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The crystal structures and doublet emission properties of hexaam(m)ine Cr(III) complexes

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Dedicated to Professor A.W. Adamson on the occasion of his 80th birthday

Contents

Abbreviations: en, $H_2N(CH_2)_2NH_2$; pn, (*R*,*S*)-$H_2NCH(CH_3)CH_2NH_2$; tn, $H_2N(CH_2)_3NH_2$; chxn, *trans*-*RR*,*SS*-1,2-diamino-cyclohexane; Me_2tn, $H_2NCH_2C(CH_3)_2CH_2NH_2$; 3,3-tri, $H_2N(CH_2)_3NH(CH_2)_3NH_2$; 2,3-tri, $H_2N(CH_2)_2NH(CH_2)_3NH_2$.

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Abstract

Hexaam(m)ine Cr(III) complexes are reviewed on which X-ray data were published or of which the phosphorescence was measured in the crystalline state. In addition complexes of the type *mer*-$[Cr(NH_3)(diamine)(triamine)]^{3+}$ have been prepared. In all cases, the complex cations were crystallised as chloromercury(II) salts and single-crystal X-ray structures have been determined for six systems. Apart from *mer*-$[Cr(NH_3)(Me_2tn)(2,3\text{-tri})]HgCl_5\cdot 1.5H_2O$ (**5**) (monoclinic, $C2/c$) which has both *endo* and *exo* forms in the lattice, the other six complexes adopt the *exo*–*mer*-triamine configuration. The 1,2-diaminopropane (pn) ligand in *mer*-$[Cr(NH_3)(pn)(3,3\text{-tri})]HgCl_5\cdot 2H_2O$ (**2**) (monoclinic, $P2_1/c$) is end-for-end disordered and the 1,2-cyclohexane diamine ligand (chxn) is the *trans*-(*RR*,*SS*)-isomer in both *mer*-$[Cr(NH_3)(chxn)(3,3\text{-tri})]HgCl_5$ (**3**) (monoclinic, $P2_1/n$) and *mer*-$[Cr(NH_3)(chxn)(2,3\text{-tri})]HgCl_5\cdot 2H_2O$ (**6**) (monoclinic, $P2_1c$). In **2**, **3**, **5** and **6** above, the chloromercury(II) formula unit is a distorted tetrahedral $HgCl_4^{2-}$ plus an isolated Cl^- ion. The $Hg_2Cl_7^{3-}$ formula unit in *mer*-$[Cr(NH_3)(tn)(2,3\text{-tri})]Hg_2Cl_7\cdot H_2O$ (**4**) (triclinic, $P\bar{1}$) adopts an $HgCl_3^-$ plus $HgCl_4^{2-}$ arrangement. A novel $[Hg_4Cl_{17}]^{9-}$ stoichiometry is found in *mer*-$[Cr(NH_3)(en)(3,3\text{-tri})]_3[HgCl_4]_4\cdot Cl\cdot 3H_2O$ (**1**) (triclinic, $P1$). The ^2E_g–$^4A_{2g}$ (O_h) intercombination bands were measured at 20 K both in absorption and emission. The phosphorescence decay curves of selected single emission lines were determined at temperatures $18 < T < 200$ K. Quantitative correlation were found between the intensity of the vibronic sidebands and the deviation from octahedral symmetry and between the phosphorescence decay times and the mean N′–Cr–N–H torsion angle. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chromium(III); Amines; Chloromercury(II); Phosphorescence

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1. Introduction

The early photochemical and photophysical studies of coordination compounds were mostly done in aqueous solutions or in glassy matrices. Those were the subjects of several reviews [1–4]. At that time, internal effects were the main object as one can read in the disputes about the photoactive state or Adamson's rules, where Adamson was one of the protagonists [5–9]. In the following, hexaam(m)ine Cr(III) complexes are reviewed on which X-ray data were published or of which the phosphorescence was measured in the crystalline state. Then we present new data of a series of complexes of the type *mer*-$[Cr(NH_3)(diamine)(triamine)]^{3+}$ with the diamines being en, pn, tn, chxn and Me_2tn and the triamines 3,3-tri and 2,3-tri. An abbreviated nomenclature is used, where only the varied ligands are stated as for example 2,3-en for $[Cr(NH_3)(1,4,8\text{-triazaoctane})(1,2\text{-diaminoethane})]^{3+}$.

In recent years X-ray structure determinations of coordination compounds became more popular and provide a basis for spectroscopic and theoretical studies.

For experimental studies the complexes of the hexaam(m)inechromium(III) class, $[Cr(N_6)]^{3+}$, are especially suitable, because their ^2E_g–$^4A_{2g}$ transitions exhibit sharp lines with well resolved vibronic sidebands both in absorption as well as in emission. They can be prepared in a large variety of ligand arrangements and single crystals appropriate for crystal structure analysis can be obtained. Most of the classical complexes have been characterised by X-ray crystallography. Table 1 summarizes the CrN_6 complex ions for which structural and luminescence data exist. Although their number is quite impressive there are only rather few cases that match in the counter ions. Nevertheless, few studies exist where the emission spectra were obtained from the same samples as the X-ray data.

Kirk and Güdel [10,11] studied the luminescence and doublet absorption spectra of multidentate hexaamine Cr(III) complexes with particular interest in the ligand induced distortions from O_h symmetry. They observed an increase in intensity of the vibronic origins relative to the intensity of the side bands with deviation from centrosymmetry.

Detailed angular overlap calculations on CrN_6 complexes were performed by Hoggard et al. [12–16]. The calculations indicated that the ^2E_g splittings are sensitive to deviation from the ideal octahedral geometry. Hoggard [10] found “generally good agreement between the observed splittings and those calculated using a constant set of interelectronic and spin orbit coupling parameters”. Further theoretical work uses or predicts structural parameters [17–22]. A density functional study [23] on $[Cr(NH_3)_6]^{3+}$ showed the distortion of the $^4T_{2g}$. An elongation of 0.15 Å in the equatorial plane and a contraction of 0.03 Å along the third axis was in good agreement with Wilson and Solomon’s spectroscopic results [24]. Mingos and Rohl [25] calculated molecular surface and shapes from van der Waals radii in order to estimate packing effects in the solid state.

2. Crystal structure and doublet emission properties of six *mer*-$[Cr(NH_3)(diamine)(triamine)]Hg_xCl_y$ complexes

2.1. Experimental

2.1.1. Syntheses

The trichlorotriaminechromium(III) complexes *mer*-$CrCl_3$(3,3-tri) and *mer*-$CrCl_3$(2,3-tri) [26,27] were converted into *mer*-[CrCl(diamine)(triamine)]$ZnCl_4$ salts as previously described [26,28,29] (diamine = en, pn, chxn, Me_2tn, tn) using the commercially available diamines (pn = racemic 1,2-diaminopropane, chxn = 50:50 mixture of *trans*-(*RR*,*SS*)- and *cis*-(*R*,*S*)-isomers of 1,2-diaminocyclohexane).

Samples of *mer*-$[Cr(NH_3)(diamine)(triamine)]Hg_xCl_y$ were prepared from the chloro analogs using liquid NH_3 described previously [28]. Crystals suitable for single crystal X-ray analysis were grown by room temperature evaporation of small samples of the $Hg_xCl_y^{n-}$ salts dissolved in 3 M HCl (in the dark).

All complexes have been characterised by single-crystal X-ray structural analysis. Compositions, preparative yields and quartet absorption data are presented in Table 2.

