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Preparation and structural characterization of η^5-pentamethylcyclopentadienylcobalt(III) complexes of α-amino acids with coordinating side chains

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Abstract

The complexes [(η^5-Cp*)CoCl(L-phe)] (**3**) and [(η^5-Cp*)CoCl(L-pro)] (**4**), which contain bidentate α-amino acidate ligands, were prepared by the reaction of [(η^5-Cp*)Co(μ-Cl)$_3$Co(η^5-Cp*)]FeCl$_4$ (**1**) with the appropriate α-amino acid at room temperature. An analogous complex [(η^5-Cp*)CoCl(DL-pipe)] (DL-pipeH = DL-pipecolinic acid) was synthesized, as were the remaining complexes, using [(η^5-Cp*)Co(μ-Cl)Cl]$_2$ (**2**) instead of **1** and its structure was established by an X-ray study. Tridentate coordination of the cobalt atoms by α-amino acidate ligands is observed for [(η^5-Cp*)Co(L-his)]PF$_6$ (**6b**), [(η^5-Cp*)Co(L-aspH$_{-1}$)] (**7a**), [(η^5-Cp*)Co(L-penH$_{-1}$)] (**8**) and [(η^5-Cp*)Co(L-met)]FeCl$_4$ (**9a**). An X-ray study of **9a** confirmed an N, O, S coordination of the chiral cobalt atom. In [(η^5-Cp*)Co(L-aspH$_{-1}$)] $\cdot$ LiCl $\cdot$ 3H$_2$O (**7b**) the [L-aspH$_{-1}$]$^{2-}$ dianion adopts a μ_3-($1\kappa^3N,O,O'$:$2\kappa^1O'$:$3\kappa^1O'$) coordination mode in bridging the cobalt and two lithium atoms. A μ_2-($1\kappa^3N,O,S$:$2\kappa^1O'$) mode is displayed by the [L-S-Mecys] anion in [(η^5-Cp*)Co(μ-L–S–Mecys)CoCl$_3$] (**11**), which contains Co$^{\mathrm{III}}$ and Co$^{\mathrm{II}}$ atoms.

Key words: Cobalt; Cyclopentadienyl; Amino acid; Crystal structure

1. Introduction

In recent years there have been a number of reports of the preparation and structural characterization of half-sandwich complexes of α-amino acids. These include (η^6-arene)Ru$^{\mathrm{II}}$ (arene = C$_6$H$_6$ or *p*-cymene), (η^6-C$_6$H$_6$)Os$^{\mathrm{II}}$, (η^5-Cp*)Rh$^{\mathrm{III}}$ and (η^5-Cp*)Ir$^{\mathrm{III}}$ derivatives (Cp* = C$_5$Me$_5$), in which the amino acidate ligands are bi or tridentate [1–7]. Such organometallic compounds exhibit chirality both in the ligand and at the metal centre and offer considerable potential for enantioselective synthesis. Of particular interest is the reaction of α-amino acid esters with half-sandwich complexes of the type [(η^5-Cp*) MCl(diglyR)] (M = Rh or Ir; digly = diglycinate; R = Me or Et), which leads to peptide chain expansion at the coordinated amino group of the diglycine ester [8]. It is reasonable to assume that the formation of a new peptide bond proceeds via a template process.

In extension of the above work we now report the synthesis and structural characterization of (η^5-Cp*)Co$^{\mathrm{III}}$ complexes of the following potentially bi or tridentate amino acids: L-phenylalanine (L-pheH), L-proline (L-proH), DL-pipecolinic acid (DL-pipeH), L-histidine (L-hisH), L-histidine methyl ester (L-hisMe), L-aspartic acid (L-aspH), L-penicillamine (L-penH), L-methionine (L-metH), L-methionine methyl ester (L-metMe) and L-S-methylcysteine (L-S-MecysH). The source of the (η^5-Cp*)Co$^{\mathrm{III}}$ fragment was either [(η^5-Cp*)Co(μ-Cl)$_3$Co(η^5-Cp*)]FeCl$_4$ (**1**) or [(η^5-Cp*)Co(μ-Cl)Cl]$_2$ (**2**) [9,10].

2. Experimental details

IR spectra were recorded on a Perkin–Elmer 983 or 1760 spectrometer as KBr discs, FAB (MS) on a Fisons VG AutoSpec spectrometer, and ^{1}H nuclear magnetic resonance (NMR) spectra on a Bruker WP80 (80 MHz)

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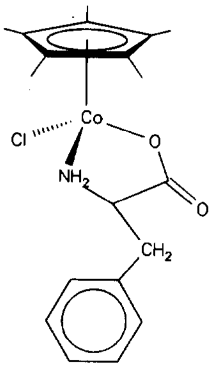


(3)

or AM400 (400 MHz) instrument with δ values determined relative to the solvent as internal standard. Elemental analyses were performed with a Perkin–Elmer 240 or a Carlo Erba 1106 instrument. Unless specified, all reactions were carried out in purified solvents under argon. Compounds **1** and **2** were prepared by published procedures [9,10]. Amino acids were purchased from Sigma or Fluka (L-S-MecysH).

3. Preparation of complexes 3–11

3.1. [(η⁵-Cp*)CoCl(L-phe)] (3)

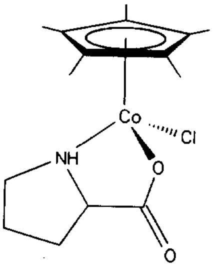
L-pheH (33 mg, 0.2 mmol) was added to 70 mg (0.1 mmol) of **1** in 10 ml of methanol and the solution was stirred for 2 h at room temperature. The solvent was removed from the violet solution and the resulting solid redissolved in acetone. The addition of diethyl ether produced a blue precipitate of **3** (yield, 80%).

(Anal. Found: C, 58.3; H, 6.7; N, 3.3. $C_{19}H_{25}NO_2CoCl$ ($M = 393.8$) Calc: C, 57.9; H, 6.4; N, 3.5%. IR: $\nu(NH_2)$ 3220, 3305, $\nu(CO_2)$ 1600 cm^{-1}. ^1H NMR (400 MHz, D_2O), 1.0 (s, 15H, Cp*); 2.94; 3.12 (2m, 2H, β-CH_2); 3.83 (m, 1H, α-CH); 7.3 (m, 5H, C_6H_5) ppm.

3.2. [(η⁵-Cp*)CoCl(L-pro)] (4)

L-proH (30 mg, 0.26 mmol) was added to 90 mg (0.13 mmol) of **1** in 10 ml of methanol and the solution was stirred for 2 h at room temperature. The solvent was removed from the light-blue solution and the resulting solid redissolved in CH_2Cl_2. The addition of pentane gave a precipitation of blue **4** (yield, 85%).

