interaction is diminished for the sulfur ligands because of the lack of $p\pi^*$–$d\pi$ interactions.

It has been established[5,6] that there is significant electron transfer from the cobalt atom to dioxygen in oxycobalto-hemoglobin and oxycobaltomyoglobin. The comparison of ^{Co}A values in Table I for the dioxygen complexes is interesting. The values increase in the order of $CoMbO_2 \sim Co(p\text{-}OCH_3)TPP\cdot(amine); O_2 < CoPPIX\cdot ME, O_2, CoPPIX\cdot MTE; O_2 < CoPPIX\cdot O_2$. This is consistent with sulfur being a better donor than nitrogen and that there is $d\pi$–$p\pi^*$ back-donation from cobalt to nitrogen but not to sulfur.

In conclusion, this EPR study showed that N_6, N_5S, N_5, and N_4S have clearly distinguishable g and hyperfine values. The assignment of EPR spectra of the various pH-dependent conformational states of Co(cyt c)[10] has been verified as a result of this work.

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Registry No. CoPPIX·py, 36544-46-4; CoPPIX·im, 41188-38-9; CoPPIX·MTE, 58512-28-0; CoPPIX·ME, 58512-29-1; CoPPIX·2py, 58526-82-2; CoPPIX·O₂, 58503-65-4; CoPPIX·MTE·O₂, 58503-64-3; CoPPIX·ME·O₂, 58503-63-2.

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(3) Abbreviations: EPR, electron paramagnetic resonance; Co(cyt c), cobaltocytochrome c; NMR, nuclear magnetic resonance; CoPPIX, cobalt protoporphyrin IX dimethyl ester; MTE, 2-(methylthio)ethanol; ME, mercaptoethanol; py, pyridine; TPP, tetraphenylporphyrin.
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d-Orbital Energies and Low-Lying Excited States of Cobalt Porphyrins

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With assumed values of the Racah parameters, B and C, and the spin–orbit coupling parameter, ζ, it was found possible to deduce the relative d-orbital energies of cobalt porphyrin systems from their ESR data. The method consisted of diagonalizing the matrix of the combined ligand field, electrostatic, and spin–orbit coupling energies and using the ground-state eigenvectors thus obtained to calculate $g_\parallel$ and $g_\perp$. The sets of the d-orbital energies which satisfied the experimental $g_\parallel$ and $g_\perp$ were used to discuss the electronic structure of the various systems. Besides the ^2E state which was the only one considered in earlier works, a ^4E state and a $^4A_2$ state were found to be important in determining the nature of the $^2A_1$ ground state. For uncoordinated cobalt porphyrins, a $^4B_2$ state was further found to be very important and the experimental $g_\parallel$ could not be accounted for without it.

Introduction

Recently, an attempt was made to calculate the d-orbital energies in cobalt porphyrins from ESR data.[1] It was found that reasonable values of the relative energies of $d_{x^2-y^2}$, d_{z^2}, and (d_{xz}, d_{yz}) could be obtained through the use of the expressions for $g_\perp$, $A_\parallel$, and $A_\perp$, derived from the first-order perturbation treatment of the spin–orbit interaction. Although the energy of d_{xy} could also be calculated from the second-order equation for $g_\parallel$, the values obtained were always too high. It was suggested that low-lying quartet states which mixed in through spin–orbit coupling might not justify the use of the perturbation technique. In the present work, the spin–orbit interaction matrix is diagonalized together with the ligand field and the electrostatic energy. The ground state (a Kramers doublet) thus derived can be used to calculate $g_\parallel$ and $g_\perp$. It is hoped that by varying the orbital energies by trial and error one may find one set of energies which will yield calculated $g_\parallel$ and $g_\perp$ in agreement with the experimental ones.

Preliminary Considerations

Griffith's original designation[2] which was used in the previous work[1] is used again here, viz.

