Monatshefte für Chemie 110, 663—676 (1979)

Monatshefte für Chemie

Ligational Behaviour of Thiosemicarbazide and Thiosemicarbazone-(III): Tetragonal Complexes of Cobalt(II) Derived From 4-Benzylamidothiosemicarbazide and 1-(α-) Furyl-4-Benzylamidothiosemicarbazone

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(Received 13 December 1977. Accepted 23 January 1978)

A number of new complexes of cobalt(II) have been prepared with 4-benzylamidothiosemicarbazide (*BTSC*) and 1-(α-)furyl-4-benzylamidothiosemicarbazone (*FBTS*) which conform to the general formula $\mathrm{Co}L_2X_2$ (where $L = BTSC$ and *FBTS* and $X =$ Cl, Br, I, NO_3 and NCS). These have been characterized by chemical analyses and physical measurements. The tetragonal symmetry has been proposed on the basis of electronic spectral studies for all these complexes. The explanation for the slightly lower magnetic moments for cobalt(II) complexes has been sought in the possible presence of low symmetry component. The tetragonal radial parameters $Dq(E)$, $Dq(A)$, Dt and Ds and molecular orbital parameters dπ and dσ have been evaluated. The S—N, bidentate nature of the ligands and the presence of the various anions in the coordination sphere have been confirmed on the basis of additional Co—N, Co—S and Co—X frequencies in the far infrared spectra of the complexes. The nitrato and thiocyanato groups act as monodentate and are coordinated through oxygen and nitrogen atoms, respectively.

[Keywords: Cobalt(II) complexes; Coordination chemistry; Magnetic data]

Thiosemicarbazide und Thiosemicarbazone als Liganden III. Tetragonale Kobalt(II)-Komplexe mit 4-Benzylamidothiosemicarbazid und 1-(α-)Furyl-4-benzylamidothiosemicarbazon

Es wurden eine Anzahl von neuen Kobalt(II)-Komplexen von 4-Benzylamidothiosemicarbazid (*BTSC*) und 1-(α-)Furyl-4-benzylamidothiosemicarbazon (*FBTS*) von der allgemeinen Zusammensetzung $\mathrm{Co}L_2X_2$ ($L = BTSC$, *FBTS*; $X =$ Cl, Br, I, NO_3 and NCS) synthetisiert. Die Untersuchungen erfolgten mittels Elementaranalyse, magnetischer Messungen, Elektronenanregungsspektroskopie und IR-Spektroskopie (einschließlich des fernen IR); aus diesen Messungen ließ sich eine im wesentlichen tetragonale Symmetrie für alle Komplexe dieser Reihe ableiten.

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0026-9247/79/0110/0663/$ 02.80

Table 1. *Analytical data of cobalt(II) complexes*

Complex	μ_{eff} BM	Observed percentage of					Calculated percentage of				
		C	H	N	M	X	C	H	N	M	X
$Co(C_9H_{12}N_4OS)_2 Cl_2$	4.64	37.45	4.18	19.47	10.31	12.03	38.38	4.15	19.38	10.20	12.11
$Co(C_9H_{12}N_4OS)_2 Br_2$	4.66	32.69	3.65	16.62	8.89	23.73	32.39	3.60	16.79	8.84	23.97
$Co(C_9H_{12}N_4OS)_2 I_2$	4.61	28.61	3.34	14.79	7.65	33.50	28.39	3.15	14.72	7.75	33.36
$Co(C_9H_{12}N_4OS)_2 (NO_3)_2$	4.63	34.12	3.82	22.17	9.32	—	34.23	3.80	22.19	9.34	—
$Co(C_9H_{12}N_4OS)_2 (NCS)_2$	4.57	38.45	3.82	22.48	9.41	—	38.52	3.85	22.47	9.46	—
$Co(C_{14}H_{14}N_4O_2S)_2 Cl_2$	4.62	45.69	3.85	15.25	8.01	9.78	45.79	3.81	15.26	8.03	9.66
$Co(C_{14}H_{14}N_4O_2S)_2 Br_2$	4.61	40.19	3.37	13.65	7.19	19.47	40.84	3.40	13.61	7.16	19.42
$Co(C_{14}H_{14}N_4O_2S)_2 I_2$	4.65	36.62	3.09	12.27	6.34	27.45	36.65	3.05	12.22	6.43	27.68
$Co(C_{14}H_{14}N_4O_2S)_2 (NO_3)_2$	4.59	42.65	3.51	17.81	7.52	—	42.70	3.56	17.79	7.49	—
$Co(C_{14}H_{14}N_4O_2S)_2 (NCS)_2$	4.60	46.32	3.49	17.99	7.54	—	46.21	3.60	17.97	7.56	—

