Preparation, Characterization and Crystal Structure of Bis(1,2,6,7-tetracyano-3,5-dihydro-3,5-diiminopyrrolizinido)-palladium(II)–1,2-dimethoxyethane (1/2)

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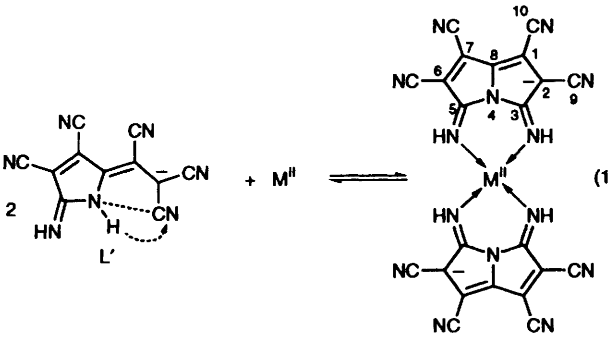
The neutral, planar complex [PdL$_2$] (L = 1,2,6,7-tetracyano-3,5-dihydro-3,5-diiminopyrrolizinide) is described along with the crystal structure of its adduct with 1,2-dimethoxyethane; structural and electronic features are discussed and correlated with previously reported data for the analogous [NiL$_2$] complex.

The anion $C_{11}N_7H_2^-$, L′, which we synthesized for the first time starting from tetracyanoethylene,[1] readily cyclizes to the pyrrolizinide anion upon interaction with transition-metal(II) cations,[2] which promote the proton shift and the formation of a C–N bond, affording centrosymmetric planar complexes [ML$_2$].



(1)

[ML$_2$]

Complexes [ML$_2$] may be of practical importance in molecular materials owing to their electronic properties, extraordinarily similar to those of metal phthalocyanine complexes,[3] and for their electron acceptor capability, given the high number of substituent –C≡N groups.

Our studies previously concentrated on [ML$_2$] complexes with first-row transition metals.[4] In this communication, the complex [PdL$_2$]·2dme **1**·2dme (dme = 1,2-dimethoxyethane), is described and compared with the previously reported [NiL$_2$] **2**.[4a]

Complex **1** is readily obtained† by addition of a stoichiometric amount of $[PdCl_4]^{2-}$, dissolved in water, to a water–acetone solution of the ligand L′; on reversing the reagent addition order or using an excess of metal, a dinuclear species, of 1 : 1 Pd : L ratio, is instead formed.‡

The crystal structure§ of **1**·2dme is shown in Fig. 1. The palladium atom is surrounded by four imino groups from two chelating ligands, in a square-planar arrangement, and there are no interactions with crystallographically equivalent complex units.

The Pd–N co-ordination distance of 1.997(4) Å is comparable with those found in other related palladium–imino complexes[8] (1.93–2.03 Å), and 0.10 Å longer than that found in the analogous, square-planar [NiL$_2$]·ttf·2thf complex (ttf = tetrathiafulvalene, thf = tetrahydrofuran), as expected on the basis of the covalent radii of Ni and Pd. The other bond lengths in the ligand system of **1** and **2** are strictly comparable, this confirming the influence of the metal co-ordination geometry on the ligand electronic distribution, as noted elsewhere.[4a] Two 1,2-dimethoxyethane molecules are laterally adducted and involved in two weak hydrogen bonds, as already found in the analogous [FeL$_2$]·2dme and [CoL$_2$]·2dme complexes.[4b]

Complex **1** is more stable than **2**, given the tendency of *n*d^8-metal ions to form square-planar complexes, which increases in the order $Ni^{2+} < Pd^{2+}$. Thus, in contrast to **2**, complex **1** (*i*) does not dissociate in solution, even in the presence of a 10^3 excess of water; (*ii*) follows the Lambert–Beer law in the concentration range 10^{-3}–10^{-4} mol dm^{-3}; (*iii*) exhibits a solid state reflectance spectrum which is identical

