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Synthesis and characterisation of some $[M(C_3S_5)_2]^{n-}$ complexes (M = Ni, Pd, Pt). Single crystal structure of $[PPN][Ni(C_3S_5)_2] \cdot MeOH$

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Abstract—The synthesis and characterisation of some anionic Ni, Pd and Pt complexes of the ligand, $Na_2C_3S_5$, ($C_3S_5^{2-}$ = 1,3-dithiole-2-thione-4,5-dimercapto = dmit) are reported. The complexes were isolated as PPN$^+$ [PPN$^+$ = bis(triphenylphosphine)iminium] salts. The monoanionic complexes [PPN] $[Ni(C_3S_5)_2]$ and [PPN] $[Pd(C_3S_5)_2]$ were further oxidised with iodine in acetonitrile to afford $[PPN]_{0.25}[Ni(C_3S_5)_2]$ and $[PPN]_{0.25}[Pd(C_3S_5)_2]$. The partially oxidised complexes have electrical conductivities of 1.2×10^{-2} and 0.64 S cm^{-1} at room temperature for compacted pellets. Cyclic voltammetry, electronic, IR and ESR spectra of the complexes are discussed. A single crystal X-ray determination of [PPN] $[Ni(C_3S_5)_2] \cdot MeOH$ was carried out. The average value of Ni—S bond length is one of the highest observed for a $[Ni(dmit)_2]$ complex. © 1997 Elsevier Science Ltd

Keywords: d^8 metals; square planar; dmit; PPN; molecular conductor.

Anionic square planar complexes derived from the sulfur rich ligand $C_3S_5^{2-}$ ($C_3S_5^{2-}$ = 1,3-dithiole-2-thione-4,5-ditholate-dmit) have been investigated extensively in recent years [1–4]. This system has yielded several low temperature molecular metals and superconductors. At present seven superconductors, $TTF[Ni(dmit)_2]_2$ [5], α-$TTF[Pd(dmit)_2]_2$ [6], α'-$TTF[Pd(dmit)_2]_2$ [6], $[NMe_4][Ni(dmit)_2]_2$ [7], β-$[NMe_4][Pd(dmit)_2]_2$ [8], $[NMe_2Et_2]$ $[Pd(dmit)_2]_2$ [9] and α-[EDT-TTF]$[Ni(dmit)_2]$ [10] (EDT-TTF = ethylenedithiotetrathiafulvalene) are known among the $M(dmit)_2$ (M = d^8 metal ion) salts. Intramolecular S···S contacts form an effective electronic conduction band in the crystal. The cation plays a crucial role in determining the packing of the planar $[M(dmit)_2]$ units and hence the physical properties of the non-stoichiometric salts. The cations of large size prevent the establishment of close S···S contacts in simple complexes. However, non-stoichiometric complexes in which cation:anion ratio is low (*ca* < 1), exhibit relatively high conductivity. For example, $[n\text{-}Bu_4N]_{0.29}[Ni(dmit)_2]$ shows a very good conductivity of 10 S cm^{-1} at room temperature [11]. $[Ph_4As]$ $[Ni(dmit)_2]_4$ is another fractional oxidation state salt with a bulky cation which has high conductivity of 10–15 S cm^{-1} [12]. More recently $[Co(\eta\text{-}C_5H_5)_n][M(C_3H_5)_2]$ salts (M = Ni or Pd, n = 2 or 1) containing another bulky cobalticenium ion have been reported [13]. This paper reports the preparation and spectroscopic properties of $[M(dmit)_2]$ complexes (M = Ni, Pd, Pt) with the bulky cation, PPN$^+$. The conductivities of oxidized complexes and the crystal structure of $[PPN][Ni(dmit)_2] \cdot MeOH$ are also described.

EXPERIMENTAL

All the reactions were carried out under nitrogen with standard Schlenk techniques unless otherwise stated.

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Preparations

[PPN]$_2$[Ni(dmit)$_2$] (**1**). 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione [14] (812 mg, 2 mmol) was dissolved in sodium methoxide solution (7 cm^3, 2 M) to give a dark red solution. To this was added a methanol (50 cm^3) solution of $NiCl_2 \cdot 6H_2O$ (238 mg, 1 mmol) followed by a methanol (20 cm^3) solution of bis(triphenylphosphine)iminium chloride (PPN^+Cl^-, 1.15 g, 2 mmol). The reaction mixture was then stirred for 30 min. The dark green solid which precipitated out was filtered, washed with methanol and recrystallized from acetone-isopropanol mixture (1 : 1). Yield: 79%. Found: C, 59.6; H, 3.7; N, 1.6. Calc. for **1**: C, 61.3; H, 3.9; N, 1.8%.

