

Tetranuclear Cu(II) complex with octaazamacrocycle and bridging bicyclic dicarboxylato ligands

ZORAN M. MIODRAGOVIĆ^{1*}, GORDANA VUČKOVIĆ¹ and VUKADIN M. LEOVAC^{2#}

¹Faculty of Chemistry, University of Belgrade, P.O. Box 158, YU-11001 Belgrade and ²Institute of Chemistry, Faculty of Science, Trg D. Obradovića 3, YU-21000 Novi Sad, Yugoslavia

(Received 19 March 2001)

A new tetranuclear copper(II) complex of the formula $[\text{Cu}_4\text{L}(\text{tpmc})_2](\text{ClO}_4)_6 \cdot 4\text{NaClO}_4$ (tpmc = *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane; L = *endo*-bicyclo[2.2.1]-hept-5-en-2,3-*cis*-dicarboxylate dianion) has been isolated. The complex was characterized by elemental analysis, magnetic and conductometric measurements, electronic and IR spectroscopy and cyclic voltammetry (CV). This is one of the rare cases when a tetranuclear complex with tpmc is formed, with the bulky bicyclic dicarboxylate as the bridging ligand between two tpmc units in which two copper(II) ions are coordinated in the *exo* position.

Keywords: tetranuclear complex, bicyclic dicarboxylato ligand, octaazamacrocycle, copper(II).

INTRODUCTION

A great variety of coordination modes of carboxylato and dicarboxylato ligands with transition metals is known¹ depending on the reaction conditions, central metal

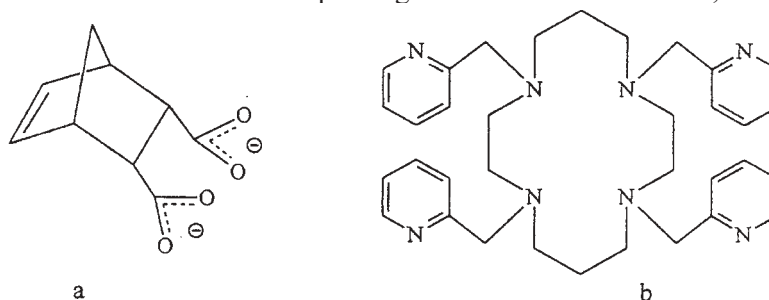


Fig. 1. a) Dianion of the bicyclic dicarboxylate ligand L (*endo*-bicyclo[2.2.1]-hept-5-en-2,3-*cis*-dicarboxylate); b) *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc).

* Author for correspondence (Fax: +381-11-638-785, E-mail: evuckogo@ubbg.etf.bg.ac.yu)

Serbian Chemical Society active member.

ion, etc. In our previous papers^{2,3} we described Co(II) and Co(III) mono- and binuclear mixed-ligand complexes with a bicyclic dicarboxylato ligand (Fig. 1a) and tetra- or octaazamacrocyclic ligand (tpmc, Fig. 1b). In addition, we succeeded in preparing the first tetranuclear complex with tpmc (tpmc = *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) containing the additional malonato ion as a bridging ligand.³ It was observed that cobalt(II) under similar conditions formed a binuclear, but copper(II) a tetranuclear complex. This is ascribed to the greater tendency of bulky ligands to form tetranuclear species with Cu(II), and to the coordination ability of Co(II) to easily adopt both coordination numbers, five and six. In the work reported the same was confirmed in the case of the Cu(II) complex containing the bicyclic dicarboxylato ligand L besides tpmc.

EXPERIMENTAL

Warning! Perchlorate salts of metal complexes containing organic ligands should be handled with great care! They are potentially explosive!

Preparation

The ligand tpmc,⁴ dipotassium salt of bicyclic dicarboxylate (K_2L)^{2,5} and the starting complex $[Cu_2tpmc](ClO_4)_4$ ⁶ were prepared according to the described procedures.

