Table VII. Shape-Determining Dihedral Angles (Deg) of [Co(terpy)BH_4] (Based on Neutron Results)

	e_1	e_2	e_3
trigonal bipyramid	53.1	53.1	53.1
[Co(terpy)BH_4]	37.2 (3)[41]	82.4 (3)[41]	17.9 (3)
tetragonal pyramid	75.7	75.7	0

middle ring differ sufficiently in shift to show a first-order coupling pattern. This behavior is most readily explained in terms of the magnetic characteristics of the compound, which has a solid-state susceptibility (Guoy method, corrected for diamagnetism) corresponding to an effective magnetic moment of 1.01 μ_B at 299 K and 0.70 μ_B at 78 K.[42] This weak paramagnetism in an essentially low-spin molecule could be responsible for shifting the resonances from their normal positions and could also account for the failure to observe ^{11}B ($I = {}^3/_2$, 81% natural abundance) coupling to the tetrahydroborato protons. This coupling normally results in the observation of these resonances as a quartet which collapses as the rate of quadrupolar spin–lattice relaxation increases, e.g., as the correlation time which characterizes the molecular tumbling is increased by lowering the temperature.[43] The paramagnetism would provide another mechanism for increasing the rate of spin–lattice relaxation of the boron nuclei and would hence decouple them from the protons. The limited solubility of the molecule in inert solvents precluded variable-temperature NMR studies.

The origins of the weak paramagnetism are themselves interesting. The small temperature dependence is consistent with a TIP contribution, but the magnitude and temperature dependence are rather large for that to be the sole origin of the moment. It seems likely that the observed magnetic behavior arises from a combination of factors, e.g., the presence of a ground state which exhibits TIP together with a thermally accessible triplet state, but a definitive interpretation will only be possible after a much more complete study of the magnetic behavior.

Solutions of [Co(terpy)BH_4] are extremely air sensitive and decomposed even when exposed to prepurified argon, possibly by a chain reaction. In contrast, crystalline samples could be handled in air for several minutes without visible evidence of deterioration. The compound reacts readily with a wide variety of reagents, including organolithium compounds, alkyl halides, and donor ligands such as alkyl phosphines. The only tractable product which could be isolated from any of these reactions was the bis(terpyridine)cobalt dication, formed in several instances when an aqueous isolation procedure was used.

Acknowledgment. We thank E. Whitten and W. Reiff of Northeastern University for carrying out the solid-state magnetic susceptibility measurements and for valuable discussions (N.J.C.), and F. Takusagawa for many helpful suggestions (W.M.C.). The technical assistance of J. Henriques in operating the neutron diffractometer is appreciated. We gratefully acknowledge financial support from the National Science Foundation (Grant No. CHE-77-19899 to W.N.L. and Grant No. CHE-75-04124 to E.J.C.). Research at Brookhaven National Laboratory was supported by the Department of Energy, Office of Basic Energy Sciences.

Registry No. Co(terpy)BH_4, 78891-42-6; Co(terpy)BD_4, 78891-41-5; Co(terpy)Cl_2, 14854-50-3.

Supplementary Material Available: Tables of observed and calculated structure factors for the X-ray and neutron analyses (29 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Materials Research Center,
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(Tetramethylporphyrinato)nickel 7,7,8,8-Tetracyanoquinodimethane, Ni(TMP)TCNQ. Synthesis, Structure, and Physical Properties

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Single crystals of the 1:1 charge-transfer complex (tetramethylporphyrinato)nickel(II) 7,7,8,8-tetracyano-*p*-quinodimethane, Ni(TMP)TCNQ, were afforded by the reaction of Ni(TMP) in benzene with TCNQ in acetonitrile. The compound crystallizes in the space group C_{2h}^5-$P2_1/n$ of the monoclinic system with four formula units in a cell of dimensions $a = 17.542$ (11) Å, $b = 6.868$ (5) Å, $c = 22.597$ (13) Å, and $\beta = 98.42$ (2)° at 116 K. Full-matrix least-squares refinement of 407 variables gives a final value of the conventional R index (on F^2) of 0.093 for 5190 observations. The conventional R index on F for 3095 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.053. The structure consists of stacks of alternating, parallel Ni(TMP) and TCNQ molecules which are tilted with respect to the stacking axis. The short intrastack interplanar spacing between Ni(TMP) and TCNQ molecules (~3.30 Å) and the presence of two broad charge-transfer bands at 9100 and 11100 cm^{-1} suggest that there is some charge-transfer interaction in the complex. The visible and middle-infrared spectrum of Ni(TMP)TCNQ is essentially a superposition of the spectra of the individual neutral component molecules, so the degree of charge transfer in Ni(TMP)TCNQ is small. An analysis of the bond distances in the TCNQ molecule indicates that the amount of charge transfer is less than 0.2 e. The Ni(TMP)TCNQ complex is diamagnetic, and the conductivity along the single-crystal needle axis is low ($<10^{-5}$ Ω^{-1} cm^{-1}).

Introduction

Charge-transfer complexes composed of various organic and inorganic donors and acceptors have been known for many years and have been the objects of much study.[1,2] Formation of these complexes is assisted if the donors and acceptors are planar, conjugated molecules. Metalloporphyrins have an ideal structure for forming charge-transfer complexes, and there have been several spectroscopic studies of charge-transfer complexes of metalloporphyrins with aromatic organic acceptors.[3-8] However, the main focus of these studies has been

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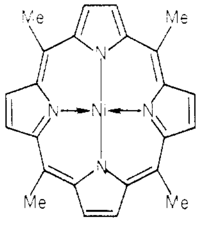
on the behavior of the complexes in solution, and only in a few cases have they been isolated as solids.[9-11]

Our interest in charge-transfer complexes involving metalloporphyrins stems from our studies of quasi-one-dimensional systems displaying anisotropic physical properties. We have found that (tetramethylporphyrinato)nickel(II), Ni(TMP) (I), reacts with iodine to form a highly electrically conducting linear chain system.[12] This has prompted us to explore the possibility of using acceptors other than iodine with the donor Ni(TMP) molecule. The organic acceptor tetracyanoquinodimethane, TCNQ (II), has received much attention because of the highly conductive complex it forms with the organic donor tetrathiafulvalene (TTF).[13,14] We know of only one study of the interaction of TCNQ with metalloporphyrins; in this case, charge-transfer complexes of Zn(TPP)[15] and M(Etio-I)[15] (M = Ni, Cu, Zn, ClFe) were investigated.[5] Complex formation at low temperature was followed spectroscopically, but these complexes were unstable at room temperature and could not be isolated.



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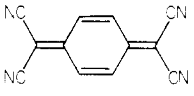

II

In this paper, we report the preparation, structure, and physical properties of the 1:1 charge-transfer complex Ni(TMP)TCNQ. This is the first such structure in which a metalloporphyrin is the donor molecule.[16]

Experimental Section

Preparation of Ni(TMP)TCNQ. Ni(TMP) was prepared as described previously.[17] TCNQ was purchased from Aldrich Chemical Co. and purified by sublimation. Crystals of Ni(TMP)TCNQ suitable for diffraction study were grown in an H-tube by diffusing together a benzene solution of Ni(TMP) and an acetonitrile solution of TCNQ. Elemental analyses were performed by Galbraith Laboratories and gave results corresponding to a 1:1 stoichiometry. Anal. Calcd for $C_{36}H_{24}N_8Ni$: C, 68.92; H, 3.86; N, 17.86; Ni, 9.36. Found: C, 69.01; H, 3.82; N, 17.68; Ni, 9.35. This stoichiometry was later confirmed by the X-ray structure determination.

