# One-dimensional System of Square-planar Bis(1,2-dicyanovinylene-1,2-dithiolato)metal Complexes. I. The Crystal Structure of $[(C_4H_9)_4N]_2[Ni(mnt)_2]$ and $[(C_2H_5)_4N][Ni(mnt)_2]$

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X-Ray crystal structure analyses of $[(C_4H_9)_4N]_2[Ni(mnt)_2]$ (I) and $[(C_2H_5)_4N][Ni(mnt)_2]$ (II) {mnt: 1,2-dicyanovinylene-1,2-dithiolato $C_4N_2S_2^{2-}$} have been carried out from the viewpoint of one-dimensional system. Crystals of (I) belong to triclinic system: $a=12.360(6)$, $b=11.138(12)$, $c=9.833(9)$ Å, $\alpha=118.43(9)$, $\beta=92.05(6)$, $\gamma=91.91(6)°$, space group $P\bar{1}$ with $Z=1$. The compound (II) forms monoclinic crystals, $P2_1/a$: $a=20.018(18)$, $b=16.079(9)$, $c=7.118(6)$ Å, $\beta=110.43(6)°$, $Z=4$. Both structures, solved by the heavy-atom method, have been refined anisotropically by least-squares procedure to $R=0.049$ and 0.050 for (I) and (II), respectively. The bond distances of diamagnetic $Ni(mnt)_2^{2-}$ anion and paramagnetic $Ni(mnt)_2^{1-}$ anion are compared. A columnar structure was found in the structure of (II). The $Ni(mnt)_2^{1-}$ ions form a diadic unit, that is a repeating unit of two anions, within the columns. The electrical conductivity data are measured along the direction parallel to the $Ni(mnt)_2^{1-}$ stacks in the temperature range from room temperature to 373 K. This compound behaves as a semiconductor in this temperature range.

Recent studies of high conductive platinum complex of $K_2Pt(CN)_4Br_{0.3}\cdot xH_2O$ and TCNQ salts[1] have revealed their metallic behavior. Their magnetic, electrical and optical properties are also originated from one-dimensional interactions associated with a columnar crystallographic structure.[1] Like TCNQ, bis(1,2-dicyanovinylene-1,2-dithiolato)metal complexes are known in some cases to form compounds with high electrical conductivities.[2,3] Furthermore these dithiolene complexes form a series of stable compounds with the same central metal ion in different oxidation states *e.g.*, in the Ni, Pd, Pt, the 0, −1, −2 charged complexes are well known.[4]

We report here X-ray diffraction studies on single crystals of tetrabutylammonium salt of diamagnetic $Ni(mnt)_2^{2-}$ and tetraethylammonium salt of paramagnetic $Ni(mnt)_2^{1-}$. Electrical conductivity measurements were also performed on single crystals of $[(Et)_4N][Ni(mnt)_2]$ by the use of the four-probe methods. We are interested in the relationship between the crystal structures and electrical properties of one-dimensional system.

## Experimental

*Data Collections and Structure Analyses.* The compounds $[(n\text{-}Bu)_4N]_2[Ni(mnt)_2]$ (I) and $[(Et)_4N][Ni(mnt)_2]$ (II) were prepared by the published method.[4] The tetrabutylammonium salt and tetraethylammonium salt were chosen because we could obtain suitable single crystals for experiments. The red crystals of (I) and black crystals of (II) were obtained from the original product through recrystallization by slow evaporation from acetone solution. For the purpose of the X-ray diffraction work, a specimen $0.25\times0.20\times0.37$ mm was used for (I) and $0.075\times0.125\times0.38$ mm for (II). The intensity data set were collected with monochromatized Mo$K\alpha$ radiation by the $\omega$-$2\theta$ scan technique out to $2\theta=60°$. Reflections were scanned at a rate of 2 ° minute in $2\theta$. Background counts of 10 s were taken at each end of the scan range. Independent 3559 significant reflections for which $|F|\geqq3\sigma(F)$ were obtained for (I) and 2635 for (II), respectively. The data were corrected for Lorentz and polarization effects. No corrections were made for absorption.

The crystal data are as follows:

| $[(n\text{-}Bu)_4N]_2[Ni(mnt)_2]$ (I) | $[(Et)_4N][Ni(mnt)_2]$ (II) |
|---|---|
| triclinic $P\bar{1}$ | monoclinic $P2_1/a$ |
| $a=12.360(6)$ Å | $a=20.018(18)$ Å |
| $b=11.138(12)$ | $b=16.079(9)$ |
| $c=9.833(9)$ | $c=7.118(6)$ |
| $\alpha=118.43(9)°$ | $\beta=110.43(6)°$ |
| $\beta=92.05(6)$ | $V=2147.0$ Å$^3$ |
| $\gamma=91.91(6)$ | $Z=4$ |
| $V=1187.7$ Å$^3$ | $d_m=1.24$ g/cm$^3$ |
| $Z=1$ | $d_c=1.235$ g/cm$^3$ |
| $d_m=1.07$ g/cm$^3$ | $\mu=13.23$ cm$^{-1}$ |
| $d_c=1.074$ g/cm$^3$ | |
| $\mu=6.29$ cm$^{-1}$ | |

Since Wilson's statistics indicated the presence of a center of symmetry, the space group $P\bar{1}$ was assumed for (I). For solution and refinement of the structure usual heavy-atom methods were employed. The atomic parameters were refined by the block-diagonal least-squares method, using anisotropic temperature factors for all the nonhydrogen atoms and isotropic ones for hydrogen atoms. The effects of the anomalous dispersion of Ni and S atoms were included in the calculation. Final reliability factors are: (I), $R=0.049$, (II), $R=0.050$. The positional and thermal parameters of all atoms are presented in Tables 1 and 2.

