A New One-pot Synthesis of Bis(macrocyclic) Complexes: Preparation and Characterization of Nickel Complexes with Bis(pentaazamacrocyclic) Ligands

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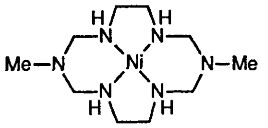
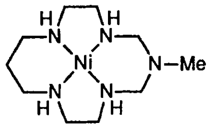
Template condensation of $[Ni(2,3,2\text{-tet})]^{2+}$ with formaldehyde and aliphatic diamines result in new type of nickel(II) bis(pentaazamacrocylic) complexes; the spectral and electrochemical data indicate the absence of electronic interactions between the metal centres.

The synthetic approaches to preparation of monomacrocyclic complexes of transition metals are extensively developed at present,[1] but relatively few studies dealing with preparation of bis(macrocyclic) compounds are available and in most cases multistep syntheses are needed.[2] Bis(macrocyclic) complexes containing two connected metal ions are of interest also as models for polynuclear metalloenzymes and as multielectron redox reagents and catalysts.

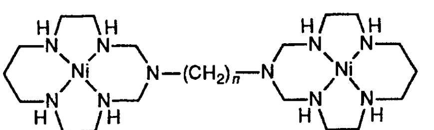
To devise a new method for the synthesis of bis(macrocyclic) compounds it seems appropriate to use the template



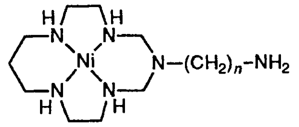
$[NiL^1]^{2+}$



$[NiL^2]^{2+}$



$n = 2$ $[Ni_2L^3]^{4+}$
$n = 3$ $[Ni_2L^4]^{4+}$
$n = 4$ $[Ni_2L^5]^{4+}$



$[NiL^6]^{2+}$

condensation reactions with participation of amines and formaldehyde. For example, the preparation of $[NiL^1]^{2+}$ complex by the template condensation of ethylenediamine, formaldehyde and alkylamines in the presence of a metal ion has been previously reported.[3] When $[Ni(2,3,2\text{-tet})]^{2+}$(2,3,2-tet = 1,9-diamino-3,7-diazanonane) was used as a template agent, $[NiL^2]^{2+}$ was obtained.[4]

We believe that utilization of primary diamines instead of monoamines in such a reaction can open the way to preparation of bis(macrocyclic) complexes. In fact, the reactions of stoichiometric quantities of $[Ni(2,3,2\text{-tet})](ClO_4)_2$ with CH_2O and $H_2N\text{-}(CH_2)_n\text{-}NH_2$ (n = 2,3,4) in boiling methanol-water (4 : 1) solution lead to formation of yellow compounds whose properties are in accordance with bis(macrocyclic) structure.† The following reasons allow us to reach such a conclusion.

(*i*) The disappearance of sharp bands in the IR spectra of products attributed to N–H stretches of coordinated secondary amino groups in $[Ni(2,3,2\text{-tet})]^{2+}$ (3395, 3345 and 3265 cm^{-1}) and the presence of a single absorption near 3200 cm^{-1} attributed to the ν_{N-H} stretch of coordinated secondary aminogroups in the macrocyclic complexes $[NiL^1]^{2+}$ and $[NiL^2]^{2+}$[3,4] shows that cyclization reactions took place. These data also give us the possibility to discard from consideration the structure $[NiL^6]^{2+}$ with pendant $-NH_2$ groups in the macrocyclic backbone.

(*ii*) The electronic spectra and electrochemical data of the complexes under consideration were found to be very similar to those of monomacrocyclic compounds $[NiL^2]^{2+}$ (see Table 1), as well as for $[NiL^1]^{2+}$.[3] Visible spectra are typical of square-planar nickel(II) complexes with 14-membered tetradentate macrocycles.[5] This suggests a similar structure of the chromophore for all the complexes studied. The spectra of complexes in aqueous solution are unaffected by pH change in the range $2 < pH < 12$. This also implies that complexes of type $[NiL^6]^{2+}$ are not the product of cyclization reactions, insofar as macrocyclic nickel complexes with ligand containing pendant amino groups exist in alkaline solutions in blue or violet high-spin form.[6]

Table 1 Electronic spectra and cyclic voltammetric data for the nickel(II) complexes in aqueous solution (295 K)

Complex	$\nu/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})[a] NaClO$_4$(0.1 mol dm^{-3})	$E_{1/2}$/V[b] NaClO$_4$ (0.1 mol dm^{-3})	$E_{1/2}$/V[b] Na$_2$SO$_4$ (0.5 mol dm^{-3})
$[NiL^2]^{2+}$	22.3(50) 48.0(11 000)	0.81	0.53
$[Ni_2L^3]^{4+}$	22.3(62) 48.2(11 500)	0.79	0.51
$[Ni_2L^4]^{4+}$	22.3(63) 46.0(11 800)	0.79	0.51
$[Ni_2L^5]^{4+}$	22.4(64) 47.0(12 000)	[c]	0.51

[a] Extinction coefficients for all complexes were calculated per overall nickel(II) ion concentration. [b] *vs.* SCE, sweep rate 50 mV s^{-1}, platinum electrode. [c] Poorly soluble in perchlorate containing solutions.

