Inorganica Chimica Acta, 163 (1989) 93–98

The First Example of a Stacked Structure Containing the 5,6-Dihydro-1,4-dithiin-2,3-dithiolate Ligand: the Crystal Structure of $[(C_2H_5)_4N][Pt(DDDT)_2]$

JANE HANNA WELCH, ROBERT D. BEREMAN* and PHIRTU SINGH

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204 (U.S.A.)

(Received January 24, 1989; revised April 17, 1989)

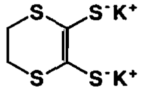
Abstract

The crystal structure of $[(C_2H_5)_4N][Pt(DDDT)_2]$ where $DDDT^{2-}$ = 5,6-dihydro-1,4-dithiin-2,3-dithiolate belongs to the monoclinic space group $C2/c$ with unit cell dimensions $a = 22.199(6)$, $b = 8.206(2)$, $c = 17.698(4)$ Å, $\beta = 130.87(1)°$, $Z = 4$. The Pt and N atoms lie on an inversion center and a two-fold axis, respectively. The PtS_4 core exhibits square planar coordination with an average Pt–S bond length of 2.270(6) Å. This structure represents the first transition metal complex of the $DDDT^{2-}$ ligand containing stacks of planar anions. The stacks interlock to form a layer. The molecular packing diagram shows alternating cation and anion layers.

Introduction

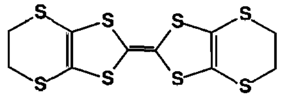
The first report of an 'organic metal', tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ), appeared fifteen years ago and was the impetus for the massive research effort which has led to the synthesis of organic superconductors. This charge transfer complex exhibited metallic behavior between room temperature and 66 K [1]. The crystal structures of TTF–TCNQ [2], and the superconducting perchlorate [3], hexafluoroarsenate [4], and hexafluorophosphate [5] salts of tetramethyltetraselenafulvalene, $(TMTSF)_2X$, have elucidated many structural features necessary for the conduction of electrons. The requirements for the metallic state, both structural and electronic, have been addressed in several reviews [6–14]. A prerequisite for conductivity is a planar molecule which forms segregated stacks in the crystal lattice.

The discovery of the first totally sulfur-based organic superconductor, bis(ethylenedithiolotetrathiafulvalenium)rhenate [15] $(BEDT–TTF)_2ReO_4$, offered further stimulus to the potential of the 'TTF' framework. We recently reported a new 1,2-dithiolene, 5,6-dihydro-1,4-dithiin-2,3-dithiolate ($DDDT^{2-}$), which was synthesized as the potassium salt. Complexes of this ligand with Ni, Pd, Pt, Cu, and Co have been synthesized with the general formula $M(DDDT)_2^-$ and isolated as tetraalkylammonium salts [16–19].

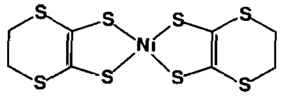


K₂DDDT

A structural study of this series of complexes began with the crystal structure of $[(C_2H_5)_4N]$-$[Ni(DDDT)_2]$ [16]. The $Ni(DDDT)_2^-$ anion exhibits square planar coordination. A crystallographic analysis showed the anion to have structural features quite similar to the BEDT–TTF partially oxidized cation.



BEDT-TTF



Ni(DDDT)$_2^-$

The packing of the tetraethylammonium salt showed sheets of $Ni(DDDT)_2^-$ anions instead of stacks yet this produced some close S···S contacts resulting in long-range antiferromagnetic interactions evidenced in magnetic measurements [16]. This observation has led us to continue to study these complexes.

The significant role of the counter ion on crystal structure and thus physical properties has been established. An investigation into the effect of the counter ion on the crystal structures of $DDDT^{2-}$ complexes was initiated by the synthesis of the tetrabutylammonium and trimethylammonium salts of $Cu(DDDT)_2^-$ [18]. Subsequently, the structures of the

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

© Elsevier Sequoia/Printed in Switzerland

tetramethylammonium and tetrabutylammonium salts of $Ni(DDDT)_2^-$ have been reported [20, 21]. While decreases in S···S contacts have been observed in some cases, none exhibit segregated stacking of planar anions in the crystal lattice. More recently, the structure of the Co complex was determined and found to be dimeric [19]. The intradimer S···S contacts are shorter than the interdimer distances with three significantly less than the van der Waals distance of 3.70 Å. We believe this to be a measure of the theoretical limit of S···S contacts in these systems.

