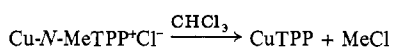


Experimental Section

To prepare $\text{Cu-}N\text{-MeTPP}^+\text{Cl}^-$, a fivefold molar excess of $\text{CuCl}\cdot 2\text{H}_2\text{O}$ was added to $H\text{-}N\text{-MeTPP}$ in methanol and stirred overnight. The methanol was evaporated and the resulting solid taken up in benzene and filtered. The solution was passed through a dry alumina column and eluted with benzene to remove CuTPP . The copper-chloro complex was eluted with 1% MeOH in C_6H_6 and the solvent was immediately removed by flash evaporation. The complex was then dried under vacuum at 100°C . Anal. Calcd for $\text{Cu-}N\text{-MeTPP}^+\text{Cl}^-$, $\text{C}_{45}\text{H}_{31}\text{N}_4\text{CuCl}$: C, 74.37; N, 7.71; H, 4.30; Cu, 8.74. Found: C, 74.50; N, 7.54; H, 4.64; Cu, 8.77. Absorption band of $\text{Cu-}N\text{-MeTPP}^+\text{Cl}^-$ in CHCl_3 (25°C): 672 nm ($\log E_{\text{max}} = 3.60$), 617 nm (3.82), 537 nm (3.80), 452 nm (4.95).

Results and Discussion

When dissolved in CHCl_3 , $\text{Cu-}N\text{-MeTPP}^+\text{Cl}^-$ spontaneously transforms into CuTPP in a first-order fashion. The reaction shows no deviation from first-order kinetics over 3 half-lives and the observed rate was independent of total porphyrin concentration from ca. 10^{-4} to 10^{-6} M. The half-life was 75.0 ± 1.0 min at 25.5°C ; $\Delta H^\ddagger = 24.4 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = +3.7 \pm 1.0$ eu. Excellent isosbestic points were found as the reaction proceeded and the product CuTPP was identified by the position and intensities of its absorption bands. Acid demetalation of the resulting CuTPP produced H_2TPP . The NMR spectra of a distilled fraction of the product solution gave a singlet at 3.1 ppm characteristic of CH_3Cl and flushing the solution with nitrogen caused the resonance of the gaseous CH_3Cl to disappear. Spectrophotometrically, 1 mol of CuTPP was produced from 1 mol of reactant. The reaction is



This reaction also occurred in C_6H_6 , CH_2Cl_2 , and CCl_4 but was orders of magnitude slower in CH_3OH or $\text{CH}_3\text{OH}-\text{C}-\text{HCl}_3$. The methanol presumably solvates the porphyrin and chloride, forming the outer-sphere adduct ($\text{Cu-}N\text{-MeTPP}^+\text{Cl}^-$) which is less reactive than the inner-sphere ion-pair form.

This free base $H\text{-}N\text{-MeTPP}$ shows no evidence of demethylation after weeks in CHCl_3 . As another indication of the metal ion specificity of such reactions, $\text{Zn-}N\text{-MeTPP}^+\text{Cl}^-$ can be refluxed without change for hours in CHCl_3 , while the copper adduct decomposes in minutes under similar conditions.

This simple reaction is novel insofar as the spontaneous demethylation of a metallo- N -methylporphyrin in the absence of added nucleophiles has not been reported. The fact that this copper porphyrin type has never heretofore been isolated may be due to its spontaneous decomposition under the usual porphyrin recrystallization conditions and it is noted that this adduct has always been prepared in situ for solution studies.⁷ Further work is in progress on the anion, metal, and porphyrin influences in these presumed ion-pair, metal-assisted acid-base reactions.

Acknowledgment. We thank ERDA, Contract No. E-(40-1)-4047, for financial support.

Registry No. $\text{Cu-}N\text{-MeTPP}^+\text{Cl}^-$, 51552-51-3; CuTPP , 14172-91-9; MeCl , 74-87-3.

