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## Structures of [PhCNSSN]<sub>2</sub>[Pt(mnt)<sub>2</sub>] and [(*p*-ClC<sub>6</sub>H<sub>4</sub>CNSSN)<sub>2</sub>Cl][Pt(mnt)<sub>2</sub>] (mnt = Maleonitriledithiolato Ligand)

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### Abstract

4-Phenyl-1,2-dithia-3,5-diazolium bis(maleonitriledithiolato)platinum(II), [PhCNSSN]<sub>2</sub>[Pt(mnt)<sub>2</sub>] (1), and bis-[4-(4-chlorophenyl)-1,2-dithia-3,5-diazolium] chloride-bis(maleonitriledithiolato)platinum(III), [(*p*-ClC<sub>6</sub>H<sub>4</sub>CNSSN)<sub>2</sub>Cl][Pt(mnt)<sub>2</sub>] (2), contain essentially planar [Pt(mnt)<sub>2</sub>]<sup>n-</sup> anions [*n* = 2 for complex (1), *n* = 1 for complex (2)], with square-planar coordination of Pt. The Pt—S bonds are slightly, but significantly, shorter for the Pt<sup>III</sup> complex (2). The cations contain planar CNSSN five-membered rings with an aryl substituent Ar (Ph or *p*-ClC<sub>6</sub>H<sub>4</sub>) on C. In (1), the cations are discrete, but in (2), they are associated in pairs with a Cl<sup>-</sup> anion to give an approximately planar [(ArCNSSN)<sub>2</sub>Cl]<sup>+</sup> cationic unit, with S...Cl contacts in the range 2.845 (3)–2.970 (4) Å. In (1), the cations and anions are arranged all parallel in mixed cation–anion stacks, each anion being sandwiched between two cations. In (2), the cations and anions form sheets which are buckled into an unusual wave-like configuration.

### Comment

During the study of the chemistry of the 4-phenyl-1,2-dithia-3,5-diazolium cation [PhCNSSN]<sup>+</sup>, a variety of salts have been prepared. Those which have planar or almost planar cyclic sulfur–nitrogen anions give low-dimensional stacking arrangements in the solid state, generally of an ABBA type, as has been found for [PhCNSSN][S<sub>3</sub>N<sub>3</sub>] (3), [PhCNSSN][S<sub>3</sub>N<sub>2</sub>]Cl (4) and [(PhCNSSN)<sub>2</sub>Cl][S<sub>3</sub>N<sub>3</sub>] (5) (Banister, Clegg, Hauptman, Luke & Wait, 1989; Banister, Hansford, Hauptman, Luke, Wait, Clegg & Jørgensen, 1990). In such compounds the rings are held together by secondary interactions between cations and anions within each stack. The lowest unoccupied molecular orbital (LUMO) of the [PhCNSSN]<sup>+</sup> cation is antibonding with respect to both the S—N and S—S bonds; consequently, charge-transfer interactions between the anions and cations in these stacked structures take place at the expense of S—N and S—S bonding within the cations. These S—N and S—S bonds are observed to be longer than in salts without such interactions, for example [PhCNSSN][AsF<sub>6</sub>] (Scholz, Roesky, Schimkowiak & Noltemeyer, 1989). However, in some salts, such as the chloride, interactions in the plane of the cation are found (Hazell & Hazell, 1988); these involve a higher-energy molecular orbital of different symmetry, resulting in a shortening of the cation bonds through a net three-centre bonding interaction.

As an extension of this work, we have examined other salts containing soft anions, with the aim of enhancing these structurally influential secondary interactions. We report here structures containing [Pt(mnt)<sub>2</sub>]<sup>n-</sup> anions (*n* = 2 and 1) with formal Pt<sup>II</sup> and Pt<sup>III</sup> oxidation states, respectively.

The asymmetric unit of (1) consists of a complete cation, the Pt and one ligand of the anion. The asymmetric unit of (2) comprises four cations, one complete complex anion, two half anions with Pt on inversion centres and Cl<sup>-</sup> anions on one general position and two inversion centres.

