The Crystal Structures of $K[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ and $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ *

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The crystal structures of $K[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ and $NH_4[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ are described. The former has a structure consisting of an equidistant columnar stack of anions, whereas in the latter compound the anions are arranged as dimers in an eclipsed Pd over Pd arrangement.

During the past six years there has been renewed interest in metal dithiolene complexes.[1–5] This has come about because of the discovery that salts of the complex anions $[M\{S_2C_2(CN)_2\}_2]^-$ (where M is Ni, Pd, or Pt) with small cations can exhibit unusual co-operative phenomena in the solid state. For example, $[NH_4][Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ exhibits the properties of a Heisenberg antiferromagnetic chain at room temperature but at low temperatures the ground state is a singlet with the monoanions associated as dimers.[3,4] The non-stoicheiometric compound $[H_3O]_{0.33}Li_{0.8}[Pt\{S_2C_2(CN)_2\}_2]\cdot 1.67H_2O$ exhibits metallic properties at room temperature but undergoes the Peierls instability at $\approx$220 K to become a semiconductor.[2]

Previous *X*-ray studies on the structures of the $[M\{S_2C_2(CN)_2\}_2]^-$ monoanions (where M = Ni or Pt) have shown that when the cation is large and bulky {*e.g.* $[N(C_2H_5)_4]^+$} the anions are associated as dimer pairs in a staggered configuration with a metal on sulphur arrangement.[6,7] With small Group 1 cations or $[NH_4]^+$ as the counter ion the structure appears to be dependent on the central metal. *X*-Ray studies have shown $[NH_4][Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ to possess an equidistant anion stack structure whereas $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$ and $[H_3O][Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$ possess dimer pairs of anions in an eclipsed Pt over Pt configuration.[4,7,8]

It is not easy to predict whether the $[Pd\{S_2C_2(CN)_2\}_2]^-$ monoanion salts of small cations will adopt the equidistant stack structure found for the nickel complex or the dimeric structure observed for the platinum complexes. We have recently shown that $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot 0.5H_2O$ is the first palladium dithiolene complex to exhibit metallic behaviour under pressure.[9] In this compound the anions are associated as dimer pairs but not in a columnar stack arrangement as found for $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$.[8,10] We now report the structures of $K[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ and $NH_4[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$, to establish the effect of cation size on the structure of $[Pd\{S_2C_2(CN)_2\}_2]^-$ monoanion salts of Group 1 cations.

Experimental

Single crystals of $K[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ were prepared by electrocrystallisation, at a constant voltage of 1.5 V, of an aqueous acetone solution (10% v/v) of $K_2[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ (0.02 mol dm^{-3}) and urea (0.1 mol dm^{-3}). The platinum anode was replaced after 24 h and single crystals of the product grew on the second anode over a period of 10 d (Found: C, 21.65; H, 0.55; N, 12.20; Pd, 24.7. Calc. for $C_8H_2KN_4OPdS_4$: C, 21.60; H, 0.45; N, 12.6; Pd, 24.05%).

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for $K[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$

Atom	*x*	*y*	*z*
Pd(1)	0	5 000	5 000
S(1)	849.9(14)	3 582.4(59)	4 332.4(6)
S(2)	−1 571.8(14)	6 361.4(57)	4 612.9(5)
C(1)	−173(5)	4 328(18)	3 940(2)
C(2)	−1 207(5)	5 603(20)	4 058(2)
C(10)	76(6)	3 548(19)	3 466(2)
N(10)	225(5)	2 909(19)	3 096(2)
C(20)	−1 969(6)	6 298(21)	3 702(2)
N(20)	−2 536(6)	6 944(21)	3 405(2)
O(1)	−1 936(6)	1 900(27)	2 500
K(1)	−3 570(2)	−2 997(7)	2 500

Single crystals of $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ were prepared from $[NH_4]_2[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ by electrocrystallisation in aqueous solution as described above for $K[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ (Found: C, 21.95; H, 1.35; N, 15.70; Pd, 25.6. Calc. for $C_8H_6N_5OPdS_4$: C, 21.70; H, 1.85; N, 15.90; Pd, 24.1%). ^{1}H N.m.r. of $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ [in $(CD_3)_2SO$]: δ 4.99 (s, O-H, exchangeable with D_2O); 7.49 (s), 7.09 (s), 6.23 p.p.m. (s) (N-H); J_{N-H} 51.0 Hz, lit.[11] 52.7 ± 0.2 Hz.

