Preparation and Characterization of Cobalt(III), Nickel(II), and Copper(I) Complexes Containing 5,8-Diphenyl-5,8-diphospha-2,11-dithiadodecane (L), $CH_3SCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2SCH_3$, and Molecular Structure of [Ni(*rac*(*P*)-L)$_2$](BF$_4$)$_2$

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Δ-RR,Λ-SS-[Co(acac)$_2$(*rac*(*P*)-L)]$^+$ and [Co(acac)$_2$(*meso*(*P*)-L)]$^+$ were obtained by reaction of [Co(acac)$_3$] (acac=2,4-pentanedionate ion) with 5,8-diphenyl-5,8-diphospha-2,11-dithiadodecane (L) in 1:1 molar ratio in dichloromethane in the presence of active charcoal, no *Δ-SS,Λ-RR* isomer of the *rac*(*P*)-L complex being formed. Five-coordinate [Ni(*rac*(*P*)-L)$_2$]$^{2+}$ and [Ni(*meso*(*P*)-L)$_2$]$^{2+}$ were yielded by reaction of Ni(II) and L in 1:2 molar ratio in methanol, and the molecular structure of less soluble [Ni(*rac*(*P*)-L)$_2$](BF$_4$)$_2$ was determined by X-ray analysis. Crystal data: monoclinic, space group $P2_1/n$, a=17.136(3), b=20.134(5), c=14.106(3) Å, β=93.30(2)°, V=4859(2) Å^3, Z=4, R=0.089 for 8001 reflections. The Ni atom is surrounded square pyramidally by four P atoms in the basal plane and one S atom at the apical position with distances of the Ni–P: 2.214(2)—2.234(2) Å and the Ni–S: 2.603(2) Å. Both [Ni(*rac*(*P*)-L)$_2$]$^{2+}$ and [Ni(*meso*(*P*)-L)$_2$]$^{2+}$ in CH_2Cl_2 solutions exchange four $-SCH_3$ groups at the apical positin on the NMR time scale. White [Cu(*rac*(*P*)-L)]BF$_4$ was precipitated selectively by reaction of Cu(BF$_4$)$_2$·6H$_2$O and L in 1:1 molar ratio in ethanol.

In our previous papers, we have reported the preparation and stereochemistry of octahedral cobalt(III) complexes with linear quadridentate phosphine ligands of the PNNP[1–4] and NPPN[5–7] types for donor atoms. The ligand of the latter type has two chiral phosphorus donor atoms and forms various stereoisomers depending on the chirality. This paper reports the preparation and characterization of cobalt(III), nickel(II), and copper(I) complexes of 5,8-diphenyl-5,8-diphospha-2,11-dithiadodecane, $CH_3SCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2SCH_3$ (L), together with the X-ray crystal structure of [Ni(*rac*(*P*)-L)$_2$](BF$_4$)$_2$. The ligand is also a linear quadridentate ligand with two chiral phosphorus and two sulfur donor atoms. However, ligand L was found to act as a bidentate in Co(III), a bidentate and a terdentate in Ni(II), and a quadridentate in Cu(I) complexes.

To our knowledge, only two papers have appeared for metal complexes of the SPPS-type ligand. Issleib and Gans[8] prepared [MX(NH$_3$)(SCH$_2$CH$_2$PHCH$_2$CH$_2$PHCH$_2$CH$_2$S)] (M=Co, X=Br; M=Rh, X=Cl) and [M{SCH(R)CH$_2$PHCH$_2$CH$_2$PHCH$_2$CH(R)S}] (M=Ni, Pd, Pt; R=H, CH$_3$). However, detailed stereochemistry for Co(III) and Rh(III) complexes was not reported. Schmelzer and Schwarzenbach[9] reported the X-ray crystal structures of *rac*(*P*)- and *meso*(*P*)-isomers of [Ni(SCH$_2$CH$_2$P(C$_6$H$_5$)CH$_2$CH$_2$CH$_2$P(C$_6$H$_5$)CH$_2$CH$_2$S)], but experimental details and chemical properties were not described.

Experimental

The phosphine ligand was handled under an atmosphere of nitrogen until it formed metal complexes. All solvents used for the preparation of the ligand and complexes were made oxygen-free by bubbling nitrogen for 20 min immediately before use. Absorption and ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi U3400 and a R-90H spectrometer, respectively.

Preparation of 5,8-Diphenyl-5,8-diphospha-2,11-dithiadodecane (L). A 15% hexane solution of butyl lithium (53 cm^3, 0.086 mol) was added dropwise with stirring to a dry tetrahydrofuran solution (600 cm^3) of 1,2-bis(phenylphosphino)ethane[10] (8.3 g, 0.034 mol). The solution changed from red to orange in color and gave yellow precipitate of $C_6H_5P(Li)CH_2CH_2P(Li)C_6H_5$. The precipitate was dissolved by warming at 50 °C. To the solution was added 2-chloroethyl methyl sulfide (7.5 g, 0.067 mol). The mixture was stirred at 50 °C for 5 h, and cooled to room temperature. Water (800 cm^3) was added to the solution dropwise with stirring. The ethereal layer was separated, dried over MgSO$_4$ (5 g) overnight, filtered, and the filtrate was evaporated to leave an oily product. This was used for the preparation of metal complexes without further purification. Yield: 13.2 g (98%).

