

2. Liu, C. S., Sucov, E. W. and Weaver, L. A., *Appl. Phys. Lett.*, 1973, **23**, 92.
3. Chen, C. J., *J. Appl. Phys.*, 1974, **45**, 4663.
4. Chen, C. J., *Appl. Phys. Lett.*, 1974, **24**, 499.
5. Weaver, L. A., Liu, C. S. and Sucov, E. W., *IEEE. J. Quant. Elect.*, 1974, **QE10**, 140.
6. Dwight, E. Gray, *American Institute of Physics Handbook*, McGraw-Hill, New York, 1972, p. 4.
7. Shelton, R. A. J., *Trans. Faraday. Soc.*, 1961, **57**, 2113.
8. Robert, C. W., *CRC handbook of chemistry and physics*, Boca Raton, Florida, CRC Press, 1983-84, pD-196.
9. Holstein, T., *Phys. Rev.*, 1951, **83**, 1159.
10. Srigouri, K., Ramaprabhu, S. and Prasada Rao, T. A., *J. Appl. Phys.*, 1986 (communicated).
11. Nerheim, N. M., *J. Appl. Phys.*, 1977, **48**, 1186.
12. Milan Brandt and Piper, J. A., *IEEE. J. Quant. Elect.*, 1981, **QE17**, 1107.

SPECTROSCOPIC EVIDENCE FOR STERIC ENHANCEMENT OF RESONANCE IN COMPLEXES

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THE phenomenon of steric enhancement of resonance was discovered by Baliah and Uma¹ while studying the electric dipole moments of some substituted anisoles and acetophenones. Since its discovery, several physico-chemical investigations have been carried out in support of this view²⁻⁶. In the present work the electronic, infrared and ¹H NMR spectral data of a few palladium(II) complexes with suitable substituted phenyl methyl sulphides as ligands synthesized⁷⁻⁹ are taken for substantiating this phenomenon.

It is observed that the electron-releasing substituent present in the ligand decreases the $\nu(\text{Pd-S})$ stretching frequency, whereas electron withdrawing group increases^{10,11}. The $\nu(\text{Pd-S})$ stretching frequency in the complex $\text{trans-PdCl}_2(\text{p-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$ is at 277 cm^{-1} (table 1) which is much less than the corresponding frequency in $\text{trans-PdCl}_2(\text{C}_6\text{H}_5\text{SCH}_3)_2$ ^{7,12,13}. This decrease is caused by p-OCH₃, an electron-releasing group. The $\nu(\text{Pd-S})$ stretching frequency in $\text{trans-PdCl}_2(\text{m-CH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$ is 297 cm^{-1} which is almost the same as that of the parent compound. The $\nu(\text{Pd-S})$ stretching frequency in $\text{trans-PdCl}_2(4\text{-OCH}_3\text{-3-CH}_3\text{C}_6\text{H}_3\text{SCH}_3)_2$ is at 270 cm^{-1} , which is less than that of $\text{trans-PdCl}_2(\text{p-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$, because the 3-methyl group in 4-methoxy-3-methylphenyl methyl sulphide exerts an accelerating influence of the conjugation of methoxy group with the phenyl ring. The methyl group makes the methoxy assume a trans-orientation and hence the probability of the methoxy group attaining planarity with the aromatic ring increases. There can, therefore, be enhanced interaction of the methoxy group with the aromatic

Table 1 Infrared, electronic and ¹H NMR spectra of the complexes

Complex	IR $\nu(\text{Pd-S})$ cm^{-1}	Electronic spectra		¹ H NMR			
		λ_{max} nm	ϵ	-SCH ₃ (δ)	-CH ₃ (δ)	-OCH ₃ (δ)	Ph protons (δ)
$\text{trans-PdCl}_2(\text{C}_6\text{H}_5\text{SCH}_3)_2$	298	332 277	11,600 7,100	2.66	—	—	7.2-7.86
$\text{trans-PdCl}_2(\text{m-CH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$	297	335 277	11,900 6,600	2.49	2.26	—	7.09-7.49
$\text{trans-PdCl}_2(\text{p-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$	277	365 277	10,000 6,800	2.52	—	3.69	6.69-7.67
$\text{trans-PdCl}_2(4\text{-OCH}_3\text{-3-CH}_3\text{C}_6\text{H}_3\text{SCH}_3)_2$	270	372 277	10,800 8,700	2.52	2.18	3.80	6.66-7.66
$\text{trans-PdCl}_2(3,5\text{-di-CH}_3\text{-4-OCH}_3\text{C}_6\text{H}_2\text{SCH}_3)_2$	312	356 277	10,400 5,700	2.46	2.18	3.60	7.12-7.32

The solvent in all cases was C₆H₆.

ring, resulting in a greater mesomeric electron release to the sulphur of $-\text{SCH}_3$. Indeed the expected steric inhibition of resonance is found in $\text{trans-PdCl}_2(3,5\text{-di-CH}_3\text{-4-OCH}_3\text{C}_6\text{H}_2\text{SCH}_3)_2$. The $\nu(\text{Pd-S})$ 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 $L(\pi) \rightarrow L(\pi)^*$ 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 $\text{trans-PdCl}_2(p\text{-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$ is due to the presence of electron repelling $-\text{OCH}_3$ in p-position. The λ_{max} value still increases to 372 nm in the complex $\text{trans-PdCl}_2(3\text{-CH}_3\text{-4-OCH}_3\text{C}_6\text{H}_3\text{SCH}_3)_2$ which is due to steric enhancement of resonance.

