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LETTER

Novel synthesis of *trans*-$Cr(NH_3)_4(CN)_2^+$: a facile entry to the *trans*-tetraamminechromium(III) series

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trans-Diacidotetraammine complexes have played an important role in kinetic [1, 2] and photochemical [3, 4] studies of chromium(III). Two ways of access to the *trans*-$Cr(NH_3)_4XY^{z+}$ family have been so far described in the literature: either ammonation of *trans*-$Cr(py)_4F_2^+$ to *trans*-$Cr(NH_3)_4F_2^+$ [5], or acid cleavage of the binuclear chloro–erythro complex to yield *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ [6, 7]. The general stereoretentivity of chromium(III) substitution in aqueous media [8] then allows coordination of a variety of *trans* X and/or Y ligands. Both methods, however, involve several laborious steps, some of which are under drastic conditions.

We report here a new, short route to this class of compounds, devised in the course of our investigations of chromium(III) cyano-ammine species [9–12]. Its key feature is the straightforward obtainment of *trans*-$Cr(NH_3)_4(CN)_2^+$ in fairly good yield, starting from readily available materials. This affords an example of synthetic application of the *trans* effect in octahedral complexes.

Experimental

Reagents and techniques

Dimethyl sulfoxide (Me_2SO) was dried with 4 Å molecular sieves. $[Cr(NH_3)_5(Me_2SO)](ClO_4)_3$ was obtained by heating $[Cr(NH_3)_5(H_2O)](ClO_4)_3$ [13] in Me_2SO, as already described [9]. An improved procedure to precipitate the product without using (expensive) $LiClO_4$ in methanol, was 1.5:1 dilution with water of the cooled reaction mixture, followed by addition of an equal volume of either aqueous 10 M $NaClO_4$ or 70% $HClO_4$. The yield of crude product was *c*. 95%.

Caution. The above mixture must be diluted with water before adding $HClO_4$, in order to avoid possible explosion. In addition, although no nuisance was experienced in this preparation, perchlorate salts of complexes with organic groups should be regarded as potentially explosive, specially when ether-damp. Working with cyanide requires an efficiently ventilated hood.

Chromium, ammonia and cyanide were determined by reported methods [10]. Absorption spectra were recorded by a Cary 17 spectrophotometer. Emission spectra were measured by a Perkin-Elmer 650-10S spectrofluorometer.

trans-Dicyanotetraamminechromium(III) perchlorate

Due to the photosensitivity of chromium(III), all operations were performed in dim light. A 5.0-g portion of NaCN (*c*. 100 mmol) was dissolved on heating in 75 ml of Me_2SO in a stoppered flask. Following addition of 5.0 g of $[Cr(NH_3)_5(Me_2SO)](ClO_4)_3$ (*c*. 10 mmol), the mixture was heated at 60 °C for 60 min with stirring. The color turned from purple to orange and some yellow solid, consisting of $[Cr(NH_3)_5(CN)](CN)_2$, separated. A 100-ml volume of 3 M $LiClO_4$ in MeOH was then added and the suspension was kept at 60 °C for 12–15 h under magnetic stirring and maintaining the flask closed. A lemon-yellow powdery salt progressively accumulated. After cooling this was removed by centrifugation, washed with ethanol, then with ether, and vacuum-dried over P_2O_5. The yields ranged between 1.0 and 1.3 g, or 40–50%. The crude product was recrystallized by dissolution of 1.0 g in 150 ml of water at 40 °C, filtration, and slow addition of 60 ml of aqueous 10 M $NaClO_4$ to the stirred, cool solution. After ice-cooling for 2–3 h, the crystalline *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$ was collected by filtration and washed and dried as above. Recovery was *c*. 90%. The maxima of the ligand-field (LF) absorption spectrum in aqueous solution occur at 440 (ϵ 42.6) and 344 (ϵ 41.5) nm, as those reported previously [10].

Aquation products

trans-$[Cr(NH_3)_4(H_2O)(CN)]Cl_2$ was prepared by stirring a suspension of 1.0 g of *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$ (3.7 mmol) in 38 ml of 0.10 M HCl for 30 min at 25 °C. Dissolution proceeded with CN^- aquation and involved acid consumption. The amount of HCl was such that the pH of the final, orange solution was 2.5–3.0. Dropwise addition of 10 ml of aqueous 16 M LiCl precipitated the

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product. After ice-cooling for 2–3 h, the yellow–orange crystals were filtered off, washed with ethanol, then with ether, and vacuum-dried over P_2O_5. A typical yield was 0.8 g or 90%. *Anal.* Calc. for $[Cr(NH_3)_4(H_2O)(CN)]Cl_2$: Cr, 22.12; NH_3, 28.98; CN, 11.07. Found: Cr, 21.8; NH_3, 28.7; CN, 10.9%. The LF maxima in aqueous 10^{-3} M $HClO_4$ are at 468 (ϵ 48) and 354 (ϵ 32) nm and match those given earlier for the *trans*-cyanoaquo ion isolated in solution [10].

