The Synthesis of Bis(trifluoromethyl)-1,2-diseleneten and *cis*-1,2-Ditrifluoromethylethylene-1,2-diselenato-complexes

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THERE has been surprisingly little investigation of complexes which have selenium donor ligands.[1] In view of the extensive chemistry of the *cis*-1,2-disubstituted ethylene-1,2-dithiolato-complexes of transition metals, it seemed reasonable that the corresponding selenates could be prepared.

We have synthesised the novel heterocycle, bis(trifluoromethyl)-1,2-diseleneten, by the reaction of selenium vapour with hexafluorobut-2-yne. The deep red liquid (b.p. 78°/87 mm.) forms bis- and tris-complexes with transition metals in reactions analogous[2] to those of the related heterocycle $S_2C_2(CF_3)_2$. The reaction of $Se_2C_2(CF_3)_2$ with $Ni(CO)_4$ in pentane, under a nitrogen atmosphere, gives dark blue $[NiSe_4C_4(CF_3)_4]$, which cannot be recrystallised without decomposition and is markedly less stable than its sulphur analogue. By selective reduction of this compound, we obtained both the light green paramagnetic ($S = \frac{1}{2}$), $[Ph_4As][NiSe_4C_4(CF_3)_4]$, m.p. 161—162°, and the orange brown, diamagnetic $[Ph_4As]_2[NiSe_4C_4(CF_3)_4]$, m.p. 256—257°. Polarography of the compounds in dichloromethane[3] revealed two waves of roughly equal diffusion current with half-wave potentials identical to those of the corresponding sulphur complexes at $+0{\cdot}89$ and $-0{\cdot}17$ volts *versus* standard calomel electrode, (S.C.E.). The e.s.r. spectra of $[Ph_4As][NiSe_4C_4(CF_3)_4]$ in a DMF–$CHCl_3$ glass at $-170°$ showed the pronounced g value anisotropy characteristic of similar systems $g_1 = 2{\cdot}008$, $g_2 = 2{\cdot}116$, $g_3 = 2{\cdot}193$. Clearly resolvable electron–nucleus hyperfine interaction arising from the 23·74% of those molecules having one ^{77}Se ($I = \frac{1}{2}$, abundance 7·5%) was found about g_1 with $|A_1| = 69 \pm 2$ gauss.

The similarities evidenced above between selenium complexes and their sulphur congeners is also found for complexes with other transition elements. Tris-complexes can be readily obtained, *e.g.*, the purple paramagnetic ($S = \frac{1}{2}$) $[Ph_4As]_2[VSe_6C_6(CF_3)_6]$, m.p. 190° (decomp.). Salts of the mono-anion $[VSeC_6(CF_3)_6]^-$ are, however, less stable than the corresponding sulphur complexes and decompose on standing. Polarographic studies of the $[VSe_6C_6(CF_3)_6]^z$ ($z = -1, -2$) species show irreversible waves of $+0{\cdot}07$ and $-1{\cdot}05$ volts *versus* S.C.E.

More detailed studies on these and related 1,2-diselenato-complexes will be reported subsequently.

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