Table I. Summary of Crystal Data and Intensity Collection

compd	Ni(TMP)TCNQ
formula	$NiC_{36}H_{24}N_8$
formula weight	627.36
space group	C_{2h}^5-$P2_1/n$
cell: a	17.542 (11) Å
b	6.868 (5) Å
c	22.597 (13) Å
β	98.42 (2)°
V	2693 Å^3
Z	4
density: calcd (temp)	1.547 g/cm^3 (116 K)[a]
obsd[b] (temp)	1.50 (2) g/cm^3 (298 K)
cryst shape	needle with faces of the forms {100}, {010}, and {001} with separations of 0.109, 0.806, and 0.060 mm, respectively
cryst vol	0.00533 mm^3
radiation	graphite-monochromated Mo Kα (λ(Mo Kα_1) = 0.709 30 Å)
μ	7.65 cm^{-1}
transmission factors	0.91–0.96
takeoff angle	2.6°
receiving aperture	5.5 mm high × 5.5 mm wide; 34 cm from crystal
scan speed	1°/min
scan width	1.2° below Kα_1 to 0.85° above Kα_2
bkgd counts	40 s total with rescan option[c]
data collected	$\pm h, k \geqslant 0, l \geqslant 0$; $3.4° \leqslant 2\theta \leqslant 51.5°$
unique data	5190
unique data with $F_o^2 \geqslant 3\sigma(F_o^2)$	3095
final no. variables	407
error in observations of unit weight	1.17 e^2
R } for last cycle on F_o^2	0.093
R_w } for last cycle on F_o^2	0.125
R } on F_o for data with $F_o^2 \geqslant 3\sigma(F_o^2)$	0.053
R_w } on F_o for data with $F_o^2 \geqslant 3\sigma(F_o^2)$	0.055

[a] The low-temperature system is based on a design by J. C. Huffman (Ph.D. Thesis, Indiana University, 1974). [b] Flotation in $ZnCl_2/H_2O$. [c] The diffractometer was run under the disk-oriented Vanderbilt system (Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568–570).

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 283 double-beam spectrometer. Visible and near-infrared spectra were obtained with a Cary Model 14 recording spectrophotometer. Solid samples were examined in KBr pellets and as Nujol mulls between KBr plates. Four-probe single-crystal conductivity measurements were made along *b*, the needle axis, using procedures described previously.[18] The small dimensions (~0.1 mm) of the crystal in directions perpendicular to the *b* axis precluded any other single-crystal conductivity measurements. Magnetic susceptibility measurements were carried out on a powder sample by the Faraday method. Electron paramagnetic resonance measurements were made at room temperature and 77 K on both single crystal and powder samples using a modified Syva Frat X-band spectrometer.

Crystallographic Data for Ni(TMP)TCNQ. On the basis of Weissenberg and precession photographs, crystals of Ni(TMP)TCNQ were assigned to the Laue group $2/m$. Systematic absences were observed for $h0l$, $h + l$ odd, and $0k0$, k odd, consistent with the space group C_{2h}^5—$P2_1/n$. The cell constants of a = 17.542 (11) Å, b = 6.868 (5) Å, c = 22.597 (13) Å, and β = 98.42(2)° at 116 K were determined by a least-squares refinement of the setting angles of 13 reflections on a FACS-I diffractometer.

Intensity data were collected at 116 (2) K with use of the θ–2θ scan technique and graphite-monochromated Mo Kα radiation.[19] The

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(15) Abbreviations used: TMP, 5,10,15,20-tetramethylporphyrinato; TPP, 5,10,15,20-tetraphenylporphyrinato; TPrP, 5,10,15,20-tetra-*n*-propylporphyrinato; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinato; Etio-I, 2,7,12,17-tetramethyl-3,8,13,18-tetraethylporphyrinato; Deut, 2,7,12,18-tetramethyl-3,8-diacetyl-13,17-bis(2-carboxyethyl)-porphyrinato; TCNQ, 7,7,8,8-tetracyano-*p*-quinodimethane; TTF, tetrathiafulvalene.

(16) There are, however, two structurally characterized metalloporphyrin π complexes which do not have a 1:1 stoichiometry: the 1:2 π-complex between Ni(Etio-I)[15] and tetrafluorenone[11] in which the porphyrin is acting as a donor and the 2:1 π-complex between M(TPP)[15] (M= Mn,[43a] Zn,[43b] Cr[43c]) and two toluene molecules of solvation in which the porphyrin is acting as an acceptor.

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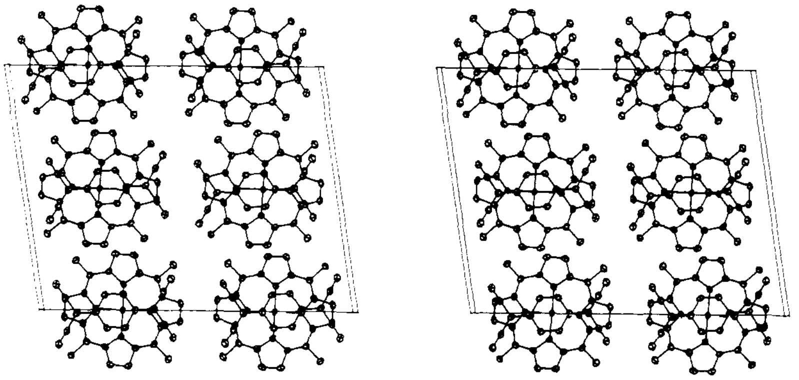

Figure 1. Stereoview of a unit cell of Ni(TMP)TCNQ. The *x* axis is pointing toward the top of the page, the *y* axis is perpendicular to the paper pointing toward the reader, and the *z* axis is horizontal to the right. Vibrational ellipsoids are at the 50% probability level. H atoms have been omitted.

intensities of six standard reflections measured after every 100 reflections showed no evidence of crystal decomposition over the course of data collection. Of the total 5798 reflections collected, 5190 were unique and 3095 were found to have $F_o^2 > 3\sigma(F_o^2)$. Crystal data and experimental details are given in Table I. The data were processed[20] with use of a value of 0.04 for *p* in the estimation of standard deviations. Intensities were corrected for Lorentz and polarization factors and absorption.[21]

Solution and Refinement of the Structure. The positions of all nonhydrogen atoms were located with the use of direct methods.[21] Initial cycles of refinement were carried out on $|F_o|$, using the 3095 reflections having $F_o^2 > 3\sigma(F_o^2)$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weight *w* is $4F_o^2/\sigma^2(F_o^2)$. Refinement of an isotropic model converged to values of 0.074 and 0.087 for *R* and R_w, respectively.

The final cycles of refinement were carried out on F_o^2 using all 5190 reflections and included anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atom positions were located in Fourier difference maps; their idealized positions (C–H = 0.95 Å) were used and not varied. The isotropic thermal parameter of a hydrogen atom was assumed to be 1.0 Å^2 greater than that of the carbon atom to which it is attached. The final values for *R* and R_w on F_o^2 are 0.093 and 0.125, respectively. The values for *R* and R_w on F_o for the reflections having $F_o^2 > 3\sigma(F_o^2)$ are 0.053 and 0.055, respectively. A final difference Fourier map is essentially featureless.

The final positional and thermal parameters appear in Table II, and the root-mean-square amplitudes of vibration are in Table III.[22] A listing of observed and calculated structure amplitudes is also available.[22]

Structural Results

Description of the Structure. The structure consists of alternating Ni(TMP) and TCNQ molecules which stack along the *b* axis. A stereoview of the packing in the unit cell is shown in Figure 1. Intramolecular distances and angles are given in Tables IV and V.