Preparation of Metal Complexes. [Co(acac)$_2$(*meso*(*P*)-L)]SbF$_6$ (A-I) and *Δ-RR,Λ-SS*-[Co(acac)$_2$(*rac*(*P*)-L)]SbF$_6$ (A-II). A mixture of [Co(acac)$_3$][11] (0.19 g, 0.53 mmol), L (0.21 g, 0.53 mmol) and active charcoal (0.03 g) in dichloromethane (20 cm^3) was stirred for 10 h. Active charcoal was filtered off, and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in a mixture of water and methanol (2:1, 50 cm^3), and the solution was applied on a column (ϕ3 cm×120 cm) of SP-Sephadex C-25. By elution with a 0.1 mol dm^{-3} NaCl aqueous solution two large dark-red bands (**A-I** and **A-II** in the order of elution) and several small bands appeared. Each eluate of the two large bands was shaken with chloroform to extract the complex. The extract was evaporated to dryness and the residue was dissolved in water. On addition of excess NaSbF$_6$ the solution yielded orange brown crystals, which were collected by filtration and recrystallized from a hot mixture of water and methanol (1:1). Yield: 93 mg (19%) for **A-I** and 99 mg (21%) for **A-II**. Found for **A-I**: C, 40.61; H, 4.83%. Found for **A-II**: C, 40.89; H, 4.81%. Calcd for [Co(acac)$_2$L]SbF$_6$=$C_{30}H_{42}O_4S_2P_2SbF_6Co$: C, 40.61; H, 4.77%. The complexes are soluble in methanol, ethanol, chloroform, and acetone, and slightly soluble in water and diethyl ether.

$[\mathrm{Ni}(\mathit{rac}(P)\text{-L})_2](\mathrm{BF}_4)_2$ (B-I) and $[\mathrm{Ni}(\mathit{meso}(P)\text{-L})_2](\mathrm{BF}_4)_2$ (B-II). $\mathrm{Ni(BF_4)_2 \cdot 6H_2O}$ (0.54 g, 1.6 mmol) and L (1.2 g, 3.1 mmol) were mixed in methanol (15 cm^3) with stirring at room temperature, and then the mixture was cooled at 0 °C. After 30 min a red-brown precipitate (**B-I**) which appeared was collected by filtration and recrystallized from hot methanol. Yield: 0.43 g (27%). The filtrate was allowed to stand to evaporate slowly, yielding red-brown crystals (**B-II**). They were recrystallized from hot methanol. Yield: 0.23 g (15%). Found for **B-I**: C, 47.03; H, 5.56%. Found for **B-II**: C, 47.15; H, 5.64%. Calcd for $[\mathrm{Ni(L)_2}](\mathrm{BF_4})_2 = \mathrm{C_{40}H_{56}P_4S_4B_2F_8Ni}$: C, 47.04; H, 5.53%. The complexes are soluble in chloroform and methanol, and insoluble in water and diethyl ether.

Table 1. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors of $[\mathrm{Ni}(\mathit{rac}(P)\text{-L})_2](\mathrm{BF}_4)_2$

Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^2$
Ni	3950.1(4)	2137.0(3)	3941.1(4)	2.4
S1	5069 (2)	3213 (1)	247 (2)	6.8
S2	5431 (2)	3324 (2)	7571 (2)	7.1
S3	870 (1)	3671 (1)	3555 (2)	7.1
S4	4604 (1)	1234 (1)	5043 (1)	3.8
P1	4945 (1)	2124 (1)	2991 (1)	3.1
P2	4513 (1)	3050 (1)	4552 (1)	3.1
P3	2802 (1)	2348 (1)	4552 (1)	2.8
P4	3361 (1)	1275 (1)	3239 (1)	2.9
F1	1522 (6)	2974 (4)	968 (10)	12.0
F2	2681 (5)	3318 (5)	1525 (6)	9.8
F3	1737 (9)	4045 (5)	1107 (19)	17.0
F4	2351 (8)	3453 (8)	28 (6)	13.4
F5	−3028 (13)	4863 (8)	3088 (18)	17.5
F6	−3350 (16)	4998 (9)	2002 (15)	17.8
F7	−2408 (17)	4246 (10)	2081 (34)	25.3
F8	−3312 (17)	3829 (9)	2771 (20)	19.2
C1	4669 (13)	3969 (7)	661 (12)	10.4
C2	5389 (4)	2821 (4)	1338 (6)	5.2
C3	4709 (4)	2605 (4)	1908 (5)	4.7
C4	5390 (3)	1367 (3)	2589 (4)	3.4
C5	5209 (4)	1120 (4)	1684 (5)	4.5
C6	5567 (5)	531 (4)	1399 (6)	5.7
C7	6070 (5)	198 (4)	1985 (7)	5.8
C8	6257 (4)	440 (4)	2863 (7)	5.9
C9	5915 (4)	1010 (4)	3190 (5)	4.3
C10	5777 (4)	2532 (4)	3655 (5)	4.4
C11	5475 (4)	3180 (4)	4027 (6)	4.9
C12	4060 (4)	3851 (3)	4302 (4)	3.5
C13	4057 (4)	4365 (4)	4963 (6)	4.8
C14	3777 (5)	4985 (4)	4707 (8)	5.9
C15	3485 (5)	5097 (4)	3808 (7)	5.6
C16	3447 (5)	4594 (4)	3130 (6)	5.6
C17	3733 (4)	3973 (4)	3406 (5)	4.7
C18	4692 (4)	3002 (3)	5856 (5)	4.2
C19	5424 (4)	3323 (5)	6283 (6)	5.5
C20	4873 (9)	4058 (8)	7755 (7)	8.7
C21	−99 (6)	3510 (7)	3875 (8)	7.7
C22	1350 (4)	2969 (4)	4139 (5)	4.4
C23	2180 (3)	2914 (4)	3809 (4)	3.9
C24	2754 (3)	2660 (3)	5757 (4)	3.4
C25	2847 (4)	2225 (4)	6498 (5)	4.8
C26	2871 (6)	2477 (7)	7426 (5)	6.9
C27	2788 (6)	3119 (6)	7615 (6)	6.9
C28	2692 (5)	3569 (6)	6866 (8)	7.0
C29	2675 (4)	3342 (4)	5931 (5)	4.7
C30	2267 (3)	1563 (3)	4545 (4)	3.3
C31	2356 (3)	1212 (3)	3604 (5)	4.0
C32	3242 (3)	1185 (3)	1953 (4)	3.5
C33	3431 (4)	589 (4)	1498 (5)	4.9
C34	3294 (5)	539 (5)	523 (6)	6.2
C35	2994 (5)	1075 (5)	−2 (6)	6.2
C36	2821 (5)	1644 (5)	451 (5)	6.0
C37	2947 (4)	1715 (4)	1433 (5)	4.4
C38	3831 (4)	503 (3)	3684 (5)	4.0
C39	3996 (4)	512 (3)	4732 (5)	4.0
C40	4676 (6)	1170 (5)	6310 (5)	6.1
B1	2077 (6)	3460 (5)	903 (7)	5.8
B2	−3181 (10)	4424 (9)	2460 (9)	9.2

$[\mathrm{Cu}(\mathit{rac}(P)\text{-L})]\mathrm{BF}_4$. Mixing of $\mathrm{Cu(BF_4)_2 \cdot 6H_2O}$ (0.13 g, 0.53 mmol) and L (0.21 g, 0.53 mmol) in methanol (10 cm^3) with stirring resulted in immediate formation of a white precipitate. It was collected by filtration and washed with water. Yield: 0.09 g (31%). Found: C, 44.03; H,5.16%. Calcd for $[\mathrm{Cu(L)}]\mathrm{BF_4} = \mathrm{C_{20}H_{28}P_2S_2BF_4Cu}$: C, 44.10; H, 5.18%. The complex is soluble in chloroform, but insoluble in water, methanol, and diethyl ether.

