the same intensity ratio as for the solid state, we can evaluate a contribution of this isomer of 30% to the band at 1981 cm^{-1}. Due to the value of the small splitting (9 cm^{-1}) of the two frequencies 1990 and 1981 cm^{-1}[2] and to their relative intensities (4.7 and 10.0, respectively) it sounds quite reasonable to assign them to the trans isomer in which the angle between the two CO vibrators is 113° (*vide infra*). Thus starting from *cis*-[RhCl(CO)PMe$_2$Ph]$_2$ in the solid state, a mixture of cis and trans isomers occurs in cyclohexane solutions. Inversely, the cis isomer is the only one recovered from these solutions and the trans isomer disappeared upon isomerization.

Similarly, we have studied the complex [RhCl(CO)PMe$_3$]$_2$. All crystals studied correspond to the cis isomer; *i.e.*, two CO stretching bands at 1984 cm^{-1} (9.2) and 1969 cm^{-1} (10.0) are found. In cyclohexane solutions, we also observed a mixture of both isomers, with the following assignments: *cis*-[RhCl(CO)PMe$_3$]$_2$, 1995 cm^{-1} (14% of total intensity) and 1980 cm^{-1} (15%); the trans isomer, 1989 cm^{-1} (16%) and 1980 cm^{-1} (55%).

The complex [RhCl(CO)P(NMe$_2$)$_3$]$_2$ exhibits two CO bands at 1971 and 1962 cm^{-1} in the solid state. The occurrence of a small splitting of frequencies (9 cm^{-1}) and a rather small intensity ratio (5.6/10.0) prompt us to assign a trans geometry to this complex. In solution, a small proportion of cis isomer also is detected (1994 and 1978 cm^{-1}) in addition to the trans one (1988 and 1978 cm^{-1}).

From X-ray determinations, the angle between both CO vectors was calculated to be $\omega = 80.4°$. Using the usual approximation in which each CO oscillator is treated as a dipole vector,[16] the angle ω can be calculated from the intensities of the symmetric (I_{sym}) and antisymmetric bands (I_{asym}) with the formula $I_{\text{sym}}/I_{\text{asym}} = \cot^2(\omega/2)$. In the case of the compound *cis*-[RhCl(CO)(PMe$_2$Ph]$_2$ of C_s symmetry such a calculation gives $I_{\text{sym}}/I_{\text{asym}} = 58/42$ from $\omega = 80.4°$ whereas the experimental ratio of higher and lower frequency bands is $\sim 44/56$!

In the trans isomer of [RhCl(CO)PMe$_2$Ph]$_2$ the same ambiguity does not occur, the angle ω between CO vibrators being calculated as 113°, a value consistent with both CO groups in trans positions.

The discrepancy in the case of the cis isomer is under investigation.[17]

Registry No. *cis*-[RhCl(CO)PMe$_2$Ph]$_2$, 53187-76-1; *trans*-[RhCl(CO)PMe$_2$Ph]$_2$, 53187-77-2; *cis*-[RhCl(CO)PMe$_3$]$_2$, 53187-78-3; *trans*-[RhCl(CO)PMe$_3$]$_2$, 36713-90-3; *cis*-[RhCl(CO)P(NMe$_2$)$_3$]$_2$, 53187-79-4; *trans*-[RhCl(CO)P(NMe$_2$)$_3$]$_2$, 53187-80-7.

Supplementary Material Available. Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC40493V.

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Hindered Ligand Systems. VIII. Syntheses of the Iron(III), Cobalt(III), and Nickel(II) Compounds of *cis,cis*-1,3,5-Tris(salicylaldimino)cyclohexane and the Crystal Molecular Structure of the Cobalt(III) Complex

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The Fe(III), Co(III), and Ni(II) complexes of *cis,cis*-1,3,5-tris(salicylaldimino)cyclohexane ((sal)$_3$tach) have been prepared and characterized. The diamagnetic Co(III) and high-spin Fe(III) compounds are mononuclear but the Ni(II) complex has been shown to be Ni$_3$((sal)$_3$tach)$_2$ with a magnetic moment of 3.2 BM/Ni atom. The crystal structure of Co((sal)$_3$tach) was determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the hexagonal space group $P\bar{3}$ with two molecules in the unit cell whose dimensions are $a = 11.80$ (2) and $c = 9.52$ (1) Å. Least-squares refinement of the structure led to a final residual, R, of 0.052 for the 616 unique reflections. The complex, which has crystallographic threefold symmetry, has a twist angle of 59°. The anomalously long Co–N bond distance of 1.942 (4) Å, the nonplanar nature of the chelate rings, and rotations about C=N bonds as well as those about the C—C bonds immediately adjacent are ascribed to the rigidity of the cyclohexane backbone and the overwhelming tendency of the Co atom to introduce large twist angles.

