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Mesocyclic Complexes.[1] VI.
Synthesis of Four- and Five-Coordinated Cobalt(II) Complexes with Saturated Mesocyclic Diamines

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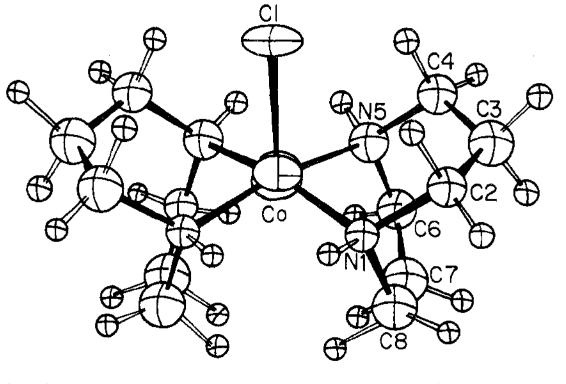
Cobalt(II) complexes of mesocyclic diamines without π-electron systems (1,5-diazacyclooctane = daco; 1,4-diazacycloheptane = dach) have been synthesized. Four general classes of complexes have been prepared: $CoLX_2$ (I), CoL_2X_2 (II), CoL_2XY (III), and CoL_2Y_2 (IV), where L = daco or dach; $X^- = Cl^-, Br^-, I^-$, or SCN^-; and $Y^- = ClO_4^-$ or BF_4^-. Tetrahedral complexes of class I are stable, deep blue, soluble but nonconducting in ethanol and have properties similar to common tetrahedral amine complexes of CoX_2. Square-pyramidal complexes of class II are formed in ethanol in the presence of excess ligand. Class III complexes can be precipitated by the addition of ClO_4^- or BF_4^- to ethanolic solutions of class II complexes. The physical properties of class II and III complexes containing Br^- or Cl^- are similar; the complexes are square pyramidal with uncoordinated perchlorate and are unique examples of five-coordinated cobalt(II) without π-bonding ligands. Complexes of class IV have only been formed with daco, *i.e.*, $Co(daco)_2(ClO_4)_2$. It is shocking pink and its structure has not been determined unequivocally. It appears to have an almost square-planar structure with either a slight tetrahedral distortion or an extremely weak axial interaction. An iodide complex of class II is most unusual. $Co(daco)_2I_2 \cdot EtOH$ is pale orange and square pyramidal at <75°, but its spectral properties are identical with those of $Co(daco)_2(ClO_4)_2$ above this temperature. The color change is reversible.

In previous work with copper(II) and nickel(II),[1,2] mesocyclic diamines (1,5-diazacyclooctane = daco; 1,4-diazacycloheptane = dach) were shown to be versatile chelating agents in that they often conferred unusual geometries on the metal ion: daco complexes were always planar; dach complexes were either planar or square pyramidal.[3] When this study was extended to cobalt(II), both amines caused the cobalt(II) ion to adopt a five-coordinated square-pyramidal geometry when the amine to cobalt(II) ratio was 2:1 and at least one chloride or bromide anion was present. As expected, when the ratio of amine to cobalt(II) was 1:1 tetrahedral complexes were formed.

The structures of these cobalt(II) complexes are noteworthy in that they may be the first square-pyramidal cobalt complexes reported which do not contain a π-electron system in the ligand. As a representative member of this class of compounds, the crystal structure determination of the square-pyramidal chlorobis(1,5-diazacyclooctane)cobalt(II) chloride was carried out and is reported elsewhere.[4]



A shocking pink diperchlorate complex, $Co(daco)_2(ClO_4)_2$, can be prepared in dilute ethanol and an unusual diiodide, $Cu(daco)_2I_2 \cdot EtOH$, was prepared which may be five-coordinated at room temperature but appears identical with the diperchlorate at >75°.

Experimental Part

I. Synthesis and Analytical Data. Synthesis of Bis Complexes (Table IA). A. The preparation was carried out using vacuum techniques. Anhydrous cobaltous halide (0.005 mol) was heated under vacuum at 110° for 12 hr. After cooling to −196°, anhydrous ethanol (50 ml) was condensed into the flask containing the cobalt(II) halide and the mixture was warmed to room temperature. The solution was stirred until the cobalt(II) halide completely dissolved. The cobalt(II) solution was frozen and daco[1] (0.04 mol) (dried with BaO) was condensed (sublimed with dach[1]) into the flask. The mixture was slowly warmed to room temperature with stirring yielding CoL_2X_2 (with $Co(dach)_2Cl_2$, the volume of solution was reduced to about half under vacuum before a brick red solid formed). The product was transferred to a drybox and the solution was filtered under vacuum. The solid was washed with anhydrous ether and vacuum-dried at room temperature.