$[Cu_4(L)(tpmc)_2](ClO_4)_6 \cdot 4NaClO_4$. To a solution of 0.146 mmol (159.0 mg) of $[Cu_2tpmc](ClO_4)_4$ in 1 cm³ mixture of acetonitrile-water (10:1, v/v), a solution of 0.219 mmol (60.0 mg) of $K_2L \cdot H_2O$ in 6 drops of water was added dropwise with stirring. The reaction mixture was heated to 75 °C during 3 h with continuous stirring. The colour of the solution changed from violet to blue-green. To facilitate crystallization, small amounts of water and solid $NaClO_4$ were added to the solution. On cooling in a refrigerator overnight, a green-blue deposit appeared. It was separated by vacuum filtration and washed several times with cold water. Recrystallization was achieved from warm acetonitrile and further procedure repeated as for the crude product. The obtained green-blue microcrystalline product was kept in a desiccator over $CaCl_2$. On standing in open atmosphere for a longer period, the crystals can lose their transparency, although the substance is stable. Yield: 122 mg (52 %). Anal. Calcd. for $Cu_4C_{77}H_{96}N_{16}O_{44}Cl_{10}Na_4$: C, 34.90; H, 3.65; N, 8.46 %. Found: C, 35.56; H, 4.05; N, 8.15 %.

Measurements

Elemental analysis (C, H, N) was carried out by standard micromethods at the Center of Instrumental Analysis, University of Belgrade. The electronic absorption spectrum in acetonitrile solution ($c = 1 \times 10^{-3}$ mol/dm³) was recorded using a GBC UV/VIS 911 A spectrophotometer. IR spectra (KBr disc technique) were recorded on a Perkin-Elmer FTIR 31725 X spectrophotometer. The magnetic measurement was carried out at room temperature (19 °C) with a magnetic balance MSB-MKI, Sherwood Scientific Ltd., Cambridge, England, using $HgCo(NCS)_4$ for calibration. The data were corrected for diamagnetic susceptibilities by using the Pascal's constants. Molar electrical conductivities of the complex ($c = 1 \times 10^{-3}$ mol/dm³) and $NaClO_4$ ($c = 4 \times 10^{-3}$ mol/dm³) solutions in acetonitrile were measured at room temperature using a Jenway 4010 conductometer.

Electrochemical measurements were performed in a standard three-electrode cell: Pt as the auxiliary, saturated calomel (SCE) as the reference, and a glassy carbon electrode (GC) (GC20 Tokay) as the working electrode. The GC electrode was prepared according to the previously described procedure.⁷ The measurements were carried out in a mixture of aqueous solution of NaOH ($c = 0.1$ mol/dm³) and acetonitrile (60:1, v/v), the total volume being 30 cm³. The concentrations of the solutions were about 1×10^{-3} mol/dm³. Cyclic voltammetry (CV) was carried out by changing the po-

tential at a rate of 50 mV/s in the potential range from -0.8 to $+0.4$ V vs. SCE, and at 20, 10, 5 and 2 mV/s in the range from -1 to $+1$ V. A MA54450 Iskra polarograph was used as the generator of a triangular linear signal. An XY Graph REC 61 Servograph-Copenhagen was used. Oxygen was removed from the system by constant bubbling with nitrogen (pyrogallol, NaOH). The CV of the supporting electrolyte itself (the scanning rate was 50 and 2 mV/s), as well as of the solutions of tpmc, K_2L , $Cu(ClO_4)_2$ and $[Cu_2tpmc](ClO_4)_4$ (the scanning rate was 2 mV/s) were previously scanned in the range of potential from -1 to $+1$ V (blank test).

