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STUDIES ON THE OPTICAL ROTATORY DISPERSION OF ALDIMINES OF AMINO SUGARS AND METAL CHELATES

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Various amino sugars, including D-glucosamine, condense with aromatic o-hydroxy aldehydes to yield aldimines. By adding various transitional metal ions, these aldimines give chelate compounds. N-Pyridoxalidene amino sugars, derived from amino sugars and pyridoxal, form intensive blue fluorescent chelates with Zn(II) in pyridine-methanol solution and this reaction has been applied to the micro-determination of amino sugars[1]. The metal chelates of the aldimines derived ffom α-amino acids or optical active amines showed Cotton effects, of which the signs depended on the configuration of amino groups[2]. Therefore the ORD curves of these chelates were measured to elucidate the conformation in solution and the correlation with the configuration of amino groups.

Various N-salicylidene amino sugars as model compounds were synthesized. N-Pyridoxalidene amino sugars were prepared in methanol by mixing amino sugars and pyridoxal (1 : 1). To the resultant aldimin solutions metal ion solutions were added to yield metal chelates. N-Salicylidene or N-pyridoxalidene amino sugars absorb at about 400, 335 and 255 mμ. When a metal ion, such as Cu (II), Ni(II), Mn(II), Zn(II) and Co(II), is added, the absorption band at 400 mμ is shifted about 30 mμ towards shorter wavelengths (370∼390 mμ) and the absorption band at 335 mμ disappears : this indicates some kind of chelate formation. It has been found that anomalous ORD curves associated with these chelate absorption bands. Chelates with Cu(II), Ni(II), Zn(II), Co(II) and Mn(II) exhibit Cotton effects respectively at the chelate absorption bands and have lager molecular amplitudes as compared with those of free aldimines. Cu(II)-chelate exhibits the most intensive Cotton effect.

The aldimines which exhibited a feeble Cotton effect, such as N-salicylidene and N-pyridoxalidene methyl 3-amino-3-deoxy-α-D-mannopyranoside, also showed a distinct Cotton effect by formation of the chelate with Cu(II) ion.

1,3,4,6-Tetra-O-acetyl-N-salicylidene and -N-pyridoxalidene glucosamine exhibits a positive Cotton effect at its chelate absorption band, but its amplitude does not increae. The amplitude of Cotton effect may be highly dependent on the vicinal hydroxy groups. Table I and II summarized the relationship between the absolute configuration of amino groups and the sign of the Cotton effect. It has seen from Tables that the metal chelates of the C-2 and C-3 N-salicylideneamino- and N-pyridoxalideneamino-derivatives having the D (S) configuration showed positive sign as well as aldimines [3]. Whereas the ones having the L (R) configuration exhibited negative sign except 2-amino-2-deoxy-D-mannose. The aldimine of D-mannosamine in which amino group at C-2 is axial configuration in C-1 conformation exhibits negative Cotton effect corresponding with L (R) configuration of amino group, but the chelate with Cu(II) or Ni(II) ion undergoes a sign inversion resulting in an annomalous positive Cotton effect. On the other hand, the aldimine of methyl 3-amino-3-deoxy-D-allopyranoside in which amino group at C-3 is axial showed positive sign corresponding with its amino group configuration, D (S), but the chelate with Cu(II) or Ni(II) does not undergo a sign inversion.

The detile discussion will be represented elsewhere.

References

1) M.Maeda, T.Kinoshita and A.Tsuji ; Presented to the 88th Annual Meeting of the Pharmaceutical Society of Japan. (April, 1968).

2) M.Torchinsky and L.G.Koreneva ; Biochimija, 30, 39 (1965).

3) S.Inouye ; Chem. Pharm. Bull., 15, 1557 (1967).

Table 1 ORD data of N-Salicylidene Amino Sugars and their Metal Chelates

Compounds	$[\phi]_1$ (λ_1)	$[\phi]_2$ (λ_2)	a*	Sign	ε (mμ)	
I	1300(325)	-200(386)	15	+	3900(318)	100(402)
Cu(II)	11500(392)	-12500(340)	240	+	4900(374)	
Ni(II)	5200(380)	-4800(344)	100	+	3500(377)	
Co(II)	3500(390)	-3100(310)	66	+	2600(368)	
Mn(II)	3300(410)	-1600(362)	49	+	1700(386)	
Zn(II)	6200(380)	-2800(336)	90	+	2700(338)	
II	950(427)	100(384)	9	+	2600(318)	710(410)
Cu(II)	6300(396)	-6000(340)	123	+	3500(370)	
Ni(II)	3500(386)	-2300(340)	58	+	2300(373)	
III	2900(427)	400(370)	25	+	2800(318)	1500(404)
Cu(II)	3800(396)	-3400(340)	72	+	3700(374)	
Ni(II)	2600(390)	-650(350)	33	+	3000(378)	
IV	1300(426)	-650(350)	19	+	2500(318)	2100(403)
Cu(II)	2300(390)	-3700(330)	60	+	5800(367)	
Ni(II)	450(390)	-440(330)	9	+	2600(360)	
V	1400(420)	-900(358)	23	+	2700(313)	1800(398)
Cu(II)	1700(394)	-300(360)	20	+	5800(363)	
VI	5500(335)	-1600(300)	71	+	4600(320)	
Cu(II)	3300(400)	-2000(340)	53	+	4000(384)	
Ni(II)	3600(390)	-1700(340)	53	+	3300(388)	
VII	-1500(420)	0(380)	-15	-	3200(318)	870(400)
Cu(II)	1400(400)	-2500(340)	39	+	3600(373)	
Ni(II)	2500(390)	-1800(338)	43	+	5300(373)	
VIII	-1800(370)	2900(320)	-47	-	2800(319)	1700(404)
Cu(II)	-5100(390)	8300(340)	-134	-	4600(373)	
Ni(II)	-2400(382)	3800(352)	-62	-	4800(368)	
IX	2400(425)	0(376)	24	+	2700(317)	1000(403)
Cu(II)	8200(396)	-7800(340)	160	+	3700(369)	