Table 1
Survey of crystal structure determinations and emission studies of crystalline CrN_6-complexes (reports, where the compositions match, are shown in bold type)

Complex ion		Further constituents	
Name of ligand	Formula	Structure determinations[a]	Emission spectra[b,c]
Ammonia	$[Cr(NH_3)_6]^{3+}$	$[Ni(CN)_5]^{3-}\cdot 2H_2O$ [39] $[ZnCl_4]^{2-}\cdot Cl^-$ [40] $[MnCl_5H_2O]^{3-}$ [41] $[MnF_6]^{3-}$ [42] $[CuCl_5]^{3-}$ [43,44] $[CuBr_5]^{3-}$ [45] $[CuBr_3\,Cl_2]^{3-}$ [46] $[HgCl_5]^{3-}$ [47,48] $[Ni(H_2O)_6]\cdot 5Cl^-\cdot 1/2NH_4Cl$ [49] $NH_4^+\cdot$4(1,5-di-*p*-tolylpenta-azadienide)$\cdot 4H_2O$ [50]	$(ClO_4)_3$ [52–54] $(ClO_4)_3$ (deuterated) [52–54] $(PF_6)_3$ [54] Polycarboxylates [55]
	$[Cr(NH_3)_5NH_2(^tBu)]^{3+}$	**$[ZnCl_4]^{2-}\cdot Cl^-$** [51] **$3ClO_4\cdot 2H_2O$** [51]	**$[ZnCl_4]^{2-}\cdot Cl^-$** [56] **$3ClO_4\cdot 2H_2O$** [56]
1,2-Diaminoethane	$[Cr(en)_3]^{3+}$	**$3Cl^-\cdot 3H_2O$** [57] $3NCS^-$ [58,59] $3NCS^-\cdot 0.75H_2O$ [60,61] $[ZnCl_4]^{2-}\cdot Cl^-$ [62] $3/2[HgCl_4]^{2-}$ [63] $[FeCl_6]^{3-}\cdot 6Cl^-\cdot H_2O$ [64] $[FeCl_4]^-\cdot 2Cl^-\cdot 9H_2O$ [64] $[Co(CN)_6]^{3-}\cdot 6H_2O$ [65] $[Ni(CN)_5]^{3-}\cdot 1.5H_2O$ [66] $[MoO(CN)_4OH]^{3-}\cdot H_2O$ [67] $Li^+\cdot$2D-tartrate$\cdot 3H_2O$ [68] $[Co(en)_3]^{3+}\cdot 6Cl^-\cdot 6.1H_2O$ [69]	$3ClO_4^-$ [52,53,83] $3ClO_4^-$ (deuterated) [52,53,83] $3ClO_4^-$ {Rh}[d] [52] $3ClO_4^-$ {Rh}[d] (deuterated) [52] $3NO_3^-$ [52] $3NO_3^-$ (deuterated) [52] **$3Cl^-$** [52,84] $3Br^-$ [52] $3/2Cl^-\cdot 1/2KCl\cdot 3H_2O$ [83–85] $3/2Cl^-\cdot 1/2KCl\cdot 3H_2O$ (deuterated) [83]

Table 1 (*Continued*)

Complex ion		Further constituents	
Name of ligand	Formula	Structure determinations[a]	Emission spectra[b,c]
	$[(+)Cr(en)_3]^{3+}$	$3Cl^-\cdot 2H_2O$ [70,71]	
		$3Br^-\cdot 0.6H_2O$ [72,73]	
		$3I^-\cdot H_2O$ [74]	
		$[(+)Rh(en)_3]^{3+}\cdot 6Cl^-\cdot 6H_2O$ [75]	
		$[(+)Rh(en)_3]^{3+}\cdot 6NCS^-\cdot 1.5H_2O$ [76]	
	$[(-)Cr(en)_3]^{3+}$	$3NCS^-$ [77]	
		$[(+)Co(en)_3]^{3+}\cdot 6Cl^-\cdot 6H_2O$ [78]	
		$[(+)Co(en)_3]^{3+}\cdot 6NCS^-$ [79,80]	
		$[(+)Co(en)_3]^{3+}\cdot 6NCS^-\cdot 6H_2O$ [81]	
	cis-$[Cr(en)_2(CH_3NH_2)_2]^{3+}$	$3ClO_4$ [82]	
1,3-Diaminopropane	$[Cr(tn)_3]^{3+}$	$[Ni(CN)_5]^{3-}\cdot 2H_2O$ [39,86]	$3Cl^-$ [45]
	$[Cr(tn)_2en]^{3+}$	$3I^-\cdot H_2O$ [87]	
	$[Cr(en)_2tn]^{3+}$	$3Br^-\cdot H_2O$ [87]	
	$[Cr(tn)_2(NH_3)_2]^{3+}$		
	trans-	Unpublished work mentioned in [10]	$3ClO_4$ [e] [10]
	cis-		$3ClO_4$ [10]
1,4,7-Triazaheptane	$[Cr(dien)_2]^{3+}$		
	mer-	$[Hg_2Cl_7]^{3-}$ [88]	
		$[HgCl_5)^{3-}$ [63]	
	fac-	$[Hg_2Cl_7]^{3-}$ [63,88]	
trans-1,2-Diaminocyclo-hexane	$[Cr(chxn)_3]^{3+}$	$3NO_3^-\cdot 3H_2O$ [89]	$3Cl^-$ [90]
1,4,8,11-tetraaza-Cyclotetradecane	$[Cr\ cyclam(NH_3)_2]^{3+}$		
	trans-	**$ClO_4\cdot 2Cl^-$** [30]	$3ClO_4^-$ [e] [11]
			$3ClO_4^-$ (deuterated) [11]
			$ClO_4\cdot 2Cl^-$ [30]

Table 1 (*Continued*)

Complex ion		Further constituents	
Name of ligand	Formula	Structure determinations[a]	Emission spectra[b,c]
	cis-	$3I^-\cdot H_2O$ [91]	$NO_3\cdot 2ClO_4^-$ [11] $NO_3\cdot 2ClO_4^-$ (deuterated) [11]
	cis-[Cr cyclam en]$^{3+}$	**$3ClO_4^-$** [92]	**$3ClO_4^-$** [93]
	cis-[Cr cyclam pn]$^{3+}$		**$3ClO_4^-$** [94]
6,13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane	[Cr *trans*-diammac]$^{3+}$	**$3ClO_4^-$** [95]	**$3ClO_4^-$** [f] [96]
1,4,7,10,13,16-Hexaazacycloocta-decane	[Cr[18]aneN6]$^{3+}$	**$3Br^-$** [97,98]	**$3Br^-$** [e] [10]
1,4,7,11,14,17-Hexaazacycloeico-sane	[Cr[20]aneN6]$^{3+}$	**$3Br^-\cdot H_2O$** [98]	**$3Br^-$** [10]
4,4′,4″-Ethylidynetris-3-azabutan-1-amine	[Cr sen]$^{3+}$	$3Br^-$ [99]	**$3Br^-$** [e] [10,99] $3ClO_4$ {Rh}[d] [99]
1,4,7-Tris(amino-propyl)-1,4,7-triazacyclononane	[Cr taptacn]$^{3+}$		$3Br^-$ [e] [10]
1,6-Diamino-3,6,10,13,16,19-hexaazabicyclo [6.6.6]eicosane	[Cr diamsar]$^{3+}$	$3Cl^-\cdot H_2O$ [100] $[Ln(pic)_3]^{3-}\cdot 8H_2O$ [101] (Ln = La–Lu, Y; dipic = pyridine-2,6-dicarboxylate	

[a] Sources: Cambridge Structural Database (CSD) and Inorganic Crystal Structure Database.

[b] The presence of water of crystallization might have been neglected in the spectroscopic studies.

[c] Composition relative to chromium.

[d] Isomorphic host.

[e] Single crystals.

[f] Sample identical to Ref. [95].

2.1.2. X-ray structural analysis

Crystallographic data solution procedures and refinement outcomes are presented in Table 3. The 130(2) K data collection and subsequent structure solution and refinement followed procedures previously outlined [28]. All compounds (**1**–**6**) gave acceptable solution refinements.

2.1.3. Spectroscopic measurements

The absorption and emission spectra were taken from single crystals of the same crops that were used for the X-ray structural analysis. The samples were mounted on an Air Products helium closed cycle cryostat and VIS and phosphorescence spectra, respectively, were recorded as previously outlined [30].

