

The coefficient 2 in eq. 16 is necessary because both the forward and reverse reactions of eq. 10 contribute to the observed electron transfer. Since the system is at equilibrium, the rates of these two reactions are equal. Consequently, the forward reaction of eq. 10 is only responsible for half the observed electron transfers.¹⁹ Substitution of $k_3 = 12.1 \pm 1.6 M^{-1} \text{ sec.}^{-1}$ and $k_6 = 57.6 \pm 2 M^{-1} \text{ sec.}^{-1}$ gives $k_5 = 33.4 \pm 2.6 M^{-1} \text{ sec.}^{-1}$ at 25.0° and ionic strength 3.0 *M*. A comparison of the magnitudes of these rate constants shows that the electron exchange between Fe^{2+} and FeCl^{2+} proceeds mainly by a chlorine atom transfer mechanism (provided, as seems reasonable, the third-order term involving Fe^{2+} , Fe^{3+} , and chloride may be neglected).

The chlorine atom transfer presumably occurs in a chloride-bridged, inner-sphere activated complex, while the electron transfer may occur in either an outer-sphere activated complex or in a water-bridged, inner-sphere activated complex. It is of interest that reaction *via* the chloride-bridged path is only about three

(19) J. Silverman, Ph.D. Thesis, Columbia University, New York, N. Y., 1951.

times as rapid as reaction *via* the outer-sphere or water-bridged paths. This small difference, and indeed the relatively small effect of chloride on the iron(II)–iron(III) exchange, contrasts markedly with its effect on the iron(II)–chromium(III) and chromium(II)–chromium(III) reactions. In the latter systems, chloride bridging increases the rates of the reactions by factors of 10^4 and more than 2×10^6 , respectively.¹⁸ Moreover, the chromium(II)-catalyzed dissociation of CrCl^{2+} is slower by a factor of more than 10^4 than the Cr^{2+} – CrCl^{2+} exchange.²⁰ The difference in the chloride effects cannot be ascribed to any difference in the mechanisms of the reactions since these studies show that it is very likely that the chloride-catalyzed iron(II)–iron(III) exchange, like the chloride-catalyzed chromium(II)–iron(III) and chromium(II)–chromium(III) reactions, proceeds *via* an inner-sphere activated complex.

Acknowledgment.—The authors wish to acknowledge helpful discussions with R. W. Dodson.

(20) H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, NEW YORK 10027]

The Electronic Structures of Square-Planar Metal Complexes. V. Spectral Properties of the Maleonitriledithiolate Complexes of Nickel, Palladium, and Platinum

BY S. I. SHUPACK,^{1a} E. BILLIG, R. J. H. CLARK, RAYMOND WILLIAMS,^{1b} AND HARRY B. GRAY

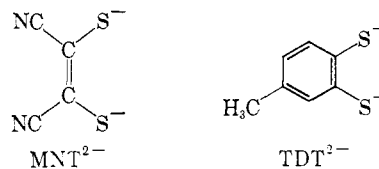
RECEIVED JUNE 8, 1964

The results of molecular orbital calculations of the square-planar nickel complexes of maleonitriledithiolate are reported. Electronic spectra of the nickel, palladium, and platinum complexes are assigned on the basis of the derived energy levels for the dinegative nickel complex. The observed bands are due to d–d, ligand-to-metal and metal-to-ligand charge transfer, and intraligand transitions. The spectral assignments are consistent with the known spectra of square-planar halides, cyanides, and simple derivatives of maleonitriledithiolate. The orbital parameter Δ_1 is reported for all the complexes, affording a comparison of the $x^2-y^2 \rightarrow xy$ splitting for several complexes containing a nickel-group central metal. Evidence is presented for the assignment of the highest filled orbital as $4a_g(x^2-y^2)$ in D_{2h} symmetry for the dinegative complexes of the nickel group.

Introduction

For several years we have been investigating the syntheses, electronic structures, and reaction mechanisms of square-planar metal complexes. Until very recently, the square-planar geometry was restricted to the diamagnetic, d^8 complexes of Ni(II), Pd(II), Pt(II), Rh(I), Ir(I), and Au(III), except for a few paramagnetic ($S = 1/2$), square-planar Co(II) and Cu(II) complexes containing fairly complicated ligands. It is clear that one of the important problems in inorganic chemistry is the preparation and study of square-planar complexes containing as many different transition metals and with as many different ground states as possible. From such research we can hope to help determine the relative energies of the molecular orbitals in planar metal complexes, a problem for which many different solutions have been suggested in the past few years.^{2–11}

From the results of our initial theoretical work, we believe that one way to stabilize the square-planar geometry is to involve the metal d_{xz} , d_{yz} , and p_z valence orbitals in an extensive π -orbital network spanning the entire complex, thus allowing as much delocalization of charge as possible. Two ligands which have good donor atoms and also a considerably delocalized π -orbital system are the dianions of maleonitriledithiol (MNT²⁻) and toluene-3,4-dithiol (TDT²⁻), which are shown below. Whether or not for the reason given above,



(6) S. Kida, J. Fukita, K. Nakamoto, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **31**, 79 (1958).

(7) (a) R. F. Fenske, D. S. Martin, and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962); (b) D. S. Martin and C. S. Lenhardt, to be published.

(8) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

(9) J. Ferguson, *J. Chem. Phys.*, **34**, 611 (1961).

(10) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962, p. 114, and references therein.

(1) (a) NIH Postdoctoral Fellow, 1963–1964; (b) NSF Graduate Fellow, 1963–1964.

(2) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

(3) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162 (1958); **29**, 1129 (1958).

(4) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **71**, 538 (1959).

(5) M. I. Ban, *Acta Chim. Acad. Sci. Hung.*, **19**, 459 (1959).

MNT²⁻ and TDT²⁻ have proved to be excellent stabilizers for the square-planar geometry. From studies of the complexes formed by these ligands, to date the following *new* square-planar complexes have been characterized:

- (1) a square-planar complex with $S = 1$; Co(TD-T)₂⁻¹²
- (2) a square-planar rhodium complex with $S = 1/2$; Rh(MNT)₂⁻¹³
- (3) square-planar copper complexes with $S = 0$; Cu(TDT)₂⁻, Cu(MNT)₂^{-12,14}
- (4) square-planar nickel, palladium, and platinum complexes with $S = 1/2$; Ni(TDT)₂⁻, Pd(TDT)₂⁻, Pt(TDT)₂⁻, Ni(MNT)₂⁻, Pd(MNT)₂⁻, Pt(MNT)₂^{-12,14,15}
- (5) square-planar iron complexes with $S = 1/2$ and $3/2$; Fe(TDT)₂⁻, Fe(MNT)₂^{-12,15}

Independent of the MNT²⁻ and TDT²⁻ work, Schrauzer and co-workers¹⁶ have made a significant contribution to the solution of the general problem by characterizing many new planar complexes in the M(S₂C₂(C₆H₅)₂)₂ⁿ and related systems.

It is important to have a consistent theoretical framework for the discussion of these new square-planar complexes. Accordingly, we have carried out molecular orbital calculations on the Ni(MNT)₂²⁻ and Ni(MNT)₂⁻ complexes. It is the purpose of this paper to present these calculations and to discuss the spectral properties of the Ni, Pd, and Pt complexes. Subsequent papers will present the results of our work on the MNT²⁻ complexes of Co, Rh, Fe, Cu, and Au, and the TDT²⁻ complexes of Fe, Co, Ni, Cu, Pd, Pt, and Au.