X-*Ray Structure Determinations.*—Crystals of the two compounds were mounted on glass fibres. Following preliminary photography, unit-cell parameters in each case were obtained by least-squares refinement of the setting angles for 25 automatically centred reflections measured on a CAD4 diffractometer. Intensities were recorded in the $\omega/2\theta$ scan mode with graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å) as previously described in detail.[12] Semi-empirical absorption corrections were applied in each case.[13] The structures were solved *via* routine heavy-atom procedures and refined *via* application of full-matrix least squares. For the final refinements, a weighting scheme of the type $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ was used. Atomic scattering factor data were taken from ref. 14 and all calculations were made using SHELX 76.[15]

Crystal data for $K[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$. Black needles, $C_8H_2KN_4OPdS_4$, M = 443.88 orthorhombic, space group *Pnma*, a = 12.176(2), b = 3.778(1), c = 29.614(4) Å, U = 1 362.3 Å^3, Z = 4, D_c = 2.16 g cm^{-3}, D_m = 2.17 g cm^{-3}, μ(Mo-K_α) = 20.95 cm^{-1}, $F(000)$ = 856. Total data recorded 1 188 ($1.5 \leqslant \theta \leqslant 23°$), unique 953, observed [$I > 1.5\sigma(I)$] 624. Number of parameters 96, g parameter 0.0001, final R = 0.0315,

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* Potassium and ammonium bis(1,2-dicyanoethylene-1,2-dithiolato)palladate(1−) hydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

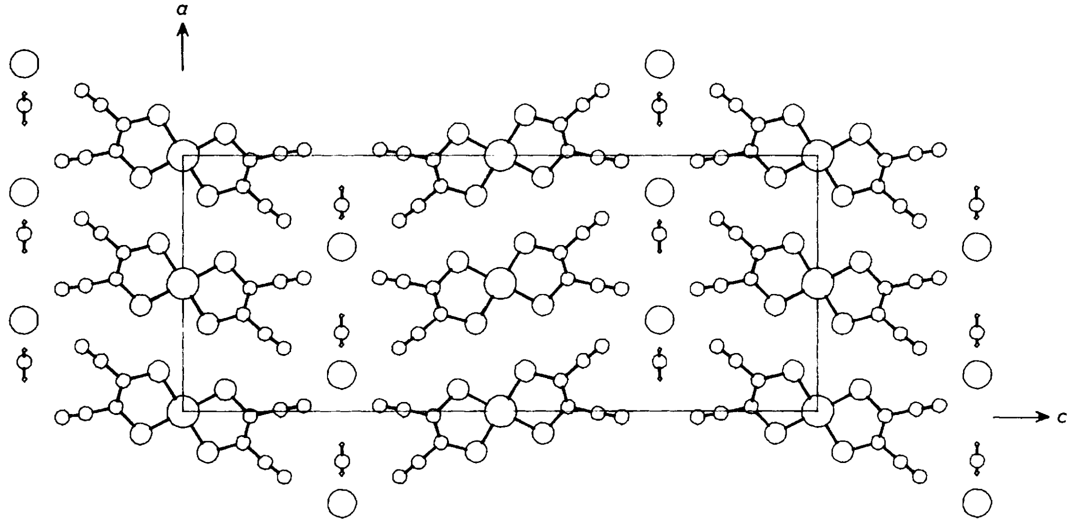

Figure 1. A projection of the structure of $K[Pd\{S_2C_2(CN)_2\}_2]{\cdot}H_2O$ as viewed down the *b* axis

