59. Metal Complexes with Macrocyclic Ligands. XVI[1]). Spectrophotometric and Thermodynamic Studies of Solvents and Unidentate Ligands Interaction with the Pentacoordinate Co^{2+}-, Ni^{2+}- and Cu^{2+}-Complexes of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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Summary

The interaction of solvents and of unidentate ligands such as N_3^-, SCN^-, OCN^- and OH^- with the Co^{2+}-, Ni^{2+}- and Cu^{2+}-complexes of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) have been studied by spectrophotometric and calorimetric techniques. The spectra in different solvents *(Table 2)* show that the Ni^{2+}- and probably also the Cu^{2+}-complex with TMC exist as square planar or pentacoordinate species or as a mixture of both, depending on the donor properties of the solvent. The $[Co(TMC)]^{2+}$-complex is pentacoordinate in all the solvents studied.

Ternary complexes $[(M(TMC)X]^{n+}$ are also formed by the unidentate ligands $X = N_3^-$, OCN^-, OH^-, F^- and NH_3 and their stability constants have been determined. Interesting is the high selectivity of $[Ni(TMC)]^{2+}$ towards the addition of a further donor *(Table 3)*. Only small ligands such as those listed above form stable adducts, whereas the larger ones such as imidazole or pyridine do not. This is a consequence of the special structure of the complex and of the *trans-I-(RSRS)*-conformation of the ligand in these complexes. Since the four methyl groups are all on the side of the macrocycle to which the additional unidentate ligand binds, steric interaction between the four methyl groups and the larger ligands prevents the formation of the adducts.

The calorimetric measurements show that the stability of the complexes $[M(TMC)X]^{n+}$ is due to both an enthalpic and entropic contribution which differ in their magnitude *(Table 4)*. This indicates that several antagonistic factors are important in determining the overall stability.

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Introduction. - Since the discovery of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) it was realized [2] [3] that its metal complexes do not show the usual square planar or octahedral coordination geometry as do the analogous complexes with the unsubstituted 1,4,8,11-tetraazacyclotetradecane (Cyclam) [4], but that they exhibit either square pyramidal or trigonal bipyramidal structures.

A clear example of it is given by the X-ray structures of $[Ni(TMC)N_3]^+$ [5] and $[Zn(TMC)Cl]^+$ [6] in which the metal ion is surrounded by the four N-atoms of the macrocycle at the base of a square pyramid and the unidentate ligand is bound in the axial position. In solution, however, ^{13}C-NMR. and ^{1}H-NMR. spectra of the Ni^{2+}- and Zn^{2+}-complexes indicate fluxional behaviour of a species with trigonal bipyramidal structure [6] [7].

In the Ni^{2+}-complex prepared from TMC and free metal ion the ligand exists in the *trans-I-(RSRS)*-[8] structure *(Fig.)*. The *trans-III-(RSSR)*-configuration has also been found in the Ni^{2+}-complex when preformed $[Ni(Cyclam)]^{2+}$ is alkylated with CH_3I in DMSO [9]. The *trans-I-(RSRS)*-$[Ni(TMC)]^{2+}$-complex is in aqueous solution a mixture of a blue (pentacoordinate) and a yellow (square planar) isomer and some of their properties have been described [7]. However, less is known about the geometry and the properties in solution of the Cu^{2+}- and Co^{2+}-complexes. This study was undertaken to obtain more information about these complexes and especially to determine which factors are responsible for the axial coordination of solvent and unidentate ligand molecules.

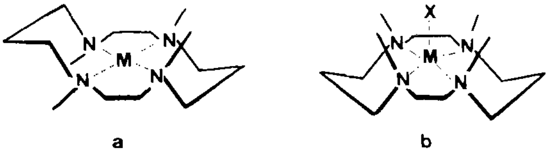

Figure. *Structure of the* trans-*III*-(RSSR)- (a) *and* trans-*I*-(RSRS)-*[Ni(TMC)]*$^{2+}$ (b)

Experimental Part. - 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) [2] [3], $Ni(TMC)(ClO_4)_2$ [3] and $Cu(TMC)(ClO_4)_2$ [3] were prepared according to the literature. All other reagents were of analytical grade and were used without further purification except NaOCN [10] and the buffer bases which were distilled.

