Spectroscopic Analysis, Coordination Geometry, and X-ray Structures of Nickel(II) Compounds with Sterically Demanding Tris(pyrazolyl)borate Ligands and Azide or (Thio)cyanate Anions. Crystal and Molecular Structures of Bis[(μ-thiocyanato-*N,S*)(hydrotris(3-isopropyl-4-bromopyrazol-1-yl)borato)nickel(II)]-3-Heptane and (Thiocyanato-*N*)(hydrotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borato)nickel(II)

S. Trofimenko,[†] J. C. Calabrese,[†] J. K. Kochi,[‡] S. Wolowiec,[‡] F. B. Hulsbergen,[§] and J. Reedijk*,[§]

Du Pont Company, Experimental Station, Wilmington, Delaware 19898, Department of Chemistry, The University of Houston, Houston, Texas 77204, and Department of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Received October 23, 1991

Ligand-field spectra and infrared spectra of compounds with stoichiometry M(LLL)X, where X is one of the pseudohalides NCS^-, NCO^-, and N_3^-, LLL^- is a tridentate-substituted pyrazolylborate monoanionic ligand, and M = Ni (as well as a number of Co and Zn compounds for comparison), are described. The spectral data and X-ray powder isomorphism between the Ni(II) and the Co(II) and Zn(II) compounds for the same ligands have been studied in detail and have been used to assign one of the following two structure types: (a) monomeric, trigonally distorted tetrahedral M, with a MN_3N' chromophore; (b) dinuclear, five-coordinated M with two anionic bridges. Most of the compounds belong to group a and are mononuclear with the NCS^-, NCO^-, and N_3^- ligands coordinating via N, forming a tetrahedrally based NiN_3N' chromophore. As an example of a mononuclear structure, the X-ray structure has been determined for $[Ni\{HB[N_2C_3H(Me)(C_4H_9)]_3\}(NCS)]$ (I), which crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 9.594$ (5) Å, $b = 17.429$ (4) Å, $c = 17.933$ (7) Å, $\beta = 98.43$ (3)°, $Z = 4$, $\mu = 7.47$ cm^{-1}, and $D_c = 1.209$ kg/dm^3. The Ni–N distances are quite short for tetrahedral Ni(II) (1.93–2.00 Å) and the deviations from tetrahedral angles are significant (93–123°), as a result of the tripodal bite angles of LLL. From the compounds of type b, a dinuclear species with two bridging anions was deduced from a crystal structure determination for a thiocyanate. The bridging (μ-*N,S*) bis(thiocyanate) mode is a symmetrical one, as proven by the single-crystal structure analysis for the representative example $[NiC_{19}H_{25}N_7Br_3BS]_2{\cdot}3C_7H_{16}$ ($[Ni\{HB[N_2C_3H(Br)(C_3H_7)]_3\}(NCS\text{-}\mu\text{-}N,S)]_2{\cdot}3C_7H_{16}$ (II)). This compound crystallizes in the monoclinic space group $C2/c$, with $a = 21.301$ (8) Å, $b = 12.740$ (6) Å, $c = 30.198$ (8) Å, $\beta = 107.04$ (2)°, $\mu = 36.1$ cm^{-1}, and $D_c = 1.43$ kg/dm^3. A chromophore $NiN_3N'S$ has been found for each Ni(II) in the centrosymmetric dinuclear species (Ni–Ni = 5.55 Å). Heptane was found present in the crystal lattice. The Ni–N distances vary from 2.034 to 2.083 Å, whereas the Ni–S distance amounts to 2.430 Å. The coordination geometry around Ni(II) is square pyramidal, with equatorial trans angles of 166–188°. Infrared spectra are also conclusive with regard to the proposed geometries. Tetrahedral M(II) ions with N-coordinated NCS have the $\nu_{C{=}N}$ stretch at 2050 cm^{-1}. In case of the dinuclear species a strong band at 2150 cm^{-1} is indicative of the bridging NCS^- anion. For the azide and cyanate compounds the C=N stretch is found at about 2070 and 2220 cm^{-1}, respectively. This is in agreement with end-on N coordination. The ligand-field spectral data for tetrahedral Co(II) indicate a very strong, trigonally distorted tetrahedral crystal field with *Dq* values varying 640–680 cm^{-1}.

Introduction

The coordination chemistry of poly(pyrazol-1-yl)borate ligands is currently undergoing a renaissance after their discovery, now more than 25 years ago.[1] The renewed and rapidly growing interest, especially for the tripodal tris(pyrazolyl)borates, stems from the fact that regiospecific substituents in the pyrazole rings allow control of steric factors. This has resulted in the synthesis and structure determination of complexes capable of e.g. activation of small molecules like dinitrogen and dioxygen and the study of the catalytic properties of such compounds.[2]

Recently some of us have described[3] the synthesis of some new tris(pyrazolyl)borates with bulky substituents at the position 3 in the ring (see Figure 1 for a general formula of the ligands LLL1–LLL8) and investigated some metal complexes. The synthesis of LLL3 is described below in detail; it was selected with a 2-fold objective: increasing its hydrolytic stability (compared with respect to LLL5) by protecting the BH end with three flanking methyl groups and tightening the "bite" at the metal end though nonbonding repulsions of the above methyl

---

[†] Du Pont.

[‡] The University of Houston.

[§] Leiden University.

(1) Trofimenko, S. *Chem. Rev.* **1972,** *72,* 497 and references cited there. Trofimenko, S. *Prog. Inorg. Chem.* **1986,** *34,* 115.

(2) See for some recent examples: Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990,** *29,* 2452. Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989,** *28,* 3444. Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989,** *29,* 3210. Egan, J. W., Jr.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990,** *112,* 2445 and references cited there. Bucher, U. E.; Langweiler, T.; Nanz, D.; von Philipsborn, W.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 548. Degnan, I. A.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1990,** *123,* 1347. Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989,** *111,* 375. Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989,** *111,* 5480. Ghosh, C. K.; Rodgers, P. S.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1988,** 1511. Gorrell, I.; Looney, A.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1990,** 220. Cano, M.; Heras, J. V.; Jones, C. J.; McCleverty, J. A.; Trofimenko, S. *Polyhedron* **1990,** *9,* 619. Kitajima, N.; Koda, T.; Iwata, Y.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990,** *112,* 8833. Kitajima, N.; Fujisawa, K.; Moro-oka, Y.; Toriumi, K. *J. Am. Chem. Soc.* **1989,** *111,* 8975. Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 205–6. Eichhorn, D. M.; Armstrong, W. H. *Inorg. Chem.* **1990,** *29,* 3607. Gorrell, I. B.; Looney, A.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990,** *112,* 4068. Han, R.; Parkin, G. *J. Am. Chem. Soc.* **1990,** *112,* 3662.

0020-1669/92/1331-3943$03.00/0

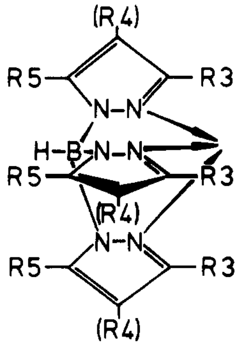

Figure 1. Schematic drawing of the ligands LLL1–LLL8. Substituents are as follows: LLL*n* = 3,4,5-trisubstituted tris(pyrazolyl)borate; LLL1 = 3-isopropyl-5-methyl; LLL2 = 3-neopentyl; LLL3 = 3-*tert*-butyl-5-methyl; LLL4 = 3-isopropyl; LLL5 = 3-*tert*-butyl; LLL6 = 4-bromo-3-isopropyl; LLL7 = 3-*p*-tolyl; LLL8 = 3-*p*-methoxyphenyl.

groups. Due to the steric effects, the metal ions are usually forced into a tetrahedral geometry, which is uncommon for metal ions like Ni(II). In a few cases, however, an additional ligand was found to bind to M(II), either as a solvent molecule or as a bridging ligand, thereby yielding a five-coordinate geometry.

The spectroscopic properties of these compounds were not yet studied in detail, and only a limited number of structures have become available so far. Therefore, we have undertaken a spectroscopic study on a variety of compounds with the general formula Ni(LLL)X, with X = NCS, NCO, or NNN, with special attention to their ligand-field spectra and possible effects of the trigonal crystal field; for comparison some related Co(II) and Zn(II) compounds have been prepared to compare their solid-state structures. Using ligand-field, IR, NMR, and powder-diffraction data, conclusions have been drawn about their geometries. Two more compounds of this group have been studied in full detail by single-crystal X-ray diffraction.

Experimental Section

Starting Materials and Synthesis of the Complexes. The ligands LLL1,[3c] LLL4,[3b] LLL5,[3a] and LLL6[3b] and several of the metal complexes were prepared by literature methods;[3] the synthesis and chemistry of LLL2 are reported elsewhere (J. C. Calabrese and S. Trofimenko, submitted for publication in *Inorg. Chem.*). The synthesis of LLL3, LLL7, and LLL8 is described below; also the coordination compound synthesis is described below.

Hydrotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate (=LLL3). The 3-*tert*-butyl-5-methylpyrazole (HPz*) was prepared by reaction of 2,2-dimethyl-3,5-hexanedione, prepared according to the literature method,[4a] with hydrazine hydrate. It was purified by sublimation and melted sharply at 168 °C (lit.[4b] mp 169–171 °C). A mixture of 3-*tert*-butyl-5-methylpyrazole and KBH_4 in a 6:1 molar ratio (at lower 3-*tert*-butyl-5-methylpyrazole/KBH_4 ratios premature solidification occurred) was heated until no more dihydrogen was evolved. The melt was allowed to solidify under dinitrogen and was then broken up and crushed. Excess 3-*tert*-butyl-5-methylpyrazole was sublimed out of the mixture at 200 °C/1 Torr. The residue was dissolved in acetonitrile, and the turbid KLLL3 solution was filtered through Celite and then added dropwise to boiling heptane, so that acetonitrile distilled out slowly. The cooled slurry was filtered, and the dried product was obtained in 74% yield. It is sublimable in vacuo. Mp (DSC): 308 °C. IR: 2450 cm^{-1} (BH). Anal. Calcd for $C_{24}H_{40}BKN_6$: C, 62.3; H, 8.66; N, 18.2. Found: C, 61.9; H, 8.57; N, 17.7. This ligand was characterized as the salt TlLLL3, prepared by mixing a THF solution of KLLL3 with aqueous $TlNO_3$ and extraction with methylene chloride. The product was purified by recrystallization from toluene/heptane. Mp (DSC): 184 °C IR: 2550, 2530 cm^{-1} (BH). NMR (ppm): d, 5.8 (J = 12.6, 1 H); s, 2.37 (3 H); d, 1.3 (J = 10.1, 27 H). ^{13}C NMR (ppm): s (5-CH_3), 13.4; d (J = 197.4, C(*C*H3)3), 32.4; d (J = 35.9, 4-C), 102.3; s (5-C), 143.8; d (J = 59.4, 3-C), 161.9. Anal. Calcd for $C_{24}H_{40}BTlN_6$: C, 45.9; H, 6.38; N, 13.4. Found: C, 46.0; H, 6.13; N, 13.2. The new metal complexes were prepared as described below for Ni(NCS)(LLL3).

Synthesis of Ni(LLL3)(NCS) and of Related Complexes. This complex was made by adding a thf solution of KLLL3 to an excess of aqueous $Ni(NO_3)_2$ containing 4 equiv of KNCS. The product was extracted with methylene chloride, purified by chromatography on alumina, dried in vacuo, and recrystallized from toluene/heptane. Dark violet crystals were isolated, mp 289 °C. NMR (ppm): 87.2 (4-H), 7.01 (Me), −14 (H–B), 4.46 (Bu^t). Anal. Calcd for $C_{25}H_{40}BN_7NiS$: C, 55.6; H, 7.41; N, 18.2. Found: C, 55.5; H, 7.16; N, 18.0.

Other M(LLL3)X complexes were prepared similarly, using KNCO or NaN_3, instead of KNCS, and $Co(NO_3)_2$ or $Zn(NO_3)_2$, instead of $Ni(NO_3)_2$.

Ni(LLL3)(NCO): Violet, mp 305 °C dec. Anal. Calcd for $C_{25}H_{40}BN_7NiO$: C, 57.3; H, 7.63; N, 18.7. Found: C, 57.5; H, 7.64; N, 18.9.

Ni(LLL3)(N_3): Violet, mp 260 °C dec. Anal. Calcd for $C_{24}H_{40}BN_9Ni$: C, 55.0; H, 7.63; N, 24.0. Found: C, 55.0; H, 7.54; N, 23.8.

Co(LLL3)(NCO): Blue, mp 328–330 °C dec. Anal. Calcd for $C_{25}H_{40}BN_7CoO$: C, 57.3; H, 7.63; N, 18.7. Found: C, 57.5; H, 7.56; N, 18.1.

Co(LLL3)(NCS): Blue, mp 302 °C (DSC; a second peak at 348–350 °C). Anal. Calcd for $C_{25}H_{40}BN_7CoS$: C, 55.6; H, 7.41; N, 18.2. Found: C, 55.6; H, 7.36; N, 18.1.

Co(LLL3)(N_3): Blue, mp 314 °C dec. Anal. Calcd for $C_{24}H_{40}BN_9Co$: C, 55.0; H, 7.63; N, 24.0. Found: C, 54.9; H, 7.35; N, 23.7.

Zn(LLL3)(NCS): White, mp 300–301 °C. NMR (ppm): s, 5.81; s, 2.38; S, 1.40 (1:3:9 ratio). Anal. Calcd for $C_{25}H_{40}BN_7ZnS$: C, 55.0; H, 7.33; N, 18.0. Found: C, 55.2; H, 7.20; N, 17.9.

Zn(LLL3)(NCO): White, mp 325–327 °C. NMR (ppm): s, 5.80; s, 2.38; s, 1.39 (1:3:9 ratio). Anal. Calcd for $C_{25}H_{40}BN_7ZnO$: C, 56.6; H, 7.55; N, 18.5. Found: C, 56.9; H, 7.60; N, 18.7.

Zn(LLL3)(N_3): White, mp 316–318 °C dec. NMR (ppm): s, 5.82; s, 2.40; s, 1.37 (1:3:9 ratio). Anal. Calcd for $C_{24}H_{40}BN_9Zn$: C, 54.3; H, 7.55; N, 23.8. Found: C, 54.0; H, 7.78; N, 24.1.

Hydrotris(3-*p*-tolylpyrazol-1-yl)borate (=LLL7). This ligand was prepared from 3-*p*-tolylpyrazol (made from 4-methylacetophenone and ethyl formate by the method used for 3-phenylpyrazole[3a]) [mp 78–80 °C (lit.[5] mp 82 °C). NMR (ppm): d, 7.67; d, 7.12; d, 6.55; s, 2.34 (2:1:2:1:3 ratio). Anal. Calcd for $C_{10}H_{10}N_2$: C, 76.0; H, 6.33; N, 17.7. Found: C, 76.4; H, 6.44; N, 17.1] and KBH_4 by the method used for HB(3-phenylpyrazole)$_3$K, and it was characterized as the Tl(LLL7) salt, mp 246–247 °C, which was recently also reported by others.[6] The various M(LLL7) complexes were prepared as was LLL3.

Ni(LLL7)(NCS): Chestnut brown, mp 243–245 °C. Anal. Calcd for $C_{31}H_{28}BN_7NiS$: C, 62.0; H, 4.67; N, 16.3. Found: C, 62.3; H, 4.75; N, 16.0.

Ni(LLL7)(NCO): Reddish brown, mp 235–237 °C. Anal. Calcd for $C_{31}H_{28}BN_7NiO$: C, 63.7; H, 4.79; N, 16.8. Found: C, 63.9; H, 4.76; N, 16.8.

Ni(LLL7)(N_3): Maroon, mp 220–222 °C. Anal. Calcd for $C_{30}H_{28}BN_9Ni$: C, 61.6; H, 4.79; N, 21.6. Found: C, 61.8; H, 4.84; N, 21.8.

Co(LLL7)(NCO): Blue, mp 232–233 °C dec. Anal. Calcd for $C_{31}H_{28}BN_7CoO$: C, 63.7; H, 4.79; N, 16.8. Found: C, 63.9; H, 4.87; N, 16.6.

Co(LLL7)(NCS): Blue, mp 234–236 °C. Anal. Calcd for $C_{31}H_{28}BN_7CoS$: C, 62.0; H, 4.67; N, 16.3. Found: C, 61.8; H, 4.39; N, 16.0.

Co(LLL7)(N_3): Blue, mp 220–222 °C dec. Anal. Calcd for $C_{30}H_{28}BN_9Co$: C, 61.6; H, 4.79; N, 21.6. Found: C, 61.7; H, 4.74; N, 21.7.

Zn(LLL7)(NCS): White, mp 263–266 °C. NMR (ppm): d, 7.79 (H5); A_2B_2 tolyl pattern as doublets at 7.53 and 7.40; d (H4), 6.47; s, 2.40 (1:1:2:2:3 ratio). Anal. Calcd for $C_{31}H_{28}BN_7ZnS$: C, 61.5; H, 4.63; N, 16.2. Found: C, 61.4; H, 4.87; N, 16.0.

---

(3) (a) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507. (b) Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091. Cano, M.; Heras, J. V.; Trofimenko, S.; Monge, A.; Guiterrez, E.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3577.

(4) (a) Swamer, F. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1953**, *72*, 1352. (b) Dayton, P. G. *Compt. Rend.* **1953**, *236*, 2515. (c) Egan, J. W.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445.

(5) Grimmett, M. R.; Richard Lim, K. H.; Weavers, R. T. *Aust. J. Chem.* **1979**, *32*, 2204.

