erview of research progress in this area is available.[27]

Finally, it should be noted that it is amazing that the rate of *intra*molecular electron transfer for the mixed-valence cations in **2** and **3** is greater than $\sim 10^{10}$ s$^{-1}$ (or even $\sim 10^{7}$ s$^{-1}$) at 4.2 K. Obviously, there is no thermal energy available at this temperature. The infrared spectra for these two compounds indicate that there is a potential energy barrier for electron transfer. The inescapable conclusion is that the *intra*molecular electron transfer in **2** and **3** at temperatures in the liquid-helium temperature range proceds by an electron and nuclear tunneling mechanism. If this is the case, there is a reasonably good probability that a large fraction of the electron transferring at room temperature also proceeds by a tunneling mechanism.

**Acknowledgment.** We are grateful for support from National Institutes of Health Grant HL13652 (to D.N.H.).

**Registry No. 2**, 56030-43-4; **3**, 88005-31-6; **4**, 88005-33-8.

**Supplementary Material Available:** Observed and calculated structure factors and thermal parameters for compounds **2** and **4**; figure showing the infrared spectra for **2** at 298 and 50 K and for 1′,6′-diiodobiferrocene at 298 K (14 pages). Ordering information is given on any current masthead page.

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[27] Hendrickson, D. N.; Oh, S. M.; Dong, T.-Y.; Moore, M. F. *Comments Inorg. Chem.*, in press.

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# A Series of Edge-Sharing Bioctahedral, M–M Bonded Molecules: Non-Monotonic Bond Length Variation and Its Interpretation

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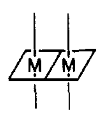
**Abstract:** Three new stoichiometrically homologous compounds, $Ta_2Cl_6(dmpm)_2$ (**1**), $Mo_2Cl_6(dppm)_2$ (**2**), and $Ru_2Cl_6(dmpm)_2$ (**3**), have been prepared and their structures determined. Crystal data are as follows. **1**: $P2_1/n$, $a = 7.263$ (3) Å, $b = 15.536$ (3) Å, $c = 10.827$ (2) Å, $\beta = 93.73$ (2)°, $V = 1219$ (1) Å$^3$, $Z = 2$. **2**: $C2/c$, $a = 23.083$ (4) Å, $b = 10.866$ (4) Å, $c = 23.254$ (5) Å, $\beta = 124.25$ (3)°, $V = 4821$ (4) Å$^3$, $Z = 4$. **3**: $I2/a$, $a = 12.479$ (5) Å, $b = 15.330$ (6) Å, $c = 13.212$ (4) Å, $\beta = 113.91$ (3)°, $V = 2310$ (1) Å$^3$, $Z = 4$. These three compounds, as well as the previously described $Nb_2Cl_6(dmpm)_2$ and $Re_2Cl_6(dppm)_2$, consist of molecules in which two octahedra share an edge via $\mu$-Cl atoms, thus forming a central, planar $Cl_2M(\mu\text{-}Cl)_2MCl_2$ unit with bridging dmpm or dppm molecules connecting pairs of adjacent axial positions above and below the central plane. The M–M distances in these five molecules are the following: Nb–Nb, 2.711 (3) Å; Ta–Ta, 2.692 (2) Å; Mo–Mo, 2.789 (1) Å; Re–Re, 2.616 (1) Å; Ru–Ru, 2.933 (1) Å. The up, down, up variation on proceeding through the $d^2$–$d^2$, $d^3$–$d^3$, $d^4$–$d^4$, $d^5$–$d^5$ series of metal atom pairs is consistent with the following electronic configurations: $\sigma^2\pi^2$, $\sigma^2\pi^2\delta^{*2}$, $\sigma^2\pi^2\delta^{*2}\delta^2$, $\sigma^2\pi^2\delta^{*2}\delta^2\pi^{*2}$. The relationship of this structurally indicated ordering of the orbitals is discussed in the light of molecular quantum mechanical calculations on model systems, and it is shown that the overall experimental and theoretical picture is internally consistent.

The juxtaposition of two metal atoms in the edge-sharing bioctahedron type of structure I affords the opportunity to study metal–metal (M–M) bonding under conditions that are, in principle, under control yet widely variable. The situation is not only inherently interesting but relevent to M–M interactions that are of importance, but less amenable to systematic study, in solid-state chemistry.



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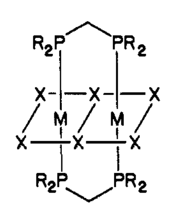

II
R=CH$_3$, C$_6$H$_5$
X=Cl

Before the *potentially* available opportunities to study systematically such complexes can actually be exploited, synthetic methods are required that allow us to make, by design, species whose behavior is expected to be interesting. In this laboratory we are developing such synthetic methods and a few reports have already appeared.[1-3] We have also conducted several studies of the M–M bonding in these complexes using structural and magnetic data as well as molecular orbital calculations.[1-4] Further synthetic work and spectroscopic studies are also in hand and will be reported shortly along with pertinent structural and magnetic data.

For a particular series of structurally homologous compounds, namely those for which the general representation is II, with R = CH$_3$ or Ph, and the metal atoms are from groups V, VI, VII, and VIII, we now have data that allow us to provide what we believe is direct evidence for the ordering of the molecular orbitals responsible for M–M bonding in this general type of interaction. We have previously reported the compounds of the type II in which M = Nb[2] and Re.[1] We now have the compounds with M = Ta, Mo, and Ru. A comparison of the first of these with the niobium compound shows that the differences (at least structural ones) caused by changing from a second transition series metal to its congener in the third transition series, or vice versa, are not critical.

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[1] Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

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[4] Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Fang, A.; Ilsley, W. H.; Kolthammer, B. W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 5078.

