Notes

Crystal Structure and Electrical Conduction Properties of $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$.† The Precursor of a One-dimensional Metal

Munir M. Ahmad, Derek J. Turner, and Allan E. Underhill *
Department of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW
Akiko Kobayashi and Yukiyoshi Sasaki
Department of Chemistry, The University of Tokyo, Hongo 113, Japan
Hayao Kobayashi
Department of Chemistry, Tokyo University, Funabashi, Chiba 274, Japan

The preparation, crystal structure, and electrical conduction properties of $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ are described. The planar anions are arranged in a dimeric eclipsed configuration to form a columnar stacked structure. The room-temperature conductivity in the platinum atom chain direction is 2.5×10^{-5} Ω^{-1} cm^{-1} and the compound behaves as a semiconductor.

The discovery of a new type of one-dimensional metallic complex based on bis[(*Z*)-1,2-dicyanoethylene-1,2-dithiolato]platinate anions has aroused considerable interest in this class of compound.[1,2] Dithiolate complexes exist as a series of compounds with the same central metal ion in different formal oxidation states; for example, the 0, −1, and −2 charged complexes of nickel, palladium, and platinum are well known.[3] Compounds with integral oxidation states have been shown to exhibit low electrical conductivities and behave as semiconductors or insulators whereas compounds with non-integral oxidation states, *e.g.* $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$, exhibit high conductivities and metallic properties in the platinum atom chain direction.[4,5]

It is very important, therefore, to elucidate the chemical factors which determine whether or not metallic complexes of non-integral oxidation state can be formed. There appear to be two principal factors.

(*a*) In this class of one-dimensional metal the ligand π-system (with a major contribution from the sulphur orbitals) is involved in the intra-chain overlap to form the conducting band.[1] Thus they differ from the non-integral oxidation state tetracyanoplatinates and bis(oxalato)platinates in which the conduction band is thought to arise from overlap of the platinum d_{z^2} and p_z orbitals.[6] Therefore the electron distribution within the π system of the complex is very important. The failure to obtain metallic complexes with $S_2C_2R_2^{2-}$ where R = Ph, H, or Me, in which the π-distribution is very different from that of the cyano-substituted complex, supports this view.[4,7]

(*b*) The one-dimensional metallic complex $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ possesses a columnar stack structure with the anions arranged in an eclipsed configuration.[8] ‡ This arrangement of anions is unusual since previous studies have shown the dianion salts to contain isolated anions whereas the monoanion salts often possess columnar stacks containing anion dimers with a staggered configuration.[9] Those studies were made, however, on salts of bulky organic cations. The influence of small cations on the structure adopted by these complex anions may be crucial for the establishment of the eclipsed columnar stack structure necessary for the formation of highly conducting metal complexes.

We now report the first structure determination and electrical conductivity study of a monoanion metal dithiolate salt containing a small alkali metal cation.

Experimental

$Rb_{0.8}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ was obtained as a black microcrystalline powder under the same conditions used for the preparation of $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ [1] (Found: C, 17.4; H, 0.4; N, 9.7; Rb, 11.4. Calc. for $C_8H_4N_4O_2PtRb_{0.8}S_4$: C, 16.6; H, 0.7; N, 9.7; Rb, 11.8%). Unfortunately no single crystals were obtained. Attempted recrystallisation of the black powder from IMS (industrial methylated spirits), however, yielded black crystals of the integral oxidation state salt $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ (Found: C, 16.6; H, 0.3; N, 9.6; Pt, 33.1; Rb, 12.9. Calc. for $C_8H_4N_4O_2PtRbS_4$: C, 16.1; H, 0.7; N, 9.4; Pt, 32.7; Rb, 14.3%).

X-Ray Data Collection and Structure Analysis.—Crystals of $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ are black (triclinic) parallelepipeds.

Crystal data. $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$, $M = 596.93$, triclinic, space group $P1$, $a = 14.659(17)$, $b = 7.179(6)$, $c = 6.734(7)$ Å, $\alpha = 98.37(7)$, $\beta = 97.39(11)$, $\gamma = 92.55(10)^\circ$, $U = 693.89$ Å^3, $Z = 2$, $D_c = 2.858$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu = 148.98$ cm^{-1}.

