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Sulphur Chelates 33. Preparation, Characterization and X-Ray Structure Determination of (Chloro)-(pentane-2,4-dithionato)(triethylphosphine)nickel(II), Ni(SacSac)(PEt_3)Cl, an Asymmetric Complex which displays Fluxional Behavior in Solution on the NMR Time Scale

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*The title compound has been prepared and characterized spectroscopically and by single-crystal X-ray crystallography (refined to $R_1 = 0.052$, $R_w = 0.064$ with 1837 data having $I > 3\sigma(I)$). The dithioacetylacetonate (SacSac) methyl groups are NMR equivalent at room temperature, but can be resolved at temperatures below 288 K. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 7.6107(3) Å, b = 18.1466(28) Å and c = 11.5270(5) Å; β = 98.459(3)°, V = 1574.12(25) Å^3, and Z = 4. The coordination about the nickel(II) is planar. Important nickel–ligand lengths are Ni–S (*trans *Cl) 2.108(2) Å, Ni–S (*trans *P) 2.154(2) Å, Ni–Cl 2.206(2) Å, Ni–P 2.232(2) Å with angles SNiS 97.9(1)°, SNiCl 85.6(1)°, SNiP 91.4(1)° and ClNiP 85.2(1)°. Two of the triethylphosphine ethyl groups lie in a plane approximately normal to the rest of the molecule. The dithioacetylacetonate dimensions are similar to those in Ni(SacSac)$_2$, although the chelate bite is smaller, and there may be some asymmetry in the C–S bonding in Ni(SacSac)PEt_3Cl. The molecules pack with their chelate rings approximately parallel.*

Introduction

We have reported [1–4] the structures of the species ML(PR_3)Cl (M = Ni, Pd, Pt, L = S_2CNEt_2, R = Ph, Et). These compounds serve as models for comparing the donor-atom behaviour of sulphur and selenium, furnish structural data to augment our studies on C–N bond rotation [5] and ^{77}Se NMR [6, 7], and provide a convenient series with which to probe the *trans* effect of P, Cl, S and Se. The structures of the symmetric chelates ML_2 from which these compounds were synthesized are known [8–11] and so the series also allows a study of the effects of substitution for one of the ML_2 ligands.

The rationalization of apparently conflicting dynamic NMR spectroscopic data for the M(S_2CNR_2)(PR_3)Cl complexes [5, 12] was possible upon recognizing the steric requirements of the various phosphine ligands. In particular, a distortion of the phosphine ethyl groups in NiLPEt_3Cl was observed such that two of them are found in a plane approximately perpendicular to the nickel–donor atom plane. The larger palladium(II) and platinum(II) centers are able to accommodate the bulky and less deformable triphenylphosphine more comfortably than is nickel(II).

Additionally, it was demonstrated [3, 5] that at least three processes equilibrate the dithiocarbamate alkyl groups on the NMR time scale. They are identified as C⋯N bond rotation, a stericly-induced phosphine exchange, and a dissociative process involving either the halide or the chelate ligand.

We have extended studies of asymmetric complexes to the preparation, characterization and structural determination of the complex Ni(SacSac)(PEt_3)Cl. This compound (1) presents an additional measure of the distortions associated with the phosphine with a stericly demanding dithio ligand, (2) provides alkyl groups unable to equilibrate by C⋯N bond rotation, and (3) probes further the interaction of Lewis bases with sulphur chelates, an area of considerable current interest [5, 12–15]. The structures of Ni(SacSac)$_2$ and the analogous Ni(NH_2Sac-NH_2Sac)$_2$ are known [16, 17] and hence provide the basis for detailed comparisons.

Our successful high-yield synthesis of Ni(SacSac)(PEt_3)Cl supports the generality of the metathetical route to these asymmetric chelates and provides a useful synthesis of complexes of the elusive [18] dithioacetylacetonate ligand. Moreover, since several Ni(acac)$_2$/alkylating agent/phosphine mixtures exhibit catalytic activity [19], the present compound is expected to be a catalyst or catalyst precursor with an activity modified by the different chemical and

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TABLE I. Crystal Data for Ni(SacSac)PEt_3Cl.

