

longer than the N–C bond in free NMe₃, 1.454(2) Å.

The \angle Al–N–C angle in Cl₃AlNMe₃ is larger than the corresponding angles in H₃AlNMe₃ and Me₃AlNMe₃, 109.0(0.3)° and 109.3(0.4)°, respectively, although the difference is of marginal statistical significance. Such a difference might easily be explained as the result of increased steric interaction between donor and acceptor due to the shortening of the Al–N bond.

The Al–Cl bond distance is in excellent agreement with the mean Al–Cl bond distance found in the crystal, 2.123 Å. Just as the N–C bond distances in the complexes X₃AlNMe₃ are longer than in free NMe₃ and appear to increase in length with increasing acceptor strength of X₃Al, so the Al–Cl bond distances in complexes of the type Cl₃Al–L are longer than the Al–Cl bond in free AlCl₃ and appear to increase with increasing donor strength of the base L: The Al–Cl bond in Cl₃AlNMe₃ is significantly longer than the mean Al–Cl bond distance in the complex of AlCl₃ with propionyl chloride,⁹ 2.093(3) Å, which in turn is significantly longer than the Al–Cl bond in free AlCl₃, 2.06 ± 0.01 Å.⁹

The shrinkage of the Cl...C(*trans*) distance was found to be 0.12(6) Å.

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Preparations of *trans*-Bis(2-picolylamine) Complexes of Chromium(III)

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In a recent paper,¹ two series of octahedral *cis*-bis(2-picolylamine) complexes of chromium were described (2-picolylamine = 2-aminomethylpyridine). The ligands in the *cis*-positions were Cl⁻, Br⁻, and H₂O. This paper reports the preparation of a series of the corresponding *trans*-complexes.

Only one type of geometrical isomer occurs, probably a *trans,trans,trans* isomer (Fig. 1. a). It is likely that the other imaginable isomer, the *trans,cis,cis* (Fig. 1 b), does not exist because of sterical hindrance.

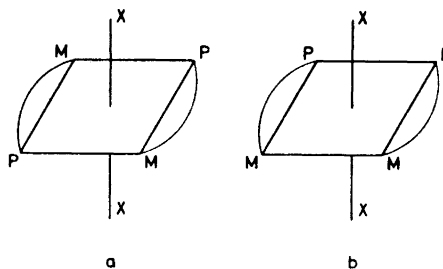


Fig. 1. The geometrical isomers of the *trans*-[Cr(C₆H₈N₂)₂X₂]ⁿ⁺ ion. P symbolizes the pyridine nitrogens, M, the methylamine nitrogens. a. The *trans,trans,trans* isomer. b. The *trans,cis,cis* isomer.

The preparations are based upon the reaction between the so-called α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl¹ and moist silver oxide. The resulting solution apparently contains both *trans*- and α -*cis*-[Cr(C₆H₈N₂)₂OH·H₂O]²⁺. By means of conc. nitric acid *trans*-[Cr(C₆H₈N₂)₂(H₂O)₂](NO₃)₃ is isolated from the reaction mixture and used as an initial material for *trans*-[Cr(C₆H₈N₂)₂Cl₂]Cl and *trans*-[Cr(C₆H₈N₂)₂Br₂]Br.

The assignment of geometric configuration is based entirely upon the colours of

Table I. Spectral data of $trans-[Cr(en)_2X_2]^{n+}$ and $trans-[Cr(C_6H_8N_2)_2X_2]^{n+}$.

