Preparation of Sodium Bis(L-aspartato)rhodate(III)

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Synopsis Bis(L-aspartato) rhodate(III) complex was prepared and separated into three isomers, and their absorption, CD curves and ^{1}H NMR spectra are presented. The geometrical configurations of three isomers are assigned mainly on the basis of the spectral analogy between this complex and the $[Co(L\text{-}asp)_2]^-$ complex.

Numerous studies of cobalt(III) complexes containing amino carboxylate ion have been reported,[1-3] but only a few rhodium(III) complexes with amino carboxylate ion have been studied.[4] As both cobalt(III) and rhodium(III) have the same low spin d^6 electronic configuration, the spectral features of the rhodium(III) complexes should resemble those of the cobalt(III) complexes having the same ligands. Smith and Sawyer[4] have reported on the preparation and the characterization by ^{1}H-NMR spectra of rhodium(III) complexes having iminodiacetate ion (=ida) and *N*-methyliminodiacetate ion (=mida), in which UV and ^{1}H-NMR spectra of these complexes resemble those of the cobalt(III) complexes having the same ligand. The present paper deals with the preparation and the assignment of Bis(L-aspartato) rhodate(III).

Experimental

To a hot solution (20 cm^3) containing 2g of $Rh(NO_3)_3$ (0.007 mol) 4 mol dm^{-3} KOH solution was added untill the pH of the solution reached 7. The precipitate was centrifuged and suspended in 80 cm^3 of water containing 1.84 g of aspartic acid (0.0138 mol) in a pyrex tube and heated at 120—130 °C for five hours. After cooling, the tube was opened carefully and a small quantity of metallic rhodium removed by filtration. This solution was loaded on a QEA-Sephadex A-25 anion exchanger column (50×300 mm). After the elution of the cation and non charged complexes with water, the column was eluted with 0.1 mol dm^{-3} NaCl solution. Five bands descended and showed yellow or yellow brown color (R1, R2, R3, R4, and R5; those are named in the order of elution). The bands R1, R2, and R3 were the desired isomers as established below. The separation of R2 and R3 was not good. The complexes corrsponding to bands R4 and R5 did not possess one minus charge because these bands gradually spread with 0.1 mol dm^{-3} NaCl solution. Each eluate was concentrateed by using a rotary evaporator at room temperature. Calcd for $Na[Rh(L\text{-}asp)_2]\ 2H_2O$ C, 21.80; H, 4.12; N, 6.36%. Found (R1): C, 21.75; H, 4.01; N, 6.55%. Found (R2): C, 21.86; H, 4.36; N, 6.37. Found (R3): C, 22.00; H, 4.05; N, 6.45%.

Spectral Measurements. Visible absorption and circular dichroism spectra were measured with JASCO-UV505 and JASCO-J20 spectrometers in aqueous solution. ^{1}H NMR spectra were measured with a Varian FT-80A spectrometer in D_2O solution with TSP (sodium 3-(trimethylsilyl) propionate) as an internal standard.

Results and Discussion

Figure 1 shows the possible isomers of $[Rh(L\text{-}asp)_2]^-$. These complexes are composed of one

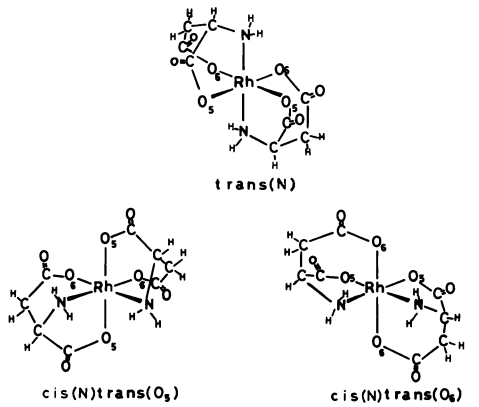

Fig. 1. The three possible isomers of $[Rh(L\text{-}asp)_2]^-$.