Introduction

In our previous communications[1–4] 4-benzylamidothiosemicarbazide and 1-(α-)furyl-4-benzylamidothiosemicarbazone have been reported as chelating agents for a number of salts of various transition metal ions since both the ligands contain nitrogen and thioketo-sulphur atoms ideally situated for chelation. The present communication describes the isolation and characterization of the cobalt(II) complexes derived from 4-benzylamidothiosemicarbazide and 1-(α-)furyl-4-benzylamidothiosemicarbazone by means of chemical analyses, magnetic measurements, electronic and infrared including far infrared spectral studies.

Results and Discussion

All the cobalt(II) complexes of both the ligands exhibit rather low magnetic moments in the range 4.66–4.57 BM at room temperatures. The magnetic moment of Co(II) ion having a $^4T_{1g}$ ground term in the octahedral field is expected to be associated with large orbital contribution showing values as large as 5.36 BM. It was in the fitness of things to examine the dependance of magnetic moment on temperature for this series of complexes and therefore as a representative complex Co(*BTSC*)$_2$Cl$_2$ was subjected to low temperature (down to liquid nitrogen temperature) magnetic susceptibility measurements and was found to obey *Curie-Weiss* law with a small value of θ (2K). The lower magnetic moments can be explained on the basis of the presence of low symmetry components which tend to quench the orbital contribution and the value approaches the spin-only value. In such a situation the dependance of magnetic moment on temperature also tends to decrease. This behaviour of the magnetic moment with temperature for the present chloro complex of *BTSC* points towards the presence of low symmetry components[5] where as the orbital contribution has been quenched to a considerable extent.

Table 2. *Magnetic data of* Co(*BTSC*)$_2$Cl$_2$ *at various temperatures*

Temperature (K)	$\chi_{M'} \times 10^6$(cgs)	μ_{eff} (BM)
80	31,614	4.50
96	26,527	4.51
117	21,892	4.53
154	16,966	4.57
203	13,003	4.60
295	9,115	4.64

In octahedral symmetry the Cobalt(II) ion having the ground term $^4T_{1g}$ exhibits[6] three spin-allowed bands conforming to the transitions $^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ (ν_1); $^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ (ν_2) and $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ (ν_3). In D_{4h} symmetry, however, the ν_1 band is observed to split into two[7,8] components ($^4B_{2g}$, ^4E_g) to the extent depending upon the magnitude of distortion produced by the axial ligands. Further in this symmetry[7,8] the ν_3 band is also expected to split giving rise to the terms $^4A_{2g}$, ^4E_g [$^4T_{1g(P)}$ in octahedral field] and the $^4B_{1g}$ transition [coming from $^4A_{2g(F)}$ octahedral] is usually too weak to be observed. In the electronic spectra of the complexes under study the splitting of ν_1 and ν_3 bands have been observed in all the cases but for $[Co(BTSC)_2(NO_3)_2]$ and $[Co(FBTS)_2(I)_2]$ in which only ν_1 has been found to split. Thus four bands have been observed in all the cases (except for the above two complexes) in the range 7,270-6,350 cm^{-1} (ν_1), 9,280-8,580 cm^{-1} (ν_1), 18,690-17,240 cm^{-1} (ν_3) and 24,000-23,260 cm^{-1} (ν_3) which have been assigned on the basis of D_{4h} symmetry as $^4T_{1g(F)} \rightarrow {}^4B_{2g}$ (ν_1); $^4T_{1g(F)} \rightarrow {}^4E_g$ (ν_1); $^4T_{1g(F)} \rightarrow {}^4E_g$ (ν_3) and $^4T_{1g(F)} \rightarrow {}^4A_{2g}$ (ν_3).