3. Results

3.1. Structures

The atom labelling schemes are shown in Figs. 1–3. Selected bond angles and bond lengths for **1**–**6** are given in Tables 4 and 6 and selected bite and dihedral angles in Table 5.

3.1.1. Anionic structures

The present set of am(m)ine complexes represents a series of reasonably similar $+3$ cations that were precipitated as $Hg_xCl_y^{n-}$ salts and recrystallized with a standard procedure. This might have been expected to produce a series of salts with constant anion stoichiometry and composition. It is obvious that such expectation was not realized, and the $Hg_xCl_y^{n-}$ stoichiometry observed is dependent on subtle

Table 2
Composition, preparative yields and quartet absorption data[a] for **1**–**6**

Composition	Preparative yield (%)[b]	Quartet absorption λ/nm (ε/M^{-1} cm^{-1})
$[Cr(NH_3)(en)(3,3\text{-tri})]_3[HgCl_4]_4Cl\cdot 3H_2O$ (**1**) (3,3-en (**1**))	56	467 (52); 357 (53)
$[Cr(NH_3)(pn)(3,3\text{-tri})]HgCl_5\cdot H_2O\cdot$(**2**) (3,3-pn (**2**))	63	468 (50); 357 (52)
$[Cr(NH_3)(chxn)(3,3\text{-tri})]HgCl_5$ (**3**) (3,3-chxn (**3**))	51	468 (51); 358 (49)
$[Cr(NH_3)(tn)(2,3\text{-tri})]Hg_2Cl_7\cdot H_2O$ (**4**) (2,3-tn (**4**))	33	462 (72); 355 (64)
$[Cr(NH_3)(Me_2tn)(2,3\text{-tri})]HgCl_5\cdot 1.5H_2O$ (**5**) (2,3-Me_2tn (**5**))	74	465 (71); 356 (59)
$[Cr(NH_3)(chxn)(2,3\text{-tri})]HgCl_5\cdot 2H_2O$ (**6**) (2,3-chxn (**6**))	51	463 (68); 359 (58)

[a] Because of the poor solubility of the hexaam(m)ines, the samples were prepared by dissolving the compounds in a few drops of dimethylformamide followed by dilution with 0.1 M HCl. Measurements were taken at room temperature.

[b] Related to the chloropentaammine starting material.

Table 3
Crystal data and structural refinement[a,b,c]

	$[Cr(NH_3)(en)(3,3\text{-tri})]_3[Hg_4Cl_{17}]\cdot 3H_2O$ (**1**)	$[Cr(NH_3)(pn)\text{-}(3,3\text{-tri})]\ HgCl_5\cdot H_2O$ (**2**)	$[Cr(NH_3)(chxn)\text{-}(3,3\text{-tri})]\ HgCl_5$ (**3**)	$[Cr(NH_3)(tn)(2,3\text{-tri})]\ Hg_2Cl_7\cdot H_2O$ (**4**)	$[Cr(NH_3)(Me_2tn)\text{-}(2,3\text{-tri})]\ HgCl_5\cdot 1.5H_2O$ (**5**)	$[Cr(NH_3)(chxn)\text{-}(2,3\text{-tri})]\ HgCl_5\cdot 2H_2O$ (**6**)
Crystal data						
Empirical formula	$C_8H_{30}Cl_{5.67}CrHg_{1.33}N_6O$	$C_9H_{30}Cl_5CrHgN_6O$	$C_{12}H_{34}Cl_5CrHgN_6$	$C_8H_{28}Cl_7CrHg_2N_6O$	$C_{10}H_{35}Cl_5CrHgN_6O_{1.5}$	$C_{11}H_{36}Cl_5CrHgN_6O_2$
Formula weight (g mol^{-1})	746.72	668.23	692.29	927.71	693.28	714.30
Crystal size (mm)	0.64 × 0.28 × 0.10	0.76 × 0.30 × 0.08	0.44 × 0.18 × 0.18	0.51 × 0.16 × 0.06	0.44 × 0.26 × 0.16	0.58 × 0.21 × 0.17
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P1$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/c$
Unit cell dimensions						
a (Å)	7.9880(10)	7.9490(10)	10.717(2)	8.071(2)	28.317(7)	12.447(12)
b (Å)	9.052(2)	31.568(9)	11.372(2)	13.028(3)	10.606(2)	14.317(13)
c (Å)	23.899(6)	9.207(2)	18.758(4)	24.160(5)	15.825(6)	13.62(2)
α (°)	96.240(10)	90	90	80.24(3)	90	90
β (°)	96.82(2)	100.25(2)	90.62(3)	89.35(3)	97.26(3)	102.25(8)
γ (°)	102.570(10)	90	90	79.14(3)	90	90
Volume (Å^3)	1658.5(6)	2273.5(9)	2286.0(8)	2458.2(8)	4715(2)	2372(4)
Z	3	4	4	4	8	4
D_{calc} (Mg m^{-3})	2.237	1.952	2.012	2.501	2.013	1.989
Absorption coefficient (mm^{-1})	10.422	7.819	7.777	13.666	7.554	7.503
$F(000)$	1059	1292	1348	1716	2776	1380
Data collection						
θ Range (°)	2.33–23.99	2.34–22.49	1.00–25.00	2.14–22.50	2.05–22.47	2.09–25.08
Index ranges	$0 \le h \le 19$, $-10 \le k \le 10$, $-27 \le l \le 27$	$-8 \le h \le 2$, $-1 \le k \le 33$, $-9 \le l \le 9$	$-12 \le h \le 0$, $0 \le k \le 13$, $-22 \le l \le 22$	$0 \le h \le 8$, $-13 \le k \le 13$, $-25 \le l \le 25$	$-1 \le h \le 30$, $-1 \le k \le 11$, $-17 \le l \le 16$	$-14 \le h \le 0$, $0 \le k \le 16$, $-15 \le 1 \le 15$

Table 3 (*Continued*)

	$[Cr(NH_3)(en)(3,3\text{-tri})]_3[Hg_4Cl_{17}]\cdot 3H_2O$ (**1**)	$[Cr(NH_3)(pn)\text{-}(3,3\text{-tri})]\ HgCl_5\cdot H_2O$ (**2**)	$[Cr(NH_3)(chxn)\text{-}(3,3\text{-tri})]\ HgCl_5$ (**3**)	$[Cr(NH_3)(tn)(2,3\text{-tri})]\ Hg_2Cl_7\cdot H_2O$ (**4**)	$[Cr(NH_3)(Me_2tn)\text{-}(2,3\text{-tri})]\ HgCl_5\cdot 1.5H_2O$ (**5**)	$[Cr(NH_3)(chxn)\text{-}(2,3\text{-tri})]\ HgCl_5\cdot 2H_2O$ (**6**)
R indices (all data) R_1						
Reflections collected	4667	3501	4057	6534	3274	3949
Independent reflections	4667	2633	4025	6037	2746	3741
R_{int}	0.0000	0.0541	0.0537	0.0303	0.0314	0.0526
Max/min transmission	0.60433/0.22085	0.75679/0.23888	0.57050/0.23883	0.38210/0.06110	0.726/0.369	0.35186/0.28070
Refinement						
Data/restraints/parameters	4667/3/415	2633/24/239	4024/0/227	6036/60/453	2746/30/289	3740/6/236
Goodness-of-fit on F^2	0.801	0.915	0.822	1.023	0.958	1.022
Final *R* indices $[I>2\sigma(I)]$ R_1 (wR_2)	0.0438 (0.1104)	0.0438 (0.1240)	0.0381 (0.1024)	0.0540 (0.1194)	0.0489 (0.1234)	0.0627 (0.1472)
R indices (all data) R_1 (wR_2)	0.0506 (0.1136)	0.0622 (0.1313)	0.0623 (0.1235)	0.0904 (0.1389)	0.0817 (0.1531)	0.1146 (0.1830)
Largest difference peak and hole (e Å^{-3})	1.765 and −1.780	1.744 and −1.420	0.938 and −1.284	2.720 and −1.950	0.671 and −0.629	1.157 and −1.129

[a] Radiation (Å) = Mo–K_α ($\lambda = 0.71073$ Å).

