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A New Phosphine Stabilized Sulphido Trinuclear Rhodium(III) Species. Synthesis and Structure of $[Rh_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)(\mu_2\text{-}Cl)_2(PEt_3)_6]PF_6$

FRANCO CECCONI, CARLO A. GHILARDI,
STEFANO MIDOLLINI, ANNABELLA ORLANDINI,
ALBERTO VACCA

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, 50132 Florence, Italy

and JOSÉ A. RAMIREZ

Dep. Quimica Inorganica, Fac. Quimicas, Universidad de Valencia, Valencia, Spain

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The recognized importance of transition metal–sulphur clusters both in biological and in catalytic processes has stimulated an ever-increasing interest in the synthesis, reactivity and characterization of new metal–sulphido species [1].

In recent years we have succeeded in the synthesis of iron, cobalt and nickel sulphur clusters, by reacting the related aquo-ions with hydrogen sulphide in the presence of monotertiary phosphines [2]. Now we report the synthesis and X-ray structural characterization of the new polynuclear rhodium system $[Rh_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)(\mu_2\text{-}Cl)_2(PEt_3)_6]^+$ (1). Interestingly, in spite of the propensity of rhodium to form large carbonyl clusters, only rare examples of sulphido stabilized polynuclear rhodium species have been reported [3].

The reaction of H_2S with $Rh_2(\mu\text{-}Cl)_2(COD)_2$ in the presence of an excess of PEt_3 and $NaBPh_4$ afforded a brown oil from which triethylphosphine sulphide and a mixture of rhodium–phosphine complexes were separated by chromatography. The ^{31}P NMR spectra (121.418 MHz, $CDCl_3$, H_3PO_4 ext.) of this orange mixture show a strong singlet at 55 ppm attributable to $(PEt_3)_3PS$ and a series of well-shaped multiplets in the range 2–26 ppm. The high resolution $[^{31}P-^{31}P]$ - COSY45 NMR spectrum of the mixture allowed identification of at least four different rhodium–phosphorus species. Further chromatographic separation and addition of $[n\text{-}Bu_4N]PF_6$ allowed the crystallization of one of these derivatives. H_2S was bubbled through a deoxygenated solution of $Rh_2Cl_2(COD)_2$ (500 mg, 1 mmol) and triethylphosphine (708 mg, 6 mmol) in methylene chloride (20 ml) for *ca.* 5 min. After addition of $NaBPh_4$ (340 mg, 1 mmol) in n-butanol (10 ml) the solvent was slowly evaporated in air at room temperature. The resulting brown oil was chromatographed on silica gel thick-layer plates (eluent: $CHCl_3$ (85%)/CH_3CN (15%)). The first, principal deep orange fraction, after evaporation of the solvent, gave an orange oil. Successive chromatography of this latter by using $CHCl_3$ (85%)/C_6H_6 (10%)/CH_3CN (5%) as eluent produced a further separation in six fractions. The solvent was removed from the first orange fraction and the residue was recrystallized from ethanol/CH_2Cl_2 in presence of $[n\text{-}Bu_4N]PF_6$. Large brown–orange crystals of **1** were mechanically separated from colourless crystals of $[n\text{-}Bu_4]PF_6$. Yield, 55 mg (6% based on the metal). The deep-brown crystals so obtained analyse as $C_{36}H_{90}Cl_2F_6P_7Rh_3S_3$ (**1**).

The molecular structure of **1** has been established by a complete X-ray analysis. The crystal are monoclinic, space group $P2_1/n$ with $a = 14.605(9)$, $b = 24.128(15)$, $c = 16.336(10)$ Å, $\beta = 92.84(6)°$ and $Z = 4$. Data collection was carried out on an Enraf Nonius CAD4 diffractometer using the ω–2θ technique and graphite monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å) within $2\theta \leqslant 45°$. The structure was solved by the heavy atom method and refined by full-matrix least-squares refinement to the conventional R and R_w factors of 0.078 for both for 3091 absorption-corrected ($\mu = 12.7$ cm^{-1}) reflections having $I \geqslant 3\sigma(I)$.

The molecular structure consists of discrete units of $[Rh_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)(\mu_2\text{-}Cl)_2(PEt_3)_6]^+$ and PF_6^- anions. A perspective view of the cluster unit is given in Fig. 1. The cation is built up of a triangle of rhodium atoms, symmetrically capped by two triply bridging sulphur atoms; moreover, the three rhodium fragments are linked to each other by two doubly bridging chlorine atoms and by one double bridging sulphur atom. The Rh_3SCl_2 moiety is almost perfectly planar, the largest deviation of the bridging basal ligands from the Rh_3 plane being less than

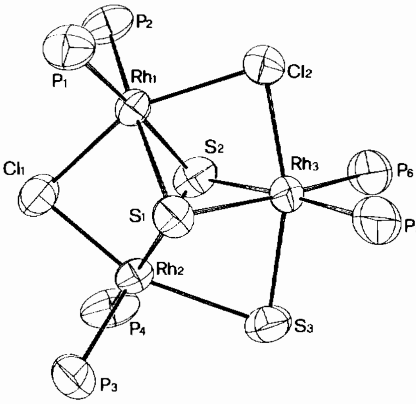

Fig. 1. Perspective view of the skeleton of $[Rh_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)(\mu_2\text{-}Cl)_2(PEt_3)_6]^+$. ORTEP drawing with 30% probability ellipsoids. Selected bond distances: Rh1–Rh2, 3.172(3); Rh1–Rh3, 3.188(3); Rh2–Rh3, 3.247(3) Å; Rh–P (av), 2.340 Å; Rh–S(ap) (av), 2.379 Å; Rh–S(bas) (av), 2.55 Å; Rh–Cl (av), 2.42 Å.