Both structures contain essentially planar [ArCNSSN]<sup>+</sup> cations and [Pt(mnt)<sub>2</sub>]<sup>n-</sup> anions, as shown in Figs. 1 and 2. The r.m.s. deviation of the CNSSN ring atoms from their mean plane is 0.023 Å in (1) and 0.008, 0.007, 0.003 and 0.006 Å for the independent cations of (2), with the aryl substituent almost in the same plane [dihedral angles 3.1° for (1); 14.0, 14.1, 8.3 and 11.5° for (2)]. In the anions, the PtS<sub>4</sub> unit is strictly planar in (1) and in some of the anions of (2), with Pt on an inversion centre; the crystallographically unconstrained anion in (2) has an r.m.s. deviation of 0.039 Å for the PtS<sub>4</sub> atoms from their mean plane. The r.m.s. deviations for the complete anions are 0.064 Å in (1) and 0.092, 0.041 and 0.030 Å in (2).

In each complex anion the coordination geometry of Pt is essentially undistorted square planar, with S—Pt—S angles deviating by less than 1° from the ideal 90°. The

Pt—S bond lengths are greater in the Pt<sup>II</sup> complex (1) [2.280 (3) and 2.288 (2) Å] than in the Pt<sup>III</sup> complex (2) [2.256 (3)–2.264 (3) Å], as expected.

The [PhCNSSN]<sup>+</sup> cations in (1) are discrete, the closest contacts being within mixed stacks of approximately parallel (dihedral angle between mean planes = 6.9°) cations and anions; each anion is symmetrically sandwiched between two cations and each cation has an anion and another cation as nearest neighbours (Fig. 3). The shortest

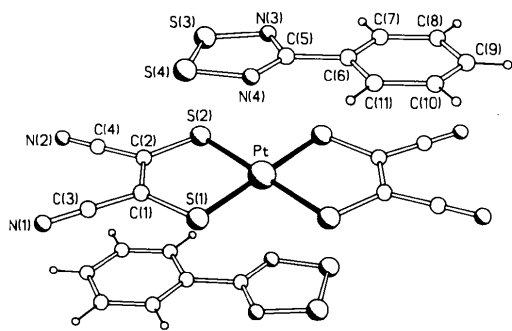


Fig. 1. The structure (two asymmetric units) of salt (1), showing the numbering of the independent non-H atoms.

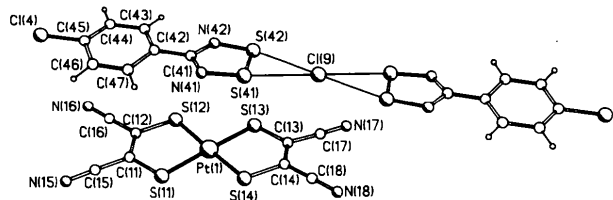


Fig. 2. The structure of representative anions and composite cationic units of salt (2). Analogous numbering schemes apply to the other ions in the asymmetric unit.

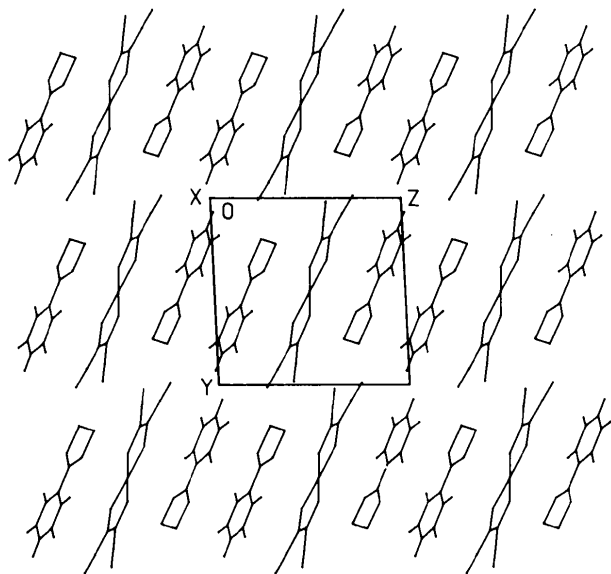


Fig. 3. Packing in the salt (1), showing the parallel ions, viewed in parallel projection along the *a* axis.