[PPN][Pd(dmit)$_2$] (**2**). The complex was obtained by using $PdCl_2$ in place of $NiCl_2 \cdot 6H_2O$ in the above reaction. Yield: 76%. Found: C, 49.3; H, 3.5; N, 1.4. Calc. for **2**: C, 48.6; H, 2.9; N, 1.3%.

[PPN][Pt(dmit)$_2$] (**3**). The dibenzoylester (812 mg, 2 mmol) was dissolved in sodium methoxide (7 cm^3, 2 M) and stirred for 30 min. To the dark red coloured solution was added K_2PtCl_4 (415 mg, 1 mmol) dissolved in deoxygenated water (50 cm^3). After stirring for another 30 min, a methanolic solution of bis(triphenylphosphine)iminium chloride (1.15 g, 2 mmol, 20 cm^3 methanol) was added. The black precipitate was collected by filtration, washed with methanol and dried *in vacuo*. Recrystallization was accomplished from 1 : 1 acetone–isopropanol mixture. Yield: 90%. Found: C, 44.4; H, 2.8; N, 1.3. Calc. for **3**: C, 44.8; H, 2.7; N, 1.2%.

[PPN][Ni(dmit)$_2$] (**4**). [PPN]$_2$[Ni(dmit)$_2$] (1.5 g, 1 mmol) was dissolved in acetone (60 cm^3) and air was bubbled through the solution for 30 min. The volume of the solution was reduced to above 30 cm^3 under reduced pressure. Methanol (30 cm^3) was added to this to give a brown precipitate of [PPN][Ni(dmit)$_2$]. The solid was collected by filtration and dried *in vacuo*. Yield: 65%. Found: C, 51.3; H, 3.3; N, 1.6%. Calc. for **4**: C, 51.0; H, 3.0; N, 1.4%.

[PPN]$_{0.25}$[Ni(dmit)$_2$I] (**5**). Complex **4** (1.02 g, 1 mmol) was dissolved in acetonitrile (25 cm^3). To this was added an acetonitrile solution (20 cm^3) of iodine (125 mg, 1 mmol). The mixture was kept overnight in the fridge to get a black precipitate of [PPN]$_{0.25}$[Ni(dmit)$_2$I]. Yield: 28%. Found: C, 25.5; H, 1.0; N, 0.49%. Calc. for **5**: C, 25.3; H, 1.0; N, 0.49%.

[PPN]$_{0.25}$[Pd(dmit)$_2$I] (**6**). The complex was prepared from **2** by following the above procedure. Yield: 25%. Found: C, 23.0; H, 0.9; N, 0.47%. Calc. for **6**: C, 23.7; H, 1.0; N, 0.46%.

Physical measurements

Elemental analyses for C, H and N were carried out with a Carlo Erba Elemental Analyser Model 1106. IR spectra were obtained using a Perkin–Elmer Model 681 spectrophotometer. UV–vis spectra in acetonitrile solution were recorded with a Shimadzu UV-260 spectrophotometer. ESR studies were performed with Varian E-line century series X-band E-112 EPR spectrometer. Cyclic voltammetric studies were performed on EG & G Princeton Applied Research Potentiostat Model 273. Cyclic voltammetric experiments were carried out with two Pt wires as working and auxillary electrodes in solution of acetonitrile containing tetrabutylammonium perchlorate as supporting electrolyte and Ag/AgCl electrode as a reference. Electrical resistivities of the complexes were measured for compacted pellets by the conventional two-probe method.

X-ray crystallography. [PPN][Ni(C_3S_5)$_2$] · MeOH **4**

Crystal data and the details of the measurements are listed in Table 1. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo–Kα radiation ($\lambda = 0.71069$ Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflection in the range $20.80 < 2\theta < 24.45°$ corresponded to a triclinic cell. The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 50.0°. Of the 8206 reflections which were collected 7879 were unique ($R_{int} = 0.059$). The intensities of three representative reflections which were measured after every 150 reflections remained throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo–Kα is 9.9 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.85 to 1.00. The data was corrected for Lorentz and polarisation effects.

