To 5.64 g (0.0125 mole) of $(C_6H_5)_4P_2N_3H_4Cl$ in 700 ml of refluxing anhydrous benzene was added with stirring 9.37 g (0.0375 mole) of $C_6H_5PCl_4$ in 100 ml of benzene. The reaction mixture was kept under an atmosphere of dry nitrogen and refluxed for a period of 24 hr. The reaction mixture separated into two layers. The lower layer was removed and found to contain a large quantity of unreacted phenyltetrachlorophosphorane. The upper benzene layer was washed with eight 100-ml portions of water to remove unreacted phosphorane and dried with anhydrous sodium sulfate. Removal of the benzene by vacuum distillation gave 6.02 g of impure product. Recrystallization from acetonitrile gave 4.48 g (64% yield) of white needles, mp 150–151°.

Anal. Calcd for $C_{30}H_{25}ClP_3N_3$: C, 64.81; H, 4.53; Cl, 6.38; P, 16.72; N, 7.56; mol wt, 556. Found: C, 64.78; H, 4.41; Cl, 6.20; P, 16.52; N, 7.28; mol wt, 567 (cryoscopic in benzene).

Chloropentaphenylcyclotriphosphazatriene is readily soluble in benzene, acetonitrile, methylene chloride, and *sym*-tetrachloroethane and insoluble in ether and hydrocarbon solvents.

Preparation of $(C_6H_5)_5(OH)P_3N_3$.—A solution of 2.1 g (3.8 mmoles) of $(C_6H_5)_5ClP_3N_3$ and 0.10 g (5.6 mmoles) of water in 10 ml of pyridine was allowed to react for 30 min at room temperature. The removal of pyridine left 2.0 g of a white crystalline material, equivalent to a 97% yield. Recrystallization from ethanol gave white, prismatic crystals, mp 275–276°.

Anal. Calcd for $C_{30}H_{26}P_3N_3O$: C, 67.04; H, 4.88; N, 7.82; P, 17.29. Found: C, 66.83; H, 5.08; N, 7.77; P, 17.18.

Preparation of $[(C_6H_5)_5P_3N_3]_2O$.—A solution of 0.98 g (1.8 mmoles) of $(C_6H_5)_5ClP_3N_3$ and 0.95 g (1.8 mmoles) of $(C_6H_5)_5(OH)P_3N_3$ in 25 ml of benzene and 25 ml of pyridine was refluxed for 1 hr. The solvents were then removed under reduced pressure. The solid which remained was treated with boiling acetonitrile and the undissolved, unreacted $(C_6H_5)_5(OH)P_3N_3$ was removed by filtration. Upon cooling, the filtrate yielded 0.20 g of white needlelike crystals of $[(C_6H_5)_5P_3N_3]_2O$, mp 238–239°.

Anal. Calcd for $C_{60}H_{50}P_6N_6O$: C, 68.18; H, 4.74; N, 7.95; P, 17.61; mol wt, 1057. Found: C, 68.80; H, 4.96; N, 7.96; P, 17.65; mol wt, 1070 (vapor pressure lowering in benzene).

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Crystal Field Spectra of Some Tris(salicylaldimine)cobalt(III) Chelates

BY A. CHAKRAVORTY, K. C. KALIA, AND T. S. KANNAN

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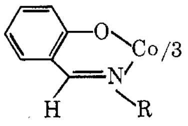
Hexacoordinated metal complexes containing three unsymmetrical bidentate ligands can exist in two geometrically isomeric forms: *cis* and *trans*. Considering coordinated atoms only, the two isomers belong to the point groups C_{3v} and C_{2v}, respectively. Tris(N-alkyl salicylaldimine)cobalt(III) (**1**) can be isolated only in the sterically less hindered *trans* form (**2**) as proved conclusively by nuclear resonance[1] and dipole moment[2] data in solution. The same is true of tris(N-alkylpyrrole-2-aldimine)cobalt(III)[1] (**3**). Diamagnetic Co(III) in crystal fields of O_h symmetry shows two spin-allowed transitions: ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and $\rightarrow {}^1T_{2g}$, the latter being at higher energy and often masked by strong ultraviolet absorptions when the ligand contains conjugated organic fragments, as is true for the compounds under the present investigation.



