erence, over the statistical values, for reaction in the positions *cis* to the substituent and this may be associated with the ability of the incoming solvent molecule to hydrogen bond with the electronegative substituent. The *cis* product in each instance is optically pure ($\pm 2\%$) and this excludes any appreciable amount of the alternative form of the trigonal bipyramid.

The results may be contrasted with those obtained for the induced aquations of *trans*-$[Co(NH_3)_4(ND_3)N_3]^{2+}$ and *trans*-$[Co(NH_3)_4(ND_3)X]^{2+}$[8] (X = Cl, Br) where no rearrangement was observed. The difference between the two sets of data may result from the possible stabilization of the trigonal bipyramid in the $[Co(en)_2X]$ system by bonding the filled p orbitals of appropriate symmetry on the substituent to the vacated cobalt orbital as suggested by Basolo and Pearson.[21] This possibility does not arise when X = NH_3 so that to be consistent with this proposal full retention of configuration should be observed in the induced aquations of *cis*-$[Co(en)_2NH_3N_3]^{2+}$ and *cis*-$[Co(en)_2NH_3Cl]^{2+}$. These systems are at present being examined. Also initial studies show that full retention of configuration occurs in the analogous reactions of the [Co(tetraethylenepentamine)X]$^{2+}$ isomers (X = N_3, Cl, Br).[22]

It seems unlikely that these and previous results[2-8] can be explained by coincidences in the reactivity pattern for the reaction intermediates $RCoNNNO^{3+}$ and $RCoClHg^{4+}$ over a range of complexes and for several methods of detecting their behavior. It is more logical to argue that the common results obtained for the isotopic fractionation factor, the competition studies, and the stereochemistry of the products for the sets of complexes are explained by a common cause, rather than by multiple coincidences.

Acknowledgment.—The authors thank the Microanalytical Unit of the John Curtin School of Medical Research for the C, H, and N microanalyses.

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(21) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 133.

(22) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, to be published.

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Synthesis, Nuclear Resonance, and Electronic Spectra of Tris(2-hydroxypropiophenimine)cobalt(III)

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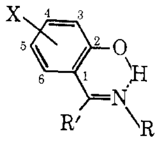
Several tris(N-alkyl-2-hydroxypropiophenimine)cobalt(III) compounds have been synthesized by a nonaqueous chelation reaction. Tris(N-methyl-2-hydroxypropiophenimine)cobalt(III) exists as a 1:1 dichloromethane adduct in which dichloromethane is held very strongly in the crystal lattice. The chelates exist exclusively in the *trans* form. The aromatic region of the nuclear resonance spectra of the chelates is discussed in some detail, and it is shown that definite assignments can be made for several signals. The crystal field spectra of the chelates are compatible with an essentially octahedral field having a rhombic component. This component clearly splits the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition in some cases. A shoulder around 24,000 cm^{-1} presumably represents the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition.

Introduction

As part of our general program[1,2] on the studies of transition metal complexes derived from ligands of type **1**, we recently reported the nuclear resonance and crystal field spectra of 2-hydroxyacetophenimine chelates of trivalent cobalt[1] (**3**, R = alkyl, X = H). These complexes belong to the class $Co(A-B)_3$ where A–B is an unsymmetrical bidentate ligand. The *trans* geometry of **2** and **3** was demonstrated unequivocally by proton resonance spectra.[1,3] In the present paper we report the synthesis, nuclear resonance, and electronic spectra of the corresponding 2-hydroxypropiophenimine chelates **4** (R = alkyl, X = H or 5-CH_3). Synthesis of **3** required a nonaqueous chelation reaction in most cases. The same is found to be true for **4**, as one might intuitively expect. The salicylaldimines, **2**, can, on the other hand, be made in general by aqueous chelation.[3,4]



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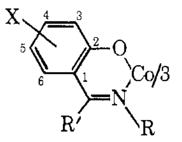

2, R′ = H
3, R′ = CH_3
4, R′ = C_2H_5

The nuclear resonance spectra of **4** both in alkyl and aromatic regions are compatible only with the expected *trans* structure. To facilitate analysis of the spectrum in the aromatic region in detail, complex **3** (R = CH_3, X = 4,5-$(CH_3)_2$) was synthesized.

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(1) A. Chakravorty and K. C. Kalia, *Inorg. Chem.*, **6**, 690 (1967).

