Nucleophilic Substitution Reactions of Co-ordinated Xanthates and Dithiocarbamates

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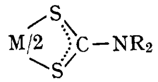
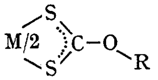
REACTIONS of co-ordinated ligands are important in chemical and biological systems,[1] though the influence of the metal ion often has been poorly understood.[2] Metal ions affect the physical properties of dithiocarbamates[3] and xanthates,[4,5] but little is known[6] of metal-influenced ligand reactions with these species.

We have found that certain metal dithiocarbamates (I), notably those formed with nickel(II), palladium(II), and platinum(II) ions undergo a ligand reaction in which the $-NR_2$ group is replaced cleanly by the nucleophile. For example, if $Ni(S_2CNH_2)_2$ in acetone is treated with an excess of morpholine, a high yield (50—90%) of the bis-morpholyl dithiocarbamate complex is obtained. [The m.p. and i.r. spectrum are identical with those from the nickel(II) complex formed directly from the morpholinium morpholyl dithiocarbamate.] With piperidine and $Ni(S_2CNH_2)$, a similar *trans-ammination* reaction occurs in acetone to form the piperidine product with a yield $> 80\%$.



(I)

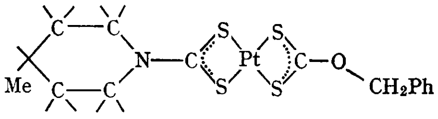


(II)

Since the $-NH_2$ appeared to be a "leaving group" in the above reaction, it seemed likely that metal xanthates (II) would behave similarly. When $Ni(S_2COEt)_2$ was treated with piperidine in acetone, the dithiocarbamate indeed resulted. The reaction is complicated, however by concomitant cleavage of the O–R bond with certain bases and alkyl groups.[7]

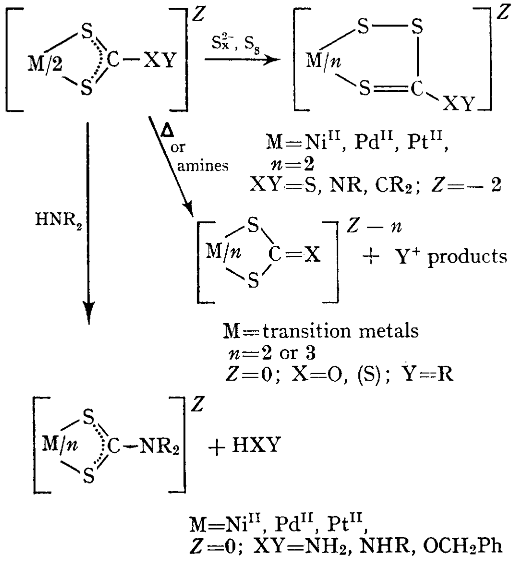
Preliminary studies of the reaction of base with the non-labile platinum(II) complex of benzoyl xanthate (II; $R{=}CH_2Ph$), suggest that the reaction occurs without rupture of the metal-sulphur bonds. When a toluene solution of $Pt(S_2CO{\cdot}CH_2Ph)_2$ reacts with an excess of 4-methyl-piperidine, the spectrum slowly (*ca.* 1 hr.) becomes that of the 4-methylpiperidine carbamate complex of platinum(II). A series of solutions containing various ratios of base-to-complex develop isosbestic points in the 400 to 500 $m\mu$ region which clearly indicate the formation of the mixed ligand (1 : 1) complex (III). Equilibria are slowly (*ca.* 1 hr.) achieved between the xanthate and the mixed ligand complex with difficiencies of base, and between the mixed ligand complex and the dithicarbamate in excess of base.

With nickel(II) xanthates and certain dithio-carbamates the reaction with strong bases gives high-spin "octahedral" adducts.[5] This imparts some lability to the ligands. Hence the reaction with the nickel(II) complexes may be different from the reaction with the platinum(II) complexes which are low-spin. However, direct nucleophilic attack appears to be the most reasonable way to account for the conversions which are observed.



(III)

Three different metal-influenced ligand reactions have now emerged from out studies of the 1,1-dithio-complexes. Each of these reactions, *sulphur oxidative addition*,[7] *carbon–oxygen cleavage*,[6] and the *nucleophilic substitution* appear to be metal-ion influenced. Studies of the role of the metal ion are currently in progress.



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