The Ni(TMP) Molecule. A drawing of the Ni(TMP) molecule showing the labeling scheme and bond distances is presented in Figure 2. Best weighted least-squares planes are given in Table VI. The coordination about the Ni atom is essentially square planar with a standard deviation of only 0.006 Å for the best least-squares plane through the Ni atom and its four coordinated pyrrole N atoms. The four pyrrole rings deviate only slightly from planarity with the angles between the planes of adjacent rings ranging from 3.00 to 8.59°. The Ni(TMP) molecule is slightly more ruffled than other planar nickel porphyrins such as Ni(Deut)[23] and the triclinic form of Ni(OEP),[24] which have angles between adjacent pyrrole groups of 1.9–5.2 and 2.1°, respectively. In contrast, S_4-ruffled porphyrins such as the tetragonal form of Ni(OEP)[25] have angles between adjacent pyrrole groups of approximately 30°.

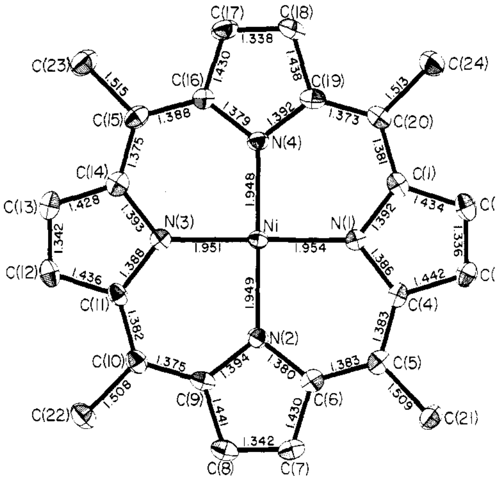

Figure 2. Drawing of the Ni(TMP) molecule with labeling scheme and bond distances. Vibrational ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

The Ni(TMP) molecule has no crystallographically imposed symmetry; however, chemically equivalent bond distances and angles agree very well, and their averaged values are included in Table VII, along with similar data for several other nickel(II) porphyrins. All bond distances and angles of the Ni(TMP) molecule from Ni(TMP)TCNQ agree within experimental error with those of the unreacted Ni(TMP) molecule,[17,26] as can be seen in Table VII. The Ni–N bond distance of 1.950 (4) Å is in the range expected for a planar nickel porphyrin. The only significant difference between the meso-substituted Ni(TMP) molecule and the pyrrole-substituted Ni(Deut) and Ni(OEP) molecules is the larger M–C_m distance in Ni(TMP). This lengthening was noted previous-

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Table II. Positional and Thermal Parameters for the Atoms of Ni(TMP)TCNQ

ATOM	X[a]	Y	Z	B11[b] OR B,A^2	B22	B33	B12	B13	B23
NI	0.998780(33)	0.324504(85)	0.745022(21)	11.02(22)	60.5(13)	5.58(13)	-0.95(42)	1.48(10)	-1.25(32)
N(1)	1.10647(18)	0.24280(51)	0.76203(13)	11.4(12)	47.7(83)	6.87(64)	-6.1(26)	1.12(70)	-0.2(18)
N(2)	0.99456(19)	0.34249(56)	0.83054(14)	11.0(12)	88.9(96)	6.69(64)	-4.1(28)	1.65(69)	-3.3(21)
N(3)	0.89102(18)	0.40383(52)	0.72816(14)	12.0(12)	61.6(89)	7.30(67)	-1.4(27)	1.37(72)	-1.0(20)
N(4)	1.00308(19)	0.30815(56)	0.65950(13)	12.9(12)	88.0(96)	5.35(63)	-3.4(28)	0.82(69)	-3.2(20)
C(1)	1.15387(22)	0.18336(68)	0.72115(17)	12.3(14)	54.2(99)	9.83(80)	-4.8(33)	3.07(85)	-2.6(25)
C(2)	1.22656(23)	0.11841(69)	0.75225(19)	12.2(15)	95.(12)	12.68(91)	-2.4(33)	3.97(97)	-0.5(26)
C(3)	1.22523(23)	0.13990(66)	0.81083(17)	13.9(15)	69.(12)	9.50(82)	1.3(32)	-0.02(86)	4.6(25)
C(4)	1.15095(23)	0.21965(64)	0.81755(17)	11.1(14)	60.(11)	9.17(81)	-1.2(30)	-0.79(84)	1.5(23)
C(5)	1.12927(23)	0.26324(68)	0.87245(17)	13.7(15)	68.(11)	9.06(83)	-11.3(33)	0.50(89)	1.8(24)
C(6)	1.05423(24)	0.31577(68)	0.87687(17)	15.9(16)	61.(11)	8.30(79)	-1.3(34)	0.72(88)	-0.2(26)
C(7)	1.02820(25)	0.34324(73)	0.93337(17)	19.2(17)	103.(12)	6.25(77)	-5.2(37)	-0.87(88)	-1.3(26)
C(8)	0.95258(26)	0.38303(70)	0.92235(18)	20.1(17)	90.(12)	8.13(84)	-6.9(36)	5.13(96)	-1.8(25)
C(9)	0.93093(23)	0.38762(65)	0.85836(17)	15.6(15)	53.(10)	6.78(76)	-10.2(32)	3.59(85)	-4.9(23)
C(10)	0.85871(23)	0.43860(67)	0.83049(17)	13.2(14)	78.(11)	9.48(84)	0.0(33)	2.91(88)	-3.9(25)
C(11)	0.84205(22)	0.45169(66)	0.76892(17)	9.6(14)	71.(11)	9.19(82)	-4.1(31)	2.85(84)	-6.7(24)
C(12)	0.76897(23)	0.51822(69)	0.73867(18)	12.3(15)	75.(11)	12.88(97)	4.6(33)	3.32(91)	-0.5(26)
C(13)	0.77194(24)	0.50412(74)	0.67982(18)	12.2(15)	107.(13)	12.12(94)	2.3(35)	-0.95(93)	1.5(28)
C(14)	0.84656(24)	0.43324(66)	0.67255(17)	15.1(15)	59.(11)	9.44(84)	-2.7(33)	0.95(89)	3.8(24)
C(15)	0.86974(24)	0.40092(69)	0.61782(17)	15.7(15)	82.(11)	7.65(81)	-6.6(34)	-0.93(89)	1.8(24)
C(16)	0.94465(23)	0.34510(68)	0.61304(17)	13.0(15)	76.(11)	6.97(76)	-3.4(33)	1.59(84)	-0.5(24)
C(17)	0.97123(26)	0.31684(77)	0.55680(17)	19.0(17)	141.(13)	5.96(78)	-9.9(39)	0.19(88)	-5.7(28)
C(18)	1.04525(25)	0.26276(74)	0.56777(18)	18.9(17)	122.(12)	7.60(81)	-3.8(38)	5.11(94)	-4.2(26)
C(19)	1.06558(25)	0.25350(67)	0.63172(17)	19.0(16)	57.(10)	7.07(80)	-3.8(33)	2.90(91)	-2.8(23)
C(20)	1.13711(24)	0.19808(67)	0.65967(17)	15.0(15)	66.(11)	9.00(80)	-3.1(33)	4.54(87)	-1.9(25)
C(21)	1.18664(24)	0.24863(73)	0.92895(17)	13.8(15)	125.(12)	8.46(83)	-2.5(35)	-1.25(90)	4.5(26)
C(22)	0.79673(24)	0.48404(77)	0.86814(19)	15.0(16)	135.(13)	12.17(94)	-5.3(38)	5.35(97)	-8.1(29)
C(23)	0.81267(25)	0.42246(79)	0.56101(19)	19.1(17)	149.(14)	9.97(91)	-5.4(39)	-1.3(10)	1.4(29)
C(24)	1.19858(25)	0.14854(78)	0.62160(18)	18.1(16)	148.(14)	10.98(89)	5.7(39)	3.99(97)	-8.6(29)
N(5)	1.14073(22)	0.75769(65)	0.95386(15)	19.5(15)	151.(11)	9.97(77)	-5.6(33)	2.51(89)	-3.3(24)
N(6)	0.89474(22)	0.91721(62)	0.93473(15)	21.0(15)	131.(11)	10.10(76)	-0.2(33)	3.28(88)	-0.4(24)
N(7)	0.86924(22)	0.90299(63)	0.56612(16)	21.4(15)	140.(11)	11.12(80)	6.1(34)	1.32(91)	-0.6(25)
N(8)	1.11103(21)	0.71044(63)	0.58806(15)	17.9(14)	153.(12)	9.26(73)	-1.2(33)	1.05(83)	-8.2(24)
C(25)	0.99807(24)	0.81595(68)	0.69793(17)	16.9(16)	60.(11)	8.47(80)	-2.1(34)	2.41(88)	1.5(25)
C(26)	1.06876(23)	0.76845(66)	0.73596(18)	11.4(14)	59.(10)	10.87(85)	2.6(31)	4.37(88)	-4.0(24)
C(27)	1.07404(23)	0.77706(67)	0.79565(17)	13.1(15)	79.(11)	8.97(82)	-4.5(33)	1.06(88)	-1.0(25)
C(28)	1.00939(23,	0.83015(66)	0.82371(18)	12.0(15)	43.(10)	10.88(83)	-3.9(31)	2.94(87)	0.3(26)
C(29)	0.93791(23)	0.87620(69)	0.78645(18)	12.3(15)	91.(12)	10.31(85)	-4.8(33)	2.86(88)	-3.5(25)
C(30)	0.93228(24)	0.86904(69)	0.72615(18)	12.5(15)	96.(12)	9.79(85)	-7.8(34)	0.43(89)	-3.5(26)
C(31)	0.99309(25)	0.81201(70)	0.63670(18)	16.7(16)	72.(11)	9.55(83)	-3.6(34)	2.25(91)	-2.5(27)
C(32)	1.01436(24)	0.83619(69)	0.88556(18)	13.5(15)	74.(11)	10.06(83)	-3.6(34)	3.29(88)	-1.3(27)
C(33)	1.08474(26)	0.79290(67)	0.92360(18)	19.9(17)	64.(11)	9.26(84)	-9.0(35)	5.7(10)	-4.7(25)
C(34)	0.94848(25)	0.88229(72)	0.91385(18)	15.9(16)	116.(13)	7.59(83)	0.7(36)	0.30(94)	1.6(26)
C(35)	0.92395(26)	0.86147(70)	0.59757(18)	17.7(17)	89.(12)	8.32(83)	-3.9(35)	2.49(96)	-4.1(25)
C(36)	1.05771(25)	0.75538(71)	0.60892(18)	16.2(16)	97.(11)	7.51(81)	-2.9(35)	-0.35(95)	0.2(25)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H1C(2)	1.269	.054	.735	2.8	H2C(22)	.747	.448	.848	3.1
H1C(3)	1.266	.109	.843	2.6	H3C(22)	.805	.416	.906	3.1
H1C(7)	1.060	.337	.973	2.7	H1C(23)	.821	.544	.541	3.3
H1C(8)	.917	.401	.952	2.8	H2C(23)	.818	.320	.534	3.3
H1C(12)	.726	.505	.757	2.6	H3C(23)	.761	.424	.570	3.3
H1C(13)	.731	.536	.647	3.0	H1C(24)	1.229	.041	.639	3.4
H1C(17)	.942	.335	.518	3.3	H2C(24)	1.177	.115	.582	3.4
H1C(18)	1.078	.235	.538	2.9	H3C(24)	1.232	.258	.620	3.4
H1C(21)	1.172	.149	.954	2.7	H1C(26)	1.113	.731	.717	2.4
H2C(21)	1.237	.242	.920	2.7	H1C(27)	1.122	.743	.820	2.5
H3C(21)	1.189	.370	.951	2.7	H1C(29)	.895	.917	.805	2.6
H1C(22)	.736	.521	.877	3.1	H1C(30)	.884	.898	.702	2.6

