

## References and Notes

- (1) (a) Partial support of this research by the Public Health Service (Grant AM 14341) is gratefully acknowledged. (b) Presented in part at the 163d National Meeting of the American Chemical Society, New York, N.Y., Aug 1972.
- (2) D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, **11**, 2361 (1972).
- (3) Abbreviations for the macrocyclic ligands: [14]tetraeneN<sub>4</sub>, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; [14]dieneN<sub>4</sub>, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.
- (4) A. M. Tait, M. Z. Hoffman, and E. Hayon, *J. Am. Chem. Soc.*, **98**, 86 (1976).
- (5) D. P. Rillema and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 8711 (1972).
- (6) (a) M. P. Liteplo and J. F. Endicott, *Inorg. Chem.*, **10**, 1420 (1971); (b) D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Am. Chem. Soc.*, **94**, 394 (1972).
- (7) D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971).
- (8) D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Am. Chem. Soc.*, **95**, 6987 (1973).
- (9) B. Durham and J. F. Endicott, work in progress.
- (10) For example we found half-lives of the order of 7 s in the "Co'tetraene" solution about 10<sup>-4</sup> M in reductant at pH 4 (see supplementary material), where Tait et al.<sup>4</sup> would predict a 0.06-s half-life for (5) under these conditions. It should be noted that these reducing solutions appeared to be stoichiometrically oxidized by various species including Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Co(en)<sub>3</sub><sup>3+</sup>, and Co([14]-4,11-dieneN<sub>4</sub>)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> with apparent second-order rate constants of about 6 × 10<sup>3</sup>, 3 × 10<sup>2</sup>, and 1.4 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively (ionic strength 0.1 M, 25 °C).
- (11) We wish to thank Dr. C. Y. Mok for assistance with these experiments.
- (12) (a) J. F. Endicott, R. R. Schroeder, D. H. Chidester, and D. R. Ferrier, *J. Phys. Chem.*, **77**, 2579 (1973); (b) M. D. Glick, J. M. Kusaj, and J. F. Endicott, *J. Am. Chem. Soc.*, **95**, 5097 (1973); (c) M. D. Glick, W. G. Schmonsees, and J. F. Endicott, *ibid.*, **96**, 5661 (1974).
- (13) (a) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963); (b) *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).
- (14) These expressions may be obtained as follows: for (2),  $\Delta G^{\circ}_{Cr,Co} \approx 1/8(\lambda_{Cr} + \lambda_{Co}) + \Delta G^{\circ}_2/2 + \dots$ ; for (3),  $\Delta G^{\circ}_{Cr,X} \approx 1/8(\lambda'_{Cr} + \lambda_X) + \Delta G^{\circ}_3/2 + \dots$ ; for (4),  $\Delta G^{\circ}_{X,Co} \approx 1/8(\lambda_X + \lambda'_{Co}) + \Delta G^{\circ}_4 + \dots$ . The reorganizational parameters are defined with regard to the reactions specified with the exception that we have assumed a single value for  $\lambda_X$ ; i.e., since  $\lambda_X$  must be relatively small for the catalytic pathways, small differences between  $\lambda'_X$  for oxidation of Co([14]tetraeneN<sub>4</sub>) and  $\lambda''_X$  for reduction of Co<sup>II</sup>([14]tetraeneN<sub>4</sub>) may be ignored. Owing to the similar half-reactions involved,  $\Delta G^{\circ}_2 - \Delta G^{\circ}_3 - \Delta G^{\circ}_4 = 0$ , so we may consider  $\Delta G^{\circ}_{Cr,Co} - \Delta G^{\circ}_{Cr,X} - \Delta G^{\circ}_{X,Co} \approx 1/8[(\lambda_{Cr} + \lambda_{Co}) - (\lambda'_{Cr} + \lambda'_{Co} + 2\lambda_X)] = \Delta \Delta G^{\circ}$ . In order for the catalytic pathway to be significant,  $\Delta \Delta G^{\circ} > 0$ ; hence we have the expression in the text.
- (15) While the d<sup>7</sup> complexes are axially distorted in the solid state,<sup>12b,12c</sup> the d<sup>8</sup> nickel(II) analogues tend to be square planar, perhaps owing to somewhat weaker axial interactions. For examples see: (a) M. F. Bailey and I. E. Maxwell, *Chem. Commun.*, 883 (1966); (b) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 1 (1966).

