structural differences produced by replacing bromide by iodide than is the higher energy band. Another difference in the behavior of these two complexes is seen in their thermogravimetric analyses (Figure 3). The iodide shows a clear break when four pyridine molecules are lost, while the bromide curve consistently breaks when ~3.5 pyridine molecules are removed. This also may reflect structural and bonding differences.

The complex $CrI_2 \cdot 4py$ probably has a structure similar to the structures of $NiI_2 \cdot 4py$ and $CoI_2 \cdot 4py$,[29] which are known to be tetragonal, containing four coplanar pyridines and halogens in *trans* axial positions. This molecule might be expected to have a spectrum characteristic of a tetragonal species, thus displaying at least two bands. However, due to the presence of a low-energy charge-transfer absorption, only the band near 12,000 cm.$^{-1}$ is observed. The presence of this charge-transfer band, not present at similar energies in $CrI_2 \cdot 6py$, is consistent with the expected metal–halogen bonding of the $CrI_2 \cdot 4py$ and the lack of such bonding in the $CrX_2 \cdot 6py$ complexes.

Acknowledgments.—The support of the National Science Foundation, GP-196, is gratefully acknowledged. We also wish to thank Prof. Louis Gordon for the use of the thermogravimetric balance.

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[29] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford, 1962, p. 915.

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High-Spin Hexa-, Penta-, and Tetracoordinated Complexes of Cobalt(II) with Schiff Bases Formed from Salicylaldehydes and N,N-Substituted Ethylenediamines

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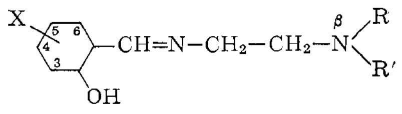
The Schiff bases formed from ring-substituted salicylaldehydes and N,N-substituted ethylenediamines react with cobalt(II) to give high-spin complexes with the generic formula [X–SALen–(R)R′]$_2$Co (I). When neither R nor R′ is an aryl group the solid complexes have either a *cis*-octahedral configuration or a five-coordinate distorted square-pyramidal configuration. The latter group of compounds is the first in which high-spin square-pyramidal cobalt(II) has been found. When R and R′ are both phenyl groups the complexes have a tetrahedral configuration. When R is hydrogen or a methyl group and R′ is an aryl group the stereochemistry of the complex is not known. In solution octahedral, pyramidal, and tetrahedral species exist in an equilibrium mixture.

Introduction

In previous papers[1,2] it was shown that complexes of nickel(II) with two molecules of Schiff bases of the general formula



can have octahedral, square-planar, or pentacoordinate configurations according to the nature of the substituents X, R, and R′.

We have now prepared various cobalt(II) complexes with analogous ligands, given the generic formula [X–SALen–N(R)R′]$_2$Co (I), and studied their properties by means of spectrophotometric, magnetic, and dipole moment measurements.

Experimental

Preparation of the Compounds.—All the compounds were prepared and collected under a nitrogen atmosphere in order to avoid oxidation by atmospheric oxygen. Two different preparative methods were used: (A) A solution of 0.025 mole of the appropriate N-substituted ethylenediamine in 15 ml. of ethanol was added to a suspension of 0.010 mole of bis(X-salicylaldehydato)-cobalt(II) dihydrate in 50 ml. of ethanol. (B) A solution of 0.010 mole of cobaltous acetate in 15 ml. of water was added to a solution of 0.020 mole of X-salicylaldehyde and 0.025 mole of N-substituted ethylenediamine in 50 ml. of ethanol.

In both cases the reaction mixture was then heated on a water bath until a clear red solution was obtained. Hot water (about 75 ml.) was then added and the solution was allowed to cool at room temperature. The resulting crystals were filtered, washed with aqueous ethanol and ether, and then dried under a nitrogen atmosphere. These compounds are soluble in chloroform, benzene, and pyridine, slightly soluble in ethanol, dioxane, and cyclohexane, and insoluble in diethyl ether and petroleum ether. The analytical data for these compounds are summarized in Table I.

Spectrophotometric Measurements.—The absorption spectra were recorded with a Beckman DK2 spectrophotometer. The solvents were purified by the standard procedures used for spectrophotometric measurements. The reflectance spectra were recorded using the standard Beckman reflectance attachment and magnesium oxide as a reference. Concentrations of the solutions were in the range 0.01–0.02 *M*.

