ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 1, pp. 133–136. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © S.B. Larionov, L.I. Myachina, E.G. Boguslavskii, R.V. Andreev, G.I. Borodkin, V.E. Shubin, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 1, pp. 139–142.

Complexes of Cu(II) and Pd(II) with 2-R-1,3,11,11*c*-Tetraazacyclopenta[*c*]phenanthrenes

S. B. Larionov[a], L. I. Myachina[a], E. G. Boguslavskii[a],
R. V. Andreev[b], G. I. Borodkin[b], and V. E. Shubin[b]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,*
pr. Akad. Lavrent'eva 3, Novosibirsk, 630090 Russia
e-mail: lar@che.nsk.su

[b] *Vorozhtsov Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*

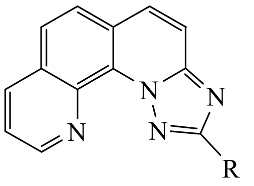
Received March 26, 2009

Abstract—Paramagnetic complexes $CuL^1SO_4\cdot0.5H_2O$, $CuL^2SO_4\cdot2H_2O$ and diamagnetic $Pd(HL^2)Cl_3$ (L^1 = 2-methyl-1,3,11,11*c*-tetraazacyclopenta[*c*]phenanthrene complex (L^2 = 2-phenyl-1,3,11,11*c*-tetraazacyclopenta-[*c*]phenanthrene) were synthesized. The most probable structure of the complexes was suggested on the basis of the IR and ESR spectra. Coordination units of paramagnetic complexes contain N atoms of the bidentate cycle-forming ligands, L^1 and L^2 molecules. The square $PdCl_3N$ unit of the diamagnetic complex includes the N atom of the triazole fragment of the monodentate ligand, $(HL^2)^+$ cation.

DOI: 10.1134/S1070363210010184

Complexes of metals with nitrogen heterocycles form one of the most studied classes of coordination compounds. Of great interest are those nitrogen heterocycles which can play the role of bidentate cycle-forming ligands due to their structure. Widely known ligands of such type are 2,2'-dipyridyl and 1,10-phenanthroline containing two pyridine fragments [1–4]. These heterocycles are classical analytical reagents. Coordination compounds with these ligands have various functional properties. In particular, copper complexes with 1,10-phenanthroline have nonlinear optical properties [5]. Heteroligand complexes of lanthanides containing 1,10-phenanthroline are promising luminescent materials [6]. Complexes with nitrogen heterocycles with two different heterocyclic fragments attract appreciable attention of researchers [7–10]. Complexes of Pd(II) and Pt(II) with triazolopyrimidine were synthesized, and anticancerogenic activity of the platinum complexes was studied [10].

The aim of this work was to synthesize and study complexes of Cu(II) (an intermediate acid according to Pearson) and Pd(II) (a soft acid according to Pearson) with 2-R-1,3,11,11*c*-tetraazacyclopenta[*c*]phenanthrenes L^1 and L^2 containing pyridine and 1,2,4-triazole fragments.



R = Me (L^1), Ph (L^2).

The complex compounds $CuL^1SO_4\cdot0.5H_2O$ (**I**) and $CuL^2SO_4\cdot2H_2O$ (**II**) were obtained with high yields by the reactions of $CuSO_4$ with L^1 and L^2 (the mole ratio Cu:L = 1:2) in the EtOH–H_2O medium. The values of μ_{eff} for paramagnetic complexes **I** and **II** equal to 1.85 and 2.2 BM, respectively, point to the d^9 electron configuration of the Cu^{2+} ion.

In the IR spectrum of free L^1 bands at 1633, 1594, and 1535 cm^{-1} are observed, which can be assigned to the stretching vibrations of conjugated C=C and C=N bonds. In the IR spectrum of complex **I** there are also three bands in the range of 1640–1500 cm^{-1} (1636, 1598, and 1549 cm^{-1}). The shift of bands in the spectrum of complex **I** in comparison to the spectrum of L^1 points to the coordination of nitrogen atoms of ligand L^1 to the ion Cu^{2+}, where L^1 is apparently a bidentate cycle-forming ligand. Such coordination mode results in the formation of the hexatomic chelate cycle CuC_2N_3. The intensive split band at 1192 and 1175 cm^{-1} and the band at 1079 cm^{-1} in the IR

