

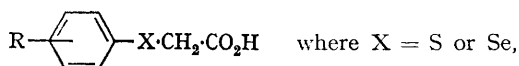
## A Comparison of the Donor Properties of Group VIB Elements

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WHILE oxygen co-ordinates preferentially with class (a) metals, sulphur and selenium form more stable complexes with class (b) metals.<sup>1</sup> They are therefore regarded as 'soft' acids while oxygen is regarded as 'hard'.<sup>2</sup> As a result of the paucity of quantitative data on the stabilities of complexes formed between organosulphur and organoselenium ligands and metal ions, sulphur and selenium are generally considered to be of approximately equal 'softness' and the high stability of the complexes they form with class (b) (soft) metal ions is usually explained by the introduction of back-co-ordination and  $d_{\pi}-d_{\pi}$  bonding.

We have synthesized 21 organosulphur and 20 organoselenium ligands, HL, of similar structure:



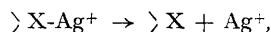
and measured the stability constants of the complexes  $\text{AgL}$ ,  $\text{AgHL}^+$ , and  $\text{AgL}_2^-$ , which they form with silver ions [typically class (b)], using a high precision potentiometric technique. In all cases the selenium ligands formed more stable complexes than the analogous sulphur ligands which, in turn, were more stable than the oxygen analogues. For example, for phenoxyacetic acid,

$\log K_{\text{AgL}} = 1.4$  while for the sulphur and selenium analogues ( $\text{R}=\text{H}$ ) the values are:

	$\log K_{\text{AgL}}$	$\log K_{\text{AgHL}}$	$\log K_{\text{AgL}_2}$
Thiophenoxy-acetic acid	.. 2.83	2.31	2.0
Selenophenoxy-acetic acid	.. 3.71	2.97	2.62

Omitting compounds with *ortho*-substituents, the differences,  $\log K_{\text{X}=\text{Se}} - \log K_{\text{X}=\text{S}}$ , for comparable ligands were remarkably constant, being  $0.83 \pm 0.04$  for the  $\text{AgL}$  and  $0.65 \pm 0.05$  for the  $\text{AgHL}$  complexes. Hence selenium is distinctly 'softer' than sulphur.

The dissociation of the silver complexes,



may be considered analogous to the proton dissociation of phenols,  $-\text{O}-\text{H} \rightarrow -\text{O}^- + \text{H}^+$ , apart from the difference in charges involved. The dissociation of phenols is closely analogous to that of benzoic acids and can be expressed, to a high degree of precision, by the Hammett equation,

$$\log K_{\text{R}=\text{R}'} - \log K_{\text{R}=\text{H}} = \rho\sigma$$

particularly if the Hammett functions,  $\sigma$ , for *para*-substituents showing large resonance contributions,

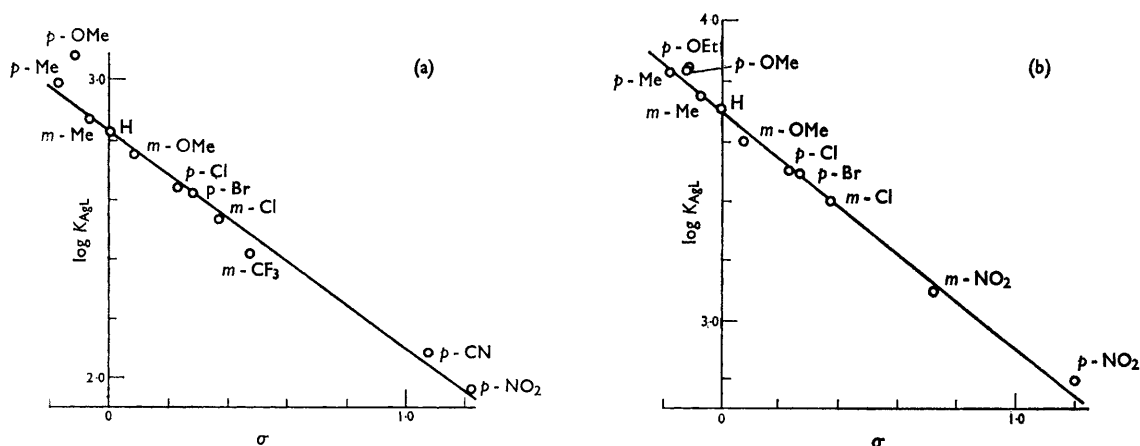


FIGURE. The relationship between the stability constants of silver complexes,  $\text{AgL}$ , of (a) substituted organosulphur ligands and (b) substituted organoselenium ligands and the Hammett functions ( $\sigma$ ) of the substituents, R.

are corrected for phenols.<sup>3</sup> If the measured stability constants for *meta*- and *para*-substituents are plotted against the Hammett functions for those substituents (rather than the phenolic  $pK$  values since this would limit the data available) straight lines are obtained for the protonated and unprotonated (AgHL and AgL) silver complexes of both sulphur and selenium ligands. The graphs are reproduced for the AgL species.

The slope ( $\rho$ ) of the graph of  $pK_{\text{phenol}}$  against  $\sigma$  is  $-2.23$ ; for the silver-sulphur complexes it is  $-0.86$  and for the silver-selenium complexes  $-0.82$ . A large difference in gradient between that for the proton dissociation and those for the silver dissociations is to be expected as a result of large differences in field-effects due to differences in size and charge of the atoms concerned and the orbitals involved. However, it is clear from the

graphs that the inductive and resonance effects which influence the phenolic proton dissociations appear to influence the sulphur-silver and selenium-silver dissociations in exactly the same way. Electron attractive groups such as nitro-, for instance, markedly increase the acidity of phenols and decrease the stability of the silver complexes. The introduction of back co-ordination and  $d_{\pi}-d_{\pi}$  bonding, which cannot be present in phenols, would therefore appear to be unnecessary; rather it may be considered to be contrary to the experimental data since back co-ordination sufficient to markedly influence the enthalpy of complex formation (and hence the stability constants since entropy changes in all cases would be comparable) should reverse the sign of the gradient ( $\rho$ ) of the  $\log K$  against  $\sigma$  graphs.

(Received, October 9th, 1967; Com. 1067.)

<sup>1</sup> S. Ahrland, J. Chatt, and N. Davies, *Quart. Rev.*, 1958, **12**, 265.

<sup>2</sup> R. G. Pearson, *Science*, 1966, **151**, 172.

<sup>3</sup> A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, 388.