218. Metal Complexes of Macrocyclic Ligands

Part XXIII1)

Synthesis, Properties, and Structures of Mononuclear Complexes with 12- and 14-Membered Tetraazamacrocycle-*N*,*N*′,*N*″,*N*‴-tetraacetic Acids

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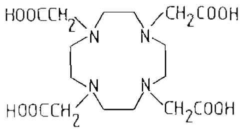
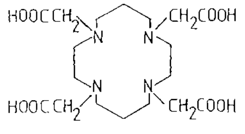
(7.VIII.86)

The two tetraazamacrocycle-*N*,*N*′,*N*″,*N*‴-tetraacetic acids H_4dota and H_4teta form with Ni^{2+}, Cu^{2+}, and Zn^{2+} (M^{2+}) mononuclear complexes MLH_2 and M′[ML], M′ being an alkaline earth ion. The structures of Ni(H_2dota) and Cu(H_2dota) have been solved by X-ray structure analysis. The metal ions are in a distorted octahedral geometry coordinated by four amino N-atoms and two carboxylates. In the case of Cu^{2+}, the distortions are more pronounced than for Ni^{2+} indicating that the *Jahn-Teller* effect is operating. Starting from these two structures, the coordination geometry of the other complexes is discussed using VIS and IR spectra.

Introduction. – The chemistry of tetra-*N*-substituted tetraazamacrocycle tetraacetic acids and their metal-complex formation has been described in several papers. *Stetter et al.* [2] [3] first published the synthesis of a series of such ligands and claimed that they would bind alkaline earth ions better than edta [2]. A more detailed investigation of the complexation equilibria showed that, besides the complexes ML^{2-} described by *Stetter et al.*, also protonated species have to be considered [4]. *Delgado* and *Frausto da Silva* also observed that in some cases Na^+ and K^+ are complexed so that Et_4NOH and $Et_4N^+(NO_3^-)$ must be used as titrating base and as inert electrolyte, respectively [4]. H_4dota and H_4teta were also studied by NMR techniques in regard to their complexation with lanthanides [5], and a proposal was made to use these complexes as NMR-shift reagents [6]. During these studies, a structure analysis of Eu(Hdota)·H_2O was solved [7], showing an ennea coordinate metal ion: Eu^{3+} is lying between the plane of the four N-atoms and that of the four O-atoms and binding an additional H_2O molecule. In a preparative study of the metal complexes of a H_4teta analogon, it was found that these ligands form different complexes with stoichiometry MLH_2, M′[ML], and M_2L [8]. VIS, IR, and NMR spectra were used to deduce the structures of these species. In continuation of such studies, we



H_4 dota



H_4 teta

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1) Part XXII: [1].

have now prepared a series of Cu^{2+}, Ni^{2+}, and Zn^{2+} complexes with the ligands H_4dota and H_4teta in order to understand better the complexation properties of these ligands.

Experimental. – H_4dota [9][3] and H_4teta [10][3] were prepared according to the literature.

Metal Complexes from Acidic Soln. Equimolar amounts (0.2–0.5 mmol) of ligand and a metal salt (chloride or sulfate) were dissolved in 50–100 ml H_2O. In the case of H_4dota, the solns. were adjusted to pH 2.5 and were left for several days to crystallize. In the case of H_4teta, which was dissolved by addition of a small quantity of 0.1M NaOH the complexation is slower, so that we had to heat and increase the pH in order to obtain the complexes. After the reaction had taken place, the pH was adjusted to 3.5–4.0 and the soln. were left for crystallization.

Ni(H_2dota). Violet crystals (80%). Anal. calc. for $C_{16}H_{26}N_4NiO_8$ (461.12): C 41.68, H 5.68, N 12.15; found: C 41.61, H 5.67, N 12.14.

Cu(H_2dota). Light-blue crystals (69%). Anal. calc. for $C_{16}H_{26}CuN_4O_8$ (465.95): C 41.24, H 5.62, N 12.02; found: C 41.37, H 5.63, N 11.93.

Zn(H_2dota). Colourless crystals (72%). Anal. calc. for $C_{16}H_{26}N_4O_8Zn$ (467.77): C 41.08, H 5.60, N 11.98, Zn 13.97; found: C 41.11, H 5.62, N 11.78, Zn 13.9.

