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Coordination Compounds of Hydrazine Derivatives with Transition Metals. X. Cobalt(II) Aroylhydrazone Complexes

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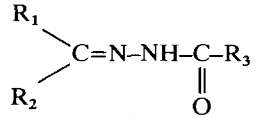
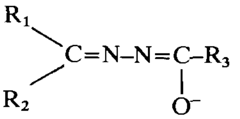
The reactions of some aroylhydrazones (HL) with cobalt(II) salts were investigated and chelates of the types $[Co(HL)_2X_2]$ and $[Co(L)_2]$ were isolated. Analytical data, infrared studies, magnetic moments and solution spectra as well as some conductivity measurements were used to characterise these chelates. The $[Co(HL)_2X_2]$ chelates were found to possess octahedral configuration in solid state but dissociate in DMF solutions. Attempts were made to identify the dissociation products. A dimeric pentacoordinate structure was tentatively assigned for the neutral $[Co(L)_2]$ chelates.

Introduction

Due to their biological activity, especially as potent inhibitors for many enzymes, the coordination chemistry of aroylhydrazines and related compounds was the subject of extensive studies.[1–12] In this respect, the nickel(II) and copper(II) chelates with ligands of type (I) were isolated and characterised.[8–10] However, much less data were reported for the corresponding cobalt(II) chelates.[8,10]


(I-a)


(I-b)

In continuation of our studies on the chelating properties of aroylhydrazines and their azomethine derivatives[7–9,11,12] the present work describes the isolation and properties of cobalt(II) chelates with some aroylhydrazones (I).

Results and Discussion

The reaction of aroylhydrazones of the type (I-a) with cobalt(II) nitrate or chloride gave the corresponding bis chelates of the general formula $[Co(HL)_2X_2]$, where HL refers to the neutral aroylhydrazone molecule. However, in the presence of excess bromide or thiocyanate ions the reaction of cobalt(II) nitrate with (I-a) afforded the corresponding bromo and thio-

TABLE I. Analytical and Magnetic Data for Cobalt(II) Chelates.

R_1	R_2	R_3	X	M.p. °C Decomp.	Co%[a]	N%[a]	X%[a]	μ_{eff} (°K)
i) $Co(R_1R_2C{=}N{-}NHCOR_3)X_2$								
H	C_6H_5	C_6H_5	Cl	272	9.8 (10.2)	9.5 (9.7)	12.8 (12.3)	4.92(299)
H	p-$CH_3OC_6H_4$	C_6H_5	Cl	288	9.6 (9.3)		10.9 (11.1)	4.91(299)
CH_3	CH_3	C_6H_5	Cl	259	12.1 (12.1)		14.3 (14.7)	4.72(293)
CH_3	CH_3	C_6H_5	Br	245	10.4 (10.3)		27.4 (28.0)	4.67(294)
CH_3	CH_3	C_6H_5	SCN	242	11.2 (11.2)	16.2 (16.1)		4.91(293)

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TABLE I. (Cont.)

R_1	R_2	R_3	X	M.p.°C Decomp.	Co%[a]	N%[a]	X%[a]	μ_{eff}(°K)
CH_3	CH_3	C_6H_5	NO_3	218	11.0 (11.0)	15.8 (15.9)		
CH_3	CH_3	o-HOC_6H_4	Cl	300	11.5 (11.5)		13.4 (13.8)	4.83(301)
CH_3	CH_3	o-HOC_6H_4	Br	294	9.9 (9.7)		26.0 (26.6)	4.58(301)
CH_3	CH_3	o-HOC_6H_4	SCN	267	10.9 (10.5)	14.2 (14.0)		4.92(295)
CH_3	CH_3	o-HOC_6H_4	NO_3	117	10.2 (10.3)	14.5 (14.8)		4.37(302)
CH_3	CH_3	p-$CH_3OC_6H_4$	Cl	273	11.0 (10.8)		12.8 (13.1)	4.85(299)
CH_3	CH_3	p-$CH_3OC_6H_4$	SCN	256	10.3 (10.0)	14.8 (14.9)		4.94(299)
CH_3	CH_3	p-$NO_2C_6H_4$	Cl	278	10.5 (10.2)		12.2 (12.4)	4.78(298)
CH_3	CH_3	p-$NO_2C_6H_4$	SCN	236	9.7 (9.5)	17.8 (18.0)		4.88(299)
C_5H_{10}		C_6H_5	Cl	265	10.5 (10.4)		12.5 (12.6)	4.82(299)
C_5H_{10}		C_6H_5	SCN	220	9.2 (9.7)	12.8 (13.0)		4.93(299)
C_5H_{10}		C_6H_5	NO_3	230	9.5 (9.5)	13.7 (13.7)		4.52(298)
C_5H_{10}		o-HOC_6H_4	Cl	290	9.7 (9.9)		11.6 (11.9)	4.78(298)
C_5H_{10}		o-HOC_6H_4	SCN	300	9.1 (9.2)	12.5 (12.5)		4.81(299)
C_5H_{10}		o-HOC_6H_4	NO_3	300	8.9 (8.5)	12.9 (13.0)		4.63(298)
ii) $Co(R_1R_2C{=}N{-}N{=}COR_3)_2$								
H	C_6H_5	C_6H_5		211	11.6 (11.7)	11.0 (11.1)		4.88(301)
H	p-$CH_3OC_6H_4$	C_6H_5		217	10.7 (10.4)	10.1 (9.9)		4.82(301)
CH_3	CH_3	C_6H_5		196	14.3 (14.3)	13.8 (13.8)		4.95(299)
CH_3	CH_3	p-$NO_2C_6H_4$		290	10.5 (10.9)	15.3 (15.6)		4.90(298)
CH_3	C_6H_5	C_6H_5		195	10.1 (11.0)	10.2 (10.5)		4.90(301)
CH_3	C_6H_5	p-$NO_2C_6H_4$		266	9.3 (9.4)	13.4 (13.5)		4.55(301)
C_5H_{10}		C_6H_5		210	12.3 (12.1)	11.3 (11.4)		5.00(301)
C_5H_{10}		p-$NO_2C_6H_4$		189	9.8 (10.1)	14.3 (14.5)		5.12(301)
iii) $Co(R_1R_2C{=}N{-}N{=}COR_3)_2 \cdot 2Py$								
CH_3	CH_3	C_6H_5		170	10.8 (10.3)	14.7 (14.8)		5.02(300)
CH_3	CH_3	p-$NO_2C_6H_4$			9.5 (8.9)	16.9 (17.0)		4.91(300)
C_5H_{10}		C_6H_5		215	8.8 (9.0)	15.2 (15.3)		4.93(300)

