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NICKEL(II) COMPLEXES WITH NOVEL TETRADENTATE AMINOCARBOXYLATE LIGANDS

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Nickel(II) chelates with 1,4-diazacycloheptanediacetate(dachda) and its alkyl derivatives were newly obtained, and characterized by their electronic spectra and magnetic moments. The crystal structure of one of them, studied by X-ray diffraction method, confirmed the proposed square planar structure.

Cyclic diamines such as 1,5-diazacyclooctane (daco) and 1,4-diazacycloheptane (dach)[1,2] form stable planar chelates with nickel(II), $[Ni(diamine)_2]^{2+}$, while common linear-chain diamines tend to form octahedral species, such as the dihydrate complex, $[Ni(diamine)_2(OH_2)_2]^{2+}$.[3] This difference is certainly due to the steric effect of the diaza rings in the former ligands, which strongly shield the axial sites above and below the chelate plane. As to the nickel(II) chelates of the aminocarboxylate derivatives of these cyclic diamines, only one example has been reported, i.e., the peculiar 5-coordinate complex $[Ni(dacoda)(OH_2)]$ where dacoda means 1,5-diazacyclooctanediacetate.[4-8] No corresponding complex containing 1,4-diazacycloheptanediacetate (dachda) has been reported, however, probably owing to the difficulty to get it in pure crystalline form.

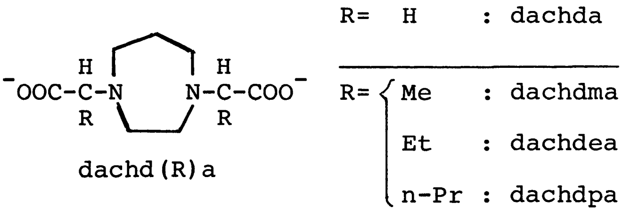

Fig. 1. 1,4-Diazacycloheptanedicarboxylate.

Recently, we could obtain the nickel(II) chelates of dachda and of its alkyl derivatives, dachdma, dachdea and dachdpa (cf. Fig. 1), by mixing equimolar amounts of aqueous solutions of Ni^{2+} and the ligand prepared from dach and (X)CH(R)COOH (X=Cl or Br). The green or orange crystals which precipitated were recrystallized from water. Some of their properties will be reported in this communication.

Among the complexes in Table 1, the dachda complex could be obtained in a very poor yield, so that only the elementary analysis and magnetic measurements could be done. It is green and paramagnetic (high-spin) dihydrate, so is most probablly $[Ni(dachda)(OH_2)_2]$. The chelates with other ligands are anhydrous,

Table 1. Color, analytical and magnetic data of the complexes obtained

Complex	Color	C(%)[a]	H(%)[a]	N(%)[a]	μ_{eff}/BM[b]
$[Ni(dachda)(OH_2)_2]$	Green	34.86(34.99)	5.88(5.89)	9.03(9.07)	3.23
[Ni(dachdma)]	Orange	43.90(43.89)	6.03(5.98)	9.31(9.07)	dia.
[Ni(dachdea)]	Orange	47.10(47.46)	6.83(6.74)	8.43(8.51)	dia.
[Ni(dachdpa)]	Orange	49.46(50.46)	7.40(7.33)	7.73(7.85)	dia.

a) Calculated values are shown in parentheses. b) At room temperature; dia.= diamagnetic.

Table 2. Crystal data, bond lengths and angles around the central metal atom of [Ni(dachdea)]

$C_{13}H_{22}N_2O_4Ni$, MW=329.0, orthorhombic, space group $P2_12_12_1$; (1 Å=0.1 nm), a=7.845(9)Å, b=25.48(2)Å, c=7.216(5)Å, U=1442(8) $(Å)^3$, Z=4, Dx=1.52 g/cm^3, Dm=1.54 g/cm^3; μ(Mo Kα; λ=0.7107Å)=1.42 cm^{-1}, F(000)-548, 1350 reflections ($|Fo| > 2\sigma(|Fo|)$), R=0.118.

