yield of this intermediate (β-cyanoethyl-5'-thymidylate, II) was 652 optical density units (0.067 mmole, 33.5%). For use in the subsequent condensation, the barium salt was converted into the pyridinium salt as described above for thymidylate.

The protected pyridinium thymidylate (0.066 mmole) was dissolved in 5 ml. of dry pyridine and concentrated to dryness *in vacuo*. Dowex 50 W-X8, pyridinium cycle (prepared by converting the hydrogen form with 5% aqueous pyridine and subsequent suspension of the resin in absolute pyridine), 200 λ, was added to the residue, and the mixture was again dried by coconcentration with a few ml. of dry pyridine. Finally, 0.1 mmole of $N^6,O^{3'}$-diacetyldeoxyadenylic 5'-acid (pyridinium salt) was added and the drying process repeated several times. The residue was dissolved in 0.5 ml. of anhydrous pyridine, and 103 mg. of dicyclohexylcarbodiimide was added. The resulting mixture was tightly stoppered, agitated for several minutes, and allowed to stand in the dark for 72 hr. Water (2 ml.) was added and, after further standing at room temperature for 36 hr., the mixture was concentrated to a volume of approximately 0.5 ml. Concentrated ammonia (1.5 ml.) was added, and the mixture was heated for 1 hr. at 55°; a second portion of ammonia (1.5 ml.) was added and heating continued for another hour. The vessel was cooled and its content diluted with 5 ml. of water. The insoluble components were centrifuged in a clinical centrifuge and the supernatant portion was decanted. The residue was washed several times with water and the mixture was centrifuged each time. The combined aqueous phase was concentrated to a small volume to remove the bulk of pyridine and then brought up to a volume of 30 ml. with distilled water. After adjustment to a pH of 8.8 with ammonia, the solution was applied to the top of a column (2.5 × 15 cm.) of DEAE-cellulose in the bicarbonate cycle. Irrigation with a gradient of 0.3 M triethylammonium bicarbonate (pH 7.5, 1.5 l.) into a like volume of distilled water resulted in the elution (at around 0.1 M buffer strength) of the desired d-pTpA (IV). Fractions of the symmetrical peak were combined, concentrated to a small volume, and lyophilized. In agreement with its composition, this material had an absorption maximum in the ultraviolet at 260 mμ, 280/260 = 0.43, 250/260 = 0.79 (all measurements at pH 2). A yield of 315 optical density units corresponds to 0.0154 mmole, or 23.4%, based on protected thymidylic acid. This material traveled somewhat slower than pT in the buffered isobutyrate paper-chromatographic system[21] (R_f 0.34) and gave rise to pT and pA (in the ratio of 1.00:1.07) upon treatment with purified venom diesterase.[16] It had an $\epsilon/2P = 20,500$. Upon complete degradation to mononucleotides with the latter enzyme, an 11% rise in the absorptivity was noted.[13]

Deoxyadenylyl-(5' → 3')-thymidine-5' Triphosphate (VI).—Dinucleotide IV (25 optical density units, 1.2 μmoles) was dissolved in 25 λ of water, transferred to a reaction vessel fashioned from a piece of Pyrex tubing (diameter 3 mm., length 15 cm., sealed at one end) by means of a Pasteur pipet, and the transfer completed by washing with another 25 λ of water. Morpholine (0.8 λ) and 25 λ of a solution of dicyclohexylcarbodiimide (251 mg.) in *t*-butyl alcohol (6.25 ml.) were added, and the open end of the tube was sealed by drawing out in a burner. The tube was immersed in a test tube containing mineral oil, and the latter was placed in a heating bath (mineral oil) which was kept at 132° for 4 hr. The temperature of the inner bath fluctuated between 105 and 110°. The reaction vessel was cooled and opened by means of a triangular file, and the contents were streaked on 7 cm. of Whatman filter paper grade No. 3MM. The paper was saturated

with a 0.05 M solution of triethylammonium bicarbonate, pH 7.5 (care being taken not to elute or displace the applied product), and subjected to electrophoresis in the apparatus of Markham and Smith[22] at an applied voltage of 1200 v. for a period of 80 min. Under these conditions, the starting dinucleotide had moved a distance of 28 cm. toward the anode; the desired morpholidate V—the major portion—had migrated only 18 cm. in the same direction. The latter, extracted with water and concentrated to a dry residue, had the properties: $\lambda_{max}^{pH\ 2}$ at 260 mμ, 280/260 = 0.49, 250/260 = 0.85; total extracted: 18.9 optical density units (75.6%).