RESULTS AND DISCUSSION

The results of elemental analysis (Experimental) are consistent with a tetranuclear structure of the obtained complex, the proposed formula of which is: $[Cu_4L(tpmc)_2](ClO_4)_6 \cdot 4NaClO_4$. It is, after the corresponding malonato analogue,³ the second isolated tetranuclear complex, among numerous binuclear complexes with tpmc described till now. The complex was obtained by the reaction of $[Cu_2tpmc](ClO_4)_4$ and $K_2L \cdot H_2O$ in 1:1.5 mole ratio. The compound is a stable microcrystalline solid, well soluble in acetonitrile.

The molar conductivity (λ_M) value in acetonitrile (1×10^{-3} mol/dm³) of 994 S cm²mol⁻¹ is very high, indicating the great possibility that the assumption about a 1:6 complex electrolyte type is correct, even through there is not sufficient literature data about such an electrolyte type.^{3,8} The conductivity of a $NaClO_4$ solution in acetonitrile (4×10^{-3} mol/dm³) of 540 S cm² mol⁻¹ indicates that the greater part of the conductivity of the solution of this complex originates from the $NaClO_4$ incorporated in the crystal lattice. Nevertheless, the λ_M value for the complex is still very high, as the complex cation of 6+ charge is very voluminous and poorly mobile, which considerably reduces its contribution to the electric conductivity.

The electronic absorption spectrum of the complex in acetonitrile shows a broad maximum at about 663 nm ($\epsilon = 577$ dm³ mol⁻¹ cm⁻¹), corresponding to d-d transitions of the pentacoordinated Cu(II) complexes¹ and to the related complexes with tpmc^{3,6,9} with the same chromophore. However, the molar coefficient of absorptivity is considerably higher than in the corresponding binuclear complexes^{1,6,9} and similar to the analogous tetranuclear μ -malonato one,³ suggesting a tetranuclear structure.

In the IR spectrum, a sharp strong band at 1611 cm⁻¹ (ascribed to skeletal vibration of the pyridine ring), a characteristic broad very strong band at 1092 cm⁻¹ ($\nu(ClO_4)$) and a sharp medium band at 626 cm⁻¹ ($\delta(ClO_4)$) were found.⁹⁻¹¹ A weak broad band at 2931 cm⁻¹ originates from the stretching vibrations of CH, and two medium bands at 1485 and 1448 cm⁻¹ from CH₂ bending vibrations.¹²

No band of "free" C=O groups at about 1700 cm⁻¹ were observed in the IR spectrum of the complex. Since, there is no possibility for the participation of eventually uncoordinated carboxylic O atoms in the formation of hydrogen bonds, it is assumed that all four oxygen atoms of the dicarboxylato ligand L take part in coordination, as in the corresponding tetranuclear μ -malonato Cu(II) complex with tpmc.³ The difference between the asymmetric and symmetric OCO stretching vibrations ($\Delta\nu = \nu(OCO)_{asym} -$