$$|\epsilon\rangle = (1/\sqrt{2})(|2\rangle + |-2\rangle) = d_{x^2-y^2}$$

$$|\theta\rangle = |0\rangle = d_{z^2}$$

$$|\mu\rangle = (1/\sqrt{2})(|2\rangle - |-2\rangle) = id_{xy}$$

$$|1\rangle = (1/\sqrt{2})(d_{xz} + id_{yz})$$

$$|-1\rangle = (1/\sqrt{2})(d_{xz} - id_{yz})$$

In C_{4v} or D_4 symmetry, $|\epsilon\rangle$ belongs to b_1, $|\theta\rangle$ to a_1, $|\mu\rangle$ to b_2, and $|1\rangle$ and $|-1\rangle$ to e. In a truly square-planar complex such as an uncoordinated metalloporphyrin, the b_1 orbital is very much higher than all of the others which are closely spaced among themselves. Molecular orbital theory as exemplified by the extended Hückel calculations of Zerner and Gouterman[3] placed a_1 slightly above e, which in turn, was placed slightly above b_2. Simple crystal field theory, on the other hand, would place b_2 above both a_1 and e. In the presence of solvent molecules, coordinated to the fifth and/or the sixth position, a_1 would be raised above both b_2 and e. How much so would depend upon the particular case. A recent work by Walker[4] showed the gradual increase of a_1 above e in cobalt tetraphenylporphyrin systems by a series of ligands, the effect being reflected in the decrease of $g_\perp$ from 3.2 to 2.2 with the simultaneous increase of $g_\parallel$ from 1.7 to 2.05. No quantitative interpretation was offered.
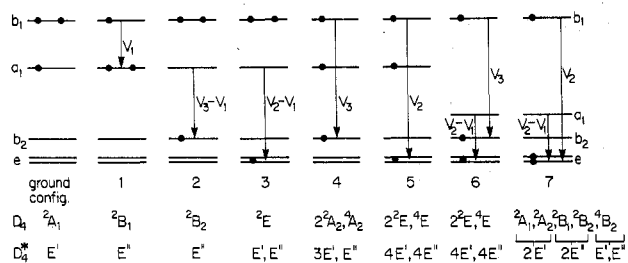
Figure 1. Ground, singly, and some doubly excited configurations in the three-hole (d⁷) system. (Note that configurations 6 and 7 are drawn with a low a_1 orbital.)

Table I. The 9 Basis Functions Which Belong to E' of D_4*

Config'n	Multiplets	States
$(b_1)^2 a_1$	$^2A_1$	$|\psi_0\rangle = |\overset{+-+}{\epsilon\bar\epsilon\theta}|,\ |\psi_0'\rangle = |\overset{+--}{\epsilon\bar\epsilon\bar\theta}|$
$(b_1)^2 e$	^2E	$|\psi_1\rangle = |\overset{+--}{\epsilon\bar\epsilon1}|,\ |\psi_1'\rangle = |\overset{+-+}{\epsilon\bar\epsilon-1}|$
$(b_1)(a_1)(e)$	^4E	$|\psi_2\rangle = |\overset{+++}{\epsilon1\theta}|,\ |\psi_2'\rangle = |\overset{---}{-1\epsilon\theta}|$
	$^2E, {}^2E, {}^4E$	$|\psi_3\rangle = |\overset{-\ -+}{\epsilon-1\theta}|,\ |\psi_3'\rangle = |\overset{-++}{1\epsilon\theta}|$
		$|\psi_4\rangle = |\overset{-\ +-}{\epsilon-1\theta}|,\ |\psi_4'\rangle = |\overset{-++}{1\epsilon\theta}|$
		$|\psi_5\rangle = |\overset{+\ --}{\epsilon-1\theta}|,\ |\psi_5'\rangle = |\overset{+++}{1\epsilon\theta}|$
$(b_1)(a_1)(b_2)$	$^2A_2, {}^2A_2, {}^4A_2$	$|\psi_6\rangle = |\overset{++-}{\epsilon\mu\theta}|,\ |\psi_6'\rangle = |\overset{-\ -+}{\epsilon\mu\theta}|$
		$|\psi_7\rangle = |\overset{+-+}{\epsilon\mu\theta}|,\ |\psi_7'\rangle = |\overset{-+-}{\epsilon\mu\theta}|$
		$|\psi_8\rangle = |\overset{-++}{\epsilon\mu\theta}|,\ |\psi_8'\rangle = |\overset{+--}{\epsilon\mu\theta}|$

In the solvent-coordinated cobalt porphyrins, one can be pretty sure that the ground state is a $^2A_1$. With uncoordinated complexes, such as cobalt porphyrins diluted in free bases, the ground state is less certain. However, past and present works have so far shown that other alternative assignments yielded totally unreasonable results.[1,2]

In the presence of the spin–orbit interaction, the $^2A_1$ state belongs to the E' (or Γ_6 in the Bethe notation) representation of the double group, D_4^* (or C_{4v}^*). In principle, all states belonging to E' mix with the ground state. Since there are 120 states in the d⁷ (or "three hole") system and since there are only two irreducible representations (E'(Γ_6) and E"(Γ_7)) appropriate for an odd-electron system, one may roughly estimate a total of 60 states which would have to be considered. Clearly, a substantial reduction in this number is highly desirable if the calculation is to be reasonably manageable.