inter-ion S··S distances are 2.998 Å within stacks and 4.826 Å between adjacent stacks. These secondary S··S interactions result in partial charge transfer from the anion to the cation LUMO, which lengthens the S—N and, more particularly, the S—S bonds. Comparison of various salts of [ArCNSSN]<sup>+</sup> with planar anions, together with other derivatives (Table 5), indicates that the S—S bond length is a sensitive probe of the degree of cation–anion interaction. It can be seen that the donor capacity of the [Pt(mnt)<sub>2</sub>]<sup>2-</sup> anion is similar to that of [S<sub>3</sub>N<sub>3</sub>]<sup>-</sup>; extended Hückel calculations have already indicated that [S<sub>3</sub>N<sub>3</sub>]<sup>-</sup> donates approximately 0.86 e charge into the CNSSN π system in (3) (Banister *et al.*, 1990). Addition of a whole electron to the cation, to give the neutral complex (in the form of its dimer), increases the S—S bond length to 2.089 (5) Å (Vegas, Pérez-Salazar, Banister & Hey, 1980).

The [ArCNSSN]<sup>+</sup> cations in (2) are associated in pairs with a Cl<sup>-</sup> anion, to give an [(ArCNSSN)<sub>2</sub>Cl]<sup>+</sup> cationic unit (Fig. 2). Such a unit has been observed previously in (5) (Banister *et al.*, 1990). Although a direct comparison between S—S distances in [*p*-ClC<sub>6</sub>H<sub>4</sub>CNSSN] and [PhCNSSN] rings cannot be made at this stage because of the dearth of data for the chloro-substituted system, the data available for [*p*-ClC<sub>6</sub>H<sub>4</sub>CNSSN][AsF<sub>6</sub>] (Hursthouse, Rickard, Banister, Luke & Rawson, 1993) and [*p*-ClC<sub>6</sub>H<sub>4</sub>CNSSN]<sub>2</sub> (Clegg, McCamley, Banister & Lavender, 1993), in comparison with their non-substituted analogues, would suggest that chloro-substitution in the *para* position does not greatly affect the chemistry or geometry of dithiazole and dithiazolium rings (Table 5).

In (5), the [(PhCNSSN)<sub>2</sub>Cl]<sup>+</sup> unit is approximately planar, the Cl<sup>-</sup> interacting weakly with all four S atoms at distances in the range 2.897 (2)–3.082 (2) Å. Such in-plane interactions strengthen and shorten the S—S bond of the cation, although simultaneous out-of-plane interactions with the [S<sub>3</sub>N<sub>3</sub>]<sup>-</sup> anion induce bond lengthening. The overall effect is thus to make the S—S bond slightly longer in (5) than in [PhCNSSN][AsF<sub>6</sub>]. In (2), bond shortening through four Cl··S interactions per Cl<sup>-</sup> anion [in the range 2.845 (3)–2.970 (4) Å] makes the S—S distance somewhat shorter than in [*p*-ClC<sub>6</sub>H<sub>4</sub>CNSSN][AsF<sub>6</sub>]. However, the interactions between the associated [(*p*-ClC<sub>6</sub>H<sub>4</sub>CNSSN)<sub>2</sub>Cl]<sup>+</sup> cation and the [Pt(mnt)<sub>2</sub>]<sup>-</sup> anion would appear to be somewhat weaker than those observed between [(PhCNSSN)<sub>2</sub>Cl]<sup>+</sup> and [S<sub>3</sub>N<sub>3</sub>]<sup>-</sup> in (5) (mean S··S interaction distance 3.056 Å). Cations and anions stack approximately parallel to each other in (2), with a markedly greater cation–anion separation (around 3.5 Å) than in (1). Such a dramatic reduction in cation–anion interactions in going from (1) to (2) can be considered to arise through (a) the lower charge on the anion and (b) the secondary interactions with the anionic chloride in the associated [(ArCNSSN)<sub>2</sub>Cl]<sup>+</sup>

cation. The overall packing arrangement for (2) produces unusual wave-like sheets of ions (Fig. 4).