X-X	Amine	$\lambda_{max}(1)$	$\epsilon(1)$	$\lambda_{max}(2)$	$\epsilon(2)$	$\lambda_{max}(3)$	$\epsilon(3)$	Ref.
H ₂ O	en	508	22.5	442.5	29.3	361	39.2	2
H ₂ O	C ₆ H ₈ N ₂	~ 510	~ 18	443.5	28.1	~ 360	~ 34	
Cl	en	578	24.5	453	22.8	396	34.0	3
Cl	C ₆ H ₈ N ₂	578	27.1	445	24.6	393	42.1	
Br	en	607	34.9	~ 460	~ 24	406	30.7	4
Br	C ₆ H ₈ N ₂	605	43.3	~ 465	~ 23	405	50.2	

the compounds and a comparison of their visible absorption spectra with those of known bis (ethylenediamine) analogous (Table 1).^{2,3,4}

Experimental. α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl·H₂O was prepared as described before.¹ All other reagents were reagent grade and used without further purification.

trans-Diaquabis (2-picolyamine) chromium (III) nitrate, [Cr(C₆H₈N₂)₂(H₂O)₂](NO₃)₃. 1.40 g α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl·H₂O (3.57 mmol) was added to moist silver oxide, freshly prepared from 3.0 g silver nitrate (18 mmol). After 5 min the violet solution was filtered and acidified with conc. nitric acid. During stirring and ice-cooling 250 ml ethanol (99 %) was added slowly to precipitate yellow-orange crystals of presumed *trans*-[Cr(C₆H₈N₂)₂(H₂O)₂](NO₃)₃. They were filtered and washed with ethanol and acetone. 0.78 g. The recrystallization was performed by dissolving the crystals in 5–6 ml boiling water, filtering and cooling on ice after the addition of 1 ml conc. nitric acid. Yield: 0.65 g (36 %) of filtered needles. (Found: Cr 10.24; C 28.3; N 19.4; H 4.40. Calc. for [Cr(C₆H₈N₂)₂(H₂O)₂](NO₃)₃·H₂O: Cr 10.23; C 28.4; N 19.3; H 4.36).

trans-Dichlorobis (2-picolyamine) chromium (III) chloride, [Cr(C₆H₈N₂)₂Cl₂]Cl. 1.40 g *trans*-[Cr(C₆H₈N₂)₂(H₂O)₂](NO₃)₃·H₂O (2.75 mmol) was heated on a water-bath (100°) with 6–7 ml conc. hydrochloric acid. A violet solution soon formed and grey-green, shining crystals separated. After cooling on ice, they were filtered and washed with conc. hydrochloric acid and acetone. 0.65 g. The compound was recrystallized from 30 ml boiling 6 M hydrochloric acid. Washing as above. Yield: 0.54 g (47 %). (Found: Cr 12.69; C 34.6;

N 13.5; Cl 25.5. Calc. for [Cr(C₆H₈N₂)₂Cl₂]Cl·2.25H₂O: Cr 12.52; C 34.7; N 13.5; Cl 25.6). The hydrogen analyses for this and the following compound failed to come out reproducibly.

trans-Dibromobis (2-picolyamine) chromium (III) bromide, [Cr(C₆H₈N₂)₂Br₂]Br. 1.00 g *trans*-[Cr(C₆H₈N₂)₂(H₂O)₂](NO₃)₃·H₂O (1.97 mmol) was heated on a water-bath (100°) with 10 ml hydrobromic acid (48 %). A grass-green precipitate, probably *trans*-(Cr(C₆H₈N₂)₂Br₂]Br·Br₂ soon formed. Approx. 300 mg ascorbic acid was added and the heating continued, until the tribromide had been transformed to the more soluble, darkgreen bromide. After cooling on ice the compound was filtered and washed with ice-water and acetone. Yield 0.54 g (52 %). Recrystallization was not necessary. (Found: Cr 9.82; C 27.5; N 10.6; Br 45.7. Calc. for [Cr(C₆H₈N₂)₂Br₂]Br·H₂O: Cr 9.88; C 27.4; N 10.7; Br 45.6).

Electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer. Data for the maxima are given in Table I as (λ, ϵ), the wavelength λ in $m\mu$, the molar extinction coefficient ϵ in $l\ mol^{-1}\ cm^{-1}$. Medium 0.1 M hydrochloric acid.

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