Inorganica Chimica Acta, 27 (1978) 265–267
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Synthesis of *trans*[$Cr(NH_3)_4(NCS)_2$]$^+$, *trans*[$Cr(NH_3)_4NCSF$]$^+$ and [$Cr(NH_3)_5NCS$]$^{2+}$

A. D. KIRK and C. F. C. WONG

Department of Chemistry, University of Victoria, Victoria, B.C. V8W 2Y2, Canada

Received August 11, 1977

Preparation of trans-[$Cr(NH_3)_4(NCS)_2$]$^+$, trans-[$Cr(NH_3)_4NCSF$]$^+$ *and* $Cr(NH_3)_5NCS$]$^{2+}$ *by anation in acidic methanol is described. Spectral data (uv/vis) for the compounds is given and for* [$Cr(NH_3)_5$-NCS]$^{2+}$ *suggests that the product is significantly purer than from the pre-existing literature method.*

Introduction

Recently [1] the preparation of some *trans* diacido tetrammine chromium(III) complexes by a procedure involving anation, in methanol solution, of acidoaquotetrammine starting materials was described. We report here the utility of analogous procedures for preparation of the new compounds *trans*-[$Cr(NH_3)_4NCSF$]$^+$ and *trans*-[$Cr(NH_3)_4(NCS)_2$]$^+$. We also describe improvements (in our hands) to the preparation of *trans*-[$Cr(NH_3)_4F_2$]$^+$. The procedure also has significant advantages for preparation of [$Cr(NH_3)_5NCS$]$^{2+}$ salts and yields a much purer product in better yield than the previous method [2].

Experimental

trans-[$Cr(NH_3)_4F_2$]ClO_4

This compound was prepared by a modification of the method described by Wirth *et al.* [1]. 7 g of *trans*-[$Cr(NH_3)_4(H_2O)_2$]$(ClO_4)_3$ [3], and 7 g of NH_4F in 100 ml of methanol containing 0.1 ml of 60% $HClO_4$ were vigorously stirred at 28–30 °C for 24 h. The resulting violet powder was filtered and washed with methanol and ether. Recrystallization, by dissolving in 40 ml of 0.01 N HCl at ~60 °C, adding 4 ml of 60% $HClO_4$ and cooling to 0 °C, yielded 2.7 g of product (70%). The spectral data, Table I, are in excellent agreement with those in the literature [1], and consistent with the bisethylenediamine analogue [4].

trans-[$Cr(NH_3)_4(H_2O)F$]$(ClO_4)_2$

This compound was prepared as described [1].

trans-[$Cr(NH_3)_4(NCS)F$]ClO_4

A mixture of 3.0 g of *trans*-[$Cr(NH_3)_4(H_2O)F$]-$(ClO_4)_2$ and 3.0 g of NH_4NCS in 60 ml of methanol containing 0.1 ml of 60% $HClO_4$ was vigorously stirred at 28–30 °C for 24 h. The solid residue was filtered off and washed with methanol. To ensure that the product was entirely in the perchlorate form, it was dissolved in a minimum of 0.01 *M* HCl at 40 °C and precipitated by dropwise addition of 70% $HClO_4$ (~1/10 volume) to the cooled solution. The product was recrystallized by dissolving in a minimum of 0.01 *M* HCl at 40 °C, filtering the solution, and cooling the filtrate on ice. The beautiful pinkish–red needles obtained were filtered off, washed with methanol and

TABLE I. Spectral data for *trans*-[$Cr(NH_3)_4(NCS)_2$]$^+$, *trans*-[$Cr(NH_3)_4(NCS)F$]$^+$, *trans*-[$Cr(NH_3)_4F_2$]$^+$ and Their Ethylenediamine Analogues.

	λ_{max}	λ_{min}	λ_{max}	Ref.
trans-[$Cr(NH_3)_4(NCS)_2$]$^+$	374 (47.0)	425 (19.2)	502 (84.6)	This work
trans-[$Cr(en)_2(NCS)_2$]$^+$	365 (62.1)	414 (25.2)	487 (87.1)	6
trans-[$Cr(NH_3)_4(NCS)F$]$^+$	386 (31.0)	435 (13.7)	512 (36.3)	This work
trans-[$Cr(en)_2(NCS)F$]$^+$	375 (33.9)	422 (20.8)	502 (41.2)	5
trans-[$Cr(NH_3)_4F_2$]$^{+\,a}$	357 (11.4)	404 (11.1)	490 (15.3) 540 (13.8)	This work
	358 (11.6)	403 (11.3)	490 (15.4) 540 (13.7)	1
trans-[$Cr(en)_2F_2$]$^{+\,a}$	350 (14.5)	400 (12.8)	466 (21.1) 525 (16.3)	4

[a] Data are all for absorption maxima.

