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Contribution from the Department of Chemistry, Simon Fraser University,
Burnaby, British Columbia, Canada V5A 1S6

Crystal and Molecular Structure of (η-*p*-Di-*tert*-butylbenzene)carbonylbis(trichlorosilyl)ruthenium, $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2$

F. W. B. EINSTEIN* and T. JONES

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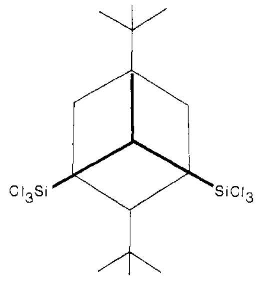
The crystal and molecular structure of $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2\cdot{}^1/_2C_6H_5CH_3$ has been determined. The crystal system is triclinic, space group $P\bar{1}$, with $a = 9.208$ (1) Å, $b = 10.718$ (1) Å, $c = 14.856$ (2) Å, $\alpha = 94.25$ (1)°, $\beta = 84.03$ (1)°, and $\gamma = 117.47$ (1)°. Intensity data were measured for 4580 independent reflections ($2\theta \leq 50°$). Refinement was based upon 3846 observed ($I \geq 2.3\sigma(I)$) reflections and yielded a final discrepancy index $R = 0.039$. The molecule adopts a "piano stool" arrangement. The conformation of the arene ring with respect to the $Ru(CO)(SiCl_3)_2$ moiety is roughly 10° from a staggered arrangement. The carbon atoms of the ring attached to the *t*-Bu groups are slightly out of the plane made by the other four-ring carbons. These features of the structure and others are discussed in relation to similar structures.

Introduction

The literature contains a number of structural reports[1-16] concerning complexes of the type $(arene)M(CO)(L)_2$ (M = Cr, Ru; L = CO, $PMePh_2$, or $GeCl_3$). Even for the less complicated chromium tricarbonyl systems[1-14] $(arene)Cr(CO)_3$, a variety of different structures arise as a result of different conformations of the arene ring with respect to the chromium tricarbonyl moiety. In some cases[1-7] these conformations can be reasonably explained in terms of electronic effects of the arene substituents. Other conformations,[8-14] however, are not readily explicable in these terms. This situation becomes even more confusing when one considers the conformations adopted by the more complicated complexes such as $(C_6H_6)Ru(CO)(GeCl_3)_2$, which is eclipsed,[15] and $(arene)RuCl_2(PMePh_2)$ (arene = benzene or *p*-isopropyltoluene), both of which are staggered and exhibit nonplanarity of their six-membered rings.[16]

The present study on $(p\text{-}t\text{-}Bu_2C_4H_6)Ru(CO)(SiCl_3)_2$ was intended to shed further light upon the factors influencing the conformations adopted in these compounds. Further interest arose since, in solution, it exhibits restricted rotation, on the NMR time scale, of the arene ring about the ruthenium atom.[17] On the basis of NMR evidence, the eclipsed structure I was proposed to be the preferred conformation at low temperatures in solution and probably in the solid state.



I

Experimental Section

The crystal data is given in Table I. A crystal suitable for data collection was mounted in a Lindemann capillary tube. Weissenberg and precession photographs were used to determine the diffraction symbol and approximate cell dimensions. Accurate cell dimensions were determined by least-squares refinement of 20 accurately centered reflections (2θ = 25–32°; Mo Kα = 0.709 26 Å). Data were collected with an automatic Picker FACS-I four-circle diffractometer with a graphite monochromator and a scintillation counter with pulse height discrimination. The takeoff angle was 3°, and a symmetrical θ–2θ scan (2°/min) of $(1.6 + 0.692 \tan \theta)°$ was used. Stationary-crystal, stationary-counter background counts of 10% of the scan time were taken at each side of the scan. The peak profile of each reflection was analyzed and used to derive its intensity and associated error.[18] Intensity measurement of 2 standards every 70 reflections showed no evidence of crystal deterioration nor instability of detector.

Intensities were measured for 4580 independent reflections ($2\theta \leq 50°$), of which 3846 were classified as observed [$I \geq 2.3\sigma(I)$]. Lorentz, polarization, and absorption corrections have been made.

