or to an isolated Mn(III) ion.[30] These spin-state changes indicate structural changes of the Mn coordination sphere, which presumably bring about altered magnetic coupling between Mn ions in the cluster. A chloride requirement has also been noted for photoactivation of the disassembled Mn cluster, a process by which all four dissociated Mn(II) ions and Cl^- can rebind to the depleted protein complex to restore water oxidation.[31] If only Mn rebinding is assayed, an anion requirement is also observed.[32] Both the disassembly[33,34] and the reassembly of the Mn cluster indicate cooperative processes most likely associated with a discrete Mn cluster of 3–4 coupled Mn ions.

The present study has shown that depending on the nature of the counterion in solution, Mn(II) chelates with H_2dapd can assemble into monomeric Mn bis chelate complexes with noncoordinating counterions such as Br^- and ClO_4^-, while Cl^- induces assembly into an oligormic, probably dimeric or tetrameric, complex in solution. The special capability of Cl^- to serve as a bridging ligand between Mn(II) ions is thus established. Other factors are clearly important, such as the solvent and Mn oxidation state, both of which are different for the functional photosynthetic Mn site. A role for Cl^- in the initial assembly of the Mn cluster can be speculated with some justification now.

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Supplementary Material Available: Tables SI, SII, SIV, and SV, listing H atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, independent magnetic susceptibility data, and isothermal susceptibility data for **1**, respectively (3 pages); Table III, listing observed and calculated structure factors for **1** (6 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal Structure of [Ni(hMedbtaa)][TCNQ]. A Mixed-Stack Donor–Acceptor Molecular Solid

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A donor–acceptor molecular solid with formula [Ni(hMedbtaa)][TCNQ] (Ni(hMedbtaa) = (hexamethyldibenzotetraazaannulenato)nickel(II); TCNQ = tetracyanoquinodimethane) was obtained on mixing methylene chloride solutions of the neutral reagent compounds. The structure consists of integrated stacks (along *a*) of planar donor macrocycles and acceptor molecules. The distance between the centers of the nonparallel donor and acceptor molecules within these stacks is half the *a*-axis dimension, or 3.99 Å. Donor and acceptor molecules also alternate along axes parallel to the *b* axis, forming a two-dimensional donor–acceptor array parallel to the (110) plane. The intramolecular bond distances and the physical properties of this compound indicate a non-charge-transferred ground state. Crystal data: $C_{36}H_{30}N_8Ni$, monoclinic, space group $P2_1/a$ (No. 14), $a = 7.975$ (1) Å, $b = 21.845$ (5) Å, $c = 8.683$ (1) Å, $\beta = 98.95$ (1)°, $V = 1494.3$ (5) Å^3, $Z = 2$, $D_{calc} = 1.41$ g/cm^3.

The electrical properties of π-donor–acceptor compounds, molecular solids that result from the interaction of planar molecular donor (D) and electron-acceptor (A) species, have been investigated for nearly 30 years.[2-5] Overlap of the molecular π-orbital systems in the stacks of donor and acceptor species that typically occur in these solids, along with, in some situations, intermolecular charge transfer, makes possible cooperative electronic or magnetic phenomena.

For example, in the prototypical "organic metal" [TTF]-[TCNQ], segregated stacks of planar tetrathiafulvalene and tetracyanoquinodimethane form, through intermolecular charge transfer, partially occupied, electronic bands, which enable high, anisotropic electronic conductivity.[6] While most of the work in the development of charge-transfer solids has involved organic molecules as both donor and acceptor species, transition-metal complexes have been used successfully as acceptor,[7] donor,[8] and both acceptor and donor[9] in the preparation of two-component π-D–A compounds. Indeed, a molecular solid formed with transition-metal complexes may have properties that derive from cooperative interactions of electrons in metal-centered orbitals as well as from interactions of ligand π-electronic systems. The planar tetraaza[14]annulene transition-metal complexes (Figure 1), having both kinds of electronic systems, can function as donor species. Redox potentials of these macrocyclic metal complexes may be tuned through substitution of peripheral hydrogen atoms or variation of the metal center. Cutler, Alleyne, and Dolphin[10] found improved solubility and ease of preparation in various methyl-substituted dibenzo macrocycles, formed from diaminobenzenes and propyl diacetals in metal template reactions. Hunziker[11-13] and others[14-16] have reported the structures and properties of several highly conductive, nonstoichiometric compounds in which substituted dibenzotetraaza[14]annulene (dbtaa)

