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

Sandwich Ion Associate Structure of Bis(1-ethyl-4-carbomethoxypyridinium) Bis(maleonitriledithiolato)nickelate(II)

IAN G. DANCE,* PRISCILLA J. SOLSTAD, and J. C. CALABRESE

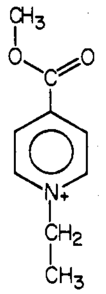
Received February 6, 1973

The crystal structure of the title compound contains planar centrosymmetrical $[Ni(mnt)_2]^{2-}$ dianions sandwiched between planar (excepting the alkyl groups) 1-ethyl-4-carbomethoxypyridinium cations (KOS^+). Within this sandwich ion associate the dihedral angle between the $Ni(mnt)_2$ and KOS planes is 10.8° and the closest anion–cation contacts are Ni- -C = 3.41 Å, S- -N = 3.68 Å, S- -C = 3.70 Å, and C- -O = 3.39 Å, which are interpreted as the van der Waals contact distances for this structure. Other interion contacts in the crystal are not significant in determining the packing. Crystal data are as follows: $a = 10.688$ (3) Å, $b = 8.974$ (2) Å, $c = 15.747$ (3) Å, $\beta = 91.44$ (2)°; space group $P2_1/c$; $Z = 2$; $d_{\text{obsd}} = 1.4801$ g cm^{-3}, $d_{\text{calcd}} = 1.4767$ g cm^{-3}. The structure was solved from 993 reflections observed with the Syntex $P\bar{1}$ diffractometer (Mo Kα radiation). Final structure factor residuals are $R_1 = 4.1\%$, $R_2 = 4.4\%$.

Introduction

Square-planar transition metal–dithiolene complexes which are relatively electron rich (that is, the most reduced complexes[1] $[M(S\text{-}S,R)_2]^{2-}$ of the latter transition metals cobalt, nickel, and copper) have been considered to be coordinatively unreactive, in contrast to their more oxidized forms, and consequently have not been fully investigated. This is in part due to early observations on the lack of additional coordinative interaction of these complexes with traditional Lewis base ligands.[2] More recently Pearson has found that $[Ni(mnt)_2]^{2-}$ [1] and related complexes are remarkably resistant to substitution.[3] However, Schrauzer[4] has demonstrated the nucleophilic reactivity of the sulfur atoms in the reduced nickel, palladium, and platinum complexes, and Coucouvanis[5] has utilized the Lewis basicity of some reduced nickel–dithiolene complexes with respect to strong class b acceptors $(Ph_3P)_2Ag^+$ and $(Ph_3P)_2Cu^+$. The ion association of $(C_2H_5)_4N^+$ and $[Ni(mnt)_2]^{2-}$ in acetonitrile solution has been measured.[6]

We have studied these reduced complexes and their coordinative reactions, many of which involve very small free energy changes. The weak interaction between $[Co(mnt)_2]^{2-}$ and pyridine has been demonstrated electrochemically.[7] Using pyridinium cations, in particular 1-ethyl-4-carbomethoxypyridinium (KOS^+) we have prepared a series of transition metal mnt and tfd complexes, some of which manifest anion → cation charge-transfer spectroscopic transitions in crystalline and solution phases.[8] The crystal structure of $(KOS)_2Ni(mnt)_2$, a charge-transfer ion associate, has been determined to aid interpretation of the anion–cation electronic interactions and is reported here.



KOS^+

Experimental Section

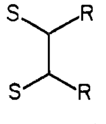
Crystal Growth. The preparation and characterization of $(KOS)_2Ni(mnt)_2$ are described elsewhere.[8] Crystals were grown from an acetone–2-propanol solution by slow evaporation. The predominant crystal form was a red-black prismatic needle, although some very thin plates, approximately hexagonal and appearing red by transmitted light, were also obtained. Only the needles were examined crystallographically.

Crystal Data. Preliminary Weissenberg photographs indicated a monoclinic cell with systematic absences for $h0l$, $l = 2n + 1$. The space group is $P2_1/c$ with b^* parallel to the needle axis and a^* normal to the largest face of the needle. The unit cell dimensions were calculated from a least-squares procedure[9] based on the refined diffraction angles for 15 reflections accurately positioned with the Syntex $P\bar{1}$ diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å): $a = 10.6883$ (26) Å, $b = 8.9742$ (20) Å, $c = 15.7473$ (28) Å, $\beta = 91.444$ (17)°, unit cell volume 1509.97 (56) Å^3. The molecular weight is 671.48 amu. With $Z = 2$ the calculated density is 1.477 g cm^{-3}, whereas the density measured by flotation in a carbon tetrachloride–heptane mixture is 1.480 g cm^{-3}.

