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Preparation and X-ray Structure of a Trinuclear Rhodium Complex with the Polydentate 1,8-Naphthyridine-2-one (Onapy) Ligand: $[Rh_3(\mu_3\text{-Onapy})_2(CO)_2(cod)_2](ClO_4)\cdot 1.5C_2H_4Cl_2$

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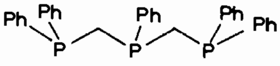
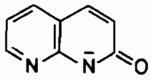
As part of our studies exploring the use of polydentate nitrogen-donor ligands for the construction of bi- and polynuclear rhodium(I) and iridium(I) complexes we have examined the coordinative behaviour of 1,8-naphthyridine (napy) [1] and 7-azaindole [2]. These ligands have the same structural elements as bis(diphenylphosphino)methane (dppm), *i.e.* two donor centers bonded through a single carbon atom but in a rigid framework. On the other hand, these bidentate nitrogen-donor ligands promote a *cis*-$Rh_2(\mu\text{-N–C–N})_2$ arrangement in their binuclear complexes that differs from the usual *trans*-$Rh_2(\mu\text{-dppm})_2$ disposition for the related bis(diphenylphosphino)methane complexes [3].

Balch and coworkers have reported the preparation and properties of trinuclear rhodium(I) complexes with the ligand bis(diphenylphosphinomethyl)phenylphosphine (dpmp) (A) [4]. In this context,



A



B

we have recently hypothesized the ability of the 1,8-naphthyridine-2-one ligand (B) to promote the formation of trinuclear rhodium complexes [5], and herein we describe the preparation and X-ray structure of one of the trinuclear complexes formed by the polydentate 1,8-naphthyridine-2-one ligand (Onapy).

The trinuclear complex $[Rh_3(\mu_3\text{-Onapy})_2(CO)_2(cod)_2](ClO_4)$ can be prepared by slow addition of the solvated intermediate $[Rh(CO)_2(Me_2CO)_x](ClO_4)$ (0.1 mmol) to a dichloromethane solution of the yellow mononuclear compound [Rh(Onapy)(cod)] (cod: 1,5-cyclooctadiene) (0.2 mmol). After working-up, the complex was isolated and characterized by elemental analyses, conductivity measurements and IR spectroscopy. Furthermore, violet prismatic crystals of $[Rh_3(\mu_3\text{-Onapy})_2(CO)_2(cod)_2](ClO_4)\cdot 1.5C_2H_4Cl_2$, suitable for an X-ray analysis, were obtained by slow diffusion of pentane into a solution of the complex in 1,2-dichloroethane at −10 °C. One of them, with approximate dimensions 0.20 × 0.25 × 0.30 mm, was used for the data collection.

Crystal Data

$C_{37}H_{40}Cl_4N_4O_8Rh_3$, M = 1119.27, triclinic, $a = 18.558(4)$, $b = 19.044(4)$, $c = 12.398(6)$ Å, $\alpha = 69.79(2)$, $\beta = 88.86(2)$, $\gamma = 88.56(2)°$, $V = 4110(2)$ Å^3 (by least-squares refinement of the θ values of 30 selected reflections accurately measured in the range 11–22°), space group $P\bar{1}$, $Z = 4$, $D_c = 1.81$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 14.88$ cm^{-1}, $F(000) = 2228$. Philips PW 1100 diffractometer, $\omega/2\theta$ mode; monochromated Mo Kα radiation ($\lambda = 0.71069$ Å); 12 419 reflections measured ($3 \leqslant \theta \leqslant 24°$), of which 8706 unique reflections were considered observed [$I \geqslant 3\sigma(I)$]; usual Lorentz and polarization reduction; absorption correction was applied using a semi-empirical method with maximum and minimum corrections of 1.26 and 1.00 [6]. The structure was solved by direct (MULTAN) and conventional Fourier methods. Full matrix least-squares refinement was carried out with anisotropic thermal parameters for the metals and atoms directly bonded to them (excepting those of the diolefinic ligands). Three independent solvent molecules were found, one of them being partially disordered. Three positions were assigned for the atoms disordered with occupancy factors 0.4 [Cl(23), C(23)], 0.3 [Cl(33), C(33)] and 0.3 [Cl(43), C(43)]. No attempt was made to calculate the hydrogen atoms. Weighting scheme used: $w = 1.6868/[\sigma^2(F_o) + 0.005\ F_o^2]$. Final R and R' values were 0.059 and 0.073. Final atomic coordinates for the non-hydrogen atoms are given in Table I. Thermal parameters and a list of structural factors are available from the authors on request.