Calculations Using the 9-Function Basis Set

A schematic diagram showing the d-orbital energies is shown in Figure 1. The relative energies V_1, V_2, and V_3 are defined as $V_1 = E(b_1) - E(a_1)$, $V_2 = E(b_1) - E(e)$, and $V_3 = E(b_1) - E(b_2)$. States derivable from each configuration in group D_4 or D_4^* symmetry are also shown in the figure. When a_1 is well above b_2 and e, such as in the case of solvent-coordinated complexes, only singly excited configurations (configurations 1–5) need be considered. All doubly excited configurations are very much higher in energy. States $^2B_1$ and $^2B_2$ from configurations 1 and 2 do not mix with the ground state through spin–orbit coupling while the remaining three singly excited configurations do. The relevant states, one ground and eight excited, which belong to E' in D_4^*, are listed in Table I. The seemingly arbitrary choice of phases is designed so that the matrices formed from the two components of E' are identical.

The matrix for the combined ligand field, electrostatic, and spin–orbit energy for the 9-function basis set is shown in Table II (supplementary material). Configuration interaction has been neglected in the electrostatic energy. When numerical values are assigned to the Racah parameters B and C, the spin–orbit coupling parameters ζ, and the ligand field energies V_1, V_2, and V_3, the total energy matrix can be diagonalized
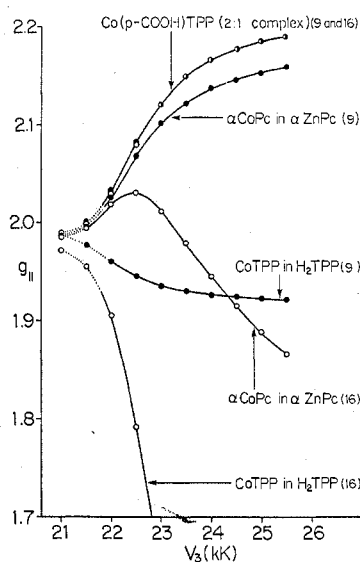
Figure 2. Plot of $g_\parallel$ against V_3. The values within the parentheses indicate the number of functions in the basis set. Dotted portions of the curves indicate that the ground state is not $^2A_1$.

Table III. Some Calculations of V_3 Using the 9-Function Basis Set

System	$g_\parallel$	$g_\perp$	Ref	Sign choice $(A_\parallel, A_\perp)$	V_1, kK	V_2, kK	V_3, kK
Co(p-COOH)TPP in py (2:1)	2.054	2.236	5	(+, −)	16.0	23.6	22.2
Co(p-OCH₃)TPP in toluene + py (1:1)	2.025	2.327	6	(+, −)	20.1	24.0	22.1
Co(p-OCH₃)TPP in toluene + py (1:1)	2.025	2.327	6	(+, +)	19.6	23.6	22.0
α-CoPc in α-ZnPc	2.007	2.422	7	(+, −)	19.3	21.1	a
α-CoPc in α-ZnPc	2.007	2.422	7	(+, +)	21.9	23.7	21.7
CoTPP in H₂TPP	1.798	3.322	9	(+, +)	31.8	28.6	b

a Ground state ^4E; $g_\parallel \approx 6$. b No proper V_3 could be obtained; $g_\parallel > 1.92$.

numerically. The eigenvector corresponding to the lowest eigenvalue

$$|+\rangle = \sum_{i=0}^{8} \eta_i |\psi_i\rangle$$

can be used for the calculation of $g_\parallel$. Thus

$$g_\parallel = 2\langle+|L_z + 2S_z|+\rangle = 2 - 2\eta_1^2 + 6\eta_2^2 - 6(\eta_3^2 + \eta_4^2 + \eta_5^2) + 8\eta_0(\eta_7 - \eta_8) \tag{1}$$

The first set of calculations was carried out with $B = 1.115$, $C = 4.366$, and $\zeta = 0.515$ kK, all free-ion values, and V_1 and V_2 previously obtained from the first-order treatment of the spin–orbit interaction.[1]

V_3 was varied and the corresponding $g_\parallel$ was calculated as described above. A plot of $g_\parallel$ against V_3 for some of the typical calculations is shown in Figure 2; see curves marked with (9). From the curves, V_3 corresponding to the experimental $g_\parallel$ can be read and some of the results are listed in Table III.

