Structural Studies of Substituted Hydrazine Complexes. Part 2.[1] Crystal and Molecular Structure of (η-Cyclo-octa-1,5-diene)tris(*NN*-dimethylhydrazine)hydridoruthenium(II) Hexafluorophosphate

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The crystal and molecular structure of the title complex has been determined by *X*-ray diffraction methods from counter data. The colourless crystals, M = 535.6, are monoclinic with space group $P2_1/n$, a = 14.96(2), b = 16.34(2), c = 9.78(2) Å, β = 92.6(1)°, and Z = 4. The structure has been solved by the heavy-atom method and refined by least-squares to R 0.063 for 1 780 observed reflections (graphite-monochromatized Mo-K_α radiation). The co-ordination geometry of the cation is approximately octahedral with the six sites occupied by a bidentate cyclo-octa-1,5-diene ligand, a hydride ligand (unlocated), and a *fac* configuration of NH_2NMe_2 ligands, bonded to the ruthenium *via* NH_2 nitrogen atoms. The bond from ruthenium to the nitrogen atom *trans* to the hydride ligand [2.28(1) Å] is significantly longer than those to the other two co-ordinated nitrogen atoms [mean 2.19(1) Å]. The small N–Ru–N angles (82, 84, and 86°), short non-bonded distances between the NH_2 and NMe_2 nitrogen atoms (2.87, 2.89, and 2.93 Å), and the symmetrical arrangement of the hydrazine ligands are indicative of hydrogen bonding between these ligands.

FEW transition-metal complexes containing alkyl-substituted hydrazine ligands have so far been reported and most of these are unstable and difficult to characterize.[2] Possible reasons for this instability are (*i*) the ease with which hydrazines undergo redox or deprotonation reactions [3,4] and (*ii*) steric effects which prevent bonding of the more basic substituted nitrogen atom to the metal. However, we have recently isolated a range of stable † ruthenium(II) complexes containing hydrazine ligands, *viz.* $[Ru(cod)(NH_2NHR)_4]^{2+}$ (1; R = H or Me), $[RuH(cod)(NH_2NR^1R^2)_3]^+$ (2: $R^1 = R^2$ = H or Me; R^1 = H, R^2 = Me), and $[\{RuX(H)(cod)\}_2(NH_2NMe_2)]$ (X = Cl or Br) (cod = cyclo-octa-1,5-diene) which are ideal precursors for the synthesis of an extensive series of cationic and neutral ruthenium(II) complexes.[5] During this preparative study we noticed that *NN*-dimethylhydrazine behaved differently to the other hydrazines. For example, under the same conditions used for the preparation of the dications (1) the ionic complex $[RuCl(cod)(NH_2NMe_2)_3]Cl$ was the only product with NH_2NMe_2. However, in the presence of water the hydrido-cation $[RuH(cod)(NH_2NMe_2)_3]^+$ was rapidly formed, whereas the analogous complexes (2: R^1 = R^2 = H; R^1 = Me, R^2 = H) could be isolated only after a much longer period. This difference in reactivity may be ascribed to either steric hindrance by a co-ordinated NMe_2 ligand, or to the weaker binding properties of NH_2NMe_2 which is the least basic of the hydrazines studied.[6]

Since the two relevant *X*-ray structural studies so far reported [7] on monosubstituted hydrazine derivatives are insufficient to elucidate all possible co-ordination modes of substituted hydrazines, we decided to carry out *X*-ray crystallographic analyses of the structures of certain of these derivatives. We were interested to discover (*i*) the conditions which stabilize co-ordination of hydrazines, and (*ii*) how alkyl or aryl groups affect the ligating ability of the substituted nitrogen atom and the configuration of the complex. We considered that the determination of the structure of the salt $[RuH(cod)(NH_2NMe_2)_3][PF_6]$, in view of its manner of preparation, solution properties,[5] and high reactivity,[8] would provide a suitable starting point in this programme. In addition, this appears to be the first *X*-ray diffraction study of the structure of a metal complex containing *NN*-disubstituted hydrazine ligands.

