Co-ordination of Organophosphorus Anions. Part III.[1] Spectral Studies of some Five- and Six-co-ordinate Cobalt(II) and Zinc(II) Halides and Pseudohalides

By **Marie H. Youinou** and **Jacques E. Guerchais,*** Laboratoire de chimie moléculaire inorganique, U.E.R. des Sciences, Université de Bretagne Occidentale, 29283 Brest, France

The anions $[P(CHCOCH_2R)O(OEt)_2]^-$ [R = NEt_2(L^2), $\overline{NCH_2CH_2OCH_2CH_2}$ (L^3), or $\overline{NCH_2CH_2CH_2CH_2CH_2}$ (L^4)] form five-co-ordinate complexes [MX(L)] (M = Co^{II}, L = L^2, L^3, or L^4 and X = Br, I, NCS, or NCSe; M = Zn^{II}, L = L^3 or L^4, and X = Cl, Br, or I). A trigonal-bipyramidal stereochemistry is ascribed to these complexes, essentially on the basis of electronic and vibrational spectra and of *X*-ray powder and single-crystal results. Such a structure may be attained by polymerization using X, the phosphorus and carbonyl oxygen atoms, and the nitrogen atom of the ligand, but depends on the metal ion and the steric demands of the ligands. Under suitable conditions, six-co-ordination is attained for the complexes $[Co(NCY)(L^3)(OH_2)]$ (Y = S or Se), the stability of which is attributed to the formation of hydrogen bonds.

VARIOUS studies have shown that the choice of ligands often determines the kind of arrangement adopted by metal ions. For a five-co-ordinate structure, a trigonal-bipyramidal, square-pyramidal, or intermediate distorted geometry [2-4] may be preferred. Generally, the shape and the size of the ligands influence the geometry of the co-ordination.[5] It appears that the stability of neutral five-co-ordinate complexes may be attributed to the high lattice-energy arising from intramolecular attractions between cationic and anionic ligands.[6,7] Finally, hydrogen bonding plays an important part in stabilizing anionic complexes: [8-11] the counter ion, which is not involved in the crystal field, must be necessarily bulky and possess one or more donor atoms susceptible to bonding in the crystal lattice.

Previously, we have studied halogenozinc(II) complexes, [ZnX(L)], formed with the anionic ligand $[P(CHCOCH_2R)O(OEt)_2]^-$ [R = NMe_2 (L^1) or NEt_2 (L^2)].[1,12] Although this ligand is bulky and multidentate, its bidentate nature seems to be more consistent with the suggested tetrahedral arrangement of the complexes. In the present study, the size and the shape of the group R, as well as the nature of the central atom, were also found to be relevant factors in deciding the stereochemistry. Cobalt(II) complexes of stoicheiometry [CoX(L)] were investigated with R = NEt_2(L^2), $\overline{NCH_2CH_2OCH_2CH_2}$ (L^3), or $\overline{NCH_2CH_2CH_2CH_2CH_2}$ (L^4) and X = Br, I, NCS, or NCSe. In order to establish comparisons, we have extended our previous studies on zinc(II) complexes to those where R is a cyclic amine.

EXPERIMENTAL

Preparations.—Ligands. The synthesis of $P(CH_2COCH_2R)O(OEt)_2$ [R = NMe_2 (HL^1), NEt_2 (HL^2) $\overline{NCH_2CH_2OCH_2CH_2}$ (HL^3), and $\overline{NCH_2CH_2CH_2CH_2CH_2}$ (HL^4)] has been described previously.[13]

Halogenocobalt complexes, [CoX(L)] (X = Br *or* I; L = L^2, L^3, *or* L^4). The complexes were prepared by the following general method. Hydrated cobalt(II) bromide, $CoBr_2 \cdot 2OH_2$ (5 mmol), or anhydrous cobalt(II) iodide, CoI_2, dissolved in the minimum of acetone, was added to 0.01 mol of HL. This procedure was adapted to each HL. A further quantity (2.5 mmol) of HL^2 was necessary to change the colour of the mixture from blue to purple. To decrease the precipitation in the case of $[CoX(L^4)]$, the ligand was added to the cobalt(II) solution as a solution in acetone (*ca.* 5 cm^3). This was also necessary for HL^3 in order to avoid simultaneous precipitation of a white powder together with the expected complex. The white powder has the formula $\overline{CH_2CH_2OCH_2CH_2N}H_2X$ (X = Br or I) {Found (by potentiometric titration with $Ag[NO_3]$: I, 58.5. Calc.: I, 59.0%}. The i.r. spectra showed a broad band at *ca.* 3 410 cm^{-1} assigned to the N–H stretching and another band at 1 600 cm^{-1} due to δ(HNH); n.m.r. data were also consistent with this formula. The complexes $[CoBr(L^2)]$ and $[CoI(L^3)]$ were obtained as crystals mixed with the powder, and the other complexes were obtained as crystalline precipitates; they were filtered off, washed with a slight amount of acetone, and dried *in vacuo*.

Halogenozinc complexes, [ZnX(L)] (X = Cl, Br, *or* I; L = L^3 *or* L^4). The general procedure described [12] for the complexes [ZnX(L)] (L = L^1 or L^2) was followed with the exception that HL^3 and HL^4 were utilized as solutions in ethanol. Addition of an ethanolic solution (5 cm^3) of zinc(II) halides (2.5 mmol) to HL (5 mmol) in ethanol (*ca.* 5 cm^3) gave an immediate microcrystalline powder, except in the case of $[ZnCl(L^3)]$ for which the solution afforded crystals of this complex. When the quantity of solvent was reduced (to *ca.* 3 cm^3), single crystals of the complex $[ZnBr(L^4)]$ formed slowly.

Pseudohalide complexes. These were prepared from the corresponding bromide complexes and K[NCS] or K[NCSe] in acetone.

