Journal of Organometallic Chemistry, 192 (1980) 235—251

THE CRYSTAL AND MOLECULAR STRUCTURES OF DI(NITRATO-*O*)(η-PENTAMETHYLCYCLOPENTADIENYL)-TRIPHENYLPHOSPHINERHODIUM(III) (A) AND (NITRATO-*O*)(NITRATO-*O,O'*)(η-PENTAMETHYLCYCLOPENTADIENYL)-RHODIUM(III) (B); A STRUCTURAL COMPARISON OF MONO- AND BI-DENTATE NITRATO-LIGANDS

MICHAEL B. HURSTHOUSE, K.M. ABDUL MALIK, D. MICHAEL P. MINGOS * and STEPHEN D. WILLOUGHBY

Department of Chemistry, Queen Mary College, University of London, Mile End Road, London E1 4NS (U.K.)

(Received December 14th, 1979)

Summary

The crystal and molecular structures of the title compounds have been determined by single crystal X-ray analyses. Compound A crystallizes in the monoclinic system with a 11.925(2), b 14.616(2), c 15.709(3) Å, β 92.45(2)°, space group $P2_1/n$ and $Z = 4$, and B in the orthorhombic system with a 13.012(2), b 14.866(2), c 14.274(2) Å, space group $Pbca$ and $Z = 8$. The structure of A was refined to an R value of 0.032 using 5143 observed ($F_0 \geqslant 3\sigma(F_0)$) intensities, and B to an R value of 0.043 using 2711 observed intensities measured on an automatic diffractometer.

Both A and B have a "piano stool" arrangement of ligands and provide a unique opportunity for comparing the structural parameters of the mono- and bi-dentate nitrato-ligand. In addition the infrared criteria for distinguishing these alternative coordination modes in this type of organometallic complex are discussed.

Considerable interest has been shown in the electronic structures of nitrato-complexes [1], and in the catalytic chemistries of platinum metal nitrato-complexes [2]; however, the structural characterisation of nitrato-complexes has received less attention [3]. The recent synthesis and spectroscopic characterisation of $Rh(\eta\text{-}C_5Me_5)(NO_3)_2$ [4] suggested that this complex might have

---

* Present address: Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR.

within one coordination sphere both a mono- and bidentate nitrato-ligand, and therefore provided an excellent opportunity for making a detailed and self consistent comparison of the structural parameters for these alternative coordination modes. This paper describes the results of this structural determination, together with those for the related complex $Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)$.

Experimental

Suitable single crystals of $Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)$, (A) were grown from methanol/ether and those of $Rh(\eta\text{-}C_5Me_5)(NO_3)_2$, (B) from acetone, and mounted in Lindemann capillaries. Unit-cell parameters were initially determined from oscillation and Weissenberg photographs and later refined using setting angles for 15 high angle reflections ($16 < \theta(\text{Mo-}K_\alpha) < 17°$) automatically centered on a Nonius CAD4 diffractometer. The space groups, $P2_1/n$ (No. 14) for (A) and *Pbca* (No. 61) for (B), were uniquely determined by the systematic absences, $0k0$ for k odd and $h0l$ for $h + l$ odd, and $0kl$ for k odd, $h0l$

TABLE 1

CRYSTAL DATA AND DETAILS OF STRUCTURAL ANALYSES

Crystal data	A	B
Formula	$Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)$	$Rh(\eta\text{-}C_5Me_5)(NO_3)_2$
MW	624.4	362.2
Crystal System	monoclinic	orthorhombic
a (Å)	11.925(2) [a]	13.012(2)
b (Å)	14.616(2)	14.866(2)
c (Å)	15.709(3)	14.274(2)
α (°)	90	90
β (°)	92.45(2)	90
γ (°)	90	90
U (Å^3)	2735.5	2761.1
Space Group	$P2_1/n$ (No. 14)	*Pbca* (No. 61)
Z	4	8
Dc (g cm^{-3})	1.516($D_{\text{flot.}}$ = 1.52)	1.742($D_{\text{flot.}}$ = 1.74)
F(000)	1280	1456
Crystal Size (mm)	0.2 × 0.4 × 0.25	0.25 × 0.25 × 0.35
μ(Mo-K_α (cm^{-1})	6.4	11.3
Data Collection		
θ min, θ max (°)	1.5—24	1.5—24
Scan width parameters A, B in width = $A + B \tan\theta$	0.80, 0.30	0.70, 0.30
Total Unique Data	8667	4024
Observed Data $F_O > 3\sigma(F_O)$	5143	2711
Refinement		
No. of parameters	361	188
Weighting scheme coefficient, g, in $\omega = 1/[\sigma^2\lvert F_O\rvert + g\lvert F_O\rvert^2]$	0.00034	0.00052
Final $R = \Sigma\Delta F/\Sigma(F_O)$	0.032	0.043
$R' = (\Sigma\omega\Delta F^2/\Sigma\omega F_O^2)^{1/2}$	0.038	0.048

[a] The estimated standard deviations are given in parentheses, in this and other Tables throughout this paper.

for l odd and $hk0$ for h odd, respectively. The crystal data and details of data collection and structure refinement are presented in Table 1.

Intensity data for A and B were recorded on the CAD4 diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71069 Å) and an ω — 2θ scan technique, in the manner described previously [5]. During data collection the crystals showed no indications of decomposition. The data were corrected for Lorenz and polarization effects, but not for absorption.

The structures of both compounds were solved via Patterson and electron density syntheses and refined by full matrix least squares techniques with anisotropic temperature factors assigned to all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions (with C—H 1.08 Å) and their contribution included in the computation of F_c. One common isotropic tempera-

TABLE 2

FRACTIONAL COORDINATES (Rh × 10^5; others × 10^4) OF NON-HYDROGEN ATOMS IN $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2PPh_3]$