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[a] Figures in parentheses indicate the required percentages. [b] Isolated as dihydrate.

cyanato complexes. The $[Co(HL)_2X_2]$ chelates are generally insoluble in non polar solvents such as benzene, carbon tetrachloride, sparingly soluble in ethanol and acetonitrile but moderately soluble in dimethylformamide. On the other hand, the reaction of cobalt(II) acetate with (I-a) in ethanol afforded chelates of the type $[Co(L)_2]$ where L refers to the deprotonated ligand (I-b). These chelates are sparingly soluble in ethanol, moderately soluble in benzene and soluble in pyridine. The prepared $[Co(HL)_2X_2]$ and $[Co(L)_2]$ together with their elemental analyses are listed in Table I.

$Co(HL)_2X_2$ Chelates

Magnetic measurements (Table I) reveal that all $[Co(HL)_2X_2]$ chelates are paramagnetic. With the exception of the nitrate complexes, the values of the magnetic moments (μ_{eff}) varies from *ca.* 4.8–4.92 BM which are within the range reported for high spin pseudooctahedral cobalt(II) chelates.[13] The values of μ_{eff} are sensitive to the nature of X and decrease in the order $SCN > Cl > Br > NO_3$. The observed low μ_{eff} values of the nitrate complexes may be due to strong tetragonal distortion resulting from the relatively weak ligand field strength of the nitrate ion.

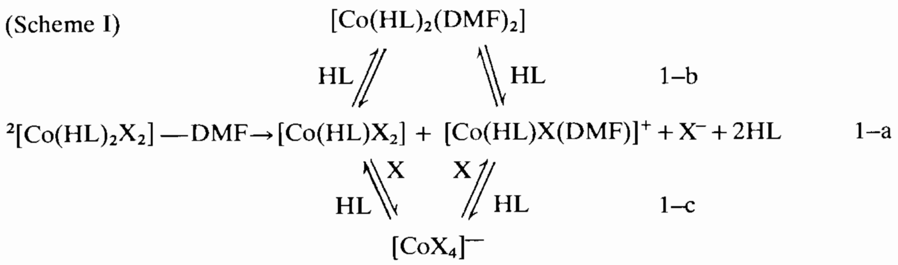
The Nujol mull electronic spectra of these chelates (Table II) are consistent with an octahedral environment around the cobalt(II) ion.[14] The spectra show a split band at *ca.* 20 kK and a broad band at *ca.* 10.0 kK besides very weak bands or shoulders at 14.0 to 15.0 kK. The first and second bands can be, respectively, attributed to $^4T_{1g}\rightarrow{}^4A_{2g}$ and $^4T_{1g}\rightarrow{}^4T_{2g}$ transitions in idealized O_h symmetry. The weak bands are most probably due to different forbidden transitions usually observed in the spectra of octahedral Co(II) complexes.[13, 14] Grinding of the bis thiocyanate complexes for mull spectral measurements caused a change of colour from rose pink to faint blue. The spectra show intense bands in the 15.0–16.0 kK region besides those characteristic of octahedral Co(II) chelates. The position and intensity of the additional bands suggest the presence of tetrahedral species. Such change in colour was previously observed for aroylhydrazine cobalt(II) chelates.[11]

The infrared spectra of $[Co(HL)_2X_2]$ chelates (Table II) are similar to those of the parent aroylhydrazone ligands. The spectra of these chelates show bands characteristic of ν(N–H) stretching, amide I $\nu(C=O)$, azomethine $\nu(C=N)$ and amide II.[15] Both $\nu(C=O)$ and $\nu(C=N)$ bands are usually lowered by *ca.* $20 \pm 5\ cm^{-1}$ with respect to the values of the corresponding parent ligands. Accordingly the hydrazone residue in these chelates acts as a neutral bidentate ligand and is coordinated to the central Co(II) ion via the carbonyl oxygen and azomethine nitrogen. Apart from the bands characteristic of the organic ligands, the infrared spectra of the thiocyanate complexes possess a strong (C–N) stretching band at $2070\ cm^{-1}$ suggesting N-coordinated thiocyanate group.[16–18] The spectra of the nitrate complexes also show bands in the $1250–1290\ cm^{-1}$ region besides a broad absorption at $1050\ cm^{-1}$ characteristic of monodentate nitrate ion.[19] Based on magnetic, electronic and infrared spectral data it is suggested that the two X anions are coordinated to the central Co(II) probably in *trans* axial positions completing the pseudooctahedral symmetry.

