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Synthesis and stereochemistry of diene-ruthenium(II) complexes of sulphur-containing α-amino acids

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Abstract

Diene-ruthenium(II) complexes of the sulphur-containing amino acids *d,l*-methionine (*d,l*-metH), *d,l*-penicillamine (*d,l*-penH) and *d,l*-cysteine (*d,l*-cysH) and of *d,l*-methionine methyl ester (*d,l*-metme) have been prepared by their reaction of the amino acids or esters with $[(diene)RuCl_2]_n$ (diene = norbornadiene (nbd), 1,5-cyclooctadiene (cod)) in methanol at reflux. Crystal structures are reported for $[(nbd)Ru(d,l\text{-metme})Cl_2]$ (**1**), $[(nbd)Ru(d,l\text{-met})Cl] \cdot CH_3OH$ (**2**) and $[(nbd)Ru(d,l\text{-penH}_{-1})]_2 \cdot EtOH \cdot HCl$ (**3**), in which the amino acid ligands are respectively bi-, tri- and tetra-dentate, with *S,N*-, *S,N,O*- and *S,S,N,O*-coordination. Spectroscopic evidence suggests that, in contrast to **3**, the *d,l*-cysteinate ligands are tridentate (*S,S,N*-coordination) in dimeric $[(cod)Ru(d,l\text{-cys})Cl]_2$ (**4**).

Introduction

Reaction of $[(diene)RuCl_2]_n$ (diene = norbornadiene (nbd), 1,5-cyclooctadiene (cod)] with α-amino acids (aaH) such as glycine (glyH), *d,l*-alanine (*d,l*-alaH) or *l*-phenylalanine (*l*-phe) in aqueous solution at reflux leads to the formation of complexes of the type $[(diene)Ru(aa)_2]$ [1,2]. As established by an X-ray structural study, the Δ diastereomer of $[(nbd)Ru(l\text{-phe})_2]$ is obtained by recrystallisation of this complex from methanol [2]. Both of the phenylalaninate ligands participate in five-membered chelate rings with N(ammine),O(carboxyl)-coordination. An ammine nitrogen of the first and a carboxyl oxygen of the second amino acid ligand are sited *trans* to nbd double bonds, so that the coordination may be described as *OC*-6-32 [3]. In contrast, reaction of $[(diene)RuCl_2]_n$ with α-amino acids (aa = gly, *d,l*-ala, *d,l*-val, *d,l*-phe) in methanol at reflux leads to the isolation of oligomeric complexes $[(diene)RuCl(aa)]_n$, in which the amino acid ligand must be tridentate [2]. A crystal structure study of tetrameric $[(cod)RuCl(d,l\text{-phe})]_4$ confirms that there is N(ammine),O(carboxyl),O(carboxyl′) coordination, with symmetrical carboxyl bridges

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between individual ruthenium atoms. We recently reported the preparation and structural characterisation of (η^6-arene)ruthenium(II) complexes of α-amino acids with coordinating side chains (aa = *l*-penicillamine *l*-penH, *l*-histidine *l*-hisH, triglycine glyglyglyH) [4]. The *l*-penicillaminate ligands in $[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})]_2Cl_2 \cdot H_2O$ are tridentate, with the deprotonated sulphur atoms adopting a bridging position between two ruthenium atoms to give a four-membered RuSRuS ring. The coordination spheres of the ruthenium atoms are completed by respective amino nitrogen atoms, which participate in five-membered chelate rings. We now describe the synthesis and structural characterization of dieneruthenium(II) complexes of the sulphur containing amino acids, or in one case an ester, *d,l*-methionine methyl ester (*d,l*-metme), *d,l*-methionine (*d,l*-met), *d,l*-penicillamine (*d,l*-pen) and *d,l*-cysteine (*d,l*-cys). Crystal structures have been determined for [(nbd)Ru(*d,l*-metme)Cl_2] (**1**), [(nbd)Ru(*d,l*-met)Cl] · CH_3OH (**2**) and [(nbd)Ru($d,l\text{-penH}_{-1}$)]$_2$ · EtOH · HCl (**3**), in which the amino acid ligands are respectively bi-, tri- and tetra-dentate. In contrast to complex **3**, the *d,l*-cysteinate ligands in dimeric [(cod)Ru(*d,l*-cys)Cl]$_2$ (**4**) appear to be tridentate as indicated by IR data. The carboxyl groups are protonated and do not participate in coordination to the Ru atoms.

Experimental

All reactions were carried out under argon. Solvents were dried and distilled before use. IR spectra were recorded as 1% KBr discs on a Perkin Elmer 297 spectrometer. ^{1}H NMR spectra were recorded on a Bruker WP 200 spectrometer for **1** and **2** and on a Bruker AM 400 for **3** and **4**. The α-amino acids were purchased from Sigma Chemie GmbH and used as received. $RuCl_3 \cdot 3H_2O$ was a gift from Degussa AG. $[Ru(cod)Cl_2]_n$ and $[Ru(nbd)Cl_2]_n$ were prepared as previously described [5–7].

*Preparation of complexes **1–4***

[(nbd)Ru(d,l-metme)Cl_2] (1). A mixture of $[Ru(nbd)Cl_2]_n$ 162 mg, 0.61 mmol and *d,l*-methionine methyl ester (258 mg 1.29 mmol) in 10 ml of absolute methanol was stirred for 30 h under reflux. The dark orange solution was filtered hot then cooled to −30 °C to yield orange needle shaped crystals of **1**. Yield 185 mg (70%). **1**: Anal. found: C, 36.2; H, 4.88; N, 3.3. $C_{13}H_{21}Cl_2NO_2SRu$ (*M*, 427.4) calcd.: C, 36.54; H, 4.95; N, 3.27%. IR: 3320, 3260 $\nu(NH_2)$, 1750 ν(CO), 1580 cm^{-1} $\delta(NH_2)$. ^{1}H NMR (CD_2Cl_2/TMS): 1.52, 1.85 (2s, 3H, *d,l*-metme S-CH_3), 3.71 (s, 3H, *d,l*-metme, COO-CH_3), 1.96–4.78 (superimposed signals of *d,l*-metme CH, CH_2; nbd CH, CH_2).