Atom	x/a	y/b	z/c
Rh	18 602(2)	16 880(1)	13 983(1)
P	3 004(1)	2 378(1)	370(1)
N(1)	—366(2)	1 825(2)	447(2)
N(2)	1 455(2)	3 667(2)	1 835(2)
O(11)	678(2)	1 668(1)	324(1)
O(12)	—799(2)	1 526(2)	1 076(2)
O(13)	—891(2)	2 278(2)	—98(2)
O(21)	979(2)	2 923(1)	1 577(1)
O(22)	2 432(2)	3 654(2)	2 097(2)
O(23)	880(2)	4 365(2)	1 805(2)
C(1)	3 081(3)	1 167(2)	2 346(2)
C(2)	2 848(2)	483(2)	1 705(2)
C(3)	1 685(3)	253(2)	1 745(2)
C(4)	1 211(2)	791(2)	2 395(2)
C(5)	2 078(3)	1 351(2)	2 753(2)
C(11)	4 207(3)	1 499(3)	2 646(3)
C(21)	3 698(3)	—8(3)	1 204(2)
C(31)	1 070(3)	—445(2)	1 214(3)
C(41)	47(3)	701(3)	2 713(3)
C(51)	1 937(4)	2 005(3)	3 480(2)
C(112)	3 580(3)	2 105(2)	—1 313(2)
C(113)	3 727(3)	1 597(3)	—2 042(2)
C(114)	3 288(3)	728(3)	—2 102(2)
C(115)	2 695(3)	364(3)	—1 447(2)
C(116)	2 567(2)	871(2)	—709(2)
C(111)	3 024(2)	1 738(2)	—630(2)
C(122)	3 358(3)	4 259(2)	14(2)
C(123)	3 001(3)	5 119(3)	252(3)
C(124)	1 910(3)	5 265(2)	—515(2)
C(125)	1 162(3)	4 550(2)	—528(2)
C(126)	1 504(3)	3 683(2)	—265(2)
C(121)	2 606(2)	3 530(2)	17(2)
C(132)	5 302(2)	1 932(2)	334(2)
C(133)	6 414(2)	1 992(2)	633(2)
C(134)	6 714(2)	2 580(3)	1 286(2)
C(135)	5 919(3)	3 110(2)	1 651(2)
C(136)	4 800(2)	3 065(2)	1 363(2)
C(131)	4 487(2)	2 478(2)	696(2)

ture factor (U_{iso}) was refined for methyl hydrogen [final value 0.117(5) Å^2 for A and 0.110(6) Å^2 for B] and another for phenyl hydrogens in structure A [final value 0.068(3) Å^2].

For A, an empirical isotropic extinction parameter, χ, in the modified expression for the calculated structure factor $F_c' = F_c(1 - \chi F_c^2/\sin\theta)$ was also varied in the least-squares, and this refined to a value of 21(±7) × 10^{-5}. The weighting scheme used in the refinement took the form $\omega = 1/[\sigma^2|F_0| + g|F_0|^2]$, with the parameter g chosen to give flat agreement analyses. The final difference maps showed no peaks of intensity greater than 0.5 e Å^{-3}.

Final fractional coordinates and anisotropic thermal parameters of the non-hydrogen atoms are given in Tables 2 and 3 for A and Tables 4 and 5 for B.

TABLE 3

ANISOTROPIC VIBRATIONAL AMPLITUDES (Å^2 × 10^4) OF NON-HYDROGEN ATOMS IN [Rh(η-C_5Me_5)$(NO_3)_2PPh_3$] [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh	257(1)	252(1)	277(1)	—11(1)	6(1)	5(1)
P	237(3)	314(3)	317(3)	11(3)	14(2)	3(3)
N(1)	312(12)	469(16)	555(16)	—41(13)	—62(11)	—27(11)
N(2)	526(16)	339(12)	343(13)	—53(10)	29(11)	50(11)
O(11)	280(9)	483(12)	413(11)	—77(10)	—57(8)	54(9)
O(12)	372(13)	1124(25)	933(22)	377(18)	151(14)	18(14)
O(13)	470(13)	723(18)	750(18)	75(15)	—192(13)	137(12)
O(21)	394(11)	330(10)	484(12)	—78(9)	6(9)	54(9)
O(22)	496(14)	515(14)	725(17)	—179(13)	—46(12)	—27(11)
O(23)	897(19)	364(13)	699(17)	—95(12)	—49(15)	228(13)
C(1)	470(17)	410(16)	401(16)	129(13)	—132(13)	52(13)
C(2)	411(15)	351(15)	404(15)	104(12)	20(12)	110(12)
C(3)	512(17)	257(13)	368(14)	19(11)	—21(12)	17(12)
C(4)	449(16)	347(15)	394(15)	82(12)	93(13)	—5(12)
C(5)	691(21)	319(14)	303(14)	36(12)	—22(14)	—19(14)
C(11)	634(24)	638(25)	858(29)	309(21)	—422(21)	—208(19)
C(21)	630(22)	614(23)	649(23)	151(19)	148(18)	348(18)
C(31)	791(25)	350(17)	633(23)	—53(16)	—172(19)	—85(17)
C(41)	638(23)	750(27)	760(27)	178(22)	286(21)	—24(21)
C(51)	1227(38)	569(23)	375(18)	—112(17)	33(21)	—10(24)
C(112)	425(16)	571(19)	368(15)	47(14)	51(13)	—13(15)
C(113)	473(18)	908(29)	307(15)	54(17)	70(13)	123(19)
C(114)	554(20)	774(26)	331(16)	—139(17)	—25(15)	206(19)
C(115)	589(19)	514(20)	478(19)	—93(15)	—69(16)	93(16)
C(116)	392(15)	421(16)	367(14)	—36(13)	3(12)	49(12)
C(111)	280(12)	442(15)	292(12)	—5(12)	3(10)	52(12)
C(122)	448(17)	397(17)	714(23)	151(16)	—18(16)	—70(14)
C(123)	745(25)	437(19)	773(27)	176(19)	—70(21)	—114(18)
C(124)	802(26)	392(18)	503(20)	78(15)	—8(18)	82(17)
C(125)	545(19)	563(21)	470(18)	88(16)	—55(15)	175(16)
C(126)	419(16)	422(16)	445(17)	61(14)	—52(13)	34(13)
C(121)	360(14)	351(15)	334(14)	43(11)	29(11)	11(11)
C(132)	293(13)	489(17)	477(17)	—1(14)	12(12)	36(12)
C(133)	287(14)	557(19)	661(22)	39(17)	13(14)	69(13)
C(134)	285(15)	560(20)	738(24)	104(18)	—92(15)	—47(14)
C(135)	408(17)	494(20)	635(21)	—45(16)	—97(15)	—83(14)
C(136)	320(14)	418(16)	543(18)	—29(14)	—26(13)	—10(12)
C(131)	262(12)	366(14)	401(14)	51(12)	—21(11)	1(11)

[a] The anisotropic temperature factor exponent takes the form: $2\pi^2(h^2a^{*2}U_{11} + \ldots 2hka^*b^*U_{12})$

TABLE 4

FRACTIONAL COORDINATES (Rh × 10^5, OTHERS × 10^4) OF NON-HYDROGEN ATOMS IN [$Rh(\eta\text{-}C_5Me_5)(NO_3)_2$]