Dissolving the pink chloride and thiocyanate complexes in dimethylformamide (DMF) afforded blue solutions. The molar conductances (Table IV) of these solutions approach those reported for 1:1 electrolytes.[20] The electronic spectra at room temperature indicate the formation of tetrahedral species. The spectra show dependence on the concentration of both the free ligand and the anion as well as on the temperature. Typical spectral variations on varying the free ligand concentration are shown in Figure 1. It is apparent that as the concentration of the free ligand increases the absorption due to the tetrahedral species in the range 16.6 to 14.3 kK decreases without any noticeable change in their band position. Meanwhile, an increase in the absorbance due to octahedral species at 20.0–18.2 kK is observed. The isobestic points at 17.7 and 13.7 kK imply a reversible octahedral $\rightleftharpoons$ tetrahedral equilibria involving the free ligand molecule. Such spectral behaviour and the observed low molar conductance may suggest the disproportionation reaction (I-a in scheme I).

In the case of the thiocyanate complexes the formation of the solvated tetrahedral species $[Co(HL)(SCN)DMF]^+$ is much favoured than $[Co(HL)(SCN)_2]$ as evident from their high molar conductance as compared to the chloride complexes. In pres-

(Scheme I)



$$\begin{tikzcd}
 & & {[Co(HL)_2(DMF)_2]} & & \text{1–b} \\
{^2[Co(HL)_2X_2]} \arrow[r, "DMF"] & {[Co(HL)X_2]} \arrow[ur, shift left, "HL"] \arrow[dr, shift left, "X"] & + & {[Co(HL)X(DMF)]^+} \arrow[ul, shift left, "HL"'] \arrow[dl, shift left, "X"'] & {+X^- + 2HL \quad \text{1–a}} \\
 & & {[CoX_4]^-} \arrow[ul, shift left, "HL"] \arrow[ur, shift left, "HL"'] & & \text{1–c}
\end{tikzcd}$$

TABLE II. The Electronic Spectra of Solid Co($\overset{R_1}{\underset{R_2}{>}}$C=N–NH–COR$_3$)$_2X_2$ Chelates.[a]

R$_1$	R$_2$	R$_3$	X		$^4T_{1g}\rightarrow{}^4T_{1g}(P)$									$^4T_{1g}\rightarrow{}^4T_{1g}$	
CH$_3$	CH$_3$	C$_6$H$_5$	Cl	21.05	19.61		18.35	16.95					12.50		
CH$_3$	CH$_3$	C$_6$H$_5$	Br	20.20	19.23			17.39					11.70	10.93	10.20b
CH$_3$	CH$_3$	C$_6$H$_5$	SCN	21.98	21.05		18.35	16.39					11.43		10.53
CH$_3$	CH$_3$	C$_6$H$_5$	NO$_3$	22.73	21.05	19.05	17.86	16.67					11.36	10.64	10.00
CH$_3$	CH$_3$	*o*-HOC$_6$H$_4$	Cl	20.62	19.42	17.86	16.00	15.15					11.56	10.81	10.15
CH$_3$	CH$_3$	*o*-HOC$_6$H$_4$	Br	21.50	20.41			16.95				13.33	11.63	10.99	10.31
CH$_3$	CH$_3$	*o*-HOC$_6$H$_4$	SCN	21.98	20.41	19.05			17.24	16.00		12.99	11.36	10.81	10.00
CH$_3$	CH$_3$	*o*-HOC$_6$H$_4$	NO$_3$	21.74	20.62			17.39					13.33	11.11	10.53
CH$_3$	CH$_3$	*p*-CH$_3$OC$_6$H$_4$	Cl	20.41	19.23	17.86	15.38	14.49					11.36	10.75	
CH$_3$	CH$_3$	*p*-CH$_3$OC$_6$H$_4$	SCN	22.22	20.41	19.42			16.67	15.75	15.04		11.76	10.87	10.10
CH$_3$	CH$_3$	*p*-NO$_2$C$_6$H$_4$	Cl	21.05	19.80	18.18	16.00	15.15							
CH$_3$	CH$_3$	*p*-NO$_2$C$_6$H$_4$	SCN	19.80	18.69				16.95	15.63	14.93			11.76	
C$_5$H$_{10}$		C$_6$H$_5$	Cl	20.83	19.41(sh)	18.01(sh)		15.03						10.86	10.30b
C$_5$H$_{10}$		C$_6$H$_5$	SCN	22.22	20.40(sh)	18.86(sh)			16.49(sh)	15.87				10.75	10.52
C$_5$H$_{10}$		C$_6$H$_5$	NO$_3$	22.72b	19.60(sh)	17.09									
C$_5$H$_{10}$		*o*-HOC$_6$H$_4$	Cl	20.83	19.80	17.85		14.08(wsh)						10.98b	
C$_5$H$_{10}$		*o*-HOC$_6$H$_4$	SCN	22.22	20.40	18.86(sh)			16.66(sh)	15.87				10.98	10.41
C$_5$H$_{10}$		*o*-HOC$_6$H$_4$	NO$_3$	22.72(sh)	19.23	16.94(wsh)		15.15(wsh)						11.11	10.81

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[a] b = broad band, sh = shoulder, wsh = weak shoulder.

