PREPARATION, SPECTROSCOPIC, MAGNETIC, CONDUCTOMETRIC AND POLAROGRAPHIC CHARACTERIZATION OF COBALT(II)-1-PHENYL-4,6-DIMETHYLPYRIMIDINE-2-THIONE COMPLEXES

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The following coordination compounds of cobalt(II) with 1-phenyl-4,6-dimethylpyrimidine-2-thione: $CoLX_2 . n H_2O$ ($X = Cl^-$, $n = 1$; $X = Br^-$, $n = 2$; $X = SCN^-$, $n = 0$; $X = NO_3^-$, $n = 4$), $Co_2L_3Cl_4 . H_2O$, CoL_2X_2 ($X = Br^-$, I^-, SCN^-, NO_3^-), $CoL_2X_2 . n H_2O . p Me_2CO$ ($X = I^-$, ClO_4^-, $n = p = 2$; $X = NO_3^-$, $n = 1$, $p = 0$), $CoL_3(ClO_4)_2 . 0.5 Me_2CO$, $Co_2L_5(NO_3)_4$ and $Co_2L_7X_4$ ($X = Cl^-$, Br^-, I^-) have been isolated and characterized by chemical analyses, visible and IR spectra, paramagnetic susceptibility, conductivity and polarographic measurements. Solid phase IR spectra suggest that the heterocyclic ligand is almost always bonded through non-substituted ring nitrogen and exocyclic sulfur atoms. The solid compounds with the exception of the $[CoL(SCN)_2]_2$, $[CoL_2(H_2O)_2][CoCl_4]$ and $[CoL_3][CoCl_4] . H_2O$ have originally a distorted octahedral geometry. By grinding the solid $[CoL_2(SCN)_2]$, $Co_2L_7Cl_4$ and all the bromide complexes the cobalt(II) coordination undergo octahedral → tetrahedral geometry change. Spectral evidences and polarographic results in DMF solution have shown that for these and $[CoL(SCN)_2]_2$, $[CoL_2(H_2O)_2][CoCl_4]$ and $[CoL_3][CoCl_4] . H_2O$ complexes, the solvolysis gives rise to equilibria between tetrahedral anionic $[CoX_4]^{2-}$ ($X = SCN^-$, Cl^-), $[CoX_3(DMF)]^-$ ($X = SCN^-$, Cl^-, Br^-) and some possible $[Co(DMF)_6]^{2+}$, $[CoX(DMF)_5]^+$, $[CoXL(DMF)_4]^+$, $[CoL(DMF)_5]^{2+}$ (L = N-monodentate ligand) cationic octahedral species. Polarographic data for perchlorate complexes and for $[Co(DMF)_6](ClO_4)_2$–L system at increasing ligand concentration have shown that in DMF solution the solvated ions $[Co(DMF)_6]^{2+}$ are the prevailing species and that the thiopyrimidine-containing species $[CoL(DMF)_5]^{2+}$ ($\beta = 3.78 . 10^5$) and $[CoL_2(DMF)_4]^{2+}$ ($\beta = 9.59 . 10^7$) can be formed only in presence of a large excess of the free ligand.

The current interest in the coordination chemistry of the thiopyrimidine derivatives arises from the significant role played by these heterocyclic bases in many biological systems (the ring system being an integral part of several nucleic acids, vitamins, coenzymes etc.), from their application as anti-tumor and anti-thyroid agents[1 – 3], and from the variety of coordination modes exhibited by them towards transition metal ions. Typical bonding modes including S-donation, N,S-chelation or bridging as well as

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N-donation have been spectroscopically inferred and sometimes structurally established[4].

As part of our systematic investigation concerning studies on the coordinating properties of oxo- and thiopyrimidine analogues with metal ions, in this communication, we report the preparation and physico-chemical characterization of some new cobalt(II) complexes with 1-phenyl-4,6-dimethylpyrimidine-2-thione (L).

Since it has been found that some $-\overset{|}{N}-H$ (refs[5 – 7]) and $-\overset{|}{N}-CH_3$ (refs[8,9]) thiopyrimidine derivatives coordinate to cobalt(II) ions strongly by non-substituted ring nitrogen atom and more weakly by the exocyclic sulfur atom, we were interested to examine the influence of the bulky N-phenyl group (which suppress thione $\rightleftharpoons$ thiol tautomerism) on the coordination mode and on the stoichiometry of L–cobalt(II) complexes.

EXPERIMENTAL

The 1-phenyl-4,6-dimethylpyrimidine-2-thione (L) was prepared by the method reported previously[10].

Preparation of Complexes

$[CoL_2(H_2O)_2][CoCl_4]$, $[CoL(H_2O)_2I_2]$, $[CoL(SCN)_2]_2$ and $[CoL_2(H_2O)_2]I_2 . 2 Me_2CO$: Solid L (4 mmol) was added slowly under stirring for 4 h at room temperature, to a solution of anhydrous $Co(SCN)_2$ (4 mmol) in acetone (30 cm^3) or of the appropriate hydrated halide salt (4 mmol). After three days the solid compounds were filtered.

$[CoL_3][CoCl_2] . H_2O$, $[CoL_2(H_2O)(NO_3)](NO_3)$ and $[CoL_2X_2]$, ($X = Br^-, I^-, SCN^-$): A solution of 3 mmol of anhydrous $Co(SCN)_2$ or of the corresponding hydrated salt in 10 cm^3 of acetone was added to a stirred suspension of L (6 mmol) in 30 cm^3 of acetone at room temperature. The reaction mixture was boiled under reflux for 4 h and kept at room temperature. After some days the solid compounds were filtered.

$Co_2L_5(NO_3)_4$, $[CoL_3](ClO_4)_2 . 0.5 Me_2CO$ and $Co_2L_7X_4$ ($X = Cl^-, Br^-, I^-$): Two millimoles of the appropriate hydrated salt were dissolved in 3 cm^3 of acetone (5 cm^3 for the perchlorate) and 7 cm^3 of triethylorthoformate (TEOF) as dehydrating agent, and the solutions allowed to stand at room temperature for 3 days in stoppered flasks. The solutions were added to a suspension of L (8 mmol) in 15 cm^3 of acetone with stirring at room temperature. The resulting solutions were heated under reflux for 6 h giving homogeneous compounds which after three days were filtered.

For $Co_2L_7X_4$ ($X = Cl^-, Br^-, I^-$) and $Co_2L_5(NO_3)_4$ compounds repeated attempts to obtain single crystals suitable for X-ray structure determination have so far failed.

$[CoL(H_2O)_4](NO_3)_2$: To an acetone solution (25 cm^3) of $Co(NO_3)_2 . 6 H_2O$ (8 mmol), 4 mmol of solid L were added with stirring at room temperature. After standing overnight the crystalline compound was filtered. On cooling for several days, the purple mother liquor afforded again brik-red crystals suitable for X-ray diffraction measurements.

$[CoL_2(NO)_3](NO_3)$: 4.5 mmol of $Co(NO_3)_2 . 6 H_2O$, were dissolved in 10 cm^3 of TEOF and 5 cm^3 of acetone and the solution allowed to stand for 3 days in a stoppered flask. On addition of solid L (4.5 mmol) and refluxing under stirring for 5 h, the initial pink solution turned to brown-purple and a yellow compound deposited. After two days the solid was filtered.

$[CoL_2(H_2O)_2](ClO_4)_2 . 2 Me_2CO$: The compound was obtained dissolving under stirring for 5 h at room temperature the solid complexing agent L (5 mmol) in an acetone solution (20 cm^3) containing 2.5 mmol of $Co(ClO_4)_2 . 6 H_2O$. After standing overnight the resulting yellow-ivory compound was filtered.