All the *X*-ray diffraction intensities were measured on a Rigaku automatic four-circle diffractometer with ω—2θ scan mode using graphite-monochromated Mo-K_α radiation. The intensities were corrected for the absorption effect and 3 305 independent reflections ($|F_o| > 3\sigma|F_o|$) were used. The dimensions of the crystal were $0.33 \times 0.19 \times 0.04$ mm. The structure was solved by the usual heavy-atom method. Atomic scattering factors for anomalous scattering were taken from International Tables.[10] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The function minimized was $w(|F_o| - |F_c|)^2$, where $w = 0.2$ for $|F_o| < 15$ and $w = 1/[\sigma(F_o)^2 + c|F_o|^2]$ otherwise ($c = 0.003$). The final R value was 0.045. Fractional atomic co-ordinates are in Table 1.

---

† Rubidium bis[(*Z*)-1,2-dicyanoethylene-1,2-dithiolato]platinate(1−) dihydrate.

Supplementary data available (No. SUP 23920, 12 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

‡ This compound was initially reported as $Li_{0.75}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ (ref. 1) but recent low-temperatue *X*-ray studies indicate that it should be shown as $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$.

Table 1. Fractional atom co-ordinates (× 10^5) for Rb[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	1 707(3)	27 453(6)	4 844(7)	C(5)	32 130(81)	42 235(150)	13 307(156)
Rb	46 059(9)	19 497(17)	77 056(18)	C(6)	26 607(81)	46 830(156)	51 017(161)
S(1)	15 268(21)	31 054(39)	−7 043(41)	C(7)	−22 899(83)	5 137(162)	−40 915(161)
S(2)	8 636(20)	37 432(41)	37 000(41)	C(8)	−28 518(82)	10 216(154)	−2 932(156)
S(3)	−5 302(21)	17 266(39)	−27 104(41)	N(1)	39 788(71)	45 374(146)	12 642(148)
S(4)	−11 837(21)	24 009(40)	16 760(41)	N(2)	32 383(77)	50 725(155)	64 085(145)
C(1)	22 709(75)	38 561(139)	14 633(150)	N(3)	−28 420(84)	−779(160)	−53 961(146)
C(2)	19 789(73)	41 049(142)	33 597(147)	N(4)	−36 003(75)	6 012(157)	−1 987(154)
C(3)	−16 220(78)	12 474(140)	−23 766(154)	O	48 169(68)	78 850(126)	62 640(126)
C(4)	−19 154(74)	15 285(143)	−4 818(152)				

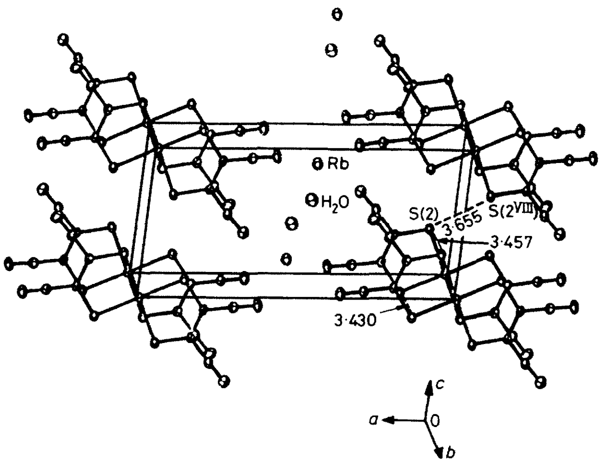

Figure 1. Crystal structure of Rb[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ (*b* * projection)

Results and Discussion

Figure 1 shows the *b** axis projection of the crystal structure of Rb[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$. The [Pt{$S_2C_2(CN)_2$}$_2$]$^-$ anion is almost planar with average bond lengths Pt–S 2.260 and S–C 1.697 Å (Table 2). The planar anions are arranged face to face in an eclipsed configuration to form a columnar stacked structure. Rb[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ possesses a dimeric structure (see Figure 2), the interplanar spacing within the dimer being 3.356 Å and between dimers, 3.512 Å. This is different from the structure found for the one-dimensional metal $Li_{0.82}$[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ in which all the inter-anion distances within the columnar structures are equal.[8] In Rb[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ there are short S···S distances between anions in adjacent stacks (3.655 Å, Table 3) similar to those found in the Li compound (3.682 and 3.743 Å).[8]

Apart from the dimerisation of the anions, the structure of the rubidium salt is very similar to that of $Li_{0.82}$[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$. In both structures the columns of anions form two-dimensional sheets with close S···S contacts. These sheets are separated by the cations and water molecules, the cation being co-ordinated by the oxygen atoms of the water molecules and the cyano-group of the anions.