In Table III, the system CoTPP in H₂TPP represents the case in which the cobalt porphyrin is not coordinated. No proper V_3 value can be found, calculated $g_\parallel$ values being all

Table IV. Additional 7 Basis Functions in the 16-Function Basis Set

Config	Multiplets	States
$(b_1)(e)^2$	$^2A_1$, $^2A_2$	$|\psi_9\rangle = |\epsilon \overset{+}{1}\overset{+}{1}\overset{-}{1}|$, $|\psi_9{}'\rangle = |\epsilon \overset{-}{-}\overset{+}{1}\overset{-}{-}\overset{-}{1}|$
		$|\psi_{10}\rangle = |\epsilon \overset{+}{-}\overset{+}{1}\overset{+}{-}\overset{-}{1}\overset{-}{1}|$, $|\psi_{10}{}'\rangle = |\epsilon \overset{-}{1}\overset{+}{1}\overset{-}{1}|$
	$^4B_2$	$|\psi_{11}\rangle = |\epsilon \overset{-}{1}\overset{-}{-}\overset{-}{1}|$, $|\psi_{11}{}'\rangle = |\epsilon \overset{+}{1}\overset{+}{-}\overset{+}{1}|$
$(b_1)(b_2)(e)$	^4E	$|\psi_{12}\rangle = |\epsilon \mu \overset{+}{-}\overset{+}{1}|$, $|\psi_{12}{}'\rangle = |\epsilon \mu \overset{-}{1}\overset{-}{-}|$
	^2E, ^2E, ^4E	$|\psi_{13}\rangle = |\epsilon \mu \overset{-}{1}\overset{+}{1}|$, $|\psi_{13}{}'\rangle = |\epsilon \mu \overset{+}{-}\overset{+}{1}|$
		$|\psi_{14}\rangle = |\epsilon \mu \overset{-}{1}\overset{+}{1}|$, $|\psi_{14}{}'\rangle = |\epsilon \mu \overset{+}{-}\overset{-}{1}|$
		$|\psi_{15}\rangle = |\epsilon \mu \overset{+}{1}\overset{-}{-}\overset{-}{1}|$, $|\psi_{15}{}'\rangle = |\epsilon \mu \overset{-}{-}\overset{+}{-}\overset{+}{1}|$

higher than the experimental values. Other systems of free base diluted cobalt porphyrins ran into the same trouble. In the next section, it will be shown that, for uncoordinated cobalt porphyrins, it is more appropriate to include some doubly excited configurations. Again, in Table III, the system Co-$(p$-COOH)TPP in pyridine (pyridine:porphyrin = 2:1) is representative of a six-coordinated complex. Other similar systems yielded similar results. As shown in ref 1, 1:1 solvent-coordinated cobalt porphyrins and α-CoPc in α-ZnPc represent intermediate cases. In the case of α-CoPc, the calculation suggested that the (+, +) sign combination is the correct choice while in the case of the 1:1 complex, no such decision can be made.

In concluding this section, one may say that the present calculation yields resonable values of V_3 ($\sim$22 kK) for solvent-coordinated cobalt porphyrins and for the special case of α-CoPc. It places b_2 at approximately the same level as the e orbitals. Previous calculations,[1] using the perturbation technique alone, yielded V_3 in the order of only a few kilokaysers which was totally unreasonable.

Calculations Using the 16-Function Basis Set

When the a_1 orbital is at approximately the same level as b_2 and e, as in the case of a free base diluted system, some doubly excited configurations should be included. This can be seen from Figure 1. Only two of the doubly excited configurations, 6 and 7, have been included, for these are the only ones with ligand field energies comparable to that of the singly excited configurations. All other doubly excited configurations have much higher energies.

All E' states mix with E' from the $^2A_1$ ground state. The additional states to be considered besides the nine already listed in the previous section are now listed in Table IV. The augmented portion of the 16 × 16 matrix of the ligand field, the electrostatic and the spin–orbit energies, is shown in Table V (supplementary material). Once again, the configuration interaction has been neglected.

