov, *J. Amer. Chem. Soc.*, **89**, 6467 (1967). [d] 5-Aminotetrazole monohydrate: K. Britts and I. L. Karle, *Acta Crystallogr.*, **22**, 308 (1967). [e] Sodium tetrazolate monohydrate: G. J. Palenik, *ibid.*, **16**, 596 (1963). [f] Hydrazinium 5-aminotetrazolate: J. H. Bryden, *ibid.*, **11**, 31 (1958). [g] 2-Methyl-5-aminotetrazole: J. H. Bryden, *ibid.*, **9**, 874 (1956). [h] 1,3-Dimethyl-5-aminotetrazole: J. H. Bryden, *ibid.*, **8**, 211 (1955).

bon. It is also comparable with the independent Au(III)–CN distances of 1.95 (2) and 1.99 (2) Å determined for $[H_5O_2][Au(CN)_4]$,[41] but somewhat shorter (at the furthermost edge of statistical significance) than the gold(III)–C(alkyl) bond lengths found for

$[(CH_3)_2AuOH]_4$, (2.05 Å)[42,43]


$o\text{-}(C_6H_5)_2PC_6H_4C(CH_2Br)AuBr_2$, (2.10 (3) Å)[44]

and 
$o\text{-}(C_6H_5)_2PC_6H_4C(H)_2C(H)(CH_2Br)AuBr_2$ (2.13 (4) Å)[44]

The tetrameric dimethylgold(III) hydroxide molecule of approximately S_4 geometry occurs as an eight-membered ring in which the square-planar gold(III)'s are linked by bridging hydroxo oxygens,[43] while in the latter two complexes the planar-coordinated gold(III) is bonded to two terminal bromine atoms, a benzene-attached phosphorus atom, and a sp^3-like carbon atom of the side chain of the benzene ring, thereby resulting in a five-membered chelate ring in the one complex and a six-membered chelate ring in the other complex.[44]

In the $[Au(CN_4(i\text{-}C_3H_7))_4]^-$ anion, the fact that the pπ orbitals of each tetrazole ring (in being nearly parallel with the filled d_{xy} gold orbital) are almost at right angles with the empty 6p_z gold orbital would appear to preclude any significant ligand-to-metal π bonding. The empty antibonding tetrazole pπ orbitals are also deemed to be energetically unfavorable for any significant metal-to-ligand π bonding. Hence, it is presumed in the absence of appreciable nonbonding steric effects that the average value of 1.98 Å for the gold(III)–carbon distance primarily reflects a single-bond length.

The ^{197}Au Mössbauer isomer shift (IS) and electronic quadrupole splitting (QS) which were recently investigated[45,46] for a large number of Au(I) and Au(III) compounds, among them the two complex species $[As(C_6H_5)_4][Au(CN_4R)_4]$ and $[As(C_6H_5)_4][Au(CN_4R)_2]$ (where R is $-C_6H_{11}$),[45] shed considerable light concerning the nature of the carbon-bonded tetrazole ligand. In these studies a correlation between the observed isomer shift and the spectrochemical series of the ligands was established for a considerable number of Au(I) as well as Au(III) complexes. However, the positions for the above-mentioned tetrazolato–Au(I) and –Au(III) complexes[45] are unexpectedly at the very low end of the IS scale near those for halogeno–gold complexes, in sharp contrast with the high positive positions not only of $KAu(CN)_2$, $KAu(CN)_4$, and other gold cyanide complexes, but also of $(C_6H_5)_3PAuCH_3$[45] which has a higher position than $(C_6H_5)_3PAuCN$.[46] This startling difference appears to rule out a similarity in bonding of the $[Au(CN_4R)_4]^-$ anion with that of the $[Au(CN)_4]^-$ anion, whose high IS position is comparable with the position of the cyanide ligand in the spectrochemical series. Instead, these Mössbauer results suggest that, in contradistinction to the high σ-inductive electron-donating effect of carbon as a methyl or cyanide ligand, the carbon-bonded tetrazolato ligand appears to possess low σ-donor strength (at least in the $[Au(CN_4R)_4]^-$ and $[Au(CN_4R)_2]^-$ anions). It is noteworthy that in accord with chemical intuition the Mössbauer data provide indirect but yet definite evidence that metal-to-ligand π bonding in these anions may be neglected on the basis that such an interaction would give rise to an increase in the IS.

The differences among corresponding dimensions of the four tetrazole rings are not significant. Furthermore, the average values given in Table IV compare favorably with the corresponding bond lengths determined in previous structural determinations of various tetrazole derivatives. All of these C–N and N–N values are similarly shorter than those usually found for

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single bonds and therefore are compatible with considerable electron delocalization as also proposed for the other tetrazole systems.