Following the above assignments the calculations for the tetragonal radial parameters *Ds* and *Dt* have been made using the equations suggested by *Ballhausen*[9]. In the absence of the splitting of the ν_3 band in the two complexes referred to in above, the value of *Ds* could not be obtained. The value of *Dq*(*E*) cannot be evaluated directly from any transition but an attempt has been made to obtain this value from an approximation $10\,Dq = f$ (ligand) $\times\, g$ (metal). In the present case the value of 'f' for the ligands under study has been obtained by substituting[10] *Dq*(*E*) and *g* for the corresponding nickel(II) complexes[3]. The values of *Dq*(*A*) have been calculated by using the equation $Dq(A) = Dq(E) — 7/4\,Dt$. All the ligand field parameters have been cited in Table 3. From the perusal of the table it is apparent that the value of *Dt* increases from chloro complexes to thiocyanato complexes via nitrato complexes. A series for the anions based on the values *Dq*(*E*) has been drawn which agrees well with the one obtained for nickel(II) and copper(II) complexes of similar ligands[1,3] and is $Cl < Br < I < NO_3 < NCS$. The molecular obital parameters $d\pi$ and $d\sigma$ have also been calculated[10] and recorded in Table 3.

Infrared Spectral Studies

Infrared spectral frequencies of the ligands and their cobalt(II) complexes along with tentative assignments for the important ones have been given in Tables 4 and 5. These assignments are based on the corresponding thiosemicarbazides and thiosemicarbazones and their metal complexes[11–12].

Table 3. *Electronic spectral data of* Co(II) *complexes of BTSC and FBTS*

Complex	$^4T_{2g}$					$Dq(E)$	$Dq(A)$	Dt	$-Ds$	$(d\pi\text{-}d\sigma)$	$d\sigma$	$d\pi$
	$^4B_{2g}(\nu_1)$	$^4E_g(\nu_2)$	$^4B_{1g}(\nu_2)$	$^4E_g(\nu_3)$	$^4A_{2g}(\nu_3)$							
Co(*BTSC*)$_2$Cl$_2$	7270	9250	16390 sh	18600	23530	1118	723	226	1266	989	1475	2464
Co(*BTSC*)$_2$Br$_2$	6990	9010	17240 sh	18520	23670	1133	731	230	1333	1006	1568	2575
Co(*BTSC*)$_2$I$_2$	7120	9220	—	18180	23530	1143	723	240	1383	1050	1624	2674
Co(*BTSC*)$_2$(NO$_3$)$_2$	6470	8730	—	20620		1178	727	258	—	1129	1745	2849
Co(*BTSC*)$_2$(NCS)$_2$	6350	8660	16670 sh	17240	23530	1223	761	264	1657	1155	1990	3145
Co(*FBTS*)$_2$Cl$_2$	7250	9260	—	18680	23260	1122	722	229	1141	1002	1282	2284
Co(*FBTS*)$_2$Br$_2$	6940	9010	16390 sh	18520	23810	1131	718	236	1366	1033	1606	2639
Co(*FBTS*)$_2$I$_2$	7140	9190	—	20830		1147	719	245	—	1072	1633	2705
Co(*FBTS*)$_2$(NO$_3$)$_2$	6370	8580	15040 sh	18260	23810	1194	753	252	1430	1103	1672	2775
Co(*FBTS*)$_2$(NCS)$_2$	6480	8730	15270 sh	17290	23530	1220	771	257	1652	1124	1996	3121