It is our hope that these initial theoretical and experimental studies will point the way to new ligand systems which will afford even better stabilization of the square-planar structure. Thus it may be possible to prepare square-planar complexes of most of the transition metals exhibiting ground states from $S = 0$ up to and including $S = 5/2$.

Experimental

The complexes studied were prepared by published methods.^{14,17} All the solution electronic spectra were taken using a Cary 14 spectrophotometer and quartz cells of 0.01-, 1-, and 10-cm. path lengths. Acetonitrile was the solvent employed for the spectra reported in Tables III, IV, and V.

Structure of the M(MNT)₂ⁿ⁻ Complexes

The structure of the diamagnetic [(CH₃)₄N]₂[Ni(MNT)₂] complex has been determined by X-ray diffraction techniques.¹⁸ The Ni(MNT)₂²⁻ anion is truly planar in the solid, with only the noncoordinating

(11) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

(12) H. B. Gray and E. Billig, *ibid.*, **85**, 2019 (1963).

(13) E. Billig, S. I. Shupack, J. H. Waters, R. Williams, and H. B. Gray, *ibid.*, **86**, 926 (1964).

(14) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

(15) R. Williams, unpublished results.

(16) (a) G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962); (b) G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964); (c) G. N. Schrauzer and V. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964).

(17) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964).

(18) R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964).

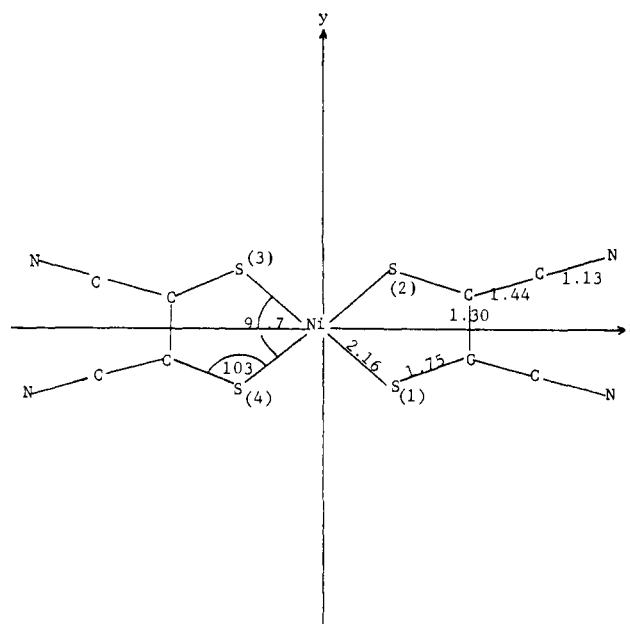


Fig. 1.—Structure of the Ni(MNT)₂²⁻ complex and coordinate system for designation of molecular orbitals.

(CH₃)₄N⁺ groups above and below the plane. The structure, with bond lengths and bond angles, is shown in Fig. 1.

The spectral and magnetic properties of Ni(MNT)₂²⁻ are essentially the same in the solid and in a number of solvents, including good coordinating ones such as pyridine, and we conclude that Ni(MNT)₂²⁻ is square-planar, with negligible axial interaction, in solution.

Since Pd(MNT)₂²⁻ and Pt(MNT)₂²⁻ are diamagnetic, we conclude that these complexes are also square-planar. The R[Ni(MNT)₂] and R[Pd(MNT)₂] complexes are also assumed to contain square-planar anions, since they are isomorphous with diamagnetic R[Cu(MNT)₂] in the R = (n-C₄H₉)₄N⁺ series. The R[Pt(MNT)₂] complex is isomorphous with R[Au(MNT)₂] with R = (C₂H₅)₄N⁺, and thus Pt(MNT)₂⁻ is undoubtedly square-planar.¹⁴

Molecular Orbitals for Ni(MNT)₂ⁿ⁻ Complexes

The coordinate system adopted for the calculation is given in Fig. 1. The metal valence orbitals are 3d, 4s, and 4p. The wave functions for the ligand π -orbitals perpendicular to the molecular plane (π_v orbitals) were obtained from a separate calculation.¹⁹ The in-plane ligand functions (σ and π_h) were taken as hybrids of the 3s and 3p sulfur orbitals, with one-third s- and two-thirds p-character.

The basis functions and group-overlap integrals in the D_{2h} symmetry are given in Table I. The calculation of the energies and valence-orbital coefficients of the molecular orbitals was carried out by a method which has been described in detail elsewhere.²⁰ For both Ni(MNT)₂²⁻ and Ni(MNT)₂⁻, an iterative procedure was used until the coulomb integrals used in the calculation corresponded to the extrapolated values appropriate for the final calculated charge distribution and orbital populations.

(19) J. Halper, W. D. Closson, and H. B. Gray, to be published.

(20) (a) A. Viste and H. B. Gray, *Inorg. Chem.*, **3**, 1113 (1964); (b) C. J. Ballhausen and H. B. Gray, *ibid.*, **1**, 111 (1962).

TABLE I
BASIS FUNCTIONS AND GROUP-OVERLAP INTEGRALS FOR
 $\text{Ni}(\text{MNT})_2^{2-}$

Irreducible representation in D_{2h}	Metal function	Ligand function ^a	G_{ij} ^b
a_g	$3d_{z^2}$	$\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$	0.128
	$4s$	$\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$	0.857
	$3d_{x^2-y^2}$	$\frac{1}{2}(\pi_{1h} - \pi_{2h} + \pi_{3h} - \pi_{4h})$	0.078
a_u	...	$\frac{1}{\sqrt{2}}(2\pi_{1,2v} + 2\pi_{3,4v})$...
	...	$\frac{1}{\sqrt{2}}(4\pi_{1,2v} + 4\pi_{3,4v})$...
	...	$\frac{1}{\sqrt{2}}(6\pi_{1,2v} + 6\pi_{3,4v})$...
	...	$\frac{1}{\sqrt{2}}(8\pi_{1,2v} + 8\pi_{3,4v})$...
b_{1g}	$3d_{xy}$	$\frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$	0.239
	$3d_{xy}$	$\frac{1}{2}(\pi_{1h} + \pi_{2h} + \pi_{3h} + \pi_{4h})$	0.000
b_{1u}	$4p_z$	$\frac{1}{\sqrt{2}}(1\pi_{1,2v} + 1\pi_{3,4v})$	0.159
	$4p_z$	$\frac{1}{\sqrt{2}}(3\pi_{1,2v} + 3\pi_{3,4v})$	0.224
	$4p_z$	$\frac{1}{\sqrt{2}}(5\pi_{1,2v} + 5\pi_{3,4v})$	0.267
	$4p_z$	$\frac{1}{\sqrt{2}}(7\pi_{1,2v} + 7\pi_{3,4v})$	0.044
b_{2g}	$3d_{xz}$	$\frac{1}{\sqrt{2}}(1\pi_{1,2v} - 1\pi_{3,4v})$	0.035
	$3d_{xz}$	$\frac{1}{\sqrt{2}}(3\pi_{1,2v} - 3\pi_{3,4v})$	0.049
	$3d_{xz}$	$\frac{1}{\sqrt{2}}(5\pi_{1,2v} - 5\pi_{3,4v})$	0.058
	$3d_{xz}$	$\frac{1}{\sqrt{2}}(7\pi_{1,2v} - 7\pi_{3,4v})$	0.010
b_{2u}	$4p_y$	$\frac{1}{2}(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4)$	0.790
	$4p_y$	$\frac{1}{2}(-\pi_{1h} + \pi_{2h} + \pi_{3h} - \pi_{4h})$	0.180
b_{3g}	$3d_{yz}$	$\frac{1}{\sqrt{2}}(2\pi_{1,2v} - 2\pi_{3,4v})$	0.017
	$3d_{yz}$	$\frac{1}{\sqrt{2}}(4\pi_{1,2v} - 4\pi_{3,4v})$	0.074
	$3d_{yz}$	$\frac{1}{\sqrt{2}}(6\pi_{1,2v} - 6\pi_{3,4v})$	0.299
	$3d_{yz}$	$\frac{1}{\sqrt{2}}(8\pi_{1,2v} - 8\pi_{3,4v})$	0.208
b_{3u}	$4p_x$	$\frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$	0.740
	$4p_x$	$\frac{1}{2}(\pi_{1h} - \pi_{2h} - \pi_{3h} + \pi_{4h})$	0.180

