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Pseudotetrahedral Co^{II} Complexes with Thio- and Seleno-carbamate Esters

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Thiocarbamate esters L=RHN–CS–OR′ act as unidentate ligands through their S atoms towards Co^{II} giving pseudotetrahedral CoL_2X_2 (X=Cl, Br, I) complexes. The complexing behaviour of L is therefore similar to that of substituted thioureas RHN–CS–NHR′, also in electronic spectral patterns and spectrochemical parameters values. However, the effect of –OR′ substituents compared to –NHR′ of thioureas reduces markedly the affinity of thiocarbonyl sulfur for Co^{II}, and results in much more limited stability and easier solvolytic displacement of thiocarbamate complexes. Selenocarbamate complexes appear to be even less stable than the corresponding thiocarbamate complexes, but nevertheless $CoL'X_2$ (L′=N–phenyl–O–methylselenocarbamate, X=Br, I) could be prepared; their electronic spectra are consistent with lower spectrochemical position and stronger nephelauxetic effect of the Se donors.

The crystal and molecular structure of one of these complexes, dibromo–bis(O–ethyl,N–phenylthiocarbamate)cobalt(II), $Co[(C_6H_5)NH–CS–(OC_2H_5)]_2Br_2$, has been determined from three-dimensional single-crystal X-ray data collected by standard film techniques. The structure has been refined by least-squares methods to a conventional R *factor of 0.078 for 1330 non zero reflections. The neutral complex crystallises in space group C2/c of the monoclinic system with a cell of dimensions* $a=25.95\pm0.02$, $b=5.82\pm0.02$, $c=15.22\pm0.02$ Å; $\beta=104.3\pm.1°$; $V=2227$ Å^3. $\rho(exp)$ *is* 1.72 ± 0.04 g/cm^3 *in good agreement with 1.73 g/cm^3 as calculated for* $Z=4$.

The molecule is crystallographically required to possess a twofold symmetry axis with cobalt occupying the 4(e) special positions of the space group.

The complex consists of a cobalt atom tetrahedrally coordinated by two bromine atoms and by sulphur atoms of the two thiocarbamate ligands. The Co–Br and Co–S distances are 2.394(2) and 2.328(3) Å respectively. A strong hydrogen bond interaction between the hydrogen belonging to nitrogen and the bromine has been revealed (H–N . . . Br=3.36 Å). Several features of the geometry within the molecule are also given and discussed.

Introduction

Thiocarbamic esters RHN–CS–OR′ are structurally similar to substituted thioureas RHN–CS–NHR′, and can be expected to behave analogously as ligands towards appropriate metal centers whenever S–bonded, although replacement of –NHR′ through the more negative –OR′ grouping may considerably effect the donor properties of the thiocarbonyl group. Unlike thioureas, whose complex chemistry has been widely investigated, thiocarbamate esters have received however until now little or no attention as ligands. We have investigated recently[1,2] complex formation between Pd^{II} or Pt^{II}, and N–phenyl– or N–allyl, O–alkylthiocarbamates, and found that they are bonded through S like N,N′–disubstituted thioureas, but, unlike the latter, prefer chelating behaviour under exploitation of other donor functions in their molecules, which results in lower c.n. and different stereochemistry.[1,2] Thus, although thiocarbamates and thioureas use the same functional group as donor in metal complexation, their complexing behaviour is considerably different: thiocarbamates are not trivial analogs of thioureas, and relative investigation of their behaviour as ligands may offer several points of interest.

In the present paper we report preparation of complexes of thiocarbamates with Co^{II}, and a comparison with Co^{II}–thiourea complexes. Since Co^{II} has a strong preference for pseudotetrahedral coordination, we expected the ligands to be forced into such preferred coordination, so as to give the same stereochemistry as with thiourea, and to allow therefore quantitative comparison of spectrochemical parameters. Indeed, the complexes of thiocarbamic esters we were able to prepare revealed, also by X-ray analysis, pseudotetrahedral coordination, and in the following section we shall report their preparation and properties, and discuss their spectra and stability.

Experimental Section

Pseudotetrahedral Co^{II} complexes of formula CoL_2X_2 have been prepared by reaction of anhydrous CoX_2 (X=Cl, Br, I) under the experimental conditions described below, with the following ligands L: O–ethyl,N–phenylthiocarbamate (eptcH), O–ethyl,N–allylthiocarbamate (eatcH), and O–methyl,N–phenylselenocarbamate (mpscH). Only $Co(eptcH)_2X_2$ (X=Cl, Br, I) and $Co(mpscH)_2X_2$ (X=Br, I) could be iso-

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(1) T. Tarantelli and C. Furlani, *J. Chem. Soc.*, (A) 1213 (1971).
(2) P. Porta, on. *J. Chem. Soc.*, (A) 1217 (1971).

lated as pure solids, while evidence for complexes with eatcH was obtained only in solution.

Starting Materials. Cobalt halides and solvents were reagent grade commercial products. The ligands and the starting materials for their preparations were obtained as follows:

Phenylisoselenocyanate, PhNCSe—. A modification of previous literature procedures[3,4,5] was found necessary in order to obtain a product of satisfactory purity. Hydrated sodium selenide, from 9.87 g or 0.125 moles Se reduced with rongalite in alkaline medium[6] is dehydrated by heating *in vacuo* 12 hours on oil bath; carefully purified N_2 at atmospheric pressure is then added, 150 ml dealreated acetone and subsequently 125 ml of a deaereated solution of 21.75 g or 0.125 moles $PhNCCl_2$ in acetone are added under magnetic stirring. After 48 hours stirring, NaCl is filtered off, and the solution evaporated at low pressure; the deep orange-red oily residue is distilled *in vacuo,* yielding in the intermediate fraction a pale yellow product (18.1 g; 80% yield) whichi can be further purified by recrystallization from petroleum ether. M.p. 14-16°C.

