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Synthesis and X-Ray Structural Study of Magnesium (1,3-Propanediaminetetraacetato)nickelate(II) Octahydrate, Mg[Ni(1,3-pdta)]•8H_2O. Structural Parameters and Strain Analysis of [M(1,3-pdta)]$^{n-}$ Complexes in Relation to Their Octahedral Distortion

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The hexadentate complex Mg[Ni(1,3-pdta)]•8H_2O (1,3-pdta = 1,3-propanediaminetetraacetate ion) was prepared and its structure established by X-ray crystallography. The complex salt crystallizes in the space group *Pnna* (# 52) of the orthorhombic crystal system with a = 13.251(2), b = 11.645(2), c = 13.818(3) Å and Z = 4. The Ni(II) ion is surrounded octahedrally by two nitrogen and four oxygen atoms of the ligand. The Mg cation is bonded octahedrally to six water molecules. Both complex ions utilize a two-fold symmetry axis that is present in the crystal. The conformations of the chelate rings were found to be *envelope* or *twist* for the glycinates and *skew-boat* for the six-membered diamine ring. A comparison of structures of hexadentate [M(1,3-pdta)]$^{n-}$ complexes shows an expected variation in their octahedral distortion depending on the central metal ion M. Some spectral characteristics of the complex studied have also been reported.

It is known that the deviation of the bonding angles from the ideal values in [M(edta)]$^{n-}$ complexes[1–7] (edta = ethylenediaminetetraacetate ion) shows significance of the ligand strain. In these kinds of complexes the ethylenediamine ring (E ring) and the two glycinate rings occupying an equatorial plane (G rings) are more strained than the two glycinate rings coordinated axially (R rings). Moreover, the G rings are usually observed to be puckered, while the R rings are observed to be more planar than the G's, and are referred to as having an *envelope* conformation.

Many structural studies have been reported on transition-metal complexes of edta and related ligands, and their molecular structures have been discussed in terms of the d-electron configuration and size of the central metal ion, M. These influence the differences in the bond lengths (M–N and M–O), ring strain and the ligand configuration.[8–18] The edta-type ligands with longer (diamine or carboxylate) chains are likely to function as hexadentate ligands with larger metal ions. Such ligands ease away any in-plane strain, thus allowing the complexes to attain octahedral angles closer to the ideal with apparently less strain in the M–L bonds by forming (as dominant) less-strained isomers.[11–30] The 1,3-pdta ligand forms a six-membered diamine (T) ring when coordinated. The size and flexibility of the T ring in such complexes, with respect to the [M(edta)]$^{n-}$,[1–7] serve to relieve some of the angular strain in the G-plane, as evidenced in the crystal structures of hexadentate [M(1,3-pdta)]$^{n-}$ chelates (M = Co(III),[27] Cr(III),[28] Rh(III),[28] Fe(III),[11] V(III),[29] or Cu(II)[30]).

Our interest in a diaminopolycarboxylate metal complexes is related to the involved stereochemistry and to study factors determining the coordination number (C.N.) and structural types of such complexes. This paper deals with the preparation of an octahedral complex, Mg[Ni(1,3-pdta)]•8H_2O (**1**), for which the data of an X-ray structural analysis have been reported. The structural parameters and strain analysis data of this complex and the other [M(1,3-pdta)]$^{n-}$ complexes of known structures are compared and discussed in relation to their octahedral distortion. Spectral data of the complex studied (IR-carboxylate region and electronic absorption) are also given and discussed.

