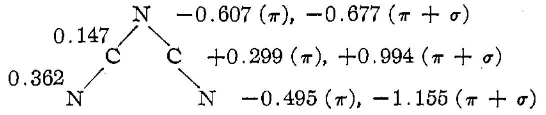
mode, whereas the first band is very probably depolarized and is assigned to the b_1 mode. Thus, the bent structure of the ion in the solid and in solution is confirmed, but the assignment of the stretching modes by Kuhn and Mecke is reversed. A recent infrared and Raman analysis of $S(CN)_2$,[32] which is isomorphous with bent $Se(CN)_2$,[33] has yielded $\nu_{C\equiv N}$ (a_1) > $\nu_{C\equiv N}$ (b_1).

The results of molecular orbital calculations of the charge densities and overlap populations for nonlinear $N(CN)_2^-$ follow. The signed quantities are the charge densities, the unsigned quantities the total π-overlap populations. These results refer to ∠C–N–C = 120°,



but show only minor variations from 110 to 160°. The charge distribution strongly resembles that in $C(CN)_3^-$ with the terminal nitrogens being the more negative. That these atoms interact with coordinating cations is evident from the increase in the C≡N stretching frequencies in copper, mercury, and lead salts compared to $NaN(CN)_2$.[30,34]

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[32] D. A. Long and D. Steele, *Spectrochim. Acta*, **19**, 1731 (1963); see also E. E. Aynsley, N. N. Greenwood, and M. J. Sprague, *J. Chem. Soc.*, 704 (1964).

[33] A. C. Hazell, *Acta Cryst.*, **16**, 843 (1963).

[34] NOTE ADDED IN PROOF.—A very recent and more complete X-ray study than that reported in ref. 8 has shown that in $NH_4C(CN)_3$ the anion is slightly nonplanar with the central carbon 0.13 Å. above the plane of the three nitrogens [C. Bugg, R. Desiderato, and R. L. Sass, *J. Am. Chem. Soc.*, **86**, 3157 (1964)]. In the transition metal salts a similar distortion and/or site symmetry effects could account for some of the infrared results. The conclusion that the structure of the anion in these salts and in $KC(CN)_3$ is essentially the same is unaffected.

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Identification of the Geometrical Isomers of Some Tris-Chelate Cobalt(III) Complexes by Nuclear Resonance

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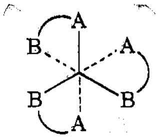
The proton resonance spectra of tris-(N-R-salicylaldimine) Co(III) complexes (R = methyl, ethyl, *p*-tolyl) and a new series of tris-(N-R-pyrrole-2-aldimine) Co(III) complexes (R = methyl, ethyl, isopropyl, *sec*-butyl) have been examined. The spectra provide unequivocal evidence for the existence of the *trans* isomer. In no case was any *cis* isomer detected. The apparent exclusive formation of the *trans* isomer is ascribed to significantly reduced steric interactions among the nitrogen substituents compared to the *cis* configuration. The more general formation of octahedral complexes in the pyrrole-2-aldimine than in the salicylaldimine series is concluded to be due to somewhat reduced steric interactions among these substituents. A general preparative method for tris(pyrrole-2-aldimine) Co(III) complexes is given.

Introduction

Tris-chelate metal complexes containing three identical unsymmetrical bidentate ligands can exist in two geometrically isomeric configurations, *cis* and *trans*. This type of isomerism is well recognized and the isomers have in some cases been identified by their ligand field spectra,[2-4] with a particular example being tris(glycinato)cobalt(III).[2] More recently, Fay and Piper[5-7] have separated *cis* and *trans* isomers of unsymmetrical β-diketones and have identified each by nuclear resonance. The *cis* isomer contains a threefold rotation axis whereas the *trans* isomer, **1**, has no symmetry. Therefore, in this isomer a given substituent on each chelate ring could in principle produce a separate resonance, but only a single resonance for the same substituent in each ring should occur in the *cis* form. This behavior has been observed in tris-(benzoylacetonato)[5] and tris(trifluoroacetylacetonato)[6] complexes of number of trivalent ions.