Anal. Calcd for C_7H_6NSe: C, 46.17; H, 2.77; N, 7.69; Se, 43.36. Found C, 45.98; H, 2.94; N, 7.90; Se, 42.90.

From PhNCSe (g 3.5 in 20 ml anhydrous methanol), *O—methyl,N—phenylselenocarbamate* $C_6H_5NH—CSe—OCH_3$ (mpscH) is obtained by addition of CH_3ONa in 5 ml methanol, after 15 hours standing at room temperature, evaporation at low pressure, drying of the residue, dissolution in ligroin over steambath, filtration and crystallisation at −15°C. Large white crystals (m.p. 99-100°C—) precipitate, which are filtered and washed with ligroin.

Anal. Calcd for C_8H_9NOSe: C, 44.87; H, 4.24; N, 6.54. Found C, 44.97; H, 4.22; N, 6.52.

O—ethyl,N—phenylthiocarbamate $C_6H_5NH—CS—OC_2H_5$ (eptcH) was obtained from C_6H_5NCS and ethanol as described in literature.[7]

Preparations of the Complexes

Dihalobis(O—ethyl,N—phenylthiocarbamate)cobalt(II) $Co(eptcH)_2Cl_2$: 1.18 g (5 mmoles) $CoCl_2 . 6H_2O$ and 1.81 g (10 mmoles) eptcH in 45 ml butanol are heated over a steambath for 30 hours in a flask filtered with reflux condenser and U-tube with $CaCl_2$ to prevent admission of air humidity. The solvent is then removed under vacuum, the residue dissolved in ca. 30 ml CH_2Cl_2 cooled at 0° and filtered; the solution is then kept under exclusion air mixture at −15°C in a flash equipped with a dropp funnel and a porous glass funnel; from the former, petroleum ether is added dropwise until turbid, then a precipitate is slowly formed which is eventually sucked through the glass frit. The product can be recrystallized from CH_2Cl_2 by repeating the above procedure. Blue crystals m.p. 140-1°C.

Anal. Calcd for $C_{18}N_{22}N_2Cl_2O_2S_2Co$: C, 43.91; H, 4.50; N, 5.69. Found 43.93; H, 4.19; N, 5.46.

Essentially by the same procedures we obtained also: *Co(eptcH)₂Br₂*, green crystals, m.p. 138-9°C.

Anal. Calcd for $C_{18}H_{22}N_2O_2S_2Br_2Co$: C, 37.19; H, 3.81; N, 4.28. Found C, 36.81; H, 5.27; N, 4.67. (The initial solvent may be ethanol instead of butanol and the initial heating can be abbreviated to 2-3 hours); *Co(eptcH)₂I₂* green crystals m.p. 134-5°C.

Anal. Calcd for $C_{18}N_{22}N_2O_2S_2I_2Co$: C, 32.02; H, 3.28; N, 4.15. Found C, 32.49; H, 3.53; N, 3.98. (Initial heating only 15'); *Co(mpscH)₂I₂*, green crystals, m.p. 110°C (dec.).

Anal. Calcd for $C_{16}H_{18}N_2O_2Se_2I_2Co$: C, 25.92; H, 2.45; N, 3.77. Found C, 25.67; H, 2.30; N, 3.62. *Co(mpscH)₂Br₂* can be obtained in crude form as green crystals by the same procedure, but is invariably decomposed as one tries to purify it by crystallization.

Apparatus. Electronic absorption spectra were obtained with Beckman DK-1A spectrophotometer and with a Shimadzu MPS-50L for single crystal.

Infrared spectra were taken with a Beckman IR-10 apparatus, using KBr disks.

Molecular weight measurements were performed with a 301-A vapor pressure osmometer (Hewlett-Packard).

Magnetic data were obtained by the Gouy Technique using $Hg[Co(NCS)_4]$ as calibrant and corrected for diamagnetism in the usual manner.

Crystal data and Structure Determination of Co(eptcH)₂Br₂. X-ray structure analysis was undertaken on one representative of the complexes prepared above, namely $Co((eptcH)_2Br_2$, $C_{18}H_{22}O_2N_2S_2CoBr_2$, $M = 581.3$. Monoclinic, $a = 25.95 \pm 0.02$, $b = 5.82 \pm 0.02$, $c = 15.22 \pm 0.02$ Å, $\beta = 104.3° \pm 1°$, $U = 2227$ Å^3, $D_m = 1.72 \pm 0.04$ g.cm^{-3} (by flotation), $Z = 4$, $D_c = 1.73$ g cm^{-3}, $F(000)) = 1156$. The observed extinctions, hkl $(h+k \neq 2n)$ and $h0l$ $(l \neq 2n)$, are consistent with the two space groups C2/c and Cc. Nickel-filtered CuKα radiation, $\lambda = 1.5418$ Å; μ(CuKα) 124.3 cm^{-1}. Cell dimensions were obtained from zero-layer Weissenberg photographs taken about the *b* and *c* axes using an improved version of Christ's method.[8] Only reflections from CuKα_1 radiation (λ taken as 1.540562 Å) were considered and the limits of errors given are estimates of maximum errors. The X-ray intensities were estimated from sets of multiple-film equi-inclination Weissenberg photographs taken about the *b* (*h0l* through *h4l*) and *c* axes (*hk*0 through *hk*3). An elongated prismatic crystal about $0.9 \times 0.06 \times 0.06$ mm (the elongation being along the *b* axis) *was* used for data collection about the main axis (*b*), whereas the same crystal was cut in a suitable shape to avoid strong absorption phenomena for data collection

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(3) H. Stolte, *Ber. 19,* 2350 (1886).
(4) C. Hasan and R. Unter, *J. Chem. Soc.,* 1762 (1935)
(5) C. Collar-Charon and M. Renson, *Bull. Soc. Chem. Belg., 71,* 531 (1962).
(6) L. Tschugaeff and W. Chlopin, *Ber., 47,* 1269 (1914).
(7) W. Walter and K. D. Dode, *Angewandte Chemie (Intern. Ed.), 6,* 281 (1967) and references therein.
(8) G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca Sci., 33,* 1113 (1963).