Experimental

Preparation of Magnesium (1,3-Propanediaminetetraacetato)nickelate(II) Octahydrate, Mg[Ni(1,3-pdta)]•8H_2O (1). After 8.43 g (0.0300 mol) of $NiSO_4$•7H_2O were dissolved in 80 ml of water, the solution was stirred at 80 °C for 10 min. To this solution, solid Ba_2(1,3-pdta)•2H_2O[30] (18.39 g, 0.0300 mol) was added and the resulting light-blue solution was then stirred at 80 °C for 3 h. During this process, the volume of the reaction mixture was maintained by the addition of hot water, and the pH of the mixture was kept at 7. After the deposited $BaSO_4$ was removed by filtration, the filtrate was reduced to 60 ml and then poured into a 5×60 cm column containing Dowex 1X8 (200–400 mesh) anion-exchange resin in the Cl^- form. After the column was washed with H_2O, a 0.05 M $MgCl_2$ solution was used for elution (ca. 0.5 ml min^{-1}). One band with 2− charge appeared on the column. The obtained eluate was reduced to 150 ml and then allowed to stand at room temperature for several days. Light-blue crystals were collected, washed with ethanol and then ether, and air-dried. Yield 10 g (63%) of Mg[Ni(1,3-pdta)]•8H_2O. The complex was recrystallized from warm water after standing at room temperature. Found: C, 24.90; H, 5.82; N, 5.32%. Calcd for Mg[Ni(1,3-pdta)]•8H_2O = $MgNiC_{11}H_{30}N_2O_{16}$ (fw = 529.36): C, 24.96; H, 5.71; N, 5.29%.

Physical Measurements. Mg[Ni(1,3-pdta)]•8H_2O (1): A blue rod crystal having approximate dimensions of 0.20 × 0.30 × 0.60 mm, obtained from an aqueous solution, was used for X-ray data collection. Intensity measurements were made on a Rigaku AFC7S diffractometer using graphite-monochromated Mo $K\alpha$ radiation $\lambda = 0.71069$ Å) at 23 °C. Crystal data: $MgNiC_{11}H_{30}N_2O_{16}$ (fw = 529.36), orthorhombic, space group *Pnna* (# 52), a = 13.251(2), b = 11.645(2), c = 13.818(3) Å, V = 2132(1) Å^3, Z = 4, D_c = 1.649 g cm^{-3}, $F(000)$ = 1112.0, $\mu(\text{Mo}K\alpha)$ = 10.20 cm^{-1}.

The structure was solved by the Patterson heavy-atom method,[31] expanded using Fourier techniques,[32] and refined by a least-squares techniques to R = 0.056 and R_w = 0.053 for 1340 reflections ($I > 3.00\,\sigma(I)$) of 2455 collected over the range $2\theta < 55.0°$. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms, excluding those of water molecules, were included, but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[33] All calculations were performed using the teXsan crystallographic software package.[34]

Lists of the structure factors, the positional parameters for the non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atom, positional parameters for the hydrogen atoms and other relevant crystallographic data have been deposited as Document No. 74022 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 154042.

IR spectra in the solid state were recorded on a JASCO FT/IR-5300 spectrophotometer using KBr pellets.

Electronic absorption spectra were recorded on a Varian Cary 17D spectrophotometer. For these measurements, about 4×10^{-2} mol dm^{-3} aqueous solutions were used.

Elemental microanalyses for carbon, hydrogen and nitrogen were performed by the Microanalytical Laboratory, Faculty of Chemistry, University of Belgrade.

Results and Discussion

Description of the Crystal Structure of Mg[Ni(1,3-pdta)]•H_2O (1). An ORTEP drawing of the complex anion, $[Ni(1,3\text{-pdta})]^{2-}$, is depicted in Fig. 1, and the selected bond lengths and valency angles are listed in Table 1.

The structural unit consists of $[Ni(1,3\text{-pdta})]^{2-}$ and $[Mg(H_2O)_6]^{2+}$ octahedra, and two water solvent molecules. In the complex anion (Fig. 1), the Ni(II) ion is encircled by all of the donating atoms (2N and 4O) of the ligand to form an octahedral geometry. The C_2 symmetry axis of the complex passes