Although considerable study has been directed to metal complexes of the adduct of pyridine-2-carboxaldehyde with *cis,cis*-1,3,5-triaminocyclohexane ((py)$_3$tach),[1-5] the corresponding complexes of *cis,cis*-1,3,5-tris(salicylaldimino)cyclohexane ((sal)$_3$tach) have received little attention.[1,6] Unlike (py)$_3$tach, the larger chelate rings of (sal)$_3$tach cannot accommodate trigonal-prismatic coordination to a metal atom without severe distortions to bond angles within the chelate rings. Thus, the twist angle[7] is expected to approach 60°. Optimal values of this angle cannot be determined from the

Table I. Analytical Data

Compd	% N		% M		Mol wt	
	Calcd	Found	Calcd	Found	Calcd	Found
$H_3(sal)_3tach$	9.75	9.51			441	441 ± 1[a]
$Co((sal)_3tach)$	8.44	8.25			497	497 ± 1[a]
$Fe((sal)_3tach)$	8.50	8.55	11.3	10.9	494	493 ± 1[a]
$Ni_3((sal)_3tach)_2$	7.98	7.93	16.8	16.1	1053	1050 ± 100[b]

[a] Determined from the parent ion peak in the mass spectrum. [b] Determined from osmometry in CH_2Br_2.

Table II. Magnetic and Spectroscopic Data

Compd	$\mu_{eff}(300°K)$,[a] BM	$\nu_{C=N}$,[b] cm^{-1}	ν_{max},[c] cm^{-1}
$H_3(sal)_3tach$		1628	
$Co((sal)_3tach)$	Diamag	1592, 1620	~12,500 (5), 17,160 (1200), 20,800 (1400)
$Fe((sal)_3tach)$	6.0	1610, 1620	~9750 (2), 20,600 (5560), 23,300 (4800), 27,600 sh (7700)
$Ni_3((sal)_3tach)_2$	3.2/Ni	1600, 1620	9100 (56), 12,500 (14), 16,400 (33)

[a] The magnetic moment was obtained by the Faraday method. [b] The infrared spectra were obtained in KBr disks. [c] The electronic spectra were obtained in CH_2Cl_2 solutions. Extinction coefficients appear within parentheses.

inspection of molecular models. However, the chiral natures of certain alkyl-substituted (sal)3tach complexes of Co(III) and Al(III) have already been deduced from nmr spectroscopy.[6]

We have begun an investigation of the complexes of this ligand and we report here the characterization of the Co(III), Fe(III), and Ni(II) compounds. We also report the crystal and molecular structure of the Co(III) compound which was chosen for examination since it should, according to theory,[3c] possess the largest twist angle.

Experimental Section

Preparation of Compounds. $H_3(sal)_3tach$. Pure[8] *cis,cis*-tach·3HCl·H_2O (0.24 g, 1.0 mmol) was dissolved in 15 ml of 0.2 *M* NaOH solution, and 0.37 g (3.0 mmol) of salicylaldehyde was added. The yellow precipitate, which formed in virtually quantitative yield after shaking, was separated by filtration. Recrystallization, accomplished according to the procedure of Lions and Martin,[1] afforded yellow needles whose characterization is given in Tables I and II.

M((sal)3tach) (M = Co, Fe). Deep red Co((sal)3tach) was prepared from the oxidation of stoichiometric quantities of the ligand and $Co(C_2H_3O_2)_2·4H_2O$ with H_2O_2 according to the method of Lions and Martin.[1] Deep red Fe((sal)3tach) was prepared similarly from $Fe(OH)(C_2H_3O_2)_2$ although, of course, oxidation with H_2O_2 was not necessary. Purification was accomplished in each case by charging a CH_2Cl_2 solution onto a short alumina column and eluting with CH_2Cl_2. A small brown fraction remained at the top of the column in each case. Analytical data and physical properties of each complex are included in Tables I and II.

