Crystal structure of [(trimethylsilyltrimethylphosphane)iminium] [tribromo(trimethylsilyltrimethylphosphane)iminenickelate(II)], $[(\text{CH}_3)_3\text{SiN}(\text{H})\text{P}(\text{CH}_3)_3]^+[\text{NiBr}_3(\text{CH}_3)_3\text{SiNP}(\text{CH}_3)_3]^-$

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Received October 9, 1997, CSD-No. 409122

Fig. 1. Anion.

Fig. 2. Cation.

Source of material: The compound is formed from NiBr_2 and excess $\text{Me}_3\text{SiNPMe}_3$ at 453 K in the presence of NaF and traces of water. After evaporation of the excess $\text{Me}_3\text{SiNPMe}_3$, extraction with CH_2Cl_2 and further evaporation and extraction with THF, deep blue single crystals crystallized from the deep blue solution at 243 K.

Selected bond lengths: $d(\text{Ni}-\text{Br}1) = 243.03(7)$ pm, $d(\text{Ni}-\text{Br}2) = 242.02(8)$ pm, $d(\text{Ni}-\text{Br}3) = 239.83(8)$ pm, $d(\text{Ni}-\text{N}1) = 202.0(3)$ pm, $d(\text{N}1-\text{P}1) = 159.3(3)$ pm, $d(\text{N}1-\text{Si}1) = 173.1(3)$ pm, $d(\text{N}2-\text{P}2) = 160.8(4)$ pm, $d(\text{N}2-\text{Si}2) = 174.6(5)$ pm. Angles: $(\text{N}1-\text{Ni}-\text{Br}1) = 114.41(9)^\circ$, $(\text{N}1-\text{Ni}-\text{Br}2) = 103.8(1)^\circ$, $(\text{N}1-\text{Ni}-\text{Br}3) = 112.8(1)^\circ$, $(\text{Br}1-\text{Ni}-\text{Br}2) = 100.97(3)^\circ$, $(\text{Br}1-\text{Ni}-\text{Br}3) = 101.80(3)^\circ$, $(\text{Br}2-\text{Ni}-\text{Br}3) = 122.88(3)^\circ$, $(\text{Ni}-\text{N}1-\text{P}1) = 117.3(2)^\circ$, $(\text{Ni}-\text{N}1-\text{Si}1) = 114.7(2)^\circ$, $(\text{P}1-\text{N}1-\text{Si}1) = 127.8(2)^\circ$, $(\text{P}2-\text{N}2-\text{Si}2) = 139.0(3)^\circ$. There is no significant hydrogen bridging between cation and anion. The bond angle sum at N(1) ($359.8(1)^\circ$) corresponds with sp^2 hybridisation. In the anion $[\text{NiBr}_3(\text{quinoline})]^-$ the Ni–N bond (202.9 pm) is found to be of the same order, whereas the Ni–Br bonds (average value 237.5 pm) are distinctly shorter (see ref. 1). Ligand geometry of the $\text{Me}_3\text{SiNPMe}_3$ group is similar to that of other complexes containing it as a neutral ligand (see ref. 2). On the other hand, the cation differs from known examples by its small bond angle $\text{Si}2-\text{N}2-\text{P}2$ (139.0° compared with 150.6° in $[\text{Me}_3\text{SiN}(\text{H})\text{PMe}_3]_2[\text{Se}_2\text{Cl}_6]$ (see ref. 3)).

$\text{C}_{12}\text{H}_{37}\text{Br}_3\text{N}_2\text{NiP}_2\text{Si}_2$, triclinic, $P\bar{1}$ (No. 2), $a = 8.3032(8)$ Å, $b = 10.742(1)$ Å, $c = 16.137(2)$ Å, $\alpha = 89.10(1)^\circ$, $\beta = 78.251(9)^\circ$, $\gamma = 68.217(7)^\circ$, $V = 1305.7$ Å³, $Z = 2$, $R(F) = 0.040$, $R_w(F^2) = 0.088$.

