TABLE III

COMPARISON OF EXPERIMENTAL AND THEORETICAL ISOTROPIC ^{1}H SHIFT RATIOS FOR PYRIDINE-TYPE BASES, L, OCTAHEDRALLY COORDINATED TO NICKEL(II)

		Experiment			Theory		
Ligand proton		Ni(acac)$_2$L$_2$[a]	Ni(acac)$_2$L$_2$[b]	NiL$_6$$^{2+}$[c]	INDO/2(σ)[d]	EHMO(σ)[e]	EHMO($\sigma + \pi^*$)[e]	EHMO($\sigma + \pi$)[e]
Pyridine	α	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	β	0.294	0.303	0.385	0.326	0.382	0.384	0.398
	γ	0.077	0.091	0.116	0.208	1.01	1.10	1.09
γ-Picoline	α	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	β	0.278	0.180	0.328	0.338	0.394	0.401	0.420
	γ-CH$_3$	−0.090	−0.091	−0.092	−0.063	0.015	−0.092[g]	−0.092[g]
β-Picolineβ	α	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	β	0.296	0.387	0.365	0.310	0.365	0.373	0.390
	γ	0.063	0.230	0.104	0.234	1.02	1.11	1.02
	β-CH$_3$	0.055	0.077	0.072	0.087	0.092	0.074	0.019
4-Vinylpyridine	α			2.13	2.94[h]	2.52	2.46	2.38
	β		1.0[d]	1.0	1.0[h]	1.0	1.0	1.0
	H$_a$		0.118[d]	0.073[f]	0.063[h]	0.241	0.380	0.266
	H$_b$		0.122[d]	0.192[f]	0.055[h]	0.055	−0.009	−0.023
	H$_c$		−0.113[d]	−0.176[f]	−0.050[h]	0.045	0.085	0.100

[a] Data from ref 8. [b] Data from ref 14. [c] Data from ref 12c. [d] Present work. [e] From ref 12c. [f] See footnote f of Table II. [g] Forced fit, see text. [h] Planar form.

ture which becomes unresolvable at higher R_p values; all are in good agreement with the spectrum of pure 4-vinylpyridine.

Finally, we compare the present INDO/2 results for the pmr shift ratios with an interpretation recently presented[12c] involving EHMO theory. In Table III are presented ratios of isotropic shifts for pyridine and three derivative ligands L in complexes of the types Ni(acac)$_2$L$_2$ and NiL$_6$$^{2+}$. No theoretical model limited to the ligand moiety can be expected to provide better agreement than that found between different systems involving the same ligand or variations observed by different investigators on the same system. Also listed in Table III are the ratios predicted on the basis of INDO/2 hyperfine coupling constant calculations. The sign of the shift is correctly predicted by these calculations in every case and reasonable semiquantitative agreement with the observed ratios is apparent. In the final three columns of Table III are given the results of an EHMO analysis of these systems.[12c] The column labeled EHMO(σ) gives the ratios of hyperfine interactions expected for spin delocalization in the highest filled σ MO. EHMO theory is of course incapable of accounting for upfield shifts and yields particularly poor results for H$_\gamma$, as noted elsewhere.[12] Cramer and Drago[12c] attributed the upfield shifts to a contribution from β-spin delocalization in the ligand π system, involving either the highest filled, π, or lowest vacant, π^*, orbital. By forcing a fit for the H$_\alpha$ and γ-CH$_3$ resonances they analyzed the spin delocalization in terms of a linear combination of σ and π mechanisms as shown in the last two columns of Table III. This procedure does not improve the agreement for H$_\gamma$ and apparently predicts an upfield shift for the H$_b$ resonance rather than for H$_c$ of 4-vinylpyridine, contrary to our observations.

We conclude that INDO/2 theory shows reasonable promise on the semiquantitative level in interpreting contact shifts of both protons and ^{13}C nuclei. The analysis presented here, which involves but a single (σ) spin delocalization mechanism, represents an alternative (to that presented in ref 15c) interpretation of contact shifts in pyridine-type bases coordinated to octahedral nickel(II).

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The Cotton Effect of Tris(1,3-diaminopropane)cobalt(III) Ion, Co(tn)$_3$$^{3+}$

Sir:

Recent assignments of the ligand field circular dichroism (CD) spectra of $\Delta(+)$-Co(tn)$_3$$^{3+}$ are at variance. Those based on a single-crystal study[1] assign the high-energy component as E$_a$ symmetric while solution studies with oxyanions suggest that this is the A$_2$ component.[2-4] Assuming both assignments to be correct we suggest an explanation for these apparently discordant results in terms of Piper's model[5-8] for the sign of the Cotton effect in trigonally symmetric tris-bidentate transition metal complex ions. This electrostatic model determines the sign of the Cotton effect in terms of distortions of the ligand atoms from exact O_h symmetry. The Cotton effect is predicted to change sign as the twist angle, ω of Figure 1, changes from less than 60° to greater than 60° taken in a Λ chiral sense.[5,7] This model predicts no optical activity for $\omega = 60°$ and neglects the chiral distribution of the ligands around the C_3 axis. Alternatively, the sign of the Cotton effect is related to the absolute configuration of the