Anal. Found: C, 52.2; H., 6.8; N, 4.8. $C_{15}H_{23}NO_2CoCl$ ($M = 343.7$) Calc.: C, 52.4; H, 6.7; N, 4.0%. IR: $\nu(NH_2)$ 3290, 3235, $\nu(CO_2)$, $\delta(NH)$ 1622, 1581 cm^{-1}. ^1H NMR (400 MHz, D_2O); 1.2 (s, 15H, Cp*); 1.87 (m, 2H, γ-CH_2), 1.95, 2.18 (2m, 2H, β-CH_2), 3.15, 3.20 (2m, 2H, δ-CH_2), 3.98 (t, 1H, α-CH) ppm.



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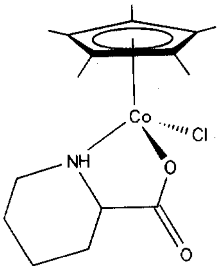
3.3. [(η⁵-Cp*)CoCl(L-pipe)] (5)

DL-pipeH (69 mg, 0.54 mmol) was added to 141 mg (0.27 mmol) of **2** in 4 ml of methanol and the solution, whose colour changed from green to blue, was stirred for 2 h at room temperature. After removal of the solvent, the resulting solid was redissolved in CH_2Cl_2 and the solution layered with hexane to yield blue crystals of **5** (yield, 77%).

Anal. Found: C, 53.3; H, 6.9; N, 4.1. $C_{16}H_{25}NO_2ClCo$ ($M = 357.8$) Calc.: C, 53.7; H, 7.0; N, 3.9%. FAB MS: m/z (%) 358(8) [$M^+ + H$], 322(52) [$M^+ - {}^{35}Cl$]. IR: $\nu(NH_2)$ 3300, 3130, $\nu(CO_2)$ 1620, cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): 1.3 (s, 15H, Cp*); 1.0–2.1 (mm, 6H, β-$CH_2\gamma$-CH_2, δ-CH_2); 3.1–4.1 (m, 3H, α-CH, ϵ-CH_2) ppm.



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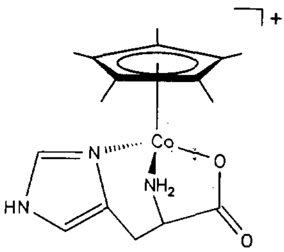
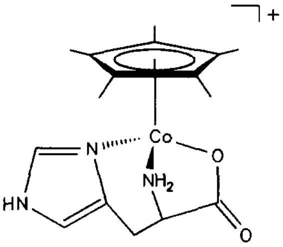
3.4. [(η⁵-Cp*)Co(L-his)]X (X = FeCl₄ (6a) or PF₆ (6b))

L-hisH (50 mg, 0.32 mmol) was added to 110 mg (0.16 mmol) of **1** in 10 ml of methanol, causing a colour change from blue to violet. After stirring for 3 h at room temperature, the solvent was removed and the resulting solid redissolved in acetone. The addition of diethyl ether led to precipitation of [(η⁵-Cp*)Co(L-his)]$FeCl_4$ (**6a**). Anion exchange of PF_6- for $FeCl_4$- was achieved by the addition of NH_4PF_6 to an acetone solution of **6a**. The solution was filtered and **6b** precipitated by addition of diethyl ether (yield, 82%). **6a** and **6b** (after anion exchange) may also be prepared by the reaction of L-hisMe with **1** under analogous conditions in the presence of an equivalent of NaOMe.

Anal. Found: C, 38.1; H, 4.5; N, 8.1. $C_{16}H_{23}N_3O_2$-F_6PCo ($M = 493.3$) Calc.: C, 38.9; H, 4.7; N, 8.5%. IR: $\nu(NH_2)$ 3210, 3137, $\nu(CO_2)$ 1625, cm^{-1}. ^1H NMR (400 MHz, D_2O): 1.1 (s, 15H, Cp*); 2.4 (m, 2H, β-CH_2); 3.4 (m, 1H, α-CH); 6.6 (s, 1H, C=CH–N); 8.4 (s, 1H, N–CH=N) ppm.



Cl^- (6a)

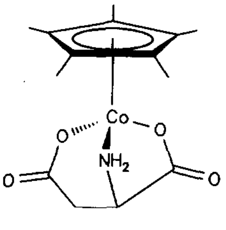


PF_6^- (6b)

3.5. $[(\eta^5\text{-}Cp^*)Co(\text{L-}aspH_{-1})]$ (7a)

L-aspH (63 mg, 0.47 mmol) was added to 125 mg (0.24 mmol) of **2** in 7 ml of methanol and the solution, whose colour changed from green to violet was stirred for 24 h at room temperature in the presence of 158 mg (0.94 mmol) of AgOAc. After filtration to remove AgCl the solvent was evaporated and the resulting solid redissolved in water–methanol. The solution was layered with diethyl ether to yield blue crystals of **7a** · H_2O (yield, 57%).

Anal. Found: C, 47.8; H, 6.4; N, 4.1. $C_{14}H_{20}NO_4Co \cdot H_2O$ (**M** = 343.3) Calc.: C, 49.0; H, 6.6; N, 4.1%. IR: $\nu(NH_2)$ 3189, 3090, $\nu(CO_2)$ 1659, 1619 cm^{-1}. ^1H NMR (80 MHz, D_2O): 1.3 (s, 15H, Cp*); 2.0–2.25 (m, 2H, β-CH_2); 3.15 (m, 1H, α-CH) ppm. Crystals of $[(\eta^5\text{-}Cp^*)Co(\text{L-}aspH_{-1})] \cdot LiCl \cdot 3H_2O$ (**7b**) suitable for X-ray analysis were obtained by slow evaporation of a methanol–isopropanol solution of **7a** containing an excess of LiCl.

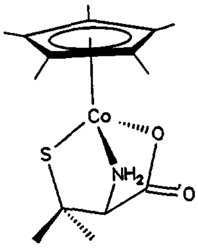


(7a)

3.6. $[(\eta^5\text{-}Cp^*)Co(\text{L-}penH_{-1})]$ (8)

L-penH (72 mg, 0.48 mmol) was added to a solution of 127 mg (0.24 mmol) of **2** in methanol–water and the deep-violet mixtures was stirred for 24 h at room temperature in the presence of 161 mg (0.96 mmol) of AgOAc. After filtration to remove AgCl the solvent was evaporated and the resulting solid redissolved in 2 ml of CH_2Cl_2. Black crystals of **8** · H_2O were obtained by layer the solution with hexane (yield, 67%).

Anal. Found: C, 48.8; H, 7.3; N, 3.9. $C_{15}H_{24}NO_2Co \cdot H_2O$ (M = 341.4) Calc.: C, 50.1; H, 7.3; N, 4.3%. IR: $\nu(NH_2)$ 3230, 3130, $\nu(CO_2)$ 1641, 1613 cm^{-1}. ^1H NMR (80 MHz, D_2O): 1.15 (s, 3H, penH$_{-1}$ CH_3): 1.35 (s, 3H, penH$_{-1}$ CH_3); 1.55 (s, 15H, Cp*); 2.9 (s, 1H, α-CH) ppm.



