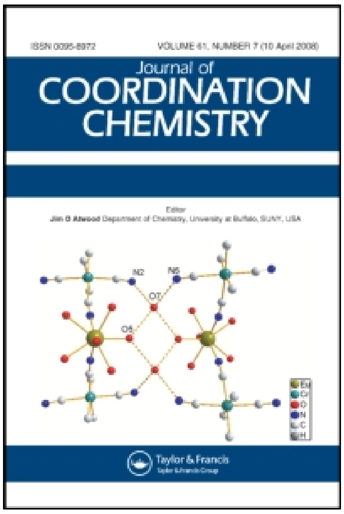

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Preparation, characterization and redox properties of o,o'-geometrical isomers of μ-α and μ-β-aminoisobuty-rato co(ii) complexes with n,n',n',n'''-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane

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PREPARATION, CHARACTERIZATION AND REDOX PROPERTIES OF O,O′-GEOMETRICAL ISOMERS OF μ-α AND μ-β-AMINOISOBUTYRATO Co(II) COMPLEXES WITH N,N′,N″,N‴-TETRAKIS(2-PYRIDYLMETHYL)-1,4,8,11-TETRAAZACYCLOTETRADECANE

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Two new dinuclear cobalt(II) complexes which, besides macrocyclic ligand N′,N′,N″,N‴-tetrakis (2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) contain α- or ß-aminoisobutyrato ions (α-*aibu*⁻ and ß-*aibu*⁻, respectively) were synthesized. The complexes having general formula $[Co_2(aibu)tpmc](ClO_4)_3$ were characterized by elemental analysis, electronic and IR spectroscopy, magnetic measurements and cyclic voltammetry. It was assumed that in both complexes an exo coordination of the macrocyclic ligand is achieved. Cobalt(II) ions are bridged with O,O′-aminoisobutyrato ligand. Both complexes are stable against air oxidation, whereas the oxidation of the complex containing the α-aibu⁻ ion by hydrogen-peroxide gave the coresponding mixed-valence Co^{II}/Co^{III} complex. The complexes are also electrochemically stable in the potential range from–0,6V to 0,4V vs SCE.

INTRODUCTION

In most hitherto described transition metal complexes with amino acids, the latter behave either as N,O-bidentate chelate or as monodentate ligands.[1] Only

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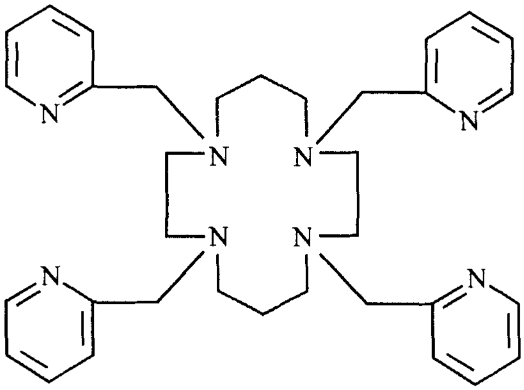


SCHEME 1

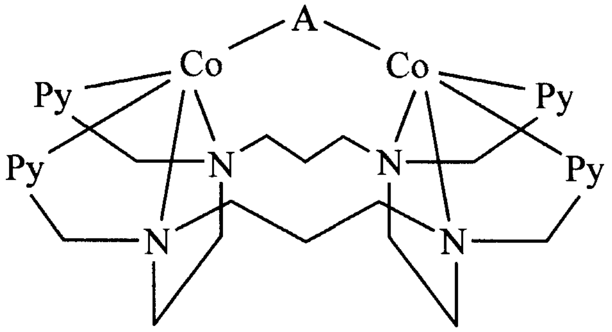
few examples are known in which these ligands form a bridge between two ions, and in that case two types of complexes may be formed. In one type the amino acid is a bridging O,O′-neutral ligand,[2] whereas in the other at the same time both chelate N,O- and a bridging O,O′-anionic ligand.[3]

The N,N′,N″,N‴-tetrakis-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (Scheme 1) belongs to the class of octaazamacrocyclic ligands derived from *cyclam*. A great number of complexes containing this class of ligands [4] (*tpmc*,[5] *taec* [6] and *tcoa* [7])[†] is described. The cited ligands coordinate two metal ions, leaving the site for an additional ligand which forms a bridge between the central ions.