The structure of Rb[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ is quite different from that found for [NEt_4][Ni{$S_2C_2(CN)_2$}$_2$] in which there are columns of anion dimers, the anions within the dimers being staggered with respect to each other.[9] This is related to the arrangement of large bulky organic cations within the lattice. In addition there are no S···S contacts between adjacent columns and indeed the closest inter-chain contacts are between cyano-groups on adjacent stacks.

Table 2. Selected intramolecular bond lengths (Å) and angles (°)

Pt–S(1)	2.255(3)	C(3)–C(4)	1.388(15)
Pt–S(2)	2.270(3)	C(3)–C(7)	1.434(14)
Pt–S(3)	2.264(3)	C(4)–C(8)	1.431(16)
Pt–S(4)	2.252(3)	C(1)–C(5)	1.411(16)
S(1)–C(1)	1.709(10)	C(2)–C(6)	1.438(14)
S(2)–C(2)	1.694(11)	C(7)–N(3)	1.134(14)
S(3)–C(3)	1.672(12)	C(8)–N(4)	1.137(16)
S(4)–C(4)	1.711(10)	C(5)–N(1)	1.143(16)
C(1)–C(2)	1.388(15)	C(6)–N(2)	1.134(14)
S(1)–Pt–S(2)	90.6(1)	S(1)–C(1)–C(2)	122.0(8)
S(3)–Pt–S(4)	90.2(1)	S(2)–C(2)–C(1)	122.9(8)
Pt–S(1)–C(1)	102.4(3)	S(3)–C(3)–C(4)	122.5(8)
Pt–S(2)–C(2)	102.1(4)	S(4)–C(4)–C(3)	122.2(8)
Pt–S(3)–C(3)	102.9(4)	C(5)–C(1)–C(2)	118.8(9)
Pt–S(4)–C(4)	102.2(3)	C(6)–C(2)–C(1)	118.0(10)
		C(7)–C(3)–C(4)	117.9(10)
		C(8)–C(4)–C(3)	119.6(9)

Table 3. Intermolecular bond lengths (Å)

Pt···Pt^{IX}	3.899(1)	Rb···N(3^{IX})	2.993(11)
Pt···Pt^{II}	3.440(1)	Rb···N(1^{VI})	3.076(10)
S (2)···S(2^{VIII})	3.655(6)	Rb···N(4^{V})	3.084(11)
S (3)···S(2^{IV})	3.760(4)	Rb···N(4^{X})	3.104(11)
S (2)···S(3^{II})	3.457(4)	Rb···N(1^{III})	3.131(10)
Rb···O^{III}	2.922(9)	Rb···N(2^{I})	3.214(11)
Rb···O^{VII}	2.981(9)		

Key to symmetry operations

I	x, y, z	VI	$x, y, -1 + z$
II	$-x, 1 - y, -z$	VII	$x, 1 + y, z$
III	$1 - x, 1 - y, 1 - z$	VIII	$-x, 1 - y, 1 - z$
IV	$x, y, 1 + z$	IX	$-x, -y, -z$
V	$1 + x, y, 1 + z$	X	$-x, -y, 1 - z$

The d.c. conductivity (two-probe) of Rb[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ parallel to the columnar stack of anions ($\sigma_{\parallel}$) at room temperature is 2.5×10^{-5} Ω^{-1} cm^{-1}. This is not dissimilar to that observed for [NEt_4][Ni{$S_2C_2(CN)_2$}$_2$] (2.8×10^{-6} Ω^{-1} cm^{-1}) in spite of the differences in the mode of overlap between the anions in the dimer. This is probably because the magnitude of the conductivity will be controlled by an inter-dimer rather than intra-dimer hopping mechanism. The conductivity is very much lower than that observed for single crystals of $Li_{0.82}$[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ (10^2 Ω^{-1} cm^{-1})[1] or for compressed discs of the non-integral oxidation state, $Rb_{0.8}$[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ (0.5 Ω^{-1} cm^{-1}).