Atom	x/a	y/b	z/c
Rh	19 520(2)	17 692(1)	15 884(1)
N(1)	3 090(4)	625(3)	718(3)
N(2)	3 654(3)	3 037(3)	1 403(3)
O(11)	3 207(3)	790(3)	1 569(2)
O(12)	2 332(4)	995(3)	335(3)
O(13)	3 681(4)	112(3)	302(3)
O(21)	2 995(3)	2 651(3)	889(2)
O(22)	3 676(3)	2 846(4)	2 227(3)
O(23)	4 310(4)	3 521(4)	1 114(4)
C(1)	922(3)	1 204(3)	2 578(3)
C(2)	1 384(3)	1 997(3)	2 962(3)
C(3)	1 103(3)	2 737(3)	2 380(3)
C(4)	499(3)	2 416(3)	1 623(3)
C(5)	363(3)	1 457(3)	1 762(3)
C(11)	1 003(4)	268(3)	2 978(4)
C(21)	2 021(4)	2 038(5)	3 831(4)
C(31)	1 410(4)	3 706(31)	2 528(5)
C(41)	27(4)	2 955(3)	861(4)
C(51)	–227(4)	833(3)	1 152(4)

Lists of observed and calculated structure factors may be obtained from the authors on request.

Neutral atom scattering factors were taken from reference 6 for Rh, reference 7 for P, O, N and C, and reference 8 for H. The scattering factors of the

TABLE 5

ANISOTROPIC VIBRATIONAL AMPLITUDES (Å^2 × 10^4) OF NON-HYDROGEN ATOMS IN [$Rh(\eta\text{-}C_5Me_5)(NO_3)_2$] [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh	450(2)	363(2)	447(2)	4(1)	81(1)	50(1)
N(1)	1044(38)	552(23)	630(27)	36(21)	270(26)	265(24)
N(2)	482(21)	829(29)	481(23)	–91(20)	74(17)	–158(20)
O(11)	981(31)	882(29)	541(21)	107(18)	159(19)	514(24)
O(12)	1089(32)	823(25)	503(20)	–67(19)	79(21)	237(25)
O(13)	1647(48)	966(32)	885(33)	–43(25)	553(32)	648(34)
O(21)	713(24)	935(28)	523(21)	–40(20)	47(16)	–128(19)
O(22)	608(24)	1451(40)	817(30)	134(28)	–34(20)	–23(26)
O(23)	1229(42)	1322(38)	997(35)	–54(32)	258(32)	750(35)
C(1)	468(20)	428(19)	451(21)	40(16)	38(17)	26(17)
C(2)	465(22)	531(22)	411(21)	51(17)	84(17)	–2(18)
C(3)	398(20)	395(20)	640(26)	–102(18)	133(18)	21(15)
C(4)	410(19)	427(20)	597(25)	58(18)	51(18)	27(16)
C(5)	473(22)	427(19)	510(24)	49(17)	18(18)	–14(18)
C(11)	750(33)	503(24)	682(31)	191(24)	–34(25)	–29(24)
C(22)	659(34)	952(39)	518(28)	–141(29)	–49(23)	–68(28)
C(31)	659(34)	398(22)	1050(43)	–199(26)	162(32)	–14(21)
C(41)	636(30)	563(26)	805(38)	176(25)	6(26)	99(24)
C(51)	809(36)	536(27)	714(33)	22(24)	234(29)	101(25)

[a] The anisotropic temperature factor exponent takes the form: $2\pi^2(h^2a^{*2}U_{11} + \ldots 2hka^*b^*U_{12})$

heavier elements were modified for anomalous dispersion effects taking $\Delta f'$ and $\Delta f''$ values from reference 9.

All the calculations were performed on the Queen Mary College ICL 1904S and University of London CDC7600 computers using the programmes SHELX for structure determination and refinement [10], XANADU for least-squares calculations [11] and PLUTO for molecular diagrams [12].

Description and discussion of structures

The molecular structure of $Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)$, is illustrated in Figure 1. Selected intramolecular distances and angles are given in Table 6.

$Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)$ has the "three-legged piano stool" arrangement of ligands common to many cyclopentadienyl complexes, with the cyclopentadienyl ligand forming the seat and the two monodentate nitrato-ligands and the triphenylphosphine ligands making up the three legs. The cyclopentadienyl ligand in this complex does not show idealised five fold symmetry and the rhodium—carbon distances vary significantly within the limits 2.161—2.207 Å and the carbon—carbon distances also vary from 1.407 to 1.438 Å; however no correlation between these distances and the metal to ring carbon distances could be discerned. The cyclopentadienyl ring carbon atoms define a good plane with the individual carbon atoms deviating less than 0.0045 Å from the best least squares plane through these atoms (see Table 7). The rhodium atom lies

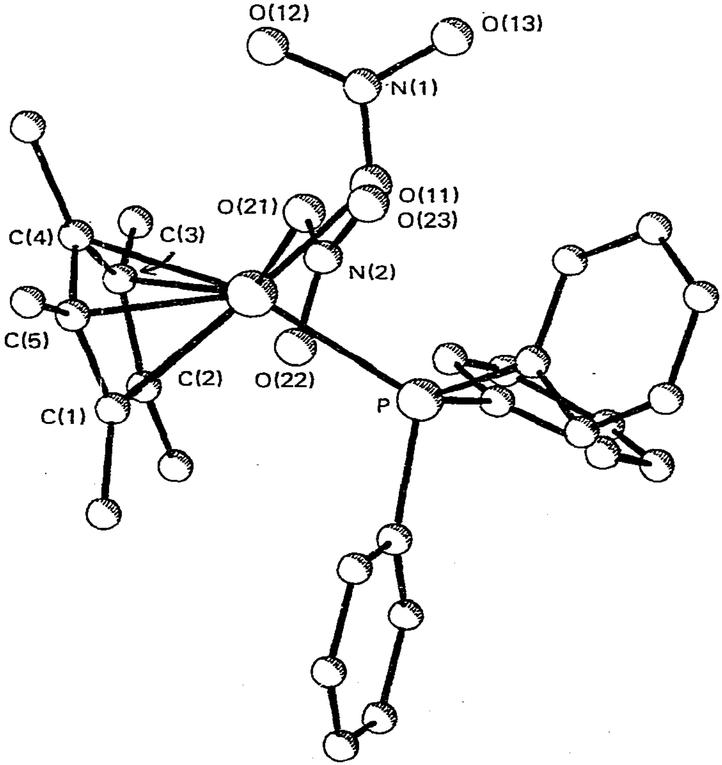


Fig. 1. Molecular structure of $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)]$.