B. This procedure was the same as procedure A except that tetra-*n*-butylammonium perchlorate (0.01 mol) was added before condensing daco (subliming with dach) into the flask. The product, CoL_2XClO_4, was vacuum-dried at room temperature for 12 hr.

C. This procedure was also similar to procedure A except that equimolar quantities (0.0025 mol) of anhydrous cobalt(II) halide and $Co(EtOH)_6(ClO_4)_2$[5] or $Co(EtOH)_6(BF_4)_2$ were placed in a flask and vacuum-dried at room temperature for 12 hr before the ligand was condensed into the flask.

D. $Co(daco)_2(ClO_4)_2$ could be prepared only under extremely dilute conditions. Two separate solutions were prepared in the drybox. One solution contained 0.001 mol of $Co(EtOH)_6(ClO_4)_2$ dissolved in 100 ml of anhydrous ethanol and the second solution contained 0.002 mol of daco dissolved in 100 ml of anhydrous ethanol. Both solutions were deaerated with a stream of nitrogen gas for 1/2 hr and combined. The final solution was further agitated with a stream of N_2 as the complex slowly precipitated from solution. The product was filtered under vacuum in the drybox and washed with 30 ml of anhydrous ether. The shocking pink $Co(daco)_2(ClO_4)_2$ was vacuum-dried at room temperature. No tetrafluoroborate salt could be obtained under these conditions.

E. The best method for recrystallizing the complexes is to place a small amount of the powdered product in a Carius tube and then condense anhydrous ethanol (20 ml) and about 0.5 g of the amine into the tube under vacuum. After sealing the tube under vacuum, the mixture is heated at 110° to give a deep blue solution. On cooling, brick red crystals form, which, on powdering, give pale pink solids.

Synthesis of Mono Complexes (Table IB). The mono-daco and -dach complexes of $CoCl_2$ and $CoBr_2$ have also been isolated. The synthesis of the mono complexes was normally accomplished by mixing a solution containing anhydrous cobalt(II) halide (0.005 mol) in 30 ml of anhydrous ethanol with another solution containing

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(1) W. K. Musker and M. S. Hussain, *Inorg. Chem.*, **5**, 1416 (1966).

(2) W. K. Musker and M. S. Hussain, *Inorg. Chem.*, **8**, 528 (1969).

(3) M. S. Hussain and H. Hope, *Acta Crystallogr., Sect. B*, **25**, 1866 (1969).

(4) E. D. Steffen and E. Stevens, *Inorg. Nucl. Chem. Lett.*, **9**, 1011 (1973).

(5) P. W. N. M. van Leeuwen, *Recl. Trav. Chim. Pays-Bas*, **86**, 247 (1967).

Table I. Analytical Data of Mesocyclic Diamine Complexes of Cobalt(II)

Complex	Color (method of synthesis)	Dec pt, °C	% C		% H		% N	
			Calcd	Found	Calcd	Found	Calcd	Found
		A. Bis Complexes						
$Co(daco)_2Cl_2$	Pale pink (A)	60[e]	40.25	40.44[b]	7.82	7.72[b]	15.65	15.80[b]
$Co(daco)_2Br_2$	Pale pink (A)	64[e]	32.23	31.61[b]	6.27	6.57[b]	12.53	11.91[b]
$Co(daco)_2I_2 \cdot EtOH$	Pale orange (A)	184[d]	28.63	28.60[a]	5.79	5.79[a]		
$[Co(daco)_2Cl]ClO_4$	Pale pink (B, C)	218	34.14	34.38[b]	6.64	6.81[b]	13.28	13.06[a]
$[Co(daco)_2Br]ClO_4$	Pale pink (B, C)	167	30.88	30.80[b]	6.01	6.29[b]		
$[Co(daco)_2I]ClO_4$	Shocking pink (C)	182	28.06	28.76[b]	5.46	5.88[a]		
$[Co(daco)_2SCN]ClO_4$	Pink (C)	217	35.10	35.07[b]	6.30	6.41[b]	15.75	15.75[a]
$Co(daco)_2(ClO_4)_2$	Shocking pink (D)	182	29.64	29.49[b]	5.76	5.82[b]	11.53	10.73[a]
$Co(dach)_2Cl_2 \cdot EtOH$	Red brick (A)[f]		38.32	37.57[c]	7.98	8.11[c]	14.90	14.96[c]
$Co(dach)_2Cl_2$	Pale pink (A)[g]	80-85[d]	36.37	36.81[c]	7.28	7.26[c]		
$Co(dach)_2Br_2$	Red brick (A)[f]	155-160[d]	28.66	28.05[b]	5.73	5.88[b]		
$Co(dach)_2I_2$	Pale pink (A)[g]	233-237	23.40	22.94[a]	4.68	4.74[a]		
$[Co(dach)_2Cl]ClO_4$	Red brick (B, C)[f]	186	30.47	30.80[b]	6.09	6.22[b]		
$[Co(dach)_2Br]ClO_4$	Red brick (B, C)[f]	169					12.78	12.03[a]
$Co(dach)_2(ClO_4)_2 \cdot EtOH$	Pink-brown (A)	190-197	28.55	28.05[b]	5.95	5.29[b]		
		B. Mono Complexes						
$Co(daco)Cl_2$	Deep blue	221	29.29	29.48[b]	5.70	5.83[b]	11.39	11.98[b]
$Co(daco)Br_2$	Deep blue	218	21.51	21.77[a]	4.18	4.28[a]		
$Co(dach)Cl_2$	Blue	205	26.13	29.48[b]	5.22	5.93[b]		
$Co(dach)Br_2$	Blue	163	18.80	18.61[a]	3.76	3.87[a]		

