

The Interconversion of Some μ -Alkylthio- and Alkyl-trithiocarbonato-complexes of Nickel

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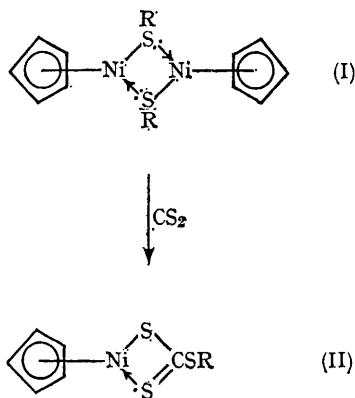
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CARBON disulphide insertion reactions are probably more common than is generally realised. Thus

the preparation of some *NN*-dialkyldithiocarbamate-derivatives recently reported by Bradley

and Gitlitz¹ provides additional examples of a reaction that has been used to convert nickel methoxide into bis-(*O*-methylxanthato)nickel,² and copper(I) *n*-butylmercaptide into an unstable *n*-butyltrithiocarbonato-complex.³

We have obtained substantial evidence that the μ -alkylthio-complexes⁴ (I; R = Me, Et) also undergo insertion reactions with carbon disulphide. In C₆D₆ solution the n.m.r. spectra of (I; R = Me, Et) are reconcilable with the proposed structures,



but in carbon disulphide solution the n.m.r. spectra are "time-dependent". The changes observed over 2 hours in the "zero-time" spectrum of the ethyl derivative are shown in Fig. 1. The appearance of the final spectrum is unchanged after 24 hours. The methyl derivative (I; R = Me) shows essentially similar behaviour but the phenyl derivative is unreactive. Accompanying these changes in the n.m.r. spectra, the solutions turn from a brown to a dichroic red-green colour, but the n.m.r. spectra reveal that only the μ -alkylthio-complex is obtained after complete removal of the solvent. Subsequent chromatography of the ethyl derivative (I; R = Et) causes some decomposition to [Ni(SET)₂]₆. Treatment of iodocarbonylcyclopentadienylnickel⁵ with sodium ethyltrithiocarbonate and a gross excess of carbon disulphide at -78°, produced a turquoise blue solution which became red-green as it lost CO on warming to room temperature; both (I; R = Et) and [Ni(SET)₂]₆ were obtained from this reaction after chromatography, but without excess of

carbon disulphide in the reaction, [Ni(SET)₂]₆ was the only isolable product.

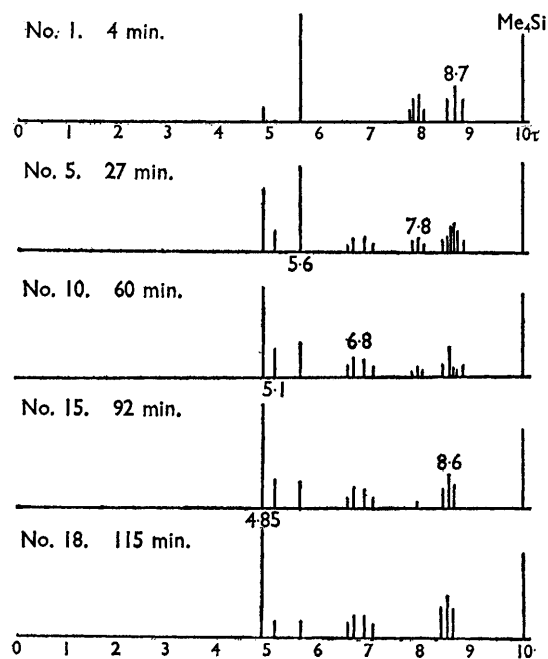


FIGURE 1.

A comparison of the n.m.r., u.v., and visible spectra of several stable trithiocarbonato, and trithiocarbonato-manganese, -iron, and -nickel complexes,^{6a} and the corresponding μ -alkyl(aryl)thio-derivatives,^{6b} with those obtained from this solution of (I) indicates that an unstable alkyltrithiocarbonatocyclopentadienylnickel complex (II; R = Me, Et) is formed. The decay of the τ 5.6 resonance (Figure 1) is first-order but the production of (II) is more complicated; the methyl derivative (I; R = Me) reacts slightly faster. It is noteworthy that paramagnetic intermediates do not interfere.

By contrast to (II) a more stable nickel complex (III) is obtained as green crystals, m.p. 94.5°, from sodium ethyltrithiocarbonate and anhydrous nickel chloride, although the other product,

¹ D. C. Bradley and M. H. Gitlitz, *Chem. Comm.*, 1965, 289.

² M. Nehmé and S. J. Teichner, *Bull. Soc. chim. France*, 1960, 659.

³ W. E. Duncan, E. Ott, and E. E. Reid, *Ind. Eng. Chem.*, 1931, **23**, 381.

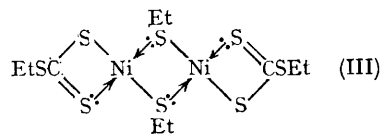
⁴ W. K. Schropp, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1688.

⁵ E. O. Fischer and C. Palm, *Chem. Ber.*, 1958, **91**, 1725.

⁶ (a) R. Bruce and G. R. Knox, in the press.

(b) M. Ahmad, R. Bruce, and G. R. Knox, unpublished observations.

$[\text{Ni}(\text{SEt})_2]_6$, presumably arises from the decomposition of (III). This black, crystalline, hexameric⁷ nickel mercaptide (m.p. 227—229°) is different from the previously reported polymeric material⁸; in spite of their bridging mercaptide type structure, neither of these will react with carbon disulphide.



⁷ R. G. Hayter and F. S. Humiec, *J. Inorg. Nuclear Chem.*, 1964, **26**, 807, have reported analogous $[\text{Pd}(\text{SR})_2]_6$ complexes.

⁸ K. A. Jensen, *Z. anorg. Chem.*, 1944, **252**, 227.