Intensity Data Collection. The data were collected using the 2θ scan technique with variable scan speeds from 2 to 24°/min, determined as a function of the peak intensity. The stationary backgrounds were counted for a total of 0.8 of the time used for the scan count. Two standard peaks monitored every 50 reflections showed no significant deviation in intensity. A total of 1650 reflections were measured and treated in the usual manner for Lorentz and polarization effects.[10] The data were then merged to give 993 independent observations for which $F > 2\sigma(F)$. The effects of absorption ($\mu = 9.49$ cm^{-1}) were ignored as the variation in absorption be-

---

[1] Abbreviations for the 1,2-dithiolene ligand (S-S,R)



mnt when R = CN; tfd when R = CF_3; $KOS^+ \equiv$ 1-ethyl-4-carbomethoxypyridinium cation.

[2] (a) H. B. Gray, *Transition Metal Chem.*, 1, 239 (1965); (b) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, 3, 663 (1964); (c) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Amer. Chem. Soc.*, 88, 43 (1966).

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

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

[5] D. Coucouvanis and M. L. Caffery, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, No. INOR 114; also private communication.

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

[7] I. G. Dance, *Inorg. Chem.*, in press.

[8] I. G. Dance and P. J. Solstad, submitted for publication in *J. Amer. Chem. Soc.*

[9] "$P\bar{1}$ Autodiffractometer Operations Manual," Syntex Analytical Instruments Division, Cupertino, Calif.

[10] All preliminary calculations leading to the solution of the structure were performed on a 16K computer (Raytheon 706) using programs (J. C. C.) FOBS, SORTMERGE, FCALC, FOURIER, PEAKLIST, and CHAIN and bond length programs.

tween the maximum and minimum test reflections for the needlelike crystal was 3.5% on F.

Solution and Refinement of the Structure. The Patterson function was easily interpreted with the nickel atom located at a center of symmetry. The remaining nonhydrogen atoms were located by standard Fourier techniques. The least-squares refinement[11] minimized the residual $\Sigma w(|F_o| - |F_c|)^2$, where $w(hkl) = [\sigma\{F_o(hkl)\}]^{-2}$, and the discrepancy residuals reported are

$$R_1 = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \qquad R_2 = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w(F_o)^2}\right]^{1/2}$$

Three cycles of least-squares refinement with isotropic atomic temperature factors converged at $R_1 = 0.094$, $R_2 = 0.107$. The [Ni(mnt)$_2$] anion and the KOS cation were then separately refined with anisotropic thermal parameters, reducing the residuals to $R_1 = 0.061$, $R_2 = 0.072$. A difference Fourier at this stage revealed the largest peaks close to the expected positions of the 12 hydrogen atoms per asymmetric unit. These hydrogen atoms were assigned idealized locations (d(C–H) = 1.00 Å) and included in all subsequent structure factor calculations with $B_{\text{iso}} = 5.0$ Å^2. Further least-squares refinement with the hydrogen atoms maintained in idealized positions, culminating in full-matrix optimization of all parameters except those of hydrogen, converged at $R_1 = 0.041$, $R_2 = 0.044$. Standard errors were computed[12] from the final variance-covariance matrix.

The atomic scattering factors used were those of Hanson, *et al.*,[13a] for the nonhydrogen atoms and those of Stewart, *et al.*[13b] for the hydrogen atoms. During the final stages of refinement the anomalous dispersion corrections of Cromer[14] for nickel and sulfur were incorporated in the structure factor calculations.

The observed and final calculated structure factors are listed elsewhere.[15]

Results

Description of the Structure. The atomic identifying symbols are given in Figure 1. The atomic coordinates and anisotropic thermal parameters are listed with their standard errors in Table I. The Ni(mnt)$_2$ and 4-carbomethoxypyridine ring units are essentially planar, as shown by the best planes and individual atom deviations reported in Table II. These planar units are arranged in the lattice in sandwich fashion with two KOS cations either side of each Ni(mnt)$_2$ at a center of symmetry. The angle between the normal to the Ni(mnt)$_2$ plane and the normals to the two KOS planes which complete each sandwich is 10.8°. A projected view[16] of all atoms in the (KOS)Ni(mnt)$_2$(KOS) sandwich normal to the Ni(mnt)$_2$ plane is shown in Figure 2. Each KOS superimposes approximately half of the Ni(mnt)$_2$ chelate, with C(8) overlying Ni, N(3) overlying S(1), C(7) approximately overlying S(2), C(12) over C(2), and O(1) over C(1). The Ni–C(8) vector is rotated only 6.3° from the normal to the Ni(mnt)$_2$ plane and 14.3° from the normal to the pyridinium ring plane.

