

Cl—Mo—Cl <sup>i</sup>	105.64 (2)	Mo—N—O	172.8 (2)
Cl—Mo—N	96.3 (1)	C2—C1—C5	109.6 (3)
Cl <sup>i</sup> —Mo—N	97.3 (1)	C1—C2—C3	108.3 (3)
Cl—Mo—C <sub>p</sub>	115.5 (1)	C2—C3—C4	108.7 (4)
Cl <sup>i</sup> —Mo—C <sub>p</sub>	114.9 (1)	C3—C4—C5	107.4 (3)
N—Mo—C <sub>p</sub>	123.9 (1)	C4—C5—C1	105.9 (3)
Mo—Cl—Mo <sup>i</sup>	74.36 (2)		

Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Structure solution: Patterson methods (*FORDAP*; Zalkin, UCLA, Los Angeles, USA, unpublished). Program(s) used to refine structure: *ORFLS* (Busing, Martin & Levy, 1962). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances and angles involving H atoms, and torsion angles, as well as a packing diagram, have been deposited with the IUCr (Reference: CR1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Ru}(\text{L-ala})\text{Cl}]$

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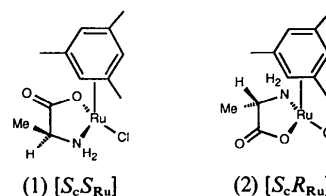
## Abstract

The structure of (L-alaninato-*N,O*)chloro( $\eta^6$ -1,3,5-trimethylbenzene)ruthenium(II),  $[\text{RuCl}(\text{C}_6\text{H}_3\text{NO}_2)(\text{C}_9\text{H}_{12})]$ , has been determined. The crystal contains

two diastereoisomers having opposite chiralities at the metal centre. There is evidence of intermolecular hydrogen bonding between the amine protons of one diastereomer and the chloride of the other.

## Comment

We have recently embarked on a study of metal complexes of biologically relevant ligands (Carter, Davies, Fawcett & Russell, 1993). As part of this programme we have synthesized some arene-ruthenium-amino acid complexes  $[(\text{arene})\text{Ru}(\text{aa})\text{Cl}]$  (aa is an aminoacidate ligand). These half-sandwich complexes are interesting in that they contain a chiral metal centre so that if an L-amino acid ligand is used two diastereoisomers may be formed. The ratio of diastereoisomers varies depending on the amino acid used (Kramer, Polborn, Wanjek, Zahn & Beck, 1990). It has been suggested that intramolecular hydrogen bonding may influence the diastereomer ratio (Sheldrick & Heeb, 1990). In order to investigate further the role of intramolecular hydrogen bonding in such complexes we have determined the structure of  $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Ru}(\text{L-ala})\text{Cl}]$ . The complex was prepared by refluxing a mixture of L-alanine (L-alaH), sodium methoxide and  $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{RuCl}_2]_2$  in a 50:50 methanol–water solution for 3 h. Evaporation of the solvent followed by extraction with dichloromethane, filtration to remove NaCl and rotary evaporation of the solvent gave  $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Ru}(\text{L-ala})\text{Cl}]$  as a yellow powder. X-ray quality crystals were grown by dissolving the solid in the minimum quantity of methanol and adding mesitylene.



The complex crystallized as a 50:50 mixture of two diastereomers having opposite chiralities at the metal centre (Fig. 1). The absolute configurations of the diastereomers were assigned from the known configuration of the amino acid. It is noteworthy that in  $\text{D}_2\text{O}$  solution the ratio of diastereomers is 60:40 rather than the 50:50 observed in the solid state. Molecule (1) displays the  $S_C S_{\text{Ru}}$  configuration while molecule (2) is  $S_C R_{\text{Ru}}$ . The configurations at the Ru atom were assigned on the basis proposed by Stanley & Baird (1975) and Sloan (1981), and are opposite to those assigned by Sheldrick & Heeb (1990) for the diastereomers of  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{L-ala})\text{Cl}]$ . The Ru—N, Ru—Cl and Ru—O distances are similar in