TABLE III. Infrared Spectra of Aroylhydrazones and Their Co(II) Chelates.[a]

R_1	R_2	R_3	X	N–H	Amide I C=O	C=N	Conj. Phenyl	C=C Phenyl	Amide II	C=C Phenyl
i) $R_1R_2C=N–NHCOR_3$										
H	C_6H_5	C_6H_5		3180m	1640s		1600m	1580w	1560m	1508
H	C_6H_5	p-$CH_3OC_6H_4$		3200m	1638s		1610s	1575s	1560m	1500sh
H	C_6H_5	o-HOC_6H_4		3200m	1640s	1610m	1600sh	1568	1550	1495
H	p-$CH_3OC_6H_4$	C_6H_5		3190m	1640s	1615s	1600s	1580s	1560m	
H	p-$NO_2C_6H_4$	C_6H_5		3200s	1645s	1618s	1605sh	1575s	1550m	1495m
H	o-$NO_2C_6H_4$	C_6H_5		3200s	1648vs	1608m	1595m	1575vs	1540s	1495w
CH_3	CH_3	C_6H_5		3200m	1665s	1640s	1610m	1585s	1540s	1500m
CH_3	CH_3	p-$CH_3OC_6H_4$		3290s	1680s	1650s		1580s	1535s	1495m
CH_3	CH_3	p-$NO_2C_6H_4$		3280s	1655s	1638s	1600s		1540s	
CH_3	CH_3	o-HOC_6H_4		3200s	1642s	1638sh	1610s	1560sh	1540s	1500m
CH_3	C_6H_5	p-$NO_2C_6H_4$		3300m	1650s	1635sh	1600	1580w	1545s	1500m
CH_3	C_6H_5	C_6H_5		3240s	1658sh	1650s	1610s	1560m	1540s	1495s
CH_3	C_6H_5	o-HOC_6H_4		3300m	1650sh	1630vs	1605s		1560s	1500m
C_5H_{10}		C_6H_5		3300s	1665vs	1620s	1605m	1580m	1540s	1495m
C_5H_{10}		p-$NO_2C_6H_4$		3300s	1655vs	1610s	1600m	1560m	1540s	1500m
C_5H_{10}		o-HOC_6H_4		3250m	1650sh	1640s	1610s	1560m	1540s	1500sh
ii) $Co(R_1R_2C=N–NHCOR_3)_2X_2$										
H	C_6H_5	C_6H_5	Cl	3180	1610		1605s	1570s	1540m	1495
H	p-$CH_3OC_6H_4$	C_6H_5	Cl	3190m	1610s		1600s	1570s	1555m	1500
CH_3	CH_3	C_6H_5	Cl	3200m	1625s	1610sh	1600sh	1575s	1540s	1520
CH_3	CH_3	C_6H_5	SCN	3200m	1620s	1610sh	1600s	1575s	1550s	1500
CH_3	CH_3	C_6H_5	NO_3		1630	1618	1600	1578s	1550	
CH_3	CH_3	o-HOC_6H_4	Cl	3295s	1625s	1610s	1600sh	1575s	1550	1495
CH_3	CH_3	o-HOC_6H_4	SCN	3260m	1620s	1608s	1595s	1570sh	1530	
CH_3	CH_3	o-HOC_6H_4	NO_3	3250m	1620s			1578	1560	1500m
CH_3	CH_3	p-$CH_3OC_6H_4$	Cl	3180m	1620s	1610s	1600sh	1570s	1550m	1510m
CH_3	CH_3	p-$CH_3OC_6H_4$	SCN	3260m	1620s	1610s		1570	1540m	1510
CH_3	CH_3	p-$NO_2C_6H_4$	Cl	3180	1625sh	1618s	1600s	1560	1540m	1490
CH_3	CH_3	p-$NO_2C_6H_4$	SCN	3325m	1635s		1600s		1540s	
C_5H_{10}		C_6H_5	Cl	3150m	1620s	1610sh	1590s	1560sh	1540sh	
C_5H_{10}		C_6H_5	SCN	3250m	1625s	1615s	1605sh	1578	1540sh	1500
C_5H_{10}		C_6H_5	NO_3	3150m	1620s	1615s	1600sh	1575	1540sh	1500m
C_5H_{10}		o-HOC_6H_4	Cl	3290	1625s	1605		1575m	1555s	1495m
C_5H_{10}		o-HOC_6H_4	SCN	3270m	1620	1605		1570	1540sh	1500m
C_5H_{10}		o-HOC_6H_4	NO_3	3250m	1630sh	1620		1575	1540	1505m
iii) $Co(R_1R_2C=N–N=COR_3)_2$						*				
H	C_6H_5	C_6H_5				1610m	1590m		1520vs	1490s
H	p-$CH_3OC_6H_4$	C_6H_5				1620m	1590s		1525vs	1490s
CH_3	C_6H_5	C_6H_5				1610sh	1600s	1578m	1540s	1500m
CH_3	C_6H_5	p-$NO_2C_6H_4$				1600sh	1598s	1570	1540s	1495m
CH_3	CH_3	C_6H_5				1640m	1590s	1550sh	1540s	1500m
CH_3	CH_3	p-$NO_2C_6H_4$				1640m	1600m	1560s	1540s	1490m
C_5H_{10}		C_6H_5				1620m				
C_5H_{10}		p-$NO_2C_6H_4$				1620m	1590m	1560s	1540s	

[a] vs = very strong, s = strong, m = medium, w = weak and sh = shoulder. * C=N–N=C.

ence of large excess of the free ligand the solvated species $[Co(HL)_2(DMF)_2]^{++}$ (eq. 1-b) are the dominating species in both series.

