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Pentamethylenetetrazole Complexes of Co(II), Ni(II) and Cu(II)

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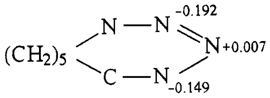
Pentamethylenetetrazole (PMT) (Fig. 1), commonly known as a cardiac drug, has been found to exhibit distinct complexation properties in spite of the very weak acid-base strength and the presence of a pentamethylene ring in its molecule [1,2]. The compound has been found to form single complexes with Co(II), Ni(II) and Zn(II), and two complexes each with Cu(II) and Ag(I) of fair thermodynamic stability in aqueous solutions [2]. It seemed thus worthwhile to study its Co(II), Ni(II) and Cu(II) complexes also in the solid state. Consequently, the purpose of this contribution was to establish their composition, the coordination structure of the central ions, their crystal field parameters and their behavior during electrolytic reduction. Cobalt(II), nickel(II) and copper(II) nitrates, purchased from POCh, Gliwice, Poland, were crystallized from double distilled water. The preparation of pentamethylenetetrazole (PMT) was described in [2]. The reflectance spectra in solid state in the 11000–30000 cm^{-1} range were taken using Li_2CO_3 pellets on a Hitachi 365 UV-VIS spectrophotometer. The remaining devices as well as the techniques used to establish the composition of the complexes, recording the IR spectra, carrying out magnetic, conductometric and cyclic chronovoltammetric measurements are described in [3,5]. Magnetic measurements at ambient temperature were run on a MSB-MKI (Sherwood Scientific Ltd.) instrument. The conductivities at 25°C of 0.001 M aqueous solutions were measured with a Radelkis OK-102/1 conductivity bridge. The distribution of charge densities in the ligands was calculated by PM3 semiempirical methods using a Hyper Chem 5.01 computer program for Windows 95 from Hypercube Inc. To 1 mmol of $M(NO_3)_2 \cdot nH_2O$ (M = Co, Ni and Cu) dissolved in 5.0 cm^3 of water, a solution



PMT

Figure 1. The charge density distribution in pentamethylenetetrazole.

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of 4 mmol of PMT in 10 cm^3 of water was added under stirring. After 24 hrs, the products were filtered off, washed with ethanol, recrystallized and dried *in vacuo* at 25°C. Elemental analyses confirmed the composition.

In Table 1 some physico-chemical characteristics of the complexes are collected. As seen, the conductometric measurements suggest that the complexes are binary electrolytes, whereas the results of magnetic measurements match those of theoretical calculations. The μ BM value is only slightly higher than the theoretical one, presumably due to orbital movement of the electrons. In the infrared spectra taken over the 4000–400 cm^{-1} range of complexes **1**–**3**, the bands in the 3100–3500 cm^{-1} range can be assigned to stretching vibrations of the water molecule. Again, those at 1650, 1665 and 1680 cm^{-1} in the spectra of the Co(II), Ni(II) and Cu(II) compounds, respectively, are due to deformation vibrations of the water molecule. Bands due to the C=N (at 1530 cm^{-1}) and C–N (at 1260 cm^{-1}) vibrations remain virtually unchanged in all the complexes studied. On the other hand, the –N=N- bands of the complexes are displaced by 30 cm^{-1} towards higher frequencies (from 1440 to 1470 cm^{-1}), thus indicating the participation of the nitrogen atom at position 2 of the heterocyclic ring of PMT in the formation of the metal–ligand bond. This conclusion is further supported by examination of the electric charge distribution in the PMT molecule (Fig. 1), which shows that the largest negative charge (–0.192) is located on N-2. Further, it is likely that the 1390 cm^{-1} bands in the spectra of the complexes are due to the nitrato group forming a dative bond by virtue of the lone electron pairs on the oxygen atoms. Again, the band at 1320 cm^{-1} is due to a noncoordinated NO_3^- group. A similar mechanism of formation of the $[ML_4NO_3]^+NO_3^-$ compounds has been reported for Co(II) complexes of 2-methylimidazole [6].

Table 1. Physical data for the complexes.

Complex	Colour	M.p. (°C)	Λ_M (cm^2 Ω^{-1} mol^{-1})	$\mu_{(BM)}$
(1)	pink	40	110	4.1
(2)	blue-green	40	106	3.3
(3)	blue	85	113	1.8

It is highly probable that the bands, due to metal-nitrogen linkages in the Co(II), Ni(II) and Cu(II) complexes, emerge respectively at 241, 269 and 293 cm^{-1}, whereas those due to metal-oxygen linkages at 444, 443 and 456 cm^{-1}. In the visible spectrum of the Co(II)–PMT complex, there is a maximum, $\overline{\nu}_3$ = 19800 cm^{-1}, characteristic of octahedral species. It can be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. A transition from the ground state to the $^4T_{2g}(\overline{\nu}_2)$ appears as a weak band on the shoulder of the main absorption band. Its position, $\overline{\nu}_2$ = 16000 cm^{-1}, was established using the Gaussian distribution.