Table 1. Parameters used for the X-ray data collection

Crystal:	deep blue, rhombus-shaped plate, size 0.21 x 0.37 x 0.55 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	55.47 cm ⁻¹
Diffractometer:	Enraf-Nonius CAD4
Scan mode:	ω
$T_{\text{measurement}}$:	203 K
$2\theta_{\text{max}}$:	52.7°
$N(hkl)_{\text{unique}}$:	5309
Criterion for I_o :	$I_o > 2\sigma(I_o)$
$N(\text{param})_{\text{refined}}$:	227
Programs:	SHELXS-97, SHELX-97

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{iso}
H(111)	2i	0.5588	0.9039	0.5618	0.11(2)
H(112)	2i	0.6177	0.7479	0.5669	0.11
H(113)	2i	0.5418	0.8423	0.6503	0.11
H(121)	2i	0.1808	1.0821	0.6095	0.12(2)
H(122)	2i	0.1416	1.0185	0.6956	0.12
H(123)	2i	0.0293	1.0252	0.6273	0.12
H(131)	2i	0.1832	0.8743	0.4663	0.10(1)
H(132)	2i	0.3597	0.7468	0.4510	0.10
H(133)	2i	0.3669	0.8904	0.4439	0.10
H(141)	2i	-0.1387	0.6529	0.7162	0.058(8)
H(142)	2i	-0.1333	0.7965	0.7242	0.058
H(143)	2i	-0.0231	0.6803	0.7739	0.058
H(151)	2i	0.1273	0.4432	0.6183	0.068(9)

Table 2. (Continued)

Atom	Site	x	y	z	U _{iso}
H(152)	2i	0.2732	0.4431	0.6666	0.068(9)
H(153)	2i	0.3050	0.4518	0.5679	0.068
H(161)	2i	−0.0401	0.8012	0.5473	0.09(1)
H(162)	2i	−0.0662	0.6643	0.5445	0.09
H(163)	2i	0.1084	0.6764	0.4929	0.09(1)
H(211)	2i	0.5479	0.0495	0.7570	0.11
H(212)	2i	0.6953	0.1031	0.7156	0.11(1)
H(213)	2i	0.4989	0.2037	0.7469	0.11
H(221)	2i	0.7868	−0.0871	0.8811	0.08(1)
H(222)	2i	0.8245	0.0016	0.9452	0.08
H(223)	2i	0.9237	−0.0189	0.8497	0.08
H(231)	2i	0.3931	0.1023	0.9466	0.08(1)

Table 2. (Continued)

Atom	Site	x	y	z	U _{iso}
H(232)	2i	0.3388	0.2564	0.9338	0.08
H(233)	2i	0.4544	0.1903	1.0001	0.08
H(241)	2i	0.8523	0.5264	0.9194	0.08(1)
H(242)	2i	0.6727	0.5167	0.9661	0.08
H(243)	2i	0.7010	0.5468	0.8700	0.08
H(251)	2i	1.1034	0.3353	0.8102	0.09(1)
H(252)	2i	0.9848	0.3271	0.7479	0.09
H(253)	2i	1.0934	0.1971	0.7880	0.09
H(261)	2i	1.0075	0.2666	0.9870	0.07(1)
H(262)	2i	0.9911	0.1389	0.9499	0.07
H(263)	2i	0.8312	0.2406	1.0153	0.07
H(1)	2i	0.635(7)	0.334(6)	0.848(4)	0.06(2)