TABLE 6

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR [Rh(η-C_5Me_5)$(NO_3)_2$(PPh_3)]

(a) Distances			
Rh—C(1)	2.175(4)	C(3)—C(31)	1.490(5)
Rh—C(2)	2.161(4)	C(4)—C(41)	1.500(5)
Rh—C(3)	2.179(3)	C(5)—C(51)	1.506(6)
Rh—C(4)	2.207(4)		
Rh—C(5)	2.189(4)	P(1)—C(111)	1.829(3)
		P(1)—C(121)	1.828(3)
Rh—O(11)	2.152(2)	P(1)—C(131)	1.826(3)
Rh—O(21)	2.114(2)		
Rh ... O(12)	3.199(4)	C(111)—C(112)	1.392(5)
Rh ... O(22)	3.140(4)	C(111)—C(116)	1.382(6)
		C(112)—C(113)	1.380(6)
Rh—P	2.383(1)	C(113)—C(114)	1.372(7)
		C(114)—C(115)	1.380(6)
N(1)—O(11)	1.289(4)	C(115)—C(116)	1.391(6)
N(1)—O(12)	1.216(5)		
N(1)—O(13)	1.231(5)	C(121)—C(122)	1.392(5)
N(2)—O(21)	1.284(4)	C(121)—C(126)	1.388(6)
N(2)—O(22)	1.219(4)	C(122)—C(123)	1.384(6)
N(2)—O(23)	1.229(4)	C(123)—C(124)	1.364(7)
		C(124)—C(125)	1.373(6)
C(1)—C(2)	1.438(6)	C(125)—C(126)	1.390(6)
C(1)—C(5)	1.407(6)		
C(2)—C(3)	1.430(6)	C(131)—C(132)	1.399(5)
C(3)—C(4)	1.425(6)	C(131)—C(136)	1.393(5)
C(4)—C(5)	1.416(6)	C(132)—C(133)	1.388(5)
		C(133)—C(134)	1.374(6)
C(1)—C(11)	1.486(5)	C(134)—C(135)	1.368(6)
C(2)—C(21)	1.494(5)	C(135)—C(136)	1.390(5)
(b) Angles			
P—Rh—O(11)	81.3(1)	Rh—P—C(111)	113.2(1)
P—Rh—O(21)	91.8(1)	Rh—P—C(121)	116.5(1)
O(11)—Rh—O(21)	78.6(1)	Rh—P—C(131)	114.8(1)
		C(111)—P—C(121)	102.9(2)
Rh—O(11)—N(1)	119.0(2)	C(111)—P—C(131)	103.5(2)
Rh—O(21)—N(2)	123.3(2)	C(121)—P—C(131)	104.3(2)
O(11)—N(1)—O(12)	120.3(3)	P—C(111)—C(112)	119.3(3)
O(11)—N(1)—O(13)	117.2(3)	P—C(111)—C(116)	121.8(3)
O(12)—N(1)—O(13)	122.5(3)	C(112)—C(111)—C(116)	118.8(4)
O(21)—N(2)—O(22)	119.8(3)	C(111)—C(112)—C(113)	120.7(4)
O(21)—N(2)—O(23)	116.9(3)	C(112)—C(113)—C(114)	119.8(4)
O(22)—N(2)—O(23)	123.3(3)	C(113)—C(114)—C(115)	120.5(4)
		C(114)—C(115)—C(116)	119.6(4)
C(2)—C(1)—C(5)	108.0(3)	C(111)—C(116)—C(115)	120.5(4)
C(2)—C(1)—C(11)	126.5(4)	P—C(121)—C(122)	123.2(3)
C(5)—C(1)—C(11)	124.6(4)	P—C(121)—C(126)	118.3(3)
C(1)—C(2)—C(3)	106.9(3)	C(122)—C(121)—C(126)	118.5(3)
C(1)—C(2)—C(21)	125.9(3)	C(121)—C(122)—C(123)	120.4(4)
C(3)—C(2)—C(21)	126.3(3)	C(122)—C(123)—C(124)	120.7(4)
C(2)—C(3)—C(4)	108.5(3)	C(123)—C(124)—C(125)	119.7(4)
C(2)—C(3)—C(31)	126.2(4)	C(124)—C(125)—C(126)	120.5(4)
C(4)—C(3)—C(31)	125.2(4)	C(121)—C(126)—C(125)	120.2(4)
C(3)—C(4)—C(5)	107.3(3)	P—C(131)—C(132)	121.5(3)
C(3)—C(4)—C(41)	126.3(4)	P—C(131)—C(136)	119.1(3)
C(5)—C(4)—C(41)	126.0(4)	C(132)—C(131)—C(136)	119.2(3)
C(1)—C(5)—C(4)	109.2(3)	C(131)—C(132)—C(133)	119.7(4)
C(1)—C(5)—C(51)	126.3(4)	C(132)—C(133)—C(134)	120.4(4)
C(4)—C(5)—C(51)	124.4(4)	C(133)—C(134)—C(135)	120.2(4)
		C(134)—C(135)—C(136)	120.6(4)
		C(131)—C(136)—C(135)	119.8(4)

TABLE 7

SELECTED LEAST-SQUARES PLANES IN [Rh(η-C_5Me_5)(NO_3)$_2$(PPh_3)]

Equations are of the form: $px + qy + rz = s$, where x, y, z are fractional coordinates σ (Å) is the r.m.s. standard deviation. Atomic deviations (Å) of individual atoms from the least squares plane are in square brackets.

Plane 1 through atoms C(1), C(2), C(3), C(4) and C(5)

p	q	r	s	σ
2.3855	−10.4402	10.3911	1.9495	0.0032

[Rh −1.8151, C(1) 0.0045, C(2) −0.0036, C(3) 0.0014, C(4) 0.0014, C(5) −0.0037, C(11) 0.2396, C(21) 0.1917, C(31) 0.0317, C(41) 0.1482, C(51) 0.0341]

Plane 2 through atoms C(11), C(21), C(31), C(41) and C(51)

p	q	r	s	σ
2.0663	−10.4943	10.4639	2.0210	0.0657

[Rh −1.9449, C(1) −0.1545, C(2) −0.1561, C(3) −0.1125, C(4) −0.0956, C(5) −0.1287, C(11) 0.0450, C(21) 0.0110, C(31) −0.0626, C(41) 0.0912, C(51) −0.0847]

Plane 3 through atoms N(1), O(11), O(12) and O(13)

p	q	r	s	σ
2.7065	12.2495	7.6335	2.4750	0.0016

[Rh 1.1635, N(1) 0.0028, O(11) −0.0009, O(12) −0.0010, O(13) −0.0009]

Plane 4 through atoms N(2), O(2), O(22) and O(23)

p	q	r	s	σ
−3.9734	−2.6031	14.7552	1.1765	0.0011

[Rh −0.2918, N(2) −0.0019, O(21) 0.0006, O(21) 0.0006, O(22) 0.0007, O(23) 0.0007]

