Synthesis of hexaamminecobalt(III) chloride – Protocol K

$$4CoCl_2 + 4NH_4Cl + 20NH_3 + O_2 \rightarrow 4[Co(NH_3)_6]Cl_3 + 2H_2O$$

Reaction. Add 240 g (1 mol) of cobalt(II) chloride hexahydrate and 160 g (3 mol) of ammonium chloride (about 200% excess) to 200 mL of water. Shake the mixture until most of the salts are dissolved. Then add 4 g of activated charcoal and 500 mL (8.25 mol) of concentrated ammonia (about 65% excess). Bubble air vigorously through the mixture until the red solution becomes yellowish brown (about 4 hours).

Isolation. Filter the crystals and charcoal on a Büchner funnel.

Purification. Add the crystals and charcoal to a solution of 15-30 mL of concentrated hydrochloric acid in 1500 mL of water. Heat the mixture and filter while it is hot. Precipitate the hexamminecobalt(III) chloride by adding 400 mL of concentrated hydrochloric acid and slowly cooling to 0 ºC. Filter the precipitate, wash first with 60% and then with 95% ethanol, and dry at 80-100 ºC.

Safety. Synthesis should be performed in a fume hood. See hazards associated with the reagents in Table 1.

Greenness Assessment. The evaluation was performed using the Green Star (GS) and the results are shown in Figure 1.

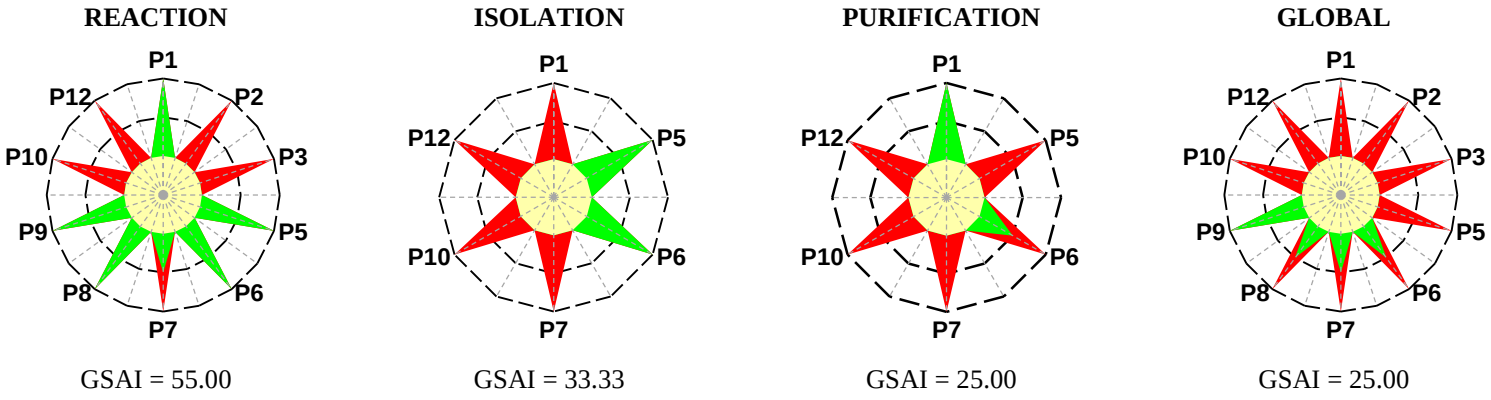

Figure 1. Greenness assessment (GS) for the synthesis of hexaamminecobalt(III) chloride

Construction of the GS

$$4CoCl_2 + 4NH_4Cl + 20NH_3 + O_2 \rightarrow 4[Co(NH_3)_6]Cl_3 + 2H_2O$$

Table 1 presents the hazards and scores associated with the substances involved and Table 2 presents the scores used to construct the green stars.