The calculations were performed on a HITAC 8700/8800 computer at the Computer Center of the University of Tokyo using a local version of UNICS.[5] The atomic scattering factors and the values of $\Delta f'$ and $\Delta f''$ were taken from the International Tables for X-Ray Crystallography.[6] The weighting scheme used were: (I), $w=1$ for $|F_o|\geqq4.25$ ($F_o$: absolute scale), $w=0.0$ otherwise; (II), $w=1$ for $|F_o|\geqq15.15$, $w=0.2$ otherwise. The $F_o$-$F_c$ tables are kept at the office of this Bulletin as Document No. 7726 and 7727.

*Conductivity Measurements.* $[(Et)_4N][Ni(mnt)_2]$ single crystals are black needles with long axis parallel to the crystallographic c axis, giving good optical reflections. Comparatively high electrical conductivity is expected for $[(Et)_4N][Ni(mnt)_2]$ single crystals because of its columnar structure:

TABLE 1. FRACTIONAL COORDINATES AND THERMAL PARAMETERS ($\times 10^4$) FOR $[(C_4H_9)_4N]_2[Ni(mnt)_2]$

Thermal parameters are for the expression $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})\}$.

a) Nonhydrogen atoms.

| Atom | $X$ | $Y$ | $Z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ni | 0 | 0 | 0 | 76(1) | 95(1) | 127(1) | −1(1) | −5(1) | 55(1) |
| S(1) | −1370(1) | −417(1) | 1073(1) | 93(1) | 108(1) | 186(2) | 0(1) | 11(1) | 75(1) |
| S(2) | −283(1) | 2168(1) | 1079(2) | 114(1) | 102(1) | 200(2) | 4(1) | 37(1) | 69(1) |
| N(1) | −3662(3) | 1270(5) | 3458(5) | 91(4) | 204(7) | 270(9) | 4(1) | 16(5) | 123(7) |
| N(2) | −2241(5) | 4628(5) | 3532(7) | 253(8) | 172(7) | 377(13) | 95(6) | 162(8) | 149(8) |
| N(3) | 2787(3) | 855(3) | 3761(4) | 66(3) | 117(4) | 141(5) | 0(3) | −10(3) | 69(4) |
| C(1) | −1914(3) | 1166(4) | 2066(5) | 78(3) | 113(5) | 137(6) | 3(3) | −2(4) | 69(5) |
| C(2) | −1434(4) | 2284(4) | 2068(5) | 101(4) | 111(5) | 138(7) | 12(4) | 12(4) | 63(5) |
| C(3) | −2884(4) | 1241(4) | 2844(5) | 83(4) | 133(6) | 179(8) | 3(4) | −11(4) | 81(5) |
| C(4) | −1881(5) | 3597(5) | 2896(6) | 137(5) | 146(6) | 230(10) | 30(5) | 59(6) | 111(7) |
| C(5) | 2576(3) | 1931(4) | 3246(5) | 79(3) | 126(5) | 143(6) | 15(3) | −2(4) | 79(5) |
| C(6) | 3521(4) | 2946(4) | 3544(5) | 95(4) | 121(5) | 164(7) | 5(4) | 8(4) | 78(5) |
| C(7) | 3232(5) | 3817(5) | 2781(6) | 149(6) | 169(7) | 200(9) | −14(5) | −13(6) | 117(7) |
| C(8) | 4044(6) | 5018(6) | 3232(8) | 180(7) | 168(8) | 334(14) | −34(6) | −8(8) | 157(9) |
| C(9) | 3720(3) | −10(4) | 2918(5) | 70(3) | 126(5) | 177(7) | 20(3) | 7(4) | 75(5) |
| C(10) | 3594(4) | −679(5) | 1149(5) | 112(5) | 167(7) | 170(8) | 42(5) | 27(5) | 67(6) |
| C(11) | 4468(4) | −1722(5) | 417(6) | 109(5) | 168(7) | 238(10) | 21(5) | 31(6) | 70(7) |
| C(12) | 4275(6) | −2992(6) | 547(8) | 164(7) | 165(8) | 394(17) | 34(6) | 46(9) | 112(10) |
| C(13) | 1726(3) | −23(4) | 3375(5) | 65(3) | 137(5) | 158(7) | −11(3) | −12(4) | 74(5) |
| C(14) | 1764(4) | −1196(5) | 3745(7) | 97(5) | 190(8) | 324(12) | −38(5) | −56(6) | 173(8) |
| C(15) | 765(4) | −2074(6) | 3240(7) | 104(5) | 205(9) | 350(14) | −38(5) | −30(7) | 168(9) |
| C(16) | 739(5) | −3261(6) | 3580(7) | 123(6) | 186(8) | 330(13) | −33(5) | −13(7) | 144(9) |
| C(17) | 3121(3) | 1534(4) | 5492(5) | 81(3) | 132(5) | 130(6) | −8(3) | −19(4) | 70(5) |
| C(18) | 2271(4) | 2358(4) | 6556(5) | 92(4) | 138(6) | 139(7) | −6(4) | −11(4) | 66(5) |
| C(19) | 2780(4) | 3227(5) | 8204(5) | 124(5) | 152(6) | 148(7) | −23(4) | −17(5) | 64(6) |
| C(20) | 1953(5) | 4082(5) | 9315(6) | 161(6) | 175(8) | 161(8) | −11(6) | −5(6) | 68(7) |

b) Hydrogen atoms.