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(B11h^2 + B22k^2 + B33l^2 + 2B12hk + 2B13hl + 2B23kl)]$. The quantities given in the table are the thermal coefficients × 10^4.

ly[27,28] in comparisons of meso- and pyrrole-substituted porphyrins and has been attributed to the fact that substitution at the meso position keeps the methine carbon atom from moving closer to the porphyrin center.[28] The increase in the M–C_m distance is accompanied by a decrease of the C_a–C_m–C_a angle as well as an increase in the N–C_a–C_m angle. The meso-substituted porphyrin Cu(TPrP)[29] shows structural trends similar to those observed for Ni(TMP).

The TCNQ Molecule. A drawing of the TCNQ molecule is presented in Figure 3, and the best weighted least-squares planes are given in Table VIII. Although the quinonoid ring

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Table IV. Bond Distances (Å) in Ni(TMP)TCNQ

atoms	dist	atoms	dist
Ni-N(1)	1.954 (4)	C(14)-C(15)	1.375 (6)
Ni-N(2)	1.949 (3)	C(15)-C(16)	1.388 (6)
Ni-N(3)	1.951 (4)	C(19)-C(20)	1.373 (6)
Ni-N(4)	1.948 (3)	C(20)-C(1)	1.381 (5)
Ni-N	av[a] = 1.950 (4)	C_a-C_m	av = 1.380 (6)
N(1)-C(1)	1.392 (5)	C(5)-C(21)	1.509 (5)
N(1)-C(4)	1.386 (5)	C(10)-C(22)	1.508 (6)
N(2)-C(6)	1.380 (5)	C(15)-C(23)	1.515 (6)
N(2)-C(9)	1.394 (5)	C(20)-C(24)	1.513 (6)
N(3)-C(11)	1.388 (5)	C_m-C_{Me}	av = 1.511 (6)
N(3)-C(14)	1.393 (5)		
N(4)-C(16)	1.379 (5)	Ni-C(5)	3.432 (4)
N(4)-C(19)	1.392 (5)	Ni-C(10)	3.431 (4)
N-C_a[b]	av = 1.388 (6)	Ni-C(15)	3.429 (4)
		Ni-C(20)	3.425 (4)
C(1)-C(2)	1.434 (6)	Ni-C_m	av = 3.429 (4)
C(3)-C(4)	1.442 (6)		
C(6)-C(7)	1.430 (6)	C(26)-C(27)	1.340 (5)
C(8)-C(9)	1.441 (5)	C(29)-C(30)	1.353 (6)
C(11)-C(12)	1.436 (6)	bond a[c]	av = 1.346 (9)
C(13)-C(14)	1.428 (6)		
C(16)-C(17)	1.430 (5)	C(25)-C(26)	1.439 (6)
C(18)-C(19)	1.438 (6)	C(27)-C(28)	1.426 (6)
C_a-C_b	av = 1.435 (6)	C(28)-C(29)	1.440 (6)
		C(30)-C(25)	1.445 (6)
C(2)-C(3)	1.336 (6)	bond b	av = 1.437 (8)
C(7)-C(8)	1.342 (6)		
C(12)-C(13)	1.342 (6)	C(25)-C(31)	1.374 (5)
C(17)-C(18)	1.338 (6)	C(28)-C(32)	1.388 (6)
C_b-C_b	av = 1.339 (6)	bond c	av = 1.381 (10)
C(4)-C(5)	1.383 (6)	C(31)-C(35)	1.433 (6)
C(5)-C(6)	1.383 (6)	C(31)-C(36)	1.428 (6)
C(9)-C(10)	1.375 (6)	C(32)-C(33)	1.429 (6)
C(10)-C(11)	1.382 (5)	C(32)-C(34)	1.436 (6)
		bond d	av = 1.431 (6)
		N(5)-C(33)	1.138 (5)
		N(6)-C(34)	1.140 (5)
		N(7)-C(35)	1.144 (5)
		N(8)-C(36)	1.150 (5)
		bond e	av = 1.143 (5)

[a] Average values are weighted. In this and subsequent tables, the error is taken to be the larger of the unweighted estimated standard deviation of a single observation and that estimated from the inverse matrix. [b] The notation is that of: Hoard, J. L. *Science* (*Washington D.C.*) **1971**, *174*, 1295–1302. [c] Bonds for the TCNQ molecule are labeled according to the nomenclature of Flandrois and Chasseau (ref 30).

