Chimia 43 (1989) 167–168

A Cationic Compound of $Ru_2^{5\oplus}$ Containing a Coordinated $PF_4O^{\ominus}$ Ion**

F. Albert Cotton* and Marek Matusz

Abstract: The compound $Ru_2(PhNNNPh)_4$ was oxidized in CH_2Cl_2 with $AgPF_6$. From a $CH_2Cl_2/(C_2H_5)_2O$ solution left to evaporate in air for one month blue-green crystals of $Ru_2(PhNNNPh)_4OPF_4$, in which the $PF_4O^{\ominus}$ ion is coordinated to one Ru atom (Ru–O: 220(1) pm), were obtained. Other principal distances are: Ru–Ru 238.5(2) pm, P–O 145.5(11) pm, P–F 159(1) pm. Angles in the $PF_4O^{\ominus}$ ion are: O-P-F 111.6(4)°, F-P-F (*cis*) 82.2(6)°, F-P-F (*trans*) 136.7(6)°.

The preparation of $Ru_2(PhN_3Ph)_4$, **1**, as well as its derivatives, **1**$(NO)_2$, **1**(*t*BuNC), and **1**$(CO)_2$ has been reported by *Lindsay* et al. [1], but they were unable to obtain crystalline material for structural characterization of **1**. In this Laboratory, we have been able to obtain the similar compound, $Ru_2(p\text{To1}N_3\,p\text{Tol})_4$, **2**, and to characterize it structurally as well as in other ways [2]. Based on the reported diamagnetic ground states of both **1** and **2** and the long Ru–Ru distance we observed [2] in **2**, viz. 2.417(2) Å, we previously proposed that **2** (and presumably **1**) have ground states based on the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*4}$, which is in contrast to the ground state $\sigma^2\pi^4\delta^2\delta^*{}^2\pi^{*2}$ for which we have recently provided evidence [3] in $Ru_2(O_2CR)_4L_2$ molecules.

Since the removal of one electron from a $\sigma^2\pi^4\delta^2\pi^{*4}$ configuration should give a $\sigma^2\pi^4\delta^2\pi^{*3}$ configuration, we would expect a compound containing one of the cations, $Ru_2(RN_3R)_4^{\oplus}$, R = C_6H_5 or *p*-$CH_3C_6H_4$, to have certain characteristics (e.g., one unpaired electron, a $\pi\rightarrow\pi^*$ absorption band as well as a $\delta\rightarrow\delta^*$ band). Of particular interest, if such a cation could be observed free of any axial ligation, the Ru–Ru distance might be expected to decrease by about 7 pm (the basis for this estimate is given in Ref. [2]), whereas if significant axial ligation occurs, the reduction would be less drastic. We have attempted the preparation of some $Ru_2(RN_3R)_4X$ compounds to test these predictions. In one case, we obtained a product with an additional feature of unusual interest, and that is described here.

Experimental

$AgPF_6$ was purchased from Strem Chemical Company and used as received. The preparation of $Ru_2(C_6H_5NNNC_6H_5)_4$ followed a literature method [1]. The product was recrystallized from toluene.

$Ru_2(PhN_3Ph)_4$, 0.595 g (1 mmol) was dissolved in 20 mL CH_2Cl_2. To this a solution of $AgPF_6$, 0.253 g (1 mmol) in 5 mL of CH_2Cl_2 was added with stirring. The color of the reaction mixture changed immediately from dark purple to deep green. After stirring at room temperature for 30 min the reaction mixture was filtered through a short Celite column to remove precipitated metallic silver. At this point it was concluded that the $Ru_2(PhN_3Ph)_4^{\oplus}$ is air stable since monitoring of the UV/VIS spectrum over a period of two days did not show any change.

Attempts to grow single crystals from different solvent mixtures failed at first. A dichloromethane-ether solution that was left for slow evaporation in air for about one month deposited some crystalline material. This solid was washed with methanol, which removed some green soluble material and the remaining solids were redissolved in dichloromethane and layered with ether. A small crop of nicely shaped crystals grew in a few days and these were used for X-ray study. UV/VIS (CH_2Cl_2 solution) $\lambda_{max} = 710$ nm, $\lambda_{max} = 318$ nm (this is the spectrum of the actual crystals used for the X-ray analysis).

X-ray Crystallography: The crystals were examined under a microscope and most of them were single crystals. The color was blue-green and the morphology was thin rectangular plates. The unit cell dimensions and the Laue class (4/m) were confirmed with axial photographs. The space group, P4/n (No. 85) was uniquely determined from systematic absences. Treatment of the data was routine to our Laboratory. Data reduction and refinement were done with an SDP-plus package software.

