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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF 2-[*p*-DIMETHYLAMINOSTYRYL]PYRIDYLMETHYL BIS[6,7-DIHYDRO-5H-1,4-DITHIEPIN-DITHIOLATO]NICKELATE(III)

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Abstract—The complex 2-(*p*-dimethylaminostyryl)pyridylmethyl bis[6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolato]nickelate(III) ([DASPM][Ni(PDDT)$_2$]) has been prepared and characterized by IR, UV–NIR and ESR. X-ray structure analysis reveals that the anions of the complex are packed in pairs and arranged as stacks along the *a*-axis. The shortest intermolecular S—S contact is 3.86 Å within a pair, and 4.00 Å between the pairs. The electrical conductivity measured for a compacted pellet at room temperature is 1.3×10^{-9} S cm^{-1}.

Over the past two decades, a massive research effort has centred on the design and synthesis of organic conductors,[1] some of which exhibit superconductivity.[2] The tetrathio-ethylene subunit is believed to be one of the key structural features that allows for the conduction of electrons.[3] At the same time, there has been a great deal of interest in conducting species of metallic complexes.[4] To combine the properties of the 'TTF type' organosulphur molecules and the inorganic systems, detailed studies on the coordination compounds of $[M(DDDT)_2]^{n-}$ (DDDT = 5,6-dihydro-1,3-dithiin-2,3-dithiolate, M = Ni, Pd, Pt, Cu, Au, Co, V)[3,5–7] and $[M(PDDT)_2]^-$ (PDDT = 6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolato, M = Ni, Cu, Pt)[8–11] have been reported. On the other hand, extensive work has been carried out on the salts of planar dithiolates with planar organic cations, such as Methylene Blue.[12]

It is well known that the planar cation [DASPM]$^+$ [DASPM = 2-(*p*-dimethylaminostyryl) pyridylmethyl] shows the largest figure of merit of electro-optic phase retardation in organic solids.[13] We synthesized the title compound (see Scheme 1) to investigate the effect of the cation on the crystal structure and physical properties.

EXPERIMENTAL

All the reagents and solvents used were analytically pure. $[Bu_4N][Ni(PDDT)_2]$ was prepared by a literature method,[9] and characterized by IR, NIR and element analysis. The solvent CH_3CN was

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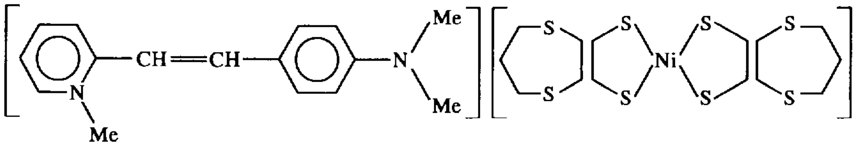


Scheme 1. Formula diagram of [DASPM][Ni(Pddt)$_2$].

dried over magnesium sulphate and freshly distilled prior to use.

Preparation

An acetonitrile solution (40 cm^3) of [Bu$_4$N][Ni(PDDT)$_2$] (29.8 mg, 0.043 mmol) was mixed with an acetonitrile solution (20 cm^3) of [DASPM]I (15.8 mg, 0.043 mmol). Dark brown crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature over 2 weeks. Found: C, 45.7; H, 4.4; N, 3.9. Calc. for $C_{26}H_{31}S_8N_2Ni$: C, 45.5; H, 4.6; N, 4.1%. IR (KBr pellet): 1587 (s), 1529 (s), 1498 (m), 1452 (m), 1411 (m), 1375 (s), 1282 (m), 1268 (m), 1165 (s), 1064 (m), 994 (m), 898 (m), 858 (m), 804 (m), 751 (m), 535 (m), 458 (w).

Physical measurements

IR spectra were recorded with KBr pellets in the 4000–400 cm^{-1} region using a Nicolet 170SX FTIR spectrophotometer. Powder electronic absorption spectra were recorded on a Hitachi U-3400 spectrophotometer. Elemental analyses were performed on a Perkin–Elmer 240C analytical instrument. ESR spectra were obtained on an FE1 XG spectrometer at 100 K. Electrical conductivity was measured for a compacted pellet by the two-probe technique at room temperature.

