ACTA CHEMICA SCANDINAVICA 19 (1965) 1175–1179

Circular Dichroism of Tris(biguanide) Complexes of Cobalt(III) and Chromium(III)

KIRSTEN MICHELSEN

Chemistry Department I, Inorganic Chemistry,
The H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

The tris(biguanide) cobalt(III) and chromium(III) ions have been resolved into their optically active enantiomers, the chromium complex for the first time, and their absorption- and circular dichroism spectra have been studied. Both absorption- and circular dichroism spectra are remarkably intense. The $(-)_D[Co(bgH)_3]^{3+}$ and the $(-)_D[Cr(bgH)_3]^{3+}$ ions have been assigned the same absolute configuration as the $(+)_D[Co(en)_3]^{3+}$ ion based on solubility and circular dichroism data.

In the last years the study of the optical rotatory power of dissymmetric molecules has obtained recognition as a means of solving spectroscopic and stereochemical problems. The understanding of the exact mechanism of the rotatory power can still be considered vague, and the intention of this work, the study of tris(biguanide) cobalt(III) and chromium(III) chloride and their circular dichroism (CD) curves, is to contribute to the great amount of experiments that may be necessary to bring a solution of the problems nearer.

The complexes are interesting because in solution they show absorption and CD bands of higher intensities in the *d—d* transition region than any other trisdiamine cobalt(III) and chromium(III) complexes so far studied. This is apparently not caused by superposition with charge-transfer bands or internal ligand bands on the normal ligand-field bands. The chelating ligand, biguanide $NH_2 \cdot C(:NH) \cdot NH \cdot C(:NH)NH_2$, has the special advantage of forming a planar ring.

Ray *et al.*[1] have resolved tris(biguanide) cobalt(III) chloride, $[Co(bgH)_3]Cl_3$, using silver *d*-tartrate as a resolving agent. The less soluble chloride *d*-tartrate showed negative rotation at the sodium D-line. In this work another method was investigated, in which ammonium *d*-bromocamphor-π-sulphonate was used as the resolving agent. The method was found to be quicker and easier than Ray's and had the advantage of being applicable to both $[Co(bgH)_3]Cl_3$ and $[Cr(bgH)_3]Cl_3$. The resolution of the latter compound has not been reported previously. Silver *d*-tartrate was tried as a resolving agent for $[Cr(bgH)_3]Cl_3$ but without success. The less soluble camphorsulphonates could easily be converted to the corresponding chlorides by means of lithium chloride in ethanol. These showed negative rotation at the sodium D-line.

Table 1. The wavelengths λ_{max} and molar extinction coefficients ε_{max} of the spectra of $(-)_D[Co(bgH)_3]Cl_3$ and $(-)_D[Cr(bgH)_3]Cl_3$ and the corresponding CD data, λ_{max} and $(\varepsilon_l - \varepsilon_d)_{max}$. In the UV region absorption and CD data cannot be correlated.

Complex	Absorption λ_{max} (mμ)	 ε_{max}	Circular dichroism λ_{max} (mμ)	 $(\varepsilon_l - \varepsilon_d)_{max}$	Assignment
$(-)_D[Co(bgH)_3]Cl_3$	477	204	513	− 3.49	$^1A_1 \rightarrow {}^1A_2$
			455	+ 4.68	$^1A_1 \rightarrow {}^1E$
	353	184	364	− 1.81	$^1A_1 \rightarrow {}^1E$
	270	3 800	295	+ 2.0	
			247	−37.0	
			218	+ 51.0	
$(-)_D[Cr(bgH)_3]Cl_3$	482	103	522	− 2.73	$^4A_2 \rightarrow {}^4A_1$
			460	+ 4.14	$^4A_2 \rightarrow {}^4E$
	368	78	375	− 1.28	$^4A_2 \rightarrow {}^4E$
			242	+ 65.0	
	222	27 600	222	−62.5	

The $(-)_D[Co(bgH)_3]^{3+}$ ion and the $(-)_D[Cr(bgH)_3]^{3+}$ ion are assigned the same absolute configuration as the $(+)_D[Co(en)_3]^{3+}$ ion based on solubility data and in agreement with a principle of Mason.[2,3]

EXPERIMENTAL

Reagents. The red inner complexes $[Co(C_2H_6N_5)_3] \cdot 2\ H_2O$ and $[Cr(C_2H_6N_5)_3] \cdot H_2O$ were prepared according to methods described in the literature.[4,5] All other chemicals were reagent grade and used without further purification.