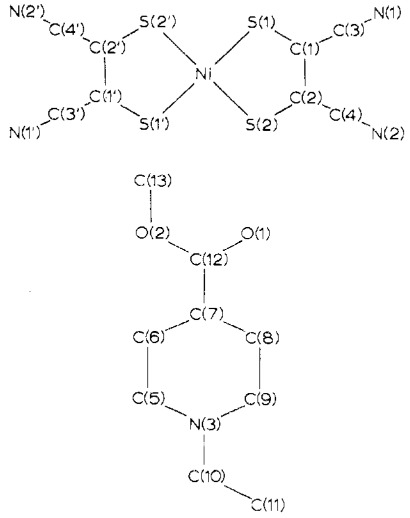


Figure 1.

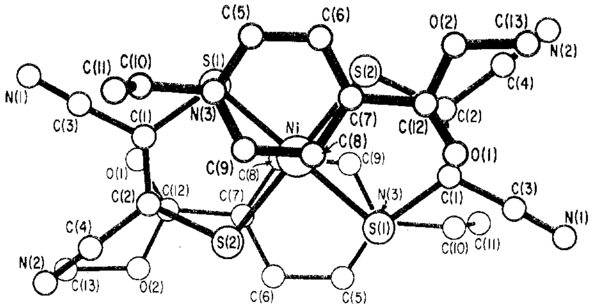


Figure 2. Projection of the (KOS)$_2$Ni(mnt)$_2$ sandwich unit onto the Ni(mnt)$_2$ plane, showing the orientation of the 4-carbomethoxypyridinium ring over the chelate atoms, and the sequence of contacts S(1)–N(3), Ni–C(8), S(2)–C(7), C(2)–C(12), C(1)–O(1), almost normal to the Ni(mnt)$_2$ plane.

As the primary interest in this structure is derived from the charge-transfer interaction between the anion and the cation, the interion contacts in the crystal have been examined in detail. The van der Waals radii of the various functionalities are assumed as follows: (a) the nickel nonbonded radius, normal to the planar chelate, not less than 1.63 Å;[17] (b) sulfur van der Waals radius, 1.80 Å;[17,18] (c) cyano nitrogen and carbonyl oxygen radii, 1.6–1.7 Å normal to the multiple bond and 1.4 Å parallel to the bond;[17] (d) half-thickness of the aromatic ring, 1.77 Å;[17] (e) ether oxygen radius, 1.52 Å;[17] (f) methyl group radius, 2.0 Å;[18] (g) hydrogen van der Waals radius, 1.2 Å;[18] (h) upper limit to C–H· · ·S hydrogen bonding, d(H–S) = 3.05 Å; (i) upper limit to C–H· · ·N(cyano) hydrogen bonding, d(H–N) = 2.6 Å. The significant interion contacts are listed in Table III, and all types except the two interanion contacts involving cyano groups are drawn in Figure 3, which shows the overall arrangement of the sandwiches in the complex from a viewpoint almost end-on to one of the Ni(mnt)$_2$ anions. From Figures 2 and 3, and Table III, it is clearly apparent that the largest number of significant interion contacts occur within the [(KOS)Ni(mnt)$_2$(KOS)] sandwich, which is the dominant feature in the crystal packing.[19] Zigzag lines of sandwiches extend through the lattice.

---

[11] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1963.

[12] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[13] (a) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964); (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[14] D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

[15] A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth 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 INORG-73-2161.

[16] C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[17] A. Bondi, *J. Phys. Chem.*, 68, 441 (1964).

[18] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 258 ff.

[19] No chemical significance other than that of lattice requirements can be attributed to the intersandwich interion contacts listed in Table III. The orientation (with respect to the constituent ions) of the short carbonyl oxygen O(1) to pyridine ring carbon C(5) contact (3.02 Å) is not interpretable as a conventional bonding interaction.

Table I. Final Atomic Parameters and Estimated Standard Deviations[a] for $(KOS)_2Ni(mnt)_2$