(6) Ferguson, G.; Jennings, M. C.; Lalor, F. J.; Shanaham, C. *Acta Crystallogr.* **1991**, *C47*, 2079.

Zn(LLL7)(N_3): White, mp 230–233 °C. NMR (ppm): d, 7.83 (H5); A_2B_2 tolyl pattern as doublets at 7.63 and 7.37; d (H4), 6.47; s, 2.41 (1:1:2:2:3 ratio). Anal. $C_{30}H_{28}BN_9Zn$: C, 61.1; H, 4.75; N, 21.4. Found: C, 61.6; H, 4.66; N, 20.9.

Hydrotris(3-(4-methoxyphenyl)pyrazol-1-yl)borate (=LLL8). The starting 3-(4-methoxyphenyl)pyrazole was prepared from 4-methoxyacetophenone and ethyl formate (by the method used for 3-phenylpyrazole[3a]) and was obtained as a solid, mp 130–131 °C (lit.[5] mp 128 °C); bp 185 °C/0.6 Torr. NMR (ppm): d, 7.67; d, 7.56; d, 6.9; d, 6.5; s, 3.87 (2:1:2:1:3 ratio). Anal. Calcd for $C_{10}H_{10}N_2O$: C, 69.0; H, 5.75; N, 16.1. Found: C, 69.0; H, 5.72; N, 16.5. A mixture of 380 g (2.18 mol) of 3-(4-methoxyphenyl)pyrazole and 20 g (0.37 mol) of KBH_4 (a 5.9:1 molar ratio) was melted together and heated gradually until about 28 L of dihydrogen, as measured by a wet-test meter, was evolved. The melt was poured into 3 L of toluene, and the slurry was refluxed briefly and filtered hot. The cooled solid was washed extensively with ether to remove excess of 3-(4-methoxyphenyl)pyrazole, producing KLLL8 in 148-g (70%) yield. It could be used as such, and it was characterized as the Tl(LLL8) salt, mp 248–250 °C. IR: 2470, 2450 cm^{-1} (BH). ^1H NMR (ppm): d, 7.75; A_2B_2 aromatic pattern as doublets at 7.56 and 6.94; d, 6.40; s, 3.83 (1:2:2:1:3 ratio). ^{13}C NMR (ppm): 30.87, 55.33, 103.16, 114.21, 126.80, 128.29, 137.01, 153.33, 159.34. Anal. Calcd for $C_{30}H_{28}BN_6O_3Tl$: C, 49.0; H, 3.81; N, 11.4. Found: C, 48.8; H, 3.91; N, 11.3. The various M(LLL8) complexes were prepared as was LLL7.

Ni(LLL8)(NCS): Green, mp 218–220 °C. Anal. Calcd for $C_{31}H_{28}BN_7NiO_3S$: C, 57.4; H, 4.32; N, 15.2. Found: C, 57.7; H, 4.59; N, 15.1.

Co(LLL8)(NCO): Blue, mp 244–246 °C. Anal. Calcd for $C_{31}H_{28}BN_7CoO_4$: C, 58.9; H, 4.43; N, 15.5. Found: C, 59.3; H, 4.62; N, 15.4.

Co(LLL8)(NCS): metallic aqua color, mp 186–188 °C. Anal. Calcd for $C_{31}H_{28}BN_7CoO_3S$: C, 57.4; H, 4.32; N, 15.2. Found: C, 57.2; H, 4.63; N, 14.9.

Co(LLL8)(N_3): Aqua, mp 234–236 °C dec. Anal. Calcd for $C_{30}H_{28}BN_9CoO_3$: C, 57.0; H, 4.43; N, 19.9. Found: C, 57.3; H, 4.66; N, 19.5.

Zn(LLL8)(NCS): White, mp 262–266 °C. NMR (ppm): d, 7.77 (H5); A_2B_2 aromatic pattern as doublets at 7.63 and 7.10; d (H4) 6.40; s, 3.85 (1:1:2:2:3 ratio). Anal. Calcd for $C_{31}H_{28}BN_7ZnO_3S$: C, 56.9; H, 4.28; N, 15.0. Found: C, 56.7; H, 4.33; N, 14.8.

Zn(LLL8)(NCO): White, mp 265–267 °C. NMR (ppm): d, 7.75 (H5); A_2B_2 aromatic pattern as doublets at 7.68 and 7.03; d (H4), 6.43; s, 3.83 (1:1:2:2:3 ratio). Anal. $C_{31}H_{28}BN_7NiO_4$: C, 58.3; H, 4.39; N, 15.4. Found: C, 57.8; H, 4.45; N, 14.9.

Zn(LLL8)(N_3): White, mp 230–233 °C. NMR (ppm): d, 7.79 (H5); A_2B_2 aromatic pattern as doublets at 7.68 and 7.08; d (H4), 6.43; s, 3.83 (1:1:2:2:3 ratio). Anal. Calcd for $C_{30}H_{28}BN_9Zn$: C, 56.4; H, 4.39; N, 19.7. Found: C, 56.1; H, 4.58; N, 19.5.

Spectroscopic and Magnetic Measurements. Solid-state ligand-field spectra were measured in the diffuse reflectance mode on a Perkin-Elmer 330 instrument equipped with a data station (33 000–4000 cm^{-1}) fitted with a reflectance attachment using MgO as reference material.

Solution ^1H and ^{13}C NMR spectra were measured on a Bruker WM-300 spectrometer. Infrared spectra from 4000 to 200 cm^{-1} were recorded as KBr pellets on a Perkin-Elmer 580 spectrometer. X-ray powder diagrams were obtained using the Guinier technique, applying Cu Kα radiation.

Crystal Growth, Data Collection, and Structure Refinements. [Ni{HB-[$N_2C_3H(Me)(C_4H_9)$]$_3$}(NCS)] (I). A purple, plate-shaped crystal of approximate size 0.35 × 0.05 × 0.55 mm was obtained using the vapor diffusion method. The crystal was mounted on an Enraf-Nonius CAD4 diffractometer. The used radiation was Mo Kα monochromatized by a graphite crystal. Cell constants and relevant data collection information are listed in Table I and the supplementary material. Intensities were measured using the ω-scan method, with a scan width of 1.2–1.5 ω and a scan speed of 1.7–5°/min. Two standard relfections were collected at regular intervals, and fluctuations were found to be at most 3%. An absorption correction was applied using DIFABS; transmission factors varied from 0.34 to 1.52.

The structure was solved by automated Patterson analysis (PHASE) and refined by full-matrix least squares on *F*. Scattering factors were taken from ref 7. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at their calculated positions and constrained to a riding motion. Final residuals are also given in Table I. Atomic coordinates are given in Table II. Tables of hydrogen atom parameters, anisotropic thermal parameters for the non-hydrogen atoms, and structure factors are deposited as supplementary material.[8]

Table I. Crystallographic Data for [Ni{HB[$N_2C_3H(Me)(C_4H_9)$]$_3$}(NCS)] (I) and [Ni{HB[$N_2C_3H(Br)(C_3H_7)$]$_3$}(NCS-μ-*N,S*)]$_2$·$3C_7H_{16}$ (II)

compd	I	II
chem formula	$NiSN_7C_{25}BH_{40}$	$Ni_2S_2Br_6N_{14}C_{59}B_2H_{98}$
fw	540.23	1686.33
a/Å	9.594 (5)	21.301 (6)
b/Å	17.429 (4)	12.740 (6)
c/Å	17.933 (7)	30.198 (8)
β/deg	98.43 (3)	107.04 (2)
V/Å^3	2966.3 (5)	7835 (9)
space group	$P2_1/n$ (No. 14)	$C2/c$
Z	4	4
D(calcd)/g cm^{-3}	1.209	1.43
μ/cm^{-1}	7.47	36.1
radiation (λ/Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
T/°C	–70	room temp
R/R_w[a]	0.067, 0.067	0.077, 0.045

[a] $R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$. $R_w = \{[\sum(\|F_o\| - \|F_c\|)^2]/\sum\|F_o\|^2\}^{1/2}$, with $w = [1/\sigma^2(F_o)]$.