Co(TMC)(NO$_3$)$_2$. After evaporating of 50 ml 0.1M $[Co(TMC)]^{2+}$-solution (see below) of pH 7.7 to dryness, the residue was taken up with 10 ml abs. EtOH, cooled to 0°, the precipitated KNO_3 filtered off and the solution concentrated. This operation was repeated until no more KNO_3 precipitated. The solution of the complex was then reduced to 5 ml and cooled to − 15° whereby red violet crystals of the product formed. Absorption spectra see *Table 2*.

$C_{14}H_{32}CoN_6O_6$ (439.38) Calc. C 38.29 H 7.34 N 19.13% Found C 38.49 H 7.47 N 19.10%

For the equilibrium studies solutions of the corresponding complexes were prepared in the following way: after dissolving 5 mmol TMC in about 50 ml water at 40° 5.5 mmol metal salt were added in small portions whereby the pH was kept at 5 for Cu^{2+} and 7 for Ni^{2+} and Co^{2+} with a KOH-solution. After complete addition of the metal ion the pH was adjusted to 12 and the precipitated metal hydroxide was filtered off. The pH of the filtrate was brought back to 7 and the solution was then diluted to the exact volume. The concentration of these solutions was determined by atomic absorption on a *Unicam SP90* spectrophotometer and was equal to the TMC-concentration indicating that no free metal ion was present. Absorption spectra were run on a *Cary 118* using the nujol technique [11] and in spectral pure solvents *(Merck Specpure)* in which the solid complexes were dissolved.

Table 1. *Experimental conditions for the spectrophotometric titrations at 25° and $I = 0.5$*

Complex and its concentration in the cell	Ligand and its concentration in the burette	Buffer and its concentration in the burette	pH	λ (in nm)
$[Co(TMC)]^{2+}$	NCO^- (1 M)	0.1 M 2,4,6-collidine	7.4	400–800
$4.8 \cdot 10^{-3}$ M	NCO^- (1 M)	0.1 M 2,4,6-collidine	8.4	400–800
	NCO^- (1 M)	0.1 M borate	9.8	400–800
	N_3^- (1 M)	0.1 M 2,4,6-collidine	7.5	400–800
	N_3^- (1 M)	0.1 M borate	8.9	400–800
	SCN^- (1 M)	0.1 M 2,4,6-collidine	7.6	400–800
	SCN^- (1 M)	0.1 M borate	9.1	400–800
$[Ni(TMC)]^{2+}$	OH^- (0.2 M)	–[a]	var.	370–450
$3.7 \cdot 10^{-3}$ M	N_3^- (0.4 M)	0.1 M 2,4,6-collidine	7.6	480–540
	OCN^- (0.1 M)	0.1 M 2,4,6-collidine	7.6	480–540
	F^- (10 M)	0.1 M 2,4,6-collidine	7.6	480–540
	NH_3 (7.7 M)	–[a]	8.9	480–540
$[Cu(TMC)]^{2+}$	SCN^- (0.5 M)	0.1 M 2,4,6-collidine	7.6	730–800
$1.5 \cdot 10^{-3}$ M	N_3^- (0.5 M)	0.1 M 2,4,6-collidine	7.6	730–800
	OCN^- (4 M)	0.1 M 2,4,6-collidine	7.6	600–670

[a] 0.01 M *t*-Butylaminoethanol was added to obtain a smooth titration.

The stability of the ternary complexes $[M(TMC)X]^{n+}$ was studied by spectrophotometric titrations using an automatic titration setup interfaced with a *Hewlett-Packard HP9820* computer [12]. The metal complex was mixed with a buffer of I = 0.5 (0.5 M (KNO_3 or $NaClO_4$)) and titrated with NaSCN, NaOCN, NaN_3, NH_4F and NaOH. All solutions were filtered through *Swinnex SX100* units with *RAWP 13000* filter. The titrations were followed at several wavelengths. The exact experimental conditions are given in *Table 1.*

The equilibrium constants were calculated at each wavelength using a non-linear least-square program based on the *Newton-Gauss-Marquard* algorithm [13].