When numerical values for B, C, ζ, V_1, V_2, and V_3 are assigned, the 16 × 16 matrix can be diagonalized. The eigenvector corresponding to the lowest eigenvalue can be expressed as

$$|+\rangle = \sum_{i=0}^{15} \eta_i |\psi_i\rangle$$

The equation for $g_\parallel$ calculated from the formula $g_\parallel = 2\langle +|L_z + 2S_z|+\rangle$ then becomes

$$g_\parallel = 2 - 2\eta_1{}^2 + 6\eta_2{}^2 - 6(\eta_3{}^2 + \eta_4{}^2 + \eta_5{}^2) + 8\eta_0(\eta_7$$
$$- \eta_8) + 4(\eta_9{}^2 - \eta_{10}{}^2) - 8\eta_{11}{}^2 + 2(\eta_{12}{}^2 - \eta_{13}{}^2 - \eta_{14}{}^2$$
$$- \eta_{15}{}^2) - 8\eta_1(\eta_{14} - \eta_{15}) \qquad (2)$$

The other component of the Kramers doublet, $|-\rangle$, has the same coefficients as $|+\rangle$ with the corresponding "primed states" $|\psi_0{}'\rangle$, $|\psi_1{}'\rangle$, ..., $|\psi_{15}{}'\rangle$. The $|+\rangle$ and the $|-\rangle$ states can
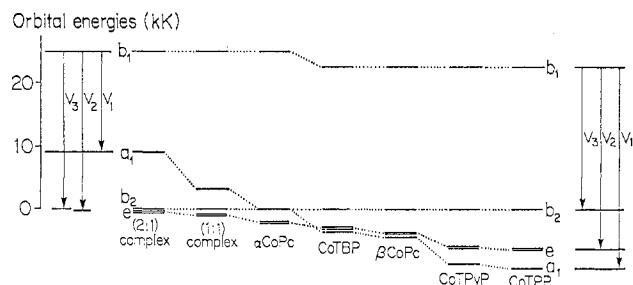
Figure 3. Derived orbital energy levels for some cobalt porphyrin systems (b_2 orbital as the reference).

be used in deriving an expression for $g_\perp$ which turns out to be

$$g_\perp = 2\langle -|L_x + 2S_x|+\rangle$$

where

$$\langle -|L_x|+\rangle = \sqrt{6}\eta_0\eta_1 - \sqrt{2}\eta_0(\eta_4 - \eta_5) - \sqrt{2}(\eta_3\eta_6 + \eta_4\eta_7$$
$$+ \eta_5\eta_8) - \sqrt{2}\eta_1\eta_{10} + \sqrt{6}\eta_2\eta_{11} - \sqrt{6}(\eta_3 - \eta_4)\eta_9$$
$$+ \sqrt{6}(\eta_6\eta_{13} + \eta_7\eta_{14} + \eta_8\eta_{15}) - \sqrt{2}\eta_{10}(\eta_{13} - \eta_{14})$$
$$+ \sqrt{2}\eta_{11}\eta_{12}$$

and

$$\langle -|2S_x|+\rangle = \eta_0{}^2 - 2\eta_2(\eta_3 + \eta_4 + \eta_5) + 2(\eta_6\eta_7 + \eta_6\eta_8$$
$$+ \eta_7\eta_8) + 2\eta_9\eta_{10} + 2\eta_{12}(\eta_{13} + \eta_{14} + \eta_{15}) \qquad (3)$$

The first calculation using the 16-function basis set was to check if the increase from 9 to 16 basis functions would result in a significant change in the calculated $g_\parallel$ values. The results of some calculations have already been included in Figure 2. One can see that, for cobalt porphyrins coordinated with two molecules of pyridine, the two curves, one for the 9 and the other for the 16 basis functions, are found to be coincident. This means that V_1 is sufficiently small (16 kK) and a_1 is sufficiently high so that all doubly excited configurations may be neglected (see Figure 1). However, for free base diluted cobalt porphyrins, the two curves are quite different. In fact, the curve for the 9 basis functions cannot reproduce the experimental $g_\parallel$ values. In such cases, the energy of a_1 is low and, in the cases studied, even below that of e ($V_1 > V_2$). The inclusion of some doubly excited configurations is found to be necessary (see Figure 1). The case of α-CoPc in α-ZnPc is intermediate in nature, and the two curves for the 9 and the 16 basis functions are nearly coincident in some region.

For uniformity of treatment, the 16-function basis set was used for all subsequent calculations, i.e., including solvent-coordinated complexes. It was found, futher, that eigenstates which yielded $g_\parallel$ in agreement with the experimental values did not reproduce the $g_\perp$ values in general. This was due to the fact that V_1 and V_2 had been derived from the perturbation technique in the calculations described so far. It was decided that the values of V_1 and V_2 from perturbation must only be used as a guide and must be allowed to vary somewhat. In what follows, V_1, V_2, and V_3 are all allowed to vary by trial and error. The final set of V_1, V_2, and V_3 which satisfactorily reproduces $g_\parallel$ and $g_\perp$ simultaneously for some representative systems is shown in Table VI.

