Inorganica Chimica Acta, 53 (1980) L43–L45

Synthesis and Characterization of some Mixed Tris(diamine)chromium(III) Complexes*

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Received September 4, 1980

The first mixed tris(diamine)chromium(III) complex was prepared by Pfeiffer, *et al.* [1] who obtained [Cr(en)$_2$pn]Cl$_3$ when either *cis*- or *trans*-[Cr(en)$_2$Cl$_2$]Cl was heated on a water bath with a 50% excess of pn. In the last decade [Cr(en)$_2$tn]Cl$_3$ was prepared by heating *cis*-[Cr(en)$_2$Cl$_2$]Cl and excess tn in DMSO [2] or ether [3]. To date one other compound, [Cr(tn)$_2$en]Cl$_3$, has been reported. It can be prepared by refluxing stoichiometric amounts of [Cr(tn)$_2$Cl$_2$]Cl and en in ether [3] or by heating a 1:1:5 molar ratio of CrCl$_3$, en and tn in DMSO [2].

Mixed tris (diamine) chromium(III) complexes are of interest because they serve as useful starting points for absolute configuration studies [2] and they provide a fertile testing ground for various models and computer programs for conformational energy calculations [3].

Experimental

The chromium(III) complexes which were used as starting, materials, *cis*-[Cr(en)$_2$Cl$_2$]Cl·1.15H$_2$O, *cis*-[Cr(tn)$_2$Cl$_2$]Cl·0.75H$_2$O, [Cr(en)$_3$]Br$_3$·4H$_2$O, [Cr(pn)$_3$]Cl$_3$·3.22H$_2$O and [Cr(tn)$_3$]Cl$_3$·4.11H$_2$O were prepared from CrCl$_3$·6H$_2$O using literature methods [4, 5]. All other chemicals were reagent grade. The visible absorption spectra of aqueous solutions were recorded at room temperature using matched quartz cells in a Cary Model 14 spectrophotometer. The purity of products was monitored by two methods. Halide was estimated by potentiometric titration [6] and chromium was measured spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide [7]. The remaining elements were determined by microanalysis†. The two synthetic methods which were employed in the synthesis of mixed tris complexes involve: (a) diamine replacement of the halide ligands in a *cis*-dichloro complex or (b) diamine replacement of one of the original diamine ligands in a tris diamine complex.

Method (a)

[Cr(en)$_2$pn]Br$_3$

cis-[Cr(en)$_2$Cl$_2$]Cl·1.15H$_2$O (1.00 g, 3.34 mmol) and 1,2-propanediamine (0.70 g, 9.70 mmol) were placed in a 50-ml round bottomed flask equipped with a water condenser and heated under reflux for 2 hr. The condenser was removed and the flask containing the reaction mixture was heated on a water bath for one hr to remove excess pn. The yellow residue was allowed to cool, slurried with absolute ethanol (100 ml), filtered, and washed successively with absolute ethanol, acetone and ether and dried under vacuum over CaCl$_2$. The crude product (1.0 g) was dissolved in a minimum amount of water at 60 °C and a saturated solution containing 1.5 g of NH$_4$Br was added. The dark yellow precipitate which formed almost immediately was filtered, washed with ethanol then ether and dried over CaCl$_2$. The analytical results of this synthesis as well as the application of Method (a) for other compounds is summarized in Table I.

[Cr(en)(tn)$_2$]I$_3$·2H$_2$O

It was necessary to modify the above method for this synthesis. A mixture of *cis*-[Cr(tn)$_2$Cl$_2$]Cl·0.75H$_2$O (1.00 g, 3.12 mmol) and en in a 1:1 molar ratio was placed in the above apparatus and heated under reflux for 5 hr. The reaction mixture was allowed to cool, ground in a mortar and pestle with absolute ethanol, filtered, washed as above and dried in vacuum over CaCl$_2$. The entire yield of crude product (1.10 g) was dissolved in a minimum amount of water, filtered onto powdered KI (2.1 g), cooled in an ice bath for 10 min and filtered. The resulting yellow residue was washed several times with 95% ethanol and dried over CaCl$_2$ for 2 hr. Yield 0.297 g, 14.1%. *Anal.* Calcd for C$_8$H$_{28}$N$_6$I$_3$Cr·2H$_2$O: I, 56.30; Cr, 7.89. Found: I, 56;36; Cr, 7.64. A second crop of unidentified green crystals was obtained from the filtrate upon further cooling.