Molecular formula	$NiC_{11}H_{22}S_2PCl$
Molecular weight	330 (fd) 353.54 (Calc)
dcalcd, g cm^{-3}	1.4
dobsd, g cm^{-3}	1.4 (by flotation)
Z, formula units per cell	4
Linear absorption μ cm^{-1}	17.2
$\lambda(MoK_\alpha)$, A	0.71073
Crystal dimensions (mm)	0.3 × 0.25 × 0.16
Systematic absences	0k0:k = 2n + 1
	h0l:h + 1 = 2n + 1
Space group	$C_{2h}^5P2_1/n$ (no. 14) monoclinic
Cell constants	
a, A	7.6107(3)
b, A	18.1406(28)
c, A	11.5270(5)
β	98.459(3)
Volume, A^3	1574.12(25)

TABLE II. Summary of Final Refinements for Ni(SacSac)-(PEt_3)Cl.

Total data collected	2205
Data used, $I/\sigma(I) \geq 3.0$	1837
Number of varied non-hydrogen parameters	145
Reflections: parameters	12.7
Final $R_1 = \{\Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|\}$	5.2%
$R_w = \{\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2\}^{1/2}$	6.4%

electronic properties resulting from substitution of sulphur for oxygen. Indeed, preliminary results indicate that cyclohexane is oligomerized by the title compound under mild conditions.

Experimental

Physical Measurements

Microanalyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee. The melting point was determined using a Laboratory Devices Mel-Temp melting point block and is reported uncorrected. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer using KBr pellets. ^1H NMR spectra were recorded on a Varian A-60A spectrophotometer. Fourier transform mode ^1H, ^{31}P and ^{13}C NMR spyctra were recorded on a Varian XL-100-15 spectrometer operated at 100.0, 40.5 and 25.16 MHz, respectively, with broad band proton decoupling where appropriate. Deuterium solvents were used as internal ^2H locks. Kinetic data were calculated from temperature variable Fourier transform ^1H NMR spectra as described previously [5].

Synthesis

$Ni(SacSac)_2$ and $Ni(PEt_3)_2Cl_2$ were synthesized and purified by literature methods [20, 21]. Solvents (Fisher Scientific) were used as received.

$Ni(SacSac)_2$ (1.00 g, 3.1 mmol) and $Ni(PEt_3)_2Cl_2$ (1.14 g, 3.1 mmol) were refluxed in benzene under nitrogen for two hours, after which time all of the $Ni(SacSac)_2$ had dissolved. The solution was filtered hot and the solvent removed with a RotaVap. The material was recrystallized in air from acetone/heptane to give dark crystals, yield 1.82 g (85%, based on $Ni(SacSac)_2$) mp 142–3 °C, soluble in benzene, chloroform and acetone. *Anal.* Calcd. for $NiC_{11}H_{22}ClPS_2$: C, 38.46; H, 6.5; P, 9.02; S, 18.66. Found: C, 38.55; H, 6.5; P, 8.73; S, 18.51. M.W. (in $CHCl_3$): Calcd: 343.5. Found: 300. The infrared spectrum shows dithioacetylacetonate [20] and triethylphosphine peaks. In particular, the ν(C=C) observed at 1485 cm^{-1} is consistent with a chelate SacSac structure [22].

