(011) and $(0\bar{1}1)$ to complete the three-dimensional interaction. The secondary hydrogen-bonded contacts involve a five-atom rather than a three-atom bridge and are expected to have a smaller contribution to the overall magnetic exchange. These interaction distances and angles as well as other pertinent hydrogen-bonding distances and angles appear in Table V.

The nature of magnetic interactions propagated over extended distances has been an area of study and speculation over the past few years.[40–43] The research of Hendrickson et al. indicate that there is no direct general relationship between the separation of the magnetic centers and the magnitude of the magnetic coupling.[41–43] More recently, Hendrickson, Stucky, et al. have also shown that saturated carbons as well as conjugated pathways are capable of propagating magnetic exchange.[44–46] They observe magnetic coupling between magnetic centers separated by several angstroms and propagated over pathways which involve saturation carbons.[44] However, the efficiency of a given pathway appears to be stronger when there is a fully conjugated pathway in the bridging skeleton.

The copper(II) complexes of pyrazinecarboxylate reported here, and a previously reported copper(II) complex of pyrazinedicarboxylate,[31] are additional examples of magnetic exchange propagated over extended distances. Moreover, these complexes show that ferromagnetic interactions may be propagated over extended distances. Lower temperature studies must be completed before the nature of the magnetic interactions in the lattice-coupled complexes can be unambiguously determined.

Registry No. CuL_2, 33135-89-6; $CuL_2(H_2O)_2$, 74172-03-5; $[Cu(HL)Cl_2]_2$, 79900-51-9.

Supplementary Material Available: Listings of final least-squares coordinates with thermal parameters for CuL_2 and $CuL_2(H_2O)_2$ (Table IIC,D), magnetic data from 6 to 300 K for CuL_2, $CuL_2(H_2O)_2$, and $[Cu(HL)Cl_2]_2$ (Table III), and observed and calculated structure factor amplitudes for CuL_2 and $CuL_2(H_2O)_2$ (17 pages). Ordering information is given on any current masthead page.

---

(40) Coffman, R. E.; Buettner, G. R. *J. Chem. Phys.* **1979**, 83, 2387.

(41) Felthouse, T. R.; Duesler, E. N.; Hendrickson, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 618.

(42) Felthouse, T. R.; Duesler, E. N.; Christenson, A. T.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 245.

(43) Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2636.

(44) Franesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2059.

(45) Kramer, L. S.; Clauss, A. W.; Franesconic, L. C.; Corbin, D. R.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2070.

(46) Franesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2078.

Contribution from the Inorganic Chemistry Institute, University of Göttingen, Göttingen, West Germany,
and the Department of Chemistry, Manchester University, Manchester, England M13 9PL

Preparation and Structural Characterization of Dipalladium(II) Tetrakis(6-methyl-2-oxypyridine), $[Pd_2(mhp)_4]$

WILLIAM CLEGG,*[1a] C. DAVID GARNER,*[1b] and M. HASSAN AL-SAMMAN[1b]

Received September 1, 1981

Palladium(II) acetate reacts with sodium 6-methyl-2-oxypyridine, Na(mhp), in CH_2Cl_2 to give a material of empirical formula $Na_2Pd(mhp)_3(O_2CCH_3)$. Subsequent treatment of this material with methanol produces the dimeric complex $[Pd_2(mhp)_4]$. The dimer crystallizes in the space group *Pbca*, with $a = 15.625$ (2) Å, $b = 16.126$ (2) Å, $c = 18.831$ (2) Å, and $Z = 8$. Refinement, based on 3243 unique diffractometer data, gave $R = 0.054$. Four mhp ligands bridge a pair of palladium(II) atoms, which are separated by 2.546 (1) Å. The properties of this molecule are discussed with respect to those of other $[M_2(mhp)_4]$ complexes and the nature of the Pd(II)–Pd(II) interaction. $[Pd_2(mhp)_4]$ is considered to possess no net direct formal metal–metal bond.

Introduction

Complexes of the type $[M_2(mhp)_4]$, where M = Cr, Mo, W,[2] Ru,[3] or Rh[4,5] and Hmhp = 6-methyl-2-hydroxypyridine, have been prepared and structurally characterized in the last few years. These complexes are of particular interest since they contain metal–metal bonds that are among the shortest observed for each metal. The molecules have approximate D_{2d} symmetry, with M–O and M–N bonds arranged trans to their own kind so that each metal atom is bonded to two oxygen and two nitrogen atoms as well as to the other metal atom. The positions of the two methyl groups at each end of the metal–metal bond effectively prevent the binding of additional axial ligands to the metal atoms.