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### Isotopic Splitting in the Sharp-Line Luminescence Spectrum of the Tetrachloroplatinate(II) Ion at 4 K

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In 1972 Patterson, Godfrey, and Khan<sup>1</sup> reported sharp-line luminescence and absorption spectra for the tetrachloroplatinate(II) ion doped in the host lattice of cesium hexachlorozirconate(IV) at 4 K. In particular, the sharp-line luminescence occurred between 19 450 and 23 190 cm<sup>-1</sup> and consisted of more than 30 distinct emission lines. Group theoretical analysis of the sharp emission lines showed that the emitting excited electronic state could only be of a certain symmetry. Also, Franck-Condon analysis showed that the Pt-Cl equilibrium separation in the excited emitting electronic state is 0.16 Å greater than in the ground state. It was argued that the reason for the splitting in the E and O peaks was that as transitions occur into the ground electronic state with more quanta of the  $\nu_1$  symmetric stretch mode excited, the complex samples to a greater extent its surroundings, and ions with

Table I. Energies of E and O Peak Components for PtCl<sub>4</sub><sup>2-</sup> Luminescence Spectrum

n value	O peak component no.	Energy, cm <sup>-1</sup>	E peak component no.	Energy, cm <sup>-1</sup>
0			10E <sub>1</sub>	22 358
1	80 <sub>1</sub>	21 888	9E <sub>1</sub>	22 022
			9E <sub>2</sub>	22 030
2	70 <sub>1</sub>	21 560	8E <sub>1</sub>	21 700
	70 <sub>2</sub>	21 565	8E <sub>2</sub>	21 705
			8E <sub>4</sub>	21 725
3	60 <sub>1</sub>	21 230	7E <sub>1</sub>	21 371
	60 <sub>2</sub>	21 236	7E <sub>2</sub>	21 379
	60 <sub>3</sub>	21 245	7E <sub>3</sub>	21 385
			7E <sub>4</sub>	21 396
			7E <sub>5</sub>	21 403
4	50 <sub>1</sub>	20 902	6E <sub>1</sub>	21 041
	50 <sub>2</sub>	20 911	6E <sub>2</sub>	21 049
	50 <sub>3</sub>	20 921	6E <sub>3</sub>	21 059
			6E <sub>4</sub>	21 070
5	40 <sub>1</sub>	20 576	5E <sub>1</sub>	20 714
	40 <sub>2</sub>	20 587	5E <sub>2</sub>	20 724
	40 <sub>3</sub>	20 598	5E <sub>3</sub>	20 736
			5E <sub>4</sub>	20 748
6	30 <sub>1</sub>	20 252	4E <sub>1</sub>	20 389
	30 <sub>2</sub>	20 263	4E <sub>2</sub>	20 401
	30 <sub>3</sub>	20 277	4E <sub>3</sub>	20 414
			4E <sub>4</sub>	20 425
7	20 <sub>1</sub>	19 924	3E <sub>1</sub>	20 061
	20 <sub>2</sub>	19 939	3E <sub>2</sub>	20 076
			3E <sub>3</sub>	20 093
			3E <sub>4</sub>	20 107
8			2E <sub>1</sub>	19 734
			2E <sub>2</sub>	19 751
			2E <sub>3</sub>	19 768
9			1E <sub>1</sub>	19 403
			1E <sub>2</sub>	19 422