[(nbd)Ru(d,l-met)Cl] (2). A mixture of $[Ru(nbd)Cl_2]_n$ (163 mg, 0.62 mmol) and *d,l*-methionine (185 mg, 1.24 mmol) in 15 ml of absolute methanol was stirred for 4 h under reflux. The solution was reduced in volume to 5 ml and then cooled to −30 °C to yield orange crystals of **2** · CH_3OH. Upon drying in vacuum the crystals lost methanol to give **2**. Yield 165 mg (71%). **2** · CH_3OH, Anal. found: C, 38.1; H, 5.41; N, 3.5. $C_{13}H_{22}NO_3SClRu$ (*M*, 408.9) calcd.: C, 38.18; H, 5.42; N, 3.42%. **2**: Anal. found: C, 37.6; H, 4.86; N, 3.9. $C_{12}H_{18}NO_2SClRu$ (*M*, 376.9) calcd.: C, 38.24; H, 4.81; N, 3.71%. IR: 3120, 3220 $\nu(NH_2)$, 1625 cm^{-1} ν(CO). ^{1}H NMR (DMSO-d_6/TMS) 3.16 (s, 3H, *d,l*-met S-CH_3), 1.49–5.27 (superimposed signals of *d,l*-met CH, CH_2; nbd-CH, CH_2).

[(nbd)Ru(d,l-penH$_{-1}$)]$_2$ · C_2H_5OH · HCl (3). A mixture of [Ru(nbd)Cl_2]$_n$ (229 mg, 0.87 mmol) and *d,l*-penicillamine (257 mg, 1.72 mmol) in 17 ml of absolute methanol was stirred for 40 h unter reflux. The solution was reduced in volume to 7 ml and acetone added until precipitation just began. The precipitate was redissolved with 1 ml ethanol. Orange-red crystals of **3** were obtained by cooling the solution to −38 °C. Yield 170 mg (52%). **3**: Anal. found.: C, 40.8; H, 5.46; N, 3.6. $C_{26}H_{41}N_2O_5S_2ClRu$ (*M*, 763.3) calcd.: C, 40.9; H, 5.41; N, 3.67%. IR: 3230, 3190, 3065, 3045 $\nu(NH_2)$, 1600, 1590 ν(CO), $\delta(NH_2)$. ^{1}H NMR (CD_3OD/TMS): 1.37 (t, 3H, ethanol CH_3), 1.53, 1.64 (2d, ^2J(H,H) 8.6 Hz, 4H, nbd-CH_2), 1.76, 1.84 (2s, 12H, pen-CH_3), 3.79 (q, 2H, ethanol-CH_2), 3.91 (m, 4H, nbd aliph CH), 4.00 (s, 2H, pen-CH), 3.83, 4.42, 4.52, 4.66 (4t, 8H, nbd olef CH), 5.75, 6.87 (2d, ^2J(H,H) 10.0 Hz, 4H, pen-NH_2).

[(cod)Ru(d,l-cys)Cl]$_2$ (4). A mixture of [Ru(cod)Cl_2]$_n$ (287 mg, 1.02 mmol) and *d,l*-cysteine (128 mg, 1.06 mmol) in 10 ml of absolute methanol was stirred for 20 h under reflux. The dark brown solution was filtered and cooled to −30 °C to yield yellow crystals of **4**. Yield 195 mg (53%). **4**: Anal. found: C, 35.6; H, 4.97; N, 3.7. $C_{22}H_{36}N_2O_4S_2Cl_2Ru_2$ (*M*, 729.7) calcd.: C, 36.21; H, 4.97; N, 3.84%. IR: 3237 $\nu(NH_2)$, 1730 ν(CO), 1590 cm^{-1} $\delta(NH_2)$. ^{1}H NMR (CD_3OD/TMS): 5.41, 6.24 (2d, ^2J(H,H) 9.7 Hz, 4H, cys NH_2), 1.90-4.51 (superimposed signals of cys-CH, CH_2; cod-CH, CH_2). EI-MS (70eV, 30 °C): *m/e* (rel. intensity) 728 (22; M^+), 658 (20; $M^+ - 2Cl$).

X-ray structural analyses of 1–3

Suitable crystals of **1** and **2** were obtained by slow crystallization of the complexes from methanol solution at −30 °C; **2** crystallized together with a methanol

(*continued on p. 380*)

Table 1

Crystal and refinement data for **1–3**

Compound	**1**	**2**·CH_3OH	**3**
Space group	*Pbca*	$P\bar{1}$	$P2_1/c$
a (Å)	17.461(2)	13.653(4)	19.802(4)
b (Å)	16.980(3)	14.718(8)	17.825(5)
c (Å)	10.693(3)	8.003(3)	17.841(4)
α (°)	90	91.19(4)	90
β (°)	90	100.26(3)	101.23(3)
γ (°)	90	95.45(4)	90
V (Å^3)	3170(2)	1574(2)	6177(5)
Z	8	4	8
D_c (g.cm^{-3})	1.79	1.73	1.64
Radiation	Cu-K_α	Mo-K_α	Mo-K_α
μ (cm^{-1})	126.2	12.8	12.2
scan type	ω–2θ	ω	ω–2θ
$2\theta_{max}$ (°)	140	50	45
Reflections collected	3064	5501	8293
Reflections observed	1674	4577	5634
Rejection criterion	$F_o^2 < 3\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$
R	0.077	0.051	0.050
R_w	0.076	0.060	0.051
P	0.014	0.002	0.014

