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Coordination Compounds of Hydrazine Derivatives with Transition Metals, XXIII

Cobalt(II) Chelates of Bis(*N*-salicylidene)dicarboxylic Acid Dihydrazides

A. El-Toukhy, A. F. M. Hefny, L. El Sayed, and **M. F. Iskander***

Chemistry Department, Faculty of Science, and University of Alexandria Research Center (UNARC), Alexandria University, Alexandria, Egypt

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The reaction of bis(*N*-salicylidene)dicarboxylic acid dihydrazides (H_4Lig) with cobalt(II) salts was investigated. Chelates of the types $Co(H_3Lig)X \cdot nH_2O$, $Co_2(H_2Lig)X_2$, $Co_3(H_3Lig)_2X_4$, $Co(H_2Lig) \cdot nH_2O$ and $Co(H_3Lig)_2 \cdot nH_2O$ (X = Cl, Br, I or SCN) were isolated and characterized by their infrared and electronic spectra as well as their magnetic properties.

[Keywords: Complexes, Co(II); Electronic spectra; Ir; Magnetic moments]

Koordinationsverbindungen von Hydrazinderivaten mit Übergangsmetallen, 23. Mitt.: Kobalt(II)-Chelate von Bis(N-salicyliden)dicarbonsäuredihydraziden

Die Reaktion von Bis(*N*-salicyliden)dicarbonsäuredihydraziden (H_4Lig) mit Kobalt(II)-Salzen ergab Chelate vom Typ $Co(H_3Lig)X \cdot nH_2O$, $Co_2(H_2Lig)X_2$, $Co_3(H_3Lig)_2X_4$, $Co(H_2Lig) \cdot nH_2O$ and $Co(H_3Lig)_2 \cdot nH_2O$ (X = Cl, Br, I oder SCN). Die Charakterisierung erfolgte mittels IR, Elektronenspektren und magnetischer Eigenschaften.

Introduction

The reaction of a series of polydentate ligands of the general formula **1** with copper(II) and nickel(II) salts were previously investigated[1]. Different modes of chelation with various degrees of deprotonation were assigned to this type of ligands. The present work is devoted to study the effect of CH_2-chain length ($n = 1$, 2, 3, 4 and 5) on the flexibility of the ligand molecule, which in turn can influence its mode of chelation as well as the stereochemistry of the isolated cobalt(II)

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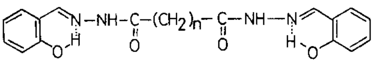
complexes. Hereafter, the ligands are generally abbreviated as $\mathrm{H}_4\mathit{Lig}$ and specifically as $\mathrm{H}_4\mathit{SM}\mathrm{H}$, $\mathrm{H}_4\mathit{SS}\mathrm{H}$, $\mathrm{H}_4\mathit{SG}\mathrm{H}$, $\mathrm{H}_4\mathit{SA}\mathrm{H}$ and $\mathrm{H}_4\mathit{SP}\mathrm{H}$ for **1**, ($n = 1$, 2, 3, 4 and 5) respectively.

Results and Discussion

The reaction of bis(*N*-salicylidene)dicarboxylic acid dihydrazides ($\mathrm{H}_4\mathit{Lig}$) with cobalt(II) salts afforded different types of cobalt(II) chelates depending on the salt used and the metal to ligand molar ratio. The isolated chelates are of the general formulae $\mathrm{Co(H_3}\mathit{Lig})X\cdot n\mathrm{H_2O}$, $\mathrm{Co_2(H_2}\mathit{Lig})X_2$, $\mathrm{Co_3(H_3}\mathit{Lig})_2X_4$, $\mathrm{Co(H_2}\mathit{Lig})\cdot n\mathrm{H_2O}$ and $\mathrm{Co(H_3}\mathit{Lig})_2\cdot n\mathrm{H_2O}$ where X is a mononegative ion, Cl, Br, I or SCN. The analytical and magnetic data of these chelates are given in Table 1.