The structure was solved by the direct methods part of the SHELXS-86 program package [4]. It revealed the dinuclear molecule on a special position (fourfold axis). A few cycles of least squares refinement and a difference Fourier map showed additional electron density on the fourfold axis that was at first assumed to be the $PF_6^{\ominus}$ anion. The P atom behaved well under refinement. However, one of the axial F atoms was missing, and the moiety was refined as PF_5 to give agreement factors $R_1 = 0.0686$ and $R_2 = 0.0912$ (all anisotropic refinement). The missing fluorine atom could not be located in a difference Fourier map and an attempt to refine it in a calculated position failed. In addition, the four equatorial fluorine atoms refused to remain in a plane containing the phosphorus atom; they always moved away from the rest of the molecule. Finally, the short distance from P to Ru(1) could not be reconciled with a P-F-Ru group having a normal P–F distance and a weak F to Ru bond. As soon as the axial ligand was assigned as PF_4O, all these difficulties were avoided. With this model the refinement (all anisotropic) converged to $R_1 = 0.0561$ and $R_2 = 0.0761$. Analysis of the data showed that two low-angle, weak reflections gave a very bad fit and these were removed from the data set. Final figures of merit are summarized in Table 1. Further crystallographic data and details are available on request.

Table 1. Crystal Data for $[Ru_2(Ph_2N_3)_4]OPF_4$.

Formula	$Ru_2PF_4ON_{12}C_{48}H_{40}$
Formula weight	1110.0
Space group	P4/n
Systematic absences	hk0: h + k ≠ 2n
a[Å]	13.370(3)
b[Å]	13.370(3)
c[Å]	12.671(5)
α[deg]	90
β[deg]	90
γ[deg]	90
V[Å^3]	2265(1)
Z	2
ϱ_{calc}[g/cm^3]	1.628
Crystal size [mm]	0.2 × 0.25 × 0.05
$\mu(Mo_{K\alpha})$ [cm^{-1}]	7.554
Data collection instrument	CAD-4
Radiation (monochromated in incident beam)	$Mo_{K\alpha}$ ($\lambda_\alpha = 0.71073$ Å)
Orientation reflections, number, range (2θ)	25, 15 < 2θ < 27
Temperature [°C]	−80
Scan method	ω–2θ
Data collection range, 2θ[deg]	4, 50
Number of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1644, 1292
Number of parameters refined	157
Trans. factors, max., min.	0.9911, 0.9233
R[a]	0.0504
R_w[b]	0.0647
Quality-of-fit indicator[c]	1.768
Largest shift/esd, final cycle	0.02
Largest peak [e/Å^3]	0.65

[a] $R = \Sigma\|\|F_o| - |F_c|\|/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

The novel molecule is depicted in Fig. 1, and the principal interatomic distances and bond angles are listed in Table 2. The molecule has crystallographic 4-fold symmetry and the P-O-Ru(1)-Ru(2) chain is strictly linear. The central Ru_2N_8 group has essentially (but not exactly) D_{4h} symmetry. The Ru–Ru distance, 238.5(2) pm is about as expected. While the loss of one π* electron might be expected to shorten it by ca. 7 pm from that in the parent neutral molecule, which would lead to a value of ca. 235 pm, the presence of a strongly coordinated axial ligand weakens the σ bond and causes an increase, resulting in the larger observed value.

Unexpectedly, the most interesting feature of this structure is the presence of a $PF_4O^{\ominus}$ ion as the axial ligand. The presence of this species is proposed on the basis

* *Correspondence:* Prof. Dr. F. A. Cotton
Department of Chemistry and
Laboratory for Molecular Structure and Bonding
Texas A&M University
College Station, TX 77843 (USA)

** *Acknowledgements:* We thank the U.S. National Science Foundation for support and Miss Charla McCaleb for the literature search.

of X-ray crystallographic data and deductions therefrom.

It does not appear that the $PF_4O^{\ominus}$ ion (nor its analogs, $AsF_4O^{\ominus}$ and $SbF_4O^{\ominus}$) has previously been obtained in an isolable chemical compound. While there is some evidence for its formation in negative-ion mass spectra[5], thermodynamic considerations were said to indicate[6] that it is distinctly unstable (by 76 kcal mol^{-1}) to the following disproportionation process:

$$2\ PF_4O^{\ominus} \rightarrow PF_6^{\ominus} + PF_2O_2^{\ominus}$$

Experimental studies have either supported this conclusion[7] or have, at the very least, failed to provide evidence for the existence[8] of the $PF_4O^{\ominus}$ ion. Experimental results for related arsenic and antimony systems show that by loss of HF from $[AsF_5(OH)]^{\ominus}$ and $[SbF_5(OH)]^{\ominus}$ only polymeric substances are obtained[9].