Crystallographic structure determination

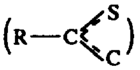
A selected single crystal with the dimensions $0.65 \times 0.15 \times 0.12$ mm was mounted on a glass fibre and the cell dimensions were obtained by a least-squares fit of 25 reflections (θ range 9.38–12.80°). Diffraction data were collected on an Enraf–Nonius CAD4 diffracometer using graphite-monochromated Mo-$K\alpha$ ($\lambda = 0.71069$ Å) radiation. The scan mode was ω–2θ. 5426 independent reflections were collected in the range $2° \leq 2\theta \leq 50°$ and 3550 observed reflections with $I > 3\sigma(I)$ were used for further computation.

The crystal of the title complex is monoclinic with space group $P2_1/n$. Formula wt 686.72, cell dimensions $a = 8.732(8)$, $b = 29.598(6)$, $c = 11.709(2)$ Å, $\beta = 95.24(6)°$, $V = 3013(3)$ Å^3, $Z = 4$, $D_{calc} = 1.51$ g cm^{-3}, $F(000) = 1428$, $\mu = 11.99$ cm^{-1}.

All calculations were performed on a MICROVAX 3100 computer using the MSC/Rigaku TEXSAN 3.1 program package. Intensity data were corrected for Lorentz-polarization effects and empirical absorption. The structure was solved by direct methods. All the remaining non-hydrogen atoms were located by successive difference Fourier syntheses. The structure was refined by a full-matrix least-squares method with anisotropic temperature factors for the non-hydrogen atoms. The final R and R_w [$w = 1/\sigma^2(F)$] were 0.047 and 0.056, respectively. Maximum shift error = 0.01, electron density in final difference map 0.32 e Å^{-3}.

Complete tables of atomic coordinates and thermal parameters, together with observed and calculated structure factors, have been deposited with the Cambridge Crystallographic Data Centre, copies are available on request.

RESULTS AND DISCUSSION

The title compound displays a very rich IR spectrum with the characteristic absorptions of monoanionic nickel dithiolenes present.[14] ν_1(C=C) at 1410 cm^{-1}, ν_2(C—S) at 1268 cm^{-1}, ν_3  at 858 cm^{-1} and ν_4(Ni—S) at 458 cm^{-1}, respectively. The IR absorptions at 1587, 1529, 1375, 1165, 994 and 804 cm^{-1} confirm the presence of [DASPM]$^+$.

Electronic and ESR spectra of [DASPM][Ni(PDDT)$_2$]

The electronic absorption spectrum of [DASPM][Ni(PDDT)$_2$] in acetonitrile shows intensive absorption at 930 nm. It may be ascribed to the electronic $\pi \rightarrow \pi$ transition of the anion.[15] The band is shifted to 976 nm in the powder absorption spectrum, indicating a significant electronic interaction in the solid state.

Figure 1 illustrates the ESR spectrum of the solid powder of the complex at 100 K. The broadening of the two ESR signals ($g = 2.131$, $g = 2.022$) is due to intermolecular interaction in the solid state.[16]

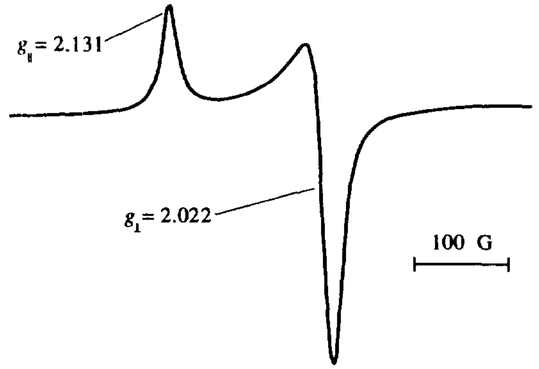


Fig. 1. Solid powder ESR spectrum of [DASPM] [Ni(PDDT)$_2$] at 100 K.

The crystal structure of [DASPM][Ni(PDDT)$_2$]

Figure 2 shows the structure and labelling scheme of [DASPM][Ni(PDDT)$_2$]. Selected bond lengths and angles for the complex are listed in Table 1.

The four sulphurs surrounding the nickel atom yield a square planar coordination with an average S—Ni—S angle of 90.0°. In the five-membered ring containing the nickel atom, the average S—Ni, S—C and C=C bond lengths are 2.148, 1.726 and 1.357 Å respectively. The corresponding values in [Et$_4$N][Ni(PDDT)$_2$] are 2.148(1), 1.726 and 1.337 Å.[8] Similar structure parameters show that the structure of [Ni(PDDT)$_2$]$^-$ anions in [DASPM] [Ni(PDDT)$_2$] is essentially the same as that in [Et$_4$N][Ni(PDDT)$_2$]. The outer seven-membered rings exist in the chair configuration. The dihedral angle between the least-square plane and the plane of the 1,3-propanediyl groups is 124.30°. The two 1,3-propanediyl groups existing in *trans* configuration with a dihedral angle of 4.70°.