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† An aqueous solution (200 cm^3) of K_2PdCl_4 (0.640 g, 1.96 mmol) was added to a stirred water–acetone (10/6) solution (100 cm^3) of NaL′[5] (1.000 g, 3.92 mmol). The resulting suspension was filtered off; the collected microcrystalline solid, washed with water and then acetone, was extracted with dme. Evaporation of the violet dme solution afforded black microcrystals of [PdL$_2$]·2dme, yield 0.880 g, 1.18 mmol (60%) (Found: C, 48.45; H, 3.25; N, 26.30; O, 8.25; Pd, 13.60. Calc. for $C_{30}H_{24}N_{14}O_4Pd$: C, 48.00; H, 3.20; N, 26.10; O, 8.50; Pd, 14.15%). Crystals suitable for X-ray crystallography were obtained after crystallization from anhydrous dme in a vial. Complex **1**·2dme is air stable in the solid state and, of ordinary *O*-donor solvents, is slightly soluble only in dme ($\approx 10^{-3}$ mol dm^{-3}).

‡ This microcrystalline species has been isolated as a $[AsPh_4]^+$ salt with microanalysis corresponding to the formula $[AsPh_4]_2[Pd_2L_2Cl_3(CN)]$; single crystals are being grown for a crystal structure determination.

§ Crystal data. $C_{30}H_{24}N_{14}O_4Pd$, $M = 751.016$, monoclinic, space group $P2_1/a$, $a = 8.176(3)$, $b = 19.959(7)$, $c = 10.318(4)$ Å, $\beta = 92.19(2)°$, $U = 1682.9(9)$ Å^3, $D_c = 1.483$ g cm^{-3}, $Z = 2$, $F(000) = 760$, μ(Mo-Kα) = 6.05 cm^{-1}; 3270 data collected, 2107 independent reflections with $I > 2\sigma(I)$, $R\ [= \Sigma|F_o - F_c|/\Sigma|F_o|] = 0.051$, $R'\ \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.038$; weighting scheme $w = 1/\sigma^2(F_o)$. A plate-like, dark blue single crystal of 0.6 × 0.5 × 0.06 mm was sealed in a glass capillary in the presence of mother-liquor. X-Ray intensity data were measured by θ–2θ scans on a computer-controlled Nicolet P2$_1$ four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Cell dimensions were determined by least-squares refinement of 25 medium-angle settings ($20 < 2\theta < 30°$). Although the linear absorption correction is small, a semiempirical correction based on a psi scan around the scattering vector of selected reflections was applied, the I_{min}/I_{max} mean ratio being 0.85. Two standard reflections were monitored every 50 during the data collection: no systematic variations in intensities were found. The structure was solved by conventional Patterson and Fourier methods, and refined by full-matrix least-squares methods, using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in their idealized positions and restrained to ride on their associated atoms. Form factors *f*′ and *f*″ were taken from ref. 6. Calculations were carried out on a Data General Eclipse 8000/II computer, by using the SIR-CAOS crystallographic program system.[7] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