Voltammograms of the complexes prepared show a single anodic and a single cathodic peaks with a peak-to-peak separation of *ca.* 100 mV. The number of methylene groups in the bridging chain has practically no effect on the $E_{1/2}$ (Table 1) value. These data suggest the absence of interaction between the two metal centres in the electrooxidation processes studied. The differences in potential observed in perchlorate- and sulphate-containing solutions are typical for nickel tetraazamacrocyclic complexes and are explained by substantial thermodynamic stabilization of nickel(III) ions owing to sulphate ion coordination.[7]

(*iii*) Close similarity in UV–VIS and ESR spectral parameters for nickel(III) bis(macrocyclic) complexes and $[Ni^{III}L^2]^{3+}$ also confirms the proposed structure of the former. These complexes are easily accessible by chemical [peroxodisulphate, hydrogen peroxide, bromate or cerium(IV)] or electrochemical (1.0–1.2 V *vs.* SCE) oxidation of common nickel(II) compounds in acidic–aqueous solutions and are characterized by absorption bands near 34 000 cm^{-1} ($\varepsilon \sim 11 000$ dm^3 mol^{-1} cm^{-1}) and 17 000 cm^{-1} ($\varepsilon \sim 100$ dm^3 mol^{-1} cm^{-1}) typical also for other nickel(III) compounds in the tetraazamacrocyclic environment.[7] ESR parameters for the bis(macrocyclic) nickel(III) complexes under consideration are practically identical for all compounds with $g_{\parallel} = 2.028$ and $g_{\perp} = 2.230$ (frozen 0,1 mol dm^{-3} sulphuric acid solution) and differ slightly from those for $[NiL^2]^{3+}$ ($g_{\parallel} = 2.033$ and $g_{\perp} = 2.216$) measured under the same conditions. These data are in accord with a d^7-electronic configuration of nickel(III) in a tetragonally distorted octahedral environment with the unpaired electron occupying d_{z^2}-orbital.

Taking into account the lack of electronic interaction between the metal ions in bis(macrocyclic) complexes it seems to be of interest to compare the kinetic features of their redox reactions with those of monocyclic analogues. For this purpose the investigation of kinetics of oxidation of nickel(II) complexes by two-electron oxidants $S_2O_8^{2-}$ and H_2O_2 was carried out. The nickel(III) complexes formation rate was found to be first order both in nickel(II) and oxidant concentrations and both for bis- and mono-cyclic compounds. But the rate constants observed were found to be several times greater for bis(macrocyclic) complexes than for the monocyclic one. So, k_{obs} for the reactions with peroxoxdisulphate (0.1 mol dm^{-3} perchloric acid, 295 K) are equal to 27, 30, 32 and 5 dm^3 mol^{-1} s^{-1}, and for the reactions with hydrogen peroxide (0.1 mol dm^{-3} sulphuric acid, 295 K) k_{obs} equals 1.5, 0.76, 0.28 and 0.01 dm^{-3} mol^{-1} s^{-1} for $[Ni_2L^3]^{4+}$, $[Ni_2L^4]^{4+}$, $[Ni_2L^5]^{4+}$ and $[NiL^2]^{2+}$ respectively. For comparison, oxidation of $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclodecane) with the same oxidants is characterized[8] by k_{obs} equal to 15 and 0.13 dm^{-3} mol^{-1} s^{-1}.

Thus, results obtained show that synthetic route proposed is convenient for preparation of bis(macrocyclic) complexes of a new type and apparently should be limited neither by type of

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† All compounds gave satisfactory elemental analyses. Unfortunately, admixture of high-spin hexa-coordinated paramagnetic forms of nickel(II) prevents the investigation by means of NMR spectroscopy. The X-ray crystallographic study of some of these complexes is now under way.

aliphatic diamines as bridging linkage nor metal ion as template. The applicability of this method to syntheses of both dicopper(II) and heterobimetallic copper–nickel bis(macrocyclic) complexes and investigation of their reactivity are currently under study in our laboratory.

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References

1 K. B. Yatsimirskii, A. G. Kolchinskii, V. V. Pavlishchuk and G. G. Talanova, *Syntheses of Macrocyclic Compounds*, Naukova dumka, Kiev, 1985; *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum Press, New York, 1979; G. W. Gokel and S. H. Korzeniovski, *Macrocyclic Polyether Synthesis*, Springer Verlag, Berlin, 1982.
2 E. K. Barefield, K. A. Foster, G. M. Freeman and C. D. Hodges, *Inorg. Chem.*, 1986, **25**, 4663; L. Fabbrizzi, L. Molnogna, A. Poggi, T. A. Kaden and L. C. Siegfried, *J. Chem. Soc., Dalton. Trans.*, 1987, 2631; A. McAuley, K. Beveridge, S. Subramanian and T. W. Whitcombe, *Can. J. Chem.*, 1989, **67**, 1657; I. Murase, S. Ueno and S. Kida, *Inorg. Chim. Acta*, 1986, **111**, 57.
3 M. P. Suh and S. G. Kang, *Inorg. Chem.*, 1988, **27**, 2544.
4 Ya. D. Lampeka and S. V. Rosokha, in the press.
5 K. B. Yatsimirskii and Ya. D. Lampeka, *Physicochemistry of Metal Complexes with Macrocyclic Ligands*, Naukova dumka, Kiev, 1985.
6 See, for example: B. Korybut-Daszkiewicz, *J. Coord. Chem.*, 1988, **19**, 101.
7 R. I. Haines and A. McAuley, *Coord. Chem. Rev.*, 1981, **39**, 77.
8 S. V. Rosokha and Ya. D. Lampeka, *Theor. Eksp. Chem.*, 1988, **24**, 577.