Table II. Relative Abundances of the Various Isomeric Species and Differences in Energies for the Case of One Quantum of the a_{1g} Symmetric Stretch Mode Excited

Complex	Calcd rel abund	Energy,[a] cm^{-1}	Energy diff, cm^{-1}
$Pt^{35}Cl_4^{2-}$	$1 \times (3/4)^4 \times (1/4)^0 = 81/256$	337.1	
			2.3
$Pt^{35}Cl_3{}^{37}Cl^{2-}$	$4 \times (3/4)^3 \times (1/4)^1 = 108/256$	334.8	
			2.4
$Pt^{35}Cl_2{}^{37}Cl_2{}^{2-}$	$6 \times (3/4)^2 \times (1/4)^2 = 54/256$	332.4	
			2.3
$Pt^{35}Cl^{37}Cl_3{}^{2-}$	$4 \times (3/4)^1 \times (1/4)^3 = 12/256$	330.1	
			2.2
$Pt^{37}Cl_4{}^{2-}$	$1 \times (3/4)^0 \times (1/4)^4 = 1/256$	327.9	

[a] Energies based on the energy of the symmetric stretch mode of K_2PtCl_4, 335 cm^{-1} [from H. Stammreich and R. Forneris, *Spectrochim. Acta, Part A*, **23**, 1137 (1967)], with the Cl atomic weight being 35.45.

Table III. Experimental Splittings of the E and O Peak Components as a Function of *n* in Comparison with Calculated Splittings for a Square-Planar (SP) and an Octahedral (Oct) Complex

n	Exptl E peak splitting	Exptl O peak splitting	Calcd splitting for SP complex	Calcd splitting for Oct complex
1	2		2.3	1.6
2	5	5	4.6	3.2
3	8	6	6.9	4.8
4	8	9	9.2	6.4
5	10	11	11.5	8.0
6	12	11	13.8	9.6
7	15	15	16.1	11.2
8	17		18.4	12.8
9	19		20.7	13.4

are present with energies as given in Table II. The separation between two adjacent isomer peaks is 2.3 cm^{-1}. If *n* quanta of the a_{1g} mode are excited in a $PtCl_4{}^{2-}$ complex, then the spacing between adjacent isomer peaks is ($n \times 2.3$) cm^{-1}. This can be proven as follows. For an isotopic species, a, undergoing an electronic transition, we can write[4]

$$\nu_a = \nu_{ea} + \sum_i \omega'_{ia}(n'_{ia} + 1/2) - \sum_i \omega''_{ia}(n''_{ia} + 1/2) \tag{3}$$

where the single prime denotes the upper electronic state and the double prime the lower electronic state. If the system is at 4 K, then expression 3 for the case of emission reduces to

$$\nu_a = \nu_{ea} - \sum_i \omega''_{ia} n''_{ia} \tag{4}$$

and if we only consider a progression in a single mode i, the difference in energy between adjacent isomer a and b peaks is

$$\Delta\nu = \nu_a - \nu_b = n''_i(\omega''_{ia} - \omega''_{ib}) \tag{5}$$

and the spacing between the isomer peaks increases linearly with *n*. Thus, the best opportunity to observe the isotope effect in inorganic complexes exists for an electronic transition which (1) exhibits sharp structure and (2) has a long Franck–Condon progression.

In Table III a summary is given of the experimental splittings of the E and O peaks as a function of *n* along with the calculated splittings for a square-planar complex and an octahedral complex. The reason that the octahedral complex calculation was carried out was to show that the emitting species is $PtCl_4{}^{2-}$. There is always the danger that some $PtCl_6{}^{2-}$ may be formed at 800 °C when the mixed crystals are grown out of the melt. The calculated results indicate that the square-planar complex is indeed the emitting species.

In Figure 1 the calculated relative intensities are shown for a square-planar complex. The intensities are in somewhat reasonable agreement with the experimental data considering the difficulty of estimating the area under the peaks.

Registry No. Cs_2PtCl_4, 13820-34-3; Cs_2ZrCl_6, 16918-86-8; $Pt^{35}Cl_4{}^{2-}$, 58832-54-5; $Pt^{35}Cl_3{}^{37}Cl^{2-}$, 58865-37-5; $Pt^{35}Cl_2{}^{37}Cl_2{}^{2-}$, 58832-55-6; $Pt^{35}Cl^{37}Cl_3{}^{2-}$, 58865-38-6; $Pt^{37}Cl_4{}^{2-}$, 58832-56-7.

