Monomeric and Dimeric Disulfide Complexes of Ni(II)

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(I) Experimental Procedure

General Considerations.

Unless stated otherwise, all operations were performed in a MBraun *Lab Master* dry box under an atmosphere of purified nitrogen. Anhydrous diethyl ether was purchased from Fischer, stirred over sodium metal, and filtered through activated alumina. Pentane and toluene were purchased from Sigma Aldrich and dried by passage through activated alumina and Q-5 columns. C_6D_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories, degassed by freeze-pump-thaw cycles, and dried over CaH_2 or activated 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated by evacuation overnight at 180°C. 1,8-bis-(di-*iso*-propylphosphino)naphthalene, $Cp_2FeBAr^F_4$, and KC_8 were prepared according to the literature.[1-3] All other chemicals were used as received. Elemental analysis were performed by Midwest Microlab (Indianapolis, IN). ^{1}H NMR spectra were recorded on a Bruker 500 MHz or 400 MHz NMR spectrometer and reported with reference to solvent resonance (for example, residual C_6D_5H in C_6D_6 at 7.16 ppm). X-ray diffraction data were collected on a Siemens Platform goniometer with a Charged Coupled Device (CCD) detector. Structures were solved by direct or Patterson methods using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

(dippnapth)Ni(cod) (1). A solution of dippnapht (360 mg in 10 mL THF, 1 mmol) was added dropwise to $Ni(cod)_2$ (275 mg in 5 mL THF, 1 mmol). The mixture was stirred for 12 hours at room temperature. The dark orange solution was filtered through celite and the solvent was removed under reduced pressure. The yellow orange residue was dissolved in a minimum amount of n-pentane and cooled to -35°C to induce crystallization. After decanting the mother

liquor, the product was isolated as dark yellow needles and dried under vacuum to give 450 mg **1** (76% yield). ^{1}H NMR (298 K, 400.13 MHz, C_6D_6): δ 7.25 (*dd*, 2H, J_{HH} = 8 Hz, J_{HH} = 1 Hz, $C_{10}H_6$), 7.16 (*m*, 2H, $C_{10}H_6$), 7.00 (*m*, 2H, $C_{10}H_6$), 5.73 (*m*, 2H, =CH), 4.38 (*m*, 2H, =CH), 3.12 (*m*, 4H, CH_2), 2.54 (*m*, 4H, CH_2), 2.01 (*m*, 2H, $CH(CH_3)_2$), 1.86 (*m*, 2H, $CH(CH_3)_2$), 0.85 (*m*, 6H, $CH(CH_3)_2$), 0.79 (*m*, 12H, $CH(CH_3)_2$), 0.66 (*m*, 6H, $CH(CH_3)_2$); $^{31}P\{^1H\}$ NMR (298 K, 161.9 MHz, C_6D_6): δ 38.93 (s). Elemental analysis for $C_{30}H_{46}NiP_2$: calculated: C% 68.33, H% 8.79; found: C% 68.09, H% 8.54.

(dippnapth)Ni(S$_2$) (**2**). A suspension of S_8 (50 mg in 10 mL toluene, 0.2 mmol, 300% excess) was added to **1** (100 mg in 5 mL toluene, 0.19 mmol) at room temperature. After stirring for 12 hours, the solution was filtered. The crude solid was recrystallized from toluene (~10 mL) at -35°C to afford 70 mg **2** (76% yield). ^{1}H NMR (298 K, 400.13 MHz, C_6D_6): δ 7.53 (*dd*, 2H, J_{HH} = 3.23 Hz, J_{HH} = 1 Hz, $C_{10}H_6$), 7.43 (*t*, 2H, J_{HH} = 5.4 Hz, $C_{10}H_6$), 7.09 (*d*, 2H, J_{HH} = 3.5 Hz, $C_{10}H_6$), 2.21 (*m*, 4H, $CH(CH_3)_2$), 1.06 (*m*, 12H, $CH(CH_3)_2$), 0.90 (*m*, 12H, $CH(CH_3)_2$); $^{31}P\{1H\}$ NMR (298 K, 161.9 MHz, C_6D_6): δ 50.95 (s); $^{13}C\{^1H\}$ NMR (298 K, 100.62 MHz, C_6D_6): δ 140.55 (t, J_{CP} = 10 Hz, $C_{10}H_6$), 136.45 (s, $C_{10}H_6$). 135.39 (s, $C_{10}H_6$), 129.40 (d, J_{CP} = 12 Hz, $C_{10}H_6$), 124.52 (*t*, J_{CP} = 4Hz, $C_{10}H_6$), 123.01 (*t*, J_{CP} = 18 Hz, $C_{10}H_6$), 28.39 (*t*, J_{CP} = 12Hz, $CH(CH_3)_2$), 18.86 (s, $CH(CH_3)_2$), 18.84 (*s*, $CH(CH_3)_2$). Elemental analysis for $C_{22}H_{34}S_2NiP_2$: calculated: C% 54.68, H% 7.09; found: C% 54.51, H% 7.22.

[(dippnapht)NiS]$_2$[BAr$^F_4$]$_2$ (**3**) *Method A*. At -35°C, **2** (100 mg in 5 mL THF, 0.207 mmol) was combined with [Cp$_2$Fe][BAr$^F_4$] (217 mg in 10 mL THF, 0.207 mmol), causing a gradual color change from orange to dark red. The reaction was allowed to warm to room temperature and stirred for an additional 2 hours. After filtering through celite, solvent was removed under reduced pressure. The resulting solid was dissolved in 5 mL Et$_2$O and layered with 15 mL pentane to afford 223 mg **3** (82% yield). Single crystals were obtained by cooling a concentrated Et$_2$O solution of **3** to -35°C.