Table 2

Atom positional parameters with equivalent isotropic temperature factors ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
1				
Ru1	−0.2155(1)	0.0785(1)	0.1616(1)	40(1)
Cl1	−0.2774(3)	0.1161(2)	0.3575(3)	53(2)
Cl2	−0.1749(3)	−0.0370(2)	0.2812(4)	54(2)
S1	−0.3022(3)	0.1684(2)	0.0629(4)	48(2)
O11	−0.4732(7)	−0.0917(6)	0.2050(11)	65(8)
O12	−0.3937(11)	−0.1343(8)	0.0673(15)	122(14)
N11	−0.2986(7)	−0.0070(6)	0.0982(12)	45(7)
C1	−0.1585(9)	0.0964(7)	−0.0175(13)	41(9)
C2	−0.1254(8)	0.0355(9)	0.0457(13)	46(9)
C3	−0.0566(9)	0.0694(8)	0.1250(12)	50(10)
C4	−0.1035(11)	0.1163(8)	0.2236(15)	62(12)
C5	−0.1363(9)	0.1780(9)	0.1624(13)	47(9)
C6	−0.1116(9)	0.1711(8)	0.0227(13)	47(10)
C7	−0.0306(10)	0.1359(9)	0.0357(15)	63(11)
C10	−0.5148(11)	−0.1656(9)	0.2011(18)	65(12)
C11	−0.4138(11)	−0.0842(10)	0.1358(16)	52(10)
C12	−0.3741(9)	−0.0041(8)	0.1517(14)	38(8)
C13	−0.4209(10)	0.0613(7)	0.942(16)	51(10)
C14	−0.3939(9)	0.1410(8)	0.1254(15)	46(9)
C15	−0.2970(14)	0.2686(9)	0.1268(16)	75(14)
2				
Ru1	0.3319(1)	0.5883(1)	0.7510(1)	24(1)
Cl1	0.3941(2)	0.4482(2)	0.6715(3)	39(1)
S1	0.2735(2)	0.4954(2)	0.9601(3)	34(1)
O11	0.2331(4)	0.6819(4)	0.8050(7)	31(2)
O12	0.0734(4)	0.7087(4)	0.7645(8)	41(2)
N11	0.2006(5)	0.5455(5)	0.5707(8)	27(2)
C11	0.1407(6)	0.6612(6)	0.7437(11)	30(2)
C12	0.1125(7)	0.5690(6)	0.6425(11)	31(3)
C13	0.0824(7)	0.4930(7)	0.7658(12)	41(3)
C14	0.1398(7)	0.5063(7)	0.9503(12)	39(3)
C15	0.3169(8)	0.5503(7)	1.1680(12)	49(3)
C111	0.4315(7)	0.6378(6)	0.5756(11)	35(3)
C112	0.3768(7)	0.7091(6)	0.6120(12)	35(3)
C113	0.4419(7)	0.7633(6)	0.7704(12)	39(3)
C114	0.4355(7)	0.6900(6)	0.9119(12)	35(3)
C115	0.4900(6)	0.6183(6)	0.8729(11)	34(3)
C116	0.5312(7)	0.6452(6)	0.7085(12)	37(3)
C117	0.5502(7)	0.7523(7)	0.7372(14)	50(3)
Ru2	−0.1996(1)	0.0842(1)	−0.2139(1)	26(1)
Cl2	−0.1464(2)	−0.0562(2)	−0.0909(4)	49(1)
S2	−0.0900(2)	0.0543(2)	−0.4040(3)	41(1)
O21	−0.1985(4)	0.2172(4)	−0.3030(7)	31(2)
O22	−0.1136(5)	0.3521(4)	−0.2791(8)	42(2)
N21	−0.0755(5)	0.1539(5)	−0.0424(9)	28(2)
C21	−0.1226(7)	0.2707(6)	−0.2439(11)	31(3)
C22	−0.0353(7)	0.2326(6)	−0.1332(12)	34(3)
C23	0.0382(7)	0.2018(7)	−0.2443(13)	44(3)
C24	−0.0115(8)	0.1596(7)	−0.4242(12)	47(3)
C25	−0.1574(9)	0.0465(9)	−0.6200(13)	66(4)
C211	−0.3182(7)	0.1435(6)	−0.1044(12)	35(3)
C212	−0.3084(7)	0.0574(7)	−0.0402(12)	39(3)

(*continued*)

Table 2 (continued)

Atom	x	y	z	U_{eq}
2				
C213	−0.3823(7)	−0.0129(7)	−0.1653(13)	45(3)
C214	−0.3307(7)	−0.0101(7)	−0.3285(12)	43(3)
C215	−0.3414(7)	0.0785(7)	−0.3879(12)	41(3)
C216	−0.3984(7)	0.1305(7)	−0.2707(12)	41(3)
C217	−0.4710(7)	0.0492(7)	−0.2207(14)	52(3)
O31	0.1213(7)	0.3609(6)	0.3662(12)	93(3)
C31	0.1838(10)	0.3004(9)	0.3046(17)	85(4)
O41	0.6830(13)	0.7869(12)	0.2348(22)	84(6)
3				
Ru1	−0.0589(1)	0.1286(1)	0.1752(1)	31(1)
Ru2	−0.1324(1)	0.0005(1)	0.2899(1)	28(1)
Ru3	0.4424(1)	0.0083(1)	0.1711(1)	31(1)
Ru4	0.3676(1)	0.1364(1)	0.2851(1)	25(1)
S1	−0.0759(1)	0.1215(1)	0.3039(1)	32(1)
S2	−0.1429(1)	0.0282(1)	0.1570(1)	32(1)
S3	0.4326(1)	0.0207(1)	0.3022(1)	32(1)
S4	0.3531(1)	0.1023(1)	0.1540(1)	28(1)
O11	0.0278(3)	0.0518(4)	0.1999(4)	38(4)
O12	0.1224(3)	0.0313(4)	0.2865(4)	50(4)
O21	−0.0381(3)	−0.0582(3)	0.2914(4)	36(4)
O22	0.0062(4)	−0.1497(4)	0.2324(4)	48(4)
O31	0.5232(4)	0.0917(4)	0.1840(4)	41(4)
O32	0.6230(4)	0.1227(4)	0.2600(5)	66(5)
O41	0.4566(3)	0.2013(4)	0.2781(4)	35(4)
O42	0.4920(4)	0.2953(4)	0.2126(4)	45(4)
N11	0.0253(4)	0.1943(4)	0.2343(4)	38(5)
N21	−0.1654(4)	−0.1047(4)	0.2383(5)	37(5)
N31	0.5332(4)	−0.0495(4)	0.2299(4)	35(5)
N41	0.3266(4)	0.2379(4)	0.2308(4)	31(4)
Cl1	0.6579(1)	−0.1129(1)	0.1592(2)	45(2)
Cl2	0.1516(1)	0.2452(2)	0.1610(2)	50(2)
C11	0.0701(6)	0.0699(5)	0.2572(6)	38(3)
C12	0.0602(5)	0.1434(6)	0.2968(6)	43(3)
C13	0.0146(5)	0.1320(5)	0.3576(5)	35(2)
C14	0.0165(6	0.2044(6)	0.4040(6)	51(3)
C15	0.0408(5)	0.0672(6)	0.4102(6)	48(3)
C21	−0.0415(5)	−0.1087(5)	0.2428(6)	36(3)
C22	−0.1118(5)	−0.1201(5)	0.1894(5)	36(3)
C23	−0.1213(5)	−0.0662(5)	0.1217(6)	38(3)
C24	−0.1852(6)	−0.0903(6)	0.0624(6)	51(3)
C25	−0.0573(5)	−0.0662(6)	0.0845(6)	45(3)
C31	0.5707(6)	0.0786(6)	0.2378(6)	45(3)
C32	0.5675(6)	0.0075(6)	0.2850(6)	46(3)
C33	0.5266(5)	0.0217(5)	0.3492(6)	39(3)
C34	0.5493(6)	0.0922(6)	0.3944(6)	50(3)
C35	0.5373(6)	−0.0472(6)	0.4024(6)	51(3)
C41	0.4470(5)	0.2508(5)	0.2266(5)	32(2)
C42	0.3751(5)	0.2549(5)	0.1770(5)	33(2)
C43	0.3658(5)	0.1962(5)	0.1118(5)	30(2)
C44	0.4270(5)	0.2004(6)	0.0695(6)	42(3)
C45	0.2986(5)	0.2117(6)	0.0564(6)	46(3)
C111	−0.0812(6)	0.1299(6)	0.0481(6)	47(3)
C112	−0.0314(6)	0.1847(6)	0.0758(6)	49(3)
C113	−0.0718(6)	0.2589(6)	0.0838(6)	56(3)
C114	−0.1056(5)	0.2367(6)	0.1524(6)	44(3)