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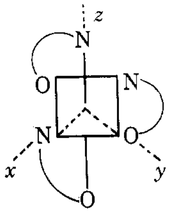

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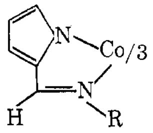

3

In fields of appropriate lower symmetry the upper states are split as shown below

O_h	C_{3v}	C_{2v}
T_{1g}	$A_2 + E$	$A_2 + B_1 + B_2$
T_{2g}	$A_1 + E$	$A_1 + B_1 + B_2$

(From here on, the g designation of states in O_h will be left out as understood.) In the *cis* form (C_{3v}) E and A have the same energy,[3] and no splitting of bands is expected; for crystal field purposes the *cis* isomer is essentially cubic.[4] In the *trans* form (C_{2v}) all components have different energies,[3] and, in principle, multiple bands are predicted. Clear-cut splittings are, however, rarely observed experimentally. Thus, of the two isomers of tris(glycinato)cobalt, one shows a broader and more asymmetric ${}^1A_1 \rightarrow {}^1T_1$ band and was hence assigned the *trans* configuration.[5] Since **1** and **3** exist only in the *trans* form, the present investigation was undertaken to determine if the C_{2v} components of the crystal field in **1** and **3** are strong enough to show clear splitting of bands. Attempts will also be made to determine the strength of the rhombic component, if any.

Experimental Section

The chelates used in the present study have all been reported previously. The salicylaldimines were made by hydrogen peroxide oxidation of an aqueous alcoholic solution containing cobalt acetate, salicylaldehyde, and the appropriate amine.[1,6,7] They form greenish black, crystalline solids. A nonaqueous chelation reaction was used for preparation of the orange-red pyrrole-2-aldimines.[1]

Anal. Calcd for **1** (R = CH_3), $C_{24}H_{24}N_3O_3Co$: C, 62.46; H, 5.24; N, 9.11. Found: C, 62.50; H, 5.00; N, 9.10. Calcd for **1** (R = C_2H_5), $C_{27}H_{30}N_3O_3Co$: C, 64.39; H, 6.01; N, 8.34. Found: 64.19; H, 5.98; N, 8.45. Calcd for **1** (R = C_4H_9), $C_{33}H_{42}N_3O_3Co$: C, 67.45; H, 7.21; N, 7.15. Found: C, 67.40; H, 7.25; N, 7.23. Calcd for **3** (R = CH_3), $C_{18}H_{21}N_6Co$: C, 56.85; H, 5.57; N, 22.11. Found: C, 56.80; H, 5.30; N, 22.00. Calcd for **3** (R = C_3H_7), $C_{24}H_{33}N_6Co$: C, 62.04; H, 7.16; N, 18.09. Found: C, 62.10; H, 6.99; N, 18.15.

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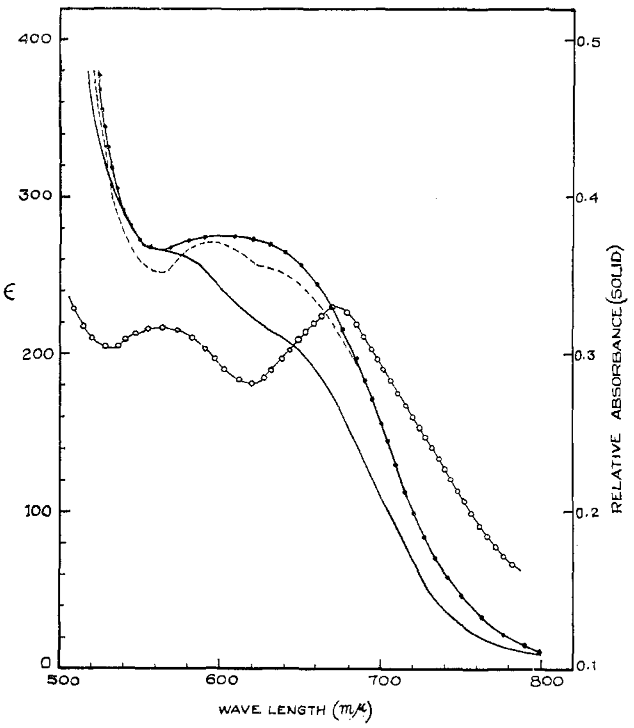