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(a) [CoX(L)] (X = NCS *or* NCSe; L = L^2 *or* L^4). A warm solution of [CoBr(L)] (2 mmol in *ca.* 10 cm^3 of dry acetone) was treated with a warm acetone solution of K[NCS] or K[NCSe] (2 mmol) and the KBr filtered off after cooling the mixture to 0 °C for some hours. Light petroleum (*ca.* 50 cm^3) was added to the filtrate, and the purple solid which was precipitated after the side of the flask had been scratched was recovered and dried *in vacuo*. The complex $[Co(NCSe)(L^4)]$ was identified by comparison of its visible and i.r. spectra with those of $[Co(NCS)(L^4)]$; the absence of KBr in the powder pattern led us to conclude that the salt is analytically pure.

(b) $[Co(NCS)(L^3)]$. The above procedure was not rigorously applied for this complex. When light petroleum or diethyl ether were added, no cloudiness appeared. After mixing stoicheiometric proportions of reactants and filtering off KBr, the solution so obtained was evaporated until it became an oil without solvent and the residue was treated with absolute ethanol (40 cm^3). A white precipitate formed immediately and was filtered off; this product was consistent with the formula $\overline{CH_2CH_2OCH_2CH_2N}H_2NCS$ by chemical analysis and i.r. and n.m.r. spectra. The filtrate when set aside overnight gave purple crystals of $[Co(NCS)(L^3)]$.

If the filtrate was evaporated only to small bulk, the products collected depended on the proportion of ethanol and acetone used. After adding ethanol (40 cm^3) to the acetone solution (*ca.* 7 cm^3), a blue powder first slowly separated from the purple solution, followed by a mixture of two solids, one blue and one purple. This was filtered off and the blue compound dissolved out with acetone and then reprecipitated on adding light petroleum. With acetone–ethanol (1 : 2), the salt first collected was $[Co(NCS)(L^3)]$ and the second was a green solid. The blue and green complexes were hydrated thiocyanate salts containing L^3 but their formulae were not determined; the salts were sticky and did not lend themselves to further investigation.

(c) $[Co(NCS)(L^3)(OH_2)]$. Pure samples of the complex were obtained from solutions in aqueous ethanol or when the solvents contained trace amounts of water. After evaporating the acetone solution as for $[Co(NCS)(L^3)]$, a mixture of 5% water and ethanol was used to dissolve the oil. A blue-purple solution resulted, from which, after adding diethyl ether, the blue solid described above was filtered off. On reducing the volume of the purple filtrate, the purple crystalline precipitate $[Co(NCS)(L^3)(OH_2)]$ formed.

(d) $[Co(NCSe)(L^3)]$ *and* $[Co(NCSe)(L^3)(OH_2)]$. The preparation of these complexes was not easy; it seems that the formation of the hydrated complex is preferred. Moreover, the experiments were not reproducible and mixtures of these two complexes were often obtained (*X*-ray powder and visible spectra). With this pseudohalide, trace amounts of water in the solvents were sufficient to precipitate $[Co(NCSe)(L^3)(OH_2)]$ in good yield. Only once, with an ethanol solution (10 cm^3), when the white solid was eliminated as for $[Co(NCS)(L^3)]$, was a purple powder rapidly collected on the filter. Elemental analyses were consistent with the formulation $[Co(NCSe)(L^3)]$; the absence of water was verified by i.r. spectroscopy.

Attempts to prepare chloro-complexes, or the analogous complexes of Ni^{II}, were unsuccessful. No solid could be isolated from the pink-violet solution obtained on mixing CoI_2 (for instance) in acetone with HL^1 even when a large excess of ligand was added.

Physical Measurements.—Carbon, hydrogen, nitrogen, phosphorus, and cobalt (for the selenocyanato-complexes only) analyses were by the Microanalysis Center of Thiais. The cobalt content was determined by titration with Ce^{4+} for the bromide complexes and by titration with ethylenediaminetetra-acetic acid in all the other cases. The methods used for the zinc halides and pseudohalides were as previously described.[12] Electrolytic conductance measurements were made on 10^{-3} mol dm^{-3} solutions in nitrobenzene, using a Tacussel conductimeter and a conventional cell which had been previously calibrated with an aqueous solution of potassium chloride (0.02 mol dm^{-3}).

Electronic diffuse-reflectance and solution spectra were recorded with a Beckman DK 2A instrument, with magnesium carbonate as reference for the solid samples and with chloroform as blank for solutions of the complexes, using 1.0 cm matched quartz cells. Infrared spectra, in Nujol mulls, were obtained over the range 200—4 000 cm^{-1}, using a Perkin-Elmer 225 spectrophotometer. A conventional Gouy balance was used for the magnetic measurements at room temperature. In all cases, diamagnetic corrections were made using Pascal's constants. N.m.r. spectra were recorded on a C60-HL JEOL spectrometer with tetramethylsilane as internal reference. Molecular weights in chloroform solutions were determined with a Microlab vapour-pressure osmometer.

The unit-cell parameters for some complexes were determined from oscillation and Weissenberg photographs with Cu-K_α radiation (λ 1.54 Å) and from precession photographs. The density of the complexes was measured by flotation in a mixture of cyclohexane and bromoform or by pycnometry with cyclohexane. The *X*-ray diffraction powder patterns were recorded either photographically with a Philips Debye–Scherrer powder camera using nickel-filtered copper radiation (circumference, 360 mm), or with a C.G.R. Theta 50 diffractometer at slow speed (0.125° min^{-1}) coupled with a quartz monochromator (Co-K_α radiation).

RESULTS

Reaction of the metal halides with HL yielded crystalline complexes of stoicheiometry [MX(L)]. On treating these latter complexes with potassium thiocyanate or selenocyanate, no change in the formulation occurred, except in the case of HL^3 when the solvent contained trace amounts of water; the formula then required is $[Co(NCY)(L^3)(OH_2)]$ (Y = S or Se). Elemental analyses (Table 1) are consistent with these compositions.

