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[Bis(diphenylphosphino)alkane]- (pentane-2,4-dithionato) complexes of nickel(II)

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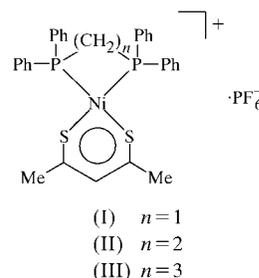
The structures of a series of four-coordinate nickel(II) complexes of the form $[\text{Ni}(\text{sacsac})\text{L}]\text{PF}_6$ (sacsac = pentane-2,4-dithione anion; $\text{L} = (\text{Ph}_2\text{P})_2(\text{CH}_2)_n$, $n = 1, 2, 3$) have been determined. These are [bis(diphenylphosphino)methane]-(pentane-2,4-dithionato-*S,S'*)nickel(II) hexafluorophosphate, $[\text{Ni}(\text{C}_{25}\text{H}_{22}\text{P}_2)(\text{C}_5\text{H}_7\text{S}_2)]\text{PF}_6$, [1,2-bis(diphenylphosphino)ethane]-(pentane-2,4-dithionato-*S,S'*)nickel(II) hexafluorophosphate, $[\text{Ni}(\text{C}_{26}\text{H}_{24}\text{P}_2)(\text{C}_5\text{H}_7\text{S}_2)]\text{PF}_6$, and [1,3-bis(diphenylphosphino)propane]-(pentane-2,4-dithionato-*S,S'*)nickel(II) hexafluorophosphate, $[\text{Ni}(\text{C}_{27}\text{H}_{26}\text{P}_2)(\text{C}_5\text{H}_7\text{S}_2)]\text{PF}_6$. All have a distorted square-planar arrangement about Ni with angles around Ni varying with the length of the hydrocarbon chain.

Comment

Although pentane-2,4-dithione (sacsac) is not stable in isolation many examples are known where the ligand is coordinated to a metal atom (Lockyer & Martin, 1980). The bis(sacsac) Co^{II} and Ni^{II} complexes (Beckett & Hoskins, 1974) both show a square-planar arrangement about the metal atom. Planar Ni^{II} mixed-ligand complexes containing phosphine and/or halide ligands have been found to act as effective catalyst precursors for olefin oligomerization and isomerization (Cavell, 1994; Cavell & Masters, 1986). Structures of two such complexes, related to the present study, are (sacsac)(P-Bu_3) ClNi (Cavell *et al.*, 1985) and (asacsac)(PET_3) ClNi (Cavell *et al.*, 1984) (asacsac is 3-allylpentane-2,4-dithione), both of which have square-planar geometry.

We describe here the structures of the hexafluorophosphate salts of pentane-2,4-dithione[bis(diphenylphosphino)methane]nickel(II), (I), $[\text{Ni}(\text{sacsac})(\text{dppm})][\text{PF}_6]$ pentane-2,4-dithione[bis-1,2-(diphenylphosphino)ethane]nickel(II), (II), $[\text{Ni}(\text{sacsac})(\text{dppe})][\text{PF}_6]$ and pentane-2,4-dithione[bis-1,3-(diphenylphosphino)propane]nickel(II), (III), $[\text{Ni}(\text{sacsac})(\text{dppp})][\text{PF}_6]$. In each case, the arrangement of the S and P

atoms about nickel is a distorted square plane with a high degree of planarity. The maximum deviation from the mean plane being 0.03 Å. The distortion from rectangular symmetry in the angles around the Ni atom arises from the variation of the size of the chelate ring increasing from four to six in the chelating phosphine ligand. Thus the P–Ni–P angles increase from 73.52 (6) in (I) to 85.39 (5) in (II) and 89.59 (3)° in (III) as the chelate ring size increases. This variation is similar to that found for other (P–P)M complexes from the Cambridge Crystallographic Database (Dierkes & van Leeuwen, 1999). The S–Ni–S angles show the opposite trend, decreasing from 101.29 (2) for (I) to 99.53 (5) in (II) and 97.22 (4)° in (III) as the strain imposed by the small chelate ring is eased.