Magnetic Susceptibility Measurements.—The magnetic susceptibility measurements were performed by the Gouy method, with the apparatus and the experimental technique described in a previous paper.[3] The sample tube was calibrated with Hg-

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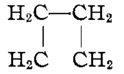
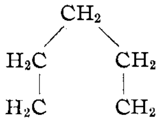
[1] L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965).

[2] L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).

[3] L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

TABLE I

SUMMARY OF PHYSICAL AND ANALYTICAL DATA FOR SOME SUBSTITUTED [X–SALen–(R)R′]$_2$Co COMPLEXES

R	R′	X	Method of prepn.[a]	Color	Formula	Calcd., % N	Calcd., % Co	Found, % N	Found, % Co
H	CH_3	H[b]	A	Orange	$C_{20}H_{26}N_4O_2Co$	13.55	18.01	13.67	18.59
H	C_3H_7	H[b]	A	Red	$C_{24}H_{34}N_4O_2Co$	11.93	12.55	11.95	12.12
		3-Cl	B	Orange	$C_{26}H_{32}N_4O_2Cl_2Co$	9.97	10.48	9.74	10.61
		5-Cl	B	Orange	$C_{26}H_{32}N_4O_2Cl_2Co$	9.97	10.48	9.72	10.72
C_2H_5	C_2H_5	H	A	Red	$C_{26}H_{38}N_4O_2Co$	11.26	11.84	11.21	11.50
		3-Cl	A	Orange	$C_{26}H_{36}N_4O_2Cl_2Co$	9.89	10.40	9.81	10.70
		5-Cl	A	Olive-green	$C_{26}H_{36}N_4O_2Cl_2Co$	9.89	10.40	9.66	10.84
		H	A	Red	$C_{28}H_{38}N_4O_2Co$	10.74	11.30	10.84	
		3-CH_3	B	Orange	$C_{30}H_{42}N_4O_2Co$	10.20	10.72	9.94	
		5-CH_3	B	Red	$C_{30}H_{42}N_4O_2Co$	10.20	10.72	10.05	
		3-Cl	B	Orange	$C_{28}H_{36}N_4O_2Cl_2Co$	9.50	9.98	9.43	
		5-Cl	B	Orange	$C_{28}H_{36}N_4O_2Cl_2Co$	9.50	9.98	9.50	9.86
H	C_6H_5	H	A	Orange	$C_{30}H_{30}N_4O_2Co$	10.43	10.97	10.35	10.74
H	o-$CH_3C_6H_4$	H	A	Red	$C_{32}H_{34}N_4O_2Co$	9.90	10.42	9.93	10.45
H	p-$CH_3C_6H_4$	H	A	Red	$C_{32}H_{34}N_4O_2Co$	9.90	10.42	9.70	10.43
CH_3	C_6H_5	H	A	Orange	$C_{32}H_{34}N_4O_2Co$	9.90	10.42	9.96	10.72
C_6H_5	C_6H_5	H	A	Orange	$C_{42}H_{38}N_4O_2Co$	8.12	8.55	8.09	8.59

[a] See Experimental section. [b] These compounds are very readily oxidizable.

[Co(NCS)$_4$][4] and freshly boiled distilled water.[4] Diamagnetic corrections were calculated from Pascal's constants.[5]

Dielectric Polarization Measurements.—The apparatus and the procedures used have been previously described.[6] The molar refractions for the sodium D-line, R_D, of the complexes were calculated by adding the proper values of bond refractions[7] to the measured molar refraction of the bis(N-cyclohexylsalicylaldiminato)cobalt(II) complex.[8] Values of the orientation polarization, P_0, were calculated by assuming a value of 20% R_D for the atom polarization.

Results and Discussion

The substituents R and R′ were chosen in a manner allowing large variation in both electron-donor ability and the bulkiness on the β-nitrogen atom. Thus alkyl, polymethylene, and aryl groups were used. Salicylaldimines substituted on the ring with chloro and methyl groups were also studied to provide a basis for comparison with analogs of nickel described earlier. Most of the compounds reported in the present study are oxidized by atmospheric oxygen, especially in solution. The solutions, usually reddish brown, darken rapidly unless they are stored in an inert gas atmosphere.

All the compounds are of the high-spin type, the values of the magnetic moments at room temperature ranging between 4.10 and 4.70 B.M. No definite correlation has been found between the stereochemistry of the complexes and the values of the moments. Perhaps this can be ascribed to a partial oxidation of some of the solids.