The acid dissociation constant of $[Co(TMC)(H_2O)]^{2+}$ was determined by potentiometric titration of a mixture of 15 ml 1 M KNO_3, 1 ml $4.8 \cdot 10^{-2}$ M $[Co(TMC)(H_2O)]^{2+}$, 1 ml 0.1 M NaOH and 13 ml water with 0.1 M HNO_3 using a *Metrohm* compensator *E388* with a *Metrohm* burette *E412* and a combined glass electrode. Calibration buffers of pH 4 and 7 were equilibrated at least 3 h at 25°. From each titration curve 29 points with pH > 7.5 were used for the determination of the pK_H value with the program *MARFIT* [14].

The magnetic moment of $[Co(TMC)(H_2O)]^{2+}$ was determined by the *Evans* method on a *Varian A60* NMR. instrument using $7 \cdot 10^{-2}$ M solutions and 2% *t*-ButOH as reference [15].

Calorimetric studies were carried out at 25° in 0.5 M KNO_3, with a *10700-1 LKB* flow-calorimeter, equipped with a *Keithley* model *150B* microvolt ammeter. A full description of this apparatus and its calibration has already been reported [16]. In a typical experiment a solution of $[M(TMC)]^{2+}$ ($M = Co^{2+}$, Ni^{2+} or Cu^{2+}) and a solution of MX ($M = Na^+$ or K^+, $X = OCN^-$, OH^-, SCN^- or N_3^-) were injected in the calorimeter by high precision electronic burettes *(Mettler DV 10).* The flow rate of the burettes and the concentration of the reactands were changed in such a way to have a ligand X to complex $[M(TMC)]^{2+}$ ratio ranging from 1:1 to 2.4:1.

Results and Discussion. – To study the geometry of the metal ion in $[Co(TMC)]^{2+}$, $[Ni(TMC)]^{2+}$ and $[Cu(TMC)]^{2+}$ we have measured their absorption spectra in different solvents *(Table 2).*

The spectral data of $[Ni(TMC)]^{2+}$ in a few solvents have been described previously [2] [7] and have been discussed by assuming an equilibrium between a square planar and a pentacoordinate species. Our additional data are in accordance

Table 2. *Absorption spectra of $Co(TMC)(NO_3)_2$, $Ni(TMC)(ClO_4)_2$ and $Cu(TMC)(ClO_4)_2$ in different solvents*

Solvent	λ in nm (ε in $M^{-1}\,cm^{-1}$)		
	$Co(TMC)(NO_3)_2$	$Ni(TMC)(ClO_4)_2$	$Cu(TMC)(ClO_4)_2$
Nujol	472, 545, 708		
Nitromethane	[a])	512 (195)	584 (230)
Acetone	476 (35), 560 (25)	388 (27), 515 (165)	588 (234)
Methanol	476 (37), 557 (24)	392 (38), 513 (170)	620 (239)
Water	472 (20), 543 (21), 725 (12)	394 (95), 512 (82), 650 (33)	640 (257)
Ethanol	477 (38), 554 (25)	392 (142), 505 (53), 655 (42)	[a])
DMSO	478 (30), 550 (22), 734 (11)	398 (105), 527 (42), 670 (27)	642 (249)
DMF	484 (34), 552 (23), 725 (10)	395 (115), 660 (30)	649 (250)

[a]) Not soluble.

with this view and show a steady change from the square planar geometry in poorly coordinating solvents such as nitromethane, acetone and methanol to the pentacoordinate species in better coordinating solvents such as DMF. In solvents with intermediate donor properties such as ethanol, water and DMSO the observed spectra can be interpreted as a superposition of the absorption of the two components. The spectra of Cu^{2+} are generally not so diagnostic for the geometric environment of the metal ion. However, the shift from 584 nm in nitromethane to 649 nm in DMF for $[Cu(TMC)]^{2+}$ indicates that the stronger donor solvent interacts with Cu^{2+} more strongly than the others. The shift to longer wavelengths is a consequence of the interaction between the solvent with Cu^{2+} in the axial position [17]. It is difficult to decide from the spectroscopic data alone, whether in poorly coordinating solvents $[Cu(TMC)]^{2+}$ is present in a square planar geometry.

