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Mixed Palladium(III)–Nickel(II) and Palladium(II)–Copper(II) Complex Salts with Biuret and the N_4-Macrocycle Cyclam†

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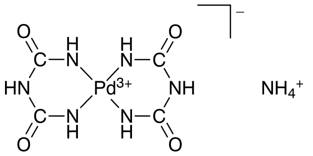
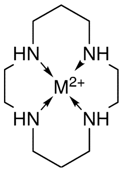
Three paramagnetic mixed salts of palladium(III) and palladium(II) complexes with biuret and Cu(cyclam)$^{2+}$ or Ni(cyclam)$^{2+}$ are obtained and their magnetic properties studied.

Recently we succeeded in obtaining a new anionic paramagnetic palladium(III)–biuret ($BiuH_2$) complex {[$Pd^{III}(Biu)_2$]$^-$} which is precipitated with NH_4^+.[1]



On the other hand it is well documented that some combinations of charged metal complex species are capable of forming metal chains which exhibit interesting magnetic properties.[2] We thus tried to obtain mixed complex species reacting [$Pd^{III}(Biu)_2$]$^-$ with Cu(cyclam)$^{2+}$ and Ni(cyclam)$^{2+}$.



M = Ni, Cu

The results obtained for the newly synthesized compounds are reported in the present paper.

Experimental

Synthesis of the Complexes—$NH_4[Pd(Biu)_2]$, [Cu(cyclam)][ClO_4]$_2$ and [Ni(cyclam)]Cl_2 were synthesized according to known procedures.[1,3,4]

The mixed complex salts [$Pd(BiuH_2)$][Ni(cyclam)]Cl_5 **1** and [$Pd(BiuH_2)$][Cu(cyclam)]Cl_4 **2** were obtained by dissolving 40 mg $NH_4[Pd(Biu)_2]$ in 25 ml of 3×10^{-2} M HCl (pH ≈ 1.5) with immediate addition of 5 ml of 1×10^{-2} M [M(cyclam)]$^{2+}$ aqueous solution, resulting in spontaneous precipitation of the salts formed.

The salt $[Pd(Biu)_2]_2$[Ni(cyclam)]·$5H_2O$ **3** was obtained by mixing aqueous solutions of $[NH_4]_2PdCl_4$ (6 ml, 5×10^{-2} M) and biuret (20 ml, 2.3×10^{-1} M) in molar ratio 1:15 and successive addition of a Ni(cyclam)Cl_2 aqueous solution (7 ml, 2×10^{-2} M) (Pd : Ni = 2:1). After adjusting the acidity of the reaction mixture (KOH solution) to pH 4.8–5.0 a yellow precipitate was formed.

The residues were filtered off, washed repeatedly with distilled water and dried over P_4O_{10} for 2 weeks.

The Ni and Cu content was determined by atomic absorption analysis (AAA) and Pd content was determined gravimetrically after treatment with conc. H_2SO_4 and following calcination at 800 °C to constant weight.

Physical Measurements—The IR spectra were recorded on a Specord IR-75 instrument (Carl-Zeiss, Jena) (Nujol muls) and EPR spectra on an X-band EPR spectrometer (Bruker B-ER 420) (temperature range 130–300 K). Magnetic susceptibility measurements were performed using the Faraday method in the temperature range 160–300 K. The thermogravimetric data were obtained on a Perkin-Elmer TGS-2 instrument and AAA was performed using a Perkin-Elmer 1100 B spectrometer.

Results and Discussion

The analytical data obtained (Table 1) show good reproducibility from batch to batch. The presence of water molecules in complex **3** is proven also by TG measurements. In the temperature range 40–170 °C a mass loss of 9.2% was registered, the theoretical value being 9.3%.

The IR data show the presence of both biuret and cyclam in the mixed complexes **1**–**3** (Table 2). In their IR spectra both $\nu_{C=O}$ and $\nu_{=NH}$ bands of biuret are present together with bands in the range 1100–1000 cm^{-1}, typical for cyclam skeletal vibrations. It should be noted also that the ν_{NH} vibrations of the cyclam molecules in the mixed complex salts are affected significantly: they are shifted from 3240 cm^{-1} (Cu–cyclam) and 3220, 3150 cm^{-1} (Ni–cyclam) to 3185 and 3140 cm^{-1}. The $\nu_{C=O}$ band of **3** is also shifted to lower frequency compared with that of $NH_4[Pd(Biu)_2]$. All these data indicate additional interactions of C=O and NH groups in the molecules of the mixed complex salts **1**–**3**, most likely due to hydrogen-bonding.