Fractional coordinates $\times 10^3$; Isotropic thermal parameters $\times 10$.

| Atom | $X$ | $Y$ | $Z$ | $B$ | Atom | $X$ | $Y$ | $Z$ | $B$ |
|---|---|---|---|---|---|---|---|---|---|
| H(1) | 198(4) | 241(5) | 380(5) | 53(12) | H(19) | 380(4) | 219(4) | 561(5) | 47(12) |
| H(2) | 237(4) | 145(4) | 214(5) | 48(12) | H(20) | 335(4) | 79(5) | 575(5) | 49(12) |
| H(3) | 422(4) | 244(5) | 332(5) | 55(13) | H(21) | 178(4) | 179(5) | 662(5) | 53(12) |
| H(4) | 360(4) | 359(5) | 462(5) | 50(12) | H(22) | 200(4) | 301(5) | 624(5) | 54(12) |
| H(5) | 252(4) | 405(5) | 301(6) | 65(14) | H(23) | 339(4) | 380(5) | 818(5) | 53(12) |
| H(6) | 319(4) | 330(5) | 173(6) | 66(14) | H(24) | 302(4) | 262(5) | 864(6) | 64(14) |
| H(7) | 378(4) | −64(4) | 337(5) | 45(11) | H(25) | 473(4) | 476(5) | 321(5) | 59(13) |
| H(8) | 441(4) | 75(5) | 338(5) | 50(12) | H(26) | 405(4) | 573(5) | 443(6) | 68(14) |
| H(9) | 362(4) | 16(5) | 93(6) | 60(13) | H(27) | 417(4) | 540(5) | 246(6) | 67(14) |
| H(10) | 281(4) | −108(5) | 92(6) | 59(13) | H(28) | 43(4) | −262(5) | 459(6) | 69(14) |
| H(11) | 527(4) | −125(5) | 80(6) | 61(13) | H(29) | 141(4) | −360(5) | 342(6) | 68(14) |
| H(12) | 441(4) | −214(5) | −84(6) | 66(14) | H(30) | 2(4) | −400(5) | 283(6) | 67(14) |
| H(13) | 158(4) | −40(4) | 222(5) | 45(11) | H(31) | 138(4) | 359(5) | 941(5) | 58(13) |
| H(14) | 120(4) | 58(5) | 411(5) | 50(12) | H(32) | 161(4) | 464(5) | 907(5) | 58(13) |
| H(15) | 176(4) | −63(5) | 499(6) | 70(15) | H(33) | 239(4) | 463(5) | 1023(6) | 62(13) |
| H(16) | 240(4) | −161(5) | 374(6) | 68(14) | H(34) | 481(4) | −361(5) | −19(6) | 67(14) |
| H(17) | 59(4) | −245(5) | 206(6) | 68(14) | H(35) | 340(4) | −340(5) | 19(6) | 68(14) |
| H(18) | 11(4) | −147(5) | 376(6) | 67(14) | H(36) | 440(4) | −279(5) | 161(6) | 69(14) |

the details of the crystal structure will be mentioned later. Four-probe resistance measurements were made on single crystals (3—6 mm long and 0.45—0.5 mm in diameter) along the needle axis paralled to the $Ni(mnt)_2^{1-}$ stacks. The crystals were attached by four 0.025 mm gold wires on a Teflon sample holder. Electrical contact was made by wetting the gold wires with silver-paste paint. The resistivity data ($R=\sigma^{-1}$) are presented in Fig. 1a, where $\ln R/R_0$ is plotted as a function of $T^{-1}$ in the limited range from room temperature to 373 K which shows straight-line behavior. Thus this compound is semiconductive. From this slope, one obtains the value of 0.35 eV for the activation energy. The room temperature resistivity parallel to $Ni(mnt)_2^{1-}$ stacks is $(3.5\pm1.2)\times10^5\ \Omega$ cm. Another type of $[(Et)_4N][Ni(mnt)_2]$ crystals (parallolepiped pillar) show different kinds of resistivity behavior in the temperature

TABLE 2. FRACTIONAL COORDINATES AND THERMAL PARAMETERS ($\times 10^4$) FOR $[(C_2H_5)_4N][Ni(mnt)_2]$

Thermal parameters are for the expression $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})\}$.

a) Nonhydrogen atoms.