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3.7. $[(\eta^5\text{-}Cp^*)Co(\text{L-}met)]X$ ($X = FeCl_4$ (9a) or PF_6 (9b))

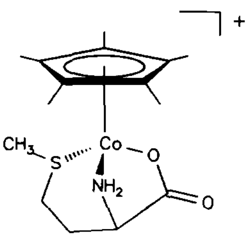
L-metH (45 mg, 0.30 mmol) was added to 100 mg (0.15 mmol) of **1** in 10 ml of methanol and the solution, whose colour changed from blue to deep red, was stirred for 2 h at room temperature. After filtration of the solution and removal of the solvent, the resulting solid was redissolved in methanol. The addition of diethyl ether led to the formation of deep-violet needle-shaped crystals of **9a** (yield, 88%).

Anal. Found: C, 33.4; H, 4.7; N, 2.5. $C_{15}H_{25}NO_2SCl_4FeCo$ (M = 540.0) Calc.: C, 33.3; H, 4.6; N, 2.6%. IR: $\nu(NH_2)$ 3280, 3200, $\nu(CO_2)$ 1660 cm^{-1}.

Anion exchange of PF_6- for $FeCl_4$- was achieved by the addition of NH_4PF_6 to an acetone solution of **9a**. The solution was filtered and $[(\eta^5\text{-}Cp^*)Co(\text{L-}met)]PF_6$ (**9b**) precipitated by the addition of diethyl ether.

Anal. Found: C, 36.6; H, 5.2; N, 2.7. $C_{15}H_{25}NO_2F_6PSCo$ (M = 487.3) Calc.: C, 37.0; H, 5.2; N, 2.9%. IR: $\nu(NH_2)$ 3280, 3210, $\nu(CO_2)$ 1646 cm^{-1}. ^1H NMR (400 MHz, D_2O): 1.3 (s, 15H, Cp*); 1.5–2.2 (mm, 4H, β-CH_2, γ-CH_2); 2.5 (s, 3H, δ-CH_3); 3.3 (m, 1H, α-CH) ppm.

9a and **9b** (after anion exchange) may also be prepared by the reaction of L-metMe with **1** under analogous conditions in the presence of an equivalent of NaOMe.

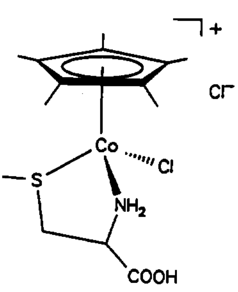


$FeCl_4^-$ (9a)

3.8. $[(\eta^5\text{-}Cp^*)CoCl(\text{L-S-MecysH})]Cl$ (10)

L-S-MecysH (64 mg, 0.48 mmol) was added to 126 mg (0.24 mmol) of **2** in 4 ml methanol and the solution stirred for 24 h at room temperature. After removal of the solvent, the resulting solid was washed with CH_2Cl_2 and redissolved in methanol. The solution was layered with diethyl ether to yield deep-violet microcrystals of **10** (yield, 65%).

Anal. Found: C, 42.3; H, 5.8; N, 3.3. $C_{14}H_{24}NO_2SCl_2Co$ ($M = 400.3$) Calc.: C, 42.0; H, 6.0; N, 3.5%. FAB MS: m/z (%) 364(25) [M^+(cation)], 328(100) [M^+(cation)-$H^{35}Cl$]. IR: $\nu(NH_2)$ 3120, 3090, $\nu(CO_2)$ 1734 cm^{-1}. ^1H NMR (80 MHz, D_2O): 1.4 (s, 15H, Cp*); 2.0 (s, 3H, δ-CH_3); 2.5–2.7 (m, 2H, β-CH_2); 4.1 (m, 1H, α-CH) ppm.



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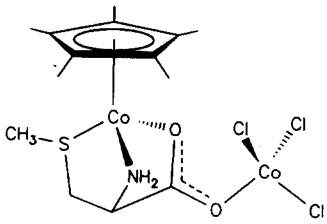
3.9. $[(\eta^5\text{-}Cp^*)Co(\mu\text{-L-S-Mecys})CoCl_3]$ (11)

Complex **10** (40 mg, 0.10 mmol) was dissolved in a mixture of water, methanol and isopropanol. Evaporation over a period of days yielded violet crystals of **11** · CH_3OH suitable for X-ray analysis. Upon drying **11** · CH_3OH loses its methanol to give **11** (yield, 59%).

Anal. Found: C, 35.2; H, 5.5; N, 4.3. $C_{15}H_{27}NO_3Cl_3Co_2$ ($M = 525.6$) Calc: C, 34.3; H, 5.2; N, 2.7%. IR: $\nu(NH_2)$ 3140, 3060, $\nu(CO_2)$ 1602 cm^{-1}.



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3.10. X-ray structural analyses

Crystal and refinement data are summarized in Table 1. Unit-cell constants were obtained for the crystals from least-squares fits to the settings of 25 reflections centred on a Siemens P4 diffractometer. Intensity data were collected on the diffractometer at varied scan rates in the ω mode for Mo Kα radiation. Semi-empirical absorption corrections (Ψ scan) were applied to the reflection intensities. The structures were solved by Patterson and difference syntheses, the latter of which revealed the presence of six water oxygen atoms in the unit cell of **7b** and a disordered methanol molecule in the asymmetric unit of **11** · CH_3OH. Four different sites were located for the oxygen atom of the latter solvate molecule. With the exception of the $[\text{L-aspH}_{-1}]^{2-}$ anions, atoms in the

TABLE 1. Crystal and refinement data for **5**, **7b**, **9a** and **11** CH_3OH

	5	**7b**	**9a**	**11** · CH_3OH
Space group	*Pbca*	$P1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	7.758(2)	9.106(3)	8.003(2)	8.623(5)
b (Å)	18.796(3)	9.959(3)	10.342(2)	15.215(2)
c (Å)	23.432(3)	11.392(4)	27.525(6)	18.001(3)
α (°)	90	107.44(3)	90	90
β (°)	90	98.41(3)	90	90
γ (°)	90	102.08(2)	90	90
Volume (Å^3)	3417.0(10)	939.3(6)	2278.3(9)	2362(1)
Z	8	2	4	4
D_c (g cm^{-3})	1.39	1.49	1.57	1.48
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (cm^{-1})	11.6	10.9	19.4	18.4
Scan method	ω	ω	ω	ω
$2\theta_{max}$ (°)	45	50	50	55
Number of independent reflections	2278	3558	2222	2669
Number of observed reflections	1357	2646	1814	1457
Rejection criterion	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$
R	0.076	0.049	0.057	0.069
R_w	0.074	0.048	0.054	0.062
p	0.0002	0.0002	0.0004	0.0002

TABLE 2. Atom coordinates ($\times 10^4$) with equivalent isotropic temperature factors.

