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# Nuclear Resonance and Electronic Spectra of Rhombic Cobalt(III) Chelates

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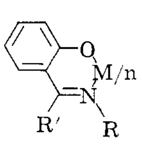
Synthesis of tris(N-alkyl-2-hydroxyacetophenimine)cobalt(III) is described. These chelates have lower hydrolytic stability than that of the corresponding salicylaldimine chelates. The chelates could be obtained only in the *trans* form as proved conclusively by nuclear resonance spectra. The crystal field spectra of the chelates are discussed in terms of an approximate $C_{2v}$ symmetry. The strength of the rhombic crystal field is calculated on the basis of a simple model.

## Introduction

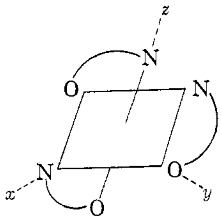
In recent years a number of interesting papers have appeared dealing with the behavior of trivalent cobalt in crystal fields of various symmetries.[1-3] Problems of geometry have been solved by elegant applications of nuclear resonance[4-6] and absolute configurations determined from studies of optical rotary dispersion in crystal field bands.[6,7] Our interest in this field centers around nuclear resonance and crystal field spectra of cobalt chelates of the general type $Co(A-B)_3$, where A–B is an unsymmetrical bidentate chelating agent. Recently we reported and analyzed the crystal field spectra of salicylaldimine chelates of trivalent cobalt.[8] The nuclear resonance spectra of these chelates were reported before.[5]

While metal chelates of salicylaldimine (**1a**) and its ring-substituted derivatives have, in general, been extensively studied, only a very limited amount of work is reported on the chelates of 2-hydroxyacetophenimines (**1b**).[9] Since **1a** and **1b** differ only in the substituent on the azomethine carbon, one may expect considerable similarities in their chemistries. While this is true to a large extent, there are significant differences in stabilities and other properties as will be pointed out in this and subsequent papers.

In this note the preparation of Co(III) chelates **1b** ($M = Co$, $n = 3$) is described. Since the bidentate ligand in **1b** is unsymmetrical, the tris chelate can exist in *cis* (1,2,3 isomer) and *trans* (1,2,6) forms. The chelate rings in the *trans* isomer are symmetrically distinct and a given magnetic nucleus (or group of equivalent nuclei) should, in principle, have different chemical shifts for the three rings. The threefold axis of symmetry in the *cis* form makes all three chelate rings equivalent. This principle has been used very effectively to determine the geometry of β-diketone,[4] salicylaldimine,[5] pyrrole-2-aldimine,[5] and α-amino acid[6] chelates of trivalent cobalt. In some cases[4,6] both *cis* and *trans* isomers could be isolated, but only the *trans* form exists in other cases.[5] Here it is unequivocally demonstrated that **1b** chelates can be isolated only in the *trans* form, **2**. The crystal field spectra of the chelates are then discussed on the basis of proven *trans* configuration.



R = alkyl
**1a**, R' = H
**1b**, R' = $CH_3$



**2**

## Experimental Section

**Preparation of Compounds.—Tris(N-methyl-2-hydroxyacetophenimine)cobalt(III).**—To a stirred aqueous alcoholic solution of 2-hydroxyacetophenone and sodium hydroxide (molar ratio 1:1) was added slowly an aqueous solution of the stoichiometric amount of cobalt acetate tetrahydrate. An orange-red solid separated. Methylamine (33% solution in water) was added in slight excess and stirring was continued for 3 hr. The mixture was kept warm throughout. The green crystalline solid was collected by filtration and twice recrystallized from alcohol. Dark green crystals were obtained, mp 229°. *Anal.* Calcd for $C_{27}H_{30}N_3O_3Co$: C, 64.50; H, 6.00; N, 8.35. Found: C, 64.40; H, 6.10; N, 8.46.

Attempts to prepare the other Co(III) chelates by the above method (replacing methylamine by an appropriate amine) led to isolation of the Schiff base as the major product. The following method was found to be of general applicability for preparation of all chelates.