Recently, we reported that, in the case of a dirhodium(II) center, it is possible for *three* mhp ligands to have their nitrogen atoms attached to one rhodium atom, with only *one* nitrogen atom bonded to the other rhodium atom.[6] A twist distortion in the ligand arrangement about the Rh–Rh bond reduces the steric interactions of the three methyl groups at one end of the molecule and, simultaneously, allows one axial ligand to bind at the other end. We found that, in two such cases, mhp itself can act as the axial ligand: in $[Rh_2(mhp)_4(Hmhp)]\cdot 0.5C_7H_8$, a fifth mhp ligand, protonated at nitrogen, is attached through its oxygen atom; in $[(Rh_2(mhp)_4)_2]\cdot 2CH_2Cl_2$, two dimeric units are linked together, one bridging mhp ligand of each unit being also axially bound to the other unit through its oxygen atom. A similar 3:1 arrangement of mhp ligands

---

(1) (a) University of Göttingen. (b) University of Manchester.

(2) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(3) (a) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowell, A. A.; Clegg, W. *Inorg. Chim. Acta* **1981**, *53*, L61. (b) Clegg, W. *Acta Crystallogr., Sect. B* **1980**, *B36*, 3112.

(4) (a) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowell, A. A.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1980**, 494. (b) Clegg, W. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2437.

(5) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 584.

(6) Berry, M.; Garner, C. D.; Hillier, I. H.; Clegg, W. *Inorg. Chim. Acta* **1980**, *45*, L209.

0020-1669/82/1321-1897$01.25/0

about a dirhodium(II) center was found for other related complexes by Cotton and Felthouse,[5] who also prepared complexes with a mixture of bridging ligands such as $[Rh_2(mhp)_2(O_2CCH_3)_2(C_3H_4N_2)]$.

As part of our continuing research on the interaction of mhp with metal centers, we have investigated the reaction of Na(mhp) with palladium(II) acetate. Herein we report the isolation and crystal structure determination of the dimeric complex $[Pd_2(mhp)_4]$. The molecule represents a valuable addition to the group of $[M_2(mhp)_4]$ complexes and allows for structural and spectroscopic comparisons of the metal–metal interactions in a homologous series of molecules, without the complications of the additional coordination of axial ligands.

Experimental Section

Reaction of Na(mhp) with Palladium Acetate. Anhydrous palladium acetate (Aldrich; 1.0 g, 4.45 mmol) and Na(mhp) (1.7 g, 12.97 mmol) were dissolved in dry CH_2Cl_2 (150 cm^3). The mixture was stirred at room temperature under an atmosphere of purified nitrogen for 48 h, during which time the solution became orange. After filtration, the solvent was removed by evaporation at room temperature under a reduced pressure. The orange-brown solid remaining was recrystallized from CH_2Cl_2; yield ca. 1.92 g, 83%. The product analyzed reasonably well for the formulation $Na_2Pd(mhp)_3(O_2CCH_3)$. Anal. Calcd for $C_{20}H_{21}N_3O_5Na_2Pd$: C, 44.8; H, 4.0; N, 7.8; Na, 8.6; Pd, 19.9. Found: C, 46.4; H, 4.8; N, 8.1; Na, 8.5; Pd, 20.1.

Preparation of $[Pd_2(mhp)_4]$. A solution of "$Na_2Pd(mhp)_3(O_2CCH_3)$" (0.5 g, 0.93 mmol) in dry methanol (10 cm^3) was stirred at room temperature for 24 h. The solution became very dark, and a dark brown precipitate was formed. This precipitate was filtered off, washed with dry methanol (2 × 2 cm^3) and dried in vacuo for 5 h. Recrystallization from CH_2Cl_2 gave pure $[Pd_2(mhp)_4]$ (ca. 0.22 g, 73%). Anal. Calcd for $C_{24}H_{24}N_4O_4Pd_2$: C, 44.7; H, 3.7; N, 8.7; Pd, 33.0. Found: C, 44.7; H, 3.7; N, 8.4; Pd, 33.3.

Crystal Structure Determination. A crystal of dimensions ca. 0.17 × 0.27 × 0.54 mm^3, sealed in a capillary tube, was examined on a Stoe-Siemens AED four-circle diffractomer, with Mo Kα radiation ($\lambda = 0.71069$ Å). All measurements were made at room temperature. Cell dimensions were derived by least-squares methods from the 2θ values ($20 < 2\theta < 25°$) of 62 centered reflections; so that systematic errors could be minimized, 2θ was measured as the difference in ω measurements on the positive and negative sides of the direct beam.[7] The space group is *Pbca*, with $a = 15.625$ (2) Å, $b = 16.126$ (2) Å, $c = 18.831$ (2) Å, $V = 4745.0$ Å^3, and $Z = 8$.

Intensity data were collected in a θ/ω scan mode for unique reflections with $2\theta < 60°$ by means of a profile-fitting procedure.[8] Empirical absorption corrections were applied on the basis of measurements of sets of equivalent reflections at a range of azimuthal (ψ) angles ($\mu = 15.3$ cm^{-1}; transmission factors vary between 0.52 and 0.57). A total of 3243 reflections with $I > 2\sigma(I)$ were used for structure refinement.

