

***NN*-Dialkyldithiocarbamates of Transition-metals of Groups IV and V**

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ALTHOUGH the dithiocarbamate group is well known to chelate transition metals, little is known of dithiocarbamate-derivatives of Group IV and V metals in their highest valencies. In attempting to dissolve dialkylamino-compounds $M(NR_2)_x$ ($M = Ti, Zr, Hf, V, Nb, Ta$) in carbon disulphide for infrared-spectral measurements we found vigorous reactions resulting in the formation of *NN*-dialkyldithiocarbamates. Doubtless an addition reaction of the type reported by Jones and Lappert¹ takes place.

In the tetrakis-compounds $M(S_2CNR_2)_4$ ($M = Ti, Zr; R = Me, Et, Pr^n$) the possibility of eight-co-ordination of the metal arises. The *NN*-dimethyldithiocarbamates are practically insoluble and non-volatile and appear to be polymeric but the higher alkyl derivatives are soluble and monomeric. The infrared and n.m.r. spectra

of tetrakis-(*NN*-diethyldithiocarbamato)titanium are consistent with the presence of chelating dithiocarbamate groups. If chelation occurs, eight-co-ordination of titanium by sulphur is involved and it is noteworthy that the first authentic eight-co-ordinated titanium compound discovered² also contained large donor atoms (*e.g.* As and Cl).

From reaction involving pentakis-dimethylaminoniobium and carbon disulphide the insoluble tetrakis-(*NN*-dimethyldithiocarbamato)-niobium(IV) and tetramethyldithiuram disulphide were produced, suggesting that the niobium cannot sustain five dithiocarbamate-groups. Under similar reaction conditions $Ta(NMe_2)_5$ was converted into $Ta(S_2CNMe_2)_5$ revealing a major difference in chemistry between niobium and tantalum.

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¹ K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1962, 358.

² R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1962, 2460.