Inorganica Chimica Acta, 115 (1986) 135–139

The Crystal and Molecular Structure of $[Rh_2(OOCCH_3)(HNOCCH_3)_3(Me_2SO)_2]\cdot 2H_2O$

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Received August 13, 1985

Abstract

One of the compounds isolated from the stepwise substitution of acetate in $[Rh_2(O_2C-CH_3)_4]$ by acetamide had composition $[Rh_2(O_2C-CH_3)(HNC(O)-CH_3)_3]$. Repeated liquid chromatography of the product of this composition shows a single band whose ^1H NMR gives four methyl proton resonances at 1.76, 1.78, 1.88 and 1.90 ppm having integrated areas in the ratio 1:1:1:1. Recrystallization from methanol containing a few drops of DMSO produced reddish, prismatic crystals of composition $[Rh_2(O_2C-CH_3)-(HNC(O)-CH_3)_3(2DMSO)]\cdot 2H_2O$ which crystallize in space group $P\bar{1}$ (No. 2). The cell constants are $a = 8.684(2)$, $b = 8.980(1)$, $c = 8.288(1)$ Å, $\alpha = 101.13(1)$, $\beta = 93.14(1)$, $\gamma = 115.92(1)^\circ$; $V = 553.9$ Å^3 and D(calc; $Z = 1$) = 1.892 g cm^{-3}. The molecule consists of a pair of metal–metal bonded Rh(II) cations bridged by three acetamides and one acetate ligands such that one Rh has a *cis* pair of amide nitrogens. The solution NMR spectrum, indicative of a single geometrical isomer (three are possible), is consistent with the molecular geometry of the isomer studied in the solid state.

Comparison of the Rh–S distances in $Rh_2(O_2C-CH_3)_4(2DMSO)$ and in $[Rh_2(O_2C-CH_3)(HNC(O)-CH_3)_3(2DMSO)]$ show the latter to be shorter by 0.038 Å. This result, coupled with similar data for the diaquo and the bis(DMSO) derivatives of the tetraacetate, tetraamide and the triamide-acetates of dirhodium complexes are shown to be consistent with an increased π interaction between the S d-orbitals and the filled Rh–Rh π^* orbitals. These conclusions, in turn, are shown to be consistent with previously reported electrochemical data comparing the solvent donor number (DN) behaviour of all six compounds.

Introduction

In recent papers we reported [1–3] detailed electrochemical and spectroscopic properties of a series of dirhodium(II) complexes with acetate and acetamidate bridging ligands, $Rh_2(ac)_n(acam)_{4-n}$ where ac = $CH_3CO_2^-$, acam = CH_3CONH^-, and n varies between 0 and 4. With each acetamidate-for-acetate substitution, the oxidation potential of the complex (in CH_3CN solution) decreased by 250 mV. As reported previously [2], the half-wave potential for $Rh_2(ac)_4$ showed an almost linear, negative shift as the donor number [4] (DN) of the solvent increased. However, a different result was observed for the acetamidate complexes when $n = 0$ or 1. The utilized solvents increased in donor number as follows: CH_3CN (14.1) < Me_2SO (29.8) < py (33.1) [4]. Thus, on the basis of an oxidation potential of $E_{1/2} = -0.27$ V *versus* Fc^+/Fc for $Rh_2(acam)_4$ in CH_3CN and -0.44 V *versus* Fc^+/Fc in py, the predicted $E_{1/2}$ for oxidation of $Rh_2(acam)_4$ in Me_2SO should be about -0.40 V *versus* Fc^+/Fc. The value observed was -0.17 V. This $E_{1/2}$ value is 230 mV more positive than expected and reflects a relative lowering of the HOMO from which the electron is abstracted which suggest that the nature of the axial interaction of Me_2SO is different in the $[Rh_2(ac)_4]^{0/+}$ and $[Rh_2(acam)_4]^{0/+}$ species. Similar results were observed for the triacetamidate complex, $Rh_2(ac)(acam)_3$ which is the compound of interest currently. The electron rich tri- and tetra-acetamidate complexes should be better π-donors and weaker σ-acceptors than the tetracarboxylate bridged complex. Rhodium → S back donation of electron density could explain the lower energy HOMO observed in Me_2SO. If such is the case, the Rh–S bond should be shorter for the Me_2SO adducts of dirhodium(II) acetamidate complexes than that found for the tetracetate complex. In order to test this theory and determine which of the three possible geometric isomers is produced in the acetamidate for acetate exchange reaction, the molecular structure of $[Rh_2(ac)(acam)_3(Me_2SO)_2]\cdot 2H_2O$ was determined. The results are reported in this paper.