Figure 3 shows how the anions and cations are packed in the unit cell. There are four molecules in each unit cell. The gross geometry of the [DASPM]$^+$ cation is also planar. The cations are almost perpendicular to the anions, with a dihedral angle of 85.30°.

The stereoview of the anion packing is shown in Fig. 4. The anions are packed in pairs and arranged as two different oriented stacks approximately along the *a*-axis. This is different from [Et$_4$N][Ni(PDDT)$_2$], where the anions form an unusual double layer array. The nearest Ni—Ni distance is 8.732 Å, which is the length of the *a*-axis. In the same stack, the shortest intermolecular S—C contact is 3.86 Å [S(2)—S(3′)] within a pair, and 4.00 Å [S(1)—S(4′)] between pairs. The contact within a pair is shorter than the corresponding values of [Et$_4$N][Ni(PDDT)$_2$] (4.13 Å) and [Et$_4$N][Ni(DDDT)$_2$] (3.98 Å). There is no close S—S contact less than 3.70 Å. This is consistent with the semi-conductive property of this complex,[17] as described later.

Electrical conductivity of [DASPM][Ni(PDDT)$_2$]

The electrical conductivity of the complex, measured using a compacted pellet at room tempera-

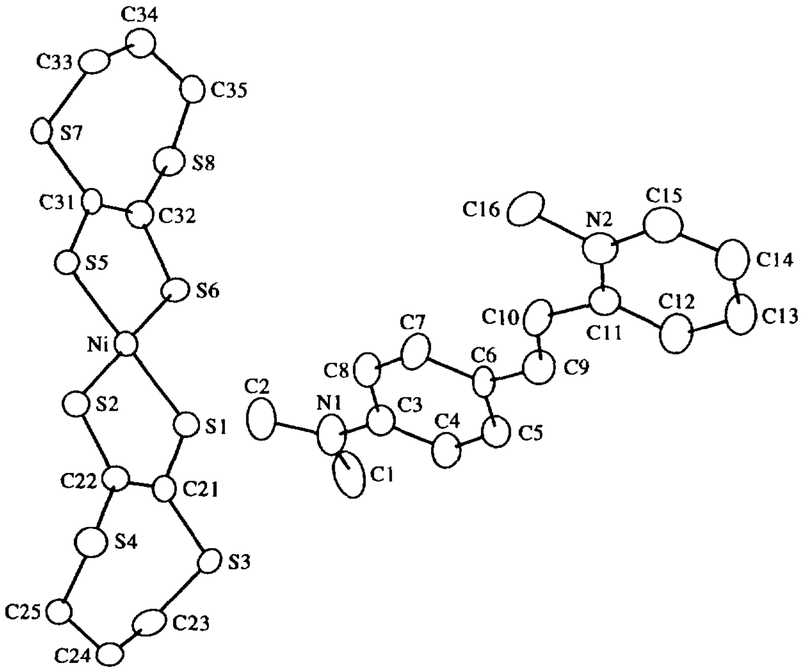


Fig. 2. Structure of [DASPM][Ni(PDDT)$_2$] with the atom labelling scheme. Hydrogen atoms are not shown.

Table 1. Selected bond lengths (Å) and angles (°) for [DASPM][Ni (PDDT)$_2$][a]

Ni—S(1)	2.143(2)	Ni—S(5)	2.149(2)	Ni—S(6)	2.149(2)
Ni—S(2)	2.152(2)	S(1)—C(21)	1.726(6)	S(2)—C(22)	1.728(6)
S(3)—C(21)	1.765(6)	S(3)—C(23)	1.812(7)	S(4)—C(22)	1.769(6)
S(4)—C(25)	1.812(7)	S(5)—C(31)	1.721(6)	S(6)—C(32)	1.730(6)
S(7)—C(31)	1.771(6)	S(7)—C(33)	1.808(7)	S(8)—C(32)	1.766(6)
S(8)—C(35)	1.809(7)	N(1)—C(3)	1.367(7)	N(1)—C(2)	1.444(9)
N(1)—C(1)	1.453(1)	N(2)—C(16)	1.483(8)	N(2)—C(15)	1.346(8)
N(2)—C(11)	1.377(7)	C(9)—C(10)	1.319(8)	C(21)—C(22)	1.358(7)
C(23)—C(24)	1.52(1)	C(24)—C(25)	1.510(9)	C(31)—C(32)	1.356(7)
C(33)—C(34)	1.514(8)	C(34)—C(35)	1.496(8)		