All the compounds obtained were washed with cold acetone, ether and dried in vacuo over KOH or P_4O_{10}.

Analyses and Apparatuses

Cobalt analyses were carried out by complexometric titration with EDTA after destruction of the complexes with concentrated H_2SO_4 and aqua regia. Carbon, hydrogen, nitrogen and sulfur were determined using an Erba 1106 Elemental Analyzer. Conductivity measurements were performed on freshly ≈ 10^{-3} mol dm^{-3} solutions in DMF at 25 °C with a Jenway 4020 Conductivity Meter.

Magnetic susceptibilities at room temperature were measured by the Gouy method and corrected for Pascal's constants.

IR spectra were recorded (4 000 – 400 cm^{-1}) in KBr pellets and in powdered polyethylene pellets (500 – 50 cm^{-1}) on a F.T.I.R. Bruker IFS113V spectrophotometer. The IR bands of the ligand, reported and discussed in previous works[10,11], were recorded with a Perkin–Elmer 180 spectrophotometer. They have been recorded again with a F.T.I.R. Bruker IFS113V spectrophotometer in order to better compared with the spectra of the new complexes. For this reason some of the wavenumbers reported in this work for L slightly differ from those given in the previous works. Electronic spectra (400 – 800 nm) of the complexes were recorded with a Cecil CE 6600S double beam spectrophotometer on solids supported on filter paper and in DMF solution using concentrations of cobalt(II) ranging from $5 . 10^{-3}$ to $3 . 10^{-3}$ mol dm^{-3} for chloro, bromo and thiocyanato complexes and $1 . 10^{-2}$ mol dm^{-3} for all the other compounds. The polarographic measurements were carried out in purified and dried DMF (Fluka) at 25 ± 0.1 °C, under a nitrogen atmosphere, with an Amel Multipolarograph 472. A satured Ag| AgCl, KCl_s, DMF electrode was used as a reference. All half-wave potentials were referred to a saturated calomel electrode (SCE). Tetrabutylammonium perchlorate was used as base electrolyte and the ionic strength of the solutions was kept constant (0.1 mol dm^{-3}). The polarographic measurements were performed: (i) on solutions $2 . 10^{-4}$ mol dm^{-3} of $[Co(DMF)_6](ClO_4)_2$ (recrystallized from DMF–TEOF) and of ligand L, with a metal-to-ligand molar ratio ranging from 1 : 0 to 1 : 42; (ii) on solutions $2 . 10^{-4}$ mol dm^{-3} of $[Co(DMF)_6](ClO_4)_2$ and KCl, KBr and NaSCN with a X^- to cobalt(II) ($X = Cl^-$, Br^-, SCN^-) molar ratio ranging from 2 : 1 to 8 : 1; (iii) on solutions of the all the chloro, bromo, thiocyanato and perchlorato complexes (cobalt(II) concentration = $2 . 10^{-4}$ mol dm^{-3}) alone and in presence of an excess of L ligand (cobalt(II) to L_{added} = 1 : 10 molar ratio). Details of the measurement procedures are identical to those previously described[11].

RESULTS AND DISCUSSION

General

Analytical results demonstrate that, under experimental conditions, 1-phenyl-4,6-dimethylpyrimidine-2-thione (L) forms with cobalt(II) salts a wider range of stoichiometries than was found for copper(I) (ref.[10]) and copper(II) (ref.[11]) complexes. In fact, it can be seen (Table I), that all molar ratios between 1 : 1 and 1 : 3.5 occur, and that for each cobalt(II) salts more than one complex exists depending upon anion, temperature, solvent and the used molar ratios of the reagents. In most cases the proposed structure of the compounds, is already expressed in their chemical formulae inferred from interpretation of the physico-chemical results. With exception of $[CoL_2X_2]$ ($X = Br^-$, I^-) complexes, the use of hydrated cobalt(II) salts in acetone afforded hydrated compounds. The anhydrous $[CoL_3](ClO_4)_2 . 0.5\ Me_2CO$, $[CoL_2(NO_3)](NO_3)$, $Co_2L_5(NO_3)_4$

TABLE I

Colour, analytical data, molar conductivities, Λ_M (Ω^{-1} mol^{-1} cm^2) in DMF solution (c = 1 . 10^{-3} mol^{-1}) at 25 °C and magnetic moments μ_{eff} (B.M.) at room temperature of the cobalt(II)–L complexes

Complex	Colour	Calculated/Found					Λ_M	μ_{eff}
		% C	% H	% Co	% N	% S		
$[CoL_2(H_2O)_2][CoCl_4]$	green	39.5	3.9	16.2	7.7	8.8	53	4.68
		39.5	3.8	16.2	7.6	8.8		
$[CoL_3][CoCl_4]$. H_2O	green-yellow	46.6	4.1	12.7	9.0	10.4	52	4.75
		46.4	4.0	12.7	8.9	10.3		
$Co_2L_7Cl_4$	yellow-brown	56.8	4.8	6.6	11.0	12.6	50	4.53
		56.8	4.7	6.5	11.0	12.6		
$[CoL(H_2O)_2Br_2]$	pale-pink	30.6	3.4	12.5	5.9	6.8	105	4.52
		30.5	3.4	12.4	5.9	6.8		
$[CoL_2Br_2]$	yellow-brown	44.2	3.7	9.0	8.6	9.8	110	4.65
		44.2	3.7	9.0	8.5	9.8		
$Co_2L_7Br_4$	yellow-brown	51.6	4.3	6.0	10.0	11.5	167	4.56
		51.6	4.3	6.0	10.0	11.4		
$[CoL_2I_2]$	brick-red	38.6	3.2	7.9	7.5	8.6	146	4.70
		38.6	3.2	7.9	7.4	8.6		
$[CoL_2(H_2O)_2]I_2$. 2 Me_2CO	light-yellow	40.1	4.5	6.5	6.2	7.1	150	4.63
		40.0	4.4	6.5	6.2	7.1		
$Co_2L_7I_4$	brown	47.1	3.9	5.5	9.1	10.5	278	4.83
		47.0	3.9	5.5	9.0	10.4		
$[CoL(SCN)_2]_2$	pale-blue	42.9	3.1	15.1	14.3	24.3	98	4.61
		42.8	3.1	15.0	14.2	24.3		
$[CoL_2(SCN)_2]$	yellow	51.3	4.0	9.7	13.8	21.1	63	4.98
		51.2	3.9	9.7	13.7	21.0		
$[CoL(H_2O)_4](NO_3)_2$	brick-red	30.6	4.3	12.5	11.9	6.8	155	4.66
		30.5	4.3	12.4	11.9	6.7		
$[CoL_2(NO_3)](NO_3)$	yellow	46.8	3.9	9.6	13.6	10.4	153	4.89
		46.7	3.9	9.6	13.6	10.4		
$[CoL_2(H_2O)(NO_3)](NO_3)$	yellow	45.5	4.1	9.3	13.3	10.1	156	4.62
		45.4	4.1	9.3	13.3	10.1		
$Co_2L_5(NO_3)_4$	brown	49.7	4.2	8.1	13.5	11.1	261	4.88
		49.6	4.2	8.1	13.5	11.0		
$[CoL_2(H_2O)_2](ClO_4)_2$. 2 Me_2CO	yellow-ivory	42.7	4.8	7.0	6.7	7.6	156	4.53
		42.6	4.8	7.0	6.7	7.6		
$[CoL_3](ClO_4)_2$. 0.5 Me_2CO	yellow-brown	48.0	4.2	6.3	9.0	10.3	148	4.74
		47.9	4.2	6.3	9.0	10.3		