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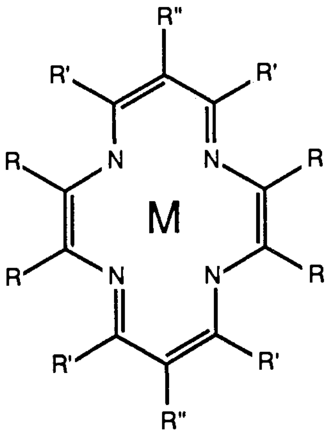

Figure 1. General form of the metallotetraaza[14]annulene macrocycle. In M(tatma) complexes, R, R″ = H and R′ = CH_3. In M(hMedbtaa), R–R = *o*-xylene, R′ = H, and R″ = CH_3.

metal complexes were partially oxidized by iodine.

In earlier studies,[9] we used the macrocyclic metal complex (tetramethyltetraaza[14lannulene)nickel(II), Ni(tatma), as the donor in preparation of π D–A compounds of the formula $[Ni(tatma)]_2[A]$ where A = TCNQ or $NiS_4C_4H_4$. Both compounds are charge-transferred and exhibit semiconductivity behavior, with room-temperature conductivities of 10^{-4}–10^{-3} $(\Omega\ cm)^{-1}$, E_a = 0.1–0.25 eV. The structure of the $[Ni(tatma)]_2[NiS_4C_4H_4]$ compound was determined by single-crystal X-ray diffraction methods. The structure of the previously studied π-donor–acceptor compound $[TTF]_2[NiS_4C_4H_4]$ indicated that, within one-dimensional stacks of TTF molecules, TTF cations formed spin-paired dimers. In like fashion, Ni(tatma) cations form spin-paired dimers in $[Ni(tatma)]_2[NiS_4C_4H_4]$. The dimer species alternate with neutral donor molecules in these two compounds to form one-dimensional stacks. The acceptor molecules, on the other hand, are not stacked, and their unpaired electrons are magnetically noninteracting. In recent work, Hoffman, Ibers, et al.[17] examined the metallic conductivity and phase transitions of a series of donor–acceptor solids that are structurally similar to $[TTF]_2NiS_4C_4H_4$. (In the new compounds selenium atoms replace sulfur in both donor and acceptor species, CF_3 groups replace H in the acceptor, and CH_3 groups replace H in the donor.)

In this paper, we report the preparation and X-ray crystal structure of an unusual compound formed of a hexamethyl-substituted Ni(dbtaa) complex and TCNQ. Although the compound is only weakly paramagnetic at room temperature, its mixed-stack structure is similar to that proposed by McConnell[18] for a D–A system that could stabilize ferromagnetic interactions. Several approaches to the preparation of ferromagnetic solids have been described in recent literature. Breslow[19,20] has reported organic donor and acceptor molecules for use in a McConnell-type mixed-stack donor–acceptor organic solid. Kahn and co-workers[21] have sought to synthesize molecular compounds whose magnetic properties result from the coupling of metal-centered spins in di-, tri-, or polynuclear transition-metal complexes. Still other charge-transfer solids are reported by Torrance[22] and by Miller, Epstein, et al.[23,24]

Table I. Crystallographic Data for [Ni(hMedbtaa)][TCNQ]