TABLE II. Spectral data for $[Cr(NH_3)_5NCS]^{2+}$ and Related Complexes.

	λ_{max}	λ_{min}	λ_{max}	Ref.
$[Cr(NH_3)_5NCS](NO_3)_2$ prep 1	363 (44.5)	411 (13.2)	483 (71.1)	This work
prep 2	(44.8)	(13.1)	(71.9)	This work
$[Cr(NH_3)_5NCS]Br_2$	(44.4)	(13.0)	(71.3)	This work
$[Cr(NH_3)_5NCS]^{2+}$	363 (53)		487 (84)	8
			500 (80)	9
	375 (42)^a	415 (15)^a		10
	370 (48)		490 (69)	11
	370 (52.5)	420 (20)	490 (83)	2
	375 (46)^a	420 (20)^a	488 (75)^a	12
	365 (45)^a	415 (14)^a	486 (70)^a	13
trans-$[Cr(en)_2(NH_3)NCS]^{2+}$	~360 sh		476 (80)	14
cis$[Cr(en)_2(NH_3)NCS]^{2+}$	~360 sh		476 (120)	14

^{a}Estimated from spectral curve in cited literature.

dried *in vacuo*. The yield was 1.4 g (56%). Spectral data are given in Table I, together with data for the bisethylenediamine analogue [5]. *Anal.* Calcd for $[Cr(NH_3)_4(NCS)F]ClO_4$: Cr, 17.53; C, 4.05; H, 4.08; N, 23.61. Found: Cr, 17.4; C, 4.1; H, 3.9; N, 23.3%.

trans-$[Cr(NH_3)_4(NCS)_2]ClO_4$

A mixture of 3.0 g *trans*-$[Cr(NH_3)_4(H_2O)_2]$-$(ClO_4)_3$ and 3.0 g of NH_4NCS was vigorously stirred in 50 ml of ethanol containing 0.1 ml of 60% $HClO_4$ for 24 h at 27–28 °C. The resulting pink powder was filtered off, washed with methanol, then ether, and air-dried. For reprecipitation as the perchlorate salt, the sample was dissolved at 35 °C in 0.01 N HCl (~100 ml), 2 ml of 70% $HClO_4$ were added, and the solution was cooled to 0 °C. The orange platelets which formed were filtered off, washed with 50/50 methanol/ether and ether, and air-dried. Addition of 10 ml of 70% $HClO_4$ to the filtrate yielded a small amount of a pink powder; no attempt was made to identify this product. The main fraction was recrystallized by dissolving in a minimum of 0.01 *M* HCl at 35 °C, adding 70% $HClO_4$ (~1 ml) to the solution to the point of incipient precipitation, and cooling in ice. The orange platelets were filtered off and washed as before. The yield was 1.1 g or about 50%. Spectral data are given in Table I and compared with the bisethylenediamine analogue [6]. *Anal.* Calcd. for $[Cr(NH_3)_4(NCS)_2]ClO_4$: Cr, 15.6; C, 7.16; H, 3.60; N, 25.03. Found: Cr, 15.6; C, 7.2; H, 3.6; N, 24.8%.

$[Cr(NH_3)_5NCS](NO_3)_2$

4.0 g of $[Cr(NH_3)_5H_2O](NO_3)_3$, prepared by the method of Mori [7], was mixed with 4.0 g of NH_4-NCS and the mixture was stirred in 100 ml of a 0.05 *M* HCl solution of 80% (v/v) methanol in water. The mixture was then vigorously stirred at 30 °C for 40 h. The light-orange product was filtered off and washed with methanol. For recrystallization, the product was dissolved in 0.01 N HCl at 35–40 °C, the solution was filtered, saturated $NaNO_3$ was added to the point of incipient precipitation and the solution was cooled to 0 °C. The yellow–orange product was filtered off, washed with methanol, and dried *in vacuo*. The yield was 1.6 g or about 43%. Spectral data with relevant literature data for comparison [8–12] are given in Table II. *Anal.* Calcd. for $[Cr(NH_3)_5$-$NCS](NO_3)_2$: Cr, 16.29; C, 3.76; H, 4.74; N, 35.10. Found: Cr, 16.4; C, 3.9; H, 5.0; N, 35.3%.

$[Cr(NH_3)_5NCS]Br_2$

The nitrate salt was dissolved in a minimum of 0.01 *M* HCl at 30 °C and saturated NaBr (about 2 ml to 1 g of starting material) was added dropwise to the stirred solution. The product was filtered and recrystallized by dissolving in 0.01 *M* HCl at 40 °C, adding saturated NaBr until the solution became slightly cloudy, warming the solution to clear, and cooling it over ~30 minutes to 0 °C. The yield was nearly quantitative. *Anal.* Calcd. for $[Cr(NH_3)_5NCS]Br_2$: C, 3.38; H, 4.26; N, 23.67. Found: C, 3.4; H, 4.0; H, 23.9%.