Table II. Atomic Fractional Coordinates (×10^4) and B_{iso} Values (Å^2) of [Ni{HB[$N_2C_3H(Me)(C_4H_9)$]$_3$}(NCS)]

atom	x	y	z	B_{iso}[a]
Ni(1)	2113 (1)	2266 (1)	2214 (1)	2.2 (1)
S(1)	3346 (4)	836 (2)	207 (1)	3.6 (1)
N(1)	2547 (10)	1715 (5)	1345 (5)	4.4 (3)
N(11)	880 (8)	3196 (4)	2127 (4)	1.8 (2)
N(12)	698 (8)	3493 (4)	2806 (4)	1.9 (2)
N(21)	3638 (8)	2723 (5)	2960 (4)	2.2 (2)
N(22)	3073 (8)	3162 (4)	3495 (4)	1.7 (2)
N(31)	1141 (9)	1788 (4)	3009 (4)	2.5 (3)
N(32)	1051 (8)	2288 (5)	3599 (4)	2.2 (2)
C(1)	2868 (11)	1355 (5)	864 (6)	2.7 (3)
C(11)	–183 (10)	4099 (5)	2719 (5)	2.1 (3)
C(12)	–563 (11)	4192 (5)	1941 (5)	2.4 (3)
C(13)	105 (10)	3619 (5)	1603 (5)	1.9 (3)
C(14)	37 (12)	3480 (6)	756 (5)	2.9 (3)
C(15)	–519 (12)	2684 (7)	568 (5)	4.3 (4)
C(16)	1468 (14)	3560 (7)	524 (6)	4.6 (4)
C(17)	–931 (14)	4058 (7)	319 (6)	5.1 (4)
C(18)	–637 (12)	4539 (5)	3342 (5)	3.1 (3)
C(21)	4153 (11)	3515 (5)	3953 (5)	2.0 (3)
C(22)	5390 (11)	3287 (5)	3716 (5)	2.4 (3)
C(23)	5018 (10)	2787 (6)	3105 (4)	2.1 (3)
C(24)	6017 (10)	2336 (6)	2688 (5)	2.4 (3)
C(25)	5698 (13)	1477 (6)	2755 (6)	3.9 (4)
C(26)	5861 (12)	2570 (6)	1847 (6)	4.0 (4)
C(27)	7523 (12)	2492 (6)	3026 (6)	4.3 (4)
C(28)	3935 (11)	4058 (5)	4553 (5)	3.0 (3)
C(31)	532 (11)	1906 (6)	4144 (5)	2.5 (3)
C(32)	259 (11)	1164 (5)	3918 (6)	2.6 (3)
C(33)	630 (11)	1105 (5)	3193 (6)	2.4 (3)
C(34)	547 (11)	425 (5)	2676 (6)	2.8 (3)
C(35)	–154 (13)	–231 (6)	3012 (7)	5.1 (4)
C(36)	2056 (13)	147 (5)	2589 (6)	4.0 (4)
C(37)	–239 (11)	614 (6)	1907 (6)	3.6 (4)
C(38)	263 (12)	2277 (6)	4866 (5)	3.6 (3)
B(1)	1514 (13)	3140 (7)	3544 (6)	2.2 (3)

[a] $B_{iso} = {}^4/_3\sum_{i=1-3}\sum_{j=1-3}(a_i \cdot a_j)\cdot\beta_{ij}$.

[Ni{HB[$N_2C_3H(Br)(C_3H_7)$]$_3$}(NCS-μ-*N,S*)]$_2$·$3C_7H_{16}$ (II). An emerald green pseudohexagonal slab having approximate dimensions 0.72 × 0.68 × 0.35 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The sample was coated with a thin layer of epoxy to retard solvent loss. The used radiation was Mo Kα monochromatized by a highly ordered graphite crystal. Cell constants and relevant data collection information are listed in Table I and the supplementary material. Laue symmetry was determined to be $2/m$, and from systematic absences noted the space group was shown to be

---

(7) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(8) (a) Supplementary material. (b) Nicolet Corp., Madison, WI 53711.

Table III. Fractional Atomic Coordinates (×10^4) and *U*(eq) Values (Å^2) for $[Ni\{HB[N_2C_3H(Br)(C_3H_7)]_3\}(NCS\text{-}\mu\text{-}N,S)]_2 \cdot 3C_7H_{16}$

	x	*y*	*z*	*U*(eq)[a]
Ni	7331 (1)	1256 (2)	4219 (1)	48 (1)
Br(1)	4490 (1)	96 (3)	3265 (1)	92 (1)
Br(2)	8590 (1)	−2445 (3)	3512 (1)	117 (2)
Br(3)	7684 (1)	4950 (3)	3081 (1)	99 (1)
S	6609 (3)	3556 (5)	5201 (2)	65 (3)
B	6953 (11)	989 (21)	3147 (8)	51 (6)
N(1)	6352 (8)	747 (12)	3351 (6)	55 (6)
N(2)	6421 (8)	770 (12)	3814 (5)	46 (5)
C(3)	5833 (10)	543 (14)	3864 (8)	51 (6)
C(4)	5384 (9)	402 (15)	3434 (7)	53 (6)
C(5)	5735 (9)	556 (15)	3084 (7)	63 (6)
C(6)	5711 (9)	465 (17)	4352 (7)	64 (6)
C(7)	5549 (10)	−695 (16)	4448 (7)	102 (7)
C(8)	5209 (9)	1332 (16)	4414 (7)	101 (6)
N(9)	7480 (7)	163 (14)	3421 (5)	55 (5)
N(10)	7697 (7)	41 (16)	3905 (5)	53 (5)
C(11)	8128 (10)	−835 (18)	4034 (9)	67 (6)
C(12)	8214 (11)	−1354 (19)	3648 (9)	90 (7)
C(13)	7821 (10)	−799 (18)	3305 (8)	80 (6)
C(14)	8385 (11)	−1286 (20)	4524 (8)	102 (7)
C(15)	8085 (11)	−2339 (17)	4585 (8)	145 (7)
C(16)	9076 (11)	−1301 (18)	4647 (8)	151 (7)
N(17)	7191 (8)	2057 (12)	3281 (6)	42 (5)
N(18)	7409 (7)	2357 (12)	3750 (6)	43 (5)
C(19)	7574 (10)	3321 (16)	3759 (7)	45 (6)
C(20)	7491 (9)	3623 (15)	3292 (8)	44 (6)
C(21)	7244 (9)	2827 (16)	3004 (8)	53 (6)
C(22)	7878 (11)	3930 (15)	4189 (7)	67 (6)
C(23)	7453 (9)	4812 (18)	4220 (6)	102 (6)
C(24)	8591 (9)	4232 (15)	4279 (7)	95 (6)
N(25)	6904 (7)	2209 (12)	4600 (5)	44 (5)
C(26)	6792 (9)	2814 (15)	4844 (7)	44 (6)
C(27)	4429 (16)	6652 (28)	3880 (13)	112 (5)
C(28)	4173 (17)	6533 (30)	3468 (15)	112 (5)
C(29)	4060 (18)	6785 (30)	3000 (16)	112 (5)
C(30)	3875 (18)	6923 (30)	2604 (15)	112 (5)
C(31)	3867 (18)	7316 (31)	2255 (15)	112 (5)
C(32)	3702 (18)	7396 (33)	1839 (15)	112 (5)
C(33)	3640 (16)	7487 (30)	1419 (13)	112 (5)
C(34)	5314 (23)	3448 (38)	2653 (20)	131 (8)
C(35)	4806 (28)	3622 (45)	2034 (19)	131 (8)
C(36)	4364 (27)	3669 (45)	1599 (19)	131 (8)
C(37)	4408 (25)	3867 (42)	1240 (19)	131 (8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Relevant Atomic Distances (Å) and Angles (deg) of $[Ni\{HB[N_2C_3H(Me)(C_4H_9)]_3\}(NCS)]$

Distances			
Ni(1)–N(1)	1.927 (9)	C(12)–C(13)	1.375 (12)
Ni(1)–N(11)	1.999 (7)	C(13)–C(14)	1.530 (12)
Ni(1)–N(21)	1.998 (7)	C(14)–C(15)	1.507 (14)
Ni(1)–N(31)	1.996 (8)	C(14)–C(16)	1.499 (15)
S(1)–C(1)	1.604 (10)	C(14)–C(17)	1.509 (14)
N(11)–N(12)	1.359 (9)	C(21)–C(22)	1.376 (13)
N(21)–N(22)	1.398 (9)	C(21)–C(28)	1.470 (12)
N(31)–N(32)	1.383 (10)	C(22)–C(23)	1.405 (12)
N(1)–C(1)	1.145 (11)	C(23)–C(24)	1.519 (13)
N(11)–C(13)	1.332 (10)	C(24)–C(25)	1.538 (13)
N(12)–C(11)	1.348 (11)	C(24)–C(26)	1.548 (13)
N(21)–C(23)	1.316 (11)	C(24)–C(27)	1.508 (13)
N(22)–C(21)	1.370 (11)	C(31)–C(32)	1.369 (12)
N(31)–C(33)	1.348 (11)	C(31)–C(38)	1.504 (13)
N(32)–C(31)	1.338 (11)	C(32)–C(33)	1.401 (13)
N(12)–B(1)	1.561 (12)	C(33)–C(34)	1.498 (13)
N(22)–B(1)	1.511 (13)	C(34)–C(35)	1.498 (14)
N(32)–B(1)	1.557 (12)	C(34)–C(36)	1.556 (15)
C(11)–C(12)	1.398 (12)	C(34)–C(37)	1.508 (13)
C(11)–C(18)	1.473 (13)		