To facilitate the discussion in the final section two graphs are presented in Figures 3 and 4. Figure 3 shows the d-orbital energy levels for some of the typical cobalt porphyrin systems as derived by the procedure described above. Figure 4 shows the corresponding zeroth-order (ligand field plus electrostatic)

Table VI. Final Sets of V_1, V_2, and V_3 Which Yield Calculated $g_\parallel$ and $g_\perp$ in Agreement with the Experimental Values, Using the 16-Function Basis Set

Systems	$g_\parallel$ (exptl)	$g_\perp$ (exptl)	Ref	V_1, kK	V_2, kK	V_3, kK	$g_\parallel$ (calcd)	$g_\perp$ (calcd)
Co(p-COOH)TPP in py (2:1)	2.054	2.236	5	16.0	25.0	25.0	2.056	2.240
Co(p-OCH$_3$)TPP in toluene + py (1:1)	2.025	2.327	6	21.9	26.0	25.0	2.026	2.342
α-CoPc in α-ZnPc	2.007	2.422	7	25.0	27.0	25.0	2.009	2.421
β-CoPc in H$_2$Pc	1.89	2.94	7	26.9	26.1	22.6	1.909	2.942
CoTBP in H$_2$TBP	1.949	2.901	8	26.0	25.7	22.6	1.950	2.906
CoTpyP in H$_2$TpyP	1.774	3.218	8	31.5	28.4	22.6	1.781	3.247
CoTPP in H$_2$TPP	1.798	3.322	9	31.8	28.55	22.5	1.792	3.325
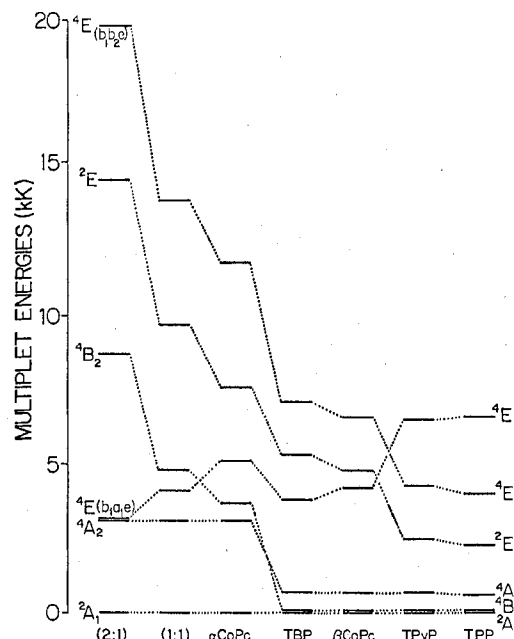
Figure 4. Zeroth-order (ligand field plus electrostatic) energies of the multiplet states for the various cobalt porphyrin systems.

energies of the important multiplet states.

Discussion

Some interesting observations and conclusions can be drawn from the present study and these are as follows.

1. By diagonalizing the matrix of the spin–orbit interaction together with the ligand field and the electrostatic energies and not merely treating the former as a perturbation, a satisfactory agreement between the calculated and the experimental $g_\parallel$ and $g_\perp$ values can be obtained.

2. Figure 3 shows that in the series going from the very ruffled TPP type [10,11] through the planar TBP type (CoTBP and βCoPc),[12,13] to the 1:1, and finally to the 2:1 solvent-coordinated complexes there is a gradual increase in the energies of both the a_1 and the e orbitals, the increase in the latter being not as prominent as that in the former. This tendency can be easily understood as follows. First, one must note that axial coordination to square-planar complexes results in the raising of a_1 through σ bonding and the e orbitals through π bonding. The ruffled structure of the TPP type porphyrins prevents the near approach of neighboring molecules in the crystal packing, while in metal phthalocyanines (β form), it has long been known that there is some axial coordination to the central metal ion by neighboring nitrogen atoms.[7,13] The effect of axial coordination due to solvent molecules, particularly those of a Lewis base, is of course most pronounced in the 2:1 and a little less in the 1:1 complexes. The crystal structure of α-CoPc is unknown but it could be that the axial coordination is somewhere in between the two extremes. In this connection, it is perhaps interesting to note the α-CoPc crystals have lower magnetic moment and higher electrical conductivity than the β polymorph.[7]

3. Although, in some cases, the a_1 orbital is calculated to be below e and b$_2$ (Figure 3), the ground state is nevertheless $^2A_1$ from configuration (b$_1$)$^2a_1$. The more favorable electrostatic energy more than offsets the less favorable ligand field energy. Although a change in the Racah parameters may alter the order of the multiplet energies, our choice is consistent with the assignment that the ground state is $^2A_1$.

