Inorganica Chimica Acta, *173* (1990) 159–162

Absorption and Emission Spectra of Tris(2,3-diamino-2,3-dimethylbutane) Chromium(III)

STEPHAN BRÖNNIMANN, ARNE ZILIAN, HANS U. GÜDEL* and ANDREAS LUDI*
Institut für Anorganische Chemie, Universität Bern, CH 3000 Bern 9 (Switzerland)

(Received November 21, 1989)

Abstract

The chromium(III) complex with the chelating diamine 2,3-diamino-2,3-dimethylbutane (tmen) is prepared by prolonged refluxing of anhydrous $CrCl_3$ with tmen in tetrahydrofurane. Compared to the parent $Cr(en)_3^{3+}$ species the absorption bands of the novel $Cr(tmen)_3^{3+}$ are red shifted and more intense with maxima at 376 and 504 nm and extinction coefficients of 140 and 154 M^{-1} cm^{-1}, respectively. A third, very weak absorption ($\epsilon \sim 1$ M^{-1} cm^{-1}) is observed at 684 nm. The low temperature luminescence is attributed to a $^2E \rightarrow {}^4A_2$ transition and is counterion dependent: chloride, nitrate and triflate salts exhibit a rather broad emission; the sulfate, tetrafluoroborate and the Cr(III) doped $Rh(tmen)_3(BF_4)_3$ show a well resolved series of very narrow signals.

Introduction

For Co(III) complexes we have demonstrated that the fully C-methylated diaminoethane, 2,3-diamino-2,3-dimethylbutane (tmen) produces a significantly smaller ligand field than the parent diaminoethane (en). The steric crowding due to the twelve peripheral methyl groups not only reduces the ligand field strength but also affects the reactivity of the $Co(tmen)_3^{3+}$ ion [1]. These observations initiated the synthesis and spectroscopic study of the hitherto unknown tmen complex of chromium(III).

Luminescence can often be used in addition to absorption spectroscopy for the study of Cr(III) complexes. The luminescent state in amine complexes is usually ^2E, and the resulting emission is often highly structured. Luminescence can thus be used as a sensitive probe for the electronic and structural properties of a complex. For $Cr(tmen)_3^{3+}$ we are particularly interested in the spectroscopic differences to $Cr(en)_3^{3+}$, i.e. the influence of the twelve peripheral methyl groups.

Experimental

Synthesis

$Cr(tmen)_3Cl_3$

A slurry of 0.98 g anhydrous $CrCl_3$ (purified by refluxing commercial $CrCl_3$ for 48 h in 18% HCl), 4.3 g tmen, and a grain of Zn in 10 ml of tetrahydrofurane was boiled under reflux for 200 h. Moisture was excluded by means of a $CaCl_2$ tube on top of the condenser. The lustrous $CrCl_3$ was converted into a very fine purple powder. After removal of the remaining Zn the solid residue was isolated by centrifugation. A water soluble, dark purple impurity was removed by washing with 2 M HCl (4X). The remaining reddish purple solid was dried *in vacuo*. Yield: 2.54 g of $Cr(tmen)_3Cl_3$ (80%). Salts with other anions were obtained by treating a suspension of the chloride in water with the appropriate silver salt. For all the compounds $Cr(tmen)_3X_3$ ($X^- = Cl^-$, BF_4^-, $CF_3SO_3^-$, NO_3^-, $\frac{1}{3}(SO_4^{2-} + HSO_4^-)$) the microanalytical results were completely satisfactory.

$Rh(tmen)_3Cl_3$

$RhCl_3 \cdot 3H_2O$ (1 g) and 3.3 g tmen in 15 ml H_2O were heated under reflux overnight. The light yellow solid residue of $Rh(tmen)_3Cl_3$ was recrystallized from water λ_{max} (ϵ_{max}): 265 nm (280 M^{-1} cm^{-1}); 316 nm (340 M^{-1} cm^{-1}).

Spectroscopy

Absorption spectra: Cary 17 D and HP 8451 A; emission spectra and lifetime measurements: Ar-laser (Spectra Physics 166) combined with Spex 1402 double monochromator and photon counting Spex DPC-2 or modulated (Bragg cell Coherent 305) Ar-laser with oscilloscope Tektronix 2430 A; low temperature experiments: flow tube technique [2].

Results and Discussion

Absorption Spectra

In contrast to the well known yellow Cr(III) coordination compounds with aliphatic amines the

---

*Authors to whom correspondence should be addressed.