Presumably the $PF_4O^{\ominus}$ ion in our compound arose by partial hydrolysis of the $PF_6^{\ominus}$ ion over the long period of time required to obtain the crystalline product, during which the solution was exposed to ordinary laboratory air that contained moisture. The resulting $PF_4O^{\ominus}$ ion may indeed be unstable, as indicated by earlier studies, in a simple ionic compound such as $CsPF_4O$, but it is able to exist in this compound by virtue of being coordinated strongly.

Received: June 7, 1989 [FC 167]

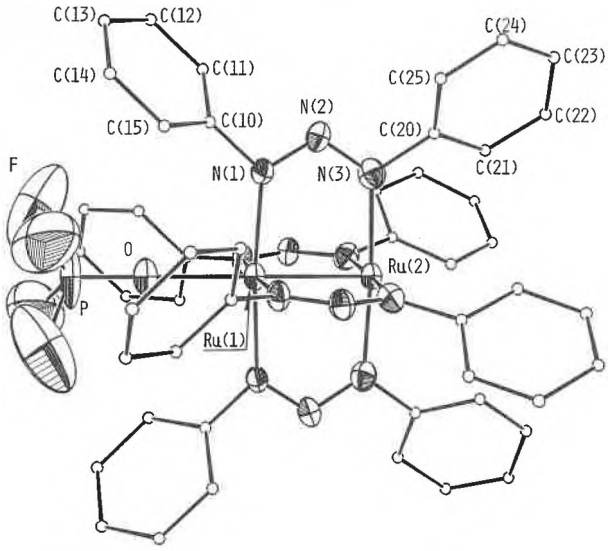

Fig. 1. The $[Ru_2(PhNNNPh)_4]OPF_4$ molecule. Atoms are represented by their ellipsoids of thermal displacement except for the carbon atoms, which are shown as arbitrarily small circles for clarity.

Table 2. Selected bond distances [Å] and bond angles [deg] for $[Ru_2(triazen)_4]POF_4$. Numbers in parentheses are estimated standard deviations in the least significant digits.

Ru(1)–Ru(2)	2.385(2)	Ru(2)–N(3)	2.013(6)	N(1)–N(2)	1.297(8)
Ru(1)–O	2.201(10)	P–O	1.455(11)	N(1)–C(10)	1.414(9)
Ru(1)–N(1)	2.038(6)	P–F	1.590(11)	N(2)–N(3)	1.321(8)
Ru(2)-Ru(1)-O	180.00(0)	N(3)-Ru(2)-N(3)	176.1(3)	Ru(1)-N(1)-N(2)	124.7(4)
Ru(2)-Ru(1)-N(1)	87.2(2)	N(3)-Ru(2)-N(3)	89.9(2)	N(1)-N(2)-N(3)	115.7(6)
N(1)-Ru(1)-N(1)	174.3(2)	O-P-F	111.6(4)	Ru(2)-N(3)-N(2)	124.4(5)
N(1)-Ru(1)-N(1)	89.9(2)	F-P-F	136.7(6)	Ru(2)-N(3)-C(20)	122.9(5)
Ru(1)-Ru(2)-N(3)	88.0(2)	F-P-F	82.2(6)		

[1] A.J. Lindsay, G. Wilkinson, M. Motevalli, M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.* (1987) 2723.
[2] F.A. Cotton, M. Matusz, *J. Am. Chem. Soc. 110* (1988) 5761.
[3] F.A. Cotton, V.M. Miskowski, B. Zhong, *J. Am. Chem. Soc.*, in press.
[4] G.M. Sheldrick, «SHELXS-86», Institut für Anorganische Chemie der Universität Göttingen, FRG (1986).
[5] T.C. Rhyne, J.G. Dillard, *Int. J. Mass Spectrom. Ion Phys. 7* (1971) 371.
[6] J.W. Larson, T.B. McMahon, *Inorg. Chem. 26* (1987) 4018.
[7] M. Lustig, J.K. Ruff, *Inorg. Chem. 6* (1967) 2115.
[8] R.D. Peacock, I.L. Wilson, *J. Chem. Soc. (A)* (1969) 2030.
[9] L. Kolditz, W. Rehak, *Z. Anorg. Allg. Chem. 300* (1959) 322; L. Kolditz, K. Haage *ibid. 301* (1959) 36; L. Kolditz, B. Nussbücker, *ibid.* 337 (1965) 191.