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(3) J. R. Gollogly and C. J. Hawkins, *Chem. Commun.*, 689 (1968).
(4) F. Woldbye, "Studier Over Optisk Activitet," Polyteknisk Forlag, Copenhagen, 1969, p 161.
(5) T. S. Piper and A. Karipides, *Mol. Phys.*, **5**, 475 (1962).
(6) T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961).
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whole complex ion, predicting that E_a be positive for Λ complex ions, *e.g.*, (+)D-$Co(en)_3{}^{3+}$ (en = 1,2-diaminoethane) irrespective of ω (Mason's model[2,9–11]).

The absolute configuration Λ has been assigned to the complex ion in (−)D-$[Co(tn)_3]Br_3 \cdot H_2O$ by X-ray structure analysis. The three ligands subtend an average angle, α, of 94.5° at the cobalt atom.[12] The Λ configuration has been similarly assigned[13] to (+)D-$Co(en)_3{}^{3+}$; the most accurately determined structure has $\alpha = 85.3°$.[14] For O_h symmetry $\alpha = 90°$ and $\omega = 60°$; it is generally considered that $\alpha > 90°$ (Λ sense) implies $\omega > 60°$,[1,2] but this conclusion is only strictly valid for mutually orthogonal bidentate ligand planes (shaded in Figure 1). The relation holds for these complex ions (Table I) and Piper's model is supported by the assignments in the CD spectra. Thus single-crystal studies assign the E_a component to the low-energy positive band of $\Lambda(+)$-$Co(en)_3{}^{3+}$ [10] and to the high-energy negative component of $\Lambda(-)$-$Co(tn)_3{}^{3+}$.[1] It is noteworthy, however, that while the change of sign of the Cotton effect is predicted, an *a priori* calculation has given the incorrect sign for the Cotton effect of (+)-$Co(en)_3{}^{3+}$.[8,9]

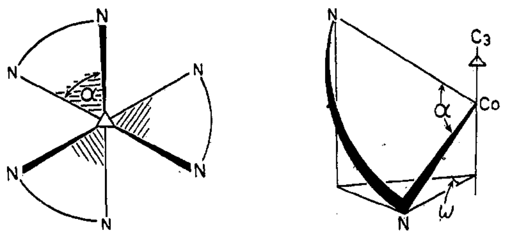

Figure 1.—Model of a tris-bidentate complex ion in the Λ configuration. The angle α is that subtended by the ligand atoms at the metal and ω is the projection of this angle on a plane perpendicular to the trigonal axis of the complex ion.

The chelate rings in (−)D$[Co(tn)_3]Br_3 \cdot H_2O$ have the chair conformation and it has been argued[3] that this geometry would be maintained in solution. Energy minimization calculations made here[15] show that a tris skew boat arrangement (lel boat[16]) has 0.9 kcal/mol less strain energy than the tris chair arrangement in the vapor state. In solution this energy difference would correspond to a tris lel boat to tris chair ratio of 4:1 if intermolecular effects are comparable. Other mixed species (*e.g.*, two chelate rings skew boat, one chair) of intermediate energy are likely but will not be considered here since they lack the C_3 symmetry required for formation of a symmetrical ion pair with a tetrahedral oxyanion such as $PO_4{}^{3-}$.[17] Boat and ob skew boat conformers are much higher in energy and they would not be present in sufficient concentration to affect the CD spectrum. Recent nmr studies show that there is a rapid flipping of the tn rings in solution, but on the addition of phosphate ion there is evidence for a degree of ion pairing not inconsistent with specific hydrogen bonding.[18,19]

From Table I it can be seen that the α and ω angles for energy-minimized $\Lambda(-)$-$Co(tn)_3{}^{3+}$ species change from 88.4 and 56.7°, respectively, for the lel boat to 93.7 and 64.3° for the tris chair. According to Piper's model for the sign of the Cotton effect, the Λ lel boat would give a positive E_a band similar to that of $\Lambda(+)$-$Co(en)_3{}^{3+}$ since $\omega < 60°$ in both cases. The Λ tris chair should give a negative E_a band. Mason's model predicts positive E_a bands for all three. It only remains to indicate which conformers of $\Lambda(-)$-$Co(tn)_3{}^{3+}$ are present in solid and solution. The chelated tn ring adopts the chair conformation in the four complexes studied;[12,15,20,21] however, in some of these bis complexes α is less than 90°. It appears that this is due to relief of ligand flattening in these complexes.[15,21] In (−)D-$[Co(tn)_3]Br_3 \cdot H_2O$ each chair ring has $\alpha > 90°$ although the complex ion does not possess an accurate C_3 axis. Crystals of (+)D-$[Co(tn)_3]Cl_3 \cdot 4H_2O$ appear to have this symmetry element,[1] although it has not been proved that the tris chair conformation exists with $\alpha > 90°$ in this crystal used for CD studies.