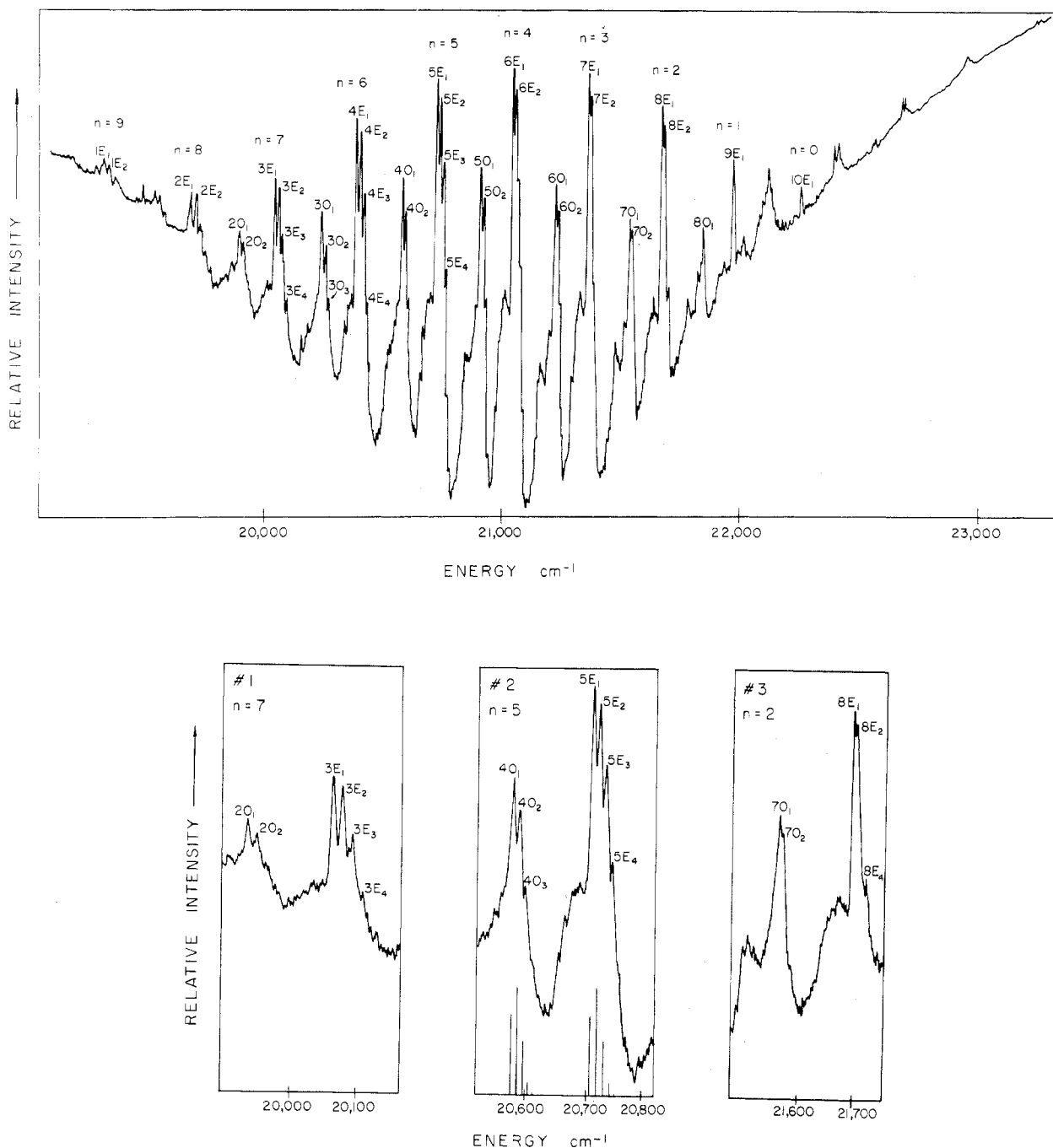
slightly less than cubic site symmetry give rise to additional peaks. In this paper a different explanation is proposed for the splittings.

The purpose of this paper is to demonstrate that the sharp splittings in the luminescence spectrum are due to the presence of <sup>35</sup>Cl and <sup>37</sup>Cl isotopes in the emitting tetrachloroplatinate(II) ion. The analysis is not dependent upon any adjustable parameters. Further, the analysis is different if the emitting species is Pt(IV) rather than Pt(II) and provides further evidence that the emitting species is indeed PtCl<sub>4</sub><sup>2-</sup> rather than PtCl<sub>6</sub><sup>2-</sup>. As far as we are aware, there have been few reports of vibrational isotopic splitting observed in electronic spectra for inorganic compounds;<sup>2-4</sup> however, this effect is well-known in Raman and infrared vibrational spectra.

### Results

In the top portion of Figure 1, the luminescence spectrum of a Cs<sub>2</sub>PtCl<sub>4</sub>-CsZrCl<sub>6</sub> single crystal at a temperature of 4 K is shown. The details of the spectroscopic measurements have been given previously in ref 1.

The Figure 1 spectrum contains two sets of peaks labeled E and O, with the E peaks having greater relative intensity than the O peaks. The progression of E peaks extends from 19 406 to 22 500 cm<sup>-1</sup> with an intensity maximum around 21 000 cm<sup>-1</sup>. In contrast, the O peak progression is very similar to the E peak progression except that the O peaks seem to extend to about 23 500 cm<sup>-1</sup>. However, if the O peak progression is carefully examined, it is found that peak 9O is broad and does not have the same general appearance as the other O peaks. Also, if the O peak splitting is measured as a function of increasing energy, it is found that the O peak splitting continually decreases until 9O, increases at 9O, and



**Figure 1.** Microphotometer tracing of a photographic plate showing the luminescence spectrum of a  $\text{Cs}_2\text{PtCl}_4\text{-Cs}_2\text{ZrCl}_6$  single crystal. The NO and NE peak labels are the same as in Figure 1 of ref 1. The  $n$  number indicates the number of  $\nu_1$  quanta excited. The calculated relative intensities for a square-planar complex are shown as a line diagram below the observed spectra for  $n = 5$ .

then decreases again. For these reasons, it is argued that the peaks observed at energies greater than 9O are due to another electronic transition.

In the bottom portion of Figure 1, we have shown the splitting of peaks O and E as the emission energy decreases. In Table I the energies of the split E and O components are tabulated. At the higher energy end of the emission spectrum the splitting between adjacent subpeaks is about  $2\text{ cm}^{-1}$  while at the lower energy end of the spectrum the splitting increases to about  $19\text{ cm}^{-1}$  in a continuous fashion.