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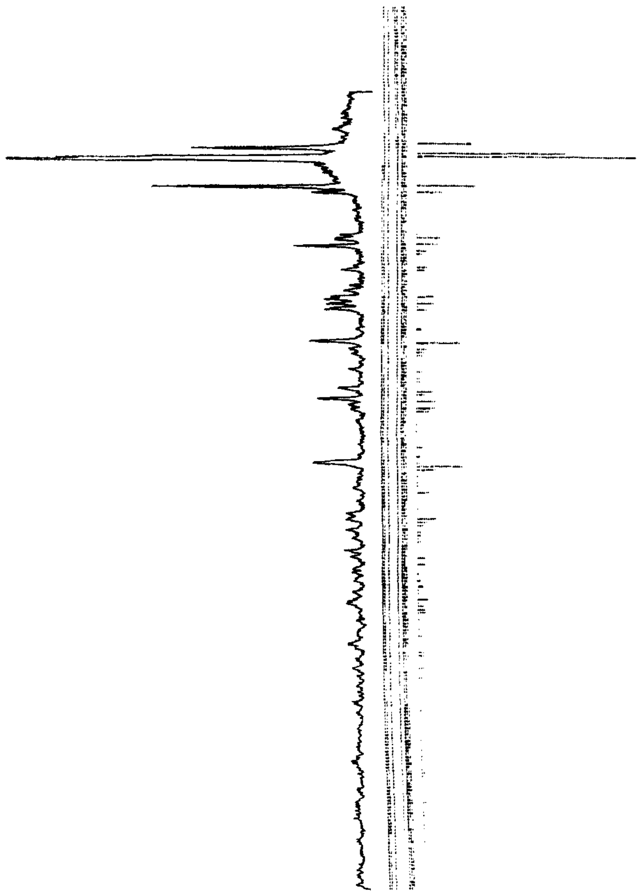

**Figure 1.** X-ray diffraction powder patterns for $Mo_2Cl_6(dppm)_2$: right, computer simulation based upon molecular structure; left, experimental.

The Mo and Ru compounds enable us to supply structural data for the uninterrupted series of $d^2$–$d^2$, $d^3$–$d^3$, $d^4$–$d^4$, and $d^5$–$d^5$ systems, where previously only representatives of the first and third types were available.

## Experimental Section

All manipulations were conducted in an atmosphere of dry argon with use of standard Schlenk techniques. THF, toluene, benzene, and hexane were dried over sodium–potassium alloy, methanol over magnesium metal, and dichloromethane over $P_2O_5$; the solvents were purged with nitrogen and distilled immediately before use. $Ta_2Cl_6(THT)_3$,[5] $K_4Mo_2Cl_8$,[6] and $Ru_2Cl(O_2CCH_3)_2(mhp)_2$,[7] where THT = tetrahydrothiophene and mhp = 6-methyl-2-hydroxypyridine, were prepared according to the literature methods. Bis(dimethylphosphino)methane (dmpm), bis(diphenylphosphino)methane (dppm), and tris(diphenylphosphino)methane were purchased from Strem Chemical Co. and used without further purification.

**Preparation of $Ta_2Cl_6(dmpm)_2$ (1).** A 10% v/v solution of dmpm (3 mL, 2.5 mmol) in toluene was added to $Ta_2Cl_6(THT)_3$ (0.84 g, 1.00 mmol) in 40 mL of benzene. After stirring for 1 day the reaction mixture was filtered, affording a red-brown solid which was washed with benzene and hexane and dried under vacuum (yield 0.5 g, 59%).

Unlike its niobium analogue, $Ta_2Cl_6(dmpm)_2$ is insoluble in common solvents. It dissolves in acetonitrile with decomposition. Single crystals were obtained by slow diffusion of the ligand (1 mL of 10% v/v solution in hexane) through 10 mL of toluene/hexane (3:2) into $Ta_2Cl_6(THT)_3$ (0.25 g in 15 mL of toluene).

**Preparation of $Mo_2Cl_6(dppm)_2$ (2).** Small, well-formed, red crystals of $Mo_2Cl_6(dppm)_2$ were obtained as a minor product in the reaction of $K_4Mo_2Cl_8$ (0.25 g, 0.40 mmol) with $HC(PPh_2)_3$ (0.22 g, 0.40 mmol) in 30 mL (1:1 v/v) of refluxing MeOH/THF. Efforts to reproduce this preparation have been unsuccessful. A reproducible bulk preparation of $Mo_2Cl_6(dppm)_2$ has been reported by Wilkinson et al.[8] Repeated attempts by us to obtain single crystals of the complex prepared in this manner have failed. However, a comparison between the powder pattern calculated from the single crystal data and that obtained by using a sample prepared by the Wilkinson method (Figure 1) confirmed that the two compounds are indeed the same.

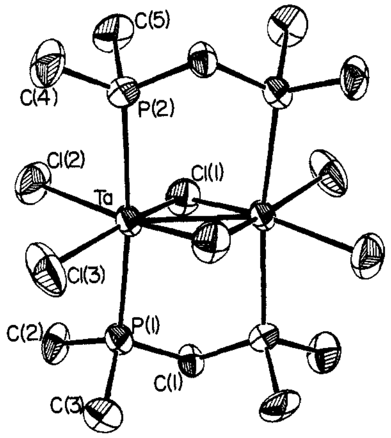

**Figure 2.** ORTEP drawing of the $Ta_2Cl_6(dmpm)_2$ molecule. The ellipsoids enclose 50% of electron density. A crystallographic inversion center relates halves of the molecule.

