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.

(47) *Cf.* T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, *Inorg. Chem.*, **5**, 1427 (1966); R. P. Taylor, D. H. Templeton, A. Zalkin, and W. D. Horrocks, Jr., *ibid.*, **7**, 2629 (1968).

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

W. P. Fehlhammer and Lawrence F. Dahl*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received March 17, 1971*

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-$\bar{1}$, shows a significant departure from an idealized D_{2h}-$2/m2/m2/m$ geometry toward a C_{2h}-$2/m$ 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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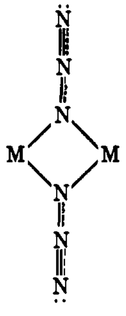
(1) W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer, and K. Feldl, *Chem. Ber.*, **100**, 2335 (1967).

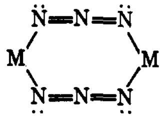
(2) W. Beck, W. P. Fehlhammer, P. Pöllmann, and R. S. Tobias, *Inorg. Chim. Acta*, **2**, 467 (1968).

(3) W. P. Fehlhammer, W. Beck, and P. Pöllmann, *Chem. Ber.*, **102**, 3903 (1969).

(4) I. Agrell, *Acta Chem. Scand.*, **21**, 2647 (1967).



I



II

However, in these and other known azido-bridged complexes, either the formation of these bridging azide rings is exclusively restricted to the crystalline state of the compound[4,6] or else decomposition rapidly occurs in solution.[7] In contrast, the azide bridges in the dimeric complexes **1–4** proved to be completely stable in solution.[8] We determined the structure of **1** in order not only to elucidate the mode of azide linkage in the $[Pd_2(N_3)_6]^{2-}$ anion but also to appraise the stereochemical differences between bridging and terminal azide ligands both coordinated to the same transition metal. It is noteworthy that an assessment of the bond lengths and angles involving the *N*-diazonium-type azide bridging ligands found[4] in $Cu(N_3)_2$ is complicated by an additional weak but significant coupling of the two independent azide groups each differently coordinated at a longer distance with a third copper atom to give for each Cu(II) an octahedral-like environment comprised of six nitrogen atoms at four normal equatorial and two longer axial Cu–N distances.

Experimental Section

Data Collection. All procedures were carried out at prevailing room temperatures of approximately 22°. Bis(tetraphenylarsonium)hexaazidodipalladate(II), $[As(C_6H_5)_4]_2[Pd_2(N_3)_6]$ (**1**), was synthesized as previously described.[1] Well-formed orange to reddish crystals were grown under nitrogen from a 1:1 chloroform–dichloromethane solution at an *n*-hexane interface. Difficulty was encountered in finding untwinned crystals. An untwinned crystal fragment approximating a rectangular prism (elongated along *a*) of dimensions 0.32 × 0.23 × 0.19 mm (along the [100], [010], and [001] directions) was finally obtained from combined optical and X-ray photographic examination and was used for all subsequent measurements. This crystal cemented to a thin glass fiber was optically aligned about the rotation axis (corresponding to the *a** reciprocal triclinic symmetry axis) on a General Electric full-circle Datex-controlled diffractometer, and 31 representative diffraction maxima then were carefully centered.[9] The lattice constants (22°) obtained by a least-squares refinement[10] of the measured angle settings of these 31 reflections were used to generate the angle settings for all data reflections.[11] Intensities for 3957 (hkl, $h\bar{k}l$, $hk\bar{l}$, $h\bar{k}\bar{l}$) reflections (corresponding to the independent hemisphere of the intensity-weighted reciprocal lattice) were measured twice with Zr-filtered Mo Kα radiation for $2\theta \leq 45°$, beyond which there were only few reflections with intensities above background. The takeoff angle for the X-ray tube was 2°; the scintillation detector with a 2-mm square aperture was placed 31 mm from the crystal, and the pulse-height analyzer was adjusted to accept approximately 90% of the Mo Kα pulse distribution. Data were collected in the θ–2θ scan mode with a 2°/min rate over a range of 2°. Background counts of 15 sec were taken at each end of a scan *via* the stationary crystal–stationary counter technique. In order to monitor periodically both electronic and crystal stability, the intensities of three standard reflections were remeasured every 100 reflections. A linear decrease in intensity of 18% was observed for the total period of data collection, and the derived structure factors were corrected for this decay. Structure factors were calculated from the intensity data by means of the data reduction program DREDGE,[12] in which the intensities were corrected for background and Lorentz-polarization effects, and $\sigma(I)$'s for each reflection were calculated as outlined in the preceding paper.[13] A data set of 2183 reflections for which $I \geq 2\sigma(I)$ was used in the structural analysis and least-squares refinements. Based on a linear absorption coefficient for Mo Kα radiation of 21.7 cm^{-1}, a general absorption correction was made with transmission coefficients ranging from 0.59 to 0.71.