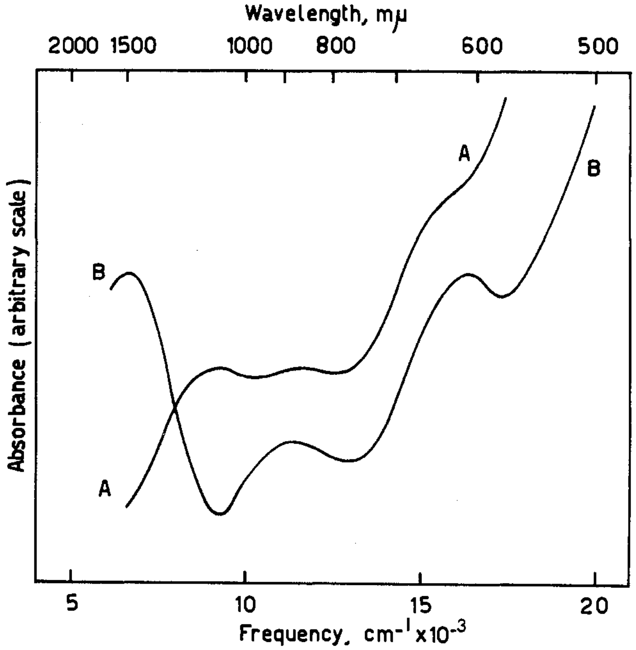


Figure 1.—Reflectance spectra of [H–SALen–N(H)CH$_3$]$_2$Co (curve A) and [5-Cl–SALen–N(C$_2$H$_5$)$_2$]$_2$Co (curve B).

The solid compounds I (X = R = H; R′ = CH_3, n-C_3H_7) give reflectance spectra in the 6000–20,000 cm.$^{-1}$ region, with bands at 9300 and 11,500 cm.$^{-1}$ and a shoulder at 15,600 cm.$^{-1}$ (Figure 1). The same spectrum is also obtained from the solutions of these compounds in benzene, chloroform, and pyridine. The molar absorbancies are: ϵ_{9300} 10, $\epsilon_{11,5000}$ 10, and $\epsilon_{15,600} \approx 12$. The fact that pyridine does not coordinate with the metal, in contrast to all the other complexes of this series, leads to the conclusion that each Schiff base behaves as a tridentate ligand. Thus these complexes of cobalt(II) are six-coordinate, as are the analogous nickel(II) compounds.[1] A regular octahedral con-

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(4) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and L. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 415.

(5) *Cf.* P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York, N. Y., 1956.

(6) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961).

(7) A. I. Vogel, W. T. Cresswell, G. H. Jeffrey, and J. Leichester, *J. Chem. Soc.*, 514 (1962).

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

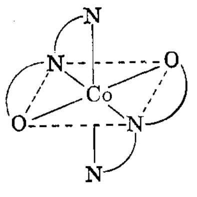
figuration, however, cannot be attained owing to the geometry of the ligands.[9] This and the fact that the ligand atoms are not equivalent explains why two bands appear in the spectrum at *ca.* 10,000 cm.$^{-1}$ instead of the single band found in regular or weakly distorted octahedral cobalt(II) complexes. In a cubic field this band corresponds to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and both states are split in fields of lower symmetry.[10] The splitting is not observable in the *trans*-octahedral adducts bis(N-alkylsalicylaldiminato)cobalt(II)·2py, indicating perhaps that in these compounds the distortion of the crystal field from regular octahedral symmetry is small.

The dipole moments of the two complexes I (X = R = H) are 6.95 D. for R′ = CH_3 and 6.60 D. for R′ = n-C_3H_7 (Table II). These high values rule out the possibility of a symmetrical *trans*-octahedral configuration of type II which should be very nearly nonpolar. Nevertheless, an estimate of the value of the dipole moment cannot be made for lack of the appropriate bond moments. They are compatible with a structure of type III in which the three donor atoms of each ligand and the cobalt atom lie approximately in one plane. Trials with Stuart's models show that the rigidity of the carbon–nitrogen double bond causes the structure III to be the most likely of a number of possible octahedral structures.