To data, six Pt dithiolene structures have been reported. Two structures show dimeric Pt complexes. Of these, one exhibits metal–metal bonding yet the dimeric units do not stack in the crystal lattice [22]. The other structure shows stacking of monomer units in which the interplanar spacing differs resulting in a dimeric association between the Pt complex anions [23]. Three structures contain monomeric Pt complexes, two of which exhibit stacking [24–26]. The most recent structure published contains monomer and dimer units that alternate in the same stack [27].

The interesting structural aspects observed in square planar complexes of $DDDT^{2-}$ and the various structural forms of Pt dithiolenes have prompted us to examine the structure of $[(C_2H_5)_4N][Pt(DDDT)_2]$. Stacking of the $Pt(DDDT)_2^-$ anions is seen along the *b* axis. This report discusses the structural features of this complex in comparison to other $DDDT^{2-}$ complexes and platinum dithiolene structures.

Experimental

Synthesis of $[(C_2H_5)_4N][Pt(DDDT)_2]$

The complex salt was synthesized by the literature method [17]. Dark red crystals suitable for X-ray analysis were grown from slow evaporation of an acetonitrile solution at 0 °C.

Single-crystal X-ray Analysis

A representative crystal was surveyed, and cell dimensions were obtained by a least-squares fit of setting angles of 20 high-angle reflections ($2\theta > 15°$). A data set was collected on a Nicolet R3m/μ diffractometer equipped with a graphite monochromator and molybdenum radiation (λ = 0.71069 Å). Systematic absences indicated that the crystal belonged to the monoclinic space group *Cc* or *C*2/*c* (hkl, $h + k = 2n + 1$; $h0l$, $h, l = 2n + 1$). The latter was confirmed as the correct space group by the successful refinement of the structure. One check reflection collected after every 49 reflections revealed no unexpected variation in intensity. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was made using a psi scan because of the large absorption coefficient (67.1 cm^{-1}). An isotropic secondary extinction correction was made (secondary extinction coefficient = 4.2×10^{-7}). Atomic scattering factors for all atoms were taken from the International Tables for X-Ray Crystallography [28]. Pertinent crystal, data collection, and refinement parameters are summarized in Table 1.

TABLE 1. Single crystal X-ray crystallographic analysis

Crystal parameters	
Formula	$PtC_{16}H_{28}NS_8$
Molecular weight	686.01
Crystallization medium	acetonitrile
Crystal size (mm)	0.25 × 0.20 × 0.01
Crystal color	deep red
Crystal habit	thin plate
Cell dimensions	$a = 22.199(6)$ Å $b = 8.206(2)$ Å $c = 17.698(4)$ Å $\beta = 130.87(1)°$
Volume	2438.0(7) $Å^3$
Space group	*C*2/*c*
Molecules/unit cell	4
Density calc. (g/cm^3)	1.87
F(000)	1348
Data collection parameters	
Radiation	Mo Kα
Temperature	298 K
2θ range	3–45°
Scan type	θ–2θ
Scan speed	variable, 4–29.3°/min
Octants collected	hkl, $hk\bar{l}$
No. reflections recorded	1837
No. reflections used ($I > 2\sigma(I)$)	1202
Background measurement	1/2 of total scan time at beginning and end of each scan
Linear absorption coefficient	67.1 cm^{-1}
Refinement parameters[a]	
Final *R* index	$R = 0.056$ $R_w = 0.068$
Goodness of fit	1.49
Largest Δ/σ	0.4
Data/parameter ratio	9.5

[a] The data fit criteria (based on reflections having $I > 2\sigma(I)$) were $R = \Sigma||F_o| - |F_c||/\Sigma F_o$; $R_w = [\Sigma w(\Delta F)^2/\Sigma F_o^2]^{0.5}$; $GOF = \Sigma(w[||F_o| - |F_c||]^2/[N_o - N_v])^{0.5}$.