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We wish to report the preparation and isomeric identification of certain tris-chelate complexes of Co(III) which form only one isomer under ordinary conditions. The complexes studied are nitrogen-substituted derivatives of tris(salicylaldimine)cobalt(III) (**2**) and tris(pyrrole-2-aldimine)cobalt(III) (**3**).

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[1] Alfred P. Sloan Foundation Fellow.

[2] F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

[3] V. Carassiti and M. Claudi, *Ann. Chim.* (Rome), **50**, 581 (1960); V. Carassiti and A. M. Marinangeli, *ibid.*, **50**, 593 (1960).

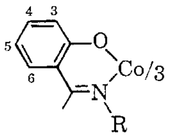
[4] H. Yoneda and S. Kida, *J. Am. Chem. Soc.*, **82**, 2139 (1960).

[5] R. C. Fay and T. S. Piper, *ibid.*, **84**, 2303 (1962).

[6] R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963).

[7] R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

The proton resonance spectra of these molecules allow an unambiguous assignment of the *trans* configuration.



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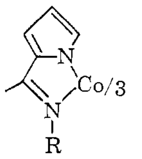

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Experimental

Preparation of Compounds.—The tris(salicylaldimine)cobalt(III) complexes were prepared following the method of West.[8] Complexes of this type have also been reported by Nishikawa, *et al.*[9]

Tris-(N-methylsalicylaldimine)cobalt(III).—Dark green crystals from dichloromethane–ethanol, m.p. 246–247°.

Anal. Calcd. for $C_{24}H_{24}N_3O_3Co$: C, 62.47; H, 5.24; N, 9.11. Found: C, 62.81; H, 5.14; H, 8.91.

Tris-(N-phenyl-5-methylsalicylaldimine)cobalt(III).—Dark green crystals from dichloromethane–ethanol, m.p.182–183°.

Anal. Calcd. for $C_{42}H_{36}N_3O_3Co$: C, 73.14; H, 5.26; N, 6.09. Found: C, 72.97; H, 5.18; N, 5.82.

The tris(pyrrole-2-aldimine) Co(III) complexes were prepared according to the following general procedure. Pyrrole-2-aldehyde and the appropriate primary amine were condensed in ethanol by allowing the solution to stand several hours at room temperature. The alcohol and water were then removed on a rotary evaporator and the resultant mass was dissolved in dry tetrahydrofuran. Potassium *t*-butoxide and $[(C_2H_5)_4N]_2(CoBr_4)$ (1 and $^1/_3$ mole, respectively, per mole of Schiff base) were added, the reaction mixture was stirred at room temperature for 5–6 hr., and then filtered. The brown filtrate was stripped down to a dark oil which was extracted with *n*-hexane. The extract on concentration gave crystals of the product, which was purified by recrystallization from dichloromethane–hexane. All complexes were isolated as orange or brown crystals except for the R = *t*-Bu derivative which was obtained as a dark violet bis complex.

Tris-(N-methylpyrrole-2-aldimine)cobalt(III).—This compound, m.p. 250–251°, has been prepared previously by reaction of cobalt oxide and the Schiff base in anisole, m.p. 250–252°.[10]

Tris-(N-ethylpyrrole-2-aldimine)cobalt(III).—M.p. 242–243°.

Anal. Calcd. for $C_{21}H_{27}N_6Co$: C, 59.71; H, 6.44; N, 19.90. Found: C, 59.85; H, 6.50; N, 20.00.

Tris-(N-isopropylpyrrole-2-aldimine)cobalt(III).—M.p. 265–268°.

Anal. Calcd. for $C_{24}H_{33}N_6Co$: C, 62.05; H, 7.16; N, 18.10. Found: C, 61.94; H, 7.25; N, 17.80.

Tris-(N-*sec*-butylpyrrole-2-aldimine)cobalt(III).—M.p. 185–195°, after four recrystallizations. The diffuse melting point is probably due to the presence of diastereoisomers.

Anal. Calcd. for $C_{27}H_{39}N_6Co$: C, 64.01; H, 7.76; N, 16.59. Found: C, 64.10; H, 7.75; N, 16.36.