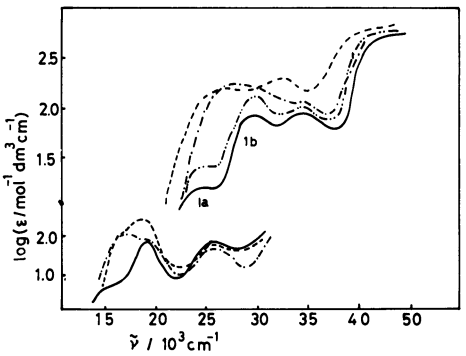

Fig. 2. Visible absorption spectra of $[Rh(L\text{-}asp)_2]^-$· (upper) R1 ——, R2 ----, R3 —·—, *trans*(N)-$[Rh(ida)_2]^-$, —··—, and $[Co(L\text{-}asp)_2]^-$· (lower) F ——, S ---- and T —·—.

trans(N) and two *cis*(N) isomers. The two *cis*(N) isomers are designated *cis*(N) *trans*(O_5) and *cis*(N) *trans*(O_6) as in the case of bis(L-aspartato) cobaltate(III) complexes.[5] Figure 2. shows the UV spectra of $[Rh(L\text{-}asp)_2]^-$ along with those of $[Co(L\text{-}asp)_2]^-$ and *trans*(N)-$[Rh(ida)_2]^-$. The lowest energy band of the R1 isomer split into well-separated components (24300 and 29400 cm^{-1}) and the splitting pattern in the first and the second absorption band regions agree with those of *trans*(N)-$[Rh(ida)_2]^-$. The isomer R1, therefore, is assigned as the *trans*(N) isomer (Fig. 1). It should be noted that the peak maximum of this isomer in the second absorption band region lies *ca.* 8000 cm^{-1} higher than that of the F isomer of $[Co(L\text{-}asp)_2]^-$[1] while the peak maximum of 1b (29400 cm^{-1}) in the first absorption band region lies *ca.* 10000 cm^{-1} higher than that of the F isomer of $[Co(L\text{-}asp)_2]^-$ (Table 1). This larger shift of the first absorption band causes the smaller seperation between the peak maxima of the first and the second absorption band than the corresponding separation for *trans*(N)-$[Co(L\text{-}asp)_2]^-$. This relation also prevails between *trans*(N)-$[Rh(ida)_2]^-$ and *trans*(N)-$[Co(ida)_2]^-$.

Table 1. AB and CD data for $[Rh(L\text{-}asp)_2]^-$ and its related complexes

	First absorption				Second absorption			
	AB		CD		AB		CD	
	$\tilde{\nu}_{max}$*	log ε*	$\tilde{\nu}_{max}$	$\Delta\varepsilon$*	$\tilde{\nu}_{max}$	log ε	$\tilde{\nu}_{max}$	$\Delta\varepsilon$
trans(N)-$[Rh(L\text{-}asp)_2]^-$	24.30	1.22	24.40	0.53	34.50	1.93	33.90	0.36
	29.40	1.93	29.85	1.08				
cis(N)*trans*(O_5)-$[Rh(L\text{-}asp)_2]^-$	25.80	2.06	24.40	−0.18	33.20	2.23	33.20	0.16
cis(N)*trans*(O_6)-$[Rh(L\text{-}asp)_2]^-$	27.03	2.24	27.03	1.12	34.48	2.07	33.90	−0.16
	29.40	2.25	31.25	−0.47				
trans(N)-$[Co(L\text{-}asp)_2]^-$	15.87	1.16	16.50	0.35	26.46	1.89	25.10	0.42
	19.53	1.90	19.40	1.42			28.40	−0.10
cis(N)*trans*(O_5)-$[Co(L\text{-}asp)_2]^-$	16.70	1.89	17.90	−1.36	26.18	1.87	26.00	0.62
cis(N)*trans*(O_6)-$[Co(L\text{-}asp)_2]^-$	17.24	2.09	17.30	3.71	26.40	1.80	25.00	−0.54
trans(N)-$[Rh(ida)_2]^-$	25.00	1.45			35.20	2.02		
	30.45	2.12						
cis(N)-$[Rh(ida)_2]^-$	27.16	2.43			33.8	2.37		

* $\tilde{\nu}/10^3$ cm^{-1}, ε/mol^{-1} dm^3 cm^{-1}.