[b] Temperature = 130(2) K.

[c] Refinement method = full-matrix least-squares on F^2.

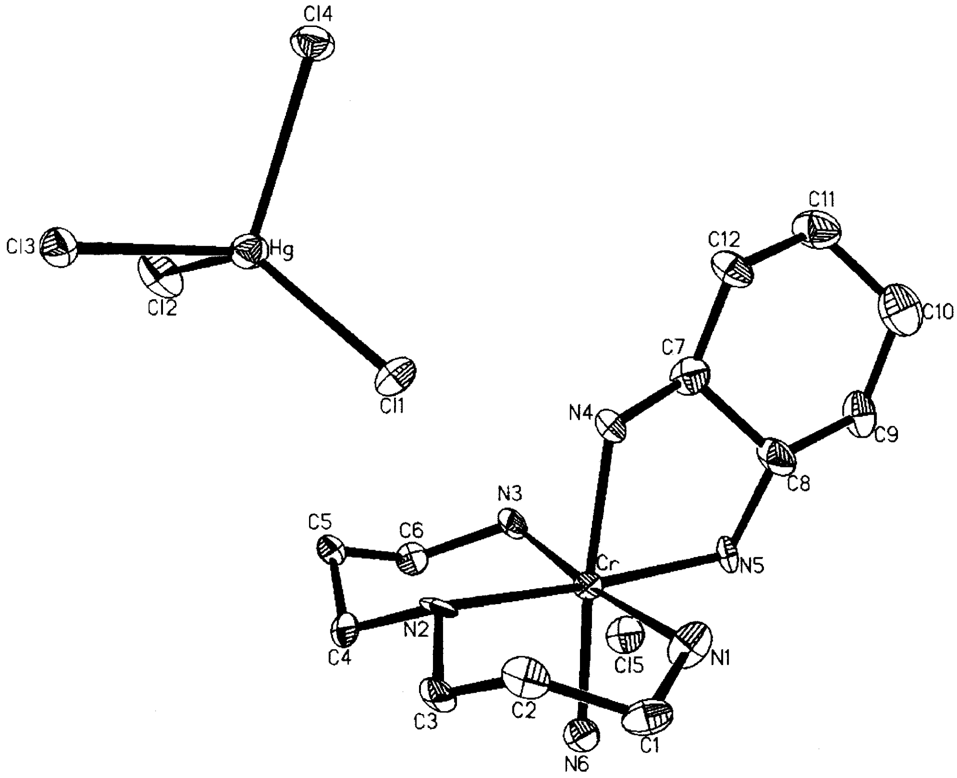

Fig. 1. A view of the cation and anion in *mer–exo*-[Cr(NH$_3$)(*trans*-chxn)(3,3-tri)][HgCl$_4$]Cl (**3**).

variations of solubility, rather than HCl/HgCl$_2$ ratios in the crystallizing solvent. The +3 cation charge requires n in the Hg$_x$Cl$_y^{n-}$ formula unit to be integral multiples of 3. The combinations HgCl$_5^{3-}$, Hg$_2$Cl$_7^{3-}$, Hg$_3$Cl$_9^{3-}$, Hg$_5$Cl$_{13}^{3-}$, Hg$_3$Cl$_{12}^{6-}$ and Hg$_4$Cl$_{14}^{6-}$ have previously been observed [31].

There are, of course, many ways in which these stoichiometries can be constructed. The HgCl$_5^{3-}$ formula unit is normally a combination of one isolated chloride ion and a distorted tetrahedral HgCl$_4^{2-}$ ion. All of the four *mer*-[Cr(NH$_3$)(diamine)(triamine)]HgCl$_5$ systems investigated here (**2**, **3**, **5**, **6**) have this arrangement but some of the Cl–Hg–Cl bond angles and Hg–Cl bond lengths (Table 6) are outside the ranges previously observed (Cl–Hg–Cl min = 92°; max = 136°; Hg–Cl min = 2.36 Å; max = 2.63 Å) [31].

A novel Hg$_4$Cl$_{17}^{9-}$ anionic formula unit has been found in *mer*-[Cr(NH$_3$)(en)(3,3-tri)]$_3$[HgCl$_4$]$_4$·Cl·3H$_2$O (**1**), as four independent HgCl$_4^{2-}$ formula units (Table 6) and one chloride ion, associated with three cations.

The other well recognized Hg$_x$Cl$_y^{3-}$ formula unit is Hg$_2$Cl$_7^{3-}$ and this occurs in the structure (**4**). The formula unit is best described as an HgCl$_3^-$ (disordered) plus HgCl$_4^{2-}$ formula unit combination. In the latter arrangement, the closest Hg···Cl inter-ion distance is 3.33 Å.

The major reason for the variation of Cl–Hg–Cl bond angles and Hg–Cl bond lengths in these complexes lies presumably in the chlorine–hydrogen contacts in combination with the highly polarisable covalent Hg–Cl bonds. Chlorine atoms with particularly long Hg–Cl distances are always fixed in a framework of hydrogen bonds to amine or crystal water protons. The closer these hydrogen bonds are, the lower the electron density in the corresponding Hg–Cl bond and the longer the resulting distance.

3.1.2. Cationic structures

Cations of the above type (triamine = 3,3-tri or 2,3-tri) have the potential to exist in *mer* and *fac* forms. To date, only the *mer*-isomers have been isolated and characterised although cations of the above type with triamine = 2,2-tri (dien) have [32,33]. In the *mer*-configuration the NH_3 ligand is *trans* to one end of the coordinated diamine but the orientation of the *sec*-NH proton in the meridonal triamine ligand may be adjacent to (*endo*) or remote from (*exo*) the NH_3 ligand.

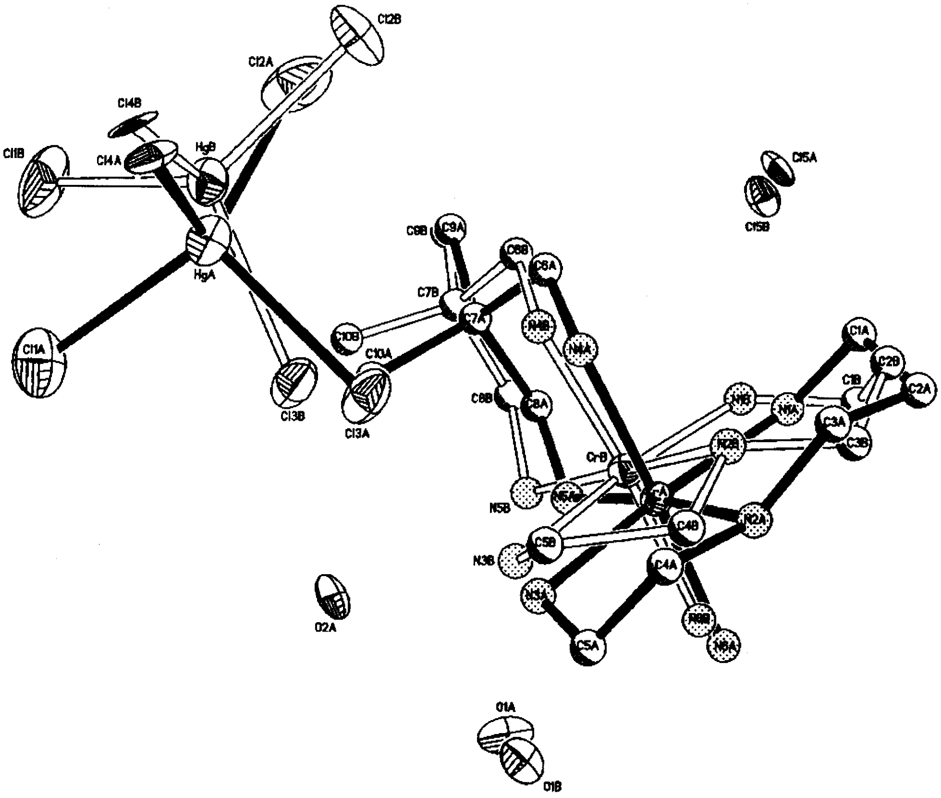

Fig. 2. A view of the cations and anions in *mer*-$[Cr(NH_3)(Me_2tn)(2,3\text{-tri})][HgCl_4]Cl\cdot 1.5H_2O$ (**5**) showing a superposition of the A (solid connections) and B (open lines) components. One cation adopts the *endo–sec*-NH proton configuration (N(2)A), while the other adopts the *exo* form (N(2)B).

