

Heteronuclear Acetate-bridged Complexes; Reaction of Palladium(II) Acetate with Bivalent Metal Acetates

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A surprising number of transition-metal acetates are polymeric in nature, containing the metal atoms linked by acetate bridges.¹ Very few are known in which there are two different metals linked in this way: examples are $\text{CaCu}(\text{OAc})_4 \cdot 6\text{H}_2\text{O}$ and $\text{CaCd}(\text{OAc})_4 \cdot 6\text{H}_2\text{O}$.² We report a series of metal acetate complexes of general formula $\text{MPd}(\text{OAc})_4 \cdot x\text{HOAc} \cdot y\text{H}_2\text{O}$ that are apparently of this type. They are simply prepared by heating equimolar amounts of palladium(II) acetate and another bivalent metal acetate (normally as the hydrate) in acetic acid.

On cooling crystals are deposited. Of the formally bivalent-metal acetates not listed here, those of Cr^{II} , Mo^{II} , Fe^{II} , and $\text{VO}(\text{II})$ cause reduction to Pd metal, and those of Rh^{II} , Pt^{II} , Mg^{II} , Hg^{II} , and $\text{UO}_2(\text{II})$ do not react appreciably. Univalent metal acetates (*e.g.* KOAc) or trivalent metal acetates [*e.g.* $\text{Fe}(\text{OAc})_3$] in stoichiometric amounts give virtually no reaction. The compounds which have been prepared are listed in the Table, with some relevant spectroscopic data. The complexes are all very soluble in water but subsequent

The complexes $\text{MPd}(\text{OAc})_4$

Compound	ν max (cm. ⁻¹)	U.v. band (HOAc soln.)		I.r. Bands (cm. ⁻¹)		$\Delta\omega$
		ϵ^a	ω_2	ω_1		
$\text{BaPd}(\text{OAc})_4 \cdot 4\text{HOAc}$.. 28,500	550	1,631	1,412	219	
$\text{SrPd}(\text{OAc})_4 \cdot 4\text{HOAc}$.. 28,500	670	1,626	1,412	214	
$\text{CaPd}(\text{OAc})_4 \cdot 4\text{HOAc}$.. 28,700	740	1,629	1,435	194	
$\text{MnPd}(\text{OAc})_4 \cdot \text{H}_2\text{O} \cdot \text{HOAc}$.. 29,200	940	1,600	1,410	190	
$\text{CdPd}(\text{OAc})_4 \cdot \text{H}_2\text{O} \cdot \text{HOAc}$.. 29,300	1,040	1,600	1,410	190	
$\text{PbPd}(\text{OAc})_4 \cdot 2\text{HOAc}$.. 29,600	860	1,597	1,404	193	
$\text{ZnPd}(\text{OAc})_4 \cdot 2\text{HOAc} \cdot 2\text{H}_2\text{O}$.. 29,600	1,280	1,626	1,395	231	
$\text{CoPd}(\text{OAc})_4 \cdot 2\text{HOAc} \cdot 2\text{H}_2\text{O}$.. 29,800	1,470	1,616	1,400	216	
$\text{NiPd}(\text{OAc})_4 \cdot \text{HOAc} \cdot \text{H}_2\text{O}^b$.. 30,400	1,240	1,600	1,400	200	
$\text{CuPd}(\text{OAc})_4^{b,c}$.. 28,500	1,000	1,608	1,449	159	

^a Based on $\text{MPd}(\text{OAc})_4$. ^b The product readily loses HOAc on standing. The material listed is that which remains.

^c A mixture of products—see text. The u.v. data are for a heated solution of a 1 : 1 $\text{Cu}(\text{OAc})_2$: $\text{Pd}(\text{OAc})_2$ mixture.

hydrolysis occurs with deposition of palladium(II) hydroxide. Dry benzene also dissolves the compounds, with $\text{CaPd}(\text{OAc})_4 \cdot 4\text{HOAc}$ being particularly soluble (> 40 g./l.). A molecular weight determination on this solution gave a value $M = 1520$ [$\text{CaPd}(\text{OAc})_4 \cdot 4\text{HOAc}$ requires $M = 623$] so the complex is obviously polymeric. In acetic solution the complexes are nonconducting, so formulations such as $M^{2+}\text{Pd}(\text{OAc})_4^{2-}$ can be discounted.

Reaction is accompanied by a pronounced change

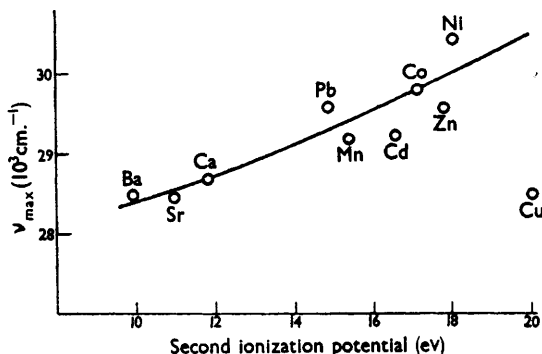


FIGURE. ν_{\max} vs. Second ionisation potential of M for the complexes $M\text{Pd}(\text{OAc})_4$. (Solvent, acetic acid).

in the absorbance spectrum of the solution with a relatively intense band appearing in the near u.v. (cf. ν_{\max} $\text{Pd}(\text{OAc})_2 = 25,100 \text{ cm}^{-1}$, $\epsilon = 220$). Apart from the copper(II) complex, the position of the band correlates with the second ionisation potential of the metal (see Figure) and also with the Irving-Williams series for the stability of transition metal complexes.³ These results show that the two metal atoms interact with each other probably through acetate bridges. This is supported by i.r. data. The Table shows that the differences between the symmetrical (ω_1) and antisymmetrical (ω_2) stretching frequencies of the $-\text{CO}_2^-$ group for each of these complexes are largely intermediate between that expected for completely symmetrical bonding ($\Delta\omega$ 164 cm^{-1}) and unidentate bonding ($\Delta\omega > 220 \text{ cm}^{-1}$).⁴ It would be expected that in a structure containing two different metal atoms linked by an acetate bridge, the acetate would interact more strongly with one metal than the other and thereby possess a certain asymmetry, though not as great as that for unidentate bonding.

Breakdown of the trimeric palladium(II) acetate by copper(II) acetate is not complete. U.v., e.s.r., and mass spectral data are consistent with a mixture of $\text{CuPd}(\text{OAc})_4$ and $\text{CuPd}_2(\text{OAc})_6$ as the product of this reaction.

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¹ See references in J. K. Kochi and P. V. Subramanian, *Inorg. Chem.*, 1965, **4**, 1527.

² D. A. Langs and G. R. Hare, *Chem. Comm.*, 1967, 890.

³ H. Irving and R. J. P. Williams, *Nature*, 1948, **162**, 746.

⁴ T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.