**Preparation of $Ru_2Cl_6(dmpm)_2$ (3).** $Ru_2Cl(O_2CCH_3)_2(mhp)_2$ (0.12 g, 0.21 mmol) in 20 mL of THF was cooled to −40 °C and $Me_3SiCl$ (0.25 mL, 3.2 mmol) and dmpm (0.06 g, 0.44 mmol) were added. The solution was then allowed to warm to room temperature and it was stirred for a further 24 h. The color of the solution changed from purple to yellow-brown. The solution was filtered and the precipitate, which was light yellow in color, was washed with THF and the washings were added to the filtrate. The resulting yellow solution was evaporated to dryness. The residue was dissolved in 10 mL of $CH_2Cl_2$. Dark brown crystals were obtained by slow evaporation of a $CH_2Cl_2$–hexane (1:1 v/v) solution. The yield was approximately 20%.

**X-ray Crystallography.** For each of the three compounds a single crystal was mounted on the tip of a glass fiber or in a glass capillary with epoxy cement. The unit cell determinations and collection of intensity data were carried out by following routine procedures used in this laboratory that have been described elsewhere.[9] Standard computational procedures[10] were used to solve and refine structures. No unusual problems were encountered. All data were corrected for Lorentz and polarization effects. An empirical absorption correction based on azimuthal scan data was also applied in each case. Pertinent crystallographic data for all three compounds are summarized in Table I.

In each case the position of the metal atom was derived from a three-dimensional Patterson map. All non-hydrogen atoms were subsequently located by an alternating series of difference Fourier syntheses and least-squares refinements. The refinements were carried out to convergence first with isotropic and then with anisotropic displacement parameters assigned to all atoms. For all three compounds the final difference Fourier map was featureless except, in the case of Ta and Ru, for some residual electron density remaining in proximity to the metal atom.

Tables of observed and calculated structure factors and anisotropic displacement parameters for the three compounds are provided as supplementary material.

## Results

Atomic positional parameters and isotropic equivalent displacement parameters for **1**, **2**, and **3** are given in Tables II, III, and IV, respectively. Table V gives selected bond distances and angles for **1**, **2**, and **3** as well as for $Nb_2Cl_6(dmpm)_2$ and $Re_2Cl_6(dppm)_2$. Complete tables of bond distances and angles are available as supplementary material.

The common feature of the structures is an edge-sharing bioctahedral configuration of the core atoms. The coordination sphere of each metal atom is comprised of four chlorine and two phosphorus atoms. Two of the chlorine atoms in each molecule

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[5] Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293.

[6] Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 351.

[7] Chakravarty, A. R.; Cotton, F. A. *Inorg. Chem.* **1985**, *24*, 2857.

[8] Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347.

[9] (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

[10] Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with the VAX-SDP software package.

**Table I.** Crystallographic Data

| | **1** | **2** | **3** |
|---|---|---|---|
| formula | $Ta_2Cl_6P_4C_{10}H_{28}$ | $Mo_2Cl_6P_4C_{50}H_{44}$ | $Ru_2Cl_6P_4C_{10}H_{28}$ |
| formula weight | 846.7 | 1173.4 | 687.1 |
| space group | $P2_1/n$ | $C2/c$ | $I2/a$ |
| systematic absences | $h0l$: $h + 1 = 2n + 1$<br>$0k0$: $k = 2n + 1$ | $hkl$: $h + k = 2n + 1$<br>$h0l$: $l = 2n + 1$ | $hkl$: $h + k + l = 2n + 1$<br>$h0l$: $h, l = 2n + 1$ |
| $a$, Å | 7.263 (3) | 23.083 (4) | 12.479 (5) |
| $b$, Å | 15.536 (3) | 10.866 (4) | 15.330 (6) |
| $c$, Å | 10.827 (2) | 23.254 (5) | 13.212 (4) |
| $\beta$, deg | 93.73 (2) | 124.25 (3) | 113.91 (3) |
| $V$, Å$^3$ | 1219 (1) | 4821 (4) | 2310 (1) |
| $Z$ | 2 | 4 | 4 |
| $d_{calcd}$, g/cm$^3$ | 2.307 | 1.617 | 1.975 |
| crystal size, mm | 0.2 × 0.1 × 0.05 | 0.2 × 0.2 × 0.1 | 0.3 × 0.2 × 0.2 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 97.14 | 10.094 | 22.535 |
| data collection instrument | Syntex P3 | CAD-4 | Syntex $P\bar{1}$ |
| radiation (monochromated in incident beam) | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| orientation reflections, no., range ($2\theta$) | 25, $13.25° < 2\theta < 34.0°$ | 25, $13° < 2\theta < 24°$ | 15, $18° < 2\theta < 25°$ |
| temp, °C | 24 | 24 | 5 |
| scan method | $\omega$–$2\theta$ | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| data col. range, $2\theta$, deg | $4.0 < 2\theta < 45.0$ | $4.0 < 2\theta < 50$ | $5 < 2\theta < 50$ |
| no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$ | 1608, 930 | 4581, 2217 | 1236, 1227 |
| no. of parameters refined | 100 | 280 | 100 |
| trans, factors, max., min. | 99.95, 48.45 | 100, 89.0 | 99.71, 70.57 |
| $R^a$ | 0.041 | 0.043 | 0.0469 |
| $R_w{}^b$ | 0.053 | 0.050 | 0.0631 |
| quality of fit indicator$^c$ | 1.017 | 1.228 | 1.511 |
| largest shift/esd, final cycle | 0.49 | 0.03 | 0.01 |
| largest peak, e/Å$^3$ | 1.400 | 0.495 | 1.1 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