| Atom | $X$ | $Y$ | $Z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ni | 432(1) | 496(1) | 2852(2) | 22(0) | 32(0) | 165(2) | 2(0) | 25(1) | 3(1) |
| S(1) | 1427(1) | 1157(2) | 3814(4) | 22(1) | 37(1) | 271(7) | 2(1) | 23(2) | 8(2) |
| S(2) | −174(1) | 1619(2) | 1871(4) | 22(1) | 35(1) | 232(6) | 2(1) | 27(2) | 5(2) |
| S(3) | 1053(1) | −607(2) | 3938(4) | 25(1) | 39(1) | 276(7) | 4(1) | 21(2) | 12(3) |
| S(4) | −553(1) | −186(2) | 1908(4) | 23(1) | 35(1) | 216(6) | 1(1) | 22(2) | 6(2) |
| N(1) | 2155(5) | 3282(6) | 4025(17) | 36(4) | 55(5) | 562(43) | −12(4) | 33(10) | 5(12) |
| N(2) | 86(5) | 3887(6) | 1355(15) | 34(3) | 42(4) | 495(36) | 5(3) | 54(9) | 24(11) |
| N(3) | 831(6) | −2895(6) | 4348(16) | 60(5) | 41(5) | 440(36) | 17(4) | 53(11) | 20(11) |
| N(4) | −1235(5) | −2348(6) | 1693(16) | 41(4) | 38(4) | 474(37) | −9(3) | 32(9) | −1(11) |
| N(5) | 1866(4) | 5083(5) | 9373(11) | 20(2) | 33(3) | 221(20) | −3(2) | 24(6) | 7(7) |
| C(1) | 1177(5) | 2179(6) | 3225(14) | 24(3) | 33(4) | 226(26) | −1(3) | 21(7) | 9(9) |
| C(2) | 471(5) | 2378(6) | 2373(14) | 24(3) | 30(4) | 234(27) | 0(3) | 37(7) | 10(8) |
| C(3) | 1721(5) | 2792(7) | 3677(17) | 29(3) | 39(5) | 339(34) | 4(3) | 34(9) | 21(11) |
| C(4) | 253(5) | 3220(7) | 1801(16) | 24(3) | 45(5) | 293(31) | −3(3) | 36(8) | 2(10) |
| C(5) | 427(5) | −1375(6) | 3448(14) | 33(3) | 32(4) | 231(28) | 4(3) | 34(8) | −2(8) |
| C(6) | −283(5) | −1199(6) | 2534(13) | 29(3) | 30(4) | 160(23) | 2(3) | 23(7) | 1(8) |
| C(7) | 667(5) | −2231(7) | 3957(16) | 34(4) | 44(5) | 281(31) | 5(4) | 34(9) | 11(10) |
| C(8) | −818(5) | −1840(6) | 2064(15) | 33(4) | 36(5) | 226(27) | 5(3) | 20(8) | 10(9) |
| C(9) | 1621(5) | 5910(6) | 8242(16) | 31(4) | 33(5) | 308(32) | 0(3) | 31(9) | 15(10) |
| C(10) | 2167(7) | 6610(7) | 8844(22) | 46(5) | 32(5) | 602(55) | −13(4) | 46(3) | 9(14) |
| C(11) | 1224(5) | 4515(6) | 8874(16) | 24(3) | 38(4) | 342(32) | −7(3) | 30(8) | 22(11) |
| C(12) | 866(6) | 4312(8) | 6597(17) | 37(4) | 55(6) | 298(34) | −8(4) | 3(9) | −12(12) |
| C(13) | 2434(5) | 4716(7) | 8579(16) | 26(3) | 47(6) | 297(30) | 1(3) | 43(8) | 3(10) |
| C(14) | 2712(6) | 3869(7) | 9399(20) | 30(4) | 43(5) | 502(46) | 7(4) | 48(11) | 4(13) |
| C(15) | 2184(5) | 5191(7) | 11619(14) | 31(3) | 60(6) | 161(24) | −1(4) | 20(7) | 2(10) |
| C(16) | 1696(7) | 5622(10) | 12463(18) | 50(5) | 107(10) | 270(34) | 1(6) | 62(11) | −32(16) |

b) Hydrogen atoms.

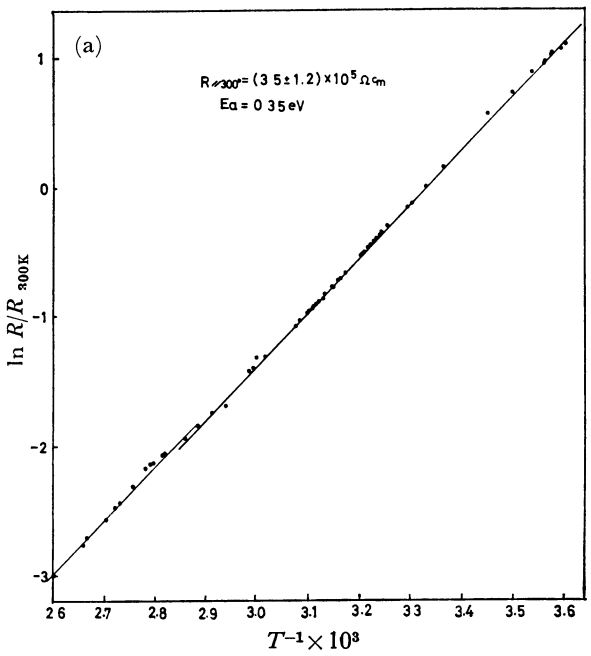
Fractional coordinates $\times 10^3$; isotropic thermal parameters $\times 10$.

| Atom | $X$ | $Y$ | $Z$ | $B$ | Atom | $X$ | $Y$ | $Z$ | $B$ |
|---|---|---|---|---|---|---|---|---|---|
| H(1) | 124(6) | 603(7) | 866(16) | 49(29) | H(11) | 220(6) | 670(8) | 1037(18) | 68(35) |
| H(2) | 145(5) | 576(6) | 655(15) | 38(26) | H(12) | 43(5) | 402(7) | 610(15) | 45(28) |
| H(3) | 85(5) | 479(7) | 942(15) | 43(27) | H(13) | 74(5) | 482(6) | 572(14) | 37(26) |
| H(4) | 137(5) | 405(7) | 996(15) | 44(28) | H(14) | 116(5) | 392(7) | 617(16) | 45(28) |
| H(5) | 282(5) | 509(7) | 878(15) | 42(27) | H(15) | 284(6) | 387(8) | 1093(17) | 60(32) |
| H(6) | 221(5) | 470(6) | 698(14) | 29(23) | H(16) | 309(5) | 368(7) | 861(16) | 45(28) |
| H(7) | 262(5) | 560(6) | 1189(13) | 25(22) | H(17) | 232(6) | 340(7) | 875(17) | 57(31) |
| H(8) | 233(5) | 460(6) | 1208(13) | 28(23) | H(18) | 133(6) | 535(8) | 1253(18) | 63(34) |
| H(9) | 201(6) | 706(7) | 778(16) | 51(30) | H(19) | 151(6) | 619(7) | 1167(16) | 49(29) |
| H(10) | 260(6) | 641(8) | 887(18) | 66(34) | H(20) | 197(7) | 581(8) | 1377(19) | 80(39) |

range of 323—363 K (Fig. 1b) and the resistivity of the room temperature is $R=(4.9\pm1.5)\times10^7\ \Omega$ cm. From the X-ray check both crystals are crystallographically identical but the latter data shows that the crystallization is bad. The accuracy of the absolute value of the conductivity is evidently limited by the crystalline imperfection.[7] It seems likely that the imperfections involved are microcracks or other large scale defects which limit the effective cross-sectional area of the samples.