Angles			
N(1)–Ni(1)–N(11)	122.4 (3)	N(32)–C(31)–C(32)	109.3 (9)
N(1)–Ni(1)–N(21)	121.1 (4)	N(32)–C(31)–C(38)	122.9 (9)
N(1)–Ni(1)–N(31)	123.3 (4)	N(31)–C(33)–C(32)	108.2 (8)
N(11)–Ni(1)–N(21)	95.5 (3)	N(31)–C(33)–C(34)	122 (1)
N(11)–Ni(1)–N(31)	93.5 (3)	C(12)–C(11)–C(18)	129 (1)
N(21)–Ni(1)–N(31)	93.5 (3)	C(11)–C(12)–C(13)	106.6 (8)
Ni(1)–N(11)–N(12)	113.0 (5)	C(12)–C(13)–C(14)	126.8 (9)
Ni(1)–N(21)–N(22)	111.0 (6)	C(13)–C(14)–C(15)	109.3 (8)
Ni(1)–N(31)–N(32)	111.8 (6)	C(13)–C(14)–C(16)	110.7 (9)
Ni(1)–N(1)–C(1)	175 (1)	C(13)–C(14)–C(17)	110.1 (9)
Ni(1)–N(11)–C(13)	140.1 (6)	C(15)–C(14)–C(16)	109 (1)
Ni(1)–N(21)–C(23)	141.6 (7)	C(15)–C(14)–C(17)	109 (1)
Ni(1)–N(31)–C(33)	140.2 (7)	C(16)–C(14)–C(17)	108 (1)
N(12)–N(11)–C(13)	106.9 (7)	C(22)–C(21)–C(28)	129 (1)
N(11)–N(12)–C(11)	110.8 (7)	C(21)–C(22)–C(23)	106.8 (9)
N(22)–N(21)–C(23)	107.3 (7)	C(22)–C(23)–C(24)	127 (1)
N(21)–N(22)–C(21)	108.8 (7)	C(23)–C(24)–C(25)	108.5 (8)
N(32)–N(31)–C(33)	107.7 (8)	C(23)–C(24)–C(26)	111.5 (8)
N(31)–N(32)–C(31)	108.5 (8)	C(23)–C(24)–C(27)	110.2 (8)
N(11)–N(12)–B(1)	119.7 (7)	C(25)–C(24)–C(26)	109.9 (8)
N(21)–N(22)–B(1)	120.8 (7)	C(25)–C(24)–C(27)	109.5 (8)
N(31)–N(32)–B(1)	120.1 (8)	C(26)–C(24)–C(27)	107.2 (9)
C(11)–N(12)–B(1)	129.5 (8)	C(32)–C(31)–C(38)	128 (1)
C(21)–N(22)–B(1)	130.2 (8)	C(31)–C(32)–C(33)	106.3 (8)
C(31)–N(32)–B(1)	131.4 (8)	C(32)–C(33)–C(34)	129.4 (9)
S(1)–C(1)–N(1)	178 (1)	C(33)–C(34)–C(35)	110 (1)
N(12)–C(11)–C(12)	105.9 (9)	C(33)–C(34)–C(36)	110.0 (8)
N(12)–C(11)–C(18)	124.8 (9)	C(33)–C(34)–C(37)	111.5 (8)
N(11)–C(13)–C(12)	109.8 (8)	C(35)–C(34)–C(36)	106.4 (9)
N(11)–C(13)–C(14)	123.4 (8)	C(35)–C(34)–C(37)	109.9 (9)
N(22)–C(21)–C(22)	107.2 (8)	C(36)–C(34)–C(37)	109 (1)
N(22)–C(21)–C(28)	123 (1)	N(12)–B(1)–N(22)	108.6 (8)
N(21)–C(23)–C(22)	110 (1)	N(12)–B(1)–N(32)	108.5 (8)
N(21)–C(23)–C(24)	123.2 (8)	N(22)–B(1)–N(32)	108.8 (8)

either *Cc* or *C*2/*c*. Intensities were measured using the ω-scan method, with a scan speed depending on the count obtained in rapid prescans of each reflection. Two standard reflections were collected after every 2 h or every 100 data, and these showed a 20% decay over the 3 days of data collection. A normalizing factor as a function of X-ray exposure time was used to account for this. In reduction of the data, Lorentz and polarization corrections were applied, as well as an empirical absorption correction based on ψ scans of 10 reflections having χ values between 70 and 90°.

Initially the molecule was thought to be a monomer with $Z = 8$ and thus space group *C*2/*c* was assumed. The structure was solved by use of the SHELXTL direct methods program, which revealed the positions of most of the non-hydrogen atoms in the asymmetric unit, consisting of a half-dimer situated about an inversion center. The remaining atoms were located in subsequent difference Fourier syntheses. The usual sequence of least-squares refinements was followed, after which all hydrogens were entered in ideal calculated positions and constrained to a riding motion. One and a half heptane molecules of heptane were in the lattice, each being massively disordered. Since *n*-heptane can exist in so many different conformations, it was impossible to model it as a rigid body. Thus only the sites having the largest residual electron density in the difference maps were refined freely, with population factors around 50%. After all shift/esd ratios were less than 0.5 (except those involving the solvent), convergence was reached at the agreement factors given in Table I. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.5 e/Å^3. Scattering factors were taken from ref 7. Atomic coordinates are given in Table III. Tables of hydrogen atom parameters, anisotropic thermal parameters for the non-hydrogen atoms, and structure factors are deposited as supplementary material.[8] All calculations were made using Nicolet's SHELXTL PLUS series of crystallographic programs.[8b]

Results and Discussion

Description of the Structure of $[Ni\{HB[N_2C_3H(Me)(C_4H_9)]_3\}(NCS)]$, [Ni(LLL3)(NCS)]. The structure of I consists of mononuclear units with a NiN_3N' tetrahedral chromophore. A projection of the molecular unit is given in Figure 2, together with the labeling system used. The butyl groups of the LLL3 ligand are away from the boron, thereby creating a pocket containing the linear thiocyanate. In fact, the butyl groups are oriented in such a way that $SCN\cdots CH_3$ contact distances are maximized (3.8–4.1 Å).

Table V. Relevant Atomic Distances (Å) and Angles (deg) for $[Ni\{HB[N_2C_3H(Br)(C_3H_7)]_3\}(NCS\text{-}\mu\text{-}N,S)]_2{\cdot}3C_7H_{16}$