**Table II.** Positional and Isotropic-Equivalent Displacement Parameters for $Ta_2Cl_6(dmpm)_2$ (**1**)[a]

| atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Ta | 0.0614 (1) | 0.06130 (5) | 0.08059 (9) | 2.98 (1) |
| Cl(1) | –0.2510 (8) | 0.0042 (4) | 0.0710 (5) | 4.4 (1) |
| Cl(2) | –0.034 (1) | 0.1239 (4) | 0.2748 (6) | 5.9 (2) |
| Cl(3) | 0.325 (1) | 0.1585 (4) | 0.0960 (8) | 6.3 (2) |
| P(1) | –0.1036 (8) | 0.1870 (4) | –0.0441 (5) | 3.1 (1) |
| P(2) | 0.2104 (8) | –0.0532 (4) | 0.2338 (5) | 3.6 (1) |
| C(1) | –0.282 (3) | 0.151 (1) | –0.160 (2) | 2.9 (4) |
| C(2) | –0.226 (3) | 0.265 (1) | 0.049 (2) | 4.3 (5) |
| C(3) | 0.050 (3) | 0.256 (2) | –0.133 (2) | 5.0 (5) |
| C(4) | 0.409 (4) | –0.018 (2) | 0.332 (2) | 5.4 (6) |
| C(5) | 0.056 (3) | –0.091 (2) | 0.348 (2) | 4.8 (6) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

bridge the dimetal unit while the remaining four chlorine atoms are terminally bound to the metal atoms. In each case the chlorine atoms and the dimetal unit form an approximately planar array. The M–P vectors are perpendicular to this plane. In all three compounds the molecule resides on a crystallographic center of inversion.

**(a) $Ta_2Cl_6(dmpm)_2$ (1).** The compound is isomorphous with the niobium analogue previously reported.[2] The molecule is shown in Figure 2. The observed Ta–Ta distance of 2.692 (2) Å is consistent with the predicted M–M double bond. The Ta–Cl distances are in the range 2.433 (6)–2.457 (6) Å with no statistically significant differences noted between the bridging and terminal Ta–Cl distances. The Ta–P distances are essentially identical at 2.620 (6) and 2.618 (7) Å.

A comparison of selected bond distances and angles in the $Ta_2Cl_6(dmpm)_2$ and $Nb_2Cl_6(dmpm)_2$ complexes can be made by referring to Table V. As has been observed in other niobium/tantalum homologues,[11] bond distances and angles are nearly the same in these two compounds. This is an expression of the well-known lanthanide contraction. Although a few differences are statistically significant, we feel that they are too small to be considered chemically or physically significant. A comparison of this type is important as it establishes the insensitivity of the structure to changes in going from a second-row transition metal to the third-row analogue.

**Table III.** Positional and Isotropic-Equivalent Displacement Parameters for $Mo_2Cl_6(dppm)_2$ (**2**)[a]

| atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Mo | 0.56576 (3) | 0.05188 (7) | 0.52692 (3) | 2.46 (1) |
| Cl(1) | 0.45525 (8) | 0.1459 (2) | 0.44201 (8) | 2.98 (4) |
| Cl(2) | 0.61207 (9) | 0.2467 (2) | 0.5225 (1) | 4.11 (5) |
| Cl(3) | 0.68615 (9) | –0.0090 (2) | 0.5994 (1) | 4.16 (5) |
| P(1) | 0.57394 (9) | 0.1366 (2) | 0.63512 (9) | 2.79 (5) |
| P(2) | 0.56958 (8) | –0.0239 (2) | 0.42363 (8) | 2.89 (5) |
| C(1) | 0.5195 (3) | 0.0432 (7) | 0.6543 (3) | 3.0 (2) |
| C(11) | 0.6150 (3) | –0.1652 (8) | 0.4297 (3) | 3.8 (2) |
| C(12) | 0.6366 (4) | –0.2485 (8) | 0.4824 (4) | 4.2 (2) |
| C(13) | 0.6677 (4) | –0.3614 (9) | 0.4829 (4) | 5.5 (3) |
| C(14) | 0.6813 (4) | –0.3817 (9) | 0.4325 (4) | 6.2 (3) |
| C(15) | 0.6652 (5) | –0.294 (1) | 0.3831 (5) | 8.1 (3) |
| C(16) | 0.6293 (4) | –0.183 (1) | 0.3782 (4) | 7.2 (3) |
| C(21) | 0.6074 (3) | 0.0885 (7) | 0.3969 (3) | 3.2 (2) |
| C(22) | 0.5681 (4) | 0.1652 (9) | 0.3402 (4) | 5.4 (3) |
| C(23) | 0.5992 (5) | 0.252 (1) | 0.3207 (5) | 7.3 (3) |
| C(24) | 0.6711 (4) | 0.2639 (9) | 0.3618 (4) | 5.7 (3) |
| C(25) | 0.7101 (4) | 0.191 (1) | 0.4163 (5) | 7.6 (3) |
| C(26) | 0.6795 (4) | 0.104 (1) | 0.4361 (5) | 7.1 (3) |
| C(31) | 0.6609 (3) | 0.1243 (8) | 0.7140 (3) | 3.6 (2) |
| C(32) | 0.6815 (4) | 0.0263 (8) | 0.7596 (4) | 4.4 (2) |
| C(33) | 0.7516 (4) | 0.019 (1) | 0.8187 (5) | 6.1 (3) |
| C(34) | 0.8010 (4) | 0.109 (1) | 0.8330 (4) | 6.3 (3) |
| C(35) | 0.7782 (5) | 0.203 (1) | 0.7869 (6) | 9.4 (4) |
| C(36) | 0.7095 (5) | 0.217 (1) | 0.7270 (5) | 7.5 (3) |
| C(41) | 0.5483 (4) | 0.2962 (8) | 0.6362 (4) | 4.1 (2) |
| C(42) | 0.5193 (4) | 0.3682 (8) | 0.5795 (4) | 4.4 (2) |
| C(43) | 0.5013 (4) | 0.4907 (9) | 0.5822 (4) | 5.6 (3) |
| C(44) | 0.5150 (6) | 0.538 (1) | 0.6417 (5) | 8.7 (4) |
| C(45) | 0.5418 (7) | 0.464 (1) | 0.6992 (5) | 13.2 (5) |
| C(46) | 0.5600 (6) | 0.340 (1) | 0.6983 (5) | 10.3 (4) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**(b) $Mo_2Cl_6(dppm)_2$ (2).** The most striking feature of the structure, Figure 3, is a long Mo–Mo distance of 2.789 (1) Å. This is appreciably longer than those found[3] previously in some

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(11) (a) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Polyhedron* **1985**, *4*, 1103. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. R. *Inorg. Chem.* **1984**, *23*, 4046.