Method B. In a manner similar to that described above, [Cp$_2$Fe][BAr$^F_4$] (139 mg, 0.132 mmol) was added to **4** (60 mg, 0.066 mmol), resulting in the isolation of 151 mg **3** (87% yield). ^{1}H NMR (298 K, 500.13 MHz, CD_2Cl_2): δ 8.24 (*m*, 4H, $C_{10}H_6$), 7.98 (*m*, 4H, $C_{10}H_6$), 7.78 (*m*, 4H, $C_{10}H_6$), 7.77 (*s*, 16H, BAr$^F_4$), 7.60 (*s*, 16H, BAr$^F_4$), 2.73 (*m*, 4H, $CH(CH_3)_2$), 2.66 (*m*, 4H,

CH(CH$_3$)$_2$), 1.25 (*m*, 24H, CH(CH$_3$)$_2$), 1.18 (*m*, 24H, CH(CH$_3$)$_2$); ^{31}P{1H} NMR (298 K, 202.46 MHz, CD$_2$Cl$_2$): δ 48.35 (s); ^{13}C{^{1}H} NMR (298 K, 100.62 MHz, CD$_2$Cl$_2$): δ 162.9. 162.4, 161.9, 161.4, 135.7, 135.2, 133.8, 133.5, 132.6, 129.4, 129.1, 125.1, 123.6, 117.9, 29.2, 28.7, 20.2, 19.0. Elemental analysis for B$_2$C$_{108}$F$_{48}$H$_{92}$Ni$_2$P$_4$S$_2$: calculated: C% 49.34, H% 3.53; found: C% 49.59, H% 3.42.

Trapping of S$_2$ from 2 and [Cp$_2$Fe][BAr$^F_4$]. In a manner similar to that described above in *Method A*, **2** (100 mg, 0.207 mmol) and [Cp$_2$Fe][BAr$^F_4$] (217 mg, 0.207 mmol) were combined in 15 mL Et$_2$O with 2,3-dimethyl-1,3-butadiene (10 fold excess). After removal of solvent, the solid was washed with 10 mL pentane and the filtrate analyzed by GC MS. GC MS (m/z) = 148.2 (m+).

[(dippnapht)NiS]$_2$ (4) *Method A*. **1** (264 mg, 0.5 mmol) and **2** (242 mg, 0.5 mmol) were combined in 10 mL THF and stirred at room temperature for 12 hours. Solvent was then removed under reduced pressure and the remaining solid washed with 30 mL Et$_2$O to afford **4** in 94% yield (423 mg). Single crystals were obtained by slow evaporation of a concentrated benzene solution at room temperature.

Method B. KC$_8$ (20 mg suspended in 10 mL THF, 0.15 mmol) was added to **3** (176 mg in 5 mL THF, 0.067 mmol) at -35°. The reaction was allowed to warm to room temperature before stirring for an additional 2 hours. After filtration through celite, the dark brown solution was reduced to dryness via vacuum and washed with 20 mL Et$_2$O. 44 mg (73% yield) of brown **4** was then isolated on a porous glass frit. ^{1}H NMR (298 K, 500.13 MHz, C$_6$D$_6$): δ 7.75 (*br*, $\Delta_{1/2}$ = 35 Hz, 4H, C$_{10}$H$_6$), 7.55 (*d*, J$_{HH}$ = 8 Hz, 2H, C$_{10}$H$_6$), 7.12 (*t*, J$_{HH}$ = 8 Hz, 2H, C$_{10}$H$_6$), 3.07 (*m*, 8H, CH(CH$_3$)$_2$), 1.52 (*d*, J$_{HH}$ = 5.5 Hz, 24H, CH(CH$_3$)$_2$), 1.36 (*d*, J$_{HH}$ = 5.5 Hz, 24H, CH(CH$_3$)$_2$); ^{31}P{1H} NMR (298 K, 202.46 MHz, C$_6$D$_6$): δ 30.37 (s); Elemental analysis for C$_{44}$H$_{68}$S$_2$NiP$_4$: calculated: C% 58.85, H% 7.60; found: C% 58.44, H% 7.41.

Method C. **2** (176 mg, 0.364 mmol) was placed in a teflon-sealed glass reaction vessel with PMe$_3$ (154 mg, 2.04 mmol, excess) and 30 mL toluene. The reaction was heated at 80°C for five days, causing a color change from yellow-green to orange. Solvent was removed under reduced pressure and the solid triturated with 50 mL Et$_2$O. **4** was collected on a glass frit, washed with 15 mL cold toluene and isolated in 56% yield (101 mg). For S=PMe$_3$: ^{1}H NMR (298 K, 500.13

MHz, C_6D_6): δ 1.01 (*dm*, J_{HP} =16 Hz); ^{31}P{1H} NMR (298 K, 202.46 MHz, C_6D_6): δ 28.0 (*octet*, J_{HP} = 16 Hz); GC MS (m/z): 108 (M$^+$).

References

(1)   Karacar, A.; Thonnessen, H.; Jones, P. G.; Bartsch, R.; Schmutzler, R. *Heteroatom Chem.* **1997**, *8*, 539.

(2)   Chavez, I; Alvarez-Carena, A.; Molis, E.; Roig, A.; Maniukiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manriquez, J. M. *J. Organomet. Chem.* **2000**, *601*, 126.

