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A Note on the Nickel(II)-Mercury(II)-Thiocynate System

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Received May 18, 1971

Conditions have been delineated under which the known sky-blue $Ni[Hg(SCN)_4],2H_2O$ *and the previosly ill-characterized* $Ni[Hg(SCN)_3]_2,H_2O$ *crystallize from aqueous media containing nickel(II) salts, mercury(II) salts and thiocyanate ion. The compounds are characterized and a comment made on their thermochromic behaviour.*

Introduction

During the attempted preparation of large samples of $M[Hg(SCN)_4]$ where M = Co, Cu and Ni by mixing aqueous solutions of MCl_2 and $K_2[Hg(SCN)_4]$ we obtained immediate precipitation for M = Co and Cu, but not for M = Ni. After a few weeks, crystals were obtained from the nickel system, but they were not the expected product. The present report clarifies the underlying chemistry.

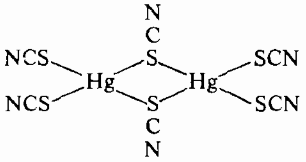
The simplest complex anions which may be present in solution containing mercury(II) ions and thiocyanate are $[Hg(SCN)_3]^-$ and $[Hg(SCN)_4]^{2-}$.

Salts of $[Hg(SCN)_4]^{2-}$ have long been known[1]: $Co[Hg(SCN)_4]$ is a highly recommended[2] magnetic standard and $Zn[Hg(SCN)_4]$ serves for the quantitative determination of zinc[3] or mercury[4]. Many metal ions, particularly those that can form tetrahedral complexes, when added to an aqueous solution of Hg^{2+} and SCN^- ions, in a molar ratio of 1:4 at a moderate concentration produce a precipitate of the corresponding $[Hg(SCN)_4]^{2-}$ salt, even when the major mercury-containing species present in solution is the $[Hg(SCN)_3]^-$ ion.[5]

Presumably the compound formed is less soluble than alternative solid products because of its extensive polymeric structure.[6]

Salts of $[Hg(SCN)_4]^{2-}$ are more common than those of $[Hg(SCN)_3]^-$.[**] The existence of $Co[Hg(SCN)_3]_2$ has been claimed[9] but not confirmed[10], although pink compounds with the formula $Co[Hg(SCN)_3]_2Ar$, where Ar is an aromatic molecule, have been characterized.[10] They readily lose the aromatic molecule and the reflectance spectrum of the product suggests that it is a mixture of $Hg(SCN)_2$ and $Co[Hg(SCN)_4]$ rather than $Co[Hg(SCN)_3]_2$; however, it has been suggested that this tri-thiocyanate species is an intermediate[11] in the decomposition.

The structure of $Co[Hg(SCN)_3]_2,C_6H_6$ has been shown[12] to consist of layers of Co^{2+} and Hg^{2+} ions joined by two types of bridging thiocyanate groups, with the benzene molecules lying between the layers. The cobalt ions are octahedrally surrounded by nitrogen atoms, and the mercury ions are in distorted tetrahedra of sulphur atoms, two of which are shared with another mercury ion.[12]



The formation of unsolvated $Ni[Hg(SCN)_3]_2$ might be thought more likely than that of its apparently non-existent cobalt analogue, because the tendency to form an insoluble salt of $[Hg(SCN)_4]^{2-}$, involving a tetrahedral environment around Ni^{2+} is less likely[13] than for Co^{2+}.

The slightly soluble, sky-blue, $Ni[Hg(SCN)_4],2H_2O$ was first prepared[14] by boiling an aqueous solution of $Ni(SCN)_2$ with an equimolar quantity of $Hg(SCN)_2$, followed by removal of solvent. Later reports[15] give no explicit practical details, and in one instance no product was obtained.[16] However, an X-ray structure analysis showing the nickel ion in an octahedral environment of four nitrogen and two oxygen atoms

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[**] Although examples of tricoordinate Hg^{2+} are known,[7] it is likely that salts of $Hg(SCN)_3^-$ will, where possible, have structures in which the environment of the Hg^{2+} is approximately tetrahedral, since Hg^{2+} is most commonly two or four coordinate.[7,8]

(1) (a) A. Rosenheim and R. Cohn, *Z. Anorg. Chem.*, 27, 280, (1901). (b) See also refs. in H. Grossmann, *Z. Anorg. Chem.*, 37, 411, (1904).

