is assumed, with J_{AB}(gem) = −13 Hz, $J_{AA'}$(vic) = 4.7 Hz, and $J_{AB'}$(vic) = 7.1 Hz. This pattern is consistent with the mode of coordination of the macrocyclic ligand in VII and also indicates a staggered conformation for the dimethylene chain, with a small difference in environment between the axial and equatorial hydrogens. This difference is most probably due to the deshielding of the axial hydrogens by electrons in the d_{z^2} orbital of the nickel(II) ion as predicted by Buckingham and Stevens.[14] Warner, Rose, and Busch[15] have also noted the difference between axial and equatorial protons of a dimethylene chain in a nickel(II) complex containing a macrocyclic ligand.

When NiTBK is heated with ethylenediamine under similar or more forcing conditions to those used with NiDMK, no reaction takes place and NiTBK is recovered unchanged from the reaction medium. It is thus apparent that the reactivity of the coordinated CO groups in complexes containing ligands of type III is dependent on the attached R group. Since the nature of the R group will affect the electron density at the carbon atom of the CO group, the extent of nucleophilic attack at that carbon atom may also be affected. The $C(CH_3)_3$ group is both electron releasing and bulky and this results in the CO group of NiTBK being less susceptible to nucleophilic attack than the CO group in NiDMK or NiMMK with methyl and phenyl substituents, respectively. We may thus conclude that reactions with amines proceed *via* attack of the amine at the carbon of the coordinated CO group, followed by elimination of a water molecule. This may be preceded by initial coordination of the amine as a unidentate ligand to the nickel. The role of the metal ion in condensations of this type is both that of an electron-withdrawing species and that of a template, holding the CO groups in cis orientation such that macrocyclic ligands may be produced by reaction with a suitable diamine.

Registry No. NiDMK, 53385-20-9; NiDMM, 53385-21-0; NiTBK, 53385-22-1.

References and Notes

(1) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
(2) D. H. Busch, *Advan. Chem. Ser.*, **No. 100**, 44 (1971).
(3) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).
(4) C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, **11**, 726 (1972).
(5) C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, **12**, 2410 (1973).
(6) G. A. Melson, *Inorg. Chem.*, **13**, 994 (1974).
(7) T. W. J. Taylor, N. H. Callow, and C. R. W. Francis, *J. Chem. Soc.*, 257 (1939).
(8) J. E. Baldwin, R. H. Holm, R. W. Harper, J. Huff, S. Koch, and T. J. Truex, *Inorg. Nucl. Chem. Lett.*, **8**, 393 (1972).
(9) V. L. Goedken and S. M. Peng, *J. Chem. Soc., Chem. Commun.*, 62 (1973).
(10) M. S. Newman and G. R. Kahle, *J. Org. Chem.*, **23**, 666 (1958).
(11) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).
(12) R. D. Archer, *Inorg. Chem.*, **2**, 292 (1963).
(13) Simulation achieved using NMRCAL, a nuclear magnetic resonance spectrum calculation program, Nicolet Instrument Corp., 1971.
(14) A. D. Buckingham and P. J. Stevens, *J. Chem. Soc.*, 4583 (1964).
(15) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 6938 (1968).

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Molecular Charge-Transfer Complexes of Metalloporphyrins with Bis(*cis*-1,2-trifluoromethylethylene-1,2-dithiolato)nickel

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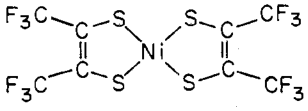
Received May 28, 1974 AIC40338G

Zinc and cobalt tetraphenylporphyrins each form 1:1 molecular complexes with the strong acceptor $Ni(S_2C_2(CF_3)_2)_2$, $Ni(tfd)_2$. The optical absorption, infrared, and electron spin resonance spectra of these 1:1 complexes have been studied. $Zn(TPP)Ni(tfd)_2$ is a Mulliken-type donor–acceptor complex with a neutral ground state showing an intermolecular charge-transfer band at approximately 1900 nm (5.26 kK). $Co(TPP)Ni(tfd)_2$ is a covalent compound having a Co–S bridging bond but nevertheless has a charge-transfer band (intramolecular) at 1370 nm (7.30 kK). The complexes disproportionate in solution, to an extent dependent on the solvent polarity. Solution thermodynamic data are presented.