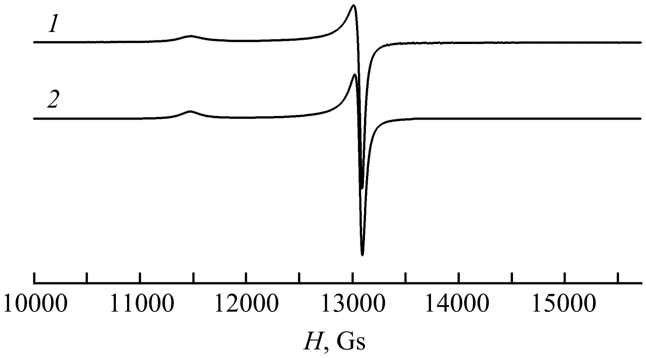


Fig. 1. (*1*) Experimental and (*2*) theoretical ESR spectra of complex **I** in *Q* range.

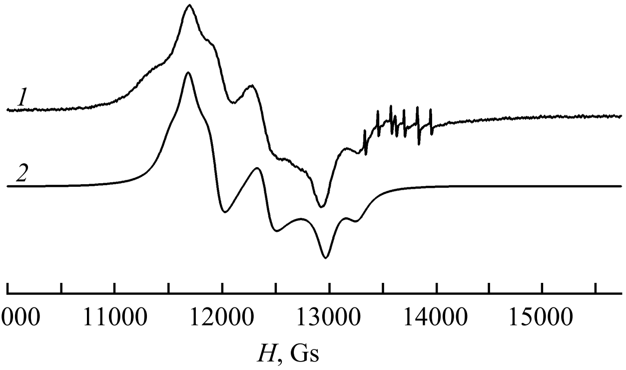


Fig. 2. (*1*) Experimental and (*2*) theoretical ESR spectra of complex **II** in *Q* range. Narrow lines in the high-field part of the spectrum correspond to the Mn^{2+} ion of a standard sample.

spectrum of compound **I** belong to the ν_3 vibrations of a coordinated SO_4^{2-} anion [11]. Apparently this ion also functions as a bidentate cycle-forming ligand. The band at 1002 cm^{-1} corresponds to the ν_1 vibration of the SO_4^{2-} anion. The wide band with a maximum at 3483 cm^{-1} belongs to a crystal water molecule. These results suggest that complex **I** contains the CuN_2O_2 unit formed due to the coordination of bidentate cycle-forming ligands L^1 and SO_4^{2-}.

This conclusion agrees with the ESR data. The ESR spectrum of complex **I** (Fig. 1) is typical for magneto-concentrated copper(II) complexes [12]. The spectrum is characterized by the axial *g*-factor, and the hyperfine structure (HFS) is averaged due to the exchange interaction of unpaired electrons of Cu^{2+} ions. The values of g-factors ($g_{||}$ 2.279, $g_{\perp}$ 2.068, and g_{av} 2.138) are usual for the Cu^{2+} ion which is present in a CuN_2O_2 coordination unit. The anisotropy of the line (90/35 Gs) width is proportional to the averaged HFS [12].

Bands at 1635, 1594, 1534, and 1515 cm^{-1} corresponding to the stretching vibrations of conjugated C=C and C=N bonds are present in the IR spectrum of coordinated L^2. Positions of similar bands in the range of 1640–1500 cm^{-1} in the IR spectrum of complex **II** (1631, 1600, 1544, and 1516 cm^{-1}) differ from those in the spectrum of free L^2, which points to the L^2 coordination to the Cu^{2+} ion through N atoms. The intensive split band at 1153 and 1135 cm^{-1} and the band at 1042 cm^{-1} in the IR spectrum of compound **II** can be assigned to the ν_3 vibration of the coordinated SO_4^{2-} anion. The band at 969 cm^{-1} corresponds to the ν_1 vibration. Unlike the IR spectrum of compound **I** containing crystal water bands, the IR spectrum of complex **II** does not contain an absorption band in the range of 3400–3600 cm^{-1}, however at lower wave numbers there is a wide absorption band of water with a maximum at 3352 cm^{-1}. Apparently, water molecules are coordinated in complex **II**.

