and the $^{31}P\{^1H\}$ NMR spectrum consisted only of resonances attributable to **2**.

(CH₃C₅H₄)₂TiS₅(PAn)₂. (AnPS₂)₂ (20 mg, 0.05 mmol) was added to a stirred solution of (MeCp)₂TiS₃(PAn) (60 mg, 0.1 mmol) in THF (10 mL) and the resulting solution stirred 24 h. Toluene (10 mL) was added, and the solution was concentrated to 5 mL and cooled to 0 °C. Schlenk filtration gave air-sensitive, purple crystalline (MeCp)₂TiS₅-(PAn)₂·0.5C₇H₈ in 80% yield (55 mg). Anal. Calcd for C₂₆H₂₈O₂S₅P₂Ti·0.5C₇H₈: C, 51.30; H, 4.93; P, 8.98; Ti, 6.94. Found: C, 51.43; H, 4.95; P, 8.90; Ti, 6.73. FDMS (*m/e*): 644, M⁺; 440, (MeCp)₂TiS₃PAn⁺. $^{31}P\{^1H\}$ NMR (40.5 MHz C₆D₆): δ 84.7 (s, 1 P); 80.8 (s, 1.2 P); 33.9 (s, 1.8 P, (MeCp)₂TiS₃(PAn)); 14.8 (s, 1.4 P, (AnPS₂)₂).

(C₅H₅)₂TiO₂S₃(PAn)₂. A mixture of Cp₂TiS₄(PAn)₂ (**2b**) (582 mg, 1.0 mmol) and acetamide (128 mg, 1.0 mmol) in THF (20 mL) was heated to reflux for 1 h. The cooled reaction mixture was evaporated to dryness and the residue extracted with diethyl ether (50 mL), from which a 97% yield (140 mg) of thioacetamide (pure by ¹H NMR) was recovered. The ether-insoluble orange residue was extracted with CH₂Cl₂ (40 mL) and filtered. Orange crystalline **6** was isolated from this filtrate by addition of methanol (10 mL), concentration to 10 mL, and cooling to −30 °C; yield 48% (280 mg). Anal. Calcd for C₂₄H₂₄TiO₄S₃P₂: C, 49.49; H, 4.15; P, 10.63; S, 16.51; Ti, 8.22. Found: C, 48.85; H, 4.16; P, 10.83; S, 15.45; Ti, 8.43. ¹H NMR (CD₂Cl₂): isomer A, δ 8.06 (q, 4 H), 7.00 (q, 4 H), 6.89 (s, 10 H), 3.87 (s, 6 H); isomer B, δ 7.45 (q, 4 H), 7.17 (s, 5 H), 6.68 (q, 4 H), 6.65 (s, 5 H), 3.79 (s, 6 H). The A:B ratio is 2.3:1 (see Figure 2). $^{31}P\{^1H\}$ NMR: δ 86.8 (s, isomer B), 83.8 (s, isomer A). FDMS (*m/e*): 626, M⁺.

From 4 and Ph₂CO. Compound **4** (24 mg, 0.035 mmol) and Ph₂CO (14 mg, 0.077 mmol) were dissolved in ca. 4 mL of dry THF in a 12-mm NMR tube. The ³¹P NMR spectrum of the solution showed that compound **3** was the predominant phosphorus species after 3 h at room temperature. After 8 h, the two isomers of (MeCp)₂TiO₂S₃(PAn)₂ (87 and 84 ppm) are fully formed. This reaction was conducted on a larger scale on a Schlenk line and worked up by chromatography on silica gel. Elution with ether/hexane gave an intense blue band containing Ph₂CS, which was crystallized from hexane at −78 °C and identified by its visible spectrum.

