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Structure of Di(tetramethylammonium)bis(maleonitrile dithiolate)nickelate(II)¹

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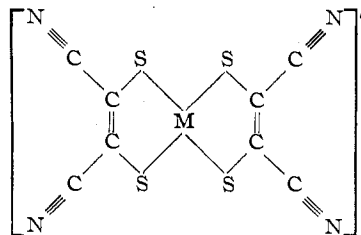
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The crystal and molecular structure of di(tetramethylammonium)bis(maleonitrile dithiolate)nickelate(II) has been determined from three-dimensional X-ray data collected from a single crystal. The material crystallizes in space group $C\bar{1}$ of the triclinic system, with two molecules in a cell of dimensions $a = 10.18$, $b = 15.79$, $c = 8.04$ Å., $\alpha = 87.1$, $\beta = 113.4$, and $\gamma = 91.9^\circ$. Although the NiS_4 portion of the anion is required by crystallographic symmetry to be planar, the entire anion need have only C_1 symmetry; the anion is found to be essentially planar and to have symmetry very near to D_{2h} . The cation has its expected tetrahedral shape.

Introduction

Since the initial report³ on the preparation of Co^{2+} and Ni^{2+} complexes containing as the ligand the dianion of maleonitriledithiol (MNT), there has been considerable activity in the preparation and characterization of a number of presumably square-planar complexes of the transition metals. The discovery⁴⁻⁶ that these compounds readily undergo reversible electron-transfer reactions to yield a wide variety of complexes with total charges of 0, -1, or -2 is of importance since it makes possible the study of similar complexes of transition metals in a series of formal oxidation states. Extensive physical measurements on the MNT systems^{7,8} as well as on related systems⁹ have been reported recently. In an earlier communication¹⁰ we provided the first crystallographic proof that in one of these compounds, namely $((CH_3)_4N)_2Ni(MNT)_2$, the anion is indeed very nearly square-planar. In this paper we describe in detail the structure determination.

Subsequent to our study the structures of other anions of the series



have been determined ($M = Co$, $q = -2^{11}$; $M = Cu$, $q = -1^{12}$; $M = Ni$, $q = -1^{13}$). The series is in fact remarkable, for the geometry of the anion appears to be independent of the metal M and the charge q .

Collection and Reduction of the X-Ray Data

The orange-red crystals of $((CH_3)_4N)_2Ni(MNT)_2$ were examined optically and by precession and Weissenberg techniques and were found to belong to the triclinic system. A Delaunay reduction performed on our initial triclinic cell failed to suggest hidden symmetry. The cell chosen for the indexing of the Weissenberg photographs is a C-centered one, with $a = 10.18 \pm 0.03$, $b = 15.79 \pm 0.03$, $c = 8.04 \pm 0.02$ Å., $\alpha = 87.1 \pm 0.1$, $\beta = 113.4 \pm 0.1$, $\gamma = 91.9 \pm 0.2^\circ$, cell volume = 1185 Å.³. The observed density of 1.35 g./cm.³ is in good agreement with the density of 1.37 g./cm.³

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(2) Participant in the Brookhaven Summer Student Program.

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(13) C. J. Fritchie, Jr., Abstract K-10, American Crystallographic Association Meeting, Bozeman, Mont., July 25-31, 1964; *Acta Cryst.*, in press.

TABLE I
 FINAL PARAMETER VALUES FOR $((\text{CH}_3)_4\text{N})_2\text{Ni}(\text{MNT})_2$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å. ²
Ni	0	0	0	3.7 (1) ^b
S ₁	0.1851 (4) ^a	-0.0715 (3)	0.1794 (5)	4.9 (1) ^b
S ₂	0.1349 (4)	0.1000 (3)	-0.0410 (5)	5.0 (1) ^b
C ₁	0.329 (1)	-0.008 (1)	0.182 (2)	4.5 (3)
C ₂	0.470 (1)	-0.040 (1)	0.288 (2)	4.7 (3)
N ₁	0.581 (2)	-0.065 (1)	0.369 (2)	7.1 (3)
C ₃	0.310 (1)	0.065 (1)	0.087 (2)	4.4 (3)
C ₄	0.423 (2)	0.117 (1)	0.088 (2)	5.2 (3)
N ₂	0.515 (2)	0.160 (1)	0.095 (2)	7.3 (3)
N _{cat}	0.034 (1)	-0.178 (1)	-0.389 (1)	4.4 (2)
C _{1cat}	0.064 (2)	-0.226 (2)	-0.208 (3)	9.4 (5)
C _{2cat}	0.136 (3)	-0.106 (2)	-0.374 (4)	11.4 (7)
C _{3cat}	-0.107 (2)	-0.139 (2)	-0.458 (3)	9.1 (5)
C _{4cat}	0.038 (2)	-0.240 (2)	-0.530 (3)	8.2 (5)