(2) (a) B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 4190, (1958). (b) M. Kral, *Coll. Czech. Chem. Comm.*, 29, 2841, (1964).

(3) G.E.F. Lundell and N.K. Bee, *Trans. Amer. Inst. Metals, 8* 146, (1914).

(4) A.I. Vogel, « A Text Book of Quantitative Inorganic Analysis, » 3rd. Ed., Longmans, London, 1966, p. 536.

(5) (a) L. Ciavatta and M. Grimaldi, *Inorg. Chim. Acta., 4,* 312, (1970). (b) See also ref. 10.

(6) (a) J. W. Jeffery, *Nature, 159,* 610 (1947). *Acta Cryst., 16,* A 66, (1963). (b) A. Korczyniki, *Roczniki Chem.*, 36, 1539, (1962). See 17(c).

(7) D. Grdenic, *Quart. Revs., 19,* 303, (1965).

(8) (a) A.F. Wells, « Structural Inorganic Chemistry », 3rd., Ed., (Oxford University Press), 1962, pp. 891-900. (b) S.E. Livingstone, *Quart. Revs., 19,* 386, (1965).

(9) H.E. Williams, « Cyanogen Compounds », 2nd. Ed., Arnold, London, 1948 p. 259. See also ref. 20.

(10) R. Baur. M. Schellenberg and G. Schwarzenbach, *Helv. Chim. Acta., 45, 775,* (1962).

(11) H.P. Fritz and J. Manchot, *Ber., 96,* 1891, (1963).

(12) R. Grønbaek and J.D. Dunitz, *Helv. Chim. Acta., 47,* 1889, (1964).

(13) (a) H.C.A. King, E. Körös and S.M. Nelson, *J. Chem. Soc.*, 5449, (1963). (b) W. Manch and W.C. Fernelius, *J. Chem. Ed., 38,* 192, (1961).

(14) P.T. Cleve, *J.Prakt. Chem., 91,* 227, (1864).

(15) (a) M.M. Chamberlain and J.C. Bailar, *J. Amer. Chem. Soc.*, 81, 6412, (1959). (b) D. Forster and D.M.L. Goodgame, *Inorg. Chem. 4,* 823, (1965).

(16) M. Czakis and A. Swinarski, *Roczniki Chem., 31,* 1101, (1957).

has appeared.[17] Other than $Ni[Hg(SCN)_3]_2,Ar$, which has not been fully investigated,[18] $Ni[Hg(SCN)_3]_2$ appears to have been mentioned[19] only once in the early literature. Incomplete and apparently incorrect analytical data were obtained.

Experimental Section

Microanalyses were performed by Dr. A. Bernhardt of Elbach über Engelskirchen. I.r. spectra were recoreded as nujol mulls with a Perkin Elmer 457 instrument and magnetic measurements were made at room temperature on a simple Gouy balance using $Co[Hg(SCN)_4]$ as the standard. Thermogravimetric analyses were recorded with a Perkin Elmer model TGSl instrument in a nitrogen atmosphere, at a heating rate or 16° $min.^{-1}$ and a recorder sensitivity of 1.0. mg f.s.d. X-ray powder photographs were obtained using a suspension in silicone oil. Whenever possible AnalaR quality reagents were used.

I. Preparation in the Absence of Halide Ions

(a) A warm aqueous solution of $Ni(NO_3)_2,6H_2O$ (2.9g in 20 ml) was added, with stirring, to a freshly prepared filtered aqueous solution of $K_2[Hg(SCN)_4]$ (4.9g in 20 ml). The resulting blue precipitate was filtered off, well washed with H_2O and dried over silica gel. Yield 2.9g.

