Inorganica Chimica Acta, 31 (1978) L429–L430

$(+)_{546}$*Trans*-dichlorobis($(+)_D$-2,4-diamino-2-methylpentane)cobalt(III)

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Received July 20, 1978

The published preparations of 2,4-diamino-2-methylpentane have described sodium-ethanol reductions of diacetonamine oxime, 4-amino-4-methylpentan-2-one oxime [1, 2] and of acetonine, 2,2,4,6,6-pentamethyl-1,2,5,6-tetrahydropyrimidine [3, 4], both being condensation products of acetone and ammonia. A more convenient Raney nickel reduction of the diacetonamine oxime is described below.

Diacetonamine oxime was prepared [2] from diacetonamine hydrogen oxalate [5] and was distilled (143–144 °C, 24 mm) immediately before use. The oxime (26 g) was dissolved in 600 ml water containing 72 g sodium hydroxide. With vigorous stirring and while maintaining the temperature at 48–50 °C, a total of 25 g powdered Ni/Al alloy (B.D.H. 50% Ni) was slowly added (approximately 2 hr). The filtrate was steam-distilled, the distillate acidified (conc. HCl) and evaporated to dryness. The amine, isolated as an upper layer by addition of conc. aqueous sodium hydroxide was dried with sodium and distilled (57 °C, 21 mm).

The amine (23.2 g, 0.2 mol) was added to *d*-tartaric acid (30.0 g, 0.2 mol) dissolved in a total three litres of ethanol/methanol/water (10/10/1 by volume). The product (41 g, 77% $|\alpha|_D$ + 21.5°, 0.05 g ml^{-1} H_2O) very slowly crystallized (5 days) and was recrystallized a further five times (10 g, 19%, $|\alpha|_D$ + 19.2°, 0.05 g ml^{-1} H_2O). *Anal.* Calcd. for $C_{10}H_{22}N_2O_6$: C, 45.1; H, 8.33; N, 10.5. Found: C, 44.9; H, 8.47; N, 10.4. The amine tartrate was treated with one mole equivalent of tartaric acid and two mole equivalents of potassium chloride in the minimum quantity of boiling water, the potassium hydrogen tartrate filtered off and the amine isolated as before; ($|\alpha|_D$ + 21.1°, 1 dm). The first mother liquor was evaporated to dryness and the residue extracted with one litre of methanol. A total 8 g was recovered from the methanol and the amine isolated as before ($|\alpha|_D$ – 18.1°, 1 dm).

Trans-dichlorobis((+)-2-4-diamino-2-methylpentane))cobalt(III) perchlorate. Anhydrous cobalt(III) chloride (Alfa) (0.49) was dissolved in 10 ml methanol and (+)amine (1.2 g) added. Carbon dioxide free air was passed through the solution for 3 hr. Then 2 ml conc. HCl was added and the mixture held at 50 °C for 5 min. Lithium perchlorate precipitated green needles which were recrystallized from a dilute HCl solution ($|\alpha|_{546}$ 46°, 0.003 g ml^{-1} nitromethane). *Anal.* Calcd. for $C_{12}H_{32}N_4Cl_3O_4Co$: C, 31,2; H, 6.93; N, 12.1. Found C, 31.0; H, 6.53; N, 12.2.

The Table shows circular dichroism and adsorption spectra for *trans*-dichlorobis((+)-2,4-diamino-2-methylpentane))cobalt(III) perchlorate. The negative, positive, negative circular dichroism mirrors that for the *trans*-dichlorobis(RR-2,4-diaminopentane)cobalt(III) ion [6] in which the two chelate rings are most certainly in the λ form.

In the present complex ion, should the chelate rings be arranged mutually *trans* with respect to their asymmetric methyl groups then there would always be considerable interference between the remaining methyl groups were the ring conformations either of twist or chair type. On the other hand, for a configuration *cis* with respect to the asymmetric methyl groups, this latter interference would be minimized

TABLE. Absorbance and Circular Dichroism Data for *trans*-Dichlorobis(pentanediamine)[a] and Bis(methylpentanediamine(cobalt)-(III) Complexes.

	Abs ν_{Max} 10^3 cm^{-1}	CD ν_{Max} 10^3 cm^{-1} $(\epsilon_l - \epsilon_r)$
trans[$CoCl_2$(RR-2,4-ptn)$_2$]	15.75 (1.63)	16.00 (+0.475)
	21.37 (1.57)	20.92 (–0.575)
	25.32 (1.81)	26.46 (+0.470)
trans[$CoCl_2$(+)me-ptn)$_2$]	15.75 (1.58)	15.04 (–0.05)
	21.05 (1.43)	20.62 (+0.36)
	25.13 (1.81)	*ca.* 26 (–)

[a] From Ref. [6].

were the chelate rings to adopt a twist rather than a chair conformation. From the circular dichroism spectrum it appears than the $(+)_{546}$*trans*-dichlorobis-($(+)_D$-2,4-diamino-2-methylpentane))cobalt(III) ion mirrors the configuration of the *trans*-dichlorobis-(RR-2,4-diaminopentane)cobalt(III) ion and by interference that the $(+)_D$ amine has S absolute configuration.

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