Introduction

Metalloporphyrins have been studied widely in recent years because of the importance of these compounds as model systems involving photosynthesis, electron-transport, and other biologically important phenomena. Receiving perhaps the greatest attention have been the redox properties and the axial coordination tendencies of these compounds.[1-5] We were interested in the possibility of synthesizing donor–acceptor complexes of metalloporphyrins and chose to investigate reactions of the zinc and cobalt tetraphenylporphyrins with bis(*cis*-trifluoromethylethylene-1,2-dithiolato)nickel, $Ni(tfd)_2$ (**1**), which had previously been shown to be a strong acceptor capable of forming donor–acceptor charge-transfer complexes in either neutral or ionic ground states.[6-8] The zinc and cobalt complexes were chosen on the basis of their published oxidation potentials, which suggested that they might act as donors when mixed with $Ni(tfd)_2$.[9] A neutral ground-state donor–acceptor complex was formed between $Ni(tfd)_2$ and the zinc complex, but a covalent compound was obtained from the reaction of the nickel and cobalt complexes. In spite of the formal difference in the two types of compounds formed, a near-infrared charge-transfer band was found in each case, indicating that relatively low-energy excited-state pathways for charge transfer exist in these compounds.



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Experimental Section

Materials. α,β,γ,δ-tetraphenylporphine (TPP) was prepared by the method of Adler, *et al.*[10] It was washed numerous times with methanol and hot water, dried under vacuum at 56°, and purified by extraction with benzene,[11,12] followed by removal of benzene under vacuum. α,β,γ,δ-Tetraphenylporphinatozinc (Zn(TPP))[13] was prepared from zinc acetate (20-fold excess) and TPP in dimethylformamide and purified by twice eluting the red-violet band with benzene on alumina. Bis(*cis*-1,2-trifluoromethylethylene-1,2-dithiolato)nickel, $Ni(tfd)_2$, was prepared by the method of Davison, *et al.*,[14] and purified by sublimation. Tetrabutylammonium bis(*cis*-1,2-trifluoromethylethylene-1,2-dithiolato)nickelate, $(Bu_4N)[Ni(tfd)_2]$, was also synthesized by the literature method.[15] Spectroquality dichloromethane and toluene were dried before use, the former by refluxing over calcium hydride for 24 hr and the latter by distillation from sodium metal. Careful drying of these solvents was necessary if spurious reduction of neutral $Ni(tfd)_2$ was to be avoided.

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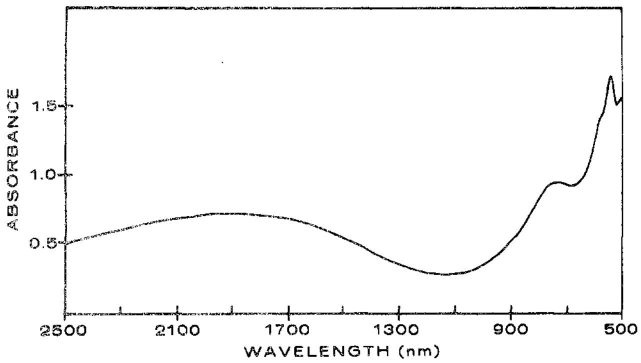

Figure 1. Optical absorption spectrum of $Zn(TPP)Ni(tfd)_2$ in KBr.

The complex between Co(TPP) and $Ni(tfd)_2$ was formed by mixing equimolar amounts of the materials in dichloromethane. The solvent was evaporated and the residue washed with pentane. Analysis was satisfactory for a 1:1 complex. *Anal.* Calcd: C, 52.80; N, 4.74; S, 10.80; H, 2.37. Found: C, 52.59; N, 4.80; S, 10.98; H, 2.58.[16] The $Zn(TPP)Ni(tfd)_2$ complex was prepared in the same fashion. *Anal.* Calcd: C, 52.50; H, 2.36; N, 4.71. Found: C, 52.54; H, 3.10; N, 4.61.[17]

Physical Measurements. Optical absorption spectra were recorded on a Beckman Model DK-1A spectrophotometer from 2500 nm to the ultraviolet cutoff for each solvent. Solid-phase spectra were obtained as pressed KBr disks. A Lauda constant-temperature circulator consisting of a thermostat, Model KB20, a cold storage vessel, Model KS, and a Model R201 electronic relay (Brinkman Instruments, Inc.) was used for obtaining spectra below room temperature. Methanol, used as the circulating liquid, was cooled in the apparatus by a methanol–Dry Ice mixture and was then pumped to the spectrophotometer cavity and circulated through an aluminum block which contained both the sample and reference cell. Infrared spectra were obtained with the Perkin-Elmer Model 225 spectrophotometer with KBr disk samples.