## Description of the Structure and Discussion

*[(n-Bu)$_4$N]$_2$[Ni(mnt)$_2$]*. Molecular geometry of the $Ni(mnt)_2^{2-}$ anion is shown in Fig. 2a. A projection of the structure as viewed along the c axis are presented in Fig. 3. This $Ni^{2+}$ complex is isomorphous with $Co^{2+}$ [8] and $Cu^{2+}$ [9] complexes. The planar diamagnetic $Ni(mnt)_2^{2-}$ ion has a center of symmetry at the nickel atom and the two tetra-*n*-butylammonium ions are related to each other by a center of symmetry. The bond lengths and angles of the anion are listed in Table 3a. The nickel atoms are very well separated with the closest distance of approach in the shortest axial length of 9.84 Å. The anion is closely planar with the sulfur atoms in a square arrangement around the nickel atom and Ni, S(1), S(2), C(1), and C(2) make the five-membered ring. The distance of the various atoms from the least-squares plane are listed in Table 4a. The average Ni–S bond length is 2.175(1) Å, S–C 1.730(5), and C–C 1.410(7), respectively. The bond distance of



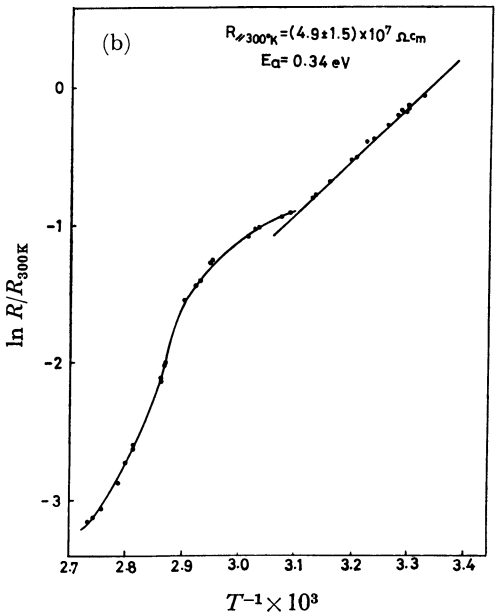




Fig. 1. Temperature dependence of electrical resistivity of $[(Et)_4N][Ni(mnt)_2]$, showing resistivity parallel to the anion stacks (crystallographic c axis).

C–C agrees well with those found in the conjugated C–C system like the benzene molecule. The S–Ni–S bond angle within the five-membered ring is found to be 92°. The bond lengths and angles of the cation is listed in Table 5a. Three of the butyl chains adopt the *trans* conformation, but one (C(9)—C(12)) adopts a *gauche* conformation. The dihedral angles for all the chains are listed in Table 6. The dihedral angle for the *gauche* chain is 72.4°.

*$[(Et)_4N][Ni(mnt)_2]$.* Molecular geometry of the anion is shown in Fig. 2b. A projection of the structure along the c axis is shown in Fig. 4. The anions are stacked in columns whose axes are parallel to c and

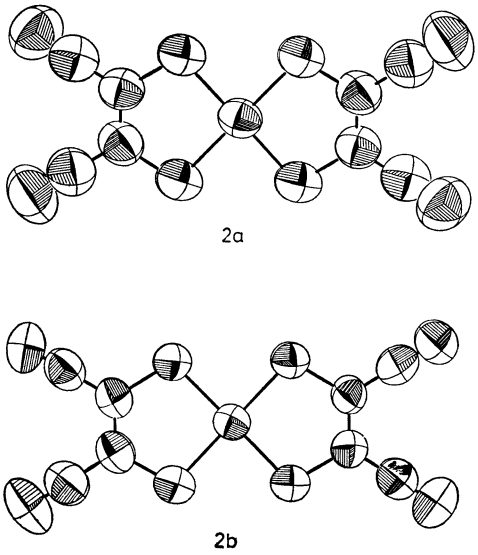



Fig. 2. Molecular geometry of the $Ni(mnt)_2^{2-}$ (2a) and $Ni(mnt)_2^{-1}$ (2b) anions. The 50% probability ellipsoids are shown.

Table 3. Bond lengths and angles of the anions

| | | | |
|---|---|---|---|
| a) $Ni(mnt)_2^{2-}$ | | | |
| Ni–S(1) | 2.176(1)Å | C(1)–C(3) | 1.428(6)Å |
| Ni–S(2) | 2.173(1) | C(2)–C(4) | 1.435(6) |
| S(1)–C(1) | 1.732(4) | C(3)–N(1) | 1.147(7) |
| S(2)–C(2) | 1.725(5) | C(4)–N(2) | 1.130(7) |
| C(1)–C(2) | 1.360(7) | | |
| S(1)–Ni–S(2) | 92.2(1)° | C(2)–C(1)–C(3) | 121.9(4)° |
| Ni–S(1)–C(1) | 103.1(1) | C(1)–C(2)–C(4) | 120.4(4) |
| Ni–S(2)–C(2) | 103.0(2) | C(1)–C(3)–N(1) | 178.4(5) |
| S(1)–C(1)–C(2) | 120.3(3) | C(2)–C(4)–N(2) | 179.2(5) |
| S(2)–C(2)–C(1) | 121.4(3) | | |
| b) $Ni(mnt)_2^{1-}$ | | | |
| Ni–S(1) | 2.147(3)Å | C(5)–C(6) | 1.370(12)Å |
| Ni–S(2) | 2.151(3) | C(1)–C(3) | 1.420(14) |
| Ni–S(3) | 2.148(3) | C(2)–C(4) | 1.437(14) |
| Ni–S(4) | 2.149(3) | C(5)–C(7) | 1.462(14) |
| S(1)–C(1) | 1.727(10) | C(6)–C(8) | 1.439(13) |
| S(2)–C(2) | 1.722(9) | C(3)–N(1) | 1.133(14) |
| S(3)–C(5) | 1.705(10) | C(4)–N(2) | 1.135(14) |
| S(4)–C(6) | 1.724(9) | C(7)–N(3) | 1.124(14) |
| C(1)–C(2) | 1.367(12) | C(8)–N(4) | 1.131(14) |
| S(1)–Ni–S(2) | 92.5(1)° | S(4)–C(6)–C(5) | 119.9(7)° |
| S(3)–Ni–S(4) | 92.5(1) | C(3)–C(1)–C(2) | 122.1(9) |
| Ni–S(1)–C(1) | 103.6(3) | C(1)–C(2)–C(4) | 120.7(8) |
| Ni–S(2)–C(2) | 103.3(3) | C(6)–C(5)–C(7) | 120.6(9) |
| Ni–S(3)–C(5) | 103.5(3) | C(5)–C(6)–C(8) | 121.8(8) |
| Ni–S(4)–C(6) | 103.3(3) | C(1)–C(3)–N(1) | 179.5(11) |
| S(1)–C(1)–C(2) | 119.8(7) | C(2)–C(4)–N(2) | 179.5(11) |
| S(2)–C(2)–C(1) | 120.7(7) | C(5)–C(7)–N(3) | 177.9(11) |
| S(3)–C(5)–C(6) | 120.9(7) | C(6)–C(8)–N(4) | 179.5(11) |