Unit Cell and Space Group. Crystals of **1** are triclinic with cell parameters given as follows: $a = 11.431\ (2)$, $b = 11.776\ (2)$, $c = 10.364\ (1)$ Å; $\alpha = 108.98\ (1)$, $\beta = 103.05\ (1)$, and $\gamma = 100.36\ (1)°$;[14] $V = 1235.7$ Å^3. The Laue symmetry C_i-$\bar{1}$ and approximate unit cell dimensions were obtained from precession films. The lattice dimensions of the originally chosen primitive cell were then transformed with the aid of the computer program RCELL[15] to the reduced (conventional) primitive cell with obtuse interaxial angles and $c < a < b$. The experimental density of 1.65 (2) g/cm^3, determined by flotation in mixtures of CCl_4 and 2-iodopropane, agrees well with the density of 1.66 g/cm^3 calculated for one formula unit, $Pd_2As_2C_{48}N_{18}H_{40}$, per cell. Of the two possible triclinic space groups, the initially assumed centrosymmetric one $P\bar{1}$ was subsequently verified by the successful refinement of the structure, the solution of which required the location of 1 palladium, 1 arsenic, 9 nitrogen, 24 carbon, and 20 hydrogen atoms corresponding to $0.5[As(C_6H_5)_4]_2[Pd_2(N_3)_6]$ per asymmetric unit. (The independent 20 hydrogens were added in the least-squares refinement after initial coordinates of the carbon atoms in the four phenyl rings were found.) The crystallographically independent atoms were each determined from the structural analysis to occupy the twofold set of general positions: $\pm(x, y, z)$.[16]

Structural Determination and Refinement. The structure was solved from interpretations of computed Patterson and Fourier maps. $P\bar{1}$ symmetry requires that the one anion per cell is dimeric about a center of symmetry, arbitrarily designated at $^1/_2$, $^1/_2$, $^1/_2$ to fix the origin of the cell.[16]

The structure was refined by full-matrix least squares, the function minimized being $\Sigma w_i(|F_o| - |F_c|)^2$, where $w_i = 1/\sigma_i^2(F_o)$. In all calculations of F_c, the atomic scattering factors used for all neutral nonhydrogen atoms were those based on the Hartree–Fock–Slater calculations as compiled by Hanson, *et al.*;[17] the atomic scattering factors of Stewart, *et al.*,[18] were utilized for the hydrogen atoms. The effects of anomalous dispersion of the palladium and arsenic atoms were included in the calculation of F_c.[19,20] An initial refinement cycle was carried out on the merged absorption-uncorrected data in which only the positional parameters of all atoms in the asymmetric unit were varied. The four phenyl rings were treated as rigid groups; the variable positional parameters for each ring included the coordinates of the ring center and three orientation

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(5) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 738 (1970); *Inorg. Chem.*, **10**, 1289 (1971).

(6) $[(C_6H_5)_3P]_2CuN_3$ is monomeric in solution; however, Ziolo, *et al.*,[5] discuss the possibility that instead of bridge-splitting, dissociation of a phosphine ligand takes place.

(7) L. Busetto, A. Palazzi, and R. Ros, *Inorg. Chem.*, **9**, 2792 (1970).

(8) Some of these complexes, **1** and **3**, can even be obtained from aqueous solution.

(9) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(10) A. S. Foust, Ph.D. Thesis, University of Wisconsin (Madison), 1970.

(11) OLDANG, a local version of the Argonne National Laboratory "Orientation and Angle Setting General Program," Program B-101, 1965.

(12) DREDGE, a local Fortran program for diffractometer data reduction.

(13) W. P. Fehlhammer and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 3370 (1972).

(14) Values in parentheses are the estimated uncertainties computed by the least-squares program.[10]

(15) S. L. Lawton and R. A. Jacobsen, "The Reduced Cell and Its Crystallographic Application," IS-1141, Ames Laboratory, Iowa State University, 1965.

(16) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969, p 75.

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

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

(19) For Mo Kα radiation, the utilized values of the dispersion corrections to the atomic scattering factors are $\Delta f' = -1.0$, $\Delta f'' = 1.3$ for palladium; $\Delta f' = 0.1$, $\Delta f'' = 2.2$ for arsenic.[20]

(20) D. H. Templeton in ref 16, Vol. III, 1962, p 215.