$C_{36}H_{30}N_8Ni$	fw 633.4
a = 7.975 (1) Å	space group $P2_1/a$ (No. 14)
b = 21.845 (5) Å	T = 25 °C
c = 8.683 (1) Å	λ = 0.71069 Å (Mo Kα)
β = 98.95 (1)°	ρ_{calc} = 1.41 g/cm^3
V = 1494.3 (5) Å^3	μ = 6.9 cm^{-1} (Mo)
Z = 2	R, R_w = 3.82, 3.93%

[Ni(hMedbtaa)][TCNQ] is the model compound for a new kind of molecular ferromagnet. Like the McConnell model, it is a mixed-stack donor–acceptor solid; like the compounds prepared by Kahn and co-workers, its metal ions are held in fixed relative positions, making possible interactions of metal-centered spins.

Experimental Section

Preparation of Compounds. 1,2-Diamino-4,5-xylene (Aldrich Chemical Co., Inc., Milwaukee, WI) was recrystallized at least three times from toluene solution; 3-ethoxymethacrolein (Aldrich) was distilled two times at reduced pressure (33 Torr, bp 106 °C) and was used as a clear, colorless liquid. Nickel acetate hydrate (Alfa-Ventron, Danvers, MA) was used as received. 7,7,8,8-Tetracyanoquinodimethane (Aldrich) was purified by vacuum sublimation at 130 °C. Solvents were distilled and deaerated immediately prior to use.

Ni(hMedbtaa). [5,14-Dihydro-2,3,7,11,12,16-hexamethyldibenzo-[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato(2−)-N^5,N^9,N^{14},N^{18}]nickel[11] was prepared by using an adaptation of literature methods for related complexes.[10,25] Nickel acetate and diaminoxylene solids were placed in a N_2-flushed reaction flask; *N*,*N*-dimethylformamide and water (3:2) were added via syringe, and the mixture was stirred at room temperature under nitrogen, forming a blue solution. Upon syringe addition of ethoxymethacrolein, the solution became yellow. Heating to 140 °C caused the solution to become red; after 30 h a fine red-purple solid was collected on a glass frit under inert atmosphere and washed with a small amount of DMF and with four 50-mL portions of water. The yield before recrystallization was 87%. The product was recrystallized two times by continuous extraction into CH_2Cl_2, yielding dark red-blue crystals. The solubility of the product in CH_2Cl_2 is ca. 0.6 mg/mL at 25 °C. Anal. Calcd for $C_{24}H_{26}N_4Ni$: C, 67.15; H, 6.12; N, 13.06. Found: C, 66.81; H, 6.23; N, 13.17.

[Ni(hMedbtaa)][TCNQ]. The compound of 1:1 stoichiometry was prepared by two methods. Very fine black needles were obtained by the room-temperature combination of 1 mM CH_2Cl_2 solutions of donor and acceptor compounds. Red Ni(hMedbtaa) and yellow TCNQ solutions were simultaneously cannula-transferred slowly under N_2 pressure into a receiving flask. After several minutes a black microcrystalline product formed; this was filtered and washed with fresh solvent and dried in vacuo. The yield was 52%. Anal. Calcd for $C_{36}H_{30}N_8Ni$: C, 68.27; H, 4.77; N, 17.69. Found: C, 68.09; H, 4.75; N, 17.80.

Black single crystals suitable for X-ray diffraction studies were obtained by the slow diffusion through solvent-swelled Sephadex LH-20 (Pharmacia LKB Biotechnology, Piscataway, NJ) of saturated CH_2Cl_2 solution of the reagent compounds. Reagents were separated at the start by ca. 2 cm of gel; after 24 h, black crystals were selected from the medium. A crystal of dimensions 0.08 × 0.14 × 0.42 mm^3 was chosen for analysis.