The ESR spectrum of complex **II** strongly differs from the spectrum of complex **I**, being characteristic for compounds containing two unpaired electrons (Fig. 2). A satisfactory simulation of this spectrum is reached with the following parameters: *S* 1, *D* 610 Gs, *E* 95 Gs, g_x 2.18, g_y 2.161, and g_z 2.153 (g_{av} 2.165). The line width *W* is 80 Gs in the *x* and *y* directions and 100 Gs in the *z* direction. Such parameters suggest a binuclear structure of complex **II**, where the exchanging pairs of Cu^{2+} ions produce states with full spins *S* 1 and *S* 0. The value of the fine structure parameter *D* in the calculations for the model of interacting point magnetic dipoles corresponds to the Cu···Cu interionic distance of 3.5 Å. The values of *g*-factors found by simulating the spectrum are non-typical for mononuclear complexes of Cu^{2+} ions and have an overestimated average value as compared to g_{av} for complex **I**. Apparently there are two $\{CuL^2(H_2O)_2\}^{2+}$ fragments in complex **II**, which are connected by two bidentate bridging SO_4^{2-} ions. Ions Cu^{2+} are included in the composition of distorted octahedral CuN_2O_4 units formed by N atoms of the bidentate cyclic L^2 ligand, O atoms of two water molecules, and bidentate bridging SO_4^{2-} ionic ligands.

The reaction of $PdCL_2$ with L^2 in ethanol acidified by HCl yields a precipitate of diamagnetic compound **III** with the composition $C_{19}H_{13}Cl_3N_4Pd$ as determined by the elemental analysis. The IR spectrum of compound **III** in the high-frequency region essentially differs from those of complexes **I** and **II**. First, there are no absorption bands in the range of 3800–3200 cm^{-1} that testifies to the absence of water in the composition of complex **III**. Second, a band at 3120 cm^{-1} is observed in the IR spectrum, which is absent from the spectra of free L^1 and L^2 and from the spectra of complexes **I** and **II**. We believe that the band at 3120 cm^{-1} is related to the stretching vibration of the N–H bond. Apparently, the ion Pd^{2+} in complex **III** coordinates not an L^2 molecule, but its protonated form as a monodentate ligand. Hence, the formula Pd(HL^2)Cl$_3$ corresponds to complex **III**. Pyridine is a stronger base (pK_a 5.17) [13] than 1,2,4-triazole (pK_a 2.45) [14]. We can assume that L^2 is protonated at the N atom of the pyridine fragment. Thus when the N atom of the triazole fragment of the monodentate cation ligand HL^{2+} and three Cl$^-$ ions are coordinated to the Pd^{2+} ion the coordination unit PdCl$_3$N is formed. According to the diamagnetism of complex **III**, its symmetry is close to square planar. It is possible that the band at 459 cm^{-1} is related to the Pd–N bond vibration. We have assigned the bands at 330 and 318 cm^{-1} to the vibrations of nonequivalent Pd–Cl bonds [15].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on an AM-400 Bruker spectrometer (working frequency 400 MHz for ^{1}H and 100.6 MHz for ^{13}C). The signals of residual protons of CDCl$_3$ (δ_H 7.24 ppm) were used as the internal standard for ^{1}H and of C atoms of CDCl$_3$ (δ_C 76.9 ppm), for ^{13}C. The mass spectra were recorded on a Finnigan MAT-8200 device. The IR spectra in the range 3800–200 cm^{-1} were recorded on Specord 75 IR and Vertex 80 spectrophotometers. Samples were prepared in the form of suspensions in mineral and fluorinated oils. Magnetic susceptibility of polycrystalline samples was measured by the Faraday method at the room temperature.

The ESR spectra were recorded on a Varian E-109 radiospectrometer equipped with a device for the analog-digital signal transformation and with a special software for the accumulation and primary treatment of spectra. The study was carried out within the *Q* range at the room temperature. Polycrystalline samples were prepared by grinding a small amount of a complex with MgO powder doped by Mn^{2+} ions in the ratio 1:5000. The ESR spectrum of Mn^{2+} ions was used for the calibration of the radiospectrometer working frequency (*g* 2.003, *a* 86.6 Gs). The cited parameters of the ESR spectra were obtained by the interpretation of the spectra and were refined by the simulation of theoretical spectra using the Simfonia program (Bruker).

Compounds L^1 and L^2 were synthesized according to a scheme given in [16]. Reagents were of the analytical or chemically-pure grade. Microanalyses were fulfilled on Hewlett Packard 185 and Carlo Erba 1106 analyzers.