X-Ray Analysis. A reddish brown crystal of $[\mathrm{Ni}(\mathit{rac}(P)\text{-L})_2](\mathrm{BF}_4)_2$with approximate dimensions, 0.30×0.28×0.25 mm^3 was used for the data collection. Crystal data: monoclinic, $P2_1/n$, $a=17.136(3)$, $b=20.134(5)$, $c=14.106(3)$ Å, $\beta=93.30(2)°$, $V=4859(2)$ Å^3, $D_x=1.40$, $D_m=1.39$ g cm^{-3}, $Z=4$, and $\mu(\mathrm{Mo}\ K\alpha)=7.53$ cm^{-1}. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). Within the range $2\theta<60°$, 8001 independent reflections with $|F_o|>3\sigma(|F_o|)$ were obtained. Absorption corrections were made by using the DABEX program.[12] The calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science with the program system UNICS III.[12]. The structure was solved by the usual heavy-atom method; the position of Ni was deduced by means of the Patterson synthesis, and all the non-hydrogen atoms were located by the subsequent Fourier synthesis. The positions of 16 among 56 hydrogen atoms were identified in the subsequent difference-Fourier maps. The structure was refined by block-diagonal least squares methods with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. The function minimized was $\sum w||F_o|-|F_c||^2$. Final R was 0.089 for 8001 observed unique reflections, and the atomic parameters of non-hydrogen atoms are listed in Table 1. Complete lists of observed and calculated structure factors, hydrogen atomic parameters, and anisotropic thermal parameters for non-hydrogen atoms are deposited as Document No. 8964 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Cobalt(III) Complexes. Two isomers (**A-I** and **A-II**) of $[\mathrm{Co(acac)_2(L)}]^+$ were obtained by reaction of $[\mathrm{Co(acac)_3}]$ with L in dichloromethane in the presence of active charcoal. The two isomers show absorption spectra very similar to each other, and give the first d-d band at 21300 (**A-I**) and 21200 cm^{-1} (**A-II**) (Fig. 1). These band positions are similar to those of $[\mathrm{Co(acac)_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}}]^+$ (20200 cm^{-1})[13] and $[\mathrm{Co(acac)_2\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}}]^+$ (23400 cm^{-1}),[14] indicating the coordination of two phosphorus atoms of L in these isomers. For $[\mathrm{Co(acac)_2L)}]^+$, there are three possible isomers, Δ-*RR*,Λ-*SS*- and Λ-*RR*,Δ-*SS*-$[Co(acac)_2(rac(P)\text{-}L)]^+$ and $[Co(acac)_2(meso(P)\text{-}L)]^+$. The *rac*(*P*)- and *meso*(*P*)-L complexes have C_2 and C_1 symmetries, respectively. In the ^1H NMR spectra isomer **A-I** exhibits six singlets for the methyl group (δ=0.96, 1.94, 2.03, 2.06, 2.16, 2.17, in $CDCl_3$) and two singlets for the methine group (δ=4.74, 5.51). Thus isomer **A-I** was assigned to the *meso*(*P*)-L complex. For isomer **A-II**, three singlet methyl signals (δ=1.04, 2.06, 2.12) and one singlet methine signal (δ=4.93) are observed, and the isomer can be assigned to the *rac*(*P*)-L complex. The assignment of either the Δ-*RR*,Λ-*SS* or Λ-*RR*,Δ-*SS* isomer was made on the basis of the chemical shift of methine proton of acac. Molecular models show that the phenyl groups of L in the Δ-*RR*, Λ-*SS* isomer are located over the acac chelate rings, while those in the Λ-*RR*,Δ-*SS* isomer are disposed away from the acac chelate rings. The methine protons of isomer **A-II** resonate at a remarkably high field (δ=4.93) compared with that (δ=5.51) of $[Co(acac)_3]$. The high field shift is attributable to the shielding effect of the phenyl group located over the acac chelate ring as has been often observed for related complexes.[3,6,7,13–15]

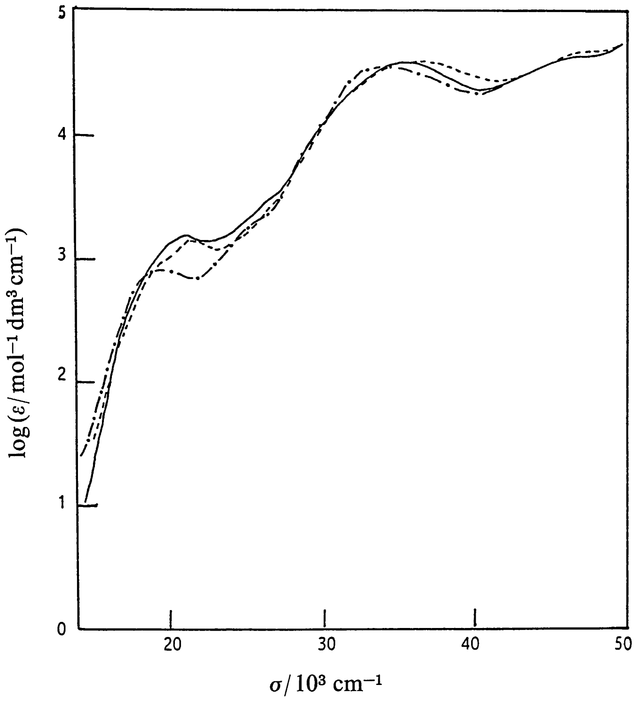

Fig. 1. Electronic spectra of $[Co(acac)_2(X)]SbF_6$ in CH_3CN solution; X=*rac*(*P*)-L (——), X=*meso*(*P*)-L (----), and $[Co(acac)_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}]PF_6$ (—·—) in ethanol.

Thus **A-II** was assigned to the Δ-*RR*,Λ-*SS*-L isomer. Two methine proton signals with a large chemical shift difference in the *meso*(*P*)-L complex (**A-I**) are consistent with molecular model considerations.