Dihedral angles between planes (°)

Planes 1 and 2	1.56	Planes 1 and 4	47.04
Planes 1 and 3	102.74	Planes 2 and 4	46.03
Planes 2 and 3	103.18	Planes 3 and 4	76.44

1.815 Å above this plane. The carbon atoms of methyl groups attached to the ring are not so planar, showing deviations up to 0.091 Å from their best plane. Also, the best plane through the methyl carbons is not coincident with the plane defined by the ring carbon atoms. The methyl ligands are effectively bent away from the rhodium atom. Similar effects have been noted previously in the structural analysis of [Rh(η-C_5Me_5)(dba)] (where dba = dibenzylidene acetone) [13] and have been attributed to rehybridisation effects at the carbon atoms of the ring which maximise the metal ligand—bonding interactions. The fact that a similar distortion is not observed in [Rh(η-C_5Me_5)(NO_3)$_2$] (vide infra) strongly suggests that the origins of this distortion lie in steric effects rather than subtle electronic effects.

As noted above both nitrato-ligands are coordinated to the metal atom in a monodentate fashion and have similar but not identical structural parameters. The rhodium—oxygen distances to the coordinated oxygen atoms are 2.152 and 2.114 Å and to the adjacent uncoordinated oxygen atoms 3.199 and 3.140 Å respectively. This large difference in metal—oxygen distances is characteristic of a monodentate nitrato-ligand, rather than an asymmetric bidentate nitrato ligand. Least squares planes through the nitrato-ligands (see Table 7)

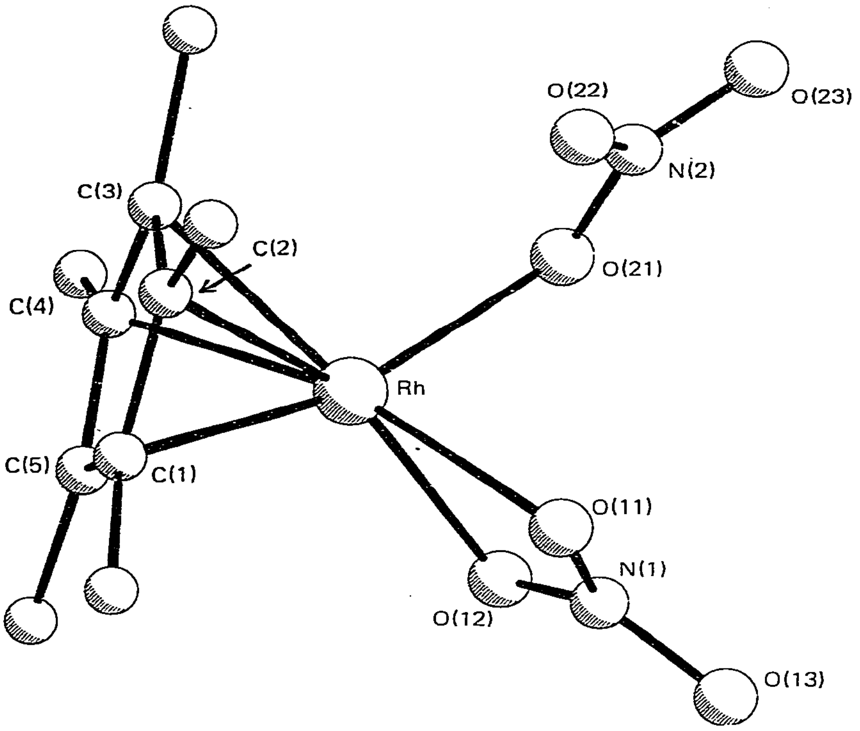


Fig. 2. Molecular structure of [Rh(η-C_5Me_5)$(NO_3)_2$].

indicate that the nitrato-ligands are planar; the metal atom however does not lie within this plane.

Figure 2 illustrates the molecular structure of [Rh(η-C_5Me_5)$(NO_3)_2$]. The important intramolecular distances and angles are summarised in Table 8. In this complex the rhodium atom is symmetrically placed with respect to the C_5Me_5 ligand and monodentate and bidentate nitrato-ligands complete the "piano-stool" ligand arrangement. Table 9 summarises the information on selected least-squares planes. As in A the cyclopentadienyl ring carbons are accurately planar (plane 1 in Table 9) but now the methyl groups also lie very close to this plane. There are some significant variations in the C—C distances within the cyclopentadienyl ring, i.e. C—C distances ranging from 1.419—1.450(6) Å, and the bond angles within the ring show significant variations from the angle anticipated for a regular pentagon. Similar distortions have been observed recently in structural determinations of [{Rh(η-C_5Me_5)Cl_2}$_2$], [{Rh(η-C_5Me_5)Br_2}$_2$] [14] and [{Rh(η-C_5Me_5)Cl}$_2$HCl] [15], and have been ascribed to subtle electronic and steric effects. Table 10 summarises these results together with those for [Rh(η-C_5Me_5)$(NO_3)_2$$(PPh_2)$] and [Rh($\eta$-$C_5Me_5$)$(NO_3)_2$] and demonstrates that the variation in C—C distance is a common feature. The average C—C bond length in the nitrato-complexes is similar to those reported previously for [{Rh(η-C_5Me_5)Br_2}$_2$] and [{Rh(η-C_5Me_5)Cl}$_2$HCl]. Table 10 also indicates that the mean Rh—ring distance as judged by the Rh—C distance or the displacement of the rhodium atom from the best least squares plane through the cyclopentadienyl ring is sensitive to the electron donating capabilities of the ligands

TABLE 8

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR $[Rh(\eta\text{-}C_5Me_5)(NO_3)]$