Addition of chloride ions to DMF solutions of $[Co(HL)_2Cl_2]$ chelates also results in profound spectral changes (Figure 2). These changes reveal the existence of at least three tetrahedral species in equilibrium. This is quite evident from the variation of the absorbance measured at 16.4 kK *versus* Cl^- (Figure 3), as well as the shift of the isobestic point initially found at 17.1 to 16.1 kK. It can be thus proposed that the initial addition of chloride ions may result in the displacement

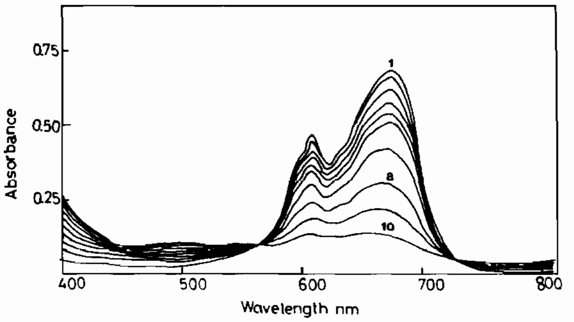


Figure 1. Electronic spectra of bis(acetone salicoylhydrazone)-cobalt(II) dichloride in DMF ($1.88 \times 10^{-3}\,M$) in presence of different concentrations of the free ligands: 1) 0.00, 2) $3.8 \times 10^{-3}\,M$, 3) $7.7 \times 10^{-3}\,M$, 4) $15.5 \times 10^{-3}\,M$, 5) $23.2 \times 10^{-3}\,M$, 6) $30.9 \times 10^{-3}\,M$, 7) $46.4 \times 10^{-3}\,M$, 8) $63.2 \times 10^{-3}\,M$, 9) $90.2 \times 10^{-3}\,M$, 10) $128 \times 10^{-3}\,M$.

of DMF molecule from $[Co(HL)_2Cl(DMF)]^+$ giving the unsolvated species $[Co(HL)Cl_2]$. Addition of excess Cl^- ions, however, results in the formation of $[CoCl_4]^{--}$ ion (eq. 1-c). In fact the spectra recorded in presence of excess Cl^- were identical to that reported for $[CoCl_4]^{--}$ in DMF solution.[21] Similar spectral changes were also observed in case of thiocyanate complexes on adding free thiocyanate ion.

At room temperature the solution spectra of $[Co(HL)_2Br_2]$ chelates in DMF suggest the existence of both octahedral and tetrahedral species. Their relative population depends on the nature of the parent ligand. When $R_1 = R_2 = CH_3$ and $R_3 = o\text{-}HOC_6H_4$, the solution is pink and the octahedral species are predominating, while in case of cyclohexanone salicoylhydrazone the solution is green and its spectrum indicates the formation of appreciable amounts of tetrahedral

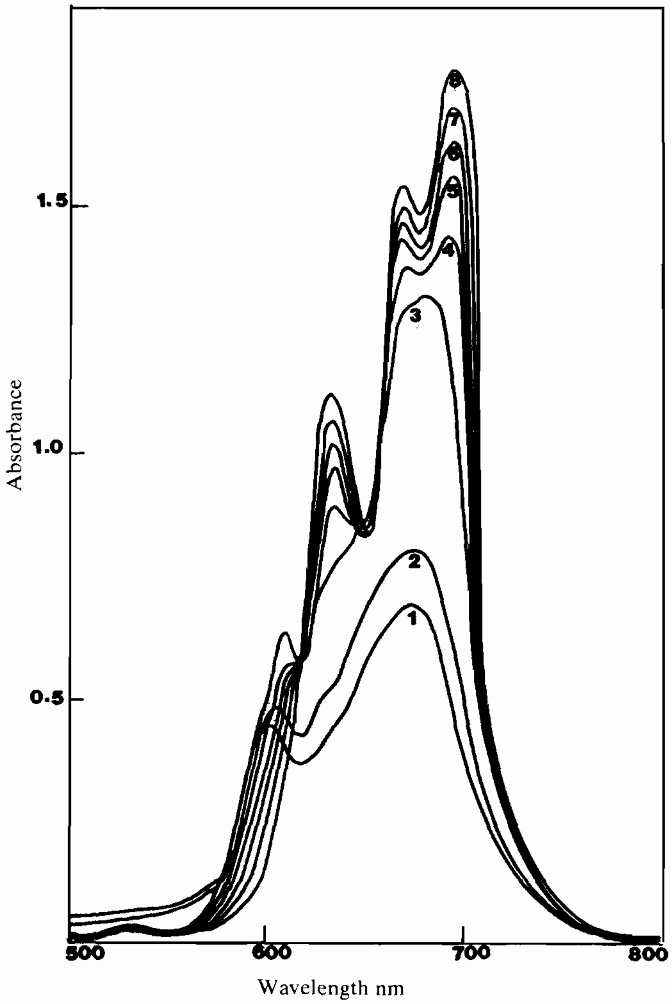


Figure 2. Electronic spectra of bis(acetone salicoylhydrazone)cobalt(II) dichloride in DMF ($2.28 \times 10^{-3}\,M$) in presence of different concentrations of chloride ion (LiCl): 1) 0.00, 2) 0.01 *M*, 3) 0.02 *M*, 4) 0.041 *M*, 5) 0.062 *M*, 6) 0.082 *M*, 7) 0.123 *M*, 8) 0.164 *M*.

