



---

## Synthesis and structure of the $(R_4Pc)Ru(TED)_2$ complex, where $R_4Pc^{2-}$ is the tetra-15-crown-5-phthalocyaninate dianion and TED is triethylenediamine

---

Yulia Yu. Enakieva, Yulia G. Gorbunova, Sergey E. Nefedov\* and Aslan Yu. Tsivadze

*N. S. Kurnakov Institute of General and Inorganic Chemistry, 119991 Moscow, Russian Federation.*

*Fax: +7 095 955 4874; e-mail: snef@igic.ras.ru*

DOI: 10.1070/MC2004v014n05ABEH001915

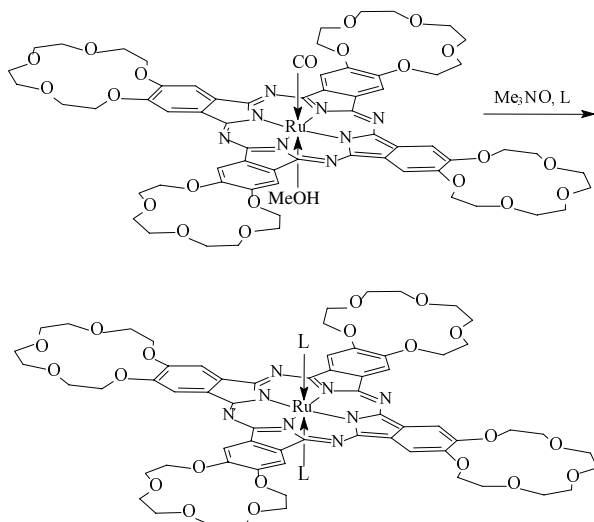
The ruthenium(II) complex  $(R_4Pc)Ru(TED)_2$  [ $R_4Pc^{2-}$  is [4,5,4',5',4'',5'',4''',5''',5''''-tetrakis-(1,4,7,10,13-pentaoxatridecamethylene)-phthalocyaninate anion]; TED is triethylenediamine] with a coordinated tetra-15-crown-5-phthalocyaninate dianion and axially arranged triethylenediamine molecules has been synthesised and characterised.

Interest in transition metal complexes with phthalocyaninate ligands primarily results from their unusual structure, chemical behaviour and physical properties.<sup>1</sup>

Previously, we found<sup>2</sup> that template condensation of dicyanobenzo-15-crown-5 with  $Ru_3(CO)_{12}$  at 250 °C (4 h) followed by the elution of products with a chloroform–methanol mixture from  $Al_2O_3$  results in ruthenium(II) tetra-15-crown-5-phthalocyaninate  $(R_4Pc)Ru(CO)(MeOH)$  **1** with axially coordinated CO and MeOH molecules.

It was shown that the reaction with trimethylamine oxide  $Me_3NO$  in the presence of N-donor ligands results in the elimination of coordinated carbon monoxide and methanol from compound **1** to give the  $(R_4Pc)Ru(NMe_3)(L)$  and  $(R_4Pc)Ru(L)_2$  complexes in different ratios depending on the nature of L and the reaction conditions (L = trimethylamine, triethylamine, pyridine, isoquinoline or pyrazine) (Scheme 1).<sup>3,4</sup>

We observed that the reaction of a solution of compound **1** in chloroform with a 4-fold excess of  $Me_3NO$  and a 100-fold



Scheme 1

excess of TED under reflux gave  $(R_4Pc)Ru(TED)_2$  complex **2** in 90% yield.<sup>†</sup>

X-ray diffraction data<sup>‡</sup> for the solvate of the complex with seven chloroform molecules, which is unstable at room temperature, showed that the  $Ru^{II}$  atom in the molecule of **2** (Figure 1) is bound to four isoindole nitrogen atoms of the tetra-15-crown-5-phthalocyanine ligand and to the nitrogen atoms of two axially coordinated triethylenediamine ligands [ $Ru-N_{iso}$  1.983(3)–1.994(3) Å;  $Ru-N_{TED}$  2.244(3) Å; the  $N_{TED}RuN_{TED}$  angle equals 180°]. The ruthenium atom is arranged exactly in the  $(N_{iso})_4$  plane.