Figure 1.—Electronic spectra of tris(N-alkyl salicylaldimine)-cobalt(III): ———, R = CH_3 in toluene; ---------, R = C_2H_5 in toluene; —●—●—, R = n-C_4H_9 in toluene; —○—○—, R = CH_3 in Nujol mull.

Spectra were measured on a Cary 14 recording spectrophotometer in silica cells. Mull spectra were recorded between silica plates.

Results and Discussion

Complexes of Type 1.—A few spectra of **1** were reported by Japanese workers,[7] who made no attempts to analyze the results. Our findings are summarized in Figure 1. Taking **1** (R = CH_3) first, the spectrum in toluene clearly shows two overlapping bands in the 550–700-mμ region. No other transitions could be located in the visible region; there is an intense band at 390 mμ (extinction coefficient, ε 8850). Attempts to locate spin-forbidden crystal field bands either in chloroform solution or in Nujol mull were not very successful, although some broad and ill-defined features were observed around 1200 mμ. The remaining discussion will refer to only the 550–700-mμ bands. Because of the overlap it is somewhat difficult to locate exactly the two absorption maxima. By visual estimation they are at 15,630 and 17,540 cm^{-1} for **1** (R = CH_3) in toluene. The energy separation is 1910 cm^{-1}. The two bands cannot be assigned to unsplit $^1A_1 \rightarrow {}^1T_1$ and $\rightarrow {}^1T_2$ for the following reasons. For octahedral and pseudo-octahedral Co(III) complexes the above transitions are generally separated[8] by ~8000 cm^{-1}. Taking the somewhat similar molecule tris(acetylacetonato)-cobalt (henceforth abbreviated as CoA_3), four bands are observed[9] at 16,890 ($^1A_1 \rightarrow {}^1T_1$), 25,000 ($\rightarrow {}^1T_2$), 9090 ($\rightarrow {}^3T_1$), and 12,500 ($\rightarrow {}^3T_2$) cm^{-1}. The spectrum fits within 3% with $Dq = 2080$, $B = 500$, $C = 4000$ cm^{-1}, where B and C are the interelectronic repulsion parameters. We used the energy expressions $10Dq - C$, $10Dq + 16B - C$, $10Dq - 3C$, $10Dq + 8B - 3C$ for the above transitions, respectively, to obtain the fit. Since the difference of the energies of the $^1T_2$ and $^1T_1$ states is $16B$, one calculates for **1** (R = CH_3) $B = 120$ cm^{-1}, if the two visible bands are assigned to the transitions to the above two states. Such a large decrease in B in going from CoA_3 to **1** is hardly possible when one remembers that B for the widely dissimilar species $Co(NH_3)_6{}^{3+}$ is 528 cm^{-1}, a value quite close to that of CoA_3. We, therefore, assign the two bands of **1** (R = CH_3) to rhombic splitting of the parent $^1T_1$ state.

