The α- and the β-Form of the Nickel(II) Diethylphosphinodithioic Acid Chelates

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Two isomeric forms of the ligand, diethylphosphinodithioic acid, Et_2PS_2H and two isomeric forms of its nickel(II) chelates have been reported by Malatesta and his co-workers.[1–3] The α-form of the ligand was prepared by the reaction of diethylphosphine with sulphur and the β-form was isolated, together with the α-form, from the reaction products of ethylmagnesium bromide and phosphorus pentasulphide. Dipole moments in benzene supported the idea that the α- and β-isomers[4] of the nickel compound were stereoisomers.

The α- and the β-form of bis(diethylphosphinodithioato)nickel(II) were prepared and isolated by the reported method,[1–3] which involved reaction between EtMgBr and P_2S_5. The two forms were separated by fractional crystallization from ethanol, the α-form being only sparingly soluble. Crystals of the α-form obtained from ethanol–acetone were blue or purple tablets (m.p. 142°; lit.[3] 140·5° and lit.[5] 142·5°).

Rod-shaped crystals of the β-form, crystallized from an ethanol solution, exhibited similar dichroic behaviour (m.p. 106—107°; lit.[2,3] 110°). Elemental analyses of the two compounds agreed with the postulated formula, $NiS_4P_2C_8H_{20}$. Crystals of the β-form were triclinic, space group $P\bar{1}$ or $P1$, $a = 7{\cdot}96$, $b = 7{\cdot}65$, $c = 7{\cdot}44$ Å, $\alpha = 89{\cdot}7$, $\beta = 104{\cdot}8$, $\gamma = 107{\cdot}0°$; $D_0 = 1{\cdot}46$ (by flotation) gave a calculated molecular weight of 376 for $Z = 1$. Crystals of the α-form were monoclinic, space group $C2/m$, Cm, or $C2$, $a = 8{\cdot}25$, $b = 12{\cdot}80$, $c = 8{\cdot}17$ Å, $\beta = 104{\cdot}2°$; $D_0 = 1{\cdot}45$ g.cm.$^{-3}$ (by flotation) and the calculated molecular weight was 365 for $Z = 2$ Despite the small difference in the molecular weights this confirmed the presence of two isomeric forms of bis(diethylphosphinodithioato)nickel(II). The i.r., u.v., visible, and ^1H n.m.r. spectra were examined and the molecular weights confirmed by mass spectrometry.

The ^1H n.m.r. spectra at 60 Mc./sec. of saturated solutions of the two forms in deuteriochloroform with Me_4Si as internal standard could not be interpreted on the basic assumption the α- and the β-form are structural isomers. The ^1H n.m.r.

spectrum of the β-form shows the presence of a multiplet centred around 4·5 p.p.m. (Figure A). The same multiplet is observed in the ^{1}H n.m.r. spectrum of bis-(*OO'*-diethyl phosphorodithioato)-nickel(II)[6] obtained under comparable conditions (Figure B), but the spectrum of the α-form shows no evidence of such a multiplet (Figure C). These spectra suggest that the crystals of the β-form contain a compound with a methylene group whose environment is identical with that of the methylene group in bis-(*OO'*-diethyl phosphorodithioato)-nickel(II). We therefore, conclude that the single crystals of the β-form of bis(diethylphosphinodithioato)nickel(II), consist of mixed crystals containing at least two structurally similar compounds with different chemical compositions.

The presence of two compounds in the crystals of the β-form was shown by carrying out a chromatographic separation. A solution of the β-form in ether was applied on a t.l.c. plate coated with silica gel G (Applied Science Laboratories Inc.) and separated into two distinct zones with a mixture of 90% v/v light petroleum and ether as eluant. No such separation occurred with the α-form. Mass spectra of the β-form between 100—120° showed the presence of two compounds with molecular weights of 364 and 396. The mass spectrum of the α-form at 125° showed a single parent peak that corresponded to a molecular weight of 364.