The cationic complexes $\mathrm{Co(H_3}\mathit{Lig})X\cdot n\mathrm{H_2O}$ (X = Cl, Br, I or SCN) were obtained with all dicarboxylic acid dihydrazones while polynuclear chelates $\mathrm{Co_2(H_2}\mathit{SS}\mathrm{H)Cl_2}$ and $\mathrm{Co_3(H_3}\mathit{SA}\mathrm{H)_2Cl_4}$ were only isolated with (**1**, $n = 2$) and (**1**, $n = 4$). Attempts to prepare the corresponding chelate with other ligands were not successful. The inner chelates of the types $\mathrm{Co(H_2}\mathit{Lig})\cdot n\mathrm{H_2O}$ and $\mathrm{Co(H_3}\mathit{Lig})_2\cdot n\mathrm{H_2O}$ were formed from the reaction of cobalt(II) acetate with the dicarboxylic acid dihydrazones in the proper molar ratio.



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The room temperature magnetic moments of all the chelates vary from 3.3 to 4.9 BM indicating that all these chelates are of high spin type and exclude any oxidation to Co(III)[2]. The observed values cannot differentiate, however, between octahedral and tetrahedral arrangement around the cobalt(II) ion since they are at the borderline between the values corresponding to the two structures. These values, also, exclude square planar arrangement around the cobalt(II) ion[2].

The infrared spectrum of $\mathrm{Co(H_3}\mathit{SM}\mathrm{H)Cl}$ (Table 2), shows a well defined band at 3 200 $\mathrm{cm^{-1}}$ due to ν (N—H) stretching vibration besides two bands at ca. 1 700 and 1 625 $\mathrm{cm^{-1}}$ due to free and coordinated amide 1 [ν (C=O)] band respectively[3–5]. Similarly, the bands at $\sim$ 1 650 and 1 615 $\mathrm{cm^{-1}}$ are also attributed to free and coordinated azomethine group [ν (C=N)] respectively. These i.r. spectral data imply that only one salicylidene acid hydrazide unit is involved in chelation while the other remains uncoordinated. Thus the ligand in the $\mathrm{Co(H_3}\mathit{SM}\mathrm{H)Cl}$ chelate reacts in the keto form and behaves as monobasic tridentate molecule.