Atom	x/a	y/b	z/c	$10^2\beta_{11}$	$10^2\beta_{22}$	$10^2\beta_{33}$	$10^2\beta_{12}$[b]	$10^2\beta_{13}$[b]	$10^2\beta_{12}$[b]
Ni	0	0	0	0.928 (15)	0.942 (19)	0.402 (7)	−0.133 (15)	−0.082 (7)	−0.064 (10)
S(1)	−0.07898 (18)	0.15537 (20)	0.08983 (12)	1.109 (23)	1.263 (31)	0.522 (11)	−0.197 (22)	0.027 (12)	−0.213 (15)
S(2)	−0.17393 (18)	−0.12606 (21)	−0.00997 (13)	1.009 (23)	1.308 (31)	0.637 (12)	−0.226 (21)	−0.064 (13)	−0.231 (16)
C(1)	−0.23126 (65)	0.09051 (81)	0.10041 (44)	1.100 (94)	1.242 (121)	0.438 (40)	−0.086 (93)	−0.120 (48)	0.001 (62)
C(2)	−0.27247 (64)	−0.03243 (76)	0.05861 (42)	0.990 (87)	1.114 (120)	0.509 (40)	−0.104 (83)	−0.204 (48)	0.032 (58)
C(3)	−0.31025 (76)	0.17167 (94)	0.15640 (55)	1.173 (110)	1.675 (154)	0.672 (56)	−0.305 (104)	−0.052 (61)	−0.175 (75)
C(4)	−0.39636 (79)	−0.09220 (84)	0.06981 (45)	1.276 (107)	1.291 (123)	0.553 (44)	−0.219 (100)	−0.133 (59)	0.036 (62)
N(1)	−0.37149 (65)	0.24169 (82)	0.20053 (47)	1.704 (111)	2.314 (155)	0.862 (53)	0.056 (103)	0.322 (57)	−0.502 (75)
N(2)	−0.49283 (64)	−0.14171 (78)	0.07897 (48)	1.229 (91)	2.398 (147)	1.031 (52)	−0.692 (97)	−0.030 (57)	0.341 (69)
N(3)	0.19090 (58)	−0.38466 (74)	0.09053 (37)	1.071 (83)	1.240 (112)	0.564 (36)	−0.098 (85)	−0.032 (44)	−0.005 (52)
C(5)	0.09753 (80)	−0.48410 (79)	0.09139 (43)	1.238 (95)	1.079 (113)	0.525 (41)	−0.048 (113)	−0.147 (52)	−0.019 (63)
C(6)	−0.01184 (70)	−0.45646 (75)	0.13197 (47)	1.069 (94)	1.102 (138)	0.544 (42)	−0.081 (84)	−0.016 (51)	−0.074 (60)
C(7)	−0.02517 (69)	−0.32207 (82)	0.17273 (44)	1.048 (96)	0.974 (124)	0.490 (43)	−0.005 (96)	−0.167 (50)	0.086 (59)
C(8)	0.07096 (84)	−0.21911 (81)	0.17173 (44)	1.487 (108)	1.095 (122)	0.504 (45)	−0.122 (110)	−0.024 (58)	−0.088 (57)
C(9)	0.17824 (78)	−0.25366 (94)	0.12954 (52)	1.432 (112)	1.242 (141)	0.584 (48)	−0.222 (100)	−0.152 (58)	0.105 (68)
C(10)	0.30786 (80)	−0.42441 (95)	0.04644 (49)	1.241 (105)	2.021 (150)	0.696 (53)	0.020 (106)	−0.042 (62)	0.106 (75)
C(11)	0.39117 (76)	−0.51425 (110)	0.10097 (56)	1.436 (111)	2.927 (199)	0.918 (58)	0.227 (125)	0.280 (63)	0.160 (95)
C(12)	−0.14111 (77)	−0.28301 (102)	0.21853 (47)	1.259 (109)	1.384 (145)	0.463 (45)	0.108 (115)	−0.195 (55)	−0.092 (67)
C(13)	−0.33727 (77)	−0.37652 (90)	0.25985 (51)	1.302 (105)	2.076 (159)	0.729 (51)	−0.092 (106)	−0.062 (58)	−0.149 (65)
O(1)	−0.16025 (50)	−0.16565 (62)	0.25219 (34)	1.665 (74)	1.499 (93)	0.722 (35)	0.194 (68)	−0.036 (38)	−0.284 (48)
O(2)	−0.22062 (49)	−0.39841 (63)	0.21728 (33)	1.003 (63)	1.777 (97)	0.856 (35)	−0.038 (67)	0.089 (38)	−0.243 (48)
HC(5)	0.108	−0.582	0.061						
HC(6)	−0.080	−0.533	0.132						
HC(8)	0.062	−0.121	0.201						
HC(9)	0.248	−0.178	0.128						
H(1)C(10)	0.353	−0.330	0.031						
H(2)C(10)	0.286	−0.481	−0.006						
H(1)C(11)	0.348	−0.610	0.115						
H(2)C(11)	0.412	−0.459	0.154						
H(3)C(11)	0.470	−0.538	0.070						
H(1)C(13)	−0.384	−0.291	0.233						
H(2)C(13)	−0.320	−0.354	0.321						
H(3)C(13)	−0.389	−0.469	0.255						