**Table IV.** Positional and Isotropic-Equivalent Displacement Parameters for $Ru_2Cl_6(dmpm)_2$ (3)[a]

| atom | *x* | *y* | *z* | *B* (Å$^2$) |
|---|---|---|---|---|
| Ru(1) | 0.15677 (6) | 0.18570 (5) | 0.23094 (5) | 2.11 (1) |
| Cl(1) | 0.2965 (2) | 0.2395 (2) | 0.3996 (2) | 2.72 (5) |
| Cl(2) | 0.0035 (2) | 0.1225 (2) | 0.0786 (2) | 4.09 (6) |
| Cl(3) | 0.0921 (2) | 0.0975 (2) | 0.3411 (2) | 3.78 (5) |
| P(1) | 0.0202 (2) | 0.2965 (2) | 0.2218 (2) | 2.97 (5) |
| P(2) | 0.2848 (2) | 0.0696 (2) | 0.2351 (2) | 2.58 (5) |
| C(1) | −0.0831 (8) | 0.2710 (9) | 0.285 (1) | 5.1 (3) |
| C(2) | −0.075 (1) | 0.3339 (9) | 0.0808 (9) | 5.3 (3) |
| C(3) | 0.0916 (7) | 0.3959 (6) | 0.2965 (7) | 2.9 (2) |
| C(4) | 0.220 (1) | −0.0169 (7) | 0.1331 (8) | 4.1 (2) |
| C(5) | 0.3471 (9) | 0.0101 (7) | 0.3669 (8) | 4.3 (3) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

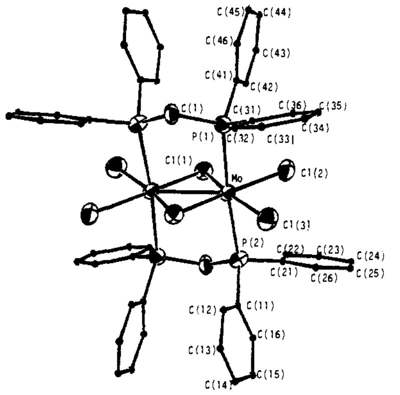

**Figure 3.** ORTEP drawing of the $Mo_2Cl_6(dppm)_2$ molecule. The atoms are represented by elliposids drawn at the 50% probability level except the phenyl carbon atoms which were assigned arbitrarily small size for the sake of clarity. A crystallographic inversion center relates halves of the molecule.

other dimolybdenum(III) compounds. Otherwise, the structure is quite similar to those of other $M_2Cl_6(dppm)_2$ compounds. Again, the bridging, 2.403 [2] Å, and terminal, 2.397 [2] Å, M–Cl distances are not significantly different.

**(c) $Ru_2Cl_6(dmpm)_2$ (3).** This molecule, Figure 4, has the very long metal–metal distance of 2.933 (1) Å but is otherwise quite similar to the others. Again, there is scarcely any difference between the mean M–Cl distances for bridging and terminal chlorine atoms, which are 2.344 [14] and 2.353 [2] Å, respectively.

## Discussion

Metal–metal interactions across the shared edge of the bioctahedral structure, represented in the most general form by I, have been discussed from a theoretical point of view several times before.[3,4,12] At the crudest level of approximation, these interactions may be viewed as overlaps between metal d orbitals; on this (inadequate) basis, one would straightforwardly anticipate a set of two-center molecular orbitals with the following order of increasing energy:

$$\sigma \ll \pi < \delta < \delta^* < \pi^* \ll \sigma^*$$

If this simple picture were reliable, one would straightforwardly predict that for species of the $d^n$–$d^n$ types with $n = 2, 3, 4$, and 5, the M–M bond orders would be $2(\sigma^2\pi^2)$, $3(\sigma^2\pi^2\delta^2)$, $2(\sigma^2\pi^2\delta^2\delta^{*2})$, and $1(\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2})$. Metal–metal distances, $D(n,n)$ as a function of $n$, would thus be expected to vary in the following sequence:

$$D(2,2) > D(3,3) < D(4,4) \ll D(5,5)$$

As first pointed out by Hoffmann et al.,[12] such a simple picture, and hence the predictions made from it, may well be incorrect because of interactions between ligand orbitals and the above-mentioned pure metal orbitals. These authors discussed all such interactions, and for a comprehensive discussion their paper should be consulted. As far as a reliable qualitative ordering of the six M–M interactions is concerned, within the limited set of compounds we are considering here, only one of these metal–ligand interactions is of crucial importance, because it affects the $\delta/\delta^*$ separation, which tends to be small in any event.