The formation of the other Λ-*RR*,Δ-*SS* isomer of the *rac*(*P*)-L complex was not observed. In this isomer the $-CH_2CH_2SCH_3$ group is disposed over the acac chelate ring, and the structure is supposed to be less stable than that of the Δ-*RR*,Λ-*SS* isomer with the phenyl group over the acac chelate ring. No acac complex containing quadridentate L, $[Co(acac)(L)]^{2+}$ was formed under the experimental conditions, in contrast to $NH_2(CH_2)_2P(C_6H_5)(CH_2)_nP(C_6H_5)(CH_2)_2NH_2$ (=NPPN, n=2[5,6], 3[6]) which formed only quadridentate ligand complexes, $[Co(acac)(NPPN)]^{2+}$ by similar reactions. The coordination ability of the $-SCH_3$ group would be weaker than that of acac toward Co(III).

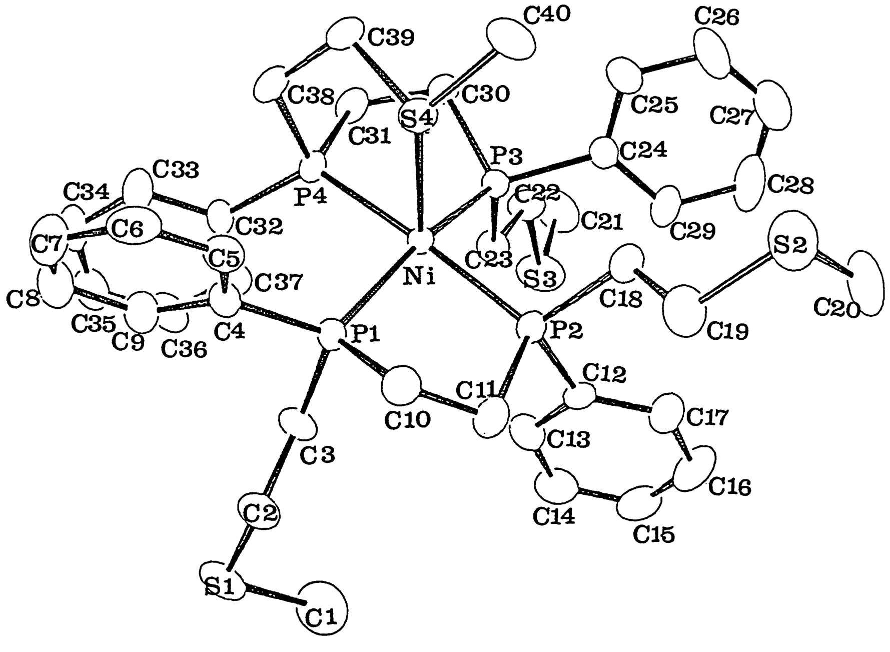

Fig. 2. A perspective view of $[Ni(rac(P)\text{-}L)_2]^{2+}$.

Nickel(II) Complexes. Two isomers (**B-I** and **B-II**) of $[Ni(L)_2](BF_4)_2$ were obtained by fractional crystallization from a methanol solution containing $Ni(BF_4)_2 \cdot 6H_2O$ and L in 1 : 2 molar ratio. The structure of the less soluble isomer (**B-I**) was determined by an X-ray diffraction method. A perspective view of the complex cation is shown in Fig. 2. The selected bond distances and angles are given in Table 2. The complex is a racemate consisting of $[Ni(RR(P)\text{-}L)_2]^{2+}$ and $[Ni(SS(P)\text{-}L)_2]^{2+}$. The chirality of the coordinating sulfur atom is *S* for the *RR*(*P*)-L and *R* for the *SS*(*P*)-L complexes. The Ni(II) ion forms a slightly distorted square pyramid with four phosphorus atoms in the basal plane and the sulfur atom at the apical position. The average Ni–P distance of 2.226(2) Å is very similar to those reported for square pyramidal diphosphine–Ni(II) complexes, $[NiBr(HQ)(H_2Q)] \cdot H_2O$ (av. 2.227(2) Å, $H_2Q{=}HO_2CCH_2P(C_6H_5)(CH_2)_2P(C_6H_5)CH_2CO_2H$, Br^- at the apical position)[16] and $[NiI(depe)_2]I$ (av. 2.224(5) Å, depe $=(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2$, I^- at the apical position).[17] The Ni–S distance (2.603(2) Å) is longer than those found in both square planar (2.22 Å) and octahedral (2.43 Å) Ni(II) complexes.[18] It is known that the apical Ni-ligand bond distance in a square pyramidal complex is, in general, fairly long compared with those in the basal plane.[19] For example, the apical Ni–S bond distance in the square pyramidal $[NiI_2\{bis(o\text{-}methylthiophenyl)phenylphosphine\}]$ complex is 2.789(10) Å, while that at the basal position is 2.189(9) Å.[20]

The deviations from the mean plane formed by four phosphorus atoms are −0.111(2), 0.126(2), 0.113(2), and −0.143(2) Å for P(1), P(2), P(3), and P(4), respectively, 0.204(1) Å for the Ni(II) and 2.753(2) Å for the S atom. The two P–P chelate rings take a nearly δ gauche conformation in $[Ni(RR(P)\text{-}L)_2]^{2+}$, while the P–S chelate ring forms a λ gauche one. The dihedral angles are 45.1(5)° for P(1)–C(10)–C(11)–P(2), 41.9(4)° for P(3)–C(30)–C(31)–P(4), and 54.7(5)° for S(4)–C(38)–C(39)–P(4). Four skeletal atoms of each uncoordinated P–C–C–S group are almost in a plane (dihedral angles: 5.7(7), 7.8(7), 13.5(5)°).