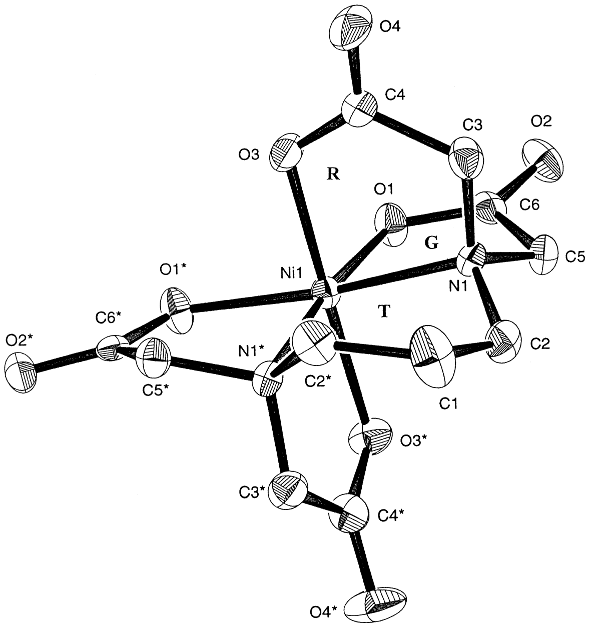

Fig. 1. Molecular Structure (ORTEP) of the $[Ni(1,3\text{-pdta})]^{2-}$ anion in Mg[Ni(1,3-pdta)]•8H_2O.

Table 1. Bond Distances (Å) and Bond Angles (°) with esd's in Parentheses for Mg[Ni(1,3-pdta)]•8H_2O (**1**)

Ni(1)–O(1)	2.026(5)	Mg(1)–O(6)	2.076(5)	O(3)–C(4)	1.269(8)	N(1)–C(5)	1.477(8)
Ni(1)–O(3)	2.078(5)	Mg(1)–O(7)	2.102(5)	O(4)–C(4)	1.233(8)	C(1)–C(2)	1.533(9)
Ni(1)–N(1)	2.073(6)	O(1)–C(6)	1.262(8)	N(1)–C(2)	1.478(8)	C(3)–C(4)	1.52(1)
Mg(1)–O(5)	2.092(5)	O(2)–C(6)	1.246(8)	N(1)–C(3)	1.479(8)	C(5)–C(6)	1.532(9)

O(1)–Ni(1)–O(1)*	99.4(3)	C(2)–N(1)–C(3)	110.7(6)
O(1)–Ni(1)–O(3)	92.1(2)	C(2)–N(1)–C(5)	110.0(5)
O(1)–Ni(1)–O(3)*	91.0(2)	C(3)–N(1)–C(5)	110.8(5)
O(1)–Ni(1)–N(1)	82.5(2)	C(2)–C(1)–C(2)*	120.7(8)
O(1)–Ni(1)–N(1)*	173.3(2)	N(1)–C(2)–C(1)	115.1(6)
O(3)–Ni(1)–O(3)*	175.1(3)	N(1)–C(3)–C(4)	115.1(6)
O(3)–Ni(1)–N(1)	82.5(2)	O(3)–C(4)–O(4)	126.3(7)
O(3)–Ni(1)–N(1)*	94.2(2)	O(3)–C(4)–C(3)	117.3(7)
N(1)–Ni(1)–N(1)*	96.3(3)	O(4)–C(4)–C(3)	116.3(7)
Ni(1)–O(1)–C(6)	115.0(4)	N(1)–C(5)–C(6)	111.0(6)
Ni(1)–O(3)–C(4)	115.7(5)	O(1)–C(6)–O(2)	125.2(7)
Ni(1)–N(1)–C(2)	111.8(4)	O(1)–C(6)–C(5)	115.3(6)
Ni(1)–N(1)–C(3)	109.2(4)	O(2)–C(6)–C(5)	119.4(7)
Ni(1)–N(1)–C(5)	104.0(4)		

*(i) = x, $1/2 - y$, $1/2 - z$.

through the Mg, Ni and C(1) atoms and bisects the N(1)–Ni–N(1)* bond angle, making the two glycinate R rings (as well as the G rings) identical. The values of the Ni–L bond distances and angles in the [Ni(1,3-pdta)]$^{2-}$ (**1**) are as expected compared with those obtained for related complexes.[7,16,26,35] The *cis* angles at the Ni(II) ion (Table 1) range from 82.5(2) to 99.4(3)° and the *trans* ones are 173.3(2) and 175.1(3)°. The six-membered (T) ring utilizes a two-fold symmetry axis in the crystal and adopts a *skew-boat* conformation (δ for the enantiomorph presented in Fig. 1 having Λ absolute configuration). The R rings are almost planar (in an *envelope* conformation), while the G-rings are much more puckered and are halfway between an *envelope* and *twist* conformations.