Table I. Fractional Atomic Coordinates and Anisotropic Thermal Parameters of the Non-hydrogen Atoms with their Estimated Standard Deviations [a].

Atoms	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0	379(5)	2500	12(0)	314(10)	44(1)	0	9(1)	0
Br	732(1)	2567(2)	2252(1)	15(1)	362(5)	60(1)	—15(1)	12(1)	38(3)
S	249(4)	—1858(6)	3805(2)	11(1)	441(13)	57(1)	27(3)	18(1)	77(6)
Cl	879(4)	—2869(17)	3965(6)	12(1)	232(38)	42(4)	—1(8)	17(4)	—36(20)
O	1069(3)	—4525(14)	4547(5)	12(1)	368(31)	51(4)	9(9)	19(3)	51(4)
N	1232(3)	—1961(17)	3558(6)	10(1)	377(37)	60(5)	35(10)	19(4)	101(22)
C2	710(4)	—5757(22)	4990(7)	11(1)	464(51)	48(5)	10(13)	20(4)	106(27)
C3	1050(5)	—7570(25)	5563(9)	19(2)	544(70)	78(8)	59(20)	31(7)	195(38)
C4	1773(3)	—2458(18)	3657(6)	10(1)	265(37)	44(4)	—30(11)	14(4)	—60(22)
C5	2025(4)	—4526(22)	4027(8)	14(2)	328(47)	63(6)	—1(13)	20(5)	—25(27)
C6	2569(4)	—4730(24)	4027(8)	13(2)	464(56)	69(7)	36(15)	29(5)	72(32)
C7	2859(4)	—3124(22)	3758(7)	17(2)	371(48)	43(5)	9(14)	18(5)	26(23)
C8	2604(4)	—1190(23)	3357(8)	12(1)	462(49)	68(6)	13(13)	27(5)	2(27)
C9	2055(4)	— 843(23)	3277(7)	13(1)	450(53)	43(5)	—7(14)	—3(4)	39(26)

[a] The anisotropic temperature factors are of the form exp $[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$. The estimated standard deviations are in parenthesis. All values are $\times 10^4$.

Table II. Fractional Coordinates ($\times 10^4$) and Assumed Isotropic Temperature Factors for Hydrogen Atoms.

Atoms [a]	x	y	z	B, Å^2
H(N)	1074	— 621	3070	7.0
H1(C2)	387	—6562	4494	»
H2(C2)	548	—4597	5418	»
H3(C3)	816	—8561	5926	»
H4(C3)	1379	—6728	6057	»
H5(C3)	1218	—8693	5134	»
H6(C5)	1808	—5884	4265	»
H7(C6)	2772	—6270	4376	»
H8(C7)	3281	—3366	3830	»
H9(C8)	2828	— 101	3095	»
H10(C9)	1854	653	2926	»

[a] The atoms to which the reported hydrogens are bonded are given in parenthesis.

about the other axis. The intensities for a total of 1545 reflections, 1330 of which independent, were recorded at room temperature (about 21°C) with nickel-filtered CuKα radiation. They were corrected for Lorentz-polarization factors and spot size of the upper layers.[9] No absorption or extinction corrections were applied. The observed structure amplitudes were placed on a common scale by the method of Hamilton, Rollett and Sparks.[10]

The structure was solved using Paterson, least-squares, and Fourier Methods. As mentioned above, the space groups consistent with the observed systematic absences are the monoclinic C2/c and Cc; the absence of any piezoelectric effect and the satisfactory agreement ultimately obtained in the refinement of the structure assigned the crystal to belong to the centrosymmetric C2/c space group. Thus the complex is crystallographically required to possess a two-fold symmetry axis with the Co atom occupying the 4e special positions of the space group, and with half a molecule representing the asymmetric unit. All non-hydrogen atoms were found by two successive difference Fourier syntheses and their positional parameters, together with isotropic thermal parameters, were refined to an R value of 0.116. After correction of several indexing errors a further four cycle of least-squares refinement were carried out by introducing anisotropic temperature factors for all non-hydrogen atoms and converging R to 0.084. At this stage the positions of hydrogen atoms were localised by means of a calculation (fixing the C–H and N–H distances at 1.08 Å) and found to agree with the approximate positions on a difference Fourier map. Four further cycles of least-squares analysis, with anisotropic temperature factors for all non-hydrogen atoms of the complex, and fixed positional and thermal parameters for the hydrogen atoms (arbitrarily fixed at 7.0 Å^2), reduced the reliability index to 0.078. A successive cycle of refinement indicated no shifts in the atomic positions and thermal parameters higher than 0.2 σ, so refinement was assumed to be concluded at the above value of R. A final difference Fourier synthesis, calculated with the use of all the final atomic parameters, has confirmed the correctness of the structure since at the sites of all atoms the value of ρ was approximately zero and certainly never exceeded the value of σ $(\rho)=0.26$ e/Å^3 calculated for the whole structure.

The quantity minimized in the least-squares analysis was $R'=w(k\,|F_o|-|F_c|)^2$ where $w=[a+bkF_o+c(kF_o)^2]^{-1}$, with $a=4.5$, $b=1.0$, and $c=0.002$.

Atomic scattering factors of Cromer[11] were used for Co, Br, S, O, N, C (those of Co, Br, and S being corrected for the real component of anomalous dispersion) and these of Hanson[12] for hydrogen.

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(9) D. C. Phillips, *Acta Cryst.*, *7*, 746 (1954).