Bis-(N-*t*-butylpyrrole-2-aldimine)cobalt (II).—M.p. 155–157°.

Anal. Calcd. for $C_{18}H_{26}N_4Co$: C, 60.49; H, 7.33; N, 15.68. Found: C, 60.73; H, 7.31; N, 15.79.

Proton Resonance Measurements.—All measurements were made on a Varian A-60 spectrometer in $CDCl_3$ solutions. Frequencies were measured by the usual side-band technique relative to tetramethylsilane as an internal reference.

Results and Discussion

The tris(pyrrole-2-aldimine) Co(III) complexes reported here are new compounds except for the R = CH_3 derivative.[10] The method of preparation of these complexes involves a nonaqueous chelation reaction, variations of which have been used to prepare tris[11] and bis[12] complexes of β-ketoamines. During the course of the reaction Co(II) is smoothly oxidized to Co(III) by air, and no other oxidizing agent is required. Only when R = *t*-Bu does aerial oxidation not take place, and a bis paramagnetic complex was isolated which is very probably tetrahedral.[13] It is to be noted that in the salicylaldimine series when R = *sec*-alkyl or *t*-Bu tetrahedral bis complexes are usually isolated[9,14] and these in general cannot be readily oxidized by air or hydrogen peroxide. In the pyrrole-2-aldimine series, however, octahedral complexes with R = *sec*-alkyl are obtained directly. In both series octahedral complexes are easily prepared when R = CH_3 or *n*-alkyl.[9] The difference in steric requirements of salicylaldimine and pyrrole-2-aldimine complexes in stabilizing a given stereochemistry is also reflected in the bis complexes which will be reported subsequently.[13]

The geometrical configuration of the tris Co(III) complexes of the salicylaldimine and pyrrole-2-aldimine series can be determined from the proton resonance spectra. Relevant chemical shift data are set out in Table I. The salicylaldimine series is considered first, and the spectrum of **2** (R = CH_3) is shown in Fig. 1a. The three distinct and equally intense resonances of the methyl group with separations of 6 c.p.s. clearly demonstrate that the predominant, if not exclusive, configuration of this complex is *trans*. Only one such

Table I

Proton Chemical Shifts in Tris(salicylaldimine) and Tris(pyrrole-2-aldimine) Co(III) Complexes

Complex[a]	Group	Chemical shifts, c.p.s.[b]
2 (N-CH_3)	N-CH_3[c]	186.3, 192.7, 198.7
	HC═N	455.0
2 (N-C_2H_5)	N-$CH_2\mathit{CH_3}$	73[d]
	HC═N	451.4
2 (N-*p*-tolyl)	N-$C_6H_4\mathit{CH_3}$	123.5 (2), 138.0
	HC═N	447.3
2 (5-CH_3,	5-CH_3	126.1
N-C_6H_5)	HC═N	445.0
3 (N-CH_3)	N-CH_3	155.3,[e] 156.9,[e] 180.4[f]
	HC═N	444.6, 453.6 (2)
3 (N-C_2H_5)	N-$CH_2\mathit{CH_3}$	61.6 (2),[g] 64.5 (1),[g]
		443.3, 452.8, 457.8
3 (N-*i*-C_3H_7)	N-CH$(\mathit{CH_3})_2$[h]	35.4, 59.0 (2), 73.1, 75.0, 82.9
	HC═N	444.6, 454.0, 463.5
3 (N-*sec*-C_4H_9)	N-CH$(\mathit{C_3H_8})$	60[i]
	HC═N	439.8, 449.8, 459.4

[a] See text. [b] Signals of a given group with twice the intensity of other signals are so designated. [c] Each signal is a doublet with J = 1.1 c.p.s. [d] Complicated feature consisting of at least seven bonds with approximate center at this frequency. [e] Overlapping. [f] Doublet with J = 1.5 c.p.s. [g] Center of triplet with J = 7.0 c.p.s. [h] Each signal is a doublet with J = 6.8 c.p.s. [i] Center of complex pattern.