Esr measurements were made with a Varian Model V-4502 spectrometer equipped with a 12-in. magnet and 100-kHz field modulation. Experiments below ambient temperature employed the E-4557-9 variable-temperature accessory. Spin concentrations of solutions containing the complexes were determined by comparing the measured signal intensity to the normalized signal intensities of a series of standard $(Bu_4N)Ni(tfd)_2$ solutions in the appropriate solvent. $Ni(tfd)_2^-$ has a single unpaired electron and in solution gives a one-line esr spectrum with a *g* value of 2.061.[14] At room temperature a working curve was prepared in which the concentration of $Ni(tfd)_2^-$ was plotted *vs.* the ratio of the intensity of the nickel line to the intensity of an internal standard sample of diphenylpicrylhydrazyl (DPPH). All spectra were run at an identical nonsaturating power level and low-modulation amplitude. The concentration of the nickel complex ion in an unknown solution was then measured by noting the intensity ratio of its resonance line to that of the DPPH standard. Similar working curves were prepared for spectra obtained on solutions below ambient temperature. Concentrations obtained in this manner were reproducible to within approximately 5%.

Results

$Zn(TPP)Ni(tfd)_2$. Zn(TPP) and $Ni(tdf)_2$ reacted to give a 1:1 molecular charge-transfer complex with a neutral ground state. This conclusion was based on the optical absorption spectrum of the solid complex in KBr (Figure 1). The absorption bands at 547 and 740 nm were assigned to neutral Zn(TPP) and neutral $Ni(tfd)_2$, respectively (see Table I for band positions and intensities of compounds pertinent to this study). No spectral evidence of a redox product, either $ZnTPP^+$ or $Ni(tfd)_2^-$, was found for the solid complex, thus eliminating the possibility of an ionic ground-state complex. The broad near-infrared band at *ca.* 1900 nm, typical of molecular complexes of $Ni(tfd)_2$, was assigned as a charge-transfer (CT) transition [$DA \rightarrow D^+A^-$, where D = Zn(TPP) and A = $Ni(tfd)_2$]. Near-infrared charge-transfer bands have been observed previously for molecular complexes of $Ni(tfd)_2$ in neutral ground states with condensed hydrocarbons[6] and in the ionic ground state with phenothiazine-type donors.[7]

Table I. Absorption Maxima and Extinction Coefficients

Compd	Matrix	λ_{max}, nm	ϵ,[a] l. mol^{-1} cm^{-1}
Cobalt tetraphenylporphine (Co(TPP))	Dichloromethane	410	3.33×10^5
		526	1.87×10^4
	Toluene	410	3.0×10^5
		522	1.85×10^4
	Nitrobenzene	435	
		529	1.34×10^4
	KBr	432	
		534	
$Ni(tfd)_2$	Dichloromethane	553	1.70×10^3
		720	1.34×10^4
	Toluene	574	3.02×10^3
		750	9.60×10^3
	Nitrobenzene	725	8.47×10^3
	KBr	563	
		716	
$(Bu_4N)[Ni(tfd)_2]$	Dichloromethane	417	2.29×10^3
		508	1.28×10^3
		810	6.53×10^3
	Toluene	412	2.20×10^3
		511	1.14×10^3
		810	6.30×10^3
	Nitrobenzene	815	6.12×10^3
	KBr	508	
		811	
Zinc tetraphenylporphine	Dichloromethane	418	4.65×10^5
		508	2.98×10^3
		541	1.92×10^4
		580	3.81×10^3
		595	3.27×10^3
	KBr	529	
		562	

The infrared spectrum of the complex gave supportive information about the polarity of the ground state. The C–C stretching frequency of metal dithiolenes has proved to be a sensitive function of the charge on the complex, since the carbon–carbon double bond character increases with increasingly negative charge on the complex.[18,19] The C–C stretching frequency reported for neutral $Ni(tfd)_2$ (1422 cm^{-1}) is considerably lower than that found in $Ni(tfd)_2^-$ (1502 cm^{-1}) or $Ni(tfd)_2^{2-}$ (1534 cm^{-1}).[20] The ir spectrum of the $Zn(TPP)Ni(tfd)_2$ complex (Figure 2) showed the C–C stretch at 1420 cm^{-1}, confirming a neutral ground state for the complex. The assignment of this band was based on a careful comparison of the spectra of the unreacted donor and acceptor components with that of the reacted complex. No ir bands except those characteristic of either Zn(TPP) or $Ni(tfd)_2$ were observed.[21]

When the Zn–Ni complex was dissolved in dichloromethane, a disproportionation occurred to give a mixture of ionic and neutral components (*i.e.*, $Ni(tfd)_2$, ZnTPP, $Ni(tfd)_2^-$, and, by inference, $Zn(TPP)^+$) but no detectable Zn–Ni associated complex. This conclusion was based on the optical absorption spectrum (Figure 3) which showed the bands of both ionic and neutral $Ni(tfd)_2$ and neutral Zn(TPP) ($Zn(TPP)^+$ has no easily diagnostic band in the visible region) but no near-ir CT band. At ambient temperature, the concentrations of components calculated from a simple Beer's law analysis of the spectrum of a 1.0×10^{-4} *F* solution were 5.7×10^{-5} *M* (ionic) and 3.6×10^{-5} *M* (neutral). The slight deviation (7%) from mass balance is considered to be due to the method of analysis and not necessarily associated with the presence of other, undetected, species in solution.