[a] Chemalytics, Inc., Tempe, Ariz. [b] Galbraith Laboratories, Inc., Knoxville, Tenn. [c] PCR, Inc., Gainesville, Fla. [d] Reversible color change at 75° (orange ⇄ pink). [e] Turned blue, $CoLX_2$. [f] Crystals. [g] Powder.

Table II. Magnetic Properties of Solid Cobalt(II) Complexes of Cyclic Bidentate Amines

Complex	Temp, °C	Diamag cor × 10^{-6}	$10^{-6} \times \chi_M^{cor}$, cgsu	μ_{eff}, BM
$Co(daco)_2Cl_2$	23	229	2830	2.59
$Co(daco)_2Br_2$	23	241	3470	2.83
$Co(daco)_2I_2 \cdot EtOH$	24	305	2586	2.48
$[Co(daco)_2Cl]ClO_4$	23	228	5316	3.55
$[Co(daco)_2Br]ClO_4$	23	239	4292	3.19
$[Co(daco)_2I]ClO_4$	24	255	5268	3.54
$[Co(daco)_2SCN]ClO_4$	24	235	5849	3.73
$[Co(daco)_2](ClO_4)_2$	24	236	7346	4.18
$Co(dach)_2Cl_2$	23	195	6285	3.86
$Co(dach)_2Br_2$	23	217	6482	3.92
$[Co(dach)_2Cl]ClO_4$	24	203	5975	3.77
$[Co(dach)_2Br]ClO_4$	24	215	7346	4.18
$Co(dach)Cl_2$	23	133	8926	4.60
$Co(daco)Br_2$	23	145	8745	4.57
$Co(dach)Cl_2$	23	121	8019	4.36
$Co(dach)Br_2$	23	143	8428	4.47

Table III. Molar Conductances of Cobalt(II) Complexes (10^{-3}–10^{-4} *M*) of Cyclic Bidentate Amines (cm^2 ohm^{-1} mol^{-1})

Complex	DMSO[a]	EtOH[b]
Nonelectrolytes		
$Co(daco)Cl_2$		7
$Co(daco)Br_2$		12
$Co(dach)Cl_2$		10
$Co(dach)Br_2$		13
Uni-univalent electrolytes		
$Co(daco)_2Cl_2$	23	28
$Co(daco)_2Br_2$	33	31
$Co(daco)_2I_2 \cdot EtOH$	31.7	33
$[Co(daco)_2Cl]ClO_4$	28	
$[Co(daco)_2Br]ClO_4$	30	
$Co(dach)_2Cl_2$	20	
$Co(dach)_2Br_2$	30	
$Co(dach)_2I_2$	40	23
$[Co(dach)_2Cl]ClO_4$	30	
$[Co(dach)_2Br]ClO_4$	40	
$n\text{-}Bu_4NClO_4$		22
$n\text{-}Bu_4NCl$		23
$[Cu(dach)_2ONO_2]NO_3$		20
Uni-divalent electrolytes		
$Co(daco)_2(ClO_4)_2$	52	
$Co(daco)_21(ClO_4)$	69	