This phenomenon also gains support from proton magnetic resonance studies (table 1). The proton signals of $-\text{SCH}_3$, $-\text{CH}_3$ and $-\text{OCH}_3$ are in the ratio 1 : 1 for 3- CH_3 , 1 : 1 for 4- OCH_3 , 1 : 1 : 1 for 3- CH_3 -4- OCH_3 and 1 : 2 : 1 for 3,5-di- CH_3 -4- OCH_3 respectively as expected. The phenyl protons in the complex $\text{trans-PdCl}_2(\text{C}_6\text{H}_5\text{SCH}_3)_2$ are in the range δ 7.2 to 7.86. In the complexes $\text{trans-PdCl}_2(m\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$ and $\text{trans-PdCl}_2(p\text{-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$ 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- CH_3 and 4- OCH_3 groups present in the phenyl ring. In the complex $\text{trans-PdCl}_2(4\text{-OCH}_3\text{-3-CH}_3\text{C}_6\text{H}_3\text{SCH}_3)_2$ phenyl protons range still decreases (δ 6.66 to 7.66) which is due to steric enhancement.

The $-\text{OCH}_3$ signal in $\text{trans-PdCl}_2(p\text{-OCH}_3\text{C}_6\text{H}_4\text{SCH}_3)_2$, δ 3.69 is shifted to δ 3.80 in the complex $\text{trans-PdCl}_2(4\text{-OCH}_3\text{-3-CH}_3\text{-C}_6\text{H}_3\text{SCH}_3)_2$. This large shift is due to the steric effect of 3- CH_3 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 $-\text{OCH}_3$ in the complex $\text{trans-PdCl}_2(3,5\text{-di-CH}_3\text{-4-OCH}_3\text{C}_6\text{H}_2\text{SCH}_3)_2$ is shifted to δ 3.60 because of the steric inhibition caused by two ortho methyl substituents.

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1. Baliah, V. and Uma, M., *Tetrahedron Lett.*, 1960, 1, 20.

2. Baliah, V. and Kanagasabapathy, V. M., *Tetrahedron*, 1978, 34, 3611.
3. Baliah, V. and Theymoli, B., *Indian J. Chem.*, 1978, B16, 599.
4. Ganapathy, K. and Jeyagandhi, P., *J. Indian Chem. Soc.*, 1979, 56, 1036.
5. Ganapathy, K., Balasubramanian, T. and Pandiarajan, K., *Curr. Sci.*, 1982, 23, 1114.
6. Ganapathy, K. and Ramanujam, M., *J. Indian Chem. Soc.*, 1983, 60, 958.
7. Clark, R. J. H., Natile, G., Belluco, U., Cattalini, L. and Filippin, C., *J. Chem. Soc.*, 1970, 659.
8. Serra, O. A., Pitombo, L. R. M. and Imamoto, Y., *Inorg. Chem. Acta*, 1978, 31, 49.
9. Baliah, V., Ganapathy, K. and Anjaneyulu, N., (unpublished work).
10. Bosolo, F. and Pearson, R. G., *Mechanism of inorganic reactions*, Wiley and Sons, New York, 1967, 2nd edn.
11. Baliah, V., Ganapathy, K. and Anjaneyulu, N., *J. Indian Chem. Soc.*, 1985 (communicated).
12. Fergusson, J. E. and Loh, K. S., *Aust. J. Chem.*, 1973, 26, 2615.
13. Allen, E. A. and Wilkinson, W., *Spectrochim. Acta*, 1972, A28, 725.

SYNTHESIS AND CHARACTERIZATION OF TRISULPHURTRINITRIDE BIS (TRIPHENYLPHOSPHINE) NICKEL(I), $\text{Ni}(\text{S}_3\text{N}_3)(\text{PPh}_3)_2$

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IN continuation of our work on small ligands of sulphur and nitrogen such as NS^{1-5} , NSO^{6-8} , NSO_2^{9} , NS_2^{10} and NS_3^{11} , we report here the formation of $\text{Ni}(\text{S}_3\text{N}_3)(\text{PPh}_3)_2$ from the reaction of S_4N_4 with $\text{NiCl}_2(\text{PPh}_3)_2$. The synthesis and characterization of S_3N_3^- anion from the reaction of azide ion and S_4N_4 in ethanol have been reported earlier^{12, 13}.

Preparation of $\text{Ni}(\text{S}_3\text{N}_3)(\text{PPh}_3)_2$

To a solution of $\text{NiCl}_2(\text{PPh}_3)_2^{14}$ (1.21 g, 2 mmol) in 60 ml acetonitrile-dichloromethane (1:1), solid $\text{S}_4\text{N}_4^{15}$ (0.37 g, 2 mmol) was added. The reaction