$Co(TPP)(tfd)_2$. It was anticipated that $Ni(tfd)_2$ would react with Co(TPP) to form a 1:1 charge-transfer molecular complex in an ionic ground state, because the one-electron oxidation of CoTPP was reported[1] to occur at a potential approximately 300 mV less positive than the *reduction* of $Ni(tfd)_2$. The

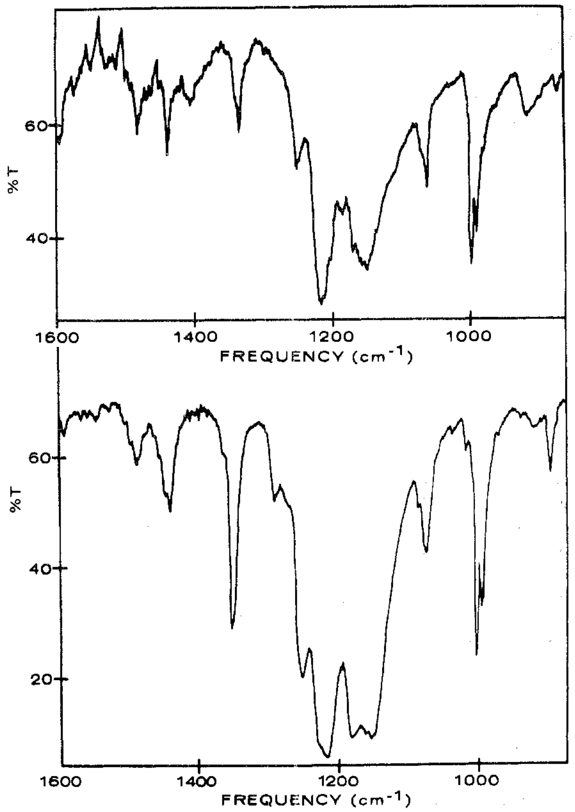

Figure 2. Partial infrared spectra (KBr disks) of Zn(TPP)Ni(tfd)$_2$ (top) and Co(TPP)Ni(tfd)$_2$ (bottom).

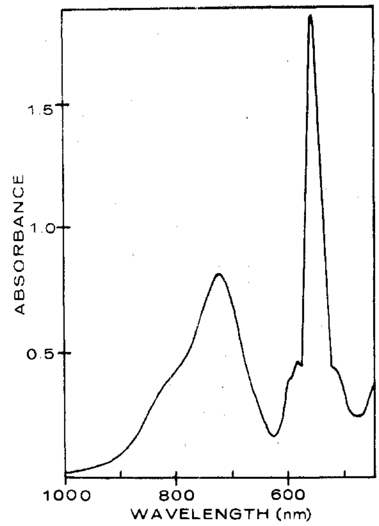

Figure 3. Optical absorption spectrum of 1 × 10^{-4} F solution of Zn(TPP)Ni(tfd)$_2$ in dichloromethane at ambient temperature.

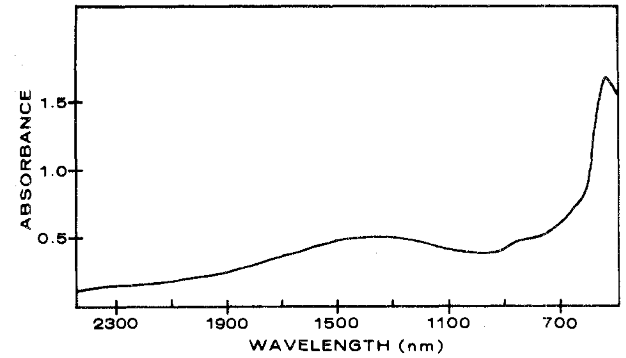

Figure 4. Optical absorption spectrum of Co(TPP)Ni(tfd)$_2$ in KBr.