The unit cell parameters, space group, and Patterson synthesis indicated that $[Pd_2(mhp)_4]$ is isostructural with $[Rh_2(mhp)_4]$.[4b] Refinement was commenced with the atomic coordinates of this rhodium compound and isotropic thermal parameters, which were subsequently made anisotropic. Hydrogen atoms, clearly revealed in a difference synthesis, were then included in the refinement, with constraints on geometry (C–H = 0.96 Å, (methyl)H–C–H = 109.5°, aromatic H on C–C–C external bisector) and on isotropic thermal parameters [$U(H) = k(U_{eq}(C))$, where U_{eq} is the equivalent isotropic parameter for the C atom;[9] $k = 1.1$ for aromatic, 1.2 for methyl H]. The weighting scheme for the least-squares refinement was $w^{-1} = \sigma^2(F) + 0.0005F^2$.

Final values for R $(=\sum|\Delta|/\sum|F_o|)$ and for R_w $[=(\sum w\Delta^2/\sum wF_o^2)^{1/2}]$ were both 0.054 ($\Delta = |F_o| - |F_c|$). All parameter shifts in the last cycles were <0.05 times the corresponding esd values. A final difference synthesis contained no significant features. An analysis of the variance showed no trends in the value of $V = (\sum w\Delta^2/\sum w)^{1/2}$ with indices, sin θ, or F_o; V, the root-mean-square deviation of an observation of unit weight on an absolute scale of $|F_c|$, was 3.73 electrons for the total data set. A normal probability plot was linear, with a slope of 1.13.[10] Tables of structure factors are available as supplementary material.

Table I. Atomic Coordinates (×10^4)

atom	*x*	*y*	*z*
Pd(1)	1247.1 (3)	1657.1 (3)	677.1 (3)
Pd(2)	1230.3 (3)	2103.5 (3)	1973.5 (3)
O(1)	2518 (3)	2181 (3)	1900 (2)
C(11)	2931 (4)	2092 (4)	1304 (4)
C(12)	3822 (4)	2193 (4)	1300 (4)
C(13)	4268 (4)	2099 (4)	681 (4)
C(14)	3847 (5)	1921 (4)	57 (4)
C(15)	2976 (5)	1829 (4)	70 (4)
C(16)	2484 (5)	1624 (6)	−585 (4)
N(1)	2518 (3)	1897 (3)	681 (3)
O(2)	1025 (3)	2848 (3)	413 (2)
C(21)	1071 (4)	3436 (4)	889 (4)
C(22)	1048 (5)	4267 (5)	638 (4)
C(23)	1087 (7)	4894 (5)	1105 (5)
C(24)	1122 (5)	4749 (5)	1820 (4)
C(25)	1132 (5)	3955 (5)	2056 (4)
C(26)	1162 (6)	3745 (6)	2821 (4)
N(2)	1126 (4)	3291 (3)	1592 (3)
O(3)	−45 (3)	1987 (3)	1964 (2)
C(31)	−442 (4)	1644 (4)	1438 (4)
C(32)	−1323 (5)	1451 (5)	1502 (4)
C(33)	−1759 (5)	1104 (5)	956 (5)
C(34)	−1330 (4)	936 (5)	330 (4)
C(35)	−487 (4)	1120 (4)	265 (4)
C(36)	−3 (5)	939 (4)	−406 (3)
N(3)	−38 (3)	1450 (3)	813 (3)
O(4)	1523 (3)	500 (3)	1012 (2)
C(41)	1476 (4)	291 (5)	1672 (4)
C(42)	1583 (5)	−546 (5)	1857 (4)
C(43)	1482 (5)	−806 (6)	2536 (5)
C(44)	1278 (6)	−221 (6)	3053 (4)
C(45)	1221 (5)	594 (5)	2896 (4)
C(46)	999 (6)	1233 (6)	3414 (4)
N(4)	1325 (3)	859 (4)	2204 (3)

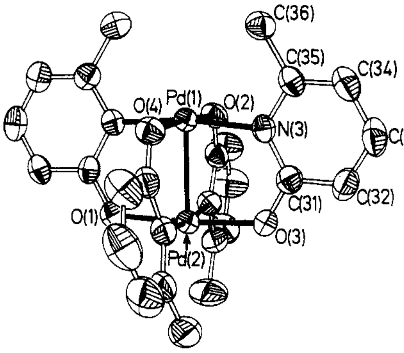

Figure 1. Molecular structure of $[Pd_2(mhp)_4]$, with thermal motion depicted as 50% probability ellipsoids.

Spectroscopic Measurements. Mass spectra were recorded on an AEI MS30 instrument using a 70-eV electron beam to produce ionization and fragmentation. Raman spectra were obtained on a Cary 82 instrument for powdered samples excited by the 5145-Å line of an argon laser, the instrument having been calibrated with cyclohexane. UV–visible spectra were recorded for CCl_4 solutions at room temperature with a Perkin-Elmer 402 spectrometer.

Results and Discussion

Description of the Structure of $[Pd_2(mhp)_4]$. The atomic coordinates are presented in Table I, and bond lengths and

---

(7) Computer programs used in this study were written by G. M. Sheldrick (SHELXTL system; Göttingen) and W. Clegg (diffractometer control progam) for the Data General Eclipse S250 computer.

