The internal monitor reactions used were:  $^{106}Cd(n,2n\beta^+)^{105}Ag$  ( $\sigma = 975 \pm 86$  mbarn) and  $^{106}Cd$ [(n,np) + (n,pn) + (n,d)]  $^{105}Ag$  ( $\sigma = 215 \pm 29$  mbarn)[21].

The cross-section values given above fit well into the systematics [22, 23] of (n,p) reaction cross-sections at 14-MeV neutron energy.

From these experiments it may be expected that, if a high-spin isomer were to exist in <sup>112</sup>Ag analogous to <sup>106m</sup> Ag and <sup>110m</sup> Ag, it should have been formed in the activation of <sup>112</sup>Cd with 14-MeV neutrons. Our experimental search, however, does not provide any evidence for such an isomer.

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# A modified preparative procedure for di-*n*-octylphenylphosphonate mediator used in calcium ion selective electrode membranes

#### (Received 20 May 1974)

A RECENT procedure [1] for preparing di-*n*-octylphenylphosphonate used as mediator in liquid ion exchanger sensors for calcium ion selective electrode membranes was based on gel permeation chromatography purification because attempted distillation of the crude phosphonate caused decomposition. Because the gel permeation chromatography stage gives low yield and is time consuming, purification by distillation has been re-examined. Di-*n*-octylphenylphosphonate product has thus been obtained in high yield and resembles the gel permeation chromatography purified product in all respects, including i.r. scans and the single spot obtained by thin layer chromatography. The refractive index,  $n_{2s}^{D}$ , of the material is 1.4747.

In the modified procedure, the crude phosphonate

product was prepared in the manner previously described [1] by treating phenylphosphonate dichloride (78g) with redistilled *n*-octanol (120g) but allowing a further 3 hr over and above the initial 2 hr reaction stage to allow for the doubled quantities of reactants. The pale straw-coloured material remaining after removing excess *n*-octanol was treated with 3.5g sodium perborate (Hopkin and Williams) and refluxed for 30 min at  $10^{-3}$  mm Hg in order to reduce the coloration[2]. The very pale yellow liquid then remaining was carefully distilled at  $5 \times 10^{-4}$  mmHg and the middle fraction (75g) collected as a colourless di-*n*-octylphenylphosphonate product with all the characteristics of the gel permeation chromatography purified material.

It is emphasised that the refluxing and final distillation

stage must be performed with great care to prevent charring and bumping of the flask contents. Thus, the pressure must be kept low, for reduced pressures of 1-2 mm Hg invariably cause charring. In order to prevent bumping it is also imperative that the reflux distillation flask be subjected to even, all-round heating with a bunsen burner held in the hand rather than with an oil bath.

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## Isomeric tricyano 2,2'-dipyridylnitrosyliron(II) complexes

## (Received 14 January 1974)

SINCE THE isolation of the nitroprusside anion[1] only alkylated derivatives of the above anion have been reported [2]. Hexaco-ordinated Fe(II) nitrosyl complexes are rare. In this communication, we wish to report the isolation and characterization of tricyano 2,2'-dipyridylnitrosyliron(II) complex in two forms.

#### EXPERIMENTAL

All reagents used were analytical grade.

Sodium nitroprusside dihydrate (1.5 g) was refluxed with 0.8 g 2.2'-dipyridyl in 20 ml dilute acetic acid (1:1) for 8 hrs to yield a reddish violet solution. The solution was evaporated to dryness and the violet residue washed several times with acetone to remove any unreacted dipyridyl or free acid. Excess dry methanol was added to dissolve unreacted nitroprusside and the sodium acetate formed. The methanolic solution was decanted from the deep violet compound. This process was repeated thrice. The compound was dissolved in methanol by warming and reprecipitated by adding acetone. The precipitate was filtered and washed with methanol and acetone and vacuum dried. The yield was 40 per cent of the theoretical value. Analysis gave the formula [FeNO(CN)<sub>3</sub>dipy]. (Found: Fe, 17.52%; N, 26.30%. Requires for the above formula: Fe, 17.46%; N, 26.25%). Another synthetic route gave a better yield. (dipy H)<sub>2</sub>[Fe(CN)<sub>5</sub>NO] salt (1g), prepared by metathesis of stoichiometric amounts of dipyridyl hydrochloride and sodium nitroprusside in methanol, was taken in a glass boat and heated in a metal block furnace at 185° in an atmosphere of dry CO<sub>2</sub> for about 5 hr when the dehydrocyanogenation reaction ceased and a dark violet mass was obtained. This was powdered and washed with water and acetone and dried in vacuum. The yield was almost quantitative. Found: Fe, 17.63%; N, 26.12%. Required for the above formula: Fe, 17.46%; N, 26.25%.

#### **RESULTS AND DISCUSSION**

The analytical results for both products are the same but they show some differences in solubility. Both are soluble in water and alcohols and insoluble in acetone and other nonpolar organic solvents but the solid phase product appears less soluble. It is only sparingly soluble in water whereas the product obtained from solution is freely soluble. Alkali decomposes the complexes with the expulsion of dipyridyl and the solid phase product is the more resistant to decomposition.

The molar conductance values of  $1.0 \times 10^{-3}$  M solutions of the two products in water are  $5 \cdot 6 \ \Omega^{-1} \ cm^2$  and  $11.0 \Omega^{-1} \text{ cm}^2$  at 23° respectively showing them to be non-electrolytes. AgNO<sub>3</sub> does not give any precipitate from their aqueous solutions. The electronic spectra in aqueous solution give gands at 201, 247, 257 (shoulder), 288, 298, 352, 490 and 522 nm for the solvent phase product and at 201, 247 (shoulder) 257 (shoulder), 288, 296, 345 and 488 nm for the solid phase product. The doublet bands at 288, 298 nm and 288, 296 nm are very intense and are due to the coordinated dipyridyl. These bands are absent for the nitroprusside anion[3], and are characteristic of the coordination of dipyridyl to a bivalent metal ion [4]. The i.r. spectra of the two complexes in nujol mulls show some interesting features. Excluding the co-ordinated dipyridyl bands, the CN-stretching and the NO-stretching frequencies for the two forms are given in Table 1.

All the bands given in Table 1 are sharp. Considering the presence of the NO and dipyridyl ligands, the point groups of both molecules should be  $C_s$ . However, both NO and dipyridyl are co-ordinating through N and in compounds like  $[M(CO)_3 dipy L]$   $(M = Cr, Mo \text{ or } W; L = py, C_6H_{11}NH_2, CH_3CN, etc.)$ , the 'E' band is not split for C, symmetry and the local symmetry corresponds to  $C_{3\nu}$  [5]. Hence, taking into account of the relative intensities as well as the sharpness of the bands, a local symmetry of  $C_{3v}$ is suggested for the solvent phase product rather than  $C_s$ . Similarly, as the low frequency CN-band of the solid phase product is strong, it may be due to the  $B_1$  mode for  $C_{2\nu}$ symmetry. However, for this symmetry the higher CN-frequency band due to the  $A'_1$  mode should be of medium intensity rather than weak. But nothing can be said conclusively because interactions between the cyanide and nitrosyl groups are likely. Moreover, further complexities may arise in solid state spectra. It may be that the solvent phase product is the cis-form and the solid phase product is the trans.