X-Ray Structural Studies

A suitable crystal (Table I) was obtained for data collection by recrystallization from acetone/heptane and mounted on a glass fibre. The X-ray data were obtained with a Syntex $P2_1$ automatic four-circle diffractometer. Standard Syntex programs for crystal centering and indexing were used with graphite crystal monochromatic MoK_α radiation. Lattice parameters were deduced at 25 °C from the angular settings of fifteen well-centered reflections, average $2\theta = 18.86°$, and were consistent with a monoclinic cell (Table I). A total of 3125 reflections with $5.0 \leq 2\theta \leq 50°$ were collected using the θ–2θ scan technique with variable scan rates from 2.0°/min to 29.5°/min. The background was measured for a time equal to half the total scan time at a point 1° to each side of the K_{α_1} and K_{α_2} peaks, and the scan count was corrected for background. During data collection, two standard reflections were monitored every fifty reflections. The maximum variation of the standard reflections was ±5% throughout data collection. The data reduction process incorporated the usual Lorentz polarization and decay factor corrections. The data were not corrected for absorbance. The systematic absences were consistent with the monoclinic space group $P2_1/n$ C_{2h}^5 (number 14) [23]. The number of reduced data with $I/\sigma(I)>$, 0.0, 3.0 and 20.0 are 2205, 1837 and 574 respectively. Programs used in the solution and refinement of the structure have been given previously [24].

TABLE III. Positional Parameters and Estimated Standard Deviations of Ni(SacSac)(PEt_3)Cl.

	x	y	z
Ni	0.43509(15)	0.37531(6)	0.20837(9)
S_1	0.26331(30)	0.37374(12)	0.04227(18)
S_2	0.44575(30)	0.49048(11)	0.23266(17)
Cl	0.42441(38)	0.25394(12)	0.19724(21)
P	0.62044(30)	0.35729(11)	0.37479(19)
C_1	0.11533(121)	0.44548(55)	−0.15176(65)
C_2	0.21864(106)	0.45556(47)	−0.02871(67)
C_3	0.26448(118)	0.52630(48)	0.1182(72)
C_4	0.35433(111)	0.54494(42)	0.12059(70)
C_5	0.37373(128)	0.62830(43)	0.14686(73)
C_6	0.71925(113)	0.44182(43)	0.45227(72)
C_7	0.81234(112)	0.29933(43)	0.35522(69)
C_8	0.51609(112)	0.30714(42)	0.48630(72)
C_9	0.91434(133)	0.33036(59)	0.25878(88)
C_{10}	0.34802(129)	0.34569(54)	0.51524(85)
C_{11}	0.86265(122)	0.42679(51)	0.55909(75)

Solution and Refinement of the Structure

The distribution plot of the X-ray intensities and the distribution of the |E|'s were in good agreement with the theoretical values for a centric space group. The nickel position was obtained from the U(1/2)W plane and the (1/2)V(1/2) line of the Patterson synthesis. A structure factor calculation using this position yielded R = 0.352, R_w = 0.425 for 574 data and a Fourier map generated by this solution revealed the nickel, two sulphur, one chlorine and one phosphorus atom positions. A structure factor calculation using these positions yielded R = 0.219, R_w = 0.269. Subsequent Fourier syntheses produced all the non-hydrogen atoms. Two cycles of full matrix isotropic refinement gave R = 0.108, R_w = 0.111 (with unit weights and 2168 data). Two cycles of full matrix anisotropic refinement with a statistical weighting scheme gave the final values (Table II). Analysis of agreement factors as functions of fixed h, k, l, sin θ/λ and F_o revealed no unaccountable trends. Atomic scattering factors for neutral atoms, Ni^{+2} and Cl^- were taken from Cromer and Waber [25]. Anomalous dispersion corrections [26] (real and imaginary) were used for the nickel in the final refinement. The final refinement, atomic positions, thermal parameters, bond distances and angles and least squares planes are summarized in Tables II–V. Figure 1 is an ORTEP drawing of the molecule.