Some cobalt (II) complexes with *tpmc* which as bridging ligands contain some simple anions or linear chain α-aminocarboxylato ions were characterized by their structural and redox properties. The general formula of described complexes was $[Co_2(A)tpmc]^{n+}$, where $A = OH^-$, CO_3^{2-}, gly^-, S-ala$^-$ or S-abu$^-$ [‡]. It was assumed that in all complexes *tpmc* adopts a boat conformation with an *exo* coordination mode (Scheme 2).[8–10] All complexes are stable against air oxidation unexpected for tetraamine Co(II) complexes. The oxidation of the complex with bridging CO_3^{2-} group by hydrogen-peroxide yielded a Co^{II}/Co^{III} mixed-valence complex as the oxidation product.[8]

[†] taec = N,N′,N″,N‴-tetrakis(2-aminoethil)-1,4,8,11-tetraazacyclotetradecane; tcoa = 1,5,8, 12,15,19,22,26-octaazatricyclo(17.9.2 5,15)-dotricontane;

[‡] gly^- = glycinato; S-ala$^-$ = S-alaninato; S-abu$^-$ = S-aminobutyrato ion;



SCHEME 2

The aim of this paper was the synthesis of dinuclear Co(II) complexes which besides *tpmc*, contain the anion of a branched chain amino acids, *i.e.*, α-aibu$^-$ or ß-*aibu*$^-$[¶] as ligands, as well as the determination of the mode of the ligand coordination and the investigation of redox properties of complexes prepared.

EXPERIMENTAL

Safety note! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should not be heated in solid state.

Syntheses

Macrocyclic ligand *tpmc* was prepared by the procedure described in the literature.[5]

[Co_2(α-aibu)tpmc](ClO_4)$_3$ (1): To a suspension of 0.142 g (0.25 mmol) *tpmc* 7 cm^3 $CH_3CN:H_2O$ (10:1, v/v), a solution containing 0.176 g (0.5 mmol) $Co(ClO_3)_3 \cdot 6H_2O$ in 2 cm^3 water, was added. The mixture was stirred for a short time and then the neutralized (pH = 8.5) solution containing 0.025 g (0.243 mmol) of α-aminoisobutyric acid, in a minimum amount of water, was added. The reaction mixture of an intense purple color was continuously stirred for 2^h. On cooling in refrigerator, a crude product containing as impurity the previously described violet complex[9] [Co_2(OH)tpmc](ClO_4)$_3$·H_2O, was

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[¶] a-aibu$^-$ = a-aminoisobutyrato, b-aibu$^-$ = b-aminoisobutyrato ion;

separated. Recrystallization from CH_3CN:H_2O (10:1, v/v) yields 0.109 g (40%) of purple crystals. Anal.: Calcd. for $C_{38}H_{52}N_9Cl_3O_{14}Co_2$: C, 42.14; H, 4.84; N, 11.64%. Found: C, 42.28; H, 5.15; N, 11.24%.

[Co_2(ß-aibu)tpmc](ClO_4)$_3$·H_2O (2): The complex was obtained in a manner similar to that described above, except for the use of a racemic ß-aminoisobutyric acid. Recrystallization from CH_3CN:H_2O (5:1, v/v) yielded 0.159 g (79%) of purple crystals. Anal: Calcd. for $C_{38}H_{54}N_9Cl_3O_{15}Co_2$: C, 41.44; H, 4.95; N, 11.45%. Found: C, 41.09; H, 5.12; N, 11.64%.

