

The Structure of Pd^{II} Complexes Containing the Tridentate Ligand Diethylenetriamine and its N-alkyl Derivatives.

Part I. Molecular Structure of Nitrodiethylenetriaminepalladium(II) Nitrate and Nitro-1,1,7,7-tetraethyldiethylenetriaminepalladium(II) Nitrate

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Earlier papers on transition metal complexes containing the NO₂⁻ ligand mainly deal with both the problems of the bond isomerism¹ (M-NO₂ ↔ M-ONO) and of the bonding mode of nitrocomplexes² (M-NO₂). With regard to the first problem it has been concluded that compounds with M-NO₂ bonding are more stable than their nitrito isomers.

As far as the nature of the bonding in nitrocomplexes is concerned, the possibility of back-donation from filled d_π metal orbitals to the empty π-antibonding orbital of NO₂⁻, mainly localized on the N atom, has been proposed. On the basis of such a model, all the factors which contribute to increase

the electronic population of the antibonding π-orbital of NO₂⁻ should provoke decrease of N-O bond order and *vice versa*. As a consequence both the symmetric and asymmetric N-O stretching frequencies must change. Thus a correlation between the π-bonding ability of neutral ligands and the N-O stretching frequencies, measured in the solid state, for a series of *cis*- and *trans*-dinitro-Pd^{II} complexes with a variety of neutral ligands containing V group donor atoms has been found³. No simple relation, however, was detected between the N-O stretching frequencies measured in solution and the electronegativity of donor atoms for a series of similar Pd^{II} and Pt^{II} dinitrocomplexes.⁴

To obtain further insight on the bonding mode in nitrocomplexes of Pd^{II}, we report a preliminary study of the structure analysis of two nitroderivatives, nitrodiethylenetriaminepalladium(II) nitrate { [Pd(dien)NO₂][NO₃] } and 1,1,7,7-tetraethyldiethylenetriaminepalladium(II) nitrate { [Pd(Et₄dien)NO₂][NO₃] }. The definitive paper will be published shortly elsewhere.

Crystal data

[Pd(Et₄dien)NO₂][NO₃·H₂O] (I), orthorhombic, space group P2₁2₁2₁, with cell parameters *a* = 21.825(9), *b* = 10.977(7), *c* = 8.233(6) Å, *d*_s = 1.48 g/cm³, *d*_c = 1.51 g/cm³ with *Z* = 4, *μ* = 9.6 cm⁻¹, *μ*-*r* = 0.06, the conventional R-factor was 0.052 for 1087 independent reflections after the last anisotropic least-squares refinement including the hydrogen atoms contribution held constant. [Pd(dien)NO₂]-

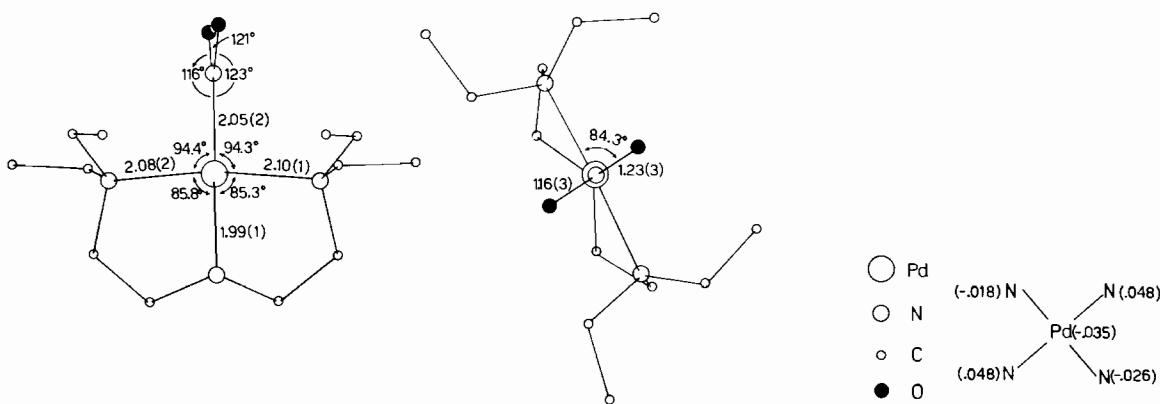


Fig. 1. Sketches of the cation [Pd(Et₄dien)NO₂]⁺ and coordination plane displacements of the Pd and N atoms. Some bond lengths and angles of interest are also reported.