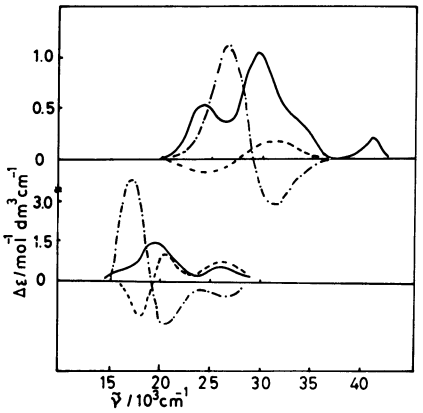

Fig. 3. CD spectra of $[Rh(L\text{-}asp)_2]^-$ (upper); R1 ——, R2 ----, and R3 —·—, and $[Co(L\text{-}asp)_2]^-$ (lower); F ——, S ----, and T —·—.

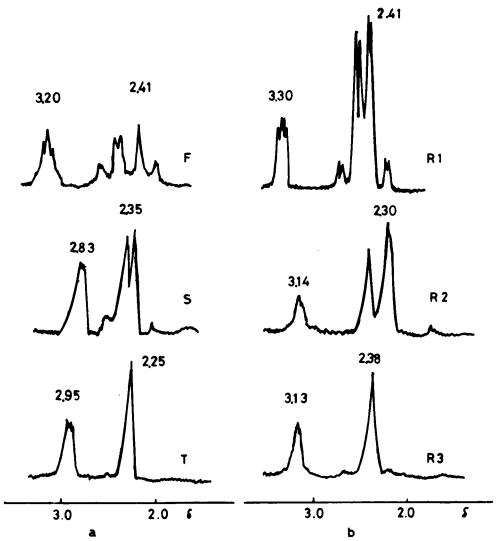

Fig. 4. ^{1}H-NMR spectra of $[Co(L\text{-}asp)_2]^-$ (left side); F, S, and T and $[Rh(L\text{-}asp)_2]^-$ (right side); R1, R2, and R3. ppm from TSP.

The three CD spectra are shown in Fig. 3 along with those of $[Co(L\text{-}asp)_2]^-$. From the crystal-structural analysis,[2] the geometry of the T isomer has been determined as a *cis*(N) *trans*(O_6) configuration. These three CD spectra of the $[Rh(L\text{-}asp)_2]^-$ complexes closely resemble those of $[Co(L\text{-}asp)_2]^-$ except that the peak maxima shift to higher energies. We assigned the R2 and the R3 isomers as *cis*(N) *trans*(O_5) and *cis*(N) *trans*(O_6).

^{1}H NMR spectra of the $[Rh(L\text{-}asp)_2]^-$ complex are shown in Fig. 4 along with those of the $[Co(L\text{-}asp)_2]^-$. The resemblance of the ^{1}H NMR spectra (80 MHz) between $[Rh(L\text{-}asp)_2]^-$ and $[Co(L\text{-}asp)_2]^-$ is notable. We have reported that when X is an oxygen atom in the moiety -CH-NH_2-Co-X (X is trans to NH_2), the methine proton signals appear at a slightly higher magnetic field than is the case where X is a nitrogen atom.[3] This trend holds for most cobalt(III) complexes. The chemical shifts of the methine proton of $[Rh(L\text{-}asp)_2]^-$ are 3.30 ppm for R1, 3.14 ppm for R2 and 3.13 ppm for R3. These values suggest that the chemical shift trend holds good in the rhodium(III) complex. However the two *cis*(N) isomers can not be distinguished only from this ternd of the ^{1}H NMR data. On the basis of the elemental analysis data and the resemblance of the spectra between the $[Rh(L\text{-}asp)_2]^-$ and the $[Co(L\text{-}asp)_2]^-$ complexes, we assigned the isomers R1,R2, and R3 as *trans*(N), *cis*(N) *trans*(O_5), and *cis*(N) *trans*(O_6).

Reference

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4) B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, **7**, 922 (1968).

5) The three isomers of $[Co(L\text{-}asp)_2]^-$ were named F, S, and T isomers in the order of elution and were assigned as *trans*(N), *cis*(N) *trans*(O_5), and *cis*(N) *trans*(O_6), respectively.