(b) A solution of $Ni(NO_3)_2,6H_2O$ (2.0g) and KCNS (3.9g) in 25 ml H_20 was added with stirring to a warm solution of $Hg(NO_3)_2,H_2O$ (3.4g in 40 ml H_2O containing a few drops of nitric acid). The precipitate was treated as above, yield 2.7g. On occasions when the precipitate and supernatant liquid were heated on the water bath, considerable amounts of hydrogen cyanide were produced.

(c) $Hg(SCN)_2$ (3.2g) was dissolved in a warm solution of KCNS (2.0g in 25 ml H_2O), undissolved solid was removed by filtration and the filtrate was added to a solution of $Ni(NO_3)_2,6H_2O$ (2.9g in 20 ml). The resulting precipitate (2.0g) was washed and dried as previously

Analytical data obtained for the above substances varied from preparation to preparation irrespective of the method employed; typical results: found C, 8.9; H, 0.2; N, 10.6; Ni, 7.5-8.8%. Usually a maximum of *ca.* 1% weight was lost after heating for 4 hrs. at 150° and 1×10^{-2} mm Hg. The $\nu C\equiv N$ band in the i.r. spectrum was usually very broad and X-ray powder photographs indicated that $Ni[Hg(SCN)_4],2H_2O$ and $Ni[Hg(SCN)_3]_2,H_2O$ as well as other substances are present in these products.

II. Preparations in the Presence of Halide Ions

A. $Ni[Hg(SCN)_3]_2,H_2O$

(a) $NiCl_2,6H_2O$ solution (23.8g in 150 ml H_2O) was added to one of $HgCl_2$ (27.2g) and NH_4CNS (30.5g) in H_2O (300 ml). After several days at 10° a quantity of Oxford blue crystals separated. These were collected, washed with water and air dried. Yield 20.7g. A further crop (20.2g) was obtained after several days from the concentrated mother liquor. Found: C, 8.7; H, 0.4; Hg, 48.8; N, 10.2; Ni, 7.2; S, 23.0%; $C_6H_2Hg_2N_6NiOS_6$ requires: C, 8.7; H, 0.2; Hg, 48.6; N, 10.2; Ni, 7.1; S, 23.3%. Dehydration: thermogravimetric, 2.3; classical, (130°) 2.2, product green; (85°) 2.1%, product blue. Required for $1H_2O$ 2.2%. Green anhydrous compound, found: C, 9.0; H, 0.0%. $C_6Hg_2N_6NiS_6$ requires: C, 8.9; H, 0.0%. Magnetic moment (21°C) = 3.1 B.M. (diamagnetic correction from Ref. 23).

(b) As preparation I(a) with KCl (3g), or preparation I(b) with KBr (3.5g) added to the nickel solution before mixing, which prevented immediate precipitation; on standing, crystals of $Ni[Hg(SCN)_3]_2,H_2O$ formed, which were identified by their X-ray powder photographs, i.r. spectrum and quantitative dehydration. Addition of $KF,2H_2O$ (2g) to preparation I(b) did not prevent immediate precipitation on mixing.

B. *$Ni[Hg(SCN)_4],2H_2O$.*

(a) A solution of $NiCl_2,6H_2O$ (2.4g) in H_2O (6 ml) was added to one of $HgCl_2$ (2.7 g) and KCNS (3.9 g) in H_2O (10 ml): warming was necessary to dissolve all the $HgCl_2$. After 3 days at 10° a quantity of sky-blue crystals had formed. These, after washing with H_2O, were air dried, yield 4.0 g. Found: C, 9.2; H, 2.0; Hg, 37.5; N, 10.6; Ni, 11.2%. Calculated for $C_4H_4HgN_4O_2S_4$: C, 9.1; H, 0.8; Hg, 38.0; N, 10.6; Ni, 11.1%. Dehydration (140°C): 6.8%. Calculated for $2H_2O$, 6.8%.