X-ray Crystallography. Orange rectangular crystals of (MeCp)₂TiO₂S₄(PAn)₂ (**3**) were obtained by slow diffusion of methanol

into concentrated dichloromethane solutions. The data collection and structural analysis was performed by Dr. C. S. Day (Crystalytics Co., P.O. Box 82286, Lincoln, NE) employing direct methods. A crystal of dimensions 0.80 × 0.75 × 0.35 mm was mounted on a thin glass fiber and was assigned the space group P$\bar{1}$ with parameters a = 9.458 (3) Å, b = 10.611 (3) Å, c = 15.975 (5) Å, α = 94.96 (2)°, β = 109.34 (2)°, γ = 105.38 (2)°, V = 11431.6 (7) Å³, and ρ_{calcd} = 1.49 g cm⁻³ for Z = 2. The data were collected on a Nicolet autodiffractomer using an ω-scanning technique over the range 3.0 < 2θ < 63.7° at ambient temperatures with monochromatized Mo Kα (λ = 0.71069 Å) radiation. Of the 9805 unique intensities processed, 7288 were observed at the 3.00σ(I) level of confidence and only these reflections were used during the refinement. The data were isotropically corrected for a 5% decline in the average intensity of 6 standards monitored every 300 reflections. The intensity data were corrected empirically for absorption effects with use of ψ scans for 8 reflections having 2θ between 7 and 41° and were then reduced to relative squared amplitudes, |F₀|², by means of standard Lorentz and polarization corrections.

The 37 non-hydrogen atoms were located and thermal parameters determined by SHELXTL, with the hydrogen atom positional parameters fixed. Successful convergence led to conventional residuals of R = 0.037 and R_w = 0.048, with all non-hydrogen atoms refined anisotropically and all hydrogen atoms refined isotropically. Atomic coordinates are presented in Table II.

Supplementary Material Available: Details of the X-ray data collection and structure solution and tables of bond lengths, bond angles, thermal parameters, complete hydrogen atom parameters, and structure factors (50 pages). Ordering information is given on any current masthead page.

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Thermodynamic Studies on Equilibria between the Branched Hexaamine N,N,N',N'-Tetrakis(3-aminopropyl)ethylenediamine (TAPEN) and Hydrogen, Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Ions

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The branched hexaamine N,N,N',N'-tetrakis(3-aminopropyl)ethylenediamine (TAPEN) has been synthesized and characterized. Potentiometric and spectrophotometric studies on the equilibria between TAPEN and hydrogen, Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions have been carried out. The equilibrium constants between TAPEN and the above-mentioned ions have been determined by potentiometry at 25 °C in 0.5 mol dm⁻³ KNO₃ as ionic medium. The presence of many hindered six-membered chelate rings in the 1:1 metal complex has been invoked to explain the low stability of these complexes and the great tendency of TAPEN to form protonated complexes. With the exception of the [Mn(TAPEN)]²⁺ complex, where all six nitrogen donor atoms are involved in the coordination, in all the 1:1 complexes TAPEN acts as a pentadentate ligand. In the case of Ni(II) the presence of a minor, square-planar, low-spin species has been detected.

Introduction

Polyamines, both cyclic and noncyclic, are the ligands studied most with respect to their basicity and coordination capability toward metal ions.[2-4] Continuing our systematic studies on the

thermodynamics of metal complex formation with polyamines as ligands, we have studied the branched polyamine N,N,N',N'-tetrakis(3-aminopropyl)ethylenediamine (abbreviated as TAPEN)