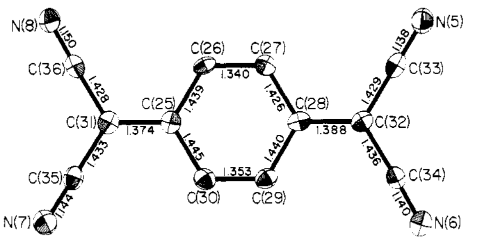

Figure 3. Drawing of the TCNQ molecule with labeling scheme and bond distances. Vibrational ellipsoids are drawn at the 50% probability level, and H atoms have been omitted.

of the TCNQ molecule is essentially planar, the molecule as a whole is nonplanar. The two dicyanomethylene groups are tilted in opposite directions and form angles of 1.69 and 2.14° with the quinonoid ring. In addition, two of the C—C≡N groups are significantly nonlinear with CCN angles of 177.9 (5) and 178.1 (4)°.

The weighted means of chemically equivalent but crystallographically independent bond lengths and angles have been included in Tables IV and V. It is possible to correlate the amount of charge transferred to the TCNQ molecule with the bond lengths of the molecule.[2] Structural parameters for several TCNQ systems are presented in Table IX and are labeled a–e according to the nomenclature of Flandrois and Chasseau.[30] The structure of Ni(TMP)TCNQ was determined at 116 K. Since most of the previous structures of TCNQ systems were determined at room temperature, comparisons must be made with caution, as some foreshortening of bond lengths in the room-temperature structures is expected. However, Blessing and Coppens[31] found that the bond lengths of TCNQ in (TTF)(TCNQ) at 100 K are not significantly different from the room-temperature values[32] (see Table IX), so the temperature dependence of these structural parameters may be small. The length of bond "c" appears to be most sensitive to the charge on the TCNQ molecule,[30] and the value of 1.380 (10) Å for bond "c" in Ni(TMP)TCNQ suggests that the amount of charge transfer is small. Flandrois and Chasseau have quantified the correlation between the degree of charge transfer and the bond lengths in TCNQ and have found that the differences (b–c) and (c–d) vary linearly with the amount of charge transferred to the TCNQ molecule. For a charge transfer of 0 (neutral TCNQ),[33] (b–c) and (c–d) are 0.069 and −0.062 Å, respectively, while for a charge transfer of −1 (e.g., $TCNQ^-$ in RbTCNQ),[34] both quantities are 0 Å. For TCNQ in Ni(TMP)TCNQ, (b–c) and (c–d) are 0.056 and −0.050 Å, respectively, and both values correspond to a charge on TCNQ of slightly less than 0.2 e. Flandrois and Chasseau consider a charge transfer of less than 0.2 e to be indicative of a nonionic charge-transfer complex.

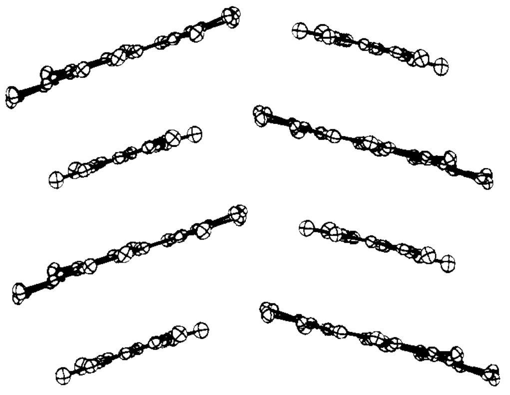

Figure 4. Projection of the structure of Ni(TMP)TCNQ onto the *ab* plane. The stacking direction is parallel to the *b* axis.

Description of the Stacking. The structure of Ni(TMP)-TCNQ consists of mixed donor–acceptor stacks, as is typical for 1:1 neutral, Mulliken-type π-molecular complexes.[35] This packing arrangement has been observed for charge-transfer complexes of TCNQ with planar organic donor molecules[36] and with transition-metal complex donors.[37–41] The Ni(TMP)

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Table V. Bond Angles (Deg) in Ni(TMP)TCNQ

atoms	angle	atoms	angle	atoms	angle
N(1)-Ni-N(2)	89.9 (1)	C(1)-C(2)-C(3)	107.9 (4)	C(25)-C(26)-C(27)	121.2 (4)
N(2)-Ni-N(3)	90.0 (1)	C(2)-C(3)-C(4)	107.1 (3)	C(26)-C(27)-C(28)	121.1 (4)
N(3)-Ni-N(4)	90.0 (1)	C(6)-C(7)-C(8)	107.3 (4)	C(28)-C(29)-C(30)	120.7 (4)
N(4)-Ni-N(1)	90.1 (1)	C(7)-C(8)-C(9)	107.4 (4)	C(29)-C(30)-C(25)	120.6 (4)
N-Ni-N	av = 90.0 (1)	C(11)-C(12)-C(13)	106.7 (4)		av = 120.9 (4)
		C(12)-C(13)-C(14)	107.9 (4)		
Ni-N(1)-C(1)	127.4 (3)	C(16)-C(17)-C(18)	107.9 (4)	C(26)-C(25)-C(30)	117.9 (3)
Ni-N(1)-C(4)	127.7 (3)	C(17)-C(18)-C(19)	106.8 (4)	C(27)-C(28)-C(29)	118.5 (4)
Ni-N(2)-C(6)	127.5 (3)	C_a-C_b-C_b	av = 107.4 (5)		av = 118.2 (5)
Ni-N(2)-C(9)	127.6 (3)				
Ni-N(3)-C(11)	127.8 (3)	C(2)-C(1)-C(20)	124.0 (4)	C(26)-C(25)-C(31)	121.3 (4)
Ni-N(3)-C(14)	128.0 (3)	C(3)-C(4)-C(5)	123.2 (4)	C(30)-C(25)-C(31)	120.8 (4)
Ni-N(4)-C(16)	127.7 (3)	C(7)-C(6)-C(5)	122.1 (4)	C(27)-C(28)-C(32)	121.2 (4)
Ni-N(4)-C(19)	127.6 (3)	C(8)-C(9)-C(10)	123.7 (4)	C(29)-C(28)-C(32)	120.2 (4)
Ni-N-C_a	av = 127.7 (3)	C(12)-C(11)-C(10)	122.8 (4)		av = 120.9 (4)
C(1)-N(1)-C(4)	104.8 (3)	C(13)-C(14)-C(15)	123.7 (4)	C(25)-C(31)-C(35)	122.7 (4)
C(6)-N(2)-C(9)	104.8 (3)	C(17)-C(16)-C(15)	122.8 (4)	C(25)-C(31)-C(36)	120.7 (4)
C(11)-N(3)-C(14)	104.2 (3)	C(18)-C(19)-C(20)	123.3 (4)	C(28)-C(32)-C(33)	121.4 (4)
C(16)-N(4)-C(19)	104.6 (3)	C_b-C_a-C_m	av = 123.2 (6)	C(28)-C(32)-C(34)	121.3 (4)
C_a-N-C_a	av = 104.6 (3)	C(4)-C(5)-C(6)	120.7 (4)		av = 121.5 (8)
N(1)-C(1)-C(2)	109.9 (3)	C(9)-C(10)-C(11)	121.5 (4)	C(35)-C(31)-C(36)	116.6 (4)
N(1)-C(4)-C(3)	110.3 (3)	C(14)-C(15)-C(16)	121.5 (4)	C(33)-C(32)-C(34)	117.3 (4)
N(2)-C(6)-C(7)	110.7 (4)	C(19)-C(20)-C(1)	121.9 (4)		av = 117.0 (5)
N(2)-C(9)-C(8)	109.7 (4)	C_a-C_m-C_a	av = 121.4 (5)	C(32)-C(33)-N(5)	179.7 (5)
N(3)-C(11)-C(12)	110.8 (3)	C(4)-C(5)-C(21)	120.5 (4)	C(32)-C(34)-N(6)	177.9 (5)
N(3)-C(14)-C(13)	110.3 (3)	C(6)-C(5)-C(21)	118.7 (4)	C(31)-C(35)-N(7)	179.1 (5)
N(4)-C(16)-C(17)	110.4 (4)	C(9)-C(10)-C(22)	119.1 (4)	C(31)-C(36)-N(8)	178.1 (4)
N(4)-C(19)-C(18)	110.2 (4)	C(11)-C(10)-C(22)	119.4 (4)		av = 178.6 (9)
N-C_a-C_b	av = 110.3 (4)	C(14)-C(15)-C(23)	120.0 (4)		
N(1)-C(1)-C(20)	125.9 (4)	C(16)-C(15)-C(23)	118.5 (4)		
N(1)-C(4)-C(5)	126.5 (4)	C(19)-C(20)-C(24)	118.7 (4)		
N(2)-C(6)-C(5)	127.2 (4)	C(1)-C(20)-C(24)	119.4 (4)		
N(2)-C(9)-C(10)	126.5 (4)	C_a-C_m-C_{Me}	av = 119.3 (7)		
N(3)-C(11)-C(10)	126.3 (4)				
N(3)-C(14)-C(15)	126.0 (4)				
N(4)-C(16)-C(15)	126.7 (4)				
N(4)-C(19)-C(20)	126.5 (4)				
N-C_a-C_m	av = 126.5 (4)				