(a) Distances			
Rh—C(1)	2.121(4)	Rh—O(11)	2.188(4)
Rh—C(2)	2.123(4)	Rh—O(12)	2.184(4)
Rh—C(3)	2.137(4)	Rh—O(21)	2.135(4)
Rh—C(4)	2.122(4)	Rh ... O(22)	2.903(5)
Rh—C(5)	2.133(4)		
		C(1)—C(2)	1.432(6)
N(1)—O(11)	1.249(6)	C(1)—C(5)	1.424(6)
N(1)—O(12)	1.255(6)	C(2)—C(3)	1.426(6)
N(1)—O(13)	1.235(5)	C(3)C(4)	1.419(6)
		C(4)—C(5)	1.450(6)
N(2)—O(21)	1.266(5)	C(1)—C(11)	1.508(6)
N(2)—O(22)	1.210(5)	C(2)—C(21)	1.493(7)
N(2)—O(23)	1.190(6)	C(3)—C(31)	1.510(6)
		C(4)—C(41)	1.484(6)
		C(5)—C(51)	1.486(6)
(b) Angles			
O(11)—Rh—O(12)	58.0(2)	C(2)—C(1)—C(5)	108.1(4)
O(11)—Rh—O(21)	85.9(2)	C(2)—C(1)—C(11)	125.8(4)
O(12)—Rh—O(21)	78.3(2)	C(5)—C(1)—C(11)	126.1(4)
		C(1)—C(2)—C(3)	107.7(4)
Rh—O(11)—N(1)	93.0(3)	C(1)—C(2)—C(21)	125.8(4)
Rh—O(12)—N(1)	93.0(3)	C(3)—C(2)—C(21)	126.5(4)
Rh—O(21)—N(2)	116.0(3)	C(2)—C(3)—C(4)	109.0(4)
		C(2)—C(3)—C(41)	125.9(4)
O(11)—N(1)—O(12)	115.7(4)	C(4)—C(3)—C(41)	125.0(4)
O(11)—N(1)—O(13)	120.9(4)	C(3)—C(4)—C(5)	107.1(4)
O(12)—N(1)—O(13)	123.4(4)	C(3)—C(4)—C(41)	127.3(4)
O(21)—N(2)—O(23)	118.2(4)	C(5)—C(4)—C(41)	125.5(4)
O(21)—N(2)—O(23)	124.0(41)	C(1)—C(5)—C(4)	108.0(4)
O(22)—N(2)—O(23)	117.5(4)	C(1)—C(5)—C(51)	125.3(4)
		C(4)—C(5)—C(51)	126.6(4)

trans to the ring. The longest metal to ring distances are observed in the hydrido- and triphenylphosphine-complexes and the shortest in the nitrato- and chloro-complexes. Such a trend is consistent with simple electrostatic and covalency considerations.

As the single crystal structural determinations of the nitrato-complexes $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)]$ and $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2]$ were undertaken in order to learn more about the bonding in the nitrato-ligand, the structural parameters associated with this ligand in these complexes are discussed in some detail below.

Structural parameters of the nitrato-ligand

In an important review in 1971 Addison and his coworkers [3] summarised the structural aspects of coordinated nitrate groups. Structural studies had resulted in the identification of four types of nitrato-ligands; symmetrical bidentate (I), unsymmetrical bidentate (II), unidentate, C_s (III) and bridging (IV).

TABLE 9

SELECTED LEAST-SQUARES PLANES IN [Rh(η-C_5Me_5)$(NO_3)_2$]

Equations are of form: $px + py + rz = s$, where x, y, z are fractional coordinates. σ (Å) is the r.m.s. standard deviation. Atomic deviations (Å) are in square brackets.

Plane 1 through atoms C(1), C(2), C(3), C(4) and C(5)

p	*q*	*r*	*s*	σ
10.6606	—2.3804	—7.8589	—1.3333	0.0105

[Rh 1.7448, C(1) 0.0036, C(2) 0.0056, C(3) —0.0127, C(4) 0.0147, C(5) —0.0112, C(11) —0.0016, C(21) —0.0080, C(31) —0.0324, C(41) —0.0179, C(51) —0.0123]

Plane 2 through atoms C(11), C(21), C(31), C(41) and C(51)

p	*q*	*r*	*s*	σ
10.6607	—2.3106	—7.8777	—1.3384	0.0046

[Rh 1.7593, C(1) 0.0122, C(2) 0.0190, C(3) 0.0069, C(4) 0.0335, C(5) 0.0006, C(11) —0.0003, C(21) 0.0040, C(31) —0.0063, C(41) 0.0061, C(51) —0.0036]

Plane 3 through atoms N(1), O(12) and O(13)

p	*q*	*r*	*s*	σ
7.5143	11.6088	—3.3992	2.7960	0.0043

[Rh 0.1847, N(1) 0.0074, O(11) —0.0024, O(12) —0.0024, O(13) —0.0026]

Plane 4 through atoms N(2), O(21), O(22) and O(23)

p	*q*	*r*	*s*	σ
—7.9958	11.4583	2.4013	0.8659	0.0168

[Rh —0.0181, N(2) 0.0292, O(21) —0.0096, O(22) —0.0094, O(23) —0.0102]

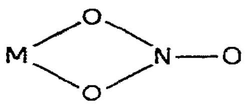
Dihedral angles between planes (°)

Planes 1 and 2	0.28	Planes 1 and 4	136.01
Planes 1 and 3	61.37	Planes 2 and 4	135.73
Planes 2 and 3	61.11	Planes 3 and 4	78;06

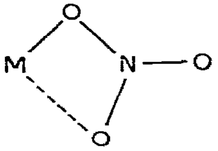
TABLE 10

A COMPARISON OF METAL-CYCLOPENTADIENYL PARAMETERS IN THE COMPLEXES [{Rh(η-C_5Me_5)Cl_2}$_2$] (A), [{Rh(η-C_5Me_5)Br_2}$_2$] (B), [{Rh(η-C_5Me_5)Cl}$_2$HCl] (C), [Rh(η-C_5Me_5)$(NO_3)_2(PPh_3)$] (D) and [Rh(η-C_5Me_5)$(NO_3)_2$] (E)

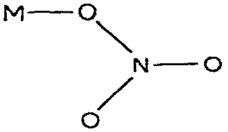
	A	B	C	D	E
Spread in Rh—C distances (Å)	2.116—2.140(4)	2.117—2.167(3)	2.109—2.178(6)	2.161—2.207(4)	2.121—2.137(4)
Average Rh—C (Å)	2.128	2.145	2.151	2.182	2.127
Spread in C—C distances (Å)	1.370—1.452(7)	1.419—1.441(10)	1.403—1.440(9)	1.407—1.438(6)	1.419—1.450(6)
Average C—C distance (Å)	1.412	1.431	1.425	1.423	1.430
Distance of Rh atom from best least-squares plane through C_5 ring in (Å)	1.756	1.769	1.777	1.815	1.745



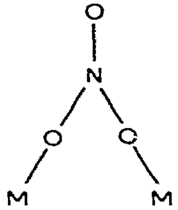
(I)



(II)



(III)



(IV)

The most commonly observed coordination mode is the symmetrical bidentate (I), and Addison et al [3] rationalised this preference in the following way. If the nitrate group is coordinated to a metal ion via one oxygen atom O_I then as shown in Figure 3, there is a relatively close approach of another oxygen O_I' to the metal ion. This close approach results from the geometry of the nitrato-group itself, taken together with the value of the MO_IN interbond angle, which is normally between 120 and 109.5°. The electrostatic interaction between the metal ion and O_I' will tend to shorten the distance MO_I' and in the extreme, give a symmetrically bidentate coordination of the nitrato-group. Alternatively, it may be argued that, because of the electronegative nature of oxygen, the donation of electron charge to the metal from a single oxygen would be less favourable than the donation of rather less charge by each of two oxygens.