It should be noted that the structure of ruthenium complexes with crown-substituted phthalocyanine ligands has been established for the first time; all conclusions about their structures were based on the analysis of spectral data in comparison with those for non-substituted analogues; X-ray diffraction analysis

<sup>†</sup> Electronic absorption spectra were recorded on a Cary-100 instrument (Varian) in rectangular quartz cells 1 cm thick. IR spectra were recorded on a Nexus FT-IR spectrometer (Nicolet); the samples were prepared as films obtained by evaporation of a solution of the complex on KRS-5 plates.

The MALDI-TOF mass spectrum was obtained on a Reflex-III mass spectrometer (Bruker Daltonics) in the positive ion mode using the reflection mode with a target voltage of 20 mV. 2,5-Dihydroxybenzoic acid was used as a matrix. ESI mass spectra were recorded on a Finnigan MAT INCOS-50 spectrometer (EI 70 eV, chemical ionisation).

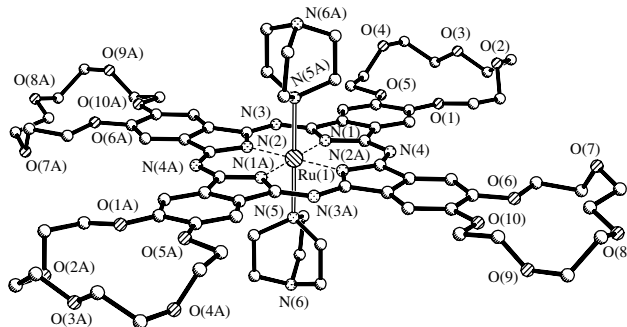
<sup>1</sup>H NMR spectra were recorded on a Bruker AC-200 spectrometer with a working frequency of 200 MHz. The samples were prepared by dissolution in  $CDCl_3$ . The chemical shifts were measured at 303 K using signals from residual protons in  $CDCl_3$  ( $\delta$  7.25 ppm) as internal standards.

Carbonyl(methanol)(tetra-15-crown-5-phthalocyaninate)ruthenium(II) **1** was synthesised from dicyanobenzo-15-crown-5 and  $Ru_3(CO)_{12}$  using the procedure described previously.<sup>2</sup>

Bis(triethylenediamine)(tetra-15-crown-5-phthalocyaninate)ruthenium(II) **2**:  $(R_4Pc)Ru(CO)(MeOH)$  (30 mg, 0.022 mmol) and  $Me_3NO$  (6.27 mg, 0.088 mmol) were dissolved in 3 ml of chloroform; triethylenediamine (234 mg, 2.2 mmol) was added, and the mixture was refluxed for 30 min. The reaction mixture was treated with 10 ml of hexane; the resulting precipitate was filtered off, dissolved in chloroform, and applied on a column (30 cm long, 1 cm in diameter) packed with neutral aluminium oxide. The blue-violet zone was eluted with a  $CHCl_3/MeOH$  mixture (99:1, v/v). The yield of compound **2** was 30.12 mg (90%).

<sup>1</sup>H NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 8.54 (s, 8H,  $H_{Ar}$ ), 4.67 (m, 16H, 1- $CH_2$ ), 4.17 (m, 16H, 2- $CH_2$ ), 3.91 (m, 32H, 3,4- $CH_2$ ), 0.73 {t, 6H,  $R_4PcRu[N(CH_2-CH_2)_3N]_2$ }, -2.36 {t, 6H,  $R_4PcRu[N(CH_2-CH_2)_3N]_2$ }. IR (main bands for the phthalocyanine and crown ether fragments,  $\nu/cm^{-1}$ ): 1610, 1496 ( $C-C_{benzene}$ ), 1278, 1202, 1114, 1065 and 940 (crown ether substituents). UV [ $\lambda_{max}/nm$  ( $\lg \epsilon$ ): 627 (4.94), 573 (sh), 375 (4.64), 321 (5.14)]. ESI MS,  $m/z$ : 1374.3 [ $M - TED_2$ ]<sup>+</sup>, calc. for  $C_{64}H_{72}N_8O_{20}Ru$  1374.38.