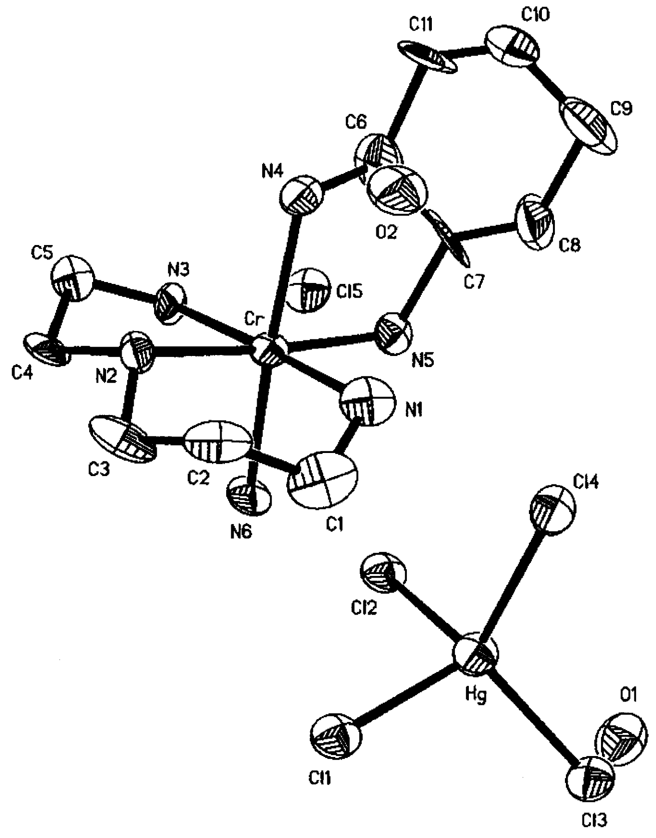

Fig. 3. A view of the cation and anions in *mer*–*exo*-[Cr(NH_3)(*trans*-chxn)(2,3-tri)][$HgCl_4$]Cl·$2H_2O$ (**6**).

Both *endo* and *exo* isomers have been isolated and characterised for *mer*-[CrCl(en)(3,3-tri)]$^{2+}$ [26,28] and both isomers coexist in the solid state form of *mer*-[Cr(Me_2tn)(2,3-tri)]$HgCl_5$ (**5**). All the other $Hg_xCl_y^{3-}$ salts (**1**–**4**, **6**) described here adopt the *exo* orientation.

Additional isomers can result if the diamine used is unsymmetrical, e.g. (*R*,*S*)-pn [33]. The structure of *exo*–*mer*-[Cr(NH_3)(pn)(3,3-tri)]$HgCl_5$·H_2O (**2**) shows the pn ligand is disordered (50%) over both potential orientations.

As one would expect, the influence of the chelating ligands is dependent on the number of atoms forming the ring. The range of N–Cr–N angles for five membered rings lies between 80.2° (N4–CrB–N5/3,3-en (**1**)) and 84.2° (N1–Cr(*exo*)–N2/2,3-Me_2tn (**5**)). The six-membered rings show correspondingly higher angles (86.5° for N4–Cr(*exo*)–N5/2,3-Me_2tn (**5**) and 95.8° for N1–CrA–N2/3,3-en (**1**)).

The alkyl bridges of the 3,3-tri ligand bend the N1–Cr–N3 axis towards the antipodal N5. The same can be observed for the N2–Cr–N4 axis which gives the whole cation roughly C_{4v} symmetry. The 2,3-tri ligands, however, bend the N1–Cr–N3 axis towards the framed N2 atom, giving the CrN_6 skeleton approximately D_{2d} symmetry.

Table 4
Cr–N bond lengths (Å) for structures **1**–**6**

		A	B	C
mer–exo-[Cr(NH$_3$)(en)(3,3-tri)]$_3$[HgCl$_4$]$_4$Cl·3H$_2$O (**1**)				
Cr–NH$_3$	N(6)	2.09(2)	2.07(2)	2.04(2)
Cr–NH$_2$(en)	N(5)	2.08(2)	2.11(2)	2.09(2)
	N(4)	2.09(2)	2.11(2)	2.11(2)
Cr–NH$_2$(3,3-tri)	N(3)	2.09(2)	2.08(2)	2.06(2)
	N(1)	2.07(2)	2.10(2)	2.08(2)
Cr–NH(3,3-tri)	N(2)	2.14(2)	2.09(2)	2.13(2)
mer–exo-[Cr(NH$_3$)(pn)(3,3-tri)][HgCl$_4$]Cl·H$_2$O (**2**)				
Cr–NH$_3$	N(6)	2.082(9)		
Cr–NH$_2$(pn)	N(5)	2.119(10)		
	N(4)	2.072(9)		
Cr–NH$_2$(3,3-tri)	N(3)	2.073(11)		
	N(1)	2.079(11)		
Cr–NH(3,3-tri)	N(2)	2.107(10)		
mer–exo-[Cr(NH$_3$)(chxn)(3,3-tri)][HgCl$_4$]Cl (**3**)				
Cr–NH$_3$	N(6)	2.072(7)		
Cr–NH$_2$(chxn)	N(5)	2.083(7)		
	N(4)	2.091(7)		
Cr–NH$_2$(3,3-tri)	N(3)	2.077(7)		
	N(1)	2.127(7)		
Cr–NH(3,3-tri)	N(2)	2.102(7)		
		A[a]	B[b]	
mer–exo-[Cr(NH$_3$)(tn)(2,3-tri)][Hg$_2$Cl$_7$]·H$_2$O (**4**)				
Cr–NH$_3$	N(6)	2.08(2)	2.09(2)	
Cr–NH$_2$(tn)	N(5)	2.07(2)	2.11(2)	
	N(4)	2.09(2)	2.08(2)	
Cr–NH$_2$(2,3-tri)	N(3)	2.11(2)	2.13(2)	
	N(1)	2.07(2)	2.08(2)	
Cr–NH(2,3-tri)	N(2)	2.08(2)	2.10(2)	
	A[a]	B[b]		
mer–exo/endo-[Cr(NH$_3$)(Me$_2$tn)(2,3-tri)][HgCl$_4$]Cl·1.5H$_2$O (**5**)				
Cr–NH$_3$	N(6)	2.10(2)	2.09(2)	
Cr–NH$_2$(Me$_2$tn)	N(5)	2.06(2)	2.09(3)	
	N(4)	2.08(2)	2.06(2)	
Cr–NH$_2$(2,3-tri)	N(3)	2.08(2)	2.12(2)	
	N(1)	2.15(2)	2.04(2)	
Cr–NH(2,3-tri)	N(2)	2.11(2)	2.11(2)	
mer–exo-[Cr(NH$_3$)(chxn)(2,3-tri)][HgCl$_4$]Cl·2H$_2$O (**6**)				
Cr–NH$_3$	N(6)	2.072(12)		
Cr–NH$_2$(chxn)	N(5)	2.057(13)		
	N(4)	2.086(13)		
Cr–NH$_2$(2,3-tri)	N(3)	2.077(12)		
	N(1)	2.114(14)		
Cr–NH(2,3-tri)	N(2)	2.071(13)		

[a] *endo* form (A) in Fig. 2.

