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Azido–amine–cobalt(III) complexes Crystal structures of *cis*-[Co(tren)$(N_3)_2$]ClO_4 and *trans*-[Co(3,2,3-tet)$(N_3)_2$]ClO_4

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Abstract

The structures of the two complexes *cis*-[Co(tren)$(N_3)_2$]ClO_4 (**I**) and *trans*-[Co(3,2,3-tet)$(N_3)_2$]ClO_4 (**II**) (tren=2,2′,2″-triamino-triethylamine; 3,2,3-tet=1,10-diamino-4,7-diazadecane) have been determined by X-ray crystallography. The compounds consist of isolated complex cations $[Co(tren)(N_3)_2]^+$ and $[Co(3,2,3\text{-}tet)(N_3)_2]^+$ with distorted octahedral geometry and ClO_4^- counter ions. The two single coordinated azido ligands are arranged *cis* and *trans* in the cations of **I** and **II**, respectively. The Co–N(azido) distances vary from 1.946(3) to 1.964(3) Å. The configurational geometry for these complexes were previously reported based on the position of the asymmetric stretching mode of vibration of the coordinated azido ligands, $\nu a(N_3)$ in the 2000–2065 cm^{-1} region. The results of X-ray studies are consistent with the previous assigned geometry based on the IR of $\nu a(N_3)$ and strongly support its use as a valuable tool for elucidating the geometrical isomerism in octahedral diazido metal complexes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Azido complexes; Cobalt(III) complexes; 2,2′,2″-Triaminotriethylamine; 1,10-Diamino-4,7-diazadecane; Crystal structure

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1. Introduction

The azide ion is a versatile ligand, it can bind metal ions in a number of coordination modes, giving rise to mononuclear, dinuclear and polynuclear complexes. In these complexes different types of bonding of the azido ligands have been observed; either simple monodentate terminal fashion [1–9] or bridging end-to-end (1,3-di-μ) or end-on (1,1-di-μ) modes [10–16]. The coordination mode of the azido ligand depends on the nature and oxidation state of the central metal ion, as well as the nature of the other coordinated ligands.

The study of metal complexes containing azide ligands is complicated by the presence of several binding modes for the azido ligands [10–16] and/or the geometrical isomers of the metal–azido core [1]. We have established a simple method to distinguish between the geometrical configuration of the mono-nuclear octahedral diazido- and triazido-metal complexes. It depends on observing the position in the IR spectrum of the asymmetric stretching vibration mode of the coordinated azide ion, $\nu a(N_3)$ in the range 2000–2065 cm^{-1}; the *cis*-diazido and *fac*-triazido species exhibit two strong absorption bands, whereas their corresponding *trans*- and *mer*-complexes show only one band [1]. A similar interpretation was also used in studying the photoisomerization and photoreduction of some square planar diazido-bis(triphenylphosphine)- and diazido-1,3-bis(diphenylphosphino)propane-platinum(II) complexes [6].

This work was undertaken to confirm our IR spectral prediction for the geometrical isomerism in octahedral azido–metal complexes based on the use of $\nu a(N_3)$ by determining the crystal structure for two of the previously characterized diazido complexes namely *cis*-[Co(tren)$(N_3)_2$]ClO_4 and *trans*-[Co(3,2,3-tet)$(N_3)_2$]ClO_4 [1].

2. Experimental

2.1. Materials

2,2′,2″-Triaminotriethylamine (tren) and 1,10-diamino-

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4,7-diazadecane (3,2,3-tet) were purchased from Aldrich Chemical Company, Milwaukee, USA. All other materials were reagent grade quality, unless otherwise indicated.

Caution: Salts of perchlorate and azide and their metal complexes are potentially explosive and should be handled with care and in small quantities.

