toroid. However it must also be borne in mind that the residual coordinating ability of nickel in $Ni_8(SCH_2COOEt)_{16}$ is very weak.

It is possible that by changing (increasing) the even number of segments the toroid size could change to accommodate guest molecules.

Conclusions

The inclusion of a molecular species, viz. an attached ester function, inside a macrocyclic polymetallic toroid $Ni_p(SR)_{2p}$, as suggested first by Dahl,[4] has been observed in $Ni_8(SCH_2COOEt)_{16}$, which is the first octagonal toroid.

The sizes of toroidal molecules $Ni_p(SR)_{2p}$ are not dominated by the stereochemistry at Ni or SR but can be determined by factors such as steric repulsions between ligand substituents (p = 4, four segments, square) or the van der Waals volume of an internal group (p = 8, eight segments, octagonal). In the absence of these factors, the hexagonal toroid with six segments is favored. It is possible that larger toroids with more than eight segments will occur as hosts for guest molecules of van der Waals diameter larger than the ethyl ester function.

Acknowledgment. We are grateful to Dr. R. O. Gould for access to unpublished results.[7] Kerry Edwards provided experimental assistance, and Don Craig collected the diffraction data. This research is funded by the Australian Research Grants Scheme.

Registry No. $Ni_8(SCH_2COOEt)_{16}$, 95045-16-2.

Supplementary Material Available: A tabulation of all atomic coordinates and thermal parameters and a listing of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of the Witwatersrand, Johannesburg, South Africa

Crystallographic and Thermodynamic Study of Metal Ion Size Selectivity in the Ligand 1,4,7-Triazacyclononane-*N*,*N'*,*N''*-triacetate

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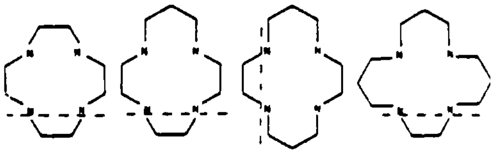
The crystal structures of $H_3O[Ni(TACNTA)]$ (I) and $[CuCl(TACNTAH_2)]$ (II) are reported (TACNTA = 1,4,7-triazacyclononane-*N*,*N'*,*N''*-triacetate). I crystallizes in space group $P3c1$, with cell constants $a = b = 8.529$ Å, $c = 12.757$ Å, $\alpha = \gamma = 90°$, and $\beta = 95.30°$. The structure was refined to a conventional R factor of 0.0833. Of particular interest was the rather short Ni–N bond length of 2.04 Å. It was concluded that this represented the high packing efficiency of the ligand around Ni(II) rather than compression. Also of interest was the hydronium ion, which was found to be disordered in the structure. The complex is unique in crystallizing as an acid, rather than having protonated carboxylate groups, as is found for other complexes of poly(amino carboxylates). Structure II crystallizes in space group $P2_12_12_1$, with cell constants $a = 13.405$ Å, $b = 11.151$ Å, $c = 10.400$ Å, and $\alpha = \beta = \gamma = 90°$. A conventional R factor of 0.0616 was achieved. The coordination sphere around copper consists of two short Cu–N bonds of 2.07 and 2.04 Å and a long Cu–N bond of 2.38 Å. The unprotonated acetate is coordinated to the copper with a normal in-plane Cu–O length of 1.96 Å, while a protonated acetate occupies the axial site with a Cu–O length of 2.56 Å. The chloride occupies a position in the plane with a Cu–Cl length of 2.30 Å. The pK_a values of TACNTA were determined to be 11.41, 5.74, 3.16, and 1.71, and log K_1 with Mg(II) was found to be 8.93, and for Ca(II) 8.81, at 25 °C in 0.1 M $NaNO_3$. The relatively high stability of the Mg(II) complex as compared with Ca(II) is discussed in terms of the size selectivity of TACNTA toward small metal ions. The unusual stability of the Ni(III) complex of TACNTA is also discussed in terms of the preference of the ligand for small metal ions.

Introduction

A point of potential interest in the chemistry of the tetraaza nitrogen donor macrocycles is the size selectivity for metal ions expected from the cavities of fairly fixed size in the ligands.[1] If we examine the actual variation in log K_1 (the formation constant) for the macrocyclic tetraaza ligands and compare this with the variation for the open-chain analogous (Table I), we see that the variability in log K_1 is no greater in the macrocycles than the open-chain ligands. This rather surprising result reflects the flexibility in the macrocyclic ring recently demonstrated by molecular-mechanics (MM) calculation.[2] Thus, a ligand such as 12-aneN_4 (see Figure 1 for structures of ligands), which in its trans-III conformation[3] has a cavity size such that metal ions with an M–N bond length of 1.82 Å fit best, is able to adapt to larger metal ions by adopting the trans-I conformer, which has a best fit M–N length of 2.11 Å. Other means of relieving steric strain with too-large metal ions are by folding of the macrocycle (the trans-V conformer) or, in the case of Ni(II), by changing spin state from the high-spin to the smaller low-spin electronic configuration.