A variety of dithiolato-metal anions are known (Davison & Holm, 1967) and their salts tend to fall into two categories: mixed stacks of cations and anions are found in the case of larger and less symmetrical cations (Zhong, Nishida, Okawa & Kidu, 1987), and segregated cation and anion stacks occur if the cation is small (Kobayashi, Sasaki, Kobayashi, Underhill & Ahmad, 1982), although the salt [perylene]<sub>2</sub>[Pt(mnt)<sub>2</sub>] shows segregated stacks (Alcácer, Novais, Pedroso, Flandroi, Coulon, Chasseau & Gaultier, 1980). Such segregated stacks often have shown anisotropic electrical conduction properties (Kutsumizu, Kojima, Ban & Tsujikawa, 1987). Although pressed pellet samples of salts (1) and (2) were not conducting, the capacity of the 1,2-dithia-3,5-diazolium ring to undergo extensive secondary interactions with donor anions indicates that it holds promise for the formation of further low-dimensional materials with novel physical (especially electrical and magnetic) properties.

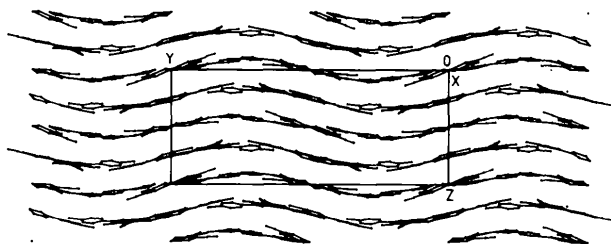
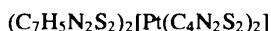


Fig. 4. The wave-like sheets of ions in the structure of salt (2), seen in parallel projection along the *a* axis.

## Experimental

### Complex (1)

#### Crystal data



$M_r = 837.95$

Triclinic

$P\bar{1}$

$a = 6.624$  (2) Å

$b = 10.165$  (3) Å

$c = 10.549$  (3) Å

$\alpha = 85.21$  (3)°

$\beta = 76.840$  (11)°

$\gamma = 79.726$  (9)°

$V = 679.8$  (3) Å<sup>3</sup>

$Z = 1$

#### Data collection

Enraf-Nonius FAST diffractometer

Scans by  $\varphi$  rotation of crystal

$D_x = 2.047$  Mg m<sup>-3</sup>

Synchrotron radiation

$\lambda = 0.910$  (5) Å

Cell parameters from 247 reflections

$\theta = 3.5$ – $30^\circ$

$\mu = 9.42$  mm<sup>-1</sup>

$T = 295.0$  (10) K

Thin plate

$0.20 \times 0.10 \times 0.01$  mm

Black

1367 measured reflections

1367 independent reflections

1309 observed reflections

$[I > 2\sigma(I)]$

Absorption correction:  
refined from  $\Delta F$  (DI-  
FABS; Walker & Stuart,  
1983)  
 $T_{\min} = 0.679$ ,  $T_{\max} =$   
1.916

### Refinement

Refinement on  $F^2$

$F[F^2 > 2\sigma(F^2)] = 0.0430$

$wR(F^2) = 0.1009$  (all data)

$S = 1.040$  (all data)

1367 reflections

178 parameters

Calculated weights

$$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 0.7694P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$\theta_{\max} = 30.49^\circ$

$h = -6 \rightarrow 6$

$k = -11 \rightarrow 11$

$l = 0 \rightarrow 11$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.36$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.17$  e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors

from Cromer & Liberman

(1970, 1981)