Bond length(Å): Ni-N1=1.96(2); Ni-N2=1.86(2); Ni-O1=1.88(2); Ni-O2=1.91(2).

Bond angle(°): N1-Ni-N2=83.7(9); N1-Ni-O1=85.8(8); O1-Ni-O2=99.3(7); O2-Ni-N2=90.8(8).

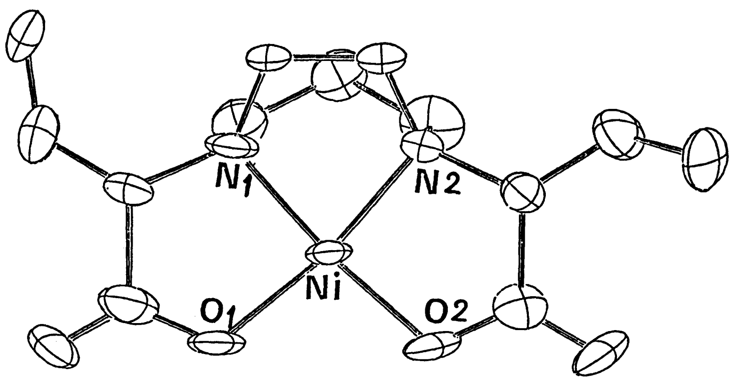

Fig. 2. Perspective view of [Ni(dachdea)].

orange and diamagnetic, and their solid reflectance spectra showed a d-d band at λ_{max}=465 nm. They are thus square planar, and should be formulated as [Ni(dachdma)], [Ni(dachdea)] and [Ni(dachdpa)], respectively.[9)]

The crystal structure of [Ni(dachdea)] was studied by means of X-ray diffraction method. It was found that the chelate has really a planar structure, with the ligand dachdea in meso form. In other words, if we ignore two ethyl groups of the ligand, the molecule has pseudo-mirror symmetry. A perspective view of the molecule is shown in Fig. 2, and some related data are given in Table 2.

For the spectral study of the dachda complex in solution, we used solutions containing Ni^{2+} ion and dachda in the molar ratio 1:1, because the stability of the complex is expected to be quite high.[10)] Figure 3 shows the

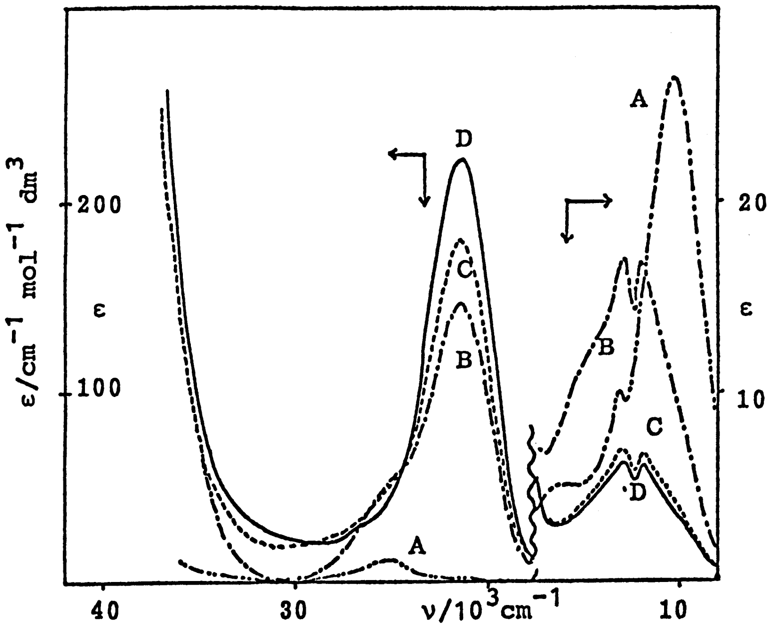

Fig. 3. Absorption spectra of Ni-dachd(R)a complexes in aqueous solutions at ca. 20 °C. A(-·······-); see text. B(-·-·-·-), C(------), and D(———) are the curves for the solutions of [Ni(dachdma)], [Ni(dachdea)], and [Ni(dachdpa)], respectively.

spectrum of such a solution (curve A). It is similar to the spectrum of octahedral [Ni(edda)$(OH_2)_2$], but is notably different from that of 5-coordinate [Ni(dacoda)(OH_2)], and the existence of the square planar species is scarcely observable at room temperature.$^{6)}$ These facts indicate that the complex exists in solution as [Ni(dachda)$(OH_2)_2$].