NO₃ (II), monoclinic, space group P2₁/c, with cell parameters $a = 11.627(7)$, $b = 7.617(6)$, $c = 17.380(9)$ Å, $\beta = 133.77(5)^\circ$, $d_s = 1.89$ g/cm³, $d_c = 1.90$ g/cm³ with $Z = 4$, $\mu = 16.5$ cm⁻¹, $\mu \cdot r = 0.15$; the conventional R-factor was 0.034 for 1351 independent reflections after the last anisotropic least-squares refinement including the hydrogen atoms contribution held constant.

Results and Discussion

The molecular structure of both complexes reveals that they are essentially square-planar, with a slightly tetrahedral distortion, as shown in Figures 1 and 2. The main difference in the two complexes deals with the orientation of the NO₂ group with respect to the coordination plane. The dihedral angle between the NO₂ and coordination planes is 84.3° in (I), whereas it is 15.8° in (II). On the contrary the Pd–NO₂ bond lengths do not appear significantly different, being $2.053(15)$ Å in (I) and $2.028(7)$ Å in (II), but slightly longer than the value of $1.984(8)$ Å found in [Pd^{II}(NH₃)₃NO₂]₂[Pd^{II}(NH₃)₄](NO₃)₄,⁵ where the nitro-group prefers coplanarity with coordination plane such as in (II). Since both the “coplanar” and “normal” (as in I) orientation of the NO₂ group are in principle consistent with the above mentioned σ - π model of the NO₂ Pd bonding (the filled d_{xz} orbital of Pd^{II}, for example, is involved in the former case, the d_{xy} being involved in the latter), the difference found may be interpreted in terms of interaction of the NO₂ group with its σ -donor ancillary ligands. When the latter donor groups are unsubstituted NH₂ or NH₃ molecules the “coplanar” orientation is the favoured one, probably because of the formation of intermolecular hydrogen bonds –NH₂–...–O₂N. Furthermore the small deviation from coplanarity (15.8°) may be due to obtain better “match” of the atoms involved in hydrogen bonding. In the compound (I) the hydrogen atoms are substituted by ethyl groups excluding the possibility of hydrogen bond formation, so that the normal orientation of the NO₂ group and the ethyl group of the Et₄dien ligand. Another geometrical difference between the two compounds is observed. The Pd–N coordination bond lengths are nearly equal in (I), whereas the length of the bond ($1.988(11)$ Å) from the central N atom of the ligand (Et₄dien) is shorter than those from the terminal N atoms ($2.082(16)$ and $2.098(13)$ Å). The latter values are in agreement with those

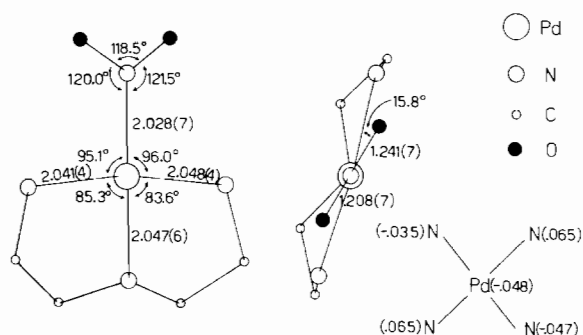


Fig. 2. Sketches of the cation [Pd(dien)NO₂]⁺ and coordination plane displacements of the Pd and N atoms. Some bond lengths and angles of interest are also reported.

found in the azide analogue [PdN₃(Et₄dien)]NO₃,⁶ which are $2.002(10)$ Å and $2.099(13)$, $2.091(12)$ Å respectively. Steric more than electronic factors are probably responsible for these differences.

Finally the geometry of the Pd–NO₂ grouping is almost the same in the two cases, with the exception of the NO₂ group orientation, within the experimental errors. Because the “normal” and “coplanar” orientations are both in agreement with the above mentioned σ - π model, we cannot exclude some amount of back-donation (Pd → NO₂) on this basis. However, if this effect is present, it must be of little effect at bond length level, because the Pd–NO₂ distances are in the range of the Pd–N distances which correspond to essentially covalent σ -bond.

Acknowledgments

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References

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