The structure was solved by direct methods [15]. The final cycle of full-matrix refinement was based on 3652 observed reflections ($I > 3.00\ \sigma(I)$) and 524 variable parameters and converged with unweighted and weighted agreement factor of $R = \Sigma \| F_0| - |F_c\| / \Sigma |F_0| = 0.054$; $R_w = [(\Sigma W(|F_0| - |F_c|)^{2-} / \Sigma W F_0^2)]^{1/2} = 0.062$.

The maximum and minimum peaks on the final difference Fourier map corresponded to 0.91 and -0.38 e/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber [16]. All calculations were performed using the Texan crystallographic software package of Molecular Structure Corporation [17] and ORTEP II [18].

RESULTS AND DISCUSSION

Crystal structure of [PPN][Ni(dmit)$_2$] · MeOH **4**

The complex crystallises in the triclinic space group $P\bar{1}$ with two molecules in the unit cell which is the same as that of [tmiz][Ni(C_3S_5)$_2$] [19] (tmiz = 1,2,3-

Table 1. Crystallographic data

Empirical formula	$C_{43}S_{10}NiNH_{34}P_2O$
Formula weight	1021.99
Crystal color, habit	black, prism
Crystal dimensions (mm)	0.200 × 0.100 × 0.450
Crystal system	triclinic
No. Reflections Used for Unit Cell Determination (2θ range)	25 (20.8–24.5°)
Lattice parameters	a = 15.605 (5) Å
	b = 17.662 (4) Å
	c = 8.256 (2) Å
	α = 96.86 (2)
	β = 94.35 (2)
	γ = 89.95 (2)
	V = 2245 (2) Å^3
Space group	$P\bar{1}$ (#2)
Z value	2
D_{calc}	1.512 g/cm^3
$F000$	1050
μ(Mo-kα)	9.86 cm^{-1}

trimethylimidazonium), $[DiPS_4][Ni(C_3S_5)_2]$ [20] ($DIPS_4$ = tetraphenyldithiapyranylidene) and $[N(CH_3)_4][Ni(C_3S_5)_2]$ [21]. A projection of the anionic unit $[Ni(C_3S_5)_2]^-$ and the cation with atom numbering is shown in Fig. 1. Intramolecular distances and angles are given in Table 2 and Table 3 respectively. The asymmetric unit consists of a discrete cation, anion and a molecule of MeOH with no significant close atom–atom contacts among them. The crystal structure can be described as being composed of stacks of $[Ni(C_3S_5)_2]^-$ units along approximately 22° with respect to the [111] plane. These stacks are arranged in layers parallel to and alternating with layers of PPN and MeOH. However, the stacking of the $Ni(C_3S_5)_2$ is very loose since the distances between the anionic layers are ≈ 10 Å. This is reflected in the very low density of the salt (1.512 g/cm^3). As a result, there is no strong interaction between the $[Ni(C_3S_5)_2]^-$ units; the shortest S···S distance is S(11)···S(42) 3.890(3) and S(12)···S(41) 3.977(3) Å.

As expected, the $Ni(dmit)_2$ is fairly close to planarity. However, in the dmit ligand the outer C atoms, C(31) and C(32) deviate significantly from the plane of inner atoms as evident from torsional angles which deviate from ideal 180°. The observed Ni—S bond lengths require some comment. The average Ni—S distance observed for compounds of general formula $[Cat][Ni(dmit)_2]$ where Cat is closed shell cation range from 2.15–2.16 Å [19]. The Ni—S bond lengths generally increase with the increase in the size of cation.