(*continued*)

Table 2 (continued)

Atom	x	y	z	U_{eq}
3				
C115	−0.1551(5)	0.1821(6)	0.1263(6)	43(3)
C116	−0.1536(6)	0.1683(6)	0.0406(6)	50(3)
C117	−0.1345(6)	0.2501(7)	0.0159(7)	64(4)
C211	−0.1589(5)	−0.0543(6)	0.3919(6)	43(3)
C212	−0.1297(5)	0.0152(5)	0.4132(6)	40(3)
C213	−0.1887(5)	0.0725(6)	0.4051(6)	45(3)
C214	−0.2098(5)	0.0761(5)	0.3161(5)	33(2)
C215	−0.2412(5)	0.0061(5)	0.2947(6)	39(3)
C216	−0.2386(6)	−0.0399(6)	0.3668(6)	51(3)
C217	−0.2480(6)	0.0239(6)	0.4242(6)	54(3)
C311	0.4137(6)	−0.0005(6)	0.0445(6)	54(3)
C312	0.4676(6)	−0.0485(7)	0.0719(7)	57(3)
C313	0.4361(7)	−0.1244(7)	0.0859(7)	64(4)
C314	0.4037(6)	−0.1050(6)	0.1563(6)	46(3)
C315	0.3493(5)	−0.0558(6)	0.1299(6)	44(3)
C316	0.3461(6)	−0.0446(7)	0.0427(7)	62(3)
C317	0.3681(8)	−0.1263(8)	0.0202(8)	84(4)
C411	0.3753(5)	0.1255(5)	0.4108(5)	35(2)
C412	0.3409(5)	0.1912(5)	0.3864(5)	36(3)
C413	0.2621(5)	0.1711(5)	0.3652(6)	40(3)
C414	0.2612(5)	0.1229(5)	0.2939(5)	36(3)
C415	0.2961(5)	0.0565(5)	0.3175(5)	33(2)
C416	0.3201(5)	0.0638(5)	0.4070(5)	36(3)
C417	0.2584(5)	0.1083(6)	0.4252(6)	43(3)
O100	0.1290(4)	−0.0975(4)	0.2395(5)	63(2)
C100	0.1506(9)	−0.1136(9)	0.1714(9)	102(5)
C101	0.1998(17)	−0.1818(19)	0.1840(18)	102(8)
C102	0.1647(17)	−0.0381(19)	0.1360(19)	102(8)
O200	0.6142(5)	0.2492(5)	0.2029(6)	89(3)
C200	0.6240(12)	0.2605(14)	0.1352(14)	161(9)
C201	0.6546(15)	0.3256(18)	0.1183(15)	214(12)

solvate molecule. **3** was crystallized from a methanol/ethanol/acetone mixture and the crystal contained protonated ethanol solvate molecules. Crystal and refinement data are summarized in Table 1, and positional parameters and isotropic temperature factors are listed in Table 2. Unit cell constants were obtained from a least-squares fit to the settings of 25 reflections recorded on an Enraf–Nonius CAD4 diffractometer at varied scan rates using Cu-K_α radiation for **1** and Mo-K_α radiation for **2** and **3**. Three monitoring reflections were examined at regular intervals during data collection; no significant decreases in intensity were observed. The structures were solved by Patterson syntheses (**1**, **2**) or direct methods (**3**) and refined by full-matrix least-squares. The asymmetric unit of **2** contains two molecules [(nbd)Ru(*d*,*l*-met)Cl] and two molecules of methanol, one of which is disordered. Only one oxygen position O41 and no carbon atom positions could be definitively located in a difference synthesis for this disordered molecule. O41 was included in the subsequent refinement with a site occupation factor (s.o.f) of 0.5. Two structural units $[(\text{nbd})\text{Ru}(d,l\text{-penH}_{-1})]_2 \cdot \text{C}_2\text{H}_5\text{OH}_2^+ \cdot \text{Cl}^-$ are contained in the asymmetric unit of **3**. Both of the protonated ethanol molecules show disorder-

ing of the CH_3 groups. For the first molecule two disordered positions C101 and C102 were located in difference syntheses and included in the refinement (s.o.f. 0.5). Although only one position C201 could be ascertained for the analogous carbon atom in the second protonated ethanol molecule; the high value of 0.214 $Å^2$ for the isotropic temperature factor suggests that this atom is also disordered. All non-hydrogen atoms in **1** and **2** except those in the methanol (**2**) were assigned anisotropic temperature factors. Anisotropic refinement of **3** was limited to non-solvate atoms heavier than carbon. Terminal reliability indices are listed in Table 1 where $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$ with weights given by $w = (\sigma^2(F_o) + p^2F_o^2)^{-1}$. Final difference syntheses were effectively contourless. Analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion were taken from ref. 8. Calculations were performed with SHELX-76 [9] and with local programs. Full details of the X-ray analyses are available from the authors.