What is needed to overcome the flexibility of the largely two-dimensional macrocycle is a three-dimensional structure, in which metal ions cannot escape compression simply by folding the macrocycle or dropping down from high spin to low spin. Such a structure is provided by the title ligand, TACNTA (Figure 1), which coordinates octahedrally to the metal ion, offering no escape from compression as long as all the acetate groups remain coordinated. TACNTA was first synthesized by Takahashi and Takamoto,[4] and a crystallographic study of the Cr(III), Cu(II),

Table I. Formation Constants of Tetraaza Macrocycles and Their Open-Chain Analogues[a]



	ligands			
	log K_1(Cu^{2+})			
open chain	20.1	23.2	21.7	17.1
macrocycle	23.3	24.4	26.5	24.4
	log K_1(Zn^{2+})			
open chain	12.0	12.8	11.3	9.4
macrocycle	16.2	15.6	15.5	15.0

[a] From: Martell, A. E.; Smith, R. M. "Critical Stability Constants Constants", First Supplement; Plenum Press: New York, 1982. The Cu(II) constants with the macrocycle are from: Thöm, V. J.; Hosken, G. D.; Hancock, R. D., submitted for publication. The broken lines indicate the bridging ethylene group to be removed from the macrocycle to generate the open-chain analogue. It is seen that the open-chain tetraaza polyamines show greater variation as the number of methylene groups in the ligand is varied than do the macrocyclic forms.

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(1) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.
(2) Thöm, V. J.; Fox, C. C.; Boeyens, J. C. A.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 5947.
(3) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

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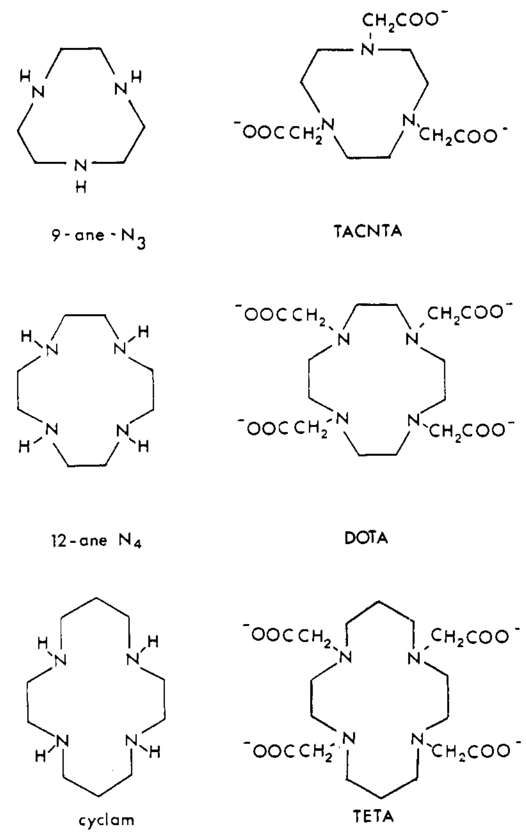

Figure 1. Ligands discussed in this paper.

and Fe(III) complexes was reported by Wieghardt et al.[5] The structure of the Ni(III) complex was recently reported by us.[6]

In this paper we report the structure of the Ni(II) complex, which is quite remarkable in that it was crystallized from nitric acid as the hydronium salt, $H_3O[Ni(TACNTA)]$. In all other comparable complexes such as the EDTA complex, any acid present protonates a carboxylate group, which is then left uncoordinated. The complex $[CuCl(TACNTAH_2)]$ was obtained for Cu(II) under similar circumstances, with the coordinated chloride ion coming from the fact that the ligand is present as a trihydrochloride salt, and its structure is also reported here. These structures are discussed in relation to the possibility that there may be compression of the M–N bonds and in relation to the ligand field (LF) parameters found for the Ni(II) complex, which are higher than those found for the tris(glycine) complex. The oxidation of the Ni(II) TACNTA complex to Ni(III) in nitric acid is also discussed as a size selectivity phenomenon in relation to the much smaller size of Ni(III) than Ni(II).

A different aspect of size selectivity was examined in the formation constants of Ca(II) and Mg(II). Normally, amino carboxylate type ligands such as EDTA complex Ca(II) more strongly than Mg(II).[7] However, Mg(II) is much smaller than Ca(II), and if, as models suggest, TACNTA has a cavity size such that small metal ions should fit best, we might expect to see a reversal of this situation. We thus report here the protonation constants for TACNTA and its formation constants with Mg(II) and Ca(II).

Experimental Section

Synthesis of the Ligand. The ligand is fairly readily synthesized by the method of Takahashi and Takamoto[4] but is extremely difficult to obtain in a pure well-defined state. Thus, Wieghardt et al.[5] were reduced to crystallizing the metal ion complexes from the reaction mixture containing the product and did not actually isolate the ligand itself. The ligand as the trihydrochloride is extremely soluble in water, which can only be removed in a drying pistol. It can thus not be recrystallized from water, and in ethanol partially esterified products are obtained. The trihydrochloride was thus adequate for synthesis of complexes, but not for the potentiometric studies. It was found that a potassium salt, $K(TACNTAH_2)$ could be obtained by adjusting the solution of the trihydrochloride to pH 7 with KOH and then leaving the solution to crystallize. Large colorless crystals of the monopotassium salt were thus obtained, which were used to prepare the stock solution for the glass electrode studies.