In addition to its homogeneity in paper electrophoresis, the material traveled as a single spot in the paper-chromatographic system 2-propanol–ammonia–water 7:1:2 (after 26 hr. of irrigation, the morpholidate had traveled 29 cm.).

Another preparation on a somewhat larger scale (125 optical density units) resulted in a slightly lower yield (65%). However, the recovery of 15.8 optical density units (12.6%) of unchanged starting material raised the over-all conversion.

The material thus obtained was used directly without further characterization in the conversion to 5'-terminal triphosphate VI. Morpholidate (81.5 optical density units) was dried by repeated coconcentration *in vacuo* with a few ml. of anhydrous pyridine, followed by dry benzene. The residue was treated with 125 λ of a solution consisting of 1 mmole of tri-*n*-butylammonium pyrophosphate in dimethyl sulfoxide (dried thoroughly by storage over a molecular sieve) and the reaction vessel was quickly stoppered and stored in a vacuum desiccator over a drying agent for 84 hr. The reaction was terminated by the addition of 1 drop of water, and most of the solvent was removed by subjecting the vessel to a high vacuum for 5 hr. The residue was then streaked on 28 cm. of Whatman filter paper grade No. 3 MM and developed in the isobutyrate system.[21] Three zones were visible by scanning under ultraviolet light: the most prominent of these, the one migrating most slowly, was extracted with water and concentrated to a small volume. A yield of 30.4 optical density units corresponds to 37.3%. Structure was assigned on the basis of the following properties. The ultraviolet spectrum was very similar to that of IV, $\epsilon^{260}/4P = 19,800$; R_f thymidylate = 0.58 in the isobutyrate system[21]; 2.09 optical density units of this material (102 mμmoles) were treated with 1 ml. of N hydrochloric acid for 1 min. at 100°.[15] An aliquot (one-fifth) was measured for inorganic phosphate: calcd. 40.8 mμmoles, found 38.8 mμmoles.

The remaining solution was spotted on Whatman filter paper grade No. 1 and developed against standards of adenosine and pTp[23] in the isobutyrate system[21]: approximately equal amounts of two spots traveling as the standards and having the required ultraviolet absorption were observed.

Another aliquot of d-pppTpA (VI) was subjected to the action of venom phosphodiesterase.[16] Paper chromatographic assay indicated the presence of pT, d-pA, and inorganic pyrophosphate in the digest.

(22) R. Markham and J. D. Smith, *Biochem. J.*, **52**, 552 (1952).

(23) The expected products of concomitant depurination of the dinucleotide. The actual event was observed in a control acid hydrolysis of d-pTpA.

COMMUNICATIONS TO THE EDITOR

Molecular and Electronic Structure of the Bis(maleonitriledithiolato)nickelate(II) Ion[1]

Sir:

The considerable recent interest in square-planar complexes,[2] particularly those containing bidentate sulfur ligands,[3] has prompted us to investigate in detail

(1) Part of the research was performed under the auspices of the U. S. Atomic Energy Commission. Part of the research was supported by the National Science Foundation.

(2) (a) R. F. Fenske, D. S. Martin, and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962); (b) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

(3) (a) G. N. Schrauzer and V. Mayweg, *ibid.*, **84**, 3221 (1962); (b) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962);

the molecular structure and the electronic energy levels of a representative example of these compounds. This communication reports the results for the bis-(maleonitriledithiolato)nickelate(II) ion, abbreviated $Ni(MNT)_2^{2-}$. The complex $[(CH_3)_4N]_2[Ni(MNT)_2]$ was chosen for the structure determination.