The platinum and four sulfur atoms were located by the direct-methods program SOLV of the crystallographic program package SHELXTL [29]. The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. The structure was refined by the block-diagonal least-squares technique using SHELXTL on a Data General Microeclipse computer. The quantity minimized was $\Sigma w(\Delta F)^2$, where $w =$

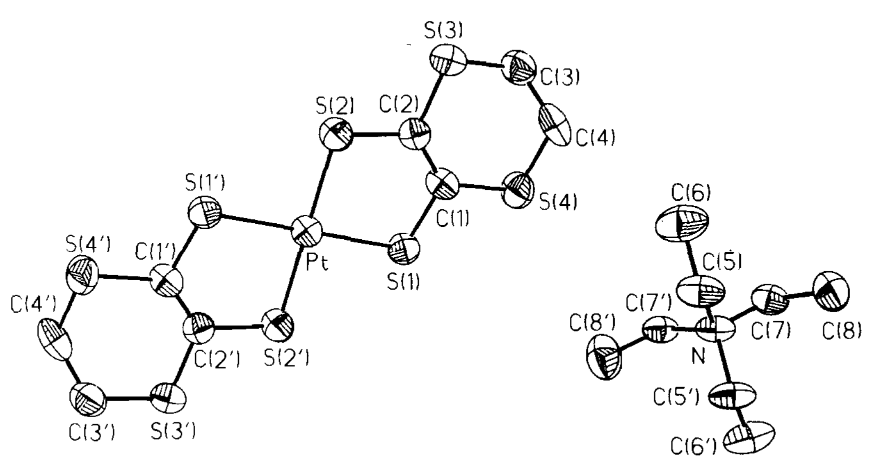


Fig. 1. Structure and numbering scheme for $[(C_2H_5)_4N][Pt(DDDT)_2]$. Thermal ellipsoids are drawn at the 50% probability level.

$1/(\sigma_F^2 + 0.001F^2)$. The non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions 0.96 Å away from the attached carbon atom and were not refined. The final *R* indices are given in Table 1. See also 'Supplementary Material'. The refined structure was plotted by using the SHELXTL graphics package.

Results and Discussion

The structure and numbering scheme of the cation and anion are shown in Fig. 1. The asymmetric unit contains only half of each ion with the Pt and N atoms occupying special positions. The Pt atom lies on an inversion center and the N atom is located on a two-fold axis. Atomic coordinates are given in Table 2. Bond lengths and bond angles are shown in Tables 3 and 4 respectively. The standard deviations of some of the positional parameters, bond lengths and bond angles are slightly high yet the structure is well established. Similar deviations were noted in the structure of the Pt complex of bis(ethylene-1,2-dithiolene) [22].

TABLE 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	U^a
Pt	2500	2500	2500	45(1)
S(1)	3159(2)	1351(5)	4556(3)	53(3)
S(2)	1361(2)	2328(5)	3379(3)	52(2)
S(3)	849(3)	1247(5)	1483(3)	58(3)
S(4)	2835(3)	220(6)	2777(4)	67(3)
C(1)	2431(9)	1062(18)	3275(10)	45(10)
C(2)	1671(10)	1495(17)	2778(11)	47(11)
C(3)	1258(10)	-83(23)	1098(12)	66(13)
C(4)	2046(10)	522(23)	1454(12)	70(14)
N	5000	2033(19)	2500	46(12)
C(5)	4281(10)	3199(23)	1945(13)	70(13)
$C(6)^b$	3498	2293	1363	.90(16)
C(7)	4948(9)	899(18)	1764(11)	53(11)
C(8)	4873(13)	1731(28)	969(15)	86(17)

^{a}Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b}The coordinates of C(6) were fixed.