$(-)_D$*[Co(bgH)₃](C₁₀H₁₄OBrSO₃)₃ · 5 H₂O.* $[Co(C_2H_6N_5)_3] \cdot 2\ H_2O$ (2.25 g, 5.7 mmoles) was treated in the cold with 3 N HCl (6 ml). The yellow past was dissolved in water (140 ml), and the pH was adjusted to 4—5 with 3 N HCl. After adding a solution of $C_{10}H_{14}OBrSO_3NH_4$ (3.00 g, 9.1 moles) in water (20 ml) the solution was shaken and allowed to stand for 5 min, after which glistening salmoncoloured crystals precipitated. The crystals were filtered, washed with icecold water (3 × 10 ml), ethanol-water (1:1, 10 ml), ethanol (10 ml) and dried in the air at room temperature. Yield 38 % (1.50 g). Recrystallization from ethanol did not increase the optical purity, but diminished the yield considerably. (Found: Co 4.37; C 31.50; N 15.07; H 5.34; Br 17.80; S 6.84. Calc. for $[Co(C_2H_7N_5)_3]\ (C_{10}H_{14}OBrSO_3)_3 \cdot 5\ H_2O$: Co 4.26; C 31.26; N 15.19; H 5.33; Br 17.73; S 6.96). $[\alpha]_D^{20} = -100$, $[M]_D^{20} = -1383$.

$(-)_D$*[Cr(bgH)₃] (C₁₀H₁₄OBrSO₃)₃ · 5 H₂O* was prepared as described above for the corresponding cobalt complex. From 2.25 g of $[Cr(C_2H_6N_5)_3] \cdot H_2O$ a yield of 2.10 g was obtained (51 %). (Found: Cr 3.81; C 31.30; N 15.16; H 5.26; Br 17.53; S 6.90. Calc. for $[Cr(C_2H_7N_5)_3]\ (C_{10}H_{14}OBrSO_3)_3 \cdot 5\ H_2O$: Cr 3.78; C 31.42; N 15.27; H 5.36; Br 17.42; S. 6.99). $[\alpha]_D^{20} = -17.8$, $[M]_D^{20} = -245$.

$(-)_D[Co(bgH)_3]Cl_3$. $[Co(bgH)_3]$ $(C_{10}H_{14}OBrSO_3)_3 \cdot 5\ H_2O$ (200 mg, 0.14 mmole) was dissolved in ethanol (20 ml). A solution of LiCl (200 mg, 4.7 mmoles) in ethanol (10 ml) was added. After 2 min yellow-orange crystals of $[Co(bgH)_3]Cl_3$ separated out. They were filtered, washed with ethanol (5 × 10 ml) and dried in the air. Yield 76 % (50 mg). $[\alpha]_D^{20} = -434$, $[M]_D^{20} = -2035$.

$(-)_D[Cr(bgH)_3]Cl_3$ was prepared by a similar method to that described for the cobalt complex. Yield from 200 mg of $[Cr(bgH)_3$ $(C_{10}H_{14}OBrSO_3)_3 \cdot 5\ H_2O$: 55 mg (78 %). $[\alpha]_D^{20} = -197$, $[M]_D^{20} = -910$. The last two compounds were identified through their absorption spectra.

The optical rotations were measured on a Perkin Elmer Model 141 polarimeter. The absorption spectra were obtained on a Cary Model 14 recording spectrophotometer. Circular dichroism measurements were performed with a Roussel-Jouan Dichrograph. All measurements were made on water solutions at room temperature.

DISCUSSION

In what follows, absorption and CD spectra for $[Co(bgH)_3]^{3+}$ are discussed in common with the analogous data for $[Cr(bgH)_3]^{3+}$, the figures and symbols in brackets referring to the chromium compound.

Under the single long-wavelength band at 477 mμ (482 mμ) two CD bands are observed. They may represent the residual wings of the bands of opposite sings due to the ^1E (^4E) and $^1A_2$ ($^4A_1$) components into which the $^1T_{1g}$ ($^4T_{2g}$) state of O_h splits in complexes of D_3 symmetry.

$^1T_{2g}$ ($^4T_{1g}$) splits into the components ^1E (^4E) and $^1A_1$ ($^4A_2$) in D_3. The CD band observed near 364 mμ (375 mμ) and beneath an absorption band at 353 mμ (368 mμ) may be ascribed to $^1A_1 \rightarrow {}^1E$ ($^4A_1 \rightarrow {}^4E$), $^1A_1 \rightarrow {}^1A_1$ ($^4A_2 \rightarrow {}^4A_2$) being forbidden.

In the ultraviolet region two very intense CD bands are observed near 247 mμ (242 mμ) and 218 mμ (222 mμ). The existence of a real peak at 218 mμ (222 mμ) may be questioned, however, since the measurements below 230 mμ approach the limits of the applicability of the dichrograph. The CD curves in this region reveal a structure which is not observable in the unpolarized absorption spectra. The fact that the bands appear at almost the same place

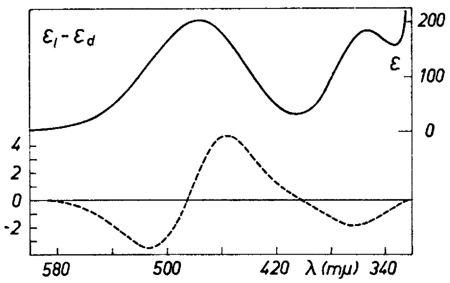

Fig. 1. Absorption spectrum (———) (2.5 × 10^{-3} M) and circular dichroism spectrum (— — —) of $(-)_D[Co(bgH)_3]Cl_3$. Vis. region.