(3)   Scwindt, M.; Lejon, T.; Hegedus, L. *Organomet.* **1990**, *9*, 2814.

(II) X-ray

     X-ray diffraction data were collected on a Siemens Platform goniometer with a Charged Coupled Device (CCD) detector. Structures were solved by direct methods using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

     Crystals of suitable size and appearance were selected under a stereomicroscope while immersed in Paratone-N oil to minimize exposure to air. Crystals were extracted from the oil using a tapered glass filament that also held the crystal during data collection. Crystals were mounted and aligned on a Bruker SMART APEX system. All images showed sharp diffractions. Frames separated in reciprocal space were collected and provided an orientation matrix and initial cell parameters. The full data sets provided final cell parameters.

A hemisphere of data was obtained at 100 K in reciprocal space to a resolution of 0.84 Å using 0.3° steps in ω using integration times of 10-30 s per frame, depending on the sample. Integration of intensities and refinement of cell parameters were completed with SAINT. Absorption corrections were applied using SADABS or psi-scans and were small. Crystals showed no visual signs of decomposition after data collection.

(dippnapth)Ni(cod) (**1**). The space group was determined to be P2(1)/n based on systematic absences and intensity statistics. Direct methods were used to locate C, Ni, and P atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined isotropically using a riding model. See Table S1 for crystal and refinement data.
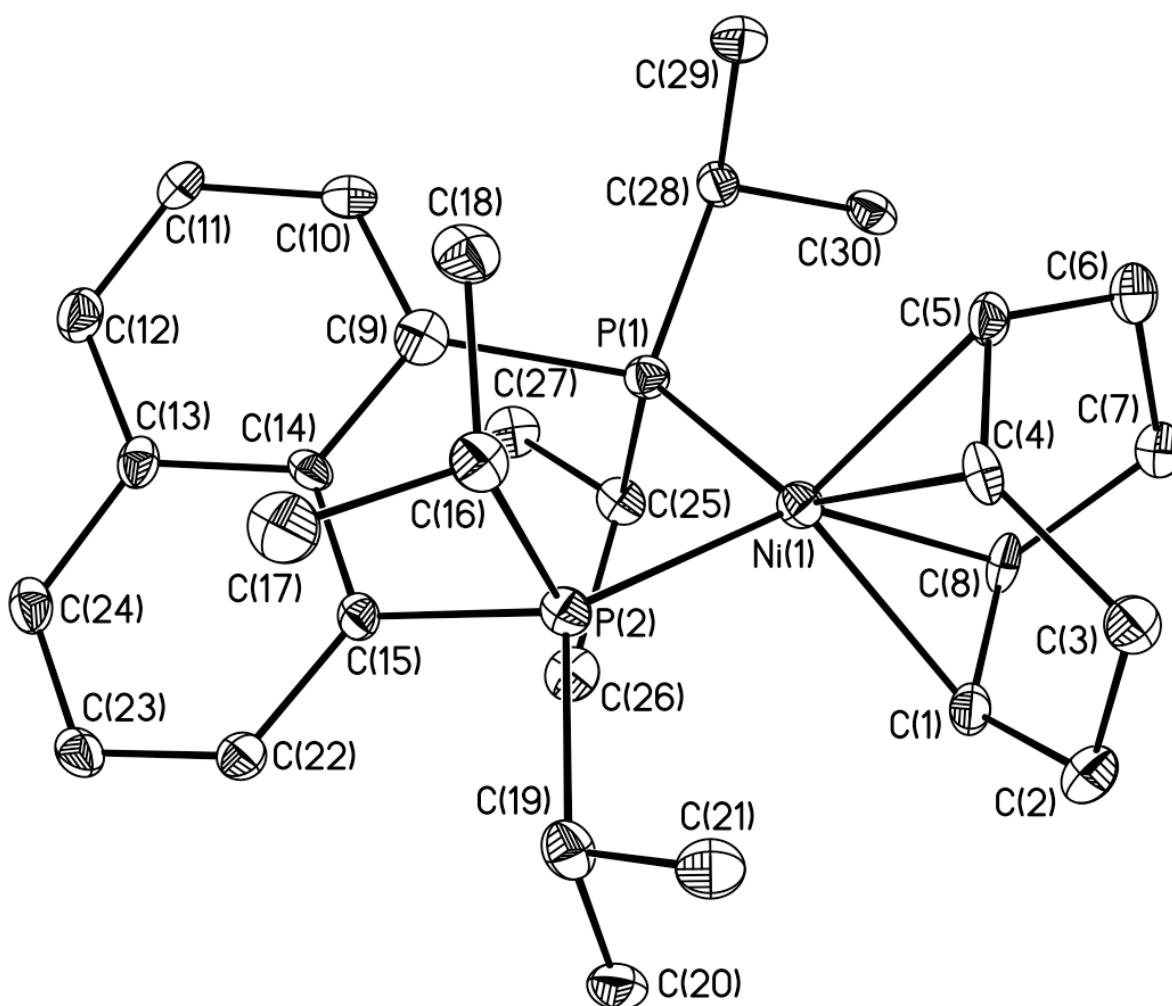
Table S1. Crystal data and structure refinement for (dippnapth)Ni(cod) (**1**).