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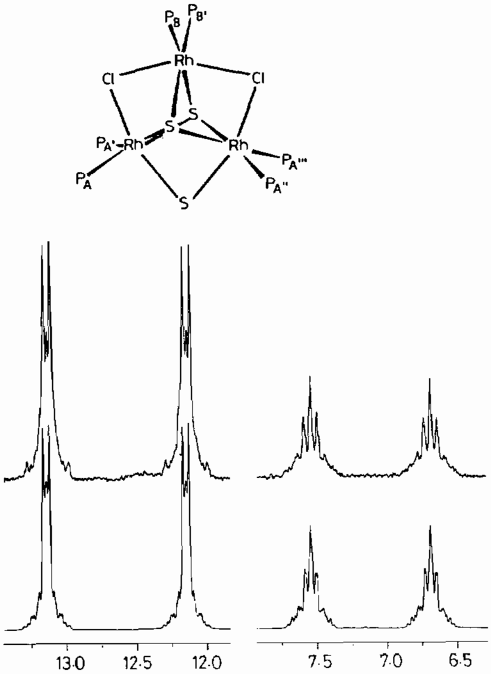

Fig. 2. Experimental (upper trace) and simulated (lower trace) phosphorus-31 NMR spectra of the P_A (lower field) and P_B (higher field) resonances.

0.01 Å. Each rhodium atom is additionally coordinated to two phosphine ligands, which complete an octahedral geometry. The values of the Rh–Rh separations (3.172(3), 3.188(3) and 3.247(3) Å) are comparable with the values reported for the trinuclear species $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ (3.053, 3.135 Å) [3], and are indicative of no significant direct metal–metal interaction.

The assignment of two chlorine atoms and one sulphur atom to the double bridging basal ligands was based on NMR considerations as well as on X-ray results. As a matter of fact, the sulphur and chlorine atoms appear generally undistinguishable by least-squares refinement; on the other hand, the $^{31}P[^{1}H]$ NMR spectrum of 1 ($CDCl_3$, room temperature; Fig. 2) with a doublet of filled-in doublets (4 P) at 12.0–13.0 ppm and a doublet of multiplets (2 P) at 6.5–7.5 ppm clearly indicates the non-equivalence of the six phosphorus atoms. This forced us to rule out the hypothesis of the three sulphur atoms all being in the basal plane.

On account of this model the NMR spectrum has been analysed, according to the spin system $[AA''B]_2X$, by computer simulation (Fig. 1). From a homonuclear (phosphorus) two-dimensional J-resolved spectrum [4], we have found that only heteronuclear ^{2}J(Rh–P) coupling constants are present. As a consequence, the nine-spin system $[AA''B]_2[X]_2Y$ can be conveniently reduced to the seven-spin system $[AA''B]_2X$. Simulation of the spectrum has been performed using a locally integrated package based on the LAOCN3 [5] and DAVINS [6] programs from the literature. It was not possible to determine all the parameters by computer least-squares refinement starting from the 'deceptively simple' experimental spectrum. Well-defined values of the chemical shifts and heteronuclear coupling constants were obtained ($\delta_A = 12.65$ ppm, $\delta_B = 7.12$ ppm, $J_{AX} = J_{A''X} = 120.5$ Hz, $J_{BX} = 104.0$ Hz), whereas it was possible to get only reliable information on the relative magnitude of the remaining constants and the combination of these values. The calculated spectrum (Fig. 2), which shows a satisfactory fit with the experimental spectrum, was obtained using the following set of parameters: $^{2}J_{AA'} = {}^{2}J_{A''A'''} = 30.0$ Hz, $^{2}J_{BB'} = 28.0$ Hz, $^{3}J_{AB} = {}^{3}J_{A''B} = -12.0$ Hz, $^{3}J_{AA''} = -10.0$ Hz; $^{3}J_{AB'} = {}^{3}J_{A''B'} = 6.5$ Hz; $^{3}J_{AA'''} = {}^{3}J_{A''A'} = 5.0$ Hz.

Crystallographic support for the above model is provided by the significant difference found in the bond distances involving the basal ligands, which definitively allowed their identification (the ligand facing the longest Rh–Rh edge shows Rh–L values significantly larger than the others (2.55 (av) *versus* 2.42 (av) Å). The presence of two chlorines and one sulphur as basal ligands could justify the deviation from a D_{3h} symmetry of the Rh_3 triangle.

Investigations are in progress to separate and characterize the other derivatives from the reaction.

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