		n=2 ; m=2	PENTEN
		n=2 ; m=3	TAPEN
		n=3 ; m=2	PTETRAEN
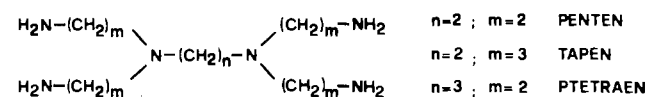
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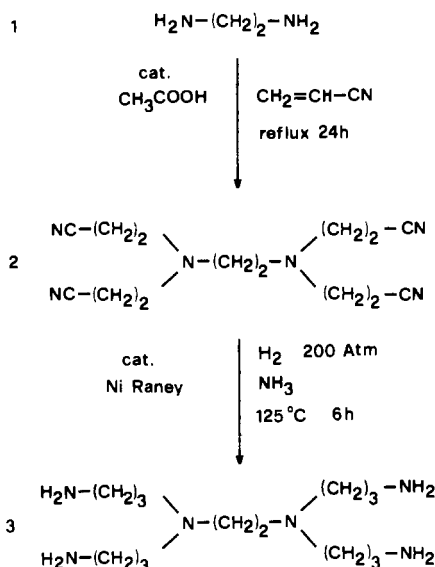
Figure 1. Reaction sequence for the synthesis of the branched hexaamine TAPEN.

and its equilibria with hydrogen, Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions. The following characteristics have made TAPEN worth studying: (i) it forms many protonated complexes; (ii) it forms metal complexes containing chelate rings of different atomicity; (iii) it can be considered the open-chain intermediate in the synthesis of polycyclic polyazamacrocycles. The coordinative behavior of TAPEN is compared with that of the two parent polyamines N,N,N',N'-tetrakis(2-aminoethyl)ethylenediamine (PENTEN)[5] and N,N,N',N'-tetrakis(2-aminoethyl)trimethylenediamine (PTETRAEN).[6]

Experimental Section

Preparation of the Ligand TAPEN. TAPEN·6HCl was prepared by modifying the procedure reported in ref 7 (see Figure 1). The tetranitrile derivative **2** was obtained, as a low-melting solid (mp 64 °C), in high yield (85%) by glacial acetic acid catalyzed cyanoethylation of ethylenediamine. Anal. Calcd for $C_{14}H_{20}N_6$: C, 61.74; H, 7.40; N, 30.86. Found: C, 62.0; H, 7.4; N, 30.7. ^{13}C NMR (CDCl$_3$): δ 17.2, 50.2, 52.9, 119.1. Mass spectrum: m/z 272. The reduction of the tetranitrile has been carried out catalytically with H_2 under pressure with a 60% yield. A 10-g sample of the tetranitrile derivative, 50 cm^3 of concentrated aqueous ammonia, and Raney nickel (5% with respect to the tetranitrile) were placed in an autoclave. The reaction mixture was kept under H_2 pressure (200 atm) at 125 °C for 6 h with stirring. The cooled reaction mixture was then filtered to remove the catalyst (*Caution!* The spent catalyst is pyrophoric when dry and must be treated with care) and rotavaporated to yield a colorless oil. The ligand TAPEN was isolated as the dihydrate hydrochloride derivative by bubbling gaseous HCl through a cooled solution of the above crude product in dry ethanol. The white crystals of TAPEN·6HCl·2H$_2$O were filtered off and washed with dry ethanol. The solid dried under vacuum yield 12.5 g of TAPEN-6HCl·2H$_2$O. Anal. Calcd for $C_{14}H_{46}N_6O_2Cl_6$: C, 30.95; H, 8.54; N, 15.47; Cl, 39.15. Found: C, 31.0; H, 8.3; N, 15.5; Cl, 39.2. ^{13}C NMR (D$_2$O): δ 27.0, 41.0, 52.5, and 53.19. The mass spectrum pattern with the expected mass units has been obtained.

Materials. The potentiometric measurements were carried out in an ionic medium of 0.5 mol dm^{-3} KNO$_3$. Erba products (high-purity grade) were purified by crystallization. Standardized CO$_2$-free solutions of NaOH were prepared as before.[8] Solutions of oxidizable metal salts were made in O$_2$-free solvents and handled under argon. The Fe(II) stock solution was maintained in the reduced form by bubbling H$_2$ gas in the presence of a small quantity of black palladium as catalyst. The concentrations of metal ion solutions were determined gravimetrically by standard methods.