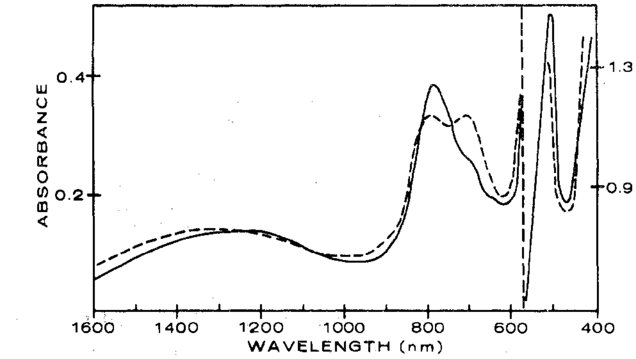

Figure 5. Optical absorption spectrum of a 1 × 10^{-4} F solution of Co(TPP)Ni(tfd)$_2$ in dichloromethane at (- - -) +15° and (——) −25°. The vertical dashed line indicates a change in the absorbance scale.

spectrum of the solid Co(TPP)Ni(tfd)$_2$ complex (Figure 4) showed a near-ir charge-transfer type absorption band and the band at 544 nm was consistent with the red shift observed in the oxidation of Co(TPP) to Co(TPP)$^+$,[1] but the spectrum did not otherwise support this expectation. The band *ca.* 800 nm, in the range of the Ni(tfd)$_2^-$ absorption, was of too low intensity (perhaps suggesting that some nickel monoanion was formed in handling or in the KBr preparation), and a new band was present at 650 nm. Confirming evidence for the covalent nature of the complex was obtained by consideration of the absorption spectra obtained at various temperatures after dissolving the complex in dichloromethane (Figure 5). It was found (*vide infra*) that mass balance calculations involving ionic and neutral uncomplexed species and the Co–Ni complex were only successful when it was assumed that the Co–Ni complex did not directly contribute to the intensity of either the 720-nm band (Ni(tfd)$_2$) or the 810-nm band (Ni(tfd)$_2^-$). This observation ruled out formulation of the Co–Ni complex as a classical donor–acceptor complex and meant that a covalent compound of Co(TPP) and Ni(tfd)$_2$ was being formed, a conclusion confirmed by the X-ray crystal structure determination of Co(TPP)Ni(tfd)$_2$ recently completed by Hermann and Wing.[22] They found that the two metal complexes were covalently bound between the cobalt atom of the Co(TPP) and one of the sulfurs in the nickel complex, with a Co–S bond distance of 2.293 Å, about 0.1 Å shorter than the Co–S bridging bond in the Co(tfd)$_2$ dimer.[22] Thus, the Co–Ni complex is better viewed as one in which oxidative addition to the cobalt compound has taken place, resulting in a formal Co(III) species. The donation of charge from the cobalt moiety to the nickel moiety allows the complex to be described formally as Co(TPP)$^{\delta+}$Ni(tfd)$_2^{\delta-}$, and the near-infrared absorption band is the result of *intra*molecular charge transfer from a charge-separated ground state to a neutral excited state. This is the analog of the *inter*molecular "reverse" charge transfer noted for ionic ground state true donor–acceptor complexes of Ni(tfd)$_2$ with other strong donors.[7] Wing and Hermann have noted[22] that the bond lengths observed in this complex are also consistent with a reduced Ni(tfd)$_2$ moiety. It was hoped that the infrared spectrum of the complex would yield supportive evidence for the polarity of the ground state, as was the case with Zn(TPP)Ni(tfd)$_2$, but the spectrum (Figure 2) is very complex in the 1400–1520-cm^{-1} region due to incomplete resolution of the bands of the nickel and cobalt moieties, and no firm conclusions could be made. It was apparent that the nickel C–C absorption had been shifted considerably above the 1420 cm^{-1} of the neutral species, however. The ir band at 900 cm^{-1} was assigned to a S=C stretch typically prominent[18] in adducts of metal dithiolenes.

Solution Behavior of Co(TPP)Ni(tfd)$_2$. The electronic absorption spectrum of a 1.0 × 10^{-4} F solution of Co-

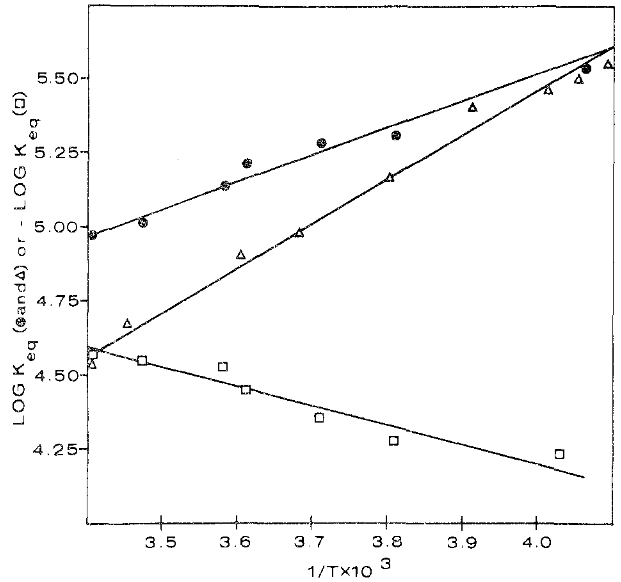

Figure 6. van't Hoff plots of equilibrium constant-temperature data for $Co(TPP) + Ni(tfd)_2 \rightleftharpoons Co(TPP)Ni(tfd)_2$ in dichloromethane (●, equilibrium 1 in eq I), $Co(TPP)Ni(tfd)_2 \rightleftharpoons Co(TPP)^+ + Ni(tfd)_2^-$ in dichloromethane (□, equilibrium 2 in eq I), and $Co(TPP) + Ni(tfd)_2$ in toluene (△).