Crystals of $[(CH_3)_4N]_2[Ni(MNT)_2]$ were examined by precession and Weissenberg techniques with Mo $K\alpha$ radiation and found to be triclinic. A convenient cell is $a = 10.16$, $b = 15.77$, $c = 8.05$ (all ±0.03 Å.), $\alpha = 87.4$, $\beta = 113.4$, $\gamma = 91.4$ (all ±0.5). The observed extinctions hkl for $h + k$ odd are consistent

(c) H. B. Gray and E. Billig, *ibid.*, **85**, 2019 (1963); (d) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 2029 (1963).
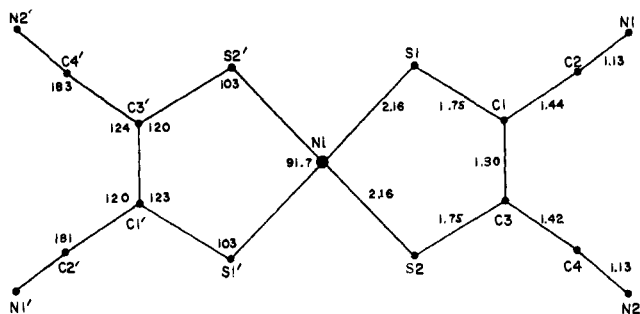
Fig. 1.—Structure of the Ni(MNT)$_2{}^{2-}$ ion. Note the center of inversion at the Ni position. Except possibly for the N atoms, the anion is planar.

Fig. 2.—Molecular orbital energy levels for the Ni(MNT)$_2{}^{2-}$ ion. Orbitals which are calculated to be approximately equal in energy are not resolved in the diagram. The molecular orbitals derived from the 3d metal orbitals are as follows: $3b_{1g}(d_{xy})$, $4a_g(d_{x^2-y^2})$, $3b_{3g}(d_{yz})$, $3a_g(d_{z^2})$, $4b_{2g}(d_{xz})$. Of these, the b_{1g} orbital is directed at the ligands and is expected to be most strongly antibonding in all M(MNT)$^{n-}$ complexes. The exact ordering of molecular orbitals which have approximately the same energy in Ni(MNT)$_2{}^{2-}$ may change depending on the charge and the nature of the central metal.

with the space groups C1 or C$\bar{1}$. The observed density of 1.35 ± 0.03 g./cm.^{3} is in good agreement with the density of 1.37 g./cm.^{3} calculated for two molecules of [(CH$_3$)$_4$N]$_2$[Ni(MNT)$_2$] in the unit cell. Intensity data were collected at room temperature by the equi-inclination Weissenberg technique. The intensities were estimated visually and reduced to values of F_0 by standard procedures.

The structure was solved by the usual combination of three-dimensional Patterson, Fourier, and least-squares techniques. The Ni atoms may be placed at (000) and ($^1/_2{}^1/_2$0). A satisfactory structure has been found for the anion on the assumption that it possesses a center of symmetry and that the correct space group is therefore C$\bar{1}$. At the present stage of refinement the conventional R factor for the 996 nonzero values of F_0 is 0.10.

Figure 1 is a sketch of the structure of the Ni-(MNT)$_2{}^{2-}$ anion. Because of the assumption of a center of symmetry the Ni-S part of the anion must be planar. On the basis of a least-squares analysis of the best plane through the anion, the Ni-S-C part of the anion is planar. Only the deviations of the N atoms from the best plane are possibly significant. The estimated standard deviations of the bond distances range from about 0.008 Å. for Ni-S up to about 0.02 Å. for C-N, and the estimated standard deviations of the bond angles are approximately 1°. Accordingly, although the anion is required to have only the symmetry C$_i$ as a result of the assumption of space group C$\bar{1}$, the symmetry of the Ni-S-C part of the anion does not differ significantly from D$_{2h}$. The molecular orbital calculation described below is consistent with the short C1-C3 distance of 1.30 ± 0.02 Å., since the predicted C1-C3 bond order is about 2.1. The tetra-methylammonium cation has its expected geometry with a mean C-N distance of 1.50 Å.

