Molecular Structure of *cyclo*-[Bis-(μ-acetato-μ-nitrosyl)-bis(di-μ-acetato-diplatinum)] and Some Aspects of the Preparation of Diacetatoplatinum(II)

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Summary A product of the preparation of diacetatoplatinum(II) by the reduction of $\mathrm{Pt^{IV}}$ in nitric acid–acetic acid has been shown by *X*-ray structure analysis to contain bridging nitrosyl as well as bridging acetato-groups and to have a molecular formula $\mathrm{Pt_4(acetate)_6(NO)_2}$.

DIACETATOPALLADIUM(II) and diacetatoplatinum(II) were reported[1] to be trimeric but not isomorphous. An *X*-ray study of diacetatopalladium has confirmed the trimeric nature of this complex and shown it to have a cyclic structure with bridging acetate groups.[2] We have now determined the crystal structure of one of the products of the preparation of the platinum complex, and find that it is tetranuclear and contains bridging nitrosyl as well as bridging acetate groups.

Crystals of the title compound were obtained as black dichroic needles of composition $\mathrm{Pt_4(CH_3COO)_6(NO)_2,2CH_3COOH}$ by recrystallising from chloroform–glacial acetic acid[1] the product obtained using the safer Davidson and Triggs modification[3] of the original preparation. The crystals are monoclinic, with unit-cell dimensions $a = 23{\cdot}723$, $b = 8{\cdot}681$, $c = 14{\cdot}195$ Å, $\beta = 92{\cdot}98°$, $U = 2919{\cdot}6$ Å^3, $D_m = 2{\cdot}97$ g cm^{-3}, $Z = 4$, $D_c = 2{\cdot}99$ g cm^{-3}, space group $C2/c$. *X*-Ray intensity data were collected on a Siemens four-circle diffractometer. Using Cu-K_α radiation a total of 1521 independent reflections were measured (to $\theta = 50°$), of which 185 were judged to be unobserved. The structure was solved by Patterson and Fourier methods, and least-squares refinement, with only platinum anisotropic, has reached $R = 0{\cdot}067$.

The Figure shows the molecular structure of the complex, together with the principal bond lengths. The molecule is tetranuclear and lies around a diad axis. The four platinum atoms form a slightly oblique rectangle, of sides 2·944 and 3·311 Å, which is not strictly planar as can be seen from Figure (a). Each of the two independent metal atoms is bonded to three oxygen atoms from bridging acetato-groups and to one nitrogen atom from a nitrosyl group, to give a square-planar co-ordination. The Pt–O distances are normal, with an average of 2·04 Å.

Ibers and his co-workers[4] have carried out a number of structure determinations of nitrosyl metal complexes and have shown that where the M–N bond is very short and the angle M–N–O is *ca.* 180° the ligand can be considered as $\mathrm{NO^+}$ while for $\mathrm{NO^-}$ the M—N distance is longer and the angle at N is *ca.* 120°. In this structure both the average Pt–N distance of 1·91 Å and the almost perfect sp^2 geometry at the bridging nitrogen are consistent with the formulation $\mathrm{NO^-}$ (see Table 7 in ref. 4),† as is also the N—O distance of 1·22(3) Å. Crystallographically confirmed bridging nitrosyl groups are rare, but recently a few have been reported.[5] It seems likely that the shortest of the Pt · · · · Pt distances within the molecule involves some metal–metal interaction.

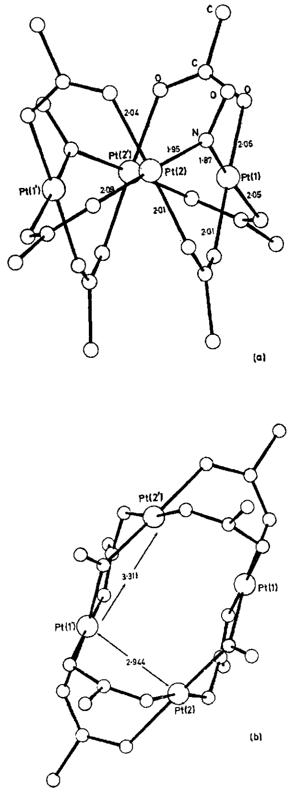

FIGURE. *Two views of the molecular structure of* $\mathrm{Pt_4(acetate)_6(NO)_2}$. *That shown in* (b) *is down a diad axis which passes through the centre of the molecule. Standard deviations are:* Pt · · · Pt, 0·002; Pt—O and Pt—N, 0·02 Å.

There is also a close approach between Pt(1) and its centrosymmetrically related neighbour in another molecule at a distance of 3·300 Å, and this separation is not spanned by any bridging group. There are many known examples of such Pt—Pt interactions[6].

We suggest that caution should be exercised as regards the identity of products in the preparation of diacetatoplatinum(II) by the reduction of $\mathrm{Pt^{IV}}$ in nitric acid–acetic acid,[1,3] since inspection of analysis results and *X*-ray powder

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† The fact that the nitrosyl groups are not carbonyl groups is confirmed by chemical analysis.

patterns shows that one of several nitrogen-containing products may be obtained. There exists an alternative, more recent, method[7] of preparing diacetatoplatinum which excludes the possibility of introducing nitrosyl ligands into the complex.

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