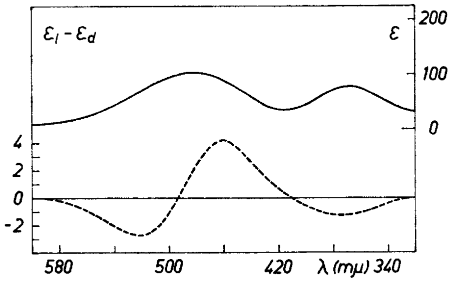

Fig. 2. Absorption spectrum (———) (2.5 × 10^{-3} M) and circular dichroism spectrum (— — —) of $(-)_D[Cr(bgH)_3]Cl_3$. Vis. region.

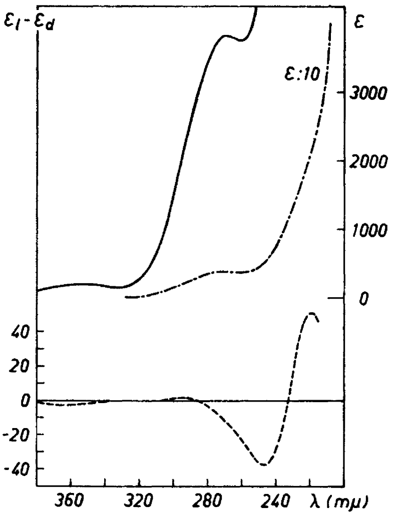

Fig. 3. Absorption spectrum (——— and — . —) (2.5×10^{-3} M and 2.5×10^{-5} M) and circular dichroism spectrum (— —) (2.5×10^{-5} M) of $(-)_D[Co(bgH)_3]Cl_3$. UV region.

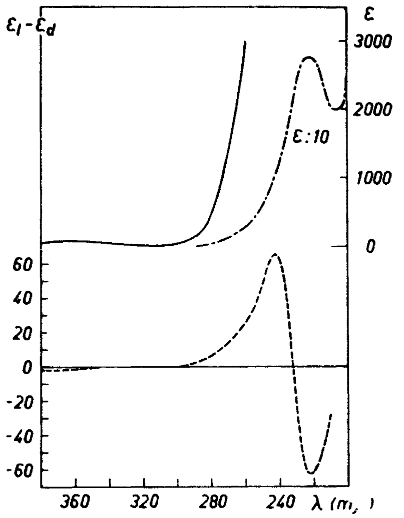

Fig. 4. Absorption spectrum (——— and — . —) (2.5×10^{-5} M) and circular dichroism spectrum (— — — —) of $(-)_D[Cr(bgH)_3]Cl_3$. UV region.

in the cobalt and the chromium complexes (and beneath an absorption band of the pure ligand at 230 mμ) suggests that they are essentially internal ligand transitions. On the other hand, it is seen that these complexes, which have similar CD spectra in the visible region and have been assigned the same absolute configuration (see below), show opposite signs in this region. This is puzzling.

According to the classical solubility assignments of chirality to dihedral complexes the $(-)_D[Co(bgH)_3]^{3+}$ ion and the $(-)_D[Cr(bgH)_3]^{3+}$ ion have the same absolute configuration as the $(+)_D[Co(en)_3]^{3+}$ ion. $(+)_D[Co(en)_3]^{3+}$ and $(-)_D[Co(bgH)_3]^{3+}$ are correlated because they both form the less soluble chloride *d*-tartrate, $(-)_D[Co(bgH)_3]^{3+}$ and $(-)_D[Cr(bgH)_3]^{3+}$ because both form the less soluble *d*-bromocamphor-π-sulphonates. Consequently, a correlation between $(+)_D[Co(en)_3]^{3+}$, $(-)_D[Co(bgH)_3]^{3+}$ and $(-)_D[Cr(bgH)_3]^{3+}$ is possible.

Mason [2,3] has suggested that the E (D_3) component gives rise to the more intense of the two CD bands beneath the first absorption band, and that a complex with a positive E component has the same absolute configuration as $(+)_D[Co(en)_3]^{3+}$. If this principle is applied here, it is possible to assign the second CD band to the E component (positive). $(-)_D[Co(bgH)_3]^{3+}$ and $(-)_D[Cr(bgH)_3]^{3+}$ would therefore have the same absolute configuration as $(+)_D[Co(en)_3]^{3+}$ in agreement with the correlation found above.

Acknowledgements. The author wishes to thank Dr. Claus Schäffer for his interest in the work and for valuable discussions.

REFERENCES

1. Ray, P. and Dutt, R. K. *J. Indian Chem. Soc.* **18** (1941) 289.
2. Mason, S. F. *Quart. Rev. (London)* **17** (1963) 26.
3. McCaffery, A. J. and Mason, S. F. *Mol. Phys.* **6** (1963) 359.
4. Ray, P. and Dutt, N. K. *J. Indian Chem. Soc.* **16** (1939) 621.
5. Rochow, E. G. (Ed.) *Inorg. Syn.* **6** (1960) 68.

Received March 18, 1965.