Results and Discussion

Structural Results

A monomeric formulation with the approximately planar nickel coordination is established by the crystallographic results. The nickel–donor atom plane makes an angle of 8° with the mean dithioacetylacetonate plane, similar [16] to that in $Ni(SacSac)_2$. This effect has been observed in related compounds

TABLE IV. Thermal Parameters[a] with Estimated Standard Deviations for Ni(SacSac)(PEt_3)Cl.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0135(3)	0.0017(3)	0.0053(3)	−0.0003(3)	−0.0002(3)	−0.0000(3)
S_1	0.0176(5)	0.0025(3)	0.0055(3)	−0.0011(3)	−0.0013(3)	0.0000(3)
S_2	0.0156(5)	0.0018(3)	0.0055(3)	0.0005(3)	−0.0006(3)	−0.0000(3)
Cl	0.0290(7)	0.0018(3)	0.0098(3)	0.0011(3)	−0.0049(3)	−0.0005(3)
P	0.0013(4)	0.0015(3)	0.0053(3)	0.0002(3)	−0.0000(3)	0.0001(3)
C_1	0.01812(21)	0.0053(5)	0.0037(7)	−0.0001(8)	−0.0029(10)	0.0005(4)
C_2	0.01111(17)	0.0039(4)	0.0062(8)	0.0010(7)	0.0022(10)	0.0011(4)
C_3	0.0152(19)	0.0028(3)	0.0058(8)	0.0002(7)	0.0017(10)	−0.0002(4)
C_4	0.0124(17)	0.0022(3)	0.0065(7)	0.0006(6)	0.0023(9)	0.0011(4)
C_5	0.0254(23)	0.0017(3)	0.0079(9)	−0.0003(8)	0.0008(11)	−0.0003(4)
C_6	0.0148(18)	0.0020(3)	0.0076(8)	0.0000(6)	−0.0028(10)	−0.0007(4)
C_7	0.0133(18)	0.0025(3)	0.0087(8)	0.0019(6)	0.0032(10)	−0.0001(4)
C_8	0.01525(18)	0.0021(3)	0.0082(8)	−0.0002(6)	0.0041(10)	0.0009(4)
C_9	0.0212(23)	0.0045(4)	0.0098(10)	0.0008(8)	0.0064(13)	0.0018(5)
C_{10}	0.0177(22)	0.0049(4)	0.0108(10)	0.0021(8)	0.0057(12)	0.0012(5)
C_{11}	0.0195(22)	0.0034(4)	0.0061(8)	−0.0005(8)	−0.0036(11)	−0.0000(4)

[a]The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE V. Significant Lengths (A), Angles (deg) for Ni(SacSac)(PEt_3)Cl.

Ni–S_1	2.154(2)	C_3–C_4	1.38(1)
Ni–S_2	2.108(2)	C_4–C_5	1.55(1)
Ni–Cl	2.206(2)	P–C_6	1.875(8)
Ni–P	2.232(2)	P–C_7	1.840(9)
S_1–C_2	1.705(9)	P–C_8	1.847(9)
S_2–C_4	1.693(8)	C_6–C_{11}	1.54(1)
C_1–C_2	1.53(1)	C_7–C_9	1.55(1)
C_2–C_3	1.39(1)	C_8–C_{10}	1.54(1)
S_1····S_2	3.214(3)	P····Cl	3.005(3)
S_1····Cl	2.962(3)	S_2····P	3.106(3)
S_1NiS_2	97.9(1)	$C_1C_2C_3$	119.4(6)
S_1NiCl	85.6(1)	$C_2C_3C_4$	126.7(6)
S_2NiP	91.4(1)	$C_3C_4C_5$	116.0(6)
ClNiP	85.2(1)	$C_3C_4S_2$	130.1(6)
NiS_1C_2	117.9(3)	$C_5C_4S_2$	113.9(5)
NiS_2C_4	118.3(3)	PC_6C_{11}	115.0(6)
$NiPC_6$	116.6(3)	PC_7C_9	111.7(6)
$NiPC_7$	113.0(3)	PC_8C_{10}	112.6(6)
$NiPC_8$	112.8(3)	C_6PC_7	104.8(4)
$S_1C_2C_1$	112.4(6)	C_6PC_8	104.8(4)
$S_1C_2C_3$	128.2(6)	C_7PC_8	103.5(4)