Atom	x	y	z	U_{eq}
Compound 5				
Co	207(2)	6083(1)	3831(1)	31(1)
Cl	−1779(4)	5664(2)	4464(1)	50(1)
O(1)	−1411(9)	6035(5)	3189(3)	41(3)
O(2)	−2792(12)	5270(4)	2611(3)	54(3)
N(2)	762(12)	5093(5)	3547(4)	32(4)
C(1)	−1760(16)	5403(7)	3002(5)	34(5)
C(2)	−842(16)	4799(6)	3319(5)	38(5)
C(3)	−519(16)	4119(5)	2963(5)	49(5)
C(4)	316(16)	3574(6)	3366(6)	60(6)
C(5)	1985(18)	3875(7)	3632(5)	57(5)
C(6)	1629(16)	4584(5)	3924(5)	39(5)
C(11)	277(15)	7174(6)	3874(5)	37(4)
C(111)	−1274(15)	7670(7)	3732(5)	53(6)
C(12)	1489(15)	6918(6)	3439(5)	32(4)
C(121)	1474(17)	7080(7)	2818(5)	48(5)
C(13)	2736(15)	6465(7)	3747(5)	39(4)
C(131)	4305(14)	6130(6)	3488(5)	42(4)
C(14)	2216(15)	6453(6)	4345(5)	33(4)
C(141)	3159(17)	6027(7)	4812(5)	51(5)
C(15)	753(16)	6882(6)	4411(5)	41(5)
C(151)	−110(17)	7068(6)	4990(5)	48(5)
Compound 7b				
Co	1944(2)	8140(2)	7940(1)	20(1)
O(41)	3389(8)	9112(6)	7154(6)	32(3)
O(11)	3424(7)	7195(7)	8547(6)	28(3)
O(42)	4681(8)	9385(7)	5719(6)	35(3)
O(12)	4715(8)	5557(8)	7820(6)	37(3)
N(1)	1438(9)	6378(8)	6419(7)	28(3)
C(1)	3773(10)	6252(9)	7656(7)	24(4)
C(2)	2930(9)	6021(9)	6335(8)	22(4)
C(3)	3864(11)	6970(8)	5743(9)	26(4)
C(4)	3965(10)	8588(8)	6240(8)	24(4)
C(11)	591(10)	7948(8)	9199(8)	30(4)
C(12)	1797(9)	9299(9)	9721(7)	29(4)
C(13)	1619(9)	10105(8)	8891(8)	33(4)
C(14)	322(10)	9288(8)	7863(7)	28(4)
C(15)	−326(9)	7965(8)	8077(7)	27(4)
C(16)	346(14)	6719(10)	9714(11)	44(5)
C(17)	3038(11)	9841(12)	10893(8)	43(5)
C(18)	2597(13)	11575(8)	9025(12)	50(5)
C(19)	−236(17)	9716(14)	6767(10)	63(7)
C(20)	−1684(12)	6781(12)	7208(12)	68(7)
Co′	8120(2)	11853(1)	2071(1)	20(1)
O(11′)	6589(7)	10753(6)	2708(6)	25(3)
O(41′)	6655(7)	12860(7)	1542(6)	32(3)
O(12′)	5378(8)	11001(7)	4261(6)	32(3)
O(42′)	5424(9)	14566(8)	1790(6)	44(3)
N(1′)	8597(7)	13312(7)	3783(6)	19(3)
C(4′)	6076(11)	13797(9)	2227(8)	31(4)
C(3′)	6178(12)	13986(11)	3612(8)	30(4)
C(2′)	7103(9)	13142(8)	4161(8)	23(4)
C(1′)	6307(10)	11525(8)	3704(8)	26(4)
Compound 7b				
C(11′)	9425(9)	12140(8)	798(8)	28(4)
C(12′)	8242(9)	10783(9)	258(7)	34(4)
C(13′)	8466(10)	9882(8)	992(8)	30(4)
C(14′)	9703(10)	10724(8)	2059(7)	30(4)
C(15′)	10332(9)	12105(8)	1925(8)	30(4)
C(16′)	9622(14)	13417(11)	356(11)	48(6)
C(17′)	6982(12)	10484(12)	−852(8)	44(5)
C(18′)	7403(14)	8429(9)	784(11)	47(5)
C(19′)	10289(13)	10236(13)	3108(9)	46(5)
C(20′)	11720(9)	13280(10)	2750(9)	33(4)
Li(1)	4935(19)	8814(17)	3982(15)	30(4)
O(1)	3013(9)	7582(8)	2901(7)	44(3)
O(2)	6391(8)	7586(7)	3592(7)	41(3)
Li(2)	4963(20)	11455(18)	5987(16)	33(4)
O(3)	6881(8)	12758(8)	7138(7)	44(3)
O(4)	3592(9)	12682(8)	6288(8)	51(4)
Cl(1)	−193(3)	6637(3)	3756(3)	38(1)
Cl(2)	200(3)	3180(3)	6501(3)	40(1)
O(5)	6474(10)	4523(8)	9394(7)	51(4)
O(6)	3541(10)	5871(10)	676(8)	62(4)
Compound 9a				
Co	5056(2)	1097(1)	8973(1)	38(1)
S	2921(3)	2263(3)	8650(1)	54(1)
S(1)	4185(9)	1421(6)	9629(2)	51(2)
O(2)	4082(11)	2846(8)	10216(2)	74(3)
N	6393(11)	2643(7)	9122(3)	45(3)
C(1)	4526(13)	2514(11)	9808(3)	52(4)
C(2)	5430(14)	3430(9)	9485(3)	51(4)
C(3)	4166(16)	4294(10)	9227(4)	63(4)
C(4)	2625(14)	3591(10)	9063(4)	62(4)
C(5)	3570(18)	3114(12)	8120(4)	76(5)
C(11)	6112(14)	−644(10)	9181(3)	53(4)
C(21)	7127(13)	−35(10)	8828(3)	50(3)
C(31)	6160(13)	97(10)	8394(3)	50(4)
C(41)	4545(13)	−406(10)	8497(3)	50(4)
C(51)	4490(12)	−857(9)	8976(4)	54(4)
C(111)	6672(18)	−989(13)	9699(4)	88(5)
C(211)	8970(13)	307(14)	8862(5)	86(5)
C(311)	6824(18)	618(13)	7913(4)	81(5)
C(411)	3163(18)	−524(12)	8115(5)	84(5)
C(511)	3057(20)	−1500(13)	9241(5)	96(6)
Fe	8342(2)	6004(2)	8358(1)	58(1)
Cl(1)	8666(4)	3965(3)	8174(1)	78(1)
Cl(2)	5728(4)	6513(3)	8210(1)	81(1)
Cl(3)	8875(6)	6251(5)	9124(1)	122(2)
Cl(4)	9889(7)	7202(5)	7900(2)	147(2)
Compound 11·CH_3OH				
Co(1)	7463(3)	6128(1)	8444(1)	25(1)
Co(2)	3001(3)	5634(2)	6768(2)	36(1)
S(1)	7603(6)	4652(3)	8612(3)	42(2)
Cl(1)	2061(5)	5080(4)	7855(3)	53(2)
Cl(2)	1727(7)	4969(4)	5824(3)	75(3)
Cl(3)	2765(7)	7111(3)	6744(4)	78(2)
O(1)	5233(12)	5264(7)	6687(7)	41(5)
O(2)	5758(12)	5988(8)	7727(7)	30(4)
N(1)	8733(14)	5921(10)	7574(9)	33(6)
C(1)	6121(19)	5482(13)	7187(11)	31(7)
C(2)	7855(20)	5200(11)	7191(10)	40(7)
C(3)	7972(20)	4398(11)	7639(10)	44(7)
C(4)	5537(20)	4272(12)	8706(11)	51(8)
C(11)	7400(21)	6382(10)	9577(8)	27(5)
C(12)	8843(19)	6659(14)	9251(11)	34(8)
C(13)	8507(19)	7291(11)	8735(11)	22(6)
C(14)	6903(25)	7422(12)	8684(12)	41(8)
C(15)	6219(22)	6808(14)	9184(14)	43(9)
C(111)	7163(25)	5730(13)	10197(10)	57(8)