those columns are surrounded by cations. This arrangement is very different from that found in $[R_4N]_2[M(mnt)_2]$, where the metal atoms are separated by about 10 Å. The dimensions of the anion are listed in

Table 4. Least-squares plane for $Ni(mnt)_2^{n-}$ anions and deviations from the planes

a) $Ni(mnt)_2^{2-}$

Plane equation:

$0.56445X+(-0.24625)Y+(0.78788)Z=0$

| Atom | Deviation (Å) | Atom | Deviation (Å) |
|---|---|---|---|
| Ni | 0.0 | C(3) | −0.0882 |
| S(1) | 0.0306 | C(4) | −0.0456 |
| S(2) | 0.0284 | N(1) | −0.1431 |
| C(1) | −0.0172 | N(2) | −0.0882 |
| C(2) | −0.0121 | | |

b) $Ni(mnt)_2^{1-}$

Plane equation:

$0.41049X+(-0.13374)Y+(-0.90201)Z+1.76906=0$

| Atom | Deviation (Å) | Atom | Deviation (Å) |
|---|---|---|---|
| Ni | 0.0107 | N(1) | 0.0020 |
| S(1) | 0.0093 | N(2) | 0.0506 |
| S(2) | −0.0387 | C(7) | 0.0124 |
| S(3) | −0.0067 | C(8) | 0.0403 |
| S(4) | 0.0122 | N(3) | 0.0147 |
| C(3) | −0.0044 | N(4) | 0.0678 |
| C(4) | 0.0176 | C(1) | −0.0014 |
| C(5) | −0.0102 | C(2) | −0.0244 |
| C(6) | 0.0115 | | |

Table 6. Dihedral angles for the four butyl chains in $(C_4H_9)_4N^+$ cation

| Plane (1) | Plane (2) | Dihedral angles |
|---|---|---|
| C(5)–C(6)–C(7) | C(6)–C(7)–C(8) | 9.45° |
| C(9)–C(10)–C(11) | C(10)–C(11)–C(12) | 72.41 |
| C(13)–C(14)–C(15) | C(14)–C(15)–C(16) | 0.41 |
| C(17)–C(18)–C(19) | C(18)–C(19)–C(20) | 0.38 |

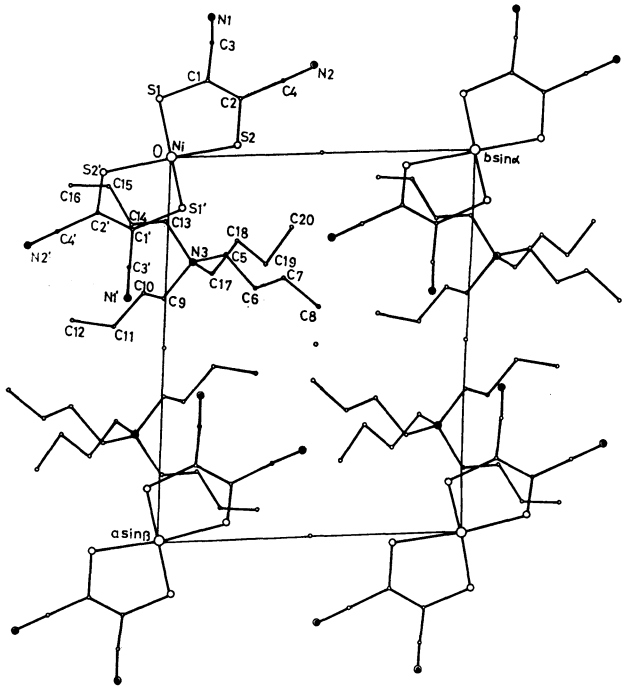



Fig. 3. A projection of the structure of $[(n\text{-}Bu)_4N]_2[Ni(mnt)_2]$ as viewed along the c axis.