I.r. spectra of the α- and the β-form in KBr discs showed marked differences. Several frequencies attributable to P–O–C vibrations (1150m, 990s, 950s, and 780s cm.$^{-1}$) were present in the i.r. spectrum of the β-form and that of the bis-(*OO'*-diethyl phosphorodithioato)nickel(II), but were not found in the spectrum of the α-form.

The locations of the absorption maxima and the values of the corresponding molar absorptivities in ethanol solutions for the α-form are: 728 ($\epsilon = 77$), 564 (91), 384 (1460), 330 (15,520), 227 mμ (10,000), and for the β-form are: 710 ($\epsilon = 72$), 550 (86), 384 (1330), 325 (15,000), 227 mμ (8900). Hence, the electronic spectra of the two compounds are similar but not identical.

These results indicate that the triclinic crystals of the β-form of bis(diethylphosphinodithioato)-nickel(II) contain two compounds. From the i.r., ^{1}H n.m.r., and mass spectral data it is evident that one of the compounds is the α-form of bis(diethylphosphinodithioato)nickel(II). The second compound is most probably the nickel(II) chelate, $Ni[S_2P(OEt)Et]_2$, bis-(*O*-ethyl ethylphosphonodithioato)nickel(II). A large scale separation of the crystals of the β-form was carried out on a Florisil column (40 cm. × 2·5 cm.). A saturated solution of the β-form in ether was added to the top of the column and eluted with a 90% v/v light petroleum–ether mixture. The deep blue α-form of bis-(diethylphosphinodithioato)nickel(II), was more strongly retained on the column than the purple coloured nickel(II) chelate of the *O*-ethyl hydrogen ethylphosphonodithioate. During separation, several batches of mixed crystals of the β-form, containing varying amounts of the two compounds, were obtained and at one stage the melting point of the mixed crystals was 110°. After repeated separation, pure triclinic crystals of bis(*O*-ethyl ethylphosphonodithioato)nickel(II) (m.p. 121°) were obtained and identified by ^{1}H n.m.r. (Figure A), and i.r. spectra, the parent peak in the mass spectrum at 115° was at $m/e = 396$.

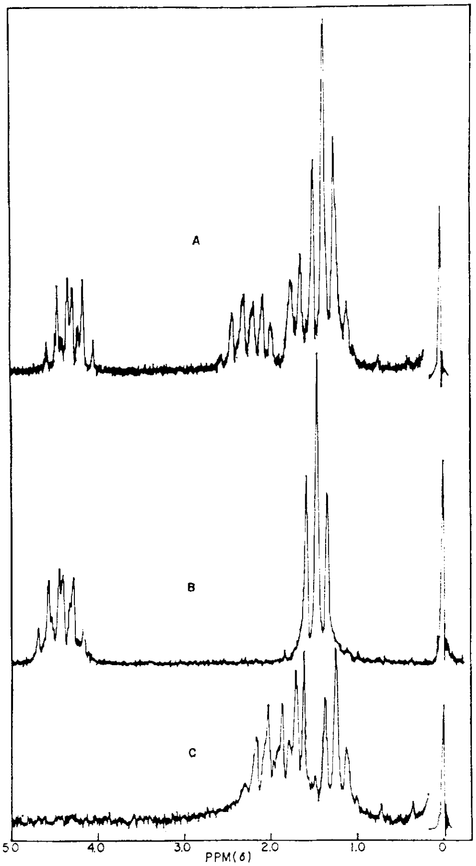

FIGURE. ^{1}H *n.m.r. Spectra in* $CDCl_3$ *with internal* Me_4Si *standard:* A, $Ni[S_2P(OEt)Et]_2$; B, $Ni[S_2P(OEt)_2]_2$; C, $Ni[S_2PEt_2]_2$.

We therefore concluded that only one form (*i.e.*, the α-form) of bis(diethylphosphinodithioato)-nickel(II) can be synthesized. The β-form consists of a mixture of two nickel(II) chelates, the α-form and bis-(*O*-ethyl ethylphosphonodithioato)nickel(II). A complete single-crystal three-dimensional structure determination of these two chelates has been undertaken which suggests tetrahedral distribution around the phosphorus atoms.

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