Molar Conductivities.—These were obtained at room temperature for nitrobenzene solutions (Table 1). The values were all very low, in agreement with the formulation of the complexes as non-electrolytes; 1 : 1 electrolytes (10^{-3} mol dm^{-3} solutions) have conductivities of 20—30 S cm^2 mol^{-1}.[14] Hence evidence for the presence of organic ligands as anions L^- is provided by the analytical and conductance results.

Magnetic Data.—The magnetic moments measured at room temperature were *ca.* 4.5 B.M. for [CoX(L)] and 4.8 B.M. for $[Co(NCY)(L^3)(OH_2)]$ (Table 2).* However, these results are of no diagnostic value in determining the metal-ion stereochemistry. They may be characteristic of distorted geometries of several symmetries: octahedral

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* 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

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TABLE 1

Analytical, conductance, and some i.r. data

	Analysis[a](%)						Conductance[b]			
	C	H	N	P	Metal	Halogen or NCX	λ/S cm^2 mol^{-1}	10^3c/mol dm^{-3}	Yield/%	ν(M–X)/cm^{-1}
[CoBr(L^2)]	32.8(32.8)	5.9(5.75)	3.5(3.45)	7.8(7.65)	14.5(14.55)	19.7(19.8)	0.9	1.00	65	232vs
[CoI(L^2)]	29.1(29.35)	5.2(5.15)	3.1(3.10)	7.0(6.85)	13.0(13.1)	28.1(28.2)	4.9	1.00	88	211vs
[Co(NCS)(L^2)]	37.3(37.8)	6.1(6.10)	7.2(7.35)	8.1(8.10)	15.5(15.45)	15.1(15.25)	2.8	1.00	57	286br
[Co(NCSe)(L^2)]	33.6(33.65)	5.4(5.40)	6.7(6.55)	7.0(7.20)	13.8(13.75)	24.4(24.5)	2.2	1.00	51	247s
α-[CoBr(L^3)]	31.8(31.7)	5.1(5.05)	3.3(3.35)	7.6(7.40)	14.6(14.15)	19.5(19.15)	1.6[c]	1.00	56	236vs
α-[CoI(L^3)]	28.8(28.45)	4.8(4.55)	3.6(3.00)	6.6(6.65)	12.5(12.7)	27.0(27.35)	2.0	1.00	68	216vs
[Co(NCS)(L^3)]	36.2(36.45)	5.4(5.35)	7.1(7.05)	8.0(7.85)	14.8(14.9)	14.5(14.7)	0.02	1.13	50	286br
[Co(NCSe)(L^3)]	30.3(32.6)	4.4(4.80)	6.0(6.35)	6.8(7.00)	12.8(13.3)	23.5(23.7)	0.06	0.15	*ca.* 10	241s
[Co(NCS)(L^3)(OH$_2$)]	35.9(34.9)	5.6(5.60)	6.8(6.80)	7.6(7.50)	14.0(14.25)	13.7(14.05)	0.03	0.42	64	280v.br
[Co(NCSe)(L^3)(OH$_2$)]	31.7(31.3)	5.0(5.05)	6.1(6.10)	6.8(6.70)	12.7(12.8)	22.1(22.8)	0.02	1.07	68	240s.br
[CoBr(L^4)]	35.1(34.7)	5.7(5.60)	3.4(3.35)	7.6(7.45)	14.3(14.2)	19.4(19.25)	1.8	1.00	72	232vs
[CoI(L^4)]	31.4(31.2)	5.3(5.00)	3.0(3.05)	6.9(6.70)	12.8(12.75)	27.7(27.45)	4.2	1.00	71	212vs
[Co(NCS)(L^4)]	37.9(39.7)	5.6(5.90)	6.8(7.10)	7.8(7.85)	14.6(15.0)	15.2(14.75)	3.3	1.00	67	281s
β-[ZnCl(L^3)]	34.8(34.85)	5.6(5.60)	3.6(3.70)	8.1(8.15)	16.7(17.25)	9.6(9.35)	0.01	1.02	40	305vs
α- + β-[ZnBr(L^3)]	31.2(31.2)	5.0(5.00)	3.1(3.30)	7.3(7.30)	15.2(15.45)	18.9(18.85)	<0.01	1.00	56	226vs
α-[ZnI(L^3)]	28.0(28.1)	4.5(4.50)	3.0(3.00)	6.6(6,60)	13.5(13.9)	27.1(26.95)	<0.01	1.00	85	206vs
[ZnCl(L^4)]	37.8(37.7)	6.1(6.15)	3.6(3.70)	8.2(8.20)	17.0(17.35)	10.0(9.40)	<0.01	1.00	40	307vs
[ZnBr(L^4)]	34.3(34.2)	5.6(5.50)	3.1(3.30)	7.3(7.35)	15.2(15.5)	19.2(18.95)	<0.01	1.00	57	219vs
[ZnI(L^4)]	30.9(30.75)	4.9(4.95)	2.8(3.00)	6.6(6.60)	13.7(13.95)	26.9(27.1)	<0.01	1.00	90	207vs

[a] Calculated values are given in parentheses. [b] For solutions in nitrobenzene. [c] Solution became green.