Table I. Logarithms of the Stepwise Protonation Constants at 25 °C in 0.5 mol dm^{-3} KNO$_3$ (Standard State 1 mol dm^{-3})

	log K		
reacn	L = TAPEN[a]	L = PENTEN[b]	L = PTETRAEN[b]
$H^+ + L = HL^+$	10.67 (2)[c]	10.08	10.24
$HL^+ + H^+ = H_2L^{2+}$	10.27 (1)	9.58	9.56
$H_2L^{2+} + H^+ = H_3L^{3+}$	9.91 (2)	8.99	9.18
$H_3L^{3+} + H^+ = H_4L^{4+}$	9.15 (1)	8.42	8.44
$H_4L^{4+} + H^+ = H_5L^{5+}$	6.72 (2)	1.33	2.50
$H_5L^{6+} + H^+ = H_6L^{6+}$	3.42 (1)		

[a] This work. [b] Taken from ref 12. [c] Values in parentheses are standard deviations in the last significant figure obtained by the computer program by using all the experimental curves.

Emf Measurements. The potentiometric titrations were carried out by using the fully automatic apparatus described elsewhere.[9] The experimental readings of the emf were not corrected for the liquid-junction potential, because this effect was negligible in the pH range investigated. The experimental details of the emf measurements have been reported as supplementary material. The computer program SUPERQUAD[10] was used to process the potentiometric data and to calculate both the basicity and the stability constants.

Electronic Spectra. The electronic spectra, at different temperatures and pHs, have been recorded on a Perkin-Elmer Lambda 9 spectrophotometer coupled with a Radiometer potentiometer, Model PHM84. The calculated spectra of the species present in the solutions used in the spectrophotometric studies (see supplementary material for experimental details) have been obtained by following the method reported in ref 11.

Results and Discussion

Protonation. The basicity constants of ligand TAPEN have been reported in Table I. For the purpose of comparison the basicity constants of the related ligands PENTEN and PTETRAEN have also been reported.[12] The polyamine TAPEN behaves as a rather strong base in the first four protonation steps, and the basicity decreases as the degree of protonation increases, due to the electrostatic repulsion between positively charged amino groups. Because of the lower local charge density in a propylenediammonium group than in an ethtlenediammonium group TAPEN is expected to be more basic, in each protonation step, than the related polyamines PENTEN and PTETRAEN. The previous considerations can be invoked to explain the relative high basicity of TAPEN even in the last protonation step (log K_6 = 3.42) as compared to that of PENTEN and PTETRAEN, for which the basicity constant is too low and cannot be measured accurately.[6,7,12]

Complex Formation Constants. In Table II we have reported the logarithms of the equilibrium constants for reactions that have been chosen in order to allow us to examine and discuss the stability of the complexes and the coordinating ability of the ligand TAPEN. TAPEN shows a great tendency to form protonated complexes. This tendency can be explained by the presence of many propylene chains in the ligand and the subsequent formation of many six-membered chelate rings in the metal complex, which are considered to be more strained than the corresponding five-membered chelate rings. The high basicity of TAPEN and the low stability of the six-membered rings will greatly facilitate the ring opening by protonation of the nitrogens bound to the metal ion and make very common protonated species. Furthermore, the high values of the equilibrium constants for the reaction ML^{2+} + H$^+$ ⇌ MLH^{3+} (see Table II), as compared to the first protonation constant of the free ligand, force us to wonder how many donor atoms of TAPEN are involved in the formation of the ML complexes. It is also interesting to compare the stabilities of the metal complexes of TAPEN with those of the related ligands