References and Notes

- (1) B. Shah, B. Shears, and P. Hambright, *J. Am. Chem. Soc.*, **93**, 776 (1971); *Inorg. Chem.*, **10**, 1818 (1971); D. K. Lavalley and A. E. Gebala, *ibid.*, **13**, 2004 (1974); R. C. Ellingston and A. H. Corwin, *J. Am. Chem. Soc.*, **68**, 1112 (1946); M. F. Hudson and K. M. Smith, *Tetrahedron Lett.*, **26**, 2223 (1974).
- (2) H. Ogoshi, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, **95**, 1666 (1973).
- (3) H. Ogoshi, E. Watanabe, N. Koketzu, and Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, 943 (1974).
- (4) H. J. Callot and T. Tschamber, *J. Am. Chem. Soc.*, **97**, 6175 (1975).
- (5) B. Shears and P. Hambright, *Inorg. Nucl. Chem. Lett.*, **6**, 679 (1970).
- (6) D. Lavalley, *Inorg. Chem.*, **15**, 691 (1976).

Contribution from the Department of Chemistry,
University of Notre Dame, Notre Dame, Indiana 46556

Stereochemistry of Low-Spin Cobalt Porphyrins. 8.
 $\alpha,\beta,\gamma,\delta$ -Tetraphenylporphinatocobalt(II)

Paul Madura and W. Robert Scheidt*

Received August 9, 1976

AIC605565

There has been considerable recent interest in the stereochemistry of low-spin cobalt porphyrins, and structure determinations for a variety of derivatives have come from our laboratories¹⁻⁷ and others.⁸⁻¹¹ Despite this, the molecular stereochemistry of the simplest member of the class, a four-coordinate cobalt(II) porphyrin, has not been determined. We report herein the molecular stereochemistry of one such four-coordinate derivative, as found in tetragonal crystals of $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II), to be written as CoTPP . CoTPP crystallizes in the same tetragonal system as that observed for the tetraphenylporphinate derivatives of iron(II),¹² nickel(II),¹³ and copper(II);¹⁴ the M(II)-N bond lengths in this sequence are thus subject to the same constraints of crystal packing.

Experimental Section

CoTPP was prepared by the method of Adler et al.¹⁵ Attempts to prepare crystals of CoTPP from a variety of solvents yielded only very fine needles, which were unsatisfactory for diffraction studies. Acceptable crystals were obtained from diethyl ether. CoTPP was placed in a Soxhlet extractor and extracted with diethyl ether for 3 days; well-formed tetragonal-bipyramidal crystals were found in the solvent flask.

Preliminary examination of crystals of CoTPP established that the Laue symmetry and systematic absences were consistent with the choice of two tetragonal space groups,¹⁶ $I4_1md$ and $I42d$. Lattice constants $a = 15.062$ (4) Å and $c = 13.954$ (5) Å (λ 0.71069 Å) came from a least-squares refinement that utilized the setting angles of 29 reflections, each collected at $\pm 2\theta$, given by the automatic centering routine supplied with the Syntex $P1$ diffractometer. These constants led to a calculated density of 1.41 g/cm³ for a cell content of four CoTPP molecules; the experimental density was 1.42 g/cm³. All measurements were made at the ambient laboratory temperature of $20 \pm 1^\circ\text{C}$. The crystal used in all measurements was a truncated tetragonal bipyramid with a basal edge of 0.45 mm and a length of 0.23 mm along the unique axis; the unique axis was approximately parallel to the mounting axis.

Diffracted intensities were measured by θ - 2θ scanning using graphite-monochromated $\text{Mo K}\alpha$ radiation. The scan range used was 0.8° below $\text{K}\alpha_1$ to 0.8° above $\text{K}\alpha_2$. Backgrounds were estimated by profile analysis.¹⁷ Two equivalent forms of data to $(\sin \theta)/\lambda \leq 0.758$ Å⁻¹ were measured and averaged. Four standard reflections, measured periodically, showed no trend with time. Variable 2θ scan rates were used as described previously;³ the slowest was $0.5^\circ/\text{min}$ and the fastest was $6.0^\circ/\text{min}$. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, without correction for the absorption of x radiation. The maximum error in any structure amplitude arising from the neglect of absorption was estimated to be $\sim 3\%$. Reflections having $F_o > 3\sigma(F_o)$ were taken to be observed. A total of 1157 unique data were taken to be observed, 82% of the theoretical number possible within the range of $(\sin \theta)/\lambda$ examined.