	Distances		
Ni–N(2)	2.061 (14)	Ni–N(10)	2.083 (19)
Ni–N(18)	2.034 (17)	Ni–N(25)	2.058 (17)
Ni–S′	2.430 (6)	Br(1)–C(4)	1.862 (18)
Br(2)–C(12)	1.713 (26)	Br(3)–C(20)	1.894 (20)
S–C(26)	1.565 (22)	B–N(1)	1.604 (33)
B–N(9)	1.583 (28)	B–N(17)	1.466 (31)
N(1)–N(2)	1.362 (23)	N(1)–C(5)	1.347 (23)
N(2)–C(3)	1.338 (29)	C(3)–C(4)	1.379 (26)
C(3)–C(6)	1.573 (33)	C(4)–C(5)	1.476 (32)
C(6)–C(7)	1.565 (30)	C(6)–C(8)	1.587 (30)
N(9)–N(10)	1.408 (21)	N(9)–C(13)	1.518 (30)
N(10)–C(11)	1.425 (28)	C(11)–C(12)	1.400 (39)
C(11)–C(14)	1.531 (34)	C(12)–C(13)	1.329 (31)
C(14)–C(15)	1.520 (34)	C(14)–C(16)	1.409 (32)
N(17)–N(18)	1.410 (23)	N(17)–C(21)	1.315 (28)
N(18)–C(19)	1.275 (26)	C(19)–C(20)	1.424 (31)
C(19)–C(22)	1.488 (28)	C(20)–C(21)	1.340 (28)
C(22)–C(23)	1.463 (31)	C(22)–C(24)	1.513 (30)
N(25)–C(26)	1.139 (26)	C(27)–C(28)	1.214 (54)
C(28)–C(29)	1.398 (64)	C(29)–C(30)	1.159 (62)
C(30)–C(31)	1.161 (63)	C(31)–C(32)	1.205 (60)
C(32)–C(33)	1.242 (59)	C(34)–C(35)	1.878 (73)
C(35)–C(36)	1.375 (70)	C(36)–C(37)	1.144 (85)
	Angles		
N(2)–Ni–N(10)	85.3 (6)	N(2)–Ni–N(18)	92.7 (6)
N(10)–Ni–N(18)	94.4 (7)	N(2)–Ni–N(25)	91.0 (6)
N(10)–Ni–N(25)	168.1 (7)	N(18)–Ni–N(25)	97.0 (7)
N(2)–Ni–S′	166.2 (5)	N(10)–Ni–S′	90.5 (4)
N(18)–Ni–S′	100.7 (4)	N(25)–Ni–S′	90.5 (4)
C(26)–S–Ni′	101.0 (7)	N(1)–B–N(9)	101.3 (17)
N(1)–B–N(17)	108.9 (19)	N(9)–B–N(17)	109.8 (15)
B–N(1)–N(2)	122.0 (14)	B–N(1)–C(5)	123.7 (17)
N(2)–N(1)–C(5)	114.3 (18)	Ni–N(2)–N(1)	114.6 (13)
Ni–N(2)–C(3)	138.3 (14)	N(1)–N(2)–C(3)	106.7 (15)
N(2)–C(3)–C(4)	109.7 (20)	N(2)–C(3)–C(6)	122.5 (16)
C(4)–C(3)–C(6)	127.9 (20)	Br(1)–C(4)–C(3)	131.0 (18)
Br(1)–C(4)–C(5)	121.6 (13)	C(3)–C(4)–C(5)	107.4 (17)
N(1)–C(5)–C(4)	101.9 (16)	C(3)–C(6)–C(7)	109.8 (17)
C(3)–C(6)–C(8)	111.7 (16)	C(7)–C(6)–C(8)	116.3 (18)
B–N(9)–N(10)	125.6 (17)	B–N(9)–C(13)	137.0 (16)
N(10)–N(9)–C(13)	96.7 (15)	Ni–N(10)–N(9)	109.8 (12)
Ni–N(10)–C(11)	139.0 (14)	N(9)–N(10)–C(11)	111.1 (18)
N(10)–C(11)–C(12)	111.9 (20)	N(10)–C(11)–C(14)	125.3 (22)
C(12)–C(11)–C(14)	122.1 (20)	Br(2)–C(12)–C(11)	140.2 (19)
Br(2)–C(12)–C(13)	118.4 (21)	C(11)–C(12)–C(13)	101.1 (21)
N(9)–C(13)–C(12)	119.0 (21)	C(11)–C(14)–C(15)	113.9 (17)
C(11)–C(14)–C(16)	108.0 (21)	C(15)–C(14)–C(16)	113.5 (20)
B–N(17)–N(18)	120.9 (16)	B–N(17)–C(21)	127.2 (18)
N(18)–N(17)–C(21)	111.9 (15)	Ni–N(18)–N(17)	116.3 (11)
Ni–N(18)–C(19)	136.6 (15)	N(17)–N(18)–C(19)	106.9 (16)
N(18)–C(19)–C(20)	106.6 (18)	N(18)–C(19)–C(22)	124.6 (19)
C(20)–C(19)–C(22)	128.3 (19)	Br(3)–C(20)–C(19)	126.8 (15)
Br(3)–C(20)–C(21)	122.7 (17)	C(19)–C(20)–C(21)	110.5 (19)
N(17)–C(21)–C(20)	104.0 (19)	C(19)–C(22)–C(23)	109.6 (16)
C(19)–C(22)–C(24)	116.5 (20)	C(23)–C(22)–C(24)	113.7 (17)
Ni–N(25)–C(26)	166.3 (14)	S–C(26)–N(25)	174.4 (19)
C(27)–C(28)–C(29)	154.1 (41)	C(28)–C(29)–C(30)	169.6 (41)
C(29)–C(30)–C(31)	155.9 (45)	C(30)–C(31)–C(32)	154.6 (43)
C(31)–C(32)–C(33)	169.6 (44)	C(34)–C(35)–C(36)	171.7 (52)
C(35)–C(36)–C(37)	133.8 (62)		

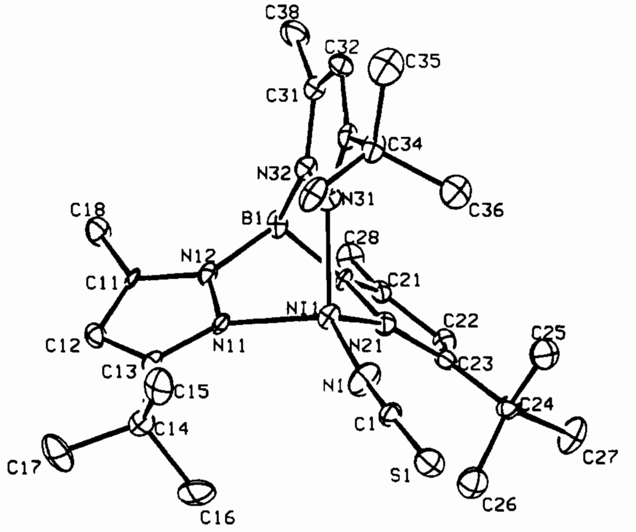

Figure 2. Numbering scheme and molecular geometry for compound I.

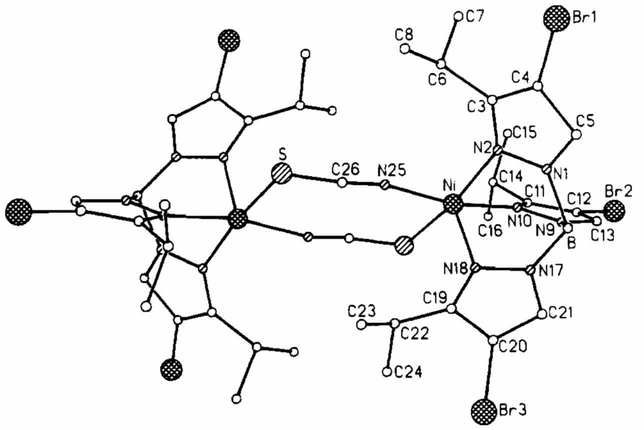

Figure 3. Numbering scheme and molecular geometry for compound II.

The Ni–N distances (1.93–2.00 Å; see Table IV) are quite short but not unusual for tetrahedral Ni.[9] As a result, a quite strong crystal field is observed in the ligand-field spectrum (vide infra). Even though the angles around Ni deviate significantly from tetrahedral (93–123°), as a result of the tripodal ligand bite, the structure can still be described as tetrahedal. The metal geometry resembles very much the related compounds [Co(LLL5)NCS][3a] and [Co(LLL6)(NCS)],[3b] only the Ni–N bonds in the present case are slightly shorter than the Co–N bonds. The structure of the molecular unit resembles very much the structure of the related Co compound with the ligand LLL6, [Co(LLL6)(NCS)], described before.[3b] Differences are minimal, with the same M–NCS distance, a linear NCS^- anion, and a linear M–N–C binding. Only the Ni–N(pyrazole) bonds appear to be slightly longer (0.03 Å) than in the Co compound. The packing of the molecular units in the crystal lattice reveals no unusual contacts.

Description of the Structure of $[Ni\{HB[N_2C_3H(Br)(C_3H_7)]_3\}(NCS\text{-}\mu\text{-}N,S)]_2{\cdot}3C_7H_{16}$, $[Ni(LLL6)(NCS)]_2{\cdot}3C_7H_{16}$. Contrary to I, the structure of II consists of dinuclear units, with end-on bridging NCS^- anions. A projection and numbering system of the compound is given in Figure 3. Relevant bond lengths and angles are given in Table V. The isopropyl groups point away from boron. However, because of the five-coordinate geometry of Ni, only two of them are pointed toward the NCS ligands (see Figure 3).

The bridging NCS anions are not unprecendented, and several dinuclear and chaintype compounds are known both for Ni(II)[10] and for other metal ions.[11] The geometry of the $Ni(NCS)_2Ni$ unit is also as usually found, i.e. with almost linear M–N–C

---

(9) Knapp, S.; Keenan, T. P.; Zhang, X.; Fikar, R.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 1882; **1990**, *112*, 3452.

(10) Haasnoot, J. G.; Driessen, W. L.; Reedijk, J. *Inorg. Chem.* **1984**, *23*, 2803. Biagini-Cingi, M.; Manotti Lanfredi, A. M.; Tiripicchio, A.; Reedijk, J.; Haasnoot, J. G. *Acta Crystallogr.* **1986**, *C42*, 427. Biagini Cingi, M.; Manotti Lanfredi, A. M.; Tiripicchio, A.; Haasnoot, J. G.; Reedijk, J. *Acta Crystallogr.* **1986**, *C42*, 1509. Driessen, W. L.; Blonk, H. L.; Hinrichs, W.; Reedijk, J. *Acta Crystallogr.* **1987**, *C43*, 1885. Bouwman, E.; Driessen, W. L.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1988**, 1337.

(11) Svelasvili, A. E. *Acta Crystallogr.* **1966**, *21*, A153. Nardelli, M.; Gaspari, G. F.; Musatti, A.; Manfredotti, A. *Acta Crystallogr.* **1966**, *21*, 910. Lipowski, J.; Andreetti, G. D. *Transition Met. Chem.* **1978**, *3*, 117. Taniguchi, M.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3277.