All intermolecular contacts appear to be normal. The closest intermolecular contacts of the Ni atom are three of the methyl carbon atoms from each of the cations at a distance of about 4 Å. The Ni atoms are well separated; the closest approach being the lattice distance of 8.05 Å.

Molecular orbitals for Ni(MNT)$_2{}^{2-}$ were constructed in the D$_{2h}$ symmetry using the following orthogonal coordinate system: the x axis bisects C1-C3 and the z axis is perpendicular to the molecular plane. The metal valence orbitals are 3d, 4s, and 4p. The four donor sulfur atoms have σ and in-plane π valence orbitals (π_h). In addition, each ligand furnishes eight π molecular orbitals perpendicular to the molecular plane (π_v orbitals).

The single-electron molecular orbital energies for the complex were calculated using a method previously described.^{4} The overlap integrals used are for the
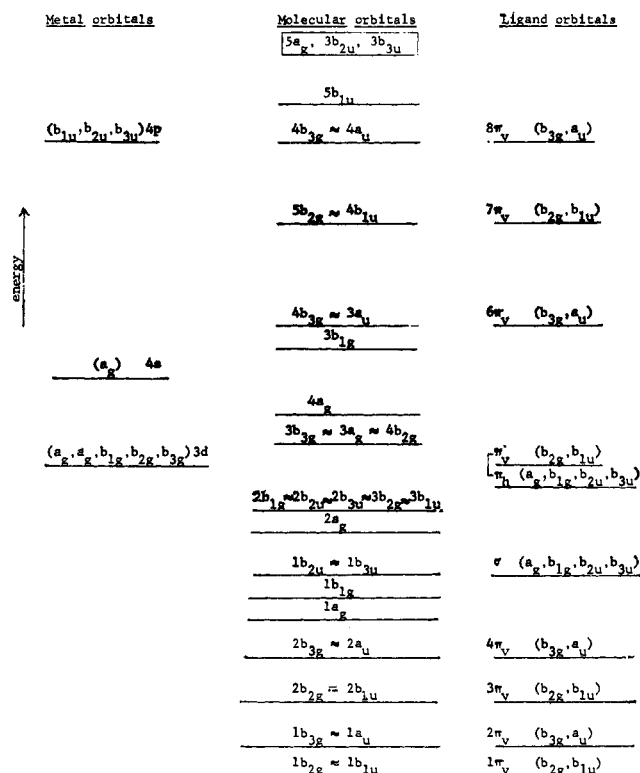
structure shown in Fig. 1. The π-orbital energies and starting wave functions for the ligand were obtained by separate calculation from an analysis of the spectra of bis(methylthio)maleonitrile and related compounds.^{5} The molecular orbital levels obtained using 3d, 4s, and 4p coulomb energies appropriate for the calculated final charge and orbital configuration of Ni are shown in Fig. 2.

The ground state of Ni(MNT)$_2{}^{2-}$ is .... (4a$_g$)^2 = ^{1}Ag. The weak absorption band observed at 11,850 cm.$^{-1}$ ($\epsilon \approx 30$) is assigned to the "d–d" transition ^{1}Ag → ^{1}B$_{1g}$ (4a$_g$ → 3b$_{1g}$). The remaining "d–d" transitions apparently are responsible for the shoulders on the first intense band. In acetonitrile, the electronic spectrum of Ni(MNT)$_2{}^{2-}$ shows four intense bands, located at 21,200 ($\epsilon \approx 3500$), 26,300 ($\epsilon \approx 6400$), 31,700 ($\epsilon \approx 24,000$), and 37,000 cm.$^{-1}$ ($\epsilon \approx 78,000$). The calculated molecular orbital levels are consistent with the following assignments.