(TPP)Ni(tfd)$_2$ in dichloromethane at 22° showed resolved bands due to Ni(tfd)$_2$, Ni(tfd)$_2^-$, Co(TPP), and the Co–Ni complex. The 590-nm band of Co(TPP)$^+$ was seen as a shoulder on the Co(TPP) 527-nm band. The situation was thus similar to that previously observed in the Ni(tfd)$_2$–phenothiazine system, successfully treated[7] in terms of the model in eq I, in which a donor–acceptor complex in an ionic

$$D + A \overset{k_1}{\rightleftharpoons} DA \overset{k_2}{\rightleftharpoons} D^+ + A^- \qquad (I)$$

ground state (*i.e.*, phenothiazine$^+$–Ni(tfd)$_2^-$) was in equilibrium with both free ions and noninteracting neutral compounds. A comparable model is appropriate in the present case (D = Co(TPP)), with the modification that the DA complex now has covalent character. The temperature dependence of the absorption spectra was such that at lower temperatures the Ni(tfd)$_2^-$ band increased in intensity and the Ni(tfd)$_2$ band decreased. When the temperature was again raised to room temperature the original spectrum was regenerated. The reversibility of the temperature effect demonstrated that the increase in Ni(tfd)$_2^-$ concentration was not caused by decomposition due to contamination of the solution by water or other reducing agents. In Figure 5 the spectra of Co(TPP)Ni(tfd)$_2$ in dichloromethane at +15 and −25° are shown. The 650-nm band seen in the solid, covalent, Co(TPP)Ni(tfd)$_2$ spectrum appeared at the lower temperatures. This band was probably hidden at higher temperatures by the more intense Ni(tfd)$_2$ band at 720 nm. Using appropriate extinction coefficients from Table I for the various components in the mixture, concentrations of the species involved in eq I were determined from the absorption spectra. Equilibrium constants obtained from these data were used to construct van't Hoff plots (Figure 6) from which the thermodynamic data involved with equilibria 1 and 2 in eq 1 were determined (Table II).

When excess tetrabutylammonium perchlorate (1.3 × 10^{-1} *F*) was added to a solution of the Co–Ni complex at room temperature, a simplified spectrum was obtained in which the only bands were at 540 nm (Co(TPP)$^+$) and 810 nm (Ni(tfd)$_2^-$), indicating that disproportionation of the complex into the free ions had occurred. The intensity of the 810-nm band indicated that the nickel complex had been totally converted to its free ionic form.

Table II. Thermodynamic Values Obtained for Equilibria 1 and 2 in Eq I from the Data of Figure 6, for the Case of $Co(TPP)Ni(tfd)_2$

Thermodynamic function	Solvent	Co(TPP)Ni(tfd)$_2$	(phenothiazine)Ni(tfd)$_2$[c]
ΔG_1	CH_2Cl_2	−6.7[a,b]	−3.5[b]
ΔG_2		6.2	5.4
ΔH_1		−5.0	−12.8
ΔH_2		−3.1	4.4
ΔS_1		5.8	−30.8
ΔS_2		−31.6	−3.3

Thermodynamic function	Solvent	Co(TPP)Ni(tfd)$_2$	Co(p-CH$_3$)(TPP)py[d]
ΔG_1	Toluene	−6.1	−3.7
ΔH_1		−7.0	−8.5
ΔS_1		−3.1	−16

[a] ΔG and ΔH values in kcal/mol; ΔS values in cal/deg mol. [b] Values for Co(TPP)Ni(tfd)$_2$ reported for 294°K; values for (phenothiazine)Ni(tfd)$_2$ reported for 300°. [c] Data from ref 7. [d] Data from ref 24.

Table III. Free-Ion Concentrations of $Co(TPP)^+$ and $Ni(tfd)_2^-$ in a 1.0 × 10^{-4} *F* Solution of $Co(TPP)Ni(tfd)_2$ in CH_2Cl_2[a]

	% ions			% ions	
Temp, °K	by esr	by optical spectroscopy	Temp, °K	by esr	by optical spectroscopy
295	36.5	33.6	248	56.4	50.2
287	41.6	37	238	65.4	
276	43.9	42	229	68.8	
267	49.2	46	208	74.0	
258	53.0	49			

[a] In the esr experiments, the Ni(tfd)$_2^-$ signal was monitored, and it was assumed that [Co(TPP)$^+$] = [Ni(tfd)$_2^-$].