TABLE 3. Bond lengths (Å)

Pt–S(1)	2.270(6)	Pt–S(2)	2.269(3)
S(1)–C(1)	1.74(1)	S(2)–C(2)	1.74(3)
S(3)–C(2)	1.78(1)	S(3)–C(3)	1.81(3)
S(4)–C(1)	1.76(2)	S(4)–C(4)	1.80(2)
C(1)–C(2)	1.34(3)	C(3)–C(4)	1.50(3)
N–C(5)	1.54(2)	N–C(7)	1.54(2)
C(5)–C(6)	1.51(2)	C(7)–C(8)	1.47(4)

The four sulfurs surround the Pt atom yielding square planar coordination with an average Pt–S bond length of 2.270(6) Å. The unique S–Pt–S angle is 88.5°. The average S–C bond length is 1.77(3) Å. When these S–C bonds are classified into ones in the five-membered ring formed through coordination with Pt and those in the periphery of the ligand the averages are 1.74(3) and 1.79(3) Å respectively. These values indicate the slight incidence of electron delocalization in the metal ligand coordination ring characteristic of transition metal dithiolenes. The C=C and C–C bond lengths within the ligand have standard values. The two outer carbons of the ligand pucker above and below the plane formed by the Pt and other ligand atoms. A least-squares calculation of this plane shows carbons 3 and 4 to lie –0.42 and +0.45 Å out of the plane respectively. A discussion of the random orientation of this $-CH_2CH_2-$ fragment is presented elsewhere [19].

Table 5 compares important bond lengths of $Pt(DDDT)_2^-$ to other reported Pt dithiolenes. The

TABLE 4. Bond angles (°)

S(1)–Pt–S(2)	88.5(2)	S(2)–Pt–S(1′)	91.5(2)
S(2)–Pt–S(2′)	180.0(1)	Pt–S(1)–C(1)	104.4(8)
Pt–S(2)–C(2)	103.8(5)	C(2)–S(3)–C(3)	102.1(8)
C(1)–S(4)–C(4)	103(1)	S(1)–C(1)–S(4)	111.3(9)
S(1)–C(1)–C(2)	121(2)	S(4)–C(1)–C(2)	128(1)
S(2)–C(2)–S(3)	111(1)	S(2)–C(2)–C(1)	122(1)
S(3)–C(2)–C(1)	127(2)	S(3)–C(3)–C(4)	112(1)
S(4)–C(4)–C(3)	112(2)	C(5)–N–C(7)	111.2(9)
C(5)–N–C(5′)	103(2)	C(7)–N–C(5′)	113(1)
C(7)–N–C(7′)	106(2)	N–C(5)–C(6)	112(1)
N–C(7)–C(8)	115(2)		

TABLE 5. Comparison of bond lengths in Pt dithiolenes [a]

Monomer/dimer	Complex				
	$PtS_4C_4H_4$ [b] dimer	$Li_{0.82}Pt[S_2C_2(CN)_2]_2 \cdot 2H_2O$ [c] monomer	$TTF[Pt(dmit)_2]_3$ [d]		$[(C_2H_5)_4N][Pt(DDDT)_2]$ [e] monomer
			monomer	dimer	
Pt–Pt	2.748(2)			2.935(3)	
Pt–S	2.297(7)	2.271	2.30(1)	2.31(1)	2.270(6)
S–C	1.68(3)	1.720	1.68(5)	1.70(6)	1.77(3)
C=C	1.40(4)	1.355	1.46(6)	1.43(8)	1.34(3)

[a] Where no deviation is shown, none was given in the original paper. [b] Ref. 22. [c] Ref. 26. [d] Ref. 27. Structure contains monomers and dimers. [e] This work.

first observation is the similarity in Pt–S distances in this structure and that of $Li_{0.82}Pt[S_2C_2(CN)_2]_2 \cdot 2H_2O$. These two structures consist of monomeric complexes only. For dimeric structures, the Pt–S length is longer as expected due to the metal–metal bond pulling the Pt atom away from the plane of the ligand. The S–C bond lengths for the monomers are longer than those for the dimers with the value for $Pt(DDDT)_2^-$ being the longest. An opposite effect is seen for the C=C distances with $Pt(DDDT)_2^-$ having the shortest value. Two conclusions can be drawn from these trends. First, the dimeric complexes have more delocalization in the metal–ligand coordination ring than monomers. Secondly, the monomer $Li_{0.82}Pt[S_2C_2(CN)_2]_2 \cdot 2H_2O$ exhibits more delocalization in this ring than in the $Pt(DDDT)_2^-$ complex. A final observation is the lack of significant difference in values for monomeric and dimeric units contained in the same structure, $TTF[Pt(dmit)_2]_3$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate).