Table II. Crystal Data for $H_3O[Ni(TACNTA)]$ and $[CuCl(TACNTAH_2)]$[a]

	$H_3O[Ni(TACNTA)]$	$[CuCl(TACNTAH_2)]$
cell const		
a, Å	8.529 (6)	13.405 (7)
b, Å	8.529 (7)	11.151 (6)
c, Å	12.757 (7)	10.400 (6)
α, deg	90	90
β, deg	95.30 (5)	90
γ, deg	90	90
V, Å^3	803.67	1554.58
d(calcd), g cm^{-3}	1.57	1.73
d(obsd), g cm^{-3}	1.57	1.73
space group	$P3c1$	$P2_12_12_1$
μr (Mo Kα = 0.719 69 Å)	23.41	15.33
F(000)	764.0	836.0
Z	2	4
no. of measd reflcns	372	1165
scan width, deg	1.2	1.1
scan speed, deg s^{-1}	0.04	0.037
θ range	θ–23	θ–23
F cutoff	$F > \sigma(F)$	$F > \sigma(F)$
Final R value	0.0833	0.0616
unexplained electron density, e Å^{-3}	0.659	0.646

[a] For the meaning of abbreviation TACNTA, see Figure 1. $TACNTAH_2$ is the diprotonated form of TACNTA. The crystallographic data collection was carried out at room temperature.

Table III. Fractional Atomic Coordinates (×10^4) for $H_3O[Ni(TACNTA)]$

atom	*x*	*y*	*z*
Ni	0000	0000	5000
O11	7629 (24)	−1564 (22)	5832 (12)
O21	4394 (22)	−194 (26)	5980 (17)
N1	−1133 (27)	−2155 (29)	4000 (14)
C11	6873 (30)	−3176 (28)	5543 (17)
C21	7729 (32)	−3766 (34)	4671 (19)
C31	−2204 (34)	−1847 (34)	3176 (20)
C41	−2703 (43)	−490 (42)	3526 (23)
H211	7118 (272)	−4768 (205)	4069 (123)
H212	8622 (244)	−3862 (335)	5212 (119)
H311	−3325 (168)	−2944 (219)	2760 (145)
H312	−1260 (232)	−1698 (277)	2525 (120)
H411	6778 (323)	−1354 (324)	4104 (164)
H412	1256 (298)	2563 (297)	2765 (154)
O3	6667	−6667	7324 (35)
O3*	6667	−6667	3299 (39)

Potentiometry. The cell and equipment for making the study have been described previously.[8] Equilibration with Ca(II) was rapid, but Mg(II) was rather sluggish, taking several minutes for a steady potential to be obtained. Data reduction was carried out with the program MINIQUAD of Sabatini et al.[9]

X-ray Crystallography. Diffraction quality crystals were selected by standard oscillation and Weissenberg techniques using Cu Kα radiation. Space groups and approximate cell constants were determined at the same time. Intensity data and accurate cell constants were obtained with a Philips PW 1100 diffractometer using Mo Kα radiation (λ = 0.71070

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(4) Takahashi, M.; Takamoto, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3413.

(5) Wieghardt, K.; Bossek, U.; Chaudhuri, P.; Herrmann, W.; Menke, B. C.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 4308.

(6) Van der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 3489.

(7) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1975; Vol. 2.

(8) Hancock, R. D. *J. Chem. Soc., Dalton Trans.* **1980**, 416.

(9) Sabatini, A.; Vacca, A.; Gans, P. *Talanta* **1974**, *21*, 53.

Table IV. Fractional Atomic Coordinates ($\times 10^4$) for the Non-Hydrogen Atoms of [CuCl($TACNTAH_2$)]

atom	*x*	*y*	*z*
Cu	2002	1421	−1846
O11	3107 (6)	274 (7)	8244 (9)
O12	−108 (7)	1242 (10)	4946 (10)
O13	2176 (11)	2072 (10)	13491 (9)
O21	4727 (7)	126 (9)	8013 (11)
O22	1338 (7)	849 (9)	5926 (10)
O23	2454 (8)	3759 (8)	12455 (9)
N1	3082 (8)	2566 (9)	7427 (10)
N2	1023 (8)	2740 (9)	7646 (11)
N3	2202 (8)	2645 (10)	10008 (11)
C11	3936 (9)	627 (12)	7828 (12)
C12	553 (10)	1370 (13)	5892 (13)
C13	2247 (11)	2726 (13)	12407 (15)
C21	3912 (10)	1733 (12)	6994 (14)
C22	188 (9)	2229 (11)	6924 (14)
C23	2084 (11)	2006 (14)	11187 (14)
C31	2567 (10)	3192 (13)	6364 (14)
C32	665 (12)	3266 (15)	8843 (16)
C33	3271 (12)	2974 (16)	9815 (16)
C41	1577 (9)	3675 (13)	6830 (14)
C42	1487 (11)	3649 (15)	9791 (15)
C43	3457 (10)	3402 (13)	8451 (13)
Cl	3271 (12)	2974 (16)	9815 (16)