The structure was solved by conventional Patterson and Fourier methods, with all atoms, including hydrogen atoms, belonging to "the NRC PDP-8e crystal structure system".[20]

Description and Discussion of Structure

The molecule $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2$ adopts a "piano stool" configuration (Figures 1 and 2). The Ru atom lies at the apex of a trigonal pyramid in which it is coordinated to a carbonyl group and two trichlorosilyl groups, all of which lie at the base of the pyramid. Above the Ru atom with its ring carbon atoms roughly equidistant from ruthenium is situated the $p\text{-}t\text{-}Bu_2C_6H_4$ group. Bond distances and angles for the molecule are given in Table III.

The conformation of the arene ring with respect to the $Ru(CO)(SiCl_3)_2$ moiety is neither staggered nor eclipsed but

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Table I. Crystal Data

compd	(η-*p*-di-*t*-butylbenzene)carbonylbis(trichlorosilyl)ruthenium
fw	634.37
formula	$C_{15}H_{22}RuCl_6Si_2O\cdot{}^1/_2(C_7H_8)$
space group	$P\bar{1}$
a, Å	9.208 (1)
b, Å	10.718 (1)
c, Å	14.856 (2)
α, deg	94.25 (1)
β, deg	84.03 (1)
γ, deg	117.47 (1)
V, Å^3	1293.23
Z	2
D_c, g cm^{-3}	1.63
crystal dimens, mm	0.08 × 0.16 × 0.13
μ, cm^{-1}	13.07

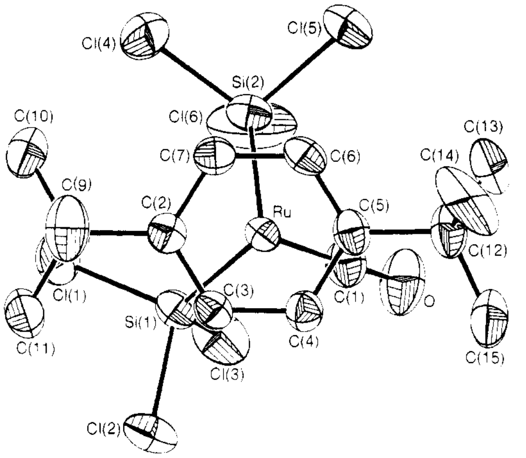

Figure 1. Projection of the $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2$ molecule approximately normal to the plane of the phenyl ring. Hydrogen atoms have been omitted (ORTEP diagram, 50% probability contours for all atoms).

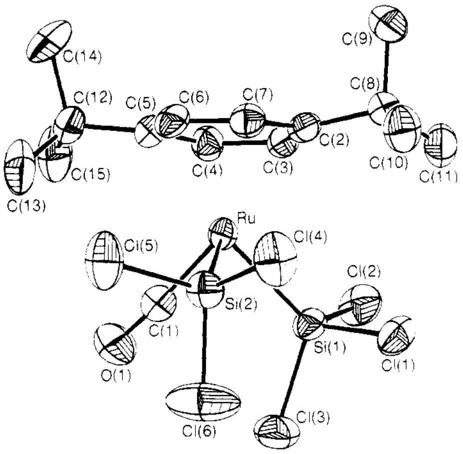

Figure 2. Molecular structure of $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2$ viewed approximately parallel to the plane of the phenyl ring. Hydrogen atoms are not included (ORTEP diagram, 50% probability contours for all atoms).