TABLE 2

Magnetic and electronic spectral data for the cobalt complexes

			Absorption maxima (cm^{-1})[d] assigned to transitions from $^4A_2'$ (F) to						
Complex	μ[a]/B.M.	State	$^4E''$(F)	$^4E'$(F)		$^4A_2'$(P)	$^4E''$(P)		
(*a*) Five-co-ordinate species									
[CoBr(L^2)]	4.47	*b*	5 200	10 400		15 300	18 300	19 500	20 700(sh)
		c		10 500 (20)		15 700 (23)	18 200 (76)	19 600 (95)	20 500 (70)
[Co(L^2)]	4.45	*b*	5 200	10 000		15 300	17 900	19 700	20 500(sh)
		c		10 200 (27)		15 200 (26)	17 900 (85)	19 700 (125)	
[Co(NCS)(L^2)]	4.45	*b*	5 400	9 600(sh)	11 600	16 100	18 800	19 700(sh)	20 700(sh)
		c		9 900(sh) (27)	11 700 (16)	16 700 (71)	18 600 (102)	19 400 (106)	
[Co(NCSe)(L^2)]	4.42	*b*	4 500	10 000(sh)	11 800	16 100	19 000	19 800	20 900(sh)
		c, e							
α-[CoBr(L^3)]	4.47	*b*	5 200	8 700(sh)	10 300	15 500	17 800	19 500	20 400(sh)
		c		8 800(sh) (10)	10 400 (12)	15 600 (20)	17 500 (66)	19 700 (72)	20 200(sh) (69)
[CoI(L^3)]	4.49	*b*	5 300	9 800		15 100	17 600	19 500	20 400(sh)
		c		8 500(sh) (24)	10 400 (31)	15 300 (51)	17 600(120)	19 600(sh) (152)	20 200 (158)
[Co(NCS)(L^3)]	4.53	*b*	4 900	9 500	11 600	16 000(sh)	18 200	20 000	21 000(sh)
		c		8 500	11 800	16 300(sh)	18 100	20 100	
[Co(NCSe)(L^3)]		*b*	5 000	9 500	11 700	16 000(sh)	18 300	20 100	21 200(sh)
[CoBr(L^4)]	4.49	*b*	5 400	9 000(sh)	10 300	15 700	17 700	19 500	20 600(sh)
		c		8 600(sh) (11)	10 400 (15)	15 600 (24)	17 500 (68)	19 700 (84)	20 400(sh) (74)
[CoI(L^4)]	4.44	*b*	5 400	9 100(sh)	10 100	15 000	17 600	19 600	20 100(sh)
		c		9 400(sh) (19)	10 100 (22)	15 400 (29)	17 400 (80)	19 800 (121)	20 100(sh) (112)
[Co(NCS)(L^4)]	4.53	*b*	5 100	9 700	11 600	16 300(sh)	18 300	20 100	21 000(sh)
		c		9 300 (17)	11 800 (24)	16 100 (50)	18 100 (98)	20 100 (123)	
[Co(NCSe)(L^4)]		*b*	5 100	9 700	11 600	16 100(sh)	18 500	20 700	
(*b*) Octahedral species				Assigned to the transitions from $^4T_{1g}$ (F) to					
				$^4T_{2g}$ (F)				$^4T_{1g}$ (P)	
[Co(NCS)(L^3)(OH$_2$)]	4.74	*b*		8 300	12 900		17 700	19 500 (sh)	20 200
[Co(NCSe)(L^3)(OH$_2$)]	4.80	*b*		8 400	12 900		17 700	19 500(sh)	20 300

[a] At room temperature. [b] Diffuse reflectance. [c] Solution in chloroform. [d] Molar absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [e] Cloudy solution.

TABLE 3

X-Ray crystallographic data

			β-Monoclinic		α-Monoclinic		
	[CoBr(L^2)]	[CoI(L^2)]	[CoBr(L^3)]	[ZnCl(L^3)]	[CoI(L^3)]	[ZnI(L^3)]	[ZnBr(L^4)]
a/Å	11.76 ± 0.02	11.78 ± 0.02	10.12 ± 0.04	9.89 ± 0.02	11.79 ± 0.04	11.83 ± 0.06	11.47 ± 0.04
b/Å	8.30 ± 0.02	8.52 ± 0.02	13.34 ± 0.02	13.39 ± 0.02	12.02 ± 0.02	12.02 ± 0.03	13.07 ± 0.02
c/Å	17.71 ± 0.03	18.01 ± 0.04	12.04 ± 0.03	11.90 ± 0.03	13.78 ± 0.02	13.79 ± 0.07	13.06 ± 0.03
β	103° 10′ ± 10′	103° 40′ ± 10′	90° 25′ ± 10′	90° 35′ ± 10′	117° 20′ ± 10′	117° 20′ ± 10′	115° 40′ ± 10′
U/Å^3	1 685 ± 15	1 755 ± 15	1 625 ± 15	1 575 ± 10	1 735 ± 15	1 740 ± 20	1 765 ± 15
D_m	1.58 ± 0.03[a]	1.71 ± 0.03[a]	1.69 ± 0.03[b]	1.58 ± 0.03[b]	1.78 ± 0.03[a]	1.80 ± 0.03[b]	1.58 ± 0.03[b]
Z	4	4	4	4	4	4	4
D_c	1.59 ± 0.02	1.70 ± 0.02	1.70 ± 0.02	1.60 ± 0.02	1.78 ± 0.02	1.80 ± 0.02	1.59 ± 0.02
Reflections							
$h0l$	$l = 2n$	$l = 2n$	$l = 2n$	$l = 2n$	$l = 2n$	$l = 2n$	$l = 2n$
$0k0$	$k = 2n$	$k = 2n$	$k = 2n$	$k = 2n$	$k = 2n$	$k = 2n$	$k = 2n$
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Test[c]	negative	negative	negative		negative		

[a] Measured by pycnometry in cyclohexane. [b] Measured by flotation in cyclohexane–bromoform. [c] Of optical-frequency doubling.

(μ = 4.7—5.2 B.M.[15]); tetrahedral (4.2—4.8 B.M.[15]); and five-co-ordinate (4.6—5.5 B.M. for a square pyramid and 4.3—4.7 B.M. for a trigonal bipyramid [16]). These data confirm the bivalent character of cobalt and allow us to conclude that it is in a high-spin state.

