Correspondence

Correlation between the Formal Partial Oxidation States Observed in the One-Dimensional Platinum Metal Complexes and the Resonating Valence Bond Theory of Metals[1]

AIC60327I

Sir:

Some years ago Pauling introduced the resonating valence bond theory of metals (RVBM)[2] and used it to assign metallic valences and to successfully correlate a vast amount of data concerning structure and interatomic distances in metals. The theory assumes the existence of a fractional metallic orbital, formally empty, which makes possible unsynchronized resonance of electron-pair bonds between adjacent metal atoms. The resulting resonance stabilization leads to the characteristic metal bond and other metallic properties. The dependence of metal–metal distance on bond number was formulated as $R_n = R_0 - 0.300 \log n$ where R_n and R_0 are metallic radii applicable to bond numbers n and 1, respectively, with $n \leq 1$. Bond number refers to the number of electron pairs involved in a bond and is assigned by means of a relation equating the valence of an atom to the sum of the bond numbers for all bonds to a given atom.

Recently, we and others[3] have characterized a number of the partially oxidized one-dimensional conducting salts of the tetracyanoplatinate and bis(oxalato)platinate variety. These contain chains of partially oxidized metal atoms in which the metal–metal bonding appears to have much in common with bonding in pure metals except that it is one dimensional. Structural and chemical data for these materials give support to two observations: (1) the concept of a single partial oxidation state which is resonance stabilized in different anionic and cationic deficient systems; (2) a correlation between oxidation state and metal–metal distance.

We believe that a basis for understanding the above observations is provided by the RVBM theory and we wish to comment on the following: (1) the relationship of oxidation state and bond number, (2) a bond number vs. metal–metal distance equation which accurately fits all experimentally characterized partially oxidized Pt 1-D complexes, and (3) evidence that Pt–Pt bond formation in the 1-D chains is resonance energy stabilized producing equivalent metal–metal distances.

Bond Number and Oxidation State. The $Pt^{2.0+}$ electronic configuration in the tetracyanoplatinate(II) anion is low spin; the highest occupied molecular orbitals are shown in Figure 1 (a).[4–7] Two electrons from each of the $Pt^{2.0+}$ ions will occupy the a_{1g} bonding and a_{2u} antibonding orbitals giving a net nonbonding result. However, since degenerate MO's of the same symmetry repel one another, the energy of the complex is lowered and a partial bond is formed. This is the case for $K_2Pt(CN)_4{\cdot}3H_2O$ which we have shown by neutron diffraction to have long 3.478-Å Pt–Pt 1-D interactions.[3b]

The bond between the metal atoms is strengthened if electrons are removed from the a_{2u} antibonding molecular orbitals by partial oxidation of the metal. Figure 1(b) represents a simplified MO description of a $Pt^{2.0+}$ complex which has been partially oxidized to a $Pt^{(2+x)+}$ state. Here x electrons per atom are removed from the a_{2u} antibonding molecular orbitals and the bonding stabilization is related to $2x$, the number of bonding electrons and therefore the metallic valence for 1-D chain bonding. The bond number is given by x, the number of bonding electron pairs involved in the bond. Since the oxidation state of Pt is $2+x+$, the bond number is equal to the increase (x) in oxidation state due to partial oxidation.

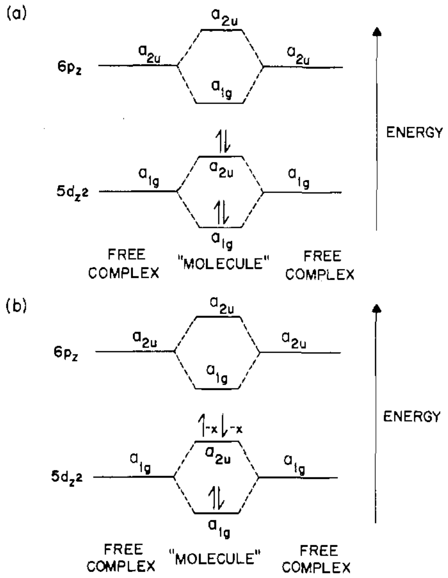

Figure 1. (a) Molecular orbital diagram of a complex formed between two $Pt^{2.0+}$ ions. (b) Molecular orbital diagram of a complex formed between two $Pt^{(2+x)+}$ ions.