[a] The estimated standard deviations shown in parentheses refer to the least significant digit(s) of the parameter value. [b] The anisotropic thermal parameter is defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Equations of Planes[a] and Distances of Selected Atoms from These Planes

Atom	Distance, Å	Atom	Distance, Å
Plane A, Including All Atoms of the $[Ni(mnt)_2]$ Dianion[b] $-0.309X + 0.561Y - 0.768Z = 0.012$			
Ni	−0.012	N(1)	0.029
S(1)	−0.045	N(2)	−0.043
S(2)	0.046	C(8)	3.40
C(1)	0.004	C(9)	3.42
C(2)	0.021	O(1)	3.33
C(3)	0.002	N(3)	3.66
C(4)	−0.003		
Plane B, Defined by the Six Ring Atoms of the KOS Cation[b] $-0.370X + 0.397Y - 0.840Z = -3.305$			
N(3)	−0.003	O(1)	0.051
C(5)	0.001	O(2)	−0.081
C(6)	0.001	Ni	3.305
C(7)	−0.001	S(1)	2.996
C(8)	−0.001	S(2)	3.675
C(9)	0.003	C(1)	3.229
C(10)	−0.033	C(2)	3.501
C(11)	−1.395	C(3)	3.098
C(12)	0.000	C(4)	3.631
C(13)	−0.099	N(1)	3.012
		N(2)	3.717

[a] The equations of the planes are given in an orthogonal angstrom coordinate system (X, Y, Z) which is related to the monoclinic fractional unit cell coordinate system (x, y, z) by the transformation $X = ax + cz \cos\beta$, $Y = by$, and $Z = cz \sin\beta$. [b] Unit weights were used for all atoms included in calculation of the plane equation. Dihedral angle between planes A and B is 10.8°.

Interatomic distances and angles within the $Ni(mnt)_2$ dianion and the KOS cation are listed in Table IV, and the anisotropic thermal ellipsoids of all nonhydrogen atoms are shown in Figure 4.

Table III. Shortest Interion Contacts and Selected Angles

A. Significant[a] KOS^{+}- -$Ni(mnt)_2{}^{2-}$ Interatomic Distances (Å) *within* each $[(KOS)Ni(mnt)_2(KOS)]$ Sandwich

Ni- -C(8)	3.41	S(2)- -C(7)	3.70
Ni- -C(9)	3.57	C(1)- -O(1)	3.39
S(1)- -N(3) $(-x, y, -z)$	3.68	C(2)- -O(1)	3.46
S(1)- -C(9) $(-x', -y, -z)$	3.69	C(2)- -C(12)	3.63

B. Intersandwich Anion–Cation Contacts

N(1)- -C(9) $(-x, {}^1/_2 + y, {}^1/_2 - z)$	3.34	Δ[b]	~−0.1 Å

C. Interanion Contacts

C(4)- -C(4) $(-1 - x, -y, -z)$	3.50	Δ	~0.1 Å
C(4)- -N(2) $(-1 - x, -y, -z)$	3.34	Δ	~0.1 Å
C(4)- -C(4) $(-1 - x, -y, -z)$- -N(2) $(-1 - x, -y, -z)$			72.6°
C(4)- -N(2) $(-1 - x, -y, -z)$- -C(4) $(-1 - x, -y, -z)$			88.4°

D. Intercation Contacts

C(5)- -O(1) $(-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.02	Δ	~−0.2 Å
C(6)- -O(1) $(-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.17	Δ	~0.05 Å
C(5)- -C(5) $(-x, -1 - y, -z)$	3.52	Δ	⩽0.05 Å
C(5)- -C(6) $(-x, -1 - y, -z)$	3.65	Δ	⩽0.15 Å

E. Possible Weak Hydrogen Bonds

S(2)- -HC(5) $(-x, -1 - y, -z)$–C(5) $(-x, -1 - y, -z)$
$d(S–H) = 2.71$ Å, $d(C–S) = 3.82$ Å
Angle C–H- -S = 167°

N(2)- -H(1)C(10) $(x - 1, y, z)$–C(10) $(x - 1, y, z)$
$d(N–H) = 2.43$ Å, $d(C–N) = 3.34$ Å
Angle C–H- -N = 140°

[a] Interatomic distances are within 0.25 Å of the van der Waals contact distance, estimated as described in the text. [b] Δ is the observed distance minus the estimated van der Waals distance.