both diastereomers. The Ru—N and Ru—O distances [average 2.118 (10) and 2.089 (9) Å, respectively] are the same as those found in [( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Ru(L-ala)Cl] (Sheldrick & Heeb, 1990), while the average Ru—Cl distance of 2.434 (3) Å is longer than that of 2.400 (7) Å found in the benzene complex. The chelate bite angles [76.4 (3) and 78.2 (3)° for molecules (1) and (2), respectively] are very similar to that observed in the related complex [( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)RuCl(pic)] (picH = picolinic acid) [77.9 (2)°] which also contains a five-membered ring (Carter, Davies, Fawcett & Russell, 1993).

chelate ring, with the C(1) and N(1) atoms 0.209 and -0.219 Å, respectively, from the best least-squares plane through the ring, while in the *R*<sub>Ru</sub> diastereomer, the chelate ring is almost flat. This arrangement of puckered and flat chelate rings is opposite to that found in the corresponding benzene complexes. The reasons for this difference, and for the almost flat chelate ring in molecule (2), are not clear.

## Experimental

### Crystal data

[RuCl(C<sub>3</sub>H<sub>6</sub>NO<sub>2</sub>)(C<sub>9</sub>H<sub>12</sub>)]

*M<sub>r</sub>* = 344.8

Monoclinic

*P*2<sub>1</sub>

*a* = 10.052 (5) Å

*b* = 17.349 (8) Å

*c* = 8.518 (5) Å

$\beta$  = 109.5 (1)°

*V* = 1400 (2) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.63 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation

$\lambda$  = 0.71073 Å

Cell parameters from 393

reflections

$\theta$  = 6.68–14.84°

$\mu$  = 1.17 mm<sup>-1</sup>

*T* = 293 K

Plate

0.62 × 0.30 × 0.12 mm

Orange

### Data collection

Stoe Stadi-2 diffractometer

$\omega$  scans

Absorption correction:

none

3092 measured reflections

3082 independent reflections

2769 observed reflections

[*I* > 3.0 $\sigma$ (*I*)]

$\theta_{\max}$  = 27°

*h* = -12 → 12

*k* = 0 → 22

*l* = 0 → 10

1 standard reflection

monitored every 50

reflections

intensity variation: none

### Refinement

Refinement on *F*

*R* = 0.0492

*wR* = 0.0522

2769 reflections

358 parameters

$w = 1/[\sigma^2(F) + 0.00046F^2]$

( $\Delta/\sigma$ )<sub>max</sub> = 0.701

$\Delta\rho_{\max}$  = 1.17 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -1.82 e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Ru(1)	0.20143 (7)	0.76056	0.11425 (9)	0.0351 (2)
Cl(1)	0.3119 (3)	0.67016 (18)	0.3393 (4)	0.0485 (10)
O(1)	0.1967 (7)	0.8382 (5)	0.2990 (10)	0.048 (3)
O(2)	0.3206 (10)	0.9154 (6)	0.5019 (12)	0.065 (4)
N(1)	0.4018 (9)	0.8139 (6)	0.1842 (12)	0.039 (3)
C(1)	0.4440 (10)	0.8417 (6)	0.3551 (13)	0.043 (3)
C(2)	0.3106 (12)	0.8683 (8)	0.3902 (14)	0.044 (4)
C(3)	0.5579 (14)	0.9042 (8)	0.3938 (18)	0.063 (5)
C(4)	-0.0216 (12)	0.7295 (8)	0.0061 (16)	0.049 (4)
C(5)	0.0584 (11)	0.6685 (7)	-0.0231 (14)	0.043 (4)
C(6)	0.1617 (12)	0.6822 (7)	-0.0993 (14)	0.045 (4)
C(7)	0.1861 (10)	0.7581 (7)	-0.1442 (10)	0.042 (3)
C(8)	0.1010 (14)	0.8186 (8)	-0.1195 (16)	0.056 (4)
C(9)	0.0001 (12)	0.8046 (8)	-0.0450 (17)	0.054 (5)
C(10)	0.0399 (15)	0.5889 (8)	0.0392 (18)	0.061 (5)