2-Hydroxyacetophenone (0.01 mole) and the appropriate amine were condensed in ethanol by heating to reflux for 1 hr. Removal of solvent left the Schiff base as a yellow solid. Potassium *t*-butoxide (0.01 mole) and $[(C_2H_5)_4N]_2(CoBr_4)$ (0.003 mole) were added to a magnetically stirred solution of the Schiff base in dry tetrahydrofuran. After overnight stirring, the reaction mixture was filtered and the filtrate was stripped to a brown gum which was extracted with boiling petroleum ether (bp 60–80°). The green solid obtained by removal of solvent from the extract was recrystallized from a dichloromethane–petroleum ether mixture to give dark green crystals.

**Tris(N-ethyl-2-hydroxyacetophenimine)cobalt(III) (Mp 171°).**—*Anal.* Calcd for $C_{30}H_{36}N_3O_3Co$: C, 66.04; H, 6.65; N, 7.70. Found: C, 66.20; H, 6.61; N, 7.44.

**Tris(N-propyl-2-hydroxyacetophenimine)cobalt(III) (Mp 167–168°).**—*Anal.* Calcd for $C_{33}H_{42}N_3O_3Co$: C, 67.44; H, 7.20; N, 7.15. Found: C, 67.41; H, 7.20; N, 7.02.

**Tris(N-*n*-butyl-2-hydroxyacetophenimine)cobalt(III) (Mp**

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169°).—*Anal.* Calcd for $C_{36}H_{48}N_3O_3Co$: C, 68.65; H, 7.68; N, 6.67. Found: C, 68.72; H, 7.62; N, 6.80.

All melting points reported herein are uncorrected.

**Proton Resonance Measurements.**—All measurements were done on Varian HR-100 spectrometer in $CDCl_3$ solution. Frequencies, accurate to ±1 cps, were measured by the side-band technique. Tetramethylsilane was used as the internal standard.

**Spectrophotometric Measures.**—A Cary 14R spectrophotometer and silica cells were used for this purpose.

## Results and Discussion

The synthesis of the chelates invites some comments. It is well known that tris(N-alkylsalicylaldimine)cobalt(III) can, in general, be prepared by hydrogen peroxide oxidation of a solution containing cobalt acetate, salicylaldehyde, and the appropriate amine.[5,10] However, this procedure, except for the methyl complex, gave very poor yields of the chelates when salicylaldehyde was replaced by 2-hydroxyacetophenone. Even in the methyl case, the reaction could be controlled better when air rather than hydrogen peroxide was used as the oxidizing agent. The nonaqueous chelation reaction, which was found to be of general applicability for the present complexes, had been used previously for the synthesis of other chelates of low hydrolytic stability, *e.g.*, β-keto amine chelates of Cr(III)[11] and Ni(II)[12] and pyrrole-2-aldimine chelates of Co(II),[5] Co(III),[5] and Ni(II).[13] Although we have made no quantitative measurements, the hydrolytic stability of the **1b** chelates seems, in general, to be lower than that of the **1a** complexes. This is a possible reason for the near failure of the chelation reaction in aqueous alcoholic solutions for most **1b** chelates. In this context, it is noteworthy that bis(N-isopropyl-2-hydroxyacetophenimine)cobalt(II) prepared by chelation in tetrahydrofuran[14] is very susceptible to hydrolysis, being quickly decomposed by moist solvents. The corresponding salicylaldimine chelate can be easily prepared in an aqueous alcoholic medium.[15] The bis Ni(II) and Cu(II) chelates of type **1b**[14] show the same trend of hydrolytic behavior.

**Nuclear Resonance Spectra.**—Representative proton resonance spectra of **1b** chelates are shown in Figure 1. Chemical shift data are set out in Table I. Examination of these leaves no doubt that the chelates have a *trans* configuration.