(8) Clegg, W. *Acta Crystallogr., Sect. A* **1981**, *A37*, 22.

(9) Willis, B. T. M.; Pryor, A. W. "Thermal Vibrations in Crystallography"; University Press: Cambridge, U.K., 1975; p 101.

(10) (a) Abrahams, S. C.; Keeve, E. T. *Acta Crystallogr., Sect. A* **1971**, *A27*, 157. (b) Hamilton, W. C. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 293.

Table II. Bond Lengths (A) and Angles (Deg)

Pd(1)···Pd(2)	2.546 (1)		
Pd(1)-N(1)	2.023 (5)	Pd(2)-O(1)	2.021 (4)
Pd(2)-N(2)	2.051 (5)	Pd(1)-O(2)	2.014 (5)
Pd(1)-N(3)	2.052 (5)	Pd(2)-O(3)	2.002 (5)
Pd(2)-N(4)	2.059 (6)	Pd(1)-O(4)	2.016 (5)
Pd(2)-Pd(1)-N(1)	87.3 (1)	Pd(1)-Pd(2)-O(1)	86.7 (1)
Pd(1)-Pd(2)-N(2)	85.9 (2)	Pd(2)-Pd(1)-O(2)	88.0 (1)
Pd(2)-Pd(1)-N(3)	85.2 (2)	Pd(1)-Pd(2)-O(3)	88.6 (1)
Pd(1)-Pd(2)-N(4)	85.7 (2)	Pd(2)-Pd(1)-O(4)	87.9 (1)
N(1)-Pd(1)-N(3)	172.4 (2)	O(1)-Pd(2)-O(3)	175.2 (2)
N(2)-Pd(2)-N(4)	171.6 (2)	O(2)-Pd(1)-O(4)	175.2 (2)
N(1)-Pd(1)-O(2)	89.3 (2)	O(1)-Pd(2)-N(2)	89.9 (2)
N(1)-Pd(1)-O(4)	88.0 (2)	O(1)-Pd(2)-N(4)	90.2 (2)
N(3)-Pd(1)-O(2)	91.0 (2)	O(3)-Pd(2)-N(2)	90.3 (2)
N(3)-Pd(1)-O(4)	91.1 (2)	O(3)-Pd(2)-N(4)	88.9 (2)

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
O(*n*)-C(*n*1)	1.303 (8)	1.306 (8)	1.293 (8)	1.290 (9)
C(*n*1)-C(*n*2)	1.402 (10)	1.420 (11)	1.416 (10)	1.404 (11)
C(*n*1)-N(*n*)	1.375 (8)	1.348 (9)	1.372 (9)	1.376 (9)
C(*n*2)-C(*n*3)	1.365 (11)	1.342 (12)	1.354 (11)	1.355 (12)
C(*n*3)-C(*n*4)	1.377 (11)	1.369 (12)	1.383 (11)	1.393 (13)
C(*n*4)-C(*n*5)	1.369 (10)	1.354 (12)	1.356 (10)	1.350 (12)
C(*n*5)-C(*n*6)	1.489 (11)	1.481 (11)	1.503 (10)	1.460 (12)
C(*n*5)-N(*n*)	1.361 (9)	1.383 (10)	1.357 (9)	1.383 (9)
Pd(*m*)[a]-O(*n*)-C(*n*1)	123.0 (4)	120.9 (4)	121.7 (4)	122.1 (4)
O(*n*)-C(*n*1)-C(*n*2)	118.9 (6)	117.1 (7)	119.7 (6)	118.9 (7)
O(*n*)-C(*n*1)-N(*n*)	121.8 (6)	123.4 (6)	122.3 (6)	122.5 (6)
C(*n*2)-C(*n*1)-N(*n*)	119.2 (6)	119.5 (6)	118.0 (6)	118.6 (7)
C(*n*1)-C(*n*2)-C(*n*3)	119.9 (7)	119.5 (8)	121.0 (7)	121.2 (8)
C(*n*2)-C(*n*3)-C(*n*4)	120.5 (7)	121.2 (8)	119.1 (7)	118.5 (8)
C(*n*3)-C(*n*4)-C(*n*5)	118.9 (7)	119.0 (8)	120.2 (7)	121.4 (8)
C(*n*4)-C(*n*5)-C(*n*6)	121.6 (7)	122.3 (8)	121.5 (6)	123.9 (7)
C(*n*4)-C(*n*5)-N(*n*)	121.9 (7)	121.7 (7)	121.3 (6)	120.0 (7)
C(*n*6)-C(*n*5)-N(*n*)	116.6 (6)	116.0 (7)	117.1 (6)	116.0 (7)
Pd(*m*)-N(*n*)-C(*n*1)	120.5 (4)	120.8 (4)	121.4 (4)	120.5 (5)
Pd(*m*)-N(*n*)-C(*n*5)	119.8 (4)	120.1 (5)	118.4 (4)	119.4 (5)
C(*n*1)-N(*n*)-C(*n*5)	119.6 (6)	119.1 (6)	120.3 (6)	120.1 (6)

[a] Pd(*m*) is Pd(1) or Pd(2) as appropriate.