0020-1693/90/$3.50

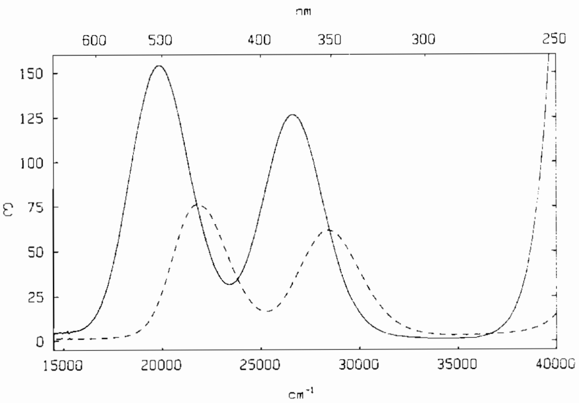

Fig. 1. Ligand field spectra of $Cr(tmen)_3^{3+}$ (——) and $Cr(en)_3^{3+}$ (– – –) in aqueous solution.

TABLE 1. Ligand field spectra of $M(tmen)_3^{3+}$ and $M(en)_3^{3+}$, M = Cr, Co

	Cr		Co	
	tmen	en[3]	tmen[1]	en[4]
λ_1 (nm)	504	459	504	464
ϵ_1 (M^{-1} cm^{-1})	154	76	177	93
λ_2 (nm)	376	350	362	338
ϵ_2 (M^{-1} cm^{-1})	140	61	177	85
Dq (cm^{-1})	1980	2180	2130	2317
B (cm^{-1})	650	640	568	587

novel $Cr(tmen)_3^{3+}$ ion is reddish purple. Its solution spectrum is shown in Fig. 1 together with that of $Cr(en)_3^{3+}$. The red shift of the spin-allowed bands for the tmen complex is accompanied by a doubling of their intensities, an indication of a stronger odd-parity ligand-field component. The low-energy part of the absorption spectrum shows the spin-forbidden $^4A_2 \rightarrow {}^2E, {}^2T_1$ excitation as a weak, rather narrow feature at 14 600 cm^{-1}. Band maxima with their intensities and the corresponding ligand-field parameters for $Cr(tmen)_3^{3+}$, $Cr(en)_3^{3+}$ and the analogous Co(III) complexes are collected in Table 1.

The shade of the color for the various complex salts of $Cr(tmen)_3^{3+}$ depends on the counterion. Mull spectra of the finely ground solid salts in paraffin oil show the $^4A_2 \rightarrow {}^4T_2$ absorption band maximum at the following energies: 19 900 (BF_4^-), 19 600 (NO_3^-), 19 400 ($CF_3SO_3^-$), 19 200 (Cl^-) cm^{-1}.

The complete methylation of the en-backbone has a remarkably similar effect on the ligand-field absorption spectra for both metal centers, Co(III) and Cr(III): a red shift of the corresponding d–d bands by about 2000 cm^{-1}. This shift in properties is also reflected in the reduction potentials. Owing to the very high substitution lability of Cr(II), only the wave for the reduction process is observed in the cyclic voltammograms. Nevertheless a significant shift of 300 mV to more positive potentials is deduced, matching the corresponding property for the Co complex [1].

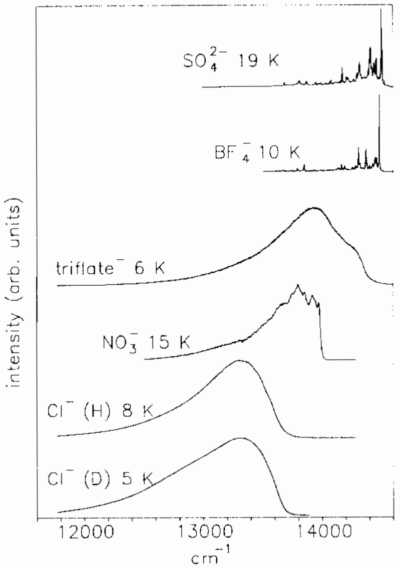

Fig. 2. Low temperature emission spectra of $Cr(tmen)_3^{3+}$ salts.

Luminescence Spectra

All the solid salts referred to in the previous section as well as $Rh(tmen)_3(BF_4)_3$ containing 2.5% Cr(III) luminesce at 10 K. With increasing temperature this luminescence is quenched at different rates for different salts. None of the compounds was found to luminesce at room temperature. Three qualitatively different emission patterns are observed below 20 K as illustrated in Fig. 2. The sulfate, tetrafluoroborate and the doped Rh tetrafluoroborate present an emission spectrum with up to 40 sharp lines with half-widths of less than 10 cm^{-1} within a spectral range of about 800 cm^{-1}. Band positions and relative intensities are listed in Table 2. The triflate, sulfate and chloride salts exhibit structureless emission bands of up to 700 cm^{-1} width. The nitrate takes an intermediate position with a partially structured emission band of approximately 600 cm^{-1} width. In addition to their different widths the emissions show a large variation of their positions, see Fig. 2.