Data collection: *MADNES* (Messerschmidt & Pflugarth, 1987) (standard reflections not applicable to this mode of data collection). Cell refinement: *MADNES*. Data reduction: *CCP4 ROTAVATA*; *CCP4 AGROVATA* (Smith & Wonacott, 1979). Program(s) used to solve structure: *SHELXL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for complex (1)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$U_{eq}$
Pt	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0393 (5)
S1	0.2493 (4)	0.3711 (2)	0.5056 (2)	0.035 (2)
S2	0.6950 (4)	0.3288 (2)	0.5966 (2)	0.036 (2)
C1	0.3533 (19)	0.2229 (10)	0.5750 (9)	0.039 (9)
C2	0.5454 (16)	0.2052 (9)	0.6175 (8)	0.030 (7)
C3	0.2437 (22)	0.1115 (12)	0.5895 (9)	0.043 (11)
C4	0.6005 (18)	0.0836 (10)	0.6892 (9)	0.038 (8)
N1	0.1575 (19)	0.0216 (11)	0.6038 (10)	0.053 (10)
N2	0.6508 (16)	-0.0126 (9)	0.7500 (9)	0.055 (8)
S3	0.9519 (5)	0.2469 (2)	0.3341 (2)	0.042 (2)
S4	0.7044 (5)	0.2203 (3)	0.2579 (3)	0.048 (2)
N3	0.9759 (15)	0.3902 (8)	0.2648 (7)	0.043 (7)
N4	0.6806 (17)	0.3667 (9)	0.1864 (8)	0.041 (8)
C5	0.8225 (17)	0.4373 (11)	0.1952 (8)	0.032 (8)
C6	0.8257 (21)	0.5769 (11)	0.1349 (9)	0.045 (10)
C7	0.9760 (22)	0.6465 (11)	0.1466 (10)	0.047 (11)
C8	0.9799 (24)	0.7747 (12)	0.0915 (10)	0.062 (12)
C9	0.8231 (26)	0.8331 (13)	0.0234 (11)	0.064 (14)
C10	0.6770 (25)	0.7602 (14)	0.0116 (11)	0.064 (13)
C11	0.6715 (22)	0.6338 (11)	0.0662 (10)	0.054 (11)

Table 2. Geometric parameters (Å, °) for complex (1)

Pt—S1	2.280 (3)	C3—N1	1.144 (16)
Pt—S2	2.288 (2)	C4—N2	1.164 (13)
S1—C1	1.719 (9)	S3—N3	1.591 (9)
S2—C2	1.705 (11)	S3—S4	2.050 (4)
C1—C2	1.420 (15)	S4—N4	1.610 (9)
C1—C3	1.430 (20)	N3—C5	1.382 (13)
C2—C4	1.429 (13)	N4—C5	1.303 (15)
S1—Pt—S2	90.85 (10)	C4—C2—S2	120.6 (8)
C1—S1—Pt	101.8 (4)	N1—C3—C1	178.4 (10)
C2—S2—Pt	102.5 (3)	N2—C4—C2	177.1 (12)
C2—C1—C3	118.2 (9)	N3—S3—S4	96.0 (4)



Table 4. Geometric parameters (Å, °) for complex (2)

