in this solvent makes the spectrum less reliable) is quite similar to that in $C_2H_4Cl_2$, as are also the reflectance and single-crystal spectra, except that, in the latter, the 15.1-kK band becomes the main maximum with shoulders at 13.7, 15.9, and 17.8 kK, and the onset of uv absorption is less intense.

Infrared spectra, with strong absorptions at 1565 and 1500 cm^{-1} (attributable to C=O stretching), 960, 935, and 915 cm^{-1} (CS stretching), and 655 cm^{-1} (OCS bending)—compare ref 7—add little information as to the stereochemistry present. However, magnetic susceptibility data offer evidence for the presence of magnetic coupling between Co(II) centers in the dimer units. In fact μ_{eff} is strongly temperature dependent, ranging from approximately 1.8 BM at 90°K to 3.1 BM at room temperature, as shown in Figure 2. The observed μ_{eff} values approximately fit the temperature dependence expected (Figure 2) according to an obvious extension of the spin-coupling model proposed by Earnshaw, Figgis, and Lewis[13] which leads, in the present case, to the equation

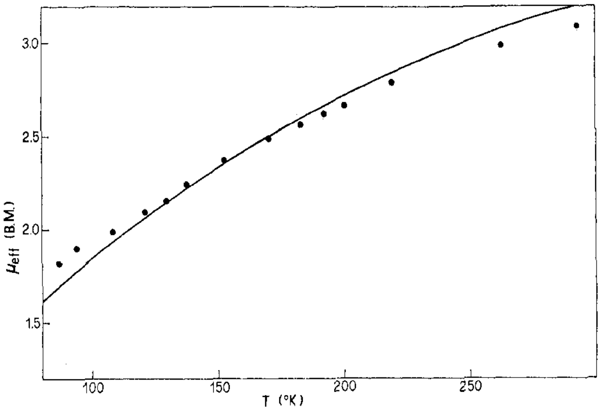

Figure 2.—μ_{eff} values for $Co_2(mtb)_4$: circles, experimental values (corrected for diamagnetism but not for TIP); full line, calculated for a binuclear cluster of $S = {}^3/_2$ ions according to eq 1 with $g = 2.31$ and $J = -63°$.

$$\mu_{eff}{}^2 \text{ (per gram-atom of Co)} = g^2(3x + 15x^3 + 42x^6)/(1 + 3x + 5x^5 + 7x^6) \quad (1)$$

where $x = \exp(2J/kT)$.

Assuming, tentatively, that $g = 2 - (8\lambda/10Dq) = 2.31$ (which would correspond to $\lambda = -0.16$ kK, and $|Dq| = 0.41$ kK, hence the order of g commonly observed for pseudotetrahedral Co(II) complexes), experimental data are consistent with $J \approx -63°$ (see Figure 2). This appears to be a unique case of magnetic coupling in polynuclear pseudotetrahedral Co(II) complexes. Despite the uncertainties, due to neglect of TIP contributions to the experimental magnetic susceptibility and to the arbitrary values assigned to the orbital g corrections, the order of magnitude of J is probably correct. It may be noted that it is in line with J values observed[13-15] in several polynuclear complexes of first-row transition metals having carboxylato bridges, such as formates, acetates, propionates, and benzoates of Cr(III) ($-J \approx$ 10–20°)[13] and Fe(III) ($-J \approx$ 40–50°).[13] Thus, monothiobenzoate $C_6H_5COS^-$ in its ligand behavior resembles, on the one hand, the mono- and dithiophosphinates (ability to promote bridged coordination) and, on the other, carboxylate ligands (efficiency of magnetic coupling through the bridging groups). This is strikingly different from the polynuclear cobalt(II) phosphinates and mono- and dithiophosphinates, which have been reported to exhibit the normal paramagnetism of tetrahedral Co(II), and it may be concluded that phosphorus-containing bridges do not allow any significant magnetic coupling to occur.

Last, monothiobenzoate is quite different from both dithiocarboxylate and dithiophosphate ligands in that it promotes pseudotetrahedral coordination of Co(II) and lacks any pronounced oxidation effect on cobalt. Instead, the dithiophosphates strongly prefer[16] pseudooctahedral coordination, and to Co(III), while the dithiocarboxylates give this coordination geometry and oxidation state exclusively.