Results and discussion

The molecular structure of [(nbd)Ru(*d,l*-metme)Cl_2] (**1**) is shown in Fig. 1; bond lengths to the ruthenium atom are listed in Tab. 3. As expected the S and N atoms of *d,l*-metme participate in a six-membered chelate ring, and have distorted chair conformation. The configurational chirality of the central ruthenium atom in this bis-bidentate complex may be designated as *R* [10]; the α-carbon atom C12 of the amino acid ligand shows *S* configuration and, the sulphur atom *S*1 *R* configuration. The enantiomer of this molecule, present in the centrosymmetric unit cell, shows the opposite Ru_S,C_R,S_S configuration. Sulphur and chlorine atoms are situated *trans* to one another in **1**, so that the ruthenium coordination sphere may be described as OC-6-42 [3]. an alternative ligand arrangement would be Cl *trans* to N (OC-6-43) or Cl *trans* to Cl (OC-6-14). The six-membered chelate ring adopts chair conformation

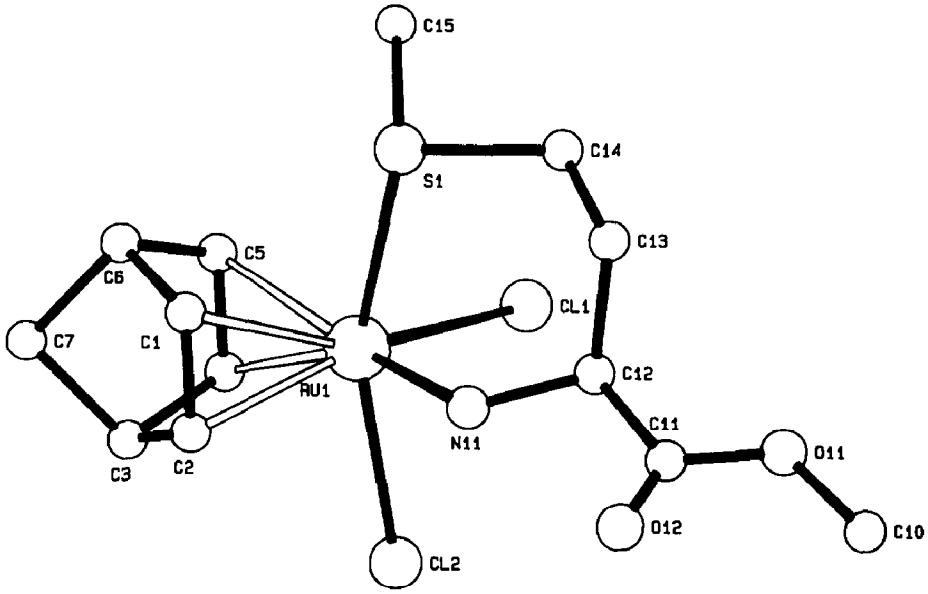

Fig. 1. Molecular structure of [(nbd)Ru(*d,l*-metme)Cl_2] (**1**) (Ru_R, C_S, S_R enantiomer).

Table 3

Bond lengths (Å) to the ruthenium atoms in **1–3**

1			
Ru1–Cl1	2.442(7)	Ru1–C12	2.446(7)
Ru1–S1	2.395(8)	Ru1–N11	2.16(2)
R1–C1	2.18(3)	Ru1–C2	2.13(3)
Ru1–C4	2.16(3)	Ru1–C5	2.18(3)
2			
Ru1–Cl1	2.418(1)	Ru2–Cl2	2.426(1)
Ru1–S1	2.381(1)	Ru2–S2	2.378(1)
Ru1–O11	2.108(3)	Ru2–O21	2.096(3)
Ru1–N11	2.126(3)	Ru2–N21	2.143(3)
Ru1–C111	2.210(4)	Ru2–C211	2.211(4)
Ru1–C112	2.212(4)	Ru2–C212	2.223(5)
Ru1–C115	2.184(4)	Ru2–C214	2.204(4)
Ru1–C116	2.204(4)	Ru2–C215	2.167(4)
3			
Ru1–S1	2.389(3)	Ru3–S3	2.395(3)
Ru1–S2	2.422(3)	Ru3–S4	2.411(2)
Ru1–O11	2.173(6)	Ru3–O31	2.162(7)
Ru1–N11	2.140(8)	Ru3–N31	2.160(7)
Ru1–C111	2.225(10)	Ru3–C311	2.223(11)
Ru1–C112	2.194(11)	Ru3–C312	2.179(11)
Ru1–C114	2.143(10)	Ru3–C314	2.158(10)
Ru1–C115	2.156(10)	Ru3–C315	2.179(11)
Ru2–S1	2.421(2)	Ru4–S3	2.419(2)
Ru2–S2	2.392(3)	Ru4–S4	2.379(2)
Ru2–O21	2.136(6)	Ru4–O41	2.133(6)
Ru2–N21	2.134(7)	Ru4–N41	2.137(7)
Ru2–C211	2.216(10)	Ru4–C411	2.228(9)
Ru2–C212	2.206(10)	Ru4–C412	2.208(10)
Ru2–C214	2.158(9)	Ru4–C414	2.155(10)
Ru2–C215	2.173(10)	Ru4–C415	2.164(9)

as demonstrated by the ring torsion angles (49.6, −63.7, 66.9, −67.9, 78.1 and −65.5°, beginning with bond Ru1–S1, clockwise direction). N11 and C14 are respectively −0.84 and 0.75 Å from the best least squares plane through the remaining four ring atoms. The S–CH_3 group is placed equatorially with respect to the chelate ring. Two resonances at 1.52 and 1.85 ppm are observed for the S–CH_3 protons in the ^{1}H NMR spectrum of **1** in CD_2Cl_2, which may be interpreted as indicating the presence of species with differing chelate ring conformations in solution. A tentative assignment would be 1.52 ppm for S–CH_3 in an axial position and 1.85 ppm for an equatorial position as observed in the solid state (Fig. 1).