Correlation of Bond Distances, Bond Numbers, and Bond Orders. Pauling has shown that the expression $D_n = D_0 - a \log n$, where

$$a = 0.600 \tag{1}$$

for n defined as bond number (n between 0 and 1) and

$$a' = 0.706 \tag{2}$$

for n' defined as bond order ($n' > 0$), successfully predicts metal–metal distances, D_n, for a wide range of metals and alloys.[8] D_0 is the expected single-bond distance ($n = 1$). Bond order is identical with bond number for materials involving no resonance stabilization but otherwise is larger, reflecting the increase in bond strength due to resonance. Bond orders may be estimated from known metal–metal distances using the above expression or from resonance bonding models. The coefficient, a, is known to vary slightly with the type of metal.

Table I lists five pseudo-one-dimensional Pt complexes which have been structurally characterized by x-ray or neutron methods. The oxidation states, the bond numbers, the metal–metal distances calculated by each of the above equations, the observed metal–metal distances, and calculated bond orders are also listed. The Pt–Pt distances calculated, using eq 2 and taking bond order equal to the known bond numbers, are on the average 0.035 Å larger than the experimentally obtained distances. These larger values would be appropriate for the lengths of the Pt–Pt bonds in these 1-D complexes if there were no stabilization by resonance.[8] However, when resonance stabilization energies are taken into account using eq 1, the fit between the calculated and experimental bond distances is within 1%. When a least-squares fit of the experimental bond distance and bond number relation is made, a log coefficient term

$$a = 0.628 \tag{3}$$

is obtained which gives experimental and calculated bond distance agreement to less than 0.2% and compares quite well

Table I. Summary

Material	Exptl oxidn state	Bond number *n*	Pt–Pt, Å Calcd from *a*	Pt–Pt, Å Calcd from *b*	Pt–Pt, Å Calcd from *c*	Pt–Pt, Å Obsd (av)	Calcd bond order (*n*′) from *a*
$K_2Pt(CN)_4Cl_{0.32}\cdot 3H_2O$	2.32	$^1/_3$	2.927	2.876	2.889	2.879	0.38
$K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$	2.30	$^1/_3$	2.927	2.876	2.889	2.890	0.39
$K_{1.75}Pt(CN)_4\cdot 1.5H_2O$	2.25	$^1/_4$	3.015	2.951	2.968	2.967	0.29
$K_{1.6}Pt(C_2O_4)_2\cdot 1.2H_2O$	2.40	$^2/_5$	2.872	2.828	2.840	2.845	0.44
$Mg_{0.82}Pt(C_2O_4)_2\cdot 5.3H_2O$	2.36	$^2/_5$	2.872	2.828	2.840	2.850	0.43
Pt metal		$^1/_2$	2.802	2.770	2.778	2.775	0.54

[a] $D_{n'} = D_0 - 0.706 \log n'$; *n*′ is bond order. [b] $D_n = D_0 - 0.600 \log n$; *n* is bond number. [c] $D_n = D_0 - 0.628 \log n$; *n* is bond number. $D_0 = 2.590$ Å (Pt–Pt single bond).

