BrO_2^+ participation. Whichever species is relevant the rate constants m and n in eq 13 are composite and may be expressed as k_mK and k_nKK_B (eq 23) where k_m and k_n are rate constants for the reactions of Hg^0

$$kK_3 = k_mK + k_nKK_B[H^+]^2 \qquad (23)$$

with BrO_3^- and BrO_2^+ (or H_2BrO_3), respectively. Using a value for K of 5.5×10^{-9} mol l.$^{-1}$ at 25°[36] $k_m = 3.7$ l. mol^{-1} sec^{-1} at 25°.

Acknowledgments. We are grateful to SRC for a postdoctoral fellowship to R. D., and to the University of Calgary for leave of absence to B. K.

[36] D. Peschanski and S. Vallados-Dubois, *Bull. Soc. Chim. Fr.*, 1170 (1956).

Ion Association and Charge-Transfer Excitation between Pyridinium Cations and Dianionic Dithiolene Complexes

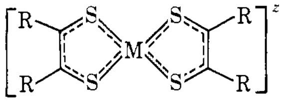
Ian G. Dance* and Priscilla J. Solstad

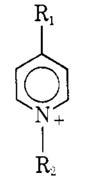
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

Received February 24, 1973

Abstract: A series of salts of anionic dithiolene complexes, $[M(mnt)_2]^{2-}$ (M = Zn, Cu, Ni, Co), $[M(mnt)_2]_n^{n-}$ (M = Cu(n = 1), Co(n = 2), Fe(n = 2)), $[Ni(tfd)_2]^{2-}$, and $[NiS_4C_4Ph_4]^-$ (mnt ≡ maleonitriledithiolate, tfd ≡ 1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate) with 1,4-substituted pyridinium cations including the 1-ethyl-4-carbomethoxypyridinium ion, KOS^+, have been prepared and characterized. The existence of a centrosymmetrical sandwich type ion associate of two planar cations enclosing a planar dianion with van der Waals separations has been demonstrated for $(KOS)_2M(mnt)_2$, M = Co, Ni, or Cu, in the crystalline state. Ion association prevails in solution, and in pyridine $K_1 = [(KOS)Ni(mnt)_2^-]/[KOS^+][Ni(mnt)_2^{2-}] = (7 \pm 4) \times 10^4\ M^{-1}$, $\beta_2 = [(KOS)_2Ni(mnt)_2]/[KOS^+]^2[Ni(mnt)_2^{2-}] = (1.1 \pm 0.7) \times 10^9\ M^{-2}$. The ion associates possess charge-transfer (anion to cation) transitions which appear in solid and solution spectra in the range 12–18 kK, with ϵ(solution) $<10^3\ M^{-1}\ cm^{-1}$. No anomalous magnetic properties occur, and it is concluded that there is negligible mutual electronic perturbation of anion and cation in the ground state. Nevertheless, the ion association is sufficient to modify the reactivity of some reduced dithiolene complexes.

Recent work on the reactivity patterns of transition metal dithiolene complexes[1] has emphasized the coordinative,[2–6] homogeneous electron-transfer,[4,7] and substitution[3,4,8,9] processes which occur for relatively oxidized, electron-poor, bisdithiolene complexes, I, z = 0, −1. Upon reduction to I, z = −2, the coordinative[6] and substitution[9,10] processes at the metal are markedly inhibited, while there is increased nucleophilicity at the sulfur donor atoms.[11] We are interested in the reactions of reduced, electron-rich, dithiolene complexes with reagents which may function as Lewis acids, cations, or oxidants and report here the results of structural and spectroscopic investigations of the compounds formed by dianionic dithiolene complexes and planar pyridinium cations, II.


I


II

Under appropriate conditions ion association would be expected;[12] the association between $Ni(mnt)_2^{2-}$ [13] and sterically encumbered, electronically insulated cations in acetonitrile has been measured.[14] It is also not unreasonable to anticipate modification of the reactivities of reduced complexes consequent upon such ion association, either *via* the reaction field[15] of the associated cations or *via* a charge-transferred excited state.[16]

Previous studies of anionic dithiolene complexes with nonspherical cations have encompassed a tropylium salt, $(C_7H_7)[Ni(tfd)_2]$,[17] a salt of the N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) cation radical $(TMPD)_2[Ni(mnt)_2]$,[18] phenothiazine and phenoxazine

---

[1] Review: J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

[2] G. R. Eaton and R. H. Holm, *Inorg. Chem.*, **10**, 805 (1971).

[3] J. K. Yandell and N. Sutin, *Inorg. Chem.*, **11**, 448 (1972); *J. Amer. Chem. Soc.*, **95**, 4847 (1973).

[4] I. G. Dance, T. R. Miller, and J. E. Cline, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, No. INOR 7.

[5] I. G. Dance and T. R. Miller, submitted to *Inorg. Chem.*

[6] I. G. Dance, *Inorg. Chem.*, **12**, 2381 (1973).

[7] I. G. Dance and J. E. Cline, submitted to *J. Amer. Chem. Soc.*

[8] (a) D. A. Sweigart and D. G. DeWit, *Inorg. Chem.*, **9**, 1582 (1970); (b) D. G. DeWit, M. J. Hynes, and D. A. Sweigart, *Inorg. Chem.*, **10**, 196 (1971).

[9] (a) I. G. Dance and T. R. Miller, *J. Chem. Soc., Chem. Commun.*, 433 (1973); *J. Amer. Chem. Soc.*, **95**, 6970 (1973); (b) I. G. Dance and T. R. Miller, unpublished work.

[10] R. G. Pearson and D. A. Sweigart, *Inorg. Chem.*, **9**, 1167 (1970).

[11] G. N. Schrauzer and H. N. Rabinowitz, *J. Amer. Chem. Soc.*, **90**, 4297 (1968).

[12] (a) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968. (b) R. A. Mackay and E. J. Poziomek, *J. Amer. Chem. Soc.*, **92**, 2432 (1970).

[13] Abbreviations: 1,2-dithiolene ligands, as in I: mnt when R = CN; tfd when R = CF_3; $S_2C_2Ph_2$ when R = Ph. Pyridinium cations, as in II: KOS^+ when $R_1 = CH_3COO$, R_2 = Et; 4-CNpyMe$^+$, 4-CNpyEt$^+$, and 4-CNpyBu$^+$ when R_1 = CN, R_2 = Me, Et, and n-Bu, respectively; pyMe$^+$ when R_1 = H, R_2 = Me.

