followed by extraction with ethyl alcohol, gave a product which was separated into two fractions: (1) an ether-soluble fraction (A) and (2) an aqueous portion (B). The ether-soluble fraction (A) gave quercetin (yield, 0·05%), identified by paper chromatography in butanol-acetic acid-water (4 : 1 : 5) and 60% acetic acid, further confirmed by the preparation of its pentaacetate and pentamethyl ether.

The aqueous fraction (B) was worked up using basic lead acetate when a yellow lead salt was precipitated. Decomposition of the lead salt gave an impure yellow residue, m.p. 222–226°, which could not be purified and hence was subjected to acid hydrolysis giving rise to a yellow flavonoid, m.p. 312–314° which on chromatographic study in 60% acetic acid and butanol-acetic acid-water (4 : 1 : 5) showed that the product, 312–314°, is only quercetin contaminated with kaempferol. The sugar moiety was examined by paper chromatography, identified as galactose.

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THE VISIBLE ELECTRONIC ABSORPTION SPECTRUM OF *BIS* (2-METHYLPYRIDINE) NICKEL (II) CHLORIDE IN 2-METHYLPYRIDINE

Quagliano *et al.*[1] first reported the preparation of *bis* (2-methylpyridine) nickel(II) chloride. On the basis of its magnetic moment, diffuse reflectance spectrum and dark blue colour, they reported the complex had a pseudotetrahedral structure in the solid state. Quagliano and different co-workers[2] later prepared the complex using the original method and claimed the absorption spectrum indicated the complex was also tetrahedral in dichloromethane, but, they did not give any spectral details.

The thermal decomposition of the complex was later studied by Allan *et al.*[3] and Beech *et al.*[4] However, Allan *et al.* claimed that the complex prepared by them, using the method of Quagliano and co-workers,[1,2] was yellow in colour and possessed an absorption spectrum characteristic of octahedral nickel (II). The difference between the yellow complex prepared by Allan *et al.*[3] and the blue complex of Quagliano *et al.*[1] was explained as due to different forms of the same complex.

We now report a new method for the preparation of *bis*(2-methylpyridine)nickel(II) chloride which yields a product of high purity, and report for the first time its visible absorption spectrum in 2-methylpyridine.

The colour of the complex is deep purplish-blue in the solid state. Solutions of it in 2-methylpyridine are the same deep colour. The agreement between the solid state spectrum and the solution spectrum in 2-methylpyridine can be seen from Fig. 1 where both spectra are shown. The absorption spectrum in 2-methylpyridine has four bands, one of low intensity at 428 mμ and three overlapping bands of high intensity at 528, 575 and 608 mμ, with maximum absorption at 608 mμ ($\epsilon \simeq 180$). The extinction coefficients and position of the absorption bands in 2-methylpyridine are consistent with those reported for tetrahedral heterocyclic base complexes of nickel(II) in solvents such as dichloromethane and chloroform.[2,5,6]

The necessity for anhydrous solvent free from other methylpyridine isomers, in order to preserve the tetrahedral structure of nickel(II) in 2-methylpyridine, may be readily demonstrated. The addition of trace amounts of either water or 3- or 4-methylpyridine to the deep purplish-blue solution of nickel(II) in 2-methylpyridine, results in a colour change to deep-green. The absorption spectrum of this green solution possesses absorption bands of low intensity characteristic of octahedral nickel(II). The susceptibility of the 2-methylpyridine solution of nickel(II) to these above-mentioned effects, which result in change of solution stereochemistry for the nickel (II)

species, is in sharp contrast to the corresponding solution of cobalt(II) in 2-methylpyridine, where the tetrahedral species of cobalt(II) is maintained even with moderate concentration of water or other methylpyridine isomers.[7]