In the crystal structure of $[Rh_3(\mu_3\text{-Onapy})_2(CO)_2(cod)_2](ClO_4)\cdot 1.5C_2H_4Cl_2$ two crystallographically independent (but practically equal) trinuclear cations and perchlorate anions are present together with three independent 1,2-dichloroethane molecules of crystallization. A view of the structure of the cation with the atomic numbering scheme is shown in Fig. 1, together with some significant bond distances (the values referring to the second independent cation are between brackets hereafter). The cationic complex, having an approximate C_2 symmetry, is trinuclear with two Onapy ligands triply bridging the metals through their two N atoms

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TABLE I. Fractional Atomic Coordinates ($\times 10^4$) with e.s.d.s in Parentheses for the Non-hydrogen Atoms

Atom	*x/a*	*y/b*	*z/c*
Rh11	7546(1)	7577(1)	1273(1)
Rh12	2338(1)	7379(1)	6670(1)
Rh21	7983(1)	6975(1)	−504(1)
Rh22	2907(1)	6958(1)	4769(1)
Rh31	8463(1)	6694(1)	−2571(1)
Rh32	3504(1)	6880(1)	2624(1)
Cl1	4770(2)	1484(2)	1410(3)
Cl2	8807(2)	−561(2)	2583(4)
O11	6750(5)	5949(6)	−210(8)
O12	1778(5)	5820(5)	4964(8)
O21	8869(5)	5826(5)	1257(7)
O22	3817(4)	5706(4)	6304(7)
O31	7487(4)	7282(4)	−2997(6)
O32	2455(4)	7366(4)	2242(6)
O41	8671(4)	7748(4)	1006(6)
O42	3419(3)	7690(4)	6482(6)
N11	7385(4)	8498(4)	−341(7)
N12	2073(4)	8334(4)	5134(7)
N21	7428(4)	7878(4)	−1679(7)
N22	2256(4)	7824(4)	3699(6)
N31	8983(4)	7740(4)	−2706(7)
N32	3907(4)	7932(5)	2698(7)
N41	8841(4)	7720(4)	−796(6)
N42	3669(4)	7789(4)	4605(6)
C11	7209(6)	6353(7)	−299(10)
C12	2202(6)	6266(6)	4890(10)
C21	8523(6)	6234(6)	582(9)
C22	3483(5)	6191(6)	5737(9)
O51	4224(6)	2055(6)	1240(9)
O52	8706(7)	99(8)	2826(11)
O61	4781(6)	1013(6)	2577(9)
O62	8587(10)	−1232(11)	3571(16)
O71	4567(7)	1019(8)	817(11)
O72	8384(11)	−613(11)	1796(17)
O81	5420(7)	1808(8)	1069(11)
O82	9543(9)	−654(9)	2387(14)
C31	7325(6)	9141(6)	−111(9)
C32	1875(6)	8945(6)	5448(9)
C41	7142(6)	9837(7)	−975(11)
C42	1539(7)	9577(7)	4684(11)
C51	6982(6)	9859(7)	−2059(10)
C52	1375(7)	9610(7)	3618(11)
C61	7071(6)	9186(6)	−2329(9)
C62	1592(5)	9010(6)	3252(9)
C71	6929(6)	9154(7)	−3435(10)
C72	1438(6)	9004(7)	2137(10)
C81	7055(6)	8511(7)	−3648(10)
C82	1699(6)	8419(6)	1816(9)
C91	7325(5)	7874(5)	−2745(8)
C92	2154(6)	7833(6)	2628(9)
C101	7283(5)	8527(5)	−1444(8)
C102	1978(5)	8383(5)	4056(8)
C111	9221(6)	8085(6)	−3794(9)
C112	4185(6)	8334(6)	1661(9)
C121	9667(5)	8691(6)	−4088(9)
C122	4569(7)	8986(7)	1485(11)
C131	9894(6)	8964(6)	−3254(9)
C132	4723(6)	9204(7)	2367(10)
C141	9633(5)	8626(5)	−2136(8)
C142	4425(6)	8791(6)	3489(9)
C151	9824(6)	8888(6)	−1224(9)
C152	4554(6)	8997(7)	4492(10)
C161	9501(6)	8588(6)	−151(9)
C162	4258(6)	8596(7)	5477(10)
C171	8994(5)	8001(5)	38(8)
C172	3753(5)	8010(5)	5535(8)
C181	9156(5)	8014(5)	−1876(8)
C182	4012(5)	8183(5)	3583(8)
C191	6489(6)	7779(7)	1730(10)
C192	1246(6)	7437(6)	7173(10)
C201	6428(9)	7873(10)	2902(14)
C202	1197(7)	7450(7)	8388(11)
C211	7105(8)	7574(8)	3647(12)
C212	1787(7)	6955(7)	9190(11)
C221	7716(6)	7330(6)	3058(9)
C222	2480(6)	6962(6)	8494(9)
C231	7751(6)	6669(6)	2800(10)
C232	2671(6)	6392(6)	8046(9)
C241	7202(8)	6087(9)	3064(13)
C242	2175(7)	5745(7)	8136(10)
C251	6492(8)	6337(9)	2465(13)
C252	1378(7)	5984(8)	7721(11)
C261	6507(6)	7100(7)	1535(10)
C262	1350(6)	6795(6)	6855(9)
C271	8104(6)	6041(6)	−3532(10)
C272	3247(6)	6241(6)	1601(9)
C281	8696(7)	5874(8)	−4226(11)
C282	3896(9)	6119(10)	933(15)
C291	9432(8)	5794(8)	−3693(12)
C292	4588(7)	6310(7)	1236(11)
C301	9479(6)	6273(7)	−2908(10)
C302	4567(6)	6631(7)	2186(10)
C311	9318(6)	5990(6)	−1730(9)
C312	4431(6)	6203(6)	3340(9)
C321	9084(7)	5166(7)	−1083(10)
C322	4277(7)	5377(7)	3772(11)
C331	8404(7)	4971(8)	−1627(11)
C332	3531(9)	5185(10)	3468(14)
C341	7956(6)	5657(6)	−2339(10)
C342	3096(6)	5835(7)	2713(10)
Cl11	4578(2)	3209(3)	4263(4)
Cl12	6446(2)	−227(3)	3570(4)
Cl21	5050(2)	4240(3)	1523(4)
Cl22	7184(2)	1443(3)	466(4)
C351	4398(9)	2984(9)	2963(13)
C352	6674(10)	266(11)	2031(16)
C361	5000(8)	3287(9)	2097(13)
C362	6998(10)	944(11)	2016(16)
Cl13	9667(3)	2550(3)	5800(5)
Cl33	9602(12)	3276(12)	8652(19)
C13	10075(14)	2477(14)	7078(23)
C33	10023(63)	3143(43)	7469(87)
Cl23	9863(9)	3842(9)	6884(14)
Cl43	9229(12)	3341(12)	7777(19)
C23	9612(38)	2915(36)	7692(55)
C43	10089(32)	3226(45)	7240(124)