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Table II. Logarithms of the Equilibrium Constants for Reactions of Complex Formations (L = TAPEN) at 25 °C in 0.5 mol dm^{-3} KNO$_3$ (Standard State 1 mol dm^{-3})

reacn	M = Mn	M = Fe	M = Co	M = Ni	M = Cu	M = Zn
M^{2+} + L = ML^{2+}	6.13 (3)^a	7.92 (1)	10.96 (4)	13.79 (8)	19.58 (2)	12.28 (2)
M^{2+} + H$^+$ + L = MHL^{3+}		17.48 (1)	20.29 (2)	22.99 (7)	29.18 (2)	21.54 (2)
M^{2+} + 2H$^+$ + L = MH$_2$L^{4+}		26.26 (1)	27.95 (1)	30.61 (8)	36.42 (1)	28.67 (3)
M^{2+} + 3H$^+$ + L = MH$_3$L^{5+}			35.61 (3)		40.46 (4)	
ML^{2+} + H$^+$ = MHL^{3+}		9.56	9.33	9.20	9.60	9.26
M^{2+} + HL$^+$ = MHL^{3+}		6.81	9.62	12.32	18.51	10.87
MHL^{3+} + H$^+$ = MH$_2$L^{4+}		8.78	7.66	7.62	7.24	7.13
M^{2+} + H$_2$L^{2+} = MH$_2$L^{4+}		5.32	7.01	9.67	15.48	7.73
MH$_2$L^{4+} + H$^+$ = MH$_3$L^{5+}			7.66		4.04	
M^{2+} + H$_3$L^{3+} = MH$_3$L^{5+}			4.76		9.61	

^{a} Values in parentheses are standard deviations in the last significant figure obtained by the computer program by using all the experimental curves.
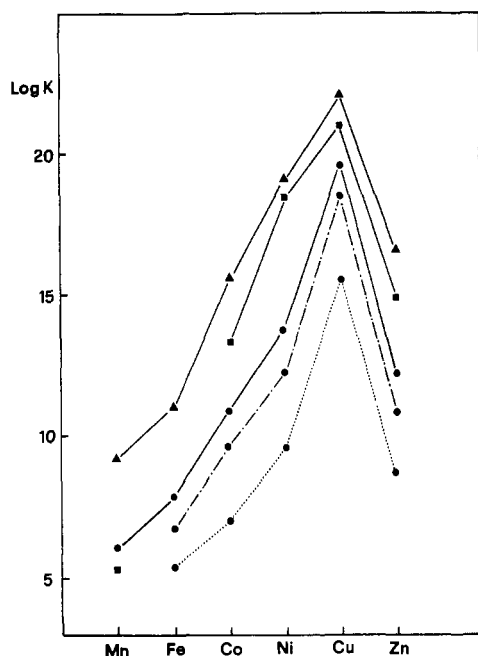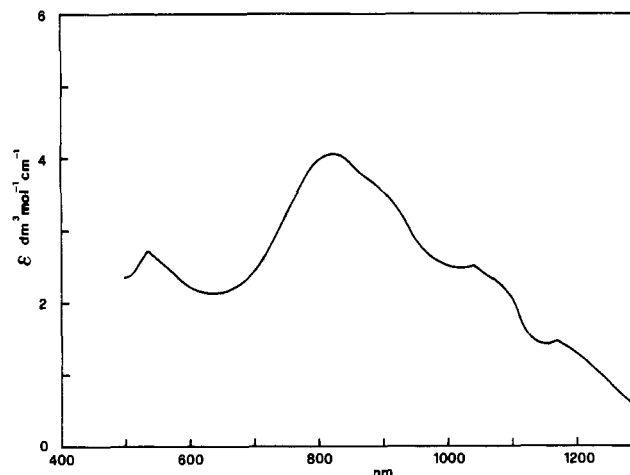

Figure 2. Plot of the logarithms of the equilibrium constants for the reaction M^{2+} + L ⇌ ML^{2+} vs. metal ion type: (−●−) L = TAPEN; (▲) L = PENTEN; (■) L = PTETRAEN; (−·●−·) L = HTAPEN$^+$; (··●··) L = H$_2$TAPEN^{2+}.