(2) A. Chakravorty, T. S. Kannan, and S. Gupta, copper and nickel complexes of **1** (R′ = CH_3), to be published.

(3) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1521 (1964).

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

TABLE I

CHARACTERIZATION OF COMPLEXES

Complex				% C		% H		% N	
R	X	Formula	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found
CH_3[a]	4,5-$(CH_3)_2$	$C_{33}H_{42}N_3O_3Co$	176–177	67.50	67.55	7.15	7.69	7.15	7.18
CH_3	H	$C_{31}H_{38}N_3O_3Cl_2Co$	203–204	59.02	58.89	6.03	6.00	6.81	6.66
CH_3	5-CH_3	$C_{33}H_{42}N_3O_3Co$	202–203	67.50	67.32	7.15	7.17	7.15	7.29
C_2H_5	H	$C_{33}H_{42}N_3O_3Co$	163–164	67.50	67.24	7.15	7.10	7.15	7.06
C_2H_5	5-CH_3	$C_{36}H_{48}N_3O_3Co$	159–160	68.69	68.65	7.62	7.69	6.67	6.30
n-C_3H_7	H	$C_{36}H_{48}N_3O_3Co$	156–157	68.69	68.64	7.62	7.67	6.67	6.71
n-C_4H_9	H	$C_{39}H_{54}N_3O_3Co$	149–152	69.77	69.56	8.04	8.29	6.25	6.02

[a] $R' = CH_3$ (type **3**); for all other chelates $R' = C_2H_5$ (type **4**).

Octahedral Co(III) generally shows two spin-allowed crystal field bands ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. In fields of lower symmetry, splitting of these bands may be expected owing to removal of degeneracies of the excited states. For the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition such splittings are observed in a few cases. The results are discussed in terms of our previous findings.[1,5]

Experimental Section

Preparation of Compounds.—**2-Hydroxypropiophenone** and **5-methyl-2-hydroxypropiophenone** were synthesized by Fries rearrangement of the corresponding phenyl esters which were made from the appropriate phenol, propionic acid, and thionyl chloride. Conditions for the rearrangement were essentially those given in "Organic Syntheses."[6]

Tris(N-methyl-2-hydroxypropiophenimine)cobalt(III).—To a methanolic solution of 2-hydroxypropiophenone and sodium hydroxide (molar ratio 1:1) was added with stirring a solution of cobalt acetate in methanol. Within a few minutes a brownish red crystalline solid separated. Methylamine (33% solution in water) was added in slight excess. A clear solution was formed which gradually turned green. After stirring for 4 hr, a green solid separated which was twice recrystallized from a dichloromethane–hexane mixture. The dark green crystals contained 1 mole of dichloromethane/mole of chelate. The crystals gradually lost their luster above 170°. Analytical data for this and other chelates are given in Table I.

Tris(5-methyl-N-methyl-2-hydroxypropiophenimine)cobalt(III) and tris(4,5-dimethyl-N-methyl-2-hydroxyacetophenimine)cobalt(III) were prepared by using the same procedure. Other chelates could not be obtained by analogous reactions in methanol. The chelation reaction involving Schiff base, potassium t-butoxide, and $((C_2H_5)_4N)_2(CoBr_4)$ in dry tetrahydrofuran was found to be of general applicability in all such cases. Details are identical with those for **3**.[1] Recrystallization was carried out from a dichloromethane–hexane mixture.

Proton resonance measurements were done on a Varian HR-100 spectrometer in $CDCl_3$ solution. Frequencies were measured by the side-band technique. Tetramethylsilane (TMS) was used as the internal standard. Intensities were measured planimetrically or by integration.

Spectral measurements in the visible and ultraviolet regions were carried out on a Cary 14 recording spectrophotometer using 1-cm silica cells.

Thermogravimetric measurements were done on an Aminco Thermobalance fitted with a precision spring, temperature programmer, and recorder. The rate of heating was 10° min^{-1} under vacuum (0.1 mm). A 149-mg sample of **4**($R = CH_3$, $X = H$)$\cdot CH_2Cl_2$ lost 20.0 mg between 170 and 230°. The calculated loss for complete removal of CH_2Cl_2 is 20.3 mg.