The other three complexes with alkylated ligands (dachd(R)a) show the spectra corresponding to the equilibrium mixtures of planar and 5-coordinate species, in which the planar species are predominant at room temperature (in Fig. 3, curves B, C, and D). The spectra of the 5-coordinate species are apparently similar to that of [Ni(dacoda)(OH_2)], while those of the planar species are just like the reflectance spectra of the same chelates (cf. above). The equilibrium between them can thus be expressed as Eq. 1, where R=Me, Et or n-Pr. As can be seen from the spectral data, it shifts to the left hand

$$[\mathrm{Ni(dachd(R)a)}] + H_2O \rightleftharpoons [\mathrm{Ni(dachd(R)a)}(OH_2)] \qquad (1)$$

side in the following order, with the increase in size of the alkyl groups on the ligand:

Ni(dachdpa) > Ni(dachdea) > Ni(dachdma) >> Ni(dacoda).$^{11)}$

All these complexes including [Ni(dachda)$(OH_2)_2$] one show thermochromism in solution. In Fig. 4, as an example, the dachda complex is shown, where the equilibrium between octahedral and planar species (Eq. 2, see below) shifts to the left hand side by heating. It should be noted here that, in the case of the dachda complex, the equilibrium shift is from the octahedral to the planar with

$$[\mathrm{Ni(dachda)}] + 2H_2O \rightleftharpoons [\mathrm{Ni(dachda)}(OH_2)_2] \qquad (2)$$

the temperature increase, while the other three chelates show the structural change from the planar to the 5-coordinate with temperature decrease (see Eq. 1). In other words, the alkyl substituent groups of dachd(R)a stabilize the planar species, so that the thermochromic change involving its formation by heating occurs at much lower temperature than that of the dachda complex.

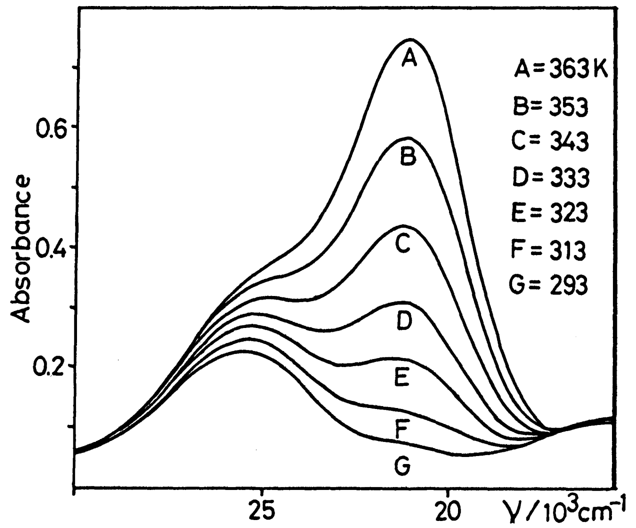

Fig. 4. Thermochromism of the aqueous solution of the dachda complex (concn: 0.023 mol/dm^3).

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10) For example, log K_1 of $[Ni(en)_2]^{2+}$ and that of [Ni(edda)], which are 7.51[12] and 13.73,[13] respectively (edda=ethylenediaminediacetate anion). The stability constant of $[Ni(dach)_2]^{2+}$(log K_1) was reported to be 8.31;[2] therefore, that of [Ni(dachda)] can be expected larger than log K_1=14 or more.
11) It is noteworthy that $[Ni(dacoda)(OH_2)]$ shows a typical 5-coordinate spectrum in aqueous solution at room temperature, where the spectrum of the planar species can scarcely be observed.[6]
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