Table I. Positional, Thermal, and Group Parameters for $[As(C_8H_5)_4]_2[Pd_2(N_3)_6]$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.60807 (7)[b]	0.56758 (7)	0.45774 (9)	0.01106 (10)	0.01112 (10)	0.01545 (14)	0.00275 (7)	0.00588 (9)	0.00458 (9)
Pd′	0.39193[c]	0.43242	0.54226	0.01106	0.01112	0.01545	0.00275	0.00588	0.00458
As	0.26345 (8)	0.11212 (9)	−0.00517 (10)	0.00843 (11)	0.00957 (11)	0.01100 (15)	0.00319 (8)	0.00318 (9)	0.00176 (10)
N(1)	0.6107 (10)	0.6834 (9)	0.3538 (11)	0.0161 (12)	0.0121 (11)	0.0196 (16)	0.0044 (10)	0.0040 (12)	0.0060 (11)
N(2)	0.7064 (10)	0.7577 (10)	0.3689 (9)	0.0132 (12)	0.0129 (12)	0.0158 (14)	0.0052 (10)	0.0068 (11)	0.0054 (11)
N(3)	0.7874 (10)	0.8307 (9)	0.3742 (11)	0.0159 (13)	0.0144 (13)	0.0258 (19)	0.0024 (11)	0.0115 (13)	0.0082 (13)
N(4)	0.7873 (8)	0.5634 (9)	0.4856 (10)	0.0098 (9)	0.0188 (13)	0.0183 (16)	0.0037 (9)	0.0050 (10)	0.0073 (12)
N(5)	0.8316 (8)	0.5620 (8)	0.3914 (10)	0.0103 (10)	0.0106 (10)	0.0147 (15)	−0.0005 (8)	0.0034 (10)	0.0027 (10)
N(6)	0.8835 (9)	0.5575 (10)	0.3069 (11)	0.0135 (14)	0.0191 (14)	0.0197 (17)	0.0027 (10)	0.0088 (12)	0.0052 (13)
N(7)	0.4276 (10)	0.5519 (11)	0.4482 (13)	0.0159 (14)	0.0214 (16)	0.0350 (26)	0.0067 (12)	0.0129 (16)	0.0180 (18)
N(8)	0.3513 (11)	0.5905 (10)	0.3800 (12)	0.0128 (13)	0.0148 (13)	0.0197 (18)	0.0023 (10)	0.0086 (13)	0.0066 (12)
N(9)	0.2850 (11)	0.6343 (14)	0.3248 (14)	0.0157 (15)	0.0325 (24)	0.0307 (25)	0.0095 (15)	0.0111 (16)	0.0203 (21)

Group	x_c[d]	y_c	z_o	ϕ	θ	δ
Ring 1	0.0676 (3)	0.2851 (3)	0.0330 (5)	−0.379 (8)	2.037 (4)	−0.256 (8)
Ring 2	0.3234 (4)	0.0430 (4)	0.2821 (5)	2.212 (4)	2.773 (3)	−1.085 (4)
Ring 3	0.4841 (4)	0.7164 (4)	0.0216 (4)	−2.508 (5)	2.273 (3)	−3.075 (5)
Ring 4	0.8289 (4)	0.1482 (4)	0.2898 (4)	−2.186 (4)	−2.672 (3)	−1.161 (4)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses given here and in other tables are estimated standard deviations in the last significant digits. [c] The coordinates of Pd′ were derived from the coordinates of Pd by inversion through the center of symmetry at $^1/_2$, $^1/_2$, $^1/_2$. The thermal parameters of Pd′ are those of Pd. [d] x_c, y_c, and z_c are fractional coordinates of the ring center; ϕ, θ, and ρ (in radians) have been defined previously.[13]

angles which have been described previously.[13] The unweighted R_1 and weighted R_2 factors[21] were 18.4 and 20.9%, respectively. Next, the absorption correction was applied. After subsequent isotropic refinement which resulted in discrepancy factors of R_1 = 7.1 and R_2 = 9.3%, anisotropic thermal parameters were introduced for the palladium, arsenic, and nitrogen atoms, and two more cycles of refinement were carried out. In these latter cycles, the four phenyl groups were again refined as rigid groups with the hydrogen atoms included and with an overall isotropic temperature factor utilized for each group. The positions of the hydrogen atoms of the phenyl rings were calculated from an assumed ring geometry of D_{6h} symmetry and a C–H distance of 1.08 Å. The final R_1 and R_2 were 5.8 and 6.9%, respectively. A difference Fourier synthesis, computed from the final parameters, showed no unusual features; the largest negative peak in the vicinity of the palladium atom had a density of −0.77 e/Å^3, while the highest positive residual peak was +0.8 e/Å^3.

Positional and thermal parameters obtained from the output of the last cycle of the least-squares refinement are listed in Table I,[22] while Table II presents the derived parameters for the phenyl carbon and hydrogen atoms. Interatomic distances and bond angles together with estimated standard deviations, calculated[23] from the full inverse matrix containing the uncertainties in lattice parameters, are given in Table III.