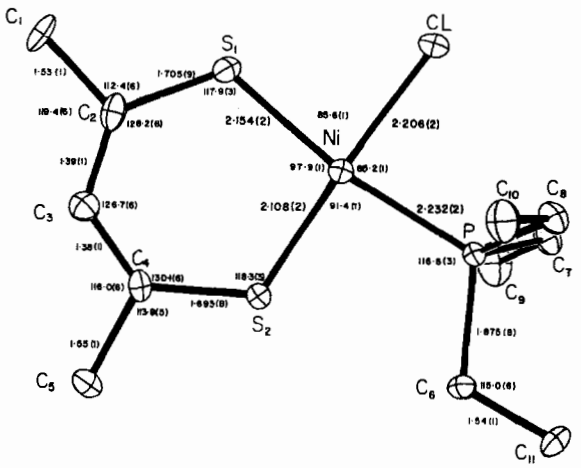

Fig. 1. An Ortep (50% probability) drawing of the molecular structure of Ni(SacSac)(PEt_3)Cl.

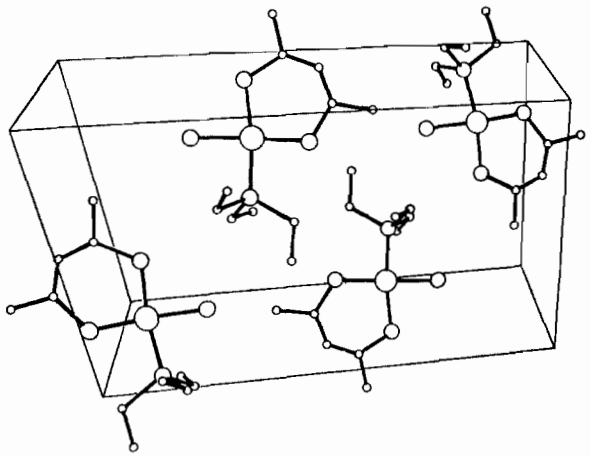

Fig. 2. A packing diagram for Ni(SacSac)(PEt_3)Cl.

[3, 4, 17, 27–30]. Perhaps the most striking feature of the structure is the alignment of the ethyl groups in a plane approximately normal to the rest of the molecule. The same phenomenon was observed in the NiL(PEt_3)Cl structures [3, 4] and can in the present case, be similarly ascribed to steric interactions between the chloride and the phosphine. The molecules pack with the chelate ligands approximately parallel, Fig. 2.

The SacSac Ligand

The dithioacetylacetonate ligand is approximately planar, its two halves making an angle of 5° at C_3. The bond lengths and angles are essentially the same as those in Ni(SacSac)$_2$. A trend towards structural asymmetry in the C–S bond lengths is observed, with C–S (*trans* P) > C–S (*trans* Cl) = C–S in Ni(SacSac)$_2$, but just as with similar trends in the M(S_2CNEt_2)(PR_3)Cl series [3], the differences are below the 3σ confidence limit for statistical significance. However, the continued observance of this trend with various asymmetric compounds suggests it to be real. Although the bite distances are the same in Ni(S_2CNEt_2)$_2$ and Ni(S_2CNEt_2)(PEt_3)Cl, that of Ni(SacSac)(PEt_3)Cl is less than that in Ni(SacSac)$_2$. This difference between the 1,1- and 1,3-dithio ligands can be related to the greater rigidity found in the four-membered chelate ring.

The chelate appears to be closer to the nickel atom in the title compound than in Hi(SacSac)$_2$. This follows from the smaller bite and shorter average Ni–S bonds in Ni(SacSac)(PEt_3)Cl, and the equivalence of the SNiS angles in the two compounds. Thus S···S interactions which are implicated by the short Ni(SacSac)$_2$ ligand separation [16] and the observed *cis* conformation of monothio-β-diketones [31, 32] possibly also lead to a greater Ni–S distance in the title compound than is observed when these S···S interactions are absent.