The packing in the structure is determined by an extended network of relatively strong hydrogen bonds predominantly involving water molecules (coordinated to Mg(II) or two water solvent molecules) and carboxylate oxygens. The two coordination polyhedra are joined by hydrogen bonds in three dimensions. The carbonyl oxygen atoms (O(2), O(2)* and O(4), O(4)*) are involved in hydrogen bonding, and such an effect causes a weakening in the C=O (1.21(3) Å)[36] bond distances (Table 1).

Structural Parameters and Strain Analysis of [M(1,3-pdta]$^{n-}$ Complexes in Relation to Their Octahedral Distortion. Some structural parameters (the mean M–L bonds and some bond angles) in [M(1,3-pdta)]$^{n-}$ chelates are given in Table 2 (complexes **1**–**7**). For complexes **1**–**6**, as expected for glycinates coordinated axially,[12–18] the mean the M–O(R) distances are slightly shorter than the mean M–O(G) distances, with an exception for complexes **1** and **5**,[11] where the equatorial M–O(G) bonds are on average shorter than the M–O(R) bonds. However, the mean M–O distances of these complexes are shorter than the mean M–N distances, and increase exactly with increasing size of the ionic radii.[37] Moreover, these bond distances are nearly equal for complexes **1** and **6** (Table 2).

Though the symmetry about Co(III) (**2**)[27] is that of an almost regular octahedron, except for the N–Co–N angle (99.0(3)°, Table 2), the other metal ions attain octahedral symmetry with varying degrees of distortion, reflecting their large ionic radii. The Ni(II) (**1**), Rh(III) (**6**)[28] and Cu(II) (**7**)[30] having a larger ionic radii than both V(III) (**4**)[29] and Fe(III) (**5**),[11] attain higher octahedral symmetry than either of these metal ions. The O(R1)–M–O(R2) angle of the V(III) complex deviates from the octahedral angle to a greater extent than does the corresponding angle of the Fe(III) complex, and *vice versa* for the O(G1)–M–O(G2) angle (Table 2). Althongh the two complexes Ni(II) (**1**) and Cu(II) (**7**)[30] show the expected distortion, a greater deviation of the O(R1)–M–O(R2) angle was realized for the tetragonally elongated complex **7**[30] than for complex **1,** and *vice versa* for the O(G1)–M–O(G2) angle. Of the three Cartesian axes, the O(R1)–M–O(R2) angles of the listed complexes deviate minimally, except for **4**[29] and **7**[30] (13.13 and 8.7°, respectively).

Strain-analysis data are available[13] for complexes of Co(III) (**2**) and Cr(III) (**3**) (Table 3). For the other 1,3-pdta complexes (**1** and **4**–**7**) the corresponding data are reported here. For a comparison, data are given in Table 3 for the M–edta complexes of known structures[1,3–7] and strain characteristics.[13,16,22b] The total deviation of the octahedral angles varies from 33° for **2**[13,27] to 104° for **5**.[11] These values, as expected, are greater for a group of edta complexes and varies from 48° for Co(III)[1,13,16] to 108° for Fe(III).[3,16] In general, these values increase with increasing size of the M ion for each ligand with exceptions for complexes of V(III) (**4**)[29] and Fe(III) (**5**)[11] and the edta complexes of Fe(III)[3,16] and Mn(III),[4,16] which deviate much more from a regular structure.