TABLE I

THE α AND ω ANGLES IN TRIS-DIAMINE COMPLEXES

Complex ion	Ligand conformation	α, deg	ω, deg	Ref
$\Lambda(+)$-$Co(en)_3{}^{3+}$	lel	85.3	54.9	*b*
	lel[a]	87.7	56.2	*c*
	ob[a]	87.2	56.2	*c*
$\Lambda(-)$-$Co(tn)_3{}^{3+}$	Chair	94.5	62.5	*d*
	Tris chair[a]	93.7	64.3	*e*
	lel boat[a]	88.4	56.7	*e*

[a] Energy minimization calculations. [b] Reference 14. [c] P. F. Crossing and M. R. Snow, unpublished energy calculations. [d] Reference 12. [e] Reference 15.

Addition of a tetrahedral oxyanion to a solution of (+)-$Co(en)_3{}^{3+}$ enhanced the A_2 component relative to the E_a component,[17] an effect rationalized in terms of an ion pair favored by the orientation of the N–H bonds in the lel conformer. A similar effect was postulated for $Co(tn)_3{}^{3+}$ where the tris chair model was the only one considered to form a favored ion pair.[2,3] It is difficult to decide on a suitable criterion for evaluating the favorability of hydrogen bonding between the tris-diamine complex ion and a $PO_4{}^{3-}$ ion. A preliminary examination of models indicates that even the N–H bonds of the previously discounted ob $Co(en)_3{}^{3+}$ may be suitably orientated to form bifurcated hydrogen bonds.

The geometry of the N–H bonds of energy-minimized

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(9) S. F. Mason, *Quart. Rev., Chem. Soc.*, **17**, 20 (1963).

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(15) R. J. Geue and M. R. Snow, to be submitted for publication. The procedure is given by M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3610 (1970).

(16) "lel" taken as the CCC plane of tn or the CC bond of en approximately parallel with the complex ion C_3 axis. "ob" taken as the CCC plane or CC bond oblique to the C_3 axis.

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TABLE II
GEOMETRY OF N–H BONDS IN TRIS-DIAMINE COMPLEXES

Complex ion	Ligand conformation	N···N, Å	H···H, Å	Angle of N–H with C_3 axis, deg	Ref
$\Lambda(+)$-Co(en)$_3{}^{3+}$	lel	2.79	2.36	14.87	*a*
	ob	2.80	2.62	30.49	*a*
$\Lambda(-)$-Co(tn)$_3{}^{3-}$	Tris chair				
	Face 1	2.79	2.55	32.86	*b*
	Face 2	2.80	2.34	24.83	*b*
	lel boat	2.80	2.34	22.98	*b*

[a] P. F. Crossing and M. R. Snow, unpublished energy calculations. [b] Reference 15.

complex ions is given in Table II. The lel boat has D_3 symmetry; the tris chair has C_3 symmetry only, one face closely resembling those of the lel boat conformer and the other approximating the geometry of the trigonal faces of the ob Co(en)$_3{}^{3+}$ ion. If linearity of hydrogen bonds (to within 25°) is considered important,[22] then, although the interoxygen atom distance in phosphate is 2.5 Å, it is not necessary that the distance between the hydrogen atoms be 2.5 Å to maintain linearity, since both the hydrogen atoms and the phosphate ion can twist about the C_3 axis with respect to the plane of nitrogen atoms. We calculate for the lel boat conformation of Co(tn)$_3{}^{3+}$ and for lel Co(en)$_3{}^{3+}$ (namely, N···N = 2.80 Å, H···H = 2.35 Å, and with N–H = 0.99 Å, O···O (of PO$_4{}^{3-}$) = 2.50 Å) that linear N–H···O bonds of length 2.73–3.22 Å require the N–H bonds to form a skew angle of 36–32° with the C_3 axis with the phosphorus atom 2.7–3.2 Å above the trigonal nitrogen atom plane. Similarly, for the tris chair face with H···H = 2.55 Å, the ideal inclination to the C_3 axis is 23–20°, the phosphorus atom being 3.0–3.5 Å from the nitrogen plane. In the absence of a more rigid criterion for hydrogen bonding it would appear that the lel boat is no less favored than the chair conformer of Co(tn)$_3{}^{3+}$ and that both are more favored than lel Co(en)$_3{}^{3+}$ in the formation of an oriented ion pair with phosphate ion.

We suggest that the conformer of $\Lambda(-)$-Co(tn)$_3{}^{3+}$ responsible for the positive low-energy E$_a$ band in oxyanion solution is the low strain energy tris lel skew boat, while that giving rise to the positive high-energy E$_a$ band in the CD crystal spectrum of $\Delta(+)$-[Co(tn)$_3$]Cl$_3\cdot$4H$_2$O is the tris chair conformer. While the assumptions of the solution oxyanion CD studies are not disproved by the single-crystal work, Mason's model is unable to explain the crystal assignment and Piper's model remains untested until the detailed geometry of the complex ion in the crystal lattice is determined.

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