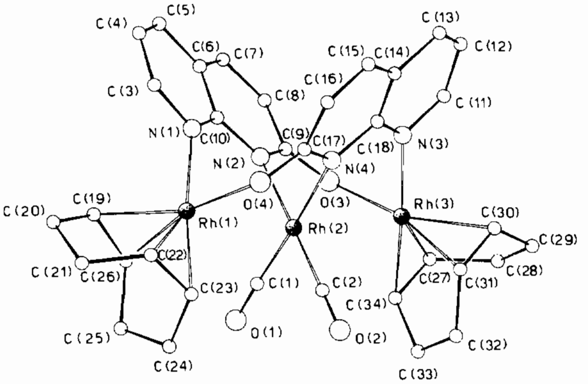

Fig. 1. View of the cationic complex $[Rh_3(\mu\text{-Onapy})_2(CO)_2(cod)_2]^+$ showing the atomic numbering scheme. Selected bond distances (Å): Rh(1)–Rh(2) 2.907(3) [2.911(3)], Rh(1)–N(1) 2.178(7) [2.185(7)], Rh(1)–O(4) 2.123(8) [2.092(6)], Rh(2)–Rh(3) 2.912(2) [2.910(2)], Rh(2)–N(2) 2.093(7) [2.095(7)], Rh(2)–N(4) 2.101(8) [2.103(8)], Rh(2)–C(1) 1.842(12) [1.847(12)], Rh(2)–C(2) 1.865(10) [1.865(9)], Rh(3)–N(3) 2.188(8) [2.188(10)], Rh(3)–O(3) 2.083(7) [2.215(7)]. The two values refer to the first and second crystallographically independent cations in the unit cell (those of the second are between brackets).

and the ketonic oxygen. If the midpoints of the olefinic bonds of the cod ligands are taken into account, all three Rh atoms show slightly distorted, but different, square planar environments. The central Rh atom, Rh(2), is bound to two N atoms of the Onapy ligands and to two carbon atoms from terminal carbonyls; the two terminal Rh atoms, Rh(1) and Rh(3), are bound to a ketonic oxygen and to a pyridinic nitrogen atom from two Onapy ligands and complete their coordination through the two olefinic bonds of a cod molecule.

The three Rh atoms show an approximate linear arrangement, the Rh(1)–Rh(2)–Rh(3) angle being 168.2(1) [167.8(1)°]. Similar linear or slightly bent trinuclear Rh complexes supported by P-donor ligands and CO or halide bridges have been recently reported [4]. As far as we know, this is the first trinuclear Rh(I) complex characterized crystallographically with a nearly linear arrangement of metal atoms supported only by a N- and O-donor ligand.

The Rh–Rh distances, 2.907(3) [2.911(3)] and 2.912(2) [2.910(2)] Å, are rather short and comparable to those found in the related binuclear complexes $[Rh_2(\mu\text{-Onapy})_2(CO)_4]$ [5] and $[Rh_2(\mu\text{-napy})_2(nbd)_2]^{2+}$ [1], 2.880(2) and 2.916(3) Å respectively; these separations are generally considered indicative of metal–metal interactions.

As in the related binuclear complex $[Rh_2(\mu\text{-Onapy})_2(CO)_4]$ [5], the two Onapy ligands are roughly planar, forming a dihedral angle between the mean planes passing through them of 125.2(2) [113.7(2)°].

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