The conformation of the 1,3-propanedimine (T) ring is that of a *skew-boat*; these chelate rings show positive total deviations (from 31° for **7** to 38° for **4**, Table 3), while the total deviations are negative for the E rings of edta complexes and of approx. 13° (except for Fe(III) (−18°)).[3,16] The bond-angle chelate-ring sums for the R and G rings are as expected.[13,16–18,22b] The total deviation for both groups of complexes varies from −1° to +1° for the R rings (except for **5** (−5°)[11] and for

Table 2. Comparison of M–L Bond Distances (Å) and Some Bond Angles (°) for [M(1,3-pdta)]$^{n-}$ Complexes

M		r_M(Å)[a]	Mean M–L Bond Distance (Å)				Ref.
			M–N	M–O(G)	M–O(R)	M–O	
Co(III)	(**2**)	0.685	1.966	1.904	1.861	1.882	27
Cr(III)	(**3**)	0.755	2.065	1.966	1.945	1.956	28
V(III)	(**4**)	0.780	2.143	1.998	1.957	1.978	29
Fe(III)	(**5**)	0.785	2.193	1.987	1.991	1.989	11
Rh(III)	(**6**)	0.805	2.032	2.044	2.003	2.023	28
Ni(II)	(**1**)	0.830	2.073	2.026	2.078	2.052	This work
Cu(II)[b]	(**7**)	0.870	2.047	1.974	2.272		30

M		Angle (°)			
		N(1)–M–N(2)	O(R1)–M–O(R2)	O(G1)–M–O(G2)	
Co(III)	(**2**)	99.0(3)	179.6(3)	92.6(3)	
Cr(III)	(**3**)	95.8(2)	184.3(2)	99.7(2)	
V(III)	(**4**)	96.67(1)	193.13(1)	102.44(1)	
Fe(III)	(**5**)	94.3 (1)	184.6(1)	112.5(1)	
Rh(III)	(**6**)	98.3 (1)	180.3(1)	97.6(1)	
Ni(II)	(**1**)	96.3 (3)	184.9(3)	99.4(3)	This work
Cu(II)[b]	(**7**)	96.8 (1)	188.7(1)	96.2(1)	

a) Ionic radius for C.N. = 6.[37] b) Tetragonally elongated octahedral complex with two equivalent axial bonds.

Table 3. Strain Analysis of $[M(1,3\text{-pdta})]^{n-}$ Complexes. For Comparison, Data Are Given for Some Edta Chelates

			$\Delta\Sigma^{b)}$			$\Delta(M–O–C)^{c)}$			
M(ligand)	r_M (Å)	$\Sigma\Delta(O_h)^{a)}$	T(E)	R	G	R	G	$\Sigma\Delta(N)^{d)}$	Ref.
(**1,3-pdta**)									
Co(III) (**2**)	0.685	33	+36	+1	−12	+7	+5	15	13,27
Cr(III) (**3**)	0.755	56	+35	+1	−10	+9	+7	14	13,28
V(III) (**4**)	0.780	75	+38	0	−11	+11	+7	14	29
Fe(III) (**5**)	0.785	104	+34	−5	−16	+8	+6	23	11
Rh(III) (**6**)	0.805	57	+36	+1	−12	+6	+4	12	28
Ni(II) (**1**)	0.830	60	+33	+1	−11	+6	+6	11	This work
Cu(II) (**7**)	0.870	64	+31	+1	−10	+3	+5	13	30
(**edta**)									
Co(III)	0.685	48	−12	−1	−9	+5	+3	18	1,13,16
Fe(III)	0.785	108	−18	−6	−13	+5	+5	31	3,16
Mn(III)	0.785	106	−12	0	−12	+11	+9	20	4,16
Ni(II)	0.830	85	−14	−1	−13	+2	+3	23	7,16
Cu(II)	0.870	83	−14	−1	−12	+1	+3	23	5,22b
Zn(II)	0.880	101	−10	0	−11	+5	+5	22	5,16
Co(II)	0.885	106	−14	0	−11	+7	+6	21	6,16

a) $\Sigma\Delta(O_h)$ is the sum of the absolute values of the deviations from 90° of the L–M–L' bite angles.

b) $\Delta\Sigma$(ring) is the deviation from the ideal of the corresponding chelate rings' bond angle sum. A mean value for the two rings (R or G) is reported because the complex ion is expected (in approximation) to have C_2 symmetry.

c) $\Delta\Sigma$(M–O–C) (ring) is the mean value of the deviation of the corresponding rings' M–O–C bond angle from 109.5°.

d) $\Sigma\Delta$(N) is the sum of the absolute values of the deviations from 109.5° of the six bond angles made by the chelate nitrogen atoms. A mean value for the two nitrogens is reported.