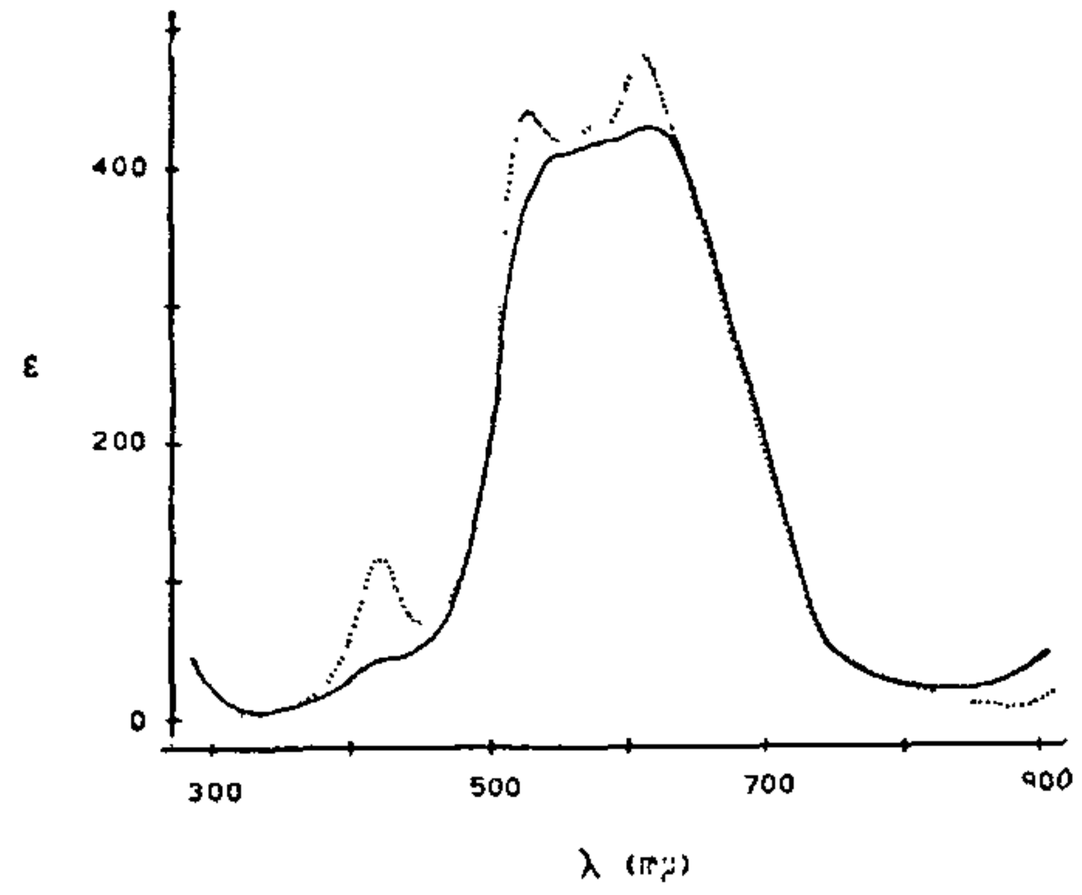

FIG. 1. Diffuse reflectance spectrum of *bis* (2-methylpyridine) nickel(II) chloride (——); Solution spectrum of $2{\cdot}72 \times 10^{-3}$ M *bis* (2-methylpyridine) nickel (II) chloride in 2-methylpyridine (....).

Experimental

Bis(2-methylpyridine)nickel(II) chloride was prepared by boiling 10 g hydrated nickel (II) chloride (Merck G.R.) with 100 ml 2-methylpyridine (Schuchardt) for 30 minutes, the solution filtered hot and allowed to cool in a stoppered flask. The cold solution was allowed to stand 24 hours after which time crystals separated out. The deep purplish-blue crystals, obtained from the 2-methylpyridine, were recrystallised twice by the same method, dried over P_2O_5 and analysed for C, H, N. Calculated for $Ni(C_6H_7N)_2Cl_2$: C, 45·6; H, 4·5; N, 8·9. Found: C, 45·2; H, 4·3; N, 8·5.

Schuchardt 2-methylpyridine was redistilled twice over potassium hydroxide and then stored over potassium hydroxide pellets. The purity of the solvent was checked by gas chromatography using a 5 ft. column of 10% triethanolamine on Chromosorb W (80/100 mesh) with an oven temperature of 70° C. Chromatograms were determined on a Varian Aerograph Model 1520.

Spectra were determined on a Zeiss PMQ II Spectrophotometer.

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SOME NEW BENZOTHIAZOLYL GUANIDINES

Several biological activities associated with substituted guanidines, *viz.*, algaecidal,[1] antibacterial,[2] antitubercular,[3] hypoglycemic,[4] etc., have stimulated the author to conduct research in this line. These benzothiazolyl guanidines have been synthesised by desulphurisation of corresponding benzothiazolyl thiocarbamides with yellow lead oxide in ethanolic alkyl amines.

Experimental

N-p-Chlorophenyl-N'-2-(substituted) benzothiazolyl thiocarbamides.—These were prepared by taking a requisite amount of 2-amino (substituted) benzothiazoles and *p*-chlorophenyl-isothiocyanate in dry benzene as reported earlier.[5]

N-p-Chlorophenyl-N'-2-benzothiazolyl-N"-n-propyl guanidine.—A mixture of N-*p*-chlorophenyl-N'-2-benzothiazolyl thiocarbamide (0·01 mole), *n*-propylamine (0·011 mole) and yellow lead oxide (0·021 mole) in ethanol (30 ml) was refluxed in a sealed tube on a water-bath for 4 hr. After removing the lead sulphide by filtration, the filtrate was concentrated to get the corresponding guanidine. It was recrystallised from ethanol.

Likewise, various N-*p*-chlorophenyl-N'-2-(substituted)-benzothiazolyl-N"-alkyl guanidines were synthesised from N-*p*-chlorophenyl-N'-2-