Ni(H_2teta). Heating over night. Recrystallized from H_2O. Light-violet crystals (78%). Anal. calc. for $C_{18}H_{30}N_4NiO_8$ (489.2): C 44.20, H 6.18, N 11.45, Ni 12.00; found: C 44.31, H 6.20, N 11.56, Ni 12.4.

Cu(H_2teta)·$2H_2O$. Reaction at pH 6, 1 h at 60°. The precipitate was filtered, dissolved in 0.1M NaOH, centrifuged from small quantity of $Cu(OH)_2$, and the pH adjusted to 3. Light-blue crystals (55%). Anal. calc. for $C_{18}H_{30}CuN_4O_8 \cdot 2H_2O$ (530.03): C 40.79, H 6.47, Cu 11.99, N 10.57; found: C 40.84, H 6.05, Cu 11.6, N 10.61.

Zn(H_2teta)·$4H_2O$. Reaction and crystallization at pH 4. Colourless crystals (15%). Anal. calc. for $C_{18}H_{30}N_4O_8Zn \cdot 4H_2O$ (567.89): C 38.07, H 6.74, N 9.87; found: C 38.01, H 6.59, N 9.81.

Complexes from Alkaline Soln. To the corresponding M(H_2dota) complexes with M = Cu^{2+}, Ni^{2+}, dissolved in a little 0.1M NaOH, an equimolar amount of $M'X_2$ (M' = Ca^{2+}, Sr^{2+}, Ba^{2+}, and X = Cl^-, NO_3^-) was added. Then the pH was adjusted to 10, and enough acetone was added, so that the soln. became turbid. From these solns. the complexes M'[M(dota)] precipitated. M'[Ni(dota)] (M' = Ca^{2+}, Sr^{2+}, Ba^{2+}): light-violet crystals, yields 79–89%; M'[Cu(dota)] (M' = Ca^{2+}, Sr^{2+}, Ba^{2+}): blue crystals, yields 72–79%. Of these, only two were analyzed, whereas the other, being very similar, were characterized only by VIS and IR spectra (see *Results*).

Ca[Ni(dota)]·$5.5H_2O$. Anal. calc. for $C_{16}H_{24}N_4O_8NiCa \cdot 5.5H_2O$ (598.27): C 32.06, H 6.05, N 9.34, Ca 6.68, Ni 9.79; found: C 32.16, H 5.88, N 9.49, Ca 7.30, Ni 9.87.

Ca[Cu(dota)]·$6H_2O$. Anal. calc. for $C_{16}H_{24}N_4O_8CuCa \cdot 6H_2O$ (612.20): C 31.39, H 5.92, N 9.15, Ca 6.54, Cu 10.38; found: C 31.26, H 5.63, N 9.26, Ca 6.36, Cu 10.30.

Measurements. IR spectra were run on a *Perkin Elmer 157G* in KBr pellets. VIS spectra were measured on a *Cary 118C* using the nujol technique [11] or in aq. soln. in 1-cm cells.

Crystal Structure. The atomic parameters of the two structures are available from the *Cambridge Crystallographic Data Centre*. University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. A list of the observed and calculated structure factors is available from the authors.

Ni(H_2dota): orthorhombic, $a = 9.280$ (2), $b = 15.248$ (3), $c = 13.092$ (6) Å, space group *Pccn*, $V = 1852.6$ (3.2) Å^3, $D_{\text{calc.}} = 1.653$, $D_{\text{exp.}} = 1.646$ gcm^{-3}, $Z = 4$, F(000) = 960.0, $\mu = 10.33$ cm^{-1}.

Cu(H_2dota): orthorhombic, $a = 9.444$ (2), $b = 15.300$ (6), $c = 13.109$ (6) Å, space group *Pccn*, $V = 1894.0$ (7.2) Å^3, $D_{\text{calc.}} = 1.634$, $D_{\text{exp.}} = 1.628$ gcm^{-3}, $Z = 4$, F(000) = 964.0, $\mu = 11.42$ cm^{-1}. For the Ni^{2+} and Cu^{2+} complexes, 2327 and 2368 reflections, respectively, were measured with MoKα radiation using the θ–2θ scan mode from $\theta = 2°$ to $\theta = 27°$ on an *Enraf Nonius CAD4* diffractometer equipped with a graphite monochromator. Unit cell parameters were obtained from accurate centring of 25 reflections. The positional parameters of the metal ions were determined by a three dimensional *Patterson* map. The remaining atoms were localized by direct methods, temporarily eliminating large structure factors of the metal ion in site symmetry, and by subsequent difference *Fourier* maps. Least-squares full-matrix refinements using 1270 and 1361 reflections ($F_0 > 2\sigma(F_0)$) gave R values of 0.073 and 0.066 for Ni^{2+} and Cu^{2+}, respectively. Programs used were developed by *Germain et al.* [12], *Sheldrick* [13] and partly by ourselves.