The free Schiff base, N-butyl-2-hydroxyacetophenimine, shows a high-field triplet (95 cps) characteristic of the methyl group in the alkyl chain and another triplet (351 cps) of correct intensity representing the $N\mathit{CH}_2$ resonance. The $CH_3C{=}N$ resonance appears as a sharp singlet at 225 cps. This spectrum (Table I) clearly establishes the relative positions of the $N\mathit{CH}_2$ and $\mathit{CH}_3C{=}N$ resonances. Except for small differences in frequencies bis(N-*n*-butyl-2-hydroxyacetophenimine)nickel(II)[14] has the same nmr spectrum as that of the free Schiff base. This is compatible with a grossly planar structure and a singlet ground state. The corresponding Co(III) chelate shows three well-separated signals assignable to $CH_3C{=}N$ resonance, thus characterizing the *trans* configuration (Table I). The same is true of the N-*n*-propyl and ethyl chelates (Figure 1, c). The methyl groups in the alkyl chain of these two chelates give rise to six and five lines, respectively (Figure 1, b and c). These can be easily analyzed into three triplets in each case: 62, 69, 76; 69, 76, 83; and 83, 90, 97 cps for the propyl complex and 116, 123, 130; 123, 130, 137; and 130, 137, 144 cps for the ethyl complex. Assuming that each triplet has the simple 1:2:1 intensity ($J$ = 7.0 cps), the observed spectral intensities (Table I) are correctly reproduced. The methyl complex (Figure 1, a) fits smoothly into the pattern giving three $CH_3C{=}N$ signals. It is interesting to note that in **1a** chelates[5] the HC=N signal appears only as a somewhat broadened single feature, while in **1b** $CH_3C{=}N$ reflects the asymmetry of the molecules most clearly.

TABLE I

| Compound | Group | Chem shift,[a-c] cps |
|---|---|---|
| **1b** (R = $CH_3$) | $NCH_3$ | 308 (2), 315 |
| | $CH_3C{=}N$ | 202, 252, 266 |
| **1b** (R = $C_2H_5$) | $NCH_2\mathit{CH}_3$ | 116, 123 (3), 130 (4), 137 (3), 144 |
| | $N\mathit{CH}_2CH_3$ | 341 (2),[d] 387[d] |
| | $CH_3C{=}N$ | 207, 257, 276 |
| **1b** (R = *n*-$C_3H_7$) | $NCH_2CH_2\mathit{CH}_3$ | 62, 69 (3), 76 (3), 83 (2), 91 (2), 98 |
| | $NCH_2\mathit{CH}_2CH_3$ | 151[e] |
| | $N\mathit{CH}_2CH_2CH_3$ | 322 (2),[d] 373[d] |
| | $CH_3C{=}N$ | 201, 252, 273 |
| **1b** (R = *n*-$C_4H_9$) | $NCH_2\mathit{C}_3\mathit{H}_7$ | 112[e] |
| | $N\mathit{CH}_2C_3H_7$ | 328 (2),[d] 375[d] |
| | $CH_3C{=}N$ | 201, 253, 276 |
| Schiff base (R = *n*-$C_4H_9$) | $NCH_2(CH_2)_2\mathit{CH}_3$ | 95[f] |
| | $NCH_2(\mathit{CH}_2)_2CH_3$ | 160[c] |
| | $N\mathit{CH}_2(CH_2)_2CH_3$ | 351[f] |
| | $CH_3C{=}N$ | 225 |

[a] From TMS. [b] Figures in parentheses show relative intensity of components for a given group. [c] For all compounds there is a complex signal around 700 cps representing aromatic protons. [d] Center of broad band. [e] Center of a complex pattern. [f] Center of triplet with $J$ = 7.0 cps.

For the methyl complex only two $NCH_3$ signals (intensity ratio 1:2) are observed (Figure 1), the *less intense* line being at *lower* field. The same is true of $NCH_2$ signals in the other chelates (Table I). Further, of the three $CH_3N{=}C$ signals shown by each complex, *two* are closely spaced at *low* field. A close look at the data of **1a**[5] and pyrrole-2-aldimine chelates[5] shows exactly similar behavior; *viz.*, (1) for substituents on the N-alkyl or N-aryl chain two of the three signals are very close to each other or merge completely; these two signals appear at *higher* field; and (2) for all other nuclei inclusive of HC=N, if two signals have identical or slightly different chemical shifts, they belong to *lower* field. It is further noted that methyl groups in *trans*-benzoylacetone[4] and alanine[6] chelates of cobalt(III) behave as in (2).