^a Radial wave functions used are given in Table VII (Appendix). The π_h orbitals are in the plane of the molecule. The eight π_v orbitals ($1\pi_v, 2\pi_v, 3\pi_v, \dots, 8\pi_v$, etc.) are the approximate π -molecular orbitals perpendicular to the plane of the molecule, obtained by separate calculation. In order of increasing energy, they are $1\pi_v, 2\pi_v, 3\pi_v, \dots, 8\pi_v$. Thus $1\pi_{1,2v}$ is the notation for the most stable ligand π_v orbital which in the metal complex includes sulfur atoms 1 and 2. Eigenvectors of the sulfur p_π orbitals in the π_v orbitals are given in Table VII (Appendix). ^b Bond distances used are given in Fig. 1.

Table II gives the calculated energies of the molecular orbitals, and the effective charge and orbital population on Ni, for both $\text{Ni}(\text{MNT})_2^{2-}$ and $\text{Ni}(\text{MNT})_2^-$. The levels of greatest spectroscopic interest in this study are shown in Fig. 2. The ground state of $\text{Ni}(\text{MNT})_2^{2-}$ is, according to our diagram, $\dots(4b_{2g})^2(4a_g)^2 = {}^1A_g$. The separation of the highest filled level ($4a_g$) and the lowest empty level ($3b_{1g}$) is called Δ_1 ; since these levels have the symmetries x^2-y^2 and xy , Δ_1 here is analogous to the Δ_1 ($xy \leftrightarrow x^2-y^2$) splitting in planar tetrahalides and tetracyanides.¹¹

Electronic Spectrum of $\text{Ni}(\text{MNT})_2^{2-}$

The electronic spectrum of $\text{Ni}(\text{MNT})_2^{2-}$ is shown in Fig. 3. There are five maxima in the region between 10,000 and 50,000 cm^{-1} ; four of the bands are quite

TABLE II
CALCULATED ORBITAL ENERGIES^a

MO	Energy (10^3 cm^{-1}) for $\text{Ni}(\text{MNT})_2^{2-}$	Energy (10^3 cm^{-1}) for $\text{Ni}(\text{MNT})_2^-$
$5a_g$	509.0	518.3
$3b_{3u}$	133.4	145.2
$3b_{2u}$	133.4	145.2
$5b_{1u}$	-12.8	-14.0
$4a_u$	-36.2	-36.2
$5b_{3g}$	-36.5	-36.2
$5b_{2g}$	-48.3	-48.3
$4b_{1u}$	-48.4	-48.5
$4b_{3g}$	-70.0	-70.0
$3a_u$	-70.4	-70.4
$3b_{1g}$	-73.2	-75.0
$4a_g$	-93.1	-94.5
$4b_{2g}$	-94.8	-96.2
$2b_{1g}$	-100.0	-100.0
$3b_{1u}$	-100.0	-100.1
$2b_{2u}$	-100.0	-100.0
$2b_{3u}$	-100.0	-100.0
$3b_{3g}$	-101.7	-106.2
$3a_g$	-103.2	-107.9
$3b_{2g}$	-107.1	-110.5
$2a_g$	-109.7	-113.2
$1b_{3u}$	-110.0	-110.3
$1b_{2u}$	-110.0	-110.3
$1b_{1g}$	-127.9	-130.6
$1a_g$	-139.7	-141.6
$2a_u$	-151.6	-151.6
$2b_{3g}$	-152.7	-152.9
$2b_{1u}$	-163.6	-163.5
$2b_{2g}$	-163.7	-163.8
$1b_{3g}$	-177.4	-177.4
$1a_u$	-177.4	-177.4
$1b_{2g}$	-186.4	-186.4
$1b_{1u}$	-186.6	-186.5
	Ni charge	Ni configuration
Input $\text{Ni}(\text{MNT})_2^{2-}$	0.25	$d^{8.85g^0.86p^0.04}$
Output $\text{Ni}(\text{MNT})_2^{2-}$	0.27	$d^{8.85g^0.84p^0.04}$
Input $\text{Ni}(\text{MNT})_2^-$	0.25	$d^{8.77g^0.84p^0.14}$
Output $\text{Ni}(\text{MNT})_2^-$	0.26	$d^{8.68g^0.86p^0.20}$

^a Coulomb integrals for the valence orbitals and eigenvectors for the MO's are given in Tables VIII and IX in the Appendix. The absurdly high energies of $3b_{2u}$, $3b_{3u}$, and $5a_g$ are of course due to the neglect of higher orbitals on Ni and S.

intense and are very likely due to allowed transitions. The band at 11,690 cm^{-1} is very weak and therefore is assigned as a parity forbidden d-d type transition. The allowed bands are due to charge-transfer transitions ($M \rightarrow L$ or $L \rightarrow M$) or to transitions localized on the ligands ($L \rightarrow L^*$).

First, a general assignment of the spectrum in terms of d-d, $L \rightarrow M$, $M \rightarrow L$, and $L \rightarrow L^*$ transitions will be attempted, after a consideration of the spectra of square-planar halide and cyanide complexes, and a suitable derivative of MNT^{2-} , bis(methylthio)maleonitrile. Second, the detailed band assignments will be made, using the molecular orbital calculation as a guide.

d-d Type Band.—Following the assignment^{7a,11} of the first spin-allowed band in simple square-planar complexes, we assign the 11,690- cm^{-1} band as the in-plane d-d type transition, ${}^1A_g \rightarrow {}^1B_{1g}$ [$4a_g \rightarrow 3b_{1g}$ ($x^2-y^2 \rightarrow xy$)]. Assuming $F_4 = 80 \text{ cm}^{-1}$ ($F_2 = 10F_1 = 800 \text{ cm}^{-1}$), the experimental Δ_1 value of $\text{Ni}(\text{MNT})_2^{2-}$ is 14,490 cm^{-1} . The calculated separation of $3b_{1g}$ and $4a_g$ is 19,900 cm^{-1} , in fair agreement with experiment.