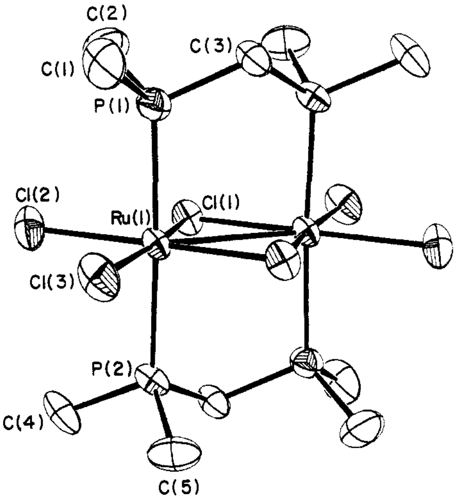

**Figure 4.** ORTEP drawing of the $Ru_2Cl_6(dmpm)_2$ molecule. The ellipsoids enclose 50% of electron density. A crystallographic inversion center relates halves of the molecule.

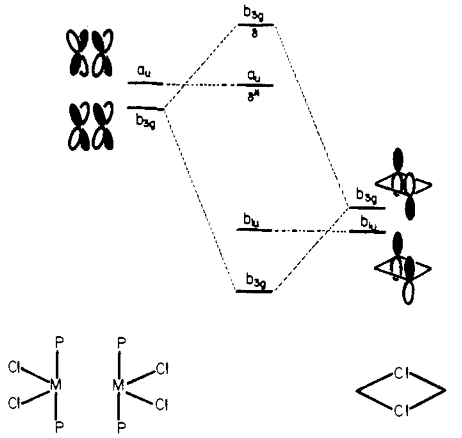

**Figure 5.** Interaction diagram for metal δ orbitals with π orbitals on bridging chlorine atoms.

As shown in Figure 5, there is a combination of π orbitals on the μ-Cl ligands that has the same symmetry ($b_{3g}$) as the bonding combination of the metal δ orbitals, whereas there is no such combination that can match the symmetry of the antibonding δ* orbital ($a_u$). Thus, if the energy of the ligand π orbitals lies below that of the metal δ orbitals, the energy of the δ orbital will be raised, relative to that of the δ* orbital, and may even be raised above that of the δ* orbital, so that the six molecular orbitals of prime importance with regard to M–M bonding would have the following order of increasing energy:

$$\sigma \ll \pi < \delta^* < \delta < \pi^* \ll \sigma^*$$

In that case, M–M distances might be expected to vary in the following order, which is qualitatively different from that deduced previously:

$$D(2,2) < D(3,3) > D(4,4) \ll D(5,5)$$

Previous quantitative theoretical treatments of this type of molecule[3,4] have shown that the relative energies of the δ and δ* orbitals will certainly depend on the particular compound considered (i.e., on the M–M separation and the identity of the ligands, especially the two μ-X ligands). They have also suggested that in many cases the separation of the δ and δ* orbitals may

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(12) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.*, **1980**, *102*, 4555.

**Table V.** Selected Bond Distances (Å) and Bond Angles (deg) for the $M_2Cl_6(LL)_2$ (LL = dppm or dmpm) Molecules

| | $Nb_2Cl_6(dmpm)_2$ | $Ta_2Cl_6(dmpm)_2$ | $Mo_2Cl_6(dppm)_2$ | $Re_2Cl_6(dppm)_2$ | $Ru_2Cl_6(dmpm)_2$ |
|---|---|---|---|---|---|
| M-M | 2.711 (3) | 2.692 (2) | 2.789 (1) | 2.616 (1) | 2.933 (1) |
| M-Cl(1) | 2.444 (4) | 2.433 (6) | 2.404 (2) | 2.389 (2) | 2.353 (2) |
| M-Cl(1)′ | 2.433 (5) | 2.433 (6) | 2.402 (2) | 2.392 (2) | 2.334 (2) |
| M-Cl(2) | 2.446 (5) | 2.457 (6) | 2.400 (2) | 2.391 (2) | 2.351 (2) |
| M-Cl(3) | 2.442 (5) | 2.435 (7) | 2.393 (2) | 2.385 (2) | 2.355 (2) |
| M-P(1) | 2.641 (5) | 2.620 (6) | 2.585 (2) | 2.478 (2) | 2.374 (2) |
| M-P(2) | 2.619 (5) | 2.618 (7) | 2.587 (2) | 2.471 (2) | 2.377 (2) |
| P(1)-C(1) | 1.86 (2) | 1.83 (2) | 1.855 (7) | 1.845 (8) | 1.838 (8) |
| P(2)-C(1) | 1.84 (2) | 1.81 (2) | 1.833 (7) | 1.839 (8) | 1.832 (8) |
| M′-M-Cl(1) | 56.0 (1) | 56.4 (2) | 54.51 (5) | 56.89 (5) | 50.96 (5) |
| -Cl(1)′ | 56.4 (1) | 56.4 (2) | 54.57 (5) | 56.78 (5) | 51.56 (5) |
| -Cl(2) | 136.8 (2) | 137.2 (2) | 137.40 (6) | 138.41 (6) | 137.52 (7) |
| -Cl(3) | 134.8 (2) | 135.1 (2) | 138.06 (7) | 139.12 (7) | 136.57 (7) |
| -P(1) | 94.2 (1) | 94.1 (1) | 92.62 (5) | 94.54 (5) | 91.78 (6) |
| -P(2) | 91.8 (1) | 92.0 (2) | 92.97 (5) | 94.47 (5) | 91.18 (6) |
| Cl(1)-M-Cl(1)′ | 112.4 (1) | 112.7 (2) | 109.08 (5) | 113.67 (5) | 102.52 (6) |
| -Cl(2) | 82.5 (2) | 82.3 (2) | 83.23 (7) | 81.83 (7) | 85.99 (8) |
| -Cl(3) | 161.3 (2) | 162.9 (2) | 166.02 (7) | 163.04 (7) | 171.68 (8) |
| -P(1) | 81.1 (1) | 81.7 (2) | 86.99 (6) | 88.23 (7) | 89.99 (8) |
| -P(2) | 96.9 (2) | 97.2 (2) | 96.34 (7) | 96.74 (7) | 91.06 (7) |
| Cl(1)′-M-Cl(2) | 160.6 (2) | 161.2 (2) | 166.51 (7) | 163.77 (8) | 171.35 (8) |
| -Cl(3) | 80.4 (2) | 80.2 (2) | 83.81 (7) | 82.62 (8) | 85.64 (8) |
| -P(1) | 103.8 (2) | 103.0 (2) | 96.47 (7) | 96.72 (7) | 92.22 (7) |
| -P(2) | 85.1 (2) | 85.1 (2) | 86.71 (6) | 88.23 (7) | 90.42 (7) |
| Cl(2)-M-Cl(3) | 88.4 (2) | 87.7 (3) | 84.55 (8) | 82.46 (8) | 85.90 (8) |
| -P(1) | 90.4 (2) | 90.0 (2) | 86.43 (7) | 88.29 (8) | 86.17 (8) |
| -P(2) | 80.7 (2) | 81.7 (2) | 89.52 (7) | 84.96 (8) | 90.98 (8) |
| Cl(3)-M-P(1) | 82.7 (2) | 84.5 (2) | 89.64 (7) | 84.93 (8) | 91.34 (8) |
| -P(2) | 97.7 (2) | 95.0 (3) | 86.14 (7) | 88.26 (8) | 87.20 (8) |
| P(1)-M-P(2) | 171.1 (2) | 171.7 (2) | 174.41 (7) | 170.99 (7) | 176.88 (8) |
| M-Cl(1)-M′ | 67.6 (1) | 67.3 (2) | 70.92 (5) | 66.33 (5) | 77.48 (6) |
| M-P(1)-C(1) | 113.1 (5) | 114.0 (7) | 110.5 (2) | 109.7 (3) | 112.6 (3) |
| M-P(2)-C(1) | 113.7 (6) | 114.3 (7) | 110.4 (2) | 110.0 (3) | 113.5 (3) |
| P(1)-C(1)-P(2) | 108.5 (8) | 110 (1) | 111.1 (4) | 109.3 (4) | 112.7 (4) |