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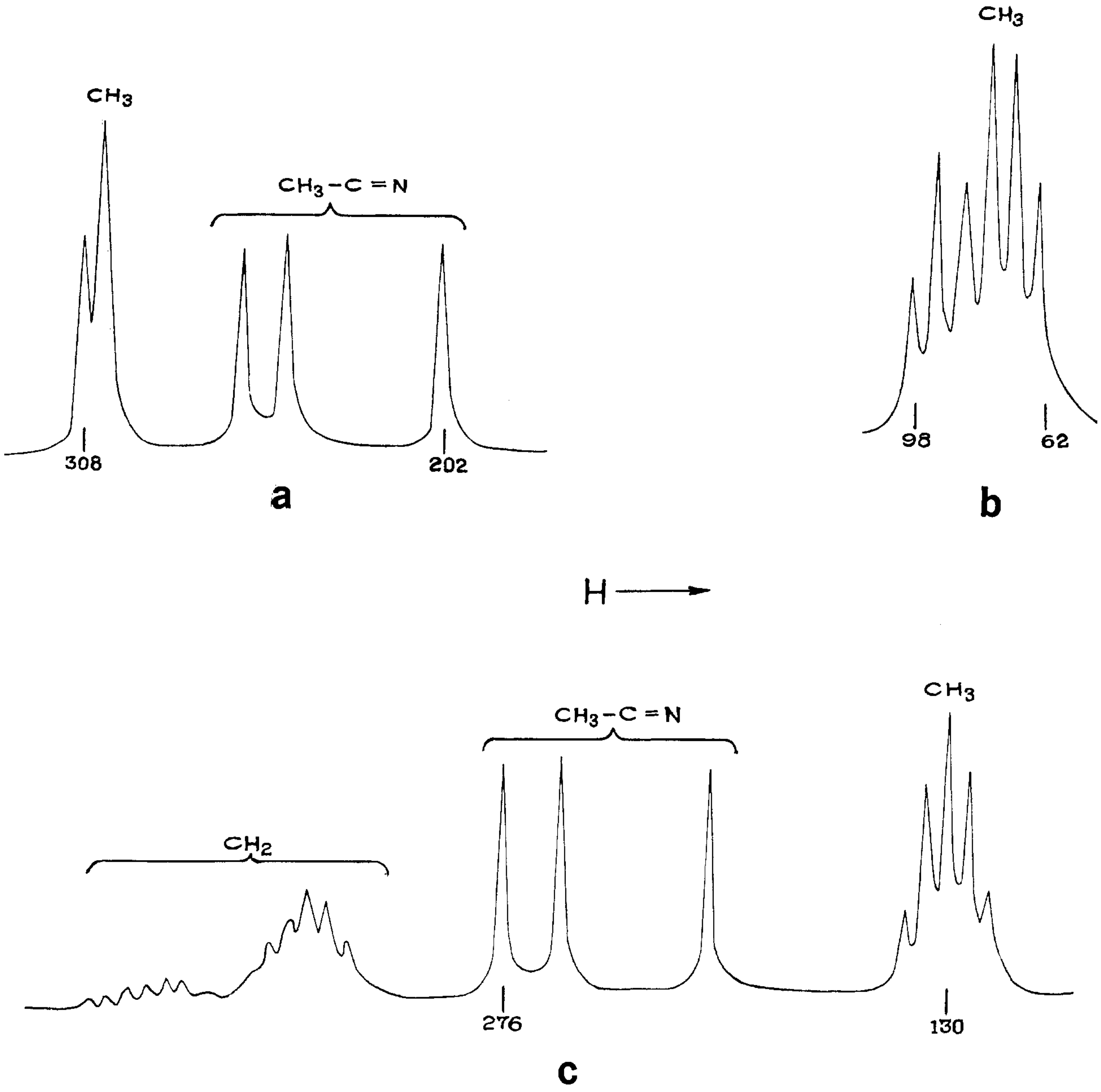

Figure 1.—Nuclear resonance spectra of tris(N-R-2-hydroxyacetophenimine)cobalt(III) in $CDCl_3$: a, R = $CH_3$; b, R = $n$-$C_3H_7$; c, R = $C_2H_5$. $CH_3$ and $CH_2$ refer to the alkyl chain on nitrogen. Numerical figures refer to chemical shifts in cycles per second from tetramethylsilane at 100 Mc/sec.