L → L* Band.—The first band in the spectrum of bis(methylthio)maleonitrile occurs at about 30,000 cm^{-1} .¹⁹ Thus we assign the band that appears at 31,300 cm^{-1} in $\text{Ni}(\text{MNT})_2^{2-}$ to a L → L* transition. The detailed assignment is ${}^1A_g \rightarrow {}^1B_{2u}$ ($3b_{1u} \rightarrow 4b_{3g}$), with a calculated one-electron energy of 30,000 cm^{-1} , in good agreement with the experimental result.

Charge-Transfer Bands.—The charge-transfer transitions in square-planar halide complexes are known to be of the L → M type.¹¹ Typically the complexes exhibit two such bands, separated by approximately 10,000 cm^{-1} , with the higher energy band being considerably more intense. Thus, we assign the bands at 26,400 and 37,000 cm^{-1} as the L → M charge-transfer transitions. The detailed assignments suggested from the calculation are as follows: the 26,400- cm^{-1} band is ${}^1A_g \rightarrow {}^1B_{2u}$, ${}^1B_{3u}$ ($2b_{3u}, 2b_{2u} \rightarrow 3b_{1g}$), which is a transition from in-plane "ligand" π -orbitals to the $3b_{1g}(\sigma^*)$ "metal" molecular orbital; the 37,000 cm^{-1} band is ${}^1A_g \rightarrow {}^1B_{2u}$, ${}^1B_{3u}$ (${}^1b_{3u}, {}^1b_{2u} \rightarrow 3b_{1g}$), which is the strongly allowed transition from "ligand" σ -bonding orbitals to the $3b_{1g}(\sigma^*)$ molecular orbital. The calculated one-electron separations are 26,800 and 36,800 cm^{-1} for the two transitions, in good agreement with the observed band positions.

The band system with a maximum at 21,000 cm^{-1} and two shoulders, at 17,500 and 19,250 cm^{-1} , remains to be assigned. We recall that the M → L charge-transfer transitions in $\text{Ni}(\text{CN})_4^{2-}$ form a closely spaced, three-band system,¹¹ and thus assign the band maximum at 21,000 cm^{-1} as the first allowed M → L transition in $\text{Ni}(\text{MNT})_2^{2-}$, ${}^1A_g \rightarrow {}^1B_{2u}$ ($4b_{2g} \rightarrow 3a_u$). The transitions responsible for the shoulders on the 21,000- cm^{-1} band cannot be assigned unambiguously, since both d-d and orbitally forbidden M → L transitions should appear in this region. The detailed assignments for the three-band system suggested by the calculation are as follows: 17,500 cm^{-1} , ${}^1A_g \rightarrow {}^1B_{3g}$ ($4b_{2g} \rightarrow 3b_{1g}$); 19,250 cm^{-1} , ${}^1A_g \rightarrow {}^1A_u$ ($4a_g \rightarrow 3a_u$); 21,000 cm^{-1} , ${}^1A_g \rightarrow {}^1B_{2u}$ ($4b_{2g} \rightarrow 3a_u$).

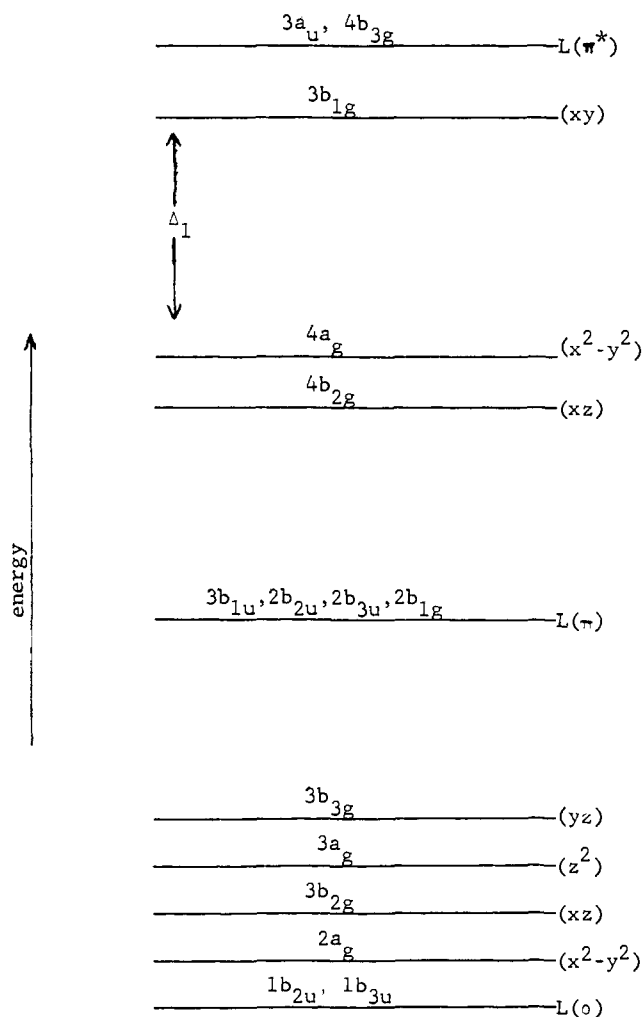
TABLE III

THE ELECTRONIC SPECTRUM OF $\text{Ni}(\text{MNT})_2^{2-}$

Band maxima, ^a cm^{-1}	ϵ	Assignments	Calculated energies, cm^{-1}
11,690	30	${}^1A_g \rightarrow {}^1B_{1g}$ ($4a_g \rightarrow 3b_{1g}$)	17,000 ^b
17,500 (sh)	570	${}^1A_g \rightarrow {}^1B_{3g}$ ($4b_{2g} \rightarrow 3b_{1g}$)	17,600 ^b
19,250 (sh)	1,250	${}^1A_g \rightarrow {}^1A_u$ ($4a_g \rightarrow 3a_u$)	17,600 ^c
21,000	3,800	${}^1A_g \rightarrow {}^1B_{2u}$ ($4b_{2g} \rightarrow 3a_u$)	18,400 ^b
26,400	6,600	${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}$ ($2b_{3u}, 2b_{2u} \rightarrow 3b_{1g}$)	26,800
31,300	30,000	${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}$ ($3b_{1u} \rightarrow 4b_{3g}$)	30,000
37,000	50,000	${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}$ ($1b_{2u}, 1b_{3u} \rightarrow 3b_{1g}$)	36,800

^a Measured in acetonitrile solutions of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Ni}(\text{MNT})_2]$. ^b Corrected for interelectronic-repulsion energy, using $F_2 = 10F_4 = 800 \text{ cm}^{-1}$; see ref. 11. ^c Correct relative energy of $4a_x$ orbital is *ca.* -88,000 cm^{-1} from the position of the ${}^1A_g \rightarrow {}^1B_{1g}$ band.

In summary then, the observed electronic spectrum of $\text{Ni}(\text{MNT})_2^{2-}$ is composed of the $x^2-y^2 \rightarrow xy$ band, the two L → M charge-transfer bands shown by square-planar halides, the M → L band system shown by square-planar cyanides, and, in addition, the L → L* transition which is known to be present in MNT^{2-} and

Fig. 2.—A diagram of the most important energy levels in $\text{Ni}(\text{MNT})_2^{2-}$ complexes.

its simple derivatives. The comparison of experimental and theoretical results is given in Table III.