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Correspondence

Distortions in Seven-Coordinate Complexes. Extension of the Dihedral Angle Method[1,2] to Inequivalent Ligand Systems

AIC50733M

Sir:

The description of the deviations of a real compound from an ideal geometry requires, as a prerequisite, an established reference structure and, second, a quantitative measure of distortion. Complexes with large coordination numbers generally fail to satisfy either criteria. Steric arguments do not confidently imply a unique ground-state geometry. Rather, a multiplicity of closely related structures, differing only slightly in energy, are generated.[3] Further, the number of coordinates necessary to describe the position of the ligands relative to an arbitrarily chosen reference structure increases rapidly with coordination number.

The difficulty is well illustrated by seven-coordinate complexes. Three ideal geometries are usually considered—the D_{5h} pentagonal bipyramid, C_{3v} monocapped octahedron, and C_{2v} monocapped trigonal prism. Although calculations based on the "points on a sphere" model[3] suggest the energy differences are small, each has been observed as an actual structural type; vide infra. When the ligands are inequivalent, so the actual symmetry is low, the assignment of a structure to one of the three classes is ambiguous or, seemingly, impossible. Thus, $[W(CO)_3(PMe_2Ph)_3I][BPh_4]$ is ". . . close to two ideal geometries, either a [monocapped trigonal prism] with I(1), C(1), C(2), P(1), P(2) in the capped quadrilateral face and P(3), C(3) in the remaining edge, or as a [monocapped octahedron] with P(3) in the capping position, C(1)–(3) in the capped face, and P(1), P(2), I(1) in the uncapped face".[4]

Muetterties and Guggenberger[2] have applied the approach of Porai-Koshits and Aslanov[1] to a variety of coordination numbers. This method describes a particular geometry by use of a specific set of dihedral angles formed by the normals to the faces of the polyhedron in question. The angles are chosen