and TCNQ molecules are nearly parallel, with a dihedral angle between their best planes of only 0.8°. The molecular planes are tilted with respect to the stacking (*b*) axis, as shown in Figure 4. The angle between the stacking axis and the normal to the molecular planes is approximately 17°, which is close to the 20–30° angle typically observed for charge-transfer complexes of this type.[2] The intrastack interplanar spacing between donor and acceptor molecules (as defined by the distance between the Ni(TMP) nickel atom and the best least-squares plane of the TCNQ quinonoid ring) is alternately 3.29 and 3.30 Å. This is well within the 3.2–3.5-Å range taken by Herbstein[2] to indicate donor–acceptor charge-transfer interaction.

It has been noted[42] that if both the donor and acceptor molecules in a π complex have a long molecular axis, these axes tend to line up when the molecules stack. Most of the structurally characterized TCNQ π complexes have involved donors which have a long molecular axis. The Ni(TMP) moiety has four-fold symmetry, and consequently the TCNQ molecule could assume a variety of orientations relative to it. The two types of overlap which occur between adjacent Ni(TMP) and TCNQ molecules in a stack are shown in Figure 5, which is a view perpendicular to the Ni(TMP) molecular plane. The overlap shown in Figure 5b is similar to that observed in the bis(toluene) solvates of M(TPP) systems[43] where the pyrrole nitrogen atom of the porphyrin bisects a bonded pair of carbon atoms from the six-membered ring. The relative orientation of donors and acceptors in the stack results from maximizing orbital overlap and minimizing unfavorable steric interactions. We cannot draw any conclusions regarding which of these two interactions is the more influential in determining the molecular orientation in this particular case; however, the overlap diagrams in Figure 5, as well as the short nonbonded distances, which are given in Table X, do give an indication of possible donor–acceptor interactions. There are three intrastack nonhydrogen contacts which are shorter than the interplanar spacing: C(1)–C(26) = 3.26 Å, C(7)–C(33) = 3.26 Å, and N(3)–C(20) = 3.28 Å. The closest interstack nonhydrogen contacts are C(17)–N(8) and C(3)–N(8) at 3.38 and 3.43 Å, respectively.

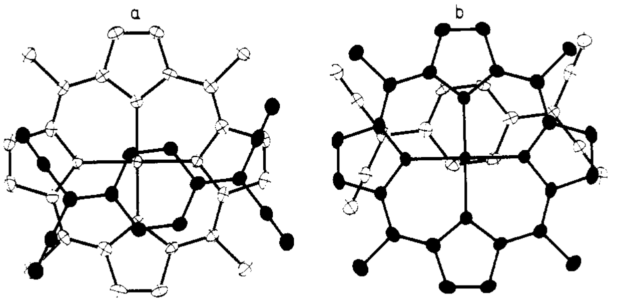

Figure 5. Projection of the TCNQ molecule at (a) *x*, *y*, *z* and (b) *x*, *y* − 1, *z* onto the molecular plane of Ni(TMP).

The possibility of interaction between the Ni d_{z^2} orbital and the TCNQ π^* orbital is of particular interest since Ni-

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Table VI. Least-Squares Planes for Ni(TMP) in Ni(TMP)TCNQ

Deviations (Å) from Planes

atoms	plane 1 Ni(TMP) molecule	2 NiN_4	3 pyrrole 1	4 pyrrole 2	5 pyrrole 3	6 pyrrole 4
Ni	0.001 (1)	0.000 (1)				
N(1)	−0.001 (4)	−0.008 (4)	−0.008 (3)			
N(2)	−0.007 (4)	0.006 (4)		−0.004 (4)		
N(3)	−0.013 (4)	−0.008 (4)			0.009 (4)	
N(4)	0.021 (4)	0.006 (4)				0.006 (4)
C(1)	−0.096 (5)		0.010 (5)			
C(2)	−0.186 (5)		−0.004 (5)			
C(3)	−0.124 (5)		−0.004 (5)			
C(4)	0.009 (4)		0.010 (4)			
C(5)	0.116 (5)					
C(6)	0.068 (5)			−0.001 (5)		
C(7)	0.045 (5)			0.010 (5)		
C(8)	−0.070 (5)			−0.013 (5)		
C(9)	−0.073 (4)			0.010 (4)		
C(10)	−0.076 (5)					
C(11)	−0.001 (5)				−0.015 (4)	
C(12)	0.096 (5)				0.011 (5)	
C(13)	0.091 (5)				−0.001 (5)	
C(14)	0.019 (5)				−0.008 (5)	
C(15)	−0.006 (5)					
C(16)	0.019 (5)					−0.004 (5)
C(17)	0.040 (5)					−0.002 (5)
C(18)	0.053 (5)					0.008 (5)
C(19)	0.019 (5)					−0.009 (5)
C(20)	−0.011 (5)					
C(21)	0.246 (5)					
C(22)	−0.144 (5)					
C(23)	−0.089 (5)					
C(24)	0.028 (5)					
std dev	0.061	0.006	0.007	0.008	0.009	0.006

Plane Equation: $Ax + By + Cz = D$

plane no.	A	B	C	D	plane no.	A	B	C	D
1	5.155	6.564	−1.226	6.364	4	3.987	6.686	−1.220	5.246
2	5.082	6.573	−1.067	6.414	5	5.952	6.460	−1.037	7.148
3	6.459	6.378	−2.207	7.021	6	5.081	6.573	−0.941	6.495