Results and Discussion. – *Structure of the Complexes.* Since the spectral studies in the VIS and IR region are not sufficient for the proposal of structures, we have solved the structures of two complexes using X-ray diffraction measurements.

In both complexes Ni(H_2dota) and Cu(H_2dota), the four N-atoms of the macrocycle and two carboxylates are bound to the metal ion, whereas the other two carboxylates are

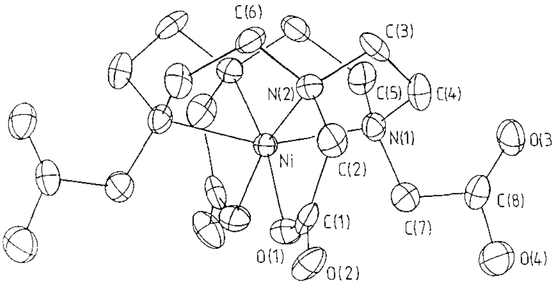

Fig. 1. *ORTEP Plot of Ni(H$_2$dota)*

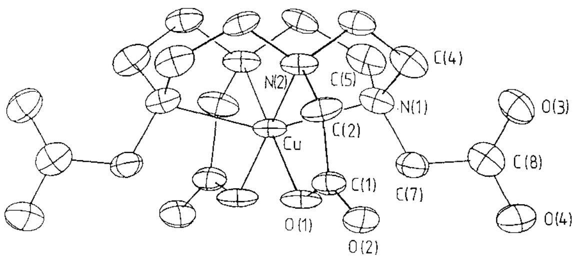

Fig. 2. *ORTEP Plot of Cu(H$_2$dota)*

Table 1. *Bond Lengths and Angles of Cu(H$_2$dota) and Ni(H$_2$dota)*

	Cu(H$_2$dota)	Ni(H$_2$dota)		Cu(H$_2$dota)	Ni(H$_2$dota)
Distances [Å]			*Angles* [°]		
M–O(1)	1.965(5)	2.025(6)	N(1a)–M–N(1b)	152.6(3)	158.6(3)
M–N(1)	2.318(6)	2.177(6)	N(2a)–M–N(2b)	105.0(3)	108.8(2)
M–N(2)	2.107(5)	2.114(7)	O(1a)–M–O(1b)	88.1(2)	87.3(2)
O(1)–C(1)	1.263(9)	1.281(10)	N(1)–M–N(2)	81.1(2)	83.0(3)
O(2)–C(1)	1.250(8)	1.224(10)	N(1)–M–O(1)	104.9(2)	101.0(2)
O(3)–C(8)	1.224(9)	1.193(10)	N(2)–M–O(1)	83.8(2)	82.4(2)
O(4)–C(8)	1.333(10)	1.333(11)	M–N(1)–C(4)	105.6(5)	106.7(5)
N(1)–C(4)	1.488(9)	1.488(11)	M–N(1)–C(5)	104.7(4)	106.3(5)
N(1)–C(5)	1.479(8)	1.499(9)	M–N(1)–C(7)	107.6(4)	109.5(5)
N(1)–C(7)	1.478(9)	1.486(11)	C(4)–N(1)–C(5)	113.9(5)	112.1(6)
N(2)–C(2)	1.502(8)	1.498(10)	C(4)–N(1)–C(7)	112.6(5)	112.1(6)
N(2)–C(3)	1.469(9)	1.487(10)	C(5)–N(1)–C(7)	111.8(6)	110.0(6)
N(2)–C(6)	1.507(–)	1.460(10)	M–N(2)–C(2)	106.9(4)	107.6(5)
C(1)–C(2)	1.531(10)	1.513(13)	M–N(2)–C(3)	109.8(4)	107.8(5)
C(3)–C(4)	1.508(12)	1.496(13)	M–N(2)–C(6)	–	106.5(5)
C(5)–C(6)	1.525(10)	1.583(–)	C(2)–N(2)–C(3)	111.2(5)	111.7(6)
C(7)–C(8)	1.491(11)	1.518(11)	C(2)–N(2)–C(6)	–	111.3(6)
			C(3)–N(2)–C(6)	–	111.5(6)
			M–O(1)–C(1)	117.5(4)	117.6(5)
			O(1)–C(1)–O(2)	125.5(7)	125.1(8)
			O(1)–C(1)–C(2)	117.4(6)	116.0(7)
			O(2)–C(1)–C(2)	117.1(6)	118.9(8)
			N(2)–C(2)–C(1)	112.6(5)	114.8(7)
			N(2)–C(3)–C(4)	113.2(5)	110.1(7)
			N(1)–C(4)–C(3)	112.1(6)	113.4(7)
			N(1)–C(5)–C(6)	112.7(6)	–
			N(1)–C(7)–C(8)	116.9(6)	115.6(7)
			O(3)–C(8)–O(4)	122.3(8)	125.1(7)
			O(3)–C(8)–C(7)	125.3(8)	124.7(8)
			O(4)–C(8)–C(7)	112.5(7)	110.1(7)