In contrast to **1**, the sulphur atoms in both of the independent molecules of [(nbd)Ru(*d*,*l*-metme)Cl] (**2**) are positioned *trans* to an nbd double bond, as shown in Fig. 2. Tridentate coordination of the amino acid ligands is observed, with the sulphur, nitrogen and oxygen atoms in a facial arrangement. The configurational chirality of the ruthenium atoms of both independent molecules in Fig. 2 may be designated as Ru_S; the methionine α-carbon and sulphur atoms have *S* configuration. As **2** crystallizes in the centrosymmetric unit cell $P\bar{1}$, the enantiomers with

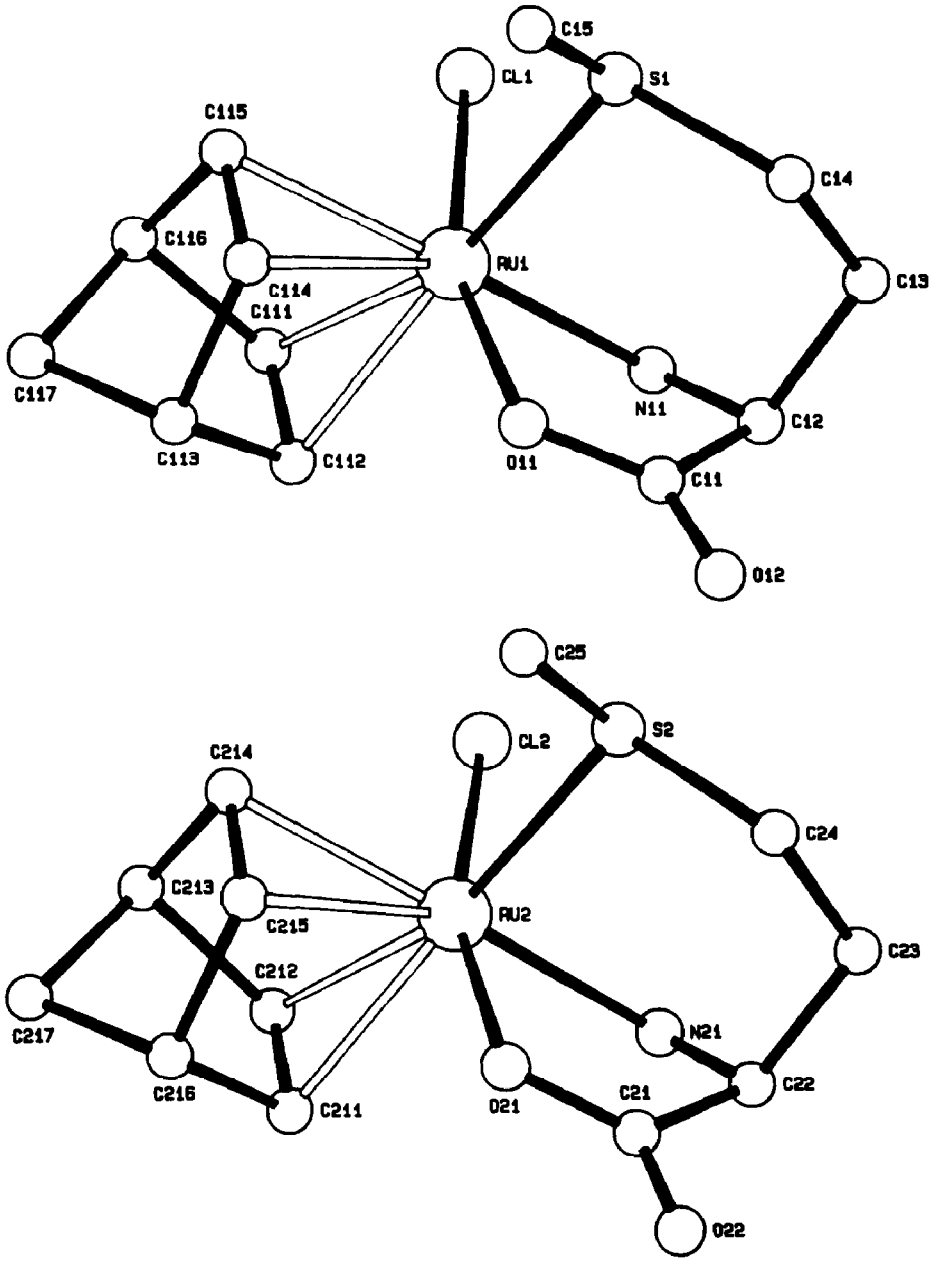

Fig. 2. Molecular structures of the two independent molecules of [(nbd)Ru(*d*,*l*-met)Cl] (**2**) (Ru_S,C_S,S_S enantiomers)

Ru_R,C_R,S_R configuration are also present in the unit cell. The ligand arrangement in **2** may be described as OC-6-35; alternative isomers would be OC-6-45 with Cl *trans* S or OC-6-45 with Cl *trans* to N. The chair conformation is adopted by the six-membered chelate rings, with S1 and C12 at distances of -0.86 and 0.84 Å, respectively, from the best least squares plane through the remaining four ring atoms in the first molecule and -0.93 and 0.83 Å in the second molecule. Exocyclic

thioether carbons C15 and C25 both lie in equatorial positions with respect to their six-membered chelate rings. Envelope conformations with the nitrogen atoms N11 and N21 in the respective flap positions are displayed by the five-membered chelate rings. The nitrogen lie away 0.59 and 0.57 Å from the best least squares planes through the remaining four ring atoms. A *trans* influence on the Ru–C(nbd) bond lengths is apparent from the following values (Å): Ru1–C111 2.210(4), Ru1–C114 2.184(4), Ru1–C112 2.212(4), Ru1–C115 2.204(4), Ru2–C211 2.211(4), Ru2–C214 2.204(4), Ru2–C212 2.223(5), Ru2–C215 2.167(4), C111–C112 1.398(6), C114–C115 1.408(6), C211–C212 1.386(6), C214–C215 1.409(6).

The longer Ru–C and shorter olefinic C–C distances *trans* to the thioether function are indicative of a lower degree of π back-bonding from ruthenium *d*-orbitals than in the bonds situated *trans* to amino nitrogen function. A significant degree of π back-bonding to the sulphur atoms may be assumed. By comparison to the free amino acid the S–CH_3 resonance in DMSO-d_6 is shifted from 2.05 [11] to 3.16 ppm in **2**. As for **1** the remaining amino acid proton resonances overlap with nbd, resonances making assignment difficult.

