Inorganica Chimica Acta, 145 (1988) 171–173

Crystal and Molecular Structure of $Rh_2(O_2CCH_3)_2(OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3)_2{\cdot}2C_5H_5N$

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(Received December 14, 1987)

Introduction

Some twenty years ago the reaction of $Rh_2(O_2CCH_3)_4$ with β-diketones was reported to give complexes with the stoichiometry $[Rh(O_2CCH_3)(\beta\text{-diketonato})L]_2$, where L is the neutral donor ligand, H_2O or pyridine [1]. Several structures were proposed for these molecules. However, the most likely one contained a $[Rh_2]^{4+}$ core, two cisoid bridging acetato ligands, one chelating β-diketonato ligand on each metal ion, and one donor ligand L on each metal ion *trans* to the metal–metal bond. We have a substantial interest in the redox chemistry of the $[Rh_2]^{4+}$ unit [2–4] and decided to prepare further examples of these molecules and explore their electrochemical properties. Before embarking on such a programme we believed it was important to determine unequivocally the structure of at least one representative compound. The compound which we chose to study crystallographically was $Rh_2(O_2CCH_3)_2(OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3)_2{\cdot}2C_5H_5N$. The results of that structure determination are now reported here.

Experimental

The compound $Rh_2(O_2CCH_3)_2(OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3)_2{\cdot}2C_5H_5N$ was prepared as reported previously [1]. Single crystals suitable for X-ray crystallographic measurement were grown by slow evaporation from a 1:1 mixture of dichloromethane and hexane.

A suitable crystal of $C_{24}H_{18}N_2O_8F_{12}Rh_2$ (M = 896, triclinic, a = 10.397(5), b = 12.620(7), c = 12.764(8) Å, α = 88.63(5), β = 70.61(4), γ = 74.20(4)°, U = 1515(1) Å, space group $P\bar{1}$, Z = 2, D_c = 1.96 g cm^{-3}, μ(Mo Kα) = 11.5 cm^{-1}, λ = 0.71073 Å, $F(000)$ = 876) was examined using a Nicolet R3m/V diffractometer. Of the 5690 independent reflections measured 3447 were observed ($|F_o^2| > 3\sigma|F_o|)^2$. The position of the two rhodium atoms in the asymmetric unit were derived from a three-dimensional Patterson map and the remainder of the structure obtained using least-squares refinement and difference electron density maps. No attempt was made to locate the hydrogen atoms in the structure. All other atoms were refined anisotropically. We note that the $-CF_3$ groups on the β-diketonato ligands are undergoing rapid rotation and that consequently the isotropic equivalent temperature factors associated with the twelve fluorine atoms are high. Refinement was by full-matrix least-squares methods to give R = 0.081, R_w = 0.071 ($w^{-1} = \sigma^2(F) + 0.00015\ F^2$). The maximum residual electron density was 1.1 e Å^{-3} which was close to $F(4)$. The maximum shift/error in the final refinement was 0.012. Computations were carried out on a Microvax II computer using the SHELXTL Plus program system [5] and published scattering factors [6]. Table I lists the fractional atomic coordinates, while Table II contains important bond distances and angles.

TABLE I. Fractional Atomic Coordinates ($\times10^4$) for $Rh_2(O_2CCH_3)_2(OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3)_2{\cdot}2C_5H_5N$