Table 1. *Analytical and magnetic data for cobalt(II) chelates*

Compound	$M\%$	N%	$X\%$	μ_{eff} (°K)
$\mathrm{Co(H_3}SM\mathrm{H)Cl}$	13.60 (13.60)	9.20 (8.80)	12.85 (12.90)	4.57 (299)
$\mathrm{Co(H_3}SS\mathrm{H)Cl \cdot 2\,H_2O}$	11.55 (12.18)	11.30 (11.58)	7.60 (7.33)	3.34 (302)
$\mathrm{Co(H_3}SS\mathrm{H)Br \cdot 2\,H_2O}$	11.10 (11.15)	10.92 (10.61)	15.08 (15.12)	3.86 (300)
$\mathrm{Co(H_3}SS\mathrm{H)I}$	10.87 (10.93)	10.68 (10.39)		4.18 (300)
$\mathrm{Co(H_3}SS\mathrm{H)SCN}$	12.14 (12.53)	15.00 (14.89)		3.59 (300)
$\mathrm{Co(H_3}SG\mathrm{H)Cl \cdot 2\,H_2O}$	11.60 (11.84)	11.01 (11.26)	7.30 (7.12)	4.81 (300)
$\mathrm{Co(H_3}SG\mathrm{H)Br \cdot 2\,H_2O}$	10.60 (10.86)	9.99 (10.33)	14.54 (14.74)	4.77 (300)
$\mathrm{Co(H_3}SG\mathrm{H)I}$	10.70 (10.65)	11.09 (10.13)		4.18 (300)
$\mathrm{Co(H_3}SG\mathrm{H)SCN}$	11.55 (12.16)	13.70 (14.46)		4.49 (300)
$\mathrm{Co(H_3}SA\mathrm{H)Cl}$	11.80 (12.38)	11.40 (11.78)	7.12 (7.45)	4.89 (300)
$\mathrm{Co(H_3}SA\mathrm{H)Br}$	11.17 (11.33)	11.54 (10.77)	15.15 (15.36)	4.77 (287)
$\mathrm{Co(H_3}SA\mathrm{H)I \cdot 2\,H_2O}$	9.32 (9.77)	10.20 (9.30)		4.55 (300)
$\mathrm{Co(H_3}SA\mathrm{H)SCN}$	12.18 (11.83)	13.60 (14.05)		4.42 (300)
$\mathrm{Co(H_3}SP\mathrm{H)Cl}$	12.63 (12.03)	11.09 (11.44)	7.10 (7.24)	
$\mathrm{Co(H_3}SP\mathrm{H)Br \cdot 2\,H_2O}$	9.94 (10.33)	9.94 (9.82)	13.90 (14.01)	4.37 (287)
$\mathrm{Co(H_3}SP\mathrm{H)I \cdot 4\,H_2O}$	8.61 (9.02)	9.06 (8.58)		4.48 (300)
$\mathrm{Co(H_3}SP\mathrm{H)SCN}$	12.10 (11.50)	13.20 (13.67)		
$\mathrm{Co_3(H_3}SA\mathrm{H)_2Cl_4}$	16.30 (16.39)	10.40 (10.36)	13.01 (13.12)	9.65 (292) 3.22
$\mathrm{Co_2(H_2}SS\mathrm{H)Cl_2}$	22.02 (21.78)	9.62 (10.35)	13.20 (13.11)	5.68 (300) 2.84
$\mathrm{Co(H_2}SM\mathrm{H) \cdot 4\,H_2O}$	11.60 (12.50)	12.04 (11.90)		3.61 (301)
$\mathrm{Co(H_2}SS\mathrm{H)}$	14.10 (14.33)	12.94 (13.62)		3.68 (300)
$\mathrm{Co(H_2}SG\mathrm{H)}$	13.80 (13.85)	12.90 (13.17)		3.25 (300)
$\mathrm{Co(H_2}SA\mathrm{H)}$	14.37 (13.41)	12.43 (12.75)		4.13 (300)
$\mathrm{Co(H_2}SP\mathrm{H) \cdot 4\,H_2O}$	11.73 (11.24)	11.69 (10.69)		4.11 (300)
$\mathrm{Co(H_3}SS\mathrm{H)_2}$	8.50 (7.69)	14.27 (14.63)		4.85 (300)
$\mathrm{Co(H_3}SA\mathrm{H)_2}$	7.07 (7.17)	12.72 (13.63)		

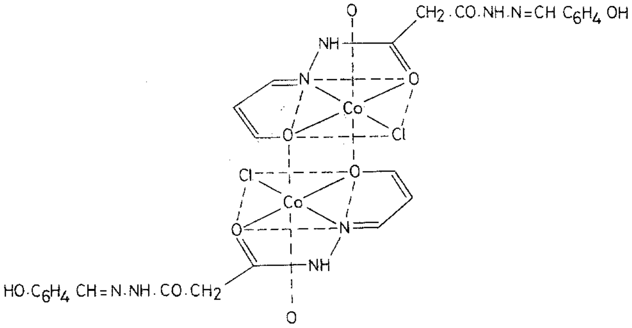
Figures in parentheses indicate the required percentage.

Table 2. *The infrared spectra of bis(N-salicylidene)dicarboxylic acid dihydrazides and their cobalt(II) chelates*