Electronic Spectra of $\text{Pd}(\text{MNT})_2^{2-}$ and $\text{Pt}(\text{MNT})_2^{2-}$

The spectra of $\text{Pd}(\text{MNT})_2^{2-}$ and $\text{Pt}(\text{MNT})_2^{2-}$ are given in Table IV. These spectra are similar to the spectrum of $\text{Ni}(\text{MNT})_2^{2-}$, and the assignments given in Table IV were made by using the $\text{Ni}(\text{MNT})_2^{2-}$ spectrum as a guide. The first spin-allowed d-d type band is assigned as the $x^2-y^2 \rightarrow xy$ transition. Each complex exhibits two intense bands spaced by *ca.* 11,000 cm^{-1} , assigned as the allowed L → M transitions, an intense band in the neighborhood of 30,000 cm^{-1} , assigned L → L*, and a slightly less intense band between 20,000 and 30,000 cm^{-1} , assigned as the first allowed M → L transition. The results will be presented according to the transition type.

d-d Type Bands.—The ${}^1A_g \rightarrow {}^1B_{1g}$ band in $\text{Pd}(\text{MNT})_2^{2-}$ is observed at 15,700 cm^{-1} . Assuming $F_4 = 60 \text{ cm}^{-1}$ ($F_2 = 10F_4 = 600 \text{ cm}^{-1}$), Δ_1 for $\text{Pd}(\text{MNT})_2^{2-}$ is 17,800 cm^{-1} . This represents a 23% increase in Δ_1 in going from $\text{Ni}(\text{MNT})_2^{2-}$ to $\text{Pd}(\text{MNT})_2^{2-}$, a very reasonable result.

Both the singlet- and the triplet-excited states arising from the $4a_g \rightarrow 3b_{1g}$ ($x^2-y^2 \rightarrow xy$) transition are observed in $\text{Pt}(\text{MNT})_2^{2-}$. The ${}^1A_g \rightarrow {}^3B_{1g}$ band is at 14,410

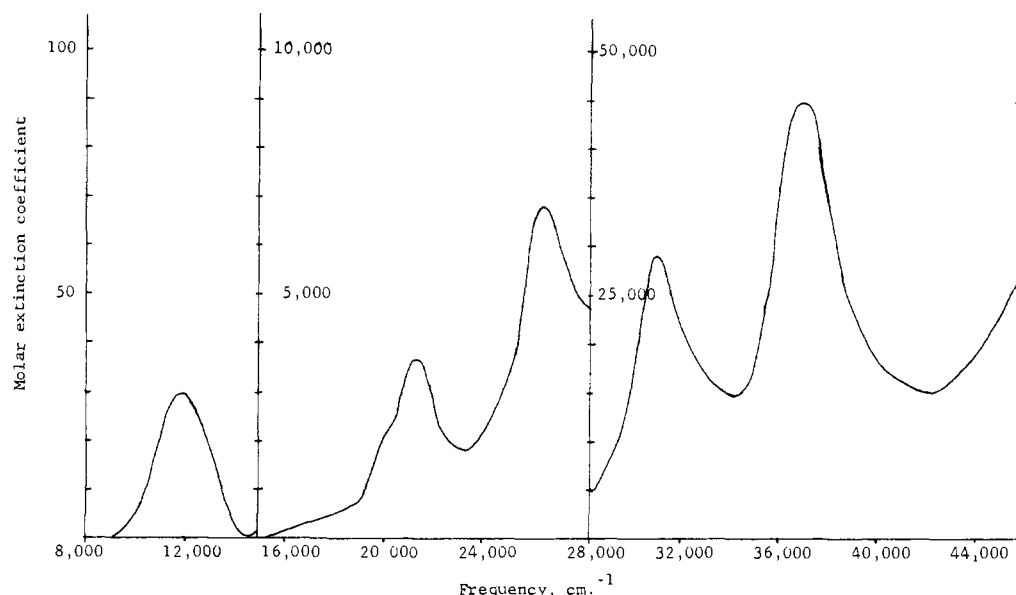


Fig. 3.—The electronic spectrum of $\text{Ni}(\text{MNT})_2^{2-}$ in acetonitrile solution.

cm^{-1} , and the ${}^1A_g \rightarrow {}^1B_{1g}$ band is at $18,500 \text{ cm}^{-1}$. If the one-electron assignment is correct, the bands should be separated by $70F_4$.¹¹ The singlet-triplet system is fitted with the reasonable value $F_4 \approx 60 \text{ cm}^{-1}$, which is good evidence for the correctness of the assignment. None of the other possible d-d type transitions is as consistent with the observed singlet-triplet system in $\text{Pt}(\text{MNT})_2^{2-}$.²¹ The weak band at $15,650 \text{ cm}^{-1}$ is tentatively assigned as the transition to the second triplet-excited state, ${}^1A_g \rightarrow {}^3B_{3g}$.

Charge-Transfer Bands.—The two allowed $L \rightarrow M$ bands in $\text{Pd}(\text{MNT})_2^{2-}$ are located at $22,700$ and $33,900 \text{ cm}^{-1}$. The less intense $M \rightarrow L$ band is found at $25,800 \text{ cm}^{-1}$. The higher energy of $M \rightarrow L$ charge transfer in $\text{Pd}(\text{MNT})_2^{2-}$ as compared with $\text{Ni}(\text{MNT})_2^{2-}$ is consistent with the known $M \rightarrow L$ energies in $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Pd}(\text{CN})_4^{2-}$.¹¹

The two $L \rightarrow M$ bands in $\text{Pt}(\text{MNT})_2^{2-}$ are found at $32,300$ and $43,800 \text{ cm}^{-1}$. The $L \rightarrow M$ charge transfer in $\text{Pt}(\text{MNT})_2^{2-}$ occurs at much higher energy than in

TABLE IV

ELECTRONIC SPECTRA OF $\text{M}(\text{MNT})_2^{2-}$ COMPLEXES WITH A...($4a_g$)² = 1A_g GROUND STATE²

Transitions	$\text{Ni}(\text{MNT})_2^{2-}$	Complexes $\text{Pd}(\text{MNT})_2^{2-}$	$\text{Pt}(\text{MNT})_2^{2-}$
d-d type			
${}^1A_g \rightarrow {}^3B_{1g} (x^2-y^2 \rightarrow xy)$	<i>b</i>	<i>b</i>	$14,410 (49)^c$
${}^1A_g \rightarrow {}^1B_{1g} (x^2-y^2 \rightarrow xy)$	$11,690 (30)$	$15,700 (64)$	$18,500 (1,220)^{c,d}$
${}^1A_g \rightarrow {}^3B_g (xz \rightarrow xy)$	<i>b</i>	<i>b</i>	$15,650 (56)^c$
${}^1A_g \rightarrow {}^1B_{3g} (xz \rightarrow xy)$	$17,500 (570)^e$	<i>b</i>	<i>b</i>
$L \rightarrow L^*$			
${}^1A_g \rightarrow {}^1B_{2u}$	$31,300 (30,000)$	$30,800 (20,200)^e$	$29,700 (15,600)$
$L \rightarrow M$ charge transfer			
${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u} (L(\pi) \rightarrow M)$	$26,400 (6,600)$	$22,700 (5,700)$	$32,300 (13,400)$
${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u} (L(\sigma) \rightarrow M)$	$37,000 (50,000)$	$33,900 (47,000)$	$43,800 (43,500)$
$M \rightarrow L$ charge transfer			
${}^1A_g \rightarrow {}^1A_u$	$19,250 (1,250)^e$	$25,800 (2,840)^e$	$18,500 (1,220)^{c,d}$
${}^1A_g \rightarrow {}^1B_{2u}$	$21,000 (3,800)$	<i>b</i>	$21,100 (3,470)$
Unassigned bands			
	None	$37,800 (45,000)$ $42,800 (34,500)$	$38,500 (17,000)^e$

^a Maxima in cm^{-1} for spectra in acetonitrile solutions; band *e*'s in parentheses. ^b Not observed. ^c Shoulder. ^d Broad shoulder probably contains two electronic transitions.