4. The deviation of $g_\parallel$ and $g_\perp$ from the free-spin values as one goes from solvent-coordinated to the planar TBP and, finally, to the ruffled TPP type complexes is due to the increased mixing of the excited states. Previously, this has been attributed to the mixing of the ^2E state (i.e., ψ_1) only.[4,8] Although Griffith's second-order equations[2] introduced the mixing of $^4E(b_1a_1e)$ and $^4A_2(b_1a_1b_2)$, these equations have never been applied until recently,[1] and that was done only with limited success. The present work shows that the inclusion of $^4E(\psi_2)$ and $^4A_2(\psi_6, \psi_7, \psi_8)$ besides $^2E(\psi_1)$ can account for the deviation of $g_\parallel$ and $g_\perp$ for solvated complexes. It further shows that the mixing of $^4A_2$ is more important than that of ^4E (see Figure 4).

5. The most interesting observation derivable from this work is that, for uncoordinated complexes, there is a $^4B_2$ state (ψ_{11}) from the (e)$^2b_1$ configuration which has an energy even closer to the ground state than the $^4A_2$ (Figure 4). The contribution of ψ_{11} to the ground state is not as large as that of the $^4A_2$ states ψ_6, ψ_7, and ψ_8, but through eq 2, its effect on decreasing the calculated $g_\parallel$ is seen to be very important. This accounts for the great difference in the two $g_\parallel$ curves for CoTPP shown in Figure 2. The 9-function basis set does not include the $^4B_2$ state and cannot reproduce the experimental $g_\parallel$ value.

6. For solvent-coordinated cobalt porphyrins, the contributions of $^4E(b_1a_1e)$ and $^4A_2$ are more important than that of $^4B_2$ (Figure 4). However, although ^4E and $^4A_2$ had been included in the second-order perturbation calculations,[1] the experimental $g_\parallel$ value could not be reproduced. Diagonalization of the spin–orbit interaction matrix is still necessary but the 9-function basis set is perhaps adequate.

7. The placing of the b$_2$ orbital above both e and a$_1$ for the uncoordinated cobalt porphyrins suggests that the bonding between cobalt and the porphyrin ring may be very ionic, in agreement with a recent comment.[8] That the bonding in cobalt porphyrins is perhaps more ionic than that in the corresponding copper complex can be understood from the fact that the ionic radius of Co^{2+} (0.70 Å) is very much smaller than that of Cu^{2+} (0.92 Å) and the rigidity of the porphyrin ring prevents a closer approach of the ligand to the central metal ion.[14]

References and Notes

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New 1,3-Dithio Chelates of Nickel(II) from Reactions of Coordinated Ligands. Their Characterization and Oxidation–Reduction Properties

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A variety of transesterification and transamination reactions of the coordinated dithio ligand *O*-ethyl thioacetothioacetate have been studied. The new nickel(II) chelates have been characterized by NMR, mass, and electronic spectroscopy, with well-defined substituent effects being discerned; these effects are particularly pronounced in the electrochemical behavior of the complexes. Also reported are the synthesis and unusual redox properties of a new type of mixed 1,2- and 1,3-dithio chelate complex, viz., [(*n*-Bu)₄N][Ni(SacSac)(MNT)].