In the case of $[Co(TMC)]^{2+}$ the absorption spectra in different solvents and the magnetic moment of 4.45 μ_B for $[Co(TMC)(H_2O)]^{2+}$ can clearly be interpreted with a pentacoordinate high-spin species [18]. The band shape is nearly constant and the small shifts in the absorption maxima indicate that the solvent can coordinate in the axial position. The $[Co(TMC)]^{2+}$-complex is remarkable because of its stability against oxygenation. Even at high pH no trace of a binuclear μ-peroxo-complex is formed when a solution of $[Co(TMC)]^{2+}$ is kept in contact with dioxygen. This seems in contrast with the chemical experience that Co^{2+}-complexes with at least three N-donor atoms rapidly pick up dioxygen [19]. However, it is possible that pentacoordination of the metal ion stabilizes the (2+)-more than the (3+)-oxidation state, since only octahedral geometry produces the large LFSE (ligand field stabilization energy) necessary for the stabilization of the trivalent ion.

Equilibrium measurements. The spectral data in different solvents, indicating that the metal complexes of TMC are at least in part pentacoordinate and that the solvent can coordinate to the axial position, prompted us to study the complexation equilibria of a series of other unidentate ligands with the complexes $[M(TMC)]^{2+}$. The reaction can be described by *Equation 1*, in which the solvent molecules have

$$[M(TMC)]^{2+} + X \xrightleftharpoons{K^{X}_{M(TMC)}} [M(TMC)X]^{2+} \qquad (1)$$

Table 3. *Comparison of the stability of the ternary complexes M(TMC)X with the binary ones NiX*

X	$\log K^{X}_{Ni(TMC)}$	$\log K^{X}_{Ni}$	$\Delta \log K_{M}$[a])
N_3^-	2.50 (5)	1.04 [23]	+ 1.46
OCN^-	3.67 (6)	1.97 [24]	+ 1.70
F^-	0.57 (7)	0.66 [25]	− 0.09
NH_3	1.10 (6)	2.80 [26]	− 1.70
CH_3COO^-	<0.3	1.43 [27]	<-1.13
Pyridine	<0.3	1.91 [28]	<-1.61
Imidazole	<0.3	3.01 [29]	<-2.71
HPO_4^{2-}	<0.3	2.08 [30]	<-1.78

[a]) $\Delta \log K_M$ is defined by *Equation 3.*

been omitted. $K^{X}_{M(TMC)}$ is the stability constant of the ternary complex. In the case of $[Ni(TMC)]^{2+}$ we have studied a large number of ligands, X being N_3^-, SCN^-, OCN^-, OH^-, F^-, NH_3, pyridine, imidazole, HPO_4^{2-}, and CH_3COO^-, whereas only the first four were studied with the other two metal ions. The spectrophotometric titration curves were analyzed and fitted with *Equation 2* taking the molar

$$E = \varepsilon_1 \cdot c_1 + \varepsilon_2 \cdot c_2 \tag{2}$$

c_1 = molar concentration of $[M(TMC)]^{2+}$; c_2 = molar concentration of $[M(TMC)X]^{2+}$

absorptivities ε_1, ε_2 and $K^{X}_{M(TMC)}$ as parameters [13]. The mean values of $\log K^{X}_{Ni(TMC)}$ obtained at different wavelengths are given in *Table 3* for a series of ligands X.