Physical Measurements. Absorption spectra were recorded with a Hewlett-Packard Model 8452 spectrophotometer. UV–visible reflectance spectra of solid samples were obtained by using an Optical Waveguide Spectrum Analyzer, Model 100 (Guided Wave, Inc.). Infrared spectra of TCNQ and [Ni(hMedbtaa)][TCNQ] as powder samples suspended in Nujol mulls were monitored with a Perkin-Elmer 1850 FTIR instrument. Elemental analyses were carried out by Desert Analytics, Tucson, AZ. X-ray powder diffraction measurements were made with a Philips APD 3520 diffractometer. [Ni(hMedbtaa)][TCNQ] formed by the direct combination of 1 mM solutions was ground to a powder and added to Scotch double cellophane tape on a glass microscope slide. The dc electrical resistance of a pressed powder sample of [Ni(hMedbtaa)][TCNQ] formed by the direct combination of reagents was measured with a Keithley 610 BR Electrometer.

Cyclic voltammetric studies of the macrocyclic nickel complex were performed with a BAS CV-27 instrument (Bioanalytical Systems, Inc., West Lafayette, IN).

The ESR signal of a polycrystalline sample was measured by using a Varian E-9 spectrometer, interfaced to a PDP-11/23 minicomputer.

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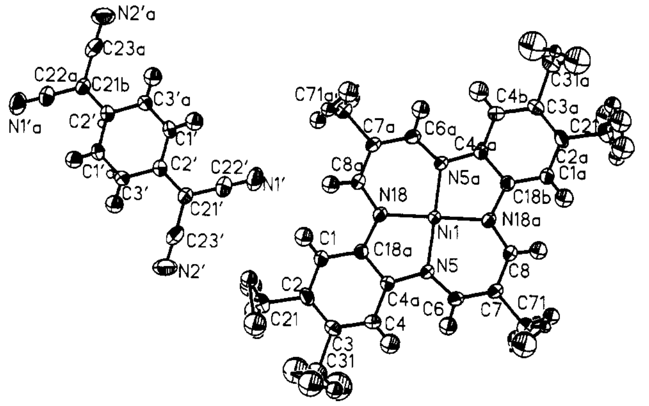

Figure 2. [Ni(hMedbtaa)][TCNQ] structure showing the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

Single-Crystal X-ray Data Collection and Reduction. Data were collected at room temperature on a Nicolet R3m diffractometer with molybdenum radiation and a graphite monochromator $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, 2357 reflections (1601 unique observed; i.e. $I > 3\sigma(I)$) were measured ($2\theta_{max} = 48°$), and Lorentz, polarization, and empirical absorption corrections ($\mu(\text{Mo}) = 6.9$ cm^{-1}) were applied. The programs of SHELXTL (Rev. 5.1) (Nicolet Corp., Madison, WI) were used for data reduction and all other calculations. Direct-phase determination followed by two Fourier cycles allowed all 23 nonhydrogen atoms in the asymmetric unit to be recognized. Atomic coordinates and anisotropic temperature factors were refined in all nonhydrogen atoms. A Fourier difference map showed peaks which indicated that all the methyl groups are present in two staggered conformations each. This model was refined per site occupation factors, with the coordinates of the hydrogen atoms riding on those of the corresponding carbon atoms. All hydrogen atoms were included in the refinement in calculated positions. The refinement converged at $R = 3.82\%$, $R_w = 3.93\%$.

Results and Discussion

The shiny black needles formed in the mixing of 1 mM solutions of Ni(hMedbtaa) and TCNQ are stable in air. The experimental X-ray powder diffraction pattern obtained from these crystals is in excellent agreement with the diffraction pattern generated from *d* spacings obtained from the X-ray diffraction study of the single-crystal sample, prepared by slow interdiffusion of the reactants.