$L \rightarrow L^*$ Band.—The $L \rightarrow L^*$ band is observed at about $30,000 \text{ cm}^{-1}$ as follows: $\text{Pt}(\text{MNT})_2^{2-}$, $30,800 \text{ cm}^{-1}$; $\text{Pt}(\text{MNT})_2^{2-}$, $29,700 \text{ cm}^{-1}$.

(21) Using $F_2 \approx 10F_4 \approx 600 \text{ cm}^{-1}$, the calculated singlet-triplet separations for $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{z^2} \rightarrow d_{xy}$, and $d_{xz}, yz \rightarrow d_{xy}$ are $4200, 6600$, and 6000 cm^{-1} , respectively. The observed separation in $\text{Pt}(\text{MNT})_2^{2-}$ is 4000 cm^{-1} . Unreasonably small F_2 and F_4 values would be required to fit this singlet-triplet system for the $d_{z^2} \rightarrow d_{xy}$ and $d_{xz}, yz \rightarrow d_{xy}$ assignments.

$\text{Pd}(\text{MNT})_2^{2-}$, a result in accord with the fact that $L \rightarrow M$ charge transfer in PtCl_4^{2-} occurs at much higher energy than in PdCl_4^{2-} . The allowed $M \rightarrow L$ band in $\text{Pt}(\text{MNT})_2^{2-}$ appears at $21,100 \text{ cm}^{-1}$, which gives the order of increasing energy of $M \rightarrow L$ charge transfer as $\text{Ni} \approx \text{Pt} < \text{Pd}$, in accord with the spectra of the square-planar cyanide complexes.¹¹ The spectrum of Pt

TABLE V
 THE ELECTRONIC SPECTRUM OF Ni(MNT)₂⁻

Band maxima, ^a cm. ⁻¹	ϵ	Assignments	General classification
8,330	329	${}^2A_g \rightarrow {}^2B_{2g}(4b_{2g} \rightarrow 4a_g)$	Parity forbidden
11,790	8,000	${}^2A_g \rightarrow {}^2B_{1u}, {}^2B_{2u}, {}^2B_{3u} (3b_{1u}, 2b_{2u}, 2b_{3u} \rightarrow 4a_g)$	$L(\pi) \rightarrow M$
16,700	500	$3b_{3g} \rightarrow 4a_g ?$	Parity forbidden
18,350	690	$3a_g \rightarrow 4a_g ?$	Parity forbidden
20,800	2,500	${}^2A_g \rightarrow {}^2B_{2u}, {}^2B_{3u} (1b_{2u}, 1b_{3u} \rightarrow 4a_g)$	$L(\sigma) \rightarrow M$
27,300	13,650	${}^2A_g \rightarrow {}^2B_{2u}, {}^2B_{3u} (2b_{3u}, 2b_{2u} \rightarrow 3b_{1g})$	$L(\pi) \rightarrow M$
31,800	42,350	${}^2A_g \rightarrow {}^2B_{2u} (3b_{1u} \rightarrow 4b_{3g})$	$L \rightarrow L^*$
36,600	42,300	${}^2A_g \rightarrow {}^2B_{2u}, {}^2B_{3u} (1b_{3u}, 1b_{2u} \rightarrow 3b_{1g})$	$L(\sigma) \rightarrow M$
43,500	23,900	Not assigned	...

^a Spectrum of [(n-C₄H₉)₄N][Ni(MNT)₂] in acetonitrile solution.

(MNT)₂²⁻ contains one extra band, a shoulder at 38,500 cm.⁻¹, for which we suggest a spin-forbidden L → M assignment.

Electronic Spectrum of Ni(MNT)₂⁻

The ground state of Ni(MNT)₂⁻ is ... (4b_{2g})²(4a_g)¹ = 2A_g . The spectrum of Ni(MNT)₂⁻ is given in Table V. The most striking feature of the spectrum of Ni(MNT)₂⁻ is the intense band at 11,790 cm.⁻¹, a very low energy. If the L → M assignments are correct for Ni(MNT)₂²⁻, we expect two additional L → M bands in Ni(MNT)₂⁻, since in the latter complex, transitions are possible to the 4a_g orbital. Although the 4a_g orbital in Ni(MNT)₂⁻ is calculated to have more ligand than metal character, the transitions from almost purely ligand levels to 4a_g are still effectively "L → M." The position of the first L → M band in Ni(MNT)₂⁻ can be estimated by subtracting Δ_1 from the first L → M band in Ni(MNT)₂²⁻. This estimate is 26,400 - 14,650 = 11,750 cm.⁻¹, in excellent agreement with the observed L → M band in Ni(MNT)₂⁻. Thus we confidently assign the intense bands at 11,790 and 20,800 cm.⁻¹ as L → M transitions. The two "regular" L → M bands are located at 27,300 and 36,600 cm.⁻¹, only very little shifted from their positions in Ni(MNT)₂²⁻. The separation of the centers of the two L → M systems in Ni(MNT)₂⁻ is ca. 15,700 cm.⁻¹, which we shall take as a reasonable estimate of Δ_1 for this complex. The L → L* band in Ni(MNT)₂⁻ appears at 31,800 cm.⁻¹, which is approximately the same energy as the L → L* band in Ni(MNT)₂²⁻.

There are three weak bands in the Ni(MNT)₂⁻ spectrum, at 8330, 16,700, and 18,350 cm.⁻¹. Since the observed one-electron separation of 4a_g and 4b_{2g} in Ni(MNT)₂²⁻ is ca. 7000 cm.⁻¹, it is reasonable to assign the band at 8330 cm.⁻¹ as 4b_{2g} → 4a_g, the first parity-forbidden transition. According to the calculation, both 4a_g and 4b_{2g} are mainly "ligand" orbitals delocalized over the four sulfur atoms in Ni(MNT)₂⁻ (see Table IX) and thus the difference in the interelectronic-repulsion energies of the 2A_g and ${}^2B_{2g}$ states is probably small. Indeed, this is very likely the case, since the Co(MNT)₂⁻ complex is diamagnetic with the probable ground state ... (4b_{2g})² = 1A_g . There is a spin-allowed band in Co(MNT)₂⁻ at 7430 cm.⁻¹, which must be interpreted as the transition 4b_{2g} → 4a_g.²²

There are several possible assignments for the weak

bands at 16,700 and 18,350 cm.⁻¹. Table V gives the assignments suggested for these bands by the calculation and summarizes all the band assignments discussed above.