	x	*y*	*z*
Rh(1)	293(1)	2098(1)	3329(1)
Rh(2)	2956(1)	1653(1)	2441(1)
N(1)	−2012(11)	2287(9)	4372(9)
N(2)	5302(11)	1043(9)	1851(9)
O(1)	669(10)	1870(7)	4785(7)
O(2)	2989(10)	1176(7)	3950(8)
O(3)	582(10)	452(7)	3092(8)
O(4)	2843(10)	164(7)	2001(8)
O(5)	−26(9)	3719(7)	3597(8)
O(6)	−155(9)	2244(7)	1893(7)
O(7)	3032(10)	2095(8)	903(8)
O(8)	3149(10)	3080(8)	2933(8)
F(1)	−870(13)	3961(9)	−77(8)
F(2)	−2354(11)	3163(10)	853(9)
F(3)	−283(12)	2216(8)	−96(8)
F(4)	−72(24)	6118(11)	2594(12)
F(5)	−249(26)	5728(10)	4101(15)
F(6)	−1893(16)	6080(12)	3712(27)
F(7)	4988(12)	4530(9)	2666(11)
F(8)	2931(15)	5023(10)	3783(13)
F(9)	3406(16)	5674(9)	2210(13)
F(10)	4440(18)	2365(15)	−1275(10)
F(11)	3516(23)	4011(14)	−1007(12)
F(12)	2315(18)	3006(18)	−850(11)
C(1)	1889(15)	1430(10)	4792(11)
C(2)	2069(17)	1139(13)	5922(12)
C(3)	1727(14)	−145(10)	2439(12)
C(4)	1785(16)	−1317(11)	2134(13)
C(5)	−395(14)	4405(10)	2944(11)
C(6)	−641(15)	4198(11)	1965(12)
C(7)	−519(14)	3156(11)	1532(10)
C(8)	−998(18)	3108(13)	526(12)
C(9)	−619(20)	5570(13)	3324(17)
C(10)	3283(15)	2991(13)	560(13)

(continued)

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TABLE I. *(continued)*

	x	y	z
C(11)	3443(17)	3847(14)	1123(15)
C(12)	3363(15)	3822(12)	2243(16)
C(13)	3649(23)	4757(15)	2776(22)
C(14)	3422(21)	3075(21)	−635(16)
C(15)	−2301(15)	1546(11)	5135(12)
C(16)	−3654(16)	1615(14)	5840(13)
C(17)	−4729(16)	2479(13)	5802(13)
C(18)	−4504(18)	3262(15)	5049(17)
C(19)	−3119(17)	3137(12)	4358(14)
C(20)	6073(16)	363(14)	914(12)
C(21)	7520(17)	−76(15)	592(14)
C(22)	8211(17)	167(13)	1266(14)
C(23)	7474(15)	860(12)	2203(11)
C(24)	6018(14)	1276(12)	2487(11)

TABLE II. Selected Bond Lengths and Angles for $Rh_2(O_2CCH_3)_2(OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3)_2{\cdot}2C_5H_5N$

Bond lengths (Å)			
Rh(1)–Rh(2)	2.523(2)	Rh(2)–O(2)	2.013(8)
Rh(1)–O(1)	2.022(8)	Rh(2)–O(4)	2.019(9)
Rh(1)–O(3)	2.032(8)	Rh(2)–O(7)	2.009(9)
Rh(1)–O(5)	1.999(8)	Rh(2)–O(8)	2.003(9)
Rh(1)–O(6)	2.028(8)	Rh(2)–N(2)	2.212(10)
Rh(1)–N(1)	2.271(11)		

Bond angles (°)	
N(1)–Rh(1)–Rh(2)	169.3(3)
O(1)–Rh(1)–N(1)	85.3(4)
O(3)–Rh(1)–N(1)	89.2(4)
O(5)–Rh(1)–Rh(2)	95.5(3)
O(5)–Rh(1)–O(1)	88.7(4)
O(6)–Rh(1)–Rh(2)	96.7(3)
O(6)–Rh(1)–O(1)	176.0(4)
O(6)–Rh(1)–O(5)	94.4(3)
O(2)–Rh(2)–Rh(1)	84.8(3)
O(4)–Rh(2)–Rh(1)	85.0(3)
O(4)–Rh(2)–O(2)	91.6(4)
O(7)–Rh(2)–N(2)	89.8(4)
O(7)–Rh(2)–O(4)	88.2(4)
O(8)–Rh(2)–N(2)	87.4(4)
O(8)–Rh(2)–O(4)	176.3(4)
O(1)–Rh(1)–Rh(2)	85.4(3)
O(3)–Rh(1)–Rh(2)	85.5(3)
O(3)–Rh(1)–O(1)	90.5(4)
O(5)–Rh(1)–N(1)	89.6(4)
O(5)–Rh(1)–O(3)	178.6(4)
O(6)–Rh(1)–N(1)	92.3(4)
O(6)–Rh(1)–O(3)	86.3(4)
N(2)–Rh(2)–Rh(1)	170.6(3)
O(2)–Rh(2)–N(2)	87.2(4)
O(4)–Rh(2)–N(2)	90.3(4)
O(7)–Rh(2)–Rh(1)	98.1(3)
O(7)–Rh(2)–O(2)	177.1(4)
O(8)–Rh(2)–Rh(1)	96.9(3)
O(8)–Rh(2)–O(2)	85.4(4)
O(8)–Rh(2)–O(7)	94.7(4)