Computer Programs. All Patterson and Fourier calculations were carried out with the Blount program,[24] while least-squares refinements were carried out with a local modification of the Busing–Martin–Levy ORFLS program.[25] Other programs used in the structural determination include DREDGE[12] for data reduction, BLANDA for calculating distances and bond angles, PLANES (Smith) for least-squares planes along with perpendicular displacements of atoms from these planes,[26] DEAR for absorption correction,[27] and ORTEP (Johnson) for drawings.[28]

Results and Discussion

The crystalline structure consists of discrete $[Pd_2(N_3)_6]^{2-}$ anions and tetraphenylarsonium $As(C_6H_5)_4^+$ cations as counterions. The fact that the closest nonbonding contacts among the individual ions in the crystal lattice are larger than the sum of van der Waals radii supports the premise that packing effects on the geometries of the ions are negligible other than for some possible angular distortions due to the optimization of the efficiency of the packing. An almost perfect separation from each other of the azidometalate anions $[Pd_2(N_3)_6]^{2-}$ is achieved by the presence of the bulky $As(C_6H_5)_4^+$ cations in the crystal lattice; the nearest contacts between the complex anions in neighboring cells amount to 4.47, 4.99, and 5.89 Å. This "crystal dilution" of the azide-containing species by large cations (or neutral ligands) is considered to be the main reason for the remarkable stability (*i.e.*, nonexplosivity) of these compounds as against those with only alkali metal counterions.[29]

In the hexaazidodipalladate(II) anion (Figure 1), the two palladium atoms are symmetrically linked together through only one of the terminal nitrogen atoms of each of the two azide bridges to give a rhombus for the Pd_2N_2 ring with the four edges measuring an average value of 2.004 (8) Å. Each Pd(II) completes its planar four-coordination through bonding with two terminal azide ligands, thus leading to a species in which the two metal atoms are literally embedded in a "cloud" of 18 nitrogen atoms. Although the Pd_2N_2 ring portion of the anion is exactly planar as required by the crystallographic site symmetry C_i-$\bar{1}$, the entire anion shows a drastic departure from an idealized D_{2h}-$2/m2/m2/m$ geometry owing to considerable deflections of the ter-

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(21) $R_1 = (\Sigma||F_o| - |F_c||/\Sigma|F_o|)100$; $R_2 = (\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2)^{1/2}100$.

(22) Observed and calculated structure factors for $[As(C_6H_5)_4]_2[Pd_2(N_3)_6]^{2-}$ 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-72-3377. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

(23) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortan Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(24) J. F. Blount, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1965.

(25) "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.

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

(27) 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).

(28) C. K. Johnson, "ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," ORNL-TM-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(29) Most of the simple alkali metal salts of the azidometallates for the heavier transition metals including palladium are highly explosive.[1]

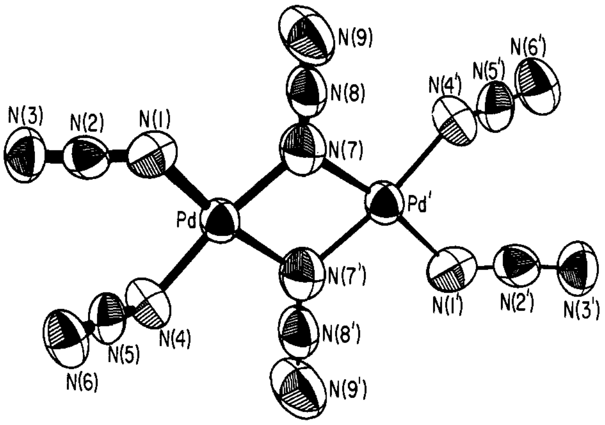

Figure 1. Configuration of the $[Pd_2(N_3)_6]^{2-}$ anion which possesses crystallographic site symmetry C_i-$\bar{1}$. All atoms are represented by 50% probability ellipsoids of thermal displacement.

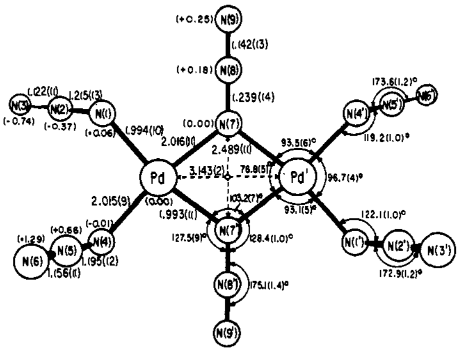

Figure 2. Principal distances and angles for the $[Pd_2(N_3)_6]^{2-}$ anion with esd's given in parentheses. Each number in parentheses preceded by either a plus or a minus sign designates the perpendicular deviation of a particular atom from the central Pd_2N_2 rhombus. The approximate coplanarity of all atoms of the $(\alpha N)_2Pd(N_3)_2Pd(\alpha N)_2$ fragment (*i.e.*, the entire anion except for the outer two nitrogen atoms of each terminal azide ligand) within 0.25 Å is observed such that this fragment may be considered to conform approximately to D_{2h} symmetry. Based on assumed equivalent orientations of the two crystallographically independent terminal azide ligands which are displaced unequally on opposite sides from the Pd_2N_2 plane, the entire $[Pd_2(N_3)_6]^{2-}$ anion ideally possesses C_{2h} symmetry.