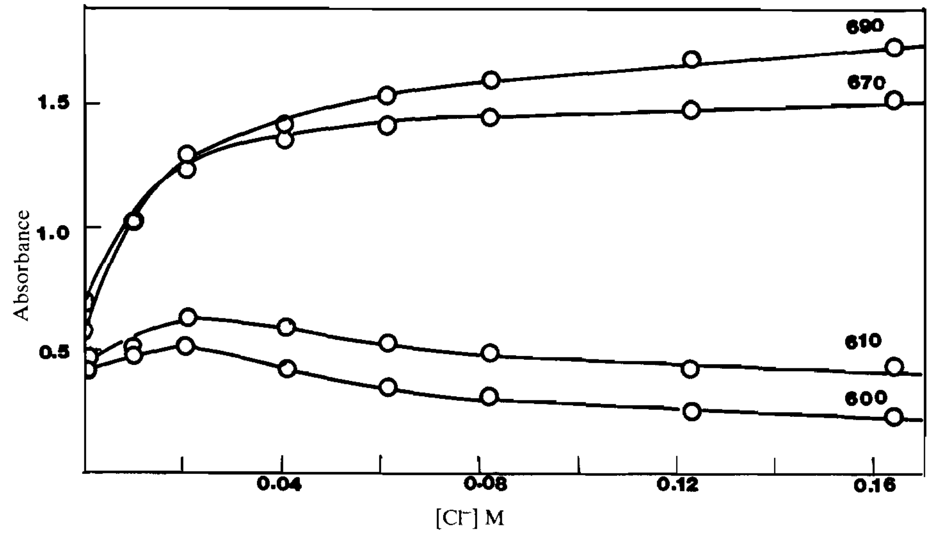


Figure 3. Variation of absorbancies of bis(acetone salicoylhydrazone)cobalt(II) dichloride in DMF (2.28×10^{-3} *M*) with varying chloride ion concentrations at different wavelengths (nm).

TABLE IV. Electrolytic Conductivities of Some Cobalt(II) Chelates of the Type $\mathrm{Co}(\genfrac{}{}{0pt}{}{R_1}{R_2}{>}C{=}N{-}NH{-}COR_3)_2X$ at 25° C.[a]

R_1	R_2	R_3	X	Λ_m ($ohm^{-1}\ cm^2\ mol^{-1}$)
CH_3	CH_3	C_6H_5	Cl	38.3
			Br	105.2
			SCN	50.8
			NO_3	133.5
CH_3	CH_3	o-HOC_6H_4	Cl	36.8
			Br	112.6
			SCN	61.2
			NO_3	142.0
C_5H_{10}		C_6H_5	Cl	39.2
			SCN	110.0
			NO_3	138.8
C_5H_{10}		o-HOC_6H_4	Cl	40.1
			SCN	62.8
			NO_3	148.2

[a] *ca.* 1×10^{-3} *M* solution.

(Scheme II)

$$[Co(HL)_2Br_2]_{++} + 2DMF \rightleftharpoons [Co(HL)_2(DMF)_2]^{++} + 2Br^- \quad \text{2-a}$$

$$[Co(HL)_2(DMF)_2] + 2DMF \rightleftharpoons [Co(HL)(DMF)_4]^{++} + HL \quad \text{2-b}$$

$$[Co(HL)(DMF)_4]^{++} \rightleftharpoons [Co(HL)(DMF)_2]^{++} + 2DMF \quad \text{2-c}$$

octahedral tetrahedral

$$\Big\uparrow\!\!\Big\downarrow Br^-$$

$$[Co(HL)(DMF)Br]^+ + DMF$$

$$\Big\uparrow\!\!\Big\downarrow Br^-$$

$$[Co(HL)(Br_2)]$$

$$\Big\uparrow\!\!\Big\downarrow Br^-$$

$$[CoBr_4]^{--}$$

species. In all cases, the addition of the free ligand greatly affects the solution spectra of these complexes. Furthermore, the molar conductances of these solutions are much higher than those reported for 1:1 electrolytes but still slightly lower than 1:2 electrolytes.[20] This behaviour is shown in scheme (II). Here again, the presence of excess Br^- ions also favours the formation of $[CoBr_4]^{--}$ ion.[22]

The spectra of all the prepared bromide complexes show reversible temperature dependence. The temperature dependent spectra are exemplified in Figure 4. It is fairly evident that there is a tetrahedral $\rightleftharpoons$ octahedral equilibrium depending on temperature. On increasing the temperature, the equilibrium (2-c) is shifted toward the formation of $[Co(HL)Br(DMF)]^+$ or $[Co(HL)Br_2]$. In presence of large excess of the free ligands, however, the equilibria are largely shifted toward $[Co(HL)_2(DMF)_2]$ and the spectra become less sensitive to temperature variations.

The nitrate complexes in DMF behave as 1:2 electrolytes.[20] Their solution spectra are diagnostic of octahedral cobalt(II). Their spectra still show depen-