Discussion

The crystal contains planar $Ni(mnt)_2$ anions sandwiched between pairs of parallel KOS cations. Consideration of all interion contacts reveals that the greatest number of interion

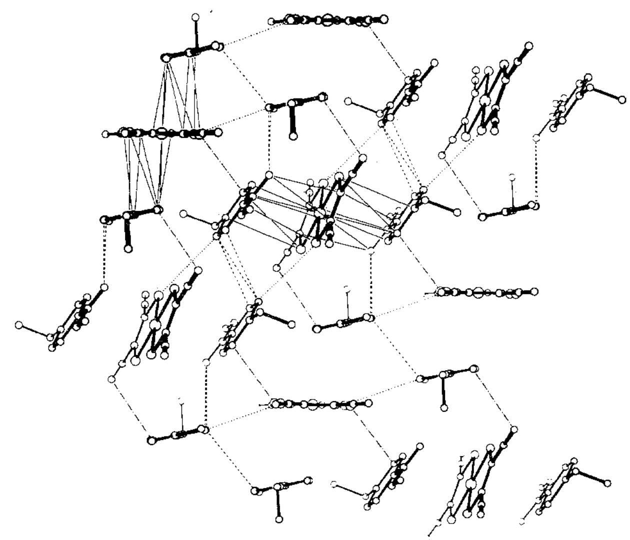


Figure 3. Packing diagram for (KOS)Ni(mnt)$_2$(KOS) showing significant interion contacts. The view direction is contained within the plane of one of the two Ni(mnt)$_2$ chelate units in the cell. The intrasandwich contacts are marked as solid lines (–) on only one (KOS)Ni(mnt)$_2$(KOS) sandwich in each of the two sandwich orientations in the cell; all other contacts have been omitted for clarity. The possible C(5)-H- -S(2) hydrogen bond is marked · · · · ·; the one intersandwich anion-cation contact N(1)- -C(9) is marked –·– –·–·; and the four intercation contacts are marked – – –. The two interanion (intersandwich) contacts are approximately normal to this diagram and are not marked.

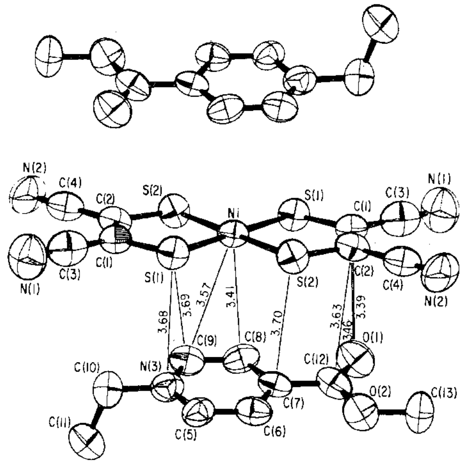


Figure 4. View of the (KOS)Ni(mnt)$_2$(KOS) sandwich unit, centrosymmetric at Ni, showing anisotropic thermal ellipsoids (at 50% probability) and the significant cation–anion contact distances.

interatomic contacts within *ca.* 0.25 Å of the estimated van der Waals nonbonded barrier occur between oppositely charged ions within the sandwich unit. The cation-dianion-cation sandwich structure is regarded as a manifestation of polar attraction between *delocalized* charges on the planar ions. If strongly localized coulombic forces were important for this compound, for instance between pyridinium nitrogen and dithiolate sulfur, they could have been satisfied with alternative lattice structures. Localized interactions of this type are apparent in the structures[20] of the *N,N'*-dimethyl-4,4'-bipyridylium salts of $CoCl_4{}^{2-}$ and $Cu_2Cl_4{}^{2-}$. Figures 2 and 4 show, however, that the rotational conformation of the KOS cation about the normal to the Ni(mnt)$_2$ plane is such as to minimize the N(3)-S(1) and C(7)-S(2) distances.

Table IV. Intraion Bond Distances (Å) and Angles (deg)

