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Amine Spectrochemical Properties in Tris(aminocarboxylate) Complexes of Chromium(III)

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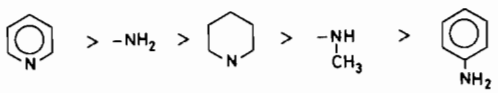
A series of CrN_3O_3 complexes with aminocarboxylate ligands was examined, and the nitrogen-containing groups could be arranged in a spectrochemical sequence in the order



Introduction

We have examined a group of tris(aminocarboxylate)chromium(III) complexes in which the amine ligands were expected to vary considerably in their electronic properties. These have been compared with respect to the spectrochemical splitting parameter, Δ_N (= 10 D_q), which may be estimated from absorption spectra. The complexes were also characterized through their luminescence spectra.

The nitrogen groups studied consisted of pyridine (in $Cr(pic)_3$; Hpic = picolinic acid, pyridine-2-carboxylic acid), piperidine ($Cr(pip)_3$; Hpip = pipecolinic acid, piperidine-2-carboxylic acid), an aliphatic secondary amine ($Cr(sar)_3$; Hsar = sarcosine, N-methylglycine), and an aromatic primary amine ($Cr(aba)_3$; Haba = *o*-aminobenzoic acid).

The picolinate complex is well known [1–5], whereas the others are not mentioned in the literature, although references to a catalytically active chromium anthranilate in several patent applications [6] may be presumed to refer to the $Cr(aba)_3$ complex reported here.

Experimental

$[Cr(pic)_3]\cdot H_2O$ and $[Cr(pic)_2OH]_2$

The earliest literature preparation, that of Ley and Ficken [1], describes the contamination by $[Cr(pic)_2OH]_2$ of the tris(picolinate) complex, a problem which is evident in subsequent references [7]. We have taken advantage of the insolubility of the dimer in acetonitrile to effect an efficient separation.

$CrCl_3\cdot 6H_2O$ (2.6 g, 0.01 mol) followed by picolinic acid (3.6 g, 0.03 mol) were dissolved in 95% ethanol (15 ml), and the solution heated on a steam bath for 20 min. A solution of NaOH (1.2 g, 0.03 mol) in 25 ml of 95% ethanol was added, and heating was continued for 15 min. The solution was filtered hot and washed with water until the filtrate was clear, whereupon the clay-like precipitate was discarded. The filtrate, with the washings, was allowed to evaporate for several days, the precipitate was collected and added to 500 ml of CH_3CN, and the solution heated to *ca.* 60 °C and stirred for 30 min. The undissolved solid was collected and further extracted with acetonitrile until the solution remained clear. Analysis was consistent with the empirical formula $[Cr(pic)_2OH]$. The violet-blue solid was somewhat soluble in methanol and dimethylformamide (DMF), and insoluble in water.

The acetonitrile filtrate was allowed to evaporate, whereupon red crystalline $[Cr(pic)_3]\cdot H_2O$ formed, which was collected, washed with ethanol, and air-dried. It was insoluble in water, somewhat soluble in methanol, and soluble in DMF. The product was dissolved in DMF and passed through a Sephadex LH-20 column, eluting with DMF as a single band. *Anal.* Calcd. for $Cr(C_6H_4NO_2)_3\cdot H_2O$: C, 49.55; H, 3.23; N, 9.63%. Found: C, 49.12; H, 3.32; N, 10.12%.

$Cr(pip)_3\cdot H_2O\cdot NaCl$

2.6 g (0.01 mol) of $CrCl_3\cdot 6H_2O$ and 3.8 g (0.03 mol) of DL-pipecolinic acid were dissolved in ethanol and heated near boiling for 30 min. 1.2 g (0.03 mol) of NaOH was dissolved in ethanol and added to the solution, whereupon a crystalline violet precipitate formed. Even after recrystallization from ethanol, NaCl appeared to have cocrystallized. Dissolved in ethanol, the product eluted as one band on Sephadex LH-20. *Anal.* Calcd. for $Cr(C_6H_{10}NO_2)_3\cdot$

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TABLE I. Electronic Absorption Spectral Data for CrL_3 Complexes, L = an Aminocarboxylate, and Calculated Values of Δ_N.