protonated and not involved in the coordination. The metal ion is, therefore, in a *cis*-octahedral geometry. The two nitrogens N(2a) and N(2b) (*trans* to each other) and the two oxygens O(1a) and O(1b), stemming from the acetate rests attached to N(2a) and N(2b), form a plane in which the metal ion is also situated. The other nitrogens N(1a) and N(1b) are in the axial position completing the octahedral geometry. The macrocycle is folded along the N(1a)–N(1b) axis and takes the *trans*-I conformation according to the nomenclature of *Bosnich et al.* [14]. The only symmetry element is a C_2 axis perpendicular to the N(2a)–N(2b) edge and lying in the N(2a)–N(2b)–O(1a)–O(1b) plane.

A comparison between the structure of Ni (H_2dota) (*Fig. 1*) and Cu (H_2dota) (*Fig. 2*) is interesting. In the case of Ni^{2+}, the octahedron is only slightly distorted: the axial Ni–N(1) bonds being 2.18 Å compared to 2.11 Å for the equatorial Ni–N(2) bonds. The Ni–O(1) bonds are as expected somewhat shorter 2.03 Å. In addition to these distortions due to bond lenghts, there are also some interesting effects, if one looks at the angles (*Table 1*). Thus, the N(1a)–Ni–N(1b) angle of 158.6° is smaller than expected (180°), which is probably due to the strain inherent in the macrocyclic structure. The N(2a)–Ni–N(2b)–, N(2)–Ni–O(1), and O(1a)–Ni–O(1b) angles are 108.8°, 82.4°, and 87.3°, respectively.

For the Cu^{2+} complex, the distortions are more pronounced. So, the axial Cu–N(1) bonds of 2.32 Å are distinctly longer than those found in the Ni^{2+} complex and also than the equatorial ones with 2.11 Å. The Cu–O(1) bonds with 1.97 Å are also somewhat shorter than those in the Ni^{2+} complex. However, the angles are similar to those observed in the Ni^{2+} complex: N(1a)–Cu–N(1b) 152.6°, N(2a)–Cu–N(2b) 105.0°, N(2)–Cu–O(1) 83.8°, O(1a)–Cu–O(1b) 88.1° (*Table 1*).

Since the Cu^{2+} and Ni^{2+} complexes are isomorphous, one must assume that the differences observed in the two structures are not due to crystal packing, but to the *Jahn-Teller* effect which is active in the d^9-ion Cu^{2+}. That the difference between equatorial and axial Cu–N bonds is not so large in Cu (H_2dota) as it is in other Cu^{2+} complexes, in which equatorial bonds between 1.95 and 2.04 Å and axial ones around 2.65 Å are found [15], is probably due to the fact that the axial N(1)-atoms are part of the macrocyclic unit and cannot be displaced to that extent. There is no indication in these structures that the two COOH groups, which point away from the metal ion, undergo any interaction with another Cu^{2+} or with another COOH group, as is found in the dimers of acetic acid [16].