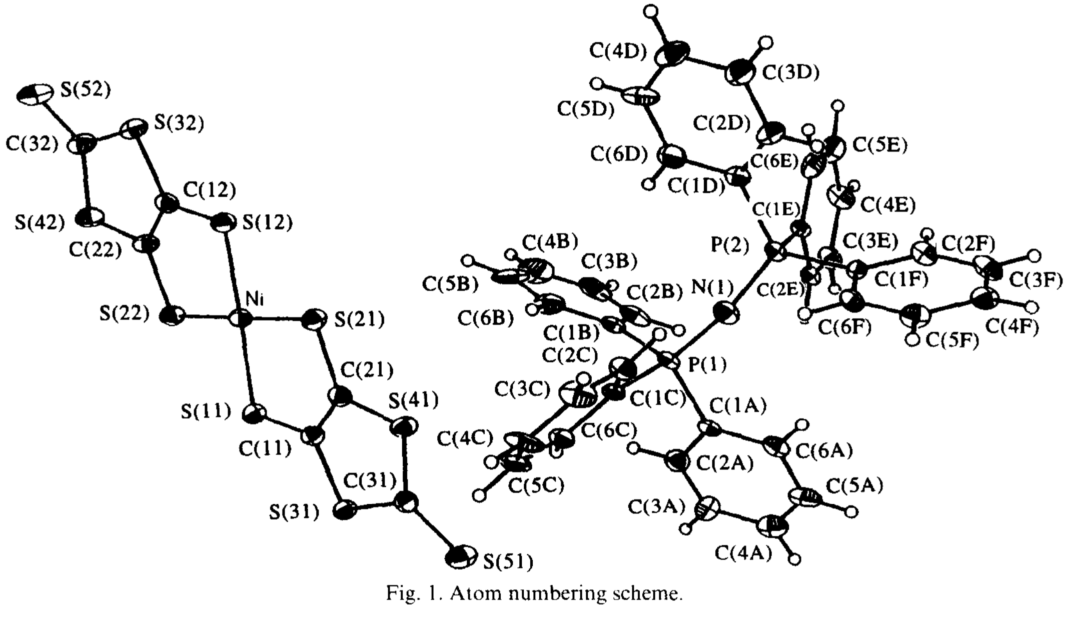

Fig. 1. Atom numbering scheme.

Table 2. Intramolecular distances involving the non-hydrogen atoms (in Å)

Ni—S(11)	2.165(2)	O(1ME)—C(1ME)	0.63(1)
Ni—S(12)	2.161(2)	C(1A)—C(2A)	1.39(1)
Ni—S(21)	2.164(2)	C(1A)—C(6A)	1.38(1)
Ni—S(22)	2.165(2)	C(1B)—C(2B)	1.37(1)
S(11)—C(11)	1.725(8)	C(1B)—C(6B)	1.38(1)
S(12)—C(12)	1.720(8)	C(1C)—C(2C)	1.37(1)
S(21)—C(21)	1.704(8)	C(1C)—C(6C)	1.377(9)
S(22)—C(22)	1.709(8)	C(1D)—C(2D)	1.37(1)
S(31)—C(11)	1.738(7)	C(1D)—C(6D)	1.38(1)
S(31)—C(31)	1.731(8)	C(1E)—C(2E)	1.382(9)
S(32)—C(12)	1.741(8)	C(1E)—C(6E)	1.382(9)
S(32)—C(32)	1.750(9)	C(1F)—C(2F)	1.37(1)
S(41)—C(21)	1.742(8)	C(1F)—C(6F)	1.385(9)
S(41)—C(31)	1.738(8)	C(2A)—C(3A)	1.36(1)
S(42)—C(22)	1.745(8)	C(2B)—C(3B)	1.37(1)
S(42)—C(32)	1.730(9)	C(2C)—C(3C)	1.36(1)
S(51)—C(31)	1.630(8)	C(2D)—C(3D)	1.35(1)
S(52)—C(32)	1.614(9)	C(2E)—C(3E)	1.38(1)
P(1)—N(1)	1.561(6)	C(2F)—C(3F)	1.38(1)
P(1)—C(1A)	1.796(7)	C(3A)—C(4A)	1.38(1)
P(1)—C(1B)	1.802(7)	C(3B)—C(4B)	1.33(1)
P(1)—C(1C)	1.805(7)	C(3C)—C(4C)	1.37(1)
P(2)—N(1)	1.555(6)	C(3D)—C(4D)	1.38(1)
P(2)—C(1D)	1.774(7)	C(3E)—C(4E)	1.37(1)
P(2)—C(1E)	1.800(7)	C(3F)—C(4F)	1.36(1)
P(2)—C(1F)	1.800(7)	C(4A)—C(5A)	1.34(1)
C(4B)—C(5B)	1.37(1)	C(4C)—C(5C)	1.36(1)
C(4D)—C(5D)	1.36(1)	C(4E)—C(5E)	1.36(1)
C(4F)—C(5F)	1.39(1)	C(5A)—C(6A)	1.37(1)
C(5B)—C(6B)	1.39(1)	C(5C)—C(6C)	1.38(1)
C(5D)—C(6D)	1.38(1)	C(5E)—C(6E)	1.36(1)
C(5F)—C(6F)	1.35(1)	C(11)—C(21)	1.35(1)
C(12)—C(22)	1.36(1)		