The results show that the rod-like ligands such as N_3^- and OCN^- form with $Ni(TMC)^{2+}$ the most stable complexes, whereas pyridine and imidazole are not coordinated at all. If we compare this with the complexation properties of Ni^{2+} we see that $[Ni(TMC)]^{2+}$ is very selective in the formation of ternary complexes. $\Delta \log K_M$ *(Eqn. 3)* has been proposed and used as a measure for the selectivity of

$$\Delta \log K_M = \log K^{X}_{M(TMC)} - \log K^{X}_{M} \tag{3}$$

the formation of ternary complexes [20]. The values of $\Delta \log K_M$ *(Table 3)* ranging from + 1.7 for OCN^- to − 2.7 for imidazole indicate the magnitude of the effect, which so far has not been observed to this extent [21]. $\Delta \log K_M$ is the equilibrium constant of *Equation 4* and describes the coordination tendency of the ligand X

$$MX + M(TMC) \rightleftharpoons M + M(TMC)X \tag{4}$$

towards M(TMC) in relation to that towards M. Thus, the value of + 1.7 means that OCN^- is more strongly coordinated to $[Ni(TMC)]^{2+}$ than to Ni^{2+} (the equilibrium *(Eqn. 4)* is shifted to the right), whereas a value of − 2.7 for imidazole indicates that this ligand practically only binds to Ni^{2+} and not to $[Ni(TMC)]^{2+}$ (the equilibrium *(Eqn. 4)* is shifted to the left). This high selectivity results from two factors: steric interactions and π-acceptor properties. The special structure of the macrocycle in the *trans-I (RSRS)* conformation with all four methyl groups on the same side as the one to which the additional ligand X must bind *(Fig.)*, induces sterical

Table 4. *Thermodynamic parameters of the adduct formation of* $M(TMC)X]^+$ *according to the reaction* $[M(TMC)]^{2+} + X^- \rightleftharpoons [M(TMC)X]^+$

$[M(TMC)]^{2+}$	X^-	$\log K^{X}_{M(TMC)}$[a]	ΔH°[a] ($kJ \cdot mol^{-1}$)	ΔS°[a] ($J \cdot mol^{-1} \cdot K^{-1}$)
$[Co(TMC)]^{2+}$	N_3^-	2.57 (3)	− 5.6 (2)	30.1 (8)
$[Ni(TMC)]^{2+}$	N_3^-	2.50 (5)	− 3.1 (2)	37.2 (9)
$[Ni(TMC)]^{2+}$	N_3^-	2.52 (5)[b]	− 15.4 (3)[b]	− 2.9 (8)[b]
$[Cu(TMC)]^{2+}$	N_3^-	1.29 (3)	− 6.3 (2)	3.8 (8)
$[Co(TMC)]^{2+}$	OCN^-	3.82 (6)	− 10.0 (4)	39.3 (9)
$[Ni(TMC)]^{2+}$	OCN^-	3.67 (6)	− 3.8 (3)	57.7 (9)
$[Ni(TMC)]^{2+}$	OCN^-	3.69 (6)[b]	− 16.0 (3)[b]	16.7 (9)[b]
$[Cu(TMC)]^{2+}$	OCN^-	1.16 (4)	~ 0	22.2 (8)
$[Co(TMC)]^{2+}$	SCN^-	3.07 (4)	− 13.7 (2)	13.0 (8)
$[Ni(TMC)]^{2+}$	SCN^-	[c]		
$[Cu(TMC)]^{2+}$	SCN^-	2.14 (3)	− 6.0 (2)	20.9 (8)
$[Co(TMC)]^{2+}$	OH^-	5.28 (3)	− 23.8 (2)	20.9 (9)
$[Ni(TMC)]^{2+}$	OH^-	3.72 (4)	− 17.5 (3)	12.5 (9)
$[Ni(TMC)]^{2+}$	OH^-	3.74 (4)[b]	− 29.7 (3)[b]	− 28.0 (9)[b]
$[Cu(TMC)]^{2+}$	OH^-	[d]		

[a] Values in parenthesis are the standard deviations on the last significant figure. [b] Referred to the reaction: $[Ni(TMC)]^{2+}$ (square planar) + $X^- \rightleftharpoons [Ni(TMC)X]^+$. [c] Precipitation of $Ni(TMC)(SCN)_2$. [d] No reaction up to pH < 12.

interaction between the methyl groups and the larger ligands such as pyridine and imidazole, so that they cannot coordinate. In addition the ligand must bind in the axial position of the square pyramidal structure. It is possible that because of the strong equatorial field of the four N-atoms of the macrocycle a π-acceptor is a better ligand than a σ-donor one. Of course N_3^-, SCN^- and OCN^- are ideal in both respects being linear and thus having only little steric hindrance with the methyl groups of TMC and being at least in part π-acceptors.