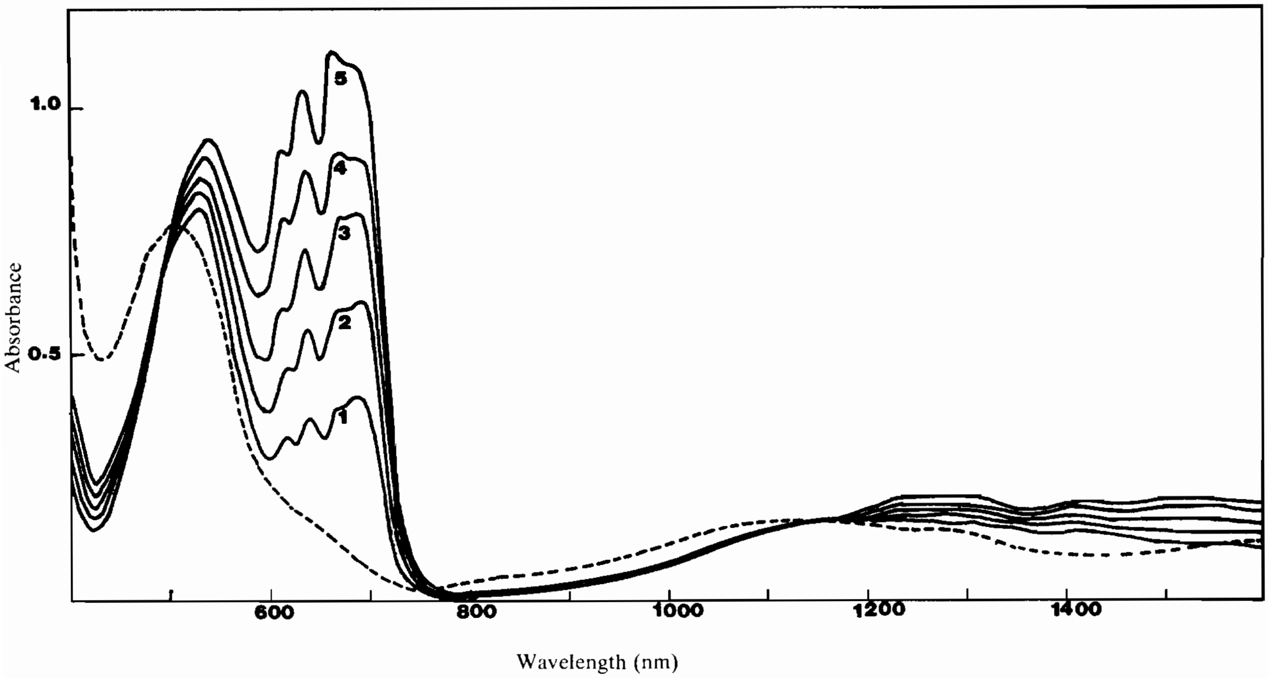


Figure 4. Effect of temperature on the spectra of bis(acetone salicoylhydrazone)cobalt(II) dibromide in DMF ($3.1 \times 10^{-2} M$): 1) 18° C, 2) 29° C, 3) 38° C, 4) 47° C, 5) 58° C. The dotted line is the spectrum in presence of excess free ligand (0.12 *M*).

dence of the free ligand concentration implying partial dissociation and equilibria (3-a and b) may exist in these solutions.

$$\mathrm{Co(HL)_2(NO_3)_2 + 2DMF \rightleftharpoons [Co(HL)_2(DMF)_2]^{++} + 2NO_3^-} \quad \text{3-a}$$

$$\mathrm{Co(HL)_2(DMF)_2 + 2DMF \rightleftharpoons [Co(HL)(DMF)_4]^{++} + HL} \quad \text{3-b}$$

Co(L)₂ Chelates

The infrared spectra (Table II) of this type of chelates indicate the deprotonation of the aroylhydrazone ligand. The spectra lack absorptions due to both ν(H–H) stretching and amide I ν (C=O), but show strong band at *ca.* 1620 $\mathrm{cm^{-1}}$ due to the $\mathrm{>C{=}N{-}N{=}C<}$ residue.

Their stoicheiometry suggests the apparent coordination number four for the central Co(II) ion. Both square planar and tetrahedral structures are accordingly possible. Molecular association, however, may give rise to five or six coordinate structures. The magnetic measurements (Table I) show that these chelates are paramagnetic with μ_{eff} varying from 4.55–5.12 BM. Thus, a square planar structure can be fairly ruled out.[13] Meanwhile, the wide range of magnetic moments provides an obstacle to assigning the actual stereochemistry of these chelates, since the range covers those reported for tetrahedral, pentacoordinate and octahedral structures.

The Nujol mull electronic spectra exhibit a split band or well developed shoulder at *ca.* 18–17 kK besides a broad band at 10.0 kK, with a prominent shoulder at 9.0 kK. The spectra in benzene (Table V) are more or less similar to those of the solid chelates measured in Nujol mull, indicating the retention of the structure in these solutions. The position of the bands as well as their intensities in both solid and solutions of non coordinating solvents cannot account for the octahedral structure but can be related to either pseudotetrahedral or dimeric pentacoordinate structures. Unfortunately, the low solubility of these chelates prevents any reliable molecular weight determination. However, a dimeric pentacoordinate structure (II) analogous to that reported for bis(N)-methylsalicylaldiminato)zinc(II)[23] may be tentatively adopted for the solid chelates on the basis of several lines of reasoning: i) the solids are slightly soluble in non coordinating solvents which may indicate some sort of association; ii) the values of μ_{eff} are rather high to account for tetrahedral arrangement; iii) the spectra of these chelates in both solid and benzene solutions are similar to the spectra reported for bis(N-methylsalicylaldiminato)cobalt(II) which was found to be isostructural with the analogous zinc(II) chelate[24]; iv) the intensity of the bands in solution spectra of these chelates in non coordinating solvents are very low (ε = 30–200) as compared to those of tetrahedral

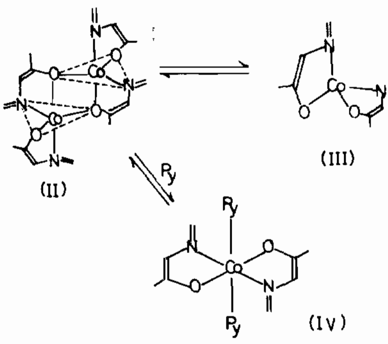
TABLE V. The Electronic Spectra of $\mathrm{Co}(\overset{R_1}{\underset{R_2}{>}}\mathrm{C{=}N{-}N{=}COR_3})_2$ Chelates.[a]