This tendency to donate charge from two oxygen atoms is also satisfied by bridging coordination. However, the ligand—ligand repulsion will be greater if a given metal coordination is achieved using bridging rather than bidentate nitrato-groups because the bridging situation cannot take advantage of the short "bite" of the nitrato-groups. Thus the symmetrical bidentate coordination of the nitrato groups maximises the metal—nitrate interaction for a given degree of nitrate—nitrate repulsion.

The unsymmetrically bidentate nitrato-groups (e.g. II) occur when there is a real (0.2—0.7 Å) difference between the distances of the metal atom from the two coordinated oxygen atoms of each nitrato-group. Addison et al [3] have suggested that unsymmetrically bidentate groups occur when either the metal electron distribution is asymmetric with respect to the two coordinated oxygens of each bidentate nitrato-groups, or the presence of a ligand with a high *trans* influence *trans* to one of the nitrato oxygen atoms.

In unidentate nitrato-complexes (III) one metal—oxygen distance is so much longer than the other (0.8—1.1 Å) that there can only be significant bonding between the metal atom and one of the oxygen atoms of each nitrato-group. It has been suggested that this coordination mode occurs when one or both of the following conditions apply:

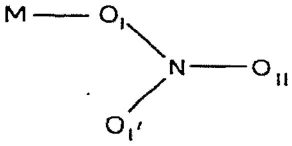


Fig. 3

(1) the number of metal—nitrate bonds which can be formed is limited to one per nitrato-group;

(2) the steric interaction with other ligands in the primary coordination sphere of the metal prevents bidentate coordination of the nitrato-group.

In the bridging coordination mode of nitrato-ligands the nitrate ligand coordinates to more than one metal atom. IV illustrates the more usual coordination mode and is found for example in α-$Cu(NO_3)_2$ [16]. A more unusual bridging mode involving bridging of two metal atoms by a single oxygen atom is found in $[Cu(NO_3)_2py_2]py$ [17].

Dimensions of nitrato-groups

In a regular environment the nitrate ion is known to be planar with all O—N—O interbond angles equal to 120°, and N—O bond lengths equal to 1.245(10) Å [3]. In all the different types of coordination nitrate groups thus identified the planarity of the nitrate ion is essentially preserved and this plane generally includes the metal ion. However, the N—O bond lengths and O—N—O interbond angles do change significantly on coordination.

The structural parameters of the bidentate nitrate ligand in $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2]$ as determined as part of the research work described in this paper are compared with those for some related nitrato-complexes in Table 11. In common with other symmetrical bidentate nitrato-ligands the terminal N—O bond length of 1.235 Å is shorter and the N—O bonds involving the coordinated oxygens are longer than the N—O bonds in the nitrate ion. However, the difference between these bond types of 0.017 Å is much smaller than those reported for other complexes containing the symmetrical bidentate ligand (0.04—0.10 Å) [3]. Addison et al [3] have noted that the changes in the N—O bond lengths which accompany coordination are related to the polarising power (as measured by the cationic charge/radius ratio) of the central metal ion in the complex. Therefore, one must conclude that although the formal charge of the rhodium atom in $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2]$ is 3+, the bond length data suggest a much smaller polarising power and net charge. This conclusion is of course in agreement with the Pauling electroneutrality principle and additionally reflects the strong covalent interaction between the metal and the cyclopentadienyl ligand in this complex. In valence bond terms the close similarity of the O—N bond lengths in $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2]$ suggest that the canonical forms B and C shown below make contributions which are as significant as that shown in A.

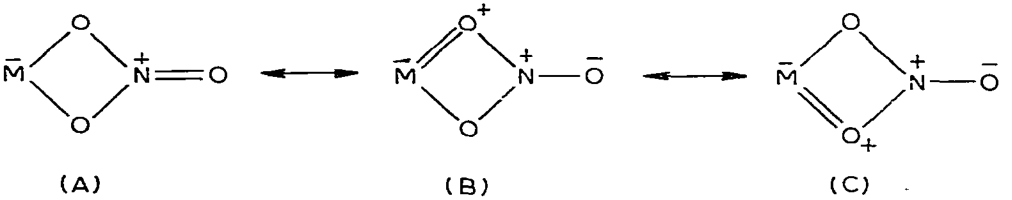
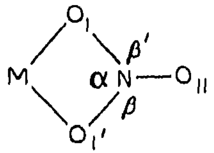


Table 11 also summarises the bond length and angle data for the monodentate nitrato-ligands in $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)]$ and $[Rh(\eta\text{-}C_5Me_5)(NO_3)_2]$. The large difference between the $Rh—O_I$ (coordinated oxygen atom) and the $Rh—O_{II}'$ distances in these complexes, i.e. 0.7 Å, clearly rules out the alterna-

TABLE 11

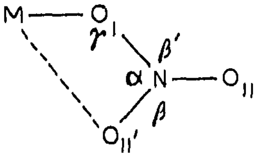
A COMPARISON OF NITRATO-LIGAND DIMENSIONS IN SOME NITRATO-COMPLEXES (DISTANCES IN Å, ANGLES IN DEGREES)

(a) Bidentate



Compound	MO_I	MO_I'	NO_I	NO_I'	NO_{II}	α	β	β'
$[Rh(\eta\text{-}C_5Me_5)(NO_3)_2]$	2.188	2.184	1.249	1.255	1.235	116	121	123
$[Cu(NO_3)(PPh_3)_2]$ [a]	2.22	2.22	1.25	1.25	1.16	118	121	121
$[Fe(NO_3)_4](AsPh_4)_2$ [a]	2.13	2.14	1.27	1.27	1.22	114	123	123

(b) Monodentate



Compound	MO_I	$MO_{II'}$	NO_I	$NO_{II'}$	NO_{II}	α	β	β'	γ
$[Rh(\eta\text{-}C_5Me_5)(NO_3)_2(PPh_3)]$	2.152	3.199	1.289	1.216	1.231	120	123	117	119
	2.114	3.140	1.284	1.219	1.229	120	123	117	123
$[Rh(\eta\text{-}C_5Me_5)(NO_3)_2]$	2.315	2.903	1.266	1.210	1.190	118	118	124	116
$[K.Au(NO_3)_4]$ [a]	2.052	2.85	1.34	1.24	1.14	118	129	114	114
$[Ni(NO_3)_2(H_2O)_4]$ [a]	2.05	2.90	1.30	1.24	1.26	121	121	118	121

[a] Ref. 3.

tive formulation of these complexes as unsymmetrically bidentate nitrato-complexes.