Table II. Derived Parameters for Phenyl Ring Carbon and Hydrogen Atoms

Atom	*x*	*y*	*z*	*B*,[a] Å^2
		Ring 1		
C(1)[b]	0.1497	0.2114	0.0161	4.6 (1)
C(2)	0.1138	0.2432	0.1397	
H(2)	0.1497	0.2106	0.2227	
C(3)	0.0318	0.3169	0.1567	
H(3)	0.0039	0.3417	0.2528	
C(4)	−0.0144	0.3589	0.0499	
H(4)	−0.0781	0.4162	0.0631	
C(5)	0.0215	0.3271	−0.0738	
H(5)	−0.0144	0.3597	−0.1567	
C(6)	0.1035	0.2533	−0.0907	
H(6)	0.1314	0.2286	−0.1868	
		Ring 2		
C(1)	0.3004	0.0699	0.1593	5.2 (1)
C(2)	0.4138	0.1299	0.2672	
H(2)	0.4839	0.1974	0.2557	
C(3)	0.4368	0.1030	0.3901	
H(3)	0.5249	0.1496	0.4740	
C(4)	0.3464	0.0161	0.4050	
H(4)	0.3643	−0.0048	0.5005	
C(5)	0.2331	−0.0439	0.2970	
H(5)	0.1629	−0.1114	0.3086	
C(6)	0.2101	−0.0170	0.1742	
H(6)	0.1220	−0.0636	0.0903	
		Ring 3		
C(1)	0.4095	0.2100	−0.0152	4.7 (1)
C(2)	0.4667	0.1599	−0.1168	
H(2)	0.4285	0.0638	−0.1908	
C(3)	0.5732	0.2335	−0.1233	
H(3)	0.6176	0.1946	−0.2023	
C(4)	0.6224	0.3572	−0.0280	
H(4)	0.7051	0.4145	−0.0330	
C(5)	0.5652	0.4073	0.0736	
H(5)	0.6034	0.5035	0.1476	
C(6)	0.4587	0.3337	0.0801	
H(6)	0.4142	0.3726	0.1591	
		Ring 4		
C(1)	0.2029	−0.0399	−0.1680	4.5 (1)
C(2)	0.2693	−0.1282	−0.1706	
H(2)	0.3456	−0.1126	−0.0779	
C(3)	0.2375	−0.2365	−0.2924	
H(3)	0.2891	−0.3051	−0.2945	
C(4)	0.1393	−0.2566	−0.4117	
H(4)	0.1146	−0.3407	−0.5064	
C(5)	0.0729	−0.1683	−0.4091	
H(5)	−0.0034	−0.1838	−0.5017	
C(6)	0.1047	−0.0600	−0.2872	
H(6)	0.0531	0.0086	−0.2852	

[a] *B* is the refined isotropic thermal parameter for the C_6H_5 groups; an additional *B* term was assigned to each carbon atom of the phenyl ring, in order to make allowance for their different thermal vibration amplitudes (C(2), C(6), 0.5; C(3), C(5), 1.0; C(4), 1.5). [b] Ring carbon and hydrogen atoms are numbered sequentially, with C(1) attached to the As, and H(*n*) attached to C(*n*).

minal azide ligands from the Pd_2N_2 plane. The coplanarity of the palladium-attached nitrogen atoms is revealed from Figure 2, which shows their perpendicular displacements from the Pd_2N_2 plane to be within 0.06 Å; the approximate planarity of the 12 atoms of the $(\alpha N)_2Pd(N_3)_2Pd(\alpha N)_2$ substructure (*i.e.*, including the entire independent bridging azide ligand but still excluding the two outer nitrogen atoms of each terminal azide ligand) is also presented in Figure 2, which discloses that their perpendicular displacements from the Pd_2N_2 plane are all within 0.25 Å. For the two terminal azide ligands connected to a given palladium atom, if their much different directional shifts on opposite sides of the Pd_2N_2 plane are considered to be equivalent, then the idealized D_{2h} geometry for the $(\alpha N)_2Pd(N_3)_2Pd(\alpha N)_2$ fragment is reduced by the inclusion of the other two nitrogen atoms per terminal azide ligand to an idealized C_{2h}-$2/m$ geometry; the retained twofold axis passes through the two Pd(II) atoms, while the remaining horizontal mirror plane contains the two bridging azide ligands. The nonbonding Pd···Pd′ distance of 3.143 (2) Å is comparatively short, as is also true for the nonbonding N(7)···N(7′) distance of only 2.49 (1) Å. This atomic overcrowding in the M_2N_2-bridged system is primarily a consequence of the small size of the bridging nitrogen atoms. Owing primarily to the mutual repulsion of the palladium atoms, the Pd_2N_2 ring exhibits a significant angular distortion as manifested in the particularly small N(7)–Pd–N(7′) angle of 76.8 (5)°. This angular decrease of 13° from 90° and the similar lowering (by 17°) of the Pd–N(7)–Pd′ angle of 103.2 (7)° from 120° is explicable as a compromise between the right-angle tendency of each Pd(II) and the tendency of a trigonal angle for each bridgehead nitrogen atom.