Interplanar Angles (Deg)

plane no.	plane no.	angle	plane no.	plane no.	angle	plane no.	plane no.	angle
1	2	0.45	2	3	5.29	3	5	3.29
1	3	4.91	2	4	3.82	3	6	5.44
1	4	3.99	2	5	3.03	4	5	6.84
1	5	2.88	2	6	0.32	4	6	3.90
1	6	0.74	3	4	8.59	5	6	3.00

Table VII. Averaged Bond Lengths (Å) and Angles (Deg) of Selected Nickel Porphyrins

bond parameter	Ni(TMP)-TCNQ[a]	Ni(TMP)[b]	Ni(OEP) triclinic[c]	Ni(OEP) tetragonal[d]
Ni-N	1.950 (4)	1.959 (10)	1.958 (2)	1.929 (3)
$N-C_a$	1.388 (6)	1.388 (4)	1.376 (6)	1.386 (4)
C_a-C_b	1.435 (6)	1.439 (5)	1.443 (4)	1.449 (5)
C_b-C_b	1.339 (6)	1.341 (10)	1.346 (4)	1.362 (5)
C_a-C_m	1.380 (6)	1.381 (7)	1.371 (4)	1.373 (5)
$Ni-C_m$	3.429 (4)	3.427 (4)	3.381 (3)	3.355 (4)
Ni-Ni-N	90.0 (1)	90.00 (9)	90.15 (9)	90.0 (1)
$Ni-N-C_a$	127.7 (3)	127.6 (2)	128.0 (2)	127.4 (2)
C_a-N-C_a	104.6 (3)	104.7 (3)	103.9 (4)	105.1 (3)
$N-C_a-C_b$	110.3 (4)	110.3 (3)	111.6 (3)	110.6 (2)
$N-C_a-C_m$	126.5 (4)	126.1 (6)	124.4 (3)	124.0 (2)
$C_a-C_b-C_b$	107.4 (5)	107.3 (3)	106.5 (4)	106.8 (3)
$C_b-C_a-C_m$	123.2 (6)	123.5 (6)	124.1 (4)	125.0 (2)
$C_a-C_m-C_a$	121.4 (5)	122.2 (2)	125.1 (3)	124.1 (2)

[a] This work; 116 K. [b] Reference 17; 123 K. [c] Reference 24; 298 K. [d] Reference 25; 298 K.

(TMP)TCNQ is the first structurally characterized TCNQ π complex in which the donor–TCNQ overlap includes a metal atom.[44] The sum of the octahedral Ni(II) covalent radius (1.39 Å)[45] and the half-thickness of a TCNQ molecule (1.72 Å)[33] is 3.1 Å, so a significant metal–TCNQ interaction could be inferred from a Ni to TCNQ distance of 3.1 Å or less. The closest Ni contacts to the TCNQ molecule are to atoms C(26) and C(30) at 3.30 and 3.34 Å, respectively, indicating that the nickel atom plays a minimal role in any charge-transfer interactions.

Physical Properties

Optical Properties. The solid-state spectrum of Ni(TMP)TCNQ in the middle infrared region (4000–400 cm^{-1}) is essentially a superposition of the spectra of the individual neutral component molecules, as is typically the case for weak π complexes. As a result of the molecular association in the solid, there are slight changes in the frequencies and intensities of some of the bands. In particular, the bending modes are

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(44) A possible exception is the 1:2 molecular complex of bis(*N*-alkyl-2-oxy-1-naphthylidenaminato)copper(II) with TCNQ (ref 40). The TCNQ nitrogen atoms participate in the tetragonal-bipyramidal coordination around the Cu atom; however, this is considered to be a localized interaction, and the major donor–acceptor overlap involves only the naphthalene portion of the ligand system.

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Table VIII. Least-Squares Planes for TCNQ in Ni(TMP)TCNQ

Deviations (Å) from Planes

atoms	plane 1 TCNQ molecule	plane 2 quinonoid ring	plane 3 dicyano-methylene group 1	plane 4 dicyano-methylene group 2
C(25)	−0.011 (5)	0.006 (5)		0.001 (5)
C(26)	−0.019 (5)	−0.006 (5)		
C(27)	0.005 (5)	0.003 (5)		
C(28)	0.015 (5)	0.000 (5)	−0.008 (5)	
C(29)	0.009 (5)	−0.002 (5)		
C(30)	−0.007 (5)	−0.002 (5)		
C(31)	−0.002 (5)			0.002 (5)
C(32)	0.018 (5)		0.011 (5)	
C(33)	0.036 (5)		0.004 (5)	
C(34)	−0.024 (5)		0.010 (5)	
C(35)	0.028 (5)			−0.006 (5)
C(36)	−0.035 (5)			−0.003 (5)
N(5)	0.046 (4)		−0.006 (4)	
N(6)	−0.074 (4)		−0.008 (4)	
N(7)	0.068 (4)			0.004 (4)
N(8)	−0.053 (4)			0.002 (4)
std dev	0.028	0.003	0.008	0.003

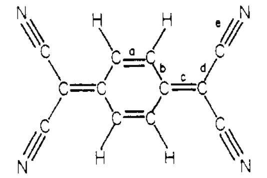
Plane Equations: $Ax + By + Cz = D$

plane no.	A	B	C	D
1	4.842	6.601	−0.975	9.550
2	4.918	6.592	−1.232	9.421
3	4.375	6.651	−0.701	9.367
4	5.288	6.548	−0.864	10.016

Interplanar Angles (Deg)

plane no.	plane no.	angle	plane no.	plane no.	angle
1	2	0.67	2	3	2.14
1	3	1.65	2	4	1.69
1	4	1.60	3	4	3.10

Table IX. Molecular Parameters of Selected TCNQ Systems (Å)[a]



bond parameter	TCNQ[b]	(TTF)-(TCNQ)[c]	(TTF)-(TCNQ)[d]	Rb(TCNQ)[e]	Ni(TMP)-TCNQ[f]
a	1.344 (3)	1.356 (3)	1.352 (4)	1.374 (4)	1.346 (9)
b	1.443 (4)	1.433 (10)	1.433 (3)	1.423 (4)	1.437 (8)
c	1.373 (3)	1.402 (3)	1.395 (3)	1.420 (4)	1.381 (10)
d	1.436 (4)	1.423 (7)	1.432 (3)	1.416 (5)	1.431 (6)
e	1.138 (3)	1.151 (6)	1.149 (3)	1.153 (5)	1.143 (5)

[a] Librational corrections have not been included. [b] Reference 33; 298 K. [c] Reference 32; 298 K. [d] Reference 31; 100 K. [e] Reference 34; 113 K. [f] This work; 116 K.

Table X. Short (<3.4 Å) Intrastack Intermolecular Contacts (Å)

atoms	dist	atoms	dist
Ni-C(26)	3.304 (5)	C(8)-N(6)	3.380 (7)
Ni-C(30)	3.344 (5)	C(11)-C(29)	3.360 (7)
N(1)-C(26)	3.359 (6)	C(15)-C(35)	3.353 (7)
N(1)-C(27)	3.355 (6)	C(16)-C(31)	3.340 (7)
N(2)-C(28)	3.365 (6)	C(16)-C(35)	3.354 (7)
N(3)-C(30)	3.278 (6)	C(17)-C(35)	3.397 (7)
C(1)-C(26)	3.257 (7)	C(17)-N(7)	3.381 (7)
C(4)-C(27)	3.333 (6)	C(18)-N(8)	3.292 (7)
C(6)-C(32)	3.379 (7)	C(19)-C(31)	3.296 (7)
C(7)-C(33)	3.261 (7)		