Results and Discussion

The molecular structure of $Rh_2(O_2CCH_3)_2(OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3)_2{\cdot}2C_5H_5N$ is depicted in Fig. 1. The molecule contains structural features in common with those described for $Rh_2(O_2CCH_3)_2(dmg)_2{\cdot}2PPh_3$ [7]. The two rhodium atoms are bridged by two acetate ligands and each rhodium is also coordinated by a chelating $[OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3]^-$ ligand. The coordination sites *trans* to the Rh–Rh bond are occupied by pyridine molecules. The Rh–Rh bond length, 2.523(2) Å, is much greater than that observed in the tetracarboxylate complex $Rh_2(O_2CCH_3)_4{\cdot}2C_5H_5N$, 2.396(1) Å [8], as would have been expected. The Rh–Rh bond distance is very similar to that found in $[Rh_2(O_2CCH_3)_2(phen)_2]$ complexes (mean: 2.558(3) Å) [9], but is significantly less than that found for $Rh_2(O_2CCH_3)_2(dmg)_2{\cdot}2PPh_3$, 2.618(5) Å, [7]. The mean Rh–N distance 2.242(11) Å is comparable with that found in $Rh_2(O_2CCH_3)_4{\cdot}2C_5H_5N$, 2.227(3) Å [8]. The geometry at the rhodium atoms is distorted octahedral with the internal angles involving the chelating ligands being significantly greater than 90° (∠O(5)–Rh(1)–O(6), 94.4(3)°;∠O(7)–Rh(2)–O(8), 94.7(4)°). The Rh–Rh and Rh–N bonds are not colinear (∠Rh(2)–Rh(1)–N(1) = 169.3(3)°; ∠Rh(1)–Rh(2)–N(2) = 170.6(3)°). The latter observation can almost certainly be attributed to unfavourable steric interactions between the $-CF_3$ groups on the chelating β-diketonates and the axial ligands. Unfavourable steric interactions also occur between the substituent groups on the different chelating ligands, with the dihedral angle between the least-squares planes defined by the atoms Rh(1)–O(5)–C(5)–C(6)–C(7)–O(6) and Rh(2)–O(7)–C(10)–C(11)–C(12)–O(8) being 23.9°. In addition the β-diketonate ligands are rotated about the Rh–Rh axis by *ca.* 14° from the eclipsed configuration (torsion angles O(5)–Rh(1)–

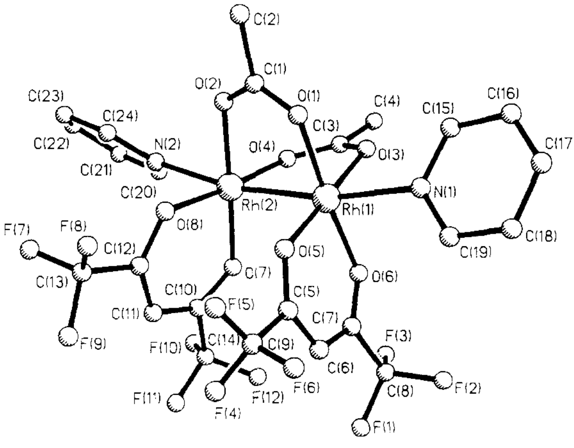

Fig. 1. Molecular structure of $Rh_2(O_2CCH_3)_2(OC{\cdot}CF_3{\cdot}CH{\cdot}CO{\cdot}CF_3)_2{\cdot}2C_5H_5N$, showing the atom labelling scheme.

Rh(2)–O(8) 14.9°; O(6)–Rh(1)–Rh(2)–O(7) 14.2°). The two bridging acetate ligands are also distorted with torsion angles about the Rh–Rh bond of 11.3° and 12.5°.

Supplementary Material

Tables of thermal parameters and observed and calculated structure factors are available from the authors on request.

Acknowledgements

We wish to thank Johnson Matthey plc for generous loans of rhodium trichloride and the S.E.R.C. for the provision of the X-ray equipment.

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