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-2yne. The deep red liquid (b.p. 78°/87 mm.) forms bis- and tris-complexes with transition metals in reactions analogous² 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 [Ph₄As]₂[NiSe₄C₄(CF₃)₄], m.p. 256-257°. Polarography of the compounds in dichloromethane³ revealed two waves of roughly equal diffusion current with half-wave potentials identical to those of the corresponding sulphur complexes at +0.89

and -0.17 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-CHCl₃ glass at -170° showed the pronounced g value anisotropy characteristic of similar systems $g_1 = 2.008, g_2 = 2.116, g_3 = 2.193$. Clearly resolvable electron-nucleus hyperfine interaction arising from the 23.74% of those molecules having one ⁷⁷Se $(I = \frac{1}{2}, abundance$ 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 $(S = \frac{1}{2})$ [Ph₄As]₂[VSe₆C₆-(CF₃)₆], m.p. 190° (decomp.). Salts of the monoanion [VSeC₆(CF₃)₆]⁻ are, however, less stable than the corresponding sulphur complexes and decompose on standing. Polarographic studies of the [VSe₆C₆(CF₃)₆]^z (z = -1, -2) species show irreversible waves of ± 0.07 and ± 1.05 volts versus S.C.E.

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

(Received, May 31st, 1967; Com. 540.)

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