Identification code	nicole59a
Empirical formula	C30 H46.50 Ni P2
Formula weight	527.82
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 8.8016(11) Å α = 90°.
	b = 33.585(5) Å β = 94.839(3)°.
	c = 18.521(3) Å γ = 90°.
Volume	5455.2(12) Å^3
Z	8
Density (calculated)	1.285 Mg/m^3
Absorption coefficient	0.845 mm^{-1}
F(000)	2276
Crystal size	.6 x .2 x .2 mm^3
Theta range for data collection	2.13 to 21.59°.
Index ranges	-9<=h<=8, -34<=k<=31, -19<=l<=19
Reflections collected	20314
Independent reflections	6303 [R(int) = 0.0718]
Completeness to theta = 21.59°	99.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6303 / 0 / 611
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.0830
R indices (all data)	R1 = 0.0528, wR2 = 0.0861
Largest diff. peak and hole	0.553 and -0.622 e.Å^{-3}

(dippnapth)Ni(S$_2$) (2).   The space group was determined to be C2/c based on systematic absences and intensity statistics. Direct methods were used to locate C, Ni, P, and S atoms. All non-hydrogen atoms were refined anisotropically.   Hydrogen atoms were placed at idealized positions and refined isotropically using a riding model. The S atom was disordered over two sites (S(10) and S(20), only S(10) is pictured below). See Table S2 for crystal and refinement data.
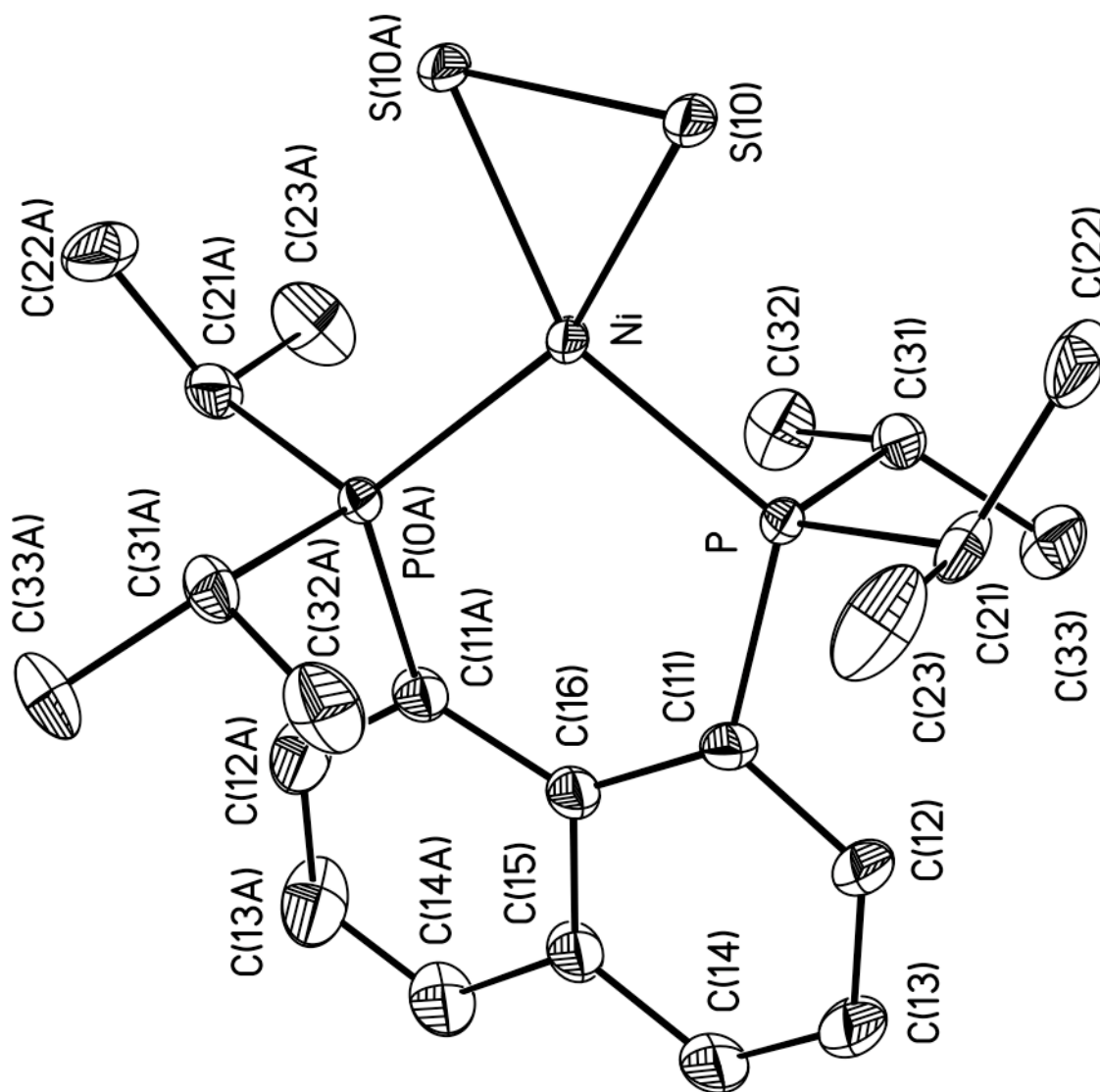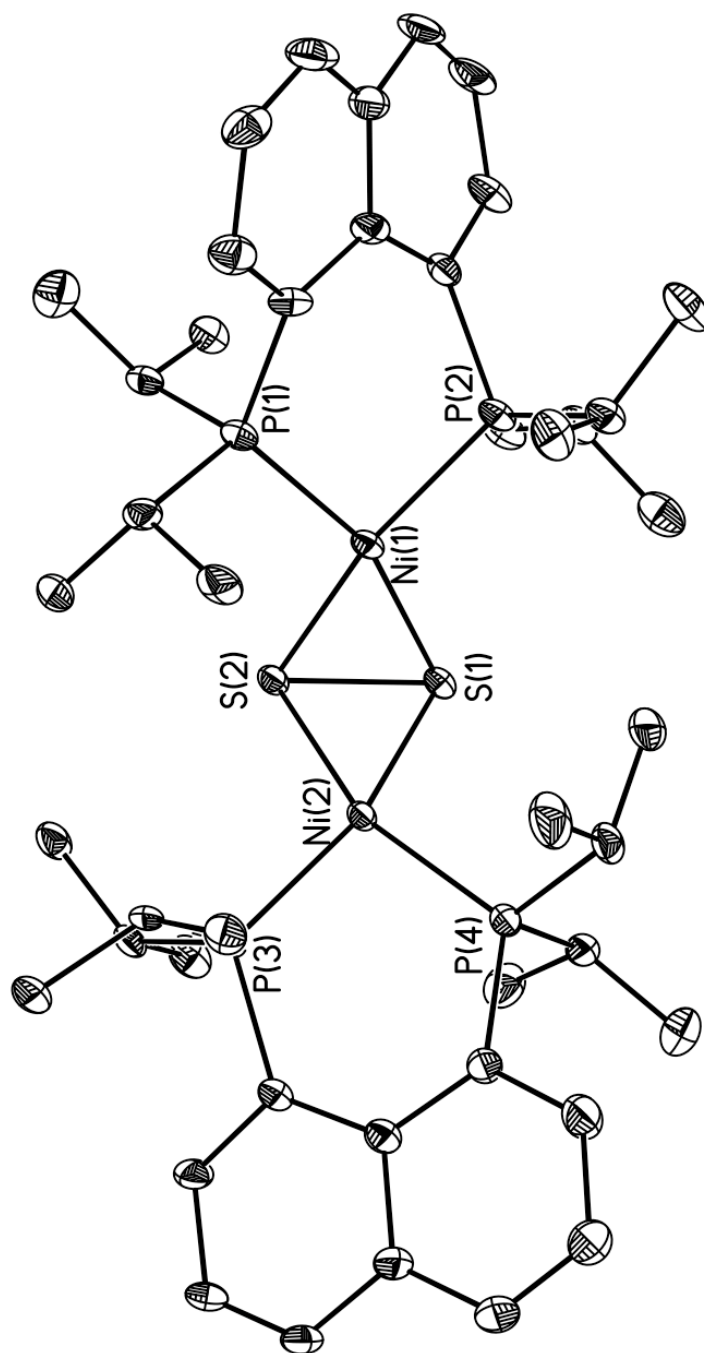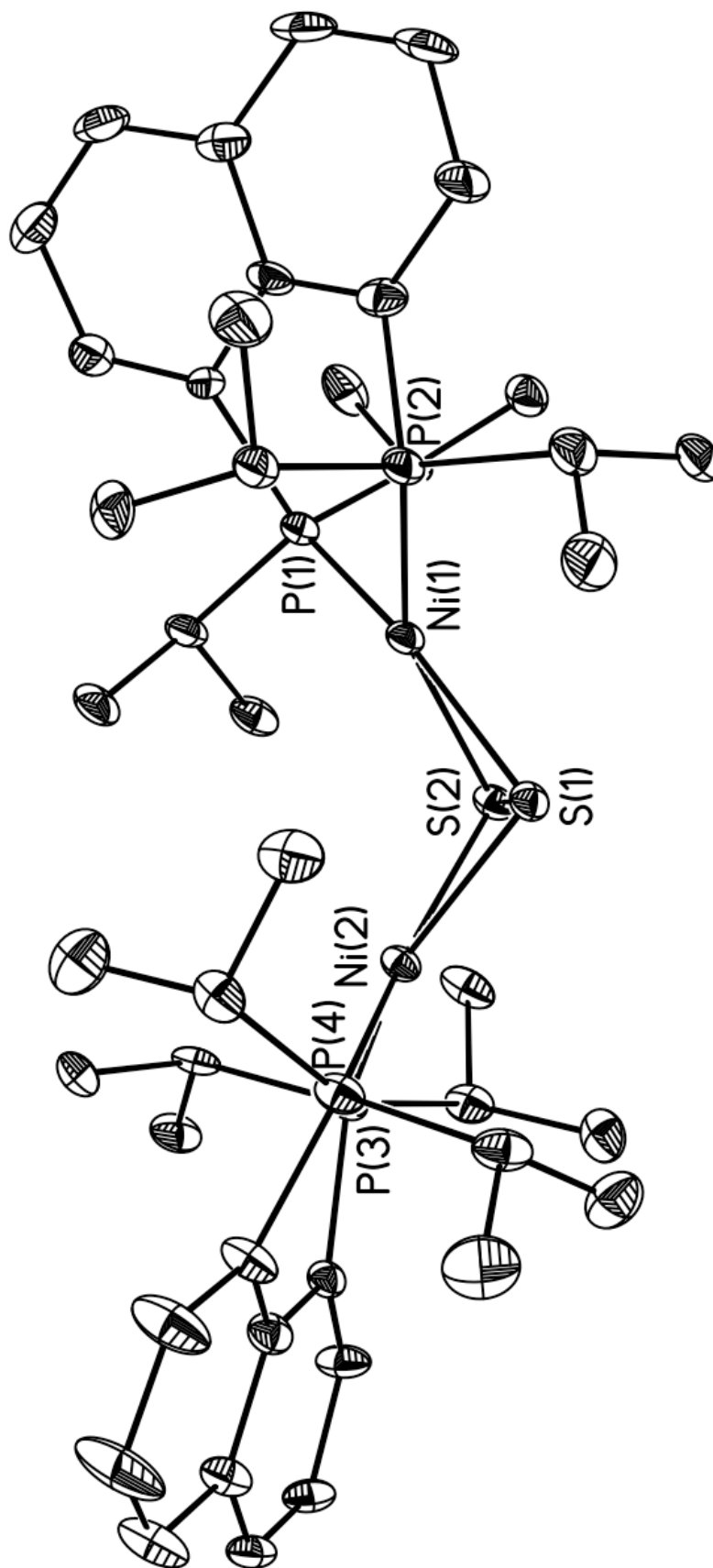
Table S2. Crystal data and structure refinement for (dippnapth)Ni(S$_2$) (**2**).

