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The Synthesis and Characterization of $(nBu_4N)_3Re(NCS)_6$, a Rhenium(III) Thiocyanate Complex

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The species present in the analytical determination of technetium and rhenium with thiocyanate ion [1–4] have recently been identified. In the case of rhenium, $Re^{IV}(NCS)_6^{2-}$ and $Re^{V}O(NCS)_5^{2-}$ are observed [5]. For the technetium system, the redox couple $Tc^{III}(NCS)_6^{3-}$ and $Tc^{IV}(NCS)_6^{2-}$ are the two species observed [6]. Recently, $Tc^{V}O(NCS)_5^{2-}$ has been isolated and its role in the thiocyanate chemistry of technetium has been explored [5]. The apparent differences in the thiocyanate chemistry of technetium and rhenium can be explained by chemical periodicity; however, isolation of $Re^{III}(NCS)_6^{3-}$ would provide additional support for the overall similarities in chemistry of these Group VII metals.

The existence of $Re^{III}(NCS)_6^{3-}$ has been postulated upon the basis of cyclic voltammetric data on the reduction of $Re(NCS)_6^{2-}$ in non-aqueous solvents [7, 8]. To date, no other evidence of the existence of $Re^{III}(NCS)_6^{3-}$ has been available. We wish to report the preparation and characterization of $(nBu_4N)_3Re(NCS)_6$.

A N_2 purged flask was charged with 0.13 gm (1.27×10^{-4} mol) $(nBu_4N)_2Re(NCS)_6$ [9]. After addition of 40 ml methanol and 10 ml THF (all solvents purged with N_2 and purified as appropriate), 0.6 ml of $N_2H_4 \cdot H_2O$ were added, turning the red solution a pale yellow brown. After a Schlenk-ware filtration, 20 ml of a saturated methanol solution of nBu_4NClO_4 were added. Crystals quickly formed and were filtered using Schlenk ware, washed with methanol, then dried *in vacuo*. The very pale yellow crystals of $(nBu_4N)_3Re(NCS)_6$ gave a satisfactory analysis: Calc.: C, 51.40; H, 8.63; N, 9.99; S, 15.25. Found: C, 50.86; H, 8.72; N, 9.87, S, 14.92%.

Infrared spectra (KBr pellet) show bands at 2104 cm^{-1} (m–w) and 2070 cm^{-1} (s) in the cyanide stretching region. As the KBr pellet is exposed to air, a new band appears at 2050 cm^{-1}, due to formation of $Re(NCS)_6^{2-}$ [9]. Although one would expect only one band in the cyanide stretching region for a complex of octahedral symmetry, the solid state spectrum of $(nBu_4N)_3Tc(NCS)_6$ also displays two bands in this region [6]. A crystal structure of $(nBu_4N)_3Tc(NCS)_6$ confirmed octahedral symmetry for the $Tc(NCS)_6^{3-}$ ions [6].

As noted previously, the complex is extremely air sensitive in solid and solution, converting to the well characterized $Re(NCS)_6^{2-}$ complex. This oxidation can be followed spectrophotometrically. Nitrogen gas purged acetonitrile solutions of $(nBu_4N)_3Re(NCS)_6$ are essentially colorless, with a strong charge transfer band at 370 nm. Upon exposure to air, this band decreases in intensity, with the concomitant appearance of an absorption band at 420 nm due to the $Re(NCS)_6^{2-}$ ion [9]. This behavior parallels the observed behavior of the technetium analogs, $Tc(NCS)_6^{3-}$ and $Tc(NCS)_6^{2-}$. It is apparent from these results and electrochemical measurements that $Re(NCS)_6^{3-}$ and $Re(NCS)_6^{2-}$ represent a completely reversible one electron redox couple:

$$Re(NCS)_6^{3-} \rightleftarrows Re(NCS)_6^{2-} + e^-$$

The effect of chemical periodicity on the stability of metal oxidation states is vividly pointed out by the difference in $E_{1/2}$ for the redox couples, $M(NCS)_6^{3-} \rightleftarrows M(NCS)_6^{2-} + e^-$: $E_{1/2} = +0.18$ V *vs.* SCE, M = Tc [6]; $E_{1/2} = -0.11$ V *vs.* SCE, M = Re [7]. Thus, it is not surprising that although $Re(NCS)_6^{3-}$ plays a role in the thiocyanate chemistry of rhenium, it has never been observed in those systems.

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References

1 W. Geilmann, *Z. Anorg. Allg. Chem., 208,* 217 (1932).
2 C. E. Crouthamel, *Analyt. Chem., 29,* 1756 (1957).
3 O. H. Howard and C. W. Weber, *Analyt. Chem., 24,* 530 (1962).
4 F. Jasim, R. J. Magee and C. J. Wilson, *Tantala, 2,* 93 (1959).
5 A. Davison, A. G. Jones, L. Muller, R. Tatz and H. S. Trop, *Inorg. Chem.,* in press.
6 H. S. Trop, A. Davison, A. G. Jones, M. A. Davis, D. J. Szalda and S. J. Lippard, *Inorg. Chem., 19,* 1105 (1980).
7 H. S. Trop, A. Davison, G. Carey, B. V. DePamphilis, A. G. Jones and M. A. Davis, *J. Inorg. Nucl. Chem., 41,* 271 (1979).
8 J. E. Hahn, T. Nimry, W. T. Robinson, D. J. Salmon and R. A. Walton, *J. Chem. Soc. Dalton,* 1232 (1978).
9 F. A. Cotton, W. R. Robinson, R. A. Walton and R. Whyman, *Inorg. Chem., 6,* 929 (1967).