Experimental

Chemical

All solvents and organic chemicals were of the highest purity available from Aldrich Chemical Company, Milwaukee, Wis., and were used without further purification. The complex $Rh_2(ac)(acam)_3$ was synthesized by the stepwise exchange reaction

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0020-1693/86/$3.50

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of $Rh_2(ac)_4$ with acetamide, as previously reported [3]. The complex is one of the four substitution products formed in this reaction. There are three possible geometric isomers of the triacetamidate complex. Only one band is observed in the liquid chromatographic separation indicating only one of these isomers is formed. Crystals for X-ray analysis were obtained from a methanol solution containing a few drops of Me_2SO.

Crystal Data Collection, Structural Solution and Refinement

The reddish, prismatic crystals of this substance were found to rapidly lose their water of crystallization at room temperature in or out of the X-ray beam. Consequently, data were collected at *ca.* −100 °C at which temperature the crystals are indefinitely stable. A crystal of approximate dimensions 0.45 × 0.30 × 0.25 mm was mounted in a random orientation on a CAD-4 Diffractometer equipped with a Mo target tube monochromatized by a dense graphite crystal [λ = 0.71073 Å].

Cell constants were obtained from least-squares fitting of the orientation angles of 25 reflections. The cell obtained was triclinic and a check on the Niggli matrix indicated no higher symmetry cell associated with this crystal. The space group, therefore, had to be either $P1$ or $P\bar{1}$ [Nos. 1 or 2]. Given the density of this substance, there is only one molecule in the unit cell.

TABLE I. Summary of X-ray Data Collection and Processing Parameters

Space group	$P1$
Cell constants	
a	8.684(2) Å
b	8.980(1) Å
c	8.288(1) Å
α	101.13(1)°
β	93.14(1)°
γ	115.92(1)°
Cell volume	V = 553.9 Å^3
Molecular formula	$C_{12}H_{31}N_3O_9S_2Rh_2$
Molecular weight	631.323 g mol^{-1}
Density (calc; Z = 1 mol/cell)	1.892 cm^{-3}
Radiation employed	Mo Kα (λ = 0.71073 Å)
Transmission coefficients	1.00 to 0.762
Data collection range	$4° \leq 2\theta \leq 64°$
Scan width	$\Delta\theta = 1.20 + 0.35 \tan\theta$
Total data collected	3964
Data used in refinement[a]	3277
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.057
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.068
Weights used	$w = [\sigma(F_o)]^{-2}$

[a]The difference between this number and the total is due to subtraction of 687 data which either were standards or did not meet the criterion that $I \geq 3\sigma(I)$.

TABLE II. Positional Parameters and their Standard Deviations for $Rh_2(ac)(acam)_3 \cdot 2Me_2SO$[a]

