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Tris(L-prolinato)nickel(II) Complex

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Only a few solid nickel(II) complexes of tris-(amino-acidato) type have been reported,[1,2] though the formation in solutions has been well established for many kinds of α-amino acids from stability constant measurements,[3,4] and from studies of $d \rightarrow d$ absorption spectra.[5,6]

Optically active prolinate ligand stands in a unique position among optically active α-amino acids because of its stereospecific coordination to a metal ion. In the case of tris(L-prolinato)cabalt-(III), the *mer(N)-Λ*[7] isomer can not exist[8] because of a large steric interaction between the ligands, and only the *fac(N)-Λ* isomer can be easily prepared because this shows no such steric interaction.[9] The other two Δ-isomers have more or less such steric interaction. However, Denning and Piper have succeeded to isolate these isomers in crystals.[8] As it seems that a similar stereo-specific situation also occurs in the case of tris(L-prolinato)nickel(II), we examined the preparation and optical properties of this complex and some of the related tris(amino-acidato)nickel(II) complexes. The following abbreviations will be used for the amino acid ligand:

gly=$CH_2(COO^-)NH_2$, L-ala=$CH_3CH(COO^-)NH_2$,
L-pro=$CH(COO^-)CH_2CH_2CH_2NH$ and
L-hypro=$CH(COO^-)CH_2CH(OH)CH_2NH$.

Experimental

Potassium Tris(amino-acidato)nickel(II). An aqueous solution containing freshly prepared nickle(II) carbonate, amino acid (L-proline, L-hydroxyproline, L-alanine or glycine) and potassium carbonate (the molar ratio was 1 : 5 : 2.5) was evaporated on a water bath at about 80°C until it became almost syrupy. After the crude product had been cooled to room temperature, the resulting blue precipitate was filtered by suction. Five grams of the blue powder obtained was suspended in 100 m*l* of methanol and it was refluxed for a few hours in order to extract the complex. The color of the solution changed from blue to dark blue. The resulting suspension was filtered and the dark blue filtrate was evaporated to dryness in a vacuum desiccator. The complex obtained was recrystallized from hot methanol and dried in a vacuum desiccator and then analyzed for C, H and N (Table 1).

Bis(amino-acidato)diaquonickel(II). Complexes of this type were prepared by a method similar to that of bis(glycinato)diaquonickel(II).[10] In the case of bis(L-prolinato) complex, dehydration of two moles of coordinated water occurred on heating *in vacuo* at 80°C for 16 hr; Found: 10.73%, Calcd of [Ni(L-$C_5H_8NO_2)_2(H_2O)_2$]: 11.15%. The content of C, H and N was determined after the sample had been dehydrated (Table 1).

The CD curves were obtained by a Roussel-Jouan dichrograph in the region of 800—300 mμ, and a Cary 14R*[1] or a Shimadzu QR-50 spectrophotometer with CD attachments in the region of 1150—800 mμ. The absorption measurements were made by a Beckman DU spectrophotometer. The absorption and CD curves are shown in Fig. 1 and the absorption data are summarized in Table 2.

Discussion

It is easily shown from the reported values of stability constants (*e.g.*, $\log \beta_1 = 5.69$, $\log \beta_2 = 10.50$ and $\log \beta_3 = 13.95$ for Ni(II)--glycinate system[4]) that no nickel(II) complexes of tris(amino-acidato) type dissociate the ligand to any extent. Therefore, the absorption curves of the present tris(amino-acidato)nickel(II) complexes agree well with that of the tris(glycinato) complex reported by Jørgensen[5] which was measured in a solution with

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2) D. R. Stephens and H. G. Drickamer, *J. Chem. Phys.*, **34**, 937 (1961).
3) S. Pelletier, *J. Chim. Phys.*, **57**, 287, 295, 301, 306, 311, 318 (1961).
4) R.-P. Martin and R. A. Paris, *Bull. Soc. Chim. Fr.* **1964**, 3170.
5) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955); *ibid.*, **10**, 887 (1956).
6) G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, **5**, 211 (1966).
7) The symdols Δ and Λ are used in this paper according to the tentative proposals by the Commission on the Nomenclature of Inorganic Chemistry of the IUPAC: *Inorg. Chem.*, **9**, 1 (1970).
8) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).
9) T. Yasui, J. Hidaka and Y. Shimura, This Bulletin, **38**, 2025 (1965).
*1 Thanks are due Professor F. Woldbye and Mag. Sci. G. Borch of Technical University of Denmark for the measurement by the Cary 14R.
10) H. Ito, *Nippon Kagaku Zasshi*, **77**, 1383, 1389 (1956).