Blue-violet single crystals of compound **2**·7 $CHCl_3$  suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of complex **2** in  $CHCl_3$  at 5 °C.

Figure 1 Structure of complex **2**.

revealed the structures of only three of the latter compounds, namely  $[(Ru(py)Pc^{2-})_2(\mu-C)]$ ,<sup>5</sup>  $(Bu_4N)[Ru(CN)(py)Pc^{2-}]$ <sup>6</sup> and  $(Bu_4N)_2[Ru(NO_2)Pc^{2-}]$ ,<sup>7</sup> where  $Pc^{2-}$  is the phthalocyaninate anion.

This study was supported by the Ministry of Industry, Science and Technologies of the Russian Federation (grant no. GK 41.002.1.1.1404), the Russian Foundation for Basic Research (grant nos. 02-03-33210 and 02-03-08013) and the Foundation for the Support of Domestic Science.

## References

- 1 *Phthalocyanines: Properties and Application*, eds C. C. Leznoff and A. B. P. Lever, VCH Publ. Inc., New York, 1993, vol. 1–3.
- 2 Yu. Yu. Enakieva, Yu. G. Gorbunova, S. G. Sakharov and A. Yu. Tsivadze, *Zh. Neorg. Khim.*, 2002, **47**, 1966 (*Russ. J. Inorg. Chem.*, 2002, **47**, 1973).
- 3 Yu. G. Gorbunova, Yu. Yu. Enakieva, S. G. Sakharov and A. Yu. Tsivadze, *J. Porphyrins Phthalocyanines*, 2004, **8**, 778.
- 4 Yu. G. Gorbunova, Yu. Yu. Enakieva, S. G. Sakharov and A. Yu. Tsivadze, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 79 (*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 74).
- 5 A. Kienast, C. Bruhn and H. Homborg, *Z. Anorg. Allg. Chem.*, 1997, **623**, 967.
- 6 M. Weidemann, H. Huckstadt and H. Homborg, *Z. Anorg. Allg. Chem.*, 1998, **624**, 846.
- 7 S. Sievertsen, M. Weidemann, H. Huckstadt and H. Homborg, *J. Porphyrins Phthalocyanines*, 1997, **1**, 379.
- 8 *SMART (control) and SAINT (integration) software*, Version 5.0, Bruker AXS Inc., Madison, WI, 1997.

Received: 4th March 2004; Com. 04/2241

<sup>‡</sup> The X-ray diffraction experiment was carried out at the Centre for Structural Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) using standard procedures<sup>8</sup> on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector ( $\lambda_{Mo}$ , graphite monochromator,  $\omega$ -scanning, scanning step of 0.3°, frame measurement time of 15 s,  $2\theta_{max} = 60^\circ$ ). For 2·7 $CHCl_3$ :  $C_{90}H_{110}Cl_{42}N_{12}O_{20}Ru$ ,  $M = 3269.87$ , space group  $P\bar{1}$ ,  $a = 12.9717(11)$ ,  $b = 15.9309(14)$  and  $c = 18.1636(16)$  Å,  $\alpha = 91.749(2)^\circ$ ,  $\beta = 107.037(2)^\circ$ ,  $\gamma = 112.993(2)^\circ$  (112 K),  $V = 3258.6(5)$  Å<sup>3</sup>,  $Z = 1$ , 18919 measured reflections including 10519 independent reflections with  $F^2 > 2\sigma(I)$ ,  $d_{calc} = 1.666$  g cm<sup>-3</sup>,  $\mu = 10.46$  cm<sup>-1</sup>,  $R_1 = 0.0775$ ,  $wR_2 = 0.1284$ .

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 250908. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.