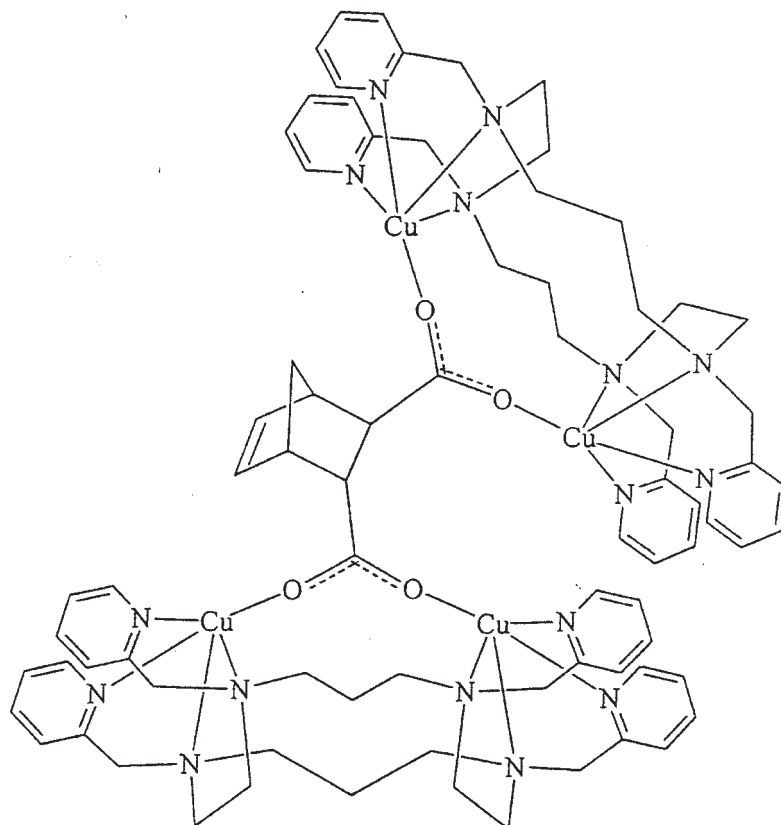


Fig. 2. The assumed structure of the tetranuclear complex cation $[\text{Cu}_4\text{L}(\text{tpmc})_2]^{6+}$.

$\nu(\text{OCO})_{\text{sym}}$) for the isolated complex (175 cm^{-1}) is slightly greater than for $\text{K}_2\text{L}\cdot\text{H}_2\text{O}$ (157 cm^{-1}), indicating a bridging mode of coordination of both dicarboxylato groups of the bicyclic ligand L.^{11,13} The results of elemental analysis, as well as the IR spectrum, allow a polymeric structure of the isolated complex. However, for such a structure a poor solubility and a small molar conductivity value is to be expected, which was not the case. So, each of the four oxygen atoms is most likely coordinated with one of each Cu(II) atoms in two "tpmc units". It is possible that one carboxylate group bridges two coppers from the same or from two different tpmc units. The former case is assumed as more probable (Fig. 2), as steric constraints might exclude the latter.

The value $\mu_{\text{eff}} = 1.44\text{ BM/Cu}$ at room temperature, being considerably lower than the spin-only value ($\mu_{\text{s.o.}} = 1.73\text{ BM/Cu}$), could indicate a magnetic interaction between the metallic centers. The same magnetic anomalies have already been found in some Cu(II) complexes, where the bridged carboxylic group and the copper(II) atoms are coplanar,¹⁴ and the Cu...Cu distance is short enough to enable such interactions.¹ This is the first Cu(II) complex with tpmc having such a small magnetic moment value. Weak interaction was observed only in the case of the binuclear $\mu\text{-OH}$ corresponding com-

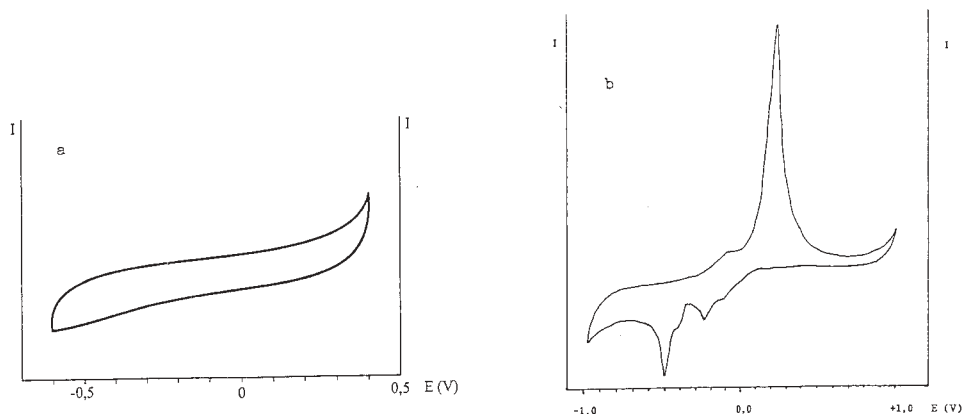


Fig. 3. Cyclic voltammograms of the isolated complex a) sweep rate 50 mV/s; b) sweep rate 2 mV/s.

