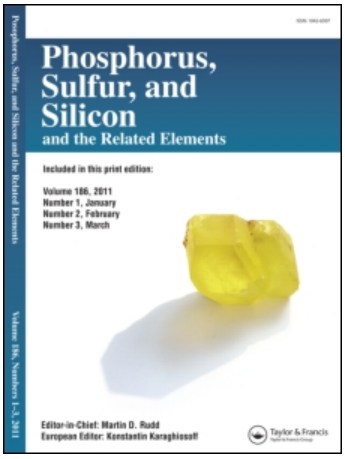

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

FURTHER COMMENTS ON THE X-RAY STRUCTURE OF *cis*-[$Pt(Me_2SO)(MeCN)Cl_2$]. LINEAR CORRELATION OF THE PT-s BOND LENGTHS IN A SERIES OF *cis*-[$Pt(Me_2SO)LCl_2$] COMPLEXES WITH "LEVER PARAMETERS" $E_L(L)$

Vadim Yu Kukushkin[a]; Vadim E. Konovalov[b]
[a] Department of Chemistry, St. Petersburg State University, Stary Petergof, Russia [b] L. Ya. Karpov Physico-Chemical Institute, Moscow, Russia

To cite this Article Kukushkin, Vadim Yu and Konovalov, Vadim E.(1992) 'FURTHER COMMENTS ON THE X-RAY STRUCTURE OF *cis*-[$Pt(Me_2SO)(MeCN)Cl_2$]. LINEAR CORRELATION OF THE PT-s BOND LENGTHS IN A SERIES OF *cis*-[$Pt(Me_2SO)LCl_2$] COMPLEXES WITH "LEVER PARAMETERS" $E_L(L)$', Phosphorus, Sulfur, and Silicon and the Related Elements, 69: 3, 305 — 307
To link to this Article: DOI: 10.1080/10426509208040651
URL: http://dx.doi.org/10.1080/10426509208040651

Phosphorus, Sulfur, and Silicon, 1992, Vol. 69, pp. 305–307
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

FURTHER COMMENTS ON THE X-RAY STRUCTURE OF *cis*-[Pt(Me_2SO)(MeCN)Cl_2]. LINEAR CORRELATION OF THE Pt—S BOND LENGTHS IN A SERIES OF *cis*-[Pt(Me_2SO)LCl_2] COMPLEXES WITH "LEVER PARAMETERS" E_L(L)

VADIM YU. KUKUSHKIN,*[a] and VADIM E. KONOVALOV[b]

[a] *Department of Chemistry, St. Petersburg State University, Universitetsky Pr. 2, 198904, Stary Petergof Russia;* [b] *L. Ya. Karpov Physico-Chemical Institute, Obukha St. 10, 103064, Moscow Russia*

(Received November 25, 1991)

Data of two X-ray structure determinations of *cis*-[Pt(Me_2SO)(MeCN)Cl_2] complex were compared. The conclusion was made that this compound can exist in different polymorphic modifications. Linear correlation of the Pt—S bond lengths in a series of *cis*-[Pt(Me_2SO)LCl_2] complexes with "Lever parameters" E_L(L) was shown. This correlation can be useful for prediction of changes in the Pt—S bond lengths in dependence of properties of associated co-ligands L.

Key words: Sulfoxide complexes of platinum; X-ray structure; polymorphic modifications; *cis*-influence; Lever parameters; Chatt constants.

The authors[1] and Rochon's group[2] independently and almost simultaneously carried out the X-ray structure determination of the *cis*-[Pt(Me_2SO)(MeCN)Cl_2] complex. Comparison of the data shows a difference in the space group ($P\bar{1}$[1] and $P2_1/n$[2]) reported for the compounds studied. The molecular structures differ in the dimethyl sulfoxide ligand rotation. In one case the coordination plane contains the carbon atom of Me_2SO ligand; the N—Pt—S—O torsion angles are 119.9 and −123.4° (for two crystallographically independent molecules).[1] In the other case, the coordination plane contains the oxygen atom of Me_2SO ligand; the N—Pt—S—O torsion angle equals 7.5°.[2] The differences (the data obtained have been carefully checked by both groups)[3] require that the *cis*-[Pt(Me_2SO)(MeCN)Cl_2] complex crystallizes in different polymorphic modifications.