Table II. Positional Parameters for $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2$[a]

atom	*x*	*y*	*z*
Ru	1009 (5)	32800 (4)	23614 (3)
Si1	11165 (17)	17232 (14)	26474 (10)
Si2	19167 (18)	39773 (16)	10608 (10)
Cl(1)	10096 (18)	2637 (15)	16346 (10)
Cl(2)	−1546 (18)	4970 (15)	37681 (10)
Cl(3)	34985 (18)	25069 (17)	30136 (13)
Cl(4)	11345 (22)	27941 (17)	−1065 (10)
Cl(5)	23224 (24)	59424 (16)	6713 (11)
Cl(6)	42585 (21)	42340 (30)	10835 (14)
O	2943 (5)	5396 (5)	3333 (3)
C(1)	1882 (6)	4573 (6)	2951 (4)
C(2)	−2668 (6)	1564 (5)	2034 (3)
C(3)	−2547 (5)	1837 (5)	2980 (3)
C(4)	−2044 (6)	3196 (5)	3367 (3)
C(5)	−1597 (6)	4379 (5)	2826 (3)
C(6)	−1609 (6)	4119 (5)	1886 (3)
C(7)	−2117 (6)	2750 (5)	1508 (3)
C(8)	−3574 (6)	68 (5)	1636 (3)
C(9)	−5357 (7)	−175 (6)	1654 (5)
C(10)	−2957 (8)	−65 (6)	665 (4)
C(11)	−3535 (7)	−1054 (6)	2192 (4)
C(12)	−1192 (7)	5856 (5)	3229 (4)
C(13)	317 (9)	6980 (6)	2726 (5)
C(14)	−2685 (10)	6072 (8)	3101 (7)
C(15)	−892 (10)	5983 (7)	4215 (5)
CS(1)	4004 (9)	8810 (8)	4521 (5)
CS(2)	6335 (8)	10103 (8)	5382 (4)
CS(3)	5355 (8)	8865 (8)	4901 (4)
CS(4)	5684 (17)	7773 (13)	4801 (9)
H(3A)	−276 (5)	118 (5)	336 (3)
H(4A)	−186 (6)	324 (5)	397 (3)
H(6A)	−132 (5)	469 (5)	151 (3)
H(7A)	−215 (5)	264 (4)	90 (3)
H(9A)	−545 (7)	58 (6)	123 (4)
H(9B)	−596 (7)	−103 (6)	133 (4)
H(9C)	−567 (6)	−15 (6)	221 (4)
H(10A)	−362 (7)	−107 (6)	41 (4)
H(10B)	−301 (6)	60 (5)	31 (4)
H(10C)	−201 (6)	17 (5)	63 (3)
H(11A)	−409 (6)	−191 (5)	192 (3)
H(11B)	−246 (7)	−92 (6)	219 (4)
H(11C)	−388 (7)	−98 (6)	280 (4)
H(13A)	5 (8)	698 (7)	210 (4)
H(13B)	53 (7)	789 (6)	296 (4)
H(13C)	131 (11)	695 (10)	285 (6)
H(14A)	−259 (7)	703 (6)	340 (4)
H(14B)	−334 (8)	555 (7)	361 (4)
H(14C)	−259 (8)	619 (7)	246 (5)
H(15A)	7 (7)	584 (6)	432 (4)
H(15B)	−182 (7)	537 (6)	458 (4)
H(15C)	−65 (7)	678 (6)	449 (4)
HS(1A)	347 (8)	811 (7)	409 (4)
HS(2A)	712 (7)	1011 (6)	563 (4)

[a] The coordinates quoted here have been multipled by 10^5 for Ru, Si, and Cl, by 10^4 for C and O, and by 10^3 for H.

closer to the former; this is indicated by the torsion angles presented in Table IVc.

Factors which may influence the conformations adopted in this type of compound include (i) electronic and steric effects of the arene ring substitutents, (ii) electronic and steric effects of the ligands in the $Ru(L)_3$ moiety and (iii) crystal packing effects.

The positions of the two *t*-Bu groups para to one another lead to equally increased electron density at all four unsubstituted ring positions. This situation, in itself, does not favor electronically any particular orientation of the arene ring for interaction with the three σ orbitals of ruthenium. Electronic effects arising as a result of the asymmetry of the $Ru(CO)(SiCl_3)_2$ moiety are also unlikely, as we might expect a similarity between the trans influence of CO and $SiCl_3$ ligands. The structure of *cis*-$Ru(CO)_4(GeCl_3)_2$ showed[21] that both types of Ru–C(carbonyl) bond are in all probability equal, which suggests that the trans influence of $GeCl_3$ and CO ligands, when bond to ruthenium are approximately the same. The trans influence of $SiCl_3$ is expected to be very similar to that of $GeCl_3$. Furthermore, in (1-*tert*-butyl-2,2-dimethylpropyl)-π-tricarbonylchromium–benzene,[13] where the $M(L)_3$ moiety is symmetrical, a very similar conformation is found. It is concluded that the conformation observed here is most probably a result of steric interactions. Some of the shorter