[a] Range of molar conductances for a series of uni-univalent electrolytes in DMSO, 20–39 cm^2 ohm^{-1} mol^{-1}, concentration 10^4–10^{-3} *M*. [b] Range of molar conductances for a series of uni-univalent electrolytes in EtOH, 38–42 cm^2 ohm^{-1} mol^{-1}, concentration 10^{-3} *M*, and for a series of uni-divalent electrolytes in EtOH, 65–75 cm^2 ohm^{-1} mol^{-1}, concentration 10^{-3} *M*.

daco (0.005 mol) dissolved in 10 ml of anhydrous ethanol. Both solutions were deaerated with nitrogen. The ligand solution was added dropwise to the cobalt(II) solution while stirring. The deep blue solid which formed was isolated by filtering the solution under vacuum, washing with ether, and drying at 100° for 12 hr.

II. Magnetic Susceptibility Measurements (Table II). The magnetic moments of the solid complexes were determined by the Gouy method at room temperature. A double-ended Gouy tube was calibrated using $Hg[CO(NCS)_4]$ as the standard. The packing was done in a drybox to minimize oxidation and contamination by moisture. The calibration was further checked by measuring the magnetic susceptibility of cobaltous acetate. Pascal's constants were used to correct the observed molar susceptibilities of the crystalline complexes for the diamagnetism of the ligands and anions involved.

Solution magnetic measurements were obtained by the methods originally described by Evans[6] in 1959 and extended by Crawford and Swanson[7] in 1971. The values for 13 different complexes in ethanol or DMSO varied between 4.2 and 4.7 BM. The $Co(daco)_2I_2$ value was slightly lower at 3.8 BM.

III. Electrolytic Conductance Measurements (Table III). Electrolytic conductance measurements were made at 50–60 cps using a conductivity bridge, Model RC 16B2, made by Industrial Instruments, Inc., Cedar Grove, N. J. The conductivity cell was a Model 3403 cell purchased from the Yellow Springs Instrument Co., Inc. (cell constant 1.000 ± 0.001).

The solutions of the mono-daco and -dach complexes (10^{-3}-10^{-4} *M*) were prepared with solvents (C_2H_5OH and DMSO) deaerated with nitrogen and solutions of the bis-daco and -dach complexes were prepared with deaerated solvents containing excess ligand. The concentration of the ligand was at least 100 times the final concentration of the complex being studied. The observed conductivity was always corrected for the specific conductance of the pure solvent in the mono-daco and -dach complexes and for the specific conductance of the ligand solution in the bis-daco and -dach complexes.

The molar conductance of the dichloride complexes was plotted against $\sqrt{C}$ to determine the effects of dilution (Figure 1).

IV. Electronic Absorption Spectra (Table IV). Near-infrared, visible, and ultraviolet spectra were measured with a Cary 14 record-

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(6) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

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Table IV. Electronic Absorption Spectra of daco and dach Complexes of Cobalt(II)

Compd	State	λ, kK (ε)					
				Bis Complexes			
$Co(daco)_2Cl_2$	Solid	45.5	30.3	21.3			
	EtOH		31.7 (98)	20.4 (41)	17.9 (38)	15.9 (31)	
	DMSO		31.3	20.8 (48)	18.7 (41)	16.7 (28)	
$Co(daco)_2Br_2$	Solid	44.4	29.9	20.8			
	EtOH	44.4	29.9	20.9			
	DMSO				17.9 (43)	16.9 (34)	15.6 sh
$Co(daco)_2I_2$	Solid		31.7 sh	21.8			
EtOH							
<25°	EtOH			20.4 (75)	17.9 (88)	16.2 (83)	
<25°	DMSO		32.8	20.6 (78)			
>75°	Solid			20.0	18.9		
$[Co(daco)_2Cl]ClO_4$	Solid		29.9	21.0			
	DMSO		29.4 sh	20.9 (41)	18.9 (37)	16.7 sh	
$[Co(daco)_2Br]ClO_4$	Solid		29.8	20.6			
	DMSO			21.1 (108)	19.2 (90)		
$[Co(daco)_2I]ClO_4$	Solid			20.2	18.9		
	DMSO			20.6 (74)	18.2 (65)		
$[Co(daco)_2](ClO_4)_2$	Solid			20.0	18.9		
	DMSO		29.7 (212)	20.8 (108)	19.2 (100)		
$Co(dach)_2Cl_2$	Solid		31.7	21.1			
	EtOH		31.7	19.8	18.9	17.5	
$Co(dach)_2Br_2$	Solid		31.3	21.3			
	EtOH		31.0 (77)	20.6 (49)	18.5 (42)	17.7 (47)	
	DMSO		31.3 (73)	20.6 (58)	18.9 (50)	17.5 sh	
$[Co(dach)_2Cl]ClO_4$	Solid		31.7	21.3			
	DMSO			20.7 (54)	19.2 (40)	16.5 sh	
$[Co(dach)_2Br]ClO_4$	Solid		31.0	21.3			
	DMSO			21.7 (66)			
$Co(dach)_2I_2$	Solid		30.3	20.2			
	EtOH			20.6 (57)	18.2 (60)		
	DMSO		32.0 (152)	21.0 (48)	19.6 (41)		
				Mono Complexes			
$Co(daco)Cl_2$	Solid		18.3	16.3	15.0	10.3	7.4
	EtOH		18.3 (117)	17.6 (143)	16.3 (208)		
$Co(daco)Br_2$	Solid		18.2		15.4	10.2	
	EtOH		17.8 (216)	17.0 (233)	16.1 (283)		
$Co(dach)Cl_2$	Solid	21.0		16.7	15.4		
	EtOH		17.4 (76)	16.3 (95)	15.9 (98)		
$Co(dach)Br_2$	Solid		18.2	15.6	14.7		
	EtOH			16.9	15.8		
$Co(dach)I_2$	Solid		16.3	15.5	14.5	10.2	