TABLE 2 (continued)

Atom	x	y	z	U_{eq}
Compound 11·CH_3OH				
C(121)	10381(19)	6254(15)	9484(12)	50(9)
C(131)	9616(26)	7796(15)	8306(14)	71(11)
C(141)	6047(26)	7997(13)	8190(16)	64(10)
C(151)	4449(21)	6701(12)	9307(13)	46(9)
C(16)	8481(42)	7607(24)	5846(22)	153(14)
O(16)	9150(24)	7297(13)	6514(13)	27(6)
O(17)	8637(49)	8386(29)	5578(24)	15(11)
O(18)	7162(99)	7191(53)	5653(45)	23(22)
O(19)	8222(70)	6814(37)	5472(33)	21(16)

Equivalent isotropic temperature factors U_{eq} are defined as one third of the trace of the orthogonalized U_{ij} tensor.

unit cell of **7b** (space group, $P1$) are related to one another via a pseudocentre of symmetry, which leads to extremely strong correlations of their positional and thermal parameters. It was therefore necessary to restrain their refinement by including bond length parameters (±0.01 Å) for equivalent distances of the two independent molecules. Hydrogen atoms were included where possible for **5**, **7b**, **9a** and **11** · CH_3OH at geometrically calculated positions with group isotropic temperature factors. Anisotropic temperature factors were introduced for all non-hydrogen atoms with the exception of the lithium atoms in **7b** and the O and C atoms of the disordered methanol molecule in **11** · CH_3OH. Terminal reliability indices are listed in Table 1, with $R_w = [\Sigma(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$, with weight given by the expression $w = (\sigma^2(F_o) + p^2F_o^2)^{-1}$. Calculations were performed with the SHELXTL program system (Siemens). Atom coordinates are listed in Table 2, and selected bond lengths and angles in Tables 3 and 4 respectively.

TABLE 3. Selected bond lengths (Å) with standard deviations

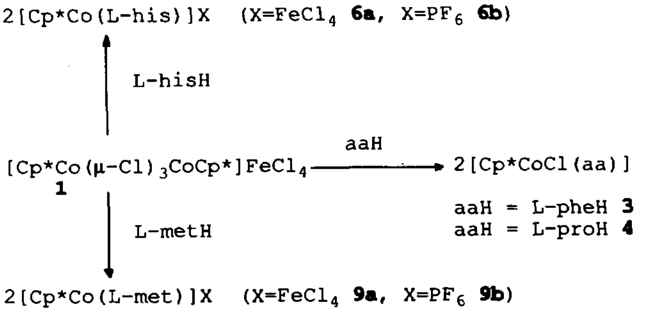
5			
Co–Cl	2.280(4)	Co–O(1)	1.962(7)
Co–N(2)	2.022(9)	Co–C(11)	2.055(10)
Co–C(12)	2.073(11)	Co–C(13)	2.099(12)
Co–C(14)	2.089(11)	Co–C(15)	2.070(12)
O(1)–C(1)	1.30(1)	O(2)–C(1)	1.24(1)
N(2)–C(2)	1.46(1)	N(2)–C(6)	1.47(1)
7b (molecule 1)			
Co–O(11)	1.956(8)	Co–O(41)	1.949(7)
Co–N(1)	1.974(7)	Co–C(11)	2.048(10)
Co–C(12)	2.051(8)	Co–C(13)	2.039(8)
Co–C(14)	2.056(10)	Co–C(15)	2.071(8)
O(11)–C(1)	1.288(10)	O(12)–C(1)	1.236(13)
N(1)–C(2)	1.484(12)	O(41)–C(4)	1.257(11)
O(42)–C(4)	1.260(12)	Li(1)–O(42)	1.95(2)
Li(1)–O(12)′	2.05(2)	Li(1)–O(1)	1.91(2)
Li(1)–O(2)	1.99(2)	Li(2)–O(42)	1.95(2)
Li(2)–O(12)′	1.99(2)	Li(2)–O(3)	1.95(2)
Li(2)–O(4)	1.92(2)		
9a			
Co–S	2.272(3)	Co–O(1)	1.965(6)
Co–N	1.967(8)	Co–C(11)	2.070(11)
Co–C(21)	2.068(10)	Co–C(31)	2.094(10)
Co–C(41)	2.073(10)	Co–C(51)	2.071(10)
O(1)–C(1)	1.263(12)	O(2)–C(1)	1.226(12)
N–C(2)	1.502(12)	S–C(4)	1.800(11)
S–C(5)	1.781(11)		
11			
Co(1)–S(1)	2.270(5)	Co(1)–O(2)	1.968(12)
Co(1)–N(1)	1.94(1)	Co(1)–C(11)	2.08(1)
Co(1)–C(12)	2.04(2)	Co(1)–C(13)	2.05(2)
Co(1)–C(14)	2.07(2)	Co(1)–C(15)	2.00(2)
Co(2)–Cl(1)	2.279(6)	Co(2)–Cl(2)	2.263(7)
Co(2)–Cl(3)	2.257(5)	Co(2)–O(1)	2.011(10)
O(1)–C(1)	1.23(2)	O(2)–C(1)	1.28(2)
N(1)–C(2)	1.50(2)	S(1)–C(3)	1.82(2)
S(1)–C(4)	1.88(2)		

