Gas-chromatographic Separation of Nickel(II), Palladium(II), and Platinum(II) Bismonothiotrifluoroacetylacetonates

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Summary The gas-chromatographic separation of three transition metals in the same group of the Periodic Table is reported for the first time.

THE successful gas chromatography of metal β-diketonates has greatly extended the application of this technique to metal analysis.[1,2] Our interest in this field has included some of the more difficult metal separations, particularly those between members of the same periodic group where we hoped that some degree of resolution might be possible. The only reported example of the separation of three metals in the same group is for the trifluoroacetylacetonates of Al^{III}, Ga^{III}, and In^{III}.[3]

We now describe the first example of the gas chromatography of metal monothiotrifluoroacetylacetonates, the first recorded chromatogram of any platinum chelate, and the successful separation of three transition metals, Ni^{II}, Pd^{II}, and Pt^{II}, in the same Periodic Group. This separation confirms the great potential of monothio-β-diketonates as suitable chelates for gas-chromatographic study,[4,5] particularly for metal ions possessing both (a) and (b) class character[6] whose β-diketonates give unsatisfactory gas-chromatographic behaviour.

Monothiotrifluoroacetylacetone (t-tfa) was prepared by the method of Livingstone *et al.*,[7] by treating a 5% solution of trifluoroacetylacetone in ethanol at −70°, with hydrogen sulphide and hydrogen chloride. The nickel chelate was prepared by shaking the ligand in n-hexane with aqueous nickel acetate solution; it was then purified by vacuum sublimation. The other chelates were made by heating the ligand under reflux with benzene solutions of $PdCl_2,2C_6H_5CN$ and $PtCl_2,2C_6H_5CN$, respectively, evaporating to dryness and purifying by vacuum sublimation. Correct microanalyses were obtained for each compound,

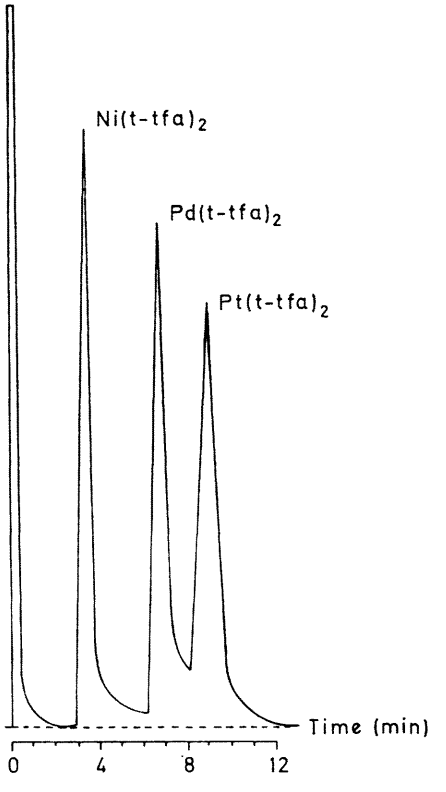

FIGURE. *Chromatogram of* Ni^{II}, Pd^{II}, *and* Pt^{II} *bis(monothiotrifluoroacetylacetonates).* 6 *ft. stainless steel column* (1/8 *in. o.d.*) *filled with* 2·5% *Apiezon L on "Universal B"* (60—85 *mesh*). *Column temperature* 170°; *injection temperature* 190°; *and detector temperature* 190°. *Nitrogen flow rate* 60 *ml./min.*

and mass spectral analysis† gave a top mass for each chelate corresponding to the molecular ion of the bis-complexes.

Gas-chromatographic studies were made with a Pye R research chromatograph equipped with a flame ionisation detector. The sharp symmetrical peaks obtained for each chelate make them particularly suitable for quantitative gas chromatography. Under the conditions given in the Figure and with the instrument operating at its optimal sensitivity, the limits of detection found for each individual chelate were: $Ni(t\text{-}tfa)_2$, 5×10^{-7} g of chelate (*ca.* $7{\cdot}5 \times 10^{-8}$ g of Ni^{II}); Pd $(t\text{-}tfa)_2$, 8×10^{-7} g of chelate (*ca.* 2×10^{-7} g of Pd^{II}); and Pt $(t\text{-}tfa)_2$, 1×10^{-6} g of chelate (*ca.* $3{\cdot}6 \times 10^{-7}$ g of Pt^{II}). These values indicate negligible sample loss by adsorption or decomposition on the long steel column used.

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† Mass spectral analysis was performed on an A.E.I. MS9 mass spectrometer using a direct insertion probe.

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