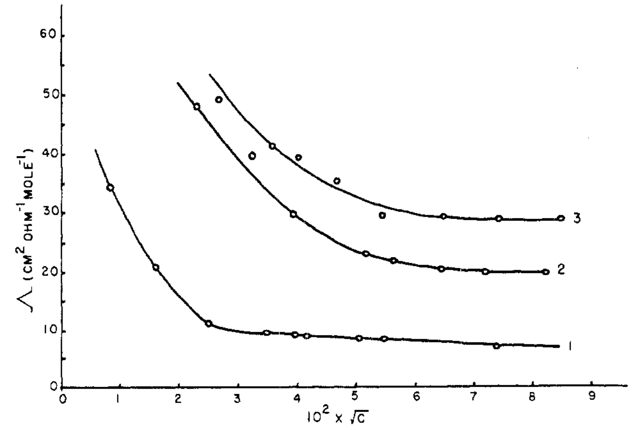

Figure 1. Molar conductance in EtOH at 25° for some selected complexes: (1) $Co(dach)Cl_2$; (2) $[Cu(dach)_2ONO_2]NO_3$; (3) $[Co(daco)_2Cl]Cl$.

ing spectrophotometer. Solution spectra were run in 1-cm and 1-mm matched quartz cells. For solid-state spectra, Nujol mulls of the complexes were soaked into Whatman No. 1 filter paper and Nujol soaked filter paper was used as the reference. If the sample was found to be too unstable in air, the Nujol mull was placed between two quartz plates.

The solutions used to obtain the molar extinction coefficient (ε) of the bis-daco and -dach dihalide complexes were prepared by mixing a deaerated solution containing cobalt halide (10^{-3}–10^{-4} *M*) with a deaerated solution containing ligand. Both solutions were deaerated with nitrogen gas for at least 30 min. The final concentration of the ligand was at least 100 times the concentration of the complex formed. The extinction coefficients (ε) of $Co(daco)_2Cl_2$ and $Co(daco)_2Br_2$ were also checked in EtOH by dissolving the complexes in deaerated solutions containing excess ligand.

The molar extinction coefficients of the halide perchlorate complexes were obtained with solutions prepared by dissolving the complexes in solvents containing a 100-fold excess of ligand. The solutions used for obtaining the molar extinction coefficients of mono-daco and -dach complexes were prepared by dissolution in solvents deaerated with nitrogen.

Results and Discussion

All the complexes were carefully recrystallized whenever possible to ensure that the isolated material was neither a mixture nor a polymer. However, analyses of crystalline rather than powdered samples of daco complexes with cobalt halides were poor, usually being higher in the percentages of carbon and hydrogen than the expected stoichiometry. The infrared spectrum of the $Co(daco)_2Cl_2$ crystals used for the X-ray investigation showed the presence of a peak in the O-H stretching region. Later in the crystal structure analysis,[4] 1 mol of ethanol was found trapped in the crystal lattice, but not coordinated to the metal. Although, thoroughly powdering the sample normally removed the solvent, $Co(daco)_2I_2 \cdot C_2H_5OH$ could not be freed from solvent even after heating under vacuum above 75° (where a reversible color change takes place). The dach complexes were more difficult to purify than the daco complexes but, by powdering and after drying the sample under vacuum for 12 hr at 25°, satisfactory analyses were normally obtained. Therefore, slight variations in the expected analytical results are probably due to the incorporation of solvent in the crystal lattice.