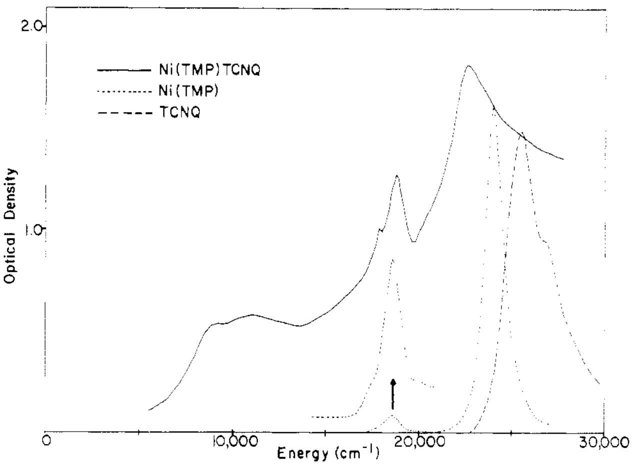


Figure 6. Visible and near-infrared spectra: (—) Ni(TMP)TCNQ in a KBr pellet; (---) Ni(TMP) in benzene; (– – –) TCNQ in acetonitrile.

most affected because of the face-to-face packing of the Ni(TMP) and TCNQ molecules. Two of the strongest bands in the spectrum of $TCNQ^0$ are the C-H bending mode (864 cm^{-1}) and the $C(CN)_2$ wagging mode (476 cm^{-1}),[46] and these bands decrease to 826 and 458 cm^{-1}, respectively, in Ni(TMP)TCNQ. The C≡N stretching frequency is found at 2228 cm^{-1} in $TCNQ^0$ and at 2219 cm^{-1} in Ni(TMP)TCNQ, a shift which is comparable with that observed for several other neutral TCNQ π complexes.[47] As expected for a weak π complex of this type, there are no bands in the region of the spectrum where the C≡N stretching modes of $TCNQ^{-}\cdot$ typically appear (2200–2180 cm^{-1}).[48]

The solid-state absorption spectrum of Ni(TMP)TCNQ in the visible and near-infrared region is shown in Figure 6, along with the solution spectra of the isolated donor and acceptor molecules. As was true for the infrared spectrum, the visible spectrum of Ni(TMP)TCNQ is composed of the sum of the spectra of the neutral component molecules. Upon formation of the complex with TCNQ, the porphyrin α band resolves to a distinct peak, and both the α and β bands shift to higher energy (~17 300 and 18 600 cm^{-1}, respectively, in Ni(TMP) vs. 17 900 and 18 900 cm^{-1} in Ni(TMP)TCNQ). This is in contrast to the results of solution studies of several metalloporphyrin charge-transfer complexes[3,10] where the porphyrin visible bands were unshifted relative to the bands of the uncomplexed porphyrin. Since the porphyrin Soret band usually broadens and decreases in intensity upon formation of a π complex in solution,[4,5] the sharp peak at 23 000 cm^{-1} probably arises from the $TCNQ^0$ $\pi \rightarrow \pi^*$ transition which occurs at 25 300 cm^{-1} in the solution spectrum of TCNQ.[49] The species $TCNQ^{-}\cdot$ has an absorption in this region as well, but we can rule out the possibility that any appreciable amount of $TCNQ^{-}\cdot$ is present since its low-energy transition[50] at 11 900 cm^{-1} is not observed.

The most interesting feature of the optical spectrum of Ni(TMP)TCNQ occurs in the near-infrared region. The two broad bands with maxima at 9100 and 11 100 cm^{-1} do not appear in the spectra of the isolated Ni(TMP) and TCNQ molecules and consequently can be assigned as intermolecular

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charge-transfer transitions (DA → D^+A^-).[51] Multiple charge-transfer bands can arise from (1) transitions from the highest filled donor orbital to several vacant acceptor orbitals or (2) transitions from several filled donor orbitals to the lowest unoccupied acceptor orbital. Since multiple charge-transfer bands are generally not observed in TCNQ π complexes, it is unlikely that the two bands in Ni(TMP)TCNQ arise from transitions to two vacant TCNQ π^* orbitals. Consequently, these bands are probably the result of electron transfer from two filled porphyrin orbitals to an unoccupied TCNQ π^* orbital with the energy difference between the two charge-transfer bands (~2000 cm^{-1}) corresponding to the energy difference between the two highest porphyrin π-molecular orbitals (a_{1u} and a_{2u}).[52]

For a series of complexes with the same acceptor, the energy of the charge-transfer transition is proportional to the ionization potential of the donor.[53] The solid-state charge-transfer band of perylene–TCNQ (10700 cm^{-1})[54] is close in energy to the Ni(TMP)TCNQ charge-transfer bands, so it appears that the ionization potentials of perylene and Ni(TMP) are very similar. The charge-transfer bands found by Sidorov[5] for several metalloporphyrin–TCNQ complexes in methylene chloride at 77 K occur at lower energies (7700–7100 cm^{-1}) than those found for Ni(TMP)TCNQ; however, it is not possible to draw any conclusions about the ionization potential of Ni(TMP) relative to the other metalloporphyrins because the experimental conditions that we used to record our spectra are so different from those used by Sidorov.

Electrical and Magnetic Properties. No conductivity along the needle axis of several Ni(TMP)TCNQ crystals could be detected at room temperature. For our apparatus, this indicates that the conductivity is less than $10^{-5}\ \Omega^{-1}\ cm^{-1}$.

Bulk magnetic susceptibility measurements show Ni(TMP)TCNQ to be diamagnetic. This is to be expected since in weak π complexes the concentration of unpaired electrons is rarely high enough to be detected by macroscopic susceptibility methods.[50] Electron paramagnetic resonance (EPR) spectroscopy is a more sensitive technique for detecting the weak paramagnetism found in several of the TCNQ π complexes.[50,55] No EPR signal was observed for Ni(TMP)TCNQ at either room temperature or 77 K; thus the degree of charge transfer is very small,[56] in agreement with spectral and structural results.

Summary

The new charge-transfer complex Ni(TMP)TCNQ has been prepared and consists of stacks of alternating Ni(TMP) and TCNQ molecules. As is typical of charge-transfer complexes with mixed stacks,[57] the conductivity of Ni(TMP)TCNQ is low ($<10^{-5}\ \Omega^{-1}\ cm^{-1}$). Since the visible and middle infrared spectrum of Ni(TMP)TCNQ is composed primarily of the sum of the spectra of neutral Ni(TMP) and TCNQ, we conclude that the intermolecular forces between adjacent molecules in the stack are weak compared with the intramolecular bonding of the component molecules. This conclusion is supported by magnetic measurements which show the compound to be diamagnetic and by a structural analysis of the TCNQ bond distances which show the amount of charge transfer to be less than 0.2 e. Charge-transfer interaction between adjacent Ni(TMP) and TCNQ molecules in the Ni(TMP)TCNQ stacks can be inferred from the presence of two charge-transfer bands in the near-infrared region of the spectrum and from the close contacts (<3.3 Å) of adjacent molecules in the stack. Although the region of donor–TCNQ overlap does include the Ni atom, the Ni–TCNQ distances are too large to permit significant interaction between the π orbitals of TCNQ and the d_{z^2} orbital of the Ni atom.

Acknowledgments. We thank Professor M. Gouterman and Professor W. C. Trogler for helpful discussions regarding the spectral results and Mr. J. Martinsen for assistance with EPR and susceptibility measurements. This research was generously supported by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR 79-23573) and by the National Science Foundation (Grant CHE80-09671 to J.A.I. and an NSF Graduate Fellowship to L.J.P.). A.U. thanks the Minna-James-Heineman-Stiftung for financial assistance.

Registry No. I, 67067-51-0; Ni(TMP)TCNQ, 78965-42-1.

Supplementary Material Available: A table of the root-mean-square amplitudes of vibration (Table III) and a listing of observed and calculated structure amplitudes (19 pages). Ordering information is given on by current masthead page.

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