Maxima, cm.$^{-1}$	Assignments
21,200	^{1}Ag → ^{1}B$_{2u}$ (4b$_{2g}$ → 3a$_u$)
26,300	^{1}Ag → ^{1}B$_{2u}$, ^{1}B$_{3u}$ (2b$_{3u}$ → 3b$_{1g}$, 2b$_{2u}$ → 3b$_{1g}$)
31,700	^{1}Ag → ^{1}B$_{2u}$ (3b$_{2g}$ → 3a$_u$, 3b$_{1u}$ → 4b$_{3g}$)
37,000	^{1}Ag → ^{1}B$_{2u}$, ^{1}B$_{3u}$ (1b$_{3u}$ → 3b$_{1g}$, 1b$_{2u}$ → 3b$_{1g}$)

The 21,200-cm.$^{-1}$ band involves metal to ligand charge transfer; the 26,300-cm.$^{-1}$ band involves charge transfer from π_h orbitals to the metal; the 31,700-cm.$^{-1}$ band arises from the first allowed ligand–

(4) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1, 111 (1962).
(5) J. Halper, W. D. Closson, and H. B. Gray, to be published.

ligand transition in the π_v orbitals.[6] A similar band appears at 29,500 cm.$^{-1}$ in the spectrum of bis(methylthio)maleonitrile; finally, the very intense band at 37,000 cm.$^{-1}$ is assigned as the strongly allowed ligand (σ^b) to metal (σ^*) charge transfer.

The electronic spectra of the $Pd(MNT)_2^{2-}$, $Pt(MNT)_2^{2-}$, and $Au(MNT)_2^-$ complexes are similar to the spectrum of $Ni(MNT)_2^{2-}$, and the observed transition energies are consistent with the above assignments.

(6) The $\pi_h \rightarrow 6\pi_v$ transitions, which are expected to appear somewhat higher than 31,700 cm.$^{-1}$, are "perpendicular" and thus much less intense than the strongly allowed bands. These transitions are probably buried under the $\sigma \rightarrow \sigma^*$ band at 37,000 cm.$^{-1}$.

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Diazonium and Carbonyl Derivatives of Polyhedral Boranes

Sir:

We have now established the scope of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ derivative chemistry[1] to be comparable to that of aromatic hydrocarbon chemistry. The key to this advance has been the preparation of several important intermediates, namely, the inner diazonium salt $B_{10}H_8(N_2)_2$ and the dicarbonyls $B_{10}H_8(CO)_2$ and $B_{12}H_{10}(CO)_2$.

The diazonium derivative is prepared from $B_{10}H_{10}^{-2}$ by reaction with a large excess (10–12 mole equiv.) of aqueous nitrous acid followed by reduction of a precipitated intermediate with $NaBH_4$ in methanol.[2]

Figure 1.

the corresponding $B_{10}H_8(ligand)_2$ species. A similar displacement occurs with amides but the stereochemistry of these products is uncertain. Minor amounts (<5%) of other isomers of $B_{10}H_8(CO)_2$ have been separated by gas chromatography; the presence of corresponding amounts of the analogous isomers of $B_{10}H_8(N_2)_2$ would not be detectable by boron n.m.r. because of the chemical shifts and line widths encountered in B^{11} n.m.r. spectroscopy.

$B_{10}H_8(CO)_2$ has been the most thoroughly studied of the ligand displacement products. It is best prepared from $B_{10}H_8(N_2)_2$ and carbon monoxide at 120–140°, in the absence of a solvent, although iron carbonyl can

TABLE I

ANALYSES OF REPRESENTATIVE SPECIES

Species	% Calcd.					% Found				
	B	C	H	N	Misc.	B	C	H	N	Misc.
$B_{10}H_8(N_2)_2$	62.8	..	4.6	32.6	Mol. wt. 172	62.1	..	4.9	33.3	169
$B_{10}H_8(CO)_2$	62.8	14.0	4.6	..	Mol. wt. 172	62.9	14.2	4.8	..	186
$B_{10}Cl_8(CO)_2$	24.1	5.4	0.0	..	Cl 63.3	24.2	6.2	0.9	..	63.3
$Cs_2B_{10}Cl_8(N_3)_2$	14.6	..	...	11.3	Cl 38.2	14.6	..	..	11.1	38.7
					Cs 35.8					35.8
$(Me_4N)_2B_{10}Cl_8(COC_6H_4NMe_2)_2$	18.0	19.9	5.0	4.6	...	17.6	19.9	4.6	4.7	...
$B_{12}H_{10}(CO)_2$	66.1	12.2	5.0	..	Mol. wt. 196	65.8	12.1	5.0	..	204
$(Me_4N)_2B_{12}H_{10}(NCO)_2$	34.9	32.3	9.2	15.0	...	34.8	32.3	9.1	15.2	...
$(Me_4N)_2B_{12}H_{10}(COOCH_3)_2$	32.0	35.5	9.9	6.9		31.9	35.1	10.0	6.9	...

