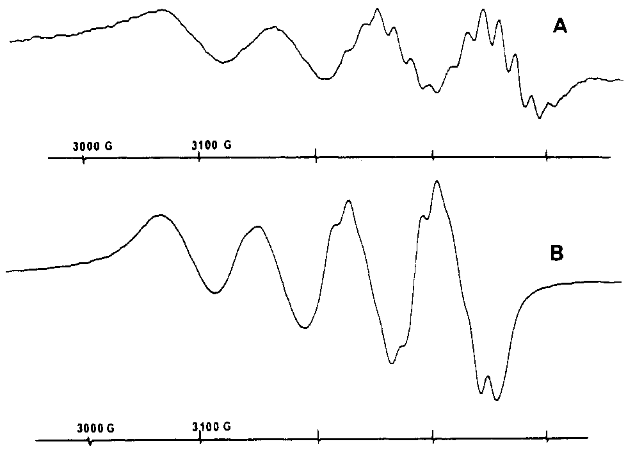

Figure 3. EPR spectra of NaCu(L$_1$-3H)·2H$_2$O (A), Cu(L$_1$-4H)Ni (B) complexes at room temperature.

Evidence that isomerization occurs upon addition of a second metal center is provided by EPR and electronic spectroscopies. Theoretically, EPR offers an easy means to determine the number of nitrogen atoms adjacent to the copper ion through the observation of the superhyperfine (shf) lines resulting from the interaction of the electron with the ^{14}N nuclei ($I = 1$).[9]

The isotropic spectra (solutions studied at room temperature) of [Cu(L$_1$-3H)]$^-$ and Cu(L$_1$-4H)Ni show the well-known hyperfine structure of four lines due to coupling of the electron with the nuclear spin ($I = {}^3/_2$) of the copper atom and, in addition, a superhyperfine structure clearly discernible on the high-field components of the hyperfine spectrum (cf. Figure 3).

In the case of [Cu(L$_1$-3H)]$^-$, seven shf lines are observed with a separation of 13.5 G, indicating that the environment of the copper ion is N$_3$O, while for Cu(L$_1$-4H)Ni, the number of shf-lines decreases to five (separation of 13.2 G) in accordance with the presence of a CuN$_2$O$_2$ chromophore. Due to the occurrence of a strong antiferromagnetic coupling, the spectrum of Cu(L$_1$-4H)Cu displays a broad signal devoid of any structure and centered at $g = 2.089$.

The change of conformation of the oxamido group in going from the mononuclear complex to the dinuclear complex is further supported by electronic spectra. Indeed the maximum of absorption (λ_{max}) suffers a significant shift from ca. 504 nm for the mononuclear species, [Cu(L$_1$-3H)]$^-$ and [Cu(L$_3$-3H)]$^-$, to ca. 560 nm for the dinuclear complexes, Cu(L$_1$-4H)Cu and Cu(L$_1$-4H)Ni. This is in accordance with the change in the coordination spheres established by EPR data and the generally accepted assumption that a shift of λ_{max} toward shorter wavelengths is associated with an increase of the nitrogen atoms adjacent to the metal centers.[10] Interestingly, identical visible spectra (λ_{max} = 450 nm) are observed for the nickel chromophores in Cu(L$_1$-4H)Ni and Ni(L$_1$-4H)Ni.

As suggested by a reviewer, the word mononuclear could be misused in the case of NaCu(L$_1$-3H)·2H$_2$O since this complex could actually display a higher nuclearity. As previously mentioned this possibility would be supported by the presence of a feeble antiferromagnetic interaction as in NaCu(L$_2$-3H)·1.33H$_2$O. A structural study would be necessary, but we have not been able to prepare crystals suitable for such a work. Nevertheless, the main conclusion of this work, the N$_3$O environment of the copper atom in the anionic entity Cu(L$_1$-3H)$^-$ and the N$_2$O$_2$ environment in Cu(L$_1$-4H)Cu and Cu(L$_1$-4H)Ni is not called into question by the absence of structural determination.