Table III. Comparison of [$M_2(mhp)_4$] Molecular Geometries

	M = Mo[a]	M = Ru[b]	M = Rh[c]	M = Pd[d]
M-M, A	2.065 (1)	2.238 (1)	2.359 (1)	2.546 (1)
mean M-N, A	2.167 (16)	2.089 (5)	2.043 (5)	2.046 (16)
mean M-O, A	2.086 (8)	2.044 (10)	2.017 (4)	2.013 (8)
mean O-M-M-N torsion, deg	−1.3 (4)	−3.5 (6)	−6.1 (9)	−6.4 (12)

[a] Reference 2. [b] Reference 3. [c] Reference 4. [d] This work.

interbond angles are listed in Table II. Molecules of [$Pd_2(mhp)_4$] have the approximate D_{2d} symmetry previously found for the other [$M_2(mhp)_4$] (M = Cr, Mo, W,[2] Ru,[3] or Rh[4]) molecules, which have been crystallographically characterized, and the intramolecular dimensions of these molecules containing the 4*d* elements are compared in Table III. The pair of palladium(II) atoms are bridged by four mhp ligands, arranged so that both atoms are coordinated to two nitrogen and two oxygen atoms and each of these ligand donor atoms is trans to its own kind (Figure 1). There are no axial ligands and no molecules of solvent of crystallization. A trimeric or tetrameric structure such as those observed for palladium(II) and platinum(II) acetates, respectively,[11] would appear to be precluded by the consequent and unfavorable steric interactions involving the methyl groups of the mhp ligands. Such steric interactions are, indeed, manifest in [$Pd_2(mhp)_4$] in that the molecule is distorted away from exact D_{2d} symmetry by a twist of the mhp ligands about the Pd···Pd axis; the torsion angles[12] O(*n*)-Pd-Pd-N(*n*) (*n* = 1-4) are −6.0 (2), −5.3 (2), −6.0 (2), and −8.3 (2)°, respectively (mean −6.4 (12)°).

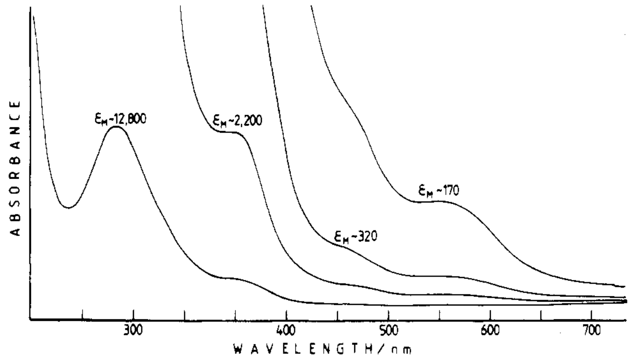

Figure 2. UV–visible spectrum of [$Pd_2(mhp)_4$] in CCl_4 solution.

The compound is isostructural with [$Rh_2(mhp)_4$];[4] indeed, almost all geometrical parameters for the two molecules are insignificantly different, except for the considerably greater metal–metal separation and angles that are obviously dependent on this separation. It is perhaps surprising that the shortening of the mean M–O and particularly M–N bonds observed across the series from [$Mo_2(mhp)_4$] to [$Rh_2(mhp)_4$] (Table III) does not continue as we move to [$Pd_2(mhp)_4$].

Spectra. The UV–visible spectrum of [$Pd_2(mhp)_4$] in CCl_4 solution has been recorded (Figure 2). ^1H and ^{13}C NMR have been measured and will be described in detail elsewhere;[13] we

---

(11) (a) Skapski, A. C.; Smart, M. L. *J. Chem. Soc., Chem. Commun.* **1970**, 658. (b) Mawby, A.; Pringle, P. E. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1989. (c) Carrondo, M. A. A. F. de C. T.; Skapski, A. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1857, 3576.

(12) Klyne, W.; Prelog, V. *Experientia* **1960**, *16*, 521.