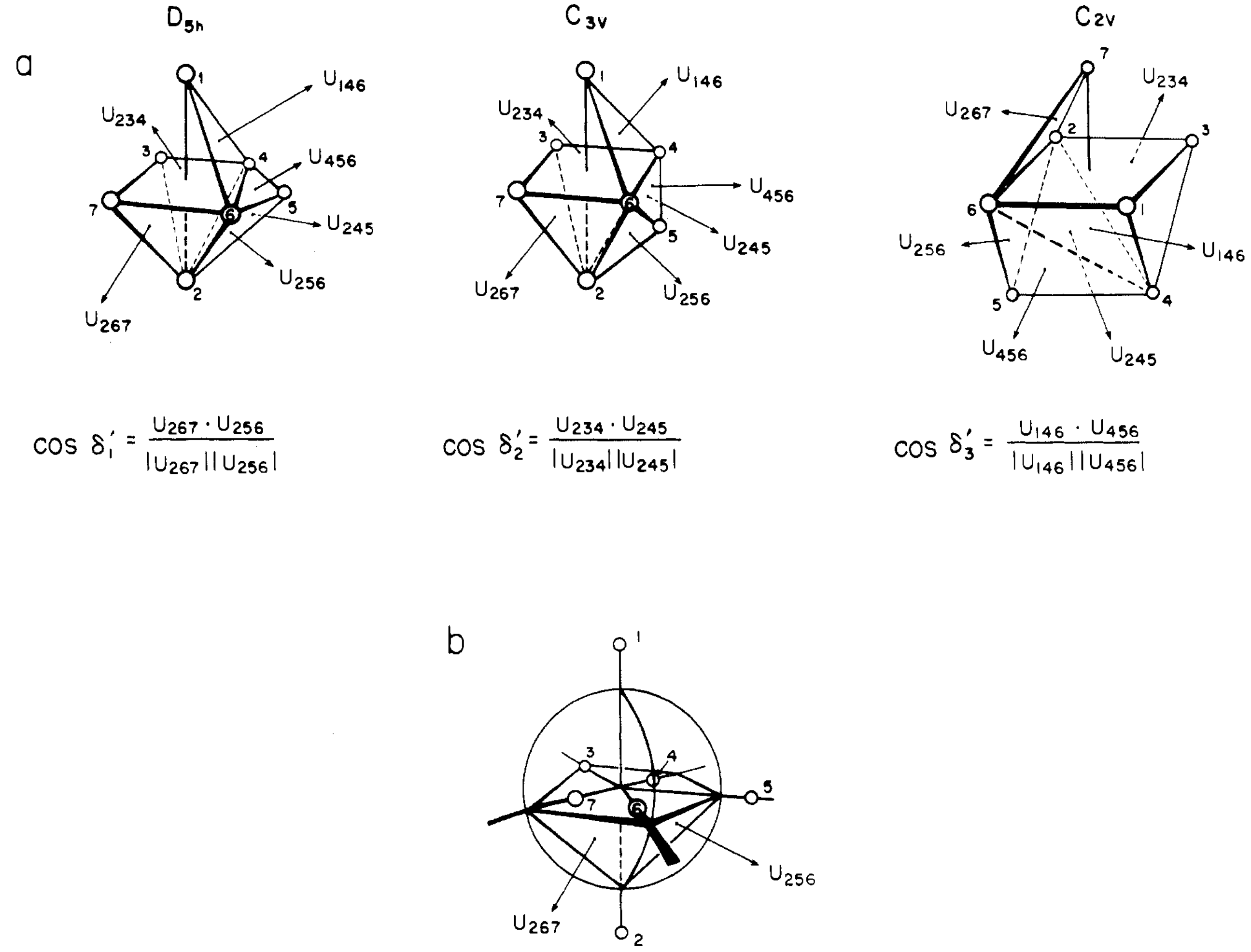

Figure 1. (a) δ_i' in the reference geometries. These angles are as chosen in ref 2 except those for D_{5h}.[22] (b) Projection of the ligands onto a unit sphere to form the inscribed polyhedron used to calculate the δ_i' in this work.

in such a way that they are sensitive to the traverse of one reference structure into another by a generalized diamond–square–diamond path.[5] Distortion is measured by the position of the complex in question along this specific reaction coordinate. The application of this method by Muetterties and Guggenberger[2] to seven-coordination is illustrated in Figure 1. Note that since only three coordinates are required to describe the traverse, this approach gives intelligible results *only if the reaction coordinate is a real one.* The δ_i' of an example which lies off the path bear, in general, nothing more than a coincidental relation to the nature and degree of deviation from the coordinate. Thus, the question of whether this method (or any which relates degree of distortion to an arbitrary reaction coordinate) is valid is reduced to whether or not it is supported by experimental evidence. Its validity can only be established by determining whether a large body of seven-coordinate complexes do, in fact, represent "frozen out" points along the path or bear a systematic relation to it.

Inasmuch as random lengthening or contraction of metal–ligand bonds does not lie along the coordinate, the δ' method is inapplicable to complexes containing inequivalent ligands, i.e., inequivalent bond lengths. This problem arises because the dihedral angles, as formulated in ref 1, are based on polyhedral shapes and not solely on ligand–metal–ligand angles. One should note that since no regular polytope with seven vertices exists, it is impossible for the ligands to experience equal repulsive potentials. Consequently, even complexes with equivalent ligands are expected to possess unequal bond lengths. Such behavior is well documented.[6] Computation of the δ_i' for ML_7 species will, therefore, introduce a deviation from the reaction path which will be geometry and, quite probably, ligand dependent (the reference structures are defined with equivalent bond lengths). This point has been noted for C_{2v} $[(t\text{-BuNC})_7\text{Mo}^{\text{II}}][\text{PF}_6]_2$.[7] Finally, the restriction to complexes of the type ML_7 is a rather severe one, since the data set is not large enough to evaluate the validity of the reaction coordinate.

If the reaction path is defined by the motion of metal–ligand vectors of unit length, the method is extended to all seven-coordinate species and the problem associated with inequivalent bond lengths in ML_7 complexes is eliminated. This corresponds to contracting or expanding the metal–ligand vectors such that they become points on a unit sphere and evaluating the dihedral angles associated with the faces of the inscribed polyhedron—a process which destroys bond length information but preserves the ligand–metal–ligand angles.

Table I represents the δ_i' calculated for a representative body of seven-coordinate structures by this, more general, procedure (see Figure 1b). From the data, it is apparent that a quantitative assessment of geometry has merit, since some of the assignments made by inspection are, *by these criteria,* in error. For example, the high-pressure form of UO_3, which reportedly resembles a puckered pentagonal bipyramid,[8] is very close to the idealized C_{2v} monocapped trigonal prism. Similarly, bis[bis(diphenylarsino)methane]dibromodicarbonylmolybdenum(II) has been said to be a distorted monocapped octahedron.[9] Our results indicate it has a marginally distorted C_{2v} structure. It is possible to make a

