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# Stereochemistry of Cobalt(III) Complexes Containing (N,O)-Five and Six-membered Aminoalcohol Chelate Rings

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$^{59}$Co NMR (94.45 MHz) has been used to study $Co^{III}$ complexes formed by reaction of cobalt(II) chloride with 2- and 3-aminoalcohols; mononuclear molecular tris-O,N-chelate complexes of $Co^{III}L_3$ ($L = NH_2CH_2CH_2O^-$ and $NH_2CH_2CH_2CH_2O^-$) are produced in both geometric *mer*- and *fac*-forms, the *mer*-isomers being thermodynamically unstable and spontaneously rearranging to the *fac*-form in solution; the analogous complex $L = NH_2CHEtCH_2O^-$ exists only in the *fac*-form; 2-aminoalcohols also yield trinuclear complexes $[Co^{II}(Co^{III}L_3)_2]^{2+}$, in which pseudo-contact interaction of the $Co^{II}$ and $Co^{III}$ atoms occurs; the crystal structure of $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}\cdot Cl_3(NH_3CH_2CH_2OH)\cdot 2H_2O$ has been determined.

When 2-aminoethanol reacts with $Co^{II}$ salts in the presence of alkali a molecular tris-O,N-chelate complex of cobalt(III) $[Co(NH_2CH_2CH_2O)_3]$[1–4] is formed which exists in two isomeric forms [$\delta_{mer}$ 1913; $\delta_{fac}$ 2066, relative to $Co(NH_3)_6Cl_3$].

The *mer*-isomer is unstable in aqueous solution (pH 7) and spontaneously isomerizes to the *fac*-form with time. In this case the *mer*→*fac* isomerization reaction is first order ($K_S = 5.2 \times 10^{-4}\ s^{-1}$; $\Delta H^‡ = 59.44$ kJ mol$^{-1}$; $\Delta S^‡ = -0.11$ kJ mol$^{-1}$ K$^{-1}$ at 25 °C). The relatively low values of the activation parameters may indicate an intramolecular character of the *mer*→*fac* isomerization process (twist-mechanism). One can assume that on dissolving the *mer*-isomer in water the dipole–dipole interaction of the complex with solvent molecules causes *mer*→*fac* isomerization, because the presence of negative charge on one side (side OOO) and positive charge on the opposite side (side NNN) increases the dipole of the *fac*-isomer. When the less polar solvent methanol is used then *mer*→*fac* isomerization proceeds four times slower than in aqueous solution. It should be noted that during *mer*→*fac* isomerization, when the concentration of both isomers became approximately equal within a short period, signals (δ 3250 and 3560) characteristic of $Co^{III}(N)_2(O)_4$ type complexes were registered in the $^{59}$Co NMR spectra. Thus, the mechanism of *mer*→*fac* isomerization can also include cleavage of the metal—ligand bond through the nitrogen atom (or complete cleavage of both cobalt—ligand bonds) with the participation of the solvent molecules. The cobalt—nitrogen bond in the *mer*-isomer can break in two different places (on N—Co—N and N—Co—O coordinates); this fact explains the presence of two bands from the intermediate complex $Co(N)_2(O)_4$ in the spectrum.

The presence of hydroxy ions in the solution causes the reverse transfer *fac*→*mer*. The kinetics of the *fac*⇌*mer* isomerization catalysed by $OH^-$ ions is described by eqns. (1) and (2),

