polarons react with, for example, the sulphate ions present according to:

$$HSO_4^- + (H_2O)^+ \rightarrow HSO_4.(H_2O) \rightarrow SO_4^-.(H_3O)^+ \quad (1a)$$

$$SO_4^{2-} + (H_2O)^+ \rightarrow SO_4^-.(H_2O) \quad (1b)$$
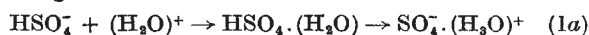
giving the radical ion SO_4^- which shows a characteristic electron spin resonance spectrum and absorbs light in the visible region with absorption maximum at 446 mμ. A corresponding process occurs in the phosphate matrices where it leads to the formation of the HPO_4^- radical ion, which shows maximum absorption at 525 mμ.

In the photochemical bleaching with light which is absorbed by these coloured radical ions an electron is transferred from the hydration shell to the radical ions, for example, according to:

$$SO_4^-.(H_2O) + h\nu \rightarrow SO_4^{2-}.(H_2O)^+ \quad (2)$$
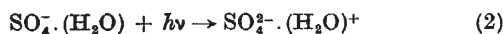
leading to the formation of a positive hole trapped in the hydration shell of the respective ions. The presence of a positive hole can be inferred from an examination of the electron-spin resonance spectra. The latter were found to be identical after bleaching of both the γ-irradiated sulphate and phosphate ice matrices. If now these colourless matrices are warmed up to a temperature of about 120° K the original colour is practically immediately restored. This procedure, that is, of photochemical bleaching and thermal restoration, corresponding to reaction (1b), can be repeated through many cycles with practically no change in the concentrations of the intermediate species involved in these processes.

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Molecular Structure of π-allyl-palladium Acetate

THE structures of π-allyl complexes of transition metal ions are of interest because the allyl ligand can be regarded as intermediate in behaviour between olefines and conjugated aromatic systems. π-Allyl palladium complexes have, in particular, assumed importance as catalytic agents in carbonylation and other reactions involving unsaturated organic halides[1,2]. The only structural analysis of an allyl complex so far reported is that of the dimeric π-allyl palladium chloride[3], the reaction of this complex with silver acetate yielding π-allyl palladium acetate[4]. A three-dimensional X-ray analysis of the structure of this molecule has now been completed, the molecular stereochemistry being shown in Fig. 1; estimated standard deviations of the observed bond lengths are 0·003 Å (Pd–Pd), 0·02 Å (Pd–O), 0·035 Å (Pd–C), 0·04 Å (O–C) and 0·05 Å (C–C) and correspond to a discrepancy index of 0·068 for 1,065 reflexions.

The π-allyl palladium residues are bridged by the two acetate groups, the overall arrangement showing considerable similarity to that of the binuclear cupric acetate dihydrate[5] in which a metal–metal bond is evidenced largely by magnetic and spectroscopic criteria (see, for example, ref. 6). The Cu–Cu bond-length of 2·64 Å is equivalent to that of 2·94 Å for the Pd–Pd distance in the present complex; the difference between the mean Cu–O (1·97 Å) and Pd–O (2·11 Å) bond-lengths can be taken as the difference between the metal radii so that judged by these data the Cu–Cu and Pd–Pd bond-lengths should differ by 0·28 Å (observed 0·30 Å). Formally, with the allyl anion acting as a four-electron donor, the present results offer a further example of the formation of a metal–metal bond between two d^8 ions, but the relation between the cupric acetate structure and the present one

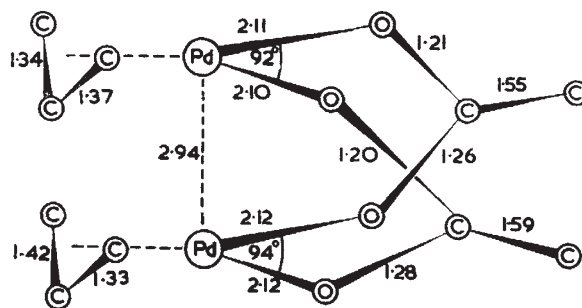
Fig. 1

is perhaps made clearer if we regard the palladium ion as interacting with the π-allylic radical since metal–metal bonds are then formed between d^9 ions in both examples. The Pd–Pd distance is 0·3–0·4 Å shorter than those reported for Pd (dimethylglyoxime)$_2$ (3·26 Å) (ref. 7), [Pd(NH$_3$)$_4$].[PdCl$_4$] — 3·25 Å (ref. 8), [Pd(NH$_3$)$_4$].[Pd(Br$_4$)] — 3·33 Å and [Pd(NH$_3$)$_4$] [Pd(SCN)$_4$] — 3·35 Å (ref. 9), in which complexes there is no ligand bridging of the d^8 palladium ions.

The palladium–allyl bonding is such that the planes of the allyl ligands make dihedral angles of 125° and 110° (± 5°) with those defined by the respective O–Pd–O groups. A re-examination of the structure of (π-C$_3$H$_5$ PdCl)$_2$ (ref. 10) shows the allyl plane in this complex to be similarly oriented at an angle of 118° with respect to the plane of the Pd$_2$Cl$_2$ system with the Pd–C (allyl) bond-lengths varying from 2·15 ± 0·02 Å in the case of the terminal carbon atoms to 2·01 ± 0·04 Å for the central atom of the allyl group. An independent examination[11] of the structure of (π-C$_3$H$_5$PdCl)$_2$ at —140° C does not, however, confirm this difference, and indeed while the mean values for these bonds in the present structure are 2·08 Å and 2·05 Å, respectively, no significance can be attached to this result, or to the observed differences in the carbon–carbon bond distances in the allyl ligands.

The configuration of the allyl ligand with respect to the palladium ion differs from that which might have been anticipated on the basis of a molecular orbital description of the electron distribution in the free ligand. As such the same conditions may apply, mutatis mutandis, to those which have been discussed elsewhere for the bonding of cyclic ligands to transition metal ions[12–14].

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