Atom	β_{11} ^c	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0144 (3)	0.0037 (2)	0.0133 (4)	0.0026 (2)	0.0064 (3)	0.0004 (2)
S ₁	0.0142 (5)	0.0044 (3)	0.0214 (7)	0.0022 (3)	0.0048 (5)	0.0019 (3)
S ₂	0.0157 (5)	0.0052 (3)	0.0214 (7)	0.0025 (3)	0.0074 (5)	0.0036 (3)

^a The estimated standard deviation in the least significant figure is given in parentheses here and in subsequent tables. ^b From the isotropic refinement. ^c The general form for the anisotropic temperature factor is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$.

calculated for two molecules in this centered cell. A very sensitive piezoelectric test¹⁴ was negative, and this provides reasonable evidence that the space group is $\text{C}\bar{1}$, rather than $\text{C}1$. The satisfactory agreement ultimately obtained is also taken as support for the choice of $\text{C}\bar{1}$. (The equivalent positions of $\text{C}\bar{1}$ are $\pm(x, y, z; 1/2 + x, 1/2 + y, z)$.)

Intensity data were collected at room temperature by the equi-inclination Weissenberg technique. Zirconium-filtered Mo $K\alpha$ radiation was employed. The layers $h0l$ to $h10l$ were photographed. The intensities of 996 independent reflections accessible within the angular range $\theta_{\text{Mo}} \leq 22.2^\circ$ were estimated visually. Because of the triclinic symmetry the intensity estimates were necessarily made from both the top and bottom portions of the films, and no corrections were applied for spot elongation. The usual Lorentz-polarization factor was applied to the intensities to yield F_o^2 values (where F_o is the observed structure amplitude) and these were then corrected for absorption. In order to carry out the absorption correction the 12 crystal faces were identified by optical goniometry and the dimensions of the faces were carefully measured. (It turns out that the volume of the crystal used in the X-ray study is approximately 0.23 mm.³ and has a calculated weight of 315 μg .) Using an absorption coefficient of 11.7 cm^{-1} we find the resultant transmission coefficients range from about 0.39 to 0.61.¹⁵ The F_o values were subsequently brought to an approximate common scale through a modification of Wilson's procedure.

Solution of the Structure

With two molecules in $\text{C}\bar{1}$ the Ni atoms may be placed at the special positions (000) and $(1/2, 1/2, 0)$

(14) We are indebted to F. Holtzberg for performing this measurement for us.

(15) The programs for the IBM 7090 used in this work were local modifications of Burnham's GNABS absorption program, Zalkin's FORADP Fourier program, and the Busing-Levy ORFLS least-squares program.

and the NiS_4 portion of the anion is necessarily planar. These features make the solution of an otherwise simple problem trivial. A complete trial structure was readily found from the usual combination of three-dimensional Patterson and difference Fourier maps and was refined by the least-squares procedure. The function minimized was $\sum w(F_o - F_c)^2$, where the weights w were assigned in the following way: $F \leq 10$ e, $w = F^2/100$; $10 < F < 30$ e, $w = 1$; $F \geq 30$ e, $w = 900/F^2$. The atomic scattering factors for the neutral atoms tabulated by Ibers¹⁶ were used. The anomalous parts of the Ni and S scattering factors were obtained from Templeton's tabulation¹⁷ and were included in the calculated structure factors.¹⁸ The contributions of the hydrogen atoms to the structure factors were ignored, since no clear indication of their positions was obtained.

Initially the refinement was carried out in which all atoms were assigned individual isotropic thermal parameters. This refinement of 53 positional and thermal parameters converged to a conventional R factor ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.15 and to a weighted R factor R' ($R' = (\sum w(F_o - F_c)^2 / \sum w F_o^2)^{1/2}$) of 0.180. A difference Fourier based on this refinement exhibited electron density as high as 2.9 $\text{e}/\text{\AA}^3$ (about 75% of the height of a carbon atom in this structure). There was clear indication of significant anisotropic thermal motion in the vicinity of the heavy atoms.