S(1)—Ni—S(6)	88.25(8)	S(1)—Ni—S(2)	90.99(8)
S(5)—Ni—S(6)	91.27(8)	S(5)—Ni—S(2)	89.49(8)
C(21)—S(1)—Ni	104.9(2)	C(22)—S(2)—Ni	104.9(2)
C(21)—S(3)—C(23)	103.6(3)	C(22)—S(4)—C(25)	104.3(3)
C(31)—S(5)—Ni	104.7(2)	C(32)—S(6)—Ni	104.3(2)
C(31)—S(7)—C(33)	106.2(3)	C(32)—S(8)—C(35)	104.8(3)
N(1)—C(3)—C(4)	121.6(6)	N(1)—C(3)—C(8)	120.8(6)
C(31)—C(32)—S(8)	125.0(4)	S(6)—C(32)—S(8)	115.0(3)
C(34)—C(33)—S(7)	117.2(5)	C(35)—C(34)—C(33)	114.5(5)
C(34)—C(35)—S(8)	116.5(4)	C(10)—C(9)—C(6)	127.8(6)
C(9)—C(10)—C(11)	124.0(6)	N(2)—C(11)—C(12)	116.1(6)
N(2)—C(11)—C(10)	120.2(6)	C(22)—C(21)—S(1)	120.0(4)
C(22)—C(21)—S(3)	124.9(4)	S(1)—C(21)—S(3)	115.1(3)
C(21)—C(22)—S(2)	119.2(4)	C(21)—C(22)—S(4)	124.7(4)
S(2)—C(22)—S(4)	115.8(3)	C(24)—C(33)—S(3)	117.3(5)
C(25)—C(24)—C(23)	115.7(5)	C(24)—C(25)—S(4)	116.8(4)
C(32)—C(31)—S(5)	119.6(4)	C(32)—C(31)—S(7)	124.5(4)
S(5)—C(31)—S(7)	115.7(3)	C(31)—C(32)—S(6)	120.4(4)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

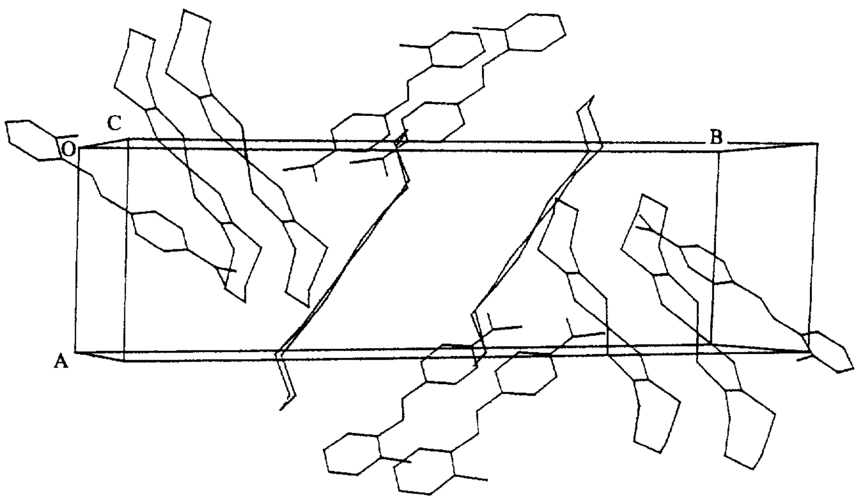


Fig. 3. Stereoview of the unit cell. The view is looking down the *c*-axis.