The ^1H and ^{13}C NMR spectra of $[Ni(rac(P)\text{-}L)_2]^{2+}$ in CD_2Cl_2 at 30 °C show a singlet signal at δ=2.16 and 16.8, respectively, for the $-SCH_3$ groups. These results indicate that the coordinating $-SCH_3$ group in the solid state dissociates or exchanges rapidly with free $-SCH_3$ groups on the NMR time scale in solution. In Fig. 3 is compared the absorption spectrum in CH_2Cl_2 solution with the reflection spectrum in the solid state. These spectra are very similar in pattern, and the band around 25000 cm^{-1} is the one characteristic of a square pyrami-

Table 2. Bond Distances (l/Å) and Angles (ϕ/°) of $[Ni(rac(P)\text{-}L)_2](BF_4)_2$

Ni–S(4)	2.603(2)	Ni–P(1)	2.228(2)	C(21)–S(3)–C(22)	98.5(5)	Ni–S(4)–C(39)	101.1(2)
Ni–P(2)	2.227(2)	Ni–P(3)	2.233(2)	Ni–S(4)–C(40)	130.5(3)	C(39)–S(4)–C(40)	100.9(4)
Ni–P(4)	2.214(2)	S(1)–C(1)	1.782(16)	Ni–P(1)–C(3)	110.8(3)	Ni–P(1)–C(4)	123.3(2)
S(1)–C(2)	1.787(8)	S(2)–C(19)	1.816(8)	Ni–P(1)–C(10)	106.5(2)	C(3)–P(1)–C(4)	105.0(3)
S(2)–C(20)	1.786(16)	S(3)–C(21)	1.776(11)	C(3)–P(1)–C(10)	108.3(3)	C(4)–P(1)–C(10)	101.9(3)
S(3)–C(22)	1.809(8)	S(4)–C(39)	1.826(6)	Ni–P(2)–C(11)	109.6(2)	Ni–P(2)–C(12)	119.1(2)
P(1)–C(3)	1.835(7)	P(1)–C(4)	1.810(6)	Ni–P(2)–C(18)	112.6(2)	C(11)–P(2)–C(12)	100.2(3)
P(1)–C(10)	1.852(7)	P(2)–C(11)	1.863(7)	C(11)–P(2)–C(18)	107.7(3)	C(12)–P(2)–C(18)	106.5(3)
P(2)–C(12)	1.815(6)	P(2)–C(18)	1.849(7)	Ni–P(3)–C(23)	113.0(2)	Ni–P(3)–C(24)	120.9(2)
P(3)–C(23)	1.845(7)	P(3)–C(24)	1.819(6)	Ni–P(3)–C(30)	105.0(3)	C(23)–P(3)–C(24)	105.2(3)
P(3)–C(30)	1.827(6)	P(4)–C(31)	1.829(6)	C(23)–P(3)–C(30)	105.0(3)	C(24)–P(3)–C(30)	104.7(3)
P(4)–C(32)	1.823(6)	P(4)–C(38)	1.843(6)	Ni–P(4)–C(31)	109.9(2)	Ni–P(4)–C(32)	123.0(2)
C(2)–C(3)	1.516(11)	C(4)–C(5)	1.389(9)	Ni–P(4)–C(38)	109.2(2)	C(31)–P(4)–C(32)	102.7(3)
C(4)–C(9)	1.399(9)	C(5)–C(6)	1.405(12)	C(31)–P(4)–C(38)	104.3(3)	C(32)–P(4)–C(38)	106.1(3)
C(6)–C(7)	1.339(12)	C(7)–C(8)	1.352(14)	S(1)–C(2)–C(3)	112.1(5)	P(1)–C(3)–C(2)	117.0(5)
C(8)–C(9)	1.380(11)	C(10)–C(11)	1.510(11)	P(1)–C(4)–C(5)	120.9(5)	P(1)–C(4)–C(9)	120.7(5)
C(12)–C(13)	1.393(10)	C(12)–C(17)	1.375(9)	C(4)–C(5)–C(6)	119.1(7)	C(5)–C(6)–C(7)	121.6(8)
C(13)–C(14)	1.379(11)	C(14)–C(15)	1.355(14)	C(6)–C(7)–C(8)	119.6(8)	C(7)–C(8)–C(9)	121.6(8)
C(15)–C(16)	1.391(13)	C(16)–C(17)	1.390(12)	C(4)–C(9)–C(8)	119.7(7)	P(1)–C(10)–C(11)	106.8(5)
C(18)–C(19)	1.507(11)	C(22)–C(23)	1.526(9)	P(2)–C(11)–C(10)	110.3(5)	P(2)–C(12)–C(13)	123.2(5)
C(24)–C(25)	1.366(9)	C(24)–C(29)	1.402(10)	P(2)–C(12)–C(17)	119.0(5)	C(12)–C(13)–C(14)	120.8(7)
C(25)–C(26)	1.402(11)	C(26)–C(27)	1.330(18)	C(13)–C(14)–C(15)	119.9(8)	C(14)–C(15)–C(16)	121.6(8)
C(27)–C(28)	1.395(15)	C(28)–C(29)	1.395(14)	C(15)–C(16)–C(17)	117.3(8)	C(12)–C(17)–C(16)	122.5(7)
C(30)–C(31)	1.520(9)	C(32)–C(33)	1.408(10)	P(2)–C(18)–C(19)	117.5(5)	S(2)–C(19)–C(18)	111.0(6)
C(32)–C(37)	1.376(9)	C(33)–C(34)	1.385(12)	S(3)–C(22)–C(23)	109.0(5)	P(3)–C(23)–C(22)	112.9(5)
C(34)–C(35)	1.390(14)	C(35)–C(36)	1.354(14)	P(3)–C(24)–C(25)	119.0(5)	P(3)–C(24)–C(29)	120.8(5)
C(36)–C(37)	1.397(10)	C(38)–C(39)	1.489(10)	C(24)–C(25)–C(26)	118.7(8)	C(25)–C(26)–C(27)	122.7(9)
				C(26)–C(27)–C(28)	119.4(9)	C(24)–C(29)–C(28)	119.4(8)
S(4)–Ni–P(1)	91.89(6)	S(4)–Ni–P(2)	100.57(6)	P(3)–C(30)–C(31)	109.3(4)	P(4)–C(31)–C(30)	110.9(4)
S(4)–Ni–P(3)	105.11(6)	S(4)–Ni–P(4)	83.61(6)	P(4)–C(32)–C(33)	121.5(5)	P(4)–C(32)–C(37)	118.1(5)
P(1)–Ni–P(2)	84.99(6)	P(1)–Ni–P(3)	162.86(6)	C(32)–C(33)–C(34)	118.9(7)	C(33)–C(34)–C(35)	120.7(9)
P(1)–Ni–P(4)	93.87(6)	P(2)–Ni–P(3)	93.77(6)	C(34)–C(35)–C(36)	119.3(8)	C(35)–C(36)–C(37)	122.0(8)
P(2)–Ni–P(4)	175.69(6)	P(3)–Ni–P(4)	86.10(6)	C(32)–C(37)–C(36)	118.7(7)	P(4)–C(38)–C(39)	112.5(4)
C(1)–S(1)–C(2)	101.5(6)	C(19)–S(2)–C(20)	100.0(5)	S(4)–C(39)–C(38)	108.8(4)		