The Ni–S distances are all comparable and average 2.146 Å which is in good agreement with other Ni(sacsac) complexes. The Ni–P distances show some variation, with those involving the smaller chelate ring being significantly smaller than those of the larger rings, average 2.204 for (I) and 2.228 and 2.237 Å for (II) and (III), respectively. The non-bonded S–P distances are all shorter than the sum of the van der Waals radii and average 3.073 Å, an effect also observed for the interligand S–S distances in $\text{Ni}(\text{sacsac})_2$. The corresponding S–P distances in the other known phosphine complexes are comparable. An explanation for this phenomenon has been advanced in terms of the planar nature of the six-membered chelate ring formed by the sacsac ligand (Beckett & Hoskins, 1974)

The sacsac ligands are all planar with maximum deviations from the mean plane being 0.06 Å for (II). The folding along the S–S vector, which has been observed for other complexes, is shown for (I) and (II) where the interplanar angles are 5.43 (6) and 7.22 (9)° respectively. For (III), the ligand is coplanar with the coordination plane. The methylene C atom of the dppe ligand lies 0.649 (2) Å from the mean plane of the Ni and P atoms in (I). In (II), the five membered ring formed by the dppe ligand has the *gauche* conformation with the two C atoms located 0.488 (6) and 0.185 (6) Å either side of the Ni–P plane. For (III), the six-membered ring formed by the dppe ligand has the chair conformation with the Ni atom 0.937 (2) Å below the plane defined by P1, C4 and their mirror related atoms and C5 is 0.678 (5) Å above the same plane.

Experimental

Complexes (I), (II) and (III) were prepared as the hexafluorophosphate salts by reaction of Ni(sacsac)₂, NiCl₂·6H₂O and the appropriate phosphine following the method described by Cavell & Masters (1986) for the tetraphenylborate salts. Sodium hexafluorophosphate was used in place of sodium tetraphenylborate. Suitable crystals were obtained by recrystallization from acetone.

Compound (I)

Crystal data

[Ni(C₂₅H₂₂P₂)(C₅H₇S₂)]PF₆
M_r = 719.27
 Monoclinic, *P*2₁/*n*₁
a = 10.89710 (10) Å
b = 17.73670 (10) Å
c = 16.7252 (2) Å
 β = 94.7930 (10)°
V = 3221.32 (5) Å³
Z = 4

Data collection

Siemens SMART diffractometer
 Area-detector ω scans
 Absorption correction: multi-scan
 (Blessing, 1995)
*T*_{min} = 0.652, *T*_{max} = 0.780
 30784 measured reflections
 7145 independent reflections

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.083$
S = 1.014
 7145 reflections
 379 parameters

D_x = 1.483 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 7505
 reflections
 $\theta = 2\text{--}27^\circ$
 $\mu = 0.936 \text{ mm}^{-1}$
T = 203 (2) K
 Prism, orange
 0.50 × 0.34 × 0.28 mm

6130 reflections with *I* > 2 σ (*I*)
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 27.43^\circ$
 $h = -13 \rightarrow 13$
 $k = 0 \rightarrow 22$
 $l = 0 \rightarrow 21$

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 1.0272P]$ where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.004$
 $\Delta\rho_{\text{max}} = 0.265 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.203 \text{ e } \text{Å}^{-3}$

Compound (II)

Crystal data

[Ni(C₂₆H₂₄P₂)(C₅H₇S₂)]PF₆
M_r = 733.30
 Triclinic, *P* $\bar{1}$
a = 11.0458 (2) Å
b = 13.4850 (2) Å
c = 14.5828 (1) Å
 $\alpha = 67.386 (1)^\circ$
 $\beta = 76.105 (1)^\circ$
 $\gamma = 72.088 (1)^\circ$
V = 1889.50 (5) Å³