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*Abbreviations used: en = ethylenediamine; pn = 1,2-propanediamine (propylenediamine); tn = 1,3-propanediamine (trimethylenediamine); *i*-bn = 2-methyl-1,2-propanediamine (isobutylenediamine); chxn = *trans*-1,2-cyclohexanediamine; DMSO = dimethyl sulfoxide.

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†Microanalysis by M-H-W Microanalytical Laboratory, Phoenix, Arizona.

TABLE I. Analytical Results[a] of Methods (a) and (b).

Compound	Method	Heating Time	Yield	%C	%H	%N	%Br
$[Cr(en)_2pn]Br_3$	(a)	2 hr	73%	17.60 (17.30)	5.33 (5.35)	17.13 (17.30)	49.51 (49.34)
$[Cr(en)_2tn]Br_3$	(a)	4 hr	75%	17.14 (17.30)	5.52 (5.35)	17.18 (17.30)	49.21 (49.34)
$[Cr(en)_2\textit{i}\text{-bn}]Br_3$	(a)	45 min	78%	19.47 (19.22)	5.88 (5.60)	16.89 (16.82)	48.10 (47.96)
$[Cr(en)_2chxn]Br_3$	(a)	4 hr	83%	23.03 (22.84)	5.97 (5.70)	15.53 (15.98)	45.72 (45.59)
$[Cr(tn)_2\textit{i}\text{-bn}]Br_3$	(b)	1 hr	71%	22.63 (22.74)	6.09 (6.12)	16.15 (15.91)	45.51 (45.39)
$[Cr(pn)_2\textit{i}\text{-bn}]Br_3$	(b)	3 hr	84%	22.62 (22.74)	5.82 (6.12)	16.04 (15.91)	45.60 (45.39)
$[Cr(pn)_2chxn]Cl_3$[b]	(b)	1.5 hr	72%	33.96 (34.23)	8.14 (8.16)	19.78 (19.97)	25.27 (25.30)

[a] Calcd percentages appear in parentheses underneath experimental percentages. [b] Halide percentage is reported as chloride.

TABLE II. Visible Absorption Maxima and Minima of $[Cr(AA)_2BB]^{3+}$ in Aqueous Solution at Ambient Temperature*.

Compound	λ_{max} nm, (ϵ)	λ_{min} nm, (ϵ)	λ_{max} nm, (ϵ)	λ_{min} nm, (ϵ)
[a] $[Cr(en)_3]Cl_3 \cdot 3.22H_2O$	458(74.4)	395(14.2)	351(60.2)	287(1.5)
[a] $[Cr(tn)_3]Cl_3 \cdot 4.11H_2O$	464(53.3)	400(11.5)	354(47.6)	295(4.4)
[a] $[Cr(chxn)_3]Cl_3 \cdot 0.98H_2O$	460(89.0)	396(16.6)	353(69.7)	275(2.2)
[b] $[Cr(pn)_3]Br_3$	457(82.9)	396(20.0)	349(69.0)	305(17.8)
[b] $[Cr(en)_2pn]Br_3$	458(71.4)	395(18.9)	350(59.6)	308(11.8)
[b] $[Cr(en)_2tn]Br_3$	460(76.4)	395(21.2)	350(70.2)	312(18.5)
[b] $[Cr(en)_2chxn]Br_3$	458(78.7)	395(23.3)	350(70.2)	312(22.7)
[b] $[Cr(en)_2\textit{i}\text{-bn}]Br_3$	462(74.1)	400(26.4)	352(66.4)	314(21.9)
[b] $[Cr(tn)_2en]I_3 \cdot 2H_2O$	460(64.5)	397(15.6)	349(62.6)	317(34.8)
[b] $[Cr(tn)_2\textit{i}\text{-bn}]Br_3$	463(69.1)	397(15.4)	352(60.2)	300(6.2)
[b] $[Cr(pn)_2\textit{i}\text{-bn}]Br_3$	457(87.6)	394(21.4)	350(73.2)	290(10.8)
[b] $[Cr(pn)_2chxn]Cl_3$	458(80.2)	396(24.0)	350(76.5)	305(29.6)

*Molar absorptivity, ϵ, in units of M^{-1} cm^{-1}. [a] Ref. 4. [b] This work.

Method (b)

A mixture of the tris diamine, $[Cr(AA)_3]Cl_3 \cdot xH_2O$ (1.00 g) and the desired diamine (BB) in a 1:3 molar ratio was heated under reflux for 1 to 3 hr. The reaction mixture was allowed to cool, slurried with absolute ethanol, washed and the resulting crude complex recrystallized as the bromide salt by the same procedure used in Method (a) above. The new compounds prepared by this method are listed in Table I.

