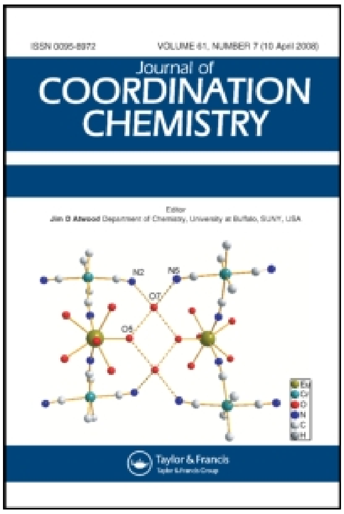

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SYNTHESIS AND PRELIMINARY STUDY OF CU(II) AND PD(II) COMPLEXES WITH A NEW CHELATING BIS(TRIAZOLYL)TRIAZENIDO LIGAND

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NOTE

SYNTHESIS AND PRELIMINARY STUDY OF CU(II) AND PD(II) COMPLEXES WITH A NEW CHELATING BIS(TRIAZOLYL)TRIAZENIDO LIGAND

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The triazenide anion in Ar-NH-N = N-Ar can bind as a monodentate (N^1 or N^3), a bidentate (N^1, N^3) or a μ, η^2 bridging (N^1, N^3) ligand[1]. On an other hand, azoles, in particular 1,2,4-triazoles, are versatile ligands which can give polynuclear metal complexes through various bridging modes[2]. Interest in *quasi*-linear polynuclear complexes liable to exhibit unusual properties prompted us to study 1,3-bis(azolyl)triazenes, which form a new class of ligands combining these two coordinating units. In this note we report the synthesis and characterization by IR absorption, micro-Raman and ^{1}H-NMR spectroscopy of complexes of Cu(II) and Pd(II) with the ligand 1,3-bis[3-(5-amino-1,2,4-triazolyl)]triazene (BATTH hereafter; Fig. 1) and chloro ligands.

EXPERIMENTAL

BATTH.2HCl(0.5H_2O)(**1**) was prepared following ref. 3 except for the synthesis of the intermediate nitrosoamino compound.[4] BATTH (**2**) was precipitated by neutralisation of **1** with KOH in methanol.

Cu(BATT)Cl(3)

A solution of $CuCl_2.2H_2O$ (1.47 mmol) in water (50 cm^3) was added to an equimolar solution of **1** in water (2 dm^3). After two days, green, dichroïc needles were filtered off and washed with water, ethanol and ether (248 mg, 55%). *Anal.* Calcd. for $C_4H_6N_{11}Cu$: Cu, 20.7; C, 15.6; N, 50.2; Cl, 11.5%. Found: Cu, 19.5; C, 16.8; N, 49.2; O, 1.6; Cl, 10.8%.

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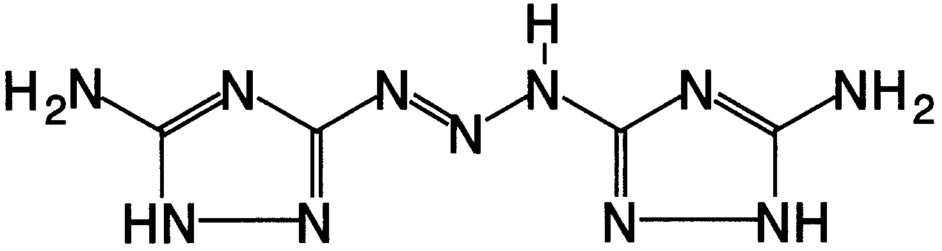

Figure 1 The ligand BATTH.

Pd(BATT)Cl.CH$_3$OH(4)

A solution of **1** (0.77 mmol) in CH_3OH (150cm^3) was added to K_2PdCl_4 (0.77 mmol) in CH_3OH (500 cm^3). A few days later, red-orange, prismatic crystals were separated from amorphous material by several decantations and then filtered off, and washed with methanol and ether (237 mg, 62%). *Anal.* Calcd. for $C_5H_{10}N_{11}OPd$:Pd, 27.9; C, 15.7; N, 40.3; O, 4.2; Cl, 9.3%. Found: Pd, 27.6; C, 15.9; N, 40.3; O, 4.4; Cl, 9.5%.

