Crystal Structure of Di-μ-sulphur dioxide-pentakis(t-butyl isocyanide)-*triangulo*-tripalladium–Dibenzene

By SEI OTSUKA,* Y. TATSUNO, and M. MIKI
(*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan*)
and T. AOKI, M. MATSUMOTO, H. YOSHIOKA, and K. NAKATSU
(*Faculty of Science, Kwansei Gakuin University, Nishinomiya, Hyogo, Japan*)

Summary A single-crystal *X*-ray analysis on the title compound revealed an interesting cluster structure involving SO_2 bridging.

SULPHUR DIOXIDE in its complexes with later transition metals *e.g.* Pt^{0},[1a,b] Ni^{0},[2] Ir^{I},[3] or Ru^{II},[3] generally shows an increased tendency to undergo oxygenation with dioxygen in ground state $^{3}\Sigma_{g}^{-}$ compared with the free molecule.[4] In contrast, the title complex of Pd^{0} was found quite inert to air. Because of the paucity in the *X*-ray structural data[5–9] on the sulphur dioxide complexes the correlations between structure and reactivity of co-ordinated sulphur dioxide are poorly understood; this prompted the present *X*-ray study.

An orange, diamagnetic cluster $Pd_3(SO_2)_2(Bu^tNC)_5,2(C_6H_6)$,† in which sulphur dioxide co-ordination is irreversible, is prepared from $Pd(Bu^tNC)_2$ and an excess of SO_2.[2] Crystals grown from benzene solution generally contain 2 mol. equiv. of solvent. The single-crystal specimens are obtained from the benzene–n-heptane solution. *Crystal data:* $Pd_3S_2O_4N_5C_{37}H_{57}$, $M = 1019$, orthorhombic $a = 26{\cdot}18(3)$, $b = 15{\cdot}99(2)$, $c = 11{\cdot}61(2)$ Å, D_m (flotation) $= 1{\cdot}40$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}39_2$ g cm^{-3}, space group $P2_12_12_1$. A total of 3230 non-zero independent reflections was collected on a four-circle automatic diffractometer with a maximum 2θ value of 50° using Zr-filtered Mo-K_α radiation.

The structure was solved by the heavy-atom method. All 51 non-hydrogen atoms were refined by a least-squares

---

† It was once formulated as a dimer, $[Pd(SO_2)(Bu^tNC)_2]_2$.[2]

method, assuming anisotropic thermal parameters for the Pd and S atoms and isotropic parameters for the other non-hydrogen atoms. The *R*-factor has converged to 0·07.

There is clearly no bonding interaction among the discrete cluster molecules and the benzene. The Figure illustrates the configuration except for the t-butyl groups. The molecule has an approximately C_2 symmetry axis bisecting the Pd(2)–Pd(3) bond and passing through the Pd(1) atom. The metal–metal bond Pd(2)–Pd(3), which has no SO_2 bridge, is significantly longer than the others. The geometry around the sulphur atoms resembles that of $Fe_2(SO_2)(CO)_8$.[8] The average Pd–S bond distance of 2·26 Å is slightly shorter than the values (av. 2·30 Å) for chalcogenide Pd complexes,[10] implying a strong bonding to the metal. The S–O bond length (av. 1·48 Å) and O–S–O bond angle (av. 111°) are close to the values (1·50 Å and 108°) found in dithionite ion ($S_2O_4^{2-}$)[11] which may be regarded as consisting of two SO_2^- groups. In spite of this considerable increase in electron density the sulphur dioxide ligand was found inactive towards electrophiles, *e.g.* dioxygen, a behaviour in contrast with the ready oxygenation observed for $Ni(SO_2)(Bu^tNC)_3$[2] and many other Group VIII metal–sulphur dioxide complexes. The sulphur atom is co-ordinatively saturated, lacking low-lying vacant and/or filled orbitals; therefore the SO_2 ligand becomes inert. The N≡C stretching frequencies (2170 and 2155 cm^{-1}) of the isocyanide groups are comparable with those found in the Pd^0 complexes, $Pd(olefin)(Bu^tNC)_2$, where the olefin ligand is electron-accepting maleic anhydride or fumaronitrile.[12] This implies that the SO_2 ligand behaves as a strong electron-accepting ligand in this cluster complex.