Table 1. Analytical results (unit in %)

Complex			C	H	N
$K[Ni(gly)_3]$	deep blue	Calcd	22.52	3.78	13.13
		Found	22.50	3.75	12.96
$K[Ni(L\text{-}ala)_3]\cdot H_2O$	deep blue	Calcd	28.43	5.30	11.05
		Found	28.77	5.11	10.97
$K[Ni(L\text{-}pro)_3]$	sky blue	Calcd	40.93	5.49	9.54
		Found	40.76	5.69	9.39
$K[Ni(L\text{-}hypro)_3]$	sky blue	Calcd	36.90	4.96	8.60
		Found	36.39	5.12	8.22
$[Ni(L\text{-}pro)_2(H_2O)_2]$	marine blue	Calcd	41.86	5.58	9.77
		Found	41.22	5.62	9.63

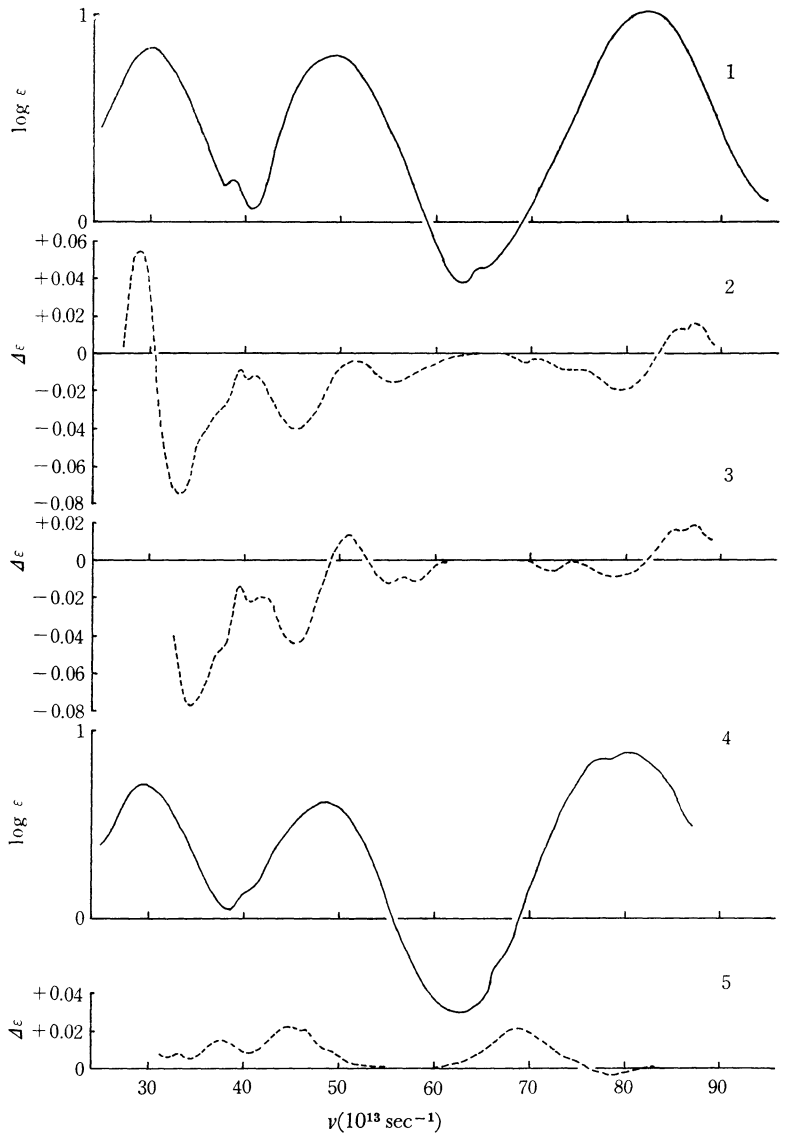

Fig. 1. Absorption curves of (1) $K[Ni(L\text{-}pro)_3]$ and (4) $[Ni(L\text{-}pro)_2(H_2O)_2]$ and CD curves of (2) $K[Ni(L\text{-}pro)_3]$, (3) $K[Ni(L\text{-}hypro)_3]$ and (5) $[Ni(L\text{-}pro)_2(H_2O)_2]$ in aqueous solutions.

TABLE 2. ABSORPTION DATA[a] OF K[Ni(amino-acidato)$_3$] AND [Ni(amino-acidato)$_2$(H_2O)$_2$]

Complex	Solvent	Band I ν_{max} (log ε_{max})	Singlet band ν_{max} (log ε_{max})	Band II ν_{max} (log ε_{max})	Band III ν_{max} (log ε_{max})
K[Ni(gly)$_3$]	H_2O	30.5(1.01)	39.7(0.35)	50.2(0.95)	83.0(1.18)
K[Ni(L-ala)$_3$]	H_2O	30.5(1.03)	39.4(0.40)	50.0(0.99)	82.4(1.20)
K[Ni(L-pro)$_3$]	H_2O	30.0(0.97)	38.8(0.27)	49.2(0.94)	82.2(1.06)
	CH_3OH	30.2(1.01)	39.0(0.32)	50.0(0.99)	82.5(1.12)
K[Ni(L-hypro)$_3$]	H_2O	30.0(0.92)	38.8(0.31)	49.0(0.88)	82.0(1.13)
[Ni(gly)$_2$(H_2O)$_2$]	H_2O	29.5(0.85)	Ca 41 sh	48.8(0.62)	80.8(0.92)
[Ni(L-pro)$_2$(H_2O)$_2$]	H_2O	29.4(0.71)	Ca 40 sh	48.0(0.60)	80.4(0.86)
	CH_3OH	29.6(0.91)	Ca 40 sh	48.4(0.82)	80.8(1.06)

a) The frequencies are given in 10^{13} sec^{-1}.