Structure of [Ni(hMedbtaa)][TCNQ]. [Ni(hMedbtaa)][TCNQ] is monoclinic, space group $P2_1/a$ (No. 14). The atom-labeling scheme is indicated in Figure 2. The unit cell consists of layers of molecules, indicated as projections onto the *bc* plane in Figure 3A,B. The bottom ($x = 0$) layer and the top ($x = 1$) layer are identical and shown in part A. The middle ($x = 0.5$) layer is shown in part B. The mixed stacks parallel to the *a* axis are shown in Figure 3C. Atomic coordinates, selected bond lengths, and selected bond angles are given in Tables II–IV. The coordination geometry around each Ni atom is pseudosquare planar. The Ni–N distances are 1.859 (2) and 1.871 (3) Å. The Ni atoms are located at alternate inversion centers on the plane $z = 0$, i.e. at (0, 0.5, 0), (0.5, 0, 0), (0.5, 1, 0), and (1, 0.5, 0). The TCNQ molecules are located such that their centers of symmetry lie at the remaining inversion centers of that plane, i.e. (0, 0, 0), (0, 1, 0), (0.5, 0.5, 0), (1, 0, 0), and (1, 1, 0). The plane $z = 0.5$ is not occupied. Therefore, both the Ni(hMedbtaa) and the TCNQ molecules repeat at intervals of the *c*-axis dimension (8.683 (1) Å) along *c*. These molecules alternate along directions parallel to *a* and *b* at $^1/_2a = 3.987$ (1) Å and $^1/_2b = 10.922$ (5) Å (Figure 3). The planes of Ni(hMedbtaa) and TCNQ form angles of 14.5° with each other and 66.5 and 64.6°, respectively, with the *c* axis. (These are angles between the plane normals and the *c* axis.)

The closest approach between molecules is along directions parallel to the *a* axis. Viewed along the *a* axis, the Ni(hMedbtaa) and TCNQ molecules alternate in the stacks as donor and acceptor species; see Figure 3. The spacing of the centers of the molecules is $^1/_2\,a = 3.987$ (1) Å, but the normal distance is 3.28 (5) Å on average. The distances of the centers of adjacent stacks are $^1/_2b = 10.922$ (5) Å and $c = 8.683$ (1) Å. Both the Ni macrocycles and the TCNQ molecules are planar, as is required by the crystallographic symmetry.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	*y*	*z*	U^a
Ni(1)	0	5000	10000	26 (1)
N(18)	473 (3)	4173 (1)	9793 (3)	29 (1)
C(18A)	1272 (4)	4037 (1)	8491 (4)	28 (1)
C(1)	1816 (4)	3468 (1)	8065 (4)	32 (1)
C(2)	2539 (2)	3394 (1)	6728 (2)	34 (1)
C(21)	3111 (1)	2753 (1)	6299 (1)	47 (1)
C(3)	2702 (2)	3900 (2)	5787 (1)	35 (1)
C(31)	3449 (1)	3839 (1)	4265 (2)	49 (1)
C(4)	2195 (4)	4473 (2)	6205 (4)	36 (1)
C(4A)	1484 (4)	4550 (1)	7569 (4)	29 (1)
N(5)	931 (3)	5103 (1)	8168 (3)	28 (1)
C(6)	1120 (4)	5635 (2)	7458 (4)	32 (1)
C(7)	674 (4)	6198 (1)	7966 (2)	33 (1)
C(71)	989 (1)	6769 (1)	7012 (1)	44 (1)
C(8)	−83 (4)	6276 (1)	9280 (4)	31 (1)
C(21′)	1104 (4)	1092 (2)	8794 (4)	35 (1)
C(22′)	915 (4)	1674 (2)	9504 (4)	41 (1)
C(23′)	1877 (5)	1085 (2)	7418 (4)	42 (1)
N1′)	736 (5)	2137 (1)	10067 (4)	59 (1)
N(2′)	2497 (4)	1061 (2)	6309 (4)	62 (1)
C(1′)	−231 (4)	548 (2)	10759 (4)	36 (1)
C(2′)	556 (4)	558 (1)	9398 (4)	34 (1)
C(3′)	759 (4)	−24 (2)	8655 (4)	36 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Lengths (Å)