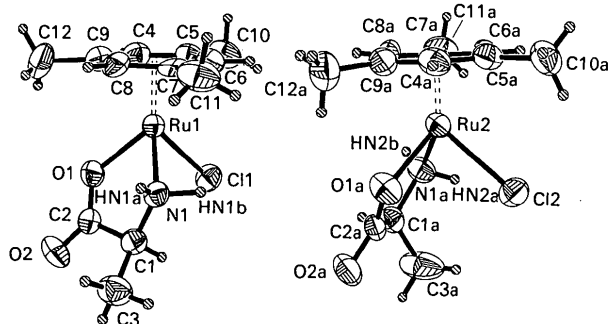


Fig. 1. The molecular structures (*SHELXTL/PC*; Sheldrick, 1990) of the two diastereomers of the title compound with anisotropic ellipsoids representing 50% probability boundaries and H atoms drawn as circles of arbitrary radii.

The structure of the related complex [( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)-Ru(L-ala)Cl] revealed intramolecular hydrogen bonding in the *S*<sub>Ru</sub> diastereomer [labelled *R*<sub>Ru</sub> by Sheldrick & Heeb (1990)] between the N—H group and Cl atom, which led to a relatively planar conformation for that chelate ring. The other diastereomer did not form hydrogen bonds and the chelate ring was puckered. In contrast, the present study revealed no evidence of intramolecular hydrogen bonding. However, in the *S*<sub>Ru</sub> diastereomer the N(1) to H(*n*1*a*) and H(*n*1*b*) bond distances are found to be 0.64 (18) and 1.08 (16) Å, respectively. This apparent asymmetry about the N(1) atom may be due to a strong intermolecular hydrogen bond between H(*n*1*b*) and Cl(2) [Cl(2)⋯H(*n*1*b*) = 2.32 (16), Cl(2)⋯N(1<sup>i</sup>) = 3.34 (1) Å and Cl(2)⋯H(*n*1*b*)—N(1<sup>i</sup>) = 158 (10)°; symmetry code: (i) 1 - *x*, - $\frac{1}{2}$  + *y*, -*z*]. The Cl(2)⋯N(1<sup>i</sup>) distance of 3.34 (1) Å is similar to the N⋯Cl distance of 3.270 (5) Å found by X-ray diffraction in [N<sup>+</sup>Pr<sub>4</sub>]<sub>2</sub>[PtCl<sub>4</sub>].*cis*-[PtCl<sub>2</sub>(NH<sub>2</sub>Me)<sub>2</sub>], where the presence of hydrogen bonding was confirmed by neutron diffraction and the H⋯Cl distance and N—H⋯Cl angle were found to be 2.318 (12) Å and 151.0 (12)°, respectively (Brammer *et al.*, 1991). In addition, the *S*<sub>Ru</sub> diastereomer has a more energetically favoured puckered conformation for the

