Communications

Lone-Pair-Lone-Pair Repulsion in the Halogen Molecules

Sir:

A simple molecular orbital treatment of the diatomic homonuclear halogens, in which the overlap integral is ignored when estimating the resonance integral, leads to the conclusion that the antibonding π^* level is raised above the atomic p level as much as the bonding π level is lowered below that level. This result is equivalent to having the eight π electrons of an X_2 molecule occupy four strictly nonbonding lone-pair orbitals. However, if the overlap integral is included in the treatment, it is found that the antibonding level is raised more than the bonding level is lowered,[1] resulting in a net π-antibonding interaction, or "lone-pair-lone-pair repulsion". One would expect the $p\pi$-$p\pi$ overlap integral of F_2 to be much greater than that of the other halogen molecules, and the corresponding high lone-pair-lone-pair repulsion has been proposed as an explanation of the extraordinary weakness of the F-F bond.[2-5] However, other plausible explanations of the weak F-F bond have been proposed[2,6-11] and no direct experimental proof of extraordinarily high lone-pair-lone-pair repulsion in F_2 has been demonstrated.

It has recently been shown that, by combining the results of valence and core photoelectron spectroscopy, the energies of molecular orbitals relative to the energies of strictly nonbonding atomic orbitals (corrected for the effects of potential and relaxation energy) can be determined.[12,13] We here report the results of applying this method to the data for both the homonuclear and the heteronuclear diatomic halogens.

By using both core and valence ionization potentials, it is possible to evaluate the ionization potentials that atomic orbitals (in molecules) would have if they were nonbonding. These localized orbital ionization potentials (LOIPs), the π and π^* ionization potentials, and the differences, Δ, between the average of the π and π^* ionization potentials and the LOIP values are presented in Table I.[14-16] A Δ value of zero corresponds to no lone-pair-lone-pair repulsion; a negative value indicates lone-pair-lone-pair repulsion. In the case of the homonuclear molecules, the only Δ value that is definitely negative (with the ±0.1-eV uncertainty of the method taken into account) is that of F_2. We believe that these data constitute the first unequivocal evidence for lone-pair repulsion in F_2. Other effects may contribute to the weakness of the F-F bond, but clearly lone-pair repulsion is very significant.

In the case of the heteronuclear molecules, the Δ values were calculated by using the average LOIPs for the two atoms. For ClF, Δ is slightly negative, suggesting weak lone-pair repulsion, and for ICl, there is no lone-pair repulsion. The positive Δ value for IBr has no obvious rationale and suggests experimental error; it would be worthwhile to reinvestigate the spectra of IBr.

Table I. LOIPs, Ionization Potentials, and Δ Values for Halogens and Interhalogens (eV)

molecule	LOIP[a]	IP(π)[b]	IP(π^*)[b]	Δ
F_2	17.94	18.80	15.84	−0.62
Cl_2	13.12	14.42	11.61	−0.10
Br_2	11.85	12.85	10.68	−0.08
I_2	10.35	11.21	9.51	0.01
ClF	15.09[c]	17.06[d]	12.79[d]	−0.16
ICl	11.56[c]	12.88	10.24	0.0
IBr	10.59[c]	12.09	9.99	0.45

[a] See ref 14 and 15. [b] Except as noted, from: Potts, A. W.; Price, W. C. *Trans. Faraday Soc.* 1971, *67*, 1242. [c] Average LOIP for the two halogen atoms of the interhalogen. [d] DeKock, R. L.; Higginson, B. R.; Lloyd, D. R.; Breeze, A.; Cruickshank, D. W. J.; Armstrong, D. R. *Mol. Phys.* 1972, *24*, 1059.

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Registry No. F_2, 7782-41-4; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; ClF, 7790-89-8; ICl, 7790-99-0; IBr, 7789-33-5.

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(1) See, for example: Ballhausen, C. J.; Gray, H. B. "Molecular Orbital Theory"; W. A. Benjamin: New York, 1964; pp 20-21.

(2) Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, *70*, 2140.

(3) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 4493.

(4) Coulson, C. A. "Valence"; Oxford University Press, London, 1952; pp 178-179.

(5) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 142-144.

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(9) Brown, M. G. *Trans. Faraday Soc.* **1959**, *55*, 9.

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(12) Jolly, W. L. *J. Phys. Chem.* **1981**, *85*, 3792.

(13) Jolly, W. L.; Eyermann, C. J. *J. Phys. Chem.* **1982**, *86*, 4834.