Results and Discussion

The 2-hydroxypropiophenimine complexes are reported for the first time. They form dark green crystalline solids. The chelates with $R = CH_3$ can in general be prepared by allowing cobalt acetate, ketone, and methylamine to react in methanolic solution (aqueous ethanolic medium used for **3** ($R = CH_3$)[1] gave poor yields for **4** ($R = CH_3$)). The remaining complexes all needed a nonaqueous chelation for synthesis. In all cases oxygen (air) served as the oxidizing agent. The nonaqueous chelation procedure has become increasingly important in the synthesis of easily hydrolyzable complexes derived from ligands of low acidity. Examples are β-ketoamine chelates of Cr(III),[7] Ni(II),[8a] Co(II),[8b] and V(III),[9] pyrrole-2-aldimine chelates of Co(II),[3] Co(III),[3] and Ni(II),[10] and 2-hydroxyacetophenimine complexes of Ni(II)[2] and Co(III).[1]

The complex **4** ($R = CH_3$, $X = H$) was isolated as a dichloromethane adduct. Infrared spectrum shows the C–Cl stretch at 740 cm^{-1}. Analytical data fit with a 1:1 composition for the adduct. This is corroborated by nuclear resonance and thermogravimetry. The nuclear resonance spectrum of the complex in $CDCl_3$ solution shows a sharp dichloromethane signal (Table II) of correct relative intensity. Under vacuum the crystalline solid loses weight in a well-defined stage, representing loss of 1 mole of dichloromethane/mole of chelate, between 170 and 230°. Above 240° there is a very rapid loss of weight which can be due either to sublimation of the complex or to decomposition giving volatile products. The high temperature needed to liberate dichloromethane is indicative of the considerable tenacity of its attachment to the crystal lattice. Since the adduct is in no way unusual when compared with other nonsolvated chelates described here either in physical appearance or in nuclear magnetic and crystal field behavior (*vide infra*), the dichloromethane is most probably present as such in the adduct and no strong chemical bonds are involved. The crystal lattice seems to be just right to trap a dichloromethane molecule very effectively. The possibility of trapping other molecules is now being investigated.

Nuclear Resonance Spectra.—From previous experience with salicylaldimine[3] and 2-hydroxyacetophenimine[1] chelates one may confidently predict that the complexes reported here will exist exclusively in

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[5] A. Chakravorty, K. C. Kalia, and T. S. Kannan, *Inorg. Chem.*, **5**, 1623 (1966).

[6] A. H. Blatt, Ed., "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 543.

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

[8] (a) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965); (b) G. W. Everett, Jr., and R. H. Holm, *ibid.*, **88**, 2442 (1966).

[9] F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1607 (1967).

[10] R. H. Holm, A. Chakravorty, and L. J. Theriot, *ibid.*, **5**, 625 (1966).

TABLE II

PROTON RESONANCE FREQUENCIES

Compound ($R = CH_3$)	Group	Chemical shift,[a,b] cps
4, $X = H$[c]	NCH_3	310, 314, 324
	$\mathit{CH}_3CH_2C{=}N$	60 (1),[d] 128 (2)[e]
	$CH_3\mathit{CH}_2C{=}N$	261 (1),[e] 299 (2)[e,f]
	CH_2Cl_2	526
	Benzene ring	616 (1),[g] 650 (3),[h] 692 (6),[h] 738 (1),[g] 748 (1)[g]
4, $X = 5\text{-}CH_3$	NCH_3	308, 310, 320
	$\mathit{CH}_3CH_2C{=}N$	63 (1),[d] 129 (2)[e]
	$CH_3\mathit{CH}_2C{=}N$	260 (1),[e] 296 (2)[e,f]
	$5\text{-}CH_3$	217, 221, 226
	Benzene ring	607 (1),[g] 680 (6),[h] 716 (1), 731 (1)
3, $X = 4,5\text{-}(CH_3)_2$	NCH_3	302, 304, 308
	$CH_3C{=}N$	201,[i] 246, 261
	$4,5\text{-}(CH_3)_2$	196 (1), 205 (3), 210 (1), 221 (1)
	Benzene ring	595 (1), 665 (1), 672 (2), 701 (1), 721 (1)