Table VI. Spectral Properties of Compounds M(LLL)(NCS) (M = Ni)

				ν/cm^{-1}		
LLL[a]	anion	type	ligand-field max/10^3 cm^{-1}	ν_{B-H}	$\nu_{C\equiv N}$ or $\nu_{N=N}$	comment
LLL1	NCS	dimer[b]	23.8, 15.2, 11.6, 7.0 vbr	2515	2130, 2040 (w)	decomposed to C_{3v}?
LLL2	NCS	C_{3v}	*28.4*, 20.3, 17.4 sh, 12.4, 11.3, 7.1, 6.0	2510	2110 (vw), 2045[d]	
LLL3	NCS	C_{3v}	*26.8*, 18.6, 16.6 sh, 12.0, 10.8, 8.5, 5.5	2542	2045	X-ray of I
LLL4	NCS	dimer[b]	24.3, 15.6, 12.1 (br), 7.1	2475	2140	X-ray in ref 3b
LLL5	NCS	C_{3v}	*26.0*, 19.3, 18.0 sh, 16.7 sh, 12.0, 10.7, 8.4, 5.5	2510	2042	X-ray in ref 3a
LLL6	NCS	C_{4v}, dimer	25.0, 16.0, 13.1, 10.3, 7.4	2510	2140, 2110 (sh)	X-ray of II
LLL7	NCS	C_{3v}	*30.0*, 20.2, 17.8 sh, 12.0, 10.7, 6.7	2504	2060	
LLL8	NCS	C_{4v}[b]	*28.6*, 25.8 sh, 16.3, 11.5, 7.0 vbr	2480	2070	
LLL2	NCO	C_{3v}	20.9, 18.5 sh, 12.4, 11.5, 9.5 sh, 6.0	2495	2205	
LLL3	NCO	C_{3v}	19.9, 18.7 sh, 12.6, 10.7, 8.5 sh, 5.7	2545	2210	
LLL4	NCO	C_{4v}[b]	24.7, 14.9, 11.5, 6.5 br	2490	2240	see ref 3b
LLL5	NCO	C_{3v}	20.9, 18.4 sh, 12.4, 11.1, 6.2	2495	2205	see ref 3a
LLL6	NCO	C_{3v}	20.7, 18.2 sh, 12.3, 10.8, 6.0	2495 br	2215 br	see ref 3b
LLL7	NCO	C_{3v}	26.5 sh, 20.6, 18.2 sh, 12.2, 10.7, 8.9 sh, 6.0	2500	2210	
LLL2	NNN	C_{3v}	*28.2*, 20.9, 18.1, 12.0, 11.2, 10.6, 6.3	2490	2080[d]	
LLL3	NNN	C_{3v}	*27.8*, 19.8, 17.3, 11.7, 10.5, 8.3 sh, 5.9	2545	2090[d]	
LLL6	NNN	C_{4v}[b]	25.0 sh, 15.2, 10.2, 7.0 vbr	2490, 2470	2120 sh, 2090	
LLL7	NNN	C_{4v}[b]	*28.3*, 22.6 sh, 16.1, 12.7, 11.5, 6.6 vbr	2470	2070 vs	

[a] LLL = 3,4,5-trisubstituted tris(pyrazolyl)borate; LLL1 = 3-isopropyl-5-methyl; LLL2 = 3-neopentyl; LLL3 = 3-*tert*-butyl-5-methyl; LLL4 = 3-isopropyl; LLL5 = 3-*tert*-butyl; LLL6 = 4-bromo-3-isopropyl; LLL7 = 3-*p*-tolyl; LLL8 = 3-*p*-methoxyphenyl; see Figure 1 for drawing. [b] Structure not proven; ligand-field spectrum indicates five-coordinate dimer. [c] Italicized bands are assigned as Ni–anion charge-transfer bands. [d] X-ray isomorphous with the corresponding Co compound (listed in Table VII).

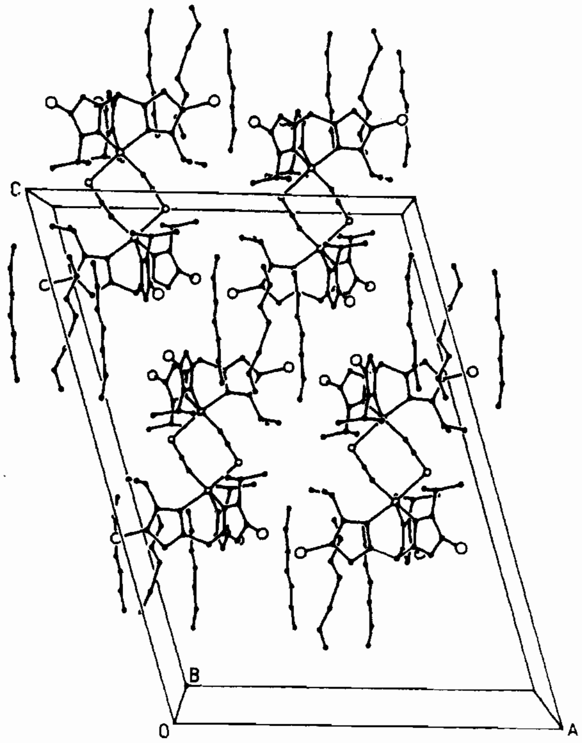

Figure 4. Packing diagram of the dinuclear units in compound II.

angles (here 166°) and a strongly bent M–S–C angle (here 101°). The Ni–S distance of 2.43 Å is significantly shorter than in the related (octahedrally coordinated) Ni(II) compounds[12] (2.54–2.63 Å). The Ni···Ni distance of 5.55 Å is about the same as found for the other compounds.[12] The geometry of the LLL6 ligand is less regular then in tetrahedral [Co(LLL6)(NCS)].[3b] The packing of the dinuclear units in the unit cell reveals no unusual features. Only van der Waals contacts are observed (Figure 4).

Ligand-Field Spectra. The ligand-field spectra for the several Ni(II) and Co(II) compounds are given in Table VI and Table VII. Two types of spectra are easily distinguished, for both Co(II) and Ni(II) compounds. The first group is in agreement with high-spin tetrahedral Co(II) and Ni(II). For Co(II) the ligand-field parameters can easily be calculated,[12] and the found value of *Dq* (640–680 cm^{-1}) is unusually high and agrees with a strong ligand field for this ligand set. In the case of Ni(II), determination of the LF parameters is more difficult, due to additional splittings. A typical Ni(II) ligand-field spectrum of this unusual geometry is redrawn together with a spectrum of a five-coordinate Ni(II) compound (in Figure 5A,B). The large number of bands in these cases is ascribed to the trigonal splitting. Such a splitting has remained unresolved for the Co(II) compounds (Figure 5C).

The second type of spectrum agrees with square-pyramidal five-coordinated Ni(II) and Co(II)[12,13] and is known for many Ni(II) compounds and a relatively small number of Co(II) compounds. The spectra cannot distinguish clearly between $[M(LLL)X]_2$ and [M(LLL)XL]. A typical example of such a Ni(II) ligand-field spectrum is included in Figure 5.

In addition to the ligand-field transitions, many of the Ni compounds also show charge-transfer bands between the anion and the nickel(II) ion. Some of these, when resolved below 32 000 cm^{-1}, have also been indicated in Table VI. It is clearly observed that in the case of tetrahedral Ni(II) the band is observed at quite low energy (down to 26 000 cm^{-1}), whereas, for the five-coordinate dinuclear Ni(II) with a significantly longer Ni–N bond, the charge-transfer band is usually observed above 29 000 cm^{-1}. Also in case of the Co(II) compounds the CT band is seen but usually above 30 000 cm^{-1}.

Infrared Spectra. The infrared spectra of all compounds clearly show the vibrations due to the ligand present. In addition the B–H stretch is easily seen in the 2400–2500-cm^{-1} range. Most interesting information, however, is obtained from the anionic stretches near 2000–2300 cm^{-1}. This range is most well studied for the thiocyanates and is almost conclusive for the binding mode. A monodentate end-on NCS$^-$ has a $\nu_{C\equiv N}$ stretch somewhat below 2100 cm^{-1}, whereas bridging NCS$^-$ has a band above 2120 cm^{-1}.[14]

For the cyanate and azide anions, usually end-on monodentate is found for cyanate, whereas for azide both 1,1-bridging and 1,3-bridging has also been observed.[14] In the present compounds the $\nu_{C\equiv N}$ and the $\nu_{N=N}$ stretches, listed in Tables VI and VII, are in the usual range for end-on N-bonded anions.[15]

Other Measurements. To characterize the Zn compounds, which often have IR spectra very similar to those of the Co(II)

---

(12) Lever, A. B. P. *Inorganic Electron Spectroscopyl* Elsevier: Amsterdam, 1985.

(13) Reedijk, J.; Verbiest, J. *Transition Met. Chem.* **1978**, *3*, 51.

(14) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1986.

(15) Burmeister, J. *Coord. Chem. Rev.* **1990**, *105*, 77.