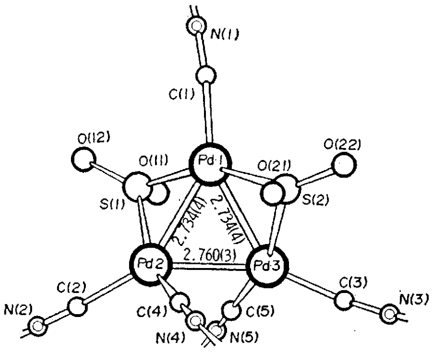

FIGURE. The configuration of $Pd_3(SO_2)_2(Bu^tNC)_5$, except t-butyl groups. The relevant bond lengths (Å) and angles (°) are; distances, Pd(1)–S(1), 2·265(9); Pd(1)–S(2), 2·267(8); Pd(2)–S(1), 2·256(8); Pd(3)–S(2), 2·254(9); Pd(1)–C(1), 2·03(3); Pd(2)–C(2), 2·04(3); Pd(3)–C(3), 1·99(3); Pd(2)–C(4), 2·11(3); Pd(3)–C(5), 2·13(3); S(1)–O(11), 1·49(3); S(1)–O(12), 1·45(3); S(2)–O(21), 1·47(3); S(2)–O(22), 1·49(2); angles, O(11)–S(1)–O(12), 113(2); O(21)–S(2)–O(22), 109(2); dihedral angles between [Pd(1), Pd(2), Pd(3)] and [Pd(1), S(1), Pd(2)] 49·2°; [Pd(1), Pd(2), Pd(3)]; and [Pd(1), S(2), Pd(3)] 46·7°.

The three isocyanide carbons C(1), C(2), and C(3) lie nearly in the metal plane with –N≡C vectors stretching equatorially. The other isocyanide carbons C(4) and C(5) lie above and below the plane, the N≡C vectors forming about 55° with the normal vector of the Pd plane. The two axial isocyanides with longer Pd–C distances appear to be nearly at a distance to form a bridging bond with the neighbour palladium atom, the average distance for Pd(2)–C(5) and Pd(3)–C(4) being 2·81 Å. This view is consistent with the ^1H n.m.r. spectrum (CH_2Cl_2) which shows a single sharp peak at 1·50 p.p.m. (Me_4Si) from −78° to 30° indicating rapid exchange between the magnetically inequivalent isocyanide ligands.[13]

(*Received*, 19*th March* 1973; *Com.* 370.)

---

[1] (a) J. J. Levison and S. D. Robinson, *Chem. Comm.*, 1967, 198; (b) T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1963, **41**, 296.

[2] S. Otsuka, A. Nakamura, Y. Tatsuno, and M. Miki, *J. Amer. Chem. Soc.*, 1972, **94**, 3761.

[3] J. Valentine, D. Valentine, Jr., and J. P. Collman, *Inorg. Chem.*, 1971, **10**, 219.

[4] T. N. Rao, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, 1969, **91**, 1616.

[5] L. H. Vogt, J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, 1965, **4**, 1157.

[6] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 405.

[7] K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1921.

[8] J. Meunier-Piret, P. Piret, and M. Van Meerssche, *Bull. Soc. chim. belges*, 1967, **76**, 374.

[9] M. R. Churchill, B. G. DeBoer, K. L. Kalra, P. Reich-Rohrwing, and A. Wojcicki, *J.C.S. Chem. Comm.*, 1972, 981.

[10] P. M. Maitlis, "The Organic Chemistry of Palladium," vol. I, Academic Press, N.Y. and London, 1971, p. 38.

[11] J. D. Dunitz, *Acta Cryst.*, 1956, **9**, 579.

[12] S. Otsuka, T. Yoshida, and Y. Tatsuno, *J. Amer. Chem. Soc.*, 1971, **93**, 6462.

[13] S. Otsuka, *et al.*, to be published.