Table 1. Hazards for the synthesis of hexaamminecobalt(III) chloride, protocol K[α]

Substances involved	Step			Hazard code	Score: hazards to...		
	R	I	Pu		HH	E	P
Stoichiometric reagents							
Ammonia (concentrated solution)	✓			H290, H314, H335, H400	3	3	2
Ammonium chloride (CAS 12125-02-9)	✓			H302, H319	2	1	1
Cobalt(II) chloride hexahydrate (CAS 7791-13-1)	✓			H302, H317, H334, H341, H350i, H360F, H410	3	3	1
Oxygen[a] (CAS 7782-44-7)	✓			H270	1	1	3
Auxiliary substances							
Solvents							
Ethanol[b] (CAS 64-17-5)			✓	H225	1	1	3
Hydrochloric acid (CAS 7647-01-0)			✓	H314, H335	3	1	1
Water[a,b]	✓		✓	-	1	1	1
Other auxiliary substances							
Activated charcoal (CAS 7440-44-0)	✓			-	1	1	1
Product							
Hexaamminecobalt(III) chloride (10534-89-1)	✓	✓	✓	H315, H319, H335	2	1	1
Waste							
Activated charcoal			✓	-	1	1	1
Ammonia (aqueous solution)		✓		H315, H318, H400	3	3	1
Ammonium chloride (excess, aqueous solution)		✓		H302, H319	2	1	1
Ethanol[b]			✓	H225	1	1	3
Hydrochloric acid (dilute solution)			✓	-	1	1	1
Water[a,b]		✓	✓	-	1	1	1

[α] R – Reaction; I – Isolation; Pu – Purification; HH – Human Health; E – Environment; P – Physical

[a] Renewable; [b] Degradable to innocuous products

Table 2. Scores used to construct the green star for the synthesis of hexaamminecobalt(III) chloride, protocol K[α]

Green Chemistry Principle	Reaction		Isolation		Purification		Global	
	s	**Explanation**	**s**	**Explanation**	**s**	**Explanation**	**s**	**Explanation**
P1 Prevention	3	Without waste	1	Excess of ammonia solution, H318 and H400	3	Waste is innocuous	1	Excess of ammonia solution, H318 and H400
P2 Atom Economy	1	Excess of reagents > 10%, formation of by-products		NA		NA	1	Excess of reagents > 10%, formation of by-products
P3 Less hazardous chemical synthesis	1	Cobalt(II) chloride hexahydrate, H334, H350, H360 and H410, ammonia solution, H314 and H400		NA		NA	1	Cobalt(II) chloride hexahydrate, H334, H350, H360 and H410, ammonia solution, H314 and H400, hydrochloric acid, H314
P5 Safer solvents and auxiliary substances	3	Solvents and auxiliary substances are innocuous	3	Solvents and auxiliary substances are not used	1	Hydrochloric acid, H314	1	Hydrochloric acid, H314
P6 Increase energy efficiency	3	Room temperature	3	Room temperature	2	0 ºC ≤ T ≤ 100 ºC	2	0 ºC ≤ T ≤ 100 ºC
P7 Use renewable feedstocks	2	Oxygen is renewable	1	Substances not renewable	1	Substances not renewable	2	Oxygen is renewable
P8 Reduce derivatives	3	One stage		NA		NA	2	Two stages
P9 Catalysts	3	Activated charcoal is innocuous		NA		NA	3	Activated charcoal is innocuous
P10 Design for degradation	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable
P12 Safer chemistry for accident prevention	1	Cobalt(II) chloride hexahydrate, H334, H350, and H360, ammonia solution, H314, and oxygen, H270	1	Excess of ammonia solution, H318	1	Hydrochloric acid, H314, and ethanol, H225	1	Cobalt(II) chloride hexahydrate, H334, H350, and H360, ammonia solution, H314, oxygen, H270, hydrochloric acid, H314, and ethanol, H225

[α]s – Score; NA – Not applicable

References

Fernelius, W.C. et al. *Inorganic Syntheses – Vol. II*. McGraw-Hill Book Company, Inc: New York, 1946, pp. 216-218.

Inorganic Chemistry Experiment, *http://webhard.gnu.ac.kr/pub.php?get.pdf* (accessed June 2011).