Figure 3. Absorption spectrum of [Fe(TAPEN)]$^{2+}$ in 0.5 mol dm^{-3} KNO$_3$.

PENTEN and PTETRAEN. In Figure 2 we have reported the stabilities of the 1:1 metal complex of TAPEN and those of the corresponding complexes of PENTEN and PTETRAEN. TA-PEN forms 1:1 metal complexes that are less stable than those of PENTEN and PTETRAEN. This behavior is expected, because in the complexes of the last two polyamines no or only one hindered six-membered chelate ring can be formed in the ML complexes. It is worthwhile to note the absence of any hydroxo species in the M(II)−TAPEN systems (see Table II). To avoid confusion in the discussion, each metal ion system will be briefly reviewed.

Mn(II). Among the metal ions investigated, Mn(II) is the only one that does not form any protonated species. This can be considered as indirect evidence that all the six nitrogen donor atoms are involved in the coordination of TAPEN to the large Mn(II) ion. Aqueous solutions of [Mn(TAPEN)]$^{2+}$ are colorless; when oxygen is present, a brownish color appears immediately.

Fe(II). In the case of Fe(II) ion three species are formed at equilibrium: [Fe(TAPEN)]$^{2+}$, [Fe(HTAPEN)]$^{3+}$, and [Fe(H$_2$TAPEN)]$^{4+}$. The high value of the equilibrium constant relative to the protonation of the 1:1 complex in forming the monoprotonated complex [Fe(HTAPEN)]$^{3+}$, as compared to the first basicity constant of the ligand, indicates that the protonation involves a nonbound nitrogen atom and TAPEN employs at most five nitrogen donor atoms in the formation of the [Fe(TAPEN)]$^{2+}$ species. In Figure 3 the UV−vis spectrum of the Fe(II)−TAPEN complex is reported. By use of the DISPOL^{13} computer program

the solution is made in such a way that a large amount of the [Fe(TAPEN)]$^{2+}$ species is present together with negligible amounts of [Fe(HTAPEN)]$^{3+}$ and [Fe(H$_2$TAPEN)]$^{4+}$. The spectrum is similar to that of [Fe(PENTEN)]$^{2+}$ reported in ref 6, indicating octahedral geometry. In the presence of oxygen an immediate precipitation of Fe(III) hydrate oxide takes place.