Pt1—S11	2.256 (3)	Pt3—S32	2.264 (3)
Pt1—S14	2.259 (3)	S31—C31	1.689 (12)
Pt1—S12	2.261 (3)	S32—C32	1.733 (12)
Pt1—S13	2.263 (3)	C31—C32	1.378 (16)
S11—C11	1.698 (13)	C31—C33	1.428 (18)
S12—C12	1.743 (12)	C32—C34	1.415 (18)
S13—C13	1.675 (13)	C33—N33	1.145 (16)
S14—C14	1.719 (12)	C34—N34	1.150 (17)
C11—C12	1.391 (16)	S41—N41	1.591 (11)
C11—C15	1.424 (19)	S41—S42	2.004 (5)
C12—C16	1.388 (18)	S42—N42	1.573 (11)
C13—C14	1.386 (17)	N41—C41	1.329 (15)
C13—C17	1.456 (19)	N42—C41	1.335 (15)
C14—C18	1.397 (19)	S51—N51	1.600 (10)
C15—N15	1.149 (17)	S51—S52	2.007 (5)
C16—N16	1.159 (16)	S52—N52	1.595 (10)
C17—N17	1.166 (17)	N51—C51	1.328 (15)
C18—N18	1.175 (18)	N52—C51	1.348 (16)
Pt2—S21	2.263 (3)	S61—N61	1.592 (11)
Pt2—S22	2.264 (3)	S61—S62	2.006 (5)
S21—C21	1.675 (13)	S62—N62	1.593 (11)
S22—C22	1.719 (12)	N61—C61	1.345 (16)
C21—C22	1.367 (17)	N62—C61	1.230 (16)
C21—C23	1.469 (18)	S71—N71	1.590 (12)
C22—C24	1.420 (18)	S71—S72	1.988 (5)
C23—N23	1.120 (16)	S72—N72	1.578 (12)
C24—N24	1.118 (15)	N71—C71	1.323 (15)
Pt3—S31	2.261 (3)	N72—C71	1.336 (16)
S11—Pt1—S14	90.01 (12)	C24—C22—S22	116.8 (9)
S11—Pt1—S12	89.76 (12)	N23—C23—C21	177.7 (16)
S14—Pt1—S12	177.70 (14)	N24—C24—C22	178.0 (16)
S11—Pt1—S13	177.38 (13)	S31—Pt3—S32	89.62 (11)
S14—Pt1—S13	89.58 (12)	C31—S31—Pt3	103.7 (4)
S12—Pt1—S13	90.76 (12)	C32—S32—Pt3	102.7 (4)
C11—S11—Pt1	103.8 (4)	C32—C31—C33	119.5 (11)
C12—S12—Pt1	103.5 (4)	C32—C31—S31	122.4 (9)
C13—S13—Pt1	103.4 (4)	C33—C31—S31	118.1 (8)
C14—S14—Pt1	102.9 (5)	C31—C32—C34	123.8 (11)
C12—C11—C15	118.1 (12)	C31—C32—S32	121.5 (9)
C12—C11—S11	122.9 (9)	C34—C32—S32	114.6 (9)
C15—C11—S11	118.8 (9)	N33—C33—C31	177.8 (13)
C16—C12—C11	122.8 (11)	N34—C34—C32	177.6 (17)
C16—C12—S12	117.1 (9)	N41—S41—S42	94.9 (4)
C11—C12—S12	120.1 (9)	N42—S42—S41	95.6 (4)
C14—C13—C17	118.3 (11)	C41—N41—S41	115.2 (8)
C14—C13—S13	122.8 (9)	C41—N42—S42	115.3 (8)
C17—C13—S13	118.8 (9)	N41—C41—N42	118.9 (10)
C13—C14—C18	123.2 (12)	N51—S51—S52	95.9 (4)
C13—C14—S14	121.1 (10)	N52—S52—S51	95.4 (4)
C18—C14—S14	115.7 (10)	C51—N51—S51	113.9 (9)
N15—C15—C11	178.0 (16)	C51—N52—S52	114.1 (8)
N16—C16—C12	178.5 (15)	N51—C51—N52	120.6 (11)
N17—C17—C13	178.1 (14)	N61—S61—S62	95.2 (4)
N18—C18—C14	179.0 (18)	N62—S62—S61	95.3 (4)
S21—Pt2—S22	89.77 (11)	C61—N61—S61	115.4 (9)
C21—S21—Pt2	102.2 (4)	C61—N62—S62	115.6 (9)
C22—S22—Pt2	102.8 (4)	N62—C61—N61	118.5 (11)
C22—C21—C23	117.4 (11)	N71—S71—S72	94.9 (4)
C22—C21—S21	124.8 (9)	N72—S72—S71	94.7 (4)
C23—C21—S21	117.9 (9)	C71—N71—S71	117.0 (10)
C21—C22—C24	122.8 (11)	C71—N72—S72	117.4 (9)
C21—C22—S22	120.4 (9)	N71—C71—N72	116.0 (11)