A study of the literature indicates that most Cu^{2+} complexes of the parent compound 1,4,7,10-tetraazacyclododecane [12]aneN_4 have square pyramidal [17] or trigonal bipyramidal [18] structures, so that a comparison with our complexes is not possible. However, there are examples of *cis*-octahedral geometry in several Co^{3+} complexes such as $[Co([12]aneN_4)(NO_2)_2]Cl$ [19], $[Co([12]aneN_4)(CO_3)](ClO_4)$ [20], and $[Co([12]aneN_4)(acac)](ClO_4)_2$ [21]. This last example is especially interesting, since it shows similar distortions from the octahedral geometry as our complex: So, N_{ax}–Co–N_{ax} is 166.1°. Another example to compare with is $[Cu([12]aneO_4)]Cl_2$, in which the macrocyclic ligand is 1,4,7,10-tetraoxacyclododecane [22]. In this compound, a distorted *cis*-octahedral arrangement is found with a folded macrocycle: the axial Cu–O bonds are distinctly longer (2.34 and 2.40 Å) than the equatorial ones (2.11 and 2.13 Å), and the angle O_{ax}–Co–O_{ax} is 135.2°.

Spectral Properties. After the structural properties of Cu(H_2dota) and Ni(H_2dota) have been discussed, one can try to derive the structures of the other complexes from their

Table 2. *Absorption Spectra of the Cu^{2+} Complexes* (λ_{max} [nm])

	Solid	Solution
$Cu(H_2dota)$	715	pH 13 740
Ca[Cu(dota)]	730	pH 7 735
Sr[Cu(dota)]	730	
Ba[Cu(dota)]	735	
$Cu(H_2teta) \cdot 2H_2O$	650	pH 13 635

spectroscopical properties. The VIS spectra (*Table 2*) were measured in the solid and in solution, whereby the pH had sometimes to be adjusted to solubilize the compounds. For a discussion of the spectra of the Cu^{2+} complexes the two papers of *Billo* [23] and *Kurganov* and *Davankov* [24] are of great help, since they allow to predict the absorption maxima from increments of each coordinated group. So, the absorption maximum of $Cu(H_2dota)$, in which we have two equatorial N, two equatorial COO^- and two axial N, is calculated to be 709 nm, which compares well with the measured value of 715 nm in the solid. There is a small shift of the maximum when $Cu(H_2dota)$ is dissolved in NaOH, or when one looks at the complexes M'[Cu(dota)], in which the two carboxylic protons have been neutralized. So, we would predict that the coordination geometry in $Cu(dota)^{2-}$ is very similar to that of $Cu(H_2dota)$. The small shift could arise from the generation of the two additional negative charges of the two carboxylate groups in $Cu(dota)^{2-}$. However, the situation in $Cu(H_2teta)$ must be completely different, since the absorption maximum is found at 650 nm in the solid and 635 nm in alkaline solution. Two possible chromophores $CuN_2O_2(H_2O)_2$ with two amino and two carboxylate groups in equatorial position and two H_2O axially coordinated, or $CuN_4(COO)_2$ with four N-atoms in the equatorial plane and two axial carboxylates would give λ_{max} 645 nm and 658 nm, respectively, and could equally well be responsible for the absorption band. It is worth pointing out that similar λ_{max} values (660 nm in the solid and 653 nm in H_2O) were also found for the Cu^{2+} complex of a H_4teta analog, for which it was suggested that the metal ion is not in the centre of the macrocycle, but is coordinated by two N-atoms and two carboxylates [8]. The X-ray structure analysis of $Ni(H_2dota)$ has demonstrated the *cis*-octahedral geometry of this compound, and indeed the absorption spectrum of $Ni(H_2dota)$ in the solid and in solution at pH3 (*Table 3*) is typical for high-spin octahedral coordination geometry. Only small shifts are observed on going from $Ni(H_2dota)$ to the complexes containing $Ni(dota)^{2-}$ so that one can assume that, as in the case $Cu(dota)^{2-}$, deprotonation of the acid functions takes place without a substantial geometrical rearrangement. The spectra of the Ni^{2+} complexes with H_4teta also do not differ dramatically from those of $Ni(H_2dota)$, so their geometry must also be octahedral. However, it is not possible to

Table 3. *Absorption Spectra of the Ni^{2+} Complexes* (λ_{max} [nm])