The choice of $I42d$ as the probable space group follows that of the isomorphous crystals of FeTPP ¹² and CuTPP and PdTPP ¹⁴ and was confirmed by all subsequent details of the structure solution and refinement. Initial coordinates for CoTPP were taken from those reported for CuTPP .¹⁴ Full-matrix least-squares refinement,¹⁸ with anisotropic thermal parameters and standard values for the atomic form factors,¹⁹ smoothly converged. A Fourier difference synthesis gave the approximate positions of all hydrogen atoms in the asymmetric unit of structure; these atoms were then assigned to theoretically calculated positions ($\text{C-H} = 0.95$ Å), with isotropic thermal parameters fixed one unit higher than those of the associated carbon atoms, and their contributions to the calculated structure amplitudes were included in subsequent cycles of refinement. Inclusion of the

Table I. Structural Parameters of the Atoms in Crystalline CoTPP^a

Atom type	Fractional coordinates			Anisotropic thermal parameters, Å ²					
	10 ⁴ x	10 ⁴ y	10 ⁴ z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Co	0	0	0	2.10 (4)	2.10 (4)	3.50 (3)	0	0	0
N	1117 (2)	652 (2)	-17 (2)	2.4 (1)	2.2 (1)	3.9 (1)	0.0 (1)	0.0 (1)	-0.1 (1)
C ₁	1959 (2)	328 (2)	181 (3)	2.2 (1)	2.9 (1)	4.5 (2)	-0.1 (1)	-0.3 (1)	0.0 (1)
C ₂	2594 (2)	1031 (2)	169 (4)	2.4 (1)	3.2 (1)	6.4 (2)	-0.4 (1)	-0.4 (1)	0.0 (2)
C ₃	2160 (2)	1781 (2)	-67 (4)	2.7 (1)	2.9 (1)	6.5 (2)	-0.6 (1)	-0.5 (2)	0.4 (2)
C ₄	1234 (2)	1550 (2)	-164 (3)	2.6 (1)	2.7 (1)	4.1 (2)	-0.3 (1)	-0.1 (1)	0.1 (1)
C ₅	568 (2)	2169 (2)	-303 (3)	2.8 (1)	2.2 (1)	3.8 (2)	-0.1 (1)	-0.2 (1)	0.1 (1)
C ₆	815 (2)	3102 (2)	-556 (3)	2.6 (1)	2.4 (1)	4.5 (2)	-0.1 (1)	-0.4 (1)	0.3 (1)
C ₇	1319 (3)	4822 (2)	-1041 (4)	4.8 (2)	3.0 (2)	6.5 (2)	-0.8 (1)	-0.5 (2)	0.8 (1)
C ₈	1020 (3)	3313 (2)	-1488 (3)	4.8 (2)	3.0 (1)	4.7 (2)	-0.3 (1)	0.1 (2)	0.3 (1)
C ₉	1270 (4)	4178 (3)	-1734 (4)	6.2 (2)	3.7 (2)	5.6 (2)	-0.9 (2)	0.7 (2)	0.9 (2)
C ₁₀	856 (3)	3758 (2)	132 (3)	6.0 (2)	3.0 (1)	4.6 (2)	-0.9 (1)	0.0 (2)	0.1 (1)
C ₁₁	1104 (3)	4618 (2)	-103 (4)	6.2 (2)	2.8 (1)	5.9 (2)	-0.8 (1)	-0.6 (2)	-0.3 (2)

^a The figure in parentheses following each datum is the estimated standard deviation in the last significant figure.