The temperature dependence of $\sigma_{\parallel}$ for a single crystal of Rb[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ and $Rb_{0.8}$[Pt{$S_2C_2(CN)_2$}$_2$]·$2H_2O$ is shown in Figure 3 and was found to be reproducible from crystal to crystal. The non-integral oxidation state salt

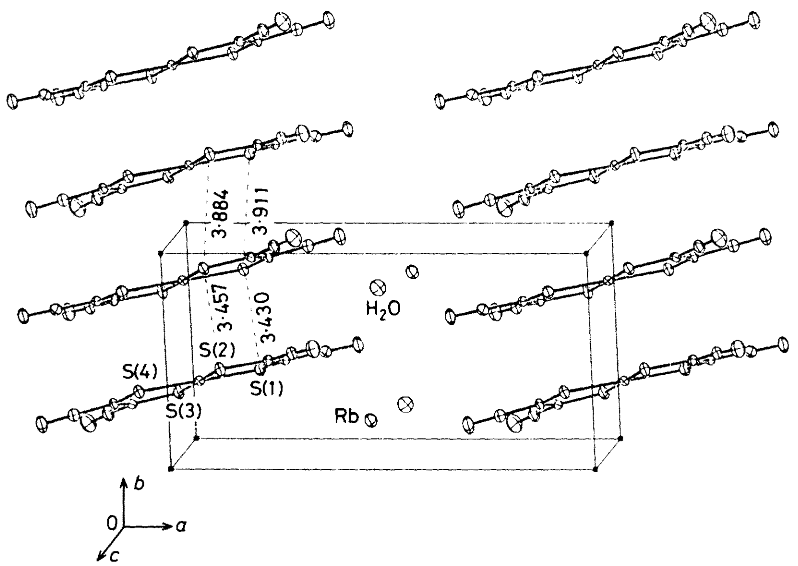

Figure 2. Crystal structure of $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot2H_2O$ (c^* projection) showing the dimer unit

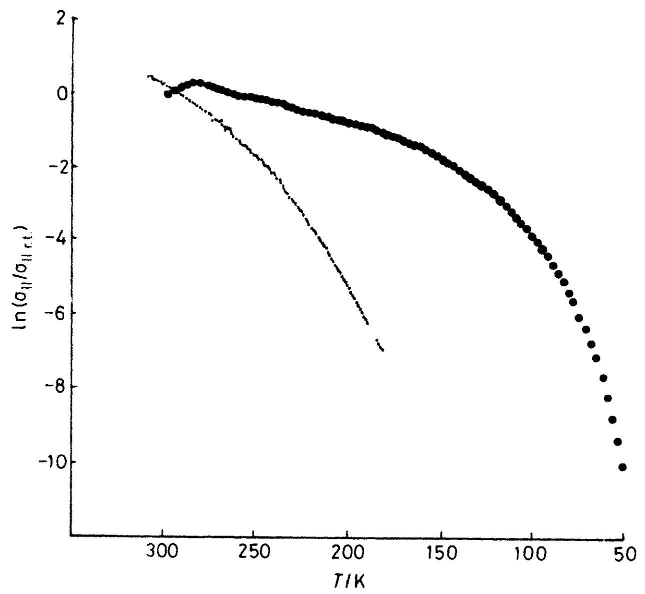

Figure 3. Temperature dependence of $\sigma_{\parallel}$ for $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot2H_2O$ (·····) and $Rb_{0.8}[Pt\{S_2C_2(CN)_2\}_2]\cdot2H_2O$ (● ● ●); $\sigma_{\parallel r.t.}$ = room-temperature conductivity

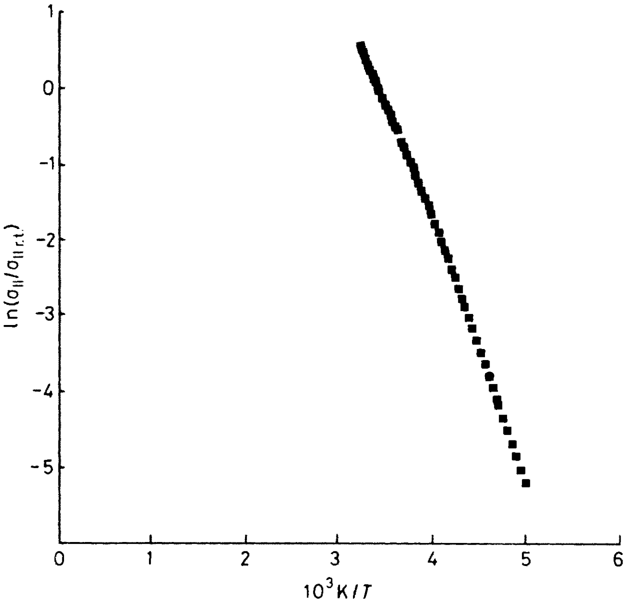

Figure 4. Variation of ln $\sigma_{\parallel}$ with inverse temperature for $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot2H_2O$; $\sigma_{\parallel r.t.}$ = room-temperature conductivity