EXPERIMENTAL

Crystal Data.—$[RuH(cod)(NH_2NMe_2)_3][PF_6]$, M = 535.6, Monoclinic, space group $P2_1/n$, a = 14.96(2), b = 16.34(2), c = 9.78(2) Å, β = 92.6(1)°, U = 2 388.2 Å^3, D_m (by flotation) = 1.47, Z = 4, D_c = 1.49 g cm^{-3}, $F(000)$ = 1 104, Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 7.73 cm^{-1}.

The space group was determined from preliminary oscillation and Weissenberg photographs. Final lattice parameters were obtained from a least-squares refinement of the setting angles of 24 reflections. The complex was prepared as previously reported,[5] and a colourless crystal of dimensions 0.12 × 0.28 × 0.36 mm was used for data collection on the Philips PW 1100 four-circle diffractometer at the N.P.R.L., C.S.I.R. Intensity measurements (graphite-monochromatized Mo-K_α radiation) were based on the ω—2θ scan routine, in the range θ 3—20°. Each reflection was scanned for 30 s and the same time was spent on the background count. 1 780 Reflections out of 2 195 were considered observed on the basis of $I > 3\sigma(I)$. Standard reflections (131), $(3\bar{1}5)$, and $(\bar{2}55)$, remeasured every hour, changed respectively by 1.7, 1.0, and 2.1% during the 42 h of data collection. Corrections were made for Lorentz and polarization effects but not for extinction, absorption [μ(Mo-K_α) 7.73 cm^{-1}], or decomposition.

Structure Solution and Refinement.—The structure was solved by a conventional heavy-atom method. Refinement was carried out, using anisotropic thermal parameters

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† Sufficient for isolation and easy manipulation.

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for Ru, P, and F atoms, and isotropic thermal parameters for C and N. No hydride atom was located. The residual, R, converged to 0.063 with unit weights assigned to the observations. All the calculations were made on a CDC CYBER 174 computer with the program SHELX-76.[9] Atomic scattering factors and dispersion corrections were taken from ref. 10. Figures were drawn by the ORTEP program of Johnson.[11] Observed and calculated structure factors and the thermal parameters from the final least-squares cycle are listed in Supplementary Publication No. SUP 22277 (14 pp.).* Atomic co-ordinates are listed in Table 1, bond lengths and angles in Tables 2 and 3, and selected intramolecular separations in Table 4. Figure 1 gives the numbering system in the cation, while Figure 2 shows the arrangement of the hydrazine ligands around the ruthenium atom.

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ru	990(1)	2 006(1)	2 308(1)
C(1)	596(8)	999(8)	1 001(13)
C(2)	1 425(8)	822(8)	1 677(13)
C(3)	1 574(9)	236(9)	2 913(14)
C(4)	895(9)	391(8)	4 032(14)
C(5)	600(8)	1 312(8)	4 092(13)
C(6)	−170(8)	1 603(8)	3 387(12)
C(7)	−797(9)	1 079(9)	2 471(14)
C(8)	−294(9)	576(8)	1 378(13)
N(11)	1 778(6)	2 535(6)	728(9)
N(12)	1 606(7)	3 385(6)	337(10)
C(121)	2 415(10)	3 691(9)	−362(15)
C(122)	795(10)	3 432(10)	−592(16)
N(21)	2 272(6)	2 158(6)	3 633(9)
N(22)	3 097(7)	2 379(7)	2 936(11)
C(221)	3 648(10)	2 933(10)	3 864(15)
C(222)	3 594(11)	1 625(10)	2 631(17)
N(31)	767(7)	3 275(6)	2 974(10)
N(32)	1 258(8)	3 619(7)	4 177(12)
C(321)	724(11)	3 462(11)	5 389(17)
C(322)	1 364(12)	4 522(11)	3 967(17)
P	−2 022(3)	3 863(3)	2 519(4)
F(1)	−2 327(10)	4 138(7)	1 061(10)
F(2)	−2 731(15)	3 259(14)	2 387(23)
F(3)	−2 522(15)	4 540(14)	3 087(17)
F(4)	−1 254(13)	4 466(13)	2 672(19)
F(5)	−1 759(11)	3 571(9)	4 006(11)
F(6)	−1 373(14)	3 291(14)	1 959(17)