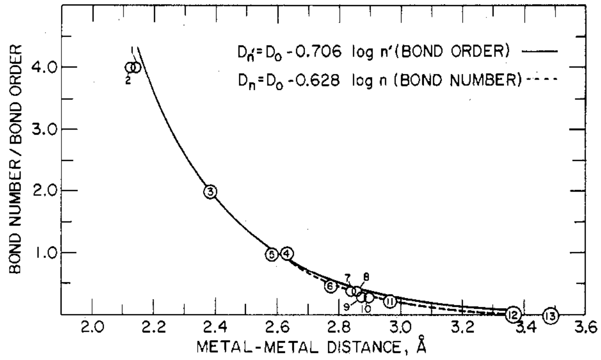

Figure 2. A bond number/order vs. metal–metal bond distance plot of the theoretical bond number and bond order curves and the experimental data: 1, $Mo_2Cl_8^{4-}$;[17] 2, $Mo_2(O_2CCH_3)_4$;[10] 3, $Mo_2Cl_8^{3-}$;[17] 4, Mo_6Cl_{12};[10] 5, μ-5-cyclopentadienylcyclopentadiene-bis(π-cyclopentadienyl)diplatinum;[18] 6, Pt metal;[9] 7, $K_{1.6}Pt(C_2O_4)_2\cdot 1.2H_2O$;[15] 8, $Mg_{0.82}Pt(C_2O_4)_2\cdot 5.3H_2O$;[16] 9, $K_2Pt(CN)_4Cl_{0.32}\cdot 3H_2O$;[14] 10, $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$;[13] 11, $K_{1.75}Pt(CN)_4\cdot 1.5H_2O$;[3c–e] 12, Pt_6Cl_{12};[10] 13, $K_2Pt(CN)_4\cdot 3H_2O$.[3b]

with the coefficient of 0.62 which Pauling has suggested as possibly preferable for a resonance-stabilized metal system.[2a] It should be emphasized that the above equations may not apply to all 1-D metal complexes, especially those where large ligands or counterions may force a larger metal–metal spacing than would be otherwise predicted.

Resonance Nature of the Metal–Metal Chain. Figure 2 shows plots of metal–metal bond distances as a function of bond number for several 1-D complexes and a selection of Pt and Mo compounds. The smooth curves result from application of eq 2 and 3 to Pt and Mo which have almost identical single-bond radii (Pt, 1.295 Å; Mo, 1.296 Å).[9] All five partially oxidized materials fall on the smooth curve calculated by eq 3, as does Pt metal, thus indicating the existence of resonance stabilization in 1-D Pt chains. The fit of the Mo complexes to the curve calculated by eq 2 is quite good, since there is no resonance stabilization to cause metal–metal bond shortening. Pt_6Cl_{12}[10] and $K_2Pt(CN)_4\cdot 3H_2O$[3b] have metal–metal distances which correspond to an expected bond number of ~0 while Pt metal displays the expected bond number of $^1/_2$.[9]

Since resonance effects are clearly shown to be important in these complexes, the coexistence of two oxidation states, i.e., $Pt^{2.0+}$ and $Pt^{4.0+}$, is not justified and a single Pt–Pt distance should result. This is in good agreement with the ^{195}Pt Mössbauer spectra[11] and photoelectron spectra (ESCA)[12] results for several of these complexes. The small differences in Pt–Pt spacings observed experimentally are probably not electronically significant, i.e.: $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$, 2.888 (6), 2.892 (6) Å;[13] $K_2Pt(CN)_4Cl_{0.32}\cdot 3H_2O$, 2.870 (2), 2.878 (2) Å[14a] and 2.867 (10), 2.903 (10) Å;[14b] $K_{1.75}Pt(CN)_4\cdot 1.5H_2O$, 2.967 (1), 2.976 (1) Å[3c] and 2.961 (1), 2.965 (1) Å;[3d] $K_{1.6}Pt(C_2O_4)_2\cdot 1.2H_2O$, 2.833 (2), 2.857 (2) Å.[15] In $Mg_{0.8}Pt(C_2O_4)_2\cdot 5.3H_2O$ because of the orthorhombic symmetry only one Pt–Pt distance of 2.850 Å is found.[16]

Registry No. $K_2Pt(CN)_4$, 562-76-5; Cl_2, 7782-50-5; Br_2, 7726-95-6; $K_2Pt(C_2O_4)_2$, 35371-78-9; $MgPt(C_2O_4)_2$, 38686-00-9; Pt, 7440-06-4.

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Calculation of Natural Abundances of Isotopic Isomers—an Aid in Spectral Synthesis

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Sir:

Many types of spectra exhibit complications due to the presence of isotopic isomers. Interpretation of such spectra may be sought in terms of the sum of individual component spectra each weighted according to its natural (or known enriched) abundance.[1] This correspondence points out how the weighting may readily be calculated through the use of