The tetraethylammonium counterion exhibits characteristic bond lengths with averages for N–C and C–C distances of 1.54(2) and 1.49(4) Å respectively. The expected tetrahedral structure contains a unique C–N–C angle of 111.2(9)°. Carbon 6 presented some problems in the final stages of structure refinement. Large shifts occurred for this atom in each least-squares cycle. The shifts were oscillating in the *y* direction. Disorder of this type has been noted resulting in high thermal parameters and inaccurate bond lengths [19, 20, 30]. In order to assure that shifts for other atoms were small, we fixed the coordinates of C6. It is worth comment that the *R* value did not decrease as a result of these fixed coordinates. Thus, the *R* factor is a true indication of structure refinement.

A stereoview of the cell packing is shown in Fig. 2 looking down the *b* axis. The anions form stacks along this axis. The anions in adjacent stacks are tilted oppositely and overlap to form a layer of interlocking stacks. The counterions are located between these layers of $Pt(DDDT)_2^-$ anions creating an alternating pattern of cation and anion sheets. The cell packing of the tetraethylammonium salt of $Ni(DDDT)_2^-$ was also described as layered yet the anions did not form stacks [16]. The tilting and interlocking of anions has been reported for the tetramethylammonium salt of $Ni(DDDT)_2^-$ however, the stacks in this salt consist of alternating cations and anions [20].

Another feature of conducting organo–sulfur compounds is close S···S contacts within the crystal lattice. A key interest in the crystallographic analysis of square planar $DDDT^{2-}$ complexes is the determina-

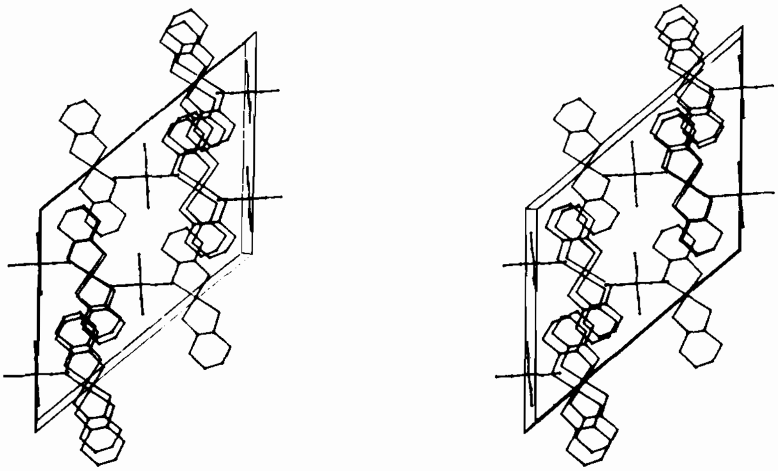


Fig. 2. Stereoview of the molecular packing for $[(C_2H_5)_4N][Pt(DDDT)_2]$.

tion of these contact distances. Unfortunately, the Pt anions in the stacks are separated by 8.2 Å, the length of the *b* axis, disallowing any close S···S contacts in this area. There are only two values less than 5 Å, 4.65 and 4.48 Å, that correspond to S2–S2′ and S3–S3′, respectively. These contacts occur in the interlocking region between stacks where the anions overlap. To date, the closest S···S contacts for $DDDT^{2-}$ complexes occur in the Co species [19].

Supplementary Material

Tables of anisotropic temperature factors and hydrogen coordinates (1 page), and a listing of calculated and observed structure factors (10 pages) are available from the authors on request.