L[a]	Solvent	λ_1^{max}, nm	λ_2^{max}, nm	Δ_N[d], cm^{-1}
pic	DMF	515	[b]	21,700
pip	C_2H_5OH	545	395	19,600
aba	CH_3OH	590	[b]	16,800
sar	H_2O	550	400	19,270
gly	DMF	528[c]	393[c]	20,800

[a]Abbreviations: pic = picolinate, pip = 2-piperidinecarboxylate, aba = *o*-aminobenzoate, sar = sarcosinate, gly = glycinate. [b]Obscured by UV tail. [c]From Ref. 9. [d]Assuming $\Delta_o = 17{,}100\ cm^{-1}$.

$H_2O \cdot NaCl$: C, 42.15; H, 6.29; N, 8.19%. Found: C, 41.71; H, 6.57; N, 8.30%.

$Cr(aba)_3 \cdot 5H_2O$

2.6 g (0.01 mol) of $CrCl_3 \cdot 6H_2O$ and 4.1 g (0.03 mol) of *o*-aminobenzoic acid were dissolved in methanol and heated near boiling for 1 hr. 1.2 g (0.03 mol) of NaOH, dissolved in methanol, was then added, whereupon a crystalline green precipitate formed. This was recrystallized from methanol and dried *in vacuo*. The solid was soluble in methanol, ethanol and other polar organic solvents. Dissolved in methanol, it eluted as one band on a Sephadex LH-20 column. *Anal.* Calcd. for $Cr(C_7H_6NO_2)_3 \cdot 5H_2O$: C, 45.82; H, 5.13; N, 7.63%. Found: C, 45.53; H, 4.77; N, 7.86%.

$Cr(sarc)_3 \cdot 3H_2O \cdot 2/3NaCl$

2.6 g (0.03 mol) of sarcosine was dissolved in ethanol and reacted as in the above preparations. A crystalline purple precipitate formed, in which NaCl either was present as an impurity or cocrystallized. The solid was insoluble in ethanol but somewhat soluble in water. Dissolved in water, it eluted as one band on a Sephadex G-10 column. *Anal.* Calcd. for $Cr(C_3H_6NO_2)_3 \cdot 3H_2O \cdot 2/3NaCl$: C, 26.41; H, 5.91; N, 10.27%. Found: C, 26.83; H, 6.04; N, 9.99%.

Physical Measurements

Absorption spectra were recorded on a Cary 14 spectrophotometer. Luminescence spectra were obtained with an apparatus, previously described [8], based on a Spex 1400-II 0.75 m double monochromator. The samples were in microcrystalline form, maintained at 12 K.

Results

Absorption spectral data for tris(aminocarboxylato)chromium(III) complexes are listed in Table I.

TABLE II. Luminescence Spectral Data for CrL_3 Complexes.

L[a]	λ_{max}[b], nm	δ[c], cm^{-1}
pic	790	500
pip	728(718)[d]	750
aba	775	270
sar	716(740)[d]	850

[a]Abbreviations as in Table I. [b]Measured on samples in KBr pellets (*ca.* 1:1) at 12 K; uncorrected. [c]Full width at half height. [d]Shoulder.

It has been noted [9] that the band positions for $[Cr(gly)_3]$ vary considerably with solvent. In the present instance there was no common solvent, and so some uncertainty must attach to the comparison. However, spectra of $[Cr(pic)_3]$ in several solvents were recorded, without the large variation noted for the glycinate complex (in general, less than 3 nm).

This point is of interest because our value for the first absorption maximum of $[Cr(pic)_3]$, 515 nm, is at odds with the previous literature values, 543 [10] and 540 nm [11]. These wavelengths are, however, not consistent with the red color of the solid. An explanation may lie in the confusion by the previous workers of $[Cr(pic)_3]$ with the dimer, for which we find absorption maxima, in methanol, at 545 and 406 nm. Alternatively, the meridional isomer, for which we have found no evidence, may have been present in their samples.