The spectrum of **1** (R = C_2H_5) is very similar to that of the methyl analog but with a smaller splitting (bands at 15,610 and 16,950 cm^{-1}) (Figure 1). For **1** (R = n-C_4H_9) only one broad feature is observed. However, the band envelope is very similar to that of the ethyl analog, and it is reasonable to assume that the broad absorption contains two overlapping bands. Since substituents on the azomethine nitrogen may conceivably have an effect on its precise position (relative to phenolic oxgen) in the spectrochemical series *via* inductive and steric factors, the variation of the splitting with the nature of the R group is not surprising. However, in the absence of detailed knowledge of bonding and molecular structure (hence of the origin of the C_{2v} component), we postpone any further speculation on the issue. Another noticeable feature is the increase in intensity of the bands with increasing size of the R group (Figure 1). Similar trends in band position and intensity as a function of R are observed in some related tetragonal copper chelates which will be discussed elsewhere.[10]

In C_{2v} symmetry one may expect three components of the parent $^1A_1 \rightarrow {}^1T_1$ transition: $^1A_1 \rightarrow {}^1B_2$, $\rightarrow {}^1A_2$, $\rightarrow {}^1B_1$. Using crystal field and molecular orbital methods, Yamatera has shown[3] that these three bands of *trans*-ML_3P_3 (L, P = ligand) are separated by ν, 2ν, and 3ν, respectively, from the $^1A_1 \rightarrow {}^1T_1$ transition of the parent octahedral complex ML_6 [Yamatera's symbols were δ_l (crystal field model) and $^1/_4\delta_\sigma + {}^1/_4\delta_\pi$ (molecular orbital model) for our parameter ν]. ν, which, in the ionic model, essentially measures the change in the electrostatic effects due to ligand replacement, may be taken as an index of the rhombic component. To proceed further, one notes that of the three transitions, $^1A_1 \rightarrow {}^1B_2(y)$ and $\rightarrow {}^1B_1(x)$ are electronically allowed, but $^1A_1 \rightarrow {}^1A_2$ is not. Thus, one of the bands may be expected to be weaker compared to the other two which should have similar intensities. For **1** only two bands are experimentally observed. After correction for the overlap with the tail, they will undoubtedly have very comparable intensities. The following assignments can then be made: **1** (R = CH_3), $^1A_1 \rightarrow {}^1B_2$, 15,630; $\rightarrow {}^1B_1$, 17,540 cm^{-1}, with reference to the axes system shown in 2. This assignment implies that the phenolic oxygen creates a weaker ligand field than azomethine nitrogen. One then caculates $2\nu = 1910$ cm^{-1}. Simi-

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larly, for **1** (R = C_2H_5), $2\nu = 1340$ cm^{-1}. However, we are assuming that $^1A_1 \rightarrow {}^1A_2$ is not observed owing to small intensity. This is an unsafe assumption since a transition can gain considerable intensity by indirect means, *e.g.*, vibronic coupling. Thus the possibility that the higher energy band is $^1A_1 \rightarrow {}^1A_2$ ($\rightarrow {}^1B_1$ being masked by the ultraviolet tail) cannot be ruled out. With this assignment ν will have twice the previous value.

Comparison of the Nujol mull spectrum (bands at 14,930 and 17,540 cm^{-1}) of **1** (R = CH_3) with the solution spectrum shows a difference in splitting (Figure 1). For **1** (R = C_2H_5 and n-C_4H_9) mull and solution spectra are identical. We are unable to explain the anomaly of the methyl complex. The crystal structure is not known.

In conclusion, it may be mentioned that tris(benzoylacetonato)cobalt can be isolated[11] in *cis* and *trans* forms. They differ very little in absorption spectra and show an unsplit $^1A_1 \rightarrow {}^1T_1$ band in solution. This result is not surprising since the two types of oxygen atoms are expected to be very similar for crystal field purposes. However, the $^1A_1 \rightarrow {}^1T_1$ band of the very similar CoA_3 is known, from polarized spectral studies,[12] to be composite, the two components being separated by 800 cm^{-1}. The splitting is assigned to[12] the D_3 symmetry of the crystal field under which T_1 goes to A_2 + E. Particular mention of this observation is being made here because in the analysis of our results the chelate rings were completely neglected. Consideration of the chelate rings in **1** removes all symmetry; however, the number of bands predicted remains the same since all degeneracies are already lifted under C_{2v}. Interaction of metal d orbitals with the chelate rings, *e.g.*, *via* π bonding, can, of course, seriously affect the magnitude of splittings and intensities of the bands.