trans-$[Cr(NH_3)_4(H_2O)(CN)](ClO_4)_2$ was obtained by slowly adding 25 ml of 3 M $LiClO_4$ in MeOH to a filtered, stirred solution of 1.0 g of the chloride salt in *c.* 20 ml of water at pH 3.5 ($HClO_4$). Ice-cooling for 2–3 h completed precipitation. The perchlorate salt was recovered by filtration, washed with ice-cold ethanol (in which it is slightly soluble) and ether, and air-dried. This was recrystallized from water at pH 3.5 by addition of 10 M $NaClO_4$ and washed and dried as above. The yield of pure product was 1.0 g or 67%. *Anal.* Calc. for $[Cr(NH_3)_4(H_2O)(CN)](ClO_4)_2$: Cr, 14.32; NH_3, 18.76; CN, 7.17. Found: Cr, 14.1; NH_3, 18.6, CN, 7.0%. The LF spectrum is identical with that of the chloride salt.

trans-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$ was prepared by stirring a suspension of 1.0 g of *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$ (3.7 mmol) into 20 ml of 1.5 M HCl for 60 min at 40 °C. Treatment of the cooled solution with an equal volume of 70% $HClO_4$ and ice-cooling for 2–3 h precipitated a pinkish salt, which was collected, washed with ethanol and ether, and vacuum-dried. Yield: 1.4 g or 85%. The LF spectrum shows one shoulder at 520 nm (ϵ 17) and two maxima at 475 (ϵ 20) and 368 (ϵ 29) nm, in agreement with literature data [7].

Results and discussion

The present synthesis of *trans*-$Cr(NH_3)_4(CN)_2^+$ is much simpler and more efficient than the one we reported earlier [10], whereby conversion of the initial chromium(III) salt to the final product required at least 7 preparative stages. In essence, this procedure enables a 'one-pot' passage under mild conditions from the easily obtainable pentaammines to the less accessible *trans*-tetraammines of chromium(III).

The preliminary process is smooth anation of $Cr(NH_3)_5(Me_2SO)^{3+}$ by CN^- (eqn. (1)). As already pointed out [9, 10], the ligand to be replaced must not be H_2O, since coordinated water is readily deprotonated by the basic cyanide ion even in non-aqueous media. The Cr–O bond would thus be strengthened, and decomposition of the unstable hydroxo complex would successfully compete with anation. In addition, the dipolar aprotic solvent excludes CN^- hydrolysis and enhances ion association [14], hence, anation. If needed, the $Cr(NH_3)_5(CN)^{2+}$ intermediate may be isolated at this point in high yield [9].

$$Cr(NH_3)_5(Me_2SO)^{3+} + CN^- \xrightarrow{Me_2SO} Cr(NH_3)_5(CN)^{2+} + Me_2SO \qquad (1)$$

The subsequent phase (eqn. (2)) takes advantage of two factors: (i) the *trans* directing power of CN^- and (ii) the insolubility of *trans*-$Cr(NH_3)_4(CN)_2^+$ in methanol, which prevents further reactions. The Cr–NH_3 bonds of acidoammine complexes in general, and those of $Cr(NH_3)_5X^{z+}$ ions in particular, are known to be very stable and to persist throughout the substitution reactions of the acido groups [1, 2]: ammonia displacement of the pentaammine with $X = CN^-$ may be thus regarded as an exception. Once the first cyanide has entered the coordination sphere, the *trans* NH_3 ligand is selectively substituted by another CN^-. The atypical behavior was not quite unexpected, however, in the light of our kinetic results with *trans*-$Cr(NH_3)_4(CN)X^{z+}$-type complexes [11, 12] quantifying *trans* effects in chromium(III) and supplementing literature data for octahedral cobalt(III) systems [15]. It may be also noted that, unlike the earlier reported interaction of tetraammine species with CN^- in Me_2SO solution resulting in mixtures of the two dicyano isomers [10], the heterogeneous process in methanol appears to be stereospecific, at least on a preparative scale.

$$Cr(NH_3)_5(CN)^{2+} + CN^- \xrightarrow{MeOH} trans\text{-}Cr(NH_3)_4(CN)_2^+ + NH_3 \qquad (2)$$

Attempts to obtain $Cr(NH_3)_4(CN)_2^+$ species from $[Cr(NH_3)_5(CN)](CN)_2$ at high temperature by analogy with the solid-state, inner–outer sphere exchange of other acidopentaammines [1], were unsuccessful.

Authentication of the *trans*-dicyano complex was by means of its UV–Vis absorption features, as well as by its emission in room-temperature solution, centered at 698 nm [10]. The isomeric purity was confirmed by the spectrum of the final aquation product, *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$, markedly different from that of the *cis* form [7].

trans-$Cr(NH_3)_4(CN)_2^+$ has been demonstrated to undergo acid-catalyzed stepwise aquation of the CN^- groups with complete retention of configuration [10], as is generally true for aqueous chromium(III) systems [8]. Since the rates for the first and the second solvation stage differ by two orders of magnitude [11], both *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ and *trans*-

$Cr(NH_3)_4(H_2O)_2^{3+}$ can be obtained separately in good amounts under the appropriate acidity, and precipitated.

The perchlorate salt of the diaquo ion represents a convenient parent compound for various *trans*-tetraammines of chromium(III).

The monoaquo species, *trans*-$[Cr(NH_3)_4(H_2O)(CN)](ClO_4)_2$, reacts efficiently in methanol suspension with good nucleophiles, as thiocyanate and fluoride, forming *trans*-$Cr(NH_3)_4(NCS)(CN)^+$ and *trans*-$Cr(NH_3)_4(CN)F^+$, as described elsewhere [16]. The latter exhibit uncommon ground-state [12] and excited-state [16] behaviors, related to the considerable difference in the electronic and bonding properties of the two axial ligands. Obtainment of these complexes is again facilitated by the *trans* labilizing ability of cyanide.

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