In a second round of calculations the Ni and S atoms were allowed to vibrate anisotropically, while the other atoms were restricted to isotropic vibration. This refinement of 68 positional and thermal parameters converged to the values $R = 0.107$ and $R' = 0.130$.

(16) J. A. Ibers, "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. 3, Table 3.3.1A.

(17) D. H. Templeton, *ibid.*, Table 3.3.2C.

(18) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

TABLE II OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (X10) FOR ((CH3)4N)2Ni(MNT)2

Table with multiple columns labeled H L OBS CAL, H L OBS CAL, L OBS CAL, H L OBS CAL, H L OBS CAL, H L OBS CAL, H L OBS CAL, H L OBS CAL, H L OBS CAL, H L OBS CAL, H L OBS CAL, H L OBS CAL. It contains a dense grid of numerical data points representing structure amplitudes.

According to Hamilton's¹⁹ R-factor test this improvement is highly significant. The highest peak on the difference Fourier based on this refinement is 0.8 e/Å.³, about 20% the height of a carbon atom. There were no discernible features on this map that suggested an inadequate treatment of thermal motion; rather it appeared as though the limit of refinement consistent with the quality of the data had been reached. Nevertheless, in a final series of calculations the atoms in the cation were restricted to isotropic vibration, while all nine atoms in the anion were allowed to vibrate anisotropically.²⁰ This refinement of 98 positional and thermal parameters converged to the values R = 0.104 and R' = 0.126. There were no

significant shifts of the positional parameters away from the positions found in the previous refinement. Moreover, the improvement in the value of R' is significant at only about the 25% level¹⁹ and there is thus little justification for this refinement of additional thermal parameters. Accordingly in Table I we list as final parameters for this structure those that were obtained from the second calculation in which only the Ni and S atoms were allowed to vibrate anisotropically. The final values of F_o are based on these parameters; in Table II we list 10F_o and 10|F_o| (in electrons) for the 996 observed reflections. Since

(20) Since the scale factors of the separate layers were also adjusted in the least-squares procedure, it is not possible to carry out a complete anisotropic refinement. As long as a reasonable fraction of the atoms are restricted to isotropic vibration there is little correlation between the scale factors and the values of β₂₂ of those atoms that are vibrating anisotropically.

(19) W. C. Hamilton, Acta Cryst., in press.

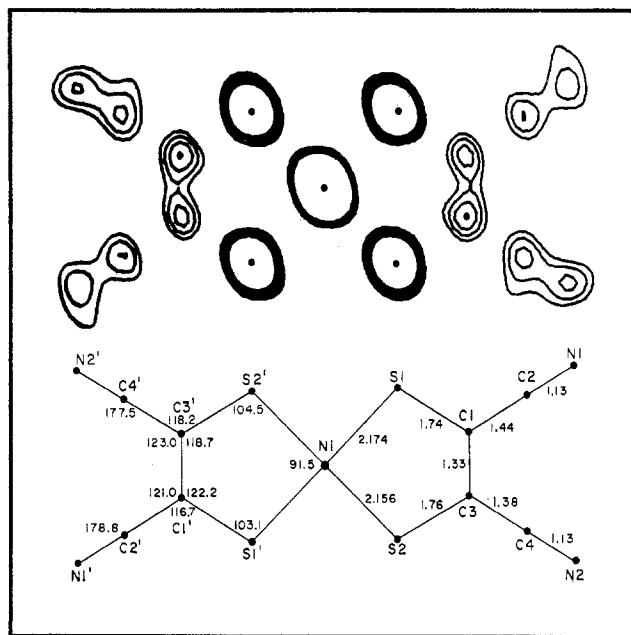


Figure 1.—A sketch of the $\text{Ni}(\text{MNT})_2^{2-}$ ion showing approximate dimensions and angles and also the electron density in the best least-squares plane through the anion. The electron density map was drawn by the cathode ray tube plotter on-line to the IBM 7094. The lowest contour is $1.46 \text{ e}/\text{\AA}^3$ and contours above $5.10 \text{ e}/\text{\AA}^3$ have been omitted. The contour interval of $0.73 \text{ e}/\text{\AA}^3$ nicely displays the density of the light atoms, but is too small to allow the heavy-atom contours to be resolved. The dots in the centers of the heavy atoms designate the atomic centers.

none of the intensities calculated for the unobserved but accessible reflections exceeds our estimate of a minimum observable intensity value, $|F_o|$ values for unobserved reflections are omitted from Table II.