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Table III. Bond Distances (Å) and Angles (Deg)

Ru–Si(1) = 2.338 (1)
Ru–Si(2) = 2.340 (1)
Ru–C(1) = 1.843 (5)
Ru–C(2) = 2.432 (5)
Ru–C(3) = 2.334 (4)
Ru–C(4) = 2.320 (5)
Ru–C(5) = 2.379 (5)
Ru–C(6) = 2.327 (4)
Ru–C(7) = 2.337 (5)

C(1)–O = 1.141 (7)

C(2)–C(3) = 1.419 (7)
C(3)–C(4) = 1.405 (7)
C(4)–C(5) = 1.423 (7)
C(5)–C(6) = 1.403 (7)
C(6)–C(7) = 1.409 (7)
C(7)–C(2) = 1.398 (7)

C(2)–C(8) = 1.531 (7)
C(8)–C(9) = 1.537 (8)
C(8)–C(10) = 1.522 (8)
C(8)–C(11) = 1.524 (7)
C(5)–C(12) = 1.538 (7)
C(12)–C(13) = 1.521 (9)
C(12)–C(14) = 1.528 (9)
C(12)–C(15) = 1.503 (9)

Si(1)–Cl(1) = 2.064 (2)
Si(1)–Cl(2) = 2.090 (2)
Si(1)–Cl(3) = 2.072 (2)
Si(2)–Cl(4) = 2.055 (2)
Si(2)–Cl(5) = 2.079 (2)
Si(2)–Cl(6) = 2.048 (2)

Si(1)–Ru–Si(2) = 89.13 (5)
Si(1)–Ru–C(1) = 83.6 (2)
Si(1)–Ru–C(2) = 98.6 (1)
Si(1)–Ru–C(3) = 94.0 (1)
Si(1)–Ru–C(4) = 115.1 (1)
Si(1)–Ru–C(5) = 149.6 (1)
Si(1)–Ru–C(6) = 160.4 (1)
Si(1)–Ru–C(7) = 125.6 (1)

C(1)–Ru–C(2) = 162.6 (2)
C(1)–Ru–C(3) = 128.3 (2)
C(1)–Ru–C(4) = 100.8 (2)
C(1)–Ru–C(5) = 95.1 (2)
C(1)–Ru–C(6) = 116.0 (2)
C(1)–Ru–C(7) = 150.4 (2)

Ru–Si(1)–Cl(1) = 116.99 (7)
Ru–Si(1)–Cl(2) = 111.98 (7)
Ru–Si(1)–Cl(3) = 119.66 (8)
Cl(1)–Si(1)–Cl(2) = 103.75 (8)
Cl(1)–Si(1)–Cl(3) = 102.42 (9)
Cl(2)–Si(1)–Cl(3) = 99.56 (8)

Ru–Si(2)–Cl(4) = 116.98 (8)
Ru–Si(2)–Cl(5) = 110.73 (8)
Ru–Si(2)–Cl(6) = 120.06 (8)
Cl(4)–Si(2)–Cl(5) = 101.15 (9)
Cl(4)–Si(2)–Cl(6) = 103.19 (11)
Cl(5)–Si(2)–Cl(6) = 102.19 (11)

Ru–C(1)–O = 177.1 (5)
C(7)–C(2)–C(8) = 122.0 (4)
C(3)–C(2)–C(8) = 121.9 (4)
C(6)–C(5)–C(12) = 120.8 (4)
C(4)–C(5)–C(12) = 123.0 (5)

Si(2)–Ru–C(1) = 84.4 (2)
Si(2)–Ru–C(2) = 112.8 (1)
Si(2)–Ru–C(3) = 147.3 (1)
Si(2)–Ru–C(4) = 155.6 (1)
Si(2)–Ru–C(5) = 121.0 (1)
Si(2)–Ru–C(6) = 94.1 (1)
Si(2)–Ru–C(7) = 90.7 (1)