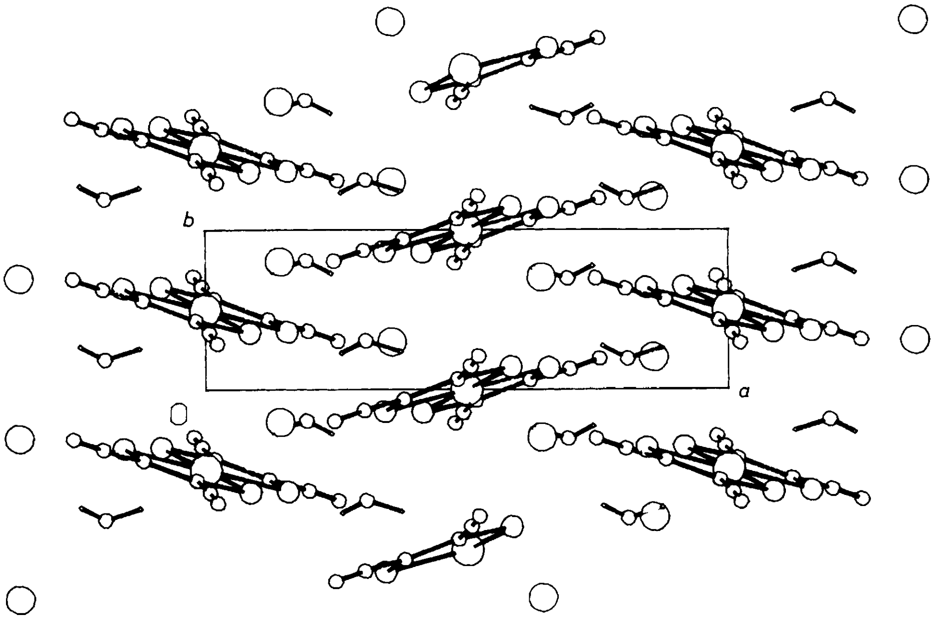

Figure 2. A projection of the structure of $K[Pd\{S_2C_2(CN)_2\}_2]{\cdot}H_2O$ as viewed down the *c* axis showing the arrangement of the components in the anions and cations of water sheets

$R' = 0.0294$. Non-hydrogens anisotropic, hydrogens experimentally located and refined with a common U_{iso} value. Final fractional atomic co-ordinates are given in Table 1.

Crystal data for $[NH_4][Pd\{S_2C_2(CN)_2\}_2]{\cdot}H_2O$. Black needles, $C_8H_6N_5OPdS_4$, $M = 422.8$, triclinic, space group $P\bar{1}$, $a = 14.689(4)$, $b = 7.153(4)$, $c = 6.724(1)$ Å, $\alpha = 97.83(4)$, $\beta = 97.13(2)$, $\gamma = 92.95(4)°$, $U = 692.8$ Å^3, $Z = 2$, $D_c = 2.03$ g cm^{-3}, $D_m = 2.02$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 17.7$ cm^{-1}, $F(000) = 414$. Total data recorded 2 640 ($1.5 \leqslant \theta \leqslant 25°$), unique 2 428, observed $[I > 1.5\sigma(I)]$ 1 680. Number of parameters 172, *g* parameter 0.001, final $R = 0.0479$, $R' = 0.0565$. Non-hydrogens anisotropic. Hydrogen atoms could not be reliably located and refined, and were not included. Final fractional atomic co-ordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Structure of $K[Pd\{S_2C_2(CN)_2\}_2]{\cdot}H_2O$.—The complex $K[Pd\{S_2C_2(CN)_2\}_2]{\cdot}H_2O$ is isostructural with $[NH_4][Ni\{S_2C_2(CN)_2\}_2]{\cdot}H_2O$.[4] Figure 1 shows the crystal structure as viewed down the *b* axis. Interatomic distances and interbond angles are given in Table 3. The structure contains equidistant anionic stacks repeating along the short *b* axis in which the co-ordination planes are tilted with respect to this axis. Within the stack the closest interionic atom–atom distances are the S • • • S and Pd • • • Pd repeat distances. These distances of 3.778 Å are considerably shorter than those observed in $[NH_4][Ni-$