Thermodynamic properties. In general the stability of the ternary complexes $[M(TMC)X]^+$ *(Table 4)* is given by a favorable entropic term and except for the $[Cu(TMC)]^{2+}/OCN^-$ system also by a favorable enthalpic contribution ($\Delta H^{\circ} < 0$). For the hydroxo-complexes $[M(TMC)OH]^+$ ($M = Co^{2+}, Ni^{2+}$) which are between the most stable ones, the enthalpy contributes to about 80% to the stability. In other cases as for $[Ni(TMC)]^{2+}/OCN^-$, however, the entropic contribution predominates. Finally there are examples ($[Co(TMC)]^{2+}/OCN^-$) in which the two contributions are nearly equal in magnitude. This clearly indicates that several antagonistic effects must exist, which finally determine the overall stability of the ternary complex. The formation of the M,X-bond is an exothermic effect which stabilizes the complex together with a diminished orientation capability, due to a partial charge neutralization, which causes an increase in entropy (desolvation). Opposed endothermic effects are the breaking of the M,OH_2-bond and the desolvation of the ions. Comparing the $[Co(TMC)]^{2+}$- and $[Ni(TMC)]^{2+}$-complexes one finds *(Table 4)* that the formation of the adducts is more exothermic (ΔH° more negative) for the Co^{2+}- than for the analogous Ni^{2+}-system. This also is reflected in a higher stability of the $[Co(TMC)]^{2+}$-adducts compared to the corresponding $[Ni(TMC)]^{2+}$-species.

The different exothermicity probably results from a different interaction of the metal ion with the donor atom of the ligand X, since this is the most important enthalpic contribution. The structural studies on $[Ni(TMC)N_3]^+$ [5] and $[Zn(TMC)Cl]^+$ [6] have shown that in both complexes the metal ion is pentacoordinate with square pyramidal geometry. In these complexes the metal ion is placed above the plane defined by the four N-atoms of the macrocycle by 0.33 Å in the case of Ni^{2+} and by 0.57 Å in the case of Zn^{2+}, which is the larger ion. It is therefore possible that in $[Co(TMC)]^{2+}$ the Co^{2+}-ion, also larger than the Ni^{2+}-ion, is less 'submerged' into the macrocyclic ring. Thus, a stronger interaction with X, a stronger M,X-bond and also a larger reaction enthalpy results. The entropy of formation of the adducts favors (ΔS° more positive) the $[Ni(TMC)]^{2+}$-over the $[Co(TMC)]^{2+}$-complexes. Only in the case of the complexation with OH^- the $[Co(TMC)]^{2+}$-complex has a more positive entropy change than that of $[Ni(TMC)]^{2+}$. The same considerations about the size of the metal ion made for the enthalpic contribution can be used to interpret the entropy change. The axial M,X-bond in the adducts produces a higher steric interaction between the methyl groups of the macrocycle and the hydrated ligand X in the case of the smaller Ni^{2+}-compared to the larger Co^{2+}-ion. Thus a larger desolvation of X and an increase in translational entropy is expected.

The Cu^{2+}-complexes are less stable than those of the other metal ions studied. It is astonishing that $[Cu(TMC)]^{2+}$ does not bind a OH^- up to pH 12 although its high hydrolytic tendency is well-known [22], whereas both $[Co(TMC)]^{2+}$ and $[Ni(TMC)]^{2+}$ form stable hydroxo-species.

Finally in the case of $[Ni(TMC)]^{2+}$ one can calculate the thermodynamic parameters for the yellow diamagnetic square planar form, since the equilibrium constant between the square planar and the pentacoordinate species has been determined [7]. For the square planar $[Ni(TMC)]^{2+}$ the values of ΔH° are more exothermic, whereas those of ΔS° are smaller *(Table 4)*.