(14) LOIPs were calculated from the relation LOIP = IP(ref) + 0.8[E_B − E_B(ref)], where ref refers to reference molecules (the hydrogen halides) in which the $p\pi$ halogen lone pairs are completely nonbonding. The required E_B values were taken from the compilation of Bakke et al.[15] The valence ionization potentials of the hydrogen halides were taken from ref 16.

(15) Bakke, A. A.; Chen, H. W.; Jolly, W. L. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 333.

(16) Frost, D. C.; McDowell, C. A.; Vroom, D. A. *J. Chem. Phys.* **1967**, *46*, 4255.

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Syntheses and Structures of a One-Dimensional Palladium(II)-Palladium(IV) Mixed-Valence Complex and Its Parent Palladium(II) and Palladium(IV) Complexes with 1,4,8,11-Tetraazacyclotetradecane

Sir:

One-dimensional M(II)-M(IV) mixed-valence complexes of Pt, Pd, and Ni have attracted much interest from the viewpoint of the chemistry and physics of low-dimensional compounds.[1] Crystal structures of some of these complexes, mostly of Pt, have been reported.[2] In this study, we have

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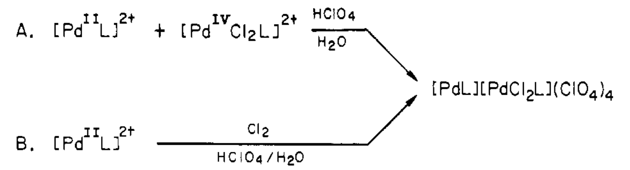
(1) (a) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1. (b) Yamashita, M.; Nonaka, Y.; Kida, S.; Hamaue, Y.; Aoki, R. *Inorg. Chim. Acta* **1981**, *52*, 43. (c) Aoki, R.; Hamaue, Y.; Kida, S.; Yamashita, M.; Takemura, T.; Furuta, Y.; Kawamori, A. *Mol. Cryst. Liq. Cryst.* **1982**, *81*, 301. (d) Clark, R. J. H.; Kurmoo, M.; Galas, A. M. R.; Hursthouse, M. B. *Inorg. Chem.* **1981**, *20*, 4206 and references cited therein.

0020-1669/83/1322-1566$01.50/0

Scheme I



successfully prepared a new Pd(II)–Pd(IV) mixed-valence complex with the titled tetraaza macrocyclic ligand (L), $[Pd^{II}L][Pd^{IV}Cl_2L](ClO_4)_4$ (**1**), along with discrete Pd(II) and Pd(IV) complexes having the same in-plane ligand L, $[Pd^{II}L](ClO_4)_2$ (**2**) and $[Pd^{IV}Cl_2L](NO_3)_2\cdot H_2O\cdot HNO_3$ (**3**). Generally, compounds of Pd(IV) are fairly unstable, and very few structural studies have been reported. We used the ligand L as the in-plane ligand, because earlier studies[3] suggest that a fully saturated tetraazacycloalkane produces, in some cases, stable compounds of metal ions in high oxidation states when the effective hole size of the macrocyclic ligand is slightly smaller than the metal ion.

The Pd(II) complex **2** was prepared by the reaction of palladium(II) acetate with L in H_2O and subsequent addition of $HClO_4$. The Pd(IV) complex **3** was obtained by nitric acid oxidation of a chloride salt of **2** and recrystallization from dilute aqueous HNO_3. Two routes for the synthesis of the mixed-valence complex **1** are shown in Scheme I.[4,5] The mixed-valence complex **1** forms lustrous green needles, exhibiting remarkable dichroism, i.e., strongly colored for light polarized along the needle axis and only slightly colored for light polarized perpendicular to the needle axis.

Molecular and crystal structures of **1**–**3** have been determined by X-ray diffractometry.[6]

