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Abstract

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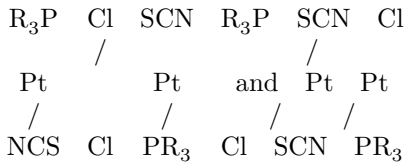
ON COMPOUNDS WITH THE COMPLEX ANION $[Hg(SCN)_4]^{2-}$ AND THEIR PRECIPITATES

The complex tetraiodomercurate ion ($K_{diss} \sim 10^{-22}$ ([1])) is characterized by the presence of a strong covalent mercury–sulfur bond of the thiocyanate group ([2–4]). However, it should be borne in mind that the thiocyanate ion possesses lone pairs of electrons both on the sulfur atoms and on nitrogen, and the donor properties of nitrogen are just as pronounced (or even more so) as the donor properties of oxygen ([5]). Consequently, in theory the thiocyanate ion can coordinate around metal atoms by means of any of the lone electron pairs of the sulfur or nitrogen atoms. Indeed, if in the complex $[Hg(SCN)_4]^{2-}$ the thiocyanate type of bond Me—SCN is realized, then in the tetrathiocyanate complexes of zinc and cobalt the isothiocyanate type Me—NCS occurs, while the complex $[Cd(SCN)_4]^{2-}$ is characterized by an intermediate type of bond ([2]). A similar phenomenon is observed also in the more thoroughly studied complex compounds with cyano groups as addends, where the carbon–metal bond does not prevent the formation of a coordination bond between nitrogen and another metal atom; this may lead to the formation of "supercomplex" compounds or even polynuclear complexes ([5], p. 64), in which the cyano group acts as a bridge. The fact that platinum compounds exist in isomeric forms ([5], p. 61) points to an analogous role of the thiocyanate group:



If, in the tetraiodomercurate complex, the donor properties of the sulfur of the thiocyanate groups are considered exhausted through formation of the covalent Hg—S bond, then the donor properties of nitrogen remain uncompensated. On the basis of these considerations it is natural to expect interaction of the tetraiodomercurate ion with various cations, with formation of a thiocyanate-isothiocyanate type of bond Hg—SCN—Me. Such a dual function of anions of

Fig. 1. Uptake isotherms of barium (I), strontium (II), and calcium (III) by precipitates of $Me^{II}[Hg(SCN)_4]$. pH 5.5, 6 h, 25°C

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this kind may ultimately lead to polymerization of inorganic compounds ([6]). It is known ([7]) that formation of a donor π-bond through interaction of the *d*-orbitals of a metal atom with vacant *p*- or *d*-orbitals located in the vacant shell of the addend atoms leads to an increase in the stability of complex compounds. Consequently, the formation of stable molecular forms constructed according to the thiocyanate-isothiocyanate type of bond Hg—SCN—Me should be expected above all for cations capable of forming donor π-bonds, i.e., for cations prone to complex formation. This capacity is possessed by most elements of the side subgroups of the periodic table. Indeed, such cations as Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} probably form covalent-type bonds so strong that the entire complex molecule $Me^{II}[Hg(SCN)_4]$ proves to be built according to a predominantly covalent type of bond; this circumstance accounts for the low solubility in water of the tetraiodomercurates of these elements ([8]).

The formation of thiocyanate-isothiocyanate groupings is indicated, in some cases, by a change in the color of solutions and precipitates. Thus, whereas aqueous solutions containing simple Co^{2+} ions are characterized by a red color,

coloration, the presence of complex ions $[Co(NCS)_4]^{2-}$ causes an intense blue coloration of the solution; the interaction of Co^{2+} ions with the colorless anion $[Hg(SCN)_4]^{2-}$ leads to the precipitation of $Co[Hg(SCN)_4]$, which likewise has an intense blue color.

Cations of alkali and alkaline-earth metals, which do not possess the ability to form donor π-bonds, give water-soluble compounds with the $[Hg(SCN)_4]^{2-}$ ion, in which the bond of the metal with the complex anion has a predominantly ionogenic character ([2]).

Until now it has been considered that the reaction with the $[Hg(SCN)_4]^{2-}$ ion is analytically specific only for certain cations, such as Zn^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+} ([8]). However, taking into account the above-mentioned features of the ion $[Hg(SCN)_4]^{2-}$, it was of interest to trace the behavior of various cations in the process of precipitation of sparingly soluble tetraisothiocyanatomercurates. As macrocomponents, precipitates of the tetraisothiocyanatomercurates of zinc, cobalt, and cadmium were chosen; their solubility in water, according to our data, is respectively $1.72 \cdot 10^{-4}$, $5.92 \cdot 10^{-4}$, and $2.11 \cdot 10^{-3}$ mol/l at 25°.

Fig. 1. Uptake isotherms of barium (*I*), strontium (*II*), and calcium (*III*) by precipitates of $Me^{II}[Hg(SCN)_4]$. pH 5.5, 6 h, 25°C

Determination of the absolute magnitude of uptake of microimpurities by precipitates was carried out by the "two indicators" method developed by us, which in principle is analogous to the Cameron method ([9]), known in physicochemical analysis and used for determining the composition of precipitates in ordinary systems. The "two indicators" method consists in the following: into the solution under study, containing micro- and macrocomponents, an analytically or radiochemically readily determinable impurity that is not sorbed by the precipitate is introduced, or, as we call it, a "second indicator." The radioactivity of the microcomponent is taken as the first indicator. The macrocomponent is then precipitated according to the adopted scheme. After formation of the precipitate and attainment of equilibrium between the precipitate and the mother liquor, the precipitate is separated, as completely as possible, from the main mass of the mother liquor. The precipitate and the mother liquor are then analyzed for the content of the microcomponent (by radioactivity) and for the amount of the "second indicator."