and $Co_2L_7X_4$ ($X = Cl^-, Br^-, I^-$) halide complexes were conveniently prepared by refluxing solutions of the ligand and the corresponding hydrated cobalt(II) salt in an acetone–TEOF solution. All the solid compounds appear quite stable in an inert atmosphere. The complexes are soluble in DMF, but in some cases their dissolution is accompanied by changes in colour relative to those of the solids, indicating a strong solvolytic effect of the coordinating solvent. In this solvent the molar conductivities of the complexes show that the mono- and bis-ligand bromide complexes approach those reported for 1 : 2 electrolytes while the $[CoL_2(H_2O)_2][CoCl_4]$, $[CoL_3][CoCl_4] \cdot H_2O$, $Co_2L_7Cl_4$ and both the thiocyanate complexes have a molar conductivity that is between the ranges proposed for 1 : 1 and non-electrolytes[12]. All the other anhydrous and solvated bis-ligand complexes, the $[CoL(H_2O)_4](NO_3)_2$, $[CoL_3](ClO_4)_2 \cdot 0.5\ Me_2CO$ and $Co_2L_7Br_4$ are 1 : 2 electrolytes, while both $Co_2L_5(NO_3)_4$ and $Co_2L_7I_4$ compounds may be formulated as 1 : 3 electrolytes (Table I).

IR Spectral Studies

Comparison of the IR spectra of the complexes with those of the free complexing agent gives diagnostic indication on the donor atom(s) of the ligand, the bonding mode of the counter-ion and the presence in the solid compounds of possible solvent molecules. As reported in Table II, the hydrated complexes exhibit in the IR spectra one or two broad bands in the 3 450 – 3 200 cm^{-1} region, characteristic of $\nu(O-H)$ absorptions while the medium bands in range 390 – 340 cm^{-1} (Table III), are assignable to a $\nu(Co-OH_2)$ modes of the coordinated aqua molecules[6 – 8]. In addition, a sharp absorption at about 1 715 cm^{-1} ($\nu(C=O)$) is a clear indication for the presence of acetone in the $[CoL_2(H_2O)_2]X_2 \cdot 2\ Me_2CO$ ($X = I^-, ClO_4^-$) and $[CoL_3](ClO_4)_2 \cdot 0.5\ Me_2CO$ compounds.

Like in copper(I) (ref.[10]) and in copper(II) (ref.[11]) complexes, the very strong ligand bands in the range 1 600 – 1 300 cm^{-1}, assigned to a combination of C=C and C=N skeletal stretching vibrations of the pyrimidine ring, upon complexation are shifted to low- or high-frequency sides indicating a N-coordination through the non-substituted ring nitrogen atom. Furthermore, the strong ligand bands at 1 232 and 1 198 cm^{-1}, to which an important $\nu(C=S)$ contribution was assigned[10], are lowered in intensity and both, or one of them, are shifted to lower frequencies in the spectra of the complexes indicating an involvement of the exocyclic sulfur atom in the complexation.

Although the metal–ligand vibrations, especially those involving nitrogen and sulfur atoms of a $=N-\overset{|}{C}=S$ group which form part of heterocyclic ligands, may suffer strong coupling with ring vibrations, the relative constancy in position of the bands found for the cobalt(II)–L complexes in the 310 – 250 and 240 – 190 cm^{-1} regions (Table III) with the change of the anion and of the stoichiometry, together with the very close assignments reported reported for other metal complexes with similar ligand[6,7,10 – 13], suggest that these bands are due to modes with prevalent $\nu(Co-N)$ and $\nu(Co-S)$ character, respectively.

TABLE II
Principal IR bands (cm^{-1}) of L and its cobalt(II) complexes

Compound	ν(O–H)	ν(C=O)	ν(ring)		$\nu(C'=S) + \nu(NCN) + \nu(NCS)$		$\delta(C=S) + \pi$(ring)	
L			1 611 vs 1 521 vs	1 422 s 1 344 vs 1 335 s	1 272 vs 1 252 m	1 232 vs 1 198 m, sh	474 vs	
$[CoL_2(H_2O)][CoCl_4]$	3 435 m, sh 3 285 m, br		1 610 vs, sh 1 605 vs 1 525 vs	1 422 m, sh 1 324 w 1 315 vw	1 281 vs 1 257 w	1 243 m 1 200 w	493 m	471 m
$[CoL_3][CoCl_4] . H_2O$	3 436 m, br 3 224 m, sh		1 609 vs 1 524 vs	1 426	1 280 vs 1 242 m	1 201 w 1 180 w	490 m	471 m
$Co_2L_7Cl_4$			1 607 vs 1 523 vs	1 426 m, sh 1 346 m 1 335 m, w	1 276 vs 1 237 m, s	1 200 m 1 182 m	490 m	474 m 467 m, sh
$[CoL(H_2O)_2Br_2]$	3 455 vs 3 263 vs		1 615 vs 1 605 vs 1 531 vs	1 429 m 1 335 w 1 315 w	1 281 vs 1 254 m	1 245 m, sh 1 206 w	494 m	471 m 467 m, sh
$[CoL_2Br_2]$			1 604 vs 1 524 vs	1 430 m, sh 1 324 w 1 316 w	1 280 vs	1 243 s 1 201 m, w	491 s	476 m
$Co_2L_7Br_4$			1 605 vs 1 520 vs	1 429 m, sh 1 335 m 1 315 w	1 274 vs	1 237 s 1 201 m,w	491 s	474 s 467 s, sh
$[CoL_2I_2]$			1 603 vs 1 519 vs	1 428 m 1 328 m 1 320 w	1 281 vs	1 243 s 1 201 m, w	491 s	474 m
$[CoL_2(H_2O)_2]I_2 . 2 Me_2CO$	3 337 s 3 225 s	1 711 s	1 618 s 1 531 s	1 427 m 1 330 vw 1 315 w	1 281 vs 1 247 m	1 222 m 1 212 w	494 s	472 m

TABLE II
(*Continued*)

Compound	ν(O–H)	ν(C=O)	ν(ring)		ν(C=S) + ν(NCN) + ν(NCS)		δ(C=S) + π(ring)	
$Co_2L_7I_4$			1 604 vs 1 520 vs	1 427 m 1 335 m 1 316 w	1 280 vs	1 237 m 1 202 w	494 m,s	474 m, s 470 m, sh
$[CoL(SCN)_2]_2$			1 616 vs 1 526 s	1 435 s 1 330 w 1 315 w	1 280 vs 1 260 m	1 225 w 1 209 w	492 m	472 m, br
$[CoL_2(SCN)_2]$			1 603 vs 1 523 vs	1 430 m 1 333 m, sh 1 315 w	1 279 vs 1 256 m	1238 s 1 200 w	488 vs	472 s
$[CoL(H_2O)_4](NO_3)_2$	3 438 s 3 385 s, br 3 267 s, br		1 619 m, s 1 605 m, s 1 531 m	1 430 m 1 325 m, sh	1 281 s 1 253 m, w	1 240 w 1 205 m	493 m	474 w 464 w
$[CoL_2(NO_3)](NO_3)$			1 606 vs 1 525 s	1 431 s 1 332 w	1 281 vs	1 240 m 1 202 m, w	494 m	472 m, w 463 w, sh
$[CoL_2(H_2O)(NO_3)](NO_3)$	3 400 m, sh 3 300 m 3 206 m		1 610 vs 1 530 s, sh	1 435 s, sh 1 323 m	1 282 vs 1 245 m	1 234 m 1 205 m, w	492 vs	472 m, w 460 w, sh
$Co_2L_5(NO_3)_4$			1 607 vs 1 525 vs	1 431 s 1 334 m	1 280 vs 1 270 m, sh	1 238 m 1 206 w	494 m	472 m, w 462 m, sh
$[CoL_2(H_2O)_2](ClO_4)_2 . 2 Me_2CO$	3 244 vs 3 191 vs 3 167 vs	1 719 m,s	1 613 vs 1 535 s	1 430 s 1 335 w 1 318 w	1 281 vs 1 243 s	1 220 w 1 205 w	492 s	472 m, s
$[CoL_3](ClO_4)_2 . 0.5 Me_2CO$		1 713 m	1 618 vs 1 524 vs	1 427 s	1 280 vs 1 241 ms	1 225 m, w 1 202 w	490 vs	472 m, s 462 m, sh