Table III. Distances (Å) and Angles (deg) for $[As(C_6H_5)_4]_2[Pd_2(N_3)_6]$[a]

A. Bond Lengths

Palladium to Nitrogen	
Pd–N(1)	1.994 (10)
Pd–N(4)	2.015 (9)
Pd–N(7)	2.016 (11)
Pd–N(7′)[b]	1.993 (11)
	2.004 (av)
Nitrogen to Nitrogen Terminal Azide Groups	
N(1)–N(2)	1.215 (13)
N(2)–N(3)	1.122 (11)
N(4)–N(5)	1.195 (12)
N(5)–N(6)	1.156 (11)
Bridging Azide Groups	
N(7)–N(8)	1.239 (14)
N(8)–N(9)	1.142 (13)
Arsenic to Phenyl Carbon	
As–C(1-1)	1.902 (12)
As–C(2-1)	1.906 (11)
As–C(3-1)	1.894 (9)
As–C(4-1)	1.896 (10)
	1.900 (av)

B. Bond Angles

Nitrogen–Palladium–Nitrogen	
N(1)–Pd–N(4)	96.7 (4)
N(1)–Pd–N(7)	93.1 (5)
N(4)–Pd–N(7′)	93.5 (6)
N(7)–Pd–N(7′)	76.8 (5)
Palladium–Nitrogen–Palladium	
Pd–N(7)–Pd′	103.2 (7)
Palladium–Nitrogen–Nitrogen	
Pd–N(1)–N(2)	122.1 (10)
Pd–N(4)–N(5)	119.2 (10)
Pd–N(7)–N(8)	128.4 (10)
Pd–N(7′)–N(8′)	127.5 (9)
Linearity of the Azide Groups	
N(1)–N(2)–N(3)	172.9 (12)
N(4)–N(5)–N(6)	173.6 (12)
N(7)–N(8)–N(9)	175.1 (14)
Carbon–Arsenic–Carbon	
C(1-1)–As–C(2-1)	107.6 (11)
C(1-1)–As–C(3-1)	107.5 (11)
C(1-1)–As–C(4-1)	115.1 (10)
C(2-1)–As–C(3-1)	110.6 (11)
C(2-1)–As–C(4-1)	107.0 (10)
C(3-1)–As–C(4-1)	109.0 (10)
	109.5 (av)

C. Selected Nonbonding Distances

Near-Neighbor Distances[c] within the $[Pd_2(N_3)_6]^{2-}$ Anion	
N(1)···N(4)	3.00 (1)
N(1)···N(5)	3.13 (1)
N(2)···N(4)	3.10 (1)
N(2)···N(5)	2.97 (1)
N(2)···N(6)	3.37 (1)
N(3)···N(5)	3.35 (1)
N(3)···N(6)	3.49 (1)
N(1)···N(8)	3.07 (1)
N(4)···N(7′)[a]	2.92 (1)
N(4)···N(8′)	3.06 (1)
N(7)···N(7′)	2.49 (1)
Pd···Pd′	3.143 (2)

Near-Neighbor Distances between Ions

Nitrogen to Phenyl Carbon Contacts[d]		
N(1)···C(2-3)	$(1-x, 1-y, 1-z)$	3.23 (1)
N(1)···C(2-4)	$(1-x, 1-y, 1-z)$	3.47 (1)
N(1)···C(3-3)	$(1-x, 1-y, 1-z)$	3.33 (1)
N(1)···C(3-5)	$(1-x, 1-y, -z)$	3.44 (1)
N(2)···C(2-3)	$(1-x, 1-y, 1-z)$	3.43 (1)
N(2)···C(2-4)	$(1-x, 1-y, 1-z)$	3.18 (1)
N(3)···C(1-6)	$(1-x, 1-y, -z)$	3.37 (1)
N(3)···C(2-4)	$(1-x, 1-y, 1-z)$	3.27 (1)
N(3)···C(4-6)	$(x, 1+y, z)$	3.24 (1)
N(4)···C(1-3)	$(1-x, 1-y, 1-z)$	3.47 (1)
N(6)···C(1-4)	$(1+x, y, z)$	3.50 (1)
N(9)···C(3-3)	(x, y, z)	3.48 (1)
N(9)···C(3-4)	(x, y, z)	3.49 (1)
Nitrogen to Phenyl Hydrogen Contacts[e]		
N(1)···H(3-5)	$(1-x, 1-y, -z)$	2.44
N(3)···H(1-6)	$(1-x, 1-y, -z)$	2.30
N(6)···H(1-4)	$(1+x, y, z)$	2.71
N(6)···H(1-5)	$(1-x, 1-y, -z)$	2.67

[a] Estimated standard deviations of the last significant figures are given in parentheses. [b] Primes refer to atoms related by the crystallographic center of symmetry at 1/2, 1/2, 1/2 to atoms in the asymmetric unit. [c] Below 3.5 Å. [d] To 3.5 Å. [e] Below 2.8 Å.