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[13] A. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc. A*, 1656 (1966).

[14] K. Kambe, *J. Phys. Soc. Jap.*, **5**, 48 (1950).

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Hindered-Ligand Systems. VI. Trigonal-Prismatic to Octahedral Coordination *via* Hydrogenation of Acyclic C=N Functional Groups

BY R. A. D. WENTWORTH

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The hexadentate ligand, *cis,cis*-1,3,5-tris(pyridine-2-carboxyaldimino)cyclohexane, ($(py)_3$tach), undergoes trigonal-prismatic coordination with Zn(II), Mn(II), and Co(II) ions[1,2] but may be capable of near-octahedral coordination in the Fe(II) and Ni(II) derivatives.[2,3] It is now found that the reaction of the Co(II), Ni(II), and Zn(II) complexes with BH_4^-, which affects the hydrogenation of the acyclic C=N bonds, gives the corresponding complexes of *N,N′,N″*-tris(2-picolyl)-*cis,cis*-1,3,5-triaminocyclohexane ($(pic)_3$tach) which are basically octahedral. Although the hydrogenation of Schiff's bases with BH_4^- is fairly well known,[4] these reaction products have a greater significance. If only conformational restraints of the acyclic C=N functional groups are responsible for the unusual coordination geometries in complexes of $(py)_3$tach, then removal of these restraints by hydrogenation of those groups should lead exclusively to chiral and basically octahedral coordination. This conclusion is consistent with experimental observations. It has also been found

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[1] W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *Chem. Commun.*, 843 (1969).

[2] W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *Inorg. Chem.*, **9**, 1825 (1970).

[3] A X-ray diffraction study of $Ni[(py)_3tach](ClO_4)_2$ has been undertaken by C. Huffman and W. E. Streib. Although not yet complete, the results show that the coordination geometry about the Ni atom is very nearly halfway between an octahedron and a trigonal prism.

[4] See for example K. Harada in "The Chemistry of the Carbon-Nitrogen Double Bond," S. Patai, Ed., Interscience, New York, N. Y., 1970, p 281.

that oxidation of Co[(pic)$_3$tach]$^{2+}$ yields the corresponding octahedral Co(III) complex ion.

Experimental Section

Preparation of M[(pic)$_3$tach](ClO$_4$)$_2$·0.5H$_2$O (M = Co, Ni, Zn).—Both the Ni(II) and Zn(II) compounds were prepared by the same general method. Aqueous solutions of the appropriate M[(py)$_3$tach](ClO$_4$)$_2$[2] and a tenfold excess of NaBH$_4$ were allowed to sit overnight at room temperature. The solutions were then evaporated (a slight cloudiness in the Zn(II) solution was removed by the addition of glacial acetic acid) until crystallization commenced. Solid NaClO$_4$ was then added to the hot solution. After cooling, the crystals (pink and white for the Ni(II) and Zn(II) compounds, respectively) were filtered, washed with water, and recrystallized in the same manner. Both compounds were dried in air. The amine groups in the Zn(II) compound were labeled with deuterium by recrystallization from D$_2$O.

The Co(II) complex was prepared in a somewhat different manner. About 0.3 g of Co[(py)$_3$tach](ClO$_4$)$_2$ was placed in 100 ml of H$_2$O, and a tenfold excess of NaBH$_4$ was added to this mixture. After sitting overnight, a black precipitate (perhaps a Co(I) derivative) had formed. The addition of 5 ml of glacial acetic acid caused the precipitate to dissolve and discharged the excess BH$_4^-$. The filtered, yellow solution was treated with solid NaClO$_4$ until the crystallization of the light-yellow compound was nearly complete. The compound was washed with ethyl alcohol and dried under vacuum.

The infrared spectra of these compounds, taken in Nujol mulls, indicated the presence of water of crystallization. The analytical results correspond best to the hemihydrates. *Anal.* Calcd for Co[(pic)$_3$tach](ClO$_4$)$_2$·0.5H$_2$O: C, 43.1; H, 4.67; N, 12.6. Found: C, 42.7; H, 4.59; N, 12.4. Calcd for Ni[(pic)$_3$tach](ClO$_4$)$_2$·0.5H$_2$O: C, 43.1; H, 4.67; N, 12.6. Found: C, 43.2; H, 4.69; N, 12.4. Calcd for Zn[(pic)$_3$tach](ClO$_4$)$_2$·0.5H$_2$O: C, 42.7; H, 4.62; N, 12.4. Found: C, 42.7; H, 4.75; N, 12.2.