2-Methyl-1,3,11,11*c*-tetraazacyclopenta[*c*]phenanthrene. To a suspension of 0.30 mmol of 1-amino-1,10-phenanthrolinium mesitylenesulfonate [17] in 0.4 ml of a 2 M KOH solution 0.4 ml of CH$_3$CN was added dropwise with stirring. The mixture was stirred for 8 h at room temperature, and then diluted with water (7 ml), and the reaction product was extracted by CHCl$_3$ (3×5 ml). The organic layer was dried with Na$_2$SO$_4$, filtered, and then the solvent was distilled off. The residue was chromatographed on a column (sorbent Al$_2$O$_3$, eluent CHCl$_3$). Yield 18 mg (26%). Colorless powder, mp 175–176°C. ^{1}H NMR spectrum (CDCl$_3$), ppm (J_{HH}, Hz): 2.85 s (C*H*$_3$), 7.68 d.d (H^9, *J* 8.2, 4.3), 7.88 (H^5 or H^4, *AB* system, *J* 8.6), 7.93 (H^4 or H^5, AB system, *J* 8.6), 7.91 (H^7, AB system, *J* 9.2), 7.98 (H^6, AB system, *J* 9.2, 0.3), 8.35 d.d.d (H^8, *J* 8.2, 1.8, 0.3); 9.43 d.d (H^{10}, *J* 4.3, 1.8). ^{13}C NMR spectrum (CDCl$_3$), ppm: 164.5, 151.7 (C^2, C^{3a}); 139.4, 130.3, 129.2, 124.1 (C^{5a}, C^{7a}, C^{11a}, C^{11b}); 150.7 (C^{10}); 136.4, 130.5, 126.9, 125.6, 122.3, 116.3 (C^4, C^5, C^6, C^7, C^8, C^9); 15.2 (CH$_3$). Found: *M* 234.09145. C$_{14}$H$_{10}$N$_4$. Calculated: *M* 234.09054.

2-Phenyl-1,3,11,11*c*-tetraazacyclopenta[*c*]phenanthrene was synthesized analogously. Yield 34 mg (36%). A sample was recrystallized from a benzene-hexane mixture, mp 211–212°C. ^{1}H NMR spectrum (CDCl$_3$), ppm (J_{HH}, Hz): 7.44–7.56 m (H$^{3'}$, H$^{4'}$, H$^{5'}$), 7.70 d.d (H^9, *J* 8.2, 4.2), 7.89 (H^5 or H^4, AB system, *J* 8.6), 7.94 (H^4 or H^5, *AB* system, *J* 8.6), 8.01 (H^6 or H^7, AB system, *J* 9.8), 8.02 (H^7 or H^6, AB system, *J* 9.8), 8.36 d.d (H^8, *J* 8.2, 1.7), 8.48–8.57 m (H$^{2'}$, H$^{6'}$), 9.46 d.d (H^{10}, *J* 4.2, 1.8). ^{13}C NMR spectrum (CDCl$_3$), ppm: 164.7, 152.2 (C^2, C^{3a}); 139.6, 131.0, 130.5, 129.2, 124.4 (C^{5a}, C^{7a}, C^{11a}, C^{11b}, C$^{1'}$); 150.7 (C^{10}); 136.2, 130.7, 129.9, 128.5, 127.7, 126.8, 125.8, 122.4, 116.7 (C^4, C^5, C^6, C^7, C^8, C^9, C$^{2'}$-C$^{6'}$); 15.2 (CH$_3$). Found: *M* 296.10620. C$_{19}$H$_{12}$N$_4$. Calculated: *M* 296.10619.

CuL^{1}SO$_4$·0.5H$_2$O (I). Warm (~50°C) solutions of 0.042 g of CuSO$_4$·5H$_2$O in ~0.7 ml of water and 0.079 g of L^1 in 1.5 ml of EtOH were mixed. A green precipitate was formed on mixing, which was filtered after 3 h, washed with EtOH and hexane, and dried in air. Yield 0.068 g (91%). IR spectrum, cm^{-1}: 3483, 3098, 3073, 3044, 1636, 1598, 1549, 1483, 1446, 1387, 1377, 1192, 1175, 1079, 1002, 860, 676, 575, 478, 399, 328, 315. Found, %: C 41.7; H 2.7; N 13.4. $C_{14}H_{11}Cu\cdot N_4O_{4.5}S$. Calculated, %: C 41.7; H 2.75; N 13.9.

$CuL^2SO_4\cdot 2H_2O$ (II). Warm solutions of 0.050 g of $CuSO_4\cdot 5H_2O$ in 1 ml of water and 0.118 g of L^2 in 3 ml of EtOH were mixed. On cooling the solution to room temperature a yellow precipitate was formed, which was treated in the same way as the precipitate of complex **I**. Yield 0.118 g (~100 %). IR spectrum, cm^{-1}: 3352, 3078, 1631, 1599, 1544, 1516, 1447, 1315, 1299, 1153, 1135, 1042, 969, 852, 739, 721, 693, 658, 574, 450, 416, 365, 331, 308, 302. Found, %: C 45.7; H 3.0; N 11.2. $C_{19}H_{16}CuN_4O_6S$. Calculated, %: C 46.3; H 3.2; N 11.5.