(10) W. C. Hamilton, R. S. Rollett and R. A. Sparks, *Acta Cryst.*, *18*, 129 (1965).

(11) D. T. Cromer and J. B. Mann, *Acta Cryst.* A *24*, 321 (1968).

Table III. Observed and Calculated Structure Factors

H L	FO	FC
**** K = 0 ****		
0 2	194	-202
0 4	10	3
0 6	151	-165
0 8	153	159
0 10	34	-31
0 12	19	-21
0 16	23	19
2 0	187	201
2 2	55	-50
2 -2	215	-254
2 4	249	318
2 -4	127	141
2 6	256	-284
2 -6	18	10
2 8	222	227
2 -8	10	8
2 10	74	-74
2-10	30	29
2 12	32	36
2 14	39	-34
2-14	30	28
2-18	16	17
4 0	69	59
4 2	128	-114
4 -2	74	-69
4 4	65	69
4 -4	219	-244
4 6	180	-200
4 -6	122	131
4 8	149	163
4 -8	27	-23
4 10	49	-47
4-10	64	60
4 12	99	91
4-12	47	-45
4 14	75	-76
4-14	15	13
4 16	27	31
4-16	23	18
6 0	234	-235
6 2	60	58
6 4	79	-79
6 -4	183	-204
6 6	49	-51
6 -6	126	121
6 8	57	53
6 -8	54	54
6 10	61	-57
6 12	56	50
6-12	36	-31
6 14	49	-45
6-14	21	-20
6 16	26	31
6-16	57	48
6-18	30	-37
8 0	59	-58
8 2	182	193
8 -2	24	-22
8 -4	47	-44
8 -6	32	33
8 8	57	-56
8 -8	63	60
8 10	29	26
8-10	158	-166
8 12	10	-8
8-12	71	69
8 14	40	-37
8-14	46	-37
8 16	32	16
8-16	39	33
8-18	46	-44
10 0	158	147
10 2	77	76
10 -2	112	-111
10 4	66	-61
10 -4	120	122
10 6	25	21
10 -6	155	-151
10 8	54	-58
10 -8	132	129
10 10	51	50
10-10	168	-169
10 12	32	-29
10-12	66	65
10-14	51	-55
10-16	46	44
10-18	16	-15
12 0	139	139
12 2	31	21
12 -2	352	-347
12 4	110	110
12 -4	223	230
12 6	85	-82
12 -6	140	-125
12 -8	142	135
12 10	61	54
12-10	109	-117
12-12	60	58
14 0	133	120
14 2	196	-187
14 -2	214	-202
14 4	186	193
14 -4	174	164
14 6	103	-103
14 -6	41	-36
14 8	36	35
14 -8	92	93
14 10	14	14
14-10	30	-30
14 12	39	34
14-14	44	46
16 0	88	75
16 2	81	-77
16 -2	131	-133
16 4	137	145
16 -4	76	69
16 6	108	-103
16 -6	87	81
16 8	50	51
16 10	66	-67
16-10	31	33
16 12	71	58
16-12	19	-19
16-14	43	38
16-16	12	-14
18 0	55	-49
18 -2	40	34
18 4	81	66
18 -4	41	18
18 6	64	-67
18 -6	115	114
18 8	37	35
18 -8	105	-110
18 10	48	-44
18-10	49	-49
18 12	26	24
18-14	46	45
18-16	12	-11
18-18	26	-26
20 0	96	-92
20 2	56	51
20 -2	61	56
20 8	13	-18
20 -8	106	-105
20 10	25	-29
20 12	28	29
20-12	47	49
20-14	45	-48
22 0	94	-93
22 -2	35	33
22 -4	30	24
22 6	36	39
22 -6	61	-57
22 8	26	-27
22 -8	30	23
22-10	65	-64
22-12	52	52
22-14	24	-23
22-16	24	17
24 2	32	-28
24 -2	52	-50
24 -4	70	64
24 6	25	26
24 -6	76	-73
24 -8	64	57
24-10	36	-33
24-12	69	74
24-14	43	-39
26 0	36	33
26 2	46	-51
26 -2	55	-49
26 4	50	43
26 -4	111	112
26 -6	66	-64
26 -8	37	34
26-10	13	-23
26-12	37	40
26-14	9	-11
28 0	57	55
28 2	62	-55
28 -2	13	-15
28 4	52	51
28 -4	58	63
28 6	13	-13
28 -6	46	-43
30 0	23	23
30 2	47	-44
30 -2	21	21
30 -4	17	14
30 -6	19	-20
30 -8	39	-32
30-10	30	28
32 -2	27	28
32 -4	26	-25
**** K = 1 ****		
1 0	46	49
1 1	162	-212
1 -1	31	-25
1 2	159	-177
1 -2	111	-114
1 3	411	512
1 -3	132	-149
1 4	116	-129
1 -4	107	115
1 5	162	-186
1 -5	160	174
1 6	48	-51
1 -6	53	-56
1 7	25	25
1 -7	24	-21
1 8	92	90
1 -8	22	28
1 9	49	-54
1 -9	60	-61
1 10	36	-36
1-10	15	-15
1 11	70	65
1-11	26	23
1-12	17	21
1 13	9	-8
1-13	17	-18
1-14	28	-24
1 15	14	-21
1-15	44	45
1-16	15	14
1-17	28	-20
3 0	114	104
3 1	94	-82
3 -1	47	38
3 2	26	-20
3 -2	78	-64
3 3	168	188
3 -3	52	52
3 4	57	61
3 -4	14	12
3 5	122	-130
3 -5	21	-21
3 6	134	-146
3 -6	36	-37
3 7	76	61
3 -7	129	146
3 -8	113	109
3 9	125	-126
3 -9	118	-121
3-10	43	-42
3 11	105	109
3-11	47	49
3 12	15	13
3 13	34	-33
3-13	33	-31
3 14	22	-19
3-14	34	-28
3-15	49	47
3-18	14	-9
5 0	179	168
5 1	61	54
5 -1	180	-188
5 2	32	-31
5 -2	52	-46
5 3	21	-18
5 -3	262	255
5 4	47	52
5 -4	114	111
5 5	16	-17
5 -5	61	-66
5 6	33	-33
5 -6	50	-55
5 7	33	35
5 -7	142	155
5 8	55	55
5 -8	31	31
5 9	76	-79
5 -9	102	-111
5 10	33	-29
5-10	53	-53
5 11	70	70
5-11	25	24
5-12	20	17
5 13	33	-31
5 14	26	-23
5-14	17	-23
5 15	32	30
5-15	9	11
5-16	24	28
5 17	26	-20
5-19	16	-15
7 0	135	128
7 1	169	173
7 -1	270	-277
7 2	13	8
7 -2	93	-90
7 3	97	-97
7 -3	147	140
7 4	112	113
7 -4	20	15
7 5	99	104
7 6	39	-43
7 -6	82	-75
7 7	76	-81
7 -7	38	43
7 8	52	59
7 -8	83	83
7 -9	72	-72
7-10	44	-37
7 11	35	33
7-11	17	-16
7 12	29	26
7-12	23	22
7-13	71	72
7 14	15	-15
7-15	42	-42
7-16	25	23
7 17	19	-17
7-19	16	-14
9 0	79	72
9 1	89	80
9 -1	124	-118
9 2	32	-29
9 -2	146	-135
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14 -9	15	12
14 11	9	9
14-11	32	-32
16 0	42	38
16 1	15	-22
16 -1	29	25
16 2	54	-52
16 -2	20	-17
16 -3	51	-41
16 4	53	51
16 5	38	-34
16 6	46	-44
16 8	27	27
16 -9	26	24
16 10	22	-20
16-10	30	26
16-11	14	-16
16-12	17	-24
16-14	13	15
18 -2	11	13
18 -3	48	-42
18 -4	20	-20
18 5	24	-24
18 -5	15	21
18 6	23	-23
18 -6	50	46
18 -7	20	25
18 8	30	26
18 -8	50	-47
18-10	10	15
18-11	16	-19
20 0	35	-31
20 1	32	21
20 2	30	31
20 -2	50	47
20 -4	31	-30
20 5	33	-34
20-14	9	-12
22 0	13	-17
22 2	23	22
22 3	31	31
22 4	25	-24
22 6	21	19
22 -8	13	28
22-10	11	-16
22-11	10	-13
22-12	15	16
24 -2	21	-24
24 3	12	17
24 -4	12	18
24 -5	18	20
24 -6	27	-26
24 -8	45	39
24-10	34	-26
24-11	27	-17
26 0	22	19
26 1	8	-12
26 2	14	-16
26 -2	26	-35
26 -4	36	36
26 -5	26	27
26 -6	30	-25
26 -8	13	16
28 -2	18	-22
28 -4	10	13
28 -5	29	33
**** K = 5 ****		
1 0	17	17
1 1	103	-84
1 -1	72	58
3 1	60	-50
3 -1	46	42
5 0	35	30
5 1	19	24
5 -1	19	-20
7 0	30	31
7 1	37	32
7 -1	19	-20
7 -2	62	-48
9 0	17	23
9 1	30	35
9 -2	55	-43
11 -1	33	27
11 -2	31	-22
13 1	45	-54
13 -1	60	55
15 1	30	-36
15 -1	38	45
19 1	15	18
19 -1	27	-21
21 1	13	14
21 -1	35	-23
**** K = 6 ****		
0 0	43	-35
0 2	37	30
2 2	22	22
4 0	21	22
4 -2	37	-30
6 0	41	36
6 -2	36	-29
8 0	40	39
8 1	21	-26
8 -2	39	-31
10 1	17	-25
12 0	14	-26
14 0	13	-28
14 2	16	24
18 1	16	-14
18 -2	25	-18
**** K = 7 ****		
1 -1	13	-17
5 1	16	-21
5 -1	18	18
7 1	13	-19
7 -1	24	22
9 1	14	-17