2.2. Synthesis of the complexes

2.2.1. Cis-[Co(tren)(N_3)$_2$]ClO_4 (I)

To an aqueous solution (30 ml) containing $Co(NO_3)_2.6H_2O$ (1.45 g, 5 mmol) and tren (0.73 g, 5 mmol), NaN_3 (0.65 g, 10 mmol) dissolved in H_2O (10 ml) was added drop by drop with stirring. To complete the oxidation of the metal ions the resulting dark brown solution was air bubbled for 2 h, filtered and treated with 1 ml of saturated solution of $NaClO_4$, and this was followed by slow evaporation on steam-bath to ca 15 ml. Upon cooling at room temperature, dark fine red crystals were separated out. These were collected by filtration, washed with ethanol, acetone, ether and air dried (yield: 1.1 g, 57%). Found: C, 18.7; H, 4.7; N, 35.5; Calc. for $C_6H_{18}N_{10}ClO_4Co$: C, 18.5; H, 4.7; N, 36.0%. Single crystals suitable for X-ray measurements were obtained from dilute solution upon standing at room temperature for one week.

2.2.2. Trans-[Co(3,2,3-tet)(N_3)$_2$]ClO_4 (II)

The complex was prepared in a similar fashion as described above for **I** (yield: 0.90 g, 43%). Found: C, 23.2; H, 5.2; N, 33.2. Calc. for $C_8H_{22}N_{10}ClO_4Co$: C, 23.1; H, 5.3; N, 33.6%.

Table 1
Crystal data for *cis*-[Co(tren)(N_3)$_2$]ClO_4 (**I**) and *trans*-[Co(3,2,3-tet)(N_3)$_2$]ClO_4 (**II**)

Compound	I	II
Empirical formula	$C_6H_{18}ClCoN_{10}O_4$	$C_8H_{22}ClCoN_{10}O_4$
Formula weight	388.68	416.74
Color	deep red	deep red
System, space group	Monoclinic, I2/a	Orthorhombic, Pbca
a (Å)	13.996(4)	23.432(6)
b (Å)	15.182(4)	13.075(3)
c (Å)	14.548(4)	10.897(3)
α (°)	90	90
β (°)	108.43(2)	90
γ (°)	90	90
V (Å^3)	2932.7(14)	3339(2)
Z	8	8
μ(MoKα) (mm^{-1})	1.390	1.227
Normal. transmission factors	1.000–0.470	1.000–0.583
D_{calc}/D_{obs} (Mg/m^3)	1.761/1.75(3)	1.658/1.65(3)
Approx. crystal size (mm)	0.32×0.22×0.14	0.30×0.24×0.20
θ range of data collection (°)	2.95–26.00	2.99–26.00
Reflections collected	3554	3763
Independ. refl./R_{int}	2879/0.0376	3271/0.0274
Parameters	253	239
Goodness-of-Fit on F^2	1.073	1.062
$R1/wR2$	0.0433/0.1010	0.0449/0.0980
Weighting factors[a]: a/b	0.0566/2.8200	0.0432/2.3828
Largest peak/hole (e/Å^3)	0.423/−0.456	0.400/−0.352

[a] $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

2.3. Physical measurements

Infrared spectra were measured on a Perkin–Elmer System 2000 NIR FT-Raman spectrophotometer as KBr pellets. Elemental analyses were performed at the Micro-analytical Laboratory of Kuwait University using Elemental Analyzer LECO CHN 932.

2.4. X-ray crystal structure analyses

A modified STOE four-circle diffractometer was used for single crystal X-ray measurements. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data from 67 reflections in the θ range 8.0–15.6° (compound **I**) and 33 reflections in the θ range 8.8–15.9° (compound **II**), respectively. Data were collected at 298(2) K using graphite crystal-monochromatized Mo-Kα radiation (λ=0.71069 Å) and the ω-scan technique. The intensities were corrected for Lorentz-polarization effects, and for absorption. Crystallographic data and processing parameters are given in Table 1.

The structures were solved by Direct methods and subsequent Fourier analyses. Anisotropic displacement parameters were applied to non-hydrogen atoms in full-matrix least-squares refinements based on F^2. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical restraints. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The program DIFABS [17], and the SHELXTL/PC [18] program package were used for computations. Selected bond distances and bond angles are given in Tables 2 and 3.

3. Results and discussion

3.1. IR spectra

The IR spectra of the complexes under investigation display the characteristic strong absorption bands due to the asymmetric stretching vibration of the coordinated azido ligands, νa(N_3). The complex [Co(tren)(N_3)$_2$]ClO_4 (**I**) exhibits two bands at 2054 and 2025 cm^{-1}, whereas [Co(3,2,3-tet)(N_3)$_2$]ClO_4 (**II**) shows a single band at 2011 cm^{-1}. These spectral data are consistent with those reported earlier for the two complexes and suggest *cis* geometry for **I** and *trans* geometry for **II** [1].