C(2)–C(8)–C(9) = 103.4 (4)
C(2)–C(8)–C(10) = 112.3 (4)
C(2)–C(8)–C(11) = 113.9 (4)
C(9)–C(8)–C(10) = 109.5 (5)
C(9)–C(8)–C(11) = 108.8 (5)
C(10)–C(8)–C(11) = 108.8 (4)

C(5)–C(12)–C(13) = 111.3 (5)
C(5)–C(12)–C(14) = 105.4 (5)
C(5)–C(12)–C(15) = 112.0 (5)
C(13)–C(12)–C(14) = 109.2 (6)
C(13)–C(12)–C(15) = 108.3 (5)
C(14)–C(12)–C(15) = 110.6 (6)

C(2)–C(3)–C(4) = 122.1 (4)
C(3)–C(4)–C(5) = 121.6 (4)
C(4)–C(5)–C(6) = 116.1 (4)
C(5)–C(6)–C(7) = 121.6 (4)
C(6)–C(7)–C(2) = 122.9 (4)
C(7)–C(2)–C(3) = 115.5 (4)

Table IV. Mean Planes and Torsion Angles for $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2$ and Related Compounds

(a) Mean Planes Calculations[a]

plane	equation	χ^2
1[b]	$0.9873x + 0.1446y - 0.0661z - 6.2755 = 0$	0.00

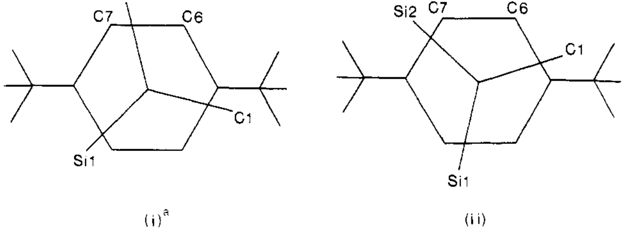
(b) Deviations from Best Planes (Å)

atom[c]	1[b]	attached substituent	2[d]	attached substituent	3[e]	attached substituent
C(2)	0.060 (6)[f]	*t*-Bu	0.074[f]	$CH(CMe_3)_2$	0.22	$POCl(C_6H_2\text{-}t\text{-}Bu_3)$
C(3)	0.000 (6)		−0.005		0.02	
C(4)	0.000 (6)		0.005		−0.02	
C(6)	0.000 (6)		−0.005		0.02	
C(7)	0.000 (6)		0.005		−0.02	
C(5)	0.035 (6)[f]	*t*-Bu	0.010[f]		0.12	*t*-Bu

(c) Torsion Angles in Present Compound[g]

C(3)–CR–Ru to CR–Ru–Si(1) = 19.3°
C(5)–CR–Ru to CR–Ru–C(1) = 19.7°
C(7)–CR–Ru to CR–Ru–Si(2) = 22.8°

[a] The equations of the planes are referred to orthogonal axes *a*, *b*′, and *c**. [b] Present compound. [c] The nomenclature of the previously reported compounds has been changed to be consistent with the present study. [d] (1-*tert*-butyl-2,2-dimethylpropyl)-π-tricarbonylchromium-benzene: ref 13. This mean plane calculation was performed in this laboratory. [e] Bis(2,4,6-tri-*tert*-butylphenyl)phosphinic chloride: ref 22. [f] These atoms are not included in mean planes calculations. [g] CR denotes the centroid of the arene ring.