Low-temperature luminescence lifetimes for four selected salts are represented in Fig. 3. They too show a rather large variation of more than one order of magnitude at 10 K. The most conspicuous difference is that between the hydrated and the deuterated chloride salts, 9 and 150 μs, respectively. There is no obvious correlation of the decay behavior and the shape of the spectra.

The pronounced differences in the luminescence spectra and lifetimes are surprising. The luminophore is expected to be $Cr(tmen)_3^{3+}$ in each of the samples.

TABLE 2. Peak positions (cm^{-1}) and intensities of low-temperature narrow-band emission spectra of Cr(tmen)$_3{}^{3+}$

[Cr(tmen)$_3$](SO$_4$)(HSO$_4$)·6H$_2$O 19 K			[Cr(tmen)$_3$](BF$_4$)$_3$ 10 K			[Rh(tmen)$_3$](BF$_4$)$_3$, 2.5% Cr 6 K		
ν	Relative intensity	$\Delta\nu$	ν	Relative intensity	$\Delta\nu$	ν	Relative intensity	$\Delta\nu$
14533	9	−25	14512	3	−25	14470	100	
14508	100		14487	100		14382	12	88
14462	37	46	14461	19	26	14357	21	113
14443	32	65	14452	19	35	14294	21	176
14418	50	90	14373	30	114	14177	9	293
14414	52	94	14312	32	175	14152	9	318
14321	33	187	14168	11	319	13837	7	633
14300	18	208	13853	11	634	13780	5	690
14179	26	329	13797	9	690			
14085	10	423						
13875	8	633						
13816	9	692						

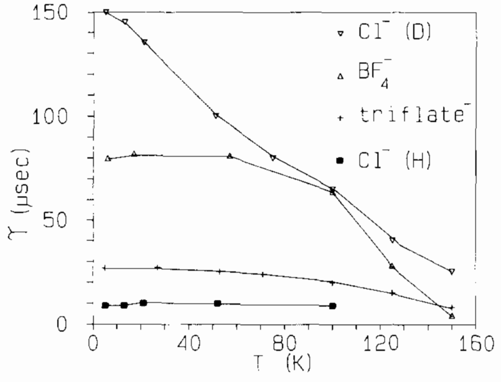

Fig. 3. Luminescence decay times vs. temperature for four selected Cr(tmen)$_3{}^{3+}$ salts.

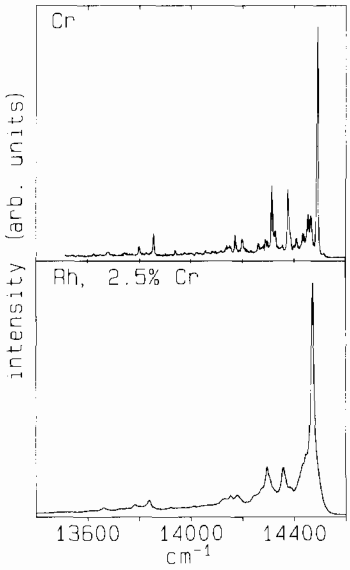

Fig. 4. Comparison of 10 K emission spectra of Cr(tmen)$_3$(BF$_4$)$_3$ and Cr(III) doped Rh(tmen)$_3$(BF$_4$)$_3$.

There is little ambiguity about the nature of the 10 K luminescence in the BF$_4{}^-$ salt. In Fig. 4 it is compared with the spectrum of Cr(III) doped Rh(tmen)$_3$(BF$_4$)$_3$. The two spectra are identical in their intensity distribution, very close in energy (red shifted in the diluted compound by 17 cm^{-1}), but with significantly narrower lines in the pure compound. This is in good agreement with their X-ray powder patterns which demonstrate the Cr and Rh complex salts to be isostructural. We can thus safely conclude that the observed emission is an intrinsic property of the Cr(tmen)$_3{}^{3+}$ complex in this crystalline environment. The onset of the emission around 14 500 cm^{-1} corresponds to the weak narrow band observed in the absorption spectrum. It is thus straightforward to assign it to the $^2E \rightarrow {}^4A_2$ transition.