Similar corresponding bond angles are found[4] in the Cu_2N_2 ring of polymeric $Cu(N_3)_2$.

The most prominent structural feature in the $[Pd_2(N_3)_6]^{2-}$ anion is that the independent bridging azide ligand and the two independent terminal azide ligands each exhibit a pronounced asymmetry in their two N–N bond lengths, with the longer distance occurring between the middle nitrogen atom and the nitrogen atom attached to the palladium atom. The two distinctly different N–N bond lengths within the bridging azide ligand are 1.239 (14) and 1.142 (13) Å and within the two terminal azide ligands average 1.205 (9) and 1.139 (8) Å. The surprisingly close similarity in the corresponding bond lengths indicates a large *structural equivalency* between the bridging and terminal azide ligands which suggests that there is no appreciable change in the degree of asymmetry 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 azido-bridged ligand of the *N*-diazonium type.[30–32]

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(30) The near structural equivalence between the bridging and terminal azide ligands in the $[Pd_2(N_3)_6]^{2-}$ anion as evidenced by the comparison of bond lengths is in accord with the experimental observations by Beck, *et al.*,[2] that the frequencies of the $\nu_{as}(N_3)$ infrared bands assigned to the azide bridges in 1–4 lie only slightly higher than the corresponding stretching modes of the terminal azide ligands (*viz.*, 2060–2080 *vs.* 2020–2060 cm^{-1}).

(31) In general, the extent of σ donation from a ligand orbital may markedly affect the electronic character of the ligand. For example, Fenske and coworkers[32] have shown that the 5σ orbital of the carbonyl group, which predominantly is comprised of the carbon AO's, is sufficiently antibonding between the carbon and oxygen atoms such that σ donation from this orbital by interaction with appropriate metal orbitals leads to a C–O σ-bond strengthening and therefore has an important effect on the carbonyl's force constant. At least in the case of the $[Pd_2(N_3)_6]^{2-}$ anion, the observed similarities in the corresponding bond lengths of the terminal and bridging ligands together with the anion's infrared spectrum[2,30] provide support that the differences in combined effects of σ and π bonding between terminal and *N*-diazonium-

Unsymmetrical N-N distances of similar magnitude have also been ascertained from X-ray diffraction studies for the terminal azide ligands in HN_3,[33] CH_3N_3,[34] $[Co(N_3)(NH_3)_5](N_3)_2$,[35] and in $[Cu(N_3)_2(NH_3)_2]$[36] as well as for the bridging azide ligands in $Cu(N_3)_2$,[4] in contrast with the N-N distances not differing significantly for the terminal azide ligands in ionic azides,[35,37] $[As(C_6H_5)_4]_2[Fe(N_3)_5]$,[38] and in $[Ru(N_3)(N_2)(NH_2CH_2CH_2NH_2)_2]PF_6$.[39] The Pd-N-N angles of 119.2 (1.0) and 122.1 (1.0)° for the terminal azide ligands in the $[Pd_2(N_3)_6]^{2-}$ anion are as anticipated for the attachment of trigonal-like nitrogen atoms to the metal atom. Both the terminal and bridging azide groups are found to be nearly linear. The two independent Pd-N(bridging) and two independent Pd-N(terminal) bonds also show structural equivalency in possessing identical average lengths of 2.004 (8) Å; this value, which is in agreement with the sum of the covalent radii of the Pd and N elements ($1.31 + 0.70 = 2.01$), is indicative of single-bond character.

Although the di-μ-azido-bis(diazidopalladate(II)) anion, being a pseudohalide complex, corresponds stereochemically to the electronically equivalent di-μ-chloro-bis(dichlorogold(III)) complex, Au_2Cl_6, there is a significant structural difference in that in the gold dimer[40] the Au-Cl(bridging) bonds of average value 2.34 (2) Å are considerably longer than the Au-Cl(terminal) bonds of average value 2.24 (2) Å.

In the least-squares refinement of **1**, the phenyl rings of the $As(C_6H_5)_4^+$ cation were treated as rigid groups each described by three positional and three angular parameters. The four independent As-C bond lengths ranged from only 1.894 to 1.906 Å. Of the six independent C-As-C angles, five, of range 107.0-110.6°, are close to the normal tetrahedral angle, and one is of somewhat larger value of 115.1°. The rotational orientations of the planes of the phenyl groups about their respective As-C_{n1}-C_{n4} axes are such that the $As(C_6H_5)_4^+$ cation does not approximate to any symmetrical conformation.[41-47]

Acknowledgment. We are most pleased to acknowledge the financial support of this research by the National Science Foundation (No. GP-4919X). 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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bridging azide ligands are markedly less than those found from spectral and bond-length changes between terminal and bridging carbonyl ligands.

(32) *Cf.* R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, 10, 38 (1971); M. B. Hall and R. F. Fenske, *ibid.*, in press.

(33) E. Amble and B. P. Dailey, *J. Chem. Phys.*, 18, 1422 (1950).