Table 4. *Infrared spectral bands of the*

BTSC (1)	Co(*BTSC*)$_2$Cl$_2$ (2)	Co(*BTSC*)$_2$Br$_2$ (3)	Co(*BTSC*)$_2$I$_2$ (4)
3290 (s)	3230 (m)	3060 (m)	3240 (m)
3245 (s)	3200 (m)	3200 to	3225 (m)
3160 (s)	3110 (s)	3085 (br.n)	3080 (m)
3090 (s)	3050 (m)	3040 (w)	3025 (m)
3040 (s)			
2940 (m)	2940 (m)	2937 (m)	2945 (m)
—	—	—	—
—	—	—	—
—	—	—	—
1625 (s)	1600 (s)	1607 (s)	1605 (s)
1565 (s)	1560 (s)	1562 (s)	1565 (s)
1495 (s)	1492 (m)	1495 (m)	1497 (m)
1450 (s)	1455 (s)	1450 (m)	1445 (s)
1420 (s)	1430 (m)	1430 (s)	1425 (s)
1365 (m)	1358 (m)	1362 (m)	1355 (m)
1335 (m)	1330 (s)	1335 (s)	1330 (sh.w)
1315 (m)	1310 (w)	—	1320 (m)
1290 (s)	1268 (s)	1270 (s)	1265 (m)
1230 (m)	1220 (m)	1225 (w)	1235 (m)
1200 (w)	—	1200 (w)	1200 (w)
1080 (m)	1075 (m)	1078 (m)	1072 (sh.m)
1070 (sh.m)	1055 (s)	1060 (sh.w)	1062 (s)
1050 (s)	—	1042 (m)	—
1035 (sh.s)	1030 (m)	1025 (m)	1030 (m)
970 (m)	972 (m)	970 (m)	965 (s)
955 (s)	950 (m)	960 (m)	955 (m)
920 (w)	925 (w)	—	—
900 (w)	—	900 (w)	900 (w)
795 (m)	790 (m)	792 (m)	785 (m)
755 (m)	752 (m)	755 (m)	760 (m)
730 (s)	728 (s)	730 (s)	728 (s)
715 (s)	710 (s)	712 (m)	709 (s)
685 (s)	687 (s)	685 (s)	682 (sh.s)
670 (s)	672 (s)	675 (s)	672 (s)
658 (m)	655 (s)	660 (m)	662 (sh.s)
632 (s)	627 (s)	635 (s)	628 (s)
		617 (w)	
572 (s)	570 (m)	587 (w)	574 (m)
542 (s)	540 (m)	572 (m)	540 (w)
		540 (w)	
487 (s)	485 (m)	480 (m)	486 (s)
480 (sh.m)	469 (w)	472 (sh.w)	462 (sh.m)
—	432 (m)	428 (m)	430 (m)
	412 (w)		410 (w)

