Gas Chromatography of Transition-metal Monothioacetylacetonates

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Summary The gas chromatography of transition-metal bis(monothioacetyl-acetonates) is reported for the first time.

THE gas chromatography of metal β-diketonates has become important for the determination of small amounts of certain metal ions.[1] Successful chromatography has been largely confined to complexes of the type M^{III} ligands$_3$. We report the preparation and g.l.c. separation of some transition-metal bis(monothioacetylacetonates).

Monothioacetylacetone (ta) was prepared by a variation of the method of Chaston *et al.*,[2] by treatment of a 5% solution of acetylacetone in absolute ethanol at −70° with hydrogen sulphide and hydrogen chloride. The ligand was isolated as the lead complex and regenerated as required by treatment of a dry ethereal suspension of the lead complex with dry hydrogen sulphide. Cobalt(II), nickel(II), and palladium(II) bis(monothioacetylacetonates) were prepared by adding an aqueous solution of the metal ion to an ethereal solution of the ligand. The chelates were recovered by evaporation of the ethereal layer. The nickel(II) chelate[2] and the cobalt(III) chelate[3] have been

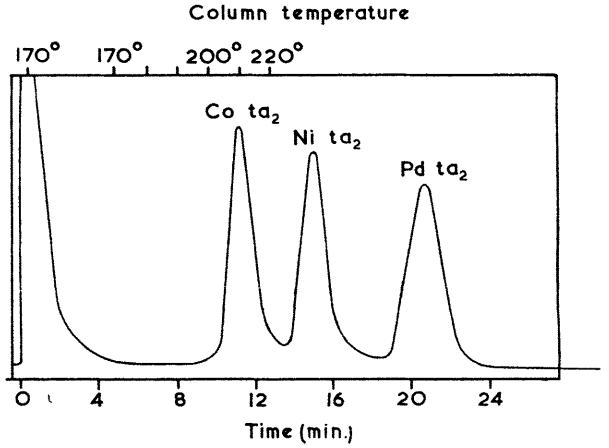

FIGURE. *Chromatogram of* Co^{II}, Ni^{II}, *and* Pd^{II} *bis(monothioacetylacetonates). Eluted from a* 3 *ft. Teflon column* (3/16 *in. o.d.*) *packed with* 5% *Apiezon on Universal B* (60—85 *mesh*) *support. Column programmed from* 170° to 220°. *Injection port*, 240°. *Nitrogen flow rate*, 120 *ml./min.* Co^{II} *and* Ni^{II} *complexes*, 40 μg.; Pd^{II} *complex*, 60 μg. *in* $CHCl_3$ *solution.*

reported previously, but not the cobalt(II) and palladium(II) chelates. The cobalt(II) and nickel(II) complexes were purified by preparative scale gas chromatography and the palladium complex by recrystallisation from carbon disulphide.

Mass spectral analysis† indicated the molecular ion of the bis-complex as the top mass for each complex. Gas chromatographic analysis was carried out on a Philips PV 4000 research chromatograph equipped with a flame ionisation detector.

The symmetrical peak shape observed for the bis(monothioacetylacetonates) gives good prospects for quantitative analytical applications. General chromatographic characteristics are superior to those of most volatile metal tris-(β-diketonates) and adsorption and decomposition are minimal. Furthermore the metals forming volatile bis-(monothioacetylacetonates) are those whose β-diketonates are not readily chromatographed. The great thermal stability of the complexes is indicated by the elution of the Ni^{II} complex at 240° without decomposition.

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

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[2] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Austral. J. Chem.*, 1965, **18**, 673.
[3] S. H. H. Chaston and S. E. Livingstone, *Austral. J. Chem.*, 1967, **20**, 1065.