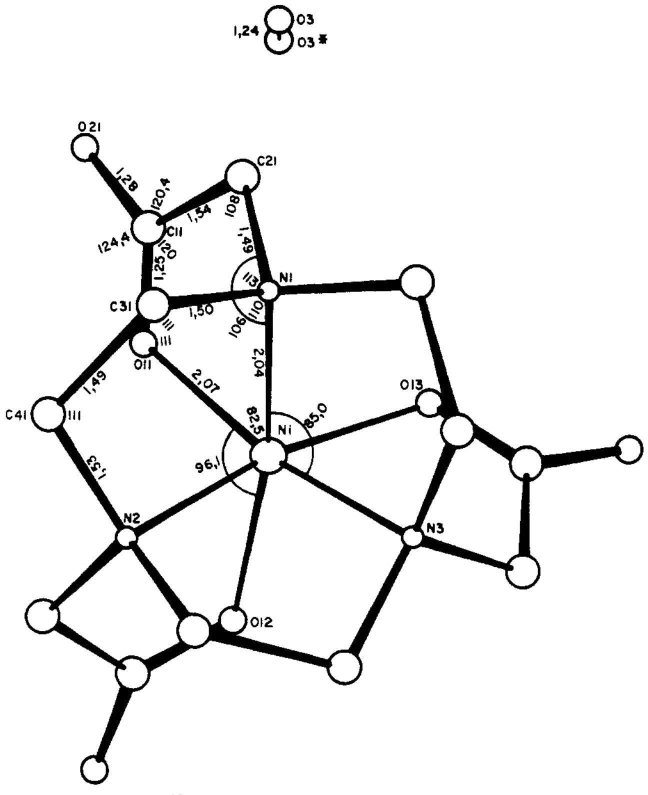

Figure 2. ORTEP[19] drawing of the H_3O[Ni(TACNTA)] structure, showing important bond lengths and bond angles. The two atoms indicated as O3 and O3* are the disordered oxygens of the hydronium ion, each having site occupancy factors of 50%, and are 1.24 Å apart.

Å). The structures were determined by Patterson and Fourier techniques, using the SHELX program.[10] The crystal data are seen in Table II. Fractional atomic coordinates for H_3O[Ni(TACNTA)] are seen in Table III and for [CuCl($TACNTAH_2$)] are in Table IV. The anisotropic thermal parameters given as supplementary material are coefficients in the expansion $T = \exp[-2\Pi^2 \sum_i \sum_j h_i{}^* a_j{}^* u_{ij}]$. The numbering schemes and important bond angles and lengths are seen in Figures 2 and 3. Stereoscopic views of the complexes are seen in Figures 4 and 5.

Spectroscopic Measurements. Electronic spectra were recorded on a Cary 2300 UV–visible spectrophotometer.

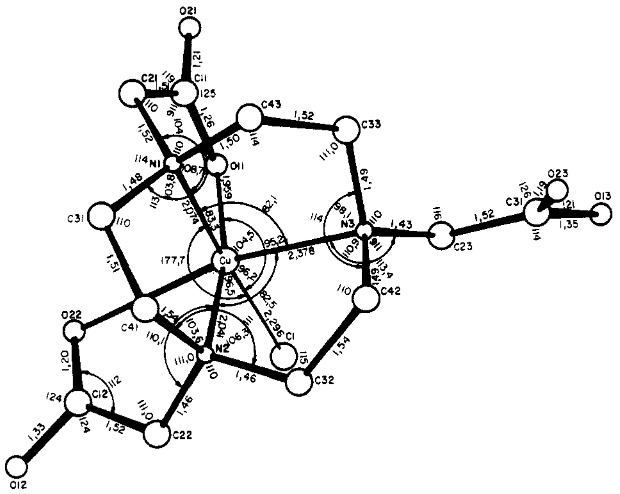

Figure 3. ORTEP[19] drawing of the complex [CuCl($TANCTAH_2$)], showing the numbering scheme and important bond lengths and bond angles.

Table V. Metal-to-Ligand Bond Lengths and Twist Angles in TACNTA Complexes[a]

metal ion	M-N[b]	M-O[b]	twist angle[c]	ref
Ni(III)	1.92	1.92	6.9	6
Ni(II)	2.04	2.08	12.0	this work
Cr(III)	2.06	1.96	11.0	5
Cu(II)[d]	2.12	2.07	33.4	5
Fe(III)[d]	2.18	1.96	35.0	5

[a] For definition of twist angle, see text. [b] Units are Å. [c] Units are deg. [d] Type II structure, whereas all other complexes have type I, as discussed in text.

Results and Discussion

The hydronium ion in the structure of H_3O[Ni(TACNTA)] was found to be disordered, as seen in Figures 2 and 5. That this is actually a hydronium ion, and not a water molecule, is shown by dissolving the complex in water, when acidic solutions with pH values in line with what would be expected if H_3O[Ni(TACNTA)] is a strong acid are obtained. Two possible arrangements exist for the acetate groups on the pseudooctahedral complexes of TACNTA. The base fragment 9-aneN_3 is chiral once coordinated to a metal ion. For a given arrangement of the 9-aneN_3 base fragment, the acetate groups may thus be oriented in a clockwise or anticlockwise fashion. We have designated[6] these two forms the type I and type II forms. The type I form is as seen in Figures 2 and 5 for Ni(II) and is also found[5,6] in Cr(III) and Ni(III). The type II form is found in Fe(III) and in a distorted form in Cu(II).[5] In Figure 6 is shown a stereoview of [Fe(TACNTA)] down the threefold axis, illustrating the type II form. (At the time of the appearance of the paper of Wieghardt et al.[5] reporting the structure of the Fe(III) complex, we had also completed this structure, and our results are in complete agreement with those of Wieghardt et al.)