TABLE III

Far-IR spectral bands (400 – 50 cm^{-1}) of the cobalt(II)–L complexes and their tentative assignments

Compound	ν(Co–OH_2)	$(Co–X)_{modes}$	ν(Co–N)	ν(Co–S)	Ligand and other bands
$[CoL_2(H_2O)][CoCl_4]$	360 m, br	326 vs, 285 vs 255 s, 123 m	308 m, sh	240 m, sh 193 m, br	390 w, sh, 143 m, 123 m, 110 m, sh, 93 m, w, 60 m, br
$[CoL_3][CoCl_4]$. H_2O		331 m, 291 vs, 256 ms, 127 m	302 vs, sh	240 m, sh 195 m	391 vw, 216 m, 160 m, 93 m, br, 70 m, 56 m
$Co_2L_7Cl_4$		247 vs, 127 ms	299 m	218 m	390 w, 339 mw, 283 m, sh, 156 mw, 115 m, sh, 90 w, 68 w
$[CoL(H_2O)_2Br_2]$	372 m, 343 ms	191 s, 175 s	297 mw	243 m	335 m, sh, 287 w, 208 m, sh, 141 s, 85 m, sh, 66 s
$[CoL_2Br_2]$		183 vs, 158 ms	301 mw, 264 mw	224 s	339 mw, 289 m, sh, 137 w, sh, 102 w, sh, 66 w
$Co_2L_7Br_4$		184 vs, 158 m	301 m, 265 m	224 s	390 w, sh, 337 mw, 137 w, sh, 66 w, sh
$[CoL_2I_2]$		150 s, 127 m	303 m, 262 m	228 ms	390 w, sh, 336 mw, 285 w, 190 w, 67m
$[CoL_2(H_2O)_2]I_2$. 2 Me_2CO	390 m, 364 m		305 m, 260 m, sh	247 vs, 218 m	334 m, 279 w, 193 m, 170 mw, 143 m, 90 w, 67 s
$Co_2L_7I_4$		150 vs, 127 w	303 m, 262 m	229 ms	390 w, 334 mw, 285 w, 89 mw, 67 ms

TABLE III
(*Continued*)

Compound	ν(Co–OH$_2$)	(Co–X)$_{modes}$	ν(Co–N)	ν(Co–S)	Ligand and other bands
[CoL(SCN)$_2$]$_2$		290 vs, 275 vs, 199 m[a]	masked	238 m, sh, 217 s, sh	390 w, 334 mw, 183 s, sh, 154 m, sh, 130 w, 91 w, 72 mw
[CoL$_2$(SCN)$_2$]		276 vs	297 s, sh	233 vs	390 w, 334 mw, 179 m, 160 ms, 143 w, 118 mw, 85 m, 59 m
[CoL(H$_2$O)$_4$](NO$_3$)$_2$	386 m, sh, 370 m		293 m	251 m	335 mw, 283 m, sh, 198 m, sh, 177 s, 116 ms, 81 ms
[CoL$_2$(NO$_3$)](NO$_3$)		243 vs	309 ms, 260 s, sh	masked	391 vw, 334 mw, 280 mw, 198 w, 172 m, 148 m, 135 m, 120 m, 62 m
[CoL$_2$(H$_2$O)(NO$_3$)](NO$_3$)	351 m, br	230 vs	309 ms, 264 m	256 ms, 241 s, sh	388 w, 334 m, 280 m, 170 m, 133 s, 122 s, sh, 91 m, 78 m, 53 w
Co$_2$L$_5$(NO$_3$)$_4$		243 vs	309 m, 258 s, sh	masked	391 w, 334 w, 282 w, 172 m, 148 m, 135 m, sh, 116 ms, 66 ms
[CoL$_2$(H$_2$O)$_2$](ClO$_4$)$_2$. 2 Me$_2$CO	388 s, 374 m, sh		303 m, 258 m	241 s, 222 ms	336 mw, 283 mw, 189 w, 164 ms, 143 ms, 116 w, 102 w, 71 s, 59 m
[CoL$_3$](ClO$_4$)$_2$. 0.5 Me$_2$CO			297 m, 251 s	245 s, sh, 208 s	391 w, 334 mw, 283 mw, 177 m, 128 w, 91 m, 70 ms, 56 m

[a] Probably ν(Co–SCN).

With regard the inorganic anions, the most interesting features are found in the IR spectrum of the mono-ligand thiocyanate complex (Table IV). Effectively in the 2 150 – 2 000 cm^{-1} region, we find three well resolved bands of roughly equal intensity with a shoulder on the low-frequency side, which can be assigned to ν(CN) stretching vibrations. Splittings of this order have previously been shown to occur when different thiocyanate coordination modes are present in the same molecule[14]. The position of the bands at 2 130 and 2 116 cm^{-1} is consistent with that proposed for thiocyanate-bridged compounds[15,16], while the bands at 2 092 and 2 077 cm^{-1} fall in the range expected for terminal N-bonded thiocyanate[17]. Also the position of the bands in the ν(CS), δ(NCS) and ν(Co–NCS) (refs[18 – 20]) regions (Table III), agree with this suggestion.

From stoichiometric considerations and in accord with solid state spectral and magnetic results, the splittings of the ν(CN), ν(CS), δ(NCS) and ν(Co–NCS) absorptions may be related to the formation of centrosymmetric dimers $[CoL(SCN)_2]_2$ in which both the cobalt(II) ions, bridged by two thiocyanate groups, achieve a five-coordinated arrangement through a N,S-chelate pyrimidine and a N-bonded thiocyanate ligand.

Alternatively, the compound might be considered to have a dinuclear or polynuclear structure consisting of cationic $[CoL_2]^{2+}$ and tetrahedral anionic $[Co(SCN)_4]^{2-}$ units[21], thiocyanate ion(s) from the latter completing a five-coordination or a distorted octahedron about the cobalt(II) ions in the $[CoL_2]^{2+}$ units as proposed for $[Co(2,5\text{-dithiahexane})Cl_2]$ compound[22].

For the $[CoL_2(SCN)_2]$ complex, the ν(CN), ν(CS), δ(NCS) and ν(Co–NCS) absorption bands fall in the regions expected for monomeric pseudo-octahedral cobalt(II) compounds with trans N-bonded thiocyanate anions.

