The Gas Chromatography of Transition-metal Chelates of Bisacetylacetone-ethylenedi-imine and its Analogues

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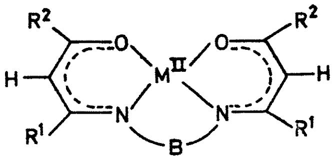
Summary The first gas-chromatographic separations of volatile quadridentate metal chelates of bisacetylacetone-ethylenedi-imine and its analogues are reported.

THERE are numerous examples of the analytical determination of metals by g.l.c. and mass spectroscopy of volatile metal chelates.[1] Considerable emphasis has been placed on the study of monomeric thermally stable complexes of the type $M^{III}(\beta\text{-diketone})_3$, but relatively little success has been achieved for chelates of the type $M^{II}(\beta\text{-diketone})_2$ which are often readily oxidised or are polymeric or solvated. In particular, if M^{II} is a transition-metal ion having a co-ordination number greater than four, the neutral chelate molecule may act as a Lewis acid forming stable base adducts, the presence of which precludes ready volatilisation.[2]

We have reported the g.l.c. of Co^{II}, Ni^{II}, Pd^{II}, and Pt^{II} chelates of both non-fluorinated and fluorinated monothio-β-diketonates[3] and considered their analytical potential particularly for metal ions possessing both (a) and (b) class character.[4] Miyazaki *et al.* have reported a study of the g.l.c. characteristics of Cu^{II} and Ni^{II} chelates of some β-ketoamine derivatives of acetylacetone and salicylaldehyde, only bis-(4-aminopent-3-en-2-ono)Ni^{II} showing sufficient stability for quantitative chromatography.[5]

In view of the enhanced stability of tetradentate β-ketoamino complexes of the structural type (1),[6] formed by the condensation of one mole of the appropriate diamine with two moles of a β-diketone, it might be predicted that these neutral complexes could be volatilised and gas-chromatographed unchanged. We have thus prepared Cu^{II}, Ni^{II}, Pd^{II}, and Pt^{II} chelates of this type where $R^1 = R^2 = Me$ or $R^1 = Me$, $R^2 = CF_3$ and $B = (CH_2)_2$ or CH_2CHMe. The ligands were made by direct reaction of the appropriate diamine with either acetylacetone or trifluoroacetylacetone, followed by recrystallisation from water for the former and from diethyl ether or light petroleum for the latter compounds. The ligands may be referred to by the following abbreviated



$R^1,R^2 = Me, CF_3$;

$B = (CH_2)_2\ (CH_2)_3,\ CH_2\cdots CHMe.$

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forms: bisacetylacetone-ethylenedi-imine, $H_2(enAA_2)$; bistrifluoroacetylacetone-ethylenedi-imine, $H_2(enTFA)_2$; bisacetylacetonepropylenedi-imine, $H_2(pnAA_2)$ and bistrifluoroacetylacetonepropylenedi-imine, $H_2(pnTFA_2)$.‡

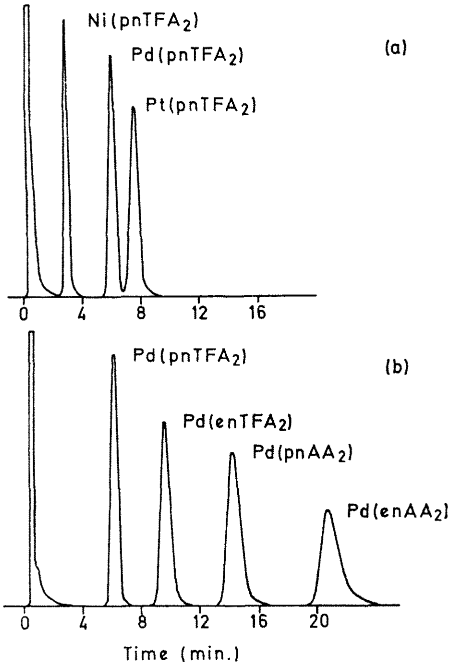

FIGURE. *Chromatograms of* (a) *separation of* Ni^{II}, Pd^{II}, *and* Pt^{II}, (20 *μg in* $CHCl_3$ *solution*) *chelates of* $H_2(pnTFA_2)$, (*b*) *quadridentate* Pd^{II} *complexes* (*each* 20 *μg in* $CHCl_3$ *solution*). 6 *ft. stainless-steel column* ($\frac{3}{16}$ *in. o.d.*) *packed with* 5% *Apiezon L on 'Universal B'* (60—85 *mesh*). *Column temperature* 250°; *injection temperature* 270°, *and detector temperature* 260°. *Nitrogen flow rate* 75 *ml* min^{-1}.

The Ni^{II} and Cu^{II} chelates were prepared either by heating suspensions of the anhydrous metal hydroxide under reflux with acetone solutions of the ligand or by treating the aqueous metal ammine complexes with the free ligand in aqueous or acetone solution. The Pd^{II} and Pt^{II} chelates were made by heating the ligand under reflux with benzene solutions of $PdCl_2,2PhCN$ and $PtCl_2,2PhCN$, respectively. All chelates were purified by vacuum sublimation. Correct microanalyses were obtained for each compound and mass-spectral analysis§ gave a top mass for each chelate corresponding to the molecular ion of the quadridentate complex.

G.l.c. studies were made with a Pye R research chromatograph equipped with a flame ionisation detector. Typical separations are shown in the Figure. The Ni^{II}, Pd^{II}, and Pt^{II} complexes show no sign of thermal decomposition at the high column temperatures employed and resolution and peak shape are excellent. It is noteworthy that for a given metal, the presence of trifluoromethyl groups and the substitution of a methyl group for hydrogen in the bridging group both increase volatility. The Cu^{II} complexes were somewhat less stable, only $Cu(pnTFA_2)$ being eluted with no signs of decomposition. In general, copper and nickel complexes of the same ligand exhibit virtually identical retention times and cannot be resolved on this column. Thermogravimetric studies have confirmed the great thermal stability of the Ni^{II}, Pd^{II}, and Pt^{II} chelates at temperatures above 300° and both quantitative and qualitative g.l.c. and mass-spectral analyses of this class of chelate appear to have considerable potential.

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‡ Non-systematic nomenclature is used because it indicates structure, mode of preparation and relationship with the parent diketones more closely than does the systematic nomenclature.

§ Mass spectral analysis was performed on an AEI MS9 mass spectrometer using a direct insertion probe.

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