In Table V are shown metal-to-ligand bond lengths and twist angles in TACNTA complexes. The twist angle (ϕ) is the amount by which the upper three oxygen donor atoms are rotated in projection around the C_3 axis relative to the value for a regular octahedron. Thus, ϕ is zero for regular octahedral coordination, and 60° for trigonal-prismatic coordination. It is seen that the structure of the Fe(III) complex is more nearly trigonal prismatic than octahedral with a value of ϕ of 35°. Table V suggests that the change from type I to type II structure comes as a response to increasing M–N bond length, which forces the metal ion up out of the 9-aneN_3 ring. This causes increasing tension in the M–O bond, which is relieved by switching to the type II structure. The source of this relief to steric strain is seen in that the type II structure has the acetate groups in a much more vertical position with respect to the plane of the 9-aneN_3 base fragment than is

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(10) Sheldrick, G. M. "SHELX Program System"; University of Cambridge: Cambridge, England, 1976.

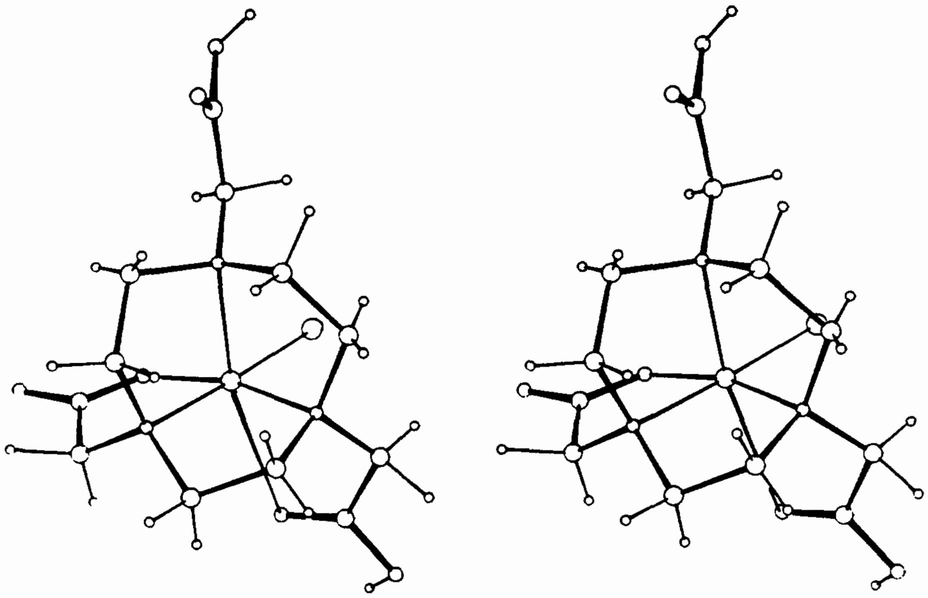

Figure 4. Stereoview of [CuCl(TACNTAH$_2$)] (ORTEP[19]). A point of particular interest is the coordinated protonated carboxylate, with the very long Cu–O bond length of 2.56 Å.

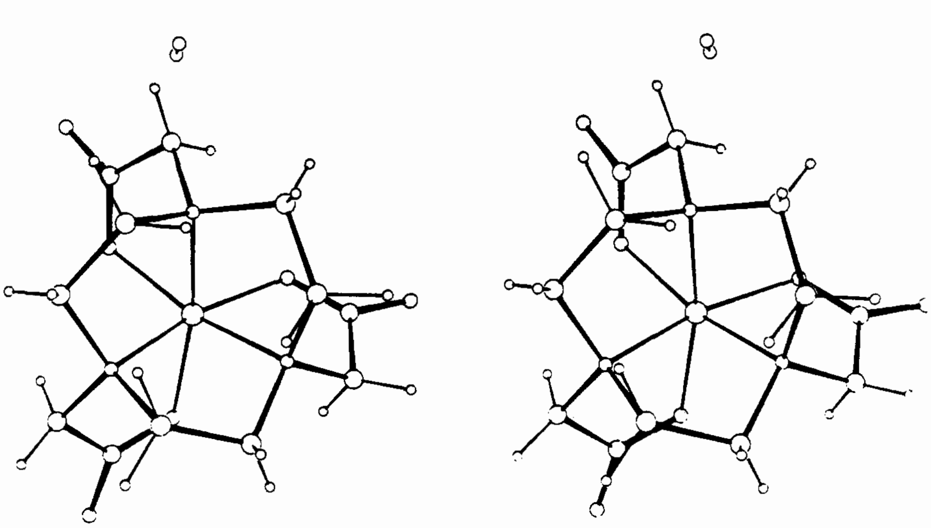

Figure 5. Stereoview[19] of the [Ni(TACNTA)]$^-$ anion, plus disordered hydronium ion. The complex anion has the type I structure defined in the text. This should be compared with the type II structure of the Fe(III) complex in Figure 6.

the case for the type I structure. This is evident from examining Figures 5 and 6. The acetates in the type II structure thus can reach much higher above the plane than is the case for type I and, therefore, accommodate a much larger metal ion.