TABLE 3. CD SIGNS OF NICKEL(II) AND COBALT(III) COMPLEXES IN THE REGION OF THEIR FIRST ABSORPTION BANDS

Complex[a]	Predominant Configuration	Sign of CD Component: Longer wavelength comp.	Sign of CD Component: Shorter wavelength comp.	Ref.
[Ni(*d*-pn)$_3$]$^{2+}$	Λ(lel)	(+)	(−)	13)
[Ni(*d*-2,3-bn)$_3$]$^{2+}$	Λ(lel)		(−)	13)
[Ni(*l*-chxn)$_3$]$^{2+}$	Δ(lel)	(−)	(+)	12)
[Ni(L-pro)$_3$]$^-$	fac(N)-Λ	(+)	(−)	b)
[Ni(L-hypro)$_3$]$^-$	fac(N)-Λ		(−)	b)
Λ(lel)-[Co(*d*-pn)$_3$]$^{3+}$		(+)	(−)	c)
Λ(lel)-[Co(*d*-2,3-bn)$_3$]$^{3+}$		(+)	(−)	13)
Δ(lel)-[Co(*l*-chxn)$_3$]$^{3+}$		(−)	(+)	d)
fac(N)-Λ-[Co(L-pro)$_3$]		(+)	(−)	9)
fac(N)-Λ-[Co(L-hypro)$_3$]		(+)	(−)	9)

a) Abbreviation: pn=propylenediamine, 2,3-bn=2,3-diaminobutane, and chxn=*trans*-1,2-diaminocyclohexane.
b) This work.
c) K. Ogino, K. Murano and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).
d) T. S. Piper and A. G. Karipides, *J. Amer. Chem. Soc.*, **86**, 5039 (1964).

excess of glycinate, and the absorption spectrum of tris(L-prolinato) complex in methanol is almost the same as that in aqueous solution (Table 2). Recently Katzin and Gulyas[11] reported the circular dichroism (CD) spectra of solution complexes in the systems of nickel(II) and amino acids, but curiously enough excluded the possibility of existence of tris(amino-acidato) complexes. As shown in Fig. 1, the CD spectrum of the tris(L-prolinato) complex differs markedly from that of the bis(L-prolinato)diaquo complex; the CD bands of the latter complex are less intense than those of the former complex. The absorption and CD spectra of the tris(L-hydroxyprolinato) complex are similar to those of the tris(L-prolinato) complex; the only difference is that, in the former complex, the band II ($^3A_{2g}\rightarrow{}^3T_{1g}$(F) transition in an O_h approximation) has a positive component besides two or three negative components while the latter complex has only two negative components in this region.

As mentioned above, four isomers, whose stabilities differ markedly from each other, are possible for a tris(amino-acidato) complex; but, in the case of the tris(L-prolinato)nickel(II) complex, the CD spectrum presented in Fig. 1 is assumed to be predominantly that of the most stable *fac(N)*-Λ isomer because of lability of the nickel(II) complexes. Treptow[12] and Woldbye[13] have already assumed similar situations in the cases of [Ni(*l*-trans-1,2-diaminocyclohexane)$_3$]$^{2+}$ and [(Ni(*d*-2,3-diaminobutane)]$^{2+}$, respectively. Table 3 compares the CD band signs of five nickel(II) complexes, with those of the corresponding cobalt(III) complexes, whose comfigurations are the same as those of the nickel(II) complexes existing predominantly in solutions. It is evident from this Table that the sign characteristics in band I of the nickel(II) complexes ($^3A_{2g}\rightarrow{}^3T_{2g}$ in an O_h

11) L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, **91**, 6940 (1969).

12) R. S. Treptow, *Inorg. Chem.*, **7**, 1229 (1968).
13) F. Woldbye, "Studies over Optisk Aktivitet," Polyteknisk Forlag, Copenhagen (1069).

approximation) are almost the same as those in band I of the cobalt(III) complexes ($^1A_{1g} \rightarrow {}^1T_{1g}$ in an O_h approximation). The behavior of the CD spectra in the region of bands II and III is rather irregular.

In conclusion, the absolute configuration of a nickel(II) complexes is reflected in the signs of its CD components in the region of the longest wavelength $d \rightarrow d$ absorption band as in the case of cobalt(III) complexes.