Table 5. S—S bonds (Å) in [ArCNSSN]<sup>+</sup> salts and derivatives

Compound	S—S	Reference
[PhCNSSN]Cl	1.990 (3)	Hazell & Hazell (1988)
[p-ClC <sub>6</sub> H <sub>4</sub> CNSSN] <sub>2</sub> Cl][Pt(mnt) <sub>2</sub> ]	2.001 (8)	This work
[p-ClC <sub>6</sub> H <sub>4</sub> CNSSN][AsF <sub>6</sub> ]	2.010 (5)	Hursthouse <i>et al.</i> (1993)
[PhCNSSN][AsF <sub>6</sub> ]	2.023 (2)	Scholze <i>et al.</i> (1989)
[(PhCNSSN) <sub>2</sub> Cl][S <sub>3</sub> N <sub>3</sub> ]	2.040 (1)	Banister <i>et al.</i> (1990)
[PhCNSSN] <sub>2</sub> [Pt(mnt) <sub>2</sub> ]	2.050 (4)	This work

[PhCNSSN][S <sub>3</sub> N <sub>2</sub> ]Cl	2.055 (2)	Banister <i>et al.</i> (1990)
[PhCNSSN][S <sub>3</sub> N <sub>3</sub> ]	2.064 (2)	Banister <i>et al.</i> (1990)
[p-ClC <sub>6</sub> H <sub>4</sub> CNSSN] <sub>2</sub>	2.085 (2)	Clegg <i>et al.</i> (1993)
[PhCNSSN] <sub>2</sub>	2.089 (5)	Vegas <i>et al.</i> (1980)

Stoichiometric reaction of [Et<sub>4</sub>N]<sub>2</sub>[Pt(mnt)<sub>2</sub>] (1 mmol) with [PhCNSSN][AsF<sub>6</sub>] (2 mmol) in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN or liquid SO<sub>2</sub> readily produced insoluble powders of [PhCNSSN]<sub>2</sub>[Pt(mnt)<sub>2</sub>] (1) at room temperature, with yields in excess of 75%. Similarly, [Et<sub>4</sub>N][Pt(mnt)<sub>2</sub>] (1 mmol) reacted with [PhCNSSN][AsF<sub>6</sub>] (1 mmol) to give [PhCNSSN][Pt(mnt)<sub>2</sub>]; the same product was obtained from a 1:1 reaction of [Et<sub>4</sub>N][Pt(mnt)<sub>2</sub>] and [PhCNSSN]Cl, but a 1:2 reaction gave instead [(PhCNSSN)<sub>2</sub>Cl][Pt(mnt)<sub>2</sub>]. Entirely analogous reactions were observed for substituted-phenyl derivatives [ArCNSSN]<sup>+</sup>, including [p-Cl-C<sub>6</sub>H<sub>4</sub>CNSSN]<sup>+</sup>. In all cases the salts were formed as highly insoluble black precipitates, giving satisfactory chemical analyses. Crystals of (1) suitable for X-ray study were grown by slow diffusion of [Et<sub>4</sub>N]<sub>2</sub>[Pt(mnt)<sub>2</sub>] through a graded sinter into a concentrated solution of [PhCNSSN][AsF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub>. Crystals of (2) were prepared by slow diffusion of [Et<sub>4</sub>N][Pt(mnt)<sub>2</sub>] through a graded sinter into a concentrated solution of [p-ClC<sub>6</sub>H<sub>4</sub>CNSSN]Cl in MeCN over excess solute and under an atmosphere of SO<sub>2</sub>.