[b] *exo* form (B) in Fig. 2.

Table 5
Bite angles, dihedral angles[a] and ring conformations in *exo–mer*-$[Cr(NH_3)(diamine)(triamine)]^{n+}$ cations[b]

(Diamine)(triamine)		Diamine (N–Cr–N)	en(tri) (N–Cr–N)	tn(tri) (N–Cr–N)	tn(tri)	Formula unit
$[Cr(NH_3)(en)(3,3\text{-tri})]_3[HgCl_4]_4\ Cl\cdot 3H_2O$ (**1**)						
NH_3 (**1**)	A	81.6(7)		95.8(7)	90.7(7)	$Hg_4Cl_{17}^{9-}$
		[48.2] δ		[68.8–74.0]	[64.7–67.1]	
	B	80.2(7)		90.1(7)	95.2(7)	
		[−45.5] λ		[71.0–69.2]	[81.6–70.7]	
	C	81.7(7)		94.6(7)	92.1(7)	
		[52.2] δ		[76.7–70.6]	[71.9–72.8]	
$[Cr(NH_3)(pn)(3,3\text{-tri})]HgCl_4\cdot Cl\cdot H_2O$ (**2**)						
NH_3 (**2**)		81.8(4)		91.0(4)	95.1(4)	$HgCl_5^{3-}$
		[−59.2] λ		[72.9–69.6]	[72.9–73.4]	
		[50.2] δ				
$[Cr(NH_3)(chxn)(3,3\text{-tri})]HgCl_4\ Cl$(**3**)						
NH_3 (**3**)		82.1(3)		90.9(3)	94.5(3)	$HgCl_5^{3-}$
		[54.7] δ		[72.2–70.2]	[64.6–79.9]	
$[Cr(NH_3)(tn)(2,3\text{-tri})][Hg_2Cl_7]\cdot H_2O$ (**4**)						
NH_3 (**4**)	A	89.0(6)	82.1(6)	92.5(6)		$Hg_2Cl_7^{3-}$
		[68.3–68.2]	[53.5] δ	[69.5–69.3]		
	B	87.9(7)	82.6(6)	91.2(7)		
		[66.5,-65.8]	[58.3] δ	[74.8–72.8]		
$[Cr(NH_3)(Me_2tn)(2,3\text{-tri})]HgCl_4\cdot Cl\cdot 1.5H_2O$ (**5**)						
NH_3 (**5**)	A-*exo*	86.5(9)	84.2(9)	90.3(9)		$HgCl_5^{3-}$
		[62.6–61.7]	[43.8] δ	[71.3–73.8]		
	B-*endo*	89.6(8)	81.9(8)	90.8(9)		
		[61.9–62.1]	[−52.1] λ	[69.2–67.4]		
$[Cr(NH_3)(chxn)(2,3\text{-tri})]HgCl_4\cdot Cl\cdot 2H_2O$ (**6**)						
NH_3 (**6**)		81.3(6)	83.9(5)	91.0(5)		$HgCl_5^{3-}$
		[47.6] δ	[52.5] δ	[72.3–71.8]		

[a] N–C–C–N or N–C–C–C dihedral angles in square brackets.

[b] See also Ref. [29].

The 3,3-en (**1**) crystallises in the rare *P*1 space group. Because of the uneven number of cations in the unit cell and their unsymmetrical distribution this assignment is unambiguous. The three crystallographically independent cations show different conformations of the ethylenediamine rings (CrA, CrC = δ, CrB = λ). The bite angles also differ as shown in Table 5, which makes this compound especially valuable for spectroscopic investigations.

Finally this series illustrates the utility of metal ions in stereoselective coordination. The commercially available cyclohexanediamine (chxn) was supplied as an approximate 50:50 mixture of the *trans*-(*RR*,*SS*)-racemic and *cis*-(*R*,*S*)-*meso* forms and was used without prior separation in this study to produce a single isomeric form of *mer*-$[CrCl(chxn)(triamine)]ZnCl_4$ (triamine = 3,3-tri, 2,3-tri). The structures of the resulting amines (**3** and **6**) show that only the *trans*-(*RR*,*SS*)-chxn isomer has coordinated.

3.2. Absorption and emission spectra

The absorption and emission spectra of compounds **1**–**6** are presented in Fig. 4, the corresponding lifetimes for **1**–**5** in Fig. 5. Because of the complex behaviour of the lifetimes of 2,3-chxn (**6**), these data are presented in tabular form (Table 7).

The analysis of the spectra is complicated by the occurrences of energy transfer and trap emissions. Such emissions can be distinguished from vibronic side bands by having no counter peaks in absorption, by differing life times and temperature dependence. The most likely emitting impurities in chloromercurates are pentaam(m)inechloro species. Their electronic origins can be expected to be about 200–400 cm^{-1} lower in energy than that of the corresponding hexaam(m)ines [4,30].

3.2.1. 3,3-tri-Complexes

The doublet–quartet spectra of the 3,3-complexes were apparently rather simple. Two prominent and sharp lines appeared on the long wavelength side in absorption

Table 6
Bond lengths (Hg–Cl) and bond angles (Cl–Hg–Cl) in $HgCl_4^{2-}$ formula units[a]

Salt		Bond angles (°) (top line) Bond lenghts (Å) (bottom line)			
$[Cr(NH_3)(en)(3,3\text{-tri})]_3[HgCl_4]_4\cdot Cl\cdot 3H_2O$ (**1**)	A	99.4	104.2	105.2	108.2
		2.383	2.410	2.560	2.625
	B	89.6	94.3	96.7	114.5
		2.374	2.403	2.440	2.846
	C	93.6	96.3	100.8	116.2
		2.403	2.432	2.438	2.728
	D	100.1	101.0	108.7	110.0
		2.441	2.454	2.469	2.576
$[Cr(NH_3)(pn)(3,3\text{-tri})]HgCl_4\cdot Cl\cdot H_2O$ (**2**)		93.29	94.63	100.03	116.04
		2.402	2.448	2.461	2.746
$[Cr(NH_3)(chxn)(3,3\text{-tri})]HgCl_4\cdot Cl$ (**3**)		94.01	98.22	103.71	108.07
		2.388	2.433	2.553	2.591
$[Cr(NH_3)(Me_2tn)(2,3\text{-tri})]HgCl_4\cdot Cl\cdot 1.5H_2O$ (**5**)					
	A	96.7	100.8	102.5	107.4
		2.382	2.434	2.54	2.588
	B	101.0	101.3	108.7	111.0
		2.411	2.419	2.495	2.63
$[Cr(NH_3)(chxn)(2,3\text{-tri})]HgCl_4\cdot Cl\cdot 2H_2O$ (**6**)		101.5	103.0	109.5	111.7
		2.417	2.452	2.500	2.546

[a] See also Ref. [31].