complexes of cobalt (II) with BTSC

Co($BTSC$)$_2$(NO$_3$)$_2$ (5)	Co($BTSC$)$_2$(NCS)$_2$ (6)	Tentative Assignments (7)
3240 (m)	3280 to	
3220 (s)	3110 (br. m)	NH and NH$_2$ stretch
3150 (m)	3060 (m)	
3045 (m)	—	
2940 (m)	2935 (m)	ν(CH$_2$)
—	2070 (s)	ν(CN) of NCS
1758 (m)	—	unidentate Nitrate
1742 (m)	—	
1595 (s)	1610 (s)	Amide-I and NH$_2$ bend
1575 (s)	1570 (s)	Amide-II and CN starch
1535 (m)	1497 (m)	
1490 (m)	1480 (w)	
1457 (m)	1450 (s)	
1410 (m)	1425 (m)	
1360 (m)	1362 (m)	
1330 (m)	1325 (m)	
1305(w)	1310 (w)	
1275 (s)	1280 (s)	CS and CN stretch
1265 (m)	1232 (m)	Amide (III)
—	1195 (w)	
1065 (m)	1085 (m)	
1055 (m)	1065 (m)	N—C—N stretch and C=S stretch
—	1037 (w)	
1025 (s)	1020 (m)	
1000 (w)		
962 (m)	965 (m)	
945 (w)	950 (w)	NN stretch
910 (w)	910 (w)	
—	865 (m)	
790 (m)	787 (m)	
752 (w)	755 (w)	δ(NCO)
732 (s)	725 (s)	CS and CN stretch
712 (m)	710 (s)	
680 (s)	690 (s)	
665 (s)	672 (s)	
655 (sh. m)	660 (m)	(C=O) out of planebend
640 (s)	632 (s)	
572 (s)	572 (m)	ν(C=S)
560 (m)	562 (w)	ν(C—C)
545 (w)	540 (w)	
490 (m)	490 (m)	
475 (m)	480 (sh. m)	ring deformation
	460 (m)	
432 (m)	427 (m)	ν(Co—N)
382 (m)	385 (m)	
	370 (sh. w)	

Table 4 (continued)

BTSC (1)	Co(*BTSC*)$_2$Cl$_2$ (2)	Co(*BTSC*)$_2$Br$_2$ (3)	Co(*BTSC*)$_2$I$_2$ (4)
378 (m)	376 (m)	372 (m)	380 (m)
340 (w)			
—	338 (m)	335 (m)	338 (m)
—	307 (m)	302 (w)	298 (w)
300 (m)	282 (w)	285 (w)	282 (w)
—		272 (w)	—
—	230 (m) (Co—Cl)	—	—
—	—	217 (w) (Co—Br)	—

Table 5. *Infrared spectral bands of the*

FBTS (1)	Co(*FBTS*)$_2$Cl$_2$ (2)	Co(*FBTS*)$_2$Br$_2$ (3)	Co(*FBTS*)$_2$I$_2$ (4)
3140 (s)	3120 (s)	3125 (s)	3190 (w)
3090 (s)	3080 (m)	3080 (s)	3080 (s)
3040 (s)	3060 (m)	3055 (s)	3045 (s)
		3025 (m)	
2935 (m)	2937 (m)	2940 (m)	2935 (m)
—	—	—	—
—	—	—	—
1615 (s)	1617 (s)	1620 (s)	1617 (s)
1575 (s)	1547 (s)	1545 (m)	1550 (m)
1500 (s)	1495 (m)	1500 (m)	1497 (m)
1475 (s)	1470 (m)	1472 (m)	1478 (s)
1455 (s)	1445 (m)	1442 (s)	1440 (m)
1430 (m)	1420 (m)	1415 (m)	1420 (w)
1415 (s)	—	1405 (w)	—
1395 (s)	1390 (s)	1392 (s)	1390 (s)
1340 (m)	1350 (m)	1340 (m)	1352 (w)
1325 (w)	1320 (m)	—	1330 (w)
			1315 (w)
1280 (s)	1267 (m)	1265 (m)	1270 (m)
1235 (w)	1235 (w)	1232 (sh. w)	1240 (w)
1200 (m)	1200 (w)	1205 (m)	1200 (w)
1155 (m)	1152 (m)	1150 (m)	1148 (m)
1100 (w)	—	—	—
1070 (s)	1075 (s)	1080 (s)	1072 (s)
1025 (m)	—	1020 (w)	1015 (s)
1015 (s)	1015 (m)	1010 (m)	—