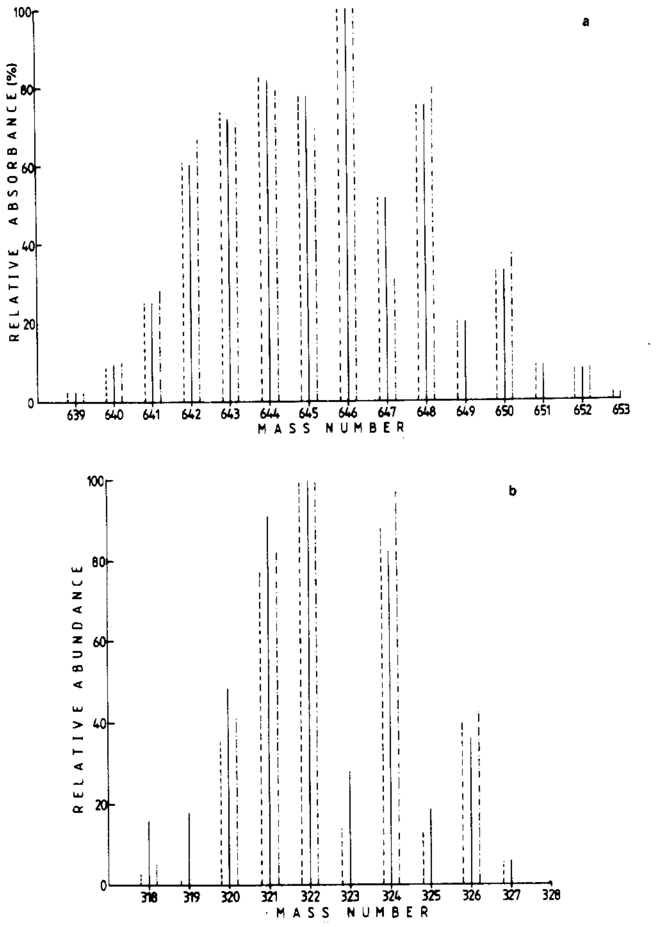

Figure 3. *m/e* intensity profiles observed in the mass spectrum of $[Pd_2(mhp)_4]$: (a) for the parent ion (—), compared with those calculated for Pd_2^+ (–·–) and $Pd_2(mhp)_4^+$ (---) on the basis of the naturally occurring isotopic composition of these elements; (b) between *m/e* 318 and 328 (—), compared with that of Pd^+(–·–) and that calculated for $Pd(mhp)_2^+$ (---).

note here, however, that these measurements indicate that $[Pd_2(mhp)_4]$ is essentially diamagnetic.

The higher *m/e* features in the mass spectrum are readily interpreted in terms of the formation of the $Pd_2(mhp)_n^+$ ($n = 4, 3, 2$) and $Pd(mhp)_n^+$ ($n = 2, 1$) ions, despite the complication that the highest *m/e* value for a $Pd_2(mhp)_n^+$ ion is the same as that for a $Pd(mhp)_{n+1}^+$ ion. The highest *m/e* feature consists of a set of adjacent peaks, spanning the *m/e* values from 639 to 652, with a profile similar to that expected for a Pd_2 moiety (Figure 3a). The slight deviation of the observed profile from that calculated for Pd_2 is attributed to the presence of the heavier isotopes of the C, H, N, and O atoms. Similar profiles are observed for the groups of adjacent peaks between *m/e* values in the ranges 532–542 and 422–437, and these are attributed to the $Pd_2(mhp)_3^+$ and $Pd_2(mhp)_2^+$ ions, respectively; the profile of the latter suggests, however, the formation of a small amount of $Pd(mhp)_3^+$. The most intense peak above *m/e* 150 occurs at 322, as part of a profile which is similar to that expected for $Pd(mhp)_2^+$ (Figure 3b), but the details suggest the presence of some (ca. 25%) Pd_2^+ and (ca. 7%) $Pd(mhp)(mhp\text{-}H)^+$. The intensity profile of the peaks with *m/e* between 210 and 220 is also more consistent with that expected for $Pd(mhp)^+$ than for Pd_2^+. The fragmentation patterns for $[M_2(mhp)_4]$ (M = Cr, Mo, W,[2,13] Ru, Rh[13]) exhibit sets of peaks corresponding to the formation of the $M_2(mhp)_n^+$ ($n = 0\text{–}4$) ions, with very much smaller quantities of $M(mhp)_n^+$ species being formed as compared with $[Pd_2(mhp)_4]$. We attribute this difference to the lack of a net formal direct metal–metal bond in $[Pd_2(mhp)_4]$ (vide infra), whereas the other $[M_2(mhp)_4]$ complexes are considered[2-4] to have metal–metal bonds with a formal bond order of 4 (Cr, Mo, W), 2 (Ru), or 1 (Rh).

Although the metal–metal stretching frequency is clearly apparent in the Raman spectra of the other $[M_2(mhp)_4]$ complexes[2,13] and the Raman spectrum of $[Pd_2(mhp)_4]$ contains peaks corresponding to vibrations of the ligands and the metal–ligand framework, we observe no feature that can be readily assigned to the ν(Pd–Pd) vibration. It is possible that, in view of the marked decrease in the metal–metal stretching frequency across the $[M_2(mhp)_4]$ series (Mo 432, Ru 281, Rh 184 cm^{-1}), the corresponding vibration for $[Pd_2(mhp)_4]$ occurs at such a low frequency that it is obscured under the envelope of the exciting line.