Method (b) was also used to prepare the compounds that were prepared by Method (a). This method gives products of comparable purity. The reaction times and yields of products using Method (b) reading from the top of Table I down are: 2 hr, 88%; 3 hr, 78%; 2 hr, 86% and 3 hr, 82%, respectively.

Results and Discussion

The general formula for mixed tris(diamine) chromium(III) complexes is $[Cr(AA)_2BB]^{3+}$. Many years after Pfeiffer reported the synthesis of the first mixed tris diamine complex (where AA = en and BB = pn), the same compound was obtained in small yield from $CrF_3 \cdot 3.5H_2O$ in a multistep synthesis [8] involving a reaction time in excess of 24 hr. Two different approaches patterned after successful syntheses of $[Cr(AA)_3]^{3+}$ in DMSO (4) or ether (9) have been used to prepare the other two previously reported compounds (where AA = en or tn and BB = en or tn). The synthesis in DMSO gives both possible products which must be separated by fractional precipitation whereas in ether anhydrous reactants are required and reaction times exceed 12 hr.

The results presented here show that the original Pfeiffer synthesis (Method a) is also applicable to the other two previously reported compounds. Its advantages are: solvent is eliminated, anhydrous reagents are not required, reaction times are shorter and in one case the yield is greatly improved. The lower yield for the reaction of $[Cr(tn)_2Cl_2]^+$ and en seems to be due to insufficient liquid to maintain good reflux when the reactants are in a 1:1 molar ratio. Excess en cannot be tolerated because this would result in the replacement of tn as well as the halide ions. The new method (Method b) was used to prepare five new mixed tris diamine complexes. The method appears to be a general one and is advantageous in cases where the *cis* or *trans* dichloro parent complex is difficult to obtain [7, 10].

Theory predicts [11] that the spin allowed transitions of Cr(III) in an octahedral field in order of increasing energy are: $^4A_{2g} \rightarrow {}^4T_{2g}$; $^4A_{2g} \rightarrow {}^4T_{1g}(F)$; and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$. These transitions lead to three broad bands in the visible absorption spectrum which are often referred to as band I, II and III in order of decreasing wavelength. In many cases the $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transition (band III) is obscured by the intense charge transfer band which arises in the UV region. The visible absorption spectra of some tris diamine and the mixed tris diamine complexes are given in Table II below. This table shows that the intensity of band II increases when $[Cr(AA)_2BB]^{3+}$ is compared with $[Cr(AA)_3]^{3+}$ in all cases except where AA = en and BB = pn. All the compounds in this table are yellow.

It has been observed [4] that chloride salts of tris diamine complexes have a water of crystallization content that can vary between 0 and 4 molecules of water per metal atom depending on their history. On the other hand, bromide salts of tris pn complexes show little or no water content [12]. Table I shows that the mixed tris diamine bromide salts prepared by the methods described here contain no water of crystallization.

References

1 P. Pfeiffer, T. Gassman and H. Pietsch, *Z. Anorg. Allgem. Chem., 57,* 312 (1908).
2 E. Rancke-Madsen and F. Woldbye, *Acta Chem. Scand., 26,* 3405 (1972).
3 E. N. Duesler and K. N. Raymond, *Inorg. Chim. Acta, 30,* 87 (1978).
4 E. Pedersen, *Acta Chem. Scand., 24,* 3362 (1970).
5 C. L. Rollison and J. C. Bailar, Jr., *J. Am. Chem. Soc., 65,* 250 (1943).
6 W. C. Cain and J. A. McLean, Jr., *Inorg. Chem., 4,* 1416 (1965).
7 R. R. Barona and J. A. McLean, Jr., *Inorg. Nucl. Chem. Lett., 5,* 385 (1969).
8 J. W. Vaughn and J. Marzowski, *Inorg. Chem., 12,* 2346 (1973).
9 H. L. Schläfer and O. Kling, *Z. Anorg. Allgem. Chem., 302,* 1 (1959).
10 J. A. McLean, Jr and N. A. Maes, *Inorg. Nucl. Chem. Lett., 8,* 147 (1972).
11 H. L. Schläfer, *J. Phys. Chem., 69,* 2201 (1965).
12 P. Andersen, F. Galsbøl and S. E. Harnung, *Acta Chem. Scand., 23,* 3027 (1969).