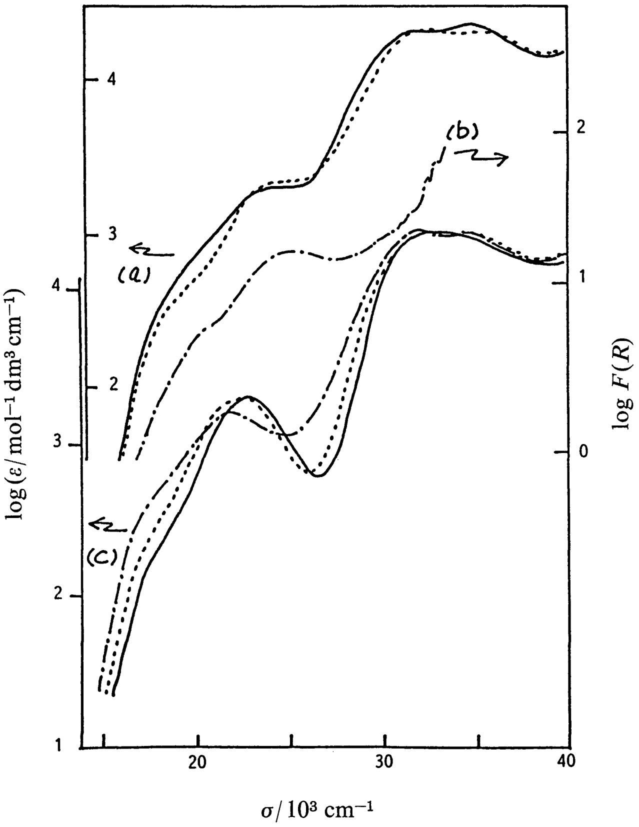

Fig. 3. Electronic spectra of Ni(II) complexes: (a) [Ni(*rac*(*P*)-L)$_2$](BF$_4$)$_2$ in CH$_2$Cl$_2$ (——), [Ni(*meso*(*P*)-L)$_2$](BF$_4$)$_2$ in CH$_2$Cl$_2$ (-----), (b) [Ni(*rac*(*P*)-L)$_2$](BF$_4$)$_2$ in the solid state (—·—), (c) [Ni(*rac*(*P*)-L)$_2$](BF$_4$)$_2$ in CH$_2$Cl$_2$ in the presence of LiCl (——), LiBr (-----), and KI (—·—).