[14] P. J. Lingane, *Inorg. Chem.*, **9**, 1162 (1970).

[15] W. Liptay, *Angew. Chem., Int. Ed. Engl.*, **8**, 177 (1969).

[16] E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965).

[17] R. M. Wing and R. L. Schlupp, *Inorg. Chem.*, **9**, 471 (1970).

[18] M. J. Hove, B. M. Hoffman and J. A. Ibers, *J. Chem. Phys.*, **56**, 3490 (1972).

Table I. Analytical Results[a]

Compound	Mp, °C	C	H	N	S
$(KOS)_2Co(mnt)_2$	176–177.5 (d)	45.98 (46.49)	3.57 (3.60)	12.70 (12.51)	
$(4\text{-}CNpyBu)_2Co(mnt)_2$	151–152	51.26 (50.82)	4.61 (3.96)	17.05 (16.93)	
$(pyMe)_2Co(mnt)_2$	209–211	45.60 (45.53)	3.04 (3.06)	15.97 (15.93)	
$(Bu_4P)_2[Co(mnt)_2]$	159–160	56.22 (55.98)	8.35 (8.46)	6.50 (6.53)	
$(KOS)_2[Co(mnt)_2]_2$	>250	40.54 (40.39)	2.45 (2.39)	13.93 (13.85)	
$(KOS)_2[Fe(mnt)_2]_2$		40.87 (40.64)	2.49 (2.41)	14.23 (13.94)	25.52 (25.53)
$(pyMe)_2[Fe(mnt)_2]_2$	255–259	38.89 (39.07)	1.66 (1.87)	16.13 (16.27)	
$(KOS)_2Ni(mnt)_2$	197.5–198.5	46.68 (46.51)	3.23, 4.19 (3.60)	12.57 (12.52)	18.53 (19.10)
$(4\text{-}CNpyMe)_2Ni(mnt)_2$		45.62 (45.77)	2.36 (2.44)	19.09 (19.41)	
$(4\text{-}CNpyEt)_2Ni(mnt)_2$		47.89 (47.61)	2.83 (3.00)	18.65 (18.51)	
$(4\text{-}CNpyBu)_2Ni(mnt)_2$	198–199	50.49 (50.84)	3.81 (3.96)	16.88 (16.94)	
$(pyMe)_2[Ni(mnt)_2]$	223.5–224	45.28 (45.55)	3.07 (3.06)	15.95 (15.94)	24.47 (24.32)
$(Bu_4P)_2[Ni(mnt)_2]$	166–167	56.35 (56.00)	8.32 (8.46)	6.66 (6.53)	
$(KOS)[Ni(mnt)_2]$	210–210.5	40.52 (40.41)	2.48 (2.39)		25.04 (25.38)
$(KOS)_2Ni(tfd)_2$		37.21 (37.03)	2.93 (2.87)	3.19 (3.32)	15.38 (15.21)
$(4\text{-}CNpyMe)_2Ni(tfd)_2$	184.5–186.5	35.41 (35.26)	1.64 (1.88)	7.38 (7.48)	
$(Bu_4P)_2[Ni(tfd)_2]$	159.5–161	47.47 (46.65)	7.08 (7.05)		12.76 (12.45)
$(KOS)[NiS_4C_4Ph_4]$	208.5–210	62.79 (62.62)	4.59 (4.55)	1.87 (1.89)	
$(KOS)_2Cu(mnt)_2$	172.5–173.5	46.08 (46.18)	3.50 (3.57)	12.30 (12.43)	18.84 (18.96)
$(KOS)_2Zn(mnt)_2$	128–130	46.41 (46.05)	3.54 (3.57)	12.25 (12.39)	
$(4\text{-}CNpyMe)_2Zn(mnt)_2$	194–195.5	45.18 (45.24)	2.42 (2.42)	19.55 (19.19)	
$(Bu_4P)_2[Zn(mnt)_2]$	108–108.5	55.88 (55.57)	8.17 (8.39)	6.55 (6.48)	

[a] Found (calculated) percentages

cation radical salts[19] of $[Ni(tfd)_2]^-$, and some cationic triphenylphosphine complexes of copper(I) and silver(I).[20]

Results

Synthesis of Complexes. Standard synthetic procedures were used to prepare the anionic dithiolene complexes $[M(mnt)_2]^{2-}$ (M = Zn, Cu, Ni, Co), $[M(mnt)_2]_n^{n-}$ (M = Cu(n = 1), Ni(n = 1), Co(n = 2), Fe(n = 1), $[M(tfd)_2]^{2-}$ (M = Ni, Co), and $[NiS_4C_4Ph_4]^-$ in solution, normally with ethanol as the primary solvent and in some cases with removal of Na^+ by precipitation of sodium chloride. On addition of aqueous or alcoholic solutions of the pyridinium cations (as iodide salts), the desired salts of the dithiolene complexes were readily crystallized. Salts with the electronically inert tetra-n-butylphosphonium cation (Bu_4P^+) have also been prepared for reference purposes. Microanalytical and melting point data characterizing all new compounds are presented in Table I.

In some cases a reduced dithiolene complex in association with a pyridinium cation is more susceptible to oxidation by molecular oxygen than is the complex with an inert cation. Thus the salts of $[Co(mnt)_2]^{2-}$ and $[Ni(tfd)_2]^{2-}$ with pyridinium cations must be prepared and purified in the absence of oxygen, and in addition a reducing agent was maintained in solution. This enhanced susceptibility to oxygen is so pronounced in the case of pyridinium salts of $[Co(tfd)_2]^{2-}$ that it has not been possible to isolate them in pure form.