Although the mono-daco complexes are very soluble in anhydrous solvents including methanol, ethanol, propanol, butanol, acetone, and chloroform without decomposition, the mono-dach complexes are less soluble and slight traces of water bring about their rapid decomposition. However, both the mono-daco and -dach complexes are decomposed in aqueous solution to give first a green solid followed by a yellow-green solution. These solutions are basic to pH paper suggesting that displacement of the amine ligand had occurred.

The mixed halide-perchlorate complexes of both the bis-daco and -dach complexes ($[CoL_2X]ClO_4$) are extremely insoluble in both methanol and ethanol; however, these complexes can be dissolved in deaerated DMSO in the presence of excess ligand to give reddish pink solutions associated with the formation of the bis-amine complexes. The solid bis-daco and -dach halide complexes (CoL_2X_2) dissolve in deaerated anhydrous methanol, ethanol, and DMSO with loss of 1 mol of ligand to give the blue tetrahedral $CoLX_2$ in solution. However, the equilibrium can be reversed by the addition of excess ligand to give the reddish pink solutions containing the bis-amine complexes. It is necessary to add larger quantities of dach to solutions of both $Co(dach)_2Cl_2$ and $Co(dach)_2Br_2$ to repress dissociation than to the corresponding daco complexes. $Co(daco)_2(ClO_4)_2$ is also insoluble in ethanol or methanol but can be dissolved in DMSO to give a reddish pink solution without the addition of excess ligand.

Crystals of both bis-daco and -dach halide complexes (CoL_2X_2) change color in air; the daco complexes become deep brown. Crystalline mixed halide-perchlorate complexes ($[CoL_2X]ClO_4$) are more stable and change color more slowly than the CoL_2X_2 complexes. Elemental analysis of the sample of $Co(daco)_2Cl_2$ exposed to oxygen or water cannot be rationalized in terms of the amount of O_2 or H_2O absorbed. The shocking pink $Co(daco)_2(ClO_4)_2$, when exposed to air, also slowly turns brown during a 72-hr period.

The absorption maxima of solid samples of the cobalt complexes mulled in Nujol, along with the maxima and molar extinction coefficients in selected solvents, are given in Table IV. Figure 2 shows that the mull spectrum of the five-coordinated complex[4] $[Co(daco)_2Cl]Cl$ is identical with those of $[Co(daco)_2Cl]ClO_4$ and $[Co(dach)_2Cl]ClO_4$. Since the crystal structure of $[Co(daco)_2Cl]Cl$ is known,[4] the spectrum which it displays can be used as a model for square-pyramidal cobalt(II) complexes. Its spectrum is quite similar to those of all other mesocyclic cobalt(II) complexes which contain at least one halide ion. It is also quite similar to that of a cobalt(II) complex reported by Cohn[8] but differs from those of many other five-coordinated complexes[9] which contain π-bonding ligands which can interact with the d orbitals of the metal.

It is clear that the spectra of the five-coordinated species are easily distinguished from those of the tetrahedral species, but it is more difficult to distinguish the five-coordinated complexes from other geometries which the cobalt(II) ion commonly adopts. It is also rather surprising that, although the spectra are similar, the magnetic moments of $Co(daco)_2Cl_2$ (2.6 BM) and $[Co(daco)_2Cl]ClO_4$ (3.5 BM) are different. Perhaps the variation is due to atmospheric oxidation since it was observed that the crystals of $Co(daco)_2Cl_2$ used in the crystal structure analysis decomposed rapidly unless oxygen was rigorously excluded. Although the usual precautions were taken, the finely powdered sample used in the Gouy method is highly susceptible to oxidation and could lead to spurious experimental results. It is also unfortunate that the solid bis complexes decompose rapidly in the near-infrared, even with cooling, and any absorption in this region is questionable.

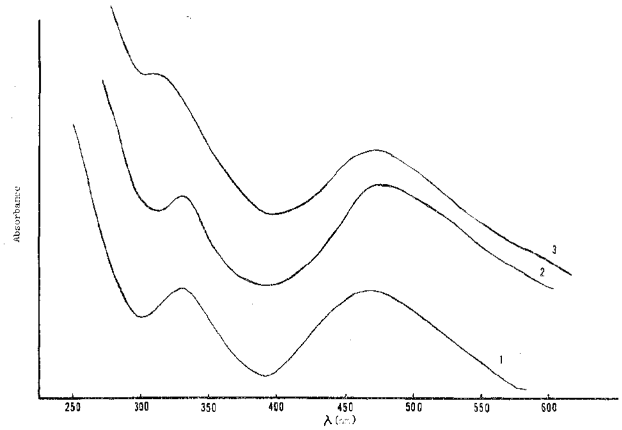

Figure 2. Solid-state absorption spectra: (1) $[Co(daco)_2Cl]Cl$; (2) $[Co(daco)_2Cl](ClO_4)$; (3) $[Co(dach)_2Cl](ClO_4)$.