$$K_{f\to m} = A[OH]^2 \quad (1)$$

$$K_{m\to f} = K_S + K_{[OH]}[OH]^2 \quad (2)$$

where $A$ is a constant, $K_{[OH]}$ the reaction rate constant, being catalysed only by $OH^-$ ions and $K_S$ the spontaneous *mer*→*fac* isomerization rate constant. Acidification by a solution (pH 5) containing the molecular complexes *fac*- and *mer*-$[Co(NH_2CH_2CH_2O)_3]$ first leads to the formation of cationic complexes $[Co(NH_2CH_2CH_2OH)_3]^{3+}$ ($\delta_{mer}$ 1205, $\delta_{fac}$ 1320), then breakage of the chelate rings through the oxygen atom takes place with time and complexes containing monodentate aminoalcohol *mer*- and *fac*-$[Co(NH_2CH_2CH_2O)_3(H_2O)]^{3+}$ (δ 2590, 2710) are formed. The tris-molecular complex $[Co(NH_2CH_2CH_2O)_3]$, containing O,N-bidentate six-membered 3-aminopropan-1-ol ligands, occurs in *mer*- and *fac*-forms. The *mer*-isomer is thermodynamically unstable and with time spontaneously isomerizes to the *fac*-form, the speed of isomerization being considerably higher in this case than for the analogous tris(2-aminoethanol) complex.

The tris complex $[Co(NH_2CHEtCH_2O)_3]$, containing five-membered O,N-chelate rings, of racemic [(*S*)- and (*R*)-forms] 2-aminobutan-1-ol, should also exist in *mer*- and *fac*-forms. In addition, each of these geometric isomers can form four different diastereoisomers $Co(S)_3$; $Co(S)_2(R)$; $Co(S)(R)_2$ and $Co(R)_3$ having enantiomeric Λ,Δ-configurations. The total number of expected diastereoisomers is 12, as previously recorded by $^{59}$Co NMR for solutions with the related tris-chelating complex $[Co(pn)_3]^{3+}$ with racemic propane-1,2-diamine (pn).[5,6] However, only four bands (δ 2160, 2120, 2225, 2290) from the diastereoisomers of *fac*-configuration were recorded in the $^{59}$Co NMR spectrum of freshly prepared $[Co(NH_2CHEtCH_2O)_3]$. The presence of only the *fac*-isomer for $[Co(NH_2CHEtCH_2O)_3]$ was also confirmed by $^{13}$C NMR spectral analysis. It is interesting to note that the formation of $K_3[Co(cysu)_3]$ containing a five-membered N,S-bidentate ligand, cysu = $[NH_2CH(CO_2)CH_2S(O)_2]^{2-}$, occurs stereoselectively and the only compound obtained is the *fac*-isomer.[7,8] In the course of reaction (3) the *fac*-configuration of the complex

$$[Co(NH_2CHEtCH_2O)_3] \xrightarrow[H_2O]{H^+} [Co(NH_2CHEtCH_2OH)_3]^{3+} \quad (3)$$

remains unchanged, *i.e.* the diastereoisomers (δ 1511, 1515, 1509, 1495) formed in the acidic medium from the cation complex are *fac*-isomers. An attractive peculiarity of the complex *fac*-$[Co(NH_2CH_2CH_2O)_3]$ is its ability to act as a ligand while interacting with $Co^{II}$ salts and to form polynuclear complexes of different compositions by means of the three oxygen atoms.[9,10] We obtained complexes $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}Cl_2$ **1**, $\{Co^{II}[Co^{III}(NH_2CH_2CH_2CH_2O)_3]_2\}Cl_3\cdot NH_3CH_2CH_2OH\cdot 2H_2O$ **2** and $\{Co^{II}[Co^{III}(NH_2CHEtCH_2O)_3]_2\}Cl_2)$ **3** from methanol solutions. In **1**–**3** aminoalcohols act as O,N-bidentate ligands and form two octahedral tris-chelating complexes with the two $Co^{III}$ atoms, hving *fac*-configurations ($Co^{III}N_3O_3$), which are bridge-bonded by $Co^{II}$ into a trinuclear fragment through six O atoms ($Co^{II}O_6$).