Crystal Structure Data. The crystal structure of $(KOS)_2Ni(mnt)_2$ has been determined.[21] The primary feature of the lattice is a sandwich-type association of two planar KOS cations with each planar, centrosymmetric $Ni(mnt)_2$ complex. The intrasandwich cation–anion dihedral angle (10.8°), the orientation of the cation over the anion, and the cation–anion contact distances have been interpreted as a manifestation of delocalized anion–cation coulombic attraction, upon which is superimposed secondary localized attractions between the dithiolene sulfur atoms (with residual atomic charge negative[11]) and the 1,4 positions of the pyridinium ring (positive). The cation–anion contacts do not penetrate the estimated van der Waals barrier; the ion triplet in the crystal lattice is tight, but there is no structural evidence for anion–cation bonding overlap or mutual electronic perturbation. It is presumed that $[Ni(tfd)_2]^{2-}$ salts take the same structure, and that the different 1,4 substituents deployed on the pyridinium ring do not disrupt the sandwich ion associate.[22] A contrasting structural type is that[18] of $(TMPD)_2Ni(mnt)_2$ in which each dianion is immediately surrounded by six cations inclined to it by 59°.[21] However the cation in this compound is an odd electron species, and the structure has been interpreted as being a consequence of cation–cation interactions.

The polycrystalline sample diffraction data[23] reveal that $(KOS)_2M(mnt)_2$, M = Co, Ni, and Cu, possess very similar lattice dimensions and intensity distributions, and therefore the sandwich ion associate must also occur for the cobalt and copper compounds. The zinc homolog does not crystallize with the same lattice symmetry. It has been generally assumed, but not confirmed, that $Zn(mnt)_2^{2-}$ possesses pseudotetrahedral stereochemistry, in which case more localized cation–anion coulombic attractions are probable. The KOS^- salts of the oxidized iron and cobalt complexes, $(KOS)_2[M(mnt)_2]_2$, are not isostructural.

Magnetic Properties. The magnetic susceptibilities of polycrystalline samples of the KOS^+ salts at room temperature are not different from those of the corresponding salts with more inert cations.

---

[19] W. E. Geiger, Jr., and A. H. Maki, *J. Phys. Chem.*, **75**, 2387 (1971).

[20] D. Coucouvanis and M. L. Caffery, Abstracts, National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, No. INOR 114, and private communication.

[21] I. G. Dance, P. J. Solstad and J. C. Calabrese, *Inorg. Chem.*, **12**, 2161 (1973).

[22] In $(KOS)_2Ni(mnt)_2$ the N-alkyl chain is twisted toward the periphery of the sandwich. The melting points (Table I) of the salts are all very similar.

[23] See paragraph at end of paper regarding supplementary material.

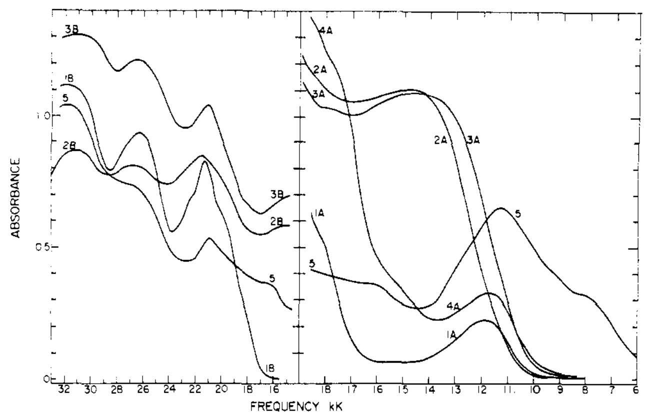


Figure 1. Diffuse reflectance spectra of polycrystalline compounds $(cation)_2Ni(mnt)_2$ and $(Bu_4P)[Ni(mnt)_2]$ (trace 5). Cation legend: 1, Bu_4P^-; 2, KOS^+; 3, 4-CNpyEt$^+$; 4, pyMe$^+$. $(Bu_4P)[Ni(mnt)_2]$ was diluted strongly with MgO for both traces; for the other compounds the traces labeled A refer to the undiluted powder while those labeled B are for the compound diluted with MgO or $MgSO_4$.

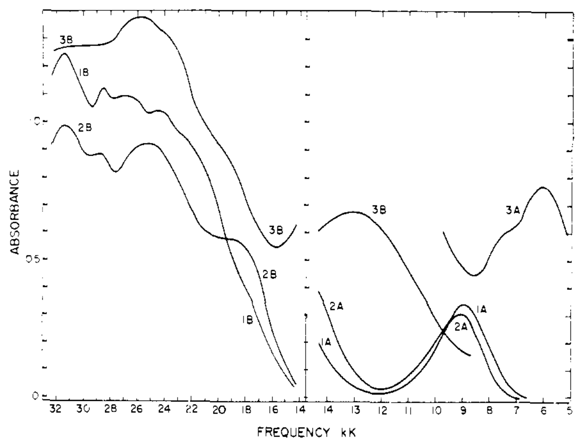


Figure 2. Diffuse reflectance spectra of polycrystalline $(Bu_4P)_2Cu(mnt)_2$ (traces 1), $(KOS)_2Cu(mnt)_2$ (traces 2), and $(Bu_4P)[Cu(mnt)_2]$ (traces 3). The labels A and B refer to undiluted and diluted samples, respectively.

Electronic Spectra. Solid State. Diffuse reflectance spectra have been recorded for polycrystalline samples of all complexes with reference (n-Bu_4P^+) and pyridinium cations, over the range 5–33 kK. Representative spectra for derivatives of $M(mnt)_2{}^{2-}$, M = Ni, Co, Cu, or Zn, are displayed in Figures 1–4, while additional spectra for $Ni(tfd)_2{}^{2-}$ and a complete tabulation of all spectral data are recorded separately.[23] Bands characteristic of the oxidized form of the dithiolene complex are absent in all cases, and new absorptions which are not characteristic of the cation or anion are apparent. These are assigned as the charge-transfer (ct) transitions. In $(KOS)_2Ni(mnt)_2$, $(4\text{-}CNpyEt)_2Ni(mnt)_2$, $(KOS)_2Ni(tfd)_2$, $(4\text{-}CNpyR)_2Ni(tfd)_2$, $(KOS)_2Co(mnt)_2$, and $(4\text{-}CNpyR)_2Zn(mnt)_2$ (R = Me, Et, and n-Bu) the additional absorption is clearly resolved as a very broad (*ca.* 5 kK band width at half-height) moderately intense transition at a frequency lower than the intense intraanion transitions in the visible and uv region. However, in pyMe$^+$ salts of $Ni(mnt)_2{}^{2-}$, $Ni(tfd)_2{}^{2-}$, and $Co(mnt)_2{}^{2-}$, and in $(4\text{-}CNpyBu)_2Co(mnt)_2$ and $(KOS)_2Zn(mnt)_2$, the additional absorptions overlap the region of intense anion absorptions. Even though there is no resolved maximum, the approximate frequency of the ct transition is still readily distinguished.