[a] From TMS. [b] Figures in parentheses show relative intensity of components for a given group. [c] Dichloromethane adduct. [d] Center of triplet with $J = 7.5$ cps. [e] Center of quartet (1:3:3:1) with $J = 7.5$ cps. [f] Partially overlaps with NCH_3 signals. [g] Center of doublet with $J = 8.0$ cps. [h] Approximate center of complex pattern. [i] Overlaps with $4,5\text{-}(CH_3)_2$ signals; assignment based on analogy with other 2-hydroxyacetophenimine complexes.[1]

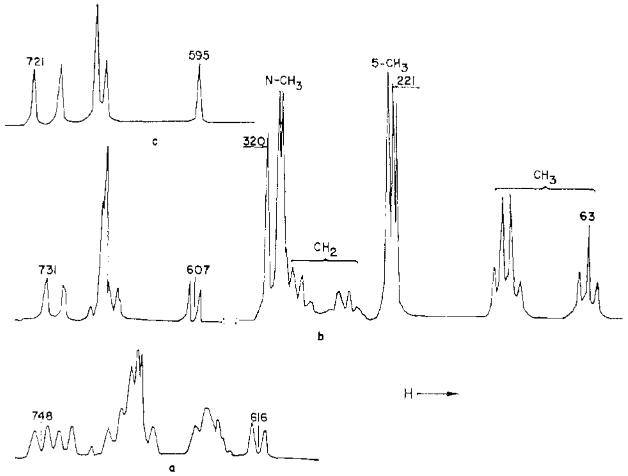

Figure 1.—Nuclear resonance spectra of: a, tris(N-methyl-2-hydroxypropiophenimine)cobalt(III)–dichloromethane in the aromatic region; b, tris(5-methyl-N-methyl-2-hydroxypropiophenimine)cobalt(III); c, tris(4,5-dimethyl-N-methyl-2-hydroxyacetophenimine)cobalt(III) in the aromatic region. Numerical figures refer to chemical shifts in cycles per second from TMS at 100 Mc/sec. Solvent is $CDCl_3$ in all cases.

trans configuration. This configuration, having no symmetry elements, requires that a given magnetic nucleus (or group of equivalent nuclei) should produce different chemical shifts for the three chelate rings. Data for selected complexes are presented in Figure 1 and Table II. The NCH_3 group in each case gives rise to three distinct signals, two of which are closely spaced at *higher* field. The azomethine CH_3 group of **4** ($R = CH_3$, $X = H$ or $5\text{-}CH_3$) gives rise to a 1:2:1 triplet (~60 cps) and a quartet (~128 cps). The latter may be resolved into two overlapping 1:2:1 triplets. Thus in effect there are three triplets of equal intensity, two of which are very closely spaced at *lower* field. The methyl group in the benzene ring of the $5\text{-}CH_3$ complex also produces three signals (Figure 1b). In the corresponding salicylaldimine complex[3] there is only one $5\text{-}CH_3$ and one broadened $HC{=}N$ signal. The asymmetry of **4** (and **3**[1]) is reflected very convincingly in substituents both on the azomethine carbon and on the benzene ring.

No attention has been given previously to resonances of aromatic protons in complexes **2** or **3**.[1,3] By comparing the behavior of several chelates, it is possible to make partial assignments of these resonances at least for the cases studied (Figure 1, Table II). Before we proceed further, it may be noticed that the aromatic signals move to higher fields with methylation of the benzene ring. This is generally true for alkyl substitution in simple aromatic compounds and can be ascribed to the electron-donating character of alkyl groups.[11]

In **4** ($R = CH_3$, $X = H$) (Figure 1a), apart from complex patterns at 650 and 692 cps, there are three doublets (616, 738, and 748 cps) of equal intensity and each is characterized by a coupling constant of 8.0 cps. This constant is consistent with the coupling of two protons in the *ortho* position. In the corresponding $5\text{-}CH_3$ complex (Figure 1b), while the doublet at highest field (607 cps) is retained, the two low-field features (716 and 731 cps) become singlets with very ill-defined signs of splitting probably due to *meta* and/or *para* coupling. This leads us to conclude that the two low-field absorptions represent two of the three expected (since each chelate ring is, in principle, distinct) 6-H signals. In the $5\text{-}CH_3$ chelate there is no absorption corresponding to the broad and complex feature of the unsubstituted chelate at 650 cps. This signal can then be assigned to 5-H with reasonable certainty. It is of correct intensity to contain all "three" 5-H resonances. The doublet at highest field for the two chelates can be due to 3-H or 4-H. The choice between the alternatives becomes clear when one considers **3** ($R = CH_3$, $X = 4,5\text{-}(CH_3)_2$) (Figure 1c). It has two low-field signals (701 and 721 cps) of equal intensity which are assigned to 6-H. The singlet at highest field (595 cps) is reasonably taken to correspond to the doublet (~610 cps) of the previous two chelates. Thus the highest field signal is assigned to 3-H in all three cases. No definitive assignment is possible for the remaining signals. In **4** ($R = CH_3$, $X = H$ and $5\text{-}CH_3$) the complex pattern at ~685 cps contains two 3-H, three 4-H, and one 6-H absorptions. In **3** ($R = CH_3$, $X = 4,5\text{-}(CH_3)_2$) there are two alternatives: one 6-H or one 3-H at 665 cps and two 3-H or one 3-H plus one 6-H at 672 cps. Although the spectra of aromatic protons are not amenable to complete analysis, they con-