Data for (1) were measured on an Enraf-Nonius FAST diffractometer at the SERC Daresbury Laboratory synchrotron source. Cell parameters were determined from reflections covering a  $\varphi$  range of 180°. The primary beam intensity was monitored continuously with an ion chamber around the exit of the collimator and appropriate corrections applied from a smooth curve fitted to the monitored intensity. All collection and processing of the data were performed with MADNES software (Messerschmidt & Pflugrath, 1987) modified for synchrotron radiation use (Papiz & Andrews, 1987). Profile fitting (Kabach, 1988) was used to improve the estimation of the intensities. Data scaling and merging were performed by the programs ROTAVATA and AGROVATA of the CCP4 package at Daresbury (Smith & Wonacott, 1979).

H atoms were constrained to lie on ring-angle external bisectors with C—H = 0.92 Å and U(H) = 1.2U<sub>eq</sub>(C).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71442 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1046]

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## Bis( $\eta^5$ -*tert*-butylcyclopentadienyl)dichloroniobium(IV)

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### Abstract

The monomeric molecule of the title compound,  $[\text{NbCl}_2(\text{C}_9\text{H}_{13})_2]$ , is best described as a paramagnetic pseudo-tetrahedral complex of niobium(IV). The two *tert*-butylcyclopentadienyl ligands are asymmetrically bound

to the Nb atom [Nb—C bond-length range 2.394 (6)–2.470 (6) Å]. The asymmetry is accounted for in terms of the steric demand of the <sup>t</sup>Bu groups and Cl ligands. Pseudo-tetrahedral geometry is completed by two Cl ligands [Nb—Cl 2.477 (2) and 2.483 (2) Å, Cl—Nb—Cl 84.15 (6)°].

### Comment

Bis(cyclopentadienyl)metal complexes have been of interest for many years, finding applications in catalysis and organic synthesis. The use of alkyl-substituted cyclopentadienyl ligands, notably the pentamethylcyclopentadienyl ligand, has been shown to enhance the solubility and stability of metal complexes. The title complex,  $[\text{NbCl}_2(\eta^5\text{-C}_9\text{H}_{13})_2]$  (1), is of interest since it represents a versatile precursor to a wide range of bis(*tert*-butylcyclopentadienyl)niobium(IV) compounds.

The Nb—Cl bond lengths and Cl—Nb—Cl bond angle are normal and comparable with other published data (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974; Lanfredi, Tiripicchio, Kapon & Reisner, 1990). The *tert*-butylcyclopentadienyl rings are bound in a staggered relative orientation. The Nb—ring-centroid distances are 2.103 and 2.094 Å and the intra-ring C—C distances do not differ significantly.

The crystal structures of  $[\text{NbCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$  (2) (Lanfredi *et al.*, 1990),  $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4\text{CMe}_3)_2]$  (3) (Howie, McQuillan, Thompson & Lock, 1986) and  $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$  (4) (Antinolo *et al.*, 1987) have been determined previously. All have essentially the same staggered orientation of rings, with substituents positioned approximately perpendicular to the Cl—M—Cl bisector, as in Fig. 1. Relevant data for structures (1)–(4) are given in Table 3. The most striking change on moving from 16-electron zirconium(IV) to 17-electron niobium(IV) complexes is the reduction of the Cl—M—Cl angle. This has been observed previously in the unsubstituted  $[\text{MCl}_2(\eta^5\text{-C}_5\text{H}_5)_2]$  analogues (Prout *et al.*, 1974) and is a consequence of the presence of an extra electron in a non-bonding but sterically significant orbital of approximate ' $d_{z^2}$ ' description (Hoffmann & Lauher,

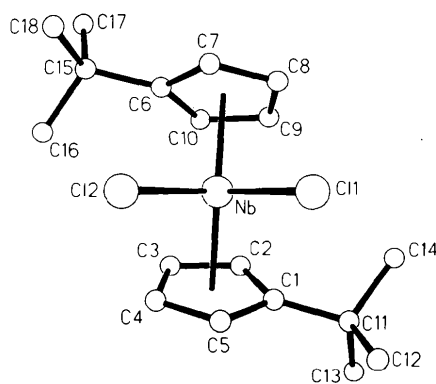


Fig. 1. Molecular structure of (1) without H atoms.