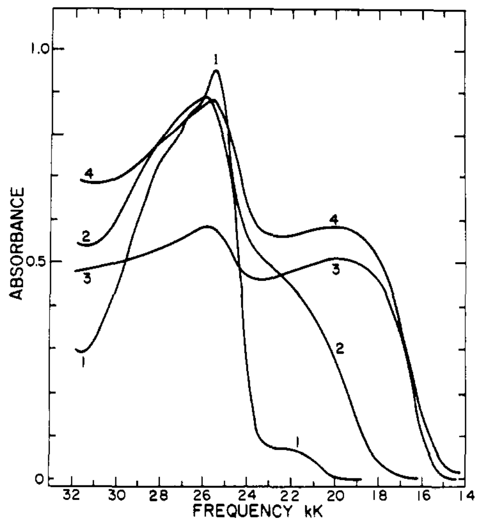


Figure 3. Diffuse reflectance spectra of polycrystalline compounds $(cation)_2Zn(mnt)_2$. Cation legend: 1, Bu_4P^+; 2, KOS^+; 3, 4-CNpyMe$^+$; 4, 4-CNpyEt$^+$. All samples are diluted with $MgSO_4$.

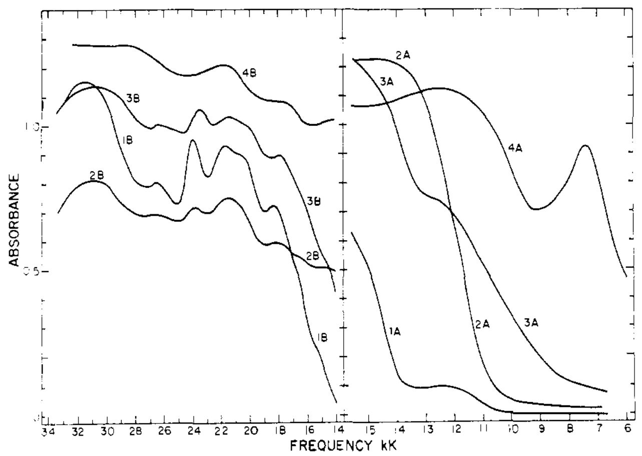


Figure 4. Diffuse reflectance spectra for polycrystalline compounds $(cation)_2Co(mnt)_2$ and $(Bu_4P)_2[Co(mnt)_2]_2$ (traces 4). Cation legend: 1, Bu_4P^+; 2, KOS^+; 3, pyMe$^+$. The labels A and B refer to undiluted and diluted samples, respectively.

The ct frequencies are listed in Table II. The width (and, in some cases, shape) of the ct absorptions are in-

Table II. Charge-Transfer Transition Frequencies from Diffuse Reflectance Spectra

Compd	Freq,[a] kK	Compd	Freq,[a] kK
$(KOS)_2Ni(mnt)_2$	14.8	$(pyMe)_2Ni(tfd)_2$	18.1
$(4\text{-}CNpyMe)_2Ni(mnt)_2$	13.0(sh), 15.3	$(KOS)_2Co(mnt)_2$	14.8
$(4\text{-}CNpyEt)_2Ni(mnt)_2$	13.3(sh), 14.7	$(4\text{-}CNpyBu)_2Co(mnt)_2$	13.2
$(4\text{-}CNpyBu)_2Ni(mnt)_2$	15.2	$(pyMe)_2Co(mnt)_2$	14–16[b]
$(pyMe)_2Ni(mnt)_2$	14–18[b]	$(KOS)_2Cu(mnt)_2$	18[b]
$(KOS)_2Ni(tfd)_2$	14.0	$(KOS)_2Zn(mnt)_2$	21.5[b]
$(4\text{-}CNpyMe)_2Ni(tfd)_2$	12.4	$(4\text{-}CNpyMe)_2Zn(mnt)_2$	19.7
$(4\text{-}CNpyBu)_2Ni(tfd)_2$	12.8	$(4\text{-}CNpyEt)_2Zn(mnt)_2$	20.0

[a] All bands are very wide; the quoted precision represents the frequency of the maximum and is not an indication of band width.
[b] Unresolved absorption.

dicative that more than one transition may be present, but for none of the compounds has it been possible to resolve such structure at room temperature. In the reflectance spectra of pyridinium salts of $Ni(mnt)_2^{2-}$, $Ni(tfd)_2^{2-}$, and $Cu(mnt)_2^{2-}$, at frequencies higher than the first ct transition, there are indications of absorption not due to the cation or anion, and it is possible that higher frequency ct transitions exist.

The spectra of $(KOS)_2[Co(mnt)_2]_2$ and $(KOS)_2[Fe(mnt)_2]_2$ in the crystalline state show the bands characteristic of the dimeric form of the anion in each case, with no additional cation-dependent transitions.

Solution Spectra and Equilibria. Solution spectra in various solvents have been recorded for most of the new complexes. Although there are several influences on the appearance of the ct absorptions in solution, as described below, solution spectra very similar to those observed for the crystalline compounds can be obtained. Intensities of the ct bands are concentration and solvent dependent in aprotic solvents (*e.g.*, acetone, acetonitrile, pyridine) and decrease markedly on addition of water. The behavior is generally consistent with the expected ion-association equilibria, shown in eq 1 and 2 for $(KOS)_2Ni(mnt)_2$ which has been studied

$$KOS^+ + [Ni(mnt_2)]^{2-} \rightleftharpoons [(KOS)Ni(mnt_2)]^- \quad K_1 \qquad (1)$$

$$KOS^+ + [(KOS)Ni(mnt_2)]^- \rightleftharpoons [(KOS)_2Ni(mnt)_2] \quad K_2 \qquad (2)$$

in greatest detail. At various degrees of ion association in solution only one type of ct spectrum is observed. Since the transition frequency is very close to that of the 2:1 sandwich ion associate known in the crystal, it can be concluded either that the ct frequencies of the 1:1 and 2:1 ion associates are sufficiently similar to be unresolved or that the concentration of the 1:1 associate is always very much less than that of the 2:1 associate. The former interpretation is the more plausible.

