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).

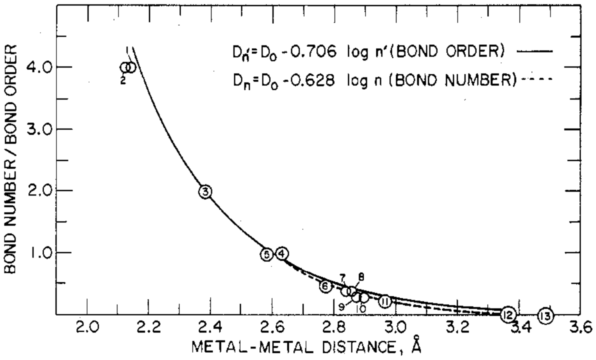

Figure 2. A bond number/order vs. metal–metal bond distance plot of the theoretical bond number and bond order curves and the experimental data: 1, $Mo_2Cl_8^{4-}$;[17] 2, $Mo_2(O_2CCH_3)_4$;[10] 3, $Mo_2Cl_8^{3-}$;[17] 4, Mo_6Cl_{12};[10] 5, μ-5-cyclopentadienylcyclopentadiene-bis(π-cyclopentadienyl)diplatinum;[18] 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

AIC60287I

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

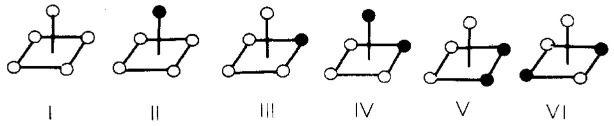

Figure 1.

Table I. Isotopic Isomer Abundances for B_5H_9

Stoichiometry of isotopic isomer	Structure of isomer	σ_i	Fractional abundance
$^{11}B_5H_9$	I	4	$\frac{4}{4}(0.804)^5 = 0.336$
$^{10}B^{11}B_4H_9$	II	4	$\frac{4}{4}(0.804)^4(0.196) = 0.082$
$^{10}B^{11}B_4H_9$	III	1	$\frac{4}{1}(0.804)^4(0.196) = 0.328$
$^{10}B_2{}^{11}B_3H_9$	IV	1	$\frac{4}{1}(0.804)^3(0.196)^2 = 0.080$
$^{10}B_2{}^{11}B_3H_9$	V	1	$\frac{4}{1}(0.804)^3(0.196)^2 = 0.080$
$^{10}B_2{}^{11}B_3H_9$	VI	2	$\frac{4}{2}(0.804)^3(0.196)^2 = 0.040$
$^{10}B_3{}^{11}B_2H_9$	VI	2	$\frac{4}{2}(0.804)^2(0.196)^3 = 0.010$
$^{10}B_3{}^{11}B_2H_9$	V	1	$\frac{4}{1}(0.804)^2(0.196)^3 = 0.019$
$^{10}B_3{}^{11}B_2H_9$	IV	1	$\frac{4}{1}(0.804)^2(0.196)^3 = 0.019$
$^{10}B_4{}^{11}BH_9$	III	1	$\frac{4}{1}(0.804)(0.196)^4 = 0.005$
$^{10}B_4{}^{11}BH_9$	II	4	$\frac{4}{4}(0.804)(0.196)^4 = 0.001$
$^{10}B_5H_9$	I	4	$\frac{4}{4}(0.196)^5 = 0.0003$

symmetry numbers.

The general formula to be used for the fractional abundance of a particular isotopic isomer, denoted f_i, is

$$f_i = \frac{\sigma}{\sigma_i} a^w b^x c^y \ldots \qquad (1)$$

where σ is the symmetry number[2] of the parent molecule considered as isotopically pure, σ_i is the symmetry number of the particular isotopic isomer, a is the natural abundance of an isotope occurring w times in the isomeric species, b is the natural abundance of isotope occurring x times, etc.

As an example, the NMR spectrum of B_5H_9 may be considered to consist of the spectra of all of the possible isotopic isomers drawn in Figure 1[3], where the darkened circles represent either ^{10}B (fractional natural abundance 0.196, nuclear spin quantum number 3) or ^{11}B (fractional natural abundance 0.804, spin $^3/_2$). The results of applying eq 1 to these data are given in Table I. The boron-11 NMR spectrum of B_5H_9 is a weighted average of the spectra of the isomers given in Table I.

Derivation. A necessary and sufficient assumption for the derivation of eq 1 is that the probability of a particular isotope occupying any particular site is given by its fractional natural abundance—i.e., it is assumed that no isotopic fractionation has occurred in the course of compound formation and that random distribution of the isotopes over the various sites occurs. Under this assumption the abundance of any particular isotopic isomer will be the product of the fractional isotopic abundance for a given stoichiometry (denoted as f_s) with the ratio of the distinguishable[7] configurations which a given isomer may have (denoted as c_i) to the total number of distinguishable configurations for the given stoichiometry (denoted as c_t). Algebraically this is given by

$$f_i = \frac{c_i}{c_t} f_s = \frac{\sigma}{\sigma_i} a^w b^x c^z \ldots \qquad (2)$$

where

$$c_t = P_1{}^n \qquad (3)$$

$$c_i = \sigma/\sigma_i \qquad (4)$$

$$f_s = P_1{}^n a^w b^x c^y \ldots \qquad (5)$$

$P_1{}^n$ is the number of distinguishable permutations possible for the isotopic atoms among the n sites and is found by evaluating $n!/w!x!y!\ldots$. The rotation group of the isotopic isomer is a subgroup of the rotation group of the parent geometry. The ratio σ/σ_i is simply the index of this subgroup and gives the number of distinct cosets plus one for the subgroup itself.[6] This is the number of operations producing distinguishable configurations of a given isomer. Equation 5 is commonly used by mass spectroscopists to calculate relative abundances of isotopic species from the stoichiometry alone but has also been used in spectral synthesis in cases where each stoichiometry leads to a single isomer.[1a]

References and Notes

(1) See (a) W. G. Schneider and A. D. Buckingham, *Discuss. Faraday Soc.*, **34**, 147 (1962), for an example involving NMR spectroscopy, or (b) H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967), for an example involving ir spectroscopy.

(2) The number of equivalent orientations of the molecule available by rotations alone, hence the order of the rotation group of the species (excluding all operations associated with C_∞).

(3) These may readily be drawn by inspection. For more complex cases, the complete expansion of the Polya cycle index provides both an enumeration[4] and a guide to formulation[5] of the isomers.

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Additions and Corrections

1976, Volume 15

R. Romeo*, D. Minniti, and M. Trozzi: Uncatalyzed Cis–Trans Isomerization and Methanol Solvolysis of Arylbromobis(triethylphosphine)platinum(II) Complexes. A Different Role for Steric Hindrance in Dissociative and Associative Mechanisms.

Page 1136. Equation 4 should read $k_1 = k_s k_Y[Y]/(k_{-s}[X^-] + k_Y[Y])$.—R. Romeo

Motoharu Tanaka: Solvent Exchange at Some Bivalent Metal Ions.

Page 2325. In the left column, first line of third paragraph, "dissociation" should read "dissociative".

Page 2327. Reference *h* in Table II should read: H. Levanon and Z. Luz, *J. Chem. Phys.*, **49**, 2031 (1968).—M. Tanaka