Nickel Environment

The NiS_2PCl core is essentially planar (rms deviation of fitted atoms from the plane 0.0391 Å). Just as in other compounds of this type [3, 4, 33], an asymmetry in the metal–sulphur bonding is evident,

TABLE VI. Selected Interatomic Dstances (A) for Ni(SacSac)(PEt_3)Cl, Ni(SacSac)$_2$ [16], Ni(Et_2dtc)(PEt_3)Cl [3] and Ni(Et_2dtc)$_2$ [8].

	Ni(SacSca)(PEt_3)Cl	Ni(SacSac)$_2$	Ni(Et_2dtc)(PEt_3)Cl	Ni(Et_2dtc)$_2$
Bite S···S	3.214 (3)	3.235 (2)	2.807 (3)	2.806 (4)
Interligand S···S	–	2.852 (2)	–	3.392 (3)
S···Cl	2.962 (3)	–	3.352 (3)	–
S···P	3.106 (3)	–	3.247 (3)	–
P···Cl	3.005 (3)	–	3.120 (3)	–
Ni–S *trans* P	2.154 (2)	2.156 (1)	2.241 (2)	2.201 (3)
Ni–S *trans* Cl	2.108 (2)		2.184 (2)	
C–S *trans* P	1.705 (9)	1.685 (3)	1.723 (7)	1.706 (8)
C–S *trans* Cl	1.693 (8)		1.728 (7)	
Ni–P	2.232 (2)	–	2.188 (2)	–
Ni–Cl	2.206 (2)	–	2.190 (2)	–

with Ni–S (*trans* P) > Ni–S (*trans* Cl). Additionally, the Ni–S (*trans* P) bond length is approximately equal to the Ni–S bonds in Ni(SacSac)$_2$ which are longer than Ni–S (*trans* Cl). The Ni–Cl bond length is comparable to those in [35] *cis*-$NiCl_2\{P(C_6H_{11})_2H\}_2$ (2.20(1) Å) but longer than those [34] in *trans*-$NiCl_2\{PPh(C_8H_{14})_2\}_2$ (2.166(1) Å [3] Ni(S_2CNEt_2)(PEt_3)Cl (2.190(2) Å) and [4] Ni(Se_2CNEt_2)(PEt_3)Cl (2.191(4) Å). The Ni–P bond is considerably longer than those [35] in *cis*-$NiCl_2\{P(C_6H_{11})_2H\}_2$ (2.15(1) Å) and the analogous [36, 37] Ni(acac)(PPh_3)Et (2.137(4) Å), Ni(acac)(Pcy_3)Me (2.159 Å) and [3] Ni(S_2CNEt_2)(PEt_3)Cl (2.188(2) Å), but shorter than those in square-planar [38, 39] *trans*-$NiBr_2(PPh_2(CH_2Ph))_2$ (2.263(7) Å), *trans*-$NiBr_2$(PEt_3)$_2$ (2.26 Å) and [34] *trans*-$NiCl_2\{PPh(C_8H_{14})\}_2$ (2.227(1) Å). Reductions of Ni–P bond lengths from that expected for a single bond in square planar nickel(II) complexes (2.28 Å) have been ascribed to increased π bonding. The longer Ni–P bond in Ni(SacSac)(PEt_3)Cl compared to the actylacetonate analog is then consistent with the presence of a greater π bond character in the Ni–S bond than in the Ni–O bond.

A steric interaction between a cyclohexyl ring and the methyl group of Ni(acac)(Pcy_3)Me has been suggested [37] but it does not appear to be as pronounced as in the asymmetric sulfur ligand complexes.

A comparison between the Ni$L(PEt_3)$Cl (L = S_2CNEt_2 and SacSac) structures reveals decreases in S···Cl, S···P and P···Cl and increases in Ni–P and Ni–Cl distances as L changes from S_2CNEt_2 to SacSac (Table VI). Thus, the larger (greater bite) and closer SacSac ligand has more difficulty accommodating the phosphine and chloride in coordination about nickel(II).