The first transition predicted by crystal field theory for octahedral Co(II) complexes, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, emerges in the near infrared region at $\overline{\nu}_1$ = 8300 cm^{-1}. The Racah's parameter calculated on the basis of $\overline{\nu}_1$ and $\overline{\nu}_2$ is 853 cm^{-1}, whereas the orbital d split Dq is 939 cm^{-1}. The d-d absorption spectrum of the Ni(II)–PTM complex is characteristic of six coordinate species of the ion. A low-energy absorption due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition appears in the near infrared region at $\bar{\nu}_1 = 9900$ cm^{-1}. The next two bands seen in the visible and ultraviolet range at $\bar{\nu}_2 = 16300$ cm^{-1} and $\bar{\nu}_3 = 26600$ cm^{-1} are due to electron transitions from the ground state $^3A_{2g}$ to $^3T_{1g}(F)$ and $^3T_{1g}(P)$ respectively. Crystal field parameters determined on the basis of $\bar{\nu}_2$ and $\bar{\nu}_3$ [7], B = 819 cm^{-1} and Dq = 1020 cm^{-1}, reveal a weak ligand field and locate pentamethylenetetrazole before imidazole and pyrazole in the spectrochemical series.

With the Cu(II)–PMT complexes, the shape of the absorption bands differs from the Gaussian bell-shapes curve. It is broad, diffuse and extends over the near infrared range with a maximum centered at 14400 cm^{-1}. Such a shape of the bands results from superposition of three single bands at 15440, 13440 and 9524 cm^{-1}. The bands can be assigned respectively to the following electronic transitions: $B_{1g} \rightarrow {}^2A_{1g}$, $B_{1g} \rightarrow {}^2E_g$, $B_{1g} \rightarrow {}^2B_{2g}$ [8].

The solutions under study were 0.001 M in Co(II), Ni(II) and Cu(II) and their PMT complexes. 1 M $NaNO_3$ was the supporting electrolyte. In order to suppress hydrolysis, the electrolytes were 0.001 M in HNO_3. Cyclic voltammetric curves recorded for Co–PMT, Ni–PMT and Cu–PMT are shown in Fig. 2 (A, B, C respectively). In addition, curves of the aqua complexes of Co(II), Ni(II) and Cu(II) have been included. Potentials of the cathodic and anodic peaks for these systems are collected in Table 2.

Table 2. Cathodic and anodic peak potentials of the solutions studied.

Solutions	E_{p1} mV	E_{p2} mV	E_{p3} mV	E_{p4} mV
Co^{2+}	320	–400	–	1010
Co^{2+}-PMT	200	–470	–290	–
Ni^{2+}	350	–380	250	1050
Ni^{2+}-PMT	230	–450	–400	–
Cu^{2+}	200	–110	50	800
Cu^{2+}-PMT	310	550	230	920

As seen in Fig. 2, the reductions proceed in two steps, and peaks on the cathodic branch can be assigned to the following reactions; M(II) + e → M(I) (peaks 1a and 1b) and M(I) + e → M(0) (peaks 2a and 2b). On the other hand, the maxima on the anodic branches correspond to the processes M(0) → M(I) + e (peaks 3a and 3b) and M(I) → M(II) + e (peaks 4a and 4b). The observed lowering of peaks 1b relative to 1a on the cathodic branches of the solutions shows that the PMT complexes of the metals undergo more reluctantly reduction than the corresponding aqua complexes. Accordingly, the complexation inhibits the formation of the Co(I), Ni(I) and Cu(I) ions. On the other hand, peaks 2b are only slightly higher than peaks 2a, which points that the reduction of M(I) to M(0) proceeds more readily than that of M(II) → M(I). It is likely that PMT can catalyze the formation of a monolayer of the metals on the surface of Pt electrode. At a more negative potential of the electrode, hydrogen ions undergo