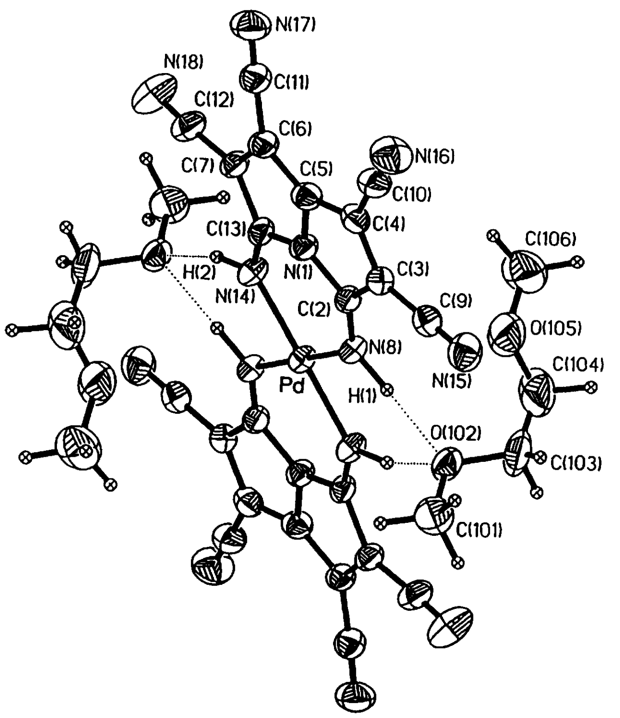

Fig. 1 Perspective view and numbering scheme of complex **1**, showing the square-planar palladium moiety and the imino-hydrogen-bonded dimethoxyethane molecules. Thermal ellipsoids are at 30% probability level. Relevant bonding parameters (mean values) are: Pd–N 1.997(4), C=NH 1.285(7), N(1)–C(2) and N(1)–C(13) 1.372(7), C(2)–C(3) and C(7)–C(13) 1.453(7)

to the solution spectrum (Fig. 2); (*iv*) exhibits a ^{13}C NMR spectrum* which does not reveal the presence of free L′ (expected to exhibit eleven different signals).[9] The infrared-allowed M–N stretching vibrations (B_{2u} and B_{3u} in D_{2h}) fall in the same frequency region for both complexes [229 and 283 cm^{-1} for **1**·2dme; 235 cm^{-1} (mean value) of the multiple Ni–O and Ni–N vibrations for $\mathbf{2}\cdot 2H_2O\cdot 3\overline{OCH_2CH_2OCH_2CH_2}$] despite the large metal mass difference. Two further striking differences between **1** and **2** are evident, which are not a consequence of their difference in stability. (*i*) The lowest energy electronic absorption band of **1** (λ_{max} = 738 nm) is red-shifted by about 80 nm with respect to **2** (λ_{max} = 662 nm) and (*ii*) complex **1** is more easily electrochemically reduced than **2**† ($\Delta E_{\frac{1}{2}} = 0.15$ V). These differences can be rationalized in terms of increased π conjugation through the metal over the two pyrrolizinido moieties in **1** relative to **2**. In **2** (M = Ni) the four frontier orbitals, two lowest-unoccupied (LUMOs) (a_u, b_{3g}) and two highest-occupied molecular orbitals (HOMOs) (b_{1u}, b_{2g}) are π_v ligand orbitals with negligible metal character; this means that the first electronic band (Q band), corresponding to a $\pi \longrightarrow \pi^*$ intraligand transition and localized on one pyrrolizinido moiety, is calculated (623 nm) to be close to the first electronic transition in the metal-free pyrrolizinide anion (594 nm).[3] In **1** (M = Pd) the π out-of-plane (π_v) metal orbitals ($4d_{xz}$, $4d_{yz}$, $5p_z$) are probably involved to a greater extent with the π_v ligand orbitals so that the degree of π conjugation increases and extends over the entire molecule; as a consequence the HOMO–LUMO energy gap is reduced and the lowering of the LUMO orbitals increases the electron affinity of the molecule, leading to its easier reduction. This increase of π conjugation has a further effect on the electronic spectrum of **1**: in the appearance of rather intense (ε = 8000 dm^3 mol^{-1} cm^{-1}) absorption bands (charge-transfer interligand or M→L transitions) in the 500 nm region, whereas **2**, like metal phthalocyanine complexes, is essentially transparent in this region.

