ring, resulting in a greater mesomeric electron release to the sulphur of -SCH₃. Indeed the expected steric inhibition of resonance is found in trans-PdCl₂(3,5-di-CH₃-4-OCH₃C₆H₅SCH₃)₂. The ν(Pd-S) stretching frequency is at 312 cm⁻¹ which is higher due to the inhibition of resonance caused by two methyl groups adjacent to the methoxy group.

In the electronic spectral data (table 1), the band at 277 is due to L(π) - L(π)⁺ transition. The other intense one is of ligand to metal charge transfer band. The large bathochromic shift of the charge transfer band (332 nm to 365 nm) in the complex trans-PdCl₂(p-OCH₃C₆H₅SCH₃)₂ is due to the presence of electron repelling -OCH₃ in p-position. The λmax value still increases to 372 nm in the complex trans-PdCl₂(3-CH₃-4-OCH₃C₆H₅SCH₃)₂ which is due to steric enhancement of resonance.

This phenomenon also gains support from proton magnetic resonance studies (table 1). The proton signals of -SCH₃, -CH₃ and -OCH₃ are in the ratio 1 : 1 for 3-CH₃, 1 : 1 for 4-OCH₃, 1 : 1 : 1 for 3-CH₃-4-OCH₃ and 1 : 2 : 1 for 3,5-di-CH₃-4-OCH₃ respectively as expected. The phenyl protons in the complex trans-PdCl₂(C₆H₅SCH₃)₂ are in the range δ 7.2 to 7.86. In the complexes trans-PdCl₂(m-CH₃C₆H₅SCH₃)₂ and trans-PdCl₂(p-OCH₃C₆H₅SCH₃)₂ the phenyl protons are in the range δ 7.09 to 7.49 and δ 6.69 to 7.67 respectively. The shift to up field in these complexes is due to the electron-releasing nature of 3-CH₃ and 4-OCH₃ groups present in the phenyl ring. In the complex trans-PdCl₂(4-OCH₃-3-CH₃C₆H₅SCH₃)₂, phenyl protons range still decreases (δ 6.66 to 7.66) which is due to steric enhancement.

The -OCH₃ signal in trans-PdCl₂(p-OCH₃C₆H₅SCH₃)₂, δ 3.69 is shifted to δ 3.80 in the complex trans-PdCl₂(4-OCH₃-3-CH₃C₆H₅SCH₃)₂. This large shift is due to the steric effect of 3-CH₃ group, which restricts the free rotation of the methoxy group, thereby increasing the probability of the latter to attain the planarity with the benzene ring. It is also of interest to note that signal for -OCH₃ in the complex trans-PdCl₂(3,5-di-CH₃-4-OCH₃C₆H₅SCH₃)₂ is shifted to δ 3.60 because of the steric inhibition caused by two ortho methyl substituents.

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SYNTHESIS AND CHARACTERIZATION OF TRISULPHURTRINITRIDEIS (TRIPHENYLPHOSPHINE) NICKEL(II), Ni(S₃N₃)(PPh₃)₂

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In continuation of our work on small ligands of sulphur and nitrogen such as NS⁺⁻, NSO⁻⁻, NSO₅⁻, NS⁺⁺ and NS₃, we report here the formation of Ni(S₃N₃)(PPh₃)₂ from the reaction of S₃N₄ with NiCl₂(PPh₃)₂. The synthesis and characterization of S₃N₃ anion from the reaction of azide ion and S₃N₄ in ethanol have been reported earlier²⁻¹³.

Preparation of Ni(S₃N₃)(PPh₃)₂

To a solution of NiCl₂(PPh₃)₂ (1.21 g, 2 mmol) in 60 ml acetonitrile-dichloromethane (1:1), solid S₃N₄ (0.37 g, 2 mmol) was added. The reaction
mixture, which turned brown within 5 min, was stirred for 2 hr. It was concentrated at reduced pressure to about 20 ml whereby the brown crystals of Ni(S₃N₃)(PPh₃)₂ separated out which were filtered, washed several times with n-hexane and dried under vacuum. The yield was 1.16 g (87%). Anal. Caled for C₃₉H₅₆N₉P₂S₃Ni: C, 59.94; H, 4.16; N, 5.82; S, 13.32%. Found: C, 59.8; H, 4.1; N, 6.0; S, 13.5%. IR spectrum, 3045, 1585, 1570, 1480, 1425, 1310, 1180, 1160, 1150, 1098, 1074, 1032, 1000, 925, 850, 745, 720, 695, 680, 655, 645, 530, 510, 490, 410, 384 and 320 cm⁻¹. Magnetic moment μ = 1.85 B.M. at 295°K.

Carbon, hydrogen, nitrogen and sulphur analysis were performed at the Microanalytical Laboratory, Göttingen, FRG. IR spectrum was recorded as KBr pellets on a Perkin Elmer Model 511 Spectrophotometer in the range 4000-300 cm⁻¹. Magnetic moment was measured by Gouy balance.

Reaction of tetrasulphurtetranitride with dichlorobis(triphenylphosphine)nickel(II) results in the formation of a brown compound which is isolated satisfactorily for the formula Ni(S₃N₃)(PPh₃)₂. It decomposes slowly in air. The magnetic moment for Ni(S₃N₃)(PPh₃)₂ at 295°K is 1.85 B.M. IR spectrum shows absorption bands at 1032 S, 925 VW, 655 S, 645 S and 384 cm⁻¹ due to S₃N₃⁻ ligand which shift slightly towards higher wavenumber from free S₃N₃⁻ ion¹³ 320 cm⁻¹ due to u(Ni-N) and bands due to triphenylphosphine. The mass spectrum shows decomposition of Ni(S₃N₃)(PPh₃)₂ (table 1) and fragments due to PPh₃ and Ni(S₃N₃). The magnetic behaviour shows the oxidation state of nickel ion as +1 and S₃N₃⁻ moiety is bonded as S₃N₃⁻ in this complex.


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