TABLE 2

Bond lengths (Å)

Ru–N(11)	2.17(1)	Ru–C(1)	2.15(1)
Ru–N(21)	2.28(1)	Ru–C(2)	2.14(1)
Ru–N(31)	2.20(1)	Ru–C(5)	2.18(1)
N(11)–N(12)	1.46(1)	Ru–C(6)	2.17(1)
N(21)–N(22)	1.48(1)	C(1)–C(2)	1.41(2)
N(31)–N(32)	1.47(1)	C(2)–C(3)	1.55(2)
N(12)–C(121)	1.50(2)	C(3)–C(4)	1.55(2)
N(12)–C(122)	1.48(2)	C(4)–C(5)	1.57(2)
N(22)–C(221)	1.50(2)	C(5)–C(6)	1.40(2)
N(22)–C(222)	1.48(2)	C(6)–C(7)	1.53(2)
N(32)–C(321)	1.48(2)	C(7)–C(8)	1.57(2)
N(32)–C(322)	1.50(2)	C(8)–C(1)	1.56(2)
P–F(1)	1.54(1)	P–F(4)	1.52(2)
P–F(2)	1.45(2)	P–F(5)	1.56(1)
P–F(3)	1.46(1)	P–F(6)	1.47(1)

RESULTS AND DISCUSSION

The crystal contains discrete cations and anions. The closest contacts are between F atoms of the hexafluorophosphate anion and N atoms of the hydrazine ligands of the cation. All are greater than 3.2 Å (Table 4). The $[PF_6]^-$ anion exhibits the high thermal motion of F atoms usually associated with this anion.

TABLE 3

Bond angles (°)

N(11)–Ru–N(21)	83.7(3)	C(1)–Ru–C(2)	38.3(5)
N(11)–Ru–N(31)	86.0(4)	C(5)–Ru–C(6)	37.5(4)
N(21)–Ru–N(31)	82.2(4)	C(1)–Ru–C(5)	90.1(5)
N(11)–Ru–C(1)	91.4(4)	C(1)–Ru–C(6)	81.6(5)
N(11)–Ru–C(2)	88.4(4)	C(2)–Ru–C(5)	81.8(5)
N(11)–Ru–C(5)	162.2(4)	C(2)–Ru–C(6)	97.3(5)
N(11)–Ru–C(6)	160.0(4)	C(1)–C(2)–C(3)	126(1)
N(21)–Ru–C(1)	128.5(4)	C(2)–C(3)–C(4)	112(1)
N(21)–Ru–C(2)	90.2(4)	C(3)–C(4)–C(5)	112(1)
N(21)–Ru–C(5)	81.4(4)	C(4)–C(5)–C(6)	122(1)
N(21)–Ru–C(6)	115.3(4)	C(5)–C(6)–C(7)	125(1)
Ru–N(11)–N(12)	118.1(7)	C(6)–C(7)–C(8)	113(1)
N(11)–N(12)–C(121)	108(1)	C(7)–C(8)–C(1)	112(1)
N(11)–N(12)–C(122)	110(1)	C(8)–C(1)–C(2)	123(1)
C(121)–N(12)–C(122)	111(1)	F(1)–P–F(2)	86.1(8)
Ru–N(21)–N(22)	117.5(7)	F(1)–P–F(3)	89.8(9)
N(21)–N(22)–C(221)	108(1)	F(1)–P–F(4)	95.3(9)
N(21)–N(22)–C(222)	109(1)	F(1)–P–F(5)	177.4(9)
C(221)–N(22)–C(222)	111(1)	F(1)–P–F(6)	90.8(9)
Ru–N(31)–N(32)	121.2(7)	F(2)–P–F(3)	99(2)
N(31)–N(32)–C(321)	108(1)	F(2)–P–F(4)	178(1)
N(31)–N(32)–C(322)	109(1)	F(2)–P–F(5)	91.6(9)
C(321)–N(32)–C(322)	110(1)	F(2)–P–F(6)	92(2)
F(4)–P–F(5)	87.0(9)	F(3)–P–F(4)	83(1)
F(4)–P–F(6)	87(1)	F(3)–P–F(5)	89.4(9)
F(5)–P–F(6)	90.6(9)	F(3)–P–F(6)	169(2)
N(31)–Ru–C(1)	148.7(4)	N(31)–Ru–C(5)	101.7(4)
N(31)–Ru–C(2)	171.0(4)	N(31)–Ru–C(6)	90.4(4)