N-Salicylidene (N-Pyridoxalidene) Derivative of

I 2-Amino-2-deoxy-D-glucose
II 2-Amino-2-deoxy-D-galactose
III Methyl 2-amino-2-deoxy-α-D-glucopyranoside
IV 2-Amino-2-deoxy-D-glucuronic acid
V 2-Amino-2-deoxy-D-glucitol
VI 1,3,4,6-O-Acetyl2-amino-2-deoxy-D-glucopyranose
VII 2-Amino-2-deoxy-D-mannose
VIII Methyl 3-amino-3-deoxy-α-D-mannopyranoside
IX Methyl 3-amino 3-deoxy-D-allopyranoside
X Mehyl 6-amino-6-deoxy-D-glucopyranoside
XI Chondrosine

$$*a = \frac{[\phi]_1 - [\phi]_2}{100}$$

Table 2 ORD Data of N-Pyridoxalidene Amino Sugars and their Metal Chelates

Compounds	$[\phi]_1$ (λ_1)	$[\phi]_2$ (λ_2)	a	Sign	ε (mμ)	
I	1200(450)	500(410)	7	+	3200(335)	1700(399)
Cu(II)	9600(414)	-8100(359)	177	+	6700(393)	800(464)
Ni(II)	6700(419)	-5400(360)	121	+	4800(393)	4700(404)
Co(II)	3500(420)	-2900(330)	64	+	3300(386)	
Mn(II)	1400(428)	-800(365)	22	+	1400(400)	
Zn(II)	5200(395)	-3600(345)	88	+	2900(389)	
II	1400(440)	450(400)	10	+	4000(336)	1100(420)
Cu(II)	12200(410)	-10000(360)	222	+	6700(394)	
Ni(II)	8900(415)	-4800(360)	137	+	6300(392)	
III	1290(450)	400(390)	8	+	1700(333)	680(410)
Cu(II)	1700(433)	-900(375)	26	+	3000(394)	
Ni(II)	1500(420)	-200(375)	17	+	400(405)	
IV	620(445)	-400(360)	10	+	2400(321)	2000(410)
Cu(II)	2300(405)	-3200(352)	55	+	2600(400)	
Ni(II)	6100(418)	-7800(355)	139	+	6800(408)	
V	1600(446)	-1300(378)	29	+	4000(335)	2000(215)
Cu(II)	3000(430)	-670(386)	37	+	7700(389)	
Ni(II)	2700(446)	-2000(396)	47	+	7500(392)	sh(404)
VI	2100(355)	-400(310)	25	+	5000(288)	2000(337)
Cu(II)	2800(416)	-1900(365)	47	+	1800(397)	
Ni(II)	1100(420)	200(380)	9	+	670(409)	
VII	-1600(445)	-1100(410)	-5	-	3700(337)	500(470)
Cu(II)	4400(415)	-2800(358)	72	+	7500(354)	500(470)
Ni(II)	3600(415)	-3400(350)	70	+	4400(394)	4300(405)
VIII	-1000(455)	300(400)	-13	-	3200(336)	1300(420)
Cu(II)	-6900(415)	11100(355)	-170	-	5600(388)	
Ni(II)	-5900(414)	7700(355)	-136	-	5600(391)	5500(405)
IX	700(445)	200(400)	5	+	3600(335)	700(422)
Cu(II)	6500(412)	-3100(372)	96	+	5000(388)	
Ni(II)	3600(420)	-350(360)	40	+	4200(393)	
X	2100(350)	0(310)	21	+	3200(335)	
Cu(II)	3600(405)	-2300(345)	59	+	5000(387)	
Ni(II)	5900(410)	-4900(340)	108	+	4600(393)	
XI	1500(446)	0(390)	15	+	3600(355)	1100(410)
Cu(II)	7100(410)	-8200(356)	153	+	6100(393)	
Ni(II)	5700(414)	-5300(356)	110	+	6700(392)	