In the crystal structure of **1**, the four-coordinate Pd(II) and six-coordinate Pd(IV) units in **1**, both of which have a 2+ charge, are stacked alternately in the direction of the *c* axis, constructing linear chains of ···Cl–Pd^{IV}–Cl···Pd^{II}··· segments (Figure 1). The 14-membered macrocyclic ligands in the Pd(II) and Pd(IV) units in **1** adopt the same, most stable ring conformation,[7] but successive macrocycles are rotated by approximately 180° about the chain axis. Neighboring Pd(II) and Pd(IV) units are linked by two hydrogen bonds, NH···O···HN (2.956 (9), 3.046 (9) Å). It has been pointed out that such anion-bridged hydrogen bonds play an important role on the formation of M(II)–M(IV) mixed-valence complexes of this type.[2] Regarding the type of the hydrogen bonds, the compound **1** appears to be a unique example.[8] As has been observed previously for most M(II)–M(IV) mixed-valence compounds of this type,[2] the bridging Cl atoms are disordered. The Cl atom was located at two positions equidistant from two Pd atoms with populations of 0.5.[9] The shorter Pd–Cl distance (2.319 (3) Å) corresponds to the distance between the Pd^{IV} and Cl atoms, whereas the longer one (3.219 (3) Å) is for the separation of the Pd^{II} and Cl atoms. No positional disorder was found for the organic ligand moieties.[10] Thus the molecular dimensions within the [PdL] moiety of the Pd(II) and Pd(IV) units are crystallographically the same. This observation may be rationalized when bond distances and angles within the [PdL] moieties in **1**, especially the Pd–N distance,

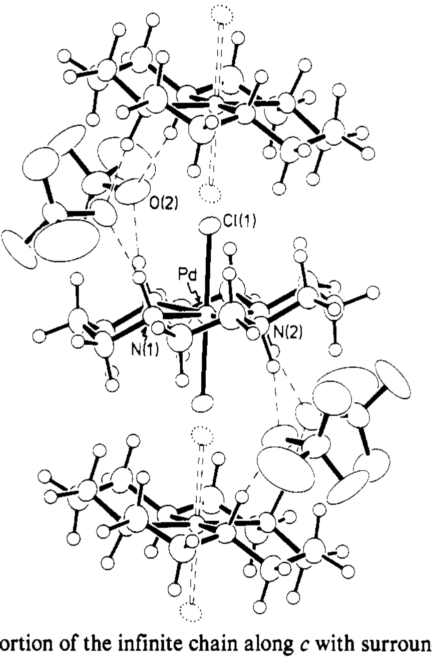


Figure 1. Portion of the infinite chain along *c* with surrounding ClO_4^- ions. Disordered perchlorate oxygens with minor occupancy factors are omitted for clarity. The dashed spheres and bonds represent the disordered positions of the Pd–Cl bonds. The dashed lines correspond to hydrogen bonds.

Table I. Average Bond Distances (Å) and Angles (deg)[a]

compd	1	2	3
Pd^{IV}–Cl	2.320 (3)		2.303 (1)
Pd^{II}· · ·Cl	3.219 (3)		
Pd–N	2.055 (3)	2.051 (5)	2.062 (1)
Cl–Pd–N	86.7 (2)[b] 89.4 (2)[c]		88.41 (3)
N–Pd–N (5*)	84.9 (2)	83.1 (3)	84.72 (4)
Pd–N–C (5*)	106.7 (6)	108.1 (4)	106.82 (8)
Pd–N–C (6*)	115.6 (5)	115.6 (4)	115.64 (7)

[a] Abbreviations: 5*, five-membered ring; 6*, six-membered ring. [b] Cl(1)–Pd–N(1). [c] Cl(1)–Pd–N(2).

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(2) (a) Matsumoto, N.; Yamashita, M.; Kida, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3514. (b) Breer, H.; Endres, H.; Keller, H. J.; Martin, R. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2295. (c) Fanwick, P. E.; Huckaby, J. L. *Inorg. Chem.* **1982**, *21*, 3067. (d) Tanaka, M.; Tsujikawa, I.; Toriumi, K.; Ito, T. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2793 and references cited therein.

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(4) In a similar way, analogues of the mixed-valence complex **1** having a general formula $[Pd^{II}Y][Pd^{IV}X_2Y]Z$ have been synthesized, where Y = L or 1,4,8,12-tetraazacyclopentadecane, X = Cl^- or Br^-, and Z = ClO_4^-, BF_4^-, or PF_6^-.

(5) Elemental analyses of the compounds **1**–**3** gave satisfactory results.

