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A NOVEL HIGH NUCLEARITY PLATINUM ISOCYANIDE CLUSTER

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A new isocyanide cluster of platinum, $Pt_7(C_9H_9N)_{12}$, was prepared by reduction of dichloro-bis(2,6-xylyl isocyanide)platinum(II) with sodium amalgam.

Metal clusters are of current interest as plausible models of surfaces in the heterogeneous catalysis.[1] Recently metal clusters of nickel(0),[2] palladium(0)[2,3], and platinum(0)[4] in which isocyanides are the only ligands have been known. These skeltons consist of only three or four metals, while various high nuclearity carbonyl clusters were well known.[5] We wish to describe a novel isocyanide cluster containing seven platinum atoms.

Dichloro-bis(2,6-xylyl isocyanide)platinum(II) is treated with sodium amalgam in THF at room temperature for 1 h. The resulting dark brown solution was chromatographed on deactivated alumina (containing 10% H_2O) to give dark brown air stable crystalline compound 1 formulated as $Pt_7(C_9H_9N)_{12}$.[6,7] The infrared spectrum showed the presence of terminal and bridging isocyanide groups.

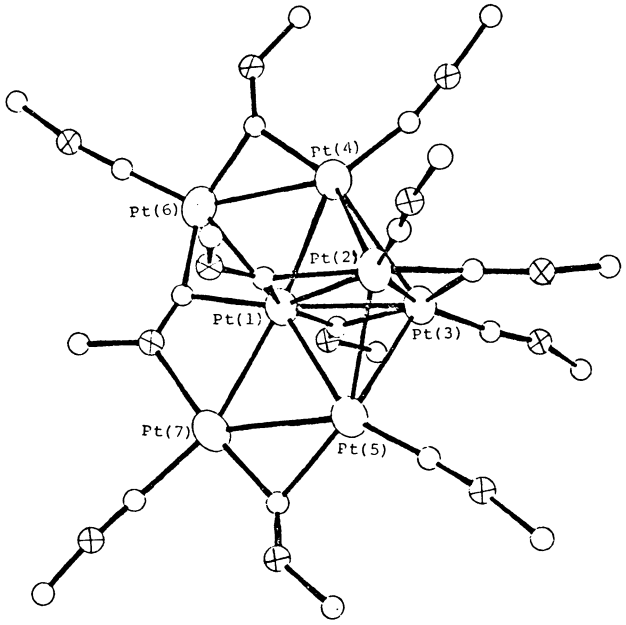
Crystals of 1 belong to the monoclinic space group $P2_1/c$. Unit cell data are $a = 28.565(6)$, $b = 26.694(25)$, $c = 15.278(3)$ Å, $\beta = 119.66(2)°$, and $Z = 4$. The 6356 reflections having $Fo > 3\sigma(Fo)$ and $2\theta < 45°$ were collected using MoKα radiation and a Rigaku four-circle diffractometer. Intensities were corrected for Lorentz, polarization, and absorption effects ($\mu = 110.4$ cm^{-1}). The calculated transmission factors varied from 0.59 to 0.87. The positions of the Pt atoms were determined by a direct method, and the N and C atoms appeared in successive electron-density maps. The final R value was 0.0985 (The Pt atoms were refined with anithotropic thermal parameters and others with isotropic ones. The molecule, shown in Figure 1, contains a metal atom cluster derived from the distorted trigonal bipyramidal unit to which two extra atoms, Pt(6) and Pt(7), have been attached in the bridging position between one basal platinum atom (Pt(1)), and each apical one (Pt(4) and Pt(5)). The two Pt-Pt bonds on one edge having a bridging platinum atom, Pt(1)-Pt(4) and Pt(1)-Pt(5), are shorter than those on the others, Pt(2)-Pt(4), Pt(3)-Pt(4), Pt(2)-Pt(5), and Pt(3)-Pt(5). The dihedral angle between the Pt(1)Pt(4)Pt(6) and the Pt(1)Pt(5)Pt(7) plane is 175.6°, showing that both planes lie in the nearly same one. The platinum framework has a pseudo C_{2v} symmetry.

A characteristic bonding mode of the coordinated isocyanide ligand is that one isocyanide ligand coordinates to three platinum atoms (Pt(1), Pt(6), and Pt(7)) by four electrons derived from the C=N- group. A similar type of coordination has been noted in $Os_6(CO)_{18}(p\text{-}CH_3C_6H_4NC)_2$.[8]

The preparation of the related complexes and their chemistry are now in progress.

Figure 1 Perspective view of $Pt_7(C_9H_9N)_{12}$. The 2,6-xylyl groups are omitted for clarity.

○ carbon atom ⊗ nitrogen atom



Relevant data: Pt(1)-Pt(4) = 2.733(5) Å, Pt(1)-Pt(5) = 2.683(4) Å, Pt(2)-Pt(4) = 3.013(4) Å, Pt(3)-Pt(4) = 3.013(4) Å, Pt(2)-Pt(5) = 2.978(5) Å, Pt(3)-Pt(5) = 3.013(4) Å, Pt(1)-Pt(2) = 2.717(3) Å, Pt(1)-Pt(3) = 2.711 Å, Pt(2)-Pt(3) = 2.619 Å.

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References and Notes

1) a) R.Ugo, Catal.Rev., 11, 225 (1975). b) F.L.Muetterties, Bull.Soc.Chim.Belg., 84, 959 (1975). c) E.L.Muetterties, ibid., 85, 451 (1976).
2) M.G.Thomas, W.R.Pretzer, B.F.Beier, F.J.Hirsekorn, and E.L.Muetterties, J.Amer. Chem.Soc., 99, 743 (1977).
3) E.O.Fischer and H.Werner, Chem.Ber., 95, 703 (1962).
4) M.Green, J.A.K.Howard, M.Murray, J.L.Spencer, and F.G.A.Stone, J.C.S.Dalton, 1509 (1977).
5) P.Chini, G.Longoni, and V.G.Albano, Adv.Organometal.Chem., 14, 285 (1976).
6) Compound 1 are also prepared from the reaction of $Pt(COD)_2$ with 2,6-xylyl isocyanide. The reaction of $Pt(COD)_2$ with tert-butyl isocyanide has been noted to give $Pt_3(t\text{-}BuNC)_6$.[4]
7) Elementary analysis: C, 44.50(44.13); H, 3.75(3.70); N, 5.51(5.72); Pt, 45.49 (46.45). M.p. 232-234°C(decomp.); IR(KBr): 2102(b), 1667(b) cm^{-1}; Electronic spectrum(CH_2Cl_2): 507(1.09×10^4), 418(3.78×10^4), 352(6.12×10^6), 318(8.21×10^6) nm.
8) A.V.Rivera and G.M.Sheldrick, Acta Cryst. B34, 1985 (1978).

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