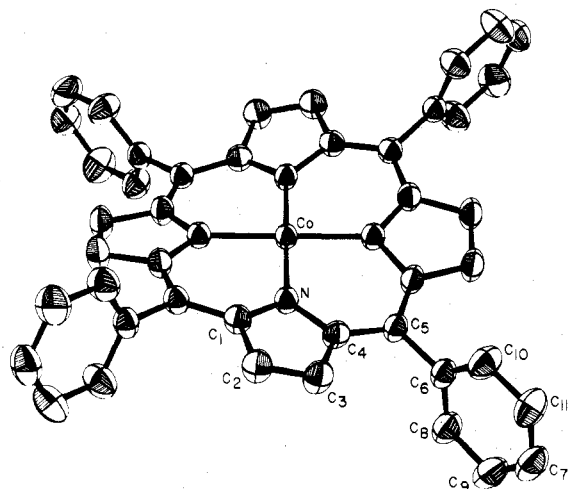


Figure 1. Computer-drawn model in perspective of the CoTPP molecule. Each atom is represented by a thermal ellipsoid drawn at the 50% probability level. Each unique atom is identified with the symbol used throughout the paper.

imaginary component $\Delta f''$ of the form factor of the cobalt atom²⁰ in the refinement enabled us to conclude that the experimentally measured intensities were those of the set $\{h\bar{k}l\}$ rather than those of the originally assumed set $\{hkl\}$.

Final least-squares refinement led to a conventional residual (R_1) of 0.049 and a weighted residual (R_2) of 0.053 and an error of fit of 1.31. A final difference synthesis displayed peak density of 0.5 e/Å³ at the origin and a pair of smaller peaks (0.4 e/Å³) lying on the c axis at ± 0.92 Å from the metal atom. The atomic coordinates and the associated thermal parameters in the asymmetric unit of structure are listed in Table I. A listing of observed and calculated structure amplitudes is available.²¹

Discussion of Results

Figure 1 presents a perspective view of the CoTPP molecule. This figure also illustrates the numbering scheme employed for the unique atoms. Individual bond parameters for the porphyrinato core are presented in Table II. With four CoTPP molecules in the unit cell, the space group $I42d$ requires that the molecule observe S_4 - $\bar{4}$ symmetry. The out-of-plane displacements of individual atoms of the S_4 ruffled porphyrinato core are illustrated in Figure 2. The departures from planarity are comparable, in both magnitude and sign, to those observed in the isomorphous crystals of FeTPP,¹² CuTPP,¹⁴ and the tetragonal form of the free base, H₂TPP.²²

The unique Co-N complexing bond has a length of 1.949 (3) Å. This distance is significantly shorter than the 1.977 (6)–2.000 (4) Å range of average Co-N bond distances²³ observed in several five- and six-coordinate cobalt(II) por-

Table II. Bond Parameters of the Core in CoTPP^a

Bond Lengths, Å			
Co-N	1.949 (3)	C ₂ -C ₃	1.346 (5)
N-C ₁	1.387 (4)	C ₃ -C ₄	1.443 (5)
N-C ₄	1.378 (4)	C ₄ -C ₅	1.384 (5)
C ₁ -C ₂	1.426 (5)	C ₅ -C _{1'}	1.396 (5)
Bond Angles, Deg			
NC ₁ N'	90.00 (2)	C ₁ NC ₄	105.0 (3)
NC ₁ N''	178.6 (5)	C ₁ C ₂ C ₃	107.5 (3)
CoNC ₁	127.5 (2)	C ₂ C ₁ C _{5'}	124.6 (3)
CoNC ₄	127.4 (2)	C ₂ C ₃ C ₄	106.8 (3)
NC ₁ C _{5'}	124.9 (3)	C ₃ C ₄ C ₅	123.4 (3)
NC ₁ C ₂	110.4 (3)	C ₄ C ₅ C ₆	119.0 (3)
NC ₄ C ₅	126.0 (3)	C ₁ 'C ₅ C ₆	118.8 (3)
NC ₄ C ₃	110.3 (3)		

^a The figure in parentheses is the estimated standard deviation in the last significant figure.