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REFERENCES

[1] *L. Hertli & Th.A. Kaden*, Helv. Chim. Acta *64*, 33 (1981).
[2] *E.K. Barefield & F. Wagner*, Inorg. Chem. *12*, 2435 (1973).
[3] *R. Buxtorf, W. Steinmann & Th.A. Kaden*, Chimia *28*, 15 (1974); *R. Buxtorf & Th.A. Kaden*, Helv. Chim. Acta *57*, 1035 (1974).
[4] *N.F. Curtis*, in 'Coordination Chemistry of Macrocyclic Compounds' (Ed. G.A. Melson), Plenum Press, New York 1979, p. 219.
[5] *M.J. d'Aniello, M.T. Mocella, F. Wagner, E.K. Barefield & J.C. Paul*, J. Am. Chem. Soc. *97*, 192 (1975).
[6] *N.W. Alcock, N. Herron & P. Moore*, J. Chem. Soc. Dalton *1978*, 1282.
[7] *N. Herron & P. Moore*, Inorg. Chim. Acta *36*, 89 (1979).

[8] *B. Bosnich, C.K. Poon & M.L. Tobe*, Inorg. Chem. *4*, 1106 (1965).
[9] *F. Wagner & E.K. Barefield*, Inorg. Chem. *15*, 408 (1976).
[10] *C.E. Vanderzee & R. Myers*, J. Phys. Chem. *65*, 153 (1961).
[11] *R.H. Lee, E. Grieswald & J. Kleinberg*, Inorg. Chem. *3*, 1278 (1964).
[12] *G. Hänisch, Th.A. Kaden & A.D. Zuberbühler*, Talanta *26*, 563 (1979).
[13] *A.D. Zuberbühler & Th.A. Kaden*, Talanta *26*, 1111 (1979).
[14] *H. Gampp, M. Maeder, A.D. Zuberbühler & Th.A. Kaden*, Talanta *27*, 513 (1980).
[15] *J. Löliger & R. Scheffold*, J. Chem. Educ. *49*, 667 (1972).
[16] *C. Bianchini, L. Fabbrizzi & P. Paoletti*, J. Chem. Soc., Dalton *1975*, 1036.
[17] *E.J. Billo*, Inorg. Nucl. Chem. Lett. *10*, 613 (1974); *A. Kurganov & V. Davankov*, Inorg. Nucl. Chem. Lett. *12*, 73 (1976).
[18] *M. Ciampolini*, Structure and Bonding *6*, 52 (1969); *Th.A. Kaden, B. Holmquist & B.L. Vallee*, Inorg. Chem. *13*, 2585 (1974).
[19] *S. Fallab*, Angew. Chem. *79*, 500 (1967).
[20] *H. Sigel*, Met. Ions Biol. Syst. *2*, 63 (1973).
[21] *H. Sigel*, in 'Coordination Chemistry-20' (Ed. D. Banerjea), Pergamon Press, Oxford 1980, p. 27.
[22] *J. Burgess*, 'Metal ions in solution', Wiley, New York 1978, p. 259.
[23] *F. Maggio, V. Romano & L. Pellerito*, J. Electroanal. Chem. *15*, 227 (1967).
[24] *A. Lodzinska*, Roczniki Chem. *41*, 1007 (1967).
[25] *S. Ahrland & K. Rosengreen*, Acta Chem. Scand. *10*, 727 (1956).
[26] *P.F. Derr & W.C. Vosburg*, J. Am. Chem. Soc. *65*, 2408 (1943).
[27] *D.W. Archer & C.B. Monk*, J. Chem. Soc. *1964*, 3117.
[28] *M.S. Sun & D.C. Brewer*, Can. J. Chem. *45*, 2729 (1967).
[29] *A. Chakravorty & F.A. Cotton*, J. Phys. Chem. *67*, 2878 (1963).
[30] *H. Sigel, K. Becker & D.B. McCormick*, Biochim. Biophys. Acta *148*, 655 (1967).