$Co(\mathit{BTSC})_2(NO_3)_2$ (5)	$Co(\mathit{BTSC})_2(NCS)_2$ (6)	Tentative Assignments (7)
335 (m)	332 (w)	ν(Co—S)
320 (w)	307 (w)	
312 (w)	290 (w)	
285 (w)	—	ν(Co—x)
270 (w)	240 (w) (Co—NCS)	
220 (w)	220 (w)	

complexes of cobalt (II) with FBTS

$Co(\mathit{FBTS})_2(NO_3)_2$ (5)	$Co(\mathit{FBTS})_2(NCS)_2$ (6)	Tentative Assignment (7)
3135 (s)	3120 (s)	
3085 (s)	3055 (s)	ν(NH)
3045 (s)	3025 (s)	
3015 (s)		
2935 (m)	2940 (m)	$\nu(CH_2)$
—	2065 (s)	ν(CN) of NCS
1752 (m)	—	unidentate nitrate
1743 (m)	—	
1615 (s)	1620 (s)	Amide-I
1552 (m)	1565 (m)	Amide-II^+ (CN)
1495 (m)	1492 (m)	
1472 (s)	1470 (s)	
1450 (sh.m)	1442 (m)	
1435 (m)	—	
1410 (w)	1417 (m)	
1392 (s)	1395 (m)	
1345 (m)	1340 (m)	
1322 (m)	1325 (w)	
1272 (m)	1267 (m)	CS and CN stretch
1262 (m)	1230 (w)	Amide III
1240 (w)	1210 (s)	
1200 (w)		
1150 (s)	1055 (m)	
—	1095 (w)	
1075 (s)	1065 (m)	
1020 (s)	1017 (m)	NCN stretch and C=S stretch
—	1005 (m)	

Table 5 (continued)

FBTS (1)	Co(*FBTS*)$_2$Cl$_2$ (2)	Co(*FBTS*)$_2$Br$_2$ (3)	Co(*FBTS*)$_2$I$_2$ (4)
950 (m)	955 (m)	960 (s)	955 (m)
935 (s)	930 (s)	937 (s)	937 (s)
905 (w)		900 (w)	
885 (s)	882 (s)	885 (s)	880 (m)
845 (s)	842 (m)	847 (m)	840 (w)
835 (sh. m)	825 (m)	830 (w)	825 (w)
750 (s)	755 (s)	752 (s)	757 (s)
735 (s)	730 (s)	725 (s)	730 (m)
705 (s)	700 (m)	—	700 (s)
694 (s)	690 (s)	687 (m)	692 (m)
650 (s)	652 (s)	650 (s)	655 (m)
592 (s)	592 (s)	585 (s)	590 (s)
580 (sh. s)	576 (sh. s)	542 (m)	582 (sh. m)
548 (s)	545 (s)	518 (w)	542 (m)
	530 (w)	500 (m)	505 (w)
498 (s)	495 (w)	480 (w)	—
437 (m)	442 (m)	445 (m)	455 (w)
	435 (w)	438 (w)	
—	425 (m)	425 (w)	430 (m)
387 (m)		407 (w)	412 (w)
387 (m)	385 (w)	380 (w)	372 (w)
			360 (w)
—	348 (m)	350 (m)	346 (w)
346 (m)	328 (m)	322 (m)	305 (w)
330 (m)	318 (w)	315 (w)	292 (w)
255 (w)	265 (w)	308 (w)	
—	232 (w) (Co—Cl)	252 (w)	262 (w)
—	—	220 (w) (Co—Br)	250 (w)
—	—	—	230 (w)

The bands around 1,290 cm^{-1} have been assigned to ν (CS) vibrations. These vibrations do change either in energy or in intensity and in most of the cases intensity decreases as also the energy is lowered on complexation. These vibrations are not free from the contribution of other vibrations especially CN vibrations. The contribution of CN is greater to the band observed ~ 730 cm^{-1} and smaller to that observed at 1,290 cm^{-1}, since the former changes to smaller extent than the later. These changes in the frequencies of CS vibrations suggest that the thioketosulphur is taking part in coordination[13, 14].