Techniques

Chromium was determined spectrophotometrically at 373 nm (ϵ = 4820 l mol^{-1} cm^{-1}) after basic peroxide oxidation to chromate ion.

Microanalyses for carbon, hydrogen and nitrogen were performed using a Perkin–Elmer Analyzer 240.

Uv–visible spectra were obtained on a Cary 17 spectrophotometer.

Discussion

Spectral data (uv/vis) for the *trans* diacidotetrammines and their bisethylenediamine analogues are given in Table I. For all the *trans* diacido compounds they are consistent with expectations based on ligand field theory, and analogy to the corresponding bisethylenediamine compounds [1, 5]. The data for [Cr(NH$_3$)$_5$NCS]$^{2+}$ differ significantly from most of the previously published values, Table II, but agree quite well with those of Waggener *et al.* [13]. We believe that this is indicative of the higher purity of our complex based on the following observations.

1) Ion exchange chromatography of our [Cr(NH$_3$)$_5$NCS]$^{2+}$ compounds under well established conditions yielded a predominant peak the area of which was $\geq$99% of all eluted bands (non-elutable species, including triply charged ions would not have been observed); the main impurity elutes faster than [Cr(NH$_3$)$_5$NCS]$^{2+}$ and may therefore be a singly charged positive ion.

2) In an earlier study [14] we found it impossible by repeated solvent extractions and recrystallizations to remove completely a (singly charged?) impurity from the analogous compound, *trans*-[Cr(en)NH$_3$NCS]$^{2+}$.

3) Our spectral data fit with a generalization [15] that for the first ligand field band ϵ(*cis*-Cr(en)$_2$NH$_3$X) > ϵ(*trans*-Cr(en)$_2$NH$_3$X) > ϵ(Cr(NH$_3$)$_5$X) while the majority of the published data for [Cr(NH$_3$)$_5$NCS]$^{2+}$ do not fit with this.

4) The published data in Table II show significant variability, even for preparations conducted in the same laboratory, while different preparations under our conditions give compounds with identical uv–visible spectra, Table II.

5) The lower temperature at which the preparation described here is carried out is likely to favour cleaner anation. In earlier work [14] it was noted that ready anation of [Cr(en)$_2$NH$_3$NCS](NCS)$_2$ occurred, either on heating or on solution in non-aqueous solvents. Other studies [16] show a significant rate constant for ammonia loss from [Cr(NH$_3$)$_5$NCS]$^{2+}$ leading to the possibility of formation of *cis* and *trans* acidoaquo, diaquo or diacido species, under the higher temperature aqueous conditions of the earlier method.

Acknowledgements

The authors acknowledge gratefully the financial support of National Research Council and University of Victoria Faculty Research Fund. Thanks are due to Dr. McGillivray of this department for performing the C, H & N analyses.

References

1 G. Wirth, C. Bifano, R. T. Walters and R. G. Linck, *Inorg. Chem., 12,* 1955 (1973).
2 M. Linhard, H. Siebert and M. Weigel, *Z. Anorg. Allg. Chem., 278,* 287 (1955).
3 D. W. Hoppenjans, J. B. Hunt and C. R. Gregoire, *Inorg. Chem., 1,* 2506 (1968).
4 S. C. Pyke and R. G. Linck, *Inorg. Chem., 10,* 2445 (1971).
5 C. F. C. Wong and A. D. Kirk, to be published.
6 C. Bifano and R. G. Linck, *Inorg. Chem., 13,* 609 (1974).
7 M. Mori, *Inorg. Synth., 5,* 131 (1957).
8 E. Zinato, R. Lindholm and A. W. Adamson, *J. Am. Chem. Soc., 91A,* 7076 (1969).
9 A. W. Adamson and A. H. Sporer, *J. Inorg. Nucl. Chem., 8,* 209 (1958); *J. Am. Chem. Soc. 80,* 3865 (1958).
10 A. W. Adamson, *J. Inorg. Nucl. Chem., 13,* 275 (1960).
11 E. Kyuno, M. Kamada and N. Tanaka, *Bull. Chem. Soc. Japan, 40,* 1848 (1967).
12 F. Seel, A. Hauser and D. Wesemann, *Z. anorg. Allg. Chem., 283,* 351 (1966).
13 W. C. Waggener, J. A. Mattern and C. H. Cartledge, *J. Am. Chem. Soc. 81,* 2958 (1959).
14 A. D. Kirk and T. L. Kelly, *Inorg. Chem., 13,* 1613 (1974).
15 C. F. C. Wong and A. D. Kirk, *Can. J. Chem., 53,* 3388 (1975).
16 C. S. Garner and D. A. House, in "Transition Metal Chemistry", Vol. 6, p. 182, edited by R. C. Carlin, Marcel Dekker, New York (1970).