New Route to the Directed Synthesis of Mixed Metal Chain Oligomers. Identification of a Platinum Complex having an Intense Emission in the Visible Spectrum in Aqueous Solution

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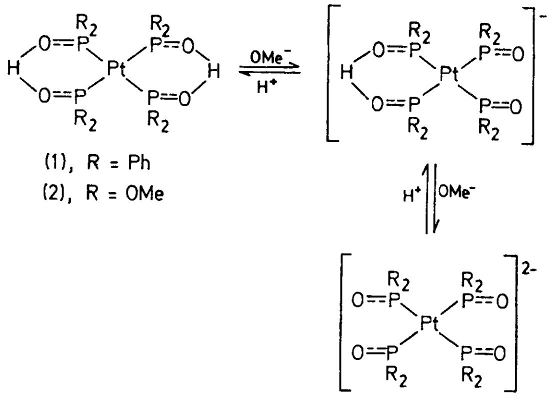
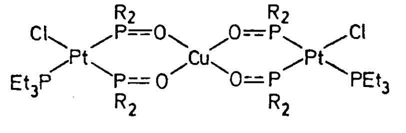
Summary The anion $[PtCl\{OP(OMe)_2\}_2(PEt_3)]^-$ and compound $[Pt\{OP(OMe)_2\}_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) have been co-ordinated to a second metal M (M = Cu^{II}, Co^{II}, Ni^{II}, Zn^{II}, Th^{IV}, or UO_2^{VI}) through the oxygens; the unexpected photophysical properties of $[Pt\{OP(OH)_2\}_2\{P(OH)_3\}_2]$ are reported.

Recently we and others have been investigating the co-ordination chemistry of substituted phosphinous and phosphonous acids. The results of these studies indicate that when a phosphinous or phosphonous acid ligand and its conjugate base anion are both bonded to a platinum metal through phosphorus, the proton is symmetrically bonded to the two oxygen atoms.[1,2] We now report that removal of this acidic proton can yield an anionic platinum complex which will function as a chelating ligand through the oxygens for a second transition metal ion. Additionally we report the unique photophysical properties of the compound $[Pt\{OP(OH)_2\}_2\{P(OH)_3\}_2]$.



(**1**), R = Ph
(**2**), R = OMe

When the complexes (**1**),[2,3] or (**2**),[4] are titrated with base they behave as dibasic acids. In a conductivity titration against added sodium methoxide, (**1**) shows a single break in the curve corresponding to the addition of 2 equiv. of base. For (**2**), however, we find two distinct breaks which correspond to the addition of 1 and 2 equiv. of base. These



(**5**), R = OMe
(**6**), R = OPh

platinum containing anions structurally resemble acetylacetonate or imidodiphenylphosphate[5] ion, and can be expected to have comparable ligating properties through the oxygens toward a second metal ion. Thus the single acidic proton in $[PtCl\{OP(OR)_2\}\{HOP(OR)_2\}Q]$ [R = OMe or OPh, Q = PEt_3; R = OMe, Q = PPh_3 (**3**)] can be replaced by BF_2, Cu^{II}, Co^{II}, $U^{VI}O_2$, or Th^{IV} to yield $[\{PtCl[OP(OMe)_2]_2PEt_3\}_2BF_2]$ (**4**), $[\{PtCl[OP(OR)_2]_2PEt_3\}_2Cu]$ [(**5**), R = Me; (**6**), R = Ph], $[\{PtCl[OP(OMe)_2]_2PEt_3\}_2UO_2]$ (**7**), $[\{PtCl[OP(OMe)_2]_2PPh_3\}_2Co]$ (**8**), and $[\{PtCl[OP(OMe)_2]_2PPh_3\}_4Th]$ (**9**). Similarly, treating $[Pt\{OP(OMe)_2\}_2(dppe)]$ or $[Pt\{OP(OMe)_2\}_2(diars)]$ with the appropriate metal ion yields $[\{Pt[OP(OMe)_2]_2(dppe)\}_2Cu][ClO_4]_2$ (**10**), $[\{Pt[OP(OMe)_2]_2(dppe)\}_2Co][ClO_4]_2$ (**11**), $[\{Pt[OP(OMe)_2]_2(dppe)\}_2Ni][ClO_4]_2$ (**12**), $[\{Pt[OP(OMe)_2]_2$-