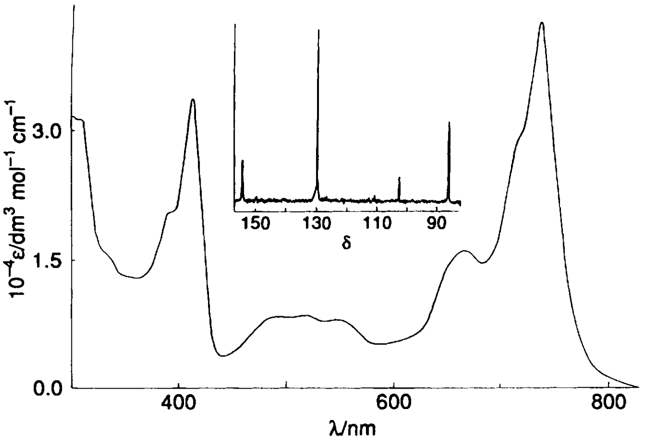

Fig. 2 Electronic absorption spectrum of complex **1** in dme (0.8×10^{-3} mol dm^{-3}) and (inset) ^{13}C NMR spectrum of the same solution + 10% [$^2H_6$]acetone as internal reference (B_0 4.7 T; T = 300 K)

In conclusion, [PdL_2] **1** is a more promising compound than [NiL_2] **2** for producing molecular materials, either as a functional dye, owing to the red-shifting of the Q band, or as an electron acceptor, owing to its easier reduction.

Acknowledgements

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References

1 G. Dessy, V. Fares, A. Flamini and A. M. Giuliani, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 426.
2 M. Bonamico, V. Fares, A. Flamini and N. Poli, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1049.
3 S. Nakamura, A. Flamini, V. Fares and M. Adachi, *J. Chem. Phys.*, 1992, **96**, 8351.
4 (*a*) M. Bonamico, V. Fares, A. Flamini and N. Poli, *Inorg. Chem.*, 1991, **30**, 3081; (*b*) M. Bonamico, V. Fares, A. Flamini and N. Poli, *J. Chem. Soc., Dalton Trans.*, 1992, 3273; (*c*) M. Bonamico, V. Fares, A. Flamini, N. Poli and G. Mattei, *Polyhedron*, 1993, in the press.
5 A. Flamini and N. Poli, *Ital. Pat.*, 22867-A/89, 1989.
6 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
7 M. Camalli, D. Capitani, G. Cascarano, S. Cerrini, C. Giacovazzo and R. Spagna, *Ital. Pat.*, 3543c/86, 1986.
8 H. Adams, N. A. Bailey, T. N. Briggs, J. A. McCleverty and H. M. Colquhoun, *J. Chem. Soc., Dalton Trans.*, 1982, 1521; M. Hunziaker, B. Hilti and G. Rihs, *Helv. Chim. Acta*, 1981, **64**, 82; K. M. A. Malik, S. Z. Haider and A. Hashem, *Acta Crystallogr., Sect. C*, 1985, **41**, 29; A. L. Rheingold and D. L. Staley, *Acta Crystallogr., Sect. C*, 1988, **44**, 572; M. Tsutsui, R. L. Bobsein, G. Cash and R. Pettersen, *Inorg. Chem.*, 1979, **18**, 758; H. Wanjek, U. Nagel and W. Beck, *Chem. Ber.*, 1988, 1021.
9 M. Bonamico, V. Fares, A. Flamini, A. M. Giuliani and P. Imperatori, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1447.

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* Although only four signals appear instead of six, a tentative assignment of the spectrum is possible, assuming that the most intense peak (δ 129.6) corresponds to the three carbon atoms (C^1, C^9 and C^{10}), which in the analogous [ZnL_2] complex have similar chemical shifts (δ 109.8, 110.2, 112.4);[2] the least intense peak (δ 102.5) corresponds to C^8 and the remaining two peaks (δ 86.0, 154.3) correspond to the most and the least shielded carbon atoms, C^2 and C^3, respectively, as in [ZnL_2] (δ 94.7 and 156.9).[2]

† By cyclic voltammetry, carried out for **1** (10^{-3} mol dm^{-3}) in dme–MeCN (1 : 1) containing 0.1 mol dm^{-3} NEt_4ClO_4.