Finally, converging arguments gained from spectroscpic data support the view that, in spite of its symmetrical structure, the ligand L$_1$ can be used to prepare heterodinuclear complexes involving two equivalent N$_2$O$_2$ coordination sites. This is realized via the isolation of a stable mononuclear copper complex with a CuN$_3$O chromophore and subsequent reaction with a second metal ion.

Registry No. NaCu(L$_1$-3H), 120206-19-1; Cu(L$_1$-4H)Cu, 120206-20-4; Cu(L$_1$-4H)Ni, 120206-21-5; Ni(L$_1$-4H)Ni, 120206-22-6; diethyl oxalate, 95-92-1; 7-amino-4-methyl-5-aza-3-hepten-2-one, 89376-43-2; *N*,*N*′-bis(4-methyl-5-aza-3-hepten-2-on-7-yl)oxamide, 120206-18-0.

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Surprisingly High Stability of Alkali-Metal Complexes of the Ligand Tris(2-pyridylmethyl)amine (TPA)

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During the last 15 years many complexing agents for alkali-metal ions have been synthesized and studied.[2] It seems to be accepted that an efficient replacement of bound water molecules by alkali-metal ions can only be achieved with ligands that offer an optimal distribution of hard donor atoms around the central cation.

High stabilities and high selectivities have been obtained by the use of macrocyclic polyethers (crown ethers, **1**) (Figure 1) and polycyclic polyethers (cryptates, **2**). In both cases the high stability is ascribed to the high structural organization of the ligands. Holes of the right dimension to fit a specific alkali-metal ion are assumed to be preformed in the ligands.[2]

Vögtle has shown that open-chain polypodal compounds based on glyme polyethers can form stable complexes with alkali-metal and alkaline-earth-metal ions[3] (open-chain cryptates).

In the present paper it is shown that alkali-metal complexes with high stability can also be formed with polypodal ligands **3** (Figure 1) without glyme ether functions. In this case a cavity of the right dimension seems to be formed from the assembly of two bowl-shaped hemispheres.

In an investigation of the quadridentate ligand tris(2-pyridylmethyl)amine (tpa) it was discovered that this ligand forms very stable complexes with sodium and potassium.

It is suggested that the structures of these complexes are similar to those of the sodium complexes of the macrobicyclic polypyridine cryptate ligands recently reported by Lehn.[3,4]

The ligand tpa was first described by Anderegg et al.,[5,6] who showed that it forms surprisingly stable 1:1 metal complexes with most of the divalent metal ions in the first transition series.[6]

Tris(2-pyridylmethyl)amine is a symmetric quadridentate ligand of the same general type as tris(2-aminoethyl)amine (tren). In the [Cu(tpa)Cl]PF$_6$ complex tpa ligands were coordinated in a symmetric fashion with the amine nitrogen and the chloride ion situated at the molecular 3-fold axis[7] of a *pseudo* trigonal bipyramid. On the other hand, if tpa is coordinated to a metal(II) ion in order to form a *pseudo*octahedral complex, two adjacent

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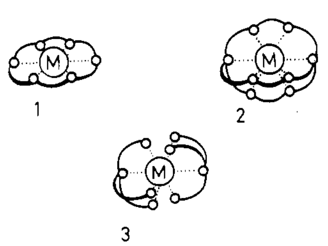

Figure 1. Schematic representation of metal complexes of macrocycles (**1**), cryptands (**2**), and polypodal ligands (**3**).

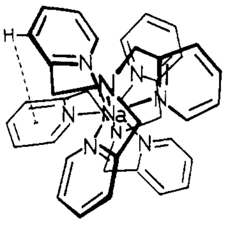

Figure 2. Suggested structure of $[Na(tpa)_2]^+$.

coordination sites of the metal ion would be available for coordination by other ligands. Recently the binuclear complexes $[(tpa)Cr(OH)_2Cr(tpa)](ClO_4)_4$[8] and $[(tpa)Mn(O)_2Mn(tpa)]_2(S_2O_6)_3$[9] have been structurally characterized. The fact that similar complexes are known for 2,2'-bipyridine (bpy) suggests that one tpa has donor properties similar to those of two bpy ligands. This is indeed demonstrated by the fact that *cis*-$[Fe(tpa)(NCS)_2]$ is a spin-crossover system similar to *cis*-$[Fe(bpy)_2(NCS)_2]$.[10] The high ligand field strength of tpa is unexpected as the coordination of this ligand may not be stabilized by π back-donation.