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(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 258.

vincingly demonstrate the effect of asymmetry of the chelates.

Neglecting chemical shifts due to asymmetry, the electron-withdrawing azomethine group and electron-donating phenolic oxygen may be expected[11] to produce the following order of deshielding: 6-H > 4-H > 5-H ~ 3-H. Taking **4** ($R = CH_3$, X = H), the signals at 738 (and 748) (6-H), 692 (4-H), 650 (5-H), and 616 (3-H) cps do approximately follow this order. However, this agreement is somewhat fortuitous since a certain set of signals was chosen. Thus considering an alternative set—692 (6-H, 4-H, 3-H) and 650 (5-H) cps—the above order is no longer clearly observable. The asymmetry of the molecule spreads out one signal (the one at *higher* field) from the remaining two particularly for 6-H and 3-H, and, conceivably, this can offset the order expected from substitution effects alone. In chelates where the complication due to lack of symmetry does not arise, *e.g.*, in bis(N-alkyl-2-hydroxyacetophenimine)nickel(II) or the corresponding Schiff base, the aromatic protons do show the following order of deshielding: 6-H > 4-H > 5-H ~ 3-H.

Crystal Field Spectra.—The 2-hydroxypropiophenimines show a prominent feature in the visible region around 16,000 cm^{-1}. The spectra are quite similar to those of **2**[5] and **3**.[1] Spectral data for the three classes of complexes are set out in Table III. Selected spectra for **4** are shown in Figure 2.

TABLE III

FREQUENCIES (CM^{-1}) AND EXTINCTION COEFFICIENTS ($L. MOLE^{-1} CM^{-1}$) OF CRYSTAL FIELD BANDS IN BENZENE

	Compound		Frequency (extinction coefficient)	δ, cm^{-1}
	R	X		
2	CH_3	H	17,400 (265), 15,600 (208) sh[a]	900
	C_2H_5	H	16,950 (271), 15,600 (252) sh	680
	n-C_4H_9	H	16,400 (275)[b]	. . .
3	CH_3	H	16,950 (333), 15,600 (301) sh	680
	C_2H_5	H	16,000 (337)[b]	. . .
	n-C_3H_7	H	16,000 (340)[b]	. . .
	n-C_4H_9	H	16,000 (366)[b]	. . .
	CH_3	4,5-$(CH_3)_2$	16,700 (386), 15,400 (350) sh	650
4	CH_3	H	16,950 (324), 15,400 (291) sh	780
	C_2H_5	H	15,800 (335)[b]	. . .
	n-C_3H_7	H	15,800 (346)[b]	. . .
	n-C_4H_9	H	15,800 (353)[b]	. . .
	CH_3	5-CH_3	16,700 (387), 15,400 (356) sh	650
	C_2H_5	5-CH_3	15,500 (391)[b]	. . .

[a] sh is shoulder. [b] Approximate center of asymmetric broad band.