Earlier it has been shown that the Pt—S bond length in complexes of the *cis*-[Pt(Me_2SO)LCl_2] series is an indicator of the ligand L *cis*-influence.[1] Based on the decreasing interatomic distance of Pt—S, the L ligands are arranged in following *cis*-influence range: Me_2SO[4,5] > C_2H_4[6] > MeCN[1,2] ~ $PhCH_2CN$[6] > Py[7] ~ 2MePy[8] > H_2O[9] > NH_3.[10] Here we consider a linear correlation between these Pt—S distances in the *cis*-[Pt(Me_2SO)LCl_2] with the E_L(L) Lever parameters†[11] (Figure 1).

* The author to whom correspondence should be addressed.

† The E_L(L) parameter is defined as 1/6 of the redox $Ru^{III}L_6/Ru^{II}L_6$ couple in MeCN has fairly recently been proposed to predict the redox potentials of Ru complexes; E_L(L) values for more than 200 ligands of various type are shown in the paper cited.

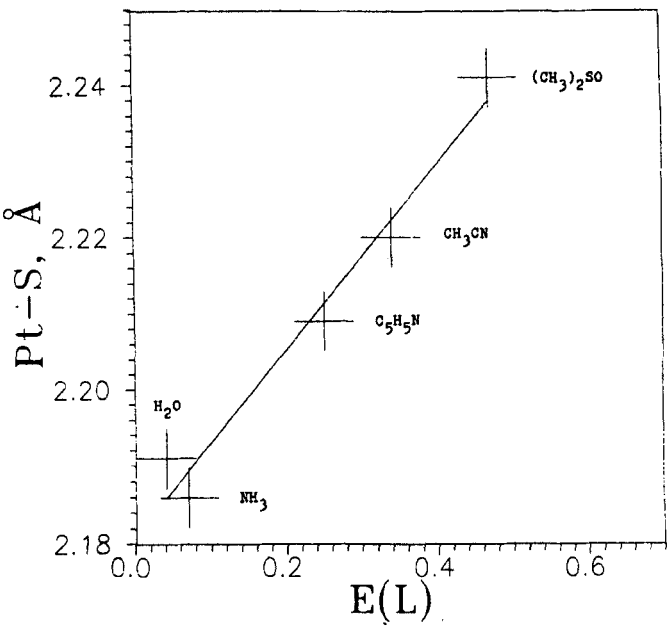

FIGURE 1 Plot of Pt—S bond lengths in *cis*-[Pt(Me_2SO)LCl_2] complexes vs. the E_L(L) Lever parameters.

The values of the E_L(L) Lever parameters (as well as the P_L Chatt constants)[12] are affected by the relative contribution of the σ-donor and π-acceptor constituents to the metal-ligand bond; the stronger π-acceptors are marked by larger E_L(L) and P_L values. First Chatt (for review see Reference 13) and then Constable[14] showed that there is an analogy between the σ-donors and π-acceptor abilities of ligands in the coordination compounds and also between the inductive and mesomeric effects in the aromatic compounds. Taking this analogy as a basis we also assume a similarity between the structural *cis*-influence in the *cis*-[Pt(Me_2SO)LCl_2] complexes and structural *ortho*-effect in aromatic compounds.

The relationship reported here between the Pt—S bond lengths and the magnitudes of the Lever E_L(L) parameters provides a new procedure for prediction of changes in the Pt—S bond distances in dependence of properties of associated coligands L which reflects in Lever parameters.

ACKNOWLEDGMENT

We wish to thank Prof. A. B. P. Lever for critical reading of the manuscript and for valuable suggestions.

REFERENCES

1. V. K. Belsky, V. E. Konovalov, V. Yu, Kukushkin, and A. I. Moiseