Crystal Structure of the New Low-Dimensional Metal $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot 0.5H_2O$†

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The *X*-ray crystal structure of $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot 0.5H_2O$ [where $S_2C_2(CN)_2^{2-}$ = 1,2-dicyanoethylene-1,2-dithiolate] has revealed that the $[Pd\{S_2C_2(CN)_2\}_2]^-$ anions are strongly associated as eclipsed dimer pairs. The arrangement of the anionic dimers is unusual and leads to short S • • • S contacts between dimers in two orthogonal directions. At low temperatures a three-fold superstructure along the *a* is observed. The structure is related to the metallic conductivity observed under pressure.

Over the past 15 years there has been great activity associated with the synthesis and study of low-dimensional molecular metals and superconductors.[1] Molecular metals based on columnar stacked structures of square coplanar metal complexes form an important class of these materials.[2] Early studies were concerned with tetracyanoplatinates and bis(oxalato)-platinates, but more recently studies have been extended to metal–dithiolene complexes.[3-7]

A study has been made of the preparation and properties of $[M\{S_2C_2(CN)_2\}_2]^-$ (M = Ni, Pd, or Pt) monoanion salts of small cations.[4] Since the compounds form columnar stacked structures, are stoicheiometric, and the anion carries a single negative charge, it would be expected that the Peierls instability[8a] would lead to dimerisation of the anions within the anion stack. This would be expected to result in the compound behaving as a semiconductor with a low room-temperature conductivity. This was observed in $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$.[5] It has been found, however, that the palladium complexes exhibit much higher conductivities than the corresponding nickel and platinum complexes. In particular, a caesium salt prepared by electrocrystallisation from an aqueous acetone solution of $Cs_2[Pd\{S_2C_2(CN)_2\}_2]\cdot H_2O$ aroused great interest because it exhibited a conductivity of about 5 Ω^{-1} cm^{-1} when measured along the long axis of the black plate-like crystals.[6] Further studies have shown that the compound behaves as a metal down to 1.4 K under 13 kbar hydrostatic pressure.[7] On the basis of initial analytical data and the observation that the structure contained anion dimers, the compound was thought to be stoicheiometric $Cs[Pd\{S_2C_2(CN)_2\}_2]\cdot 0.5H_2O$. Further analysis and a more detailed *X*-ray structure analysis, as reported here, reveals that it is non-stoicheiometric with composition $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot 0.5H_2O$.

Experimental

The compound $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot 0.5H_2O$ was prepared as black, plate-like crystals by electrocrysallisation of an aqueous acetone solution of $Cs_2[Pd\{S_2C(CN)_2\}_2]\cdot H_2O$[5] (Found: C, 18.65; H, 0.20; Cs, 19.9; N, 10.6; Pd, 19.5. Calc. for $C_8HCs_{0.82}N_4O_{0.5}PdS_4$: C, 19.05; H, 0.20; Cs, 21.6; N, 11.10; Pd, 21.10%). The crystal used for the *X*-ray work had dimensions 0.45 × 0.2 × 0.05 mm. All crystallographic measurements were made using a CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) operating in the ω–2θ scan mode, as previously described in detail.[8b] The crystal used showed considerable and variable mosaic spread, typical of this kind of material.

Crystal Data.—$C_8HCs_{0.82}N_4O_{0.5}PdS_4$, *M* = 504.74, orthorhombic, space group *Pnma*, *a* = 6.511(2), *b* = 29.94(2), *c* = 13.96(2) Å, *U* = 2 721 Å^3, D_m = 2.48 g cm^{-3}, *Z* = 8, D_c = 2.46 g cm^{-3}, μ(Mo-K_α) = 45.45 cm^{-1}, *F*(000) = 1 968.

Intensity data were recorded for one asymmetric unit in the range $1.5 \leqslant \theta \leqslant 25°$; and were corrected for absorption empirically;[9] of the 2 437 data recorded, 1 419 satisfied the criterion $I > 1.5\sigma(I)$ and were used for the analysis and refinement. The structure was solved *via* the heavy-atom method and refined *via* full-matrix least squares. All non-hydrogen atoms were refined anisotropically and the water hydrogens were apparent on a difference map and were included with interatomic distance constraints but free individual isotropic *U* values. Initially, the two independent Cs ions were included with full occupancies. The U_{ij} values for Cs(1) were normal, but for Cs(2) indicated considerable smearing (U_{11} = 0.22 Å^2). When the revised analytical data were obtained, indicating a non-stoicheiometric system, the occupancy factor of Cs(2) was reduced to that indicated by the analysis, and the refinement repeated. The U_{11} coefficient still indicated some smearing (U_{11} = 0.18 Å^2) but it was not possible to use these room-temperature *X*-ray results alone to explore the site occupancy further. However, results of a low-temperature study (see below) ratify the values used here. The number of refined parameters was 178 and the final *R* and *R'* values were 0.067 and 0.058 respectively with weights given by the expression $w = 1/[\sigma^2(F) + 0.0002(F_o)^2]$. Atomic scattering factor data were taken from ref. 10 and all calculations were made using SHELX 76.[11] Final atomic parameters are given in Table 1.

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

Results

The Room-temperature Crystal Structure.—The crystal structure is shown in the shortest axis (*a*) projection in Figure 1. Bond lengths and angles, together with other important distances are given in Table 2. The structure can be seen to contain sheets of anions parallel to the *ac* plane separated by

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

Non-S.I. unit employed: bar = 10^5 Pa.

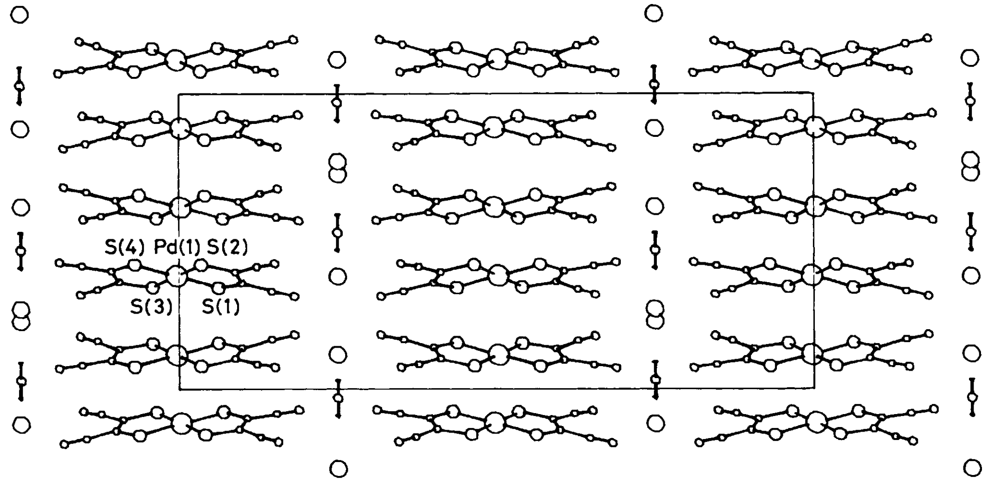

Figure 1. A view of the crystal structure down the *a* axis, showing the sheets of anions separated by sheets of Cs^+ ions and water molecules

Table 1. Fractional atomic co-ordinates (× 10^4) for $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot0.5H_2O$

Atom	*x*	*y*	*z*
Cs(1)	1 731(3)	2 500	3 825(2)
Cs(2)	6 435(8)	2 500	7 712(3)
Pd(1)	5 605(2)	−34	3 844(1)
S(1)	4 043(7)	619(1)	3 433(3)
S(2)	8 525(7)	349(2)	4 221(3)
S(3)	2 663(7)	−408(2)	3 449(3)
S(4)	7 141(7)	−692(2)	4 229(3)
C(1)	5 938(30)	994(6)	3 590(10)
C(2)	7 889(25)	880(5)	3 968(11)
C(10)	5 542(30)	1 464(6)	3 309(13)
N(10)	5 259(28)	1 813(6)	3 148(12)
C(20)	9 343(31)	1 230(7)	4 151(12)
N(20)	10 468(28)	1 514(6)	4 250(12)
C(3)	3 365(27)	−944(5)	3 633(11)
C(4)	5 262(28)	−1 063(5)	4 006(9)
C(30)	1 893(29)	−1 285(6)	3 371(11)
N(30)	735(27)	−1 552(6)	3 204(12)
C(40)	5 643(32)	−1 533(6)	4 174(11)
N(40)	5 925(30)	−1 897(6)	4 282(13)
O(1)	1 818(46)	7 500	4 662(19)

sheets of cations and water molecules. The construction of the anion sheets is very interesting (see Figure 2).

Pairs of anions in an eclipsed configuration are linked into dimers across a centre of symmetry, with a Pd ··· Pd distance of 3.329(5) Å and S ··· S contacts of 3.348 and 3.360 Å. On each anion, the pairs of S atoms not contained within the same ligands then make contacts of 3.81 and 3.85 Å with a similar pair in the facing side of the next dimer in each direction along *c*. Even shorter contacts of 3.576 and 3.681 Å are made between one of the sulphurs of each anion and a pair of sulphurs, one from each unit of a neighbouring dimer, generating links in the *a* direction and thus leading to a two-dimensional array of interanionic associations. The main contacts between the anion and cation layers seem to be Cs^+ ··· N interactions with distances of *ca.* 3.12—3.67 Å. There are no short N ··· H–O–H contacts, in contrast to the structure of $[NH_4][Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ which is also an anion–cation, water layer structure, but which has the water molecules oriented with the O–H bonds directed towards the anions.[12] In the present structure, the H–O–H

Table 2. Interatomic distances (Å) and interbond angles (°) for $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot0.5H_2O$. (*a*) Intramolecular and (*b*) Intermolecular

(*a*) Intramolecular

Pd(1)–Pd(1a)	3.329(5)	S(1)–Pd(1)	2.278(6)
S(2)–Pd(1)	2.281(7)	S(3)–Pd(1)	2.286(6)
S(4)–Pd(1)	2.273(7)	C(1)–S(1)	1.681(21)
C(2)–S(2)	1.681(17)	C(3)–S(3)	1.688(18)
C(4)–S(4)	1.683(19)	C(2)–C(1)	1.417(23)
C(10)–C(1)	1.484(24)	C(20)–C(2)	1.435(25)
N(10)–C(10)	1.085(21)	N(20)–C(20)	1.132(22)
C(4)–C(3)	1.388(22)	C(30)–C(3)	1.448(23)
C(40)–C(4)	1.447(22)	N(30)–C(30)	1.122(21)
N(40)–C(40)	1.114(22)		
H(31)–O(1)	1.061(48)	H(32)–O(1)	1.061(48)
S(2)–Pd(1)–S(1)	90.0(3)	S(3)–Pd(1)–S(1)	89.2(3)
S(3)–Pd(1)–S(2)	179.0(2)	S(4)–Pd(1)–S(1)	179.0(2)
S(4)–Pd(1)–S(2)	90.8(3)	S(4)–Pd(1)–S(3)	90.1(3)
C(1)–S(1)–Pd(1)	102.2(7)	C(2)–S(2)–Pd(1)	102.8(7)
C(3)–S(3)–Pd(1)	101.7(7)	C(4)–S(4)–Pd(1)	102.1(6)
C(2)–C(1)–S(1)	123.2(14)	C(10)–C(1)–S(1)	118.0(16)
C(10)–C(1)–C(2)	118.8(18)	C(1)–C(2)–S(2)	121.7(14)
C(20)–C(2)–S(2)	119.4(14)	C(20)–C(2)–C(1)	118.9(16)
N(10)–C(10)–C(1)	176.6(21)	N(20)–C(20)–C(2)	176.4(20)
C(4)–C(3)–S(3)	122.9(14)	C(30)–C(3)–S(3)	117.0(14)
C(30)–C(3)–C(4)	120.1(15)	C(3)–C(4)–S(4)	123.1(12)
C(40)–C(4)–S(4)	119.2(15)	C(40)–C(4)–C(3)	117.7(17)
N(30)–C(30)–C(3)	177.4(19)	N(40)–C(40)–C(4)	178.5(19)
H(32)–O(1)–H(31)	108.1(2)		

(*b*) Intermolecular contacts

S(1)–Pd(1a)	4.192	S(2)–Pd(1a)	3.927
S(3)–Pd(1a)	4.159	S(4)–Pd(1a)	3.892
Pd(1)–Pd(1b)	4.967	S(1)–Pd(1b)	4.351
S(3)–Pd(1b)	3.646	S(4)–S(1a)	3.360
S(2)–S(1c)	3.807	S(3)–S(2d)	3.681
S(2)–S(2e)	3.576	S(3)–S(2a)	3.348
S(4)–S(2e)	3.701	S(3)–S(3b)	4.198
S(4)–S(3c)	3.849		

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): (*a*) $1.0 - x, -y, 1.0 - z$; (*b*) $-0.5 + x, y, 0.5 - z$; (*c*) $0.5 + x, y, 0.5 - z$; (*d*) $-1.0 + x, y, z$; (*e*) $2.0 - x, -y, 1.0 - z$.

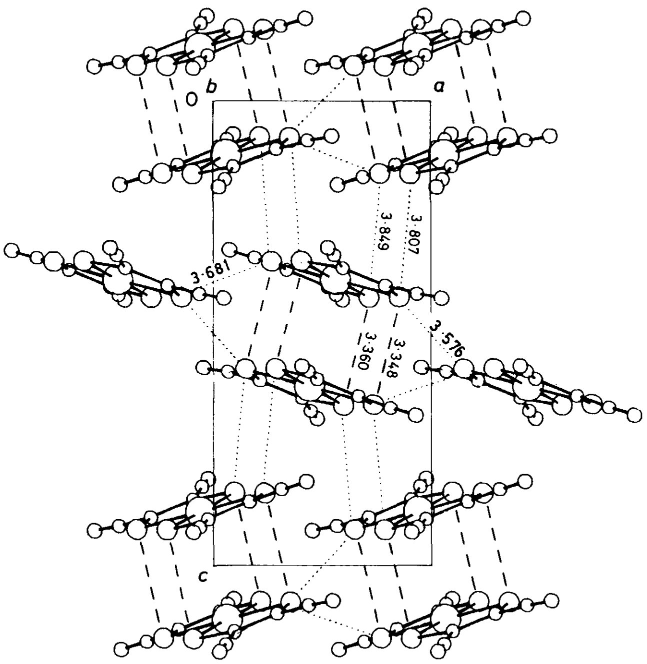

Figure 2. A view along the b axis showing the structure of the anion sheet and S $\cdots$ S contacts within the dimer indicated by bold lines

plane is coincident with the crystallographic mirror plane and the main O–H $\cdots$ contacts are with Cs^+ ions.

Low-temperature Studies.—A study has been made of the *X*-ray diffraction pattern of $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot0.5H_2O$ between room temperature and 100 K. Unfortunately the crystal quality was not sufficient for a detailed structural study. However, it is clear that as the temperature is lowered a three-fold structure develops along the a axis below about 200 K (see Figure 3). Figure 2 also shows the change in intensity of the (1, 2, 1) main peak and growth in intensity of the two satellite reflections at $(2\frac{1}{3}, 2, 11)$ and $(\frac{1}{3}, 8, 11)$ below 200 K. At 170 K the lattice constants are a = 19.186, b = 29.81, and c = 13.731 Å. The temperature dependence of the lattice parameters is given in Figure 4. The irregular change with temperature of the lattice parameter for the b axis was confirmed in a second crystal and may be due to the presence of water molecules in this direction.

Discussion

The structure of $Cs_{0.82}[Pd\{S_2C_2(CN)_2\}_2]\cdot0.5H_2O$ described above is novel for complexes of this type. The anions are strongly associated in dimer pairs, an arrangement previously observed for the $[Pt\{S_2C_2(CN)_2\}_2]^-$ monoanions. The high electrical conductivity and metallic properties under pressure must originate from the unusual arrangement of these dimers in

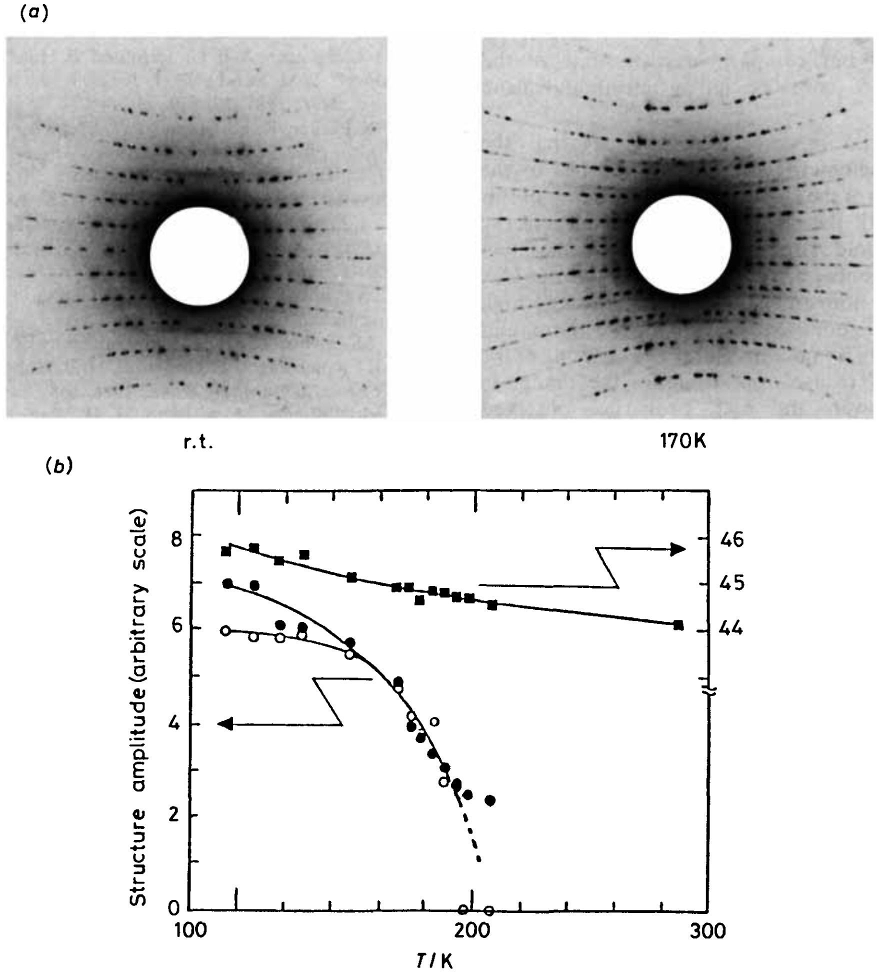

Figure 3. (*a*) *X*-Ray photographs showing tripling of the a axis on cooling to low temperatures. (*b*) Variation of intensity with temperature of (■) (1, 2, 1) main peak, and (○) $(2\frac{1}{3}, 2, 11)$ and (●) $(\frac{1}{3}, 8, 11)$ satellite peaks

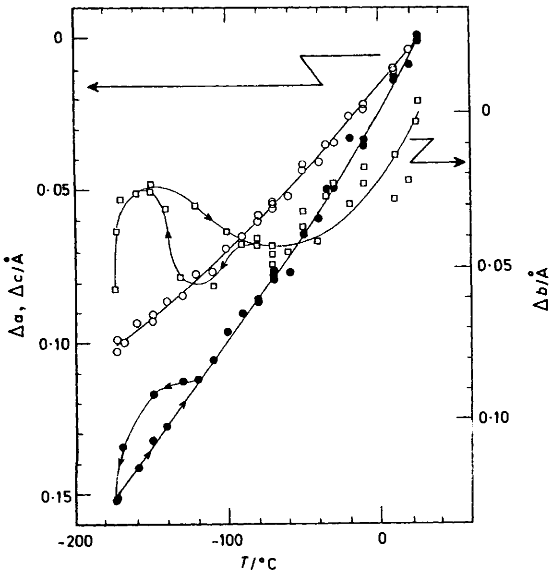

Figure 4. Temperature dependence of the cell parameters: *a* (○); *b* (□); and *c* (●)

the *ac* plane. This arrangement gives rise to the close S···S contacts between dimers as illustrated in Figure 2 and results in a two-dimensional network of short S–S contacts. The shortest inter-dimer S···S contacts in the *a* direction (3.58 Å) are considerably shorter than those found previously in $[NH_4][Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ but comparable with some of the short interstack S···S contacts in a tetrathiafulvalene compound.[13]

The Cs:Pd mole ratio reported here suggests that the compound is non-stoicheiometric and this is confirmed by the partial occupancy of one of the Cs sites. The $\frac{2}{3}$ occupancy of this site is in agreement with the chemical stoicheiometry of the compound. The three-fold structure observed in the low-temperature data presumably arises from ordering of the Cs^+ ions in these sites. The non-stoicheiometry explains the high conductivity observed at room temperature for the compound and its metal-like properties under pressure. The ordering of the cations below *ca.* 200 K is also responsible for the change in conductivity, thermopower, and e.s.r. properties observed around this temperature.[6]

High conductivity in metal complexes has usually been associated with non-stoicheiometric compounds containing an equidistant stack of anions. The structure of the Cs salt is quite different in that it contains the anions strongly associated as dimer pairs, and a non-stack structure. Dimer pairs of anions are usually associated with integral oxidation state monoanions such as those found in $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$. In the present compound it appears that the Cs^+ ion is sufficiently bulky to perturb the expected stack of dimers and facilitate close S···S inter-dimer interaction along *a*. This allows the subsequent oxidation of the $[Pd\{S_2C_2(CN)_2\}_2]_2{}^{2-}$ dimer at the anode producing the Cs salt with a partially filled band and metal-like properties. However, a full understanding of these properties must await the results of band structure calculations based on the detailed structure presented here.

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