Pd···Pd Separation. The distance of 2.546 (1) Å is the shortest approach so far observed for two Pd(II) atoms and is, moreover, shorter than *any* determined Pd···Pd distance, with the single exception of the 2.531 (1) Å separation in the unbridged Pd(I) complex $[Pd_2(CNCH_3)_6](PF_6)_2\cdot 0.5$(acetone).[14] A slightly greater distance [2.563 (1) Å] was found in the Pd(II) complex $[Pd_2(PhNNNPh)_4]$.[15] Like mhp, the PhNNNPh ligand is one of those described by Cotton et al. as ligands promoting "exceedingly short" quadruple bonds between metal atoms of the group 6 triad (Cr, Mo, W).[2,16] Otherwise, all previously determined separations between pairs of Pd(II) atoms have been greater than 2.7 Å. With chelating or bridging sulfur ligands, distances of 2.71–2.79 Å have been observed; in such complexes, a Pd–Pd bond has generally been assumed.[17] Greater separations (2.84–2.96 Å) are found when the two Pd(II) atoms are bridged by two acetate or similar ligands.[18,19] At one time, it was argued that a "rather strong interaction" must be present in such cases,[18] but more recently, the complexes have been interpreted as having no direct Pd–Pd bond,[19] except that a trinculear system has recently been described with Pd···Pd = 2.864 (1) Å, for which some Pd–Pd bonding contribution is postulated.[19e]

The 2.546 (1) Å separation in $[Pd_2(mhp)_4]$ is ca. 0.2 Å shorter than the closest approach in palladium metal (2.751 Å),[20] a fact which would once probably have led automatically to the conclusion that a strong Pd–Pd bond exists in the complex. The existence of a bond would also be suggested by this separation in view of the estimated covalent radius of 1.31 Å for Pd(II).[21] We consider, however, that there is *no* net formal direct Pd–Pd bond in $[Pd_2(mhp)_4]$ for the following reasons:

---

(13) Garner, C. D.; Al-Samman, M. H.; Berry, M., to be submitted for publication.

(14) Goldberg, S. Z.; Eisenberg, R. *Inorg. Chem.* **1976**, *15*, 535.

(15) Corbett, M.; Hoskins, B. F.; McLeod, N. J.; O'Day, B. P. *Aust. J. Chem.* **1975**, *28*, 2377.

(16) (a) Cotton, F. A.; Koch, S.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7372. (b) Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.

(17) (a) Ciullo, G.; Piovesana, O. *Inorg. Chem.* **1980**, *19*, 2871. (b) Piovesana, O.; Bellitto, C.; Flamini, A.; Zanazzi, P. F. *Ibid.* **1979**, *18*, 2258. (c) Browall, K. W.; Bursh, T.; Interrante, L. V.; Kasper, J. S. *Ibid.* **1972**, *11*, 1800. (d) Bonamico, M.; Dessy, G.; Fares, V. *J. Chem. Soc., Dalton Trans.* **1977**, 2315.

(18) (a) Churchill, M. R.; Mason, R. *Nature (London)* **1964**, *204*, 777. (b) Zocchi, M.; Tieghi, G.; Albenati, A. *J. Chem. Soc., Dalton Trans.* **1973**, 883.

(19) (a) Wong-Ng, W.; Cheng, P. T.; Kocman, V.; Lüth, H.; Nyburg, S. C. *Inorg. Chem.* **1979**, *18*, 2620. (b) Churchill, M. R.; Wasserman, H. J.; Young, G. J. *Ibid.* **1980**, *19*, 762. (c) Kuz'mina, L. G.; Struchkov, Yu. T. *Koord. Khim.* **1979**, *5*, 1558. (d) Rüger, R.; Rittner, W.; Jones, P. G.; Isenberg, W.; Sheldrick, G. M. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 382. (e) Ukhin, L. Yu.; Dolgopolova, N. A.; Kuz'mina, L. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *210*, 263.

(20) Donohue, J. "The Structures of the Elements"; Wiley: New York, 1974; p 216.

(21) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 91–164, especially pp 153–155.

1. The complexes [$M_2(mhp)_4$] with M = Mo, Ru, and Rh have been assigned formal M–M bond orders of 4, 2, and 1, respectively.[2–4] These assignments are in accordance with photoelectron spectra,[3a,4a,22] and with the observed trend in the M–M bond length in this series (Table III). The proposed electronic configurations involve progressive filling of orbitals which are M–M antibonding: for M = Mo, $(\sigma)^2(\pi)^4(\delta)^2$; for M = Ru, $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1(\pi^*)^3$; for M = Rh, $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2$. Support for this scheme comes also from SCF–Xα–SW calculations for the corresponding bridged carboxylate complexes.[23] Continuation of this pattern would lead to the σ^* orbital being occupied for M = Pd. (We note that this orbital is the next available unoccupied one, not only in any simple MO scheme but also in the SCF–Xα–SW results for Rh(II) dimers.[23b]) The resultant $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2(\sigma^*)^2$ configuration involves no net Pd–Pd bonding, a conclusion consistent with the Raman and mass spectroscopic data described above. Unfortunately, in contrast to the other [$M_2(mhp)_4$] complexes, we have been unable to measure the photoelectron spectrum of gaseous [$Pd_2(mhp)_4$] because of the involatility of the complex. It is noteworthy that the volatility of [$M_2(mhp)_4$] is another property which decreases across the series from M = Mo to M = Pd.

2. The very marked increase in metal–metal separation on going from M = Rh to M = Pd (the greatest single step in the series from Mo to Pd) reflects the loss of direct M–M bonding interaction. We would argue that this large increase is a much more significant and reliable indicator of the degree of metal–metal bonding interaction in [$Pd_2(mhp)_4$] than are comparisons with Pd⋯Pd distances in complexes with completely different ligands.