A 1.0 × 10^{-4} *F* solution of Co(TPP)Ni(tfd)$_2$ in toluene failed to show absorption due to Ni(tfd)$_2^-$. Bands due to neutral Ni(tfd)$_2$, neutral Co(TPP), and the Co–Ni complex (1360 nm) were the only ones observed. The apparent lack of free ions in this solvent was undoubtedly due to the lower dielectric constant of toluene. When intensity differences between the toluene spectra of the Co–Ni complex and those of the free neutral components were ascribed to a residuum of ionic species, an ionic content of approximately 4% of the formal concentration was calculated. Taken by itself, this would not be firm evidence for the presence of ions, but the esr results (*vide infra*) were able to confirm this level of formation of ions. The molar absorbancy coefficient for the CT band of the Co–Ni complex was calculated to be 3.6 × 10^3 l. mol^{-1} cm^{-1} (this value was 3.1 × 10^3 l. mol^{-1} cm^{-1} in CH$_2$Cl$_2$).

Variable-temperature absorption spectroscopy similar to that performed on CH$_2$Cl$_2$ solutions of the complex yielded the thermodynamic data in Figure 6 and Table II.

Measurement of the Free-Ion Concentrations by Electron Spin Resonance. The esr spectra of solutions of the Co–Ni complex were very simple, showing only the single line of Ni(tfd)$_2^-$ (g = 2.060, observed; 2.061, lit.[14]). The esr spectrum of the paramagnetic Co(TPP) is not observed in fluid solutions, and Co(TPP)$^+$ has been reported to be diamagnetic.[1] Very careful measurements of the Ni(tfd)$_2^-$ intensities *vs.* a reference, as described in the Experimental Section, allowed a determination of the ionic concentrations in these solutions which was independent of the optical spectra. Straight-line working curves were obtained using the described procedure in the concentration range 10^{-6} to 10^{-4} *M*. Table III gives a summary of the free ion concentrations of the Co–Ni complex solutions as determined by the esr method and by optical spectroscopy. The agreement was satisfactory, considering the recognized difficulty of the quantitative esr method and the complexity of the optical spectra.

Discussion

There are interesting similarities and differences in the action of Ni(tfd)$_2$ on Zn(TPP) and Co(TPP). The zinc–nickel complex is quite obviously a Mulliken-type donor–acceptor complex in a neutral ground state,[23] stabilized by nonbonding forces. Since the redox potentials of Zn(TPP) and Ni(tfd)$_2$ are so close,[9] dissolution of the Zn–Ni complex provided sufficient solvation energy of the free ions to lead to substantial, though incomplete, conversion to Zn(TPP)$^+$ and Ni(tfd)$_2{}^-$ in dichloromethane. Co(TPP) and Ni(tfd)$_2$ did not form a simple DA complex. Instead, a covalent complex similar to oxidative addition products of Co(TPP) was obtained. The enthalpy of formation of the Co(TPP)Ni(tfd)$_2$ complex in toluene, −7.0 kcal/mol, can be compared to the value found by Walker,[24] −8.5 kcal/mol, for the formation of a 1:1 complex in the same solvent between tetra(*p*-methoxyphenyl)porphinatocobalt(II) and pyridine. A fairly substantial Co–S bond is indicated by this comparison. The model proposed for the interaction of Co(TPP) and Ni(tfd)$_2$, eq I, may be seen as similar to the equilibrium reported by Schrauzer and Sibert[25] between cobalamin and thiols in aqueous solution, where the cobalt(III) aquocobalamin and the thiol reversibly form a complex in which the cobalt remains in the +3 oxidation state, but which dissociates to form Co(II) and neutral thio radicals. Our observations are also somewhat similar to those reported from interactions of Co(TPP) with tetracyanoethylene.[26]

Conclusions

Both Zn(TPP) and Co(TPP) interacted with Ni(tfd)$_2$ to form 1:1 complexes with near-infrared charge-transfer bands. Zn(TPP)Ni(tfd)$_2$ was a neutral ground-state molecular complex which disproportionated into Zn(TPP)$^+$ and Ni(tfd)$_2{}^-$ as well as Zn(TPP) and Ni(tfd)$_2$ when dissolved in polar solvents. Co(TPP)Ni(tfd)$_2$ formed a covalent compound in which a cobalt–sulfur bond bridged the two moieties, but the compound still showed a charge-transfer band in the near-infrared spectrum. This band has been assigned as an intramolecular transition, probably involving less charge separation in the excited state than in the ground state. Disproportionation into neutral reactants and free ions also occurred when the Co–Ni compound was dissolved in various solvents. The solvent polarity influenced the relative distribution of ions, neutral components, and undissociated complex. The differences in tendency toward covalent behavior of the zinc and cobalt porphyrin complexes is probably due to the availability of the unpaired electron in the out-of-plane d_{z^2} orbital in neutral Co(TPP) (the lowest unoccupied orbital in Ni(tfd)$_2$ is an out-of-plane d_{yz} orbital),[27] whereas the highest occupied orbital in Zn(TPP) is an in-plane $d_{x^2-y^2}$ orbital.[28]