dal Ni(II) complex with C_{4v} symmetry.[21] Thus it is concluded that the complex in CH$_2$Cl$_2$ solution retains the square pyramidal structure with P$_4$S donor atoms, but the coordinating -SCH$_3$ group exchanges with free -SCH$_3$ groups on the NMR time scale. The ligand field bands (20000—25000 cm^{-1}) of [Ni(*rac*(*P*)-L)$_2$]$^{2+}$ in CH$_2$Cl$_2$ are shifted to lower energy in the presence of excess halide ions (X$^-$) as shown in Fig. 3(c). The peak positions are shifted in accordance with the spectrochemical series, 29000 cm^{-1} (LiCl), 22700 cm^{-1} (LiBr), and 22000 cm^{-1} (KI). A similar spectral change was reported for square pyramidal [NiX{*o*-C$_6$H$_4$(As(CH$_3$)$_2$}$_2$]$^+$.[21] Thus [Ni(*rac*(*P*)-L)$_2$]$^{2+}$ in CH$_2$Cl$_2$ in the presence of excess halide ions would form square pyramidal [NiX(*rac*(*P*)-L)$_2$]$^+$ in which the -SCH$_3$ group is replaced by the X$^-$ ion.

To assign the more soluble isomer **B-II**, the L ligand in this isomer was liberated from the Ni(II) ion in CH$_2$Cl$_2$ by mixing with an excess aqueous KCN solution. The [Co(acac)$_2$(L)]$^+$ complex prepared with this ligand was only the *meso*(*P*)-L complex **A-I**. Thus isomer **B-II** was assigned to [Ni(*meso*(*P*)-L)$_2$]$^{2+}$. For the arrangement of chiral phosphorus atoms in [Ni(*meso*(*P*)-L)$_2$]$^{2+}$, there are two possible isomers, *trans-RS* and *trans-RR,SS*. The ^{1}H and ^{13}C NMR spectra of isomer **B-II** in CD$_2$Cl$_2$ indicate the isomer to be a single species, but the structure could not be assigned. The absorption spectrum of isomer **B-II** in CH$_2$Cl$_2$ is very similar to that of **B-I** (Fig. 3(a)), and behaves in a similar manner to isomer **B-I** when added excess halide ions. The NMR spectra in CD$_2$Cl$_2$ show only one kind of -SCH$_3$ signal. These results indicate that isomer **B-II** is also a square pyramidal complex with the -SCH$_3$ group at the apical position, and the -SCH$_3$ group exchanges with free -SCH$_3$ groups on the NMR time scale in solution. The [Ni(*rac*(*P*)-L)(*meso*(*P*)-L)]$^{2+}$ isomer was not obtained under the experimental conditions.

Copper(I) Complex. White air-stable [Cu(L)]BF$_4$ was immediately precipitated by reaction of L and Cu(BF$_4$)$_2$·6H$_2$O in methanol. The molar conductivity of 150 S cm^2 mol^{-1} in acetonitrile shows a 1:1 electrolyte for this complex.[22] The complex exhibits a singlet -SCH$_3$ signal in the ^{1}H (δ=2.16) and ^{13}C (δ=19.1) NMR spectra in CD$_2$Cl$_2$, indicating a single species. The assignment of L, *rac*(*P*) or *meso*(*P*) in the complex was made by the same method as for [Ni(*meso*(*P*)-L)$_2$]$^{2+}$. The L ligand obtained from the copper complex gave only [Co(acac)$_2$(*rac*(*P*)-L)]$^+$. Thus the copper complex is assigned as [Cu(*rac*(*P*)-L)]$^+$, and the coordination geometry should be tetrahedral. Molecular models show that *rac*(*P*)-L can coordinate to a metal ion tetrahedrally as a quadridentate ligand without strain, while one of the two -SCH$_3$ groups of *meso*(*P*)-L can not bind to the metal ion in a tetrahedral complex. The *meso*(*P*)-L complex would remain in the reaction mixture, but was not isolated in this study. The reduction mechanism of Cu(II) to Cu(I) is not clear. In general, phosphines tend to form stable complexes with Cu(I), and only a few complexes with Cu(II) are reported.[23]

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