plex with tpmc, but in this case the $\mu_{\text{eff}}/\text{Cu}$ at room temperature was equal to the spin only value.^{6,14c}

Upon examining the complex by CV in the range from -0.6 to $+0.4$ V (sweep rate 50 mV/s) no peaks were observed (Fig. 3a), confirming its electrochemical stability under these conditions. In order to examine the electrochemical behavior of the complex in detail, it was scanned over an extended range (Fig. 3b), from $+0.8$ to -0.8 V (sweep rate 2 mV/s). However, before scanning, the potential of the working electrode was kept for some time at $+1.0$ V, where the electrochemical oxidation of tpmc ($+0.75$ V) most likely occurs. Then the scanning was carried out in the cathodic direction to -0.8 V and back in the anodic direction to $+0.8$ V. A series of cathodic and two anodic peaks were observed. About the character of the cathodic peaks, with great certainty, the following can be concluded: the cathodic peak at about -0.2 V originates from the electrochemical reduction of Cu(II) from $\text{Cu}(\text{ClO}_4)_2$ or $\text{Cu}(\text{OH})_2$, as it can be assumed that at $+1.0$ V the complex was partially decomposed by the anodic oxidation of the ligand. Thus a part of the Cu(II) passes into the solution. This was proved by the occurrence of the same peak when $\text{Cu}(\text{ClO}_4)_2$ itself was scanned; – the cathodic peaks at about -0.37 and -0.45 V can be ascribed to the cathodic reduction of Cu(II) to Cu(I) or Cu, together with the reduction of Cu(I) to Cu. These peaks most likely originate from the electrochemical reduction of $\text{Cu}(\text{ClO}_4)_2$ itself under the same conditions. However, since the peak at -0.45 V in the CV of the complex is much more intensive than in the voltammogram of $\text{Cu}(\text{ClO}_4)_2$ (at approximately the same concentration of the substances), it can be assumed that (at so slow a sweep rate) the possible electrochemical decomposition of the complex occurs, and thus the peak originates from the reduction of the central metal ion at the electrode. In the anodic part of the CV curve, a peak at about -0.07 V occurs, the origin of which cannot be determined with certainty. However, since this peak is not separated from the very intensive one at $+0.27$ V, it possibly originates from the anodic

oxidation of Cu to Cu(I). The very intensive peak at about +0.27 V can, with all certainty, be regarded as originating from the dissolution of elemental Cu, which was isolated at the GC electrode in the cathodic part of the wave.

On the basis of all data obtained, it can be supposed that the structure of the complex cation of the isolated compound is as shown in Fig. 2. It is in accordance with the conclusions in our previous paper.³ Namely, it was observed that Cu(II) is mostly pentacoordinated^{3,6,9} in complexes with octaazamacrocyclic ligands. Besides, bulky bridging dicarboxylate ligands, like malonato³ or hydrogenisophthalato¹⁵ one, or bicyclic dicarboxylate L, favour the formation of tetranuclear complex ions with tpmc. The isolated compound is one of the few tetranuclear^{3,15} complexes containing Cu(II) and tpmc, among numerous binuclear ones^{3,6,9} reported till now. It is also the first Cu(II) complex with tpmc containing a μ -bonded bicyclic ligand.

Acknowledgement. This work was partially supported by the Ministry for Science and Technology of the Republic of Serbia. The authors are grateful to D. Manojlović, MSc from the Faculty of Chemistry in Belgrade for the CV measurements.