The strongest lines in this emission spectrum are in the origin region. This is another indication that the coordination geometry is not centrosymmetric. The electronic origins can gain electric dipole strength by a combination of spin–orbit coupling and the odd-parity ligand-field potential. Since there is no vibrational analysis available for a M(tmen)$_3{}^{3+}$ system we do not attempt to assign the various sharp signals of the fine structured emission. We do notice, however, that all the prominent sidebands correspond to one quantum of a vibrational mode. There are no progressions, as expected for an intraconfigurational $^2E \rightarrow {}^4A_2$ transition. The bulk of the emission intensity lies within 200 cm^{-1} from the origin. This is different from Cr(en)$_3{}^{3+}$, where the strongest sidebands are between 150 and 400 cm^{-1} from the origin, i.e. in the region of metal–ligand vibrations [5]. We conclude that for the BF$_4{}^-$ salt of Cr(tmen)$_3{}^{3+}$ low-energy modes affecting the conformation of the complex ion are strongly coupled to the

$^4A_2 \rightarrow {}^2E$ excitation. Similar conclusions can be reached for the SO_4^{2-} salt.

The apparently quite different emission pattern observed for the other salts of $Cr(tmen)_3^{3+}$ might be taken as indicative of a $^4T_2 \rightarrow {}^4A_2$ emission showing an exceptionally large Stokes shift of some 6000 cm^{-1}. Such an enormous Stokes shift could be the result of an unusually large geometric distortion in the $^4T_2$ excited state. Stokes shifts of the same order of magnitude have been observed in Cr^{3+} doped glasses [6]. However, we can rule this out. A width of 700 cm^{-1} is too small for a $^4T_2 \rightarrow {}^4A_2$ transition, the corresponding width in the room temperature absorption spectrum (Fig. 1) being 3600 cm^{-1}. In addition, the $^4T_2$ lifetime as estimated from the absorption intensity is approximately 0.5 μs. Observed luminescence lifetimes below 100 K are one to two orders of magnitude bigger and they do not discriminate between sharp-line and broad-band emitters. The significant difference in the 10 K lifetimes of the deuterated and undeuterated chloride salts clearly shows that the lifetimes are dominated by non-radiative processes down to the lowest temperatures. The efficiency of multiphonon relaxation processes at low temperatures is greatly reduced by deuteration, as was also found for $Cr(NH_3)_6^{3+}$ [7]. The value of τ = 150 μs for the deuterated chloride at 5 K is far too high for a $^4T_2 \rightarrow {}^4A_2$ transition.

We conclude that the luminescence is due to $^2E \rightarrow {}^4A_2$ transitions in all the compounds, with an exceptionally large inhomogeneous broadening in the Cl^-, NO_3^- and $CF_3SO_3^-$ salts. This broadening is due to a distribution of different geometrical sites contributing to the luminescence. It may be attributed to $Cr(tmen)_3^{3+}$ complexes in different conformations. Besides the lel and ob conformation for each ligand possible variations of the twisting angle around the trigonal axis have also to be considered in this context. In the analogous Co(III) complex the SO_4^{2-} group locks the ob_3 conformation via O•••H–N interaction [8]. We assume a similar stabilization of one conformation in the Cr(III) system for SO_4^{2-} and BF_4^- having virtually the same shape. A weaker interaction for Cl^-, NO_3^- and $CF_3SO_3^-$ will not freeze one particular conformation within the lattice and thus lead to the observed inhomogeneity. This qualitative argument is supported by molecular mechanics [9] calculations producing a difference of only 12.5 kJ mol^{-1} between ob_3 and lel_3 for the free $Cr(tmen)_3^{3+}$ complex. In addition, the infrared spectra of the solid salts are anion dependent, indicative of vibrational interactions between $Cr(tmen)_3^{3+}$ and the counterions mediated by N–H•••O, F, Cl hydrogen bonds.

Acknowledgements

We thank CIBA-GEIGY AG (Dr Monnier) for a supply of tmen and for the microanalysis.

This work was supported by the Swiss National Science Foundation, Grant No. 2.622-0.87.

References

1 P. Hendry and A. Ludi, *J. Chem. Soc., Chem. Commun.*, (1987) 891; *Helv. Chim. Acta, 71* (1988) 1966.
2 E. Krausz, C. Tomkins and H. Adler, *J. Phys. E, 15* (1982) 1176.
3 H. L. Schläfer and O. Kling, *Z. Anorg. Allg. Chem., 287* (1956) 296.
4 R. Bramley, M. Brorson, A. M. Sargeson and C. E. Schäffer, *J. Am. Chem. Soc., 107* (1985) 2780.
5 U. Geiser and H. U. Güdel, *Inorg. Chem., 20* (1981) 3013.
6 G. F. Imbusch in W. M. Yen and P. Selzer (eds.), *Laser Spectroscopy of Solids*, Springer, Berlin, 1981.
7 D. J. Robbins and A. J. Thomson, *Mol. Phys., 25* (1973) 1103.
8 J. Brunner, P. Hendry and A. Ludi, to be published.
9 T. W. Hambley, *Momec 85*, a Fortran program for strain energy minimization, Department of Chemistry, University of Sydney, Australia.