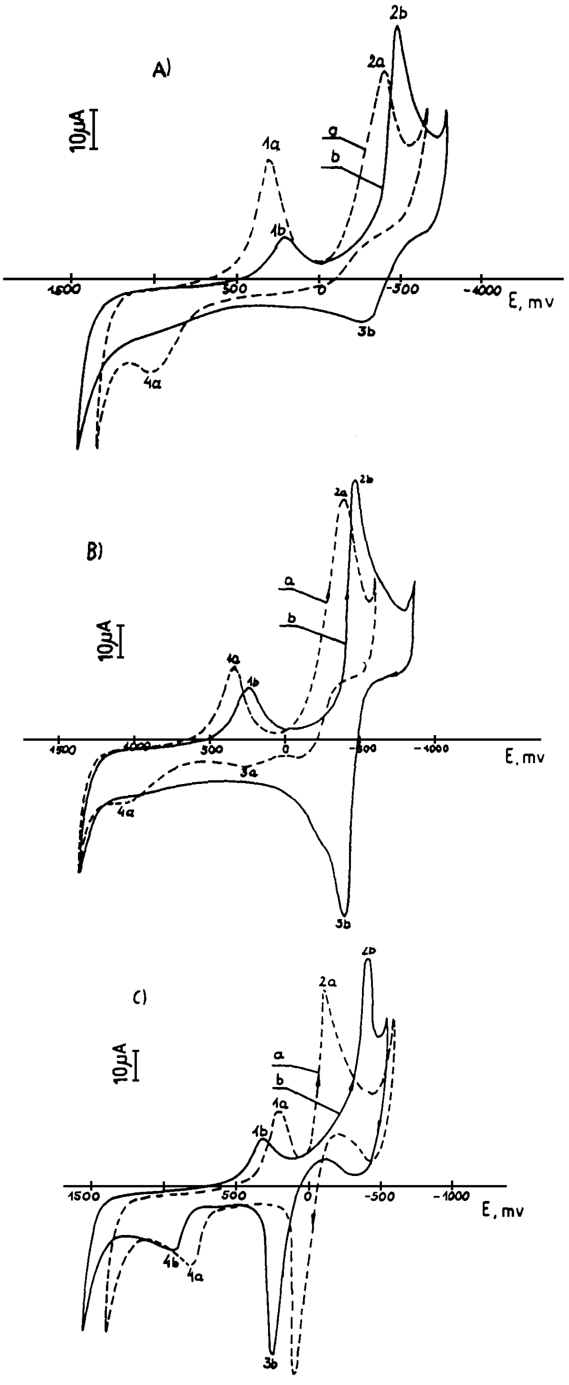

Figure 2. **A.** Cyclic voltammetric curves for: a) Co^{2+} (---) ions and b) $Co(PMT)_4(NO_3)_2\cdot H_2O$ (—) at Pt electrode. **B.** Cyclic voltammetric curves for: a) Ni^{2+} (---) ions and b) $Ni(PMT)_4(NO_3)_2\cdot H_2O$ (—) at Pt electrode. **C.** Cyclic voltammetric curves for: a) Cu^{2+} (---) ions and b) $Cu(PMT)_4(NO_3)_2\cdot H_2O$ (—) at Pt electrode. Potentials measured *vs*. saturated calomed electrode. Scan rate 50 mV/s.

reduction in all the systems studied. After reversion of the electrode potential, only one peak (3b) appears on the anodic branches for solutions of nickel and cobalt and two peaks (3b and 4b) for copper solutions (Fig. 2A, B, C). A comparison of the cobalt, nickel and copper monolayers being oxidized shows that the Co(I) compound is more electrochemically stable than analogous Ni(I) and Cu(I) compounds. Further, it can be speculated that the absence of peaks at more positive potentials indicates that either the Co(II)–PMT and Ni(II)–PMT complexes are not formed at all, or that they are electrochemically more stable than the corresponding copper(II) complexes. Upon further changes of the electrode potential, oxygen is evolved.

REFERENCES

1. Popov A., Castellani C. and Craft M., *J. Am. Chem. Soc*., **80**, 6513(1958).
2. Lenarcik B., Wiśniewski M. and Gabryszewski M., *Polish J. Chem*., **50**, 407 (1976).
3. Wiśniewski M.Z., Surga W.J. and Lenarcik B., *Trans. Met. Chem*., **15**, 63 (1990).
4. Wiśniewski M.Z. and Scendo M., *Polish J. Chem*., **72**, 1269 (1998).
5. Wiśniewski M.Z. and Głowiak T., *Polish J. Chem*., **74**, 1023 (2000).
6. Akhtar F., Hug F. and Skapski A.C., *J. Chem. Soc. Dalton Trans*., 1353 (1972).
7. Lever A.B.P., Inorganic Electronic Spectroscopy, Second ed., Elsevier, NY, 1984.
8. Kurdziel K. and Głowiak T., *Polish J. Chem*., **72**, 2181 (1998).