Final atomic positional parameters and anisotropic temperature factors, together with their estimated standard deviations, for non-hydrogen atoms, are reported in Table I. Calculated coordinates and assumed isotropic temperature factors for hydrogen atoms, are listed in Table II.

Observed and calculated structure factors are shown in Table III. The bond distances and angles within the crystal-chemical unit of the complex are reported in Table IV and in Figure 1 where a projection of the molecule along the [010] direction is shown. The equation of various planes are shown in Table V.

The calculations were carried out on the Univac 1108 electronic computer of Rome University and programs written by Albano, Domenicano and Vaciago(13) were adopted.

(12) H. P. Hanson, F. Herman, J. D. Lea, and S. Skilmann, *Acta Cryst. 17*, 1040 (1964).

(13) V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta,*, **96**, 922 (1966).

Table IV. Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations in Parenthesis.

Distances, Å		Angles, deg.	
Co-Br	2.394(2)	Co-S-Cl	111.7(4)
Co-S	2.328(3)	Br-Co-S	111.6(7)
S-Cl	1.70(1)	Br-CoBr′	115.7(1)
Cl-O	1.32(1)	N-H. . Br	170.2(5)
Cl-N	1.33(1)	S-Co-S′	112.0(2)
O-C2	1.46(1)	S-Cl-N	122.8(8)
N-C4	1.41(1)	S-Cl-O	122.4(8)
C2-C3	1.51(2)	Cl-O-C2	119.6(8)
C4-C5	1.42(2)	Cl-N-C4	130.5(9)
C4-C9	1.40(2)	O-C2-C3	105.3(9)
C5-C6	1.40(2)	N-C4-C5	124.7(1)
C6-C7	1.36(2)	N-C4-C9	115(1)
C7-C8	1.37(2)	C4-C5-C6	117(1)
C8-C9	1.42(2)	C4-C9-C8	119(1)
N-H . . . Br	3.36(1)	C5-C6-C7	124(1)
		C6-C7-C8	118(1)
		C7-C8-C9	121(1)

Table V. Deviations from Planes through Groups of Atoms, Å.