$Ni_3((sal)_3tach)_2$. This complex was prepared by mixing a hot solution of the ligand in ethyl acetate with an equimolar quantity of $Ni(C_2H_3O_2)_2·4H_2O$ in hot methyl alcohol. The green precipitate was dissolved in a minimum quantity of CH_2Cl_2 and placed on a short neutral alumina column. Elution was accomplished with pyridine. Green crystals were obtained by the addition of ethyl alcohol to the eluate. Tables I and II contain the data which are relevant to the characterization of this complex.

Instrumentation. The infrared and electronic spectra were obtained using a Perkin-Elmer 621 spectrometer and a Cary Model 14 spectrophotometer. Molecular weight measurements were made with a Mechrolab Model 301A vapor pressure osmometer. The Faraday technique was used to obtain magnetic susceptibilities.

Crystallographic Data. Crystals occurred as elongated hexagonal prisms. Precession photographs possessed $\bar{3}$ Laue symmetry with no systematic absences, requiring the space group to be either *P*3 or $P\bar{3}$. Statistical tests and packing considerations suggested the latter to be correct, and the subsequent solution confirmed this choice.

A well-formed crystal of dimensions {100} = 0.105 (2) mm, {010} = 0.128 (2) mm, {110} = 0.118 (2) mm, {001} = 0.220 (2) mm was mounted along the *c* axis on an ultrastable goniometer of our own design which has translations only. Cell dimensions and data collection were all performed at 20°. Diffractometer and crystal alignment techniques for the Picker FACS-1 utilized are described elsewhere.[9a] ω scans of three orthogonal reflections gave half-peak widths of 0.13–0.19°, indicating suitable mosaic character.[9b]

A least-squares fit of angular data from 13 reflections centered in both $\pm 2\theta$ gave cell dimensions of a = 11.80 (2) and c = 9.52 (1) Å. The measured density of 1.44 (2) g cm^{-3} as determined by flotation is in excellent agreement with the value of 1.439 g cm^{-3} calculated assuming $Z = 2$. The data were collected with Mo Kα radiation (λ 0.71069 Å), obtained from the 002 reflection of a highly oriented graphite monochromator, using a source takeoff angle of 2.2°. The crystal to source distance (target–monochromator–sample) was 23.5 cm and the crystal to detector distance was 24.9 cm. A scintillation detector with a pulse height discriminator using a window of 11.0–23.79 kV, together with a receiving aperture of 4 × 4 mm were used. Standard θ–2θ scan techniques were employed with a scan speed of 2°/min, a 2° + dispersion correction width, and 10-sec background counts recorded at the extremes of each scan. A total of 1373 redundant data were collected to $(\sin\theta)/\lambda = 0.50$. Three reflections, chosen as standards, were monitored after every 50 measurements and indicated no systematic trends, with a maximum deviation of 2.4%.

Integrated intensities, *I*, and standard errors $\sigma(I)$, were calculated as described previously,[10] and the ignorance factor, ρ, was assigned a value of 0.03 based on prior experience. The data were averaged to yield 616 unique intensities, of which 576 were nonzero. Intensities and standard errors were converted to structure factors, *F*, and errors, $\sigma(F)$, by the usual methods.[11] Preliminary scale and overall temperature factors were determined by Wilson's method.[12]

Solution and Refinement of the Structure. Direct methods were used to determine the phases of the largest 150 normalized structure factors, *E*, and a three-dimensional *E* map revealed the positions of all nonhydrogen atoms.[13] Hydrogen atoms were located from a difference Fourier synthesis obtained after three cycles of refinement[14] of the nonhydrogen atoms. A total of six cycles of isotropic refinement of all atoms gave residuals of $R(F) = 0.059$ and $R_w(F) = 0.035$, where $R(F) = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w(F) = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$ with $w = 1/\sigma(F_o)^2$. The function minimized was $w(||F_o| - |F_c||)^2$. The data were then corrected for absorption (μ = 8.16 cm^{-1} for Mo Kα) by the numerical method of Coppens, *et al.*[15] Also an isotropic extinction parameter and anomalous dispersion corrections for the Co scattering factor were introduced. The residuals after four cycles were $R(F) = 0.052$ and $R_w(F) = 0.019$. The largest Δ/σ for the last cycle was 4×10^{-3} and the goodness of fit was 0.49, the latter indicating the errors ($\rho = 0.03$) had been overestimated. The extinction parameter refined to 6.0 (8) × 10^{-7}.