Ni(1)–N(18)	1.859 (2)	Ni(1)–N(5)	1.871 (3)
Ni(1)–N(18A)	1.859 (2)	Ni(1)–N(5A)	1.871 (3)
N(18)–C(18A)	1.413 (4)	N(18)–C(8A)	1.336 (4)
C(18A)–C(1)	1.386 (4)	C(18A)–C(4A)	1.403 (4)
C(1)–C(2)	1.384 (4)	C(2)–C(21)	1.537 (2)
C(2)–C(3)	1.392 (3)	C(3)–C(31)	1.537 (2)
C(3)–C(4)	1.380 (4)	C(4)–C(4A)	1.401 (5)
C(4A)–N(5)	1.411 (4)	N(5)–C(6)	1.335 (4)
C(6)–C(7)	1.373 (4)	C(7)–C(71)	1.538 (2)
C(7)–C(8)	1.382 (4)	C(8)–N(18A)	1.336 (4)
C(21′)–C(22′)	1.431 (5)	C(21′)–C(23′)	1.428 (5)
C(21′)–C(2′)	1.377 (5)	C(22′)–N(1′)	1.142 (5)
C(23′)–N(2′)	1.150 (5)	C(1′)–C(2′)	1.422 (5)
C(1′)–C(3′A)	1.345 (5)	C(2′)–C(3′)	1.448 (5)
C(3′)–C(1′A)	1.345 (5)		

Table IV. Bond Angles (deg)

N(18)–Ni(1)–N(5)	85.5 (1)	N(18)–Ni(1)–N(18A)	180.0 (1)
N(5)–Ni(1)–N(18A)	94.5 (1)	N(18)–Ni(1)–N(5A)	94.5 (1)
N(5)–Ni(1)–N(5A)	180.0 (1)	N(18A)–Ni(1)–N(5A)	85.5 (1)
Ni(1)–N(18)–C(18A)	113.9 (2)	Ni(1)–N(18)–C(8A)	125.9 (2)
C(18A)–N(18)–C(8A)	120.2 (3)	N(18)–C(18A)–C(1)	127.0 (3)
N(18)–C(18A)–C(4A)	113.4 (3)	C(1)–C(18A)–C(4A)	119.6 (3)
C(18A)–C(1)–C(2)	121.1 (3)	C(1)–C(2)–C(21)	119.2 (2)
C(1)–C(2)–C(3)	119.3 (2)	C(21)–C(2)–C(3)	121.5 (2)
C(2)–C(3)–C(31)	121.3 (2)	C(2)–C(3)–C(4)	120.5 (2)
C(31)–C(3)–C(4)	118.2 (2)	C(3)–C(4)–C(4A)	120.4 (3)
C(18A)–C(4A)–C(4)	119.1 (3)	C(18A)–C(4A)–N(5)	113.6 (3)
C(4)–C(4A)–N(5)	127.3 (3)	Ni(1)–N(5)–C(4A)	113.5 (2)
Ni(1)–N(5)–C(6)	125.8 (2)	C(4A)–N(5)–C(6)	120.7 (3)
N(5)–C(6)–C(7)	125.4 (3)	C(6)–C(7)–C(71)	118.8 (2)
C(6)–C(7)–C(8)	122.9 (2)	C(71)–C(7)–C(8)	118.3 (2)
C(7)–C(8)–N(18A)	125.5 (3)	C(22′)–C(21′)–C(23′)	117.3 (3)
C(22′)–C(21′)–C(2′)	121.8 (3)	C(23′)–C(21′)–C(2′)	120.9 (3)
C(21′)–C(22′)–N(1′)	178.9 (4)	C(21′)–C(23′)–N(2′)	178.1 (4)
C(2′)–C(1′)–C(3′A)	122.2 (3)	C(21′)–C(2′)–C(1′)	122.6 (3)
C(21′)–C(2′)–C(3′)	120.7 (3)	C(1′)–C(2′)–C(3′)	116.8 (3)
C(2′)–C(3′)–C(1′A)	121.1 (3)		

The TCNQ bond lengths and the planarity of the molecule argue strongly for the assignment of a neutral TCNQ, implying a non-charge-transferred ground state for this compound. TCNQ bond lengths are virtually identical with those reported for neutral TCNQ.[26] (The nitrile bond of TCNQ in the compound is slightly

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(26) Long, R. E.; Sparks, R. A.; Trueblood, K. N. *Acta Crystallogr.* **1965**, *18*, 932.