The high stability of tpa complexes probably reflects a favorable geometry for an effective σ-donation in the three chelate rings.

Experimental Section

A. Ligand Synthesis. Tris(2-pyridylmethyl)amine (tpa) was prepared as described elsewhere.[10] The crude product was recrystallized from benzene. IR(KBr): 1590, 1570, 1476, 1438, 768 cm^{-1}.

Tris(2-pyridylmethyl)amine Tris(hydrogen perchlorate) ($tpaH_3(ClO_4)_3$). Another crop of crude tpa was converted into the trihydrogen perchlorate by addition of an excess of $HClO_4$ in water. The trihydrogen perchlorate was recrystallized from a 1:4 mixture of acetone and water. IR (KBr): 3060, 1627, 1152, 1095, 790, 638 cm^{-1}.

B. Metal Complexes. Sodium Bis[tris(2-pyridylmethyl)amine] Perchlorate ($[Na(tpa)_2]ClO_4$). $tpaH_3(ClO_4)_3$ (6 g, 10.1 mmol) was added to a sodium hydroxide solution (25 cm^3, 2 mol dm^{-3}) with stirring. The resulting mixture was extracted with methylene chloride (3 × 50 cm^3). The combined methylene chloride phases were dried over anhydrous magnesium sulfate and evaporated to dryness. The remaining semisolid product was recrystallized from a 1:1 mixture of tetrahydrofuran and benzene, yielding long colorless needles of $[Na(tpa)_2]ClO_4 \cdot C_6H_6$: 3.0 g (77.7%); mp 118 °C. Anal. Calcd for $C_{42}H_{42}N_8NaClO_4$: C, 64.57; H, 5.42; N, 14.34. Found: C, 64.23; H, 5.47; N, 14.01. IR (KBr): 1595, 1439, 981, 767, 627 cm^{-1}.

Thermodynamic Quantities of Complexation. Complexation between sodium(I) and tpa has been examined by calorimetry in water and acetonitrile. The ionic strength of tpa solutions was kept at 0.1 mol dm^{-3} by using $(C_2H_5)_4NClO_4$ as an ionic medium in both solvents. A tpa solution (40 cm^3) with the concentration of tpa in the range 3.2–16.2 mmol dm^{-3} was titrated with a 0.1 mol dm^{-3} $NaClO_4$ solution. Heats evolved at each titration point ranged from 0.1 to 0.9 J with a certainty of 0.01 J. Calorimetric data thus obtained were analyzed on the basis of the mass balance equations for Na^+ and tpa by assuming the formation of various sets of complexes, and formation constants and enthalpies of the complexes were simultaneously determined. The details of calorimetric measurements are described elsewhere.[11]

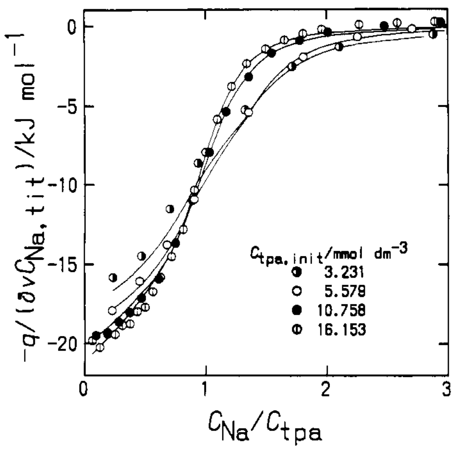

Figure 3. Calorimetric titration of tpa with $NaClO_4$ in acetonitrile solutions. The solid curves represent the best fit corresponding to the values in case 3 of Table I.