3. An alternative is to suggest that, instead of the 16 electrons of the Pd_2^{4+} center completely filling the metal–metal bonding *and* antibonding orbitals, σ nonbonding orbitals derived from the metal $5p_z$ atomic orbitals are occupied. This hypothesis was once advanced and defended[24] to explain the short metal–metal approach in Rh(II) dimers in terms of a Rh–Rh triple bond with the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(p_{z_1})^2(p_{z_2})^2$ configuration but has been ruled out by the SCF–Xα–SW calculations for bridged rhodium(II) carboxylates[23b] and by the photoelectron spectrum of [$Rh_2(mhp)_4$][4a] and has been generally discarded.[5] The slightly different configuration $(\sigma)^2(\pi)^4(\delta)^2(p_{z_1},p_{z_2})^4(\delta^*)^2$ would not be entirely inconsistent with the photoelectron spectrum profile for [$Rh_2(mhp)_4$]; it would, however, still be at variance with the SCF–Xα–SW results[23b] and with the interpretation of a Rh–Rh single bond. Furthermore, both of these configurations would lead to the two electrons possessed by Pd_2^{4+} over Rh_2^{4+} being accommodated in the metal–metal π^* level and, hence, a paramagnetic center: [$Pd_2(mhp)_4$], in common with other Pd_2^{4+} complexes[17] is essentially diamagnetic.

Effect of the Bridging mhp Ligands on the Structure. The structure of [$Pd_2(mhp)_4$] demonstrates clearly once again the ability of a set of four bridging mhp ligands (or others of a similar type[16]) to bring a pair of metal atoms into close proximity, even when direct metal–metal bonding is of low formal order or even nonexistent. As Norman and Kolari have stated,[23b] summarizing the theoretical results of Summerville and Hoffmann for another type of bridged metal–metal bonded (or nonbonded) complex:[25] "the weaker a metal–metal bond, the more likely it is to be affected by ligand preferences." The observed geometry appears to be a combination of the electronic and steric effects of the ligands and the degree of direct metal–metal bonding. Thus, in the [$M_2(mhp)_4$] system, M–M distances ranging from 1.889 (1) (M = Cr)[2] to 2.546 (1) Å (M = Pd) can be supported. Whether the geometry of [$Pd_2(mhp)_4$] represents the limit to which the system can be stretched remains to be seen. When only one mhp bridge is present, it dominates the metal–metal separation much less, as in the Cu(I) complex [$Cu_4(mhp)_4$] [Cu⋯Cu, bridged by mhp, range between 2.656 (1) and 2.709 (1) Å][26] and in the Cr(III) complex [$Cr(mhp)_2OH]_4$ [bridged Cr–Cr = 2.829 (1) Å].[27] We note in passing that the smallest and largest metal–metal separations bridged by mhp ligands so far observed are for the same metal (Cr), albeit in different formal oxidation states, with a difference of almost 1 Å.

Acknowledgment. We thank the Verband der Chemischen Industrie for financial support (W.C.) and the British Council for the award of a Scholarship (M.H.A.-S.).

Registry No. $Pd_2(mhp)_4$, 80515-22-6; Na(mhp), 13472-90-7; palladium acetate, 3375-31-3.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom parameters (22 pages). Ordering information is given on any current masthead page.

---

(22) (a) Bursten, B. E.; Cotton, F. A.; Cowley, A. H.; Hanson, B. E.; Lattman, M.; Stanley, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 6244. (b) Garner, C. D.; Hillier, I. H.; MacDowell, A. A.; Walton, I. B.; Guest, M. F. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 485. (c) Garner, C. D.; Hillier, I. H.; Knight, M. J.; MacDowell, A. A.; Walton, I. B.; Guest, M. F. *Ibid.* **1980**, *76*, 885.

(23) (a) Norman, J. G., Jr.; Kolari, H. J.; Gray, H. B.; Trogler, W. C. *Inorg. Chem.* **1977**, *16*, 987. (b) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791. (c) Norman, J. G., Jr.; Renzoni, G. E.; Case, D. A. *Ibid.* **1979**, *101*, 5256.

(24) (a) Cotton, F. A. *Acc. Chem. Res.* **1969**, *2*, 240. (b) Caulton, J. G.; Cotton, F. A. *J. Am. Chem. Soc.* **1969**, *91*, 6517. (c) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Ibid.* **1970**, *92*, 2926. (d) Cotton, F. A.; Norman, J. G., Jr. *Ibid.* **1971**, *93*, 80. (e) Caulton, K. G.; Cotton, F. A. *Ibid.* **1971**, *93*, 1914. (f) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1664.

(25) Summerville, R. H.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(26) Berry, M.; Clegg, W.; Garner, C. D.; Hillier, I. H. *Inorg. Chem.* **1982**, *21*, 1342.

(27) Akhter, L.; Clegg, W.; Garner, C. D., to be submitted for publication.