Preparation of Co[(pic)$_3$tach](ClO$_4$)$_3$.—When 0.12 g (0.2 mmol) of the Co(II) complex was placed in 10 ml of 0.01 *M* K$_2$S$_2$O$_8$ solution, the solid rapidly dissolved to give a yellow solution. The solution was filtered and reduced in volume to about 5 ml on a steam bath. The addition of solid NaClO$_4$ produced an orange, crystalline solid which was washed with ethyl alcohol and dried in air. *Anal.* Calcd for Co[(pic)$_3$tach](ClO$_4$)$_3$: C, 37.9; H, 4.11; N, 11.1. Found: C, 37.8; H, 4.05; N, 10.7.

Discussion of Results

Hydrogenation of the bound carboxaldimino C=N group will lead to a bound secondary amine whose bond angles will impart a chirality to the complex ion. Molecular models indicate that the extent of chirality should closely approach that found in chiral complexes with octahedral coordination. However, instead of regarding the coordination geometry as established by these means alone, additional evidence was sought. Infrared data have verified the hydrogenation of the carboxaldimino group, while data from pmr spectroscopy of the Zn(II) complex have supported that conclusion as well as the chiral nature of the complex. The electronic spectra of the Co(II) and Ni(II) complex ions have suggested that the ligand field is basically octahedral in nature. Finally, the close similarity of the X-ray powder patterns of these compounds allows all of the spectroscopic data to be meaningfully interrelated. Only the infrared, pmr, and electronic spectra will receive further comment.

None of the infrared spectra of these compounds contains a band which is due to the C=N stretching vibration. However, bands which originate from the stretching vibrations of the secondary amine groups (3205–3275 cm^{-1}) and bending of the acyclic methylene groups (1455–1465 cm^{-1}) are present as listed in Table I. These assignments are based on the absence of these bands in the infrared spectra of the corresponding (py)$_3$tach compounds as well as the spectrum of the compound resulting from deuteration of the amine groups in the Zn(II) complex. In that spectrum the N–D stretching frequency occurred at 2425 cm^{-1} while the methylene bending frequency remained virtually unshifted. The characteristic four bands between 1440 and 1600 cm^{-1} due to the pyridine ring[5–7] remain intact and practically unshifted from their positions in the (py)$_3$tach compounds. The pmr spectrum of the Zn((py)$_3$tach)$^{2+}$ ion (DMSO-d_6, TMS reference) contained a single, sharp signal due to the carboxaldimino proton at −8.88 ppm. In the spectrum of the Zn[(pic)$_3$tach]$^{2+}$ ion this signal was absent but signals due to the amine and acyclic methylene protons appeared as a triplet at −4.67 ppm and a doublet at −4.17 ppm, respectively, with an apparent coupling constant of 8.0 Hz. Deuteration of the amine groups removed the signal at low field, leaving a doublet with a splitting of 1.1 Hz which is located at −4.15 ppm.[8] This splitting points to the nonequivalence of the methylene protons and the chiral nature of the complex but not to the extent of the chirality.

TABLE I
VIBRATIONAL AND LIGAND FIELD SPECTRA

Compd[a]	Vibrational[b]	Electronic[c]	
	ν, cm^{-1}	ν, cm^{-1}	Assignment
CoL(ClO$_4$)$_2$·0.5H$_2$O	3260	10,500[d]	$^4T_1 \rightarrow {}^4T_2$
	1455	21,300	$^4T_1 \rightarrow {}^4T_1(P)$
CoL(ClO$_4$)$_3$[e]	3205	21,600 (ϵ 125)	$^1A_1 \rightarrow {}^1T_1$
	1465		
NiL(ClO$_4$)$_2$·0.5H$_2$O	3270	11,550 (ϵ 13)[f,g]	$^3A_2 \rightarrow {}^1E$
	1457	12,500 (ϵ 17)	$^3A_2 \rightarrow {}^3T_2$
		19,500 (ϵ 16)	$^3A_2 \rightarrow {}^3T_1$
ZnL(ClO$_4$)$_2$·0.5H$_2$O	3275		
	1456		

[a] L = (pic)$_3$tach. [b] Taken in a KBr matrix. [c] Extinction coefficients appear in parentheses. [d] Reflectance spectrum. [e] Taken in aqueous solution. [f] Taken in DMSO solution. [g] Shoulder.