The compounds whose structures are not yet confirmed are $Co(daco)_2(ClO_4)_2$, $Co(daco)_2I_2 \cdot EtOH$, and $Co(daco)_2IClO_4$. The data on these complexes will be summarized before a discussion of their structures is presented.

The spectral properties of these molecules are different from the tetrahedral and square-pyramidal complexes containing chloride and bromide. The reflectance spectrum of $Co(daco)_2(ClO_4)_2$ is similar to that of $Co(daco)_2I(ClO_4)$, but the magnetic moment of $Co(daco)_2(ClO_4)_2$ (4.2 BM) is slightly higher than that of $Co(daco)_2I(ClO_4)$ (3.5 BM). Although the solid-state spectrum of pale pink $Co(daco)_2I_2 \cdot EtOH$ is similar to that observed for five-coordinated complexes, when this complex was heated to >75° in an effort to remove the ethanol, the color changed to shocking pink and the spectrum became identical with that of $Co(daco)_2(ClO_4)_2$ (Figure 3). The color change is reversible suggesting that a simple structural change may occur on heating. A change from square-pyramidal to trigonal-bipyramidal geometry may be considered but can be ruled out since the visible and uv spectrum of solid $Co(daco)_2(ClO_4)_2$ is similar to the spectrum in DMSO solution, and conductivity data in DMSO indicate that the complex is a 2:1 electrolyte. Thus, the conductivity data along with infrared evidence that the perchlorate ion is not coordinated[10] point strongly to four-coordination for cobalt(II) in both $Co(daco)_2I(ClO_4)$ and $Co(daco)_2(ClO_4)_2$ at room temperature in $Co(daco)_2I_2 \cdot EtOH$ at 75°.

The magnetic moment found for $Co(daco)_2(ClO_4)_2$ rules out a low-spin square-planar complex and, at present, there are no known high-spin, square-planar cobalt(II) complexes. Cotton and Holm[11] initially reported the existence of high-

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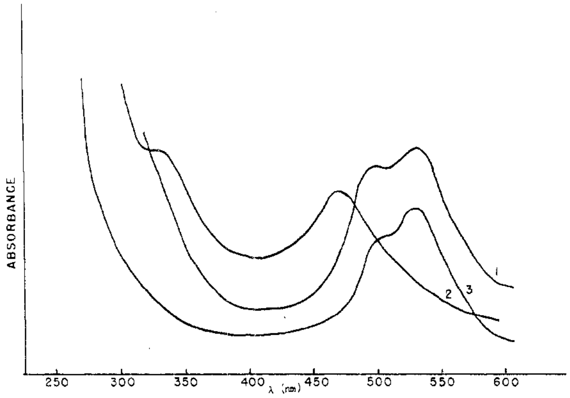

Figure 3. Solid-state absorption spectra: (1) $Co(daco)_2(ClO_4)_2$; (2) $Co(daco)_2I_2 \cdot EtOH$ at 25°; (3) $Co(daco)_2I_2$ above 75°.

spin, square-planar complexes of the $Co-O_4$ type; however, it was later proved[12] that the structure of the complexes is better described as a distorted tetrahedron. The distortion is usually in the direction of a square-planar structure. Everett and Holm[13] demonstrated the existence of the planar $\rightleftarrows$ tetrahedral equilibrium of bis(β-keto amino)cobalt(II) complexes in solution, but the square-planar complexes were all low spin.

It is pleasing to think that if the coordinated chloride was simply removed from the apical position in $[Co(daco)_2Cl]^+$ to give $[Co(daco)_2]^{2+}$, no rearrangement of the nitrogen atoms would take place, and therefore the resulting $Co(daco)_2(ClO_4)_2$ would be square planar. The corresponding nickel(II) and copper(II) complexes containing only perchlorate ions were found to have just such a square-planar structure.[1] Although present knowledge suggests that high-spin, square-planar cobalt(II) complexes may not exist, all known low-spin, square-planar cobalt(II) complexes have ligands which can engage in π bonding with the metal ion thereby stabilizing the low-spin state. Since daco does not have a π system that is capable of stabilizing the low-spin state, its complexes may have a high-spin, almost square-planar structure.