Recently a mean Ni—S distance of 2.163 Å has been reported for 1,2,3-trimethylimidazolium-bis(4,5-dimercapto-1,3-dithiole-2-thionato) nickelate(III) [19]. The longer Ni—S distance has been interpreted in terms of a more negatively charged anion. The average value of Ni—S bond length for **4** is 2.163 Å. This is one of the highest values observed for a $[Ni(dmit)_2]$ complex and is indicative of greater negative charge on the anion. It can also be explained in the terms of an oxidized Ni^{III} species. The bulky cation stabilizes the charge to give a stable complex. Figure 2 depicts a view of the packing diagram. There is no dimerisation of the $Ni(dmit)_2$ units. The Ni atom has a square planar coordination with an average S—Ni—S angle of 90.0°. The difference structure is probably determined by the cation size. The larger size of cation allows a mixed ion packing where bulky cations fill the holes between the anions.

The counter ion exhibits the expected bent configuration with P—N—P angle of 155.2(4)°. Interestingly, this is significantly higher than usually found in related PPN salts, e.g., 137.6(4)° for $(PPN^+)_2(TCNQ)_3$, [22] 143.1(2)° for PPN^+ S_4N^- [23]. The P—N bond lengths, 1.561(6) and 1.555(6) Å are shorter than observed in related complexes. Other molecular parameters in the cation are P—C = 1.796(7), 1.802(7), 1.805(7) Å and N—P—C = 110.3(3), C—P—C = 114.9(3)°.

Electrochemical and spectroscopic properties

The cyclic voltammogram of the dianionic complex **1** consists of two peaks. The cathodic peak potentials at −0.115 and −0.09, respectively correspond to the reversible $[Ni(dmit)_2]^{-1} \rightleftharpoons [Ni(dmit)_2]^{-2}$ one electron process [24]. The second quasi-reversible wave was due to $[Ni(dmit)_2]^{-1} \rightleftharpoons [Ni(dmit)_2]^0$ process. The cyclic voltammogram of **2** consists of only one reversible wave ($[Pd(dmit)_2]^{-1} \rightleftharpoons [Pd(dmit)_2]^{-2}$ (0.16 mV *vs* Ag/AgCl).

The absorption bands at ≈ 307 and ≈ 452 nm observed in the UV–vis spectra of all the complexes are ascribed to π–π^* transitions of the $C_3S_5^{2-}$ ligand. The latter band corresponds to characteristic intense bands observed for $[Na_2(C_3S_5)]$ (512 nm in methanol) and $[Zn(C_3S_5)_2]^{2-}$ (530 nm in acetonitrile) [25].

Reactions of **2** and **4** with iodine in acetonitrile afforded partially oxidized complexes. IR and ESR studies suggest a ligand centred oxidation. The

Table 3. Selected bond angles (°)

S(11)—Ni—S(12)	177.8(1)
S(11)—Ni—S(21)	93.32(9)
S(11)—Ni—S(22)	87.21(9)
S(12)—Ni—S(21)	86.51(9)
S(12)—Ni—S(22)	93.02(9)
S(21)—Ni—S(22)	178.4(1)
Ni—S(11)—C(11)	101.6(3)
Ni—S(12)—C(12)	102.2(3)
Ni—S(21)—C(21)	101.9(3)
Ni—S(22)—C(22)	102.2(3)
C(11)—S(31)—C(31)	98.3(4)
C(12)—S(32)—C(32)	97.7(4)
C(21)—S(41)—C(31)	98.5(4)
C(22)—S(42)—C(32)	98.7(4)
S(12)—C(12)—S(32)	122.3(4)
S(12)—C(12)—C(22)	121.1(6)
S(32)—C(12)—C(22)	116.6(6)
S(21)—C(21)—S(41)	122.7(4)
S(21)—C(21)—C(11)	122.1(6)
S(41)—C(21)—C(11)	115.2(6)
S(22)—C(22)—S(42)	123.2(5)
S(22)—C(22)—C(12)	121.6(6)
S(42)—C(22)—C(12)	115.3(6)
S(31)—C(31)—S(41)	111.5(4)
S(31)—C(31)—S(51)	124.5(5)
S(41)—C(31)—S(51)	124.0(5)
S(32)—C(32)—S(42)	111.7(5)
S(32)—C(32)—S(52)	123.5(5)
S(42)—C(32)—S(52)	124.8(6)