TABLE IV

IR bands wavenumbers (cm^{-1}) attributed to the SCN^- groups of cobalt(II)–L complexes

Assigments		$[CoL(SCN)_2]_2$	$[CoL_2(SCN)_2]$
ν_1	$\nu_d(CN)$	2 130 vs, 2 116 vs	
		2 092 vs, 2 077 s, sh	2 077 vs, 2033 s, sh
2 ν_2	2 δ(SCN)	964 mw	960 mw
		935 w, 918 mw	
ν_3	ν(CS)	840 m	808 m
		788 mw	
ν_2	δ(SCN)	482 m	481 m, sh
		467 m, 457 m	

The diagnostic IR band frequencies of the counter-ions, indicating ionic nature of the nitrato group in the $[CoL(H_2O)_4](NO_3)_2$ complex, are consistent with the X-ray structure of the compound[23]. Full crystallographic details for the compound will be published elsewhere together with the crystal structure of 4,6-dimethylpyrimidine-2-thione and its N-phenyl derivative. From this it follows that this compound consists of ionic NO_3^- groups and $[CoL(H_2O)_4]^{2+}$ units in which the cobalt(II) ion exhibit a distorted octahedral coordination achieved through four oxygen-bonded water molecules with Co–O distances ranging from 2.048(6) to 2.126(5) Å and a N, S-bidentate ligand molecule (Co–N = 2.196(5), Co–S = 2.481(2) Å) giving rise to a four-membered chelate ring with a S–Co–N angle on the metal of 66.4(2)°. Such values are intermediate between the mean of the values observed in $[Co(C_4H_4N_2S)_2Cl_2]$ (ref.[5]) (Co–N = 2.098, Co–S = 2.960 Å, N–Co–S = 59.12°) and in $[Co(C_6H_7N_2S)_3]$ (ref.[24]) (Co–N = 1.779, Co–S = 2.259 Å, N–Co–S = 72.4°) complexes.

In the IR spectra of the others nitrato complexes (Table V), the ν_2, ν_3 and ν_4 (in the D_{3h} symmetry) fundamental vibrational modes of NO_3^- groups, are split into two or three components and ν_1 mode becomes IR active, indicating the simultaneous presence of ionic and coordinated NO_3^- anions[25]. Lending support to our suggestion, even if the coordination mode of the nitrato groups (monodentate or bidentate) cannot be deduced unequivocally from these data, is the appearance of a strong band between 230 – 243 cm^{-1} (Table III) which is not present in the far-IR spectrum of mono-ligand nitrato complex, assignable to $\nu(Co{-}O)_{anion}$ mode[7].

For both the perchlorato complexes the splitting of ν_3 and ν_4 modes and the appearance of ν_1 mode clearly indicates that some distortion for ClO_4^- groups from T_d symmetry[25] occurs in the solid complexes caused by lattice requirements, by site-symmetry effects or by hydrogen bonds rather than Co–anion interaction.

For $[CoL_2(H_2O)_2][CoCl_4]$ and $[CoL_3][CoCl_4] \cdot H_2O$ complexes, far-IR spectra (Table III) show bands assignable to antisymmetric $\nu_d(Co{-}Cl)$ [$\nu_3(F_2)$ at 326, 285 and 331, 291 cm^{-1}], $\delta_d(Cl{-}Co{-}Cl)$ [$\nu_4(F_2)$ at 123 and 127 cm^{-1}] and symmetric $\nu_s(Co{-}Cl)$ [$\nu_1(A_1)$ at 255 and 256 cm^{-1}] modes, respectively, pointing to the presence of discrete $[CoCl^4]^{2-}$ anions[26]. Observed splittings of the fundamental ν_3 and the presence of ν_1 (IR inactive in T_d symmetry) vibrations would arise from crystal effects and/or distortions in bond angles and bond lengths caused by hydrogen bonding with water molecules.

Among the complexes with unusual stoichiometry $Co_2L_7X_4$ ($X = Cl^-, Br^-, I^-$) and $Co_2L_5(NO_3)_4$, the bromo, iodo and nitrato complexes exhibit far-IR and the iodo and nitrato derivatives also solid phase ligand field spectra, almost identical with those of the corresponding anhydrous bis-ligand complexes, for which solid state spectral results suggest to contain a distorted octahedral $[CoN_2S_2X_2]$ ($X = Br^-, I^-, O{-}NO_2^-$) chromophore. Support for a probably similar donor set for cobalt(II) in the solid $Co_2L_7X_4$ ($X = Cl^-, Br^-, I^-$) complexes comes from the position of the very strong $\nu(Co{-}X)$ frequencies[5,27] and from their ratios ($\nu(Co{-}Br_t/\nu(Co{-}Cl)_t = 0.74$, $\nu(Co{-}I)_t/\nu(Co{-}Cl)_t =$

TABLE V
IR bands wavenumbers (cm^{-1}) attributed to the NO_3^- and ClO_4^- groups of cobalt(II)–L complexes

Assigments for NO_3^- (D_{3h})		$[CoL(H_2O)_4]X_2$	$[CoL_2X]X$	$[CoL_2(H_2O)X]X$	$Co_2L_7X_4$	$[CoL_2(H_2O)_2]X_2 . 2 Me_2CO$	$[CoL_3]X_2 . 0.5 Me_2CO$	Assigments for ClO_4^- (T_d)	
		X = NO_3^-				X = ClO_4^-			
ν_3	ν_d(NO)		1 450 vs	1 444 vs	1 449 vs	1 145 vs	1 143 vs	ν_d(ClO)	ν_3
		1 386 vs	1 385 vs	1 385 vs	1 385 vs	1 114 vs	1 192 vs, br		
			1 302 vs	1 294 vs	1 301 vs	1 090 vs			
ν_1	ν_s(NO)		1 032 s	1 031 s	1 030 s	934 w	930 w	ν_s(ClO)	ν_1
ν_2	$\pi(NO_3)$	835 mw	835 w	838 w	840 m, sh	637 s	635 mw	δ_d(OClO)	ν_4
			806 m	826 w	807 m	627 s	624 s		
				810 w					
ν_4	δ_d(ONO)	715 mw	729 m	729 m	728 m				
				720 m	715 mw				

0.61), whose values are very close to those accepted for cobalt(II)–halide complexes with octahedral enviroments[28].

Nevertheless, due to impossibility to obtain crystallographic data from X-ray analysis (see Experimental) our data are not sufficient to suggest possible structures for the solid $Co_2L_7X_4$ ($X = Cl^-, Br^-, I^-$) and $Co_2L_5(NO_3)_4$ complexes since from their IR spectra (4 000 – 500 cm^{-1}) is not clear if all and how the ligand molecules are coordinated to the metal centers.

Magnetic Moments and Visible Spectra

All cobalt(II) complexes gave room temperature magnetic moments in the range 4.50 – 5.00 B.M. (Table I) as expected for high-spin tetrahedral or octahedral complexes.

The solid state and DMF solution visible spectral data (Table VI) of the cobalt(II) complexes classify them into four groups.

1) The mono-ligand chloro and $Co_2L_3Cl_4 . H_2O$ complexes furnish, both in the solid phase and in DMF solution, spectra with high-intensity absorptions in the 600 – 700 nm region and bands between 500 – 560 nm attributable to spin-allowed $^4A_2 \rightarrow {}^4T_1(P)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition, respectively, showing the co-existence of both tetrahedral and octahedral cobalt(II) species[9]. Similar composite spectral features, along with far-IR spectra, provide evidence for the formulation for these solid compounds of a salt-like structure of the type $[CoL_2(H_2O)_2][CoCl_4]$ and $[CoL_3][CoCl_4] . H_2O$, respectively.