Table I. Dihedral Angles (deg) Calculated for Seven-Coordinate Complexes

Compd	$\delta_1', \delta_2', \delta_3'$
D_{5h} reference[a]	54.4, 54.4, −72.8
$Zr_4(OH)_6(CrO_4)_5(H_2O)_2$[13]	52.8, 54.1, −69.6
$K_3[UO_2F_5]$[14]	53.3, 50.7, −66.6
$K_4[V(CN)_7]\cdot 2H_2O$[15]	53.1, 53.9, −67.4
$(NH_4)_3(ZrF_7)$[16]	54.7, 47.4, −62.0
$Rb[Fe(EDTA)(H_2O)]$[17]	50.5, 47.8, −65.8
$Rb_5[Zr_4F_{21}]$[b,11]	41.4, 35.4, −37.4
$Rb_5[Zr_4F_{21}]$[b,11]	48.5, 27.5, −46.3
C_{3v} reference[a]	24.2, 24.2, 24.2
$MoBr_2(CO)_3(diphos)$[18]	19.0, 13.2, 5.4
$Mn_3(HEDTA)_2\cdot 10H_2O$[10]	35.2, 34.5, 28.7
$[W(CO)_3(Me_2PhP)_3I][BPh_4]$[4]	32.3, 5.1, 3.2
$K_2[NbF_7]$[19]	37.6, 1.1, 6.7
UO_3[8]	44.0, 4.3, 8.9
$MoBr_2(CO)_2(Ph_2AsCH_2AsPh_2)_2$[9]	47.3, 5.2, 6.3
$[Mo(t\text{-}BuNC)_6I]I$[20]	45.0, 0.3, 0.3
$[Mo(t\text{-}BuNC)_7][PF_6]_2$[7]	39.4, 0.0, 0.0
$Na_5[Zr_2F_{13}]$[21]	40.8, 0.0, 0.0
C_{2v} reference[a]	41.5, 0.0, 0.0

[a] As discussed in the text, the choice of reference structures is arbitrary. We have followed Muetterties and Guggenberger's convention in choosing those coordinates generated by Thompson and Bartell's "points on a sphere" calculation, using an r_{ij}^{-6} potential. [b] This compound contains four unique Zr atoms in the unit cell—one is six-coordinate and one eight-coordinate; the remaining two are independent ZrF_7 polyhedra.

clear choice for $[W(CO)_3(PMe_2Ph)_3I][BPh_4]$,[4] which is closest to the monocapped trigonal prism although slightly distorted toward C_{3v}. The $Mn(EDTA)(OH_2)^{2-}$ ion in $Mn_3(HEDTA)_2\cdot 10H_2O$ is one of the few examples which is close to the reference monocapped octahedron, contrary to the original report.[10]

Inspection of Table I reveals a progression from D_{5h} to C_{3v} to C_{2v}. Small distortions from the reaction coordinate are noticable (e.g., $Rb_5[Zr_4F_{21}]$[11]); however, these arise primarily with chelating ligands,[12] which are expected to force minor deviations. We conclude that there is evidence to support the path from D_{5h} to C_{2v} via C_{3v} proposed in ref 1. However, we are unable to produce unambiguous and obvious examples connecting C_{2v} directly to D_{5h}.

It is our belief that quantitative descriptions of seven-coordinate geometries are far superior to visual inspection, particularly in cases where inequivalent bond lengths and complex ligands obscure the structure, as illustrated by the examples above.

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Registry No. $Zr_4(OH)_6(CrO_4)_5(H_2O)_2$, 58814-76-9; $K_3[UO_2F_5]$, 19426-75-6; $K_4[V(CN)_7]\cdot 2H_2O$, 38702-86-2; $(NH_4)_3(ZrF_7)$, 17250-81-6; $Rb[Fe(EDTA)(H_2O)]$, 19214-59-6; $Rb_5[Zr_4F_{21}]$, 9022-74-6; $MoBr_2(CO)_3(diphos)$, 25685-00-1; $Mn_3(HEDTA)_2\cdot 10H_2O$, 58814-75-8; $[W(CO)_3(Me_2PhP)_3I][BPh_4]$, 25640-92-0; $K_2[NbF_7]$, 16924-03-1; $MoBr_2(CO)_2(Ph_2AsCH_2AsPh_2)_2$, 20449-61-0; $[Mo(t\text{-}BuNC)_6I]I$, 36629-85-3; $[Mo(t\text{-}BuNC)_7][PF_6]_2$, 41982-05-2; $Na_5[Zr_2F_{13}]$, 12022-20-7.

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(22) Muetterties and Guggenberger[2a] left δ_3' undefined in D_{5h}, since it is an angle formed by interior faces. To illustrate the transition from one geometry to another, we have arbitrarily defined it as shown in Figure 1. Note δ_3' changes sign in going from D_{5h} to C_{3v} and vanishes in C_{2v}.

(23) The U_{ijk} in Figure 1 are computed by taking cross products of the ligand–ligand vectors associated with the ligand coordinates (generated from normalization of the metal–ligand vectors). All possible δ angles are then computed from the scalar products of the U vectors. Using these data, the polyhedron is searched for the best external threefold face as determined by the dihedral angles between the face in question and the three adjacent, edge-sharing faces. Location of this face allows the structure to be viewed relative to the C_{3v} model and the appropriate δ_i found. Alternatively, structures near D_{5h} may be referenced by finding the best axial ligands and subsequent selection of the ligand with the greatest deviation from the equatorial plane. Neither of these procedures is entirely unambiguous, and we have chosen that which is most consonant with reaction coordinates for the structure in question. It should be emphasized that small deviations within a set of δ_i cannot be considered significant for this reason.

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