TABLE 4

Selected intramolecular distances (Å)

N(11) · · · N(22)	2.87(1)	N(21) · · · F(1)	3.22(2)
N(21) · · · N(32)	2.89(1)	N(31) · · · F(6)	3.31(2)
N(31) · · · N(12)	2.93(1)	Ru · · · C(3)	3.07(1)
Ru · · · C(7)	3.08(1)	Ru · · · C(4)	3.14(1)
Ru · · · C(8)	3.13(1)		

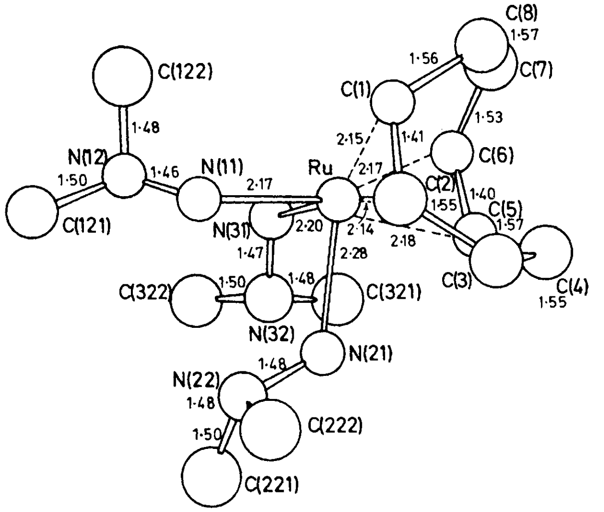

FIGURE 1 Atom-numbering scheme

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[9] G. M. Sheldrick, personal communication, 1976.

[10] 'International Tables for *X*-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

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The P–F distances range from 1.45 to 1.54 Å and the F–P–F angles from 82 to 100° and from 169 to 178°.

The co-ordination geometry of the cation is distorted octahedral with the six sites around the ruthenium occupied by a bidentate cyclo-octa-1,5-diene ligand, a hydride ligand,* and a *fac* configuration of *NN*-dimethylhydrazine ligands, co-ordinated *via* their NH_2 nitrogen atoms. The stereochemistry is as predicted,[5] with the hydrazine ligands co-ordinated *via* the less basic but more sterically favoured nitrogen atoms.

The lengths of the two approximately equal Ru–N bonds (mean 2.19 Å) to the hydrazine ligands *trans* to the olefinic groups are significantly different from that of the Ru–N bond *trans* to the hydride ligand (2.28 Å), indicating that the hydride ligand exerts the stronger structural *trans* influence. The two shorter Ru–N bond lengths (mean 2.19 Å) and the Ru–N–N angles (118, 118, and 121°) are similar to the values found[1] for the corresponding parameters in the bis(hydrazone)ruthenium(II) complex $[Ru(NH_2NCMe_2)_2\{P(OMe)_3\}_4][BPh_4]_2$. The N–N distances (1.46, 1.47, and 1.48 Å) are in the range 1.45—1.48 Å found[3] previously in structures of complexes containing either unidentate or bridging NH_2NH_2 ligands. The N–C bond lengths are normal, averaging 1.49 Å, and require no comment.