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(8) B. O. West, *J. Chem. Soc.*, 4944 (1960).

(9) H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962).

(10) B. Emmert, K. Diehl, and F. Gollwetzer, *Ber.*, **62B**, 1733 (1929).

(11) J. P. Collman and E. T. Kittleman, *Inorg. Chem.*, **1**, 499 (1962).

(12) G. W. Everett, Jr., and R. H. Holm, *Proc. Chem. Soc.*, 238 (1964).

(13) A. Chakravorty, L. J. Theriot, and R. H. Holm, to be published.

(14) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

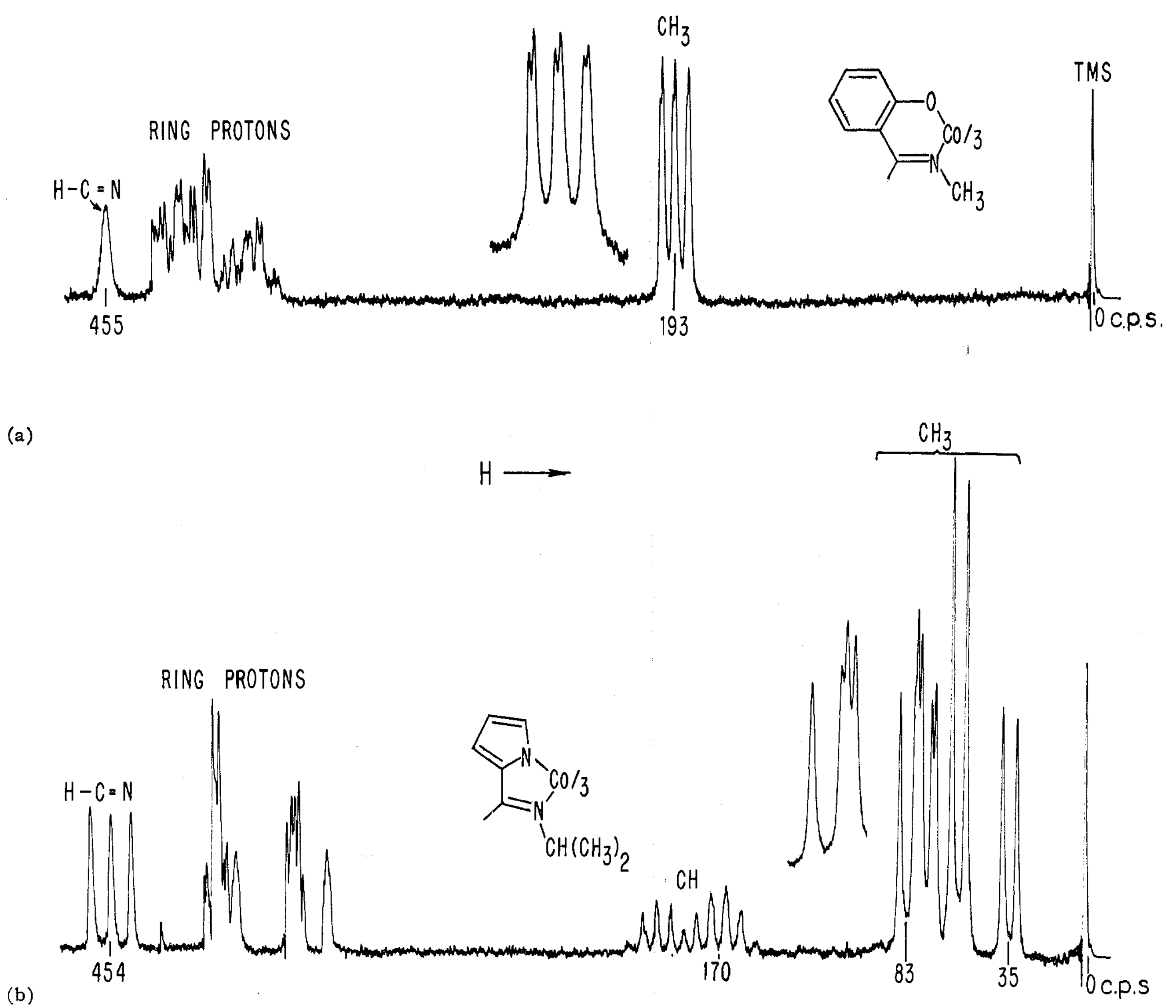

Fig. 1.—The proton resonance spectrum of (a) tris-(N-methylsalicylaldimine)cobalt(III) and (b) tris-(N-isopropylpyrrole-2-aldimine)-cobalt(III) in $CDCl_3$. The insert in (a) shows the N-CH_3 signals on an expanded scale. The insert in (b) shows a portion of the isopropyl methyl signals on an expanded scale.

resonance should occur for the *cis* isomer. The doublet feature of each signal is due to coupling with the HC=N proton (J = 1.1 c.p.s.). A similar splitting of 1.2 c.p.s. is found in the free Schiff base. The R = CH_2CH_3 complex shows at least seven methyl signals centering at about 73 c.p.s. The R = *p*-tolyl complex exhibits two methyl signals of intensity ratio 2:1 (*cf.* Fig. 2a). These observations when taken collectively are consistent only with a *trans* structure. In **2** (5-CH_3, R = C_6H_5) only one methyl signal is observed (*cf.* Fig. 2d), indicating that the chemical shift differences between the three distinct methyl groups in the *trans* form are unresolvably small unless these groups are attached to the primary chelate ring. The HC=N protons in the salicylaldimine series give only one signal, which is slightly broader than that of the free Schiff base, suggesting a composite nature.