Table VI. Ligand Field Parameters for Complexes of Ni(II) with a Total of Six Oxygen and/or Nitrogen Donor Atoms[a]

complex[b]	10*Dq*	*B*	ref
[Ni(NH$_3$)$_6$]$^{2+}$	10 750	890	19
[Ni(en)$_3$]$^{2+}$	11 500	860	19
[Ni(9-aneN$_3$)$_2$]$^{2+}$	12 350	(840)	20
[Ni(Gly)$_3$]$^-$	10 100	926	19
[Ni(9-aneN$_3$)(H$_2$O)$_3$]$^{2+}$	10 400		21
[Ni(TACNTA)]$^-$	10 820	911	this work[c]

[a] Units are cm^{-1}. The ligand field splitting parameter, 10*Dq*, and the Racah parameter, *B*, are calculated by assuming regular octahedral coordination geometry. The parentheses around the value of *B* indicate difficulties[20] with mixing of states that affect the calculation of *B*. [b] Ligand abbreviations: en = ethylenediamine, 9-aneN$_3$ = 1,4,7-triazacyclononane. [c] Calculated from the energies of the bands for this complex reported in ref 5.

What is of particular interest in relation to the chemistry of nickel with TACNTA is the very short Ni–N bond lengths of 2.04 (2) Å found for Ni(II) here. Our original suspicion was that this represented compression from the strain-free Ni–N bond lengths of 2.10 Å found for high-spin octahedral Ni(II).[11] Thus, oxidation to the smaller Ni(III) ion might be driven by relief of steric strain. As attractive as this hypothesis is, we do not believe that it is correct. One finds, in the first instance, that there is a shortening of the Ni–N bond length in high-spin octahedral Ni(II) as nitrogens are progressively replaced by oxygens. A large amount of data supports this view, with the series [Ni(en)$_3$]$^{2+}$ (Ni–N = 2.12 Å[12]), [Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$ (Ni–N = 2.09 Å[13]), and [Ni(en)(H$_2$O)$_4$]$^{2+}$ [14] (Ni–N = 2.065 Å) being a good example of the effect. We would thus, in any case, from the presence of three oxygen donors on [Ni(TACNTA)]$^-$, have expected somewhat shorter Ni–N bond lengths. A molecular-mechanics (MM) force field has been developed for high-spin Ni(II) with mixed oxygen and nitrogen donors,[15] and it is capable of reproducing the trend

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(12) Cramer, R. E.; Huneke, J. T.; *Inorg. Chem.* **1978**, *17*, 365.
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(15) Wade, P.; Hancock, R. D., to be submitted for publication.

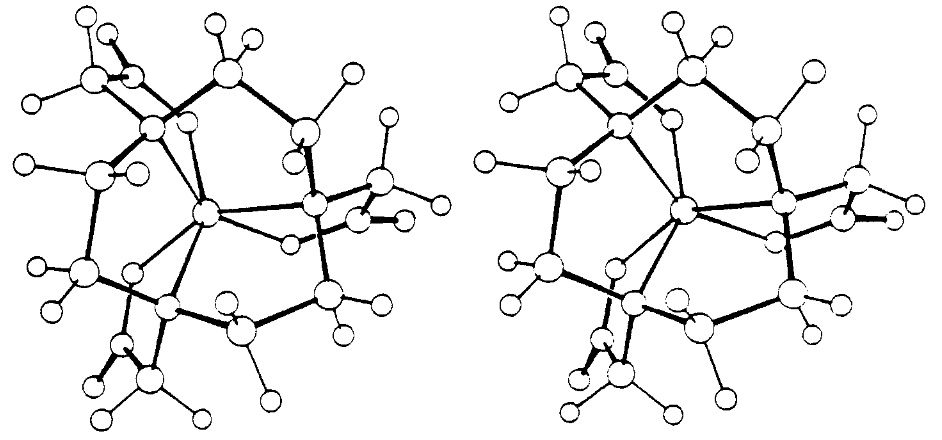

Figure 6. Stereoview[19] of [Fe(TACNTA)] down the threefold axis, demonstrating the type II structure.