Table I. Thermodynamic Quantities log β (dm^3 mol^{-1}), $\Delta H°$ (kJ mol^{-1}), and $\Delta S°$ (J K^{-1} mol^{-1}) for the Overall Formation of $[Na_p(tpa)_q]^{p+}$ in Acetonitrile at 25 °C[a]

complex		case 1	case 2	case 3
$[Na(tpa)]^+$	log β	3.41 (0.17)	3.50 (0.09)	3.18 (0.14)
	$\Delta H°$	−18.4 (0.9)	−18.0 (0.3)	−20.8 (0.9)
	$\Delta S°$	4	7	−9
$[Na(tpa)_2]^+$	log β		4.91 (0.59)	
	$\Delta H°$		−28.9 (12)	
	$\Delta S°$		−3	
$[Na_2(tpa)]^{2+}$	log β			4.78 (0.58)
	$\Delta H°$			−10.1 (6.5)
	$\Delta S°$			58
U[b]		0.1273	0.013 33	0.029 63
R[c]		0.088 11	0.028 51	0.042 52

[a] The number of calorimetric data points is 47. [b] The error square sum. [c] The Hamilton R factor.

Results and Discussion

Preparations. The ligand tpa was synthesized by the method of Toftlund et al.[10] The workup of tpa is rather tedious. In one case the method of Anderegg and Wenk[5] was followed. This procedure implies recrystallization of the trihydrogen perchlorate. During the recovery of the tpa ligand with NaOH from a solution of the perchlorate salt, an extraction with methylene chloride instead of benzene was used. As a result of this procedure the sodium salt $[Na(tpa)_2]ClO_4$ was isolated in high yield instead of the expected free tpa ligand.

Although the formation constant of the sodium tpa complex in water may be rather small, as will be shown below, the extraction seems to be efficient, probably because of the formation of a stable ion-pair complex in the organic phase.

Thermodynamics of Complexation of Na^+ with tpa. Calorimetric data obtained by titrating tpa solutions with an $NaClO_4$ solution in acetonitrile are depicted in Figure 3. The $-q/[(\delta v)C_{Na,tit}]$ values are plotted against C_{Na}/C_{tpa}, where q, δv, C_{Na}, and C_{tpa} stand for the heat evolved, the volume of an aliquot of the titrant added, and the total concentrations of sodium ion and tpa, respectively, at each titration point. $C_{Na,tit}$ denotes the concentration of $NaClO_4$ in the titrant solution. The results of the nonlinear least-squares analysis of the calorimetric data are summarized in Table I. Case 1, assuming only the formation of $[Na(tpa)]^+$, shows a rather large Hamilton R factor (0.088 11). The formation of either $[Na(tpa)_2]^+$ (case 2) or $[Na_2(tpa)]^{2+}$ (case 3) in addition to $[Na(tpa)]^+$ is assumed. As seen in Table I, the R factor is appreciably smaller for case 2 than for case 3. Furthermore, significant systematic deviations between experimental and calculated values are observed in the range $C_{Na}/C_{tpa} > 1$ in case 3. Consequently, it is concluded that the $[Na(tpa)]^+$ and

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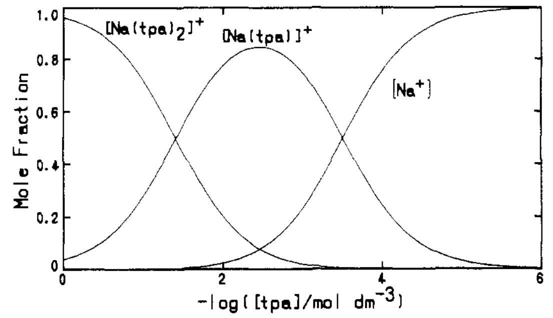

Figure 4. Distribution of species in an acetonitrile solution.

$[Na(tpa)_2]^+$ complexes are formed in acetonitrile. In fact the solid curves calculated by using the constants of the complexes (case 2) in Table I reproduce the experimental points well. They elucidate that the log K_1 and log K_2 values are 3.50 and 1.41, respectively, and the corresponding enthalpy and entropy values are −18.0 kJ mol^{-1} and 7 J K^{-1} mol^{-1} for the formation of $[Na(tpa)]^+$. It is noted that the enthalpy plays a predominant role also for the stepwise formation of $[Na(tpa)_2]^+$. The distribution of species in acetonitrile is depicted as the function of −log ([tpa]/mol dm^{-3}) in Figure 4.