Attempts to confirm these equilibria, evaluate the equilibrium constants, and calculate full spectra for the solvated ion associates are complicated by two additional phenomena. The first is that the ion-association constants for pyridinium cations with dithiolene complex anions are of similar magnitude to those with other anions such as ClO_4^- which are unavoidable gegenions if the cation concentration is to be increased. The second complication is a dependence of the charge-transfer transition frequency on the total concentration of ions, a solvatochromic effect.[24] The following series of spectral experiments demonstrates these effects and permits determination of the equilibrium constants; all results are for $(KOS)_2Ni(mnt)_2$ in pyridine, the solvent which maximizes both solubility and ion association: series A, solutions containing only KOS^+ and $Ni(mnt)_2^{2-}$, in which the intensity and frequency of the ct band both increase with the concentration of $(KOS)_2Ni(mnt)_2$; series B, solutions containing only KOS^+, Bu_4P^+, and $Ni(mnt)_2^{2-}$ at constant total ion concentration, in which the absorption frequency is *invariant* over the full range of absorption intensities; series C, solutions containing only KOS^+, $Ni(mnt)_2^{2-}$, and ClO_4^-, with $[KOS^+]_T/[Ni(mnt)_2^{2-}]_T$ ratios 2 to 50; series D, solutions containing KOS^+, Bu_4P^+, $Ni(mnt)_2^{2-}$, and ClO_4^-, $[KOS^+]_T/[Ni(mnt)_2^{2-}]_T$ ratios 0 to 50. The extrapolated limit spectrum with maximum ct absorption intensity is 91% attained at 2.0×10^{-3} *M* $(KOS)_2Ni(mnt)_2$ in series A and 96% attained when $[Ni(mnt)_2^{2-}]_T = 2.0 \times 10^{-3}$ *M*, $[KOS^+]_T = 1.4 \times 10^{-2}$ *M*, and $[ClO_4^-]_T = 1.0 \times 10^{-2}$ *M* in series C. The magnitude of the influence of ion concentration on ct absorption frequency can be illustrated by comparing spectra in series B and C. For two solutions of comparable ϵ_{max}, ν_{max} is 14.2 kK at 6×10^{-3} *M* total ions, and 14.6 kK at 57×10^{-3} *M* total ions.[25]

Quantitative analysis necessitated several approximations. The peak frequency shift was avoided by utilizing ϵ_{max} data rather than intensities at specific frequencies through the ct spectrum. Inclusion of association equilibria for all ions in solution overparametrizes the problem, and therefore the association of Bu_4P^+ with $Ni(mnt)_2^{2-}$ (possible in series B and D) and of Bu_4P^+ with ClO_4^- (possible only in series D) was neglected.[26] The remaining parameters, optimized by least-squares computations, are K_1; $\beta_2 = K_1K_2$; K_0, the ion-association constant for $KOS^+ClO_4^-$; ϵ_1, for $(KOS)Ni(mnt)_2^-$; and ϵ_2, for $(KOS)_2Ni(mnt)_2$. Calculations with separate data sets reveal that a model with only eq 1 is inconsistent with data set B and a model without eq 1 poorly reproduces data sets C and D. It is concluded that both $KOS^+–Ni(mnt)_2^{2-}$ ion associates are present in solution. A full calculation based on all data yields parameters (95% confidence limits in parentheses): $K_0 = 2.8 \times 10^4$ M^{-1} (26%), $K_1 = 6.6 \times 10^4$ M^{-1} (61%), $\beta_2 = 1.1 \times 10^9$ M^{-2} (66%), $\epsilon_1 = 180$ M^{-1} cm^{-1} (6%), $\epsilon_2 = 420$ M^{-1} cm^{-1} (2%). The discrepancy residual, $R = \Sigma|\epsilon_{obsd} - \epsilon_{calcd}|/\Sigma\epsilon_{obsd} = 0.019$, is within experimental error. It is noted that $K_2 = 1.7 \times 10^4$ M^{-1} is not much less than K_1 and that $\epsilon_1 \simeq {}^1/_2\epsilon_2$.

Discussion

The lowest frequency additional absorption band in the spectra of the ion associates is assigned as an anion to cation, $\pi \rightarrow \pi^*$ ($b\pi.a\pi$ in Mulliken's notation[27]), charge-transfer transition

$$\begin{pmatrix}\text{pyridinium}\\ \text{cation}\end{pmatrix}^{+}\begin{bmatrix}\text{dithiolene}\\ \text{dianion}\end{bmatrix}^{2-}\begin{pmatrix}\text{pyridinium}\\ \text{cation}\end{pmatrix}^{+} \xrightarrow{h\nu}$$

$$\begin{pmatrix}\text{pyridinyl}\\ \text{radical}\end{pmatrix}^{0}\begin{bmatrix}\text{dithiolene}\\ \text{monoanion}\end{bmatrix}^{-}\begin{pmatrix}\text{pyridinium}\\ \text{cation}\end{pmatrix}^{+}$$

which is analogous to the n–π^* transition in the halide and pseudohalide salts of pyridinium cations.[12,28] This assignment is confirmed by the positive correlation of the charge-transfer transition energy with the approximate free energy of electron transfer from the

---

(24) M. Mohammad and E. M. Kosower, *J. Phys. Chem.*, **74**, 1153 (1970).

(25) Owing to the high degree of association of all ions in pyridine solution the actual ionic strength will be much less than the total analytical concentration of ions, and therefore the ionic strength influence on the charge transfer transition frequency will be considerably larger than implied by the 0.4 kK shift cited.

(26) This is justifiable to the extent that (i) Bu_4P^+ is expected to associate with the anions less than KOS^+, (ii) $[Bu_4P^+]_T \ll [KOS^+]_T$ in all but several solutions, (iii) neither of the neglected associates contributes absorbance at the frequencies in question, and (iv) examination of the data fits revealed no substantial systematic deviations which could be attributed to the neglected effects. Nonetheless, the calculated association constants will be slightly in error due to this approximation.

(27) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969.

(28) G. Briegleb, W. Jung, and W. Herre, *Z. Phys. Chem.* (*Frankfort am Main*), **38**, 253 (1963).