All three complexes are paramagnetic and their effective magnetic moment (μ_{eff}) values were determined‡ at ambient temperature (293 K) (Table 3). It is evident that most likely in complex **2** the diamagnetic palladium(II) ion (square-planar coordination) is present, since the μ_{eff} value of 1.96 μ_B is typical for square-planar copper(II) complexes.[5]

Table 1 Analytical data (%)[a] for the complexes

Complex	C	H	N	Cl	Ni or Cu	Pd
[$Pd(BiuH_2)$][Ni(cyclam)]Cl_5 **1**	22.2 (22.4)	4.3 (4.5)	15.0 (15.3)	27.3 (27.2)	9.2 (9.0)	16.5 (16.5)
[$Pd(BiuH_2)$][Cu(cyclam)]Cl_4 **2**	23.1 (23.4)	4.4 (4.7)	15.6 (15.9)	23.4 (23.0)	10.4 (10.3)	16.9 (17.3)
$[Pd(Biu)_2]_2$[Ni(cyclam)]·$5H_2O$ **3**	22.5 (22.4)	4.9 (4.8)	23.7 (23.2)	—	6.5 (6.1)	22.3 (22.0)

[a]The results coincide within experimental error (±0.3%) for samples from three different batches; calculated values in parentheses.

For the other two complex salts the presence of Pd^{3+} ions might be assumed, taking into account that square-planar Ni(cyclam)$^{2+}$ complexes are diamagnetic. For the monomeric complex **1** the experimental μ_{eff} value of 1.68 μ_B is very close to the theoretical one (1.73 μ_B), while for the Pd^{3+}–Pd^{3+} species **3**, μ_{eff} of 2.50 μ_B is coincident with the

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡Calculated according the relation $\mu_{eff} = 2.828\sqrt{\chi_m T}$ with corresponding diamagnetic corrections made.

Table 2 Selected IR data for the complexes

Complex	ν_{OH}	$\nu_{=NH}$	$\nu_{NHcyclam}$	$\nu_{C=O}$	$\nu_{CN}+\delta_{CNH}$
$NH_4[Pd(Biu)_2]$	—	3320	—	1740	—
$[Cu(cyclam)][ClO_4]_2$	—	—	3240	—	1150–1050,[a] 1040–1000
$[Ni(cyclam)]Cl_2$	—	—	3220, 3150	—	1110, 1100, 1080, 1070, 1050, 1010, 1000
1	—	3320	3140	1740	1130, 1105, 1070, 1055, 1030
2	—	3320	3185	1740	1110, 1100, 1070, 1040, 1000
3	≈3480	3310	3140 (br)	1740w, 1680	1110, 1075, 1055, 1030, 1000

[a]Overlapping with $\nu_{ClO_4^-}$ (1150–1050 cm^{-1}).

Table 3 Molar magnetic susceptibility and magnetic moment for the three complexes at 298 K

Complex	χ_m	μ_{eff}/μ_B
1	1.19×10^{-3}	1.68
2	1.62×10^{-3}	1.96
3	2.63×10^{-3}	2.50

expected value (2.45 μ_B). For the latter the dependence of μ_{eff} with temperature was followed (Fig. 1) and the data obtained show a significant increase of magnetic moment with temperature, typical for antiferromagnetic exchange between the two Pd^{3+} ions.

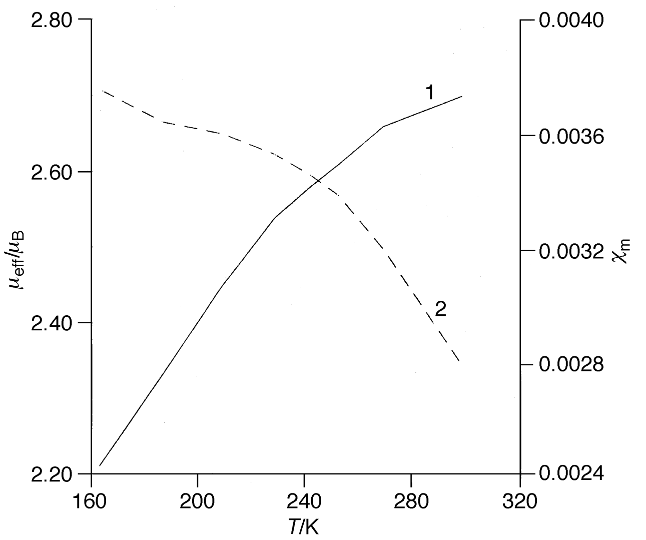
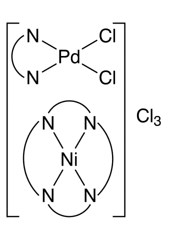


Fig. 1 Temperature dependence of the magnetic moment (curve 1) and the molar magnetic susceptibility (curve 2) for complex **3**

Additional evidence for the +3 oxidation state of palladium ion was obtained for **3** according to EPR spectroscopy. The complex exhibits a broad EPR signal (≈50 G) with a *g*-value of 2.2 which is typical for low-spin palladium(III) species.[1]

On the basis of these data the following structures are proposed:



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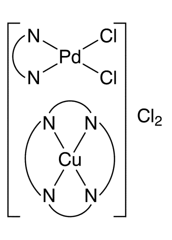

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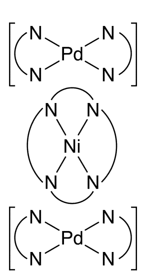

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