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Bis[bis(triphenylphosphoranylidene)ammonium] μ-tetrathiaoxalato-bis[(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II)]

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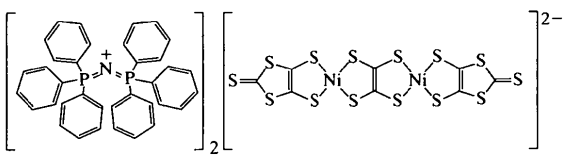
Abstract

The binuclear complex anion in $[(C_6H_5)_6P_2N]_2[(C_3S_5)Ni(C_2S_4)Ni(C_3S_5)]$, conventionally abbreviated $(PPN)_2[(dmit)Ni(tto)Ni(dmit)]$, where PPN is bis(triphenylphosphoranylidene)ammonium, dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate and tto is tetrathiaoxalate, is centrosymmetric and essentially planar, except for a small twist of 2.7 (1)° at the Ni centers. The bond lengths [average Ni—S distance 2.166 (8) Å] and angles are comparable to those reported elsewhere for other salts of the component ions. The crystal packing and the charge state of the complex anion are not favorable for electrical conduction. The binuclear complex anion was synthesized by a simpler method than that published previously.

Comment

In the last decade, considerable effort has been devoted to the synthesis and study of the electrical properties of dmit (2-thioxo-1,3-dithiole-4,5-dithiolate) ligand-based metal–dithiolate complexes, leading to the discovery of several superconducting systems containing the $[M(\text{dmit})_2]^{n-}$ (M = Ni, Pd; $0 \leq n \leq 2$) ion (Cassoux *et al.*, 1991; Olk *et al.*, 1992). The dmit-based complexes are sulfur-rich, fully conjugated and completely planar, and these structural features play a crucial role in the formation of superconducting organic materials (Cassoux & Valade, 1992; Williams *et al.*, 1992). Recently, a new class of Ni–dithiolenes, $[\text{Ni}(R_2\text{timdt})_2]$ (where R_2timdt is the monoanionic 1,3-dialkylimidazolidine-2,4,5-trithione) has been synthesized (Bigoli *et al.*, 1997).

These materials show a very intense low-energy electronic absorption (ε = 80000 dm^3 mol^{-1} cm^{-1}; λ = 1000 nm) near the emission frequency of neodymium lasers, and therefore are excellent candidates as near-IR dyes. The iodine (1310 nm) and the solid-state erbium (1540 nm) lasers lie beyond the neodymium laser wavelength (1060 nm), and the synthesis of materials that exhibit strong absorption in this range is of particular technological importance. Since both dithiolenes show unique optical and electronic properties, it is of considerable interest to synthesize the unsymmetrical mixed-ligand bis(dithiolene) nickel(II) complexes with the aim of obtaining highly conductive materials which are simultaneously highly absorbing in the near-IR. We have already prepared the unsymmetrical nickel–dithiolate anion by a ligand-exchange reaction between $[M(\text{dmit})_2]$ and $[\text{Ni}(R_2\text{timdt})_2]$ complexes in boiling tetrahydrofuran (THF) (Deplano *et al.*, 1998). In an attempt to improve the synthesis conditions, we obtained instead the bimetallic complex salt bis[bis(triphenylphosphoranylidene)ammonium] μ-tetrathiaoxalato-bis[(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II)], $(PPN)_2[(dmit)Ni(tto)Ni(dmit)]$, (I), as the major product of the reaction. The tetra-n-butylammonium salt of this complex anion was synthesized by a different method by Pullen *et al.* (1997).



(I)

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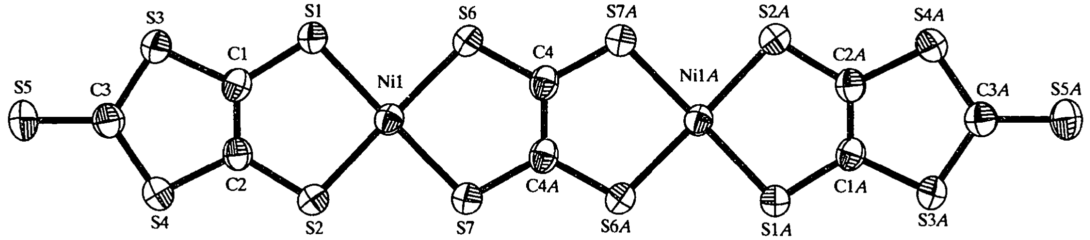

Fig. 1. The binuclear complex anion in $(PPN)_2$[(dmit)Ni(tto)Ni(dmit)]. Displacement ellipsoids are drawn at the 50% probability level. Atoms with label suffix *A* are related by an inversion center to those without the suffix.