#### Discussion.

**Analysis of Splittings in Spectrum by Means of an Isotopic Model.** Chlorine exists naturally as  $^{35}\text{Cl}$  (75%) and  $^{37}\text{Cl}$  (25%). In a square-planar complex of the type  $\text{PtCl}_4^{2-}$  this could lead to five possible isomers  $\text{PtX}_i\text{Y}_{4-i}^{2-}$  ( $i = 0-4$ ). In

Table II the relative abundances of the various isomeric species are given along with the differences in energies ( $\text{cm}^{-1}$ ) for one quantum of the  $a_{1g}$  symmetric stretch mode excited.

A normal-mode analysis of the  $\text{PtCl}_4^{2-}$  complex vibrational motions<sup>5</sup> shows that the symmetric stretch  $a_{1g}$  mode energy ( $\text{cm}^{-1}$ ) depends on the square root of the chlorine mass and not on the platinum mass. Thus

$$\bar{\nu}_{37} = \bar{\nu}_{35}(M_{35}/M_{37})^{1/2} \quad (1)$$

and the separation in  $\text{cm}^{-1}$  between  $\text{Pt}(^{35}\text{Cl})_4^{2-}$  and  $\text{Pt}(^{37}\text{Cl})_4^{2-}$  for one quantum of  $\nu_1(a_{1g})$  is

$$\Delta\bar{\nu} = \bar{\nu}_{35}[1 - (35/37)^{1/2}] = 9.2\text{ cm}^{-1} \quad (2)$$

However, in the  $\text{PtCl}_4^{2-}$  case under discussion, five isomers

**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	Ener- gy, <sup>a</sup> cm <sup>-1</sup>	En- ergy diff, cm <sup>-1</sup>
Pt <sup>35</sup> Cl <sub>4</sub> <sup>2-</sup>	1 × (3/4) <sup>4</sup> × (1/4) <sup>0</sup> = 81/256	337.1	
Pt <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sup>2-</sup>	4 × (3/4) <sup>3</sup> × (1/4) <sup>1</sup> = 108/256	334.8	2.3
Pt <sup>35</sup> Cl <sub>2</sub> <sup>37</sup> Cl <sub>2</sub> <sup>2-</sup>	6 × (3/4) <sup>2</sup> × (1/4) <sup>2</sup> = 54/256	332.4	2.4
Pt <sup>35</sup> Cl <sup>37</sup> Cl <sub>3</sub> <sup>2-</sup>	4 × (3/4) <sup>1</sup> × (1/4) <sup>3</sup> = 12/256	330.1	2.3
Pt <sup>37</sup> Cl <sub>4</sub> <sup>2-</sup>	1 × (3/4) <sup>0</sup> × (1/4) <sup>4</sup> = 1/256	327.9	2.2

<sup>a</sup> Energies based on the energy of the symmetric stretch mode of K<sub>2</sub>PtCl<sub>4</sub>, 335 cm<sup>-1</sup> [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<sup>-1</sup>. If  $n$  quanta of the  $a_{1g}$  mode are excited in a PtCl<sub>4</sub><sup>2-</sup> complex, then the spacing between adjacent isomer peaks is ( $n \times 2.3$ ) cm<sup>-1</sup>. This can be proven as follows. For an isotopic species,  $a$ , undergoing an electronic transition, we can write<sup>4</sup>

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

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

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

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

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

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<sub>4</sub><sup>2-</sup>. There is always the danger that some PtCl<sub>6</sub><sup>2-</sup> 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<sub>2</sub>PtCl<sub>4</sub>, 13820-34-3; Cs<sub>2</sub>ZrCl<sub>6</sub>, 16918-86-8; Pt<sup>35</sup>Cl<sub>4</sub><sup>2-</sup>, 58832-54-5; Pt<sup>35</sup>Cl<sub>3</sub><sup>37</sup>Cl<sup>2-</sup>, 58865-37-5; Pt<sup>35</sup>Cl<sub>2</sub><sup>37</sup>Cl<sub>2</sub><sup>2-</sup>, 58832-55-6; Pt<sup>35</sup>Cl<sup>37</sup>Cl<sub>3</sub><sup>2-</sup>, 58865-38-6; Pt<sup>37</sup>Cl<sub>4</sub><sup>2-</sup>, 58832-56-7.

## References and Notes

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# Correspondence

## Distortions in Seven-Coordinate Complexes. Extension of the Dihedral Angle Method<sup>1,2</sup> 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.<sup>3</sup> 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<sup>3</sup> 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)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>][BPh<sub>4</sub>] 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".<sup>4</sup>

Muetterties and Guggenberger<sup>2</sup> have applied the approach of Porai-Koshits and Aslanov<sup>1</sup> 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