Identification code	vlad110m
Empirical formula	C22 H34 Ni P2 S2
Formula weight	483.26
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 16.380(5) Å a= 90°.
	b = 11.628(4) Å b= 113.684(6)°.
	c = 16.757(6) Å g = 90°.
Volume	2922.7(17) Å^3
Z	4
Density (calculated)	1.098 Mg/m^3
Absorption coefficient	0.921 mm^{-1}
F(000)	1024
Crystal size	0.06 x 0.02 x 0.02 mm^3
Theta range for data collection	2.22 to 25.00°.
Index ranges	-18<=h<=19, -13<=k<=7, -19<=l<=19
Reflections collected	7472
Independent reflections	2565 [R(int) = 0.0905]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Psi-Scan
Max. and min. transmission	0.9818 and 0.9468
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2565 / 0 / 138
Goodness-of-fit on F^2	0.966
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0987
R indices (all data)	R1 = 0.0539, wR2 = 0.1014
Largest diff. peak and hole	0.630 and -0.302 e.Å^{-3}

[(dippnapht)NiS]₂[BArF₄]₂ (**3**). The space group was determined to be P2(1)/c based on systematic absences and intensity statistics. Direct methods were used to locate B, C, Cl, F, Ni, O, P, and S atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined isotropically using a riding model. Typical trifluoromethyl disorder of the BArF₄ counterion was observed, but not modeled. See Table S3 for crystal and refinement data.
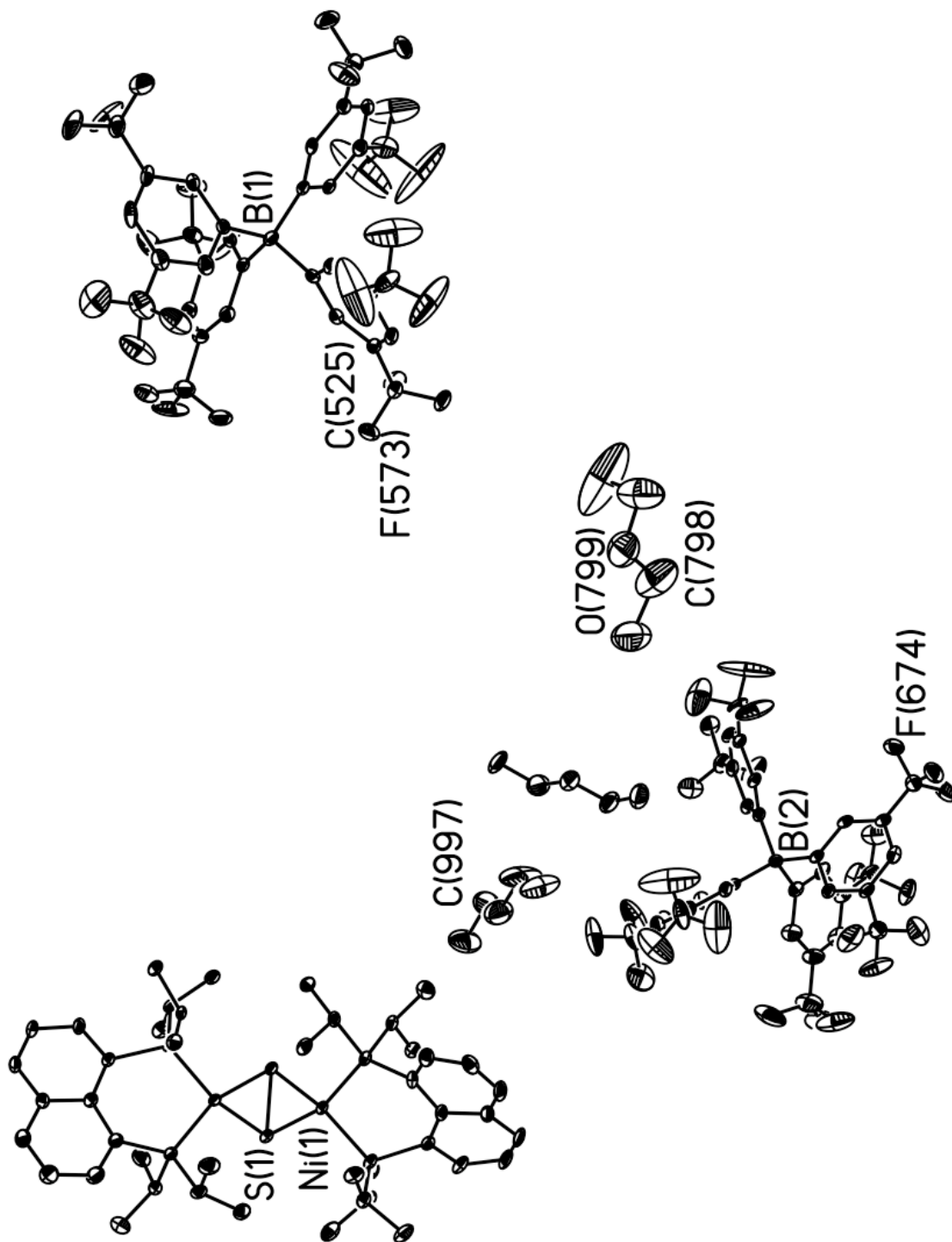
B(1)