Data collection

Siemens SMART diffractometer
 Area-detector ω scans
 Absorption correction: multi-scan
 (Blessing, 1995)
*T*_{min} = 0.654, *T*_{max} = 0.924
 17129 measured reflections
 7347 independent reflections

Z = 2
 $D_x = 1.289 \text{ Mg m}^{-3}$
 Mo *K* α radiation
 Cell parameters from 5722
 reflections
 $\theta = 2\text{--}26^\circ$
 $\mu = 0.799 \text{ mm}^{-1}$
T = 203 (2) K
 Irregular fragment, orange
 0.58 × 0.32 × 0.10 mm

5871 reflections with *I* > 2 σ (*I*)
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 26.16^\circ$
 $h = -13 \rightarrow 13$
 $k = -15 \rightarrow 16$
 $l = 0 \rightarrow 18$

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.104$
S = 1.038
 7347 reflections
 390 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1337P)^2 + 4.2975P]$ where $P = (F_o^2 + 2F_c^2)/3$
 $\Delta\rho_{\text{max}} = 0.525 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.562 \text{ e } \text{Å}^{-3}$

Compound (III)

Crystal data

[Ni(C₂₇H₂₆P₂)(C₅H₇S₂)]PF₆
M_r = 747.32
 Monoclinic, *P*2₁/*m*
a = 10.0345 (2) Å
b = 15.8632 (2) Å
c = 10.8058 (2) Å
 $\beta = 94.14^\circ$
V = 1715.58 (5) Å³
Z = 2

D_x = 1.447 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 8192
 reflections
 $\theta = 2\text{--}26^\circ$
 $\mu = 0.882 \text{ mm}^{-1}$
T = 203 (2) K
 Prism, orange
 0.30 × 0.22 × 0.18 mm

Data collection

Siemens SMART diffractometer
 Area-detector ω scans
 Absorption correction: multi-scan
 (Blessing, 1995)
*T*_{min} = 0.778, *T*_{max} = 0.857
 15834 measured reflections
 3634 independent reflections

2789 reflections with *I* > 2 σ (*I*)
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 26.38^\circ$
 $h = -12 \rightarrow 12$
 $k = -19 \rightarrow 19$
 $l = -13 \rightarrow 13$

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.0346$
 $wR(F^2) = 0.0952$
S = 0.998
 3634 reflections
 211 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.6603P]$ where $P = (F_o^2 + 2F_c^2)/3$
 $\Delta\rho_{\text{max}} = 0.335 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.263 \text{ e } \text{Å}^{-3}$

The structures were solved by Patterson and difference Fourier techniques and refined by full-matrix least squares. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups), and with *U*_{iso} constrained to be 1.2 (1.5 for methyl groups) times *U*_{eq} of the carrier atom.

Compound (III) has a mirror plane passing through the molecule and one phenyl ring shows high displacement parameters, indicative either of some disorder or deviation from true mirror symmetry. In all three complexes, the F atoms of the PF₆⁻ groups show high displacement parameters indicative of some disorder in these groups.

For (II), examination of the structure with *PLATON* (Spek, 1999) indicates the presence of a void of approximately 320 Å⁻³ between the molecules. Integration of the electron density within this void corresponds to the presence of two molecules of acetone. There are a number of small peaks of less than 2 e Å⁻³ within this volume indicating that the solvent is severely disordered. Application of the 'squeeze' function of *PLATON* and further refinement reduced $R[F < 2\sigma(F)]$ from 0.0693 to 0.0359. A final difference map, following this refinement, contained no peaks > 0.6 e Å⁻³.

For all compounds, data collection: SMART (Siemens, 1995); cell refinement: SMART; data reduction: SAINT (Siemens, 1995); program(s) used to solve structure: *SHELXS* (Sheldrick, 1990); program(s) used to refine structure:

SHELXL97 Sheldrick, (1997); software used to prepare material for publication: *SHELXL97*.

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