2) Grinding the mono- and bis-ligand bromide, the bis-ligand thiocyanate and $Co_2L_7X_4$ ($X = Cl^-, Br^-$) complexes for solid state spectral measurements, caused a change of colour to dark-green. The spectra show weak bands in the 580 – 700 nm region besides those characteristic of octahedral (500 – 570 nm) cobalt(II) complexes. The position and the intensity (increasing with the grinding) of the additional bands, indicate the formation of appreciable amounts of tetrahedral species. Such spectral behaviours of the cobalt(II) complexes are not uncommon[29 - 31]. When dissolved in DMF, all the five compounds afford dark-green or green-olive solutions and their visible spectra at room temperature seem to show a complete breakdown of the octahedral species. The spectra, in effect, reveal, besides the intense bands characteristic of tetrahedral cobalt(II) species, also the presence of weak absorptions in the 500 – 590 nm region, whose position and intensity are in the same order as the absorption bands in the corresponding octahedral cobalt(II) iodo, nitrato and perchlorato complexes and may be assigned in the same way to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions. These evidences, as well as the conductivity data, might suggest that the dissolution, with partial displacement of the ligand molecules and dissociation of the anions[30,32,33], together with a possible rearrangement of coordination mode[31,34] of the heterocyclic ligand from N,S-bidentate to N-monodentate and the breakdown[35] of the probable dinuclear $Co_2L_7X_4$ ($X = Cl^-, Br^-$) species, are responsible for the formation in DMF solution of an equilibrium between octahedral → tetrahedral complexed species containing thiopyrimidine ligand.

TABLE VI
Solid phase and DMF solution visible spectra (400 – 800 nm) of cobalt(II)–L complexes at room temperature

Compound	Solid state	DMF solution[a]
$[CoL_2(H_2O)_2][CoCl_4]$	450 sh, 530 m, 613 sh, 626 s, 645 sh, 661 s, 703 sh, 713 s	527(15), 600 sh, 608(195), 633 sh, 674(307)
$[CoL_3][CoCl_4] . H_2O$	454 sh, 532 m, 615 sh, 634 s, 648 sh, 668 s, 700 s, 711 sh	527(18), 600 sh, 608(193), 633 sh, 673(302)
$Co_2L_7Cl_4$	450 sh, 530 m, 560 m, 616 mw, 633 mw, 668 mw, 698 mw	527(22), 580 sh, 600 sh, 608(183), 633 sh, 674(282)
$[CoL(H_2O)_2Br_2]$	470 sh, 518 m, 545 m, 642 mw, 668 mw, 700 mw, 727 m	546(18), 622 sh, 642(135), 685 sh, 696(195)
$[CoL_2Br_2]$	470 sh, 538 sh, 570 m, 642 w, 666 m, 682 sh, 700 m, 723 mw	546(28), 622 sh, 642(167), 685 sh, 696(243)
$Co_2L_7Br_4$	540 sh, 573 ms, 640 m, 668 m, 700 mw, 725 sh	546(55), 583(75), 622 sh, 641(143), 685 sh, 696(196)
$[CoL(SCN)_2]_2$	446 sh, 530 sh, 562 s, 598 s, 630 sh	525(50), 588(225), 625(383)
$[CoL_2(SCN)_2]$	473 sh, 500 sh, 520 sh, 587 m, 620 mw	525(52), 588(220), 625(380)
$[CoL_2I_2]$	470 sh, 522 m, sh, 560 m, sh	527(24)
$[CoL_2(H_2O)_2]I_2 . 2 Me_2CO$	470 sh, 530 m, sh, 560 m, sh	526(25)
$Co_2L_7I_4$	460 sh, 525 m, sh, 560 m, sh	476s, sh, 525 m, sh, 570(100)
$[CoL(H_2O)_4](NO_3)_2$	468 m, 498 m, 520 m, 560 sh	430(311), 528(24)
$[CoL_2(NO_3)](NO_3)$	480 sh, 530 m, 565 sh	440(320), 528(26)
$[CoL_2(H_2O)(NO_3)](NO_3)$	475 sh, 530 m, sh, 560 m, sh	440(315), 527(25)
$Co_2L_5(NO_3)_4$	460 m, sh, 533 m, 570 m	470(678), 510(580), 550(350)
$[CoL_2(H_2O)_2](ClO_4)_2 . 2 Me_2CO$	470 sh, 520 m, 580 sh	526(23)
$[CoL_3](ClO_4)_2 . 0.5 Me_2CO$	460 sh, 542 m, 576 sh	526(22)

[a] Intensities normalized with a unit concentration of the metal ion in solution are given in parentheses.

Nevertheless, a more careful inspection of the spectra and comparing them with those displayed by $[CoL_2(H_2O)_2][CoCl_4]$ and $[CoL_3][CoCl_4] . H_2O$ complexes in DMF solution and those reported for spectrophotometric studies on $CoCl_2$ (refs[36 - 38]), $CoBr_2$ (ref.[39]) and $Co(SCN)_2$ (refs[40,41]) salts in the same solvent, also and mainly a solvolytic ionic disproportionation of the complexes into tetrahedral anionic $[CoX_4]^{2-}$ ($X = SCN^-$, Cl^-) and $[CoX_3(DMF)]^-$ ($X = SCN^-$, Cl^-, Br^-) and some possible cationic octahedral $[Co(DMF)_6]^{2+}$, $[CoX(DMF)_5]^+$, $[CoXL(DMF)_4]^+$ and $[CoL(DMF)_5]^{2+}$ ($X = Cl^-$, Br^-, SCN^- and L = N-monodentate heterocyclic ligand) species in equilibrium, cannot be ruled out.

Thus the following solvolytic reaction is proposed:

$$5\,CoL_nX_2 \xrightarrow{DMF} [CoX_{(4-y)}(DMF)_y]^{(2-y)-} + Co(DMF)_6]^{2+} + [CoX(DMF)_5]^+ +$$
$$+ [CoXL(DMF)_4]^+ + [CoL(DMF)_5]^{2+} + (5n-2)L + (4+y)X^- \qquad (A)$$

for $X = SCN^-$ $n = 1, 2$ and $y = 0, 1$;
for $X = Cl^-$ $n = 1, 1.5, 3.5$ and $y = 0, 1$;
for $X = Br^-$ $n = 1, 2, 3.5$ and $y = 1$.

This suggestion is consistent with the actual position and contour of the absorption bands due to the tetrahedral species, which for a given anion, in spite of the difference in stoichiometry of the solids, are markedly constant and closely similar to those reported for the corresponding $[CoX_4]^{2-}$, ($X = SCN^-$, Cl^-) and $[CoX_3(DMF)]^-$ ($X = SCN^-$, Cl^-, Br^-) species in DMF solution[36 - 41].

In addition, taking in consideration the complexes with the same anion, it can be observed (Table VI) that as the L to Co(II) ratio in the solid compound exceeds a given value (1 : 1 for chloro and thiocyanato and 2 : 1 for bromo complexes), the spectra show a weak but distinct increase in intensity of the bands in the 500 – 600 nm region, accompanied by a relating decrease of the absorption bands due to the tetrahedral species.

For instance, Fig. 1 shows the visible absorption spectra in DMF of the series of the bromo complexes, while Fig. 2 shows the time-dependent spectral changes of the $Co_2L_7Br_4$ complex alone and in presence of an excess of ligand (Co(II) to L_{added} = 1 : 10). Similar spectral behaviours were also observed for the other bromo derivatives and for all the chloro and thiocyanato complexes under the same experimental conditions.

These results provide a direct evidence for the existence in DMF solution of equilibria between anionic tetrahedral $[CoX_4]^{2-}$ ($X = SCN^-$, Cl^-), $[CoX_3(DMF)]^-$ ($X = SCN^-$, Cl^-, Br^-) and one or more cationic octahedral cobalt(II) species. The time-dependent composition and population of these species depend on the number of the heterocyclic ligand molecules present in the solid complexes and released by solvolysis, on the coordinating power of the counter-ion and on the relative stability constant of the new complexed species.