Compound	NH	Amide (C=O) free	Amide (C=O) coord	(C=N) free	(C=N) coord	Amide II	(C—O)
H_4*SM*H	3200	1675 vs		1660 s		1555	1535 wsh
Co(H_3*SM*H)Cl	3200	1670 s	1620	1650 vs	1610	1550	1540 sh
Co(H_2*SM*H)·4 H_2O	3250		1620		1600	1550	
H_4*SS*H	3210	1679 vs		1665		1555	
Co(H_3*SS*H)Cl·2 H_2O	3180		1640 m		1610	1558	
Co(H_3*SS*H)Br·2 H_2O	3200		1640		1610	1540	
Co(H_3*SS*H)I	3200		1640		1615	1530	
Co(H_3*SS*H)SCN	3200		1650 m		1605	1550	
Co_2(H_2*SS*H)Cl_2	3200		1625		1610	1540	
Co(H_2*SS*H)	3200		1630		1610	1540	
Co(H_3*SS*H)$_2$	3210	1670	1620	1660	1610	1560	
H_4*SG*H	3200	1670 vs		1620 vs		1550	1540 w
Co(H_3*SG*H)Cl·2 H_2O	3200		1610		1600	1540	
Co(H_3*SG*H)Br·2 H_2O	3200		1620		1605	1545	
Co(H_3*SG*H)I	3200		1620		1600	1540	
Co(H_3*SG*H)SCN	3200		1620		1600	1550	
Co(H_2*SG*H)	3200		1610		1600	1540	
H_4*SA*H	3200	1670		1650		1550	1540 sh
Co(H_3*SA*H)Cl	3200		1620		1605	1550	1530 sh
Co(H_3*SA*H)Br	3200		1620		1610	1530	1520 sh
Co(H_3*SA*H)I·2 H_2O	3200		1620		1610	1540	
Co(H_3*SA*H)SCN	3200		1610		1600	1540	
Co_3(H_3*SA*H)$_2$$Cl_4$	3200		1615		1610	1545	
Co(H_2*SA*H)	3200		1610		1600	1550	
Co(H_3*SA*H)$_2$	3210	1670	1620	1660	1610	1540	
*SP*H	3220	1680		1660		1560	1545 sh
Co(H_3*SP*H)Cl	3200		1610		1600	1550	1540 sh
Co(H_3*SP*H)Br·2 H_2O	3200		1610		1600	1540	1520 sh
Co(H_3*SP*H)I·4 H_2O	3200		1615		1605	1540	1520 sh
Co(H_3*SP*H)SCN	3200		1620		1605	1550	1530 sh
Co(H_2*SP*H)·4 H_2O	3200		1640		1600	1540	1520 sh

Coordination to the cobalt(II) ion takes place via the azomethine nitrogen, the carbonyl oxygen and the deprotonated phenolic oxygen of one salicylidene acid hydrazide unit.

The Nujol mull electronic spectrum of Co(H_3*SM*H)Cl (Table 3, as well as its magnetic moment are in accordance with an octahedral structure[2], which may be achieved through polymerization as shown in structure **2**. Cationic complexes of the same type Co(H_3*Lig*)*X*·*n*H_2O with all the other acid dihydrazide ligands (H_4*SS*H, H_4*SG*H, H_4*SA*H and H_4SPH) possess almost identical i.r. spectra but quite different from those obtained for $Co(H_3SMH)Cl$. The bands characteristic of ν (N—H), amide I [ν (C=O)] and amide II were easily identified. Both amide I and ν (C=N) bands are shifted to lower frequencies as compared to the parent organic ligands (Table 2), the absence of bands due to uncoordinated ν (C=O) and ν (C=N) groups, exhibited by $Co(H_3SMH)Cl$, reveals that both *N*-salicylidene acid hydrazide units are involved in chelation. Their electronic spectra (Table 3), suggest octahedral environment around the Co(II) ion. The position of the d-d absorption bands were found to be sensitive to the nature of *X*. A shift to lower frequencies occurs in the order NCS > Cl > Br > I in accordance with the field strength of these ligands in the spectrochemical series[6]. The position of the NCS group in this series indicates that coordination takes place via the nitrogen atom. The appearance of ν (C≡N) stretching band at 2 110 cm^{-1} is consistent with this assignment[7]. It seems that the hydrazone molecule **1** ($n = 2$, 3, 4 and 5) in these chelates acts as a monobasic pentadentate ligand with a free phenolic group, the sixth coordination site is occupied by the mononegative ion *X* as depicted in structure **3**.