	A. Within Ni(mnt)$_2$ [a]		
Ni–S(1)	2.172 (2)	S(1)–Ni–S(2)	92.03 (7)
Ni–S(2)	2.178 (2)	S(1)–Ni–S(2')	87.97 (7)
S(1)–S(2)	3.130 (5)[b]	Ni–S(1)–C(1)	103.1 (3)
S(1)–S(2')	3.021 (5)[c]	Ni–S(2)–C(2)	103.5 (3)
S(1)–C(1)	1.741 (7)	S(1)–C(1)–C(2)	121.3 (6)
S(2)–C(2)	1.743 (7)	S(2)–C(2)–C(1)	120.0 (6)
C(1)–C(2)	1.353 (9)	S(1)–C(1)–C(3)	117.1 (6)
C(1)–C(3)	1.435 (10)	S(2)–C(2)–C(4)	117.8 (5)
C(2)–C(4)	1.444 (10)	C(2)–C(1)–C(3)	121.6 (7)
C(3)–N(1)	1.153 (9)	C(1)–C(2)–C(4)	122.2 (7)
C(4)–N(2)	1.135 (9)	C(1)–C(3)–N(1)	177.5 (9)
		C(2)–C(4)–N(2)	178.7 (9)
	B. Within KOS		
N(3)–C(5)	1.339 (8)	N(3)–C(5)–C(6)	122.0 (7)
C(5)–C(6)	1.369 (9)	C(5)–C(6)–C(7)	118.5 (7)
C(6)–C(7)	1.375 (9)	C(6)–C(7)–C(8)	119.7 (7)
C(7)–C(8)	1.382 (9)	C(7)–C(8)–C(9)	119.0 (7)
C(8)–C(9)	1.375 (10)	C(8)–C(9)–N(3)	121.1 (7)
C(9)–N(3)	1.335 (9)	C(9)–N(3)–C(5)	119.9 (7)
N(3)–C(10)	1.489 (9)	C(5)–N(3)–C(10)	118.7 (7)
C(10)–C(11)	1.464 (11)	C(9)–N(3)–C(10)	121.5 (7)
C(7)–C(12)	1.491 (10)	N(3)–C(10)–C(11)	111.3 (6)
C(12)–O(1)	1.199 (8)	C(6)–C(7)–C(12)	121.9 (8)
C(12)–O(2)	1.339 (9)	C(8)–C(7)–C(12)	118.4 (8)
O(2)–C(13)	1.444 (9)	C(7)–C(12)–O(1)	125.0 (8)
		C(7)–C(12)–O(2)	110.2 (7)
		O(1)–C(12)–O(2)	124.8 (8)
		C(12)–O(2)–C(13)	116.3 (7)

[a] The prime signifies an atom transposed through the center of symmetry at Ni. [b] Same chelate. [c] Different chelate.

This is consistent with partial 1,4 localization of the positive charge in the pyridinium ring and with the conclusion of Schrauzer[4] that the sulfur atoms in dianionic dithiolene complexes are appreciably nucleophilic. Therefore the structural results are interpreted in terms of partially localized coulombic attractions superimposed on the overall coulombic attraction between the planar ions of the sandwich. It is also noted (Figure 3) that the cation is not exactly parallel to the Ni(mnt)$_2$ plane but is rotated by *ca.* 10° about the N(3)-C(7) line such that the C(8)-Ni and O(1)-C(1), C(2) distances are decreased, which is also consistent with the slightly localized attractive interactions. Two C(8) ring atoms lie very close to axial coordination positions of Ni normal to the Ni(mnt)$_2$ plane. The present structure therefore does not follow the usual structural pattern[21] for charge-transfer complexes wherein planar donor and acceptor species occur in infinite stacks.

If van der Waals radii are taken, after Bondi[17]–Ni, 1.63 Å; aromatic ring (including pyridine nitrogen) half-thickness, 1.77 Å; mnt half-thickness 1.77 Å at the C(1)-C(2) bond; S, 1.80 Å; carbonyl oxygen (O(1)), 1.65 Å normal to the double bond–then the four observed perpendicular cation–anion contacts Ni-C(8) (3.41 Å), S(1)-N(3) (3.68 Å),[22] S(2)-C(7) (3.70 Å), and O(1)-C(1), C(2) (3.33 Å) deviate from the van der Waals estimates by +0.01, +0.11, +0.13, and −0.09 Å, respectively.[23] These cation-anion contact distances support our interpretation of the structure as a sandwich type ion associate, within which the cation-anion

---

(20) C. K. Prout and P. Murray-Rust, *J. Chem. Soc. A*, 1520 (1969).

(21) F. H. Herbstein, *Perspect. Struct. Chem.*, 4, 166 (1971).

(22) The S(1)-N(3) distance may be compared with the range of 3.25, 3.47, and 3.82 Å for analogous Cl-N distances in the *N,N'*-dimethyl-4,4'-bipyridylium salts of $Cu_2Cl_4{}^{2-}$, $Cu_2Cl_6{}^{2-}$, and $CoCl_4{}^{2-}$, respectively.[20]

(23) The small deviations from the estimated van der Waals contacts may be considered to represent corrections to the van der Waals radii; the nonbonded radius of mnt sulfur may be closer to 1.9 Å and that of the ester oxygen O(1) closer to 1.6 Å.

separation is minimized without penetration of the van der Waals barrier. The compound is therefore a contact ion triplet[24] in the solid state.