(34) R. L. Livingston and C. N. R. Rao, *J. Phys. Chem.*, **64**, 756 (1960).

(35) G. J. Palenik, *Acta Crystallogr.*, 17, 360 (1964).

(36) I. Agrell, *Acta Chem. Scand.*, 20, 1281 (1966).

(37) B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959); P. Gray, *Quart. Rev., Chem. Soc.*, 17, 441 (1963).

(38) J. Drummond and J. S. Wood, *Chem. Commun.*, 1373 (1969).

(39) B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 9, 2768 (1970).

(40) E. S. Clark, D. H. Templeton, and C. H. MacGillavry, *Acta Crystallogr.*, 11, 284 (1958).

(41) After submission of the present paper for publication, X-ray diffraction studies were reported for $[N(C_2H_5)_4][Mn_2(CO)_6(N_3)_3]$[42] and $[BCl_2(N_3)]_3$.[43] The diamagnetic $[(OC)_3Mn(N_3)_3Mn(CO)_3]^-$ anion of the above salt was shown[42] to possess an $Fe_2(CO)_9$-type geometry of D_{3h} symmetry with each of the three azide ligands bridging the two Mn(I) through one nitrogen atom. Although a weak direct Mn(I)-Mn(I) interaction was suggested[42] to account for the determined metal-metal bond length of 2.893 (4) Å (being similar to those in $Mn_2(CO)_{10}$[44] and $Mn_2(CO)_8[P(C_6H_5)_3]_2$[45]) and for the Mn-N-Mn bridging bond angles of average value 88.6°, it is noteworthy that a closed-shell electronic configuration is achieved for each Mn(I) without the necessity of any electron-pair metal-metal interaction. An alternative rationalization of the observed short Mn(I)-Mn(I) distance and of the small (but not overly acute) bond angle subtended at each trigonal-like bridgehead nitrogen atom may be formulated analogous to that utilized to explain the comparatively short Pd-Pd nonbonding distance and Pd-N-Pd angle of 103.2 (7)° in the $[Pd_2(N_3)_6]^{2-}$ anion—*viz.*, atomic overcrowding in the $Mn_2(\alpha N)_3$-bridged system due primarily to *three* small-sized nitrogen atoms linking the two $Mn(CO)_3$ moieties to each other. Hence, the equilibrium geometry found for the $Mn_2(\alpha N)_3$-bridged system is presumed to arise mainly from minimization of the nonbonded nitrogen-nitrogen and metal-metal repulsions together with interorbital electron-pair interactions. These conclusions emphasize that a metal-metal distance *per se* does not necessarily offer a means of demonstrating the existence of a metal-metal interaction in a ligand-bridged complex, but rather the best means for detection of the influence of a metal-metal interaction on the geometry is given by the angular deformation of the bridged system as revealed from the much more acute M-B-M bridging angles for complexes containing M-M interactions.[46] The boron dichloride azide trimer $[BCl_2(N_3)]_3$ also contains bridging azide ligands of the *N*-diazonium type.[43] Although not completely refined, the αN-βN and βN-γN bond lengths in the bridging azide groups of the $[Mn_2(CO)_6(N_3)_3]^-$ anion tend to follow the same pattern of asymmetry established for the $[Pd_2(N_3)_6]^{2-}$ anion, whereas for $[BCl_2(N_3)]_3$ there is a much greater difference between these two N-N bond lengths of 1.260 (average) and 1.088 Å (average), respectively. These experimental observations provide additional evidence that a major factor which dictates the kind of linkage of azide ligands coordinated to two metal atoms (*viz.*, type I or II) is the nonbonding repulsions of the resulting ring system as influenced by the other ligands. The observed end-to-end bonding (mode II) of the bridging azide groups in the μ-diazido-tetrakis(triphenylphosphine)dicopper(I) rather than coordination *via* only one nitrogen atom (mode I) may be attributed at least in part to steric overcrowding of the hypothetical $Cu_2(\alpha N)_2$ system due both to the constraints imposed by the short Cu-αN bond lengths and the bulky triphenylphosphine terminal ligands. This rationalization of the actual structure of $\{[Cu(N_3)][P(C_6H_5)_3]_2\}_2$ is similar to that reached by Ziolo, *et al.*,[5] from their X-ray investigation.

(42) R. Mason, G. A. Rusholme, W. Beck, H. Engelmann, K. Joos, B. Lindenberg, and H. S. Smedal, *Chem. Commun.*, 496 (1971).

(43) U. Müller, *Z. Anorg. Allg. Chem.*, **382**, 110 (1971).

(44) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).

(45) M. J. Bennett and R. Mason, *J. Chem. Soc. A*, 75 (1968).

(46) L. F. Dahl, E. Rodulfo de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969).

(47) For a comprehensive discussion of the structural aspects of complexes containing pseudohalide terminal and/or bridging ligands including azides, see W. Beck and W. P. Fehlhammer, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, **2**, 253 (1972).