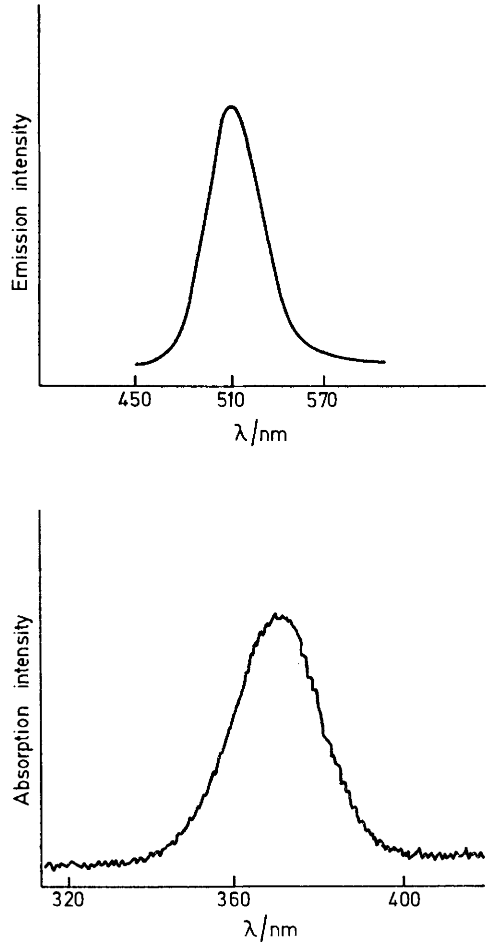


Figure. Absorption and emission spectrum of $[Pt\{OP(OH)_2\}_2\{P(OH)_3\}_2]$ in aqueous solution.

$(\mathrm{dppe})\}_2\mathrm{Zn}][\mathrm{ClO}_4]_2$ (**13**), $[\{\mathrm{Pt}[\mathrm{OP(OMe)}_2]_2(\mathrm{diars})\}_2\mathrm{Cu}][\mathrm{ClO}_4]_2$ (**14**), and $[\{\mathrm{Pt}[\mathrm{OP(OMe)}_2]_2(\mathrm{diars})\}_2\mathrm{Co}][\mathrm{ClO}_4]_2$ (**15**) (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$, and diars = $\mathrm{Me_2AsC_6H_4AsMe_2}$).†

Electronic spectra of (**5**), (**6**), (**10**), and (**14**) show the compounds to be square planar about Cu. The observed diamagnetism of (**12**) indicates a similar geometry about Ni, although a tetrahedral geometry about Co is found for (**8**) and (**11**). The electronic spectral data place the chelating *O*-bonded phosphonito-ligand in a position comparable to –NCS in the spectrochemical series. The 6-co-ordinate complex (**7**) shows the yellow colour of the linear uranyl ion indicating a square planar arrangement of the phosphonito-ligands. The novel pentametallic Th complex (**9**) is octaco-ordinate about thorium, and determination of the molecular weight by osmometry in benzene indicates only slight dissociation.

During the preparation of compound (**2**) from $\mathrm{K_2PtCl_4}$ and $\mathrm{P(OMe)_3}$ in aqueous solution we noticed a small quantity of a side product which shows an intense green emission on irradiation with u.v. light. Subsequently we have found that this material can be obtained in better yield by treating $\mathrm{K_2PtCl_4}$ with phosphorous acid in a melt. The compound is unstable to either acid or base and shows properties identical to those of $[\mathrm{Pt}\{\mathrm{OP(OH)_2}\}_2\{\mathrm{P(OH)_3}\}_2]$, previously prepared from $\mathrm{K_2PtCl_4}$ and a concentrated aqueous solution of phosphorous acid.[6] This compound is unique for a $\mathrm{Pt^{II}}$ complex in showing an intense emission spectrum in aqueous solution at room temperature. The emission band is centred at 514 nm, and results from excitation of an absorption band at 368 nm ($\epsilon = 2{\cdot}8 \times 10^2$) (Figure). This complex is the only one of these phosphonito-complexes which shows such a charge-transfer band in the edge of the visible region. For $[\mathrm{Pt}\{\mathrm{OP(OMe)_2}\}_2\{\mathrm{HOP(OMe)_2}\}_2]$ the lowest energy charge-transfer band is at 310 nm. The reason for the low energy band in $[\mathrm{Pt}\{\mathrm{OP(OH)_2}\{\mathrm{P(OH)_3}\}_2]$, along with the failure of efficient quenching at room temperature in aqueous solution, is currently being investigated. It is interesting to speculate, however, that the failure of water to quench the emission may be due to the fact that the solvent water preferentially hydrogen bonds to the ten hydroxy groups of the ligand, rather than to co-ordinate to the central metal atom. This postulate derives some support from the symmetrical unstructured nature of the emission band which makes it likely that the excited state is metal centred.

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† Satisfactory microanalytical data were obtained for all new numbered compounds.

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