$[Fe(edta)]^-$ (−6°))[3,16] and of approx. −11° for the G rings (except for **5** (−16°)).[11] The deviation of the M–O–C bond angle varies from +3° to +11° and from +4° to +7° for the R and G rings, respectively, and the value is nearly of the same order of magnitude for both kinds of rings, as was the case for $[M(edta)]^{n-}$ complexes.[13,16,22b] As expected,[22b] the corresponding Cu–O–C(R) bond angle deviates minimally for both tetragonal complexes (+3° for **7**[30] and +1° for $[Cu(edta)]^{2-}$ [5,22b]).

The effect of chelation[14] on the distortion of the tetrahedral bonding geometry of the nitrogen atoms is much greater for $[M(edta)]^{n-}$ than for $[M(1,3\text{-pdta})]^{n-}$ complexes (Table 3). The total deviation about the N atoms in complex (**1**) sums to roughly 11° and this value for 1,3-pdta complexes varies from 11 to 15° (except for **5** (23°)).[11] The total deviation about the chelating N atoms measured for the $[M(edta)]^{n-}$ complexes [13,16,22b] sums to 18–23° (except for Fe(III) (31°)).[3,16] Although the G rings of complexes considered remained relatively strained, the presence of the T rings appears to compensate for the distortion induced in the $[M(1,3\text{-pdta})]^{n-}$ coordination polyhedra.

Although ionic radius of Ni(II) is the largest among the ions whose 1,3-pdta complexes have the usual octahedral structures, the obtained structural data for the complex studied (**1**) are quite reasonable and expectable (Tables 2 and 3). On the contrary, the strain analysis data presented for complexes of V(III), Fe(III) and Mn(III) were found to be exceptional in many cases. The coordination structure of these metal ions is more flexible than that of the other metal ions, indicating that the coordination bonds in these complexes are more ionic. Therefore, the difference in the nature of the coordination bonds of these complexes would be responsible for their greater octahedral distortion with respect to the size of the ionic radii[37] than among the other complexes listed (Table 3).

Spectral Characteristics of the Complex. In an expected IR carboxylate region,[16,17,22–25b] complex (**1**) exhibits only one very strong band at 1592 cm^{-1}, assigned to the asymmetric stretch of coordinated carboxylates contained in a glycinate residue (R and G rings). One strong band appearing at 1406 cm^{-1} was tentatively assigned to the $\nu_s(COO^-)$. In this sense, the reported data have a diagnostic value in routine study of the product synthesized. The ligand field absorption spectrum of $[Ni(1,3\text{-pdta})]^{2-}$ (**1**) and the spectra of complexes $[Ni(edtp)]^{2-}$ (edtp = ethylenediaminetetra-3-propionate ion) and *trans*(O_5)-$[Ni(eddadp)]^{2-}$ (eddadp = ethylenediamine-*N,N′*-diacetate-*N,N′*-di-3-propionate ion) of known configuration[16] taken for a comparison, are given in Fig. 2 (Table 4). Complex **1** shows a broadening of the first absorption band (low-energy side, Fig. 2) due to the influence of tetragonality on the spectrochemical behavior of this complex (D_{4h} model).[38] However, its electronic absorption spectrum, as established for the Ni(II)-edta-type[16] and most other Ni(II) complexes,[39,40] can best be interpreted by using an octahedral model: $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (band I); $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (band III) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (band IV). As expected,[16] the aqueous spectrum of **1** shows a shoulder at approximately 13000 cm^{-1}, which occurs on the high-energy side of the first spin-allowed band (band II, Table 4). This band probably arises from a spin-forbidden triplet-to-singlet transition. The calculated energies of the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition from the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition, which has an energy of 10 Dq[41] (Table 4), give strong support for our use of the O_h model for a spectral interpretation. The ratio of two values (the effective value B' in Ni(II) of the complex ion (**1**) and the value of the Racah interelectronic repulsion integral B) gives $\beta = 0.72$; this value is comparable to those obtained for the edta-type[16] and other octahedral Ni(II) complexes.[42,43] The absorption maxima of edtp and eddadp