However, no heat of reaction has been observed during the titrations in water. The electronic spectrum in the wavelength range 300–500 nm and the ^1H NMR chemical shift of a tpa aqueous solution hardly changes with the addition of $NaClO_4$ in the solution. These results suggest that the complexation of sodium ion with tpa is weak and practically negligible under the experimental conditions examined.

Anderegg et al.[6] have determined the protonation constants for tpa in water. The first constant (log $K_p = 6.17$) is significantly smaller than that of similar ligands. As a constant ionic medium $\mu = 0.1$ (KNO_3) was used, it was decided to determine the correction due to the complex formation between tpa and K^+.

From ^1H NMR spectra in aqueous solutions with $\mu = 0.1$ (KCl) and C_{tpa} about 0.03 mol dm^{-3}, it was estimated that about 16–20% of the tpa was bound to potassium ions under the experimental conditions, corresponding to an underestimation of K_p by a factor of 1.2. This is of course only a modest correction (log K_p (cor) = 6.25).

IR Spectra. The pyridine deformation frequencies (ν_a and ν_b) around 1600 cm^{-1} are typically shifted 10–15 cm^{-1} to higher frequency upon coordination to a divalent transition-metal ion.[6] In the case of $[Na(tpa)_2]ClO_4$ these signals are only shifted 5 cm^{-1}, reflecting the formation of weak Na–N(py) bonds. The signals are very sharp, indicating that all six pyridine groups are coordinated with the same strength.

Magnetic Resonance. In order to get some information about the solution structure of $[Na(tpa)_2]^+$, the 400-MHz ^1H NMR spectrum in acetonitrile (0.1 mol dm^{-3}) was recorded and compared to the spectrum of pure tpa ligand. The spectra are similar. The most striking difference is an upfield shift of H(3) by 0.20 ppm on the coordination of tpa to Na^+.

From the thermodynamic measurements it is known that, in an acetonitrile solution of $[Na(tpa)_2]ClO_4$, the $[Na(tpa)_2]^+$ complex is in equilibrium with $[Na(tpa)]^+$ and tpa. With a stoichiometric concentration of 0.1 mol dm^{-3} the concentrations of the three species are of the same order of magnitude. As no additional lines are observed, the spectrum must represent a time-averaged exchange between the three species. A linear extrapolation of the shifts from the average spectrum to the pure $[Na(tpa)_2]^+$ spectrum results in a total upfield shift of 0.37 ppm for H(3).

Considering that coordination to a metal normally results in a downfield shift of the signals, it is suggested that the origin of the observed shift is due to a specific structure of the sodium tpa complex.

Among the possible structures of $[Na(tpa)_2]^+$ the one shown in Figure 2 accounts for all the spectral features. In this structure the two tpa ligands are twisted around the 3-fold axis in such a way that the whole molecular ion has a helical structure like a six-bladed propeller. The sodium ion achieves eight-coordination with a rhombohedral (S_6) site symmetry. Very recently a similar structure has been found for the $[Pb(tren)_2]Cl_2$ complex.[12]

Of special interest is the fact that H(3) of each pyridine group is placed right above the pyridine planes from the opposite part of the molecular ion. In this position it will experience a shielding from the ring current of the pyridine ring.

The proposed structure also offers an appealing explanation of the surprisingly high stability of the molecular ion. Through the helical arrangement of the pyridine planes several π–π contacts are formed, which might result in a stabilization through HOMO–LUMO interactions.

So it is suggested that the $[Na(tpa)_2]^+$ complex is related to the cryptate complex [bpy-bpy-bpy]·NaBr recently reported by Lehn et al.[3,4] in the sense that the covalent 2-C–2′-C bonds in the cryptate complex are replaced by several weak π–π interactions between the two tpa hemispheres of $[Na(tpa)_2]^+$.

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