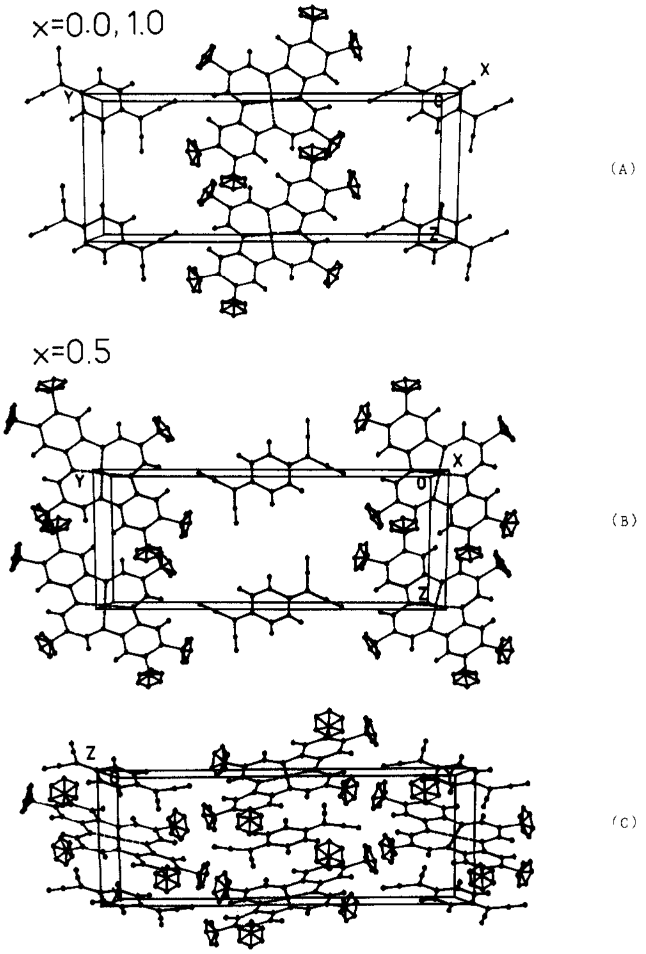

Figure 3. Views indicating molecular packing within the unit cell of [Ni(hMedbtaa)][TCNQ]. No one figure shows every molecule in the unit cell. (A) Projection onto the *bc* plane of molecules whose centers of gravity lie at $x = 0$ or $x = 1$. Note that these two "layers" of molecules are identical. (B) Projection onto the *bc* plane of molecules whose centers of gravity lie at $x = 0.5$. In the complete unit cell, this layer is sandwiched between two layers shown in part A. (C) Projection onto the *ab* plane of molecules whose centers of gravity lie at $z = 0$. The formation of mixed stacks along directions parallel to the *a* axis is indicated.

longer than that in the neutral molecule.) Furthermore, the planarity of TCNQ in this compound contrasts with the 2.6° dihedral angle formed between the plane of the $C(CN)_2$ subunits and the plane of the six-membered ring in the $TCNQ^-$ anion.[8]

Properties. Absorption maxima (extinction coefficients) of the Ni(hMedbtaa) complex in CH_2Cl_2 are at 426 nm (4.5×10^4), 452 nm (8.9×10^4), and 532 nm (9.7×10^3). The absorption spectrum of the [Ni(hMedbtaa)][TCNQ] compound dissolved in CH_2Cl_2 is only the additive sum of absorption spectra of the constituent compounds. We find no band in solution assignable to an intermolecular CT between associated D–A units.

Diffuse-reflectance UV–visible spectroscopy measured on a powder sample of [Ni(hMedbtaa)][TCNQ] shows a broad absorption that appears to be centered at 1000 nm (1000 nm is the limit of detection on this instrument), in addition to absorptions characteristic of solid samples of Ni(hMedbtaa) and TCNQ.