C(11)	0.2983 (15)	0.7708 (10)	-0.2207 (17)	0.070 (6)
C(12)	-0.0802 (18)	0.8716 (11)	-0.0066 (22)	0.087 (7)
Ru(2)	0.22941 (8)	0.11876 (5)	-0.36635 (10)	0.0384 (3)
Cl(2)	0.3490 (3)	0.20042 (19)	-0.1298 (4)	0.0516 (10)
O(1a)	0.2097 (8)	0.0409 (6)	-0.1876 (12)	0.053 (3)
O(2a)	0.3185 (9)	-0.0404 (6)	0.0115 (12)	0.060 (3)
N(1a)	0.4229 (10)	0.0575 (7)	-0.3040 (14)	0.047 (4)
C(1a)	0.4461 (11)	0.0037 (6)	-0.1602 (14)	0.044 (4)
C(2a)	0.3176 (11)	0.0020 (6)	-0.1052 (14)	0.038 (3)
C(3a)	0.5765 (14)	0.0225 (13)	-0.0174 (21)	0.097 (8)
C(4a)	0.0085 (12)	0.1546 (8)	-0.4785 (16)	0.050 (4)
C(5a)	0.0925 (12)	0.2160 (7)	-0.4952 (15)	0.046 (4)
C(6a)	0.2018 (12)	0.2025 (7)	-0.5663 (15)	0.045 (4)
C(7a)	0.2217 (10)	0.1256 (7)	-0.6208 (10)	0.041 (3)
C(8a)	0.1314 (13)	0.0680 (8)	-0.6112 (18)	0.057 (5)
C(9a)	0.0288 (12)	0.0790 (8)	-0.5355 (17)	0.055 (5)
C(10a)	0.0781 (16)	0.2946 (8)	-0.4331 (19)	0.063 (5)
C(11a)	0.3369 (14)	0.1155 (11)	-0.6972 (16)	0.065 (5)
C(12a)	-0.0589 (19)	0.0143 (10)	-0.5047 (26)	0.088 (8)

Table 2. Selected geometric parameters (Å, °)