C(525)

F(573)

O(799)

C(798)

F(674)

B(2)

C(997)

S(1)

Ni(1)

Table S3. Crystal data and structure refinement for [(dippnapht)NiS]$_2$[BAr$^F_4$]$_2$ (**3**).

Identification code	mit5a
Empirical formula	C120 H92 B2 F48 Ni2 O3 P4 S2
Formula weight	2820.98
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 24.248(3) Å a= 90°.
	b = 18.313(2) Å b= 96.573(3)°.
	c = 29.527(4) Å g = 90°.
Volume	13025(3) Å^3
Z	4
Density (calculated)	1.439 Mg/m^3
Absorption coefficient	0.487 mm^{-1}
F(000)	5704
Crystal size	0.60 x 0.20 x 0.20 mm^3
Theta range for data collection	1.40 to 25.00°.
Index ranges	-15<=h<=28, -21<=k<=21, -34<=l<=35
Reflections collected	68537
Independent reflections	22926 [R(int) = 0.1027]
Completeness to theta = 25.00°	100.0 %
Absorption correction	Psi-Scan
Max. and min. transmission	0.2813 and 0.2395
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	22926 / 0 / 1646
Goodness-of-fit on F^2	0.913
Final R indices [I>2sigma(I)]	R1 = 0.0734, wR2 = 0.1620
R indices (all data)	R1 = 0.1328, wR2 = 0.1816
Largest diff. peak and hole	1.371 and -1.079 e.Å^{-3}