The compounds were dried at 30°C at 10^{-3} torr before analysis (Analytische Laboratorien Prof. Dr. H. Malissa and G. Reuter, D-51647 Gummersbach). IR spectra were recorded with a Bruker IFS 113V FT spectrophotometer and the Raman spectra with a micro-Raman Mole S-3000 (Jobin-Yvon) using an argon ion laser source (514.5 nm). ^1H-NMR spectra were recorded with a Bruker AMX300 spectrometer (300MHz, standard $SiMe_4$). The complexes are insoluble in common solvents except DMSO (~50 mmol dm^{-3}) and DMF (~5 mmol dm^{-3}). These low solubilities precluded any determination of molecular mass by cryoscopic and osmometric measurements. Moreover, FAB MS experiments on the different complexes using various liquid matrices proved quite unsuccessful. Conductivity measurements of solutions (1 mmol dm^{-3}, 25°C) indicate the non-electrolyte nature of complexes **3** and **4** in DMF [Λ(ohm^{-1} mol^{-1} cm^2) = 3.6 and 5.1, $\Lambda_{KCl} = 69.9$] and a limited solvolysis effect for the Pd(II) complex in DMSO [Λ (ohm^{-1}mol^{-1}cm^2) = 2.41, Λ_{KCl} = 12.35]. Rotating crystal photographs (CuK_α) of needles of the Cu(II) compound grown in solution indicate that the needle axis corresponds to a crystal parameter of 7.0 Å. However these needles are actually unsuitable for a crystal structure determination as shown by the presence of multiple spots (twinning).

RESULTS AND DISCUSSION

We have performed ^{15}N isotopic substitution of the central nitrogen atom N^2 of the triazenic function of the ligand by use of $Na^{15}NO_2$ and have synthesized the isotopic forms of the complexes. The symmetric and antisymmetric stretching modes of the triazenic group can be easily identified by isotopic shifts of 10-20 cm^{-1} [ν_s (cm^{-1}) = 1253 (**1**), 1284 (**3**), 1284 and 1271 (**4**); ν_{as} (cm^{-1}) = 1486 and 1422 (**1**), 1378 (**3**), 1373 and 1360sh (**4**)]. In the IR spectra of the complexes the $\nu_s(N_3)$ stretching band is absent (**3**) or small (**4**) whereas it is very intense in the Raman spectra; the situation is quite reversed in the case of the $\nu_{as}(N_3)$ band. No such effect is present in the IR and Raman spectra of the ligand. These sharp differences suggest that the triazene acquires a symmetric C_{2v} structure[5] as a result of deprotonation in the complex (—N = N—NH—→—N$\overset{...}{-}$N$\overset{...}{-}$N—). Upon complexation two prominent lines emerge in the low wavenumber region of the Raman spectrum at 388 and 571 cm^{-1} for **3**, and at 409 and 595 cm^{-1} for **4**. In the case of the isotopic Cu(II) complex, the line at 388 cm^{-1} is shifted by 8 cm^{-1}. However, the angular deformation $\delta(N_3)$ mode shows practically no isotopic shift in the spectra of the free ligands, 1,3-diphenyltriazene[6] or ligand **1**. Considering the shift of 8 cm^{-1} recorded for $\nu_{as}(Cu\text{-}^{15}N)$ at 426 cm^{-1} in the case[7] of $[Cu(^{15}NH_3)_4]^{++}$ and the usual range of ν(Cu-N) values for haloamine complexes,[8] we attribute the line at 388 cm^{-1} to the Cu(N-N-N) stretching mode and the line at 571 cm^{-1} to the $\delta(N_3)$ angular deformation mode in the complex. This would appear to be the first example of a nitro-type mode of coordination for a triazenide group.[1] In the case of the Pd complex the isotopic sensitive line at 595 cm^{-1} (shift = 6 cm^{-1}) is consistently assigned to a Pd(N-N-N) stretching mode while the line at 409 cm^{-1} is assigned to the $\delta(N_3)$ mode. Strong coupling between these two A_1 modes of the $M(N_3)$ entity should be expected. The rather high (thought not exceptional) value of 595 cm^{-1} for ν(Pd-N) might be due to partially double bond character resulting from some π-back bonding contribution ($Pd \rightarrow N_3$). It has also to be noted that the M-Cl stretching mode is characteristic of a terminal halogen ligand[8] [$\nu(cm^{-1}) = 294$ (**3**) and 346 (**4**)].