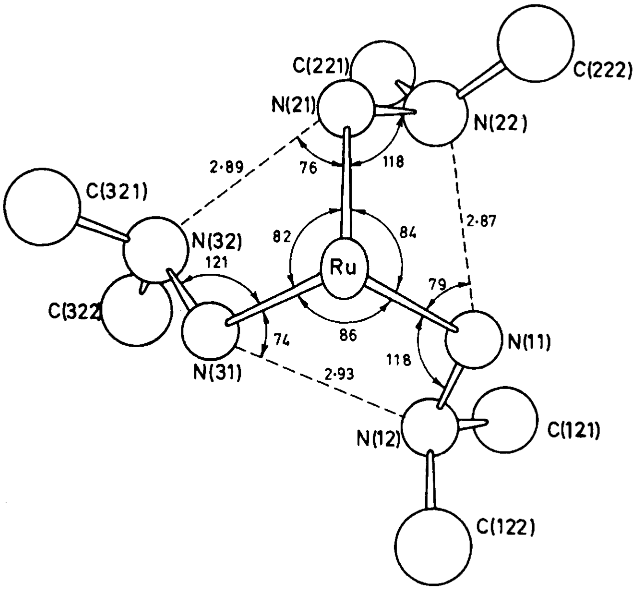

FIGURE 2 Arrangement of the hydrazine ligands around the ruthenium

A striking aspect of the structure is the evidence for three strong hydrogen bonds[12] between the substituted and unsubstituted ends of different hydrazine ligands, as shown by (*i*) the small N–Ru–N angles (82, 84, and 86°), (*ii*) the close non-bonded contacts (2.87, 2.89, and 2.93 Å) between NH_2 and NMe_2 nitrogen atoms, and (*iii*) the symmetrical arrangement of the hydrazine ligands (Figure 2; a pseudo-three-fold rotation axis passes through Ru perpendicular to the plane of the projection). The N–N–C and C–N–C angles (mean 109°) are all close (±1.5°) to the tetrahedral values.

The cod ring has the usual conformation of the four doubly bonded C atoms within bonding distance of Ru (2.14—2.19 Å) and the remaining four C atoms at non-bonding distances (3.07—3.14 Å). C–C Bond lengths average 1.55 and 1.40 Å for single and double bonds respectively.

Conclusion.—The configuration adopted by the cation is thus the one which both maximizes hydrogen-bonded contacts and minimizes the non-bonded contacts between the bulky NMe_2 ends of the hydrazine ligands. It is apparent that four *NN*-dimethylhydrazine ligands would easily fit around the Ru(cod) moiety if bonded *via* the NH_2 nitrogen atoms, and hence it could be that in the ruthenium(II) systems studied[5] the electronic properties of the hydrazine ligands are the dominant feature in determining the nature of the products.

The ^1H n.m.r. spectrum of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ exhibits an unusual feature, which can now be tentatively explained. Resonances at τ 3.83 (br, 2 H) and 5.10 (centre of an AB quartet, 4 H) were assigned to NH_2 protons from D_2O exchanges. The presence of an AB quartet[13] signifies that the two hydrogen atoms on each of the nitrogen atoms situated *trans* to the olefinic groups are non-equivalent (there is no plane of symmetry along these Ru–N bonds). This condition can only be fulfilled if ligand exchange or rotation about the Ru–N bond is slow enough to allow a magnetic distinction to be made between the two NH_2 protons. A ready explanation for this phenomenon is that rotation or dissociation of the hydrazine ligands is hindered by their strong hydrogen bonding, which is shown to be present by the molecular-structure determination.

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* The hydride ligand could not be positively identified from the final difference-Fourier map, but a peak of 0.65 e $Å^{-3}$ was observed in an approximately *trans* position to N(21), at a distance of 1.36 Å from the Ru atom.

[12] G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' W. H. Freeman and Co., San Francisco, 1960, p. 228.

[13] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, 119.