be so small that no calculation that is presently feasible can be trusted to predict the ordering with certainty. In a previous study[3] of the $d^3$–$d^3$ systems $(LL)MoCl_2(\mu\text{-}SR)_2MoCl_2(LL)$, where LL = $RSCH_2CH_2SR$ or $R_2PCH_2CH_2PR_2$, magnetic measurements showed that the $\delta$–$\delta^*$ separation was indeed only of the order of $kT$ at room temperature (i.e., a few hundred wavenumbers), but these magnetic data could not show whether the order was $\delta < \delta^*$ or $\delta > \delta^*$.

As we have pointed out above, this is a question that can, in principle, be answered by experimentally determining how the M-M distance, $D(n,n)$, varies as a function of $n$ in a series of isostructural compounds. If we have $\delta < \delta^*$ the behavior of $D(n,n)$ for $n$ = 2 to 5 should be "down, up, up", whereas for $\delta > \delta^*$ the variation should be "up, down, up". As a result of the work reported here we now have evidence for the latter pattern as shown in Figure 6.

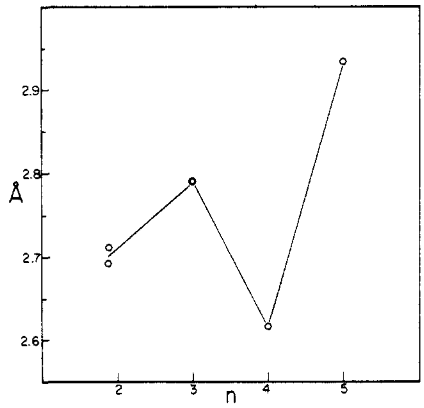

**Figure 6.** The plot of metal–metal distance vs. the number of d electrons contributed by each metal, $n$, for the $M_2Cl_6(LL)_2$ compounds.

In addition to the significance of the qualitative pattern of the data in Figure 6, we may (at the risk, perhaps, of indulging in over-interpretation) also comment on two of the quantitative aspects. The $n$ = 4 complex has the same metal–metal bond order (single bond) as the $n$ = 2 complexes, yet the M-M distance is significantly shorter (2.62 Å vs. 2.70 Å (average)). This is caused by steric effects. All distances involving the metals are shorter in the $n$ = 4 case, consistent with the trend of decreasing ionic radii with increasing atomic number. Using the differences in $M\text{–}Cl_t$ distances as a measure of the difference in ionic radii, we would expect the shortening of the M-M bond (ca. 0.08 Å) to be about twice that of the $M\text{–}Cl_t$ bond (ca. 0.05 Å). This is indeed the case. Additionally, the relatively large increase in M-M distance on going from $n$ = 4 to 5 can surely be attributed to the fact that the $\pi^*$ orbital is much more antibonding that the $\delta^*$ orbital.

Obviously, there are two additional members of this series of compounds, viz., the case of $n$ = 1, where only a M-M $\sigma$ bond would occur, and the case of $n$ = 6, where the $\sigma^*$ orbital would be doubly occupied and the net M-M bond order would be reduced to zero. Of course, there are some $d^1$–$d^1$ and $d^6$–$d^6$ cases known, but they cannot be used in connection with the present study because they are not chemically homologous and they do not contain trivalent metal atoms.[13] The appropriate compounds, namely, $M_2Cl_6(dppm)_2$ molecules with M = Zr or Hf ($d^1$–$d^1$) and M = Rh or Ir ($d^6$–$d^6$), are all, at present, unknown. If they can be made and their structures established, we would venture the predictions, by extrapolation from Figure 6, that in the $d^1$–$d^1$ cases the M-M distance would be around 2.95 Å and in the $d^6$–$d^6$ cases

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(13) The profound affect of changing metal atom charge, even though the number of electrons remains the same, has been amply documented.[14] It is also well established that changes in the ligands, even when the metal atoms are kept the same, can markedly affect the M-M distance.[1] Thus, the only satisfactory way to determine the influence of the electronic configurations on the strength of the M-M bond is that which we have employed here. This entails the comparison of compounds containing the same ligands (or very similar ones, such as dmpm and dppm) and metal atoms in the same formal oxidation state.

they would be about 3.70 Å. Here, then, is an interesting and worthwhile synthetic challenge, whereby predictions made before the fact could be tested experimentally.