Complexes of Type 3.—In toluene **3** shows only one shoulder superimposed on an ultraviolet tail. Frequencies estimated visually are 20,000 cm^{-1} (ϵ 252) for R = CH_3 and 19,500 cm^{-1} (ϵ 257) for R = $CH(CH_3)_2$. No splittings were observed. Since all coordinating atoms are nitrogen, the rhombic component is probably small. A comparative study of the electronic spectra of pseudo-tetrahedral bis(salicylaldimine)cobalt(II) and bis(pyrrole-2-aldimine)cobalt(II) (R = $C(CH_3)_3$) has similarly shown a lower effective ligand field symmetry of the CoO_2N_2 *vs.* CoN_4 coordination sphere.[13] We assign the shoulder to the transition $^1A_1 \rightarrow {}^1T_1$. Setting the interelectronic parameter $C \approx 4000$ cm^{-1} (*i.e.*, same as for CoA_3), one obtains Dq (**3**) ≈ 2400 cm^{-1}. This may be compared with Dq of other CoN_6 complexes, *e.g.*, for $Co(NH_3)_6^{3+}$, $Dq = 2490$ cm^{-1}.[8] Assuming that C values for **1** and **3** are of similar magnitude and noting that the bands for **1** are all at lower energies than the single band of **3**, one concludes that pyrrole-2-aldimine creates a stronger effective ligand field than salicylaldimine.

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Vapor Phase Reaction between Anhydrous Aluminum Fluoride and Boron Oxide[1]

BY H. N. S. LEE AND A. WOLD

Received May 2, 1966

The work of several authors[2–5] indicates that pure aluminum oxide, without contamination, can be obtained by vapor phase reactions. Most successful has been Schaffer,[5] who recently developed a chemical vapor-deposition technique for expitaxial growth of α-Al_2O_3 single crystals utilizing the reaction

$$2AlCl_3(g) + 3H_2(g) + 3CO_2(g) = Al_2O_3(s) + 3CO(g) + 6HCl(g) \quad (1)$$

Oriented crystals weighing up to 5 g were grown by this method.

The purpose of this investigation was to carry out a simple reaction in the vapor phase in order to obtain aluminum oxide crystals, in such a way as to allow convenient doping of the crystals with various transition metal ions. It was suggested by the members of the solid-state research group at Du Pont[6] that the following reaction takes place in the vapor phase with the formation of aluminum oxide crystals

$$2AlF_3 + B_2O_3 = 2BF_3 + Al_2O_3 \quad (2)$$

Since thermodynamic data are available for the compounds in the preceding equation, it is possible to calculate the standard free energy change ($\Delta G°$) and the equilibrium constant (K_p) for the reaction between 1000 and 2000°K and also to determine the optimum temperature for the formation of aluminum oxide.

It is well known that the aluminum oxide lattice is capable of accepting a variety of transition metal ions. The reaction between aluminum fluoride and boron oxide can be modified to produce doped crystals if a transition metal fluoride, for example, chromium(III) fluoride, is added to the aluminum fluoride. The thin platelets obtained by the vapor phase reaction are especially suitable for optical studies.

Experimental Section

Aluminum fluoride obtained commercially was not sufficiently pure to be used as a starting material. Aluminum fluoride can be purified by vacuum sublimation and such a procedure is described by Henry and Dreisbach.[7] Boron oxide is available as fused boric acid, but it must be fused again at 450° before it can be used.

The vapor phase reaction between aluminum fluoride and boron oxide was carried out as follows. Aluminum fluoride and boron oxide were contained in two separate crucibles, arranged

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(1) This work has been supported by the Air Force in Cambridge, Grant No. AF 19(628)-3837, and the National Science Foundation, Grant No. NSF GK-437.

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