Triethylphosphine

The bond lengths observed for the phosphine are normal, the only usual feature being the alignment of the phosphorus and C_7–C_{10} in a plane (rms deviation of fitted atoms from the plane 0.0227 Å) at 94.04° to the Ni–donor atom plane. Space filling models indicate this to be a relatively stericly unencumbered orientation, consistent with the arguments advanced earlier.

NMR Studies

The ^{1}H NMR SacSac peaks are very similar to those of Ni(SacSac)$_2$ (Table VII). The methyl groups are magnetically equivalent at room temperature in chloroform-d and acetone-d_6. At lower temperatures, however, two resonances are observed for these methyl groups, with coalescence occurring at 298 K. Table VIII contains rate data appropriate to the SacSac methyl equilibration, together with typical results for C··N bond rotations. The respective kinetic parameters are consistent with the mechanism of SacSac methyl equilibration being analogous to the low energy pathway (apparently not involving C··N bond rotation) leading to dithiocarbamate alkyl equivalence in the Ni(S_2CNR_2)(PR'_3)X compounds.

Several possible processes can lead to equilibration of the SacSac methyl groups. These include an intramolecular square planar/tetrahedral interconversion, an associative-exchange mechanism (involving solvent for example), other intermolecular associative exchange mechanisms (for example a dissociation–dimerization sequence) or a dissociative mechanism. This last mechanism could proceed via phosphine dissociation, chloride dissociation or a monodentate–bidentate equilibrium involving the chelate.

TABLE VII. NMR Parameters[a] for $Ni(SacSac)_2$ and $Ni(SacSac)(PEt_3)Cl$.

Nucleus	Compound	Temp. (K)	Solvent	SacSac		PEt_3	
				CH	CH_3	CH_2	CH_3
^1H[b]	$Ni(SacSac)_2$	303	$CDCl_3$	7.11(1)	2.73(6)	–	–
	$Ni(SacSac)(PEt_3)Cl$	303	$CDCl_3$	7.291(1)	2.390(6)	1.842 doublet of quartets	1.273 doublet of triplets
		240	$CDCl_3$	7.350(1)	2.440(3) 2.402(3)		
						$^1J_{CH_2CH_3}$ = 7.8 Hz $^2J_{PCH_2}$ = 8.8 Hz $^3J_{PCH_3}$ = 16.4 Hz	
^{31}P[c]	$Ni(SacSac)(PEt_3)Cl$	303	$CDCl_3$	–	–	17.190	
^{13}C[b]	$Ni(SacSac)_2$	303	$CDCl_3$	131.59	32.65	–	–
	$Ni(SacSac)(PEt_3)Cl$	240	$CDCl_3$[d]	131.11	32.73 (doublet $^4J_{PC}$ = 8.42 Hz) 32.01	12.88 (doublet J_{PC} = 27.2 Hz)	8.10

[a]All peaks are singlets unless stated otherwise. Integrated intensities in parentheses. [b]δ values (ppm) with respect to tetramethylsilane as internal reference (δ = 0). [c]δ values (ppm) with respect to 85% H_3PO_4 as external reference (δ = 0). [d]Essentially the same spectrum is obtained in acetone-d_6.

TABLE VIII. Kinetic Parameters[a] for the SacSac Methyl Equilibration Compared to Those for C–N Bond Rotation.

Parameter	$Ni(SacSac)(PEt_3)Cl$ in $CDCl_3$ at 298 K	$PdCl(S_2CN(i\text{-}Bu)_2)(PPh_3)$ in $C_6D_5NO_2$ at 398 K[b]
E_a (kJ mol^{-1})	113.0 ± 4.2	66.1 ± 4.2
$\Delta G^{\ddagger}$ (kJ mol^{-1})	65.7 ± 4.2	91.6 ± 4.2
$\Delta H^{\ddagger}$ (kJ mol^{-1})	110.5 ± 4.2	62.3 ± 4.2
$\Delta S^{\ddagger}$ (J deg^{-1} mol^{-1})	150.6 ± 8.4	−73.2 ± 8.4

[a]Data analyzed [5] by the NMR line shape program of G. Binsch, DNMR-3. [b]Reference 5.