R_1	R_2	R_3	State	Band Maxima in kK	(l mol^{-1} cm^{-1})					
H	C_6H_5	C_6H_5	Bz*		18.18	17.09(sh)			8.85b	
			Py		19.23(55)	17.24(28)	16.12(wsh)	10.20(sh)	9.65(5)	
H	p-$CH_3OC_6H_4$	C_6H_5	Nm		18.21	17.10(sh)		10.00(sh)		
			Bz*		18.18	17.05(sh)				
			Py		18.86(60)	16.94(31)		10.30(sh)	9.63(7)	
CH_3	CH_3	C_6H_5	Nm		18.20	17.00	16.20(wsh)			
			Bz*		18.18	16.94(sh)			8.70b	
			Py		19.60(25)	17.85(22)		10.00(sh)	9.70(4)	
CH_3	CH_3	p-$NO_2C_6H_4$	Nm		18.18	16.60(sh)				
			Bz*		18.18	16.52(sh)			8.85b	
			Py		18.20(27)	16.95(sh)		10.98(sh)	9.80(5)	
CH_3	C_6H_5	C_6H_5	Bz	20.00(sh)	18.18(85)	17.24(100)	13.60(vw)	10.00(sh)	8.77b(27)	7.22(bsh)
			Py		17.54(30)	16.40(20)		10.40(sh)	9.52(2)	
CH_3	C_6H_5	p-$NO_2C_6H_4$	Nm	20.83(sh)	18.20	17.09	13.33b	10.00(sh)		
			Bz	20.80(sh)	18.18(125)	17.09(140)	13.33b	10.00(sh)	8.85b(25)	7.30(bsh)
			Py		17.40(40)	16.40(40)		10.20(sh)	9.70(10)	
C_5H_{10}		C_6H_5	Nm		18.18	16.80(sh)				
			Bz		18.18(200)	16.94(150)				
			Py		19.23(25)	17.85(25)	12.50(wsh)	10.20(sh)	9.65(4)	
C_5H_{10}		p-$NO_2C_6H_4$	Nm		18.18	16.80(sh)				
			Bz		18.18(227)	16.94(180)				
			Py			17.70(40)	16.60(sh)	10.30(sh)	9.80(9)	

[a] Nm = Nujol mull, Bz = Benzene, Py = Pyridine.

* Saturated solution, sh = shoulder, vw = very weak, b = broad.

cobalt(II) species. Low band intensities, however, were related to a distortion from strict tetrahedral symmetry[25]; v) the apparent molar absorbance at the band maxima, per g-atom of cobalt, is dependent on temperature. An increase in temperature results in an oberved increase in band intensity without the alteration in band position. This behaviour may suggest an equilibrium between the pentacoordinate dimer (II) and the tetrahedral monomer (III) in benzene solution:



Similar equilibria were proposed for other bis Co(II) chelates.[25] The actual structure of these chelates, however, can be established only by X-ray structural determination.

In neat pyridine, the electronic spectra of $Co(L)_2$ chelates (Table V) provide evidence for the formation of octahedral dipyridinate adducts. In some cases (Table I), the solid dipyridinates were isolated. These adducts are paramagnetic (μ_{eff} = 4.95 BM) and their Nujol spectra are identical to their solution spectra in pyridine. From these results, structure (IV) can be adopted for these pyridinates in which the pyridine molecules occupy the *trans* axial positions.

Experimental

Preparation of Organic Ligands

The aroylhydrazines were prepared as previously described.[11] The following aroylhydrazones (I-a) were generally prepared by the reaction of aroylhydrazine with the corresponding ketone or aldehyde according to the method reported in literature. R_1, R_2, R_3 (m.p. °C): H, C_6H_5, C_6H_5 (212)[26], H, p-$CH_3OC_6H_4$, C_6H_5 (160)[27], CH_3, CH_3, C_6H_5 (140)[28], CH_3, CH_3, p-$CH_3OC_6H_4$ (135), CH_3, CH_3, p-$NO_2C_6H_4$ (161)[29], CH_3, CH_3, o-HOC_6H_4 (229)[30], CH_3, C_6H_5, C_6H_5, (158)[28], CH_3, C_6H_5, p-$NO_2C_6H_4$ (212)[28], C_5H_{10} (cyclohexyl), C_6H_5 (168)[27].

Preparation of Cobalt(II) complexes

Bis(aroylhydrazone)cobalt(II) chloride or nitrate complexes

A solution of cobalt(II) chloride hexahydrate (0.01 mol) in ethanol (25 ml) was treated with a solution of aroylhydrazone (0.025 mol) in ethanol (30 ml). The reaction mixture was refluxed for 1/2 hr. On cooling, the precipitated bis cobalt(II) complex was filtered, washed with ethanol then dried under vacuum. The same procedure was adopted for the preparation of bis(aroylhydrazone)cobalt(II) nitrate complexes.

Bis(aroylhydrazone)cobalt(II) thiocyanate or bromide complexes

Cobalt(II) nitrate hexahydrate (0.01 mol) was refluxed with sodium thiocyanate (0.02 mol) in the minimum amount of absolute ethanol for 10 min. The sodium nitrate formed on cooling was filtered off. The cobalt(II) thiocyanate solution was then treated with a solution of aroylhydrazone (0.02 mol) in ethanol (30 ml), and the reaction mixture was refluxed for 1/2 h during which time the thiocyanate complex was formed. The precipitate was filtered, washed with absolute ethanol and then dried under vacuum. On using sodium bromide, the bromide complexes were similarly prepared.

Bis(aroylhydrazinato)cobalt(II)

A hot solution of cobalt(II) acetate dihydrate (0.01 mol) in 50% aqueous ethanol (30 ml) was added to a boiling solution of aroylhydrazone (0.02 mol) in ethanol (30 ml). The reaction mixture was refluxed for 1 h. The precipitated complex, on cooling, was filtered, washed with hot ethanol then dried under vacuum.

Physical Measurements

Magnetic measurements, infrared and Nujol mull electronic spectra were obtained using the same procedure previously described.[9] The solution electronic spectra in DMF were recorded in the 400–1600 nm region using a Cary 17 spectrophotometer. For spectra at elevated temperatures fluid (paraffin oil) thermostated cell holders were used. The temperature of the circulating paraffin oil was maintained constant with an electric thermostat. The actual temperature of the solution was recorded by a calibrated thermocouple. Electrolytic conductance measurements were carried out using a Pye bridge and a conventional cell, previously calibrated with an aqueous solution of potassium chloride.

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