(i)[a] (ii)

Figure 3. Two alternative and equivalent conformations at low temperature in solution. (a) The conformation observed in the solid state.

intramolecular distances between the $t\text{-}Bu_2C_6H_4$ group and the $Ru(CO)(SiCl_3)_2$ moiety include the distances between Cl(1) and the hydrogen atoms H(10C) and H(11B), which are 3.24 (5) and 2.89 (5) Å, respectively, and also the distances between O and H(15A), H(15B), and H(13C), which are 3.10 (6), 3.21 (6) and 2.88 (9) Å, respectively. Although these distances are not extremely short, molecular models indicate that rotation of the arene ring to either the closest eclipsed or staggered arrangement would result in increased interaction. Molecular packing effects are also a possibility as the intermolecular distances found in this compound are of the same order as the intramolecular distances already described (a table of intermolecular distances has been deposited). The conformation adopted in the solid state is different from the eclipsed arrangement I predicted by NMR studies in solution.[17] This prediction was made on the basis of ^{13}C NMR data where the two signals assigned to the arene ring carbons in the nonrigid form were resolved into doublets at low temperature. The conformation adopted in the solid, on the other hand, if present in solution would be expected to give rise to six resonances. In the light of the present crystallographic result, the ^{13}C NMR data can readily be reinterpreted if one assumes that in solution at low temperatures, the phenyl ring rocks to and fro between the electronically equivalent positions (i) and (ii) (Figure 3) at a rate which is greater than is detectable on the NMR time scale.

An interesting feature of the present structure is the "crystallographical" nonplanarity of the arene ring. The Ru–C distances, two of which are longer than the others (Table III), and the mean plane data presented in Table IVb, clearly indicate a slight, but significant, "boating" of the arene ring at the substituted positions. An almost identical arrangement exists in (1-*tert*-butyl-2,2-dimethylpropyl)-π-tricarbonylchromium–benzene[13] (Table IV). Inequality of M–C distances in this type of compound has also been observed in (arene)-$RuCl_2(PMePh_2)$ (arene = benzene or *p*-isopropyltoluene);[16] however, the distortion of the arene ring in these compounds was of a different type and could be explained in terms of a trans effect of the halogen ligands in the $RuCl_2(PMePh_2)$ moiety. Such an explanation is not suitable in $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2$, especially when one considers the similarity in trans effects of CO and $SiCl_3$ ligands. The reason for boating is probably a result of steric interaction between hydrogens ortho to the *t*-Bu groups and hydrogens of the *t*-Bu groups, which push the para carbon atoms up out of the ring plane. These H···H distances are typically ca. 2.3 Å. This explanation rather than one involving interaction between the ring and the $Ru(CO)(SiCl_3)_2$ moiety seems more reasonable especially when one considers the marked "boating" observed in bis(2,4,6-tri-*tert*-butylphenyl)phosphinic chloride[22] where no $M(L)_3$ group is present (Table IVa).

The ring and substituent parameters are all normal (Table III) for this type of compound. The average Ru–C(ring) and Ru–C(carbonyl distances of 2.36 (4) and 1.843 (5) Å, respectively, are reasonable [cf. Ru–C(ring) = 2.20 (1) and Ru–C(carbonyl = 1.87 (2) Å in $(C_6H_6)Ru(CO)(GeCl_3)_2$[15]. The average Ru–Si distance of 2.339 (1) Å is close to the value 2.414 Å found in $Ru(SiMe_3)(CO)_2(C_8H_8(SiMe_3))$.[23] The Ru–C–O angle of 177.1 (5)° is normal. The $SiCl_3$ dimensions are similar to those observed in $(\pi\text{-}C_5H_5)FeH(SiCl_3)_2(CO)$.[24]

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Registry No. $(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2\cdot{}^1/_2C_6H_5CH_3$, 79991-87-0.

Supplementary Material Available: Listings of structure factors and final thermal parameters and a table of nonbonded distances (27 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Gorlaeus Laboratories, State University of Leiden, 2300 RA Leiden, The Netherlands

Synthesis and X-ray Structure of the Tetranuclear Heterometallic Anion Bis[μ-[*cis*-bis(D-penicillaminato(2−)-*N*,*S*)nickel(II)]-*S*,*S*′]diaurate(I)(2−) in $Na_2[Au^I_2Ni^{II}_2(SC(CH_3)_2CH(NH_2)COO)_4]\cdot x$ (solvent)