Atom	x	y	z	B_{A2}
Rh	0.44008(4)	0.34325(3)	0.43717(3)	1.282(5)
S1	0.3300(1)	0.0376(1)	0.2973(1)	1.74(2)
OW1	0.0966(5)	−0.0442(5)	0.6788(6)	4.3(1)
O1	0.2176(4)	0.3368(4)	0.3252(4)	1.78(6)
O2	0.5525(4)	0.3883(4)	0.2286(4)	1.86(6)
O3	0.2356(5)	−0.0983(4)	0.3799(5)	3.45(9)
N1	0.3337(4)	0.6275(4)	0.4451(4)	1.57(7)
N2	0.6652(5)	0.6781(4)	0.3533(4)	1.71(7)
C1	0.2086(5)	0.4805(5)	0.3549(5)	1.59(8)
C2	0.0431(6)	0.4697(6)	0.2784(6)	2.12(9)
C3	0.3557(5)	0.4550(5)	0.7682(5)	1.69(8)
C4	0.7320(6)	0.5744(6)	0.0825(5)	2.4(1)
C5	0.5052(7)	0.0012(7)	0.2312(7)	3.3(1)
C6	0.2034(6)	−0.0174(7)	0.0959(7)	3.0(1)
HN1	0.303(7)	0.687(8)	0.428(7)	4(2)*
HN2	0.743(6)	0.759(6)	0.362(6)	2(1)*
H2A	0.04(1)	0.58(1)	0.31(1)	9(3)*
H2B	0.022(7)	0.412(8)	0.160(7)	4*
H2C	−0.059(8)	0.383(8)	0.294(8)	5(2)*
H4A	0.858(7)	0.682(7)	0.122(7)	4*
H4B	0.753(7)	0.491(8)	0.043(7)	4*
H4C	0.676(8)	0.596(8)	0.008(8)	5(2)*
H5A	0.46(1)	−0.13(1)	0.14(1)	8(2)*
H5B	0.552(9)	0.072(9)	0.161(9)	6(2)*
H5C	0.574(8)	0.014(9)	0.320(9)	6(2)*
H6A	0.244(6)	0.044(6)	0.032(6)	2(1)*
H6B	0.170(7)	−0.136(7)	0.029(7)	3(1)*
H6C	0.103(8)	−0.025(9)	0.123(9)	6(2)*
HW1	0.109	−0.084	0.541	4*
HW2	0.000	−0.139	0.668	4*

[a]Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

A total of 3964 reflections were collected of which 3834 were unique. Three reflections were used as intensity standards and no change was detected throughout the period of data collection. Data were corrected for Lorentz-polarization and absorption. The latter correction was based on a series of psi-scans and the relative transmission coefficients ranged from 1.00 to 0.762. All other details of data collection and processing are given in Table I. The final values of atomic parameters are given in Table II.

The distribution of intensities shows the lattice to be centrosymmetric, which means that the molecule lies at an inversion center. The Rh atom was located from the Patterson function and all remaining atoms found in difference maps. Two of the acetamide ligands are ordered and related by the inversion center. The second, independent, acetamide and the acetate are disordered. Subsequent examination of the structure of $[Rh_2(acetamide)_4 \cdot 2DMSO] \cdot 2H_2O$ reveals that the two are isomorphous and isostruc-

TABLE III. Bond Distance (Å) of $Rh_2(ac)(acam)_3\cdot 2Me_2SO$[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Rh	Rh	2.446(0)	OW1	HW2	0.874(2)	C4	H4C	0.88(3)
Rh	S1	2.413(0)	O1	C1	1.291(2)	C5	H5A	1.12(4)
Rh	O1	2.068(1)	N1	C1	1.287(2)	C5	H5B	0.94(4)
Rh	O2	2.070(1)	N1	HN1	0.73(3)	C5	H5C	0.87(3)
Rh	N1	2.024(2)	N2	HN2	0.73(2)	C6	H6A	0.84(2)
Rh	N2	2.018(1)	C1	C2	1.492(3)	C6	H6B	0.97(3)
S1	O3	1.492(1)	C2	H2A	1.00(4)	C6	H6C	0.89(3)
S1	C5	1.777(2)	C2	H2B	0.95(3)	O1	HW2	1.965(1)
S1	C6	1.778(2)	C2	H2C	0.93(3)	O3	HW1	1.789(2)
S1	O3	1.492(1)	C4	H4A	1.06(3)			
OW1	HW1	1.137(2)	C4	H4B	0.84(3)			

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

tural and that the entire ordered part of the current molecule is identical with that of the fully ordered tetraamide [5].