3) As far as the solid pale-blue $[CoL(SCN)_2]_2$ compound is concerned, it exhibits a somewhat complicated ligand field spectrum, typical neither for six- nor four-coordination, but similar to those reported for five-coordinated trigonal-bipyramidal cobalt(II) thiocyanato complexes[31] or alternatively ascribable to compounds in which two different cobalt(II) enviroments are present. When dissolved in DMF, its green-blue solution exhibits different spectral features from the solid, but similar to those for $[CoL_2(SCN)_2]$ in the same solvent.

4) Finally, the visible spectra if all iodo, nitrato and perchlorato complexes either as solid samples or in DMF solution, are consistent with cobalt(II) in a more or less distorted octahedral field. However, their solution spectra are quite different from those of the corresponding solids, but coincident, except those of $Co_2L_5(NO_3)_4$ and $Co_2L_7I_4$ complexes with that of a solution of the pure $[Co(DMF)_6]$ $(ClO_4)_2$ (λ_{max} = 526 nm, ε = 21)(ref.[36]) in the same solvent, known to contain solvated $[Co(DMF)_6]^{2+}$ species.

These results, confirmed by polarographic data for the perchlorato complexes and for the $[Co(DMF)_6](ClO_4)_2$–L system at various ligand concentrations show that in a coordinating solvent as DMF, competitive solvent molecules displaces easily and completely thiopyrimidine ligands from these complexes. Thiopyrimidine-containing

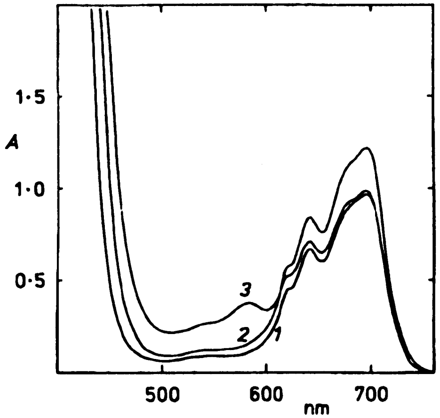

FIG. 1

Absorption spectra of: *1* $[CoL(H_2O)_2Br_2]$, *2* $[CoL_2Br_2]$, *3* $Co_2L_7Br_4$ complexes in DMF solution at 25 °C, cobalt(II) concentration = 5 . 10^{-3} mol dm^{-3}

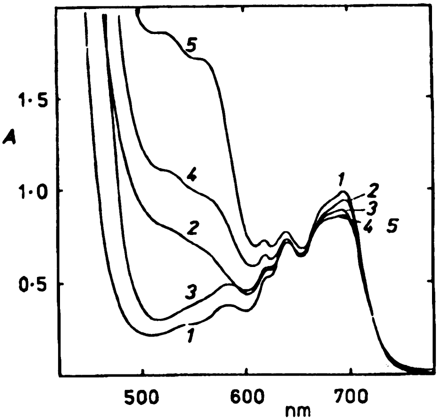

FIG. 2

Time-dependent absorption spectra of the $Co_2L_7Br_4$ complex (cobalt(II) concentration = 5 . 10^{-3} mol dm^{-3}) alone and in presence of an excess of ligand L (cobalt(II) to L = 1 : 10) in DMF at 25 °C. *1* $Co_2L_7Br_4$; *2* $Co_2L_7Br_4$, ten days later; *3* $Co_2L_7Br_4$ + 20 L; *4* and *5* $Co_2L_7Br_4$ + 20 L, three and ten days later, respectively species (Fig. 3) can be formed in solution only partially and only in presence of an excess of heterocyclic ligand.

Polarographic Behaviour of Cobalt(II)–L Complexes in DMF Solution

In order to gain a better understanding of the behaviour of the complexes under discussion in dilute DMF solution, we have carried out preliminary polarographic studies on the following systems: $[Co(DMF)_6](ClO_4)_2$, $[Co(DMF)_6](ClO_4)_2$–L at increasing L concentration, $[Co(DMF)_6](ClO_4)_2$–X (X = Cl^-, Br^-, SCN^- at increasing X concentration) and on the individual perchlorato, chloro, bromo and thiocyanato complexes alone and in the presence of a ligand excess ($(Co(II))_{complex}$ to L_{added} = 1 : 10).

Binary Systems

Polarographic measurements carried out on $[Co(DMF)_6](ClO_4)_2$, reveal a bielectronic, quasi-reversible and diffusion controlled reduction wave with $E_{1/2} = -1.195$ V. The reduction of the ligand L is an one-electron, diffusion controlled and reversible process, with $E_{1/2} = -1.710$ V (ref.[10]).

For the $[Co(DMF)_6](ClO_4)_2$–L system, the $E_{1/2}$ value of the $[Co(DMF)_6]^{2+}$ wave shifts towards more negative values with increasing ligand concentration (Table VII). This is paralleled by a decrease of diffusion current and by an increase of the reversibility of the electron transfer process (the electron transfer coefficient α shifts from 0.5 to 0.8).

In order to evaluate the species in solution and their stability constants, the Lingane plot[42] and the DeFord–Hume method[43] were used. The reversible half-wave potentials were determined according to Ayabe–Matsuda method[44].

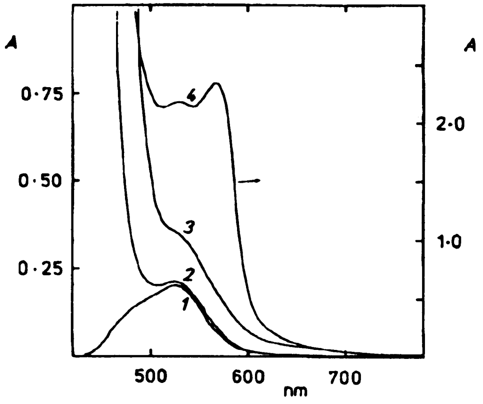

FIG. 3
Absorption spectra at 25 °C in DMF of the systems: *1* $[Co(DMF)_6](ClO_4)_2$; *2* $[CoL_2(H_2O)_2](ClO_4)_2 . 2 Me_2CO$; *3* $[CoL_2(H_2O)_2](ClO_4)_2 . 2 Me_2CO + 10$ L; *4* $[CoL_2(H_2O)_2](ClO_4)_2 . 2 Me_2CO + 10$ L after seven days. Cobalt(II) concentration = $1 . 10^{-2}$ mol dm^{-3}

The Lingane plot, reported in Fig. 4 (the slope of the straight-lines is given by log (*JRT*/*nF*), where *J* is the number of coordinated ligand molecules) shows that, for ligand-to-metal molar ratios up to about 12 : 1, the $[CoL(DMF)_5]^{2+}$ species prevails, while at higher ratios the $[CoL_2(DMF)_4]^{2+}$ species is prevalent. The predominance of $[CoL(DMF)_5]^{2+}$ on $[CoL_2(DMF)_4]^{2+}$ up to rather high ligand-to-metal molar ratios, is most probably due to a mass effect of DMF and to the weaker bonding strength of the ligand as compared to DMF. The values of the overall stability constants are $\beta\{[CoL(DMF)_5]^{2+}\} = 3.8 \cdot 10^5$ and $\beta\{[CoL_2(DMF)_4]^{2+}\} = 9.6 \cdot 10^7$, respectively.