PAUL J. M. W. L. BIRKER* and GERRIT C. VERSCHOOR

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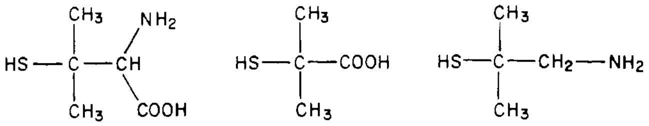
The synthesis and structural characterization of a new type of polynuclear metal thiolate compound of composition $[Au^I_2M^{II}_2L_4]^{2-}$ is described, where M is Ni or Pd and L is the deprotonated penicillamine ligand $^-SC(CH_3)_2CH(NH_2)COO^-$. The compound $Na_2[Au^I_2Ni^{II}_2L_4]\cdot x$(solvent) crystallizes in the rhombohedral space group *R*3. Described in a hexagonal lattice the unit-cell dimensions are $a = 28.27$ (7) Å and $c = 33.27$ (8) Å. Intensity data were collected on an automatic four-circle diffractometer (Mo Kα radiation; ω–θ scans). The structure was solved by direct methods and full-matrix least squares refined to a final *R* value of 0.079 for 2425 reflections with $I > 2\sigma(I)$. The structure contains two independent complex ions ($Z = 18$). The Au^I atoms are linearly coordinated by two penicillamine S atoms. The Ni^{II} atoms are cis-bidentate coordinated by two chelating penicillamine ligands. Each S atom forms a bridge between an Au^I and a Ni^{II} atom. The Au–Au distances in the two independent complex ions are 2.94 (1), and 2.99 (1) Å, which is only slightly longer than the Au–Au distance in metallic gold (2.884 Å). The formation reaction of this novel compound and the differences with the Cu^I and Ag^I containing penicillamine clusters are discussed.

Introduction

The formation of polynuclear transition-metal compounds is becoming a well-established feature of the coordination chemistry of potentially chelating thiolate ligands such as



H_2Pen H_2MIBA HDMC

D-penicillamine (H_2Pen),[1,2] α-mercaptoisobutyric acid (H_2MIBA),[3] and dimethylcysteamine (HDMC).[4] The common feature of these ligands is their capability of forming five-membered chelate rings and the presence of two alkyl substituents on the carbon atom adjacent to the sulfur atom. Their polynuclear compounds so far characterized have the composition $[M^I_8M^{II}_6L_{12}Cl]^z$, where $M^I = Cu^I$ or Ag^I and $M^{II} = Cu^{II}$, Ni^{II}, or Pd^{II} and L = Pen ($z = -5$), MIBA ($z = -5$), or DMC ($z = +7$).[1-4] In these cluster compounds the M^{II} atoms are cis-bidentate square-planar S_2N_2 or S_2O_2 coordinated by the ligands (see Figure 1). Six of these $M^{II}L_2$ units are located above the six faces of a chloride-centered M^I_8 cube so that the sulfur atoms form bridges between two M^I and one M^{II} atoms. The result is that each M^I atom is planar coordinated by a triangle of S atoms (Figure 1).

In an attempt to obtain analogues of these clusters with Au^I instead of Cu^I and Ag^I, we found much simpler complex ions of composition $[Au^I_2M^{II}_2Pen_4]^{2-}$. The X-ray crystal structure of this novel cluster compound is reported, and the different behavior of Au^I is discussed.

Experimental Section

Materials. D-penicillamine was commercially available (Aldrich, "Gold label"). Bis(thiourea)gold(I) chloride, $Au(tu)_2Cl$ was prepared according to a published method.[5] All other reagents and solvents

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* To whom correspondence should be addressed at the Unilever Research Laboratorium, P.O. Box 114, 3130 AC Vlaardingen, The Netherlands.

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(2) The abbreviations used in this article are as follows: H_2Pen = D-penicillamine, $HSC(CH_3)_2CH(NH_2)COOH$; H_2MIBA = α-mercaptoisobutyric acid, $HSC(CH_3)_2COOH$; HDMC = dimethylcysteamine, $HSC(CH_3)_2CH_2NH_2$. The deprotonated ligands are abbreviated as Pen, MIBA, and DMC, respectively. M = metal, L = ligand, and tu = thiourea.

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