Cl(1)—Ru(1)	2.439 (3)	Cl(2)—Ru(2)	2.428 (3)
O(1)—Ru(1)	2.085 (8)	O(1a)—Ru(2)	2.094 (9)
N(1)—Ru(1)	2.113 (9)	N(1a)—Ru(2)	2.123 (10)
C(4)—Ru(1)	2.188 (11)	C(4a)—Ru(2)	2.194 (11)
C(5)—Ru(1)	2.206 (10)	C(5a)—Ru(2)	2.222 (11)
C(6)—Ru(1)	2.198 (12)	C(6a)—Ru(2)	2.185 (11)
C(7)—Ru(1)	2.155 (9)	C(7a)—Ru(2)	2.146 (9)
C(8)—Ru(1)	2.158 (12)	C(8a)—Ru(2)	2.173 (13)
C(9)—Ru(1)	2.165 (11)	C(9a)—Ru(2)	2.163 (11)
C(2)—O(1)	1.262 (13)	C(2a)—O(1a)	1.271 (14)
C(2)—O(2)	1.233 (15)	C(2a)—O(2a)	1.234 (14)
C(1)—N(1)	1.456 (14)	C(1a)—N(1a)	1.495 (15)
C(2)—C(1)	1.538 (15)	C(2a)—C(1a)	1.514 (15)
C(3)—C(1)	1.532 (15)	C(3a)—C(1a)	1.496 (18)
C(5)—C(4)	1.401 (18)	C(5a)—C(4a)	1.396 (18)
C(9)—C(4)	1.414 (18)	C(9a)—C(4a)	1.436 (18)
C(6)—C(5)	1.416 (16)	C(6a)—C(5a)	1.441 (16)
C(10)—C(5)	1.513 (16)	C(10a)—C(5a)	1.486 (17)
C(7)—C(6)	1.415 (16)	C(7a)—C(6a)	1.448 (16)
C(8)—C(7)	1.413 (18)	C(8a)—C(7a)	1.371 (18)
C(11)—C(7)	1.495 (17)	C(11a)—C(7a)	1.516 (16)
C(9)—C(8)	1.386 (20)	C(9a)—C(8a)	1.400 (20)
C(12)—C(9)	1.510 (19)	C(12a)—C(9a)	1.503 (20)
O(1)—Ru(1)—Cl(1)	86.6 (3)	O(1a)—Ru(2)—Cl(2)	85.1 (3)
N(1)—Ru(1)—Cl(1)	85.3 (3)	N(1a)—Ru(2)—Cl(2)	85.8 (3)
N(1)—Ru(1)—O(1)	76.4 (3)	N(1a)—Ru(2)—O(1a)	78.2 (3)
C(2)—O(1)—Ru(1)	119.1 (7)	C(2a)—O(1a)—Ru(2)	118.3 (7)
C(1)—N(1)—Ru(1)	111.0 (7)	C(1a)—N(1a)—Ru(2)	113.4 (7)
C(2)—C(1)—N(1)	108.2 (8)	C(2a)—C(1a)—N(1a)	110.5 (9)
C(3)—C(1)—N(1)	113.4 (10)	C(3a)—C(1a)—N(1a)	112.6 (10)
C(3)—C(1)—C(2)	112.5 (10)	C(3a)—C(1a)—C(2a)	111.0 (12)
O(2)—C(2)—O(1)	124.9 (11)	O(2a)—C(2a)—O(1a)	122.5 (10)
C(1)—C(2)—O(1)	115.3 (10)	C(1a)—C(2a)—O(1a)	118.5 (10)
C(1)—C(2)—O(2)	119.8 (10)	C(1a)—C(2a)—O(2a)	118.9 (10)
C(9)—C(4)—C(5)	119.0 (11)	C(9a)—C(4a)—C(5a)	120.2 (12)
C(6)—C(5)—C(4)	120.4 (11)	C(6a)—C(5a)—C(4a)	119.4 (11)
C(10)—C(5)—C(4)	118.8 (11)	C(10a)—C(5a)—C(4a)	122.0 (12)
C(10)—C(5)—C(6)	120.6 (12)	C(10a)—C(5a)—C(6a)	118.5 (12)
C(7)—C(6)—C(5)	120.0 (11)	C(7a)—C(6a)—C(5a)	119.4 (11)
C(8)—C(7)—C(6)	118.9 (11)	C(11a)—C(7a)—Ru(2)	130.7 (6)
C(11)—C(7)—C(6)	118.6 (12)	C(11a)—C(7a)—C(6a)	116.8 (12)
C(11)—C(7)—C(8)	122.5 (12)	C(11a)—C(7a)—C(8a)	123.9 (12)
C(9)—C(8)—C(7)	120.7 (12)	C(9a)—C(8a)—C(7a)	122.2 (12)
C(8)—C(9)—C(4)	120.9 (12)	C(8a)—C(9a)—C(4a)	119.3 (11)
C(12)—C(9)—C(4)	119.6 (14)	C(12a)—C(9a)—C(4a)	117.7 (14)
C(12)—C(9)—C(8)	119.4 (14)	C(12a)—C(9a)—C(8a)	123.0 (14)

The H atoms of the NH<sub>2</sub> groups were located from a difference synthesis and their positional parameters were refined. All other H atoms were included in calculated positions (C—H = 0.95 Å) with refinement of their isotropic displacement parameters. The structure was solved by direct methods using the *TREF* option of *SHELXS86* (Sheldrick, 1986). All subsequent calculations used *SHELX76* (Sheldrick, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the IUCr (Reference: MU1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## *trans*-Tetraaquabis(*p*-nitrohippurato)-cobalt(II) Dihydrate

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## Abstract

Crystals of [Co(4-NO<sub>2</sub>-hip)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].2H<sub>2</sub>O (4-NO<sub>2</sub>-hip = *p*-NO<sub>2</sub>.C<sub>6</sub>H<sub>4</sub>CO.NHCH<sub>2</sub>CO<sub>2</sub><sup>-</sup>) contain molecules of the centrosymmetric octahedral cobalt(II) complex and lattice water molecules which are interlinked by hydrogen bonds. The Co atom lies on a crystallographic symmetry centre and has a slightly elongated octahedral environment arising from coordination by the carboxylic O atoms of two monodentate 4-nitrohippurate anions and the O atoms of four water molecules.