The complex anion (Fig. 1) is essentially identical to that found in the tetrabutylammonium salt (Pullen *et al.*, 1997). Chemically equivalent bond lengths and angles agree to within *ca* 0.02 Å and 0.4°, respectively, between the two structures. In the PPN^+ salt, the anion is located on an inversion center. The anion is essentially planar, with a very minor tetrahedral distortion at the Ni center [twist angle of 2.7 (1)° between the dmit and tto units]. The geometric parameters of the PPN^+ cation are unexceptional.

The packing consists of alternating cation and anion layers perpendicular to the [011] direction (Fig. 2). The only intermolecular contact significantly shorter than the sum of the van der Waals radii is between the S3 atoms across the inversion center at $(0,0,\frac{1}{2})$, with a contact distance of 3.513 (2) Å. Highly conducting molecular solids are characterized by numerous short intermolecular contacts and partial band filling due to partial oxidation or reduction of the constituent molecules. Neither condition is fulfilled in the present structure, and no significant electrical conduction is expected.

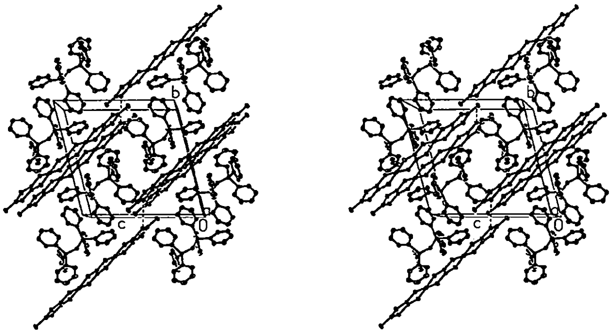

Fig. 2. Packing diagram of $(PPN)_2$[(dmit)Ni(tto)Ni(dmit)], projected approximately along the *a* axis. The dashed lines represent the shortest intramolecular S···S contact of 3.513 (2) Å. Displacement ellipsoids are drawn at the 20% probability level.

Experimental

A stirred mixture of Ni(R_2timdt)$_2$, $[N(C_4H_9)_4]Ni(dmit)_2$, and (PPN)Cl (1:1:2 molar ratio) suspended in THF was refluxed under argon for 6 d. The THF was evaporated in a rotary evaporator, and degassed acetonitrile was added to the dark-brown mixture. This mixture was refluxed under argon for 5 min and filtered while hot. The red–brown filtrate was diluted with diethyl ether and cooled in a freezer, affording red–brown crystals suitable for crystallographic analysis [m.p. 537–538 K (decomposition)].

Crystal data

$(C_{36}H_{30}NP_2)_2[Ni_2(C_2S_4)$-$(C_3S_5)_2]$
$M_r = 1739.44$
Triclinic
$P\bar{1}$
$a = 9.6507$ (2) Å
$b = 14.2770$ (3) Å
$c = 15.0369$ (4) Å
$\alpha = 75.170$ (1)°
$\beta = 82.067$ (1)°
$\gamma = 83.358$ (1)°
$V = 1976.65$ (8) Å^3
$Z = 1$
$D_x = 1.461$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5332 reflections
$\theta = 2.00$–28.26°
$\mu = 0.973$ mm^{-1}
$T = 301$ (2) K
Elongated plate
0.35 × 0.15 × 0.04 mm
Dark red–brown

Data collection

Siemens SMART CCD area-detector diffractometer
Area-detector ω scans
Absorption correction: by integration (Sheldrick, 1997)
$T_{min} = 0.800$, $T_{max} = 0.958$
12 762 measured reflections
8379 independent reflections

6033 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 28.26°$
$h = -12 \rightarrow 12$
$k = -18 \rightarrow 12$
$l = -19 \rightarrow 17$
167 standard reflections
frequency: 690 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.122$
$S = 1.105$
8379 reflections
460 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 3.5853P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni1—S6	2.1581 (12)	S4—C2	1.743 (4)
Ni1—S2	2.1633 (12)	S5—C3	1.657 (4)