Co(II). The complex [Co(TAPEN)]$^{2+}$ has a lower stability than [Zn(TAPEN)]$^{2+}$ and much lower than that of the analogous complexes of PENTEN and PTETRAEN^{12} (see Figure 2). In successive steps [Co(TAPEN)]$^{2+}$ can add up to three protons to form [Co(HTAPEN)]$^{3+}$, [Co(H$_2$TAPEN)]$^{4+}$, and [Co(H$_3$TAPEN)]$^{5+}$ (see Table II). The analogous polyamines PENTEN and PTETRAEN only form the monoprotonated species.^{12} This large tendency of forming protonated species displayed by the Co(II)−TAPEN system, obviously, is also reflected in the high values for the stepwise protonation constants of the [Co(TAPEN)]$^{2+}$ complex. In particular, the equilibrium constant for the reaction [Co(TAPEN)]$^{2+}$ + H$^+$ ⇌ [Co(HTA-PEN)]$^{3+}$ is very high and is comparable with the first basicity constant of the free ligand. Furthermore, the spectra of [Co(TAPEN)]$^{2+}$ and [Co(HTAPEN)]$^{3+}$, deposited as supplementary material, are essentially the same, which indicates that these species should have the same octahedral coordination geometry. Because in the [Co(HTAPEN)]$^{3+}$ complex only five nitrogen donor atoms are involved in the coordination to the Co(II) ion where one nitrogen atom is protonated, the same should be true also for the [Co(TAPEN)]$^{2+}$ complex. When exposed to air, the [Co(TAPEN)]$^{2+}$ aqueous solution turns from pink to "luteo". However, when the oxidized "luteo" solution is heated and N$_2$ gas is bubbled through, it tends to recover its initial pink color. Further studies on the reversibility of the oxygenation of the [Co(TA-
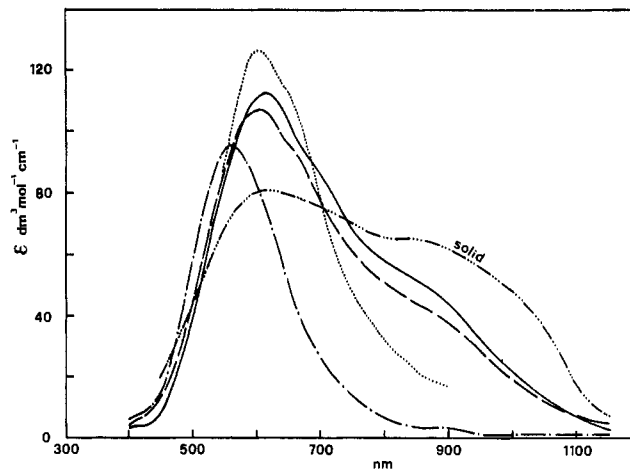
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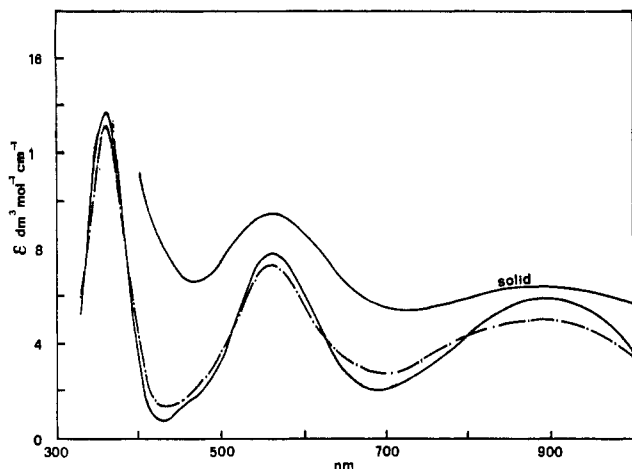
Figure 4. Calculated absorption spectrum of (—) [Ni(TAPEN)]$^{2+}$ and (−·−) [Ni(HTAPEN)]$^{3+}$ in 0.5 mol dm^{-3} KNO$_3$. The spectrum marked "solid" is the reflectance spectrum of the solid Ni(HTAPEN)(ClO$_4$)$_3$ (ordinate in arbitrary scale).

Figure 5. Calculated absorption spectra of Cu(II) complexes formed by TAPEN in 0.5 mol dm^{-3} KNO$_3$: (—) [Cu(TAPEN)]$^{2+}$; (−−) [Cu-(HTAPEN)]$^{3+}$; (−·−) [Cu(H$_2$TAPEN)]$^{4+}$; (···) [Cu(H$_3$TAPEN)]$^{5+}$; (−···) solid Cu(HTAPEN)(ClO$_4$)$_3$ (reflectance spectrum, ordinate in arbitrary scale).

PEN)]$^{2+}$ complex will be carried out.