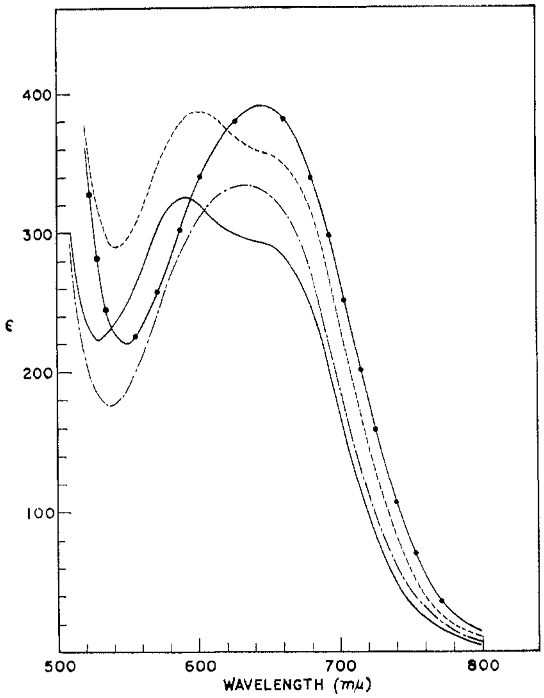

Figure 2.—Crystal field spectra of tris(X-N-R-2-hydroxypropiophenimine)cobalt(III) in benzene: ———, (X = H, $R = CH_3) \cdot CH_2Cl_2$; - - - -, X = 5-CH_3, $R = CH_3$; — - —, X = H, $R = C_2H_5$; -●—●-, X = 5-CH_3, $R = C_2H_5$.

The composite nature of the feature in the visible region can be clearly seen in all complexes with $R = CH_3$. In the remaining chelates, although no definite splitting is observed, the band is asymmetric and most probably composite. The ~16,000-cm^{-1} feature is assigned to split components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition (in O_h) by the C_{2v} (chelate rings neglected) component of the crystal field. In C_{2v}, $^1T_{1g}$ goes to $^1A_1 + {}^1B_1 + {}^1B_2$. Previously[1,5] we have applied in some detail the models of Yamatera[12] and McClure[13] to study this splitting. The effect of the rhombic component was expressed in terms of a parameter δ which measures the change in σ- and π-antibonding contributions due to ligand replacement while going from O_h to C_{2v}.[1,13] Subject to certain assumptions,[1] the energy level order is $^1B_1 < {}^1A_2 < {}^1B_2$.[14]

In cases where two bands are clearly observed in the ~16,000-cm^{-1} region the following assignments can be made: $^1A_1 \rightarrow {}^1B_1$ (~15,000 cm^{-1}) (ν_1) and $^1A_1 \rightarrow {}^1B_2$ (~17,000 cm^{-1}) (ν_3). Further,[1] $\nu_3 - \nu_1 = 2\delta$. Values of δ where ν_1 and ν_3 do not overlap too seriously are also set out Table III. Since δ is small compared to ν_1 and ν_3 and since the bands are broad, too much significance cannot be attached to small variations of δ among various complexes of types **2**, **3**, and **4**. We have not considered the $^1A_1 \rightarrow {}^1A_2$ (ν_2) transition above; the reason for this is discussed elsewhere.[1]

Certain regular trends in the intensity of the ~16,000-cm^{-1} absorption may be noted (Table III). For a given chelate type the intensity at absorption maximum (maxima) increases with the size of the R group and with methylation at the 5 position of the aromatic ring. Among different chelate types, **3** and **4** have very similar intensities while the intensity of **2** is considerably lower (for a given R group).

Previously no serious attempts were made to locate the $^1A_{1g} \rightarrow {}^1T_{2g}$ (assuming idealized O_h symmetry) transition. It was stated that for **2**[5] and **3**,[1] the transition is completely lost under strong allowed transitions in the ultraviolet region. However a more care-

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[12] H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

[13] D. S. McClure, "Advances in the Chemistry of Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 498.

[14] In ref 5 the order $^1B_2 < {}^1A_2 < {}^1B_1$ was implied. In view of the discussion in ref 1 this may now be tentatively changed to $^1B_1 < {}^1A_2 < {}^1B_2$.