[$Co^{II}Co^{III}$(α-aibu)tpmc](ClO_4)$_4$·C_2H_5OH (1a): Complex **1** was dissolved in a minimum amount of CH_3CN and oxidized by 3% H_2O_2 solution. Per each 50 mg of the complex about 5 cm^3 H_2O_2 was added dropwise, whereby the color of the solution changed from purple to brown. Addition of cold ethanol resulted in the precipitation of a brown product. The recrystallization from CH_3CN and precipitation with ethanol gave a pure product in a yield of 25%. Anal.: Calcd. for $C_{40}H_{58}N_9Cl_4O_{19}Co_2$: C, 39.10; H, 4.76; N, 10.26%. Found: C, 38.80; H, 4.59; N, 10.36%.

Measurements

Electronic absorption spectra of complexes in CH_3CN (10^{-3} mol dm^{-3}) were recorded on a GBC-UV/VIS 911A spectrophotometer.

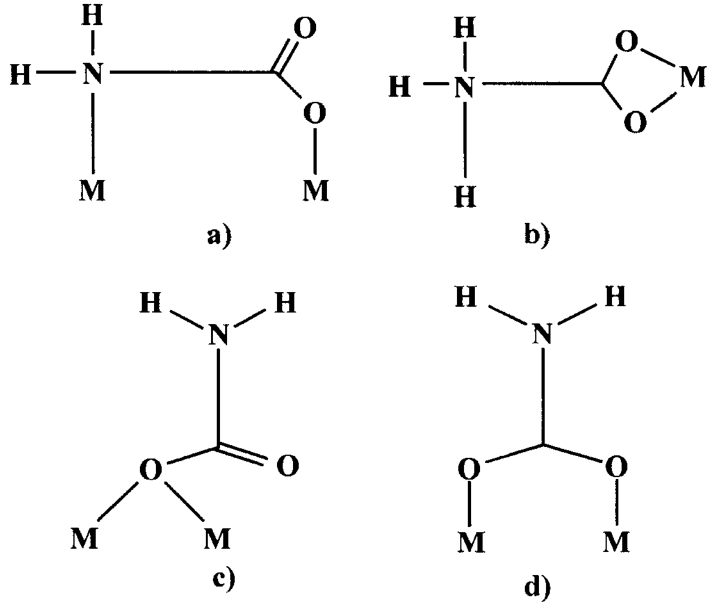
IR spectra were run on a Perkin-Elmer 31725×FTIR spectrophotometer using the KBr disc technique.

Magnetic susceptibility measurements were made at room temperature by magnetic susceptibility balance MSB-MKI Sherwood Scientific Ltd., Cambridge, England. The data were corrected for diamagnetic susceptibilities.

Electrochemical experiments were performed in a standard threelectrode cell [Pt as a counter, saturated calomel electrode (SCE) as a reference and glassy-carbon (GC, Tacusel) as a test electrode]. The GC electrode was prepared as described previously.[11] The surface of the electrode obtained was checked by CV in 100 cm^3 NaOH (0.1 mol dm^{-3}): CH_3CN (70:30, v/v). Then, it was immersed into a solution of examined complexes (10^{-4} mol dm^{-3}) for 30 min., or the complexes were added directly into the cell. CV was performed at a sweep rate of 100 mV s^{-1} whereas the potential ranged from −0.6V to 0.4V vs SCE. Other conditions and electronic equipment were as described previously.[11]

RESULTS AND DISCUSSION

Three dinuclear complexes of Co(II) and *tpmc* with a linear chain µ-α-aminoacids were described in the literature, but the mode of aminocarboxylato



SCHEME 3

ligand (N,O-, O,O′-, or N,O,O′-) coordination was not proposed.[10] In this paper for the first time Co(II) complexes which, besides the *tpmc* ligand, contain a bridging anion of a branched chain amino acid are described.

By means of an aminocarboxylato ligand the bridging between two central ions can be achieved in several simplified modes (Scheme 3).

Synthesis:

The complexes with α-aibu$^-$ and ß-*aibu*$^-$ ligands were prepared by mixing the following reactants: $Co(ClO_4)_2 \cdot 6H_2O$, *tpmc* and aminoisobutyric acid in a 2:1:1 molar ratio. Elemental analysis of complexes corresponds to the general formula $[Co_2(A)tpmc]^{3+}$, where A denotes α- or ß-*aibu*$^-$.