Results and Discussion

Addition of mercuric nitrate solution to one of nickel nitrate and potassium thiocyanate (molar ratio 1:1:4) results in the precipitation of a pale blue substance, of variable composition, containing less nickel than is required by $Ni[Hg(SCN)_4],2H_2O$. The observation[20] that no precipitate is formed when the chlorides of nickel and mercury are used, suggested that chloride ions may play an important role in this system. This was confirmed by the addition of potassium chloride to the nitrate solutions, which prevented immediate precipitation on mixing. Sodium bromide, but not potassium fluoride, behaved similarly. On standing, blue crystals formed, of $Ni[Hg(SCN)_3]_2,H_2O$ (A) which was characterized by elemental analysis, quantitative dehydration, i.r. spectroscopy and measurement of its magnetic susceptibility. The observed magnetic moment, 3.1 B.M. at room temperature, is in the range commonly found for octahedral nickel(II). Thermogravimetric analysis showed that the water molecule is smoothly lost between 120° and 160°. Classical dehydration studies at 140° (10^{-2} mm Hg) confirmed the ready loss of water to give a green substance. Since water is lost at lower temperatures

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[17] (a) K'uo-Hsiang Chou and M.A. Poraj-Košic, *Kristallografiya*, 5, 462, (1960). (b) M.A. Poraj-Košic, *Zh, Struct. Khim.*, 4, 584, (1963). (c) M.A. Poraj-Košic, *Acta. Cryst.*, 16, A42, (1963).

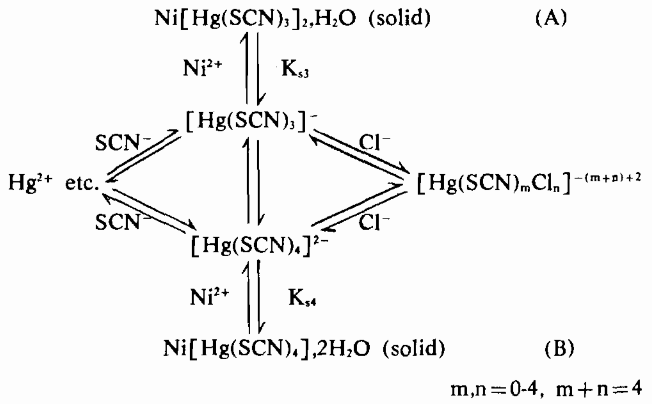
[18] See refs. 10 and 11.

[19] E.I. Orlov, *Ah. Russ. Fiz.*, 37, 1271, (1905).

[20] W. Skey, *Chem. News*, 25, (1874).

(80°) over an extended period of time (100 h) without the sample becoming green, the colour change at higher temperatures may be associated with some structural change that is not directly connected with loss of water.

When more concentrated solutions containing halide were used in attempted preparations of A the desired product was not obtained; instead the lighter blue Ni[Hg(SCN)$_4$],2H$_2$O (B) was the solid product. The following scheme explains these observations:



The stability constants[5] of the various possible species in the halide-free solutions are such that the dominant mercury-containing species in these solutions are $[Hg(SCN)_3]^-$ and $[Hg(SCN)_4]^{2-}$. Addition of chloride (or bromide) ions, capable of forming stable complexes[21] with Hg^{2+}, prevents the rapid precipitation of nickel-containing products by reducing the concentration of $[Hg(SCN)_3]^-$ and $[Hg(SCN)_4]^{2-}$ ions to such an extent that the solubility products of the respective products are not grossly exceeded, and a pure product crystallizes from solution. As the overall concentration of the solution is increased the concentration of $[Hg(SCN)_4]^{2-}$ increases faster than that of $[Hg(SCN)_3]^-$, (the former is a function of a higher power of the SCN^- concentration than the latter), and it becomes more likely that B will be formed. It is not possible to predict quantitatively the concentration at which both products have an equal likelihood of being formed since several unknown equilibrium constants,* as well as the solubility products of A (K_{s3}) and B (K_{s4}), are involved.

