

A Complex of the Hydrazidium (=N-NH₃⁺) Ligand: X-Ray Structure of [WCl(NNH₃)(PMe₃)₄]Cl₂

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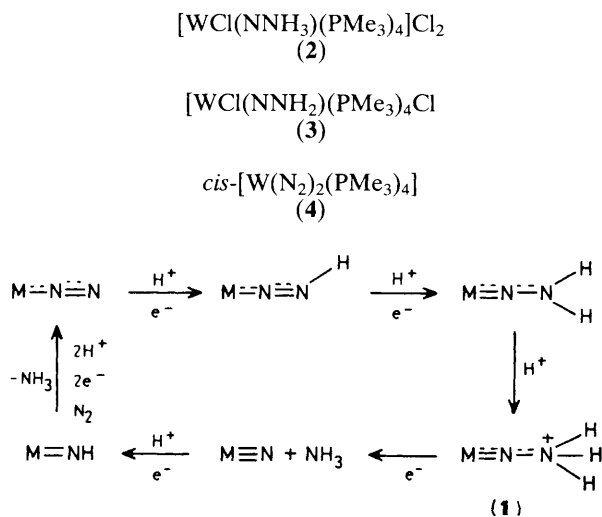
Treatment of [WCl(NNH₂)(PMe₃)₄]Cl or *cis*-[W(N₂)₂(PMe₃)₄] with HCl in methanol gives [WCl(NNH₃)(PMe₃)₄]Cl₂, whose X-ray crystal structure has been determined.

The cyclic process shown in Scheme 1 has been proposed as a reasonable model for the reduction of dinitrogen at a metal centre in complex compounds and in nitrogenase.¹

This Scheme has been proposed on the basis of isolation of examples of metal complexes of the nitrogen ligands shown and their observation in solution in reacting systems, with the exception of the hydrazidium ligand (1).

Examples of this ligand have long been sought and we report here the first example in the complex [WCl(NNH₃)(PMe₃)₄]Cl₂ (2), isolated from the reaction of [WCl(NNH₂)(PMe₃)₄]Cl (3) with anhydrous HCl in methanol as diamagnetic, red-orange crystals in 75% yield. Compound (2) may also be obtained from *cis*-[W(N₂)₂(PMe₃)₄] (4) with HCl in methanol; (3) is prepared by treatment of (4) with HCl in hexane.

Because compound (2) is only sufficiently soluble for



Scheme 1

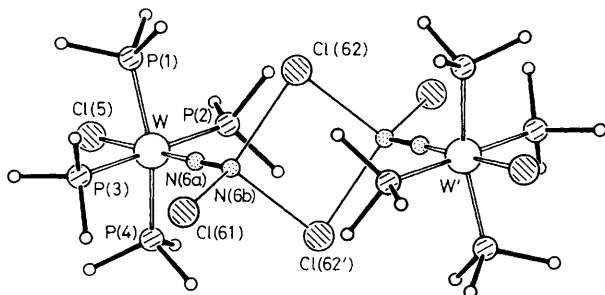


Figure 1. Molecular structure of [WCl(NNH₃)(PMe₃)₄]Cl₂ (2) showing the atom numbering scheme. Principal bond dimensions: W-P 2.499(4)–2.532(5), W-Cl(5) 2.463(4), W-N(6a) 1.785(15), N(6a)-N(6b) 1.40(2) Å; P(1)-W-P(4) 158.4(2), P(2)-W-P(3) 176.8(2), Cl(5)-W-N(6a) 179.5(3), W-N(6a)-N(6b) 179.2(10), N(6a)-N(6b) ··· Cl 108.9(8)–114.9(8)°.

spectroscopy in methanol, N-H n.m.r. spectroscopic resonances could not be observed, but it has N-H bands in its i.r. spectrum at 3420 and 3120 cm⁻¹. It has singlet ¹H (δ 1.7, rel. SiMe₄) and ³¹P [-168.6 p.p.m., rel. P(OMe₃)] resonances. Compound (2) conducts apparently as a 1:1 electrolyte (Λ_m = 595 cm² mol⁻¹ in 10⁻² mol dm⁻³ MeNO₂) and was originally formulated as [WCl(NNH₂)(PMe₃)₄]HCl₂, particularly since it is converted by treatment with Na[BPh₄] to [WCl(NNH₂)(PMe₃)₄]BPh₄, which is soluble and shows the expected spectroscopic properties for a normal hydrazido(2-) complex.¹ The X-ray structure of (2) revealed, however, that it is not an HCl₂ salt, but a dichloride containing the hydrazidium (=N-NH₃⁺) ligand (1).