Electronic Spectra:

Data along with the values for the corresponding complexes containing bridging CO_3^{2-} and OH^- ligands are listed in Table I.

TABLE I Electronic spectra in acetonitrile and μ_{eff} per metal atom at room temperature (BM)

Complexes	λ/nm ($\varepsilon/dm^{-3}mol^{-1}cm^{-1}$)			μ_{eff}
$[Co_2(\alpha\text{-aibu})tpmc](ClO_4)_3$	456(99)	514(115)	559(96)sh*	4.10
$[Co^{II}Co^{III}(\alpha\text{-aibu})tpmc](ClO_4)_4 \cdot C_2H_5OH$	431(900)sh*	519(447)sh*		5.75
$Co_2(\beta\text{-aibu})tpmc](ClO_4)_3 \cdot H_2O$	468(86)	513(74)	544(76)	4.55
$[Co_2(OH)tpmc](ClO_2)_2$**	489(60)		574(80)	4.46
$[Co_2(CO_3)tpmc](ClO_2)_2$**	484(33)	518(40)	550(32)	4.20

sh* = shoulder;
**data taken from literature[7,10]

Due to the presence of similar chromophores complexes **1** and **2** exhibit close absorption maxima (for d-d transitions) and a very similar shape of corresponding bands. A similarity with linear chain aminocarboxylato ligands is also noticed[10] indicating the same geometry.

On account of lower symmetry, Co(II) complexes with coordination number (CN) 5 have higher ε-values, in relation to the complexes with CN 6.[12] In agreement with this, ε-values for $[Co_2(OH)L]^{3+}$ complexes are in the range 60–90 $mol^{-1}dm^3cm^{-1}$, whereas for $[Co_2(CO_3)L]^{2+}$ complexes they are in the range from 32–53 $mol^{-1}dm^3cm^{-1}$, where L = *tpmc*, *taec*, *tcoa*.[7,8] Based on it, we assume that both central ions in complexes **1** and **2** have CN 5, so that possibility of N,O,O′-coordination (Scheme 3b) is excluded, since one Co(II) ion would have CN 6 in such case. In complex **1a**, the shift of absorption maximum for d-d transitions, changes in band shapes and a considerable increase in intensities with respect to the starting complex **1**, were observed. Such behavior indicates the presence of Co(III) in the oxidation product.

IR Spectra:

The complexes display the following characteristic bands: a very broad band at 3590-3220 (s) belonging to ν(O-H) from crystalline bonded solvent and ν(N-H); skeletal pyridine vibration at 1610(s); ν(COO) in the range 1670-1355 (s) (see Table II); $\nu(ClO_4^-)$ at 1100 (s, broad), and $\delta(ClO_4^-)$ sharp at 620 (m), where s and m refer to strong and medium intesities, respectively.

By comparing IR spectra of complexes with those of alkali salts of the corresponding amino acids, it is possible to suppose the mode of coordination of the aminocarboxylato ligand.[3a,13–18] From Table II it is seen that the values for Dn(COO$^-$), where $Dn = \nu_{asym} - \nu_{sym}$, for all three complexes are higher than in the case of K-aibu. That indicates that the aminocarboxylato ligands are coordinated through COO$^-$ group.