An attempt to refine nonhydrogen atoms anisotropically led to non-positive-definite thermal parameters for C(4), possibly due to the drastic reduction in the observation:parameter ratio, (7.7 for isotropic and 4.5 for anisotropic refinement). Since the residuals indicated little improvement ($R(F) = 0.049$ and $R_w(F) = 0.014$), no further attempts were made to refine anisotropically.

The observed and calculated structure factors are listed in Table III.[16] The final positional and thermal parameters are listed in Table IV. A final difference Fourier synthesis revealed no positive electron density greater than 0.53 e/Å^3.

Results and Discussion

The Complexes. All of the complexes are sufficiently volatile to obtain their mass spectra. Parent ion peaks were readily observed for Co((sal)3tach) and Fe((sal)3tach) and confirm

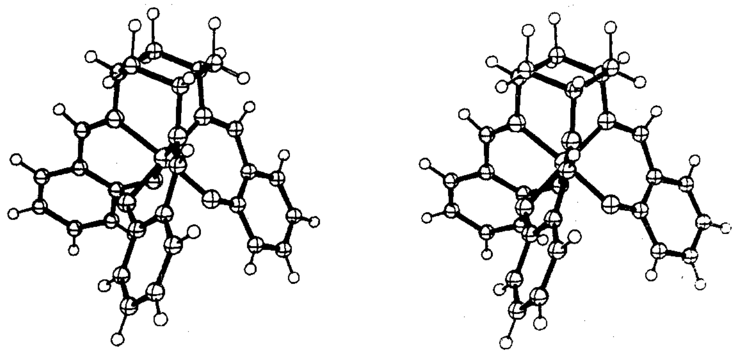

Figure 1. Stereoscopic view of the Co((sal)$_3$tach) molecule. All thermal ellipsoids are drawn to 50% probability.

Table IV. Positional and Thermal Parameters for Co((sal)$_3$tach)[a]

	x/a	y/b	z/c	B, Å^2
Co	1/3	2/3	0.0811 (2)	2.48 (4)
O(1)	0.1864 (3)	0.6020 (3)	0.2016 (4)	2.5 (1)
N(1)	0.2654 (4)	0.7559 (4)	0.9673 (6)	2.9 (1)
C(1)	0.4192 (6)	0.8068 (6)	0.7656 (10)	4.2 (2)
C(2)	0.2791 (5)	0.7546 (5)	0.8111 (9)	3.9 (1)
C(3)	0.1941 (5)	0.7996 (5)	0.0206 (7)	2.9 (1)
C(4)	0.1447 (4)	0.7794 (4)	0.1618 (6)	2.4 (1)
C(5)	0.0848 (5)	0.8487 (5)	0.2118 (7)	3.2 (1)
C(6)	0.0239 (5)	0.8204 (5)	0.3388 (7)	3.4 (1)
C(7)	0.0228 (6)	0.7246 (6)	0.4225 (9)	3.9 (2)
C(8)	0.0794 (5)	0.6539 (6)	0.3772 (7)	3.0 (1)
C(9)	0.1402 (4)	0.6771 (4)	0.2448 (6)	2.2 (1)
H(1)	0.473 (4)	0.891 (4)	0.806 (4)	3.1 (11)
H(2)	0.419 (6)	0.813 (5)	0.655 (6)	10.8 (25)
H(3)	0.244 (3)	0.817 (4)	0.779 (4)	3.5 (11)
H(4)	0.170 (5)	0.858 (5)	0.957 (5)	6.3 (13)
H(5)	0.090 (4)	0.923 (5)	0.156 (5)	6.7 (14)
H(6)	0.975 (4)	0.872 (4)	0.381 (4)	4.8 (12)
H(7)	0.992 (4)	0.692 (4)	0.508 (5)	2.6 (14)
H(8)	0.077 (3)	0.591 (3)	0.426 (4)	1.5 (10)

[a] The values in parentheses refer to the esd's of the least significant digits, in this table and in succeeding tables.