X-Ray Data.—Suitable crystals of $[\mathrm{ZnI(L^3)}]$ and $[\mathrm{CoBr(L^3)}]$ were obtained on recrystallization from benzene. Powder patterns were recorded for these products and for all directly prepared complexes. Crystal isomorphisms have been suggested in agreement with the single-crystal data collected in Table 3. From a comparison of the spectra so obtained, it appears that the complexes $[\mathrm{ZnBr(L^3)}]$ and $[\mathrm{CoBr(L^3)}]$ exist as two crystalline forms designated α and β. The complex $[\mathrm{ZnBr(L^3)}]$ as a microcrystalline precipitate from ethanol is a mixture of these two forms, the powder pattern being the sum of those of β-$[\mathrm{ZnBr(L^3)}]$ (from benzene) or its isomorph $[\mathrm{ZnCl(L^3)}]$ and of $[\mathrm{ZnI(L^3)}]$; the α form cannot be obtained pure. The powder pattern of $[\mathrm{CoBr(L^3)}]$ was analogous to that of $[\mathrm{CoI(L^3)}]$; *i.e.* it is the α form. However, single-crystal diffraction photographs showed that this complex, when recrystallized from benzene, possesses the β form: although the symmetry in both cases was monoclinic, the intensity distribution and the unit cells were different.

From this *X*-ray study, almost all the complexes have been classified according to their similarity. Isomorphism occurs with each of the following sets of complexes: (*a*) $[\mathrm{CoBr(L^2)}]$, $[\mathrm{CoI(L^2)}]$; (*b*) $[\mathrm{Co(NCS)(L^2)}]$, $[\mathrm{Co(NCSe)(L^2)}]$; (*c*) α-$[\mathrm{CoBr(L^3)}]$, $[\mathrm{CoI(L^3)}]$, α-$[\mathrm{ZnBr(L^3)}]$, $[\mathrm{ZnI(L^3)}]$; (*d*) β-$[\mathrm{CoBr(L^3)}]$ (from benzene), β-$[\mathrm{ZnBr(L^3)}]$ (from benzene), $[\mathrm{ZnCl(L^3)}]$; (*e*) $[\mathrm{CoBr(L^4)}]$, $[\mathrm{CoI(L^4)}]$, $[\mathrm{ZnBr(L^4)}]$, $[\mathrm{ZnI(L^4)}]$; and (*f*) $[\mathrm{Co(NCS)(L^3)(OH_2)}]$, $[\mathrm{Co(NCSe)(L^3)(OH_2)}]$. Recrystallization from benzene always led to formation of a product, the formula of which remained the same. In no case was the presence of solvent detected in the unit cell, as previously found for the complexes $[\mathrm{ZnX(L^2)}]$.[17]

Molecular-weight Measurements.—The mass spectrum was recorded for only one complex. A fragment containing two $[\mathrm{CoBr(L^2)}]$ units was observed; the value of *m/e* was 806, which correlated well with the calculated value of 806.2 for a dimeric structure. From osmometry in *ca.* 2×10^{-2} mol dm^{-3} chloroform solutions, molecular weights obtained were as follows (the values given in parentheses are the calculated values, assuming dimerization): $[\mathrm{ZnCl(L^3)}]$, 746 (758); $[\mathrm{CoI(L^3)}]$, 880 (928); $[\mathrm{CoI(L^4)}]$, 942 (924); and $[\mathrm{Co(NCS)(L^3)}]$, 915 (790).

Infrared Spectra (450—4 000 *cm*$^{-1}$).—The i.r. spectra of the free ligands showed several characteristic bands but we have pointed out only those which may be affected by co-ordination. As previously observed for some halogenozinc(II) complexes,[12] the most significant features were the decrease in the ν(C=O) and the ν(P=O) stretching frequencies {of *ca.* 160 and 100 cm^{-1} respectively in $[\mathrm{CoBr(L^2)}]$ from $\mathrm{HL^2}$} with a splitting of the latter absorption in some cases, and the existence of a strong band at *ca.* 1 385 cm^{-1} assigned by comparison [18] to a bending mode (O$\cdots$P$\cdots$C$\cdots$C$\cdots$O). This information provides convincing evidence that two oxygen atoms are involved in bonding with metal ion.

It is difficult to state precisely whether the R groups are involved, especially for $\mathrm{L^2}$ since there are no available data for co-ordination of an aliphatic amine through its nitrogen atom. The assignments for morpholine [19-23] and piperidine [19,23,24] have been fairly well established in complexes with these ligands containing a secondary amine: the considerable shift to lower frequencies of ν(N–H) (100—200 cm^{-1}) observed shows that the ligand is co-ordinated by means of the nitrogen atom. Their behaviour as tertiary amines is least evident. However, if co-ordination were to occur through a nitrogen or oxygen atom, there would be a change in the absorptions due to the ring C–N–C or C–O–C mode.[25,26] According to previous studies,[22,26,27] the peaks at 1 116 and 868 cm^{-1} in the free ligand $\mathrm{HL^3}$ have been assigned to the asymmetric and symmetric modes of C–O–C stretching. No shift in the frequency was observed for the complexes $[\mathrm{MX(L^3)}]$; this precludes the involvement of the ring oxygen atom in bonding with the metal ion. To our knowledge, no data have been published on the magnitude of the expected decrease in ν(C–N–C) (at 1 164 cm^{-1} in $\mathrm{HL^3}$ and 1 165 cm^{-1} in $\mathrm{HL^4}$) on co-ordination of morpholine and piperidine through their nitrogen atoms. In our complexes, the corresponding absorption was difficult to detect: a marked lowering of the intensity of this mode, as found for the thioxan [28] and thiomorpholine [29] complexes for the C–S–C vibration, may occur. Other peaks may have masked this band, *i.e.* ν(P$\rightarrow$O), absorptions due to the P(OEt) groups, or others caused by co-ordination. Although we have pointed out peaks of weak to medium intensity in the 1 100 cm^{-1} region, to attribute them to ν(C–N–C) would be without basis, as bands in this region have been also observed for $[\mathrm{CoX(L^2)}]$. Whereas direct confirmation of co-ordination of the morpholine and piperidine groups through nitrogen is difficult from the i.r. spectra, the order of co-ordinating ability of the donor atoms of the six-membered heterocyclic ligands is respected, *i.e.* N > O.[20]