The spectra of the tris(pyrrole-2-aldimine) complexes likewise give clear indication of the *trans* isomer only. In **3** (R = CH_3) two HC=N signals with a 2:1 intensity ratio and three methyl doublets, two of which partially overlap (*cf.* Fig. 2b), are observed. The intensity ratio of the two groups of methyl signals is 2:1. The slight splitting of the methyl signals (J = 1.5 c.p.s.) by the HC=N proton also appears in the free ligand (J = 1.5 c.p.s.). The R = CH_2CH_3 complex clearly shows three HC=N signals of equal intensity and two methyl triplets of intensity ratio 2:1 (*cf.* Fig. 2c). The spectrum of the R = $CH(CH_3)_2$ complex is the most interesting of any in this series and is shown in full in Fig. 1b. The complex set of signals around 386 c.p.s. is due to the pyrrole ring protons. The most conspicuous features are the three HC=N signals and the five sets of methyl doublets, one of which has twice the intensity of the others. The latter observation indicates that in the three intrinsically dissimilar isopropyl groups the methyl groups are further distinguished, presumably by the lack of sufficient rotational freedom about the N–C bond.[15] Even in the

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(15) Methyl signals in bis(N-isopropylpyrrole-2-aldimine)zinc(II), which is undoubtedly tetrahedral and thus lacking in the steric hindrance to rotation about the N–C bond, appear as one doublet at 65 c.p.s. in $CDCl_3$ solution.