In common with the bidentate nitrato-complexes discussed above the N—O_{I} bond length in the monodentate nitrato-complexes is longer than that reported for the NO_3^- ion and the N—O bond lengths to the uncoordinated oxygen atoms, i.e. O_{II} and O_{I}'. In [Rh(η-C_5Me_5)$(NO_3)_2$$(PPh_3)$] the NO_{II} and NO_{II}' bond lengths are not significantly different, and their mean value of 1.225 Å is approximately 0.06 Å shorter than NO_{I}. Similarly in [Rh(η-C_5Me_5)$(NO_3)_2$] the NO_{II} and NO_{II}' bond lengths show insigificant variation and their mean value of 1.200 Å is still approximately 0.06 Å shorter than NO_{I}. These variations have been noted previously for monodentate nitrato-complexes and two previously studied examples have been included in Table 11 for comparative purposes.

The structure determination of [Rh(η-C_5Me_5)$(NO_3)_2$] which contains both a monodentate and bidentate ligand coordinated to the same metal atom provides a unique opportunity for studying the structural differences between these alternative coordination modes. The following differences are particularly noteworthy:

(a) The Rh—O distance to the coordination oxygen atom(s) is approximately 0.05 Å shorter in the monodentate nitrato-complex.

(b) The spread in N—O bond lengths is smaller in the bidentate complex, i.e. 1.255—1.235 Å, than in the monodentate complex, i.e. 1.266—1.190 Å.

(c) Coordination of the NO_3^- ligand in a bidentate fashion leads to a significant closing up of the angle α which is defined in Table 11, as compared with the free ligand and the monodentate NO_3^- ligand.

Assignment of the nature of the nitrato coordination mode from infrared data

The unambiguous determination of the coordination mode of the nitrato-ligand in Rh(η-C_5Me_5)$(NO_3)_2$ and Rh(η-C_5Me_5)$(NO_3)_2$$(PPh_3)$ by X-ray crystallographic techniques provided the opportunity for confirming the infrared criteria for distinguishing the alternative coordination modes. It has proved to be rather difficult to differentiate the alternative coordination modes of NO_3^- by vibrational spectroscopy since the symmetry of the nitrate ion does not differ for the different modes. Originally Gatehouse [18] noted that the unidentate nitrato-ligand exhibits three bands which can be assigned to ν(NO) at approximately 1420, 1300 and 1000 cm^{-1}, whereas the chelating bidentate nitrato-ligand exhibits three ν(NO) bands at 1480, 1290 and 1020 cm^{-1}. The larger separation of the highest frequency bands has been used as the major criterion for distinguishing the alternative coordination modes.

The infrared data for the rhodium(III) complexes described in this paper are given in Table 12, together with that of [Rh(η-C_5Me_5)(*O*,*O*′-NO_3)(PPh_3)]PF_6 which we have shown to have a bidentate nitrato-ligand [4]. Those complexes with bidentate ligands show a separation of more than 280 cm^{-1} between the high frequency band which is observed at approximately 1500 cm^{-1} and the lower frequency band at approximately 1240 cm^{-1}. For the monodentate nitrato-ligand the higher frequency band which is anticipated at approximately 1420 cm^{-1} is obscured by the C—H bending vibrations originating from the other ligands in the complex, and only the lower frequency band at approximately 1280 cm^{-1} was observed. Therefore, in these cyclopentadienyl com-

TABLE 12

INFRARED FREQUENCIES OF NITRATO-LIGANDS IN RHODIUM(III) NITRATO-COMPLEXES (NUJOL AND HCBD MULLS)(cm^{-1})

Mode	$NaNO_3$	$[Rh(\eta\text{-}C_5Me_5)(O\text{-}NO_3)_2(PPh_3)]$	$[Rh(\eta\text{-}C_5Me_5)(O,O'\text{-}NO_3)(PPh_3)]PF_6$	$[Rh(\eta\text{-}C_5Me_5)(O\text{-}NO_3)(O,O'\text{-}NO_3)]$
$\nu_3(E')$	1405		1568(m, shp)	1585(w, shp)
		1280(s)	1540(s)	1280(s), 1520(s)
$\nu_1(A_1')$	1068	1002(m)	1234(m)	1005(m), 1242(m, shp)
$\nu_2(A_2'')$	831			835(m, shp) [a]
$\nu_4(E')$	692			755(m, shp) [a]

w, weak; s, strong; m, medium; shp, sharp. [a] CsI disc.

plexes the band at approximately 1580 cm^{-1} seems to be the most useful diagnostic test for the presence of bidentate nitrato-ligands.

Acknowledgements

We thank the SRC for financial support, and Johnson Mathey for a generous loan of platinum metals.

References

1 P.B. Critchlow and S.D. Robinson, Coord. Chem. Rev., 25 (1978) 69.
2 C.D. Garner, I.H. Hillier and M.F. Guest, J. Chem. Soc. Dalton, (1975) 1934; A.A. MacDowell, C.D. Garner, I.H. Hillier, C. Demain, J.C. Green, E.A. Seddon and M.F. Guest, J. Chem. Soc. Chem. Commun., (1979) 427.
3 C.C. Addison, N. Logan, S.C. Wallwork and C.D. Garner, Quart. Rev., 25 (1971) 289.
4 S.D. Willoughby, Ph.D. Thesis, University of London, 1979.
5 M.B. Hursthouse and K.M.A. Malik, J. Chem. Soc. Dalton, (1978) 1334.
6 D.T. Cromer and J.T. Waber in International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4, p. 101.
7 D.T. Cromer and J.B. Mann, Acta Cryst. A, 24 (1968) 321.
8 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
9 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
10 The SHELX Crystal Structure Analysis Program, G.M. Sheldrick, University of Cambridge, 1976.
11 G.M. Sheldrick and P. Roberts, University of Cambridge, personal communication
12 W.D.S. Motherwell, University of Cambridge, personal communication.
13 J.A. Ibers, J. Organometal. Chem., 73 (1974) 389.
14 M.R. Churchill and J.A. Stuart, Inorg. Chem., 17 (1978) 3011.
15 M.R. Churchill and J. Wormald, Inorg. Chem., 10 (1971) 572.
16 R.E. La Villa and S.H. Bauer, J. Amer. Chem. Soc., 85 (1963) 3597.
17 A.F. Cameron, K.P. Forrest, R.H. Nuttal and D.W. Taylor, Chem. Commun., (1970) 210.
18 B.M. Gatehouse, S.E. Livingston and R.S. Nyholm, J. Chem. Soc., (1957) 4222; J. Inorg. Nucl. Chem., 8 (1958) 75.