

CHROM. 3380

Separation of anionic chromium(III) thiocyanate complexes by displacement analysis*

The thiocyanate complexes of Cr(III) hold exceptional interest for studies of systematic differences among complex ions, *e.g.*, the effect of charge on adsorption. They are inert, the full set containing one through six ligands are known, and their stabilities have been measured¹. The present work concerns preparation of solutions of the anionic complexes substantially free of other anions. KAUFMAN AND KEYES² have demonstrated separation of the anionic Cr(III) thiocyanate complexes using a cellulose anion exchanger with HClO₄ in aqueous acetone as eluant. We have modified their procedure to permit displacement analysis instead of elution analysis, thereby avoiding use of acetone and contamination by extraneous anions. Prior removal of SCN⁻ was found necessary from the starting mixtures of Cr complexes; Fe³⁺-loaded cation exchanger proved useful for this purpose.

Experimental

Reagents. The salt K₃Cr(SCN)₆ was obtained from Alpha Inorganics, Inc. Our analyses indicated the presence of 2% excess KSCN by weight. Mixtures of the chromium(III)-thiocyanate complexes were obtained by heating 0.5 M K₃Cr(SCN)₆ at 50° overnight to achieve equilibrium. From the results of BJERRUM¹, we estimate that the resulting solution contained 12% Cr(SCN)₆³⁻, 28% Cr(SCN)₅²⁻, 37% Cr(SCN)₄⁻, 19% Cr(SCN)₃ and 4% Cr(SCN)₂⁺.

The cellulose anion exchanger, Cellex T, was obtained from Bio-Rad Laboratories, Richmond, Calif. This exchanger is a triethylaminoethyl cellulose with an exchange capacity of 0.53 mequiv./g.

Removal of free thiocyanate. Solutions prepared from commercial K₃Cr(SCN)₆ were used to displace the lower complexes as adjacent bands. To avoid presence of free SCN⁻ in the eluate, removal of the KSCN impurity from the K₃Cr(SCN)₆ was desired. In addition, better column behavior (*i.e.* flatter band fronts) was obtained when free SCN⁻ was removed from the mixture of complexes initially loaded on the anion-exchanger column. The mixture as originally prepared contained 1.7 moles free SCN⁻ per mole Cr(III).

A separation was developed making use of the tendency of SCN⁻ to invade Fe³⁺-loaded cation exchanger. Beads of cation exchanger in the Fe³⁺-form become red in dilute aqueous KSCN, providing visual evidence for SCN⁻ absorption. In contrast, anionic Cr(III) thiocyanate complexes are excluded from the Fe³⁺-form cation exchanger.

For the present work, 80 ml of cation exchanger was prepared using 150 mesh resin (Dowex 50W X8). Ferric nitrate in 0.001 M HNO₃ was used for conversion to the Fe³⁺-form. The converted resin was loaded into a 30 cm column with 2 cm of K⁺-form cation exchanger at the bottom. Two ml of 0.5 M K₃Cr(SCN)₆ (or two ml of the mixture of Cr(III) complexes) was added to the top of the column and eluted with water. The deep blue Cr(III) complexes were, except as noted later, eluted as a

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narrow band immediately after the column free volume (about 30 ml) was displaced. No free SCN^- could be detected in the product³. In the case of the mixture of complexes, a small fraction of the Cr was retained at the top of the column, presumably as a result of absorption of cationic complexes.

Preparation of aqueous $\text{K}[\text{Cr}(\text{SCN})_4(\text{H}_2\text{O})_2]$ and $\text{K}_2[\text{Cr}(\text{SCN})_5(\text{H}_2\text{O})]$. Columns were prepared by adding 3.2 g of anion exchange cellulose to 40 ml of 1 M KSCN, shaking vigorously to obtain a fine slurry and adding the slurry to the column while applying suction. Columns of 0.78 cm² cross-section were used; the resin bed occupied 17 cm of length and the head was adjusted to maintain a flow of 0.5 ml/min.

Two ml of the mixture of Cr complexes was treated to remove free SCN^- as described above, further diluted to 50 ml with water, and loaded onto the top of the column. Elution was carried out using 0.0033 M $\text{K}_3\text{Cr}(\text{SCN})_6$. To avoid decomposition of $\text{Cr}(\text{SCN})_6^{3-}$, the column and solutions were cooled to 10° with circulating chilled water, and the experiments were carried out in subdued light.