The independent tetraphenylarsonium cation in the $[Au(CN_4(i\text{-}C_3H_7))_4]^-$ salt approximately possesses a C_2 geometry with two phenyl rings ($n = 1, 3$) rotated by similar angles of 22.1 and 26.6° from the C_{11}–As–C_{31} plane and with the other two phenyl rings ($n = 2, 4$) rotated by similar angles of 77.9 and 80.6° from the other perpendicular C_{21}–As–C_{41} plane. The six angles between the arsenic atom and the four nearest carbon atoms of range 107.6–112.8° are close to the normal tetrahedral value of 109° 28′. The four As–C bond lengths average 1.90 Å, which is in excellent agreement with mean values found in other recent crystal structural determinations involving the tetraphenylarsonium ion.[47]

Acknowledgments. Acknowledgment of the financial support of this research is most gratefully made to the National Science Foundation (No. GP-4919X). We are especially indebted to Dr. Alan S. Foust for his helpful assistance. We also wish to acknowledge the Deutscher Akademischer Austauschdienst for a NATO research fellowship for W. P. F. and Professor Dr. Wolfgang Beck for his interest in this work. The use of the UNIVAC 1108 and CDC 3600 computers at the University of Wisconsin Computing Center was made available by partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation administered through the University Research Committee.

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Structural Characterization of the Di-μ-azido-bis(diazidopalladate(II)) Anion, $[Pd_2(N_3)_6]^{2-}$. Stereochemical Similarity between Stable Bridging Azide Ligands of the *N*-Diazonium Type and Terminal Azide Ligands

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Abstract: A single-crystal X-ray diffraction investigation of $[As(C_6H_5)_4]_2[Pd_2(N_3)_6]$ has revealed that the azido-bridged hexaazidodipalladate(II) anion contains a symmetrical planar Pd_2N_2-bridged system (involving one of the terminal nitrogen atoms of each of the two azide bridges) with a square-planar-like environment of two terminal and two bridging azide nitrogen atoms about each palladium(II). The entire anion, which possesses crystallographic site symmetry $C_i\text{-}\bar{1}$, shows a significant departure from an idealized $D_{2h}\text{-}2/m2/m2/m$ geometry toward a $C_{2h}\text{-}2/m$ geometry owing to considerable deflections of the terminal azides from the Pd_2N_2 plane. The observed angular deformations of the Pd_2N_2-bridged system are attributed to atomic overcrowding owing to the small size of the nitrogen atoms as reflected in the short nonbonding Pd···Pd′ distance of 3.143 (2) Å. The most notable structural feature in the $[Pd_2(N_3)_6]^{2-}$ anion is the similar asymmetric character in the two N–N bond lengths between the one independent azide bridging ligand (1.239 (14) Å *vs.* 1.142 (13) Å) and two independent terminal azide ligands (1.205 (9) Å *vs.* 1.139 (8) Å). This large structural equivalency between the bridging and terminal azide ligands in this anion indicates that there is no appreciable change in electronic character due to coordination of a terminal azide ligand with a second metal atom by use of a normally unshared electron pair on the trigonal nitrogen atom to give an azide-bridging ligand of the *N*-diazonium type. Crystals of $[As(C_6H_5)_4]_2[Pd_2(N_3)_6]$ belong to the triclinic system with one formula species in a unit cell of centrosymmetric symmetry $P\bar{1}$ and lattice dimensions $a = 11.43$, $b = 11.78$, $c = 10.36$ Å, $\alpha = 109.0$, $\beta = 103.1$, and $\gamma = 100.4°$. The crystal structure was determined by conventional methods and refined by full-matrix rigid-body least squares to an unweighted discrepancy index R_1 of 5.8% based on 2183 independent diffractometry-collected observations.

Within the last several years extensive studies have been directed by Beck and coworkers[1] toward the synthesis and properties of transition metal azide complexes. As part of these investigations the following new azido-bridged compounds have been produced and characterized as dimers by molecular weight determinations:[2,3] $[As(C_6H_5)_4]_2[Pd_2(N_3)_6]$ (**1**), $[(C_6H_5)_3PPd(N_3)_2]_2$ (**2**), $[(CH_3)_2Au(N_3)]_2$ (**3**), and $\{[(C_6H_5)_3P]_2Pd(N_3)\}_2(BF_4)_2$ (**4**). From their ir spectra it was not decided whether the two azide bridges in each of the above compounds possess the proposed structure I containing a four-membered M_2N_2 ring system or the proposed structure II containing an eight-membered M_2N_6 ring system.[2]

Both kinds of postulated bridging azide linkages subsequently have been ascertained from single-crystal X-ray structural determinations of polymeric $Cu(N_3)_2$ (type I)[4] and dimeric $[(C_6H_5)_3P]_2Cu(N_3)$ (type II).[5]

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