Discussion

According to the molecular orbital level scheme presented in this paper, the highest occupied MO in the d⁸ diamagnetic square-planar complexes is the in-plane π^* orbital, 4a_g. The available experimental information definitely supports this view. First, the observed singlet-triplet band system in Pt(MNT)₂²⁻ is consistent only with the assignments ${}^1A_g \rightarrow {}^3B_{1g}, {}^1B_{1g}$. Second, the 11,690-cm.⁻¹ band of Ni(MNT)₂²⁻ is not shifted in solvents with sharply different coordinating properties, such as acetone and pyridine.¹⁷ The 11,690-cm.⁻¹ band is not even affected in an acetone solution 0.1 M in the powerful ligand 1,10-phenanthroline.²² These facts strongly suggest that the 11,690-cm.⁻¹ band is due to an electronic transition localized in the plane of the molecule, or $x^2-y^2 \rightarrow xy$.

From the spectral assignments given in Tables III, IV, and V, experimental values of the orbital parameter Δ_1 (3b_{1g}-4a_g separation) were calculated. These values are presented in Table VI, along with Δ_1 values for other representative planar complexes. As ex-

 TABLE VI
 THE VALUE OF Δ_1 IN SOME PLANAR COMPLEXES^a

Complex	Δ_1 , cm. ⁻¹
Ni(MNT) ₂ ²⁻	14,490
Ni(MNT) ₂ ⁻	15,700
Ni(dtp) ₂	17,300 ^b
Ni(DTC) ₂	18,800 ^c
Ni(DΦG) ₂	25,000 ^c
Ni(CN) ₄ ²⁻	25,300 ^d
Pd(MNT) ₂ ²⁻	17,800
PdBr ₄ ²⁻	18,100 ^d
PdCl ₄ ²⁻	18,800 ^d
Pd(CN) ₄ ²⁻	>30,000 ^d
Pt(MNT) ₂ ²⁻	20,600
PtBr ₄ ²⁻	21,800 ^d
PtCl ₄ ²⁻	23,100 ^d
Pt(CN) ₄ ²⁻	>30,000 ^d

^a $F_2 = 10F_4 = 800$ cm.⁻¹ for Ni; $F_2 = 10F_4 = 600$ cm.⁻¹ for Pd and Pt. ^b Spectrum quoted in ref. 10; dtp = S₂P(OC₂H₅)₂. ^c Spectrum quoted in W. Manch and W. C. Fernelius, *J. Chem. Educ.*, **38**, 192 (1961); DTC = S₂NC(C₂H₅)₂; DΦG = diiphenylglyoxime. ^d From ref. 11.

pected, the Δ_1 values increase in the order $\text{Ni}(\text{MNT})_2^{2-} < \text{Pd}(\text{MNT})_2^{2-} < \text{Pt}(\text{MNT})_2^{2-}$. The $\text{Ni}(\text{MNT})_2^{2-}$ complex has a slightly larger Δ_1 value than $\text{Ni}(\text{MNT})_2^{2-}$, which is reasonable. A comparison of Δ_1 values in Table VI gives the spectrochemical series order $\text{MNT}^{2-} < \text{Br}^- < \text{Cl}^- < \text{dtp}^- < \text{DTC}^- < \text{D}\Phi\text{G}^- < \text{CN}^-$ for a planar situation.

We now address ourselves to an important question regarding the new square-planar complexes, which is the formulation of the ground state. The usual method of oxidation states gives M(III) and M(II) for the mononegative and dinegative complexes, respectively. We recently proposed that some of the $\text{M}(\text{MNT})_2^-$ and $\text{M}(\text{TDT})_2^-$ complexes be considered as composed of M(I) and radical-anion ligands.¹² In this formulation a filled bonding orbital must be mainly localized on the metal, adding an extra pair of electrons to be associated with the metal. Schrauzer and Mayweg had earlier made the suggestion that $\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2$ be formulated as Ni(II) and two radical-anion ligands.^{16a} The following evidence supports the radical-anion formulation for certain of these complexes.

1. According to the calculation of the $\text{Ni}(\text{MNT})_2^{2-}$ system, the $4b_{2g}$ and $4a_g$ orbitals are definitely more "ligand" than "metal," while the $3b_{2g}$ and $2a_g$ orbitals, which are bonding, are mainly localized on the metal. This means that square-planar complexes containing MNT^{2-} , in which the $4b_{2g}$ and $4a_g$ levels are *not* filled, are not best described in the usual oxidation state formalism. The diamagnetic complex $\text{Co}(\text{MNT})_2^-$, with the probable electronic structure $\dots(4b_{2g})^2(4a_g)$ empty, contains two MNT radical anions; four "metal" orbitals are filled, $3b_{2g}$, $3b_{3g}$, $3a_g$, and $2a_g$. The paramagnetic complex $\text{Ni}(\text{MNT})_2^-$, with the electronic structure $\dots(4a_g)$, contains one MNT radical anion. All the complexes with the electronic structure $\dots(4a_g)^2$ contain MNT^{2-} ligands and can safely be formulated in the usual way. That is, $\text{Ni}(\text{MNT})_2^{2-}$ contains Ni(II) and $\text{Cu}(\text{MNT})_2^-$ contains Cu(III).

2. Recently we have shown that $\text{Co}(\text{MNT})_2^-$ reacts with certain ligands to give stable five- and six-coordinated complexes.²³ For the reactions with monodentate ligands, it was observed that the five-coordinate adducts are substantially *more stable* than the six-coordinate ones, and, in many cases, the six-coordinate state was not found at all. In addition, the stabilities of the five-coordinate adducts indicate that $\text{Co}(\text{MNT})_2^-$ follows the Ahrlund, Chatt, and Davies type-B behavior,²⁴ e.g., $\text{Co}(\text{MNT})_2(\text{P}(\text{C}_6\text{H}_5)_3)^-$ is more stable than $\text{Co}(\text{MNT})_2(\text{py})^-$. Thus the *chemical* evidence in this case points to a complex in which the metal ion is effectively d^8 ; certainly the behavior of $\text{Co}(\text{MNT})_2^-$ is completely different from any usual d^6 Co(III) complex.

3. It has been possible to prepare neutral, six-coordinate complexes of the type $\text{M}(\text{TDT})_3$, with $\text{M} = \text{Ni}$ and Co .¹⁵ These complexes would call for M(VI) in the standard formulation of oxidation state. We believe this is absolutely unreasonable for a complex containing sulfur-donor ligands, and it is very likely that in these cases at least one filled bonding orbital is mainly localized on the metal.

(23) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 2958 (1964).

(24) S. Ahrlund, J. Chatt, and N. R. Davies, *Quart. Rev. (London)*, **12**, 265 (1958).

TABLE VII

A. Atomic radial functions

Atom	Orbital	Function ^a
Ni	3d	$0.5817\Phi_3(5.75) + 0.5890\Phi_3(2.20)$
	4s	$-0.02018\Phi_1(27.37) + 0.06792\Phi_2(10.60) - 0.1657\Phi_3(4.90) + 1.0013\Phi_4(1.50)$
	4p	$\Phi_4(1.40)$
S	3s	$\Phi_3(1.817)$
	3p	$\Phi_3(1.817)$

B. Eigenvectors for sulfur $3p_\pi$ functions in the π_v ligand functions^b

Orbital	$1\pi_v$	$2\pi_v$	$3\pi_v$	$4\pi_v$
S-eigenvector	0.2915	0.1427	0.4112	0.6217
Orbital	$5\pi_v$	$6\pi_v$	$7\pi_v$	$8\pi_v$
S-eigenvector	0.4895	0.2508	0.0802	0.1740

^a $\Phi_i(\mu) = N_{\mu} r^{\mu-1} e^{-\mu r}$; Ni 3d and 4s functions from J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); Ni 4p function from ref. 11.