The calculation is made by the formula:

$$A = A_1 - \frac{aQ}{q},$$

where A_1 is the total activity of the precipitate separated from the mother liquor, a is the specific activity of the mother liquor, Q is the amount of the "second indicator" determined in the precipitate, q is the specific amount of the "second indicator" in the mother liquor, and A is the activity of the microcomponent taken up by the precipitate.

A systematic study of the uptake of cations of elements of groups 1, 2, and 3 of the periodic table showed that the magnitude and character of the uptake of microimpurities by precipitates of $Me^{II}[Hg(SCN)_4]$ depend on the conditions of separation of the solid phase (pH of the solution, excess of precipitant—the ions $[Hg(SCN)_4]^{2-}$, duration of contact of the precipitates with the mother liquor), on the character of the precipitates (magnitude of the surface), and, chiefly, on the nature of the very

microcomponent. For cations characterized by a tendency to form strong rhodanide–isorhodanide groupings, a general tendency is observed toward bulk cocrystallization with the tetrarhodanomercurates of zinc, cobalt, and cadmium, or toward their separation as an independent solid phase. On the other hand, the relatively small magnitude of the uptake of alkali- and alkaline-earth-metal cations is due to their weak tendency to form covalent bonds with the rhodanide groups of the tetrarhodanomercurate complex anion. The importance of this circumstance is evident from the following: equality or a small difference in the ionic radii of magnesium and lead, calcium and cadmium, with a different character of bonding in compounds with the $[Hg(SCN)_4]^{-2}$ ion, leads to different properties of their compounds and to a difference in the character of uptake (solid solution and adsorption).

Figure 2

Figure 2: Figure 2

A characteristic feature of the uptake of cations of alkaline-earth metals and elements of the scandium–yttrium–lanthanide series by precipitates of $Me^{II}[Hg(SCN)_4]$ is the adsorption nature of the uptake. If in the case of alkali-metal cations the "two-indicator" method has proved the practical absence of uptake, then uptake of alkaline-earth-metal cations by these precipitates occurs in definite amounts (up to 5%), and the relative magnitude of uptake does not depend on the concentration of the microcomponent in solution; the uptake isotherms can be characterized by the equations of the Freundlich or Langmuir adsorption isotherm. The isotherms of absolute uptake of microamounts of alkaline-earth-metal cations, given in Fig. 1, indicate that the magnitude of uptake does not depend on the nature of the tetrarhodanomercurate precipitate, but depends chiefly on the magnitude of the surface of the precipitate and on the nature of the cation impurity.

Fig. 2. Isotherms of relative (a) and absolute (b) uptake of lanthanum by precipitates of zinc (I), cobalt (II), and cadmium (III) tetrarhodanomercurates. pH 5.5; 6 h; 25°

The isotherms of the relative uptake of trivalent cations of the scandium—yttrium—lanthanide series generally have the form shown in Fig. 2a for the case of lanthanum uptake. The absolute-uptake isotherms shown in Fig. 2b are very reminiscent of the Langmuir type of isotherms for polymolecular adsorption [10] with saturation of the adsorption monolayer (horizontal branches of the curves). From Fig. 3 it is seen that the uptake of cations of this series is in a definite dependence on the size of the cation—microimpurity. With increasing radii of the cations, their uptake by tetrarhodanomercurate precipitates also increases.

The study of the sorption of elements of the scandium—yttrium—lanthanide series from

solutions containing complex anions such as $[Hg(SCN)_4]^{-2}$ and $[Fe(CN)_6]^{-4}$ on the surface of nonpolar adsorbents (polyethylene, fluoroplastic-4) showed complete analogy in the character of the sorption isotherms and in the dependence of the amount of sorption on the nature of the cation—microimpurity—with the capture isotherms of these cations under the same conditions by precipitates of tetraodanmercurates. Taking into account the inertness of the surface of nonpolar adsorbents toward ionic forms and the selective sorption on it of substances present in molecular form, one may suppose that in the presence of an excess of complex anions, microimpurities of a number of elements can form uncharged molecular forms. In particular, for cations of alkaline-earth metals and elements of the scandium—yttrium—lanthanide series, the hypothesis of the formation in solution of molecular forms also proves valid; moreover, an increase in the strength of these formations with increasing charge and radius of the

Figure 3

Figure 3: Figure 3

cation-microimpurities will, in all probability, occur in the presence of complex anions of the type $[Hg(SCN)_4]^{-2}$, $[Fe(CN)_6]^{-4}$, and others.

Fig. 3. Dependence of the relative amount of capture of elements of the scandium–yttrium–lanthanide series on the cation radius; pH 5.5; 6 h; 25°; precipitate $Zn[Hg(SCN)_4]$.

On the basis of these propositions, in our opinion it also appears probable in a number of cases to estimate in advance the possible character of capture of a microimpurity by a given precipitate or by the surface of an adsorbent with covalent bonds. And, finally, taking into account the "bridging" nature of one or another addend in complex compounds and the nature of the "outer-sphere" cation, one may be guided in assessing the expected properties of synthesized compounds of the type considered in the present work. Thus, guided by these ideas, we obtained a number of new compounds of the tetraodanmercurate ion with various cations. In particular, sparingly water-soluble salts of thallium (+1) and indium (+3) of stoichiometric composition $Tl_2[Hg(SCN)_4]$ and $In_2[Hg(SCN)_4]_3$ were isolated.

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Note: Figure translations are in progress. See original paper for figures.