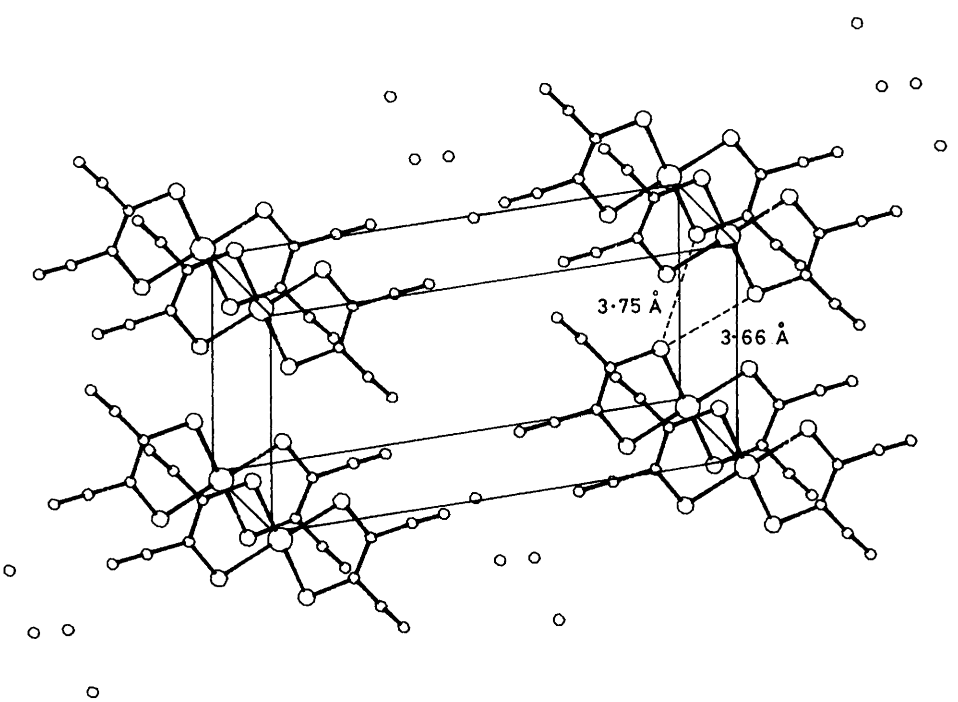

Figure 3. A projection of the structure of $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$

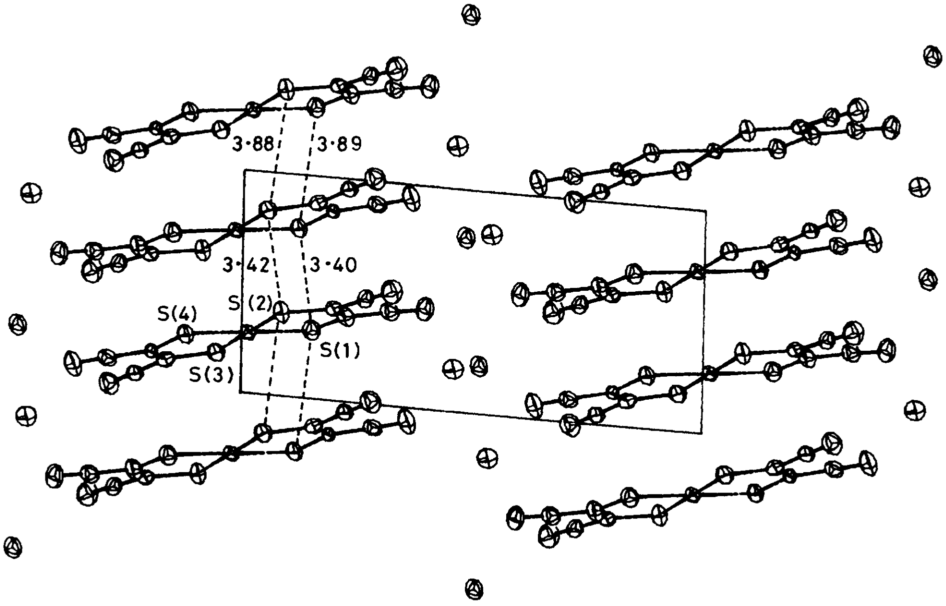

Figure 4. Crystal structure of $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ (*c* axis projection) showing the dimer unit

$\{S_2C_2(CN)_2\}_2]\cdot H_2O$ suggesting that the intrastack interactions are greater in the palladium complex.

The stacks are arranged into sheets parallel to the *ab* plane of the cell separated by sheets of cations and water molecules (see Figure 2). Within the anionic sheets, neighbouring stacks are stepped up by *b*/2 with interstack contacts of 3.73 and 3.75 Å. These are again shorter than the corresponding distances 3.79 and 3.91 Å, in the nickel complex.

Structure of $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$.—The complex $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ is isostructural with $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$[8] and $[H_3O][Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$.[7] Figure 3 shows the *b* axis projection of the crystal structure of $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$. Interatomic bond distances and interbond angles are given in Table 4. The planar anions are arranged face to face in an eclipsed configuration to form a columnar stacked structure. $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ possesses a dimeric structure (see Figure 4). The intradimer S ··· S contacts are 3.40 and 3.42 Å, and between dimers are 3.88 and 3.89 Å. These are comparable to those found in $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$[8] and $[H_3O][Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$.[7]

Between the stacks of anions there are short S ··· S contacts

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$

Atom	*x*	*y*	*z*
Pd(1)	158.7(6)	2 744(1)	10 463(2)
S(1)	1 520(2)	3 091(5)	9 210(5)
S(2)	865(2)	3 781(4)	13 681(4)
S(3)	−528(2)	1 705(4)	7 253(5)
S(4)	−1 205(2)	2 401(4)	11 680(5)
C(1)	2 252(8)	3 847(17)	11 354(19)
C(2)	1 996(8)	4 154(15)	13 305(18)
C(10)	3 208(8)	4 236(16)	11 213(17)
N(10)	3 975(7)	4 489(16)	11 090(15)
C(20)	2 677(7)	4 711(16)	15 028(17)
N(20)	3 247(7)	5 143(16)	16 306(16)
C(3)	−1 617(7)	1 187(15)	7 651(16)
C(4)	−1 940(7)	1 506(14)	9 519(17)
C(30)	−2 278(8)	444(16)	5 921(18)
N(30)	−2 836(8)	−121(16)	4 586(17)
C(40)	−2 885(8)	1 021(16)	9 736(17)
N(40)	−3 624(7)	615(16)	9 798(17)
N(1)	4 608(7)	1 917(14)	7 541(16)
O(2)	4 831(6)	7 858(14)	6 338(14)

Table 3. Interatomic distances and interbond angles for $K[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$

Bond lengths (Å)

S(1)–Pd(1)	2.295(4)	S(2)–Pd(1)	2.289(4)
C(1)–S(1)	1.726(8)	C(2)–S(2)	1.727(8)
C(2)–C(1)	1.392(10)	C(10)–C(1)	1.467(10)
C(20)–C(2)	1.428(10)	N(10)–C(10)	1.137(8)
N(20)–C(20)	1.145(9)		
H(1)–O(1)	0.894(24)	H(2)–O(1)	0.896(22)

Bond angles (°)

