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# Benzyltrimethylammonium tris(pyrimidine-2-thiolato-$\kappa^2N,S$)nickelate(II)

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.031
$wR$ factor = 0.070
Data-to-parameter ratio = 20.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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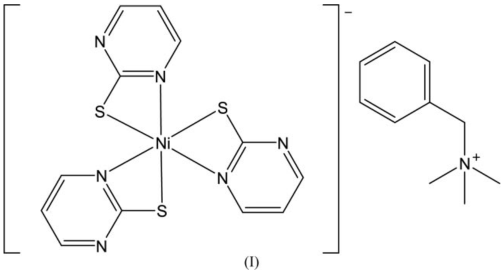
The title compound, *cis*-$[C_6H_5CH_2N(CH_3)_3][Ni(pymt)_3]$, (pymt = pyrimidine-2-thiolate, $C_4H_3N_2S$) consists of discrete cations and anions. The coordination geometry around nickel is highly distorted octahedral due to the presence of three four-membered *N,S*-chelate rings in a *cis* configuration. The Ni—S distances are in the range 2.4617 (5)–2.5290 (5) Å and the Ni—N bond distances range from 2.0490 (14) to 2.0689 (14) Å.

## Comment

Nickel aggregation through bridging by thiolate donors is well established since the discovery of a low-potential S-ligated nickel center at the active site of several hydrogenases (Thomson, 1982). Recently, an X-ray crystal structure determination on acetyl-coenzyme A synthase/carbon monoxide dehydrogenase has revealed an $[Fe_4S_4]$ cluster connected to an unexpected binuclear Ni—Ni center by S-bridging of cysteine (Darnault *et al.*, 2003). Thus, the model of thiolate-bridged nickel complexes for active sites has attracted much interest (Linck *et al.*, 2003). We report here the crystal structure of a simple mononuclear Ni$^{II}$ complex, *cis*-$[C_6H_6CH_2N(CH_3)_3]$[Ni(pymt)$_3$] (pymt = pyrimidine-2-thiolate), (I) (Fig. 1), which is different from the analogous structure, $(Ph_4P)[Ni(pymt)_3]$, reported in a previous paper (Rosenfield *et al.*, 1987).



(I)

The crystal structure of (I) consists of discrete cations and anions. The cation is notable because the Ni$^{II}$ center is bonded to three pyrimidine-2-thiolate ligands through N and S atoms, forming an octahedral geometry with a *cis* configuration. This octahedral geometry is highly distorted due to the presence of three four-membered *N,S*-chelate rings. The Ni—S distances are in the range 2.4617 (5)–2.5290 (5) Å and the Ni—N bond distances range from 2.0490 (14) to 2.0689 (14) Å. The N—Ni—N and S—Ni—S bond angles are in the range 94.69 (6)–99.25 (6) and 99.663 (18)–102.858 (17)°, respectively. These parameters are similar to those found in $(Ph_4P)[Ni(pymt)_3]$ (Rosenfield *et al.*, 1987).

## Experimental

The complex was synthesized *via* a modification to a literature method (Rosenfield *et al.*, 1987), in which $Et_4N^+$ was replaced by

$(C_6H_5CH_2)(CH_3)_3N^+$. Dark-green crystals suitable for X-ray diffraction were isolated by slowly evaporation of a solution in acetonitrile.

*Crystal data*

$(C_{10}H_{16}N)[Ni(C_4H_3N_2S)_3]$
$M_r = 542.38$
Triclinic, $P\overline{1}$
$a = 7.5730\ (8)$ Å
$b = 12.4729\ (14)$ Å
$c = 13.5236\ (13)$ Å
$\alpha = 90.205\ (4)^\circ$
$\beta = 101.633\ (5)^\circ$
$\gamma = 100.889\ (6)^\circ$
$V = 1227.5\ (2)$ Å$^3$
$Z = 2$
$D_x = 1.467$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3472 reflections
$\theta = 1.5$–$28.3^\circ$
$\mu = 1.07$ mm$^{-1}$
$T = 293\ (2)$ K
Prism, green
0.20 × 0.20 × 0.20 mm

*Data collection*

Rigaku Mercury CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{\min} = 0.746$, $T_{\max} = 0.807$
10173 measured reflections
5984 independent reflections
5426 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 28.3^\circ$
$h = -10 \rightarrow 9$
$k = -15 \rightarrow 16$
$l = -17 \rightarrow 18$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.070$
$S = 1.04$
5984 reflections
293 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.6691P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.66$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.49$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Ni1—N5 | 2.0492 (14) | Ni1—S1 | 2.4617 (5) |
| Ni1—N3 | 2.0635 (14) | Ni1—S2 | 2.4743 (5) |
| Ni1—N1 | 2.0689 (14) | Ni1—S3 | 2.5290 (5) |
| | | | |
| N5—Ni1—N3 | 94.69 (6) | N1—Ni1—S2 | 163.43 (4) |
| N5—Ni1—N1 | 96.66 (6) | S1—Ni1—S2 | 101.113 (16) |
| N3—Ni1—N1 | 99.25 (5) | N5—Ni1—S3 | 67.63 (4) |
| N5—Ni1—S1 | 162.19 (4) | N3—Ni1—S3 | 158.31 (4) |
| N3—Ni1—S1 | 97.38 (4) | N1—Ni1—S3 | 95.37 (4) |
| N1—Ni1—S1 | 68.52 (4) | S1—Ni1—S3 | 102.858 (17) |
| N5—Ni1—S2 | 95.47 (4) | S2—Ni1—S3 | 99.663 (18) |
| N3—Ni1—S2 | 68.50 (4) | | |

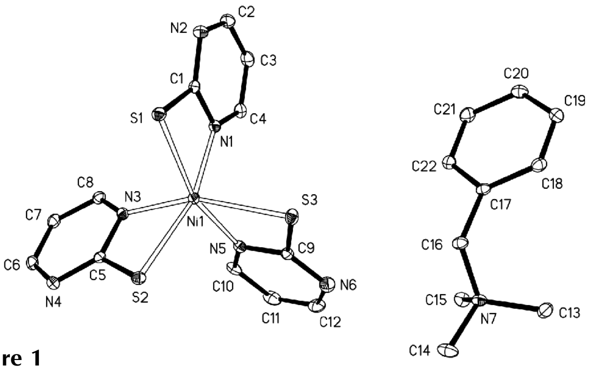


**Figure 1**
View of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

H atoms were positioned geometrically (C—H = 0.95–0.98 Å) and allowed to ride on their respective parent C atoms., with $U_{\rm iso}$= 1.5 (methyl H) or 1.2 (other H atoms) times $U_{\rm eq}$ of the parent atom.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

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