3.2. Description of the structures

3.2.1. Cis-[Co(tren)(N_3)$_2$]ClO_4 (I)

The structure consists of isolated [Co(tren)(N_3)$_2$]$^+$

Table 2
Selected bond distances (Å) and angles (°) for *cis*-[Co(tren)$(N_3)_2$]ClO_4 (**I**)

Co(1)–N(3)	1.946(3)	Co(1)–N(4)	1.945(3)
Co(1)–N(21)	1.946(3)	Co(1)–N(1)	1.953(3)
Co(1)–N(2)	1.963(3)	Co(1)–N(11)	1.964(3)
N(11)–N(12)	1.172(4)	N(12)–N(13)	1.153(5)
N(21)–N(22)	1.171(4)	N(22)–N(23)	1.145(5)
N(3)–Co(1)–N(4)	91.4(2)	N(3)–Co(1)–N(21)	96.5(2)
N(4)–Co(1)–N(21)	91.8(2)	N(3)–Co(1)–N(1)	86.94(13)
N(4)–Co(1)–N(1)	86.87(13)	N(21)–Co(1)–N(1)	176.33(14)
N(3)–Co(1)–N(2)	170.88(14)	N(4)–Co(1)–N(2)	94.41(14)
N(21)–Co(1)–N(2)	90.28(14)	N(1)–Co(1)–N(2)	86.41(13)
N(3)–Co(1)–N(11)	87.2(2)	N(4)–Co(1)–N(11)	176.7(2)
N(21)–Co(1)–N(11)	91.3(2)	N(1)–Co(1)–N(11)	90.06(13)
N(2)–Co(1)–N(11)	86.6(2)	N(12)–N(11)–Co(1)	125.1(3)
N(13)–N(12)–N(11)	175.4(4)	N(22)–N(21)–Co(1)	127.0(3)
N(23)–N(22)–N(21)	174.6(4)		

Table 3
Selected bond distances (Å) and angles (°) for *trans*-[Co(3,2,3-tet)$(N_3)_2$]ClO_4 (**II**)

Co(1)–N(21)	1.949(3)	Co(1)–N(11)	1.959(3)
Co(1)–N(4)	1.983(3)	Co(1)–N(1)	1.985(3)
Co(1)–N(2)	1.987(3)	Co(1)–N(3)	1.987(3)
N(11)–N(12)	1.192(4)	N(12)–N(13)	1.150(4)
N(21)–N(22)	1.173(4)	N(22)–N(23)	1.147(5)
N(21)–Co(1)–N(11)	177.98(13)	N(21)–Co(1)–N(4)	85.68(13)
N(11)–Co(1)–N(4)	93.45(12)	N(21)–Co(1)–N(1)	88.05(14)
N(11)–Co(1)–N(1)	90.11(14)	N(4)–Co(1)–N(1)	88.35(13)
N(21)–Co(1)–N(2)	93.66(13)	N(11)–Co(1)–N(2)	87.22(12)
N(4)–Co(1)–N(2)	179.27(12)	N(1)–Co(1)–N(2)	91.94(13)
N(21)–Co(1)–N(3)	92.42(13)	N(11)–Co(1)–N(3)	89.45(13)
N(4)–Co(1)–N(3)	93.45(12)	N(1)–Co(1)–N(3)	178.16(13)
N(2)–Co(1)–N(3)	86.26(13)	N(12)–N(11)–Co(1)	125.1(2)
N(13)–N(12)–N(11)	175.4(4)	N(22)–N(21)–Co(1)	127.0(3)
N(23)–N(22)–N(21)	176.7(5)		

cations with distorted octahedral geometry and *cis* arrangement of the two single coordinated azido ligands. As a consequence of their site symmetries, the ClO_4^- counter ions are located on split-positions with different types of disorder. A perspective view of the molecular structure together with an atom labeling scheme are shown in Fig. 1. The relevant bond distances and angles are given in Table 2. The four Co–N distances of the tren ligand [1.953(3), 1.963(3), 1.946(3) and 1.945(3) Å] are similar to the two Co–N(azido) [1.964(3) and 1.946(3) Å]. The Co–N11–N12 and Co–N21–N22 bond angles are 125.1(3) and 127.0(3)°, respectively.