The absorption bands in the region 3,290-3,040 cm^{-1} in infrared spectra of *BTSC* only have been assigned to the NH$_2$ and NH

$\mathrm{Co}(FBTS)_2(\mathrm{NO}_3)_2$ (5)	$\mathrm{Co}(FBTS)_2(\mathrm{NCS})_2$ (6)	Tentative Assignment (7)
995 (w)		
952 (m)	947 (m)	N—N stretch
935 (s)	930 (s)	
882 (s)	887 (s)	
835 (m)	870 (m)	
—	842 (m)	
790 (w)	828 (w)	
750 (s)	755 (m)	δ (NCO)
725 (m)	728 (m)	C=O and CN stretch
705 (w)	695 (m)	
685 (m)	690 (s)	
652 (m)	650 (s)	C=O out of plane bend
635 (w)		
590 (s)	592 (s)	
582 (sh.n)	—	ν (C=S)
540 (m)	540 (m)	ν (C—C)
522 (w)	498 (m)	
498 (w)	465 (w)	ring deformation
450 (w)	450 (w)	
427 (m)	425 (m)	ν (Co—N)
387 (w)	380 (w)	
362 (w)	362 (w)	
350 (w)	352 (w)	ν (Co—S)
320 (w)	322 (w)	
305 (w)	300 (w)	
280 (w)	—	
250 (w)	255 (w)	
235 (w)	245 (w) (Co—NCS)	
—	—	

vibrations[15]. Most of these vibrations shift to lower frequency as a result of the drainage of the electrons from terminal nitrogen atom of the NH.NH$_2$ group to the metal ion which is suggestive of the participation of terminal nitrogen atom in chelation.

A strong band at 1,625 cm^{-1} in *BTSC* has been observed due to the amide I and NH$_2$ bend[16]. On complexation this band shifts slightly (10–12 cm^{-1}) to lower frequency, as contribution of NH$_2$ group to this band is reduced, which suggests the participation of NH$_2$ group in chelation. On the other hand since the NH$_2$ group disappears during the thiosemicarbazone formation the amide I band is expected to be relatively free from the contribution of NH$_2$ bend and therefore it is observed at 1,615 cm^{-1} in *FBTS* (instead of 1,625 cm^{-1} as in *BTSC*). Furthermore, no change in the position of this band has been observed in *FBTS* complexes. Another strong band at 1,565 cm^{-1} in *BTSC* and 1,575 cm^{-1} in *FBTS* has been assigned to amide II and (CN) stretch vibrations[15]. In case of *BTSC* there is no change in the position of this band while in case of *FBTS* this band shifts either to low frequency (upto 20 cm^{-1}) or weakens in intensity (in few cases weakening and shift both occur). This indicates that the contribution of CN has been reduced as the nitrogen of CN group is involved in the bond formation with the metal ion.

The bands observed at $\sim$ 1,230 cm^{-1}, 750 cm^{-1} and 650 cm^{-1} have been assigned to the amide III[16], amide IV[8] (due to the major contribution of NCO) and amide VI[8] (due to the contribution of $C=O$ out of plane bending), respectively. The coordination through amide group can be excluded as no appreciable changes in the position of these bands have been observed in the infrared spectra of the complexes of both the ligands.

The S—N, bidentate nature of both the ligands is further substantiated by the appearance of the additional bands of Co—N[17] and Co—S[12] vibrations in the regions 445-425 cm^{-1} and 350-335 cm^{-1}, respectively in the far infrared spectra of the cobalt(II) complexes. The bands around 230 cm^{-1} and 217 cm^{-1} are assigned to Co—Cl[18] and Co—Br[19] vibrations, respectively. In the nitrato complexes, four bands have been observed in the regions 1,555-1,510 cm^{-1}, 1,290-1,265 cm^{-1}, 1,005-994 cm^{-1} and 808-790 cm^{-1} which have been assigned to asymmetic—NO_2 stretching, symmetric—NO_2 stretching, NO stretching and out of plane NO_2 rocking. These vibrations indicate the monodentate mode of coordination of nitrate ion[20]. One additional band is also observed in the region 1,730-1,770 cm^{-1} which has been found to split. The magnitude of this splitting, 16 cm^{-1} and 11 cm^{-1}, further suggests the monodentate mode of coordination. The N-bonded mode of coordination of thiocyanato group has been proposed because of the bands observed around 2,070 cm^{-1}, 870 cm^{-1} and 460 cm^{-1} which are assignable[21, 22] to C—N stretching of NCS group, C—S stretching of NCS group and NCS bending vibration, respectively. One characteristic additional (Co—NCS) band also observed in far infrared spectra of thiocyanato complexes at 240 cm^{-1} conform to the N-bonded mode of coordination of thiocyanato group.