Table V. Selected Interatomic Distances (Å) for Co((sal)$_3$tach)

Bonding Contacts			
Co-O(1)	1.892 (3)	C(7)-C(8)	1.372 (7)
Co-N(1)	1.942 (4)	C(8)-C(9)	1.408 (7)
N(1)-C(2)	1.497 (6)	C(9)-C(4)	1.421 (6)
N(1)-C(3)	1.289 (6)	C(1)-H(1)	0.96 (4)
O(1)-C(9)	1.316 (5)	C(1)-H(2)	1.05 (6)
C(1)-C(2)	1.510 (7)	C(2)-H(3)	1.05 (4)
C(1)-C(2')	1.526 (7)	C(3)-H(4)	1.06 (5)
C(3)-C(4)	1.436 (6)	C(5)-H(5)	1.01 (4)
C(4)-C(5)	1.405 (6)	C(6)-H(6)	1.11 (4)
C(5)-C(6)	1.360 (7)	C(7)-H(7)	0.90 (5)
C(6)-C(7)	1.378 (7)	C(8)-H(8)	0.87 (3)
Nonbonding Distances			
C(2)-C(2')	2.539 (10)	N(1)-O(1)	2.729 (6)
N(1)-N(1')	2.791 (7)	N(1)-O(1')	2.716 (6)
O(1)-O(1')	2.607 (5)		

Table VI. Selected Angles (deg)

N(1)-Co-O(1)	90.7 (2)	C(3)-C(4)-C(5)	120.1 (5)
N(1)-Co-N(1')	91.9 (2)	C(3)-C(4)-C(9)	120.1 (5)
N(1)-Co-O(1')	90.2 (2)	C(9)-C(4)-C(5)	119.3 (6)
O(1)-Co-O(1')	87.1 (2)	C(4)-C(5)-C(6)	121.1 (6)
Co-O(1)-C(9)	121.5 (3)	C(5)-C(6)-C(7)	120.2 (7)
Co-N(1)-C(2)	118.2 (4)	C(6)-C(7)-C(8)	120.6 (8)
Co-N(1)-C(3)	121.7 (5)	C(7)-C(8)-C(9)	121.3 (7)
C(1)-C(2)-C(1')	110.9 (7)	C(8)-C(9)-C(4)	117.5 (5)
C(2)-C(1)-C(2')	113.5 (7)	O(1)-C(9)-C(4)	123.0 (5)
C(1')-C(2)-N(1)	112.5 (6)	O(1)-C(9)-C(8)	119.4 (5)
C(2)-N(1)-C(3)	119.4 (5)		

their mononuclear nature. However, the highest m/e value in the mass spectrum of $Ni_3((sal)_3tach)_2$ was found to be 551 ± 1 which corresponds to the $Ni_2((sal)_3tach)$ fragment. The trinuclear nature of the complex was established by vapor-phase osmometry using CH_2Br_2 solutions (Table II).

The X-ray study of $Co((sal)_3tach)$ (see below) established that the coordination geometry is virtually that of a trigonal antiprism with a twist angle of 59°. Since chirality is favored by the ligand in order to avoid severe angular distortions within the chelate rings, it is assumed that the twist angle in $Fe((sal)_3tach)$ is much greater than 0°. Unlike the metal atom in $Co((sal)_3tach)$, the high-spin Fe(III) atom (Table II) should not exert a strong preference for octahedral coordination.[3c] However, the data on hand do not allow even an estimate of the magnitude of the twist angle. It should be recalled that no technique for the solution of this problem, other than a complete X-ray study, has been discovered. Noteworthy, however, is the fact that powder patterns of the Fe(III) and Co(III) compounds are widely disparate. This leaves open the possibility that the molecular structures are considerably different. Whether or not a different twist angle is responsible for any major structural differences remains to be seen.