^b From ref. 19.

TABLE VIII

COULOMB INTEGRAL VALUES

Nickel orbital	$-H_{ii} [\text{Ni}(\text{MNT})_2^{2-}]^a$	$-H_{ii} [\text{Ni}(\text{MNT})_2^-]^a$
3d	104,110	108,930
4s	79,450	81,914
4p	28,200	30,750
Sulfur orbital	$-H_{ij} [\text{Ni}(\text{MNT})_2^{2-} = \text{Ni}(\text{MNT})_2^-]^b$	
σ	110,000	
π_h	100,000	
$1\pi_v$	186,310	
$2\pi_v$	177,440	
$3\pi_v$	163,320	
$4\pi_v$	151,560	
$5\pi_v$	100,000	
$6\pi_v$	70,350	
$7\pi_v$	48,330	
$8\pi_v$	36,210	

^a Ionization energies for nickel with a charge and configuration listed as "input" in Table II; data from C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1952.

^b From experimental and theoretical results for bis(methylthio)maleonitrile given in ref. 19.

4. The hyperfine splitting in the e.s.r. spectrum of $\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2^-$ due to ^{61}Ni ($I = 3/2$) is only 4.5 ± 1 gauss in DMSO solution.¹⁴ Surely, with this very small metal splitting, the unpaired electron in this case is in an orbital which is delocalized over both the metal and the ligands, but is *predominantly ligand*. The composition of the $a_g(\pi^*)$ orbital is consistent with this small splitting. Although the magnetic moment of ^{61}Ni is not accurately known, both values which have been suggested give a normalized hyperfine splitting in $\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2^-$ which is smaller than the normalized splitting in $\text{Cu}(\text{MNT})_2^{2-}$. For the magnetic moment 0.3 nm.,²⁵ the ^{61}Ni splitting is 22.5 gauss/nm.; for 0.9 nm.,²⁶ the splitting is 7.5 gauss/nm. The splitting in $^{63,65}\text{Cu}(\text{MNT})_2^{2-}$ in DMF solution is approximately 49 gauss/nm.¹⁷ Thus these experimental results support the

(25) J. W. Orton, P. Auzins, and J. E. Wertz, *Phys. Rev.*, **119**, 1691 (1960).

(26) L. H. Bennett and R. L. Streever, Jr., *Phys. Rev.*, **126**, 2141 (1962).

TABLE IX
EIGENVECTORS FOR Ni(MNT)₂ⁿ⁻

MO	Valence orbitals															
	3d		4s		4p		σ		π _{1z}		π _v ^a					
	n = 1	n = 2	n = 1	n = 2	n = 1	n = 2	n = 1	n = 2	n = 1	n = 2	n = 1		n = 2			
1a _g	0.180	0.161	0.411	0.406			0.594	0.604			1	3	5	7		
2a _g	0.842	0.768							0.478	0.583	2	4	6	8	1	3
3a _g	-0.975	-0.978	0.195	0.188			0.072	0.062							2	4
4a _g	-0.546	-0.646							0.882	0.816						
5a _g	0.288	0.289	1.936	1.938			-1.914	-1.911								
1b _{1g}	0.627	0.589					0.643	0.679								
2b _{1g}									1.000	1.000						
3b _{1g}	-0.817	-0.845					0.804	0.774								
1b _{2g}	0.044	0.039									0.997	0.008	0.001	-0.000	0.998	0.006
2b _{2g}	-0.090	-0.079									0.017	-0.991	-0.004	0.000	0.014	-0.993
3b _{2g}	0.854	0.761									-0.068	-0.124	0.467	0.005	-0.057	-0.102
4b _{2g}	-0.517	-0.648									0.037	0.065	0.886	-0.005	0.045	0.077
5b _{2g}	0.016	0.017									-0.001	-0.002	-0.003	-1.000	-0.001	-0.002
1b _{3g}	0.025	0.022									0.999	0.006	-0.000	-0.000	0.999	0.005
2b _{3g}	-0.170	-0.147									0.015	-0.973	-0.001	0.001	0.012	-0.978
3b _{3g}	0.985	0.988									-0.040	-0.242	0.057	0.006	-0.038	-0.220
4b _{3g}	-0.086	-0.095									0.003	0.015	0.999	-0.003	0.003	0.016
5b _{3g}	0.027	0.028									-0.001	-0.004	-0.003	-1.000	-0.001	-0.004
1a _u											1.000				1.000	
2a _u												1.000				1.000
3a _u													1.000			1.000
4a _u														1.000		1.000
1b _{1u}					0.038	0.045					-1.006	-0.017	-0.009	-0.002	-1.006	-0.022
2b _{1u}					-0.038	-0.048					-0.003	1.008	0.008	0.002	-0.006	1.010
3b _{1u}					0.040	0.022					-0.004	-0.006	0.989	-0.001	-0.002	-0.003
4b _{1u}					-0.077	-0.066					0.009	0.014	0.025	-0.991	0.007	0.011
5b _{1u}					1.082	1.082					-0.137	-0.208	-0.326	-0.155	-0.131	-0.198
1b _{2u} , 1b _{3u}					0.057	0.013	0.954	0.989	0.001	-0.001						
2b _{2u} , 2b _{3u}					-0.023	-0.014	0.029	-0.012	-0.995	-0.997						
3b _{2u} , 3b _{3u}					1.705	1.706	-1.381	-1.356	-0.321	-0.316						

^a Numbers 1-8 refer to 1π_v-8π_v orbitals in their properly normalized combinations for the MO's under consideration; refer to Table I.

MO calculations, which suggest that the unpaired electron in $3b_{1g}$ in $\text{Cu}(\text{MNT})_2^{2-}$ is associated with the metal much more than the unpaired electron in the $a_g(\pi^*)$ orbital in $\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2^-$. In $\text{Ni}(\text{MNT})_2^{2-}$, $3b_{1g}$ is calculated to be 55.7% metal, while the metal character of $4a_g$ in $\text{Ni}(\text{MNT})_2^-$ is calculated to be only 26.0%.

Ideally, therefore, the formulation of oxidation state of the metal should take into consideration the possibility of filled bonding orbitals on the metal. Since in most cases such a procedure is necessarily arbitrary, and since the standard method of assessing oxidation state is almost certainly wrong in many of these complexes, it appears that the general MO formulation of the ground state is preferable.

Acknowledgments.—The authors gratefully acknowledge the time which Dr. James Ibers, Mr. Richard Eisenberg, Dr. Arlen Viste, Dr. James H. Waters, and Dr. Cooper H. Langford have given us for useful dis-

cussions. We thank the National Science Foundation for support of this research. This research was also supported by Public Health Service Research Grant No. CA-07016-01 from the National Cancer Institute.

Appendix

Wave Functions.—Atomic radial functions employed in the calculation are given in Table VII. The sulfur atom eigenvectors in the π_v ligand functions are also given in Table VII.

Coulomb Integrals.—The final values taken for the coulomb integrals are given in Table VIII.

Eigenvectors.—The calculation was carried out using a program written for the Columbia IBM 7094 computer by P. T. Manoharan. The method of calculation has been described in detail elsewhere.^{20a} Final eigenvectors for the molecular orbitals of $\text{Ni}(\text{MNT})_2^{2-}$ and $\text{Ni}(\text{MNT})_2^-$ are given in Table IX.