^{1}H-NMR spectra of BATTH and of the Pd(II) complex in solution in DMSO-d_6 were recorded at room temperature. In the case of the ligand the amino protons appear at 6.2 ppm, and the triazenic proton as a triplet [$J(^{14}NH) = 51$ Hz] at 7.31 ppm, whereas the triazolic protons appear as a broad peak at 11.9 and a sharper peak at 12.5 ppm. By comparison, the spectrum of the complex presents only two sharp lines in a 2:1 ratio at 6.54 (amino group) and 12.70 ppm (triazole ring). This spectrum confirms the deprotonation of the triazene group. The singlet character of the triazolic proton line of the complex is not affected by cooling to 250K in DMF-d_7 whereas the spectrum of the ligand gives a multipeak structure above 12 ppm. These data indicates that the two triazole rings are involved in the coordination of the metal and that the minimum symmetry of the Pd complex dissolves in DMF or in DMSO is C_{2v}.

IR-Raman and NMR data suggest that $BATT^-$ coordinates to the metal in a terdentate mode involving the central N^2 atom of the triazene group and two N atoms of the triazole rings. This mode should imply delocalization of the negative charge of the deprotonated triazene over the N atoms of the triazole rings. Square planar coordination around Cu(II) and Pd(II) would be completed by the chloro ligand (Fig. 2). The choice of the 1-H (1'-H) tautomeric form and the N^2 ($N^{2'}$) coordination mode for the triazole rings is supported by the following arguments: (i) conjugation of the double bond of the "quinoïd" ring with the rest of the molecule can occur only when the proton and the negative (delocalized) charge reside on the N^1 and N^2 atoms and (ii) steric interaction between the amino groups and the chloro ligand is not likely to favour N^4 ($N^{4'}$) coordination. It can be concluded that replacement of the aryls by triazoles in (1,3-disubstituted)triazenes leads to a new, nitro-type coordination mode involving the N^2 atom of the triazenide group.

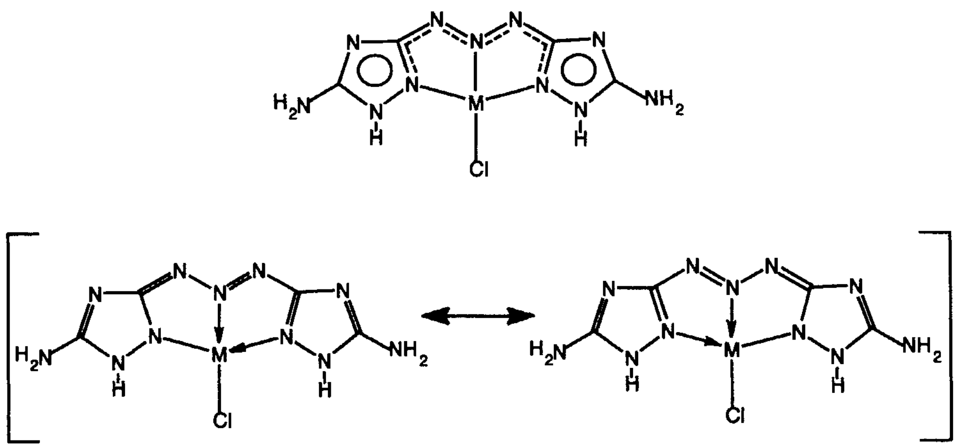

Figure 2 Proposed structural formula for complexes **3** and **4** (M = Cu, Pd).

Acknowledgements

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