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ni	2i	0.39288(7)	0.65731(6)	0.73869(3)	0.0369(3)	0.0464(3)	0.0350(3)	−0.0211(3)	−0.0173(2)	0.0127(2)
Br(1)	2i	0.27391(7)	0.52617(5)	0.83935(3)	0.0558(3)	0.0589(3)	0.0469(3)	−0.0303(2)	−0.0203(2)	0.0249(2)
Br(2)	2i	0.67338(6)	0.48730(5)	0.66936(3)	0.0436(3)	0.0589(3)	0.0534(3)	−0.0154(2)	−0.0133(2)	0.0061(2)
Br(3)	2i	0.37213(8)	0.84020(6)	0.82906(3)	0.0863(4)	0.0685(4)	0.0481(3)	−0.0477(3)	−0.0149(3)	0.0017(3)
P(1)	2i	0.1202(1)	0.6565(1)	0.63382(7)	0.0300(5)	0.0505(7)	0.0339(6)	−0.0195(5)	−0.0107(4)	0.0046(5)
P(2)	2i	0.8457(2)	0.3235(1)	0.88444(7)	0.0373(6)	0.0540(7)	0.0405(6)	−0.0252(5)	−0.0157(5)	0.0174(5)
Si(1)	2i	0.3057(2)	0.8467(1)	0.58858(8)	0.0442(7)	0.0424(7)	0.0349(6)	−0.0204(6)	−0.0147(5)	0.0144(5)
Si(2)	2i	0.6336(2)	0.1413(1)	0.86332(8)	0.0377(6)	0.0491(7)	0.0441(7)	−0.0240(6)	−0.0146(5)	0.0223(6)
N(1)	2i	0.2620(4)	0.7192(3)	0.6437(2)	0.035(2)	0.044(2)	0.035(2)	−0.022(2)	−0.016(2)	0.015(2)
N(2)	2i	0.6930(7)	0.2813(6)	0.8609(4)	0.076(3)	0.073(3)	0.153(6)	−0.058(3)	−0.087(4)	0.081(4)
C(11)	2i	0.5335(7)	0.8336(6)	0.5924(4)	0.062(3)	0.086(4)	0.069(4)	−0.050(3)	−0.019(3)	0.035(3)
C(12)	2i	0.1451(9)	1.0131(6)	0.6359(4)	0.096(5)	0.046(3)	0.084(5)	−0.011(3)	−0.016(4)	0.012(3)
C(13)	2i	0.3036(9)	0.8386(7)	0.4735(3)	0.105(5)	0.099(5)	0.042(3)	−0.064(4)	−0.030(3)	0.027(3)
C(14)	2i	−0.0653(6)	0.7018(6)	0.7223(3)	0.034(2)	0.073(4)	0.046(3)	−0.022(2)	−0.004(2)	0.003(2)
C(15)	2i	0.2176(7)	0.4781(5)	0.6201(4)	0.069(3)	0.057(3)	0.058(3)	−0.033(3)	−0.009(3)	−0.005(3)
C(16)	2i	0.0188(7)	0.7053(6)	0.5442(3)	0.047(3)	0.102(5)	0.043(3)	−0.035(3)	−0.021(2)	0.009(3)
C(21)	2i	0.5885(8)	0.1221(6)	0.7581(3)	0.087(4)	0.072(4)	0.047(3)	−0.029(3)	−0.013(3)	0.017(3)
C(22)	2i	0.8138(7)	−0.0088(6)	0.8878(4)	0.052(3)	0.068(4)	0.078(4)	−0.013(3)	−0.012(3)	0.038(3)
C(23)	2i	0.4307(7)	0.1768(5)	0.9458(3)	0.056(3)	0.056(3)	0.052(3)	−0.026(3)	−0.005(2)	0.014(2)
C(24)	2i	0.7578(8)	0.4984(6)	0.9133(4)	0.073(4)	0.063(4)	0.059(3)	−0.017(3)	−0.022(3)	0.004(3)
C(25)	2i	1.0276(8)	0.2922(6)	0.7977(3)	0.068(4)	0.084(4)	0.052(3)	−0.040(3)	0.000(3)	0.002(3)
C(26)	2i	0.9283(7)	0.2319(6)	0.9688(3)	0.050(3)	0.091(4)	0.054(3)	−0.017(3)	−0.022(3)	0.028(3)

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