The crystal[†] of (2) contains discrete, centrosymmetric, dimeric units consisting of two cations linked through Cl⁻ anions by strong hydrogen bonds, Figures 1 and 2. The N_β atom, N(6b), is approximately equidistant (3.01–3.10 Å) from three Cl⁻ anions which are arranged in an almost equilateral triangle. The N ··· Cl distances are typical of strong, linear N-H ··· Cl hydrogen bonds and this unique arrangement of such contacts implies, even without the identification of the three H atoms, that this is a hydrazidium (=N-NH₃⁺) ligand with an almost linear W-N-N group. Of the three Cl⁻ ions bound to N(6b), two are related by the centre of symmetry, and these bridge the two cations; the third is not involved in further bonding.

Presumably the hydrogen bonding is responsible for the low solubility and conductivity of (2) in solvents in which it is stable and also helps to stabilise this unique ligand in the solid state.

The formation of (2) by terminal protonation of a hydrazide ligand must be a function of the basicity of the hydrazide. Presumably the relatively high electron release from the PMe₃ co-ligands assists this basicity, since other hydrazide

[†] Crystal data for (2): C₁₂H₃₉Cl₃N₂P₄W, *M* = 625.6, monoclinic, space group *P*2₁/*c* (no. 14), *a* = 14.370(7), *b* = 13.684(4), *c* = 13.318(10) Å, β = 101.23(6)°, *U* = 2568.6 Å³, *Z* = 4, *D*_c = 1.617 g cm⁻³, *F*(000) = 1240, μ(Mo-Kα) = 51.5 cm⁻¹, λ(Mo-Kα) = 0.71069 Å.

Crystals were orange plates; crystal dimensions *ca.* 0.25 × 0.15 × 0.05 mm, mounted on a glass fibre and coated with epoxy resin. This sealing merely slowed the decomposition of the sample. After brief photographic examination, the crystal was mounted on our Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for measurement of accurate cell parameters and diffraction intensities. The intensities of two control reflections had dropped more than 40% before the data set to θ_{max} = 20° was complete, and the recording of Ψ-scan data was not satisfactory. Corrections for crystal decay and Lorentz-polarisation effects were applied and 2214 satisfactory, independent data were used in the structure analysis.

Structure determination was by the heavy atom method.^{3,4} Refinement by full-matrix least-squares methods was concluded with *R* = 0.083, *R*_w = 0.054 for all reflections,⁴ weighted *w* = σ_F⁻². Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

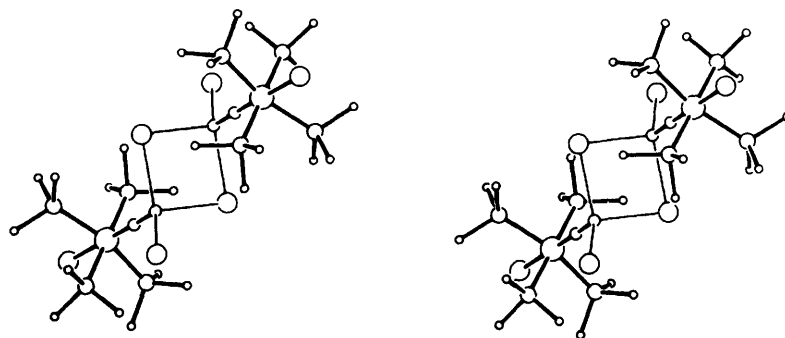


Figure 2. Stereoscopic view of (2).

complexes with less electron-releasing co-ligands do not form stable hydrazidium salts. Thus the complex $[\text{MoBr}(\text{NNH}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Br}$ does not protonate further,¹ but its analogue with the more electron-releasing $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ ligand does appear to add a third proton at nitrogen, and the structure of this complex product is under investigation.²

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