Acknowledgements

We wish to thank the National Science Foundation for funds toward upgrading our diffractometer (Grant CHE-8307022). This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References

1 J. Ferraris, D. O. Cowan, V. Walatka and J. H. Perlstein, *J. Am. Chem. Soc., 95* (1973) 948.
2 T. J. Kistenmacher, T. E. Phillips and D. O. Cowan, *Acta Crystallogr., Sect. B, 30* (1974) 763.
3 K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen and J. C. Scott, *J. Am. Chem. Soc., 103* (1981) 2440.
4 F. Wudl, *J. Am. Chem. Soc., 103* (1981) 7064.
5 N. Thorup, G. Rindorf, H. Soling and K. Bechgaard, *Acta Crystallogr., Sect. B, 37* (1981) 1236.
6 M. L. Khidekel and E. I. Zhilyaeva, *Synth. Met., 4* (1981) 1.
7 A. F. Garito and A. J. Heegar, *Acc. Chem. Res., 7* (1974) 232.
8 F. Wudl, *Acc. Chem. Res., 17* (1984) 227.
9 J. M. Williams, *Prog. Inorg. Chem., 33* (1985) 183.
10 P. M. Chaikin and R. L. Greene, *Phys. Today, 39* (1986) 24.
11 R. L. Greene and P. M. Chaikin, *Physica B + C, 126* (1984) 431.
12 R. L. Greene and G. B. Street, *Science, 226* (1984) 651.
13 D. Jérôme and H. J. Schulz, *Adv. Phys., 31* (1982) 299.
14 J. M. Williams, M. A. Beno, H. H. Wang, P. C. Leung, T. J. Emge, U. Geiser and K. D. Carlson, *Acc. Chem. Res., 18* (1985) 261.
15 S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott and R. L. Greene, *Phys. Rev. Lett., 50* (1983) 270.
16 C. T. Vance, R. D. Bereman, J. Bordner, W. E. Hatfield and J. H. Helms, *Inorg. Chem., 24* (1985) 2905.
17 C. T. Vance and R. D. Bereman, *Inorg. Chim. Acta, 149* (1988) 229.
18 C. T. Vance, *Ph.D. Thesis,* North Carolina State University, 1985.
19 J. H. Welch, R. D. Bereman, P. Singh and C. G. Moreland, *Inorg. Chim. Acta, 158* (1989) 17.
20 J. H. Welch, R. D. Bereman, P. Singh, D. Haase, W. Hatfield and M. Kirk, *Inorg. Chim. Acta, 162* (1989) 89.
21 J. H. Welch, R. D. Bereman and P. Singh, *Inorg. Chem., 27* (1988) 3680.
22 K. W. Browall, T. Bursh, L. V. Interrante and J. S. Kasper, *Inorg. Chem., 11* (1972) 1800.
23 M. M. Ahmad, D. J. Turner, A. E. Underhill, A. Kobayashi, Y. Sasaki and H. Kobayashi, *J. Chem. Soc., Dalton Trans.,* (1984) 1759.
24 I. S. Jacobs, J. W. Bray, H. R. Hart, L. V. Interrante, J. S. Kasper, G. D. Watkins, D. E. Prober and J. C. Bonner, *Phys. Rev. B, 14* (1976) 3036.
25 L. Alcacer, H. Novais, F. Pedroso, S. Flandrois, C. Coulon, D. Chasseau and J. Gaultier, *J. Solid State Commun., 35* (1980) 945.

26 A. Kobayashi, Y. Sasaki, Y. Kobayashi, A. E. Underhill and M. M. Ahmad, *J. Chem. Soc., Chem. Commun.*, (1982) 390.
27 M. Bousseau, L. Valade, J. Legros, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Am. Chem. Soc., 108* (1986) 1908.
28 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, U.K., 1974, pp. 71–102.
29 *SHELXTL*, X-ray Instruments Group, Nicolet Instrument Corp., Madison, WI, 1983.
30 J. H. Welch, R. D. Bereman and P. Singh, *Inorg. Chem.*, *27* (1988) 2862.