TABLE VII

$E_{1/2}$ values of binary systems $[Co(DMF)_6](ClO)_4)_2$–L and $[Co(DMF)_6](ClO_4)_2$–X (X = Cl^-, Br^-, SCN^-) in DMF solution, $c\{[Co(DMF)_6](ClO_4)_2\} = 2 \cdot 10^{-4}$ mol dm^{-3}, $T = 25 \pm 0.1$ °C, drop time = 1 s

c(Thione) . 10^4 mol dm^{-3}	$-E_{1/2}$, V	c(X) . 10^4 mol dm^{-3}	$-E_{1/2}$, V		
			Cl^-	Br^-	SCN^-
0	1.195	0	1.195	1.195	1.195
4.0	1.195	4.0	1.270	1.210	1.210
14.0	1.335	8.0	1.290	1.235	1.245
24.0	1.350	12.0	1.310	1.245	1.260
44.0	1.380	16.0	1.315	1.255	1.270
64.0	1.400				
84.0	1.410				

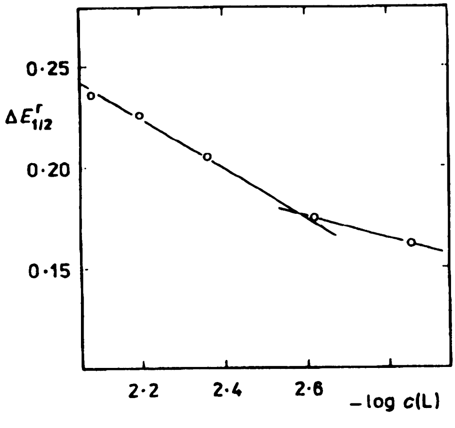

FIG. 4

Lingane plot of the system $[Co(DMF)_6](ClO_4)_2$–L in DMF at 25 °C, cobalt(II) concentration = 2 . 10^{-4} mol dm^{-3}, c(L) ligand L concentration (mol dm^{-3}), $\Delta E^r_{1/2} = E^r_{1/2}{}^M - E^r_{1/2}{}^C$

The polarographic curves of both the bis- and tris-ligand perchlorato complexes exhibit a single wave (Table VIII) with the same features found for $[Co(DMF)_6](ClO_4)_2$ and for the related binary system $[Co(DMF)_6](ClO_4)_2$–L with a Co(II) to L ratio 1 : 2.

This finding, in agreement with the electronic spectra, confirms the complete replacement of the coordinated heterocyclic ligand and water molecules by DMF molecules according to the following reactions:

$$[CoL_2(H_2O)_2](ClO_4)_2 \xrightarrow{DMF} [Co(DMF)_6]^{2+} + 2\,ClO_4^- + 2\,L + 2\,H_2O \qquad (B)$$

$$[CoL_3](ClO_4)_2 \xrightarrow{DMF} [Co(DMF)_6]^{2+} + 2\,ClO_4^- + 3\,L \qquad (C)$$

The polarographic measurements on the $[Co(DMF)_6](ClO_4)_2$–X (X = Cl^-, Br^-, SCN^-) systems were performed in order to ascertain the species present in solution with different anions and with increasing X concentration. The reduction processes are bielectronic, diffusion controlled and quasi-reversible. The $E_{1/2}$ values at increasing X concentration (X = Cl^-, Br^-, SCN^-) are reported in Table VII and used for Lingane plots. These plots (Fig. 5) indicate that, also in very dilute DMF solution, the prevailing species are $[Co(SCN)_4]^{2-}$ and $[CoX_3(DMF)]^-$ for X = Cl^-, Br^-, respectively, according the spectrophotometric measurements.

Ternary Systems

The $[CoL_n(SCN)_2]$ (n = 1, 2), $[CoL(H_2O)_2Br_2]$, $[CoL_2Br_2]$, $[CoL_3][CoCl_4]\,.\,H_2O$ and $[CoL_2(H_2O)_2][CoCl_4]$ complexes invariably display a single polarographic wave (wave I, Table VIII) showing the same features found for the corresponding binary system $[Co(DMF)_6](ClO_4)_2$–X (X = Cl^-, Br^-, SCN^-) with a $[Co(DMF)_6]^{2+}$ to X^- 1 : 2 molar

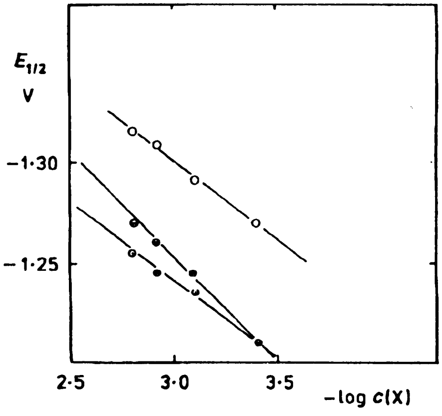

FIG. 5

Lingane plots of the $[Co(DMF)_6](ClO_4)_2$–X systems: ○ X = Cl^-, ⊙ X = Br^-, ⊖ X = SCN^- in DMF at 25 °C, cobalt(II) concentration = 2 . 10^{-4} mol dm^{-3}, c(X) halide or pseudohalide concentration (mol dm^{-3})

ratio. On the contrary, the polarograms of the $Co_2L_7X_4$ ($X = Cl^-$, Br^-) complexes, as well as those of all the above reported chloro, bromo and thiocyanato complexes in presence of an excess of ligand L added (Co(II) to L_{added} = 1 : 10), show two waves (Table VIII). The prevailing one (wave I), exhibiting the same characteristics observed for the corresponding complexes and binary systems with a $[Co(DMF)_6]^{2+}$ to X^- ($X = Cl^-$, Br^-, SCN^-) molar ratio of 1 : 2, decreases maitaining the same $E_{1/2}$ value. Wave II, which appears at more positive E values, shows a current value that increases with increasing the total ligand concentration (L added plus L molecules arising from solvolysis of the complexes). For all the systems, the sum of the currents of waves I and II remains constant.

These findings together with the $E_{1/2}$ values found for the reduction of the $[CoL(DMF)_5]^{2+}$ and $[CoL_2(DMF)_4]^{2+}$ species suggest that wave II probably corresponds to more reducible[45] Co–X–L–DMF octahedral (see electronic spectra) mixed complexes, whose composition has not been determined yet, and will be the subject of future investigation.

TABLE VIII

$-E_{1/2}$ values (in V) of cobalt(II) complexes alone and in presence of a ligand excess (cobalt(II) to L_{added} = 1 : 10) in DMF at 25 ± 0.1 °C, cobalt(II) concentration = $2 \cdot 10^{-4}$ mol dm^{-3}, drop time = 1 s

Complex	Complex alone		Complex + L_{added}	
	wave I	wave II	wave I	wave II
$[CoL(SCN)_2]_2$	1.215	–	1.215	1.050
$[CoL_2(SCN)_2]$	1.210	–	1.210	1.045
$[CoL_2(H_2O)_2][CoCl_4]$	1.270	–	1.270	1.070
$[CoL_3][CoCl_4] \cdot H_2O$	1.270	–	1.270	1.055
$Co_2L_7Cl_4$	1.270	1.070	1.270	1.040
$[CoL(H_2O)_2Br_2]$	1.210	–	1.210	1.065
$[CoL_2Br_2]$	1.210	–	1.210	1.060
$Co_2L_7Br_4$	1.210	1.060	1.210	1.055
$[CoL_2(H_2O)_2](ClO_4)_2 \cdot 2\ Me_2CO$	1.195	–	1.345	
$[CoL_3](ClO_4)_2 \cdot 0.5\ Me_2CO$	1.195	–	1.350	

The IR spectra were recorded in the Centro Interdipartimentale Grandi Strumenti of University of Modena.

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