(6) X-ray data: compound **1**, $Pd_2Cl_2C_{20}N_8H_{48}\cdot(ClO_4)_4$, monoclinic, space group $C2/c$, $a = 17.649$ (12) Å, $b = 9.738$ (8) Å, $c = 11.067$ (8) Å, $\beta = 91.33$ (6)°, $V = 1901$ (3) Å^3, $Z = 2$, $\rho_{obsd} = 1.87$ g cm^{-3}, $\rho_{calcd} = 1.89$ g cm^{-3}, $\mu(MoK\alpha) = 1.426$ mm^{-1}, $R = 0.041$ $R_w = 0.062$ for 1708 independent reflections [$2\theta < 60°$, $|F| > 3\sigma(F)$]; compound **2**, $PdC_{10}N_4H_{24}\cdot(ClO_4)_2$, orthorhombic, space group *Pbnm*, $a = 13.337$ (2) Å, $b = 14.492$ (3) Å, $c = 9.746$ (2) Å, $V = 1883.8$ (6) Å^3, $Z = 4$, $\rho_{obsd} = 1.77$ g cm^{-3}, $\rho_{calcd} = 1.78$ g cm^{-3}, $\mu(Mo\ K\alpha) = 1.297$ mm^{-1}, $R = 0.054$, $R_w = 0.067$ for 1824 independent reflections [$2\theta < 60°$, $|F| > 3\sigma(F)$]; compound **3**, $PdCl_2C_{10}N_4H_{24}\cdot(NO_3)_2\cdot HNO_3\cdot H_2O$, triclinic, space group $P\bar{1}$, $a = 9.549$ (1) Å, $b = 16.034$ (1) Å, $c = 7.863$ (1) Å, $\alpha = 86.59$ (1)°, $\beta = 111.51$ (1)°, $\gamma = 103.27$ (1)°, $V = 1089.6$ (2) Å^3, $Z = 2$, $\rho_{obsd} = 1.76$ g cm^{-3}, $\rho_{calcd} = 1.78$ g cm^{-3}, $\mu(Mo\ K\alpha) = 1.143$ mm^{-1}, $R = 0.023$, $R_w = 0.035$ for 5730 independent reflections [$2\theta < 65°$, $|F| > 3\sigma(F)$]. The procedures used for data collection as well as the methods used in the solution and refinement of the structure were standard and have been described previously (Sugimoto, M.; Fujita, J.; Ito, H.; Toriumi, K.; Ito, T. *Inorg. Chem.* **1983**, *22*, 955). Details will be reported elsewhere.

(7) Curtis, N. F. "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter 4.

(8) In most cases so far reported, all four in-plane donor atoms of the [ML] plane are involved, respectively, in the hydrogen bonds with two [ML] units above and below the plane.

(9) A palladium atom sites on a center of symmetry, and two [PdL] units bridged by the hydrogen bonds are related by a twofold axis that is perpendicular to the chain axis and passes through midpoints between the two Pd atoms and two perchlorate ions.

(10) Positional disorder of perchlorate oxygens has been observed and taken into consideration in the refinement.

are compared with those in **2** and **3** (see Table I). Total stereochemistries of the ligand L in **2** and **3** are again the same as those in **1**. Geometrical features of the [PdL] moieties in **1**, **2**, and **3** are very similar to each other irrespective of the oxidation state of Pd (note the relatively large esd's for molecular dimensions of **2**). It is likely that the occurrence of the positional disorder of the Cl atoms in the mixed-valence complex arises from this situation in addition to the weakness in packing interactions among the chains.

The Pd^{IV}–Cl distance in the chain structure **1** (2.319 (3) Å) is slightly longer than that of the complex **3** (2.303 (1) Å), indicating an electronic interaction along the chain. But the difference is surprisingly small. Preliminary measurements of the dc conductivity indicate that the compound **1** is a semiconductor and σ is on the order of 10^{-10} Ω^{-1} cm^{-1} at room temperature.[11] The solid-state electronic absorption spectrum in Nujol mull of compound **1** shows a charge-transfer band from Pd(II) to Pd(IV) at 18.9×10^3 cm^{-1}. When the compound **1** is compared with a recently reported analogue, $[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$,[12,13] the electronic interaction between Pd(II) and Pd(IV) in **1** is weaker in view of the ratio of Pd^{II}–X and Pd^{IV}–X distances[2a] and electronic spectral data.

Registry No. 1, 85337-96-8; **2**, 85337-97-9; **3**, 85337-99-1.

Supplementary Material Available: Listings of atomic coordinates, anisotropic temperature factors, and observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

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(11) The conductivity measurements were carried out on pellets by a two-probe method over the temperature range −100 to +25 °C. Conductivities of bromo derivatives $[Pd^{II}Y][Pd^{IV}Br_2Y](ClO_4)_4$[4] are on the order of ~10^{-7}–10^{-8} Ω^{-1} cm^{-1} at room temperature.

(12) Matsumoto, N.; Yamashita, M.; Kida, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2334.

(13) Beauchamp, A. L.; Layek, D.; Theophanides, T. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1158.

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