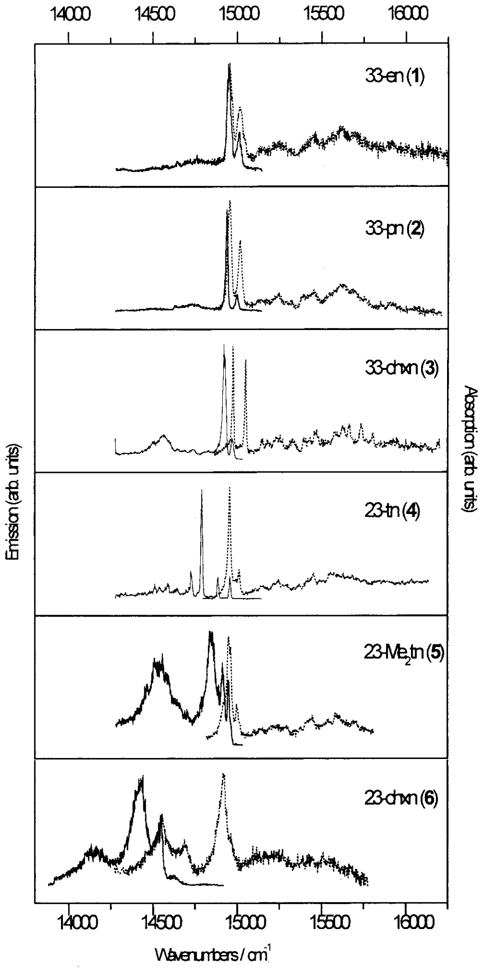

Fig. 4. Emission (solid line) and absorption (dots) spectra of compounds **1**–**6** at 20 K.

and on the short wavelength side in emission (Fig. 4). These lines are assigned to the split ^2E_g–$^4A_{2g}$ (O_h) band [4,10,34]. Closer inspection, however, revealed some significant differences within this series:

3,3-en (**1**) showed the most simple behaviour. The maxima at 14 950 and 15 010 cm^{-1} almost coincided in absorption and emission. Hence, these bands may be safely assigned to electronic origins. The phosphorescence intensities and life times (Fig. 5) were almost independent of temperature in the region $20 < T < 100$ K (low temperature region). For $T > 120$ K the maxima were bathochromically shifted in absorption. The doublet splitting of 63 cm^{-1} is similar as in other CrN_6 systems [10]. The structure determination, however, showed three different chromium complex units. The existence of several luminescent centres may be the reason for the larger half-widths as compared with that of the other 3,3 complexes and the biexponential phosphorescence decay.

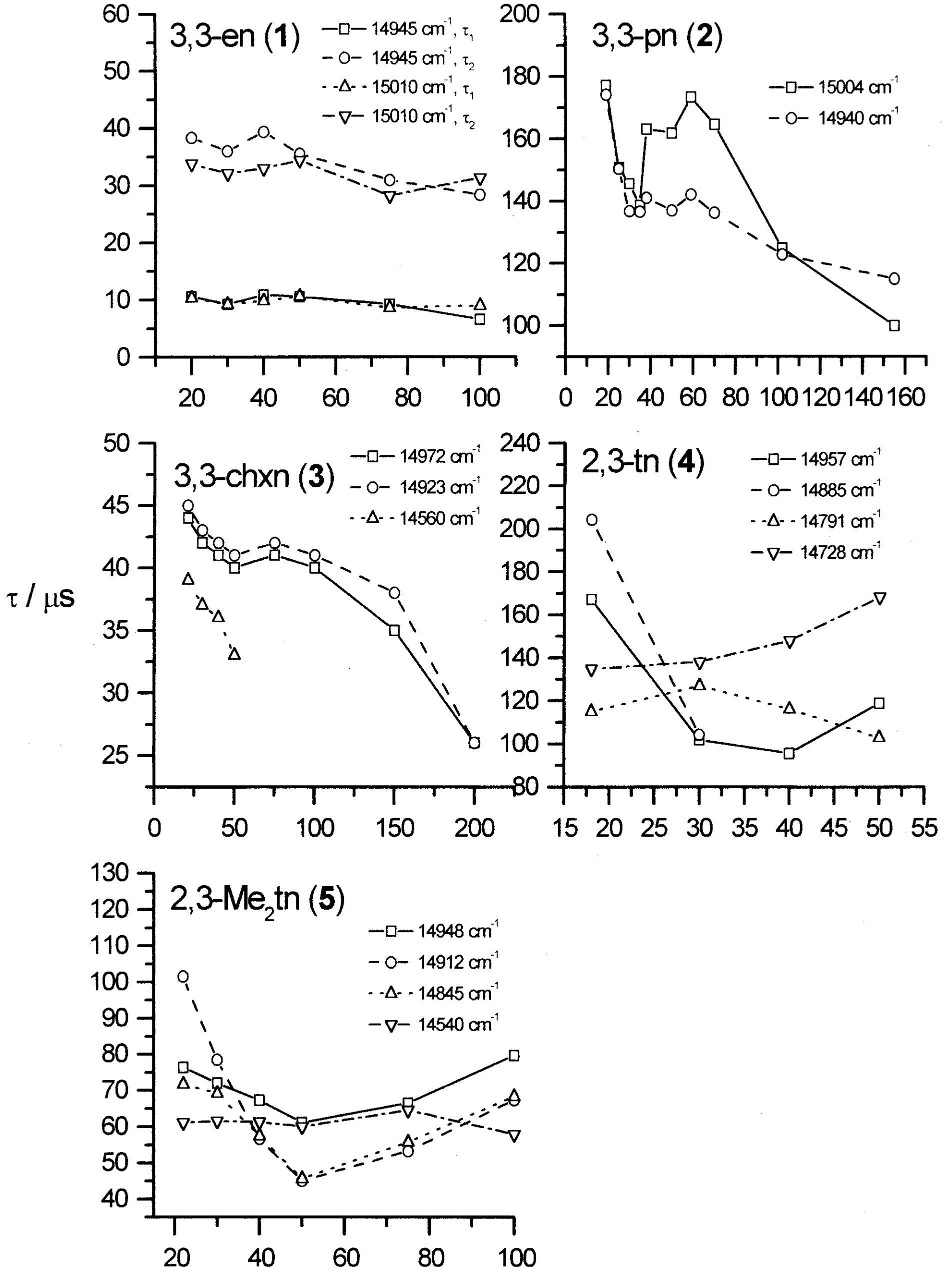

Fig. 5. Phosphorescence lifetimes of selected single emission lines of compounds **1**–**5** in the temperature range $18 \leq T \leq 200$ K.

Table 7
Phosphorescence lifetimes for selected single line emissions for *exo–mer*-[Cr(NH$_3$)(chxn)(2,3-tri)][HgCl$_4$]·Cl·2H$_2$O

T (K)	τ (μs) 14 550 cm^{-1} [a]		τ (μs) 14 430 cm^{-1} [a]		τ (μs) 14 140 cm^{-1} [b]	
20	49.2		11.3	39.0		
30	44.2		12.7	39.8		
40	31.4	97.3	12.3	38.8		
50	19.1	51.5	11	37	11	87.1
75	10.9	48.3	15.3	47.6	9.7	75.2
100			13.3	48.9	4.6	56.9

[a] Double exponential decay.

[b] Exponential rise, overlapping an exponential decay. The shorter figures give the risetimes.

In 3,3-pn (**2**) both components of the electronic origin showed a Stokes shift of 17 cm^{-1}. This indicates some relaxation in the excited state. The temperature dependence of the phosphorescence life times showed a minimum at 30 K, which indicates a phase transition.

In 3,3-chxn (**3**) only one coincidence at 14 972 cm^{-1} was observed. Considered by itself, this spectral behaviour might be explained by just one zero vibrational transition with vibronic sidebands at 14 923 and 15 050 cm^{-1} in emission and absorption, respectively. This interpretation agrees with the fact that the emissions at 14 923 and 14 972 cm^{-1} had almost the same decay kinetics (Fig. 5). If one looks at all three 3,3-complexes, however, a gradual change from the en to the chxn complex becomes evident. The en complex (**1**) had two exact coincidences, in the pn complex (**2**) both emission peaks were moderately Stokes shifted, whereas in 3,3-chxn (**3**) the shift might be so large that the high-energy emission peak coincided with the low energy absorption peak.

No characteristic structural differences could be deduced from the X-ray data.

3.2.2. 2,3-Complexes

The complexes 2,3-tn (**4**) and 2,3-chxn (**6**) showed only one pronounced coincidence at 14 956 and 14 551 cm^{-1}, respectively. In 2,3-Me$_2$tn (**5**) a small splitting of 12 cm^{-1} (14 950/14 962 cm^{-1}) was observed.