Ni1—S7	2.1678 (12)	S6—C4	1.698 (4)
Ni1—S1	2.1761 (11)	S7—C4^{i}	1.698 (4)
S1—C1	1.734 (4)	C1—C2	1.353 (5)
S2—C2	1.727 (4)	C4—C4^{i}	1.435 (8)
S3—C3	1.718 (4)	N1—P1	1.583 (3)
S3—C1	1.746 (4)	N1—P2	1.585 (3)
S4—C3	1.731 (4)		
S6—Ni1—S2	177.65 (5)	C2—C1—S3	115.9 (3)
S6—Ni1—S7	90.91 (4)	S1—C1—S3	122.8 (2)
S2—Ni1—S7	87.45 (4)	C1—C2—S2	121.7 (3)
S6—Ni1—S1	88.24 (4)	C1—C2—S4	115.8 (3)
S2—Ni1—S1	93.46 (4)	S2—C2—S4	122.4 (2)
S7—Ni1—S1	177.88 (5)	S5—C3—S3	123.0 (3)
C1—S1—Ni1	101.64 (14)	S5—C3—S4	124.1 (3)
C2—S2—Ni1	101.92 (14)	S3—C3—S4	112.9 (2)
C3—S3—C1	97.7 (2)	C4^{i}—C4—S6	118.7 (4)
C3—S4—C2	97.6 (2)	C4^{i}—C4—S7^{i}	119.4 (4)
C4—S6—Ni1	105.76 (14)	S6—C4—S7^{i}	121.9 (2)
C4^{i}—S7—Ni1	105.17 (14)	P1—N1—P2	137.4 (2)
C2—C1—S1	121.2 (3)		

Symmetry code: (i) $-x, 1-y, -z$.

H atoms were placed geometrically and refined with a riding model, and with $U_{\rm iso}$ constrained to be $1.2U_{\rm eq}$ of the carrier atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1185). Services for accessing these data are described at the back of the journal.

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(L-2-Ammonio-4-methylsulfinylbutanoic acid-κ*S*)trichloroplatinum(II)–18-crown-6–water (1/1/2)

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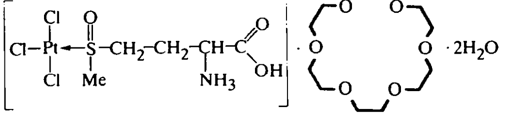
Abstract

The structure of the title compound, $[\mathrm{Pt(C_5H_{12}NO_3S)Cl_3]\cdot C_{12}H_{24}O_6\cdot 2H_2O}$, was determined by single-crystal X-ray diffraction at 223 K. The metal complex $[\mathrm{PtCl_3}(S\text{-}\mathrm{metoH_2})]$ consists of square-planar $\mathrm{Pt^{II}}$ coordinated with one *S*-bonded protonated L-methionine sulfoxide ($\mathrm{metoH_2}$) and three chloro ligands. The ammonio group of the $\mathrm{metoH_2}$ ligand forms three N—H···O hydrogen bonds to the crown ether 18-crown-6 [N···O 2.81 (2)–3.03 (3) Å]. The crystal structure consists of chains built up of these units connected by two water molecules *via* hydrogen bonds.

Comment

The anticancer activity of platinum compounds promoted investigations on platinum complexes with bioligands. Nowadays, attention is focused on $\mathrm{Pt^{IV}}$ complexes because of the lower toxicity and the possibility of oral administration (Keppler, 1993; Reedijk, 1992). In the course of our investigations on crown-ether-influenced ligand-exchange reactions in aquachloroplatinates (Steinborn, Junicke & Heinemann, 1997; Steinborn *et al.*, 1998), we found that aquapentachloroplatinic acid, $\mathrm{(H_3O)[PtCl_5(H_2O)]\cdot 2(18\text{-}cr\text{-}6)\cdot 6H_2O}$ (18-cr-6 is 18-crown-6) reacts with L-methionine sulfoxide (metoH). On reduction of $\mathrm{Pt^{IV}}$, several $\mathrm{Pt^{II}}$ complexes were formed and the title compound, $[\mathrm{PtCl_3}(S\text{-}\mathrm{metoH_2})]\cdot(18\text{-}\mathrm{cr}\text{-}6)\cdot 2\mathrm{H_2O}$, (I), was separated.



(I)

The molecular structure of (I) is shown along with the numbering scheme in Fig. 1. The complex crystallizes in space group $P2_1$. The crown ether molecule was found to be disordered over two sites (designated *a* and *b*),

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