Referring to **2** it is seen that by turning the chelate ring on the *xy* plane by 180°, keeping the rest of the molecule fixed, the *trans* form **2** can be mentally converted into the *cis* form which has identical chemical shifts for all "three signals." The chelate ring on the *xy* plane presumably generates the unique signal. This can explain observation 2 above. Observation 1 which is peculiar to nitrogen substituents in Schiff base chelates may alternatively arise from the fact that neglect of chelate rings generates a twofold axis of symmetry (*z* axis in **2**) resulting in near equivalence of the two nitrogens in the *xy* plane. The groups attached to these two nitrogens can conceivably have very similar chemical shifts.

We did not obtain evidence for the *cis* form of **1b** chelates. This is understandable[5] since in the *cis* form a prohibitively large steric crowding will arise among nitrogen substituents on the octahedral face which contains the nitrogen atoms at three corners.

**Crystal Field Spectra.**—Relevant data are presented in Figure 2. Visible absorption occurs around 630 mμ. Two bands can be clearly seen for **1b** (R = $CH_3$) in this region, while for the remaining chelates only one asymmetric feature is observable. No other transitions could be located in the visible region. The spectra are, in general, quite similar to those of **1a** chelates.[8]

If chelate rings are neglected and only coordinated atoms are considered, **2** belongs to the point group $C_{2v}$. Spin-paired Co(III) in octahedral ($O_h$) crystal fields shows two spin-allowed transitions: ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and $\rightarrow {}^1T_{2g}$, the latter appearing at higher energy. In $C_{2v}$, ${}^1T_{1g}$ is split into ${}^1A_2 + {}^1B_1 + {}^1B_2$; ${}^1T_{2g}$ is also split into ${}^1A_2 + {}^1B_1 + {}^1B_2$, but this will not concern us here since the corresponding absorption bands are completely

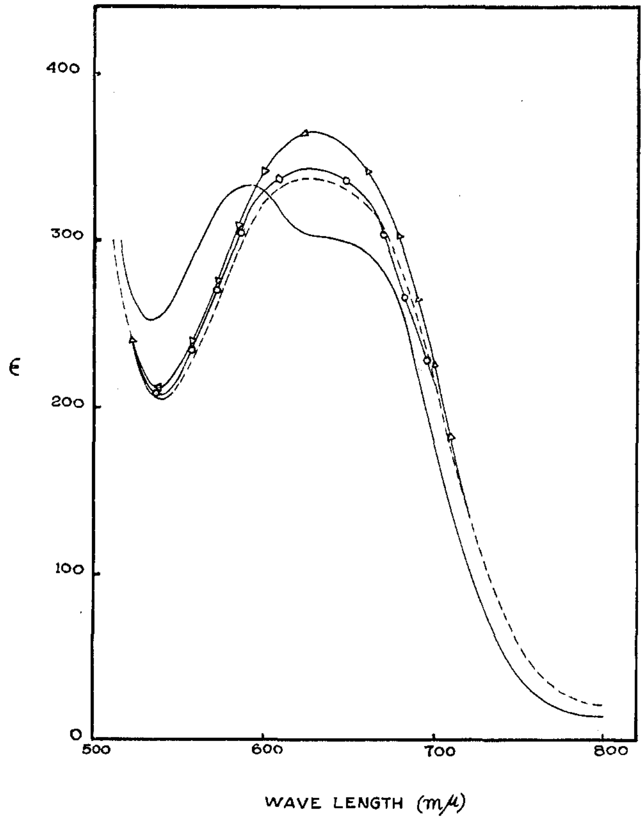

Figure 2.—Crystal field spectra of tris(N-R-2-hydroxyacetophenimine)cobalt(III) in benzene: ———, R = $CH_3$; - - - -, R = $C_2H_5$; —O—O—O—, R = $n$-$C_3H_7$; —△—△—△—, R = $n$-$C_4H_9$.

masked by ligand absorptions. We assign the visible absorption of **1b** chelates to split components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. Recently similar splittings due to rhombic crystal fields have been observed[7] in both electronic absorption and circular dichroism of other $CoO_3N_3$ chelates, *e.g.*, *trans* forms of tris(alanine)-cobalt(III) and related chelates.