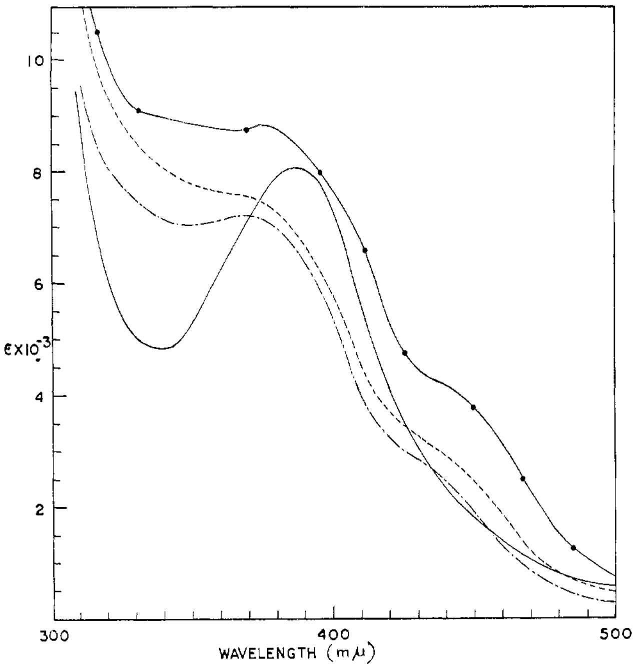

Figure 3.—Near-ultraviolet spectra of: ———, tris(N-methylsalicylaldimine)cobalt(III); — — —, tris(N-methyl-2-hydroxyacetophenimine)cobalt(III); - - - -, tris(N-methyl-2-hydroxypropiophenimine)cobalt(III)-dichloromethane; -●—●-, tris(5-methyl-N-methyl-2-hydroxypropiophenimine)cobalt(III). All spectra were taken in benzene.

ful examination now reveals a shoulder around 24,000 cm^{-1} for both **3** and **4** complexes; for **2** it is very ill defined (Figure 3). The $^1A_{1g} \rightarrow {}^1T_{2g}$ transition should be at higher energy than the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, the difference being $16B$ where B is an interelectronic repulsion parameter. B remains practically constant for a wide variety of complexes.[5,15] For tris(acetylacetonato)cobalt(III), the crystal field spectrum is consistent[5] with $B = 500$ cm.$^{-1}$ Complexes **2**, **3**, and **4** are of lower symmetry than O_h. However, since the rhombic component is small, the chelates may be roughly described as O_h particularly in cases where ν_1 and ν_3 overlap very seriously. Considering the energy of $^1A_{1g} \rightarrow {}^1T_{1g}$ to be ~16,000 cm^{-1}, one calculates $^1A_{1g} \rightarrow {}^1T_{2g}$ to be at ~24,000 cm^{-1} ($B = 500$ cm^{-1}). Thus the energy of the shoulder of **3** and **4** in the near-ultraviolet region is consistent with $^1A_{1g} \rightarrow {}^1T_{2g}$. In C_{2v} symmetry $^1T_{2g}$ splits into $^1A_1 + {}^1B_1 + {}^1B_2$. However the splitting is expected to be smaller[12,13] for $^1T_{2g}$ than for $^1T_{1g}$. This together with the fact that the ~24,000-cm^{-1} band is observed only as a shoulder on a steeply rising ultraviolet tail will explain the absence of any observable splitting for the band. Our assignment of the ~24,000-cm^{-1} band can only be tentative since the possibility that this band represents a metal–ligand rather than a crystal field transition cannot be ruled out.

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An Infrared and Chemical Investigation of the Two Isomers of the Pentaamminenitrosylcobalt Ion[1a]

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An infrared and chemical investigation of the two series of isomers known for the compounds having the empirical formula $[CoNO(NH_3)_5]X_2$ was undertaken. The infrared spectra were recorded from 4000 to 33 cm^{-1}. Previous vibrational assignments for bands above 700 cm^{-1} have been corrected by the use of ^{15}NO and deuterium isotopic substitutions. Assignments for the bands below 700 cm^{-1} which have not previously been observed are reported. On the basis of all the evidence accumulated a monomeric structure is assigned to the "black" isomers and a dimeric structure containing the hyponitrite moiety has been definitely established for the "red" isomers.

Introduction

The existence of two series of isomeric salts (hereafter referred to as red and black) having the empirical formula $[CoNO(NH_3)_5]X_2$ has been known for many years.[2] There has been a great deal of controversy over the assignment of structures to these salts for several years[3-10] which resulted from conflicting interpretations of the experimental evidence. Recently,

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[1] (a) Taken from the thesis submitted by W. A. McAllister to the University of South Carolina in partial fulfillment of the Ph.D. degree. Presented in preliminary form at the ACS Southeast–Southwest Regional Meeting, Memphis, Tenn., Dec. 2-4, 1965. (b) NDEA Fellow, 1963–1966.

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