TABLE 4. Selected bond angles (°) with standard deviations

5			
Cl–Co–O(1)	92.9(2)	Cl–Co–N(2)	92.3(3)
O(1)–Co–N(2)	80.9(4)	Co–O(1)–C(1)	115.7(7)
Co–N(2)–C(2)	106.7(7)	Co–N(2)–C(6)	119.9(7)
O(1)–C(1)–C(2)	114.8(10)	O(2)–C(1)–C(2)	120.5(11)
O(1)–C(1)–O(2)	124.6(11)	N(2)–C(2)–C(1)	107.0(9)
7b (molecule 1)			
O(11)–Co–N(1)	82.6(3)	O(41)–Co–N(1)	88.1(3)
O(11)–Co–O(4I)	92.7(3)	Co–O(11)–C(1)	113.7(6)
Co–O(41)–C(4)	130.3(5)	Co–N(1)–C(2)	104.4(4)
O(11)–C(1)–C(2)	115.1(8)	O(41)–C(4)–C(3)	121.1(8)
O(11)–C(1)–O(12)	124.7(8)	O(41)–C(4)–O(42)	121.6(7)
O(12)–C(1)–C(2)	120.2(7)	O(42)–C(4)–C(3)	117.2(8)
O(1)–Li(1)–O(2)	103.2(7)	O(3)–Li(2)–O(4)	101.0(8)
O(42)–Li(1)–O(12)′	84.5(6)	O(42)–Li(2)–O(12)′	86.1(7)
9a			
S–Co–O(1)	90.2(2)	S–Co–N	93.4(2)
O(1)–Co–N	82.1(3)	Co–O(1)–C(1)	115.8(6)
Co–N–C(2)	107.5(6)	Co–S–C(4)	104.9(4)
Co–S–C(5)	111.3(5)	O(1)–C(1)–C(2)	116.2(8)
O(2)–C(1)–C(2)	120.7(10)	O(1)–C(1)–O(2)	123.1(9)
N–C(2)–C(1)	107.6(8)		
11			
S(1)–Co(1)–O(2)	91.2(4)	S(1)–Co(1)–N(1)	85.0(4)
O(2)–Co(1)–N(1)	82.6(5)	Co(1)–O(2)–C(1)	112.2(9)
Co(1)–N(1)–C(2)	102.0(9)	Co(1)–S(1)–C(3)	95.3(5)
Co(1)–S(1)–C(4)	105.4(6)	O(2)–C(1)–C(2)	114 (1)
O(1)–C(1)–C(2)	121 (1)	O(1)–C(1)–O(2)	125 (1)
N(1)–C(2)–C(1)	106 (1)	Co(2)–O(1)–C(1)	118 (1)

4. Discussion

η⁵-Pentamethylcyclopentadienylcobalt(III) complexes of the type [(η⁵-Cp*)CoCl(aa)] (aa = L-phe (**3**) or L-pro (**4**)) were prepared by the reaction of [(η⁵-Cp*)Co(μ-Cl)$_3$Co(η⁵-Cp*)]$FeCl_4$ (**1**) with the appropriate amino acid aaH in methanol at room tempera-



Scheme 1.

ture (Scheme 1). The dimer $[(\eta^5\text{-Cp}^*)\text{CoCl}_2]_2$ (**2**) provides an alternative starting material for the synthesis of such compounds, as exemplified by the preparation of $[(\eta^5\text{-Cp}^*)\text{CoCl}(\text{DL-pipe})]$ (**5**), the structure of which was determined by an X-ray structural study (Fig. 1). Enantiomers with $R_{\text{Co}}R_{\text{C}}S_{\text{N}}$ and $S_{\text{Co}}S_{\text{C}}R_{\text{N}}$ configurations are present in the orthorhombic unit cell, the configuration at the metal centre being designated as previously specified [11,12]. As for the other complexes described in this work, the coordination of the cobalt atom may be regarded as pseudo-octahedral. The pipecolinate anions in **5** coordinate through their amino nitrogen and a carboxylate oxygen atom, leading thereby to the formation of a five-membered chelate ring, which displays an envelope conformation. The nitrogen atom N(2) is displaced by 0.64 Å from the least-squares plane through the remaining four ring atoms. In contrast, the iridium atoms lie 0.29 Å and 0.58 Å respectively from the planes defined by the O(1), C(1), C(2) and N(2) atoms in the S_{Ir} and R_{Ir} diastereomers of the analogous L-prolinate complex $[(\eta^5\text{-Cp}^*)\text{IrCl}(\text{L-pro})]$ [5,6]. A similar conformation is also observed for the five-membered chelate ring in the ruthenium complex $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{L-pro})]$ [6]. The shortening of the O(1)–M, N(2)–M and Cl–M distances to the metal atom M in **5** (M = Co) relative to those in $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{L-pro})]$ and $[(\eta^5\text{-Cp}^*)\text{IrCl}(\text{L-pro})]$ leads to a marked widening of the Cl–M–O(1) and Cl–M–N(2) angles in the cobalt complex. These are respectively 92.9(2)° and 92.3(3)° in **5** in comparison with 85.2(1)° and 82.0(1)° in the ruthenium complex and values in the range 82.9(2)–88.3(2)° in the S_{Ir} and R_{Ir} diastereomers of the iridium complex [6]. The alteration in the endocyclic angle O(1)–M–N(2) is, in contrast, less pronounced: O(1)–Co–N(2), 80.9(4)°; O(1)–Ru–N(2), 79.4(1)°; O(1)–Ir–N(2), 77.5(2) and 79.5(2)° [6]. A chair conformation with torsion angles in the range from ±52.8 to ±60.8° is observed for the six-membered piperidine ring in **5**.

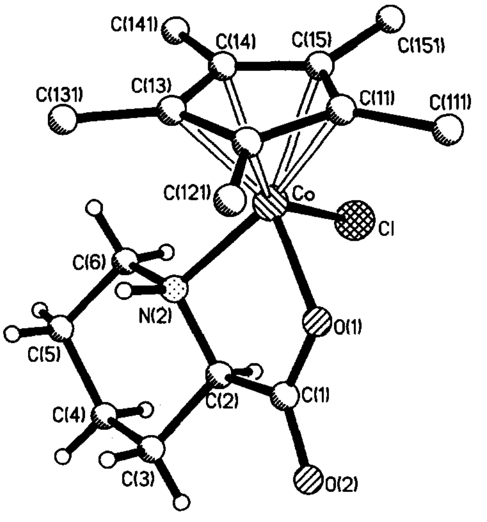
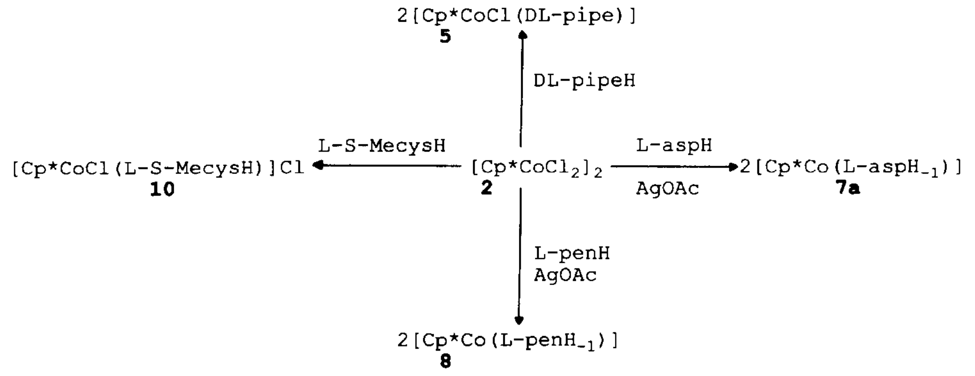


Fig. 1. Molecular structure of the $R_{\text{Co}}R_{\text{C}}S_{\text{N}}$ enantiomer of $[(\eta^5\text{-Cp}^*)\text{CoCl}(\text{DL-pipe})]$ (**5**).

