

## THE REACTION OF NICKEL(II) IONS WITH ETHYL ACETOACETATE\*

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There has recently been considerable interest in the stereochemistry of nickel(II) complexes with a stoichiometry of four coordinating groups per nickel ion. Three different structures have been observed: planar, octahedral, and tetrahedral. Structural studies of anhydrous bis(acetylacetonato)nickel(II) have shown that the compound is not tetrahedral but an octahedral trimer.<sup>1</sup> In view of this result it was decided to investigate the reaction of nickel(II) ions with the keto-ester, ethyl acetoacetate.

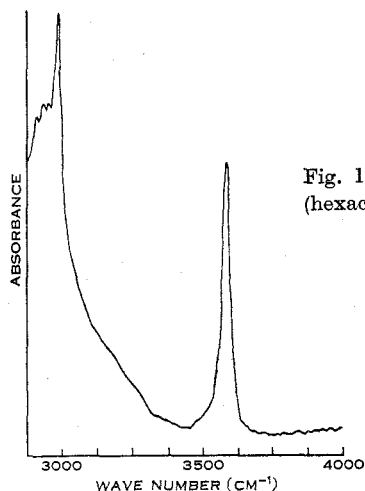


Fig. 1.—Infrared spectrum of  $\text{acet}_5\text{Ni}_3\text{OH}$ , (hexachlorobutadiene mull).

Solutions of the aqueous nickel(II) ion and ethyl acetoacetate do not yield precipitates directly, but addition of potassium hydroxide or ammonium hydroxide to the solution causes precipitation of a complex. If ammonium hydroxide is used to make the solution alkaline a pale blue complex is obtained. This compound contains coordinated ammonia, which is readily removed by heating at  $110^\circ$  to yield a pale green complex. This green complex can be recrystallized from warm dry benzene as large bright green crystals which rapidly crumble to a pale green paramagnetic powder on filtering from benzene. Analytical data are not in accord with those expected for bis(ethyl acetoacetato)nickel(II), a result previously noted by Wisliscenus.<sup>2</sup> The infrared spectrum of the complex (Fig. 1), has a very sharp band at  $3587\text{ cm}^{-1}$  due

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<sup>1</sup> Bullen, G. J., Mason, R., and Pauling, P., *Nature*, 1961, **189**, 291.

<sup>2</sup> Wisliscenus, W., and Stoeber, W., *Liebigs Ann.*, 1902, **35**, 539.

to a hydroxide ion or an OH bridge.<sup>3</sup> Cryoscopic measurements in benzene, although complicated by the rather low solubility of the complex, gave a value of  $800 \pm 50$  for the molecular weight. The visible spectrum in benzene is consistent with an octahedral complex,  $\lambda_{\text{max}}$ , 655  $\mu$ ,  $\epsilon$  15; and  $\lambda_{\text{max}}$  (shoulder) 382  $\mu$ ,  $\epsilon$  68. A strong band occurs in the ultraviolet at 283  $\mu$  (ethanol solution) which is most probably due to a  $\pi$ - $\pi^*$  transition in the enolate ion. The analytical data are in accord with the trinuclear structure  $\text{acest}_5\text{Ni}_3\text{OH}$  (mol. wt., 853), where *acest* represents the enolate ion  $\text{C}_6\text{H}_9\text{O}_3^-$ . (Preliminary n.m.r. measurements in benzene solution are also consistent with an OH bridged structure.)

Addition of pyridine to a benzene solution of the complex gives, on slow evaporation,  $\text{Niacest}_2\text{py}_2$  as bright blue crystals. Prolonged boiling of a benzene solution of the complex with ethyl acetoacetate gives the benzene-insoluble  $\text{Niacest}_2$  as a pale green crystalline powder,  $\mu_{\text{eff}}$ . (at  $20.2^\circ$ ) = 3.39 B.M., which is slightly soluble in dimethylformamide (DMF). The spectrum in this solvent has a band at 680  $\mu$ , but this is probably due to a monomeric solvate such as  $\text{acest}_2\text{Ni}(\text{DMF})_2$  rather than  $\text{acest}_2\text{Ni}$  itself and so does not provide evidence for the octahedral environment of the nickel atom in  $\text{acest}_2\text{Ni}$ .

### Experimental

*General.*—Infrared spectra were determined with a Perkin-Elmer 221 spectrophotometer. Samples were run in Nujol and hexachlorobutadiene. The ultraviolet and visible spectra were measured on a Unicam SP 700 recording spectrophotometer. The proton magnetic resonance spectra were measured with a Varian HR 60 n.m.r. spectrometer. Melting points are uncorrected. The microanalyses were performed by Dr. A. D. Campbell of the University of Otago, Dunedin.

*$\mu$ -Hydroxopenta(ethyl acetoacetato)trinickel(II).*—Nickel chloride hexahydrate (12 g) was dissolved in water (30 ml), filtered, and added to ethyl acetoacetate (13 g) in ammonia (80 ml, 4N). The pale blue complex precipitated almost immediately. The resulting product was washed with distilled water until the filtrate was free from the colour of the  $\text{Ni}(\text{NH}_3)_6^{2+}$  ion, and dried at  $110^\circ$  to a pale green powder. The major portion of this material could be recrystallized from warm dry benzene to give large bright green crystals (possibly a clathrate or solvate) which immediately crumbled to a pale green powder on filtering from benzene; the compound slowly decomposed above  $350^\circ$  (Found: C, 42.75; H, 5.7; Ni, 20.9%. Calc. for  $\text{C}_{30}\text{H}_{46}\text{O}_{16}\text{Ni}_3$ : C, 42.95; H, 5.5; Ni, 21.0%).

*Bis(ethyl acetoacetato)bis(pyridine)nickel(II).*—Pyridine (1.6 g) was added to  $\mu$ -hydroxopenta(ethyl acetoacetato)trinickel(II) (3.2 g) dissolved in the minimum of dry benzene. The solution turned blue green and on standing slowly deposited bis(ethyl acetoacetato)bis(pyridine)nickel(II). Recrystallization from benzene containing a few drops of pyridine afforded large blue crystals, m.p.  $164$ – $165^\circ$  (decomp.) (Found: C, 55.7; H, 6.2; N, 5.95; Ni, 12.4%. Calc. for  $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_6\text{Ni}$ : C, 55.6; H, 5.95; N, 5.9; Ni, 12.35%).

*Bis(ethyl acetoacetato)nickel(II).*— $\mu$ -Hydroxopenta(ethyl acetoacetato)trinickel(II) (2 g) was dissolved in dry benzene (30 ml) containing ethyl acetoacetate (4 g) and the solution refluxed for 6 hr. Pale green crystals of bis(ethyl acetoacetato)nickel(II) slowly deposited, m.p.  $233$ – $234^\circ$  (Found: C, 45.3; H, 5.9; Ni, 18.4%. Calc. for  $\text{C}_{12}\text{H}_{18}\text{O}_6\text{Ni}$ : C, 45.45; H, 5.7; Ni, 18.5%).

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<sup>3</sup> Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds." p. 75. (John Wiley: New York 1963.)