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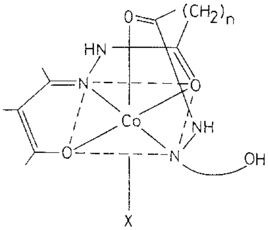

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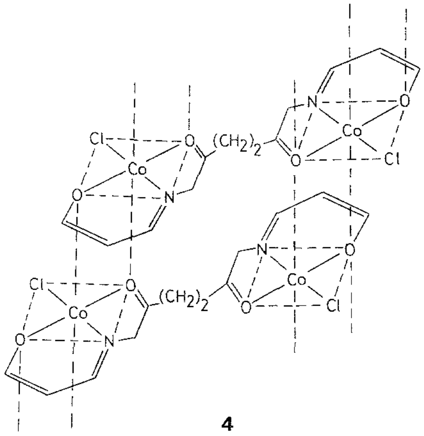
Table 3. *Nujol mull electronic spectra of cobalt(II) chelates*

Compound	Band maxima (nm)					
$\mathrm{Co(H_3}Lig\mathrm{)}X\cdot n\mathrm{H_2O}$						
$\mathrm{Co(H_3}SM\mathrm{H)Cl}$	620,	675,	950 b			
$\mathrm{Co(H_3}SS\mathrm{H)Cl\cdot 2\,H_2O}$	630,	675,	975 b			
$\mathrm{Co(H_3}SS\mathrm{H)Br\cdot 2\,H_2O}$	500 sh,	610,	720 sh,	920 b		
$\mathrm{Co(H_3}SS\mathrm{H)I}$	600,	650,	715 sh			
$\mathrm{Co(H_3}SS\mathrm{H)SCN}$	530 sh,	620,	820 sh			
$\mathrm{Co(H_3}SG\mathrm{H)Cl\cdot 2\,H_2O}$	520 sh,	620,	670,	700 b		
$\mathrm{Co(H_3}SG\mathrm{H)Br\cdot 2\,H_2O}$	550,	600,	700 b			
$\mathrm{Co(H_3}SG\mathrm{H)I}$	525,	580 sh,	880 b			
$\mathrm{Co(H_3}SG\mathrm{H)SCN}$	575,	615,	880 b			
$\mathrm{Co(H_3}SA\mathrm{H)Cl}$	520 sh,	650,	900 b			
$\mathrm{Co(H_3}SA\mathrm{H)Br}$	510 sh,	610,	700,	920 b		
$\mathrm{Co(H_3}SA\mathrm{H)I\cdot 2\,H_2O}$	515 sh,	715 sh,	775			
$\mathrm{Co(H_3}SA\mathrm{H)SCN}$	580,	620,	635,	925 b		
$\mathrm{Co(H_3}SP\mathrm{H)Cl}$	650,	790				
$\mathrm{Co(H_3}SP\mathrm{H)Br\cdot 2\,H_2O}$	530 sh,	680,	840 b			
$\mathrm{Co(H_3}SP\mathrm{H)I\cdot 4\,H_2O}$	540 sh,	800 b				
$\mathrm{Co(H_3}SP\mathrm{H)SCN}$	510 sh,	610,	830 b			
$\mathrm{Co_3(H_3}SA\mathrm{H)Cl_4}$	500 sh,	625 sh,	675,	800 b,	900 b	
$\mathrm{Co_2(H_2}SS\mathrm{H)Cl_2}$	450 sh,	525 sh,	625 sh,	675,	800 b,	915
$\mathrm{Co(H_2}Lig\mathrm{)}$						
$\mathrm{Co(H_2}SS\mathrm{H)}$	550 sh,	600 sh,	775 b,	925 b		
$\mathrm{Co(H_2}SG\mathrm{H)}$	525 sh,	600 sh,	780 b,	925 b		
$\mathrm{Co(H_2}SA\mathrm{H)}$	500 sh,	625 sh,	850 b			
$\mathrm{Co(H_2}SP\mathrm{H)}$	525 sh,	610 sh,	775 b,	875 b		

sh shoulder, b broad band.