The other structure possible for $Co(daco)_2ClO_4$, $Co(daco)_2IClO_4$, and $Co(daco)_2I_2 \cdot EtOH$ (above 75°) is a tetrahedral structure. However, one might expect to find a peak in the near-infrared region (~14,000 Å) which would confirm this assignment. Unfortunately this peak is often extremely weak and difficult to find. Even with thick mulls (0.5 mm) that absorbed most of the infrared light, no peaks in the infrared region could be observed. However, it has been established that the more a structure is distorted from a tetrahedral toward a planar geometry the weaker the peak at ~14,000 Å tends to be.[12,14] If one examines tetrahedral models of daco complexes, it appears as though this distortion may be required because of nonbonded hydrogen interactions. When each coordinated ring is in the crown form, the amine hydrogens on one ring interact with the methylene hydrogens (3 and 7 positions) of the other ring (four interactions). In the chair form half of these nonbonded interactions are removed, while in the boat form, nonbonded interactions occur only between methylene hydrogens (3 and 7 positions) of the same ring. Therefore, there should be a certain amount of angular distortion toward a square-planar structure to relieve this strain. X-Ray powder patterns of $Co(daco)_2(ClO_4)_2$ and $Ni(daco)_2(ClO_4)_2$ (square-planar complexes[2,10]) did not match. Unfortunately X-ray powder patterns are an aid in assigning structure only when they match. The exact structures (distorted tetrahedral *vs.* square planar) of $Co(daco)_2(ClO_4)_2$, $Co(daco)I(ClO_4)$, and $Co(daco)_2I_2 \cdot EtOH$ (above 75°) may be solved only when an X-ray crystal structure analysis is carried out on one of these complexes and we have not been successful in obtaining a single crystal.

The unique behavior of the daco and dach ligands as chelating agents was further confirmed from two experiments performed with the tetrahedral mono complexes in the presence of piperidine and piperazine. One might expect that if $Co(daco)Br_2$ reacts with either daco or dach to form a tetrahedral species in solution by the elimination of halide and the formation of four metal-nitrogen bonds, a monodentate secondary amine such as piperidine might also bring about the formation of a species with a similar visible and uv spectrum. However, when $Co(daco)Br_2$ (0.03 mol) was dissolved in anhydrous ethanol and piperidine was added, the solution remained blue. Increasing the amount of piperidine slowly up to a factor of 10 times the original amount had no immediate effect on the color of the solution or on the shape of the visible spectrum. After standing for 24 hr under nitrogen, the solution turned a greenish yellow with the formation of a green solid.

The experiment was repeated using piperazine in place of piperidine. Piperazine is known to be able to act as a bidentate amine with large cations such as Pt(II) and Pd(II) and as a bridging ligand with smaller cations such as Hg(II), Ni(II), and Co(II).[15,16] Therefore, one might expect piperazine to react with $Co(daco)Cl_2$ to give a product with properties similar to those of $Co(daco)_2Cl_2$, if daco is functioning as a bridging ligand. However, the results of the experiment were similar to the results obtained with piperidine. These two experiments illustrate that daco and dach are acting as chelating ligands rather than as monodentate or bridging ligands.

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Registry No. $Co(daco)_2Cl_2$, 50769-02-3; $Co(daco)_2Br_2$, 51472-48-1; $Co(daco)_2I_2 \cdot EtOH$, 51472-43-6; $[Co(daco)_2Cl]ClO_4$, 51472-41-4; $[Co(daco)_2Br]ClO_4$, 51472-45-8; $[Co(daco)_2I]ClO_4$, 51425-37-7; $[Co(daco)_2SCN]ClO_4$, 51472-47-0; $Co(daco)_2(ClO_4)_2$, 51540-09-1; $Co(dach)_2Cl_2$, 51425-38-8; $Co(dach)_2Br_2$, 51425-39-9; $Co(dach)_2I_2$, 51472-49-2; $[Co(dach)_2Cl]ClO_4$, 51425-41-3; $[Co(dach)_2Br]ClO_4$, 51425-43-5; $Co(dach)_2(ClO_4)_2$, 51425-45-7; $Co(daco)Cl_2$, 51425-46-8; $Co(daco)Br_2$, 51425-47-9; $Co(dach)Cl_2$, 51425-48-0; $Co(dach)Br_2$, 51425-49-1; $Co(dach)I_2$, 51425-50-4.

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