Convincing evidence that the complexes contain a basically octahedral coordination geometry may be derived from the electronic spectra of the chromophoric complexes (Table I). The spectroscopic parameters, derived in the usual manner for octahedral complexes, are Dq = 1205 and B = 823 cm^{-1} for Co[(pic)$_3$tach]$^{2+}$ and Dq = 1250 and B = 855 cm^{-1} for Ni[(pic)$_3$tach]$^{2+}$. The similarity of these parameters is to be expected since it is a general observation with Co(II) and Ni(II) complexes when the ligand and stereochemistry are the same.[9] The results also indicate that (pic)$_3$tach is considerably higher in the spectrochemical series than ethylenediamine and only slightly lower than 2,2′-bipyridine.

The contrast between the spectrum of Co[(pic)$_3$-

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(5) W. J. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, **82**, 4834 (1960).

(6) R. A. Krause, N. B. Colthup, and D. H. Busch, *J. Phys. Chem.*, **65**, 2216 (1961).

(7) P. E. Figgins and D. H. Busch, *ibid.*, **65**, 2236 (1961).

(8) The amine and acyclic methylene protons of the undeuterated Zn[(pic)$_3$tach]$^{2+}$ constitute an ABX system, but the resonance pattern may have the first-order appearance of an A$_2$X system under appropriate conditions, *e.g.*, $\delta_{AB} \ll J_{AB}$ and $(J_{AX} - J_{BX}) \ll J_{AB}$, where δ_{AB} is the relative chemical shift between the A and B protons. Under these conditions the apparent coupling constant is the average of J_{AX} and J_{BX}. Upon deuteration of the amine group, an AB system results with $\delta_{AB} \ll J_{AB}$ again. This condition can lead to a spectrum in which the outer lines of the expected quartet are too weak to be observed: J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959; R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(9) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, pp 204 and 212.

tach]$^{2+}$ and that of the trigonal-prismatic Co[(py)$_3$tach]$^{2+}$ is particularly vivid. The latter consists of an extremely broad band at 8430 cm^{-1} and two overlapping bands at 19,100 and 20,200 cm^{-1}.[2] The spectra of the corresponding Ni(II) compounds do not differ markedly in band position but the spectrum of the hydrogenated complex ion is somewhat less intense than that of Ni[(py)$_3$tach]$^{2+}$. However, if the spectrum of the latter is interpreted in terms of an octahedral ligand field, *B* has a remarkably high value of 980 cm^{-1}.[2] This result is undoubtedly due to the unusual coordination geometry found in that complex ion.

Oxidation of Co[(pic)$_3$tach]$^{2+}$ with $S_2O_8^{2-}$ afforded the corresponding Co(III) species whose spectra consisted of only one observable ligand field band (Table I). The band position compares favorably with the $^1A_1 \rightarrow {}^1T_1$ transition at 21,400 cm^{-1} in Co(en)$_3^{3+}$. The second spin-allowed transition in the (pic)$_3$tach complex is obscured by high-intensity transitions in the near-ultraviolet region of the spectrum. The vibrational spectrum is very similar to those of 2+ complexes.

The conclusion deduced from the experimental data is then in complete accord with that drawn from the inspection of molecular models. Consequently, it becomes clear that the trigonal-prismatic complexes of (py)$_3$tach owe their coordination geometry to the rotational barriers within the conjugated, acyclic C=N bonds.

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Metal–Metal Frequencies and Force Constants for a Platinum–Tin Cluster[1]

By Aristides Terzis, Thomas C. Strekas,
and Thomas G. Spiro*

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An unusual platinum–tin metal atom cluster was postulated recently by Lindsey, *et al.*,[2] as the basic unit of some trichlorotin complexes of platinum. The cluster was formulated as Pt_3Sn_2, a trigonal bipyramid with platinum atoms in the equatorial plane and tin atoms at the apices. Guggenberger has established this molecular configuration by X-ray crystallography[3] in the case of $L_3Pt_3(SnCl_3)_2$, where L is cycloocta-1,5-diene bound to the platinum atoms.[3] The structure is reproduced in Figure 1.