The nitrile stretching frequency we measure for neutral TCNQ is 2228 cm^{-1}, in agreement with the literature value. In the [Ni(hMedbtaa)][TCNQ] compound, this band is shifted to 2214 cm^{-1}. Chappell et al.[27] found a linear relationship between the nitrile stretching frequency and the degree of CT in a set of $TCNQ^-$ salts. According to this graph, 2214 cm^{-1} corresponds to a TCNQ charge of ca. −0.3; however, in view of the sensitivity of the CN stretching frequency to the local environment in the crystal structure, we do not attach much significance to this charge. The dc electrical resistance of a pressed powder sample was measured by a two-probe technique in a specially designed press. The observed conductivity (3.4×10^{-9} $(\Omega\ cm)^{-1}$) is consistent with insulating behavior for this π-D–A complex. As noted above, the existence of segregated donor and acceptor stacks, in addition to intermolecular charge transfer, is deemed necessary for high electrical conductivity in molecular solids. Therefore, low conductivity in this mixed-stack compound is not surprising.

The ESR spectrum of [Ni(hMedbtaa)][TCNQ] (7.5-mg sample of loosely packed needles, ca. 1 mm in length) shows two components; these signals saturate at different power levels, indicating independent origins. The more intense signal has *g* value of approximately 2.0039; the broader, less intense signal is largely obscured by the stronger signal; we could not determine its *g* value. The density of spins in a room-temperature sample of [Ni(hMedbtaa)][TCNQ] was calculated, by comparison of signal intensity to that of $Na_2[Cu(EDTA)]$, to be 7.5×10^{-5} spin/molecule, a low value consistent with a small degree of CT or, more likely, the presence of impurities or defects with unpaired electrons.

Cyclic voltammetry of the Ni(hMedbtaa) complex[28] in dichloromethane (with 0.1 M tetrabutylammonium perchlorate) shows a quasi-reversible wave at 0.23 V relative to SCE. The second reversible wave of TCNQ in the same solvent is at the same potential. The lack of appreciable CT character in [Ni(hMedbtaa)][TCNQ] is accordingly reasonable. The ready formation of a solid from solutions of these components suggests a weak donor–acceptor interaction that may develop into charge transfer in a compound formed from either a more easily oxidized analogue of the metal complex or a more easily reduced analogue of TCNQ.

Although the degree of CT in the ground state of this compound is, at best, very small, the observed structure meets the requirements proposed by McConnell[18] for stabilization of ferromagnetic coupling in a molecular solid. Specifically, [Ni(hMedbtaa)][TCNQ] consists of chains of alternating (potential) donor and acceptor molecules. Furthermore, adjacent stacks along the *y* axis (although not along the *z* axis) are out of registry by half the chain-axis repeat length, allowing the possibility of interchain spin alignment. The requirement that at least one type of radical possess an intrinsically or accidentally degenerate, partially occupied molecular orbital limits the structure of the radical to D_{2d}, $C3$, or higher, where symmetry lowering distortions do not occur.[23] Both M^{II}(hMedbtaa) (D_{2h}) and TCNQ (D_{2h}) meet this requirement.

Copper(II) and cobalt(II) analogues of Ni(hMedbtaa) would have paramagnetic metal centers. Charge transfer from the π system of the macrocycle to TCNQ could result in spin-coupling of the metal center and the oxidized macrocycle and simultaneous spin-coupling of donor and acceptor species. Our current efforts are in these directions.

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Supplementary Material Available: Tables of anisotropic thermal parameters, H atom coordinates and isotropic thermal parameters, and deviations from planes of macrocycle N and Ni atoms, TCNQ ring C atoms, and TNCQ $C(CN)_2$ fragments (8 pages); a listing of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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(27) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.

(28) Brown, P. M.; Interrante, L. V. Private communication.