$B_{10}H_8(N_2)_2$ is a colorless solid which decomposes slowly at about 125° without melting and which can be sublimed at 90–100° under vacuum. It is not shock sensitive. *However, the unreduced intermediate is exceedingly shock sensitive and should be handled with extreme caution, preferably never in the dry state.* $B_{10}H_8(N_2)_2$ is 1,10 (bisapical, see Fig. 1 for B_{10} numbering system) substituted within the detection limits of boron n.m.r. This configuration is maintained throughout reactions with amines, nitriles, ammonia, and carbon monoxide in which nitrogen is lost at 115–140° to give

(1) For an initial report on this subject see: W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

(2) This two-step synthesis of $B_{10}H_8(N_2)_2$ may be mechanistically related to the direct introduction of diazonium groups into organic aromatic species by excess nitrous acid. In the organic system, however, a reduction step is not necessary. See: J. M. Tedder and G. Theaker, *Tetrahedron*, **5**, 288 (1959).
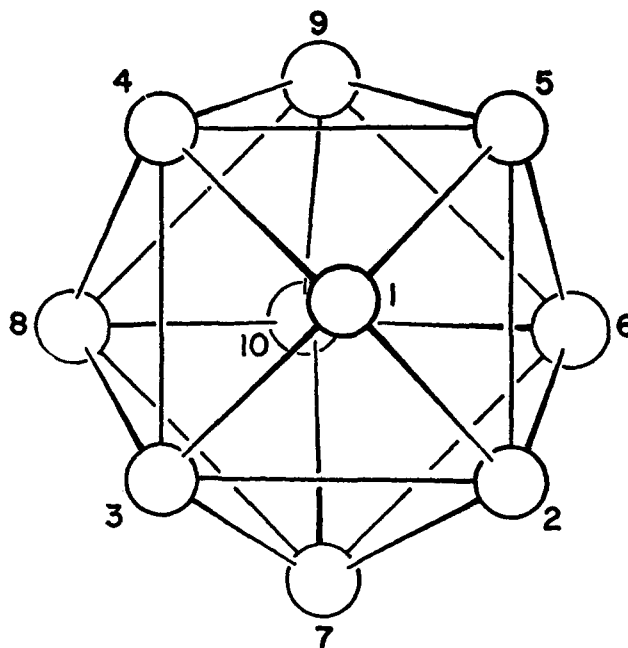
be used. If the reaction is run in the presence of cyclohexane, $C_6H_{11}B_{10}H_7(CO)_2$ and $(C_6H_{11})_2B_{10}H_6(CO)_2$ are formed, suggesting a free radical mechanism. The reaction of $B_{12}H_{12}^{-2}$ with carbon monoxide under acidic conditions has given $B_{12}H_{11}CO^-$ and $B_{12}H_{10}(CO)_2$; the latter consisting of at least two isomers according to preliminary gas chromatographic studies. The dicarbonyls of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ have very intense carbonyl stretching frequencies at 2140 and 2250 cm.$^{-1}$, respectively. These volatile compounds are easily purified by sublimation at *ca.* 100° under vacuum and do not readily undergo thermal dissociation. $B_{10}H_8(CO)_2$ (m.p. in sealed tube 155–156°) was unchanged after 2 hr. at 200° in an evacuated sealed tube, although there was evidence of decomposition at 250°.

In water the carbonyls are in equilibrium with carboxylic acid derivatives, which can be isolated as