	Solid	Solution
$Ni(H_2dota)$	385, 530, 620 (sh), 800	pH 3 385, 540, 620 (sh), 800
Ca[Ni(dota)]	385, 540, 620 (sh), 800	pH 13 385, 540, 620 (sh), 800
Sr[Ni(dota)]	385, 530, 620 (sh), 800	
Ba[Ni(dota)]	385, 530, 620 (sh), 800	
$Ni(H_2teta)$	380, 540, 620 (sh)	pH 4 345, 560, 800
$Ni(teta)^{2-}$		pH 13 345, 555, 800

predict the exact nature of the chromophore, since there are significant differences between Ni(H_2dota) and Ni(H_2teta) in the IR spectra (*vide infra*).

Important information about the structures of the complexes with H_4dota and H_4teta can also be obtained from their IR spectra listed in *Table 4*.

Table 4. *IR Spectra of the Ligands and their Complexes*

	COO^- or $COO^- \cdots M^{2+}$ [cm^{-1}]	COOH [cm^{-1}]	NH^+/OH [cm^{-1}]
H_4dota · 2HCl	–	1720	2550
Cu(H_2dota)	1590	1730	–
Ni(H_2dota)	1570	1720	–
Zn(H_2dota)	1570	1720	–
Ca[Cu(dota)]	1600–1610	–	–
Sr[Cu(dota)]	1590–1610	–	–
Ba[Cu(dota)]	1590–1600	–	–
Ca[Ni(dota)]	1590–1610	–	–
Sr[Ni(dota)]	1600	–	–
Ba[Ni(dota)]	1600	–	–
H_4teta	1620	1700	2500–2800
Cu(H_2teta)	1600	1730	2500–2800
Ni(H_2teta)	1600	1740	2600
Zn(H_2teta)	1600	1730	2550

To understand the spectra, it is important to have in mind the results collected by *Nakamoto* [25] on metal complexes with amino acids: typical bands are found at 1750–1700 cm^{-1} for COOH, at 1630–1575 cm^{-1} for COO^-, and at 1650–1590 cm^{-1} for $COO^- \cdots M^{2+}$. In addition, the OH-stretching band is observed in the region 3550–2500 cm^{-1}, NH^+-intercombination bands in the region 3400–2000 cm^{-1}. H_4dota · 2HCl shows no COO^- bands but typical ones for COOH and NH^+. So, in the solid two amino N-atoms and all carboxyl groups are protonated. This is similar to what has been found from NMR data in solution by *Desreux et al.* [26]. On going to the H_4dota complexes, we first note the disappearance of the intercombination bands at 2550 cm^{-1} and the presence of two absorptions in the carbonyl region: the peaks at 1570–1590 cm^{-1} are due to the $COO^- \cdots M^{2+}$ group, whereas those at 1730 cm^{-1} corresponds to the COOH group. This all nicely agrees with the structure obtained from X-ray diffraction. In the species $M(dota)^{2-}$ no COOH bands are found in accordance to the deprotonation of the acid groups. Although COO^- and $COO^- \cdots M^{2+}$ bands strongly overlap, and a clear separation is often not possible, some complexes $M(dota)^{2-}$ show two peaks in the region 1590–1610 cm^{-1}. The IR spectra of Cu(H_2dota), Ni(H_2dota), and Zn(H_2dota) are practically identical so that we expect the same structure for all these species.

The IR spectra of H_4teta and its complexes are somewhat different from those of the analogous H_4dota species. H_4teta exhibits strong intercombination bands between 2800 and 2500 cm^{-1} and two bands in the carbonyl region at 1620 cm^{-1} for COO^- and at 1700 cm^{-1} for COOH. All these bands also exist in the complexes M(H_2teta) so that their structure, as has been already mentioned in the discussion of the VIS spectra, must be different from those of the H_4dota complexes. The band at 1600 cm^{-1} in the complex MLH_2 could be due either to free COO^- or to complexed carboxylate $COO^- \cdots M^{2+}$ or to both, whereas the other ones can be classified as the free ligand. Although we have all this information, it is not possible at the moment to propose structures for the M(H_2teta) complexes which would account for the properties of the VIS and IR spectra.

The support of this study by the *Swiss National Science Foundation* (Project No. 2.021.0.83) is gratefully acknowledged.

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