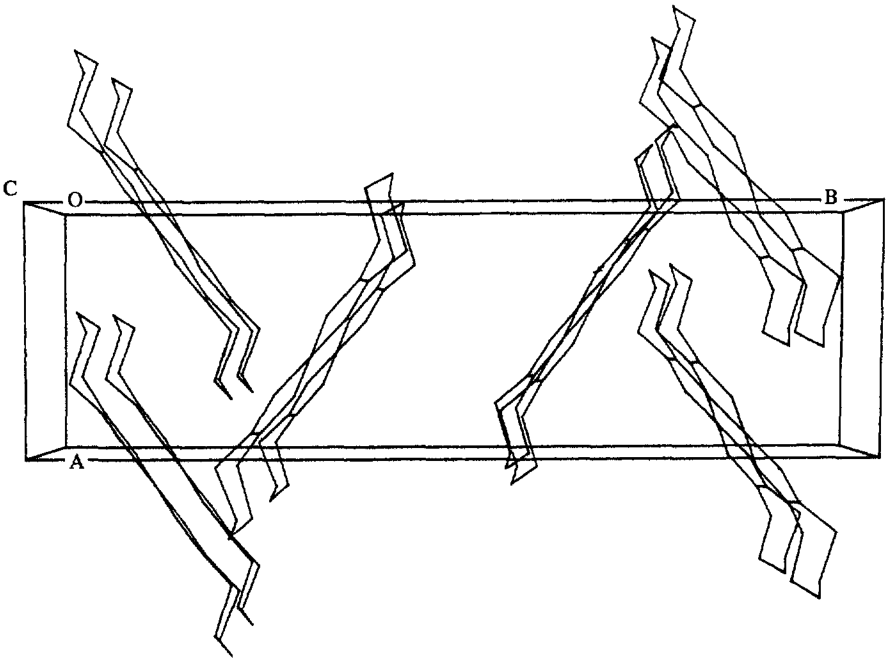


Fig. 4. Stereoview of the packing of the anions. The view is looking down the *c*-axis.

ture, is 1.3×10^{-9} S cm^{-1}. The conductivity value is smaller than that of $[Bu_4N][Ni(DMIT)_2]$ (DMIT = 4, 5 - dimercapto - 1, 3 - dithiole - 2 - thionate)[18] ($\sigma = 10^{-8}$ S cm^{-1}). It may be due to weak interactions between the $[Ni(PDDT)_2]^-$ anions as revealed in the crystal structure.

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REFERENCES

1. S. J. Lippard, J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn and A. J. Schultz, *Prog. Inorg. Chem.* 1987, **35**, 51.
2. J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkin, J. M. Kommers, S. J. Boryschuk, A. V. Strieby, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung and M. H. Whangbo, *Inorg. Chem.* 1990, **29**, 3272.
3. J. H. Welch, R. D. Bereman and P. Singh, *Inorg. Chim. Acta* 1989, **162**, 89.
4. P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.* 1991, **110**, 115.
5. J. H. Welch, R. D. Bereman, P. Singh and C. Moreland, *Inorg. Chim. Acta* 1989, **158**, 17.
6. J. H. Welch, R. D. Bereman, P. Singh and C. Moreland, *Inorg. Chem.* 1988, **27**, 2862.
7. C. T. Vance, R. D. Bereman, J. Bordner, W. E. Hafield and J. H. Helms, *Inorg. Chem.* 1985, **24**, 2905.
8. R. D. Rereman and H. Y. Lu, *Inorg. Chim. Acta* 1993, **204**, 53.
9. R. Kato, H. Kobayashi, A. Kobayashi and Y. Sasaka, *Bull. Chem. Soc. Japan* 1986, **56**, 627.
10. T. M. Yao, X. Z. You and Q. C. Yan, *Chin. J. Chem.* 1994, **12**, 248.
11. T. M. Yao, X. Z. You, C. Li, L. F. Li and Q. C. Yan, *Acta Cryst.* 1994, **C50**, 67.
12. J. S. Tonge and A. E. Underhill, *J. Chem. Soc., Dalton Trans.* 1984, 2333.
13. T. Yoshimura, *J. Appl. Phys.* 1987, **62**, 2028.
14. J. A. McLeverty, *Prog. Inorg. Chem.* 1968, **10**, 49 and references therein.
15. G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.* 1965, **87**, 3585.
16. X. Z. You, *Structure and Properties of Coordination Compounds*. Science Press, Beijing (1992).
17. G. E. Matsubayashi, K. Takahashi and T. Tanaka, *J. Chem. Soc., Dalton Trans.* 1988, 967.
18. F. Nüßlein, R. Peter and H. Kisch, *Chem. Ber.* 1989, **122**, 1023.