The magnetic moment of 3.2 BM/Ni atom which was found for $Ni_3((sal)_3tach)_2$ points to a geometry which maintains two unpaired electrons on each Ni atom. A possible structure consists of a central Ni atom bonded equally to the six phenolic O atoms of two $Ni((sal)_3tach)^-$ fragments. There are numerous examples of Schiff base–metal complexes serving as ligands to other metal ions.[17] In addition, it has been shown[18] that Co(II) will bind to two *cis*-$Co(NH_2CH_2CH_2O)_3$ moieties through the six available oxygen atoms. The $Ni((sal)_3tach)^-$ fragments should have a fairly large twist angle because of the large octahedral ligand field stabilization associated with the Ni atom and bonding requirements of the chelate rings. Assuming that this angle approaches 60°, then molecular models suggest that the NiO_6 core could have trigonal-prismatic geometry if the terminal chelates have an identical chiral sense but pseudooctahedral geometry if they have an opposite chirality. Again, arguments concerning ligand field stabilization energies[3c] suggest that the NiO_6 core should be pseudooctahedral. Thus, insofar as the original assumption about the molecular structure of this complex can be believed, the compound is predicted to have a centric structure. In view of the unsolved problem of the proper interpretation[3d,5] of the electronic spectrum of $Ni((py)_3tach)^{2+}$, no attempt will be made to interpret the spectrum of $Ni_3((sal)_3tach)_2$.

Structural Description of Co((sal)$_3$tach). This complex, which possesses crystallographic threefold symmetry, has a twist angle of 59°. The molecular structure is shown in Figure 1, while the numbering scheme for the atoms is shown in Figure 2. A packing diagram is given in Figure 3. Interatomic distances and angles are given in Tables V and VI.

The Co–O bond distance of 1.892 (3) Å is only somewhat shorter than the mean distance of 1.91 Å found for two Co(III) complexes of salen,[19,20] while the Co–N bond distance of 1.942 (4) Å is significantly longer than the mean distance of 1.88

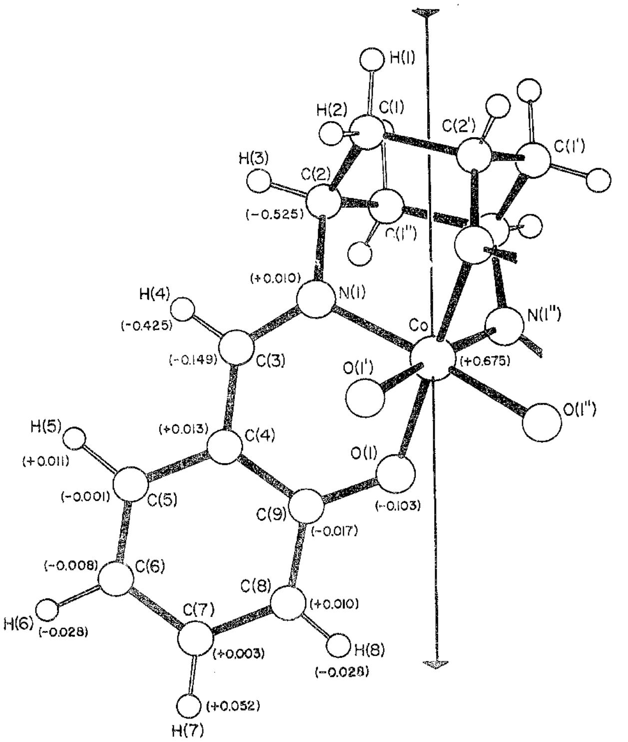

Figure 2. A view of one-third of the Co((sal)$_3$tach) molecule showing the atomic numbering systems. The numbers which appear adjacent to each atom are the distances to the least-squares plane of the phenyl ring. The equation for the plane is $7.210x + 3.197y + 4.078z = 4.192$.

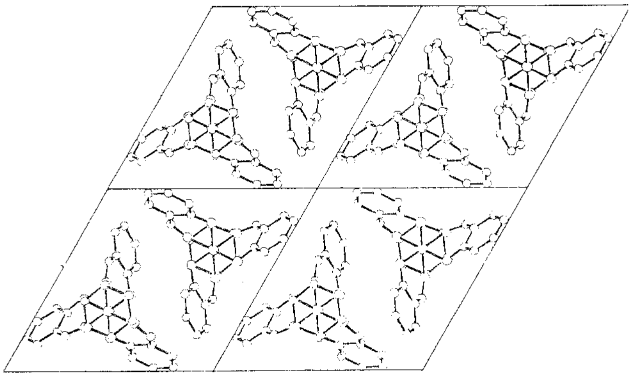

Figure 3. The molecular packing of Co((sal)$_3$tach) viewed down the *c* axis. Four unit cells are shown.

Å found in those complexes. All bond angles subtended at the Co atom are close to 90°.