Table 3b, and compared with those found for the $Ni(mnt)_2^{2-}$ anion in the $[(n\text{-}Bu)_4N]_2[Ni(mnt)_2]$. The paramagnetic anion is approximately planar, but deviations from planarity are considerably smaller than those in the $Ni(mnt)_2^{2-}$ ion. One of the cyanide group is bent a little out of the plane. The deviations of the atoms from the least-squares plane are listed in Table 4b. The average Ni–S bond length is 2.149 Å, S–C 1.725 Å, and C–C (in the five-membered ring) 1.369 Å. The S–Ni–S bond angle is 92.5°. Table 7 shows comparison of the bond lengths of $Ni(mnt)_2^{n-}$ ($n=1$, 2) in our structure analyses and those found in other $M(mnt)_2^{n-}$ structures. In $[(Et)_4N][Ni(mnt)_2]$ bond distances of the ligand agree well with our result of $[(n\text{-}Bu)_4N]_2[Ni(mnt)_2]$ and $[TMPD]_2[Ni(mnt)_2]$[11] by less than two standard deviations except Ni–S. Namely, Ni–S in (I)

Table 5. Bond lengths and angles of the cations

a) $(C_4H_9)_4N^+$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(3)–C(5) | 1.533( 7)Å | N(3)–C(9) | 1.525( 5)Å | N(3)–C(5)–C(6) | 115.4(4)° | C(5)–C(6)–C(7) | 108.7(4)° |
| C(5)–C(6) | 1.516( 6) | C(9)–C(10) | 1.531( 6) | N(3)–C(9)–C(10) | 114.8(4) | C(6)–C(7)–C(8) | 112.7(5) |
| C(6)–C(7) | 1.526( 9) | C(10)–C(11) | 1.542( 7) | N(3)–C(13)–C(14) | 114.8(4) | C(9)–C(10)–C(11) | 110.2(4) |
| C(7)–C(8) | 1.519( 8) | C(11)–C(12) | 1.491(10) | N(3)–C(17)–C(18) | 115.3(4) | C(10)–C(11)–C(12) | 113.3(5) |
| N(3)–C(13) | 1.532( 5) | N(3)–C(17) | 1.530( 5) | C(5)–N(3)–C(9) | 111.0(4) | C(13)–C(14)–C(15) | 112.9(5) |
| C(13)–C(14) | 1.515( 9) | C(17)–C(18) | 1.506( 6) | C(9)–N(3)–C(13) | 111.2(3) | C(14)–C(15)–C(16) | 116.0(6) |
| C(14)–C(15) | 1.464( 7) | C(18)–C(19) | 1.533( 6) | C(13)–N(3)–C(17) | 111.7(3) | C(17)–C(18)–C(19) | 109.9(4) |
| C(15)–C(16) | 1.509(11) | C(19)–C(20) | 1.516( 7) | C(17)–N(3)–C(5) | 110.9(3) | C(18)–C(19)–C(20) | 111.7(4) |
| | | | | C(5)–N(3)–C(13) | 105.8(3) | | |
| | | | | C(9)–N(3)–C(17) | 106.4(3) | | |

b) $(C_2H_5)_4N^+$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(5)–C(9) | 1.543(12)Å | C(9)–C(10) | 1.522(15)Å | N(5)–C(9)–C(10) | 115.1(8)° | C(9)–N(5)–C(11) | 108.0(6)° |
| N(5)–C(11) | 1.514(12) | C(11)–C(12) | 1.561(15) | N(5)–C(11)–C(12) | 114.5(9) | C(9)–N(5)–C(13) | 106.1(8) |
| N(5)–C(13) | 1.553(14) | C(13)–C(14) | 1.510(15) | N(5)–C(13)–C(14) | 114.9(9) | C(9)–N(5)–C(15) | 113.2(7) |
| N(5)–C(15) | 1.510(11) | C(15)–C(16) | 1.485(19) | N(5)–C(15)–C(16) | 112.8(9) | C(11)–N(5)–C(13) | 110.7(7) |
| | | | | | | C(11)–N(5)–C(15) | 109.1(7) |
| | | | | | | C(13)–N(5)–C(15) | 109.7(7) |

TABLE 7. COMPARISON OF BOND DISTANCES FOUND FOR $M(mnt)_2^{n-}$ ANIONS

| Bond | $[(n\text{-}Bu)_4N]_2$ $[Ni(mnt)_2]$ | $[(Et)_4N]$*[g] $[Ni(mnt)_2]$ | $[TMPD]_2$ $[Ni(mnt)_2]$[a] | $[(Me)_4N]_2$ $[Ni(mnt)_2]$[b] | $[(n\text{-}Bu)_4N]_2$ $[Cu(mnt)_2]$[c] | $[(Et)_4N]_2$ $[Cu(mnt)_2]$[d] | $[(n\text{-}Bu)_4N]$* $[Cu(mnt)_2]$[e] | $[(n\text{-}Bu)_4N]_2$ $[Co(mnt)_2]$[f] |
|---|---|---|---|---|---|---|---|---|
| M–S(1) | 2.176(1) Å | 2.148(2) | 2.173(2) | 2.16(1) | 2.286(1) | 2.264(1) | 2.174(4) | 2.163(3) |
| M–S(2) | 2.173(1) | 2.150(2) | 2.179(2) | 2.16(1) | 2.265(1) | 2.271(1) | 2.158(5) | 2.159(3) |
| S(1)–C(1) | 1.732(4) | 1.716(7) | 1.731(5) | 1.75(1) | 1.727(3) | 1.725(2) | 1.73(1) | 1.731(7) |
| S(2)–C(2) | 1.725(5) | 1.723(6) | 1.727(5) | 1.75(1) | 1.729(3) | 1.729(2) | 1.70(1) | 1.715(7) |
| C(1)–C(2) | 1.360(7) | 1.369(9) | 1.378(6) | 1.30(2) | 1.359(4) | 1.365(3) | 1.32(2) | 1.34(1) |
| C(1)–C(3) | 1.428(6) | 1.441(10) | 1.413(7) | 1.44(1) | 1.434(4) | 1.432(3) | 1.42(2) | 1.40(1) |
| C(2)–C(4) | 1.435(6) | 1.438(10) | 1.427(6) | 1.42(1) | 1.430(4) | 1.433(3) | 1.43(2) | 1.40(1) |
| C(3)–N(1) | 1.147(7) | 1.129(10) | 1.148(6) | 1.13(2) | 1.143(4) | 1.140(3) | 1.17(2) | 1.15(1) |
| C(4)–N(2) | 1.130(7) | 1.133(10) | 1.137(6) | 1.13(2) | 1.147(4) | 1.146(3) | 1.12(2) | 1.16(1) |

a) Reference 11. b) Reference 10. c) Reference 9b. d) Reference 12. e) Reference 8. f) Reference 9a.
g) The asterisk indicates the existence of the columnar structure of $M(mnt)_2^{n-}$ anions.