Co-ordination of thiocyanate and selenocyanate groups was also demonstrated by the i.r. data: ν(C≡N) at *ca.* 2 070; ν(C–S) at 827; ν(C–Se) at 654; δ(NCS) at 475; and δ(NCSe) at 430 cm^{-1}. Our complexes can be readily assigned as containing N-bonded pseudohalide by comparison of the positions and the number of peaks due to NCY with the ranges given in the literature.[30-32]

The presence of water in $[\mathrm{Co(NCY)(L^3)(OH_2)}]$ was

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confirmed by the i.r. data. In the range 3 800—3 200 cm^{-1} the OH stretching absorptions appeared as two peaks, a very sharp one at 3 660 cm^{-1} and a broader one at 3 380 cm^{-1} in the thiocyanate complex. Such splitting shows that the water molecule is very distorted and its two hydrogen atoms are non-equivalent.[33] An idea of the extent of this asymmetry is given by the difference between the two absorptions (*ca.* 280 cm^{-1}). As in hydrated salts such as $Ca[SO_4]\cdot 2OH_2$ [33] or $Ba[NO_2]_2\cdot OH_2$ [34] this i.r. pattern shows that the water molecule is asymmetrically hydrogen bonded: the downward shift from the vapour frequency is 370 cm^{-1} for the strongly and 90 cm^{-1} for the weakly hydrogen-bonded group respectively. The H–O–H deformation mode appeared as a broad and ill-defined band at *ca.* 1 660 cm^{-1}. Extra peaks were observed at 648 and 608 cm^{-1} and are probably due to H_2O rocking and wagging modes; [35] their frequencies are very close to those pointed out for $[Co(3\text{-}Etpy)_4(OH_2)_2]Br_2$ (654 and 606 cm^{-1} [36]). All these bands are relatively sharp compared with the broad absorptions observed in compounds containing lattice water, a feature which should indicate that the H_2O molecule is co-ordinated.[6]

N.M.R. Spectra.—In order to obtain more information about the influence of co-ordination on protons α to the nitrogen atoms (at 2.50 p.p.m. in HL^3 and 2.18 p.p.m. in HL^4), ^1H n.m.r. measurements of the diamagnetic complexes were made in $CDCl_3$ solutions: the peaks were so ill-resolved that no conclusion could be drawn.

Visible Spectra.—Electronic spectra in the solid state and in chloroform solutions are in Table 2. As shown in Figure 1, the spectrum of $[CoBr(L^3)]$ (α and β crystalline forms exhibit identical electronic patterns) is very similar to that of $[CoCl_3(NH_3)(L^5CH_3)]$ [6] (L^5CH_3 = *N*-methyl-1,4-diazabicyclo[2.2.2]octanium), which is isomorphous with its nickel(II) analogue. From the *X*-ray study [7] of $[NiCl_3(L^5CH_3)(OH_2)]$, the spectrum of which is comparable to that of the nickel(II) amine complex, the configuration is essentially a trigonal bipyramid only slightly distorted from C_{3v} symmetry. An analogous stereochemistry is ascribed to our complexes and assignments of their *d–d* absorptions follow those of Ciampolini and Bertini.[37] The close similarity of the spectra of all the [CoX(L)] complexes supports the assumption of a five-co-ordinate structure. The crystal field spectrum of the [Co(NCY)(L)] complexes has a band which can be correlated with that of the halide analogues, the frequency shifts being due to the different position of halide and pseudohalide in the spectrochemical series NCY > X.[38] The $^4A_2'(F)$—$^4E'(F)$ transition is split in the lower symmetry,[39] especially for the thiocyanato- and selenocyanato-complexes; when splitting was not evident, the absorption band was unsymmetrical. We must also note that, as previously found by several workers,[38–40] the band at *ca.* 15 500 cm^{-1} is hardly affected by the ligand-field strength.

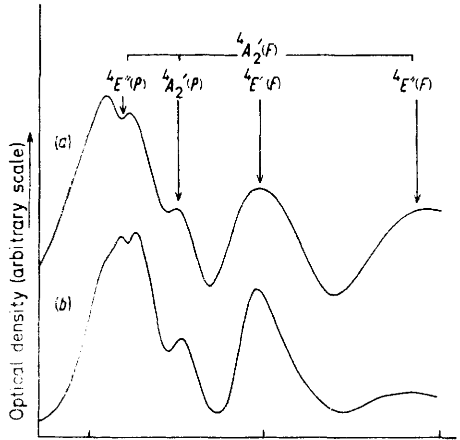

FIGURE 1 Solid-state electronic spectra of (*a*) $[CoBr(L^3)]$, (*b*) $[CoCl_3(NH_3)(L^5CH_3)]$ [6]

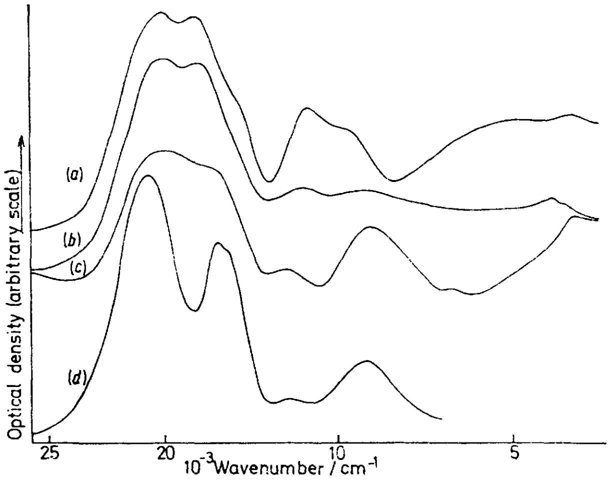

FIGURE 2 Electronic spectra of (*a*) $[Co(NCS)(L^3)]$ (reflectance), (*b*) $[Co(NCS)(L^3)]$ as a solution in chloroform, (*c*) $[Co(NCS)(L^3)(OH_2)]$ (reflectance), and (*d*) $[CoBr(L^6)]Br$ [41]