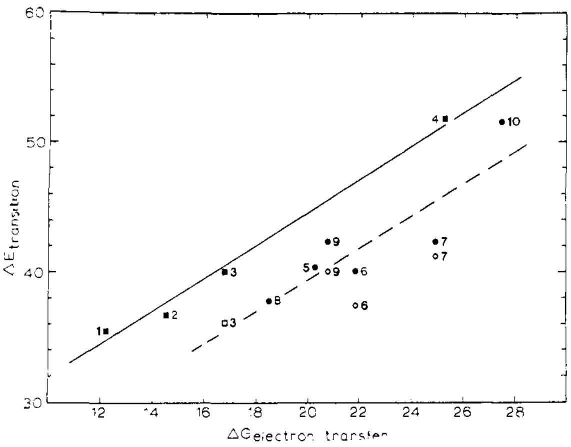


Figure 5. Charge-transfer transition energy plotted against the free energy of anion → cation electron transfer. Both energies are in kcal mol^{-1}, and the free energies of electron transfer are for acetonitrile solution: solid points represent the transition energy in the solid state, open points the transition energy in pyridine solution. Key: 1, (4-CNpyMe)$_2$Ni(tfd)$_2$; 2, (4-CNpyBu)$_2$Ni(tfd)$_2$; 3, (KOS)$_2$Ni(tfd)$_2$; 4, (pyMe)$_2$Ni(tfd)$_2$; 5, (4-CNpyMe)$_2$Ni(mnt)$_2$; 6, (4-CNpyEt)$_2$Ni(mnt)$_2$; 7, (KOS)$_2$Ni(mnt)$_2$; 8, (4-CNpyBu)$_2$Co(mnt)$_2$; 9, (KOS)$_2$Co(mnt)$_2$; 10, (KOS)$_2$Cu(mnt)$_2$. The slopes of the correlation lines are 1.28 (solid line, for Ni(tfd)$_2$$^{2-}$ compounds) and 1.13 (broken line, for M(mnt)$_2$$^{2-}$ compounds). Due to the breadth of the charge-transfer transition bands the vertical uncertainties are *ca.* 1-2 kcal mol^{-1}.

anion to the cation,[29] when both are varied over a 16 kcal mol^{-1} range by variation of both the anion and the cation. The data are plotted in Figure 5. The more precise points for solid samples of the four (cation)$_2$Ni(tfd)$_2$ compounds show good linear correlation with a slope ($\Delta E(h\nu)/\Delta G_{ct}$) of 1.25. The energy of the additional absorption in pyridinium salts of [Zn(mnt)$_2$]$^{2-}$ correlates with the ease of reduction of the cation and is indicative of charge transfer.

All evidence is consistent with interpretation of the ion-association energy in these compounds solely in terms of coulombic attraction between planar ions with delocalized charges. The ion-association free energy is considerably greater than that of almost all of the numerous charge-transfer complexes composed of neutral donor and acceptor molecules.[27,32] This is illustrated in the following set of association constants, which, for molecular complexes of planar organic molecules, are of the order 10^{-1}–10^{1} M^{-1} in solvents such as carbon tetrachloride;[32] for cobalt(II) and nickel(II) metalloporphyrins with polynitroaromatics in dichloromethane range 10^{2}–10^{3} M^{-1};[33] for Ni(tfd)$_2^-$ with the phenothiazine cation radical in dichloromethane is 1.2 × 10^4 M^{-1};[19] and for Ni(mnt)$_2$$^{2-}$ with KOS$^+$ in pyridine is 7 × 10^4 M^{-1} (and considerably larger, although unquantitated owing to low solubility, in dichloromethane).

The ct transition is thus a consequence of the association between an oxidizable anion and a reducible cation. One might expect that many such charge transfer ion associates should exist. However, the only well-documented types appear to be chloranil–TMPD,[34,35] pyridinium salts,[12,28,30] Ni(tfd)$_2^-$–phenothiazine$^+$,[19] paraquat^{2+}–MX$_4$$^{n-}$,[36] Ni(mnt)$_2$$^{2-}$–TMPD$^+$,[18,37] and those of the present work.[38]

It is appropriate to question the extent of electronic interaction of the ions in the ion associate. The extinction coefficients of the ct transitions are less than 5 × 10^2 M^{-1} cm^{-1}, comparable with those of the pyridinium halides. This together with the normal magnetic properties of the dithiolene anions, the van der Waals cation–anion separation and distribution of [Ni(mnt)$_2$]$^{2-}$ chelate bond lengths in the structure of (KOS)$_2$Ni(mnt)$_2$, indicates that there is no substantial mutual electronic perturbation of the anion and pyridinium cation in these associates. Furthermore, there is no detectable difference between the association of the first and second KOS cations with Ni(mnt)$_2$$^{2-}$. The ct transition frequencies for (KOS)Ni(mnt)$_2^-$ and (KOS)$_2$Ni(mnt)$_2$ are indistinguishable, the extinction coefficient (per Ni) for the second is twice that of the first, and K_2 is only slightly less than K_1. The light absorption process in these ion associates is essentially pure photoexcited electron transfer.

Despite these conclusions, charge-transfer ion association does influence the reactivity of the dianionic dithiolene complex. As expected, it is the electron-transfer reactivity, namely M(S-S)$_2$$^{2-}$ + O$_2$ $\rightleftharpoons$ M(S-S)$_2^-$ + O$_2^-$ in aprotic solvents, which is affected. No information bearing upon the mechanism of this cation influence is yet available. Since ion association is strongly solvent dependent, it is anticipated that this modification of reactivity will vary considerably with solvent.

In the present series of compounds an approximately linear relationship exists between $\Delta E_{charge\text{-}transfer}$ and the free energy of electron transfer between the *separated* ions, analogous to similar relationships for uncharged molecular complexes.[27,32] We have considered also the charge transfer ion associate of the phenothiazine cation radical with Ni(tfd)$_2^-$,[19] for which the data point (ΔE_{ct} ≈ 22 kcal mol^{-1}, $\Delta G_{electron\text{-}transfer}$ ≈ +3 kcal mol^{-1}) also falls on the straight line drawn for the (cation)$_2$Ni(tfd)$_2$ data in Figure 5. Extrapolation of this line yields ΔE_{ct} ~ +18 kcal mol^{-1} when $\Delta G_{electron\text{-}transfer}$ = 0. Although insufficient data are available to