Results

The brightly colored mixed band was sharply defined on the white resin as the separation began. This band was displaced down the column as $\text{Cr}(\text{SCN})_6^{3-}$ was added; the resin at the trailing edge of the mixture assumed the bright violet characteristic of adsorbed $\text{Cr}(\text{SCN})_6^{3-}$. After displacement through about 5 cm, separate dark blue and bluish-violet bands formed from the mixed band.

Chemical analyses of the eluate fractions were performed with a Cary Model 14 MR spectrometer. Chromium was determined as chromate⁴ and presence of free SCN^- was checked through formation of the ferric complex³. The number of bound SCN^- per Cr(III) was calculated using the known, fixed concentration of potassium ions in the eluate (0.01 M). The results are shown in Fig. 1.

Discussion

The results demonstrate efficient separation of the non-labile complexes $\text{Cr}(\text{SCN})_4(\text{H}_2\text{O})_2^-$ and $\text{Cr}(\text{SCN})_5\text{H}_2\text{O}^{2-}$ by displacement along a column of anion exchange cellulose. A variety of displacing anions were tried including ClO_4^- , SO_4^{2-} ,

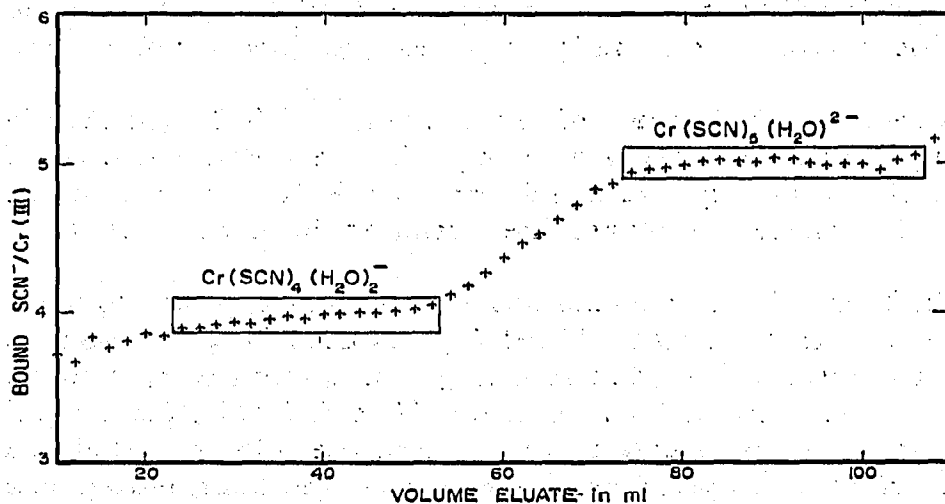


Fig. 1. Preparation of aqueous $\text{K}[\text{Cr}(\text{SCN})_4(\text{H}_2\text{O})_2]$ and $\text{K}_2[\text{Cr}(\text{SCN})_5\text{H}_2\text{O}]$ by displacement analysis on anion exchange cellulose.

$P_4O_{12}^{4-}$, $Fe(CN)_6^{4-}$ and $Cr(SCN)_6^{3-}$. Only the last of these proved at all satisfactory.

The fairly substantial volume of eluate containing both the tetra- and penta-thiocyanato complexes should not be taken to indicate that the adsorptivities of these ions are similar. Instead, it reflects primarily the tilting of the band fronts which was evident visually. Successful separations require band lengths which are great relative to the column lengths over which the tiled or fluted band fronts extend. SPEDDING AND POWELL⁴ discuss this and related requirements in connection with their pioneering work on displacement analysis of rare earths.

As pointed out by KAUFMAN AND KEYES², cellulose ion exchangers appear promising for separating a variety of inorganic ions which are strongly absorbed on conventional ion exchange resins. The relatively low density of ionic sites offers a special convenience with displacement analysis; in the present experiments, for example, each milliequivalent of adsorbed ion occupied about 8 ml of cellulose exchange bed so that rather small samples still produced bands of adequate length. From our experience, we feel displacement analysis deserves wider application in preparative inorganic chemistry.

The procedure described for removal of free SCN^- involves a novel application of ion exclusion⁵. The SCN^- ions adsorbed by the Fe^{3+} -form cation exchanger must be accompanied by K^+ to maintain charge balance. Microscopic examination of sections cut from large resin beads confirms that we are not dealing with a surface effect; the red characteristic of ferric thiocyanate complexes is evident throughout the resin. The $KSCN$ may be eluted with water, much as CH_3COOH is eluted during its separation from HCl by ion exclusion⁶. One of us (G.L.G.) has undertaken study of related systems for separation of the halides. A variety of other applications appear possible.

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