TABLE II ν_{asym} ν_{sym} and $\Delta\nu$ values of COO^- group for potassium salts of amino acids and of obtained complexes

Compound	ν_{as}	ν_s	$\Delta\nu$
K–α -aibu	1577 vs	1416 vs	161
1	1555 s	1361 w	194
1a	1670 vs 1664 vs 1655 vs	1400 m	263#
K-β -aibu	1584 vs	1408 s	176
2	1543 m	1355 m	188

vs = very strong; s = strong; m = medium; w = weak
# average value

In complexes **1** and **2** the values of ν_{asym} and ν_{sym} are lower than in the corresponding potassium salts. Such a shifting may occur when COO^- group takes part in hydrogen bond formation, or when both oxygen atoms participate in coordination.[14] Due to the steric hindrance COO^- group in complexes is less accessible for hydrogen bonding than in salts of amino acids. Since the values for ν_{asym} and ν_{sym} are still decreased, we assume that COO^- groups are coordinated through both oxygen atoms (Scheme 3d). In the case when only one oxygen is involved in coordination, the COO^- group would be more asymmetrical and values for ν_{asym} would be higher with respect to the uncoordinated group. Complex **1** has a somewhat greater $\Delta\nu$ than complex **2** which means that it has a slightly stronger Co-O bond. In complex **1a** the shift of ν_{asym} to the higher wavenumber, with respect to the complex **1** and K-aibu, is the result of a more asymmetrically bounded COO^- group. On this basis, we assume that in complex **1a** the mode of coordination is changed and the possibility of linking crystalline C_2H_5OH could not be excluded. From Table II it is also evident that in complex **1a** Co-O bond is stronger than in complex **1**.

Magnetic Properties:

All three complexes are paramagnetic and high-spin. The μ_{eff} values (Table I) for complexes **1** and **2** are higher than the spin-only value (3.87 BM). Such a behavior is usual for Co(II) complexes.[13] However, the μ_{eff} value for complex **1** is shifted to the lower limit of experimentally observed values, which can be attributed to the strong magnetic exchange between Co(II) ions.[8] The μ_{eff} value (5.72 BM/Co) for complex **1a** is unusually high, and not in agreement with the expected presence of high-spin Co(II) and low-spin Co(III) in the mixed-valence complex. The same phenomenon was observed in the oxidation product of $[Co_2(CO_3)tpmc]^{2+}$ and it was ascribed to the presence of impurities.[8] Unfortunately, all attempts to obtain less contaminated product **1a** or its single-crystals were unsuccessful.

Electrochemical Behaviour:

Cyclic voltammetry is one of the useful methods for the examination of the redox properties of complexes.[1,11,19]

CV of complex **1** is given in Figure 1a. The double layer capacity of the GC electrode is very expanded indicating the adsorption-desorption processes of the complex without any change in its structure. No charge transfer between the central metal ions and the electrode surface was observed. The holding of the potential at –0.4V also did not cause any charge transfer process.

CV of complex **2** is shown in Figure 1b. The CV clearly shows the absence of adsorption of the complex as well as any charge transfer process. On changing the potential in negative going sweep until –0.8V as well as on holding it constant at –0.4V, no signs of either adsorption or charge transfer processes were observed. Hence, the electrochemical stability is obvious for complexes **1** and **2**.

The differences observed in adsorption-desorption processes between the complexes **1** and **2** can be ascribed to the presence of different number of CH_3 groups bonded to the same C-atom, *i.e.*, complex with α-aibu⁻ ligand, due to the steric hindrance caused by the presence of two CH_3 groups linked to the same C-atom, is solvated to a smaller extent, so the adsorption-desorption processes at the electrode surface are more feasible than in the case of complex with ß-*aibu*⁻ ligand.

CV of complex **1a** (Figure 1c) clearly shows the reversible charge transfer processes between two metal ions at the GC electrode surface at –0.1V vs SCE. The observed reversible peaks remain unchanged with cycling. When holding the potential at the values before the formation of the anodic peaks (–0.150 V vs SCE) the heights of the anodic and cathodic peaks increase, indicating a relatively slow process of complex adsorption. At the electrode surface no sign of complex destruction was observed which points to a typical case of complex adsorption with electrochemically initiated charge transfer between two central metal ions.[20]