The penicillaminate ligands in **3** are tetradentate with S,S,N,O coordination. As was previously observed for $[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})]_2Cl_2 \cdot H_2O$ [4] the deprotonated

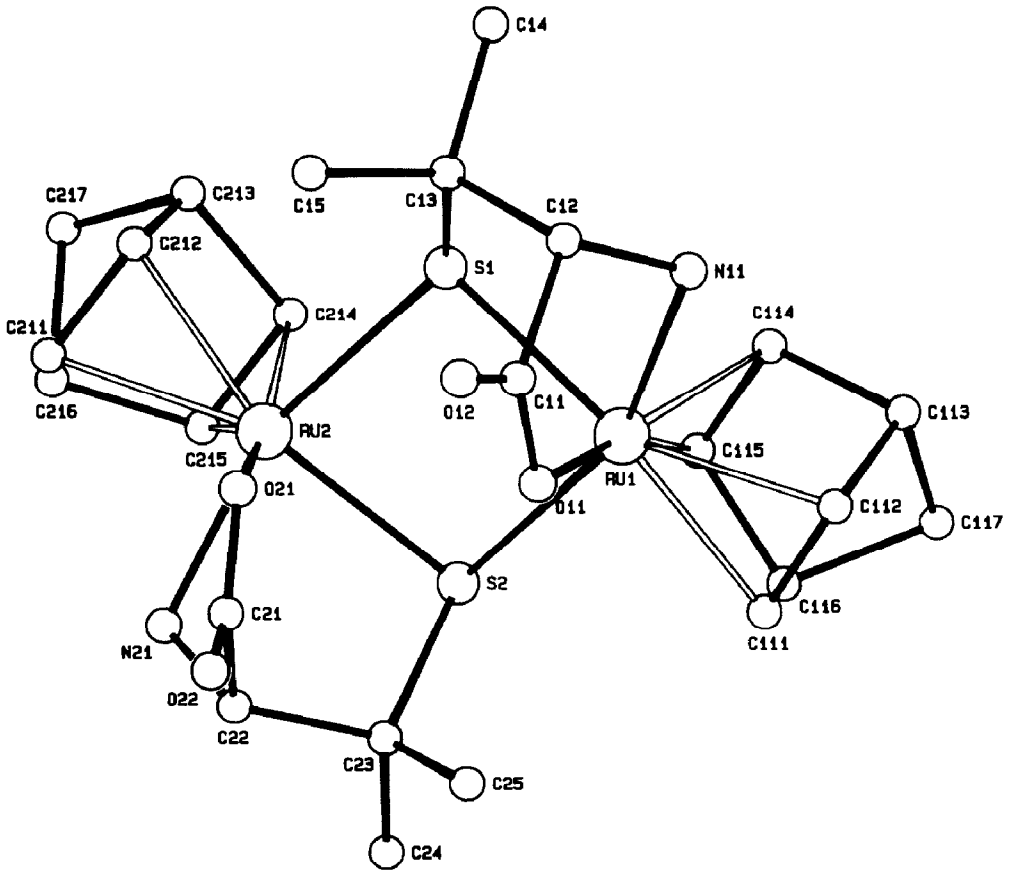

Fig. 3. Molecular structure of the first independent molecule of $[(nbd)Ru(d,l\text{-penH}_{-1})]_2$ (**3a**).

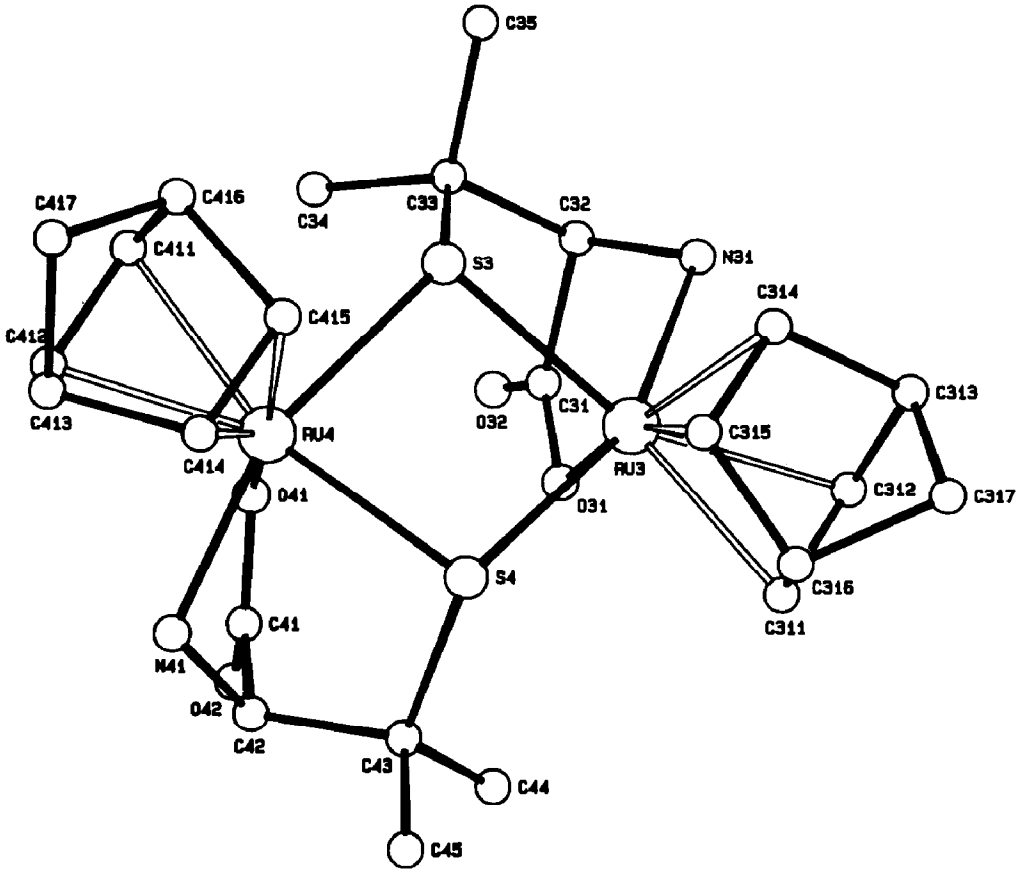

Fig. 4. Molecular structure of the second independent molecule of $[(nbd)Ru(d,l\text{-penH}_{-1})]_2$ (**3b**).

sulphur atoms adopt a bridging position between the two ruthenium atoms, thereby giving a central four-membered RuSRuS ring. Once again two independent molecules are observed in the unit cell (Fig. 3 and 4). To our knowledge [12,13] this coordination mode has not previously been observed for penicillaminate or cysteinate ligands.