exhibits metallic behaviour between 300 and 280 K and activated semiconduction (activation energy, $\Delta E = 56 \pm 2$ meV) below 170 K. This is very similar to that of single crystals of $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot2H_2O$ which exhibit an activation energy of 34 meV at low temperatures. However, $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot2H_2O$ shows activated semiconductor behaviour throughout the temperature range 310—200 K with an activation energy of 300 ± 5 meV above 250 K and 240 ± 5 meV below this temperature (Figure 4). These activation energies compare with the value of 350 meV found for $[NEt_4][Ni\{S_2C_2(CN)_2\}_2]$.[8]

The close similarities observed between the structures of $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot2H_2O$ and $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot2H_2O$ indicate that the crystal structure in the one-dimensional metal is determined by the cations and water of hydration rather than one-dimensional bonding within the chain. It appears therefore that this combination of small cation and water of hydration allows the formation of an eclipsed columnar stack structure. In addition the interactions between the ligand cyano-groups and the cations and water molecules stabilise a parallel arrangement of anion columns allowing close S···S contacts between adjacent columns resulting in a two-dimensional structure. The presence of large hydrophobic cations and the absence of water of crystallisation as in $[NEt_4][Ni\{S_2C_2(CN)_2\}_2]$ gives rise to quite a different type of structure and thus prevents the formation of a one-dimensional metal upon attempted partial oxidation.

The $[Pt\{S_2C_2(CN)_2\}_2]^{2-}$ anion is diamagnetic with two electrons in the highest delocalised π orbital of the metal–ligand system. Interaction of the π orbitals on adjacent molecules within the stack makes possible the formation of a band system within the stack direction. In $Li_{0.82}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ the band is 41% filled and one-dimensional metallic properties are observed. In $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$, where the highest occupied molecular orbital contains one electron, the band would be half filled and a Peierls distortion would be expected to produce a dimerisation of the unit cell with a band gap at the Fermi level, resulting in semiconducting properties. This is just what is observed in both the structure and electrical conduction properties of this compound.

The results presented here illustrate the importance of considering the influence of the cation and of water of crystallisation on the crystal structures of potential one-dimensional metals. Within this series of highly-conducting metal dithiolates the cations and water molecules play just as important a role as they have been shown to do in the partially oxidised tetracyanoplatinates.[11]

Acknowledgements

We would like to thank the S.E.R.C. and N.A.T.O. for support and Johnson Matthey for the loan of platinum salts.

References

1 A. E. Underhill and M. M. Ahmad, *J. Chem. Soc., Chem. Commun.*, 1981, 67; *Mol. Cryst. Liq. Cryst.*, 1982, **81**, 223; *J. Chem. Soc., Dalton Trans.*, 1982, 1065.
2 W. A. Little, *J. Phys. (Paris)*, 1983, **C3**, 819; J. R. Cooper, M. Miljak, M. M. Ahmad, and A. E. Underhill, *ibid.*, p. 1391.
3 R. P. Burns and C. A. Mcauliffe, *Adv. Inorg. Chem. Radiochem.*, 1978, **22**, 303 and refs. therein.
4 M. M. Ahmad and A. E. Underhill, *J. Chem. Soc., Dalton Trans.*, 1983, 165.
5 D. R. Rosseinsky and R. E. Malpas, *J. Chem. Soc., Dalton Trans.*, 1979, 749.
6 A. E. Underhill and D. M. Watkins, *Chem. Soc. Rev.*, 1980, **9**, 429 and refs. therein.
7 G. N. Schrauzer and H. N. Rabinowitz, *J. Am. Chem. Soc.*, 1968, **90**, 4297.
8 A. Kobayashi, Y. Sasaki, H. Kobayashi, A. E. Underhill, and M. M. Ahmad, *J. Chem. Soc., Chem. Commun.*, 1982, 390.
9 A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2650.
10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
11 A. E. Underhill, D. J. Wood, and K. Carneiro, *Synth. Met.*, 1979, **1**, 395; A. E. Underhill, *Chem. Scr.*, 1981, **17**, 179.

Received 21*st June* 1983; *Paper* 3/1053