---

(29) The free energies of electron transfer between the separated ions are obtained from the electrochemical potentials in acetonitrile, where the systems are electrochemically and chemically reversible and observed potentials closely approximate thermodynamic potentials. The anion oxidation data used are (all *vs.* SCE): [Cu(mnt)$_2$]$^{2-\rightarrow 1-}$, +0.34 V; [Ni(mnt)$_2$]$^{2-\rightarrow 1-}$, +0.23 V; [Co(mnt)$_2$]$^{2-}$ → $^1/_2$[Co(mnt)$_2$]$_2$$^{2-}$, +0.05 V (the unknown [Co(mnt)$_2$]$^{2-\rightarrow 1-}$ potential is more positive of this by the negative of the free energy of dimerization); [Ni(tfd)$_2$]$^{2-\rightarrow 1-}$, −0.12 V. The cation reduction data are essentially those of Mackay, *et al.*,[30] which differ by approximately 0.09 V from earlier values[31] but provide the internally consistent set required here: KOS$^{+\rightarrow 0}$, −0.85 V; 4-CNpyMe$^{+\rightarrow 0}$, −0.65 V; 4-CNyEt$^{+\rightarrow 0}$, −0.72 V; 4-CNpyBu$^{+\rightarrow 0}$, −0.75 V (estimated); pyMe$^{+\rightarrow 0}$, −1.21 V.

(30) R. A. Mackay, J. R. Landolph, and E. J. Poziomek, *J. Amer. Chem. Soc.*, **93**, 5026 (1971).

(31) W. M. Schwarz, E. M. Kosower, and I. Shain, *J. Amer. Chem. Soc.*, **83**, 3155 (1961).

(32) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969.

(33) (a) H. A. O. Hill, A. J. Macfarlane and R. J. P. Williams, *J. Chem. Soc. A*, 1704 (1969); (b) C. D. Barry, H. A. O. Hill, B. E. Mann, P. J. Sadler, and R. J. P. Williams, *J. Amer. Chem. Soc.*, **95**, 4545 (1973).

(34) F. H. Herbstein, *Perspect. Struct. Chem.*, 4, 339 (1971).

(35) Reference 32, p 47.

(36) (a) A. J. MacFarlane and R. J. P. Williams, *J. Chem. Soc. A*, 1517 (1969); (b) C. K. Prout and P. Murray-Rust, *ibid.*, 1520 (1969).

(37) I. G. Dance, unpublished work.

(38) (a) In an investigation of the interaction of a series of acceptor quinones with dianionic dithiolene complexes I, Burgess, *et al.*,[38b] observed only the electron transfer reactions predictable from the potentials of the separated species and found no evidence for association and charge transfer transitions. This is not surprising since *all* species in their solutions were either anionic or neutral and therefore unlikely to associate. (b) J. Burgess, K. M. C. Davis, R. D. W. Kemmitt, J. B. Raynor, and J. Stocks, *Inorg. Chim. Acta*, 4, 129 (1970).

proceed with certainty, we note that thermodynamic analysis indicates that a considerable portion of this 18 kcal mol^{-1} should be attributed to the equilibration of the Franck–Condon charge-transfer state.

Experimental Section

Electronic spectra of solutions were obtained at ambient temperature (23 ± 1°) in cells of path length 0.01–2.5 cm, using Cary 14 and Beckman DK2A spectrophotometers with exclusion of oxygen as necessary to prevent oxidation. Solid-state spectra were recorded on a Cary 14 spectrophotometer, fitted with an integrating sphere for polychromatic sample irradiation in the diffuse reflectance configuration. A block of magnesium carbonate served as reference. Samples were finely powdered, applied to a translucent adhesive tape, and directly exposed at the sample port. Sample dilution was effected by grinding with magnesium oxide or anhydrous magnesium sulfate. The background for the tape with diluent was subtracted from all spectra prior to presentation. All compounds were examined both neat and diluted, in order to maximize the detection and resolution of the weakest and strongest absorptions within the range 1900–300 nm. Spectra obtained by this technique were found to be far superior to mull transmission spectra. The almost colorless salt (Bu$_4$P)$_2$[Zn(mnt)$_2$] is light sensitive, and rapidly changes to a lemon yellow color in strong visible light, owing to an increase in absorption in the weak 22-kK band. The spectrum presented in Figure 3 was obtained from a sample which had undergone negligible photochemical change.

Polycrystalline X-ray diffraction patterns were obtained with a Phillips diffractometer fitted with a graphite monochromator between the sample and the counter; Cu Kα radiation was employed.

Magnetic susceptibilities were measured on a Faraday balance, calibrated with HgCo(SCN)$_4$. The diamagnetic corrections applied to the molar susceptibilities were -104×10^{-6} cgsu for KOS$^+$ and -112×10^{-6} cgsu for all [M(mnt)$_2$]: (KOS)$_2$Ni(mnt)$_2$, $\chi_g = -0.71 \times 10^{-6}$ cgsu (296°K), $\chi'_M = -156 \times 10^{-6}$ cgsu; (KOS)$_2$Co(mnt)$_2$, $\chi_g = 2.46 \times 10^{-6}$ cgsu (296°K), $\mu_{\mathrm{eff}}{}^{296} = 2.16$ BM; (KOS)$_2$Cu(mnt)$_2$, $\chi_g = 1.44 \times 10^{-6}$ cgsu (296°K), $\mu_{\mathrm{eff}}{}^{296} = 1.75$ BM; (KOS)$_2$[Fe(mnt)$_2$]$_2$, $\chi_g = 1.74 \times 10^{-6}$ cgsu (296°K), $\mu_{\mathrm{eff}}{}^{296}$ (per Fe) = 1.61 BM; (KOS)$_2$[Co(mnt)$_2$]$_2$, $\chi_g = -0.27 \times 10^{-6}$ cgsu (296°K), χ'_M(per Co) = $+80 \times 10^{-6}$ cgsu.

For the solution equilibria data a computer program was written, using Newton–Raphson methods, to calculate concentrations of all species in equilibria $A^+ + B^- \rightleftharpoons AB$, $A^+ + C^{2-} \rightleftharpoons AC^-$, and $2A^+ + C^{2-} \rightleftharpoons A_2C$ in terms of total concentrations and equilibrium constants. This was incorporated with a nonlinear least-squares routine to optimize equilibrium constants and species extinction coefficients from a set of observed solution absorbances.

Acetonitrile was distilled first from calcium hydride, then from P$_4$O$_{10}$ and stored over 3 Å molecular sieves. Pyridine was distilled from calcium hydride and stored over 3 Å molecular sieves. The pyridinium iodides were prepared by refluxing the substituted pyridine with the alkyl iodide in acetone, followed by cooling and crystallization. Bu$_4$P$^+$Cl$^-$ is commercially available; Bu$_4$P$^+$ salts of the dithiolene complexes were prepared by slight modifications of standard procedures.