None of the four tris complexes studied exhibited the highly structured sharp line luminescence shown by $[Cr(gly)_3]$ [12]. In each case only one main peak (two with shoulders) was evident, with, however, a considerable variation in the band widths. The data are presented in Table II.

Discussion

Luminescence Spectra

The large half-widths and lack of structure in the emission spectra indicate that a $^4T_{2g} \rightarrow {}^4A_{2g}$ fluorescence is being observed (using O_h notation) [13]. The much smaller than usual half-width for $[Cr(aba)_3]$ is, however, striking. This might be taken to indicate a significantly smaller shift of the excited state potential surface relative to the ground state, and indeed, the Stokes shift is smallest for this complex. However, the relationship between half-widths and Stokes shift is not well defined among the four complexes. An assignment of the $[Cr(aba)_3]$ emission to $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence was ruled out because of the detection of a low intensity, narrow

band in absorption at 670 nm. Even if this is the $^2T_{1g}$ rather than the ^2E_g state, the transition to ^2E_g is not likely to occur beyond 710 nm, and it would be expected to be coincident in absorption and luminescence spectra.

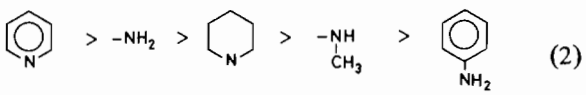
Spectrochemical Properties.

For facial CrN_3O_3 complexes, approximating the geometry as orthoaxial, the energy of the first spin-allowed band is [14]

$$\Delta E = \tfrac{1}{2}(\Delta_N + \Delta_O) \quad (1)$$

When meridional isomers are involved, the situation is more complicated, since, even neglecting spin-orbit coupling, three components of the transition will be present. But the average energy of the three components is still given by eqn. (1), and, when little splitting is observed, it should still yield a good approximation to the observed peak position.

The carboxylate ligand is common to all the complexes in this study, and Table I illustrates the considerable variation in the position of the first absorption band with the nitrogen ligand. If the ligand field strength of the carboxylate is assumed to be constant, values for Δ_N for the nitrogen groups may be calculated. A value of 17,100 cm^{-1} has been used for carboxylate in amino acid complexes [15], though the actual value used does not alter the comparison. The splitting parameters so calculated are listed in Table I, and lead to the order



(2)

Δ_N may be expressed, in the Angular Overlap Model, as $3e_\sigma - 4e_\pi$, e_σ and e_π representing the d orbital destabilization due to σ and π, bonding, respectively, so that a larger value of Δ_N may result from either a larger e_σ or a smaller e_π. In the present case, in spite of the expected variability in the extent of π-bonding, the order observed appears to reflect primarily differences in σ-bonding.

The series (2) acquires significance in that the spectrochemical properties of several of these ligating groups have not been studied because of the lack of complexes in which they appear as monodentate ligands. To place the series in perspective with respect to monodentate ligands, NH_3 and ethylenediamine would appear in approximately the same position as pyridine at the top of the series, which is just what is observed with monodentate pyridine as well [16].

Geometric Isomerism

Of the aminemonocarboxylate complexes of chromium(III), only the red glycine complex has been the subject of an X-ray structural study, it being determined to be the facial isomer [17]. The purple meridional isomer is much more difficult to prepare [12, 18]. Some cobalt(III) analogs have been investigated. Both facial and meridional isomers of [Co(gly)$_3$] are well-known [19]. [Co(pic)$_3$] and [Co(sar)$_3$] both occur as meridional isomers, the former as determined by X-ray diffraction [20], the latter from splittings in absorption spectra and other spectroscopic techniques [21].

Since no splitting of the ligand field absorption bands could be detected for any of the four tris complexes reported here, we are tempted to infer that all are facial isomers, like the glycine analog. Chromatographic behavior and invariance of the emission spectra with exciting wavelength confirm that only a single isomer is present in each case. Contrary to the situation for Co(III) complexes, however, it is probably not valid to assign the isomeric form when no splitting is observed, since the splittings are smaller for Cr(III) than for Co(III) complexes, and can easily fall within the band envelope. The existence of meridional isomers as the more stable form of some Co(III) analogs adds to the uncertainty. Nevertheless, an assignment of all complexes to the facial isomer is favored at this time.

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