3.2.2. *Trans-[Co(3,2,3-tet)$(N_3)_2$]ClO_4* (**II**)

The structure consists of isolated [Co(3,2,3-tet)$(N_3)_2$]$^+$ cations with distorted octahedral geometry and *trans* arrangement of the two single coordinated azido ligands and ClO_4^- counter ions. A perspective view together with the atom labeling scheme is illustrated in Fig. 2, and the relevant bond distances and angles are given in Table 3. The four nitrogen atoms of the 3,2,3-tet ligand and the cobalt atom are in the same plane. The four Co–N(3,2,3-tet) distances are similar [1.985(3), 1.987(3), 1.987(3) and 1.983(3) Å] and slightly longer than the two axial Co–N(azido) [1.959(3) and 1.949(3) Å]. The bond angles Co–N11–N12 and Co–N21–N22 are equal to the corresponding angles of **I**.

The Co–N(azido) distances in the two diazido complexes **I** and **II** which vary from 1.946(3) to 1.964(3) Å, are very close to those observed in *mer*-triazidotris(substituted pyridine)cobalt(III) complexes, *mer*-Co(L)$_3$$(N_3)_3$, where L=pyridine, 3,4-dimethyl-pyridine, 3,5-dimethylpyridine and 4-picoline [2,3].

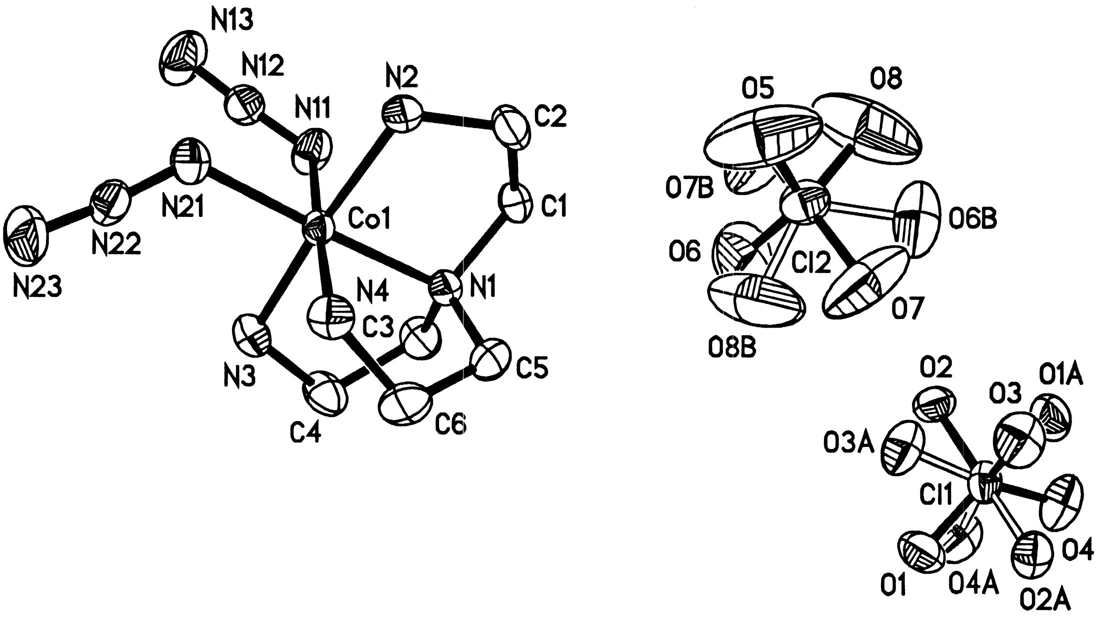

Fig. 1. Molecular structure and atom labeling scheme of *cis*-[Co(tren)$(N_3)_2$]ClO_4 (**I**). There exist different split orientations of the disordered ClO_4^- counter anion.