The IR spectra of $[(\eta^5\text{-Cp}^*)\text{CoCl}(\text{L-phe})]$ (**3**) and $[(\eta^5\text{-Cp}^*)\text{CoCl}(\text{L-pro})]$ (**4**) display $\nu_{\text{as}}(\text{CO}_2)$ absorptions at 1600 cm^{-1} and 1622 cm^{-1} respectively in the typical range for monodentate carboxylate coordination (1600–1645 cm^{-1}), and so chelate ring conformation, as in the DL-pipecolinato complex **5**, may be assumed. Diastereomers of rhodium and iridium complexes of the type $[(\eta^5\text{-Cp}^*)\text{MCl(aa)}]$ (M = Rh, or Ir; aa = L-phe or L-trp) have been shown to display separate ^{1}H NMR resonances for their Cp* methyl protons [6]. The observed differences in the chemical shifts (*e.g.* 0.33 ppm in CD_3OD solution for M = Ir, aa = L-trp) are presumably caused by the anisotropy effect of the aromatic ring of L-phe or L-trp on the Cp* protons. In contrast, the splitting of the Cp* signals is much smaller for analogous complexes of aliphatic amino acidate ligands (*e.g.* aa = gly, L-val or L-pro) and is in many cases not resolvable [5,6]. Only one set of ^{1}H NMR signals (400 MHz) was observed for the Cp* and amino acidate protons of **3** and **4** in D_2O solution. The individual resonances of the ring β–δ protons in **4** were assigned with the help of an H, C COSY spectrum. These findings suggest that one of the potential diastereomers must predominate for both **3** and **4** in aqueous solution. A strong preference for one diastereomer (about 9:1) has also been reported for the prolinate complexes $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{L-pro})]$ and $[(\eta^5\text{-Cp}^*)\text{MCl}(\text{L-pro})]$ (M = Rh or Ir) [6]. The appearance of only one set of signals for **3** and **4** also precludes the simultaneous presence of appreciable concentrations of both $[(\eta^5\text{-Cp}^*)\text{CoCl(aa)}]$ and the cation $[(\eta^5\text{-Cp}^*)\text{CoCl}(\text{D}_2\text{O})]^+$, as observed for the analogous $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}^{\text{II}}$ complexes [1–3,6].

Half-sandwich complexes of the type $[(\eta^5\text{-Cp}^*)\text{M}(\text{L-aspH}_{-1})]$ (M = Ir or Rh) and $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{L-his})]\text{Cl}$,



Scheme 2.

which contain tridentate amino acidate ligands have been reported [6], but no X-ray structures are available. We now describe the analogous (η^5-Cp*)Co^{III} complexes [(η^5-Cp*)Co(L-his)]X, (X = FeCl$_4$ (**6a**) or PF$_6$ (**6b**)) with O (carboxylate), N(amino), N(imidazole) coordination and [(η^5-Cp*)Co(L-aspH$_{-1}$)] (**7a**) with O(α-carboxylate), N(amino), O(β-carboxylate) coordination. In contrast with [(η^6-C$_6$H$_6$)Ru(L-his)]Cl, the presence of base is not required for the preparation of **6a**. The reaction of [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ with L-histidine in the absence of base yields [(η^6-C$_6$H$_6$)RuCl(L-his)]Cl, in which the bidentate amino acidate ligand is coordinated via amino and imidazole nitrogen atoms. By analogy to [(η^5-Cp*)M(L-aspH$_{-1}$)] (M = Rh or Ir), **7a** was prepared by the reaction of **2** with L-aspH in the presence of silver acetate (Scheme 2). The coordination of the carboxylate oxygen atom in **6b** is confirmed by the observation of ν_{as}(CO$_2$) at 1625 cm^{-1} in the IR spectrum.

Attempts to obtain single crystals of **6a** or **6b** and of **7a** suitable for an X-ray structural analysis were unsuccessful. However, slow evaporation of a methanol–isopropanol solution of **7a** · H$_2$O containing an excess of LiCl yielded suitable crystals of [(η^5-Cp*)Co(L-aspH$_{-1}$)] · LiCl · 3H$_2$O (**7b**), the structure of which is depicted in Fig. 2. With the exception of the [L-aspH$_{-1}$]$^{2-}$ anions, the atoms in the unit cell of **7b** (space group, $P1$) are related to one another via a pseudocentre of symmetry. It was therefore necessary to restrain the refinement by introducing bond length parameters (standard deviations, ±0.01) for equivalent distances in the two independent molecules. Both display the $S_{Co}S_C$ configuration [11,12], but whereas the first molecule is coordinated to the lithium atoms through its exocyclic β-carboxylate oxygen O(42) atom it is the exocylic α-carboxylate oxygen O(12) atom that adopts that role in the second molecule. Such a pentadentate coordination mode has not, to our knowledge, previously been reported for amino acidate ligands. The adoption of a bridging function has, however, been reported for the carboxylate group in a number of homonuclear complexes, *e.g.* [Ag(gly)]$_2$[NO$_3$]$_2$ [13] and [(cod)RuCl(DL-phe)]$_4$ [14]. Bond angles at the cobalt atoms are similar to those in the

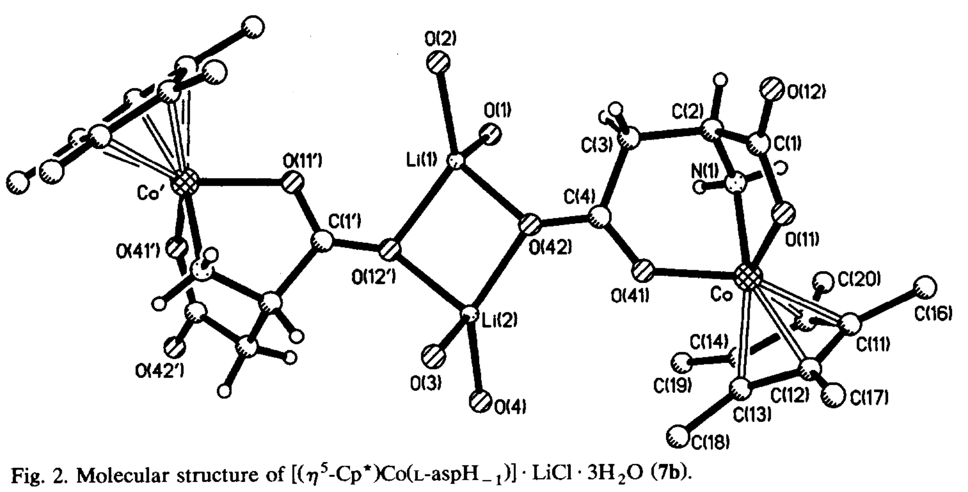


Fig. 2. Molecular structure of [(η^5-Cp*)Co(L-aspH$_{-1}$)] · LiCl · 3H$_2$O (**7b**).

bidentate complex **5**. The five-membered chelate rings in **7b** both display an envelope conformation analogous to that in the DL-pipecolinate complex. N(1) and N(1)′ are displaced 0.68 Å and 0.64 Å from the respective least-squares planes through the remaining four ring atoms (0.64 Å in **5**). The Co and N(1) atoms adopt positions 1.06 and 0.24 Å (1.09 and 0.27 Å in the second molecule) from the least-squares plane through the other atoms of the six-membered chelate ring in **7b**.