$\nu(C{=}C)$ stretching IR band of the ligand oxidized species **5** (1260 cm^{-1}) occurs at a lower wave number compared with monoionic species **4** (1370 cm^{-1}) and dianionic species **1** (1460 cm^{-1}). This negative shift is a clear indication of ligand centred oxidation. Furthermore **5** and **6** show a rather sharp, approximately isotropic powder ESR signal ($g = 2.01$) at 77 K similar to those of oxidized C_3S_5 metal complexes with ligand centred oxidation [26,27]. In the case of $[Ni(DDD)_2]^-$ (DDD = 5,6-dihydro-1,4-dithiin-2,3-dithiolate), the MO calculations suggest that the metal ion is best described by d^8 ion, and an unpaired electron in such molecule is represented by the π^* orbital of the ligand and a small contributions from the d orbitals [28]. An identical situation probably arises in the case of the PPN salts.

The powder ESR spectra were recorded at room temperature and at 77 K. All monoionic salts (**2** and **4**) except that of Pt showed apparently an isotropic broad signal at $g = 2.02$–2.03 assignable to the free radical located at the dithiolate ligand. However, complex **3** exhibited an anisotropic signal with three well separated g values; $g_{11} = 2.15$, $g_{22} = 2.07$, $g_{33} = 1.85$ and $\langle g \rangle = 2.02$. Hyperfine splitting due to the ^{195}Pt ($I = 1/2$) coupling was observed at high field resonance with coupling constants $A_{11} = 80$ gauss and $A_{22} = 90$ gauss. The decrease in the value of g most likely represents an increase in the degree of delocalization of the unpaired spin.

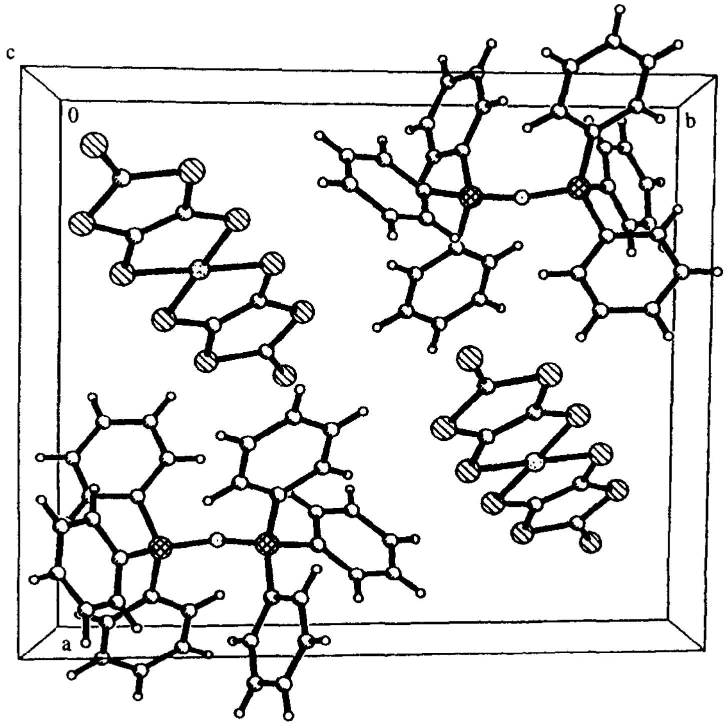

Fig. 2. Packing diagram.

The electrical conductivity of complexes **2**–**6** were measured for compacted pellets at room temperature. The complexes **2**–**4** were insulators. But the partially oxidized salts **5** and **6** showed high conductivities (1.2×10^{-2} and 0.64 S cm^{-1}, respectively). In the complexes **2**–**4** the anion moieties are separated from each other by the bulky PPN cation. However, in the partially oxidized salts the small cation to anion ratio is likely to lead to an effective packing of the anion moieties to form electron conduction pathways in the solid state [13].

In conclusion, dmit complexes of Ni, Pd, Pt with a bulky cation have been isolated. The partially oxidised complexes with low cation to anion ratio showed promising room temperature conductivities. The X-ray structure of [PPN][Ni(dmit)$_2$] consists of isolated anions with one of the longest Ni—S distances yet reported.

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