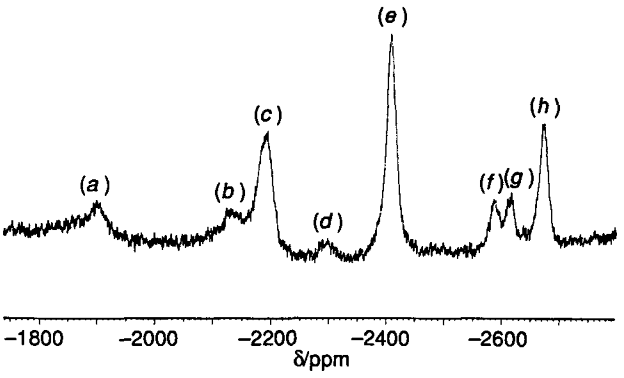

**Fig. 1** $^{59}$Co NMR spectrum of an aqueous solution of $\{Co^{II}[Co^{III}(NH_2CHEtCH_2O)_3]_2\}Cl_2$ **3**

Pseudocontact interaction with the Co$^{III}$ atoms (through the oxygen atoms) results in a shift of the $^{59}$Co NMR signals to higher field: δ $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}^{2+}$ − δ *fac*-$[Co(NH_2CH_2CH_2O)_3]$ = 4711 ppm at 25 °C due to the presence of the paramagnetic centre Co$^{II}$ in these complexes with an unpaired electron. Paramagnetic enlargement of the signal is not observed. Eight resonance lines [Fig. 1(*a*)–(*h*)] were observed in the $^{59}$Co NMR spectrum of **3**. It is worth noting that in the trinuclear complex **3** three different combinations of the Λ,Λ; Δ,Δ and Λ,Δ-configurations of monomeric tris-O,N-chelating fragments must be considered. These three combinations of fragments are enantiomers and four signals should correspond to them in the spectrum, as observed for the monomeric complex. However, non-equivalence of the O,N-chelating rings appears on formation of the trinuclear complex **3**. Thus, unlike the *fac*-monomeric complex, **3** can be formed as eight diastereoisomers *SSS*; *RSS*; *SRS*; *SSR*; *RRS*; *SRR*; *RSR*; *RRR*. It should also be noted that in this case complex asymmetry may be caused by the conformational effect.

The $\lambda \rightleftharpoons \delta$ conformational free energy differences determined for $[Co(NH_3)_4NH_2CHEtCH_2OH]^{3+}$ are not very large ($\Delta G = 1.30 \pm 0.21$ kJ mol$^{-1}$).[11] Hence it is impossible to register some conformers in the $^{59}$Co NMR spectra because of the rapid (on the NMR time scale) $\lambda \rightleftharpoons \delta$ conformation. Conformational exchange in the tris-complexes, however, must be retarded. When the tris-chelating complexes are bound into the rigid trinuclear structure **3**, the conformers become energetically non-equivalent (heterodynamic) and spectroscopically different.

The crystal structure of **2**† has a number of interesting features. The main structural unit is the trinuclear complex cation $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}^{2+}$ (Fig. 2), which consists of two crystallographically independent tris(2-aminoethanol) complexes of Co$^{III}$. Each complex shares three oxygen atoms with the central atom of the bivalent cobalt Co$^{II}$.

Coordination of Co$^{III}$ atoms is always octahedral, slightly distorted, but Co$^{II}$ forms a trigonal-extended octahedral. Three atoms of both oxygen and nitrogen of the O,N-chelate ligand forming linear fragments N—Co—O are surrounded by Co$^{III}$ atoms, causing dipolar localization on one of the facets of the octahedron. Evidently, trinuclear complex cation is formed with the bivalent cobalt in the centre for stabilization. The presence of Co$^{II}$ in the structure is confirmed by data from magnetic measurements.

