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Preliminary communication

SYNTHESIS OF THE DICYANOPENTASULFIDONICKELATE(II) ANION

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Summary

Potassium tetracyanonickelate reacts with elemental sulfur and KOH in DMF to give the $[(NC)_2NiS_5]^{2-}$ anion, which has been isolated as its $PPh_4{}^+$ and $AsPh_4{}^+$ salts. The XPS S(2*p*) binding energies of the S_5 ring sulfur are in the ratio 2(162.8 eV)/3(163.6 eV). Cyclic voltammetry shows that the compound undergoes an irreversible reduction at −1.825 V.

The nickel group of metals give a variety of catenated polysulfide complexes, but the factors determining the ring size are poorly understood. For the higher oxidation state M^{IV} (M = Pd or Pt) the tris(pentasulfido) complexes are formed [1,2]. However, for the +2 oxidation state nickel and palladium form bis(tetrasulfido) complexes [3,4]. The tetrasulfido complexes of platinum can be isolated if suitable other ligands are present, e.g. $(PPh_3)_2PtS_4$ [5]. Nickel(II) and palladium(II) form only five-membered MS_4 rings even under conditions which should favor the formation of a MS_5 moiety. Interest in these complexes arises primarily from the expectation that they will provide insight into synthetic and theoretical aspects of sulfur chemistry. Metal sulfur interactions are also of interest because of the catalyst poisoning properties of sulfur compounds.

Elemental sulfur has been used to form complexes containing the six membered MS_5 ring by oxidative addition reactions [6]. However, with the platinum group metals in d^8 electronic configuration such an oxidative addition gives disulfur complexes with increase in the coordination number [7]. We have recently shown that the MS_4 ring size can be enlarged with concomitant oxidation of palladium(II) to palladium(IV) to give $Pd(S_5)_3{}^{2-}$ using a high concentration of sulfur in polysulfide [2]. We now report the isolation of salts of the hitherto unknown complex anion $[(NC)_2NiS_5]^{2-}$.

It is known that elemental sulfur reacts only very slowly with coordinated

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cyanide. But in a basic medium the generated polysulfide in situ can react much faster [8]. The reaction between $K_2[Ni(CN)_4]$ with S_8 and KOH in DMF has been found to proceed smoothly upon stirring for 10 h, to give a very dark brown solution. The anion formed $[(NC)_2NiS_5]^{2-}$ can be isolated in its greenish brown crystalline tetraphenylphosphonium or tetraphenylarsonium salts* from DMF ether mixture.

The following scheme can be tentatively proposed taking account of the fact that cyanide in $Ni(CN)_4{}^{2-}$ is fairly labile [9].

$$S_8 + OH^- \rightarrow S_n{}^{2-} + SO_3{}^{2-} + H_2O$$

$$Ni(CN)_4{}^{2-} + S_n{}^{2-} \rightarrow (NC)_2NiS_n{}^{2-} + 2\,CN^-$$

$$S_n{}^{2-} + CN^- \rightarrow SCN^- + S_{n-1}{}^{2-}$$

The infrared spectrum (CsI pellet) of the diamagnetic salts shows ν(CN) bands at 2070(s) and 2110(sh) cm^{-1} which are at lower frequencies than the ν(CN) bands of the starting tetracyanonickelate [10], as expected for effective increase in the backbonding towards coordinated cyanide in the complexes. The appearance of corresponding ν(Ni—C) bands at 440(m) and 450(m) cm^{-1} i.e. at higher frequencies than the those of the starting compound, confirm this. The band at 283(m) cm^{-1} is assigned to ν(Ni—S) [3]. It is difficult to assign the ν(S—S) vibrations since they are masked by strong absorptions of the cation. However, we tentatively assign the vibrations at 460(w,sh), 393(w) and 385(w) cm^{-1} to ν(S—S). The electronic spectrum of the compounds in DMF show three absorptions at 17 850, 21 270 and 25 640 cm^{-1} suggesting a square planar geometry for the complex ion. Assignment of these bands are not easy since both sulfur and cyanide ligands are present [11]. In the XPS, the S(2*p*) binding energy of the salts show a broad band (FWHM 3.0 eV) which can be readily resolved to give two sets of S(2*p*) binding energies in the ratio 2S(162.8 eV)/3S(163.6 eV), respectively. Thus a distinction can be made between the sulfur attached to nickel and the sulfur attached to sulfur. (All values are relative to C(*1s*), 285.5 eV). Cyclic voltammetry of the salts in DMF using Bu_4NBF_4 as supporting electrolyte shows an irreversible reduction at —1.825 V (vs. SCE). It is noteworthy that the reaction between $Ni(CN)_4{}^{2-}$ and polysulfide in various solvents is very fast, and complete removal of the coordinated cyanide groups by the polysulfide ligand takes place; a detailed study of this process is in progress.

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References

1 K.A. Hofmann and F. Hochtlen, Chem. Ber., 36 (1903) 3090.
2 K.N. Udupa and S. Sarkar, unpublished results.
3 A. Muller, E. Krickemeyer, H. Bogge, W. Clegg and G.M. Sheldrick, Angew. Chem. Int. Ed. Engl., 22 (1983) 1006.
4 A.E. Wickenden and R.A. Krause, Inorg. Chem., 8 (1969) 779.

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*The compound gives satisfactory elemental analysis.

5 J. Chatt and D.M.P. Mingos, J. Chem. Soc. A, (1970) 1243.
6 E.G. Muller, J.L. Petersen and L.F. Dahl, J. Organomet. Chem., 111 (1976) 91.
7 A. Muller, W. Jaegermann and J.H. Enemark, Coord. Chem. Rev., 46 (1982) 245.
8 R.C. Brasted, Comprehensive Inorganic Chemistry, Vol. 8, D. Van Nostrand Company, Inc., Princeton, 1961, p. 45.
9 A.G. Sharpe, The Chemistry of Cyano complexes of the Transition Metals, Academic Press, London, 1976, p. 236.
10 G.J. Kubas and L.H. Jones, Inorg. Chem., 13 (1979) 2816.
11 A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Company, Amsterdam, 1968, p. 343.