There is only one other comparable structure determination for a planar anionic dithiolene complex with a planar cation, namely, (TMPD)$_2$[Ni(mnt)$_2$].[25-27] However this crystal does not contain the sandwich ion associates of (KOS)Ni(mnt)$_2$(KOS) but is dominated structurally by TMPD$^+$-TMPD$^+$ radical pairs. The difference between the two structures is clearly apparent in the contrast between the packing diagrams of Figure 3 (KOS$^+$ salt) and Figure 5 (TMPD$^+$ salt), both viewed almost parallel to the mnt-mnt vector of one Ni(mnt)$_2$ chelate. The dihedral angle between the TMPD$^+$ cation and Ni(mnt)$_2$ planes is 59°, contrasted with 10.8° between KOS$^+$ and Ni(mnt)$_2$ planes within the sandwich.

The crystal structures[21] of a series of charge-transfer complexes of copper and palladium oxinate chelates with TCNQ,[28] picryl azide, BTF,[28] TCNB,[28] and chloranil are all composed of chains of alternating uncharged donor and acceptor moieties and are not directly comparable with the present sandwich ion associate. In some of these neutral charge-transfer compounds there is indication of partially localized interactions involving the metal atom.

The molecular dimensions of the [Ni(mnt)$_2$]$^{2-}$ chelate are in agreement with those previously found.[5,25b,29] The bond lengths and angles of the cation are normal with one exception, the C(10)-C(11) bond length of 1.464 (11) Å in the ethyl group on the pyridinium nitrogen. This is significantly shorter than the expected single-bond distance of 1.54 Å (*cf.* 1.52 (1) Å in 1-ethyl-1-methyl-4-phenylpiperidinium perchlorate[30] and 1.54 (3) Å in 2-methyl-1-ethylquinolinium iodide[31]). The locations of the hydrogen atoms associated with C(10) and C(11) are normal, as are the carbon thermal parameters, and so no explanation for this crystallographic anomaly can be offered. It is, however, interesting that a comparable distance of 1.491 (4) Å has been obtained in a 1,1′-ethylene-2,2′-bipyridylium salt.[32]

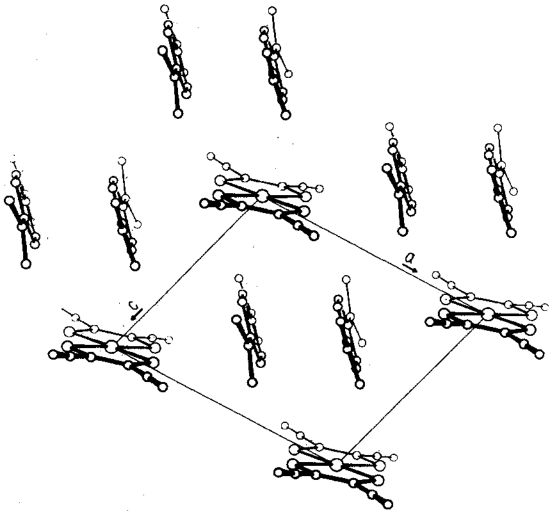


Figure 5. The *b*-axis projection of the structure of (TMPD)$_2$-Ni(mnt)$_2$ using the data of Ibers, *et al.*,[25] illustrating the 59° dihedral angle between the planar cations and planar dianion.

Registry No. (KOS)$_2$Ni(mnt)$_2$, 40635-60-7.

Acknowledgment. This work was supported by the National Science Foundation (Grant GP 24443X). The use of the Univac 1108 computer at the Madison Academic Computing Center was made possible through a grant from the Wisconsin Alumni Research Foundation through the University Research Committee.

---

[24] M. Szwarc, "Ions and Ion Pairs in Organic Reactions," Vol. I, Wiley, New York, N. Y., 1972, Chapter 1.

[25] (a) TMPD$^+$ = *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine cation radical. (b) M. J. Hove, B. M. Hoffman, and J. A. Ibers, *J. Chem. Phys.*, 56, 3490 (1972). (c) In ref 25b the fractional atomic coordinates of C(13) should read −0.25547, −0.08246, 0.47756 (J. Ibers, private communication).

[26] The structure[27] of (C$_7$H$_7$)$^+$[Ni(tfd)$_2$]$^-$ contains disordered C$_7$H$_7$ rings in a chain of alternating anions and cations inclined by 17°; the closest cation contact to the anion is 3.42 Å.

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

[28] Abbreviations: TCNQ, 7,7,8,8-tetracyanoquinodimethane; BTF, benzotrifuroxan; TCNB, 1,2,4,5-tetracyanobenzene.

[29] R. Eisenberg, *Progr. Inorg. Chem.*, 12, 295 (1970).

[30] W. Fedeli, F. Mazza, and A. Vaciago, *J. Chem. Soc. B*, 1218 (1970).

[31] S. Sakanoue, Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, and H. Mikawa, *Chem. Commun.*, 176 (1969).

[32] T. Sundaresan and S. C. Wallwork, *Acta Crystallogr., Sect. B*, 28, 3065 (1972).