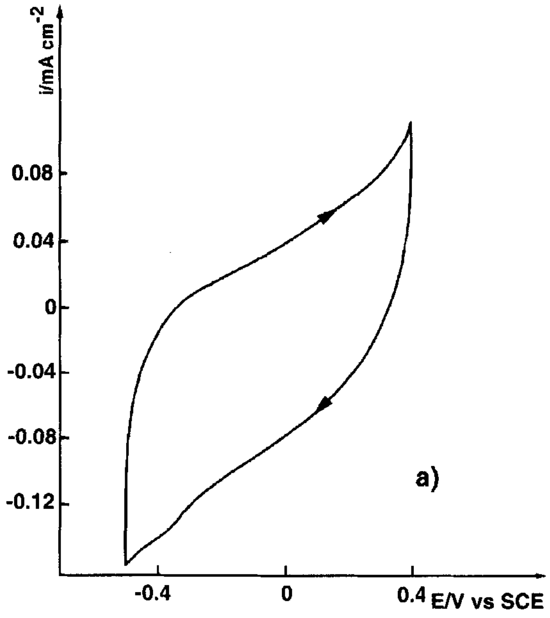


Figure 1a

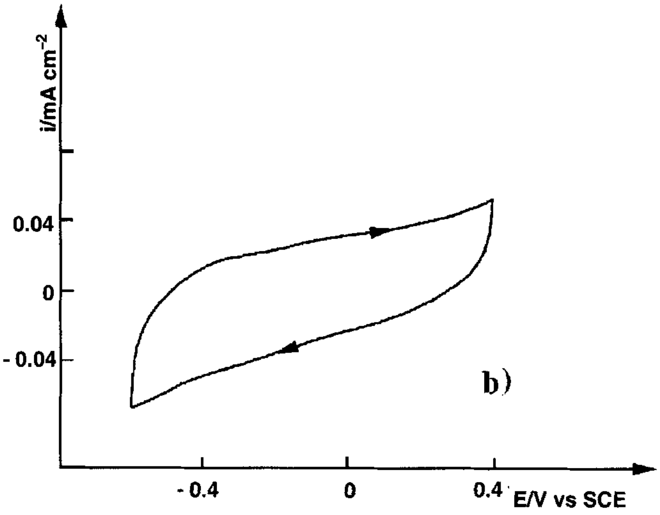


Figure 1b

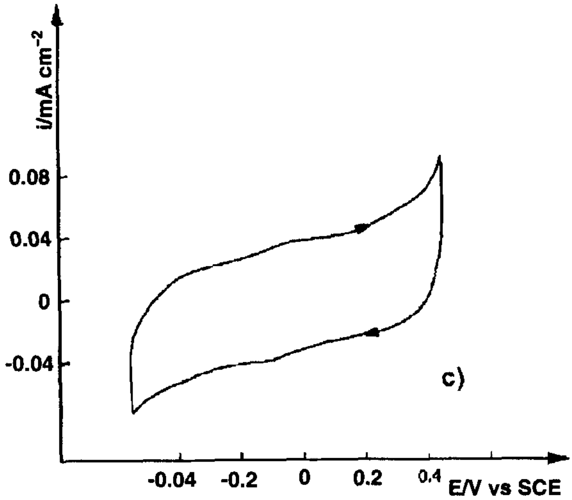
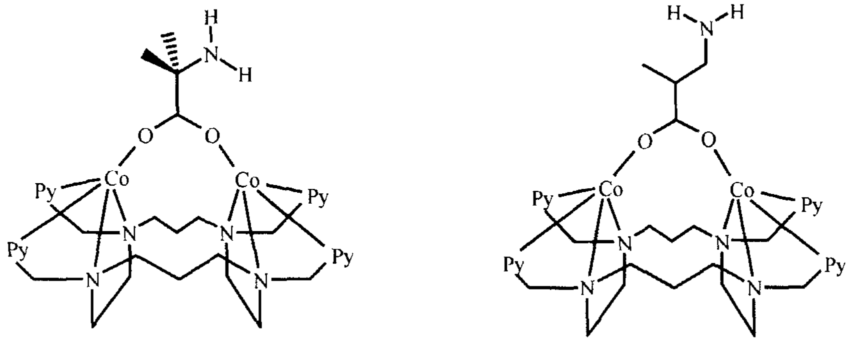


Figure 1c

FIGURE 1 CV of a stationary GC electrode in 100 cm^3 NaOH (0.1 mol dm^{-3}): CH_3CN (70 : 30, v/v) in the presence of: a) complex **1**; b) complex **2**; c) complex **1a**; sweep rate = 100 mV s^{-1}.