Concerning the selection of the proper geometrical isomer: One pair of acetamide ligands is ordered and related by the inversion center passing through the midpoint between the two Rh atoms, exactly as in the tetraamide case [5]. Consequently, as far as basal plane of each Rh atom is concerned, these two ligands provide a N and an O (*trans* to N) which are fully ordered. Therefore, no matter which of the other two basal positions is/are occupied by an amide nitrogen, the resulting geometrical isomer must have two nitrogens in *cis* configuration to each other as shown in complex **A** of Fig. 1, which means that the disorder is crystallographic (a solid state packing problem) and not molecular in nature. In what follows, we shall demonstrate that this description is consistent with the ^1H NMR of the complex.

Insofar as the present study is concerned, the most important portion of the molecule is the $(CH_3)_2$-SO–Rh1–Rh2–$SO(CH_3)_2$ and that fragment is not disordered. Thus, while we can say little about the geometrical details of the disordered pair of bridging ligands, we can give a fairly accurate description of the rest of the molecule. The bond distances and angles are presented in Tables III and IV. These

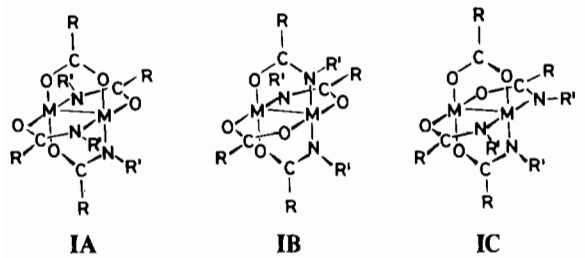

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Fig. 1. Structures for the three possible geometric isomers of $[Rh_2(O_2C-CH_3)(HNC(O)-CH_3)_3]$.

TABLE IV. Bond Angles (°) of $Rh_2(ac)(acam)_3\cdot 2Me_2SO$

Atom 1	Atom 2	Atom 3	Angle
Rh	Rh	S1	176.28(1)
Rh	Rh	O1	89.11(4)
Rh	Rh	O2	88.91(4)
Rh	Rh	N1	85.84(4)
Rh	Rh	N2	86.07(5)
S1	Rh	O1	90.81(4)
S1	Rh	O2	87.37(4)
S1	Rh	N1	94.22(4)
S1	Rh	N2	97.65(5)
O1	Rh	O2	90.09(5)
O1	Rh	N1	174.95(5)
O1	Rh	N2	88.62(6)
O2	Rh	N1	89.63(6)
O2	Rh	N2	174.83(5)
N1	Rh	N2	91.22(6)
O3	S1	C5	105.8(1)
O3	S1	C6	108.7(1)
C5	S1	C6	99.4(1)
HW1	OW1	HW2	94.2(2)
C1	N1	HN1	101.0(2)
O1	C1	N1	123.1(2)
O1	C1	C2	116.6(2)
N1	C1	C2	120.3(2)
C1	C2	H2A	114.0(2)
C1	C2	H2B	107.0(2)
C1	C2	H2C	116.0(2)
H2A	C2	H2B	118.0(3)
H2A	C2	H2C	108.0(3)
H2B	C2	H2C	92.0(2)
H4A	C4	H4B	103.0(2)
H4A	C4	H4C	106.0(2)
H4B	C4	H4C	114.0(3)
H5A	C5	H5B	101.0(3)
H5A	C5	H5C	109.0(3)
H5B	C5	H5C	118.0(3)
H6A	C6	H6B	106.0(2)
H6A	C6	H6C	114.0(3)
H6B	C6	H6C	103.0(2)

TABLE V. A. Comparison of Bond Distances for Selected Dirhodium Compounds Axially bound by Water and DMSO

Complex	Bond distances (Å)			Reference
	Rh–Rh	$Rh–OH_2$	Rh–S	
$Rh_2(ac)_4 \cdot 2H_2O$	2.385(5)	2.310(3)		6
$Rh_2(acam)_4 \cdot 2H_2O$	2.415(1)	2.352(2)		5
$Rh_2(ac)_4 \cdot 2Me_2SO$	2.406(1)		2.451(2)	8
$Rh_2(ac)(acam)_3 \cdot 2Me_2SO$	2.446(0)		2.413(0)	
$Rh_2(acam)_4 \cdot 2Me_2SO$	2.452(0)		2.414(0)	

values are certaintly comparable with the results of independent determinations of related systems (see Table V).