Table VII. Spectral Properties of Compounds M(LLL)(NCS) (M = Co, Zn)

LLL[a]	anion	type	ligand-field max/10^3 cm^{-1}	ν/cm^{-1} ν_{B-H}	$\nu_{C\equiv N}$ or $\nu_{N=N}$	comment
LLL1	NCS	only Zn		2545	2075	
LLL2	NCS	C_{3v}	18.5 sh, 16.7 sh, 16.1, 11.6, 6.8	2510	2065	
LLL3	NCS	C_{3v} = Zn[b]	17.0 sh, 16.1, 10.6, 6.7	2560, 2070		
LLL4	NCS	C_{4v}	20.0 sh, 18.5 sh, 17.8, 17.0, 13.6 sh, 8.5, 5.3	2490	2129	see ref 3b
LLL5	NCS	C_{3v}	18.7 sh, 16.0, 10.8, 6.7	2525	2060	X-ray (Co) known[3a]
LLL6	NCS	C_{3v} = Zn		2550	2075	X-ray (Co) known[3b]
LLL7	NCS	C_{3v} = Zn	18.7 sh, 16.9 sh, 16.0, 11.0, 6.6	2505	2080	
LLL8	NCS	C_{3v}	18.8 sh, 16.7 sh, 15.9, 10.7, 6.5	2495	2065	
LLL1	NNN	only Zn		2545	2085, 2035 vw	
LLL2	NNN	C_{3v}	16.9 sh, 15.7, 11.6, 6.6	2490	2070	
LLL3	NNN	C_{3v} = Zn	16.9 sh, 15.6, 10.6, 6.5	2550	2080	
LLL4	NNN	C_{3v} = Zn		2505	2085, 2040 vw??	
LLL6	NNN	C_{4v}	22.4 sh, 19.1 sh, 17.8, 15.0, 8.8, 5.9	2490, 2460	2095	Zn not isomorphous
LLL7	NNN	C_{3v}	16.8 sh, 15.7, 14.9 sh, 10.9, 6.4	2500	2075	
LLL8	NNN	C_{3v}	16.7 sh, 15.7, 11.0, 6.5	2500	2080	
LLL1	NCO	C_{3v} = Zn	18.5 sh, 17.1 sh, 15.9, 11.6, 6.5	2545	2225	
LLL3	NCO	C_{3v} = Zn	18.9 sh, 17.1 sh, 16.1, 15.4 sh, 10.7, 6.5	2550	2230	
LLL4	NCO	C_{3v} = Zn	18.0 sh, 16.3, 15.8, 11.6, 6.7	2510	2225	ref 3b
LLL6	NCO	C_{3v} = Zn	18.8 sh, 17.2 sh, 16.3, 15.9, 11.9, 6.5	2535 br	2230	ref 3b
LLL8	NCO	C_{3v}	17.5 sh, 16.2 br, 11.0, 6.7	2500	2225	

[a] For abbreviations, see Table VI. [b] The Zn compound is completely isomorphous with the Co compound (IR, X-ray).

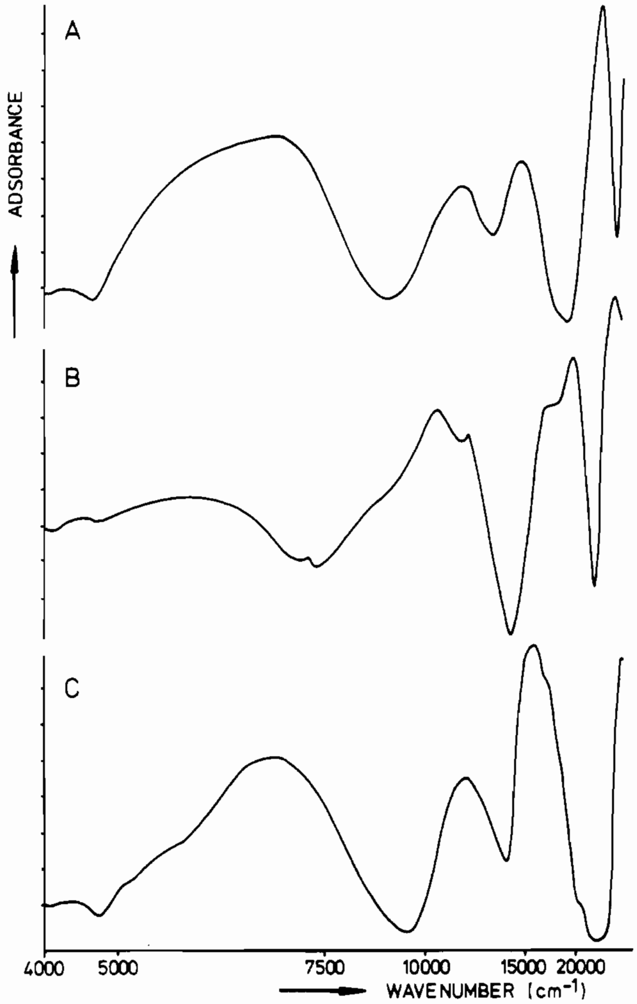

Figure 5. Typical ligand-field spectra for five-coordinate Ni(II) and tetrahedral Ni(II), as exemplified by compounds I and II, and for a tetrahedral Co spectrum, taken down to 4000 cm^{-1}: (A) [Ni(LLL4)(NCO)]$_2$; (B) [Ni(LLL3)(N$_3$)]; (C) [Co(LLL2)(N$_3$)].

compounds, Guinier X-ray powder patterns were also recorded, and the results are included in Tables VI and VII. The structural types for the Zn compounds were made on the basis of these measurements.

Table VIII. $^{13}C-^{205}Tl$ Coupling Constants (in Hz) for HB(3-Bu^t-5-Rpz)$_3$Tl Complexes

complex	C(CH$_3$)$_3$	C-3	C-4	ref
Tl(LLL5) (R = H)	171	51	14	17
Tl(LLL3) (R = Me)	197	59	36	this work

The proton NMR spectra of the Zn compounds show the usual features expected for the ligands. The Ni and Co compounds show too broad (Ni) and shifted spectra, not leading to new information. For a few samples NMR spectra in the solid state and in solution were recorded, to obtain information about the paramagnetic effects. Again only in case of the Zn compounds were sharp lines obtained, confirming the structures.

Final Remarks

The results described in the present paper have shown that the tripodal geometry of the ligands of the LLL family, given in Figure 1, usually results in tetrahedrally coordinated compounds with the pseudohalides of Co, Zn, and even Ni. Taking Ni(II) as an example, we can see the variability of its coordination mode with tris(pyrazolyl)borate ligands depending mainly on the nature of the 3-substituent and following the established hierarchy of steric hindrance as a function of the 3-R group: H < 2-thienyl[16] < Me < Ph < *i*-Pr < *t*-Bu.

Thus, for R = H, 2-thienyl, or methyl, Ni(LLL)X complexes have low stability and tend to be converted to Ni(LLL)$_2$ and NiX$_2$. For R = phenyl (where Ni(LLL)$_2$ species are possible), the Ni(LLL)X complexes are more stable, although they tend to be readily accepting of a solvent ligand. For R = *i*-Pr, including analogs with 5-Me or 4-Br substituents, Ni(LLL)X is stable and tetrahedral (red) for X = halogen or NCO but dinuclear (green) for X = NCS. Finally, for R = *t*-Bu, Ni(LLL)X complexes are inevitably tetrahedral. The trigonal distortion of the tetrahedral geometry is quite small, as deduced from the fact that the LF bands for Co(II) are hardly, if at all, split as a result of their lower symmetry.

While the major effect on the mode of coordination in LLL ligands is exerted by the 3-R group, the 5-R group also plays a role. For one thing it provides protection to the BH end of the molecule, and the nonbonding repulsions of the three 5-Me groups tend to tighten the bite of the tridentate ligand. The first effect can be seen in comparing the relative stabilities of solution of Ni(LLL5)(NCS) and Ni(LLL3)(NCS), where the latter is

---

[16] Calabrese, J. C.; Domaille, P. J.; Trofimenko, S.; Long, G. J. *Inorg. Chem.* **1991**, *30*, 2795.

indefinitely stable in air, while the former decomposes after several days. The second effect may be inferred from the significantly higher ^{13}C–^{205}Tl coupling constants in Tl(LLL3), as compared with Tl(LLL5),[17] see Table VIII. This increase in the ^{13}C–^{205}Tl coupling constants, which may be due to through-space interactions,[17] upon changing the 5-substituents from H to Me, could be interpreted in terms of a tighter ligand bite, with attendant shortening of the nonbonding Tl–C distances. However, the molecular dimensions of Tl(LLL3) are not known at present.

Acknowledgment. This research has been sponsored by the Leiden University Material Science Centre (werkgroep Fundamenteel Materialenonderzoek, WFMO), the National Science Foundation, and the R. A. Welch Foundation (Houston, TX). We thank Mr. C. Erkelens at Leiden University for recording the NMR spectra and J. D. Korp (Houston, TX) for crystallographic assistance.

Supplementary Material Available: Listings of crystal data, thermal parameters, hydrogen atom parameters, and additional bond information (5 pages). Ordering information is given on any current masthead page.

---

(17) Cowley, A. H.; Geerts, R. L.; Nunn, C. M.; Trofimenko, S. *J. Organomet. Chem.* **1989**, *365*, 19.