It is worth mention that all complexes undergo destruction at the same potential (+0.6V) which can be attributed to the oxidation of organic ligands.

On the basis of all aforesaid we propose that in complexes **1** and **2** the aminoisobutyrato ion achieved bridging O,O′-coordination between two cobalt(II) ions (CN 5), with *tpmc* in an *exo* coordination and boat conformation, as it is can be seen in Scheme 4.



a) b)

SCHEME 4

Acknowledgments

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References

[1] B.P. Straughan, O.M. Lam and A. Earnshaw, *J. Chem. Soc., Dalton Trans.*, **97** and references cited in therein (1987).

[2] C.A. Green, N. Koine, J.I. Leeg and R.D. Willett, *Inorg. Chim. Acta* **176** (1990) 87; b) J. Springborg and H. Toftlund, *Acta Chem. Scand.* Ser.A, **33** 31 (1979).

[3] C.A. McAuliffe, J.V. Quagliano and L.M. Vallariano, *Inorg.Chem.*, **5** (1996) 1996; b) B.W. Low, F.L. Hirshfeld and F.M. Richards, *J. Am. Chem. Soc.*, **81** 4412 (1959).

[4] L.F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, 1st Ed Cambridge University Press, Cambridge, 1989.

[5] N.W. Alcock, K.P. Balakrishan and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1743 (1986).

[6] I. Murase, M. Mikuriya, H. Sonoda, Y. Fukuda and S. Kida, *J. Chem. Soc. Dalton Trans.*, 953 (1986).

[7] I. Murase, G. Vučković, M. Kodera, H. Harada, N. Matsumoto and S. Kida, *Inorg.Chem.*, **30** 728 (1991).

[8] H. Harada, M. Kodera, G. Vučković, N. Matsumoto and S. Kida, *Inorg. Chem.*, **30** 1190 (1991).

[9] M. Mikuriya, S. Kida, T. Kohzuma and I. Murase, *Bull. Chem. Soc. Jpn.*, **61** 2666 (1988).

[10] G.N. Vučković and M.B. Celap, *Proceedings of the 13th Conference on Coordination Chemistry*, Smolenice, ÇSFR, **68** 339 (1991).

[11] S.P. Sovilj, G. Vučković, K. Babić, N. Matsumoto, M. Avramov-Ivić and V.M. Jovanović, *J.Coord.Chem.* **31**, 167 (1994).

[12] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd Ed., Elsevier, Amsterdam, pp. 480–505 1984.

[13] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed., J. Wiley and Sons, New York, p.483 1978.

[14] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd. Ed., (J. Wiley and Sons, New York, 1978.)

[15] M.B. Celap, D.J. Radanović, T.I. Nikolić and T.J. Janjić, *Inorg. Chim. Acta*, **2** 52 (1968).

[16] A.J. Saraceno, I. Nakagava, S. Mizusima, C. Curron and J.V. Quagliano, *J. Am. Chem. Soc.*, **80** 5018 (1958).

[17] D.T. Sawyer and J.M. McKinnie, *J. Am. Chem. Soc.*, **82** 4191 (1960).

[18] G.B. Deacon, R.J. Philips, *Coord. Chem. Rev.*, **33** 227–259 (1980).

[19] M. Beley, J.P. Collin, R. Ruppert and J.P. Sauvage, *J. Chem. Soc. Chem Commun.*, 1315 (1984).

[20] T. Hernadez-Parez, F. Momblona, G. Sanchez and I. Gonzalez, *Book of Abstracts of the 45th Annual Meeteng of ISE*, Porto, Portugal, **2**, IV-33, 1994.