$Pd(HL^2)Cl_3$ (III). To a solution of 0.036 g of $PdCl_2$ in a mixture of 1.5 ml EtOH and three drops of concentrated HCl a solution of 0.059 g of L^2 in 1.5 ml of EtOH was added. The precipitate formed was filtered off after ~4 h, washed with EtOH and hexane, and dried in air. Yellow-pink powder. Yield 0.063 g (62%). IR spectrum, cm^{-1}: 3120, 3065, 1641, 1607, 1577, 1531, 1462, 1378, 890, 847, 785, 729, 715, 644, 563, 459, 415, 362, 330, 318, 262, 235. Found, %: C 45.0; H 2.6; Cl 20.9; N 10.7. $C_{19}H_{13}C_{l3}N_4Pd$. Calculated, %: C 44.7; H 2.6; Cl 20.85; N 11.0.

ACKNOWLEDGMENTS

A.Yu. Vorob'ev took part in the experiments. The authors are grateful to V.A. Daletskii for measuring magnetic susceptibility and to L.A. Sheludyakov for taking IR spectra.

REFERENCES

1. Lindoy, L.F. and Livingstone, S.E., *Coord. Chem. Rev.*, 1967, vol. 2, no. 2, p. 173.
2. König, E., *Coord. Chem. Rev.*, 1968, vol. 3, no. 4, p. 471.
3. McWhinnie, W.R. and Miller, J.D., *Adv. Inorg. Chem. Radiochem.*, 1969, vol. 12, p. 135.
4. McKenzie, E.D., *Coord. Chem. Rev.*, 1971, vol. 6, nos. 2–3, p. 187.
5. Yu, J.-H., Lü, Z.-L., Xu, J.-Q., Bie, H.-Y., Lu, J., and Zhang, X., *New. J. Chem.*, 2004, vol. 28, no. 8, p. 940.
6. Katkova, M.A., Vitukhnovskii, A.G., and Bochkarev, M.N., *Usp. Khim.*, 2005, vol. 74, no. 12, p. 1293.
7. Ivashchenko, A.V., Garicheva, O.N., and Ivanova, T.N., *Koord. Khim.*, 1983, vol. 9, no. 11, p. 1508.
8. Escrivà, E., Garcia-Lozano, J., Martínez-Lillo, J., Nuñez, H., Server-Carrio, J., Sato, L., Carrasco, R., and Cano, J., *Inorg. Chem.*, 2003, vol. 42, no. 25, p. 8328.
9. Aakeröy, C.B., Schultheiss, N., and Desper, J., *Inorg. Chem.*, 2005, vol. 44, no. 14, p. 4983.
10. Ruiz, J., Villa, M.D., Cutillas, N., Lopez, G., de Haro, C., Bautista, D., Mareno, V., and Valencia, L., *Inorg. Chem.*, 2008, vol. 47, no. 11, p. 4490.
11. Nakamoto, K. and McCarthy, J., *Spectroscopy and Structure of Metal Chelate Compounds*, New York: Wiley, 1968, p. 216.
12. Al'tshuler, S.A. and Kozyrev, B.M., *Elektronnyi paramagnitnyi rezonans* (Electron Paramagnetic Resonance), Moscow: Nauka, 1972, p. 442.
13. Brown, H.C. and Mihm, X.R., *J. Am. Chem. Soc.*, 1955, vol. 77, no. 7, p. 1723.
14. Hansen, L.D., Baca, E.J., and Scheiner, P., *J. Heterocyclic Chem.*, 1970, vol. 7, no. 4, p. 991.
15. *Comprehensive Inorganic Chemistry*, Bailar, J.E., Emelèus, H.J., Nyholm, R., and Trotman-Dickenson, A.F., Eds., Oxford: Pergamon Press, 1973, vol. 3, p. 1284.
16. Andreev, R.V. and Borodkin, G.I., Abstracts of Papers, *Trudy konferentsii "Organicheskii sintez v novom stoletii"* (Proc. Conf. "Organic Synthesis in the New Century"), St. Petersburg: S.-Peterburg. Gos. Univ., 2002, p. 64.
17. Takeuchi, H., Hayakawa, S., Tanahashi, T., Kabayashi, A., Adachi, T., and Higuchi, D., *J. Chem. Soc., Perkin Trans. 2,* 1991, no. 6, p. 847.