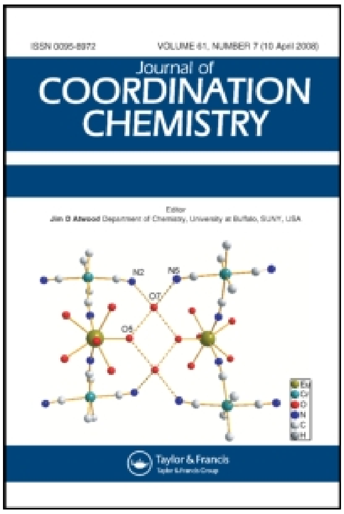

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Esr Studies of Bis[DI(2,4,5-Trimethylphenyl) Dithiophosphinato]Oxovanadium(IV). Calculation of Bonding Parameters

R. N. Mukherjee[a]; B. B. S. Shastri[a]
[a] Department of Chemistry, Indian Institute of Technology, Bombay, India

To cite this Article Mukherjee, R. N. and Shastri, B. B. S.(1989) 'Esr Studies of Bis[DI(2,4,5-Trimethylphenyl) Dithiophosphinato]Oxovanadium(IV). Calculation of Bonding Parameters', Journal of Coordination Chemistry, 20: 2, 135 — 139

To link to this Article: DOI: 10.1080/00958978909408859

URL: http://dx.doi.org/10.1080/00958978909408859

J. Coord. Chem. 1989, Vol. 20. pp. 135–139
Reprints available directly from the publisher
Photocopying permitted by license only

ESR STUDIES OF BIS[DI(2,4,5-TRIMETHYLPHENYL) DITHIOPHOSPHINATO]OXOVANADIUM(IV). CALCULATION OF BONDING PARAMETERS

R. N. MUKHERJEE* and B. B. S. SHASTRI

Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India

(Received November 23, 1988)

ESR spectra of a five-coordinate vanadyl dithiophosphinate complex correspond to the interaction of an unpaired electron with the ^{51}V nucleus and two equivalent ^{31}P nuclei. However, in the presence of moderate amounts of nitrogen and oxygen donors, only one ^{31}P superhyperfine interaction was noted. At higher ligand concentrations, the ESR reflected no ^{31}P hyperfine coupling. Bonding parameters β_1^{*2}, β_2^{*2}, ε_π^{*2} and k_v obtained for different chromophores were compared with those of $VO(acac)_2$. This leads to the decreasing sequence $VOS_4 < VOS_2N_2 < VOS_2O_2 < VOO_4$ with respect to bonding parameters for the various chromophores.

Keywords: Oxovanadium(IV), dithiophosphinate, ESR, base adducts, bonding

INTRODUCTION

The study of the oxovanadium(IV) ion is of interest because of its d^1 configuration and the high nuclear spin (7/2) of the metal. It is known that tetra- and pentacoordinate chelates of vanadium(IV) undergo substitution at vacant sites.[1,2] IR studies on addition compounds of $VO(acac)_2$ with pyridine-type donors elegantly demonstrate the existence of two types of adduct with the donor molecule in axial and equatorial positions.[3] ESR studies are inconclusive regarding the nature of adducts formed by vanadyl dithiocarbamates. However ESR will be useful to understand the type of interaction in vanadyl dithiophosphinates because of the occurrence of superhyperfine interactions. Bonding parameter calculations reflecting the covalency in these systems have received little attention. In continuation of our earlier studies[4,5] on dithiophosphinates, the present work was undertaken to inquire into the type of complexes formed between di(2,4,5-trimethylphenyl)dithiophosphinate, oxovanadium(IV), $VO(2,4,5\text{-}Me_3dtpi)_2$ and Lewis bases, and to investigate the covalency of these systems through the computation of various bonding parameters.

EXPERIMENTAL

Materials and Methods

All the chemicals used were of analytical reagent grade. The dithiophosphinic acid was synthesized by a method previously described.[6] The vanadyl dithiophosphinate complex, $VO(2,4,5\text{-}Me_3dtpi)_2$ was obtained on reaction of the sodium salt of the

---

* Author for correspondence.

ligand in methanol (2 g in 15 cm^3) with an aqueous solution of vanadyl sulphate (0.5 g in 10 cm^3). The precipitate formed was filtered, washed with methanol and dried *in vacuo* [Anal.; Calc.: V, 6.95; S, 17.46%. Found: V, 6.82; S, 17.2%].

Spectroscopic Measurements

The IR spectrum of $VO(2,4,5\text{-}Me_3dtpi)_2$ was obtained with a Pye-Unicam SP 2000 spectrophotometer and electronic spectra were recorded on a Shimadzu UV 260 spectrophotometer. Electron spin resonance spectra were run on a Varian E-112 ESR spectrometer (X-band) using TCNE (g = 2.00277) as a g-marker.