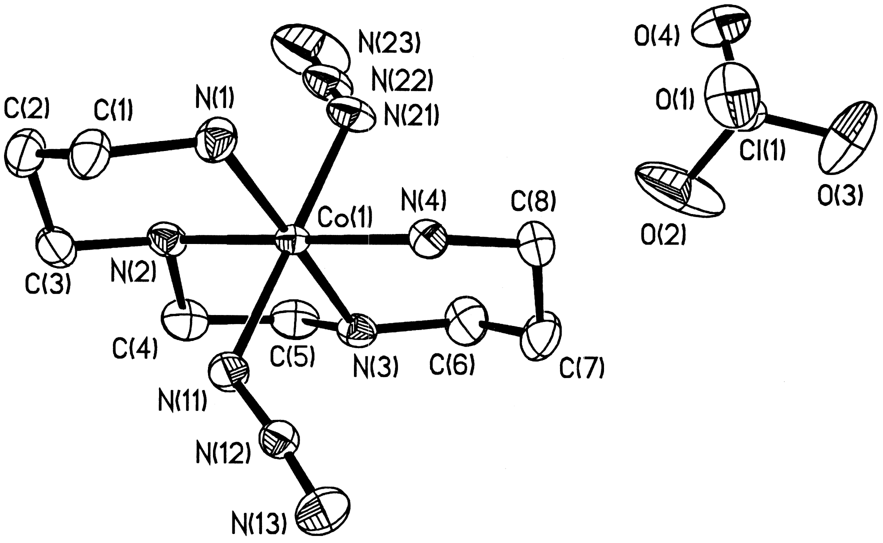

Fig. 2. Molecular structure and atom labeling scheme of *trans*-[Co(3,2,3-tet)$(N_3)_2$]ClO_4 (**II**).

The geometry of the diazido-tetraamine-cobalt(III) complex ions depends on the nature of the tetradentate amine ligand. Due to the tripodal nature, the four nitrogen donors of the tren can not adopt a planar geometry and hence enforces the formation of complexes of octahedral geometry, leaving two vacant *cis* positions available for binding two mono-dentate or bi-dentate ligand(s) [19]. In contrast, the linear nature of the 3,2,3-tet (1,10-diamino-4,7-diazadecane) amine may lead to the formation of octahedral complexes of *cis*- and/or *trans*-geometry. However, the majority of the complexes isolated with the 3,2,3-tet ligand were found to prefer *trans*-coordination [20–22]. In this case, the four nitrogen donors are oriented coplanar with the central metal ion leaving the two axial positions for binding the appropriate ligands leading to simple mono-nuclear species [16,20–22] or poly-nuclear species through bridged ligands [16,23]. The tendency of linear tetraamines for *trans*-orientation decreases in the order 3,3,3-tet (1,11-diamino-4,8-diazaundecane)>3,2,3-tet>2,3,2-tet (1,9-diamino-4,7-diazanonane)>2,2,2-tet (1,8-diamino-3,6-diazaoctane; trien) [1,16,20–25].

The X-ray structural analysis of the octahedral diazido–tetraamine–cobalt(III) complexes is in complete agreement with the assigned configuration made on the basis of the asymmetric stretching mode of vibration of the coordinated azido ligands, $\nu a(N_3)$ in the 2000–2065 cm^{-1} region. The latter method provides a simple valuable tool for the elucidation of the geometrical isomers in this class of compounds.

Attempts to obtain azido-bridged 1-D systems with cobalt ion as metal centers were not successful with above synthetic routine. In order to isolate such 1-D chains with end-to-end (EE) azido bridges, where the azido group may act as antiferromagnetic exchange pathway, the $N_3^-:ClO_4^-$ counter anion molar ratio has to be changed from 2:1 to 1:2. Such 1-D systems with EE bridging azides have been recently reported in a series of cobalt(II) azido complexes where the tetraamine ligand is replaced by four mono-dentate pyridine derivative ligands [26]. A ferromagnetically coupled dimer with trivalent metal centers has been observed in [Fe(salpn)(N_3)]$_2$, (salpnH_2=*N,N′*-bis-(salicylidene)-1,3-diaminopropane, tetra-dentate ligand), with two end-on azido bridges in *cis* orientation [27]; whereas an antiferromagnetic 1-D polymeric chain system has been observed for the corresponding manganese(III) compound, Mn(salpn)(N_3), with EE-bridging azides in *trans* arrangement [27,28].

Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers CCDC 113065 and CCDC 113064 for **I** and **II**, respectively.

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