ИЗВОД

ТЕТРАНУКЛЕАРНИ Cu(II) КОМПЛЕКС СА ОКТААЗАМАКРОЦИКЛОМ И БИЦИКЛИЧНИМ ДИКАРБОКСИЛАТО ЛИГАНДОМ У МОСТУ

ЗОРАН М. МИОДРАГОВИЋ¹, ГОРДАНА ВУЧКОВИЋ¹ И ВУКАДИН М. ЛЕОВАЦ²

¹Хемијски факултет, Универзитет у Београду, б. бр. 158, 11001 Београд и ²Институт за хемију, Природно-математички факултет, Универзитет у Новом Саду, Трг Д. Обрадовића 3, 21000 Нови Сад

Изолован је нови тетрануклеарни комплекс бакра(II), формуле $[\text{Cu}_4\text{L}(\text{tpmc})_2](\text{ClO}_4)_6 \cdot 4\text{NaClO}_4$, (tpmc = *N,N',N'',N'''*-тетракис(2-пиридилметил)-1,4,8,11-тетраазамакроциклопентан; L = дианјон *endo*-бицикло[2.2.1]-хепт-5-ен-2,3-*cis*-дикарбоксилата). Комплекс је окарактерисан елементалном анализом, магнетиним и кондуктометријским мерењима, електронском и ИЦ спектроскопијом и цикличном волтаметријом (CV). Ово је један од ретких случајева грађења тетрануклеарног комплекса са tpmc-ом, са волуминозним бицикличним дикарбоксилатом као мостним лигандом између две tpmc-јединице у којима су јонови бакра(II) координовани у *exo* положају.

(Примљено 14. марта 2001)

REFERENCES

1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, 1998
2. Z. M. Miodragović, G. Vučković, V. M. Leovac, V. M. Buzash, *Synth. React. Inorg. and Met-Org. Chem.* **30** (2000) 57
3. Z. M. Miodragović, G. Vučković, S. P. Sovilj, D. M. Manojlović, M. J. Malinar, *J. Serb. Chem. Soc.* **63** (1998) 781
4. S. Chandrasekhar, W. L. Waltz, L. Prasad, J. W. Quail, *Can. J. Chem.* **75** (1997) 1363
5. O. V. Midyanko, V. Y. Galla, V. M. Buzash, V. M. Leovac, *Trans. Metal Chem.* **15** (1990) 96
6. E. Asato, H. Toftlund, S. Kida, M. Mikuriya, K. S. Murray, *Inorg. Chim. Acta* **165** (1989) 207
7. S. P. Sovilj, G. Vučković, K. Babić, N. Matsumoto, M. Avramov-Ivić, V. M. Jovanović, *J. Coord. Chem.* **31** (1994) 167
8. W. J. Geary, *Coord. Chem. Rev.* **7** (1971) 81

9. G. Vučković, E. Asato, N. Matsumoto, S. Kida, *Inorg. Chim. Acta* **171** (1990) 45
10. V. M. Silverstein, G. C. Bassler, *Spectrometric Identification of Organic Compounds*, 2nd ed., Wiley, New York, 1967, p. 104
11. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 5th ed., Wiley, New York, 1997
12. N. C. Kneteen, S. T. Spees, *J. Inorg. Nucl. Chem.* **33** (1971) 2437
13. G. B. Deacon, R. J. Philips, *Coord. Chem. Rev.* **33** (1980) 227
14. a) A. Michalowicz, J. J. Girerd, J. Goulon, *Inorg. Chem.* **18** (1979) 3004; b) M. Julve, M. Verdager, A. Gleizes, M. Philoche-Levisalles, O. Kahn, *Inorg. Chem.* **23** (1984) 3808; c) J. J. Girerd, O. Kahn, M. Verdager, *Inorg. Chem.* **19** (1980) 274; d) V. K. Voronkova, G. Vučković, J. Jezierska, J. Mrozinski, Yu. V. Yablokov, *Inorg. Chim. Acta* **262** (1997) 147
15. M. Antonijević, G. Vučković, *XL Meeting of the Serbian Chemical Society*, Novi Sad, Yugoslavia, 2001, Abstr., NH-2U.