The fact that only one salicylidene hydrazide residue is coordinated to Co(II) ion in $\mathrm{Co(H_3}SM\mathrm{H)Cl}$ chelate is most probably due to the rigidity of the organic ligand. However by lengthening the chain between the two *N*-salicylidene units in the succinic, glutaric, adipic and pimelic acid derivatives, the molecule becomes more flexible and can accomodate itself in an octahedral arrangement around the central cobalt(II) ion without much strain.

The infrared spectra of the cationic polynuclear chelates $\mathrm{Co_2(H_2}SS\mathrm{H)Cl_2}$ and $\mathrm{Co_3(H_3}SA\mathrm{H)_2Cl_4}$ are more or less identical and show bands due to ν (N—H), ν (C=O) and ν (C=N) (Table 2), implying that both hydrazone residues react in the keto form. The stoichiometry of $\mathrm{Co_2(H_2}SS\mathrm{H)Cl_2}$, however, reveals the deprotonation of both phenolic groups and the ligand acts as a dinegative anion. Electronic spectrum of $\mathrm{Co_2(H_2}SS\mathrm{H)Cl_2}$, on the other hand, suggests that the dinegative anion $\mathrm{(H_2}SS\mathrm{H)^{2-}}$ is arranged octahedrally around the two Co(II) ions and structure **4** can be adopted for this chelate. The Nujol mull electronic spectrum of $Co_3(H_3SAH)_2Cl_4$ (Table 3), shows an intense splitted band



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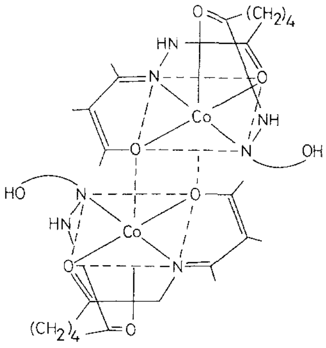
at 670 nm diagnostic of tetrahedral $(CoCl_4)^{2-}$ [8–10] besides those characteristic of octahedral Co(II) at 520 nm. Accordingly it seems reasonable to consider this chelate as $[Co_2(H_3SAH)_2]$ $(CoCl_4)$ and the arrangement of the ligand in this polynuclear chelate can be adequatly represented by structure **5**.



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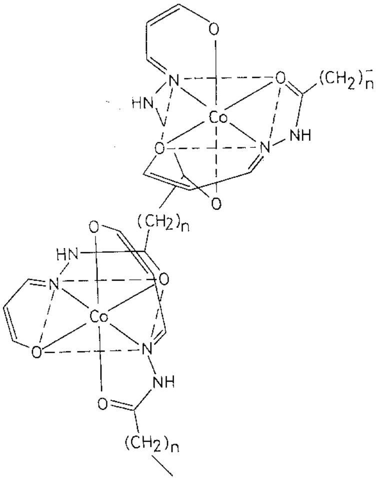
Inner chelates of the types $Co(H_2Lig) \cdot nH_2O$ and $Co(H_3Lig)_2 \cdot nH_2O$ were formed from the reaction of $Co(OAc)_2$ with the ligands in the proper molar ratio. The i.r. spectra of $Co(H_2Lig) \cdot nH_2O$ show a well developed band at 3 200 cm^{-1} due to ν (N—H) stretching besides bands due to coordinated C=O and C=N. The octahedral environment around Co(II) as indicated by their electronic spectra (Table 3), can be represented by structure **6** where the dihydrazone molecule behaves as dibasic hexadentate ligand attached to two different cobald(II) ions in a polymeric chain. The i.r. spectra of $Co(H_3Lig)_2 \cdot nH_2O$ on the contrary show both coordinated and free $C=O$ and $C=N$ bands and can best be represented by structure **7** where the ligand behaves as monobasic tridentate molecule.