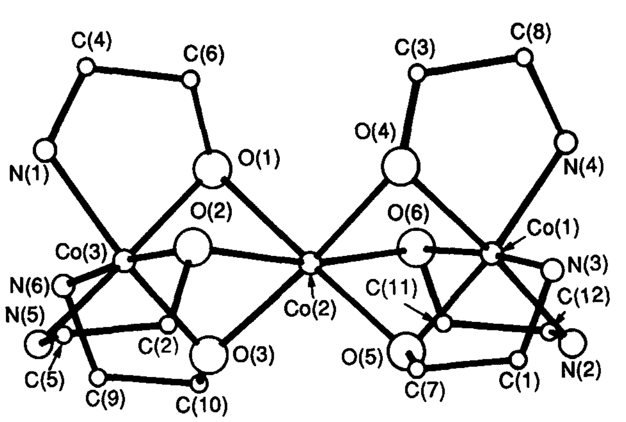

**Fig. 2** Molecular structure of the trinuclear cation $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}^{2+}$ of **2**. Bond lengths (Å) and angles (°): Co(1)—Co(2) 2.637(3), Co(2)—Co(3) 2.655(4), Co(1)—O(4) 1.95(1), Co(1)—O(5) 1.88(1), Co(1)—O(6) 1.96(1), Co(1)—N(2) 1.94(1), Co(1)—N(3) 1.93(2), Co(1)—N(4) 1.99(1), Co(2)—O(1) 2.21(2), Co(2)—O(2) 2.153(9), Co(2)—O(3) 2.074(8), Co(2)—O(4) 2.110(8), Co(2)—O(5) 2.00(1), Co(2)—O(6) 2.12(1), Co(3)—O(1) 1.96(1), Co(3)—O(2) 1.88(1), Co(3)—O(3) 1.87(1), Co(3)—N(1) 1.97(1), Co(3)—N(5) 1.92(1), Co(3)—N(6) 1.97(2); O(2)—Co(2)—O(5) 112.1(4), O(2)—Co(2)—O(6) 167.8(5), O(3)—Co(2)—O(4) 173.2(4), O(3)—Co(2)—O(5) 103.3(4), O(3)—Co(2)—O(6) 110.4(4), O(4)—Co(2)—O(5) 77.9(4), O(4)—Co(2)—O(6) 76.4(4), O(5)—Co(2)—O(6) 77.9(4).

The Co$^{III}$—N bond lengths are in the range 1.87(1) – 1.99(1) Å, while those of Co$^{III}$—O are 1.92(1)–1.99(1) Å. For Co$^{II}$ coordination the Co$^{II}$—O bond lengths vary much more: 2.00(1)–2.21(2) Å.

A trinuclear complex $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}^{2+}$ containing Co$^{II}$, is described in ref. 12.

2-Aminoethanol is an O,N-chelate ligand and forms five-membered metal rings CoNCCO. The average lengths of the C—O, C—C and C—N bonds in the chelate rings are 1.48(2), 1.42(2) and 1.50(2) Å, respectively, and are in good agreement with those found in *fac*-$Co(NH_2CH_2CH_2O)_3 \cdot 3H_2O$.[4] A non-coordinated molecule of 2-aminoethanol $NH_3CH_2CH_2OH^+$ with N—C, C—C and C—O bond lengths equal to 1.47(3), 1.51(3) and 1.38(3) Å, respectively, is present in the structure of **2**. The free molecule interacts through the nitrogen atom with an oxygen atom from one of the $H_2O$ molecules, the O(1) atom of the coordinated ligand and the intermolecular OH-group at distances of 2.83(1), 2.77(2) and 2.81(2) Å, respectively.

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† *Crystal data* for **2**: $Co_3Cl_3N_7C_{14}O_9H_{48}$, $M_r = 741.9$, monoclinic, space group *Cc*, $a = 19.617(6)$, $b = 11.578(3)$, $c = 18.061(5)$ Å, $\beta = 134.86(6)°$. Crystal dimensions $0.3 \times 0.2 \times 0.4$ mm$^3$, $U = 2907.703$ Å$^3$, $Z = 4$, $D_c = 1.69$ g cm$^{-3}$, linear absorption coefficient 20.8 cm$^{-1}$, $F(000) = 1587$, Syntex-P2$_1$ four-circle diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation, $\lambda = 0.71069$ Å, θ–2θ scan, $2\theta_{max} = 58°$, $I \geqslant 2\sigma(I)$, 1870 unique adsorption corrected intensities. The structure was solved using SHELXS-86, refinement and all further calculations were carried out using SHELXS-76. H-atoms were localized by difference Fourier methods. All non-hydrogen atoms were refined anisotropically, and all H atoms were included in structure factor calculations. Final $R = 0.044$ and $R_W = 0.034$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1 of *J. Chem. Soc., Chem. Commun.*

*Mendeleev Commun.*, 1991, 1(2), 55–57

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