Results and Discussion

It appears that only one of the three possible geometric isomers of $Rh_2(ac)(acam)_3$, shown in Fig. 1, is produced in the reaction of $Rh_2(ac)_4$ with acetamide. Liquid chromatography/mass spectrometry studies [3] of the product mixture showed that only one LC band corresponded to the molecular weight of the triacetamidate complex. The ^1H NMR of the complex in the LC band gave four methyl proton resonances at 1.76 ppm, 1.78 ppm, 1.88 ppm and 1.90 ppm with area ratios of 1:1:1:1. Since no other proton resonances were observed, and the NMR results are consistent with the molecular structure determined for $Rh_2(ac)(acam)_3$, complex **A** of Fig. 1 must be the only isomer produced in a significant amount.

The results of X-ray analysis (Fig. 2) show that the molecule contains a tetravalent cation consisting of a pair of Rh(II) axially bound to the sulfur atoms of a pair of Me_2SO molecules and bridged by three acetamidate and one acetate ions. The bonding geometry of the nitrogen and oxygen donors is that of complex **A** in Fig. 1.

Table III lists bond distances found in this study and compares them to other relevant dirhodium(II) complexes. By comparing the Rh–Rh and $Rh–OH_2$ bond distances for $Rh_2(ac)_4(H_2O)_2$ [6] and $Rh_2(acam)_4(H_2O)_2$ [7] we see the effect of the acetamidate bridge on the axial bond when the axial ligand is a pure σ-donor. As expected, the better electron-donating acetamidate bridges produce an increase in both the Rh–Rh and $Rh–OH_2$ bond distances. It should be pointed out that strong electron withdrawing equatorial ligands such as trifluoroacetate [7] cause a decrease in the $Rh–OH_2$ bond distance relative to $Rh_2(ac)_4(H_2O)_2$.

Different results are observed if we compare the Rh–S distance for $Rh_2(ac)_4(Me_2SO)_2$ [8] and $Rh_2(ac)(acam)_3(Me_2SO)_2$. The Rh–S bond distance is shorter for the latter complex by 0.038 Å. The shorter Rh–S bond for the triacetamidate complex probably results from a significant π component in

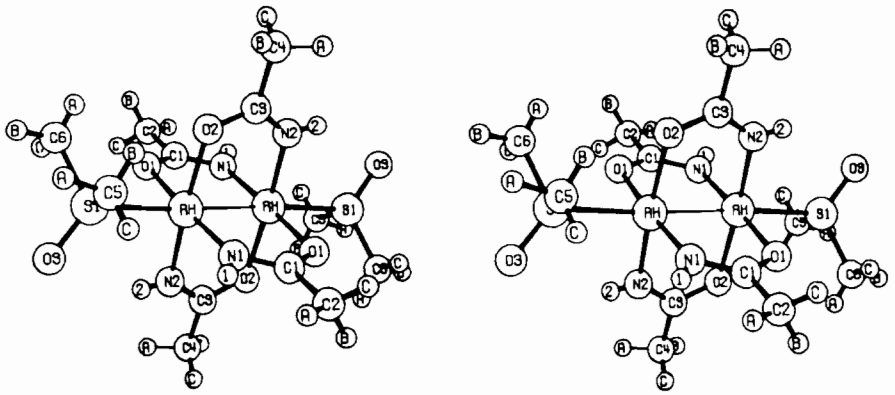

Fig. 2. Stereoview of the X-ray diffraction determined molecular structure of $[Rh_2(O_2C–CH_3)(HNC(O)–CH_3)_3(2DMSO)]$ showing the numbering system employed in labelling the atoms.

the axial interaction involving the filled Rh–Rh π^* orbitals and empty d orbitals on the sulfur atom. A significant Rh → S π donation would also explain why the oxidation potential of the acetamidate bridged complexes are more positive than expected in Me_2-SO solvent.

Acknowledgements

This research was supported by the Robert A. Welch Foundation through grants E-918 (J.L.B.) and E-594 (I.B.). Also, we thank the staff of Molecular Structure Corporation (College Station, Tex.) for collecting this low temperature data set for us.

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