Ni(II). When aqueous solutions of Ni(II) and TAPEN are mixed, a violet-blue color, characteristic of Ni(II) amine complexes, appears immediately. However, the spectra of these solutions change with time, which indicates that the kinetics of the formation of Ni(II)–TAPEN complexes is rather slow. Reproducible spectrophotometric and potentiometric results are obtained when the initial solutions, made up of Ni(II) and different amounts of neutralized ligand, are boiled for at least 15 min. Once the complexes are formed, their destruction with acid is sufficiently rapid that stable emf measurements in the titration curves are obtained a few minutes after each HCl addition. This equilibration time is also pH-dependent, being longer at lower pH. In the Ni(II)–TAPEN system there are three species: [Ni(TAPEN)]$^{2+}$, [Ni(HTAPEN)]$^{3+}$, and [Ni(H$_2$TAPEN)]$^{4+}$. The calculated spectra for [Ni(TAPEN)]$^{2+}$ and [Ni(HTAPEN)]$^{3+}$ are reported in Figure 4, together with the reflectance spectrum of the solid complex Ni(HTAPEN)(ClO$_4$)$_3$. All spectra, both in solution and in the solid state, are the same and are typical of an octahedral Ni(II) complex. The spectra of [Ni(TAPEN)]$^{2+}$ and [Ni-(HTAPEN)]$^{3+}$ are the same, once again an indication that TA-PEN behaves, at most, as a pentadentate ligand. The visible spectra of the Ni(II)–TAPEN solutions present a small maximum at 470 nm typical of the yellow, low-spin, square-planar Ni(II) complexes with tetraamines.[14] The amount of this yellow species, always very small, is pH-dependent and increases as the pH decreases. The species disappears at high pH. The above considerations allow us to hypothesize that the blue to yellow interconversion equilibrium involves the diprotonated species [Ni(H$_2$TAPEN)]$^{4+}$. If we heat a Ni(II)–TAPEN solution (pH 7) containing an excess of NaClO$_4$, its blue-violet color turns to yellow. Attempts to isolate the "yellow species" by adding acetone yields a powder with a reflectance spectrum characteristic of diamagnetic Ni(II) complexes but also containing the inert salt NaClO$_4$.

Cu(II). The Cu(II) complex with TAPEN, [Cu(TAPEN)]$^{2+}$, is the most stable of the series (see Figure 2). Cu(II) forms with TAPEN three protonated species: [Cu(HTAPEN)]$^{3+}$, [Cu-(H$_2$TAPEN)]$^{4+}$, and [Cu(H$_3$TAPEN)]$^{5+}$. The spectra for the

species of the Cu(II)–TAPEN system have been reported in Figure 5. The species [Cu(TAPEN)]$^{2+}$ and [Cu(HTAPEN)]$^{3+}$ show essentially the same spectrum, as already noticed for Co(II) and Ni(II), thereby indicating the same coordination geometry and TAPEN's behavior as a pentadentate ligand. Furthermore, these spectra show maxima at 609 nm and a shoulder at a lower frequency indicative of five-coordinated, square-pyramidal Cu(II) complexes.[15]   After a solid complex of formula Cu(HTA-PEN)(ClO$_4$)$_3$ is isolated, its reflectance spectrum shows the same pattern (see Figure 5) as those of [Cu(TAPEN)]$^{2+}$ and [Cu-(HTAPEN)]$^{3+}$ in solution. The spectrum of the [Cu-(H$_2$TAPEN)]$^{4+}$ species, where only four nitrogen donor atoms are involved in the coordination to the metal ion, shows a single wide band at 560 nm, typical of an octahedral Cu(II) complex.[3] The shift toward blue of the maximum of this species with an N$_4$ chromophore is due to the so-called "tetraamine effect".[16] Finally, the triprotonated species [Cu(H$_3$TAPEN)]$^{5+}$ shows a spectrum with a maximum at 600 nm, typical of an octahedral complex.

Zn(II). The stability of [Zn(TAPEN)]$^{2+}$ is betweeen those of the Co(II) and Ni(II) complexes; it can be protonated twice to give the species [Zn(HTAPEN)]$^{3+}$ and [Zn(H$_2$TAPEN)]$^{4+}$. Since up to now we have not measured the reaction enthalpies, the high value of the equilibrium constant relative to the protonation of the 1:1 complex, as compared to the first protonation constant of the ligand, is the only evidence that, also in the case of [Zn(TAPEN)]$^{2+}$, at most five nitrogen donor atoms are involved in the formation of the above complex. A solid complex of composition Zn(HTAPEN)(ClO$_4$)$_3$ has been isolated.

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