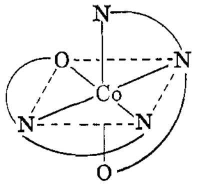
Table II

Dielectric Polarization Data for Some [X–SALen–N(R)R′]$_2$Co Complexes

R	R′	R_D, cc.	$P_{2\infty}$, cc.	P_0, cc.	μ, D.
H	CH_3	129	1150	995	6.95
H	C_3H_7	148	1070	895	6.60
CH_3	C_6H_5	171	465	260	3.55
C_6H_5	C_6H_5	210	570	320	3.95



II



III

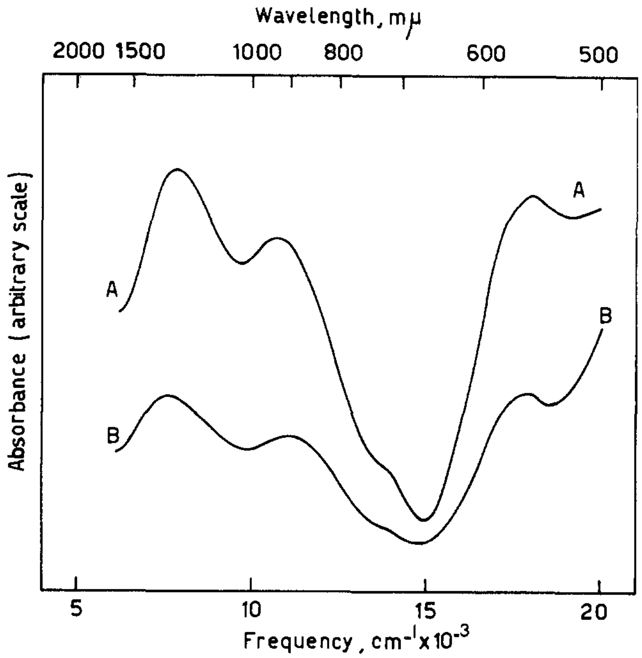
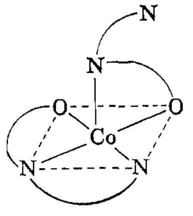


Figure 2.—Reflectance spectra of bis(N-isopropylsalicylaldiminato)cobalt(II) (curve A) and [H–SALen–N(C_6H_5)$_2$]$_2$Co (curve B).

The complexes in which two ethyl groups or a bifunctional group –(CH_2)$_n$– (n = 4, 5) are attached to the β-nitrogen atom have various structures. The complexes I (X = 5-Cl; R, R′ = –(CH_2)$_4$–) and I (X = H, 5-Cl; R, R′ = –(CH_2)$_5$–) have reflectance spectra in the solid state characteristic of the distorted octahedral configuration and so must have this stereochemistry. On the other hand the complex I (X = 5-Cl; R = R′ = C_2H_5) has been shown by X-ray diffraction measurements on a single crystal to be isomorphous and isometric with the corresponding complex of nickel(II).[9] A three-dimensional X-ray study of the latter has shown the nickel atom to be pentacoordinate with a distorted square-pyramidal structure in which one β-nitrogen atom is not bound to the central atom.[9] The same structure, IV, must therefore be assigned to the cobalt compound. This is only the second high-spin complex of cobalt(II) which has been shown definitely to possess a coordination number of five. The other pentacoordinate high-spin cobalt(II) complex, whose structure has been ascertained by X-ray analysis, is bis(N-methylsalicylaldiminato)cobalt(II). This has a distorted trigonal bipyramidal structure.[11]



IV

The reflectance spectrum of this pentacoordinate compound of cobalt(II) has three bands in the region 6000–20,000 cm.$^{-1}$ at 6700, 11,400, and 16,800 cm.$^{-1}$ (Figure 1). This spectrum is different from those of both octahedral complexes[8] and tetrahedral complexes[8] of the type illustrated in Figure 2. The solid compounds I (X = H, 3-Cl; R = R′ = C_2H_5), I (X = 3-Cl; R, R′ = –(CH_2)$_4$–), and I (X = 3-CH_3, 5-CH_3, 3-Cl; R, R′ = –(CH_2)$_5$–) have substantially the same reflectance spectrum and therefore they may be considered to have a pentacoordinate structure of the type IV.

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[9] L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

[10] C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

[11] P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Commun.* (London), 103 (1965). A high-spin probably pentacoordinate adduct of bis-(N-2,6-dimethylphenylsalicylaldiminato)cobalt(II) with one molecule of pyridine has been isolated by Professor S. Yamada (private communication).