Conclusions

(i) Tetragonality increases from halo-complexes to thiocyanato complexes via nitrato complexes. The order of the tetragonality is as follows: $Cl < Br < I < NO_3 < NCS$.

(ii) The ligand field strength in *XY*-plane, *Dq*(*E*), for a given ligand is not constant but depends largely on the nature of axial ligands and follows the same order as observed for tetragonality.

(iii) The difference, *Dq*(*E*)—*Dq*(*A*), goes exactly parallel with the difference, $d\pi$—$d\sigma$, which is a theoretical expectation.

(iv) The value of $d\pi$ and $d\sigma$ also run parallel with changing anions which is also expected theoretically.

Experimental

Preparation of the Ligands

Both the ligands (*BTSC* and *FBTS*) were prepared according to the method reported earlier[3].

Preparation of the Complexes

a) Dihalobis-(BTSC)-Cobalt(II), Dinitrobis-(BTSC)-Cobalt(II) and Corresponding Complexes of (FBTS)

For the preparation of all the complexes a general procedure has been adopted.

When 50 ml of (1.0 mmol) of the cobalt(II) salt in ethanol were mixed with 125 ml of a 2.5 mmol ethanolic solution of the ligand with constant stirring, a pink coloured solution developed. The pink mixture was refluxed on water bath for about 2 h when a deep pink coloured precipitate was obtained. It was filtered off, washed thoroughly with hot ethanol and ether and dried at 110 °C. Yield ~ 75%. Analyses correspond to general formulae $[Co(C_9H_{12}N_4OS)_2X_2]$ and $[Co(C_{14}H_{14}N_4P_2S)_2X_2]$ where, X = Cl, Br, I and NO_3.

b) Dithiocyanatobis (BTSC) Cobalt(II) and Dithiocyanatobis (FBTS) Cobalt(II)

To the pink colour obtained as a result of mixing cobalt(II) chloride and ligand in procedure (a), an ethanolic solution of ammonium thiocyanate (3.5 grams) was added. The colour of the solution turned orange immediately and a precipitate of ammonium chloride settled down in the flask. This was filtered after stirring the mixture for about 15 min, and the filtrate was refluxed for about 2 h whereby an orange coloured precipitate was obtained. It was filtered, washed and dried similar to that done for Cobalt(II) complexes in procedure (a). Yield ~ 65%. The analyses show the general formula to be $[Co(L)_2(NCS)_2]$ where L has the usual meaning.

Physical Measurements

Magnetic measurements, reflectance spectra, electronic spectra, and infrared spectra were recorded as reported earlier[1]. The sparingly soluble nature of these complexes have prevented the determination of molecular weight, conductivity and solution absorption spectral measurements which would have given more fruitful information regarding their structures. All the complexes, as expected for nitrogen-sulphur donor set[23], are sparingly soluble and posses no sharp melting points. They do, however, decompose on heating above 250 °C.

Acknowledgements

The authors are thankful to Dr. *A. K. Srivastava* for recording the electronic spectra at the University of Roma, Italy, and the authorities of Tata Institute of Fundamental Research, Bombay, for permission to carry out low temperature magnetic measurements. They are also thankful to C. S. I. R., New Delhi, and S. C. S. I. R., Lucknow, India, for financial assistance.

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