Symmetry considerations [40] and our failure to detect any effects due to paramagnetism argue against the squre-planar/tetrahedral interconversion. The large positive entropy of activation, $\Delta S^{\ddagger}$, supports a dissociative mechanism [41]. A driving force for such a dissociation is evident in the intramolecular steric pressures observed in the solid state structure. Moreover, the molecular geometry ensures an easy transition to the T or Y shaped geometries favored for three coordinate d^8 systems [42].

A 'dangling chelate' mechanism is not easily accommodated [43] by the magnitude of $\Delta S^{\ddagger}$, leaving halide and/or phosphine exchange as likely mechanisms for equilibrating the SacSac methyl groups. Either exchange can lead to methyl group equivalence and we cannot satisfactorily differentiate between them in this sytem. The dissociating ligand may be either chloride or phosphine or both as the solvent is varied.

In the presence of approximately two mol equivalents of added halide ion, as $[Me_4N]Cl$ in $CDCl_3$, a single ^1H nmr absorption is observed for the SacSac methyl groups over the temperature range 264–303 K. Thus, a different exchange process dominates in the presence of excess halide, a process which presumably involves a nucleophilic attack of the halide on the complex.

Phosphine dissociation is assumed to be small over the temperature range 213–303 K since the proton–phosphorus couplings $^2J_{P-H}$ and $^3J_{P-H}$ are maintained at 8.8 Hz and 16.4 Hz respectively. The position of the single sharp ^{31}P resonance accords well with those observed in similar species [3, 4].

The ^{13}C nmr spectra in the slow exchange limit show two absorptions attributable to the SacSac methyl carbons – a doublet downfield, and a singlet upfield of the resonances attributed to the corresponding carbons in $Ni(SacSac)_2$. The doublet splitting

is assigned as $^4J_{P-C}$ and this resonance is accordingly associated with the methyl group *trans* to the phosphine. Small $^4J_{Pt-H}$ couplings previously have been observed in related compounds [44]. The doublet becomes a broad singlet above the coalescence temperature.

Conclusions

Structural comparisons of the title compound with related compounds are made in Table VI. The differing structural *trans* effect of phosphorus and chloride, P ≫ Cl, is clearly evident, as is the steric compression about Ni (non-bond contacts) in Ni(SacSac)-(PEt_3)Cl. Tolman has elegantly demonstrated the interplay between steric and electronic effects [45] in phosphines. Obviously, both electronic and steric effects operate in the present compounds but it is not possible to resolve them exactly. The importance of steric effects is, however, emphasized by the coplanarity of two of the phosphine ethyl groups in the nickel(II) dithio and diselenocarbamato chelates. We are probing the electronic effects within this series of compounds by ESCA and electrochemistry.

This study clearly demonstrates the existence of an exchange mechanism with nickel(II) dithio chelates (not involving C⋯N bond rotation) which is disassociative. This process is considerably slower for the title compound than for the nickel(II) dithiocarbamates [5].

Interactions of Lewis bases with dithio chelates have attracted much attention recently [5, 12–15]. The metathesis employed in our synthetic work provides a convenient high yield procedure for preparing the $ML(PR_3)X$ complexes. The syntheses at reflux of species containing ligands such as $SacSac^-$ and CH_3^-, which are unstable in the absence of coordination sites, raise interesting questions concerning the mechanism(s) of ligand exchange in metathesis. We are further exploring the reaction chemistry of these $ML(PR_3)X$ compounds, and the mode of ligand exchange in their syntheses.

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