Half-sandwich complexes containing tridentate $[\text{L-met}]^-$, $[\text{L-S-Mecys}]^-$ or $[\text{L-penH}_{-1}]^{2-}$ anions have not to our knowledge been previously reported. This O,N,S coordination mode has, however, been characterized in other complexes such as [(nbd)RuCl(DL-met)] [15] or $[\text{Co(L-S-Mecys)}_2]^+$ [16]. The reaction of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ with L-penH in H_2O yields $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru(L-pen)}]_2\text{Cl}_2$, in which the deprotonated sulphur atoms adopt a bridging position between the two ruthenium atoms, leading to the formation of a four-membered RuSRuS ring [2]. The tridentate coordination of the individual ruthenium atoms is completed by the amino nitrogen atoms. Reaction of **2** with L-penH in the presence of silver acetate yields $[(\eta^5\text{-Cp}^\star)\text{Co(L-penH}_{-1})]$ (**8**), which displays a $\nu_{as}(CO_2)$ absorption in the typical range for monodentate carboxylate coordination (1600–1645 cm^{-1}), so that O,N,S coordination may be assumed (Fig. 2). $[(\eta^5\text{-Cp}^\star)\text{Co(L-met)}]\text{FeCl}_4$ (**9a**) was prepared by the reaction of **1** with L-metH in methanol and its structure established by X-ray analysis (Fig. 3). The complex exhibits the $R_{Co}S_CR_S$ configuration. If we take into account the change in the priority of the coordinated side chain in **9a** (SMe) in comparison with **7b** (β-COO), this means that the cobalt atoms in both complexes display similar arrangements of their amino acidate coordinating atoms (Figs. 3 and 4). Model building indicates that the alternative diastereomer cannot be formed for steric reasons. As in **5** and **7b**, the five-membered chelate ring adopts an envelope conformation with the amino nitrogen atom positioned 0.55 Å from the least-squares plane through the remaining four atoms. The six-membered chelate ring in **9a** has a distorted chair conformation, with N and C(4) displaced by 0.84 and −0.85 Å respectively from the best plane through the other ring atoms (deviations, ±0.075 Å or less).

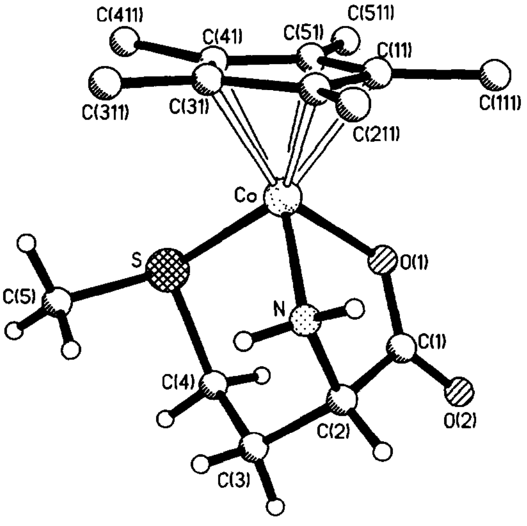


Fig. 3. Molecular structure of the cation of $[(\eta^5\text{-Cp}^\star)\text{Co(L-met)}][\text{FeCl}_4]$ (**9a**).

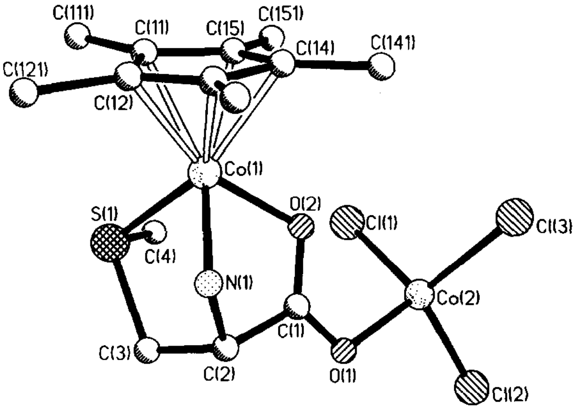


Fig. 4. Molecular structure of $[(\eta^5\text{-Cp}^\star)\text{Co}(\mu\text{-L-S-Mecys})\text{CoCl}_3]$ (**11**).

Reaction of **2** with L-S-MecysH in methanol yields $[(\eta^5\text{-Cp}^\star)\text{CoCl(L-S-MecysH)}]\text{Cl}$ (**10**), in which, in contrast with **9a** or **9b**, the amino acidate ligand is bidentate and is coordinated to the cobalt atom through its S and N atoms (Fig. 2). The $\nu_{as}(CO_2)$ absorption band at 1734 cm^{-1} confirms that the carboxylate group is protonated and is not involved in the metal coordination sphere. Attempts to crystallize **10** from a water–methanol–isopropanol mixture led unexpectedly to the formation of $[(\eta^5\text{-Cp}^\star)\text{Co}(\mu\text{-L-S-Mecys})\text{CoCl}_3]$ (**11**), in which the ligand displays a tridentate O,N,S coordination to the $(\eta^5\text{-Cp}^\star)\text{Co}^{III}$ fragment. The disproportionation of η^5-cyclopentadienylCo^{III}) complexes such as the tris(acetonitrile) cation $[\text{CpCo(NCMe)}_3]^{2+}$ in the presence of oxygen ligands (in particular traces of water) into cobalticenium and Co^{II} ions has been reported [17]. In contrast, $[\text{Cp}^\star\text{Co(H}_2\text{O)}_3]^{2+}$ may be employed for the synthesis of a wide range of $\text{Cp}^\star\text{Co}^{III}$ complexes [10]. Work is now in progress to clarify the reaction mechanism leading to the formation of **11** from **10**.

The $\nu_{as}(CO_2)$ absorption bond at 1602 cm^{-1} is in accordance with carboxylate coordination in **11** and this is confirmed by the X-ray structural analysis (Fig. 4). Indeed the carboxylate group is now bidentate adopting a bridging function between the Co^{III} and Co^{II} atoms. As for **9a** the metal centre Co(1) in **11** displays an R_{Co} configuration. The five-membered N(amino), O(carboxylate) chelate ring exhibits once again an envelope conformation with N(1) displaced 0.80 Å from the least-squares plane through the other four ring atoms. N(1) also adopts the flap position in the second five-membered ring (Co(1), N(1), C(1), C(3), S(1)). Its distance from the plane of the remaining four atoms is in this case 0.90 Å. It is interesting to compare the endocyclic bond angles at the cobalt atoms in **9a** and **11**. Whereas the S–Co–O and O–Co–N angles are very similar in both complexes, a marked narrowing of the S–Co–N angles from 93.4(2) to 85.2(5)° is observed on going from the six-membered ring in **9a** to the more strained five-membered ring in **11**. A change in the configuration from R_S in **9a** to S_S in **11** also occurs.

To our knowledge such a tetradentate μ_2-$(1\kappa^3 S,N,O:2\kappa^1 O')$ coordination has not previously been observed for sulphur-containing amino acidate ligands. Further work is now in progress to prepare and characterize structurally analogous dinuclear complexes.

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