Plane I		Plane II		Plane III	
S1	0.0140	N	0.0106	S1	0.0067
C1	—0.0146	C4	0.0287	C1	—0.0225
N	—0.0167	C5	—0.0264	N	0.0079
O	0.0516	C6	—0.0033	O	0.0079
C2	—0.0333	C7	0.0220		
C3	0.0021	C8	0.0003		
		C9	—0.0314		

Equations of the Planes ($Ax+By+Cz=D$) which refer to the crystallographic axes:

Plane I: $0.108x+0.642y+0.709z=-3.468$
» II: $0.013x+0.455y+0.859z=-4.166$
» III: $0.118x+0.662y+0.688z=-3.340$

Dihedral angles between Planes: I to II = 14.3°; II to III = 15.8°.

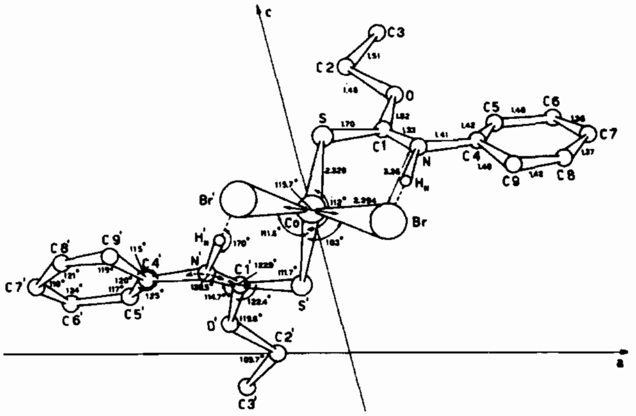

Figure 1. [010] projection of the molecule with bond distances and angles, Br′, S′, etc., refer to the atoms which are related to Br, S, etc., by the twofold symmetry axis. Only the hydrogen atom bonded to nitrogen is shown to indicate the N-H . . . Br intramolecular interaction.

Results

Physical and Chemical Properties. Solid complexes are stable in dry air, except Se-containing complexes which after longer time undergo decomposition to elemental Se; humidity causes easy decomposition. They are all soluble in CH_2Cl_2 or $C_2H_4Cl_2$, where concentrated solutions are clear and stable, while on dilution CoX_2 precipitates; to order of stability is I> Br>Cl. Solutions can be however stabilized by excess ligand, which is also capable of redissolving, although slowly, turbidity of diluted solutions. In benzene, excess of L is needed in all cases to keep complexes in solution. Acetone and others polar solvents completely prevent complex formation with thiocarbamates: addition of whatever excess of L to solutions of CoX_2 in acetone does not chenge at all the spectrum from the patterns typical of solvated pseudotetrahedral $[CoX_2(solv)_2]$ species. By contrast CoL'_2X_2 complexes with L′ = a substituted thiourea, are uneffected by acetone, where they dissolved without any practically detectable decomposition[14]. Solutions of thio - or selenocarbamate complexes in CH_2Cl_2, $C_2H_4Cl_2$ or C_6H_6 have negligible conductivity both with and without excess ligand, that is, thio - or selenocarbamates are unable to displace halides from the coordination sphere of CoL_2X_2. Molecular weight measurements with the osmometer were also unfavorably affected by the instability of solutions and yielded no satisfactory results, since there was evident decomposition of the complexes on the thermistor surface both in presence and in absence of excess ligands which resulted in irregularly low values of apparent m.w. However, clear solutions proved sufficiently stable for spectroscopic measurements, and spectra did not show any detectable change with time; addition of excess ligand did not change significantly the spectrum, which was turn substantially equal to the reflectance spectra, and of the single crystal spectra of the solids, which we took as evidence for the existence of only one kind of $[CoL_2X_2]$ chromophore as responsible for the observed spectra.

Only for iodocomplexes, dilution without excess ligands changes slightly the spectral patterns in that band components become less well resolved: this might be ascribed to partial dissociation and formation of more or less soluble polymers of $[CoX_2L_x]_n$ ($x<2$) type such as have been postulated with phosphine ligands,[15] before dissociation to insoluble CoX_2

Electronic and Vibrational Spectra. The electronic spectra show the typical patterns of pseudo tetrahedral Co^{II} and comprise two absorption regions; a rather well resolved triplet at 13-16 kK (tetrahedral $^4A_2 \rightarrow b^4T_1$), and a less intense and less resolved band around 6 kK ($^4A_2 \rightarrow a^4T_1$) (Table VI). The spectra are almost identical with those of thio- or selenoureas complexes with the same halides, not only in the frequency values of the maxima, but also in intensity and even in the shape of band contour, as is evident from the comparison reported in Figure 2. Also bathochromic shifts on replacement of Cl through Br or I, or S through Se (Figure 3), are perfectly similar to those of thioureas complexes, and of course also the values of spectrochemical parameters, as given in Table VII, are coincident or nearly so with the values of pseudo-

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[14] O. Piovesana and C. Furlani, *J. Inorg. Nucl. Chem.*, 30, 1249 (1968).

[15] M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 3, 922 (1966).

Table VI. Electronic spectra of CoL$_2$X$_2$ complexes 2.5×10^{-3} in Cl-CH$_2$-CH$_2$Cl in the presence of an excess of free L (log ε in parenthesis).