Although perhaps less likely, it is possible to interpret our observations in terms of kinetic rather than thermodynamic effects . If, as a result of a more complicated and extensive structure, the rate of nucleation of the unit cell of B is markedly more concentration-dependent than that of A, then it will become more likely that B will be formed as the overall concentration of the solution is increased.

Both A and B are thermochromic. In particular, the latter, when heated, becomes bright green; the original blue colour returns on cooling. The cycle can be repeated many times without loss of water. This colour change probably results from thermal broadening of the near u.v. charge transfer band.[22]

Table I. I.r. Spectra, in Nujol Mull (cm^{-1}) Using KBr Plates

Ni[Hg(SCN)$_4$],2H$_2$O	Ni[Hg(SCN)$_3$]$_2$,H$_2$O
3580m (br)	
3425m (br)	
2150s	2182s
	2138s
1608m (br)	1595m (br)
753w	740w
475vw	470m
453vw	438m

Table II. D-spacings from X-ray Powder Photographs Visual Relative Intensity (0-10) in Brackets

Ni[Hg(SCN)$_3$]$_2$,H$_2$O	Ni[Hg(SCN)$_4$],2H$_2$O
10.8 (5)	9.2 (9)
9.6 (10)	6.6 (6)
6.4 (9)	5.4 (10)
6.1 (4)	5.22(10)
5.7 (7)	4.83(9)
5.35(8)	4.60(7)
4.8 (10)	4.32(10)
4.65(5)	4.28(9)
4.3 (2)	3.83(9)
4.2 (2)	3.38(7)
3.81(4)	3.31(7)
3.72(8)	3.20(2)
3.67(8)	3.13(8)
3.61(5)	3.08(5)
3.58(4)	3.06(2)
3.47(6)	2.94(1)
3.38(6)	2.91(2)
3.19(4)	2.80(4)
3.14(5)	2.75(7)
3.05(1)	2.68(6)
3.02(4)	2.64(5)
2.91(4)	2.60(4)
2.85(6)	2.57(7)
2.66(6)	2.52(1)
2.59(2)	2.44(3)
2.55(7)	2.36(5)
2.41(5)	2.28(5)
2.38(1)	2.24(2)
2.34(5)	2.22(3)
2.30(4)	2.20(1)
2.26(3)	2.18(1)
2.25(4)	2.16(4)
2.23(3)	2.14(5)
2.16(2)	2.13(4)
2.09(3)	2.08(4)
2.03(4)	2.07(5)
2.00(2)	2.06(4)
	2.02(6)
	1.98(6)

Table I lists the bands observed in the i.r. spectra (250-4000 cm^{-1}) of compounds A and B. The single band for B at 2150 cm^{-1} (νC≡N) is consistent with the known structure containing one type of bridging thiocyanate group. The two bands observed for A might possibly be interpreted as arising from a structure containing two types of bridging thiocyanate, like that of Co[Hg(SCN)$_3$]$_2$,C$_6$H$_6$: however, this benzene clathrate has only a single band in the νC≡N region[10] despite the presence of two types of bridging thiocyanate.

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* Extensive data are available for the equilibria

$$Hg^{2+} + nx^- \rightleftharpoons [HgX_n]^{(n-2)-}$$

where X = halide or thiocyanate ion, but not for the mixed complexes.

(21) A.E. Martell and L.G. Sillen, « Stability Constants of Metal Ion Complexes », Special Publication No. 17, The Chemical Society, London.

(22) C.K. Jørgensen, « Absorption Spectra and Chemical Bonding in Complexes », Pergamon Press, London, 1962, p. 196. See also ref. 15b.

(23) P.W. Selwood, « Magnetochemistry », 2nd Edition, Interscience Inc., London, 1956.