Preparation of Salts of [M(mnt)$_2$]$^{2+}$ (M = Co, Ni, Cu, Zn). The normal synthetic procedure involved combination of absolute ethanol solutions of Na$_2$mnt (20 mmol) and the metal chloride or nitrate (10 mmol) under nitrogen, removal of any precipitated sodium chloride by filtration (in order to minimize complications owing to crystallization of Na$_2$M(mnt)$_2$ in subsequent stages), and addition of an ethanolic solution of the iodide of the appropriate cation (20 mmol) followed by addition of water and evaporation of ethanol as necessary to crystallize the product. Recrystallization was from acetone–2-propanol in the presence of a small excess of the cation iodide, by slow evaporation of the acetone. Further specific details, variations, and observations follow.

(KOS)$_2$Ni(mnt)$_2$. Upon addition of the KOS$^+$I$^-$ solution to the [Ni(mnt)$_2$]$^{2-}$ solution, an instantaneous green coloration was observed prior to crystallization of the product. The recrystallization was performed in air but with tri-*n*-butylamine (*ca.* 1 ml) present to inhibit complex oxidation. The red-black crystalline product is soluble in acetonitrile, pyridine, acetone, and 1:1 glyme–water but insoluble in dichloromethane, chloroform, carbon disulfide, ethyl acetate, glyme, alcohols, and water.

(4-CNpyBu)$_2$Ni(mnt)$_2$ possesses additional solubility in glyme and 1:1 methanol–water.

(4-CNpyEt)$_2$Ni(mnt)$_2$ is less soluble than the KOS$^+$ salt in most solvents and was purified by dissolution in a hot mixture of acetone and acetonitrile under nitrogen, followed by addition of isobutyl alcohol to complete crystallization.

(4-CNpyMe)$_2$Ni(mnt)$_2$ was recrystallized from hot DMSO by addition of methanol and water. It is much less soluble than the KOS$^+$ salt in pyridine and acetonitrile.

(KOS)$_2$Cu(mnt)$_2$. On combination of the metal and ligand solutions some unidentified insoluble salt of [Cu(mnt)$_2$]$^{2-}$ precipitated from the brown solution. Addition of an excess of KOS$^+$I$^-$ and digestion of the slurry at 70° for 1 hr effects conversion to the desired salt which crystallizes further on cooling.

(KOS)$_2$Co(mnt)$_2$. All operations were performed under nitrogen, and *ca.* 0.1 g of KOH was maintained in the alcoholic solutions to ensure that none of the less soluble oxidized salt, (KOS)$_2$[Co(mnt)$_2$]$_2$, was present.

(4-CNpyEt)$_2$Zn(mnt)$_2$ and (4-CNpyMe)$_2$Zn(mnt)$_2$. Small amounts of a white crystalline material, presumably Na$_2$Zn(mnt)$_2$, invariably precipitated and were removed prior to crystallization of the product. (4-CNpyMe)$_2$Zn(mnt)$_2$ was recrystallized from hot ethanol by addition of water, as red-purple flakes.

(pyMe)$_2$M(mnt)$_2$ (M = Co, Ni, Cu) was recrystallized from acetone–isobutyl alcohol; the cobalt compound was prepared in the presence of a little KOH to counter aerial oxidation.

Preparation of (KOS)[Ni(mnt)$_2$] and (KOS)$_2$[Co(mnt)$_2$]$_2$. The standard synthetic procedure was followed, with iodine as the oxidizing agent and recrystallization in the presence of a trace of iodine.

(KOS)$_2$[Fe(mnt)$_2$]$_2$. To a solution of Na$_2$mnt (7.5 g, 40 mmol) in hot absolute ethanol (200 ml) under nitrogen was added a solution of FeCl$_3 \cdot 6$H$_2$O (5.5 g, 20 mmol) in absolute ethanol (50 ml). After filtration of the precipitated sodium chloride a solution of KOS$^+$I$^-$ (6 g, 20 mmol) in water (50 ml) was added. The large black crystals which formed on cooling were collected and recrystallized twice from acetone–2-propanol.

Preparation of Salts of [Ni(tfd)$_2$]$^{2-}$. [Ni(tfd)$_2$]^0 (*ca.* 2 g) slurried in a mixture of methanol and DMF was reduced with hydrazine hydrate (*ca.* 1 ml). Filtration of the resulting yellow-orange solution into a methanolic or aqueous methanolic solution of excess of the cation iodide salt produced an initial intense blue or green color, followed by crystallization of the product. Addition of water yielded further product.

(KOS)$_2$Ni(tfd)$_2$ was recrystallized twice from acetonitrile–2-propanol containing added small amounts of hydrazine hydrate and KOS$^+$I$^-$, yielding brown platelets.

(4-CNpyMe)$_2$Ni(tfd)$_2$ was recrystallized from acetone–2-propanol and isobutyl alcohol under nitrogen.

(pyMe)$_2$Ni(tfd)$_2$ was recrystallized from acetonitrile and water in the presence of hydrazine hydrate and pyMe$^+$I$^-$, as brown plates.

(4-CNpyBu)$_2$Ni(tfd)$_2$ precipitated from the original preparative solution as beautiful green needles. Attempts at recrystallization yielded oils.

Preparation of (KOS)[NiS$_4$C$_4$Ph$_4$]. [NiS$_4$C$_4$Ph$_4$] was slurried in methanol and DMF, and reduced with hydrazine hydrate to produce the blood red solution of the monoanionic complex. This was filtered into an aqueous methanol solution of KOS$^+$I$^-$ producing a microcrystalline red precipitate, which was separated and recrystallized from a hot mixture of acetone and DMF by addition of water.

Acknowledgments. This work was supported by grants from the National Science Foundation (GP 24443X), and the Graduate School, University of Wisconsin. Dr. Carl Bowser of the Geochemical Laboratory is thanked for the use of the powder diffractometer, as is Mr. J. Kleppinger for the magnetic susceptibility determinations.

Supplementary Material Available. A listing of polycrystalline sample diffraction data, diffuse reflectance spectra of compounds (cation)$_2$Ni(tfd)$_2$, and a complete tabulation of all reflectance spectra will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7256.