Complex	$^4A_2\rightarrow a^4T_1(T_d)$	$^4A_2\rightarrow b^4T_1(T_d)$	C.T.
Co(eptcH)$_2$Cl$_2$ [a]	5.55(2.18; 6.66sh(1.98); 7.85(1.88)	13.70(2.67); 15.27 2.97); 16.53(2.78)	
Co(eptcH)$_2$Br$_2$ [a]	5.33(2.09); 6.36sh(1.93); 7.54(1.86)	13.60(2.75); 14.59(2.75); 15.87(2.73)	25.9sh
Co(eptcH)$_2$I$_2$	5.17(2.07); 6.09(2.04); 7.40(2.08)	12.93(2.99); 13.85(2.90); 14.97(2.83)	25.0 sh; 36.10(4.54)
Co(mpscH)$_2$Br$_2$ [c]	5.08(1.9) 5.88(1.8); 7.14(1.7)	13.30(2.6); 14.39(2.6); 15.67(2.7)	25.3sh
Co(mpscH)$_2$I$_2$ [d]	4.88(2.02); 5.71(1.93); 7.06(2.00)	12.47(2.92); 13.39(2.90); 14.60(2.88)	25.0sh

Excess of free ligand: [a] 1.25*M*; [b] 5x10^{-2}*M*; [c] 2.5x10^{-2}*M*; [d] 1.5x10^{-2}*M* .

Table VII. Spectrochemical parameters (in kK) of CoL$_2$X$_2$ complexes (from absorption spectra in CH$_2$Cl$_2$).

	Chromophore	Δav	ΔS (Se)	B	β	μ(R.T.) [a] B.M.	θ	λ
Co(eptcH)$_2$Cl$_2$	[CoS$_2$Cl$_2$]	3.86	4.69	0.69	0.71	4.18	—24	—.08
Co(eptcH)$_2$Br$_2$	[CoS$_2$Br$_2$]	3.70	4.55	0.67	0.69	4.54	—28	—.16
Co(eptcH)$_2$I$_2$	[CoS$_2$I$_2$]	3.60	4.55	0.63	0.65	4.62	—26	—.17$_5$
Co(mpscH)$_2$Br$_2$	[CoSe$_2$Br$_2$]	3.59	4.13	0.66	0.68	—	—	—
Co(mpscH)$_2$I$_2$	[CoSe$_2$I$_2$]	3.42	4.19	0.60	0.62	—	—	—

[a] from χ values corrected for diamagnetism of the ligands (Pascal's constants) and for t.i.p. ($=8N\beta^2/\Delta_{av}$).

tetrahedral complexes CoL′$_2$X$_2$ complexes with thio- or selenoureas (see *e.g.* ref. (14)). Wen then infer pseudotetrahedral coordination and S— (or Se—) bonding on the ground of spectroscopica evidence and of magnetic measurements (Table VII) yielding μ_{eff} values in the typical range of pseudotetrahedral Co^{II} complexes, despite inconclusiveness of m.v. measurements.

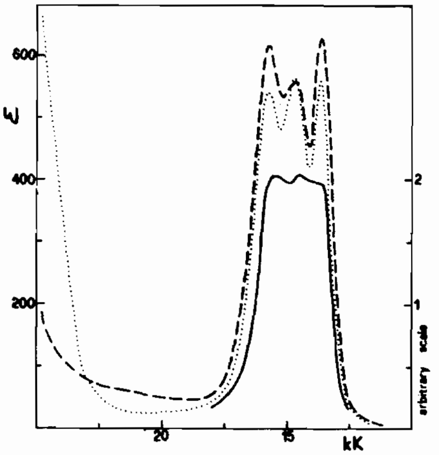

Figure 2. Electronic spectra of
·········· CoL$_2$Br$_2$(L=O-ethyl.N-phenylthiocarbamate) in CH$_2$Cl$_2$ in the presence of 20-fold excess of L
CoL$_2$Br$_2$ single crystal (unpolarised: right O.S.)
— — — — — — — CoL′$_2$Br$_2$(L′=N,N′diphenylthiourea) in CH$_2$Cl$_2$

Infrared spectra of the complexes have been measured, but will not be discussed here in detail both because of poor resolution and because they afford no further evident indications of the structure, except for one remarkable feature, namely that the NH stretching of free thiocarbamate ligands in C$_2$H$_4$Cl$_2$ solution at 3400 cm^{-1} ($\sim$3430 cm^{-1} in free thioureas) is lowered to 3210 cm^{-1} in the complexes, and falls therefore in the range of NH ... X hydrogen-bonded frequencies, as already reported for Co—thioureas complexes.[16]

Occurrence of intramolecular hydrogen bonding NH ... X, for which evidence in solution is afforded here by infrared data, is confirmed also in the solid by X-ray data (see next paragraph), and seems to be a general feature with pseudotetrahedral complexes of ligands containing a –CS–NH grouping.

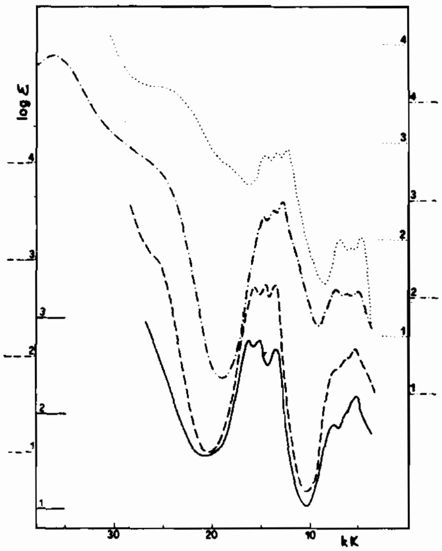

Figure 3. Absorption spectra in sim-dichloroetane of complexes of cobalt(II) with L=ethyl,N-phenyl-thiocarbamate or L′=O-methyl,N-phenyl-selenocarbamate:
CoL$_2$Cl$_2$(with excess of L)
— — — — — — CoL$_2$Br$_2$ (with excess L)
—·— ·—·— CoL$_2$I$_2$
·········· CoL′$_2$ I$_2$ (with excess L)

Description of the Structure of Co(eptcH)$_2$Br$_2$. The cobalt atom lies on a twofold axis and half a molecule

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(16) O. Piovesana and C. Furlani, *J. Inorg. Nucl Chem.* 32, 879 (1970).