Acknowledgment. The support of this work by Research Corp. is gratefully acknowledged. The authors are indebted to Dr. Richard Wing for informing us of the results of the crystal structure determination of the Co(TPP)Ni(tfd)$_2$ complex prior to publication and for very useful discussions concerning these complexes.

Registry No. Zn(TPP)Ni(tfd)$_2$, 53293-28-0; Co(TPP)Ni(tfd)$_2$, 53293-29-1; Co(TPP), 14172-90-8; Ni(tfd)$_2$, 18820-78-5; (Bu$_4$N)-[Ni(tfd)$_2$], 18958-64-0; Zn(TPP), 14074-80-7.

References and Notes

(1) A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, **92**, 2982 (1970).
(2) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, **92**, 3451 (1970).
(3) J. H. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Amer. Chem. Soc.*, **95**, 5140 (1973).
(4) J. A. Ibers, D. V. Stynes, H. C. Stynes, and B. R. James, *J. Amer. Chem. Soc.*, **96**, 1358 (1974).
(5) (a) F. A. Walker, *J. Amer. Chem. Soc.*, **95**, 1154 (1973); (b) B. M. Hoffman, C. A. Spilburg, and D. H. Petering, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 343 (1971).
(6) R. D. Schmitt, R. M. Wing, and A. H. Maki, *J. Amer. Chem. Soc.*, **91**, 4394 (1969).
(7) W. E. Geiger, Jr., and A. H. Maki, *J. Phys. Chem.*, **75**, 2387 (1971).
(8) R. D. Schmitt, Ph.D. Thesis, University of California at Riverside, Riverside, Calif., 1969.
(9) The Ni(tfd)$_2{}^0 \rightleftarrows$ Ni(tfd)$_2{}^-$ redox couple has a formal potential of +0.82 V *vs.* an aqueous saturated calomel electrode when a dichloromethane–0.1 *M* Bu$_4$NPF$_6$ electrolyte is employed. The $E_{1/2}$ potentials for the one-electron oxidation of both Zn(TPP) and Co(TPP) have been reported[1] *vs.* the sce for benzonitrile solutions (Zn, +0.79 V; Co, +0.52 V). We performed similar experiments on the metalloporphyrins in dichloromethane in order to have adequate basis for comparison with the potential measured for Ni(tfd)$_2$ and obtained (from the cyclic voltammograms) $E_{1/2}$ = +0.83 V (Zn(TPP)) and $E_{1/2}$ = +0.25 V (Co(TPP)).
(10) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).
(11) P. Rothemund and A. R. Menotti, *J. Amer. Chem. Soc.*, **70**, 1808 (1948).
(12) J. T. Horeczy, B. N. Hill, A. E. Walters, H. G. Schutze, and W. H. Bonner, *Anal. Chem.*, **27**, 1899 (1955).
(13) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
(14) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).
(15) A. Davison and R. H. Holm, *Inorg. Syn.*, **10**, 19 (1967).
(16) Analysis done by Galbraith Laboratories, Knoxville, Tenn.
(17) Analysis done by A. Bernhardt, Mülheim, West Germany.
(18) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Amer. Chem. Soc.*, **88**, 4604 (1966).
(19) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).
(20) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).
(21) A thorough study of the infrared spectra of various metalloporphyrins has previously been reported: D. W. Thomas and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 5111 (1959).
(22) R. M. Wing, private communication; A. O. Hermann, Ph.D. Thesis, University of California at Riverside, Riverside, Calif., 1972. These workers have also isolated a 2:1 Ni(tfd)$_2$–Co(TPP) complex.
(23) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969.
(24) F. A. Walker, *J. Amer. Chem. Soc.*, **95**, 1150 (1973).
(25) G. N. Schrauzer and J. W. Sibert, *Arch. Biochem. Biophys.*, **130**, 257 (1969).
(26) B. B. Wayland and D. Mohajer, *Inorg. Nucl. Chem. Lett.*, **9**, 633 (1973).
(27) R. D. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, **90**, 2288 (1968).
(28) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1966).