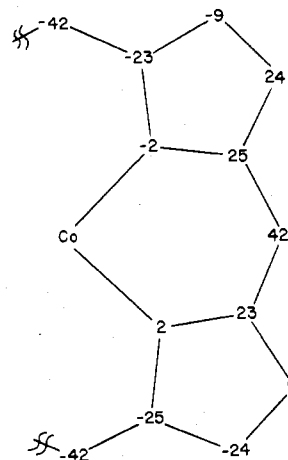


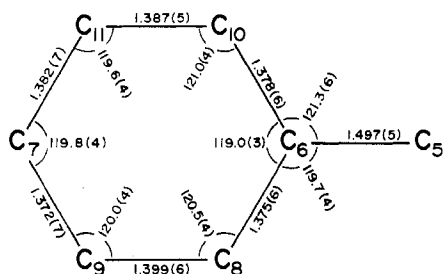
Figure 2. Diagram to illustrate the ruffling of the porphyrinato skeleton. Half of the molecule is shown, but only one-fourth of the molecule is unique. The perpendicular displacements, in units of 0.01 Å, of the atoms from the mean plane of the core are shown.

phyrins.^{3,4,6-8} This distance is also shorter than the 1.978 (6) Å average observed in two six-coordinate cobalt(II) porphyrins.^{2,9} The Co-N distance is comparable to the 1.948 (4) and 1.954 (6) Å values found, respectively, for a five-coordinate²⁴ and a six-coordinate⁵ cobalt(III) porphyrin. These two derivatives, along with CoTPP, have substantially ruffled porphyrin cores. The results for CoTPP confirm the previous suggestion⁴ that the porphyrin core conformation has a greater effect on the basal Co-N distances in the cobalt(II) and -(III) porphyrins than the oxidation state of the central cobalt atom. Thus, the Co-N distance in a cobalt(II) por-

Table III. Complexing Bond Lengths in a Sequence of Four-Coordinate Metallotetraphenylporphyrins^a

	Metal ion				
	d ⁶ Fe	d ⁷ Co	d ⁸ Ni	d ⁹ Cu	d ⁵ Mn
M-N, Å	1.972 (4)	1.949 (3)	1.928 (3)	1.981 (7)	2.082- 2.092
Spin state, <i>S</i>	1	1/2	0	1/2	5/2
Ref	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>

^a The number in parentheses is the estimated standard deviation for the bond distance. ^b Reference 12. ^c This work. ^d Reference 13. ^e Reference 14. ^f Reference 25.

**Figure 3.** Diagram of a peripheral phenyl group displaying the numbering scheme used for the atoms and the values, with estimated standard deviations, of all bond parameters.

phyrin wherein the core was nearly planar would have Co-N bond distances of 1.97–1.98 Å.

The observed M(II)-N bond distances in a sequence of MTPP derivatives are given in Table III. The presence of an electron in the $3d_{x^2-y^2}$ orbital of the d⁹ copper(II) atom and the high-spin d⁵ manganese(II) atom is clearly correlated with the M-N bond lengths and, of course, the magnetic data. The absence of such an electron in the intermediate-spin iron(II) and the low-spin cobalt(II) and nickel(II) atoms also correlates with the M(II)-N bond distances. It should be pointed out that MnTPP is anomalous not only with respect to the very large difference in the M-N bond distances but also in porphyrin core conformation. The other members of the series listed in Table III have porphyrin cores ruffled in agreement with S_4 - $\bar{4}$ symmetry; MnTPP has an expanded, nearly planar core.

The individually determined bond parameters of the peripheral phenyl group are given in Figure 3. The dihedral angle between the mean plane of the core and the phenyl ring is 80.0°. The C-C bonds of the phenyl ring that are foreshortened from the standard aromatic spacing are associated with the thermal motion of the rigid group; this phenomenon has been discussed previously.^{25,26}

The packing relationships in crystalline CoTPP are quite similar to those found in the isomorphous crystals of H₂TTP; a complete description is given in Table VI of ref 22.