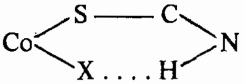
of the complex, which represents the asymmetric unit of the space group, generates the rest of the molecule by the action of the twofold axis. The cobalt atom results to be tetrahedrally coordinated by two bromine atoms and by the sulphur atoms of the thiocarbamic ligands, which behave in this compound as unidentate. The Br–Co–Br′, Br–Co–S, and S–Co–S′ (where Br′ refers to the bromine which is related to Br by the twofold symmetry axis, etc.) angles have values approximate to those of a regular tetrahedron, as shown in Figure 1 and in Table V. The Co–S distance, 2.328(3) Å, is in agreement with the values reported in the literature for similar compounds[17] as well as the Co–Br length of 2.394(2) Å agrees well with similar distances found in other bromine containing cobalt complexes.

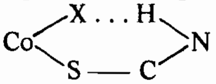
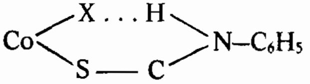
Within the thiocarbamic ligand all bond distances and angles are in close agreement with the respective values found in other structure of thio- and dithiocarbamic complexes.[2,18] It should be noted that the C1–N bond distance, 1.33 Å, implies a high degree of double bond character. A virtual planarity has been found for the S-C1 (O-C2-C3)-N and N-C4-C5-C6-C7-C8-C9 fragments, as shown in Table V, the maximum deviation from the first plane being given by O (0.05 Å) and from the second by C9 (0.03 Å). A remarkable feature within the ligand is given from the angle observed between the S–C1–O–N fragment and the phenyl group which is found to be about 16°; this is probably an indication of conjugation of the phenyl rings with the inner π-bonding network of the complex.

A final remark concerning the structure of this complex pertains to the position of the hydrogen atom on the nitrogen atom. The hydrogen is tituated, (its coordinates were found by calculation and confirmed from a difference Fourier synthesis), such as to point towards the bromine atom of the same molecule. The N–H ... Br distance and the N–H ... Br angle have been calculated to be 3.36 Å and 170° respectively so indicating, as suggested by other authors[19,20] a strong hydrogen-bond intramolecular interaction. The evidence drawn from the structure analysis regarding an intramolecular NH ... Br hydrogen bond is also supported from IR data as noted above. The shortest intermolecular contacts are in the range 3.6 Å and quite normal.

Discussion

Co^{II} complexes with thioureas are for the larger part of pseudotetrahedral $[CoL_2X_2]$ type (X = Cl, Br, I) (hexacoordinated complexes are far less common, and an earlier claim of pentacoordination in $Cotu_3Cl_2$[21] has been subsequently disproved[14]). In this respect, organic thio- and selenocarbamate esters display in their coordinating behaviour towards Co^{II} complete qualitative and quantitative similarity to substituted thioureas, as far as stereochemistry and spectroscopic bond parameters are concerned. Thus, in the complexes of $Co_2L_2X_2$ type (L = thio- or selenocarbamate esters) we have been able to prepare, a nearly regular tetrahedral coordination is established; no significant deviation from tetrahedral geometry occurs; coordinative bonding takes place through S as with thioureas, and the more negative substituent group –OR′ causes no detectable change in spectroscopic properties. The spectroscopic properties of CoL_2X_2, as described above, match almost exactly those of the corresponding complexes with thioureas; however, similarity of spectroscopic properties contrasts markedly with strongly reduced chemical stability: thus, coordinated thio- or selenocarbamates are easily displaced by solvent molecules in solvents even of relatively poor coordinating ability; this fact confines solution studies of thiocarbamate complexes to noncoordinating solvents, and practically prevents any further extensive comparative investigation of the chemical behaviour of pseudotetrahedral CoL_2X_2 complexes with both kinds of ligands.

It is still to be mentioned that coordinated thiocarbamates allow formation of six membered chelate rings  wich occur also in complexes of thioureas[16]; formation of such rings was suggested at first by infrared data and found then direct evidence from X-ray structural data; it makes probably a substantial contribution to the coordinating ability of thiocarboxylic sulfur in thioamide-type ligands, and is perhaps not the least important factors among those causing the strong similarity of geometric and spectroscopic properties in the coordinations of thiocarbamates and of thioureas to cobalt(II).

Inspection of the crystal structure suggests also occurrence of π-conjugation effects; in tetrahedral coordination no interligand conjugation can occur via the central metal as is common in quadratic d^8 complexes with ligands possessing organic π systems. However, the coordination environment around the Co atom is arranged in two mutually perpendicular planes in each of which there seems to exist extensive althuogh still imperfect conjugation throughout each chelate ring  as well as through the phenyl ring which as noted above is nearly coplanar with the former ring, making an angle of only ~16°, which probably still enables some degree of conjugation in the whole  system.

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[17] D. D. Hall, W. D. Horrocks *Jr.*, *Inorg. Chem.*, *81*, 809 (1969).
[18] G. Peyronel and A. Pignedoli, *Acta Cryst.*, *23*, 398 (1967).
[19] Chui Fan Liu and J. A. Ibers, *Inorg. Chem.*, *8*, 1911 (1969).
[20] G. A. Sim, *Acta Cryst.*, *8*, 833 (1955).
[21] K. C. Dash and V. R. Ramana Rao, *Z. Anorg. Allg. Chem.*, *345*, 217 (1966).