The individual molecules of **3** display approximately C_2 symmetry. Ruthenium atoms Ru1 and Ru2 display a Ru_S,C_S,S_R configuration, Ru3 and Ru4 the opposite Ru_R,C_R,S_S configuration. The chiralities of the individual S atoms may be established by assigning a higher priority to the Ru atom that participates in the same five-membered chelate ring, in line with Prelog's rule [14]. In contrast to $[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})]_2Cl_2 \cdot H_2O$, for which an essentially planar four-membered RuSRuS-ring was observed (deviation ± 0.008–0.009 Å, interplanar dihedral angle 1.06°), the central ring in both independent molecules of **3** is markedly folded: deviations ± 0.163 Å (**3a**), ± 0.154 (**3b**), interplanar dihedral angle RuSS RuSS 20.7° (**3a**), 19.7° (**3b**). This conformational change is presumably necessary to allow *O*-coordination in **3**, with the formation of a second five-membered chelate ring. The amino nitrogen atoms adopt the flap positions in the envelope conformations displayed by both five-membered chelate rings for each ruthenium atom. As was observed for $[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})]_2Cl_2 \cdot H_2O$, the Ru–S distances in the chelate

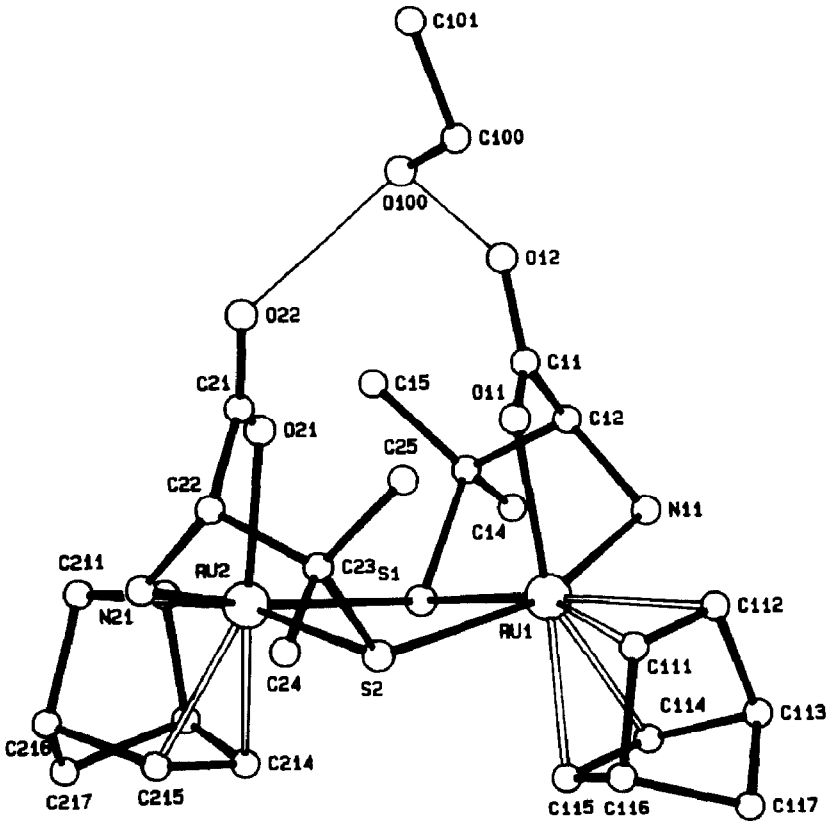

Fig. 5. Hydrogen bonding of the ethanolium cation to the carboxyl oxygens O12 and O22 in **3a**.

rings (2.379–2.395 Å) are markedly shorter than the bridging Ru–S distances in the central four-membered rings (2.411–2.422 Å).

As depicted in Fig. 5 the non-coordinated carboxyl oxygens are bridged via an ethanolium cation for both **3a** and **3b**. Full occupation of the oxygen positions O100 and O200 is observed, so that a double protonation must be assumed in order to account for the O...O distances O100...O12 2.45, O100...O22 2.58, O200...O32 2.47 and O200...O42 2.59 Å, which are indicative of O–H...O hydrogen bonding. The simplicity of the ^{1}H NMR spectrum of **3** (in CD_3OD) in comparison with those of **1** and **2** suggests that the rigid molecular structure is retained in solution. Two singlets are observed for the penicillaminate methyl protons at 1.76 and 1.84 ppm, two doublets for the amino protons at 5.75 and 6.87 ppm. In contrast to the situation in **3**, the carboxyl groups of the cysteinate ligands in **4** are protonated, as evidence by the appearance of ν(CO) at 1730 cm^{-1}. It may, therefore, be assumed that the amino acid ligands display a tridentate S,S,N coordination mode, as observed in $[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})]_2Cl_2 \cdot H_2O$. The ^{1}H NMR spectrum (CD_3OD/TMS) exhibits two doublets for the amino protons in **4**, as would be expected for a five-membered chelate ring constrained in a rigid conformation. It seems plausible that the presence of the bulkier cod ligands with a larger bite angle may prevent the tetradentate coordination of the cysteinate ligands in **4**, for which a dimeric structure $[(cod)Ru(d,l\text{-cys})Cl]_2$ with a central RuSRuS four-membered ring may be assumed, in analogy to **3**. It is interesting to note that an (nbd)Ru^{II}-complex of

d,l-cysteine could not be isolated under conditions analogous to those used for the preparation of **3**.

The present results reinforce our previous finding for $(\eta^6\text{-}C_6H_6)Ru^{II}$ complexes [4], namely that S and N coordination sites are preferred for organoruthenium(II) complexes of amino acids and peptides.

Acknowledgements

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