The electronic spectra of $[Co(NCY)(L^3)(OH_2)]$ are different from those of $[Co(NCY)(L^3)]$ (Figure 2) suggesting that structural changes occur at the metal atoms. An almost identical diffuse-reflectance spectrum (bands at 8 900, 13 400, 17 500, and 21 500 cm^{-1}) was observed for the complex $[CoBr(L^6)]Br$ [L^6 = *NN'*-di(3-aminopropyl)-piperazine] [41] the structure of which is related to that of the chloronickel complex which is described by an *X*-ray study [42] as a square pyramid formed by the four donor nitrogen atoms lying in the same plane; the nickel atom is 0.34 Å out of the plane of the nitrogen atoms in the direction of the bonded chlorine (at 2.33 Å) and the other chlorine atom lies close to the sixth co-ordination site of an octahedron (3.4 Å from the nickel atom). From these results, it is easy to understand the difficulties in differentiating an octahedral from a square-pyramidal geometry. Assuming octahedral symmetry for $[Co(NCS)(L^3)(OH_2)]$, the determination of

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Dq [43] from the transitions ν_1 and ν_3 [$^4T_{1g}(F)$ to $^4T_{2g}(F)$ and $^4T_{1g}(P)$ respectively] split into two components leads to a value of 940 cm^{-1} which is intermediate between the values found for the chromophores CoO_6 {900 cm^{-1} for $[Co(OH_2)_6]^{2+}$} and CoN_6 {1 100 cm^{-1} for $[Co(NH_3)_6]^{2+}$}.[44] The presence of two peaks in the 8 000—13 000 cm^{-1} region reflects the appreciative distortion of the ligand field from O_h symmetry. While these data do not allow an unequivocal structural assignment, nevertheless the presence of an H_2O molecule in the complex appears to play an important part in determining the final stereochemistry of these complexes.

The similarity between reflectance and absorption spectra in $CHCl_3$ solution suggests that the five-co-ordinate structure is essentially retained in solution; only the thiocyanate derivative with ligand L^3 dissolves with substantial structural changes, as shown by the spectral data (Figure 2) and molecular-weight measurements. In fact this solution spectrum bears a marked resemblance to that found by reflectance for $[Co(NCS)(L^3)(OH_2)]$. This result presumably reflects the solvation of the five-co-ordinate complex to give an octahedral structure, as often happens.[5,45] It was not possible to evaluate more precisely the nature of this molecule and whether chloroform and/or trace amounts of water are present. Moreover, we note that the positions of the two first absorption maxima are somewhat different; this is probably due to the fact that an equilibrium is set up between octahedral and five-co-ordinate species. Support for this assumption is given by the close similarity of this solution spectrum with the reflectance spectrum of the solid, which was obtained in an attempt to prepare pure $[Co(NCSe)(L^3)]$, and which appears, from X-ray powder diffraction, to be a mixture of $[Co(NCSe)(L^3)]$ and $[Co(NCSe)(L^3)(OH_2)]$.

Far-infrared Spectra (200—450 *cm*$^{-1}$).—The hydrated complexes showed a weak to medium intensity band at 363 cm^{-1} which is absent from the anhydrous complexes. With 3-ethylpyridine (3-Etpy) as ligand,[36] a band at 311—315 cm^{-1}, tentatively assigned to $Co-OH_2$ stretching, has been observed. An analogous assignment was proposed for $[Co(NCY)(L^3)(OH_2)]$; the ratio $\nu(Co-OH_2)$: ν(rock.), with a value always in the range 0.5—0.6 : 1,[46] correlates well with such an assignment, taking into account ν(rock.) at 647 cm^{-1}.

Strong absorptions due to metal–halogen stretching modes were easy to identify; their positions are in Table 1. Since it is known that they are sensitive to stereochemistry,[47] for the five-co-ordinate complexes they should lie intermediate in energy between the values observed for four- and six-co-ordinate complexes.[48] In fact, this criterion is difficult to apply, because of the influence of other ligands and of the relatively narrow range of frequencies between tetrahedral and five-co-ordinate species. Moreover, most literature data are for complexes which have two halogen ligands.[49–51] It is also expected that a zinc complex with a similar structure to the cobalt complex should have lower-frequency metal–halogen modes.[48] For the halide complexes $[MX(L)]$ ($L = L^3$ or L^4) our results are in agreement with this, thus favouring the same geometry as expected from the data of the previous X-ray study. Comparison of the i.r. spectra of $[CoX(L^2)]$ (this work) and $[ZnX(L^2)]$ [12] (X = Br and I) shows identical metal–halogen frequencies, thus implying a different stereochemistry: the suggested tetrahedral arangement for these zinc(II) complexes is thus enhanced.

Although the position of the metal–thiocyanate stretching frequency is less sensitive to changes in stereochemistry [52] and the intensity of the cobalt–nitrogen vibration is frequently weak,[53] the broad band at *ca.* 285 cm^{-1}, intermediate between the bands observed at 300 and 270 cm^{-1} in four- and six-co-ordinate complexes,[54] is assignable to this vibration. An identical result was obtained for the selenocyanato-complexes: the band at 247 cm^{-1} in $[Co(NCSe)(L^2)]$ falls within the frequencies at 260 cm^{-1} in $[NEt_4]_2[Co(NCSe)_4]$ [55] and <200 cm^{-1} in the corresponding octahedral complex $[NEt_4]_4[Co(NCSe)_6]$.[56]