Yamatera[1] and McClure[2] have treated the problem of crystal field splitting of Co(III) chelates in a variety of geometries. Yamatera[1] expressed the effect of ligand replacement in terms of a change in the overlap integral between the metal orbitals and group overlap orbitals of ligands. The same results can, however, be obtained on the assumption that the relative importance of bonding in a given direction for an orbital is proportional to the electron density in the bonding direction. This approach was extensively developed by McClure[2] for a variety of crystal field symmetries. We shall apply this model to the present chelates. In this model each ligand is supposed to exert its influence on d electrons through $\sigma$-antibonding and $\pi$-antibonding contributions which we shall designate as $\sigma$ and $\pi$, respectively. When a ligand A is replaced by a ligand B, these contributions will differ in certain directions and this may lead to splitting of energy levels. The results may be expressed in terms of the parameters $\delta\sigma$ and $\delta\pi$ defined as: $\sigma_B = \sigma_A + \delta\sigma$ and $\pi_B = \pi_A + \delta\pi$.

In going from $MA_6$ ($O_h$) to $MA_3B_3$ ($C_{2v}$, B on $+x$, $-x$, $+z$) the following contributions[2] are obtained for one-electron orbitals: $2\delta\sigma$ ($d_{x^2-y^2}$, $a_1$); $2\delta\sigma$ ($d_{z^2}$, $a_1$); $2\delta\pi$ ($d_{xy}$, $a_2$); $\delta\pi$ ($d_{yz}$, $b_2$); $3\delta\pi$ ($d_{zx}$, $b_1$). The two $a_1$ orbitals have a cross term of value $(2/\sqrt{3})\delta\sigma$. Applying these two appropriate angular functions[1] for a low-spin $d^6$ system, one can derive the following changes in energy of transition

$$\begin{array}{lll} \nu_1 & {}^1A_1 \longrightarrow {}^1B_1 & \delta\sigma - 3\delta\pi \\ \nu_2 & {}^1A_1 \longrightarrow {}^1A_2 & 2\delta\sigma - 2\delta\pi \\ \nu_3 & {}^1A_1 \longrightarrow {}^1B_2 & 3\delta\sigma - \delta\pi \end{array}$$

so that, $\nu_2 - \nu_1 = \nu_3 - \nu_2 = \delta\sigma + \delta\pi = \delta$ (say). One may consider **1a** and **1b** chelates as being formed from a parent $CoO_6$ by replacement of three oxygen atoms by nitrogen as in **2**. $\delta$ will presumably be positive since nitrogen generally creates a stronger effective ligand field than oxygen.[16] The order of increasing energy is then $B_1 < A_2 < B_2$.

Of the three possible transitions $\nu_1(x)$ and $\nu_3(y)$ are electronically allowed. **1a** (R = $CH_3$)[5] and **1b** (R = $CH_3$) clearly show two bands of about equal intensity. Even after correction for overlap with an ultraviolet tail, the intensities are quite large ($\epsilon$ 200–300), and this corroborates, at least in part, the electronic contribution. The two bands of **1b** (R = $CH_3$) (15,630 and 17,000 $cm^{-1}$) lead to $\delta$ = 650 $cm^{-1}$, if they are assigned to $\nu_1$ and $\nu_3$. For the other chelates the overlap is too serious for calculation of meaningful splitting parameters. For **1a**[5] $\delta$ has the values 950 $cm^{-1}$ (R = $CH_3$) and 650 $cm^{-1}$ (R = $C_2H_5$).[17]

Substituents on the azomethine group can affect both $\delta\sigma$ and $\delta\pi$ through inductive and steric factors. Thus variation of splitting with the nature of the R group and the substituents on azomethine carbon is not too surprising.

**Acknowledgment.**—Thanks are due Dr. B. D. Joshi of this department for helpful discussions.

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[16] $\delta\pi$ will probably be negative because of lone pairs on oxygen; $\delta\sigma$ will generally be expected to be positive for replacement of oxygen by nitrogen. $\delta\sigma$ and $\delta\pi$ work in opposite directions and $\delta\sigma + \delta\pi$ will be positive only if $|\delta\sigma| > |\delta\pi|$.

[17] It is being assumed that $\nu_2$ is not observed owing to small intensity. This is not a very safe assumption since intensity can be gained through vibronic coupling or through the fact that consideration of chelate rings removes all symmetry and makes all transitions electronically allowed. However, since only *two bands* are *experimentally* observed, this is the best we can do with the data and the simple model.