S(2)–Pd(1)–S(1)	89.9(2)	C(1)–S(1)–Pd(1)	102.5(3)
S(1)–Pd(1)–S(1)	180.0	C(2)–S(2)–Pd(1)	103.0(3)
S(2)–Pd(1)–S(2)	180.0	C(2)–C(1)–S(1)	122.8(6)
C(10)–C(1)–S(1)	117.5(6)	C(10)–C(1)–C(2)	119.7(7)
C(1)–C(2)–S(2)	121.9(6)	C(20)–C(2)–S(2)	120.3(6)
C(20)–C(2)–C(1)	117.9(7)	N(10)–C(10)–C(1)	177.2(8)
N(20)–C(20)–C(2)	176.3(8)		
H(2)–O(1)–H(1)	140.9(12)		

Selected intermolecular non-bonded distances (Å)

S(1)–Pd(1a)	5.592	S(2)–Pd(1b)	4.542
S(1)–S(1c)	4.589	S(2)–S(1c)	3.245
S(2)–S(1d)	3.746	S(2)–S(2c)	1.579
S(2)–S(2e)	3.733		

Key to symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*): (a) $0.5 - x$, $-0.5 + y$, $1.0 - z$, (b) $-0.5 - x$, $0.5 + y$, $1.0 - z$, (c) $-x$, $1.0 - y$, $1.0 - z$, (d) $-0.5 + x$, $0.5 - y$, z, (e) $-0.5 - x$, $-0.5 + y$, $1.0 - z$.

of 3.66 and 3.75 Å. These compare with values of 3.69 and 3.72 Å in $[H_3O][Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$.[7]

General Discussion.—It was pointed out in the Introduction that in the $[Ni\{S_2C_2(CN)_2\}_2]^-$ monoanion salts of small cations an equidistant stack structure is commonly found whereas for the corresponding $[Pt\{S_2C_2(CN)_2\}_2]^-$ salts the structures consist of a columnar stack of anion dimers. The present study has shown that both types of structure are found for the $[Pd\{S_2C_2(CN)_2\}_2]^-$ monoanion salts of small cations.

Table 4. Interatomic distances and interbond angles for $[NH_4][Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$

Bond lengths (Å)

S(1)–Pd(1)	2.280(5)	S(2)–Pd(1)	2.288(5)
S(3)–Pd(1)	2.275(5)	S(4)–Pd(1)	2.269(5)
Pd(1)–Pd(1c)	3.415(5)	C(1)–S(1)	1.694(14)
C(2)–S(2)	1.723(13)	C(3)–S(3)	1.685(13)
C(4)–S(4)	1.725(13)	C(2)–C(1)	1.402(18)
C(10)–C(1)	1.434(17)	C(20)–C(2)	1.431(15)
N(10)–C(10)	1.146(15)	N(20)–C(20)	1.121(15)
C(4)–C(3)	1.392(15)	C(30)–C(3)	1.441(15)
C(40)–C(4)	1.442(16)	N(30)–C(30)	1.151(15)
N(40)–C(40)	1.117(15)		

Bond angles (°)

S(2)–Pd(1)–S(1)	90.8(2)	S(3)–Pd(1)–S(1)	88.6(2)
S(3)–Pd(1)–S(2)	179.4(1)	S(4)–Pd(1)–S(1)	179.4(1)
S(4)–Pd(1)–S(2)	89.8(2)	S(4)–Pd(1)–S(3)	90.8(2)
C(1)–S(1)–Pd(1)	101.5(5)	C(2)–S(2)–Pd(1)	102.1(5)
C(3)–S(3)–Pd(1)	101.3(5)	C(4)–S(4)–Pd(1)	102.2(4)
C(2)–C(1)–S(1)	124.8(10)	C(10)–C(1)–S(1)	119.1(11)
C(10)–C(1)–C(2)	116.1(12)	C(1)–C(2)–S(2)	120.8(10)
C(20)–C(2)–S(2)	118.9(10)	C(20)–C(2)–C(1)	120.3(11)
N(10)–C(10)–C(1)	177.9(13)	N(20)–C(20)–C(2)	176.2(12)
C(4)–C(3)–S(3)	124.9(9)	C(30)–C(3)–S(3)	118.0(9)
C(30)–C(3)–C(4)	117.1(10)	C(3)–C(4)–S(4)	120.7(9)
C(40)–C(4)–S(4)	117.7(9)	C(10)–C(4)–C(3)	121.5(11)
N(30)–C(30)–C(3)	177.0(12)	N(40)–C(40)–C(4)	176.4(13)