RESULTS AND DISCUSSION

The infrared spectrum of $VO(2,4,5\text{-}Me_3dtpi)_2$ showed a V=O stretching frequency at 1005 cm^{-1} along with P–S vibrations at 580 and 650 cm^{-1}. The reflectance and chloroform solution spectra are similar and exhibit d–d bands around 14700 and 17200 cm^{-1}with a shoulder around 24400 cm^{-1}, which are attributed[7] to $b_2 \rightarrow e_\pi^*$, $b_2 \rightarrow b_1^*$ and $b_2 \rightarrow a_1^*$ transitions, respectively. The four-membered ring structure of the complex is likely to possess a tetragonal pyramidal structure[8] with C_{4v} symmetry.

TABLE I
ESR data for the oxovanadium (IV) complexes[a].

	Isotropic values			Anisotropic values					
Complex in solution	g_o	A_o^V	A_o^P	$g_\parallel$	$g_\perp$	$A_\parallel^V$	$A_\perp^V$	$A_\parallel^P$	$A_\perp^P$
$VO(2,4,5\text{-}Me_3dtpi)_2$	1.9844	90	38	1.9632	1.9550	164	50	40	37
$VO(2,4,5\text{-}Me_3dtpi)_2Py_2$	1.9720	95		1.9560	1.9810	174	55		
$VO(2,4,5\text{-}Me_3dtpi)_2PyO_2$	1.9640	100		1.9367	1.9782	184	58		

[a] All A values are given in gauss.

ESR spectra of $VO(2,4,5\text{-}Me_3dtpi)_2$ in chloroform were recorded at room temperature and at 77 K. The room temperature spectrum showed eight hyperfine lines characteristic of the vanadium nucleus (I = 7/2) split into three components with an intensity ratio of 1:2:1 arising as a result of superhyperfine interaction with two equivalent phosphorus nuclei (I = 1/2). The isotropic phosphorus constant (Table I) may be interpreted[9] in terms of a direct vanadium ($3d_{x^2-y^2}$) and phosphorus (3s) interaction. This could also arise through an interaction between the vanadium d orbital of σ symmetry and a linear combination of the two P–S bonding orbitals also of the same symmetry.[10] The isotropic splitting due to phosphorus is given by the expression

$$^{31}P_A = \frac{8\pi}{3} g_e g_n \beta_e \beta_n |\varphi 3s(O)|^2 C_s^2$$

where C_s is the contribution of the phosphorus 3s orbital to the molecular orbital containing the unpaired electron and $|\varphi 3s(O)|^2$ is the 3s electron density at the nucleus. For an unpaired electron located entirely in a phosphorus 3s orbital, the value of C_s^2 is estimated by taking the ratio of the ^{31}P superhyperfine splitting (A_{obsd}) to that calculated (A_{calcd}), as shown below.

$$C_s^2 = \frac{A_{obsd}}{A_{calcd}} = \frac{A_{obsd}}{3640\ G}$$

From the solution ESR spectrum, C_s^2 was calculated to be 0.0104. The lower value of dithiophosphinates compared to dithiophosphates (0.0135) can be accounted for by considering that the P–S bond is slightly shorter and S–P–S angle is larger, thus providing a better interaction of the unpaired electron of the metal with phosphorus in turn leading to a larger A^P value for dithiophosphates.

The complex $VO(2,4,5\text{-}Me_3dtpi)_2$ was further used to study the interaction with pyridine-type bases. Addition of these donors may result either in the expansion of coordination in which one molecule of base is attached to the sixth position or the pentacoordinate structure may be retained with strong coordination by pyridine as an equatorial ligand together with partial displacement of a sulphur ligand from the coordination sphere. In the presence of moderate amount of pyridine, the ESR spectrum showed the influence of only one phosphorus atom on the vanadium hyperfine signals in accordance with the latter structure. The decrease in the isotropic superhyperfine constant from ~40 G to ~30 G may be due to the lowering of structural symmetry caused by the interaction of pyridine which results in the reduction of delocalization of the unpaired electron of the metal over phosphorus. It may also be explained by considering that the spatial arrangement in the species formed tends to reduce the interaction between the vanadium d orbital and the P–S σ orbital of the displaced chelate. The superhyperfine splitting of the dithiophosphinate chelate which was not displaced will be modified by the asymmetry of the coordination at the other equatorial site.

From the above discussion it was expected that the addition of excess base might cause a complete destruction of the chelate structure. In the presence of excess pyridine, the room temperature ESR spectrum showed only eight lines with no phosphorus superhyperfine splitting, thus indicating that the complex species formed does not carry the coordination unit consisting of the four-membered chelate structure. Therefore it may be concluded that the addition of excess pyridine causes complete modification of the complex, which now has two unidentate sulphur ligands and two pyridine bases attached to oxovanadium(IV). Similar studies were also carried out with picolines, lutidines and some *N*-oxide donors to determine the influence of steric factors on the suggested substitution. It was also found that in the presence of these bulkier donors the pentacoordinate geometry is retained with partial displacement of both dithio ligands, thus indicating no significant steric effects on the proposed mechanism.