The complex I (X = H; R, R′ = $-(CH_2)_5-$), which is octahedral in the solid state, and the complexes I (X = 3-CH_3, 5-CH_3; R, R′ = $-(CH_2)_5-$), which are pentacoordinate in the solid, dissolve in inert solvents to give an absorption spectrum characteristic of the tetrahedral species. The molar absorbances (ϵ_{7700} 30–36, $\epsilon_{11,200}$ 20–27) are about half those found on the bis(N-alkylsalicylaldiminato)cobalt(II) complexes.[8] The other compounds with R = R′ = C_2H_5, R, R′ = $-(CH_2)_4-$ and $-(CH_2)_5-$ whether octahedral or pentacoordinate in the solid state give, in inert solvents, the absorption spectrum characteristic of the pentacoordinate species. The intensities of the bands are strongly dependent on the nature of X, R, and R′, having the largest values, ϵ_{6700} 17–34 and $\epsilon_{11,400}$ 9–13, when X = 5-Cl. The spectroscopic evidence therefore indicates the existence of a conformational equilibrium between the pentacoordinate and octahedral species. The proportion of the octahedral species present is not directly evident since this species absorbs weakly in the region concerned. In pyridine all compounds have the spectrum with two bands ($\epsilon_{10,000}$ 10, $\epsilon_{17,500}$ 18) characteristic of the octahedral adducts with two molecules of pyridine.[8]

When either or both R and R′ are aryl groups the stereochemistry of the complexes is again different. The compound I (X = H; R = R′ = C_6H_5) has a reflectance spectrum indicative of the tetrahedral configuration[8] (Figure 2), but the compounds I (X = H; R = H; R′ = C_6H_5, *o*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$) and I (X = H; R = CH_3; R′ = C_6H_5) have reflectance spectra in the solid state different from those characteristic of any known configuration.

In pyridine all aryl derivatives give spectra characteristic of the *trans*-octahedral adducts. On the other hand, in inert solvents the structure depends on R and R′. The complexes I (X = R = H; R′ = *o*-$CH_3C_6H_4$) and I (X = H; R = CH_3, C_6H_5; R′ = C_6H_5) have absorption bands usually associated with the tetrahedral species.[8] The extinction coefficients, ϵ_{7700} 53–64 and $\epsilon_{11,700}$ 32–40, indicate that almost all the molecules have the tetrahedral configuration. This conclusion gains support from the values of the dipole moments, 3.55 and 3.95 D. (Table II), for the compounds I (X = H; R = CH_3; R′ = C_6H_5) and I (X = H; R = R′ = C_6H_5), respectively, as compared with 4.1–4.7 D. for the cobalt(II) complexes with N-alkyl- and N-arylsalicyaldimines.[8] When the phenyl groups are not *ortho*-substituted, as in the compounds I (X = R = H; R′ = C_6H_5, *p*-$CH_3C_6H_4$) the solution spectra have bands with low extinction coefficients (ϵ_{7700} 23–26, $\epsilon_{11,700}$ 15–22) which may be attributed to the presence of a small proportion of the tetrahedral species.

In conclusion, a correlation can be established between the type of ligand and the stereochemistry of the complex. Indeed, the ability of β-nitrogen atoms to bond with cobalt seems to depend both on the donor ability of the β-nitrogen and on the steric requirements of the groups R and R′. When R = H and R′ = alkyl, the electron-releasing power of these groups determines the highest bonding capacity of the β-nitrogen atoms. The resulting complexes are hexacoordinate both in the solid state and in solution. Furthermore, pyridine does not substitute β-nitrogen atoms. When R and R′ are alkyl and polymethylene groups their bulkiness hinders the formation of a N–Co bond. However, pentacoordinated compounds may form and these combine in octahedral adducts with pyridine. When the substituents are aryl groups, the bonding ability of the β-nitrogen atoms is again lowered, as is shown by the appearance of tetrahedral forms. This can be attributed to steric hindrance and to the lower basicity of the β-nitrogen atoms, a consequence of the electron-withdrawing aryl substituents.

A comparison of the behavior of this type of ligand with the cations cobalt(II) and nickel(II) shows in most cases that the same coordination number is reached with the two metals. In the case of tetracoordinated complexes, however, those of cobalt are tetrahedral while those of nickel are planar.

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