Acknowledgment. We gratefully acknowledge support from the National Institutes of Health (Grant HL-15627).

Registry No. CoTPP, 14172-90-8.

Supplementary Material Available: Listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

References and Notes

- W. R. Scheidt and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8281 (1973).
- W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8289 (1973).
- W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 84 (1974).
- W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 90 (1974).
- J. A. Kaduk and W. R. Scheidt, *Inorg. Chem.*, **13**, 1875 (1974).
- P. N. Dwyer, P. Madura, and W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 4815 (1974).
- W. R. Scheidt and J. A. Ramanuja, *Inorg. Chem.*, **14**, 2643 (1975).
- R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4440 (1974).
- J. W. Lauher and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4447 (1974).
- R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4452 (1974).
- D. E. Goldberg and K. M. Thomas, *J. Am. Chem. Soc.*, **98**, 913 (1976).
- J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, *J. Am. Chem. Soc.*, **97**, 2676 (1975).
- A. A. Saylor and J. L. Hoard, to be submitted for publication.
- E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, **86**, 2342 (1964).
- A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
- "International Tables for X-Ray Crystallography", Vol. I, 3d ed, Kynoch Press, Birmingham, England, 1969, pp 199, 212.
- R. Blessing, P. Coppens, and P. Becker, *J. Appl. Crystallogr.*, **7**, 488 (1974).
- In addition to various local programs, modified versions of the following programs were employed: Busing and Levy's ORFLS least-squares, Johnson's ORTEP thermal ellipsoid plotting program, Hubbard, Quicksall, and Jacobson's ALFF Fourier program, and Busing and Levy's ORFFE error function program.
- D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968). Scattering factors for hydrogen were taken from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- Real and imaginary corrections for anomalous dispersion in the form factor for cobalt were from D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- Supplementary material.
- M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Am. Chem. Soc.*, **86**, 1938 (1964).
- All distances are cobalt-porphyrin nitrogen bond distances.
- M. E. Kastner and W. R. Scheidt, to be submitted for publication.
- J. F. Kirner, C. A. Reed, and W. R. Scheidt, submitted for publication.
- D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 6689 (1972).

Contribution from the Department of Chemistry,
University of Akron, Akron, Ohio 44325

Use of Electron Spin Resonance Data to Assist in the Assignment of Vanadyl Optical Transitions

H. A. Kuska* and J. A. Ryan

Received May 14, 1976

AIC60353G

In a review of oxovanadium(IV) chemistry Selbin¹ pointed out that more than ordering of optical assignments can fit a single set of ESR data. This is because there are two additional important variables in the appropriate equations.² They are the spin-orbit coupling constant ζ and the dipole parameter P . They have generally been considered as fixed parameters. However, it is known that they both are functions of the charge on the vanadium. Since the values of the molecular orbital coefficients are what determines the charge, it is possible to write a computer program which does an iterative charge self-consistent solution of the ESR equations, given the experimental ESR parameters and a set of optical assignments. Although this approach will not give a unique set of optical assignments for each compound, a comparison of the range of acceptable values for complexes of different covalent character should be useful in establishing the general behavior of the optical transitions.

Experimental Section

The experimental ESR values were related to the molecular orbital coefficients by²

$$g_{||} = 2.0023 - \frac{8\zeta N_{\pi_2}^2 N_{\sigma_2}^2}{\Delta\pi_2 \rightarrow \sigma_2 (I)} \left[1 - \frac{1}{2} (\lambda_{\pi_2} \lambda_{\sigma_2}) T(n) \right. \\ \left. - 3^{1/2} \lambda_{\sigma_2} S_{d,\sigma_2} - 2\lambda_{\pi_2} S_{d,\pi_2} \right] - \frac{8\zeta N_{\pi_2}^2 (1 - N_{\sigma_2}^2)}{\Delta\pi_2 \rightarrow \sigma_2 (II)} \quad (1)$$