Introduction

Reactions of coordinated ligands can provide a convenient route to complexes which are difficult to obtain by more conventional means. To this end, we have examined the transesterification and transamination reactions of bis(*O*-ethyl thioacetothioacetato)nickel(II), Ni(OEt-SacSac)₂, (Ib) with
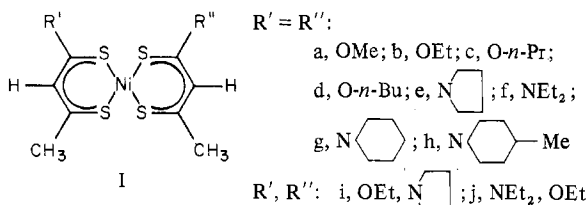
alcohols and secondary amines to provide a variety of new 1,3-dithio complexes (Ia–h). Two intermediates in the reactions have also been isolated with one 1,3-dithio ligand possessing an –OR substituent and the other an –NR₂ substituent (Ii) and (Ij). Another new type of mixed-ligand complex containing 1,2- and 1,3-dithio ligands has been formed by a ligand-scrambling reaction between Ni(SacSac)₂ and [Ni(MNT)₂]²⁻ to afford [Ni(SacSac)(MNT)]⁻ (II).
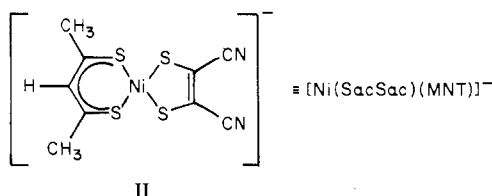
The new complexes have been characterized by spectral methods. The redox properties of these and previously known 1,3-dithio chelates of Ni(II) are compared.

Experimental Section

(A) Bis(1-ethoxy-1-thiolobut-1-ene-3-thione)nickel(II), [Ni(OEt-SacSac)₂]. This compound was prepared as previously described[1] and used as starting material in the following transesterification and transamination reactions.

(B) Bis(1-alkoxy-1-thiolobut-1-ene-3-thione)nickel(II), [Ni(OR-SacSac)₂] (R = Me, *n*-Pr, *n*-Bu). These species were prepared by the general method (B) of refluxing a basic solution of Ni(OEt-SacSac)₂ in the appropriate alcohol. Reaction times, solvents, bases, and work-up procedures are given in Table I.

(C) Bis(1-dialkylamino-1-thiolobut-1-ene-3-thione)nickel(II), [Ni(R₂N-SacSac)₂] (R₂N = Et₂N, Pyrrolidyl, Piperidyl, 4-Methylpiperidyl). These complexes were prepared by refluxing Ni(OEt-SacSac)₂ in acetone with a vast excess of the appropriate secondary amine. With pyrrolidine and piperidine, the products readily precipitated from solution. With the other amines, the disubstituted complexes were separated from mixed-ligand species by chromatography—details are in Table I.

(D) (1-Alkoxy-1-thiolobut-1-ene-3-thione)(1-dialkylamino-1-thiolobut-1-ene-3-thione)nickel(II) Compounds. (i) Ni(OEt-SacSac)(NEt₂-SacSac). Reaction of Ni(OEt-SacSac)₂ with diethylamine in acetone was followed by TLC on the reaction mixture. When the optimun yield of mixed-ligand complex was apparent, the reaction mixture was evaporated under vacuum to dryness. The pure mixed-ligand complex was obtained by chromatography and rapid recrystallization from CH₂Cl₂–petroleum ether.

(ii) Ni(OEt-SacSac)(pyrr-SacSac). The complex prepared as described in (i) was recrystallized from acetone–petroleum ether.

(E) (1-Ethoxy-1-thiolobut-1-ene-3-thione)(1,3-di(phenyl)-1-thioloprop-1-ene-3-thione)nickel(II), [Ni(OEt-SacSac)(Ph-SacPh-Sac)]. Equimolar quantities of Ni(OEt-SacSac)₂ and Ni(Ph-SacPh-Sac)₂ were refluxed in toluene for 8 h with the product distribution being monitored by TLC. The mixed-ligand complex was obtained after evaporation of solvent under reduced pressure and chromatographic separation on preparative TLC plates (silica) using toluene as solvent. This compound has only been characterized by chromatography and its NMR spectrum.

(F) Tetra-*n*-butylammonium (2-Thiolopent-2-ene-4-thione)(maleonitriledithiolato)nickelate(II), [(*n*-Bu)₄N][Ni(SacSac)(MNT)]. Equimolar quantities of Ni(SacSac)₂ and [(*n*-Bu)₄N]₂[Ni(MNT)₂] were refluxed in acetone for 3 h whereupon the solvent was removed. The residue was dissolved in CH₂Cl₂ and eluted from a silica column with CH₂Cl₂ to remove unreacted Ni(SacSac)₂. The product was then eluted with acetone. On reduction of the volume of acetone, addition of Et₂O, and cooling, crystals of the product were obtained.

Known complexes of the type Ni(R-SacR-Sac)₂, used for the redox study, were prepared by literature[2] methods and purified by chromatography.

Instrumentation. Electronic spectra were obtained on a Cary 14 spectrometer. Infrared spectra were obtained in KBr disks on a