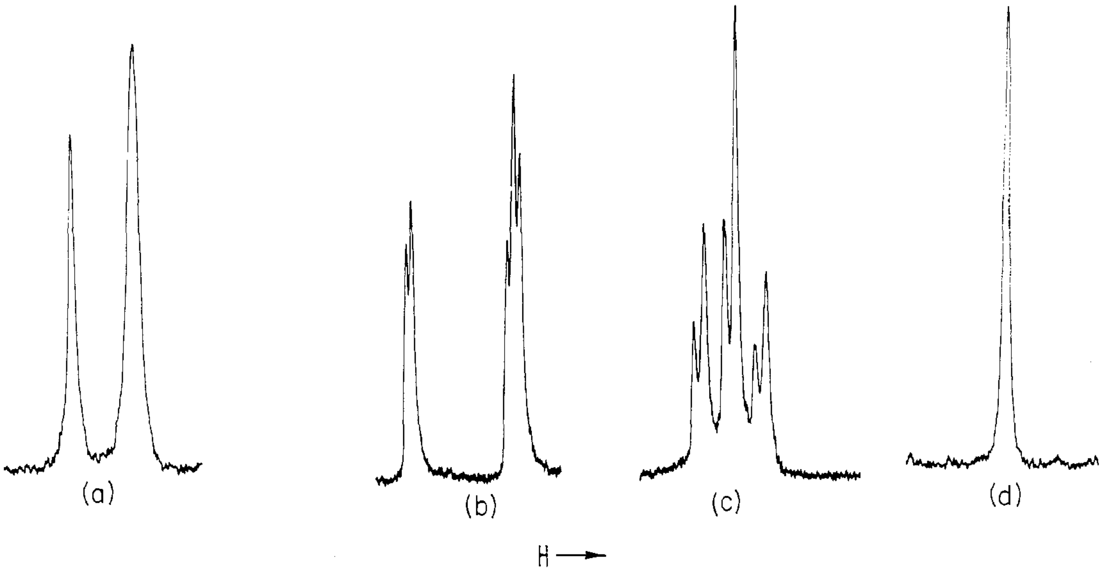

Fig. 2.—The proton resonance spectra of methyl groups in (a) tris-(N-*p*-tolylsalicylaldimine)cobalt(III), (b) tris-(N-methylpyrrole-2-aldimine)cobalt(III), (c) tris-(N-ethylpyrrole-2-aldimine)cobalt(III), (d) tris-(N-phenyl-5-methylsalicylaldimine)cobalt(III), all in $CDCl_3$ solution.

trans form of these complexes there appears to be some steric interaction between sufficiently large R groups which is most severe when R = *t*-Bu with the result that in both series bis complexes are formed.

Attempts have been made to convert the *trans* isomers of both series into the *cis* form. Heating solutions of **2** and **3** (R = CH_3) at 100° for 16 hr. produced no change in the proton resonance spectra. We conclude that in the latter complex the methyl resonance features and the appearance of only two resolvable HC═N signals do not indicate a 2:1 ratio of isomers and do correspond to the *trans* form in which the shifts of two of the three groups (probably those related by a pseudo-twofold axis) are nearly the same.

The proof of the *trans* configuration presented here substantiates certain observations and arguments made earlier in connection with the probable stereochemistry of the tris(salicylaldimine) Co(III) complexes. West[8] was unable to isolate two forms of a number of these complexes and observed that for most of these there was a tendency to be reduced to a bis Co(II) complex. West further states that because of steric overcrowding molecular models of the *cis* isomers could not be assembled and that models of the *trans* form still showed considerable steric strain. We also conclude that the apparently complete preference for the *trans* isomer, in which the nitrogen substituents project from an octahedral edge, rather than for the *cis* isomer, in which these substituents project from a common face, is predominantly due to decreased steric interactions. The increased accommodation of an octahedral structure for a given nitrogen substituent in the pyrrole-2-aldimine series can also be understood on steric grounds. In this series the N–C bonds make ~90° angles with an octahedral edge whereas in the salicylaldimines these angles are ~60°, leading to increased steric interaction in the *trans* (or *cis*) form. The disposition of the R groups nearer the HC═N protons in the pyrrole-2-aldimine series is very probably responsible for the observable separations of the resonances of these protons.

Finally, it must be mentioned that the *cis* and *trans* isomers of tris(2-hydroxy-5-methylazobenzene)cobalt(III) are claimed to have been separated by Häfelinger and Bayer,[16] who obtained by chromatography two forms of apparently identical composition and nearly identical absorption spectra. Proton resonance studies of the complex or of appropriately substituted derivatives might prove useful in investigating this claim.[17]

Acknowledgment.—Financial support of this research by the National Science Foundation (Grant GP-596) is gratefully acknowledged.

(16) G. Häfelinger and E. Bayer, *Naturwissenschaften*, **51**, 136 (1964).

(17) Note Added in Proof.—A recent dipole moment study of a series of substituted tris(salicylaldimine)cobalt(III) complexes has independently demonstrated the *trans* configuration [M. Ciampolini, F. Maggio, and F. P. Cavasino, *Inorg. Chem.*, **3**, 1188 (1964)].