The studies were further extended by carrying out the reaction of the parent complex with triphenylphosphine, a ligand which can cause further splitting on coordination. In the presence of moderate as well as excess donor, the low temperature ESR spectra remained similar to that of the parent compound, and provided no clue as to the nature of the reaction. In this connection it is of interest to note that for $VO(acac)_2$, in the presence of tributylphosphine,[11] additional hyperfine lines are observed and equatorial coordination of the phosphine was confirmed through the magnitude of the isotropic hyperfine splitting constant at the ^{31}P nucleus. This result leads to the expectation that the behaviour of vanadyl dithiophosphinate in relation to triphenyl phosphine is similar to that involving heterocyclic nitrogen donors as described above.

Electronic spectral studies have also been carried out in presence of coordinating solvents such as pyridine, picolines, pyridine-*N*-oxide and some substituted *N*-oxides. The band loated at 14700 cm^{-1} in $CHCl_3$ is shifted to 12820 and 12500 cm^{-1} in pyridine and pyridine-*N*-oxide media. The absorption found at 17240 cm^{-1} in chloroform moved to 17200 and 15625 cm^{-1} in the above solvents. However, the shoulder observed around 24400 cm^{-1} in chloroform disappeared in the presence of coordinating solvents as reported for other dithiophosphinates.[10]

A fair number of studies are available[12] regarding the use of ESR to determine bonding parameters for cupric systems having the $3d^1$ hole configuration. Such investigations have been utilised only to a limited extent for d^1 oxovanadium(IV) complexes.[13] These parameters indicate electron density contributions from molecular orbitals at different atoms. The coefficients β_1^{*2} and β_2^{*2} characterize in-plane σ and π bonding, respectively, while ε_π^{*2} represents out-of-plane π bonding. The Fermi-contact term, k_v, for the vanadium atom is associated with the s electron density at the metal nucleus (corresponding to unit spin density in the metal d orbitals) which has a negative sign, and also the direct mixing of vanadium 3d and 4s orbitals, which gives a positive contribution to the spin density. Bonding parameters have been calculated for VOS_4, VOS_2N_2 and VOS_2O_2 chromophores and are set out in Table II along with the available data[14] for the VOO_4 chromophore. In these calculations β_2^{*2} is assumed[14] to be unity, which was shown to be true by further calculations; the parameters β_1^{*2}, ε_π^{*2} and k_v have also been computed. Smaller values for these parameters reflect greater covalency in the metal-ligand bonds. The observed sequence for various chromophores is $VOS_4 < VOS_2N_2 < VOS_2O_2 < VOO_4$. This order suggests that the species formed on interaction of the parent compound with excess pyridine has a low metal–ligand covalency compared to the VOS_4 core. The covalency is further reduced for the VOS_2O_2 chromophore and is least for the $VO(acac)_2$ system.

TABLE II
Bonding Parameters for the oxovanadium(IV) complexes.

Complex	β_1^{*2}	β_2^{*2}	ε_π^{*2}	k_v
$VO(2,4,5\text{-}Me_3dtpi)_2$	0.50	1	0.33	0.68
$VO(2,4,5\text{-}Me_3dtpi)_2Py_2$	0.60	1	0.81	0.69
$VO(2,4,5\text{-}Me_3dtpi)_2PyO_2$	0.78	1	0.83	0.70
$VO(acac)_2$[a]	0.84	1	0.90	0.83

[a] Ref. 14.

ACKNOWLEDGEMENTS

One of the authors (B.B.S.S) is grateful to the Council of Scientific and Industrial Research, Government of India, New Delhi, for financial support.

REFERENCES

1. B.E. Bridgland and W.R. McCregor, *J. Inorg. Nucl. Chem.*, **32**, 1729 (1970).
2. R.L. Carlin and F.A. Walker, *J. Am. Chem. Soc.*, **87**, 2128 (1965).

3. M.R. Caira, J.M. Haigh and L.R. Nassimbeni, *J. Inorg. Nucl. Chem.*, **34**, 3171 (1972).
4. R.N. Mukherjee, S. Shankar, V.S. Vijaya and P.K. Gogoi, *Polyhedron*, **4**, 1717 (1985).
5. R.N. Mukherjee, S. Shankar and D.L. Mascarenhas, *Bull. Chem. Soc. Japan*, **59**, 3239 (1986).
6. W.A. Higgins, P.W. Vogel and W.G. Craig, *J. Am. Chem. Soc.*, **77**, 1864 (1955).
7. C.J. Ballhausen and H.B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
8. R.G. Cavell, E.D. Day, W. Byers and P.M. Watkins, *Inorg. Chem.*, **11**, 1591 (1972).
9. J.R. Wasson, *Inorg. Chem.*, **10**, 1531 (1971).
10. G.A. Miller and R.E.D. McClung, *Inorg. Chem.*, **12**, 2553 (1973).
11. N.A. Geraseva, A.A. Shklyaev, A.S. Zamina and V.S. Anufrienko, *Zh. Strukt. Khim.*, **19**, 660 (1978).
12. N.D. Yordanov and D. Shopov, *Inorg. Chim. Acta*, **5**, 679 (1971).
13. G.M. Lapin, V.V. Zelentsov, Yu.V. Rakitin and M.E. Dyatkina, *Zh. Neorg. Khim.*, **17**, 2133 (1972).
14. D. Kivelson and S.E. Lee, *J. Chem. Phys.*, **41**, 1896 (1964).