Selected intermolecular non-bonded distances (Å)

S(1)–Pd(1a)	3.967	S(2)–Pd(1a)	4.176
S(3)–Pd(1b)	3.754	S(4)–Pd(1a)	4.227
S(4)–S(1a)	3.405	S(3)–S(2c)	3.747
S(2)–S(2d)	3.658	S(3)–S(2a)	3.422
S(4)–S(2d)	3.821	S(2)–S(3b)	3.880
S(1)–S(4b)	3.887		

Key to symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*): (a) $-x$, $1.0 - y$, $2.0 - z$, (b) $-x$, $-y$, $2.0 - z$, (c) x, y, $-1.0 + z$, (d) $-x$, $1.0 - y$, $3.0 - z$.

The $[M\{S_2C_2(CN)_2\}_2]^-$ monoanion contains an unpaired electron in its highest occupied molecular orbital (h.o.m.o.). If the counter cations and solvent molecules in the lattice are relatively small and spherical, it would be expected that the most efficient crystal packing would consist of a columnar stack of the planar anions. In such an arrangement interactions between adjacent molecules in the stack due to interaction of the electrons in the half filled h.o.m.o. will be expected provided the intrastack distance is short enough. In these circumstances the electrons can either be localised on individual anions or delocalised in the stack. Electron localisation will occur if $U \gg 4t$ where U is the on-site coulomb–coulomb repulsion energy and t is the transfer integral. Such a situation will lead to an equidistant stack with the compounds exhibiting semiconducting properties and the behaviour of a Heisenberg antiferromagnetic chain as exemplified by $[NH_4][Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$.[3]

Alternatively if $U \leqslant 4t$ then electrons may be delocalised throughout the columnar structure and this might be expected to lead to metallic properties since the resulting band will be half full. However, compounds possessing a half-filled band are very susceptible to the Peierls instability which results in dimerisation and semiconducting properties. This is observed in $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$[8] and $[H_3O][Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$.[7]

The relative values of U and $4t$ depend on (*i*) the extent of delocalisation of charge on the anion and (*ii*) the spatial extension of the h.o.m.o. in the stack direction.

Both (*i*) and (*ii*) will be affected by the central metal since the metal *d* orbitals are involved in extensive metal–ligand orbital overlap. Recent extended Hückel calculations have suggested however that the charge distributions in $[Ni\{S_2C_2(CN)_2\}_2]^-$ and $[Pt\{S_2C_2(CN)_2\}_2]^-$ are not significantly different.[16] The transfer integral, *t*, would be expected to increase in the series Ni < Pd < Pt due to the influence of the increasing spatial extension of the $3d < 4d < 5d$ orbitals. Thus the dimeric structure found for the platinum complexes is a consequence of the greater '*t*' in these systems. Clearly the palladium series of compounds are an intermediate case where the two possibilities are finely balanced. In these circumstances the size of the cations appears to play a role since there is an increasing tendency to dimerisation with the large cations. Preliminary studies suggest that $Cs[Ni\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ possesses a dimerised stack structure.[17] Increasing the size of the cation could favour structures containing cavities to accommodate the larger cation. Alternatively the polarising power of the cation could influence the charge distribution in anions.

There is clearly a very subtle interplay of chemical composition, structure, and solid-state properties in the salts of metal dithiolene anions with small cations. Although the present studies have shed some light on these interactions, further structural and theoretical studies are needed to understand fully this series of compounds.

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