Table VII. Protonation Constants and Formation Constants of the Ca(II) and Mg(II) Complexes of a Variety of Ligands[a]

	TACNTA[b]	DOTA[c]	TETA[c]	THEC[d]	EDTA[e]	NTA[e]	9-aneN$_3$[f]
pK_1	11.41 (5)[g]	11.36	11.07	8.80	10.26	9.65	11.3
pK_2	5.74 (5)	9.73	9.75	8.24	6.13	2.48	7.0
pK_3	3.16 (6)	4.54	4.31	2.69	2.67	1.8	
pK_4	1.71 (6)	4.41	3.46	1.2	2.25		
log K_1(Mg^{2+})	8.93 (10)[g]	11.03	3.02	1.86	8.8	5.5	
log K_1(Ca^{2+})	8.81 (3)[g]	15.85	9.48		10.6	6.4	

[a] At 25 °C and ionic strength 0.1. For TACNTA the background electrolyte is NaNO$_3$. [b] This work. Figures in parentheses are standard deviations given by the program MINIQUAD.[9] [c] DOTA is 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetate, while TETA is 1,4,8,11-tetraazacyclotetradecane-*N,N',N'',N'''*-tetraacetate. Data from: Stetter, H.; Frank, W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 686. [d] Madeyski, C.; Michael, J. P.; Hancock, R. D. *Inorg. Chem.*, in press. THEC = tetrakis(2-hydroxyethyl)cyclam. [e] From: Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1974; Vol. 1. NTA = nitrilotriacetate, EDTA = ethylenediaminetetraacetate. [f] Marsicano, F.; Hancock, R. D., to be submitted for publication. [g] The pK_a determinations were carried out by titrating 0.01 M solutions of TACNTA with acid and base so as to cover the pH range from 2 to 11.5. The formation constant studies consisted of a repeat of these experiments with concentrations of metal ion varying from 8 × 10^{-3} to 2 × 10^{-3} M metal ion present.

above of shortening Ni–N bond lengths as en ligands are replaced by water, as well as the bond lengths of some dozen other mixed-donor complexes of Ni(II). This MM force field reproduces the structure of [Ni(TACNTA)]$^-$ very closely and suggests that the short Ni–N bond lengths are not the result of compression, but rather the very efficient packing of the TACNTA ligand around small metal ions. What emerges from calculations on ligands containing carboxylate groups is that they pack very much more efficiently than do water molecules and saturated nitrogen donors. This arises mainly because the oxygen donor on the carboxylate group carries no hydrogens, as do water molecules, which would ordinarily lead to van der Waals repulsions between adjacent coordinated groups. In addition, the carbonyl group is directed away from the coordination site and does not contribute much to the packing density around the metal ion in comparison with the methylene groups on amines such as en, where the hydrogens once again are involved in van der Waals repulsions.

We have recently[16] discussed the concept of packing density around metal ions. For some metal ions such as Co(III), the metal ion is so small that van der Waals repulsions prevent sufficiently close approach of the ligand donor atoms. Thus, the strain-free Co–N bond length is 1.925 Å, but in virtually all complexes of Co(III) with saturated amines, the Co–N bond length is much longer than this, being in the vicinity of 1.98 Å. From the very short Ni–N bond length of 1.92 Å found[6] for the Ni(III) complex with TACNTA, it can be judged that the Ni(III) ion is similar to Co(III), and also low-spin Fe(II) and Fe(III),[17] in being very small. The implication for designing ligands for stabilizing trivalent nickel is thus reasonably clear. What is required are ligands with very efficient packing around the metal ion, so that close approach to the metal ion can be achieved. Other important factors would appear to be high ligand field strength, as judged from the occurrence of Ni(III) in complexes of N donor macrocycles.[18]

In Table VI are seen ligand field (LF) parameters for several complexes of Ni(II) with nitrogen and oxygen donors. It is seen that 10*Dq* for the Ni(II) complex of TACNTA is higher than for other complexes of Ni(II) with three oxygen and three nitrogen donors, e.g. [Ni(H$_2$O)$_3$-9-aneN$_3$]$^{2+}$ and [Ni(Gly)$_3$]$^-$. This can be attributed to two effects. The first is the increasing donor strength[16] of the nitrogen as we pass from ammonia < primary amine < secondary amine < tertiary amine. This is seen for the series [Ni(NH$_3$)$_6$]$^{2+}$, [Ni(en)$_3$]$^{2+}$, [Ni(9aneN$_3$)$_2$]$^{2+}$ in Table VI. Accompanying this must be a favorable steric situation, so that the increasing donor strength is not canceled out by an increase in steric strain. Thus, the high position of 10*Dq* for [Ni(TACNTA)]$^-$ can be attributed to increasing donor strength of the tertiary nitrogens, coupled with a highly favorable steric arrangement.

The structure of [CuCl(TACNTAH$_2$)] seen in Figure 3 shows a very high level of distortion of the coordination sphere as compared with the [Cu(TACNTA)]$^-$ ion studied by Wieghardt et al.[5] Thus, the Cu–N bond lengths in the latter are 2.12, 2.20, and 2.04 Å, while in the former they are 2.07, 2.04, and 2.38 Å. The Cu–O bond lengths are respectively 1.98, 2.21, and 2.14 Å, and in contrast 1.96 and 2.56 Å, with a normal short "in-plane" Cu–Cl length of 2.30 Å. It would appear that full coordination of TACNTA in [Cu(TACNTA)]$^-$ puts considerable constraints on the amount of distortion that can occur, while in [CuCl(TACNTAH$_2$)] the breaking open of this tight coordination

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sphere, with two acetates not coordinated, or only weakly coordinated, allows considerable distortion to occur. This suggests that the reason the acetates on the Cu(II) complex of TACNTA can be protonated is that there is a stabilization produced by the distortion that occurs. In contrast, for the Ni(II) complex to be protonated would require the sterically efficient acetate group to be replaced by a bulkier water molecule, which would disrupt the tight packing of the donor atoms around the metal ion. In the EDTA complex of Ni(II), in contrast, the packing around the metal ion is not efficient, as the metal ion is considerably too large for the ligand, and thus there is no disruption of an efficiently packed set of donor atoms when an acetate is replaced by a water molecule on protonation of the acetate group.