The final R value of 0.107 is somewhat higher than we would normally expect, and we attribute this mainly to intensity errors arising from spot elongation and contraction.

The anisotropic thermal parameters (Table I) lead to the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoids tabulated in Table III. The orientations of the principal axes, which can be worked out from the data of Table I, lead us to conclude that the translational motion of the anion as a whole is somewhat smaller than motion resulting from rocking. No analysis of these vibrations in terms of a rigid-body approximation has been attempted.

Description of the Structure

The crystal structure described by the space group, the parameters of Table I, and the cell parameters

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN \AA)			
Atom	Minimum	Intermediate	Maximum
Ni	0.180 (3)	0.189 (3)	0.276 (3)
S ₁	0.198 (5)	0.265 (5)	0.274 (5)
S ₂	0.197 (5)	0.257 (4)	0.301 (6)

consists of the packing of essentially planar anions and tetrahedral cations. The anions are well-separated, the closest Ni-Ni approach being the lattice repeat of 8.04 \AA . All intermolecular contacts appear to be normal and give no indication of unusual anion-cation interactions. The closest intermolecular contacts of the Ni are three methyl carbons from each of the cations at a distance of about 4 \AA .

The dimensions of the $\text{Ni}(\text{MNT})_2^{2-}$ ion are shown in Figure 1 and tabulated in Table IV. The equation of

TABLE IV
PRINCIPAL INTRAMOLECULAR DISTANCES AND ANGLES

Atoms	Distance, \AA	Atoms	Angle, deg.
Anion			
Ni-S ₁	2.174 (6)	S ₁ -Ni-S ₂	91.5 (2)
Ni-S ₂	2.156 (6)	Ni-S ₂ -C ₃	104.5 (6)
S ₁ -C ₁	1.74 (2)	S ₂ -C ₃ -C ₁	119 (1)
S ₂ -C ₃	1.76 (1)	C ₃ -C ₁ -S ₁	122 (1)
C ₁ -C ₃	1.33 (2)	C ₁ -S ₁ -Ni	103.1 (5)
C ₁ -C ₂	1.44 (2)	S ₂ -C ₃ -C ₄	118 (1)
C ₃ -C ₄	1.38 (2)	C ₃ -C ₄ -N ₂	177 (2)
C ₂ -N ₁	1.13 (2)	C ₄ -C ₃ -C ₁	123 (1)
C ₄ -N ₂	1.13 (2)	C ₃ -C ₁ -C ₂	121 (1)
		S ₁ -C ₁ -C ₂	117 (1)
		C ₁ -C ₂ -N ₁	179 (1)
Cation			
N-C ₁	1.53 (3)	C ₁ -N-C ₂	113 (1)
N-C ₂	1.50 (3)	C ₁ -N-C ₃	111 (1)
N-C ₃	1.47 (2)	C ₁ -N-C ₄	110 (2)
N-C ₄	1.55 (2)	C ₂ -N-C ₃	104 (2)
		C ₂ -N-C ₄	110 (1)
Mean C-N	1.512	C ₃ -N-C ₄	109 (1)
		Mean angle	109.4

the best least-squares plane²¹ through the anion is $3.741x - 8.011y - 7.122z = 0$ (triclinic coordinate system). The deviations of the individual atoms from this plane (Table V) are small and presumably

TABLE V
DEVIATIONS (\AA) FROM THE LEAST-SQUARES PLANE THROUGH THE ANION

Atom	Deviation	σ (deviation)
S ₁	-0.012	0.004
S ₂	-0.004	0.004
C ₁	-0.001	0.016
C ₃	0.016	0.016
C ₂	0.024	0.016
C ₄	0.014	0.017
N ₁	0.065	0.017
N ₂	-0.036	0.017

result from packing distortions. Although the molecule is required to have only the symmetry C_i , the symmetry closely approximates D_{2h} . The geometry of the anion differs insignificantly from that of the $\text{Co}(\text{NMT})_2^{2-}$,¹¹ $\text{Cu}(\text{MNT})_2^-$,¹² and $\text{Ni}(\text{MNT})_2^{-13}$ anions.

The tetramethylammonium cation has its expected tetrahedral shape (Table IV).

(21) W. C. Hamilton, *Acta Cryst.*, **14**, 185 (1961).