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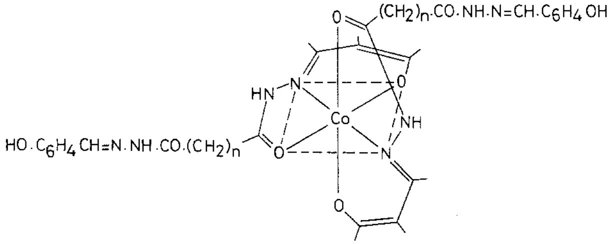

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Experimental

Preparation of Organic Ligands

Dicarboxylic acid dihydrazides and bis(*N*-salicylidene) dicarboxylic acid dihydrazides were obtained using the same procedures previously described[1].

Preparation of Cobalt(II) Chelates

$Co(H_3Lig)Cl \cdot nH_2O$ *Chelates*

To a solution of $CoCl_2 \cdot 6H_2O$ (0.01 mol) in ethanol (25 ml) was added a solution of salicylaldehyde (0.02 mol) in ethanol (25 ml) and a solution of the dicarboxylic acid dihydrazide (0.01 mol) in water (5 ml). This mixture was then refluxed for 1 h with constant stirring. The crystalline product which separated out on cooling was filtered, washed succesively with hot ethanol and ether then dried in vacuum.

$Co(H_3Lig)X \cdot nH_2O$ (X = Br, I *or* SCN) *Chelates*

A solution of $Co(NO_3)_2 \cdot 6\,H_2O$ (0.01 mol) in ethanol (25 ml) was treated with a hot solution of NH_4Br, (0.025 mol) in ethanol (20 ml). The resulting solution was cooled (0 °C) then filtered. To this filtrate, a solution of salicylaldehyde (0.02 mol) in ethanol (20 ml) was added followed by a solution of the dicarboxylic acid dihydrazide (0.01 mol) in water (5 ml). The reaction mixture was refluxed for 1 h then evaporated to half its volume. On cooling, the bromo complex which separated out was filtered, washed with ethanol and dried in vacuum. The iodo and thiocyanato complexes were similarly prepared, by using NH_4I and NH_4SCN respectively.

$Co_2(H_2SSH)Cl_2$ *Chelate*

A solution of $CoCl_2 \cdot 6\,H_2O$ (0.025 mol) in ethanol (50 ml) was refluxed for 15 min with salicylaldehyde (0.02 mol). To this boiling mixture, a solution of the dihydrazide (0.01 mol) in water (5 ml) was added with constant stirring. The whole mixture was then refluxed for 2 h; during this period, the green chelate separated out. After cooling the chelate was filtered, washed with ethanol and then dried in vacuum.

$Co_3(H_3SAH)_2Cl_4$ *Chelate*

This green complex was prepared using the same procedure described for $Co_2(H_3SSH)Cl_2$.

$Co(H_2Lig) \cdot nH_2O$ *Chelates*

A boiling solution of $Co(OAc)_2$ $4\,H_2O$ (0.01 mol) in ethanol (50 ml) was stirred for 15 min with salicylaldehyde (0.02 mol). This solution was then treated with a solution of the dihydrazide (0.01 mol) in water (5 ml). The reaction mixture was refluxed for 3 h with constant stirring, during this period, the cobalt(II) chelates of the general formula $Co(H_2Lig) \cdot nH_2O$ separated out, were filtered, washed successively with ethanol and ether then dried in vacuum.

$Co(H_2Lig)_2 \cdot nH_2O$ *Chelates*

This type of chelates was prepared by the same procedure used for $Co(H_2Lig) \cdot nH_2O$ chelates but the molar ratio of cobalt(II) acetate:salicylaldehyde:dihydrazide was 1:4:2.

Elemental Analyses

Cobalt(II) content was determined by *EDTA* titration using *EBT* as indicator[11]. The nitrogen and halogen analyses were carrried out at the microanalyses laboratory, Faculty of Science, Cairo University. The results are collected in Table 1.

Physical measurements

Magnetic, infrared and spectral data were obtained using the procedure previously described[1] (Tables 2 and 3).

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