The pK_a values and formation constants of the Mg(II) and Ca(II) complexes of TACNTA are seen in Table VII. Also shown are the values for a selection of amine and amino carboxylate ligands. The first pK_a value for TACNTA is similar to that for 9-aneN$_3$, and for other cyclic poly(amino carboxylates) such as DOTA and TETA (Figure 1). What is of particular interest in Table VII is the relative stability of the Ca(II) and Mg(II) complexes as the cavity size of the macrocycle is decreased. In TETA, with its cyclam base fragment to which the acetates are attached, the Ca(II) complex is over 6 orders of magnitude more stable than the Mg(II), while in DOTA with its 12-membered ring this difference has dropped down to a little less than 5. In TACNTA with it nine-membered ring, the progressive decrease in the relative stability of the Ca(II) complex has reached the point where the Mg(II) complex is now slightly more stable. For both open-chain poly(amino carboxylate) ligands in Table 7, NTA and EDTA, the Ca(II) complex is considerably more stable than that of Mg(II).

The ligand TACNTA shows considerable size selectivity, favoring small metal ions. This leads to stabilization of the small Ni(III) ion to an unusual extent and also a stability for the complex with the small Mg(II) ion, which is unusually high relative to that for the large Ca(II) ion. Of particular interest is the extreme stability of the Ni(II) complex, which we have isolated as a free acid. This unusual stability suggests that the short Ni–N bond lengths observed in the Ni(II) complex of TACNTA do not represent compression, because this should lead to destabilization. Rather, it appears that this shortening of the Ni–N bond is due to the highly efficient packing of TACNTA around the metal ion, which also accounts for the high stability of the complex.

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Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, and fractional atomic coordinates for hydrogen atoms (12 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Fluxional Behavior of 7-Coordinate Complexes: TpMo(CO)$_3$X (X = H, Br, I; Tp = Hydridotripyrazolylborato)

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The halogens Br$_2$ and I$_2$ react with TpMo(CO)$_3^-$ (Tp = hydridotripyrazolylborato) to give the 7-coordinate complexes TpMo(CO)$_3$X. The infrared spectra of these complexes, and of TpMo(CO)$_3$H, are consistent with a 3:4 (four-legged piano stool) structure both in the solid state and in solution. This is confirmed by the solid-state structure of TpMo(CO)$_3$Br: a, b, c = 8.305 (1), 12.032 (1), 8.570 (2) Å; α, β, γ = 104.39 (1), 93.42 (1), 92.03 (1)°; V = 826.9 (2) Å^3, space group $P\bar{1}$, Z = 2. The structure was refined with all non-H atoms anisotropic to conventional agreement indices R_1, R_2 = 0.036, 0.058 based on 1902 reflections with $I > 3\sigma(I)$. The structure may be viewed as a 3:4 piano stool or as a distorted capped trigonal prism with Br capping a quadrilateral face. The ^{1}H and ^{13}C NMR spectra of TpMo(CO)$_3$X (X = H, Br, I) show dynamic C_{3v} symmetry down to −80 °C. This behavior is interpreted in light of EHMO calculations on 3:4 and 3:3:1 (capped octahedron) isomers.

Introduction

Hydridotripyrazolylborate (Tp = HB(C$_3$H$_3$N$_2$)$_3^-$) complexes of molybdenum show many similarities to their cyclopentadienyl (Cp) analogues.[1] However, one difference in behavior is particularly noteworthy: in contrast to the numerous 7-coordinate cyclopentadienyl complexes of the general type CpML$_4$,[2] very few such derivatives have been reported for the Tp complexes. These latter are TpMo(CO)$_3$H, TpMo(CO)$_3$Me, TpMo(CO)$_3$Et,[3] TpW(CO)$_2$(CS)I,[4] and the recently reported TpTaMe$_3$Cl.[5] Even here, however, we have recently shown that the reported alkyl derivatives are in fact the 6-coordinate η^2-acyl complexes TpMo(CO)$_2$(η^2-COR).[6] Although the 7-coordinate alkyl complexes are probably intermediates in the formation of the η^2-acyl complexes from TpMo(CO)$_3^-$ and alkyl halides, these rearrange spontaneously to the 6-coordinate η^2-acyls.[7] Such facile alkyl migrations, which are not observed in CpMo(CO)$_3$R chemistry,[8] were ascribed to the steric and electronic requirements of the Tp ligand.[6,9]

Thus, TpMo(CO)$_3$H is left as the only authentic 7-coordinate Tp–Mo complex, and this hydride also exhibits different behavior when compared to the CpMo(CO)$_3$H hydride. The latter is a weak acid, and its corresponding base, CpMo(CO)$_3^-$, may be protonated with weak acids, e.g. acetic acid.[10] Furthermore, the hydrogen may be removed as a hydride by strong Lewis acids,

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