[(dippnapht)NiS]₂ (4). The space group was determined to be C2/c based on systematic absences and intensity statistics. Direct methods were used to locate C, , Ni, P, and S atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined isotropically using a riding model. See Table S4 for crystal and refinement data.
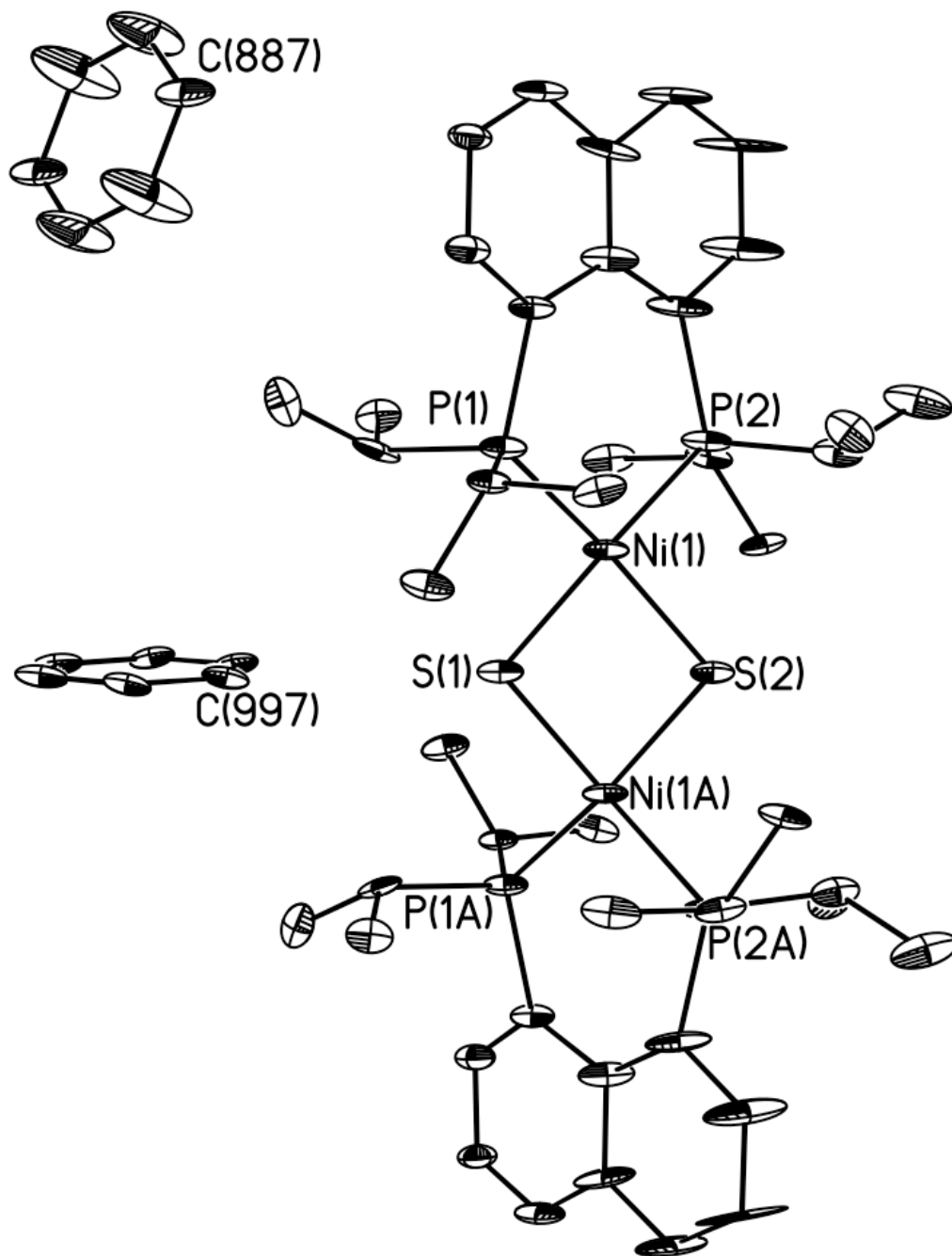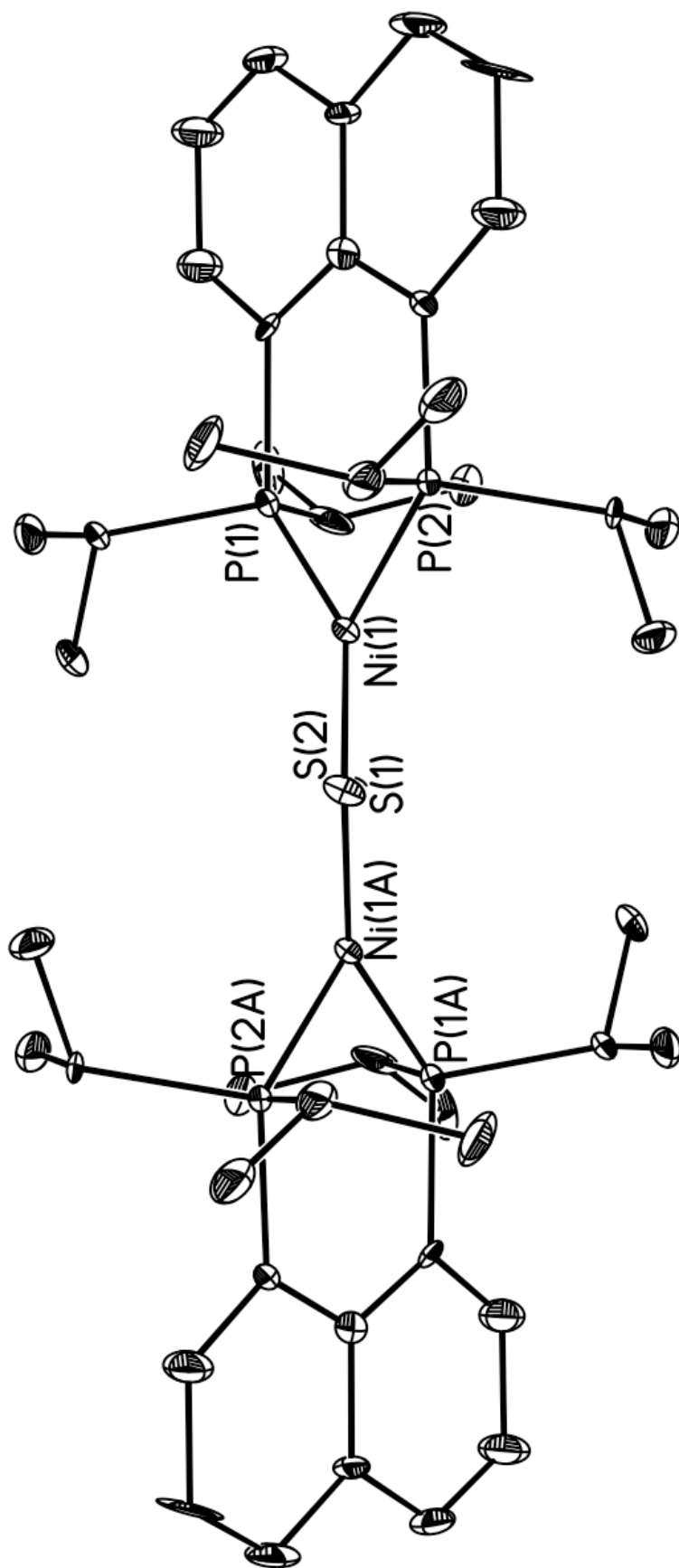
Table S4. Crystal data and structure refinement for [(dippnapht)NiS]$_2$ (**4**).

Identification code	carl111m
Empirical formula	C28 H34 Ni P2 S
Formula weight	523.26
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 28.881(17) Å a= 90°.
	b = 12.514(8) Å b= 100.912(9)°.
	c = 14.700(9) Å g = 90°.
Volume	5217(5) Å^3
Z	8
Density (calculated)	1.332 Mg/m^3
Absorption coefficient	0.961 mm^{-1}
F(000)	2208
Crystal size	0.60 x 0.20 x 0.20 mm^3
Theta range for data collection	1.44 to 22.50°.
Index ranges	-31<=h<=31, -13<=k<=13, -15<=l<=15
Reflections collected	19682
Independent reflections	3411 [R(int) = 0.2417]
Completeness to theta = 22.50°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8311 and 0.5964
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3411 / 0 / 298
Goodness-of-fit on F^2	1.262
Final R indices [I>2sigma(I)]	R1 = 0.1109, wR2 = 0.2466
R indices (all data)	R1 = 0.1190, wR2 = 0.2505
Largest diff. peak and hole	0.656 and -0.728 e.Å^{-3}