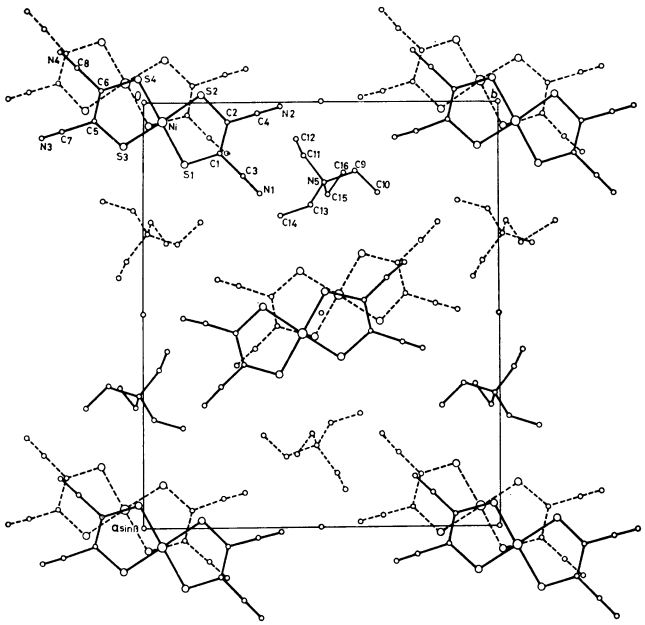



Fig. 4. A projection of the structure of $[(Et)_4N][Ni(mnt)_2]$ as viewed along the c axis.

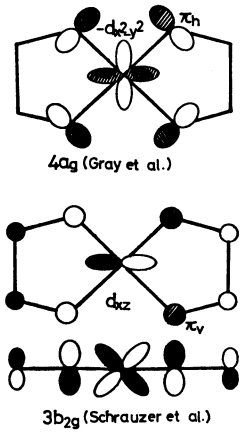



Fig. 5. Schematic drawing of highest occupied orbitals of $Ni(mnt)_2^{n-}$ ($n=1, 2$). The $\pi_v$ is the ligand $\pi$-MO vertical to the plane of the molecule and $\pi_h$ is in the plane of the molecule.

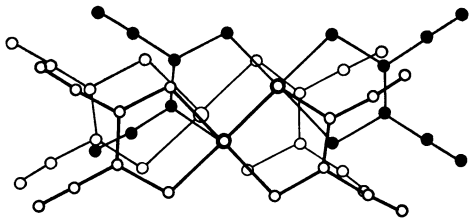


Fig. 6. Nearest neighbor overlapping within a $Ni(mnt)_2^{1-}$ column in $[(Et)_4N][Ni(mnt)_2]$.

is 2.175(1) Å and 2.149(2) Å in (II).

It is well known in organic compounds that bond lengths of molecules become longer or shorter in accordance with the change of the bond order or electronic state of molecules. When a molecular orbital which has the same sign on the neighboring two atoms is occupied with electrons, the bonding is strengthend and the bond length becomes shorter. If the sign is the reverse, the bonding is weakened. Similarly this discussion can be applied to complexes such as $Ni(mnt)_2^{n-}$ whose oxidation state could change with the molecular structure almost remaining unchanged.

The paramagnetic $Ni(mnt)_2^{1-}$ anion is thought to have the same electronic structure as that of the $Ni(mnt)_2^{2-}$ whose one electron is removed from the highest occupied level. The electronic structures of $Ni(mnt)_2^{n-}$ were studied by Gray and Schrauzer *et al.*[13,14] Gray's highest occupied orbital is $4a_g$ and Schrauzer's is $3b_{2g}$ (Fig. 5). These wave functions have the reverse sign on the Ni and S atoms, and the Ni–S bond length will be longer according to changing from $Ni(mnt)_2^{2-}$ to $Ni(mnt)_2^{1-}$. This agrees with the result of our crystal structure analyses. Similar relationship will be hold between $[(n\text{-}Bu)_4N]_2[Cu(mnt)_2]$ and $[(n\text{-}Bu)_4][Cu(mnt)_2]$ as to Cu–S bond distances (Table 7).

A characteristic feature of the crystal structure of $Ni(mnt)_2^{1-}$ complexes is the presence of columns of the $Ni(mnt)_2^{1-}$ anions weakly connected with each other. The mode of nearest neighbor overlapping within a $Ni(mnt)_2^{1-}$ column is shown in Fig. 6. The $Ni(mnt)_2^{1-}$ ions form a diadic unit within the columns. Similar columnar structure has been found in $[(n\text{-}Bu)_4N][Cu(mnt)_2]$, where columns are composed with tetradic units of $Cu(mnt)_2^{1-}$. The average interplanar

spacing of $Ni(mnt)_2^{1-}$ anion pairs in Fig. 6 is 3.5 Å and that of $Cu(mnt)_2^{1-}$ is 3.6 Å. In $Ni(mnt)_2^{1-}$ anion columns, overlapping of the Ni and S atoms is especially large, a similar columnar structure is also found in $[(n\text{-}Bu)_4N][Cu(mnt)_2]$.

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