Assignments of metal–organic ligand stretching modes must be regarded as very tentative because no isotopic substitution for the metal was utilized. Spectra were not always simple and in the case of L^3 and L^4 they were complicated by the presence of ligand vibrations. As morpholine and piperidine have similar masses, it is reasonable that the metal–nitrogen stretching frequencies should fall in a fairly narrow range. Ahuja [19] attributed strong bands at 390—300 cm^{-1} to this mode; in adducts with pentane-2,4-dionates [23] a similar range was proposed. However, Allen and Wilkinson [20] suggested that the metal–nitrogen stretching vibration in $[ZnX_2L_2]$ (L = morpholine or piperidine) lies in the range 226—205 cm^{-1}. From our results, it seems that if absorptions are expected at these frequencies they cannot always be observed because of masking by metal–bromide and –iodide vibrations. When it was possible to investigate this region, no medium to strong absorption was detected. For a given metal ion, the absorption at 350 cm^{-1} in α-$[CoBr(L^3)]$ and at 352 cm^{-1} in $[CoBr(L^4)]$ remained fairly constant, whatever the nature of X. This band is very sensitive to metal ion and the corresponding absorption follows the sequence $\nu(Co-N) > \nu(Zn-N)$ (at *ca.* 330 cm^{-1}). Such an assignment is not absolute however, because of the lack of further information.

DISCUSSION

On the basis of the experimental results, it can be deduced that the complexes $[CoX(L)]$ (X = Br, I, NCS, or NCSe) are five-co-ordinate with a trigonal-bipyramidal structure. An analogous arrangement is assigned to the zinc(II) complexes, primarily because of their isomorphism with the corresponding cobalt(II) complexes. However, a doubt may exist about [ZnCl-

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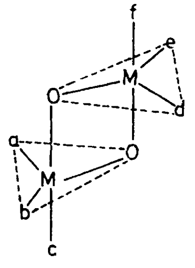
(L^3)] which has no analogue. It would be surprising if the arrangement was different, taking into account the fact that metal–chloride absorptions are unaffected when L is L^3 or L^4 (these ligands differ from each other only by replacement of an oxygen atom by a CH_2 group).

Such a structure is not always favoured and trace amounts of water are sufficient to destroy this stereochemistry. Electronic spectra of the [Co(NCY)(L^3)(OH_2)] complexes seem to be also characteristic of an octahedral structure. However, six-co-ordination must be assumed to be the more exact because the vibrational spectra seem to support bonding of the H_2O molecule to the metal ion: if a distinction between lattice and co-ordinated water is not evident, and without the aid of deuteriation, assignments must be treated with caution.[57] It is accepted that two effects (co-ordination to the metal ion and hydrogen bonding) may combine to assure bonding of a H_2O molecule. In this case, we note that no analogous complex was obtained with the ligand L^4, where the oxygen atom of morpholine is replaced by a CH_2 group. It is not surprising that the oxygen atom plays an important role in the stabilization of such a structure, by hydrogen bonding with H_2O. This kind of bonding might explain why water adds so readily to these complexes and does not add to [Co(NCY)(L^4)]. Similarly in $[NiCl_3(OH_2)(L^5CH_2Cl)]\cdot(L^5CH_2Cl)Cl$, which exhibits an i.r. pattern with two peaks separated by 160 cm^{-1} in the OH stretching region,[11] the cohesion of the crystal lattice was assumed to be due to hydrogen bonding between bound water and the free L^5CH_2Cl. Writing [Co(NCY)(L^3)(OH_2)] is hence justified and a loosely bound H_2O molecule would explain the electronic spectra.

The close similarity of the diffuse-reflectance spectra with those obtained in solution leads to the conclusion that the five-co-ordinate structure is generally stable. However, under suitable conditions the octahedral arrangement is preferred and a solvent molecule becomes attached so that the six-co-ordination is attained; this is only possible with ligand L^3. If the bonding ability to the metal ion of the oxygen atom of the morpholine group is weak, its role in attaining this kind of geometry by hydrogen bonding is not unexpected.

Five- and six-co-ordination in these complexes are presumably attained by polymerization; as the i.r. data are not consistent with the presence of halogen bridges (generally, metal–halogen modes appear below 200 cm^{-1}),[58] it is necessary to consider polymerization through the organic ligand, the oxygen atom of the carbonyl group being preferred as previously discussed.[12] From the information obtained by mass-spectral and molecular-weight measurements, it seems that the assumption of dimerization is probably correct. To attain a five-co-ordinate structure, the organic ligand must act in a tridentate manner with co-ordination through oxygen and nitrogen atoms leading to the donor set NO_3X; the sharing of an edge of the trigonal bipyramid is necessary as illustrated in (A). A binuclear centrosymetric arrangement (a = d, b = e, and c = f), like that found for the zinc(II) complex with the ligand *N*-methylsalicylaldimine,[59] may be considered as one of the most probable for the present complexes.



(A)

It is of interest to compare the [MX(L)] complexes in order to examine the factors that determine the favoured five-co-ordinate stereochemistry of Zn^{II} and Co^{II} with sterically hindered nitrogen heterocyclic ligands. As the difference between the ligands lies only in the terminal groups, it seems that five-co-ordination must arise principally through the steric requirements of ligands. When $R = NMe_2$ or NEt_2, steric hindrance to co-ordination of the terminal amine group to Zn^{II} is not sufficient, as shown by the appearance of tetrahedral binuclear forms [ZnX(L)].[12] With the cobalt complexes, this fact explains why attempts to prepare [CoX(L^1)] were unsuccessful: insufficient crowding of HL^1 leads to inhibition of such a structure. This explanation is also supported by the failure to precipitate chloride complexes with HL^2, HL^3, and HL^4. The stability of five-co-ordinate complexes follows the sequence Cl < Br < I.[60] The ease of five-co-ordination increases in the order $R = NMe_2 < NEt_2 < \overline{NCH_2CH_2CH_2CH_2CH_2} \approx \overline{NCH_2CH_2OCH_2CH_2}$, which corresponds with the steric hindrance.

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