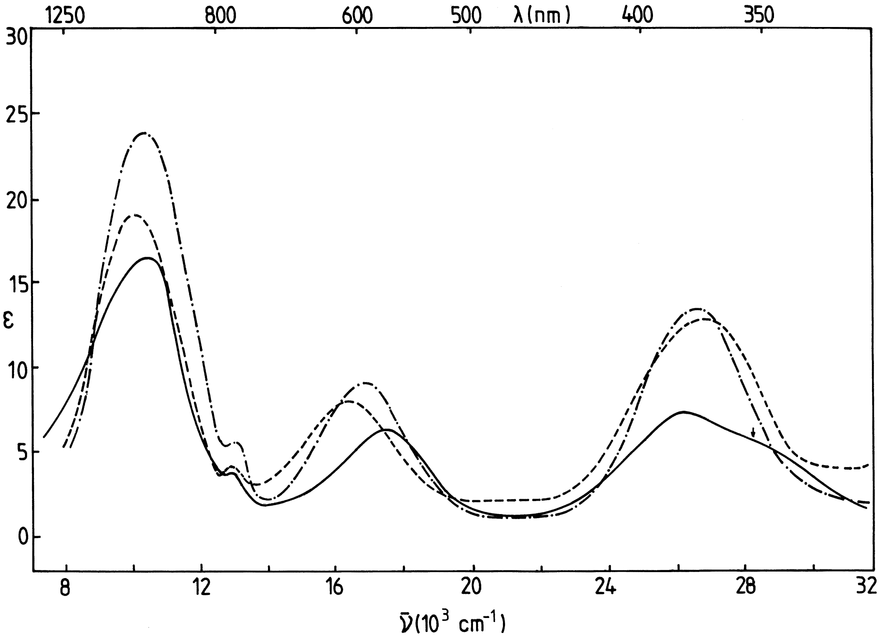

Fig. 2. Electronic Absorption Spectra of:
(---------) [Ni(edtp)]$^{2-}$, (—·—·—·) *trans*(O$_5$)-[Ni(eddadp)]$^{2-}$, and (———) [Ni(1,3-pdta)]$^{2-}$ (**1**).

Table 4. Absorption Data for [Ni(edta-type)]$^{2-}$ Complexes

Complex		Absorption[a)]			Assignments	Ref.
		ν_{obs}	ε	ν_{calc}	O_h	
[Ni(edtp)]$^{2-}$	I	10.02	19.0		$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	16
	II	13.02	4.0		$\rightarrow {}^1E_g(D)$	
	III	16.34	7.8	16.25	$\rightarrow {}^3T_{1g}(F)$	
	IV	27.02	12.6	27.02	$\rightarrow {}^3T_{1g}(P)$	
trans(O$_5$)-[Ni(eddadp)]$^{2-}$	I	10.33	24.0		$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	16
	II	12.90	5.5		$\rightarrow {}^1E_g(D)$	
	III	16.84	9.0	16.48	$\rightarrow {}^3T_{1g}(F)$	
	IV	26.68	13.4	26.68	$\rightarrow {}^3T_{1g}(P)$	
[Ni(1,3-pdta)]$^{2-}$ (**1**)	I	10.50	16.6		$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	This work
	II	12.98	3.9		$\rightarrow {}^1E_g(D)$	
	III	17.54	6.8	16.60	$\rightarrow {}^3T_{1g}(F)$	
	IV	26.37	7.6	26.37	$\rightarrow {}^3T_{1g}(P)$	
		~28.57sh				

a) In units of cm^{-1}×10^3 for the absorption maxima and mol^{-1} dm^3 cm^{-1} for the molar absorbance (ε).

complexes[16] (bands I and III, Table 4) are located at lower energies than those found for complex **1**. The ligand field strength (LFS) for these complexes increases in the order edtp < eddadp < 1,3-pdta with decreasing number of six–membered rings.

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