As part of a continuing study of the vibrational spectra of metal-cluster compounds,[4] we have examined the low-frequency Raman and ir spectra of $L_3Pt_3(SnCl_3)_2$. These provide the first opportunity to assign vibrational modes associated with the stretching of Pt–Pt bonds, and of bonds to bridging tin atoms. A simple normal-coordinate analysis provides an estimate of the force constants associated with these novel bonding features.

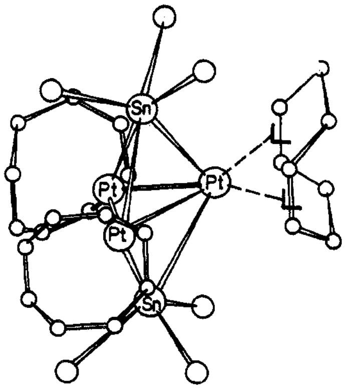

Figure 1.—The molecular configuration of $(C_8H_{12})_3Pt_3(SnCl_3)_2$ (taken from ref 3). For the normal-coordinate analysis, the cyclooctadiene rings were each replaced by two point mass ligands, effective mass 26, located at the midpoints of the double bonds coordinated to the platinum atoms. Molecular parameters: distances (Å): Pt–Pt, 2.58; Pt–Sn, 2.80; Sn–Cl, 2.39; Pt–L, 2.15; angles (deg): Cl–Sn–Cl, 109.6; L–Pt–L, 90 (see J. A. Ibers and R. G. Snyder, *J. Amer. Chem. Soc.*, **84,** 495 (1962)).

Spectral Assignments

Metal–metal stretching frequencies are expected below 250 cm^{-1}. For an isolated Pt_3Sn_2 cluster with D_{3h} symmetry there are six fundamental vibrational modes. The representations spanned by Pt–Pt and Pt–Sn internal coordinates are

$$\Gamma_{\text{Pt–Pt}} = A'_1 + E'$$
$$\Gamma_{\text{Pt–Sn}} = A'_1 + A''_2 + E' + E''$$

The A'_1 and E'' modes are Raman active only while the A''_2 mode is infrared active only and the E' modes are active in both spectra. While the crystal symmetry[3] for $L_3Pt_3(SnCl_3)_2$ is lower than D_{3h}, previous experience with metal-cluster spectra[4] suggests that site symmetry effects are unlikely to be important for the cluster modes.

Metal–metal stretching vibrations are expected to show up strongly in Raman scattering. The low-frequency Raman spectrum of a single crystal of $L_3Pt_3(SnCl_3)_2$ (Figure 2) shows four prominent bands, at 170, 143, 112, and 81 cm^{-1}, which may be assigned with some confidence to cluster modes. In addition there are several weaker bands. Mononuclear platinum cycloocta-1,5-diene complexes show four Raman bands in this region, assignable as Pt–L deformation modes: $LPtCl_2$: 186, 160, 120, and 101 cm^{-1}; $LPtBr_2$: 187, 160, 125, and 98 cm^{-1}. The only other features found in the low-frequency spectra of these reference compounds are the X–Pt–X bending frequencies, at 170 cm^{-1} for X = Cl and 116 cm^{-1} for X = Br. Accordingly we assign to Pt–L deformation modes the weak features in Figure 2 at 185, 160, 125 (sh), and 95 (sh) cm^{-1}. Other weak bands at 130, 89, and 54 cm^{-1} are shown by the normal-coordinate analysis below to be assignable to mixed Sn–Cl deformation and Pt–Sn stretching modes. The low-frequency infrared spec-

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(1) This investigation was supported by Public Health Service Grant GM-13498, from the National Institute of General Medical Sciences, and by National Science Foundation Grant GP-10122.

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(3) L. J. Guggenberger, *Chem. Commun.*, 512 (1968).

(4) (a) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **8**, 2011 (1969); (b) *ibid.*, **7**, 2365 (1968).