The C–C bond distances within the cyclohexane ring of 1.510 (7) and 1.526 (7) Å are within the rather wide range of distances reported for Zn((py)$_3$tach)(ClO$_4$)$_2$[3a] but are somewhat shorter than the average value of 1.56 Å which has been given[4] for Ni((py)$_3$tach)(ClO$_4$)$_2$. These distances compare favorably with the 1.52–1.53 Å range which has been recently found for two complexes of *cis,cis*-1,3,5-triaminocyclohexane, M(*cis,cis*-tach)$_2$(NO$_3$)$_2$ (M = Ni, Cu).[21] For comparison, cyclohexane and adamantane, according to a recent electron diffraction study,[22] have C–C bond distances of 1.534 (2) and 1.543 (9) Å, respectively. The symmetry-related atoms, C(2), C(2'), and C(2''), form an equilateral triangle which has edges of 2.539 (10) Å while the N atoms to which they are attached form a triangle with an edge length of 2.791 (7) Å. The former approaches the ideal value of 2.52 Å, which can be calculated from a C–C bond distance of 1.54 Å and tetrahedral bond angles. The increased size of the triangle of N atoms is undoubtedly due to bonding requirements of the Co atom. A similar puckering has been observed in M(*cis,cis*-tach)$_2$(NO$_3$)$_2$ (M = Ni, Cu).[21]

Table VII. Selected Dihedral Angles (deg) within the Chelate Ring

Plane	Plane	Angle
C(2)–N(1)–C(3)	N(1)–C(3)–C(4)	15.9
N(1)–C(3)–C(4)	C(3)–C(4)–C(5)	9.6
N(1)–C(3)–C(4)	C(3)–C(4)–C(9)	18.9
C(3)–C(4)–C(9)	C(4)–C(9)–C(8)	6.3
C(3)–C(4)–C(9)	C(4)–C(9)–O(1)	4.5

With two exceptions, the C–C bond lengths within the phenyl rings are identical, within experimental error, to the average values for these distances compiled by Lingafelter and Braun[23] for nine related compounds as well as the corresponding distances found for the two compounds of Co(III) with salen.[19,20] The C(4)–C(5) and C(7)–C(8) bond distances are, however, about 0.02 and 0.01 Å shorter than the corresponding distances in all of these complexes. Nevertheless, these distances are very close to values which were obtained for Co(salen)·CHCl$_3$.[24] As shown in Figure 2, the phenyl rings deviate only slightly from planarity.

All bond distances and bond angles within each chelate ring, *i.e.*, N(1)–C(3)–C(4)–C(9)–O(1), appear to be normal and compare favorably to those found in other complexes.[19,20,23] However, these rings deviate markedly from planarity as shown in Figure 2. The phenolic O atom and C(3) are approximately 0.1 Å out of the least-squares plane of the phenyl rings and are on the same side of that plane. The N atom is approximately in the plane, however. Dihedral angles between various planes of atoms within the chelate rings are given in Table VII. From these data, it is clear that a rotation of approximately 16° about the C(3)–N(1) double bond has occurred. A rotation about the C(3)–C(4) bond in the same direction has occurred also. However, this angle is not uniquely defined since C(3) is considerably out of the least-squares plane of the phenyl ring. The dihedral angle defined by the N(1)–C(3)–C(4) plane and the C(3)–C(4)–C(5) plane is 9.6° while the dihedral angle determined by the junction of the N(1)–C(3)–C(4) plane and the C(3)–C(4)–C(9) plane is 18.9°. Thus, depending upon whether the reference atom is C(5) or C(9), the rotation about the C(3)–C(4) bond is approximately either 10 or 19°. An average angle of about 15° can be used for descriptive purposes.

All independent hydrogen atoms were located by difference Fourier techniques and refined isotropically. The average C–H distance of ~1.00 Å is somewhat larger than the normal distance of 0.95 Å cited by Churchill.[25] While these positions appear to be qualitatively correct with respect to the phenyl ring, it should be pointed out that hydrogen atom positions are poorly determined in a heavy-atom structure unless special techniques are employed.