2,3-tn (**4**) showed two narrow lines in absorption at 14 956 and 15 011 cm^{-1} (Fig. 4). The line at the lower wavenumber coincided with the line at 14 957 in emission (R-line). The emission line at 14 885 differed in its temperature dependence. It did not survive 50 K. There were two more narrow lines at 14 791 and 14 728 cm^{-1} without analogues in absorption. These lines showed a similar temperature dependence of the phosphorescence intensity as the R line but differed in the life times (Fig. 5). This complex emission behaviour is in accordance with the low crystal symmetry ($P\bar{1}$) with two crystallographically independent cations. Yet it

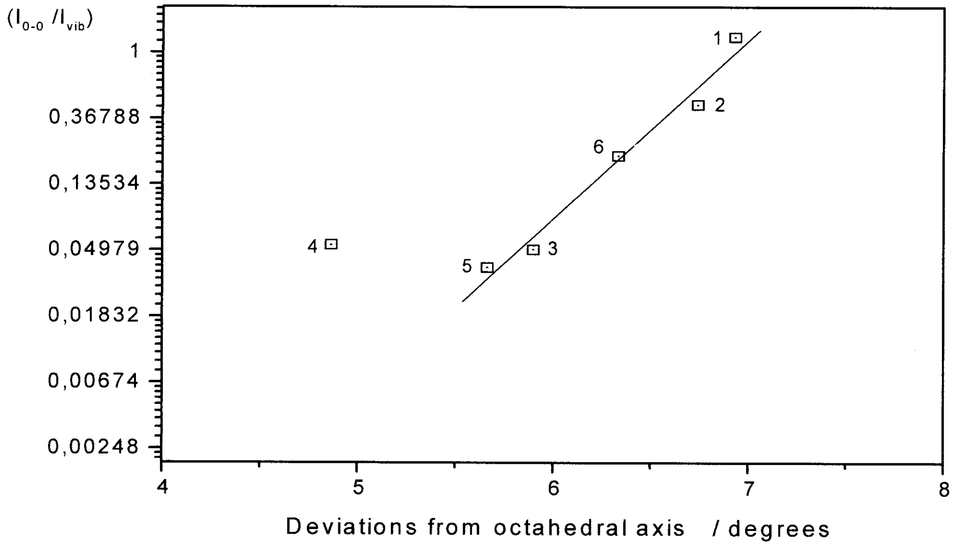

Fig. 6. Integrated intensity ratios I_{00}/I_{vib} vs. the mean deviation of the orthogonal N–Cr–N axes from 180° for compounds **1**–**6**. Point 4 was omitted in the linear regression.

is surprising that those low symmetry effects are not reflected in the absorption spectra. Hence trap emission has to be considered.

2,3-chxn (**6**) showed almost a mirror relationship between absorption and emission (Fig. 4). Its phosphorescence lifetime, however, was biexponential (Table 7). It had its doublet–quartet transition shifted ca. 400 cm^{-1} to a lower energy compared with the other complexes of this study. Impurity emission can be ruled out on account of the coincidence with absorption and its relatively high absorbance at 14 550 cm^{-1}. Therefore, the emitting species must have been present in a rather high molar ratio and should have been observed in the structure analysis. However, there also was an absorption peak at 14 981 cm^{-1}, which agrees with the electronic origins of the other complexes.

4. Discussion

4.1. Emission band intensities and doublet splittings

According to the Laporte rule, the d–d transitions in centrosymmetrical complexes are parity forbidden. Hence, the spectra of complexes with strict O_h-symmetry like $[Cr(NH_3)]^{3+}$ are dominated by intense vibronic sidebands. Increasing deviation from O_h-symmetry leads to an intensity gain of the zero-phonon-transitions. Since our set of complexes has no large variation in ligand field strength, this deviation is mainly influenced by the geometry of the coordinating atoms. The integrated intensity ratio of the zero-phonon-bands to vibronic sidebands versus the

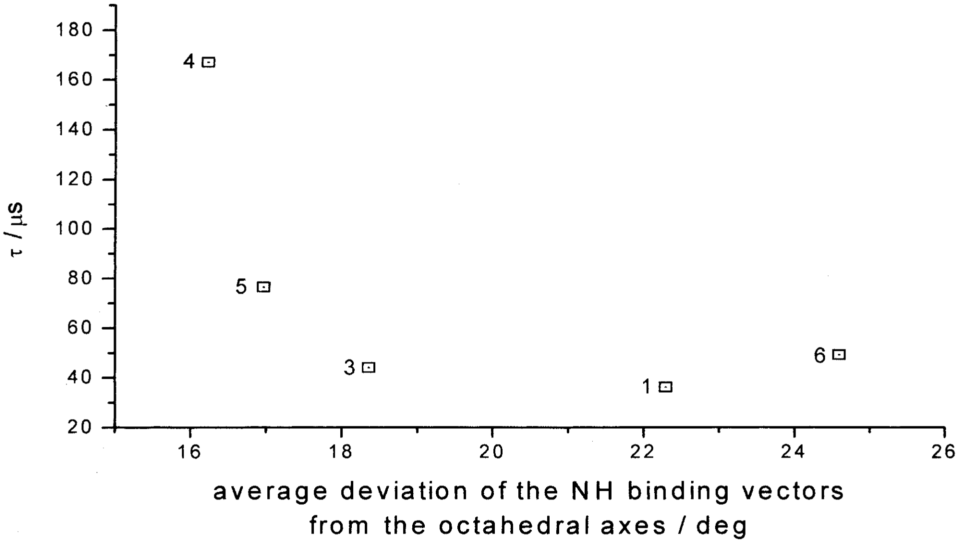

Fig. 7. Decay times of the zero-phonon-lines at 20 K vs. the average deviation of the NH binding vectors from the octahedral axes for compounds **1**–**6**.

deviation from O_h-symmetry[1] is logarithmically plotted in Fig. 6. Apart from 2,3-tn (**4**), which is closest to the ideal octahedron and which obviously shows trap emission, all data match a straight line in good correspondence. Whether this quantitative agreement makes any physical sense cannot be answered easily. The observed emission spectra are a product of a number of complex processes that are mutually influencing each other. Various different relaxation pathways can add to the observed lifetimes and band intensities.

4.2. Emission lifetimes

Previous investigations [3,35–38] relate the radiationless deactivation of the doublet emission of chromium(III) am(m)ines to the number of NH acceptor modes (N_H). This, however, can only be observed within sets of homologous complexes.

The question now arises, if in a series of complexes with the same number of NH acceptor modes, a dependency of the radiationless deactivation on the orientation of the NH binding vectors can be found. If the interaction between the t_{2g} and the NH binding orbitals is the main factor that determines the radiationless deactivation, the rate constants must in some way correspond to the mutual orientation of both orbitals.

Fig. 7 shows the measured lifetimes of the zero-phonon-bands at ca. 20 K versus the average N′–Cr–N–H torsion angle, which is a measure for the deviation of the

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[1] According to Kirk et al. [10] this deviation was calculated as the difference of the mean main axis angle from 180°, essentially giving the deviation from centrosymmetry.

NH binding vectors from the octahedron axes. The 3,3-pn (**2**) was omitted because of the disordered pn ligand.

The data clearly show a decrease in lifetime towards increasing deviation of the NH vectors. This could indicate that the mutual interaction of the corresponding orbitals is largest at a 45° angle. Since the t_{2g} orbitals lie between the octahedron axes, this compares to a parallel alignment with the binding orbitals. Taking the small number of data points, this agreement may be seen as still rather questionable. Verification of the observed trend on a broader basis should be subject to future investigations.

5. Supplementary material

Tables of: (a) fractional atomic coordinates; (b) anisotropic displacement parameters; (c) bond lengths and bond angles; (d) hydrogen atom coordinates; (e) observed and calculated structure factors are available from authors F.W. or D.A.H. on request.

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