**Acknowledgment.** We thank the National Science Foundation for financial support.

**Registry No. 1**, 99797-57-6; **2**, 99808-51-2; **3**, 99797-58-7; $Ta_2Cl_6$(THT)$_3$, 66758-43-8; $K_4Mo_2Cl_6$, 25448-39-9; $Ru_2Cl(O_2CCH_3)_2$(mhp), 96825-40-0; HC$(PPh_2)_3$, 28926-65-0.

**Supplementary Material Available:** Full list of bond distances and angles, tables of anisotropic displacement parameters, and listing of observed and calculated structure factors for all three compounds (41 pages). Ordering information is given on any current masthead page.

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# Structural Correlations between the Tetraisopropylphosphonium Cation and Triisopropylphosphonium Isopropylide: An X-ray Diffraction Study[†]

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**Abstract:** Tetraisopropylphosphonium iodide (**1a**) and tetraphenylborate (**1b**) were prepared in a three-step synthesis from triisopropylphosphine. Single-crystal X-ray diffraction data were collected for both salts, but only the structure of **1b** could be solved. Crystals of **1b** are orthorhombic, space group $P2_12_12$, $a = 9.415$ (1) Å, $b = 15.199$ (2) Å, $c = 11.157$ (1) Å, $V = 1596.6$ Å$^3$, $Z = 2$, and $R_w = 0.063$ for 181 parameters and 2519 observed reflections ($F_o \geqslant 4.0\sigma(F_o)$). Both the tetraisopropylphosphonium cations and the tetraphenylborate anions lie on a crystallographic twofold axis, but the actual cation symmetry approaches point group $S_4$ ($\bar{4}$) symmetry, in agreement with theoretical predictions for tetrahedral species with four ligands of $C_s(m)$ symmetry. The isopropyl groups are rotated pairwise in opposite directions (C1,C1*/C2,C2*) by 110° (av) away from the fully staggered $D_{2d}(\bar{4}2m)$ conformation. The triisopropylphosphonium isopropylide (**2**), obtained from **1a** and $NaNH_2$ in liquid ammonia, crystallizes in triclinic needles, space group $P\bar{1}$, $a = 7.587$ (2) Å, $b = 8.030$ (2) Å, $c = 11.521$ (2) Å, $\alpha = 86.17$ (2)°, $\beta = 106.08$ (2)°, $\gamma = 104.66$ (2)°, $V = 652.5$ Å$^3$, $Z = 2$, and $R_w = 0.055$ for 154 parameters and 1654 observables. The individual ylide molecules have approximate $C_s(m)$ symmetry, but the phosphorus–carbon skeleton is clearly reminiscent of a parent $D_{2d}(\bar{4}2m)$ symmetry. The relatively long ylidic bond P–C1 is complemented by the short aliphatic P–C4 bond. Distortions also arise from a large C—P═C angle (C3—P—C1). The ylidic carbon atom C1 exhibits a pyramidal configuration. Through these effects, the steric interactions are reduced with retention of the basic symmetry. No intra- or intermolecular hydrogen bonds between carbon atoms are present, which could account for the facile proton transfer observed in solution.

Predictions of ground-state conformations of simple molecules must often remain unconfirmed by experimental evidence, even for a number of seemingly trivial cases. It was only recently, e.g., that species with four *tert*-butyl groups attached to a central atom could be synthesized and structurally characterized, resulting in a clear corroboration of the $T(23)$ symmetry proposed on the basis of force-field calculations.[1] In the tetra-*tert*-butylphosphonium cation, the possible extreme point group symmetry $T_d(\bar{4}3m)$ is reduced to $T(23)$ through a conrotatory distortion of all *four threefold rotors* ($CC_3$) by 14° and a concomitant rotation of all $CH_3$ rotors by 11°. Both values are in excellent agreement with the theoretical figures.[2]

The problem of *four twofold rotors* of $C_{2v}(mm)$ symmetry at a common central atom could be solved experimentally with much less difficulty, since a whole series of tetraphenylated molecules with physical properties more amenable to the structural determination was readily available.[3] And yet a consistent picture was only emerging after careful consideration of the special features of individual systems.[4] (See also below, where the structure of the $BPh_4^-$ anion is reconsidered.)

Even less straightforward, both in theory and experiment, has been the approach to the conformation of four ligands with *mirror symmetry* (point group $C_s/m$) at a common central atom. A case in question was the crystal structure of tetracyclohexylsilane,[5] which was brought in line with the existing body of information only after detailed scrutiny of the molecular parameters.[6] Another example from the current literature is the evaluation of crystal structures of compounds of the pentaerythrole type, $C(CH_2X)_4$. The functionalities associated with X = OH, $NH_2$, etc., can impose strong intermolecular interactions in these materials, however, originating from dipole moments, hydrogen bonds, or other specific contacts with corresponding structural consequences.[7]

As a continuation of the work on $(t\text{-Bu})_4P^+$, it was therefore decided to investigate the structure of a phosphonium cation bearing four *isopropyl* groups, the simplest carbon skeleton of $C_s(m)$ symmetry. This cation $[(CH_3)_2CH]_4P^+$, **1**, was recently

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[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

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