From this description of the molecular structure of Co((sal)$_3$tach) it can be seen that there are at least three major distortions which deserve further comment. These are the elongated Co–N bond distances, the significant departure of C(3) and O(1) from the least-squares plane of the phenyl rings, and the rotations about the N(1)–C(3) and C(3)–C(4) bonds of about 16 and 15°, respectively. The cyclohexane backbone provides a great deal of rigidity to the base of the cavity created by the triaxial conformation of the ligand. Because of this rigidity and bond angle requirements within the chelate rings, normal metal–ligand bond distances may not be readily attained. Furthermore, the Co atom should exert an overwhelming tendency for twist angles which approach 60°. Apparently, this tendency far outweighs the rotational energy barriers within the chelate rings as well as the electronic forces which would normally place the C(3) and O(1) atoms in the plane of the phenyl ring.

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Registry No. $H_3(sal)_3tach$, 53535-00-5; $Co((sal)_3tach)$, 53516-69-1; $Fe((sal)_3tach)$, 53516-70-4; $Ni_3((sal)_3tach)_2$, 53586-50-8; *cis,cis*-tach, 26150-46-9; salicylaldehyde, 90-02-8.

Supplementary Material Available. Table III, a listing of structure factors, will appear following these pages in the microfilm edition of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40544O. Crystallographic data tables, for this paper only, are also available in microfiche for \$2.00 from the Chemistry Library, Indiana University, Bloomington, Ind. 47401. Request Molecular Structure Center Report No. 7401.

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Transition Metal Hydroborate Complexes. VIII.[1] Structure of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$. Bonding Analogies between Boron Hydrides and *nido*-Metalloboranes

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The synthesis of the complex μ-decahydrodecaborato-tetrakis(triphenylphosphine)dicopper(I) is reported. The compound crystallizes from chloroform as the solvated species $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$, the crystal and molecular structures of which have been determined in a single-crystal X-ray diffraction study. The colorless complex crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. Lattice parameters are $a = 21.189\ (3)$ Å, $b = 13.438\ (2)$ Å, $c = 13.207\ (2)$ Å, $\alpha = 102.61\ (1)°$, $\beta = 92.92\ (1)°$, and $\gamma = 88.41\ (1)°$. From 3405 unique observed reflections collected by diffractometer, the structure was solved and refined with the phenyl rings constrained as rigid groups to a final value for the discrepancy index R_F of 0.061. The $B_{10}H_{10}^{2-}$ cage ligand binds two crystallographically unique copper atoms by means of $\overline{\text{Cu–H–B–B–H}}$ chelate rings along two apical edges related to each other by an approximate S_8 operation. Each quasitetrahedral copper atom is further bonded to two triphenylphosphine ligands. Boron–boron distances within the $B_{10}H_{10}^{2-}$ cage agree well with those published for $Cu_2B_{10}H_{10}$ [B_a–B_e(av) = 1.68 (3) Å, B_e–B_e(av) = 1.81 (3) Å (a = axial, e = equatorial)]. The geometry about the copper coordination spheres is similar to that of $[(C_6H_5)_3P]_2Cu(B_3H_8)$. The average Cu–P and Cu–B distances are 2.28 (1) and 2.30 (2) Å, respectively. The mean Cu–H_a distance of 2.08 (7) Å is notably longer than the value of 1.86 (6) Å found for the mean Cu–H_e distance, a result that is rationalized from the geometry of the $B_{10}H_{10}^{2-}$ cage by assuming equivalent Cu–B interactions in the three-center Cu–H–B bridge bonds. The molar conductivity of the compound in dichloromethane indicates strong covalent interaction between bis(triphenylphosphine)copper(I) and the cage ligand in solution. The bonding in $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ is discussed with reference to the geometries and electronic requirements known or postulated for other *nido*-metalloboranes.

Introduction

Earlier papers in this series have reported the molecular structures of $[(C_6H_5)_3P]_2CuX$ complexes, where $X^- = BH_4^-$, $B_3H_8^-$, or $NCBH_3^-$.[2] In each case the hydroborate anion was found to be coordinated to the copper atom through three-center Cu–H–B bridge bonds of the kind well-known in boron hydride chemistry.[3] The present study was undertaken to determine whether bis(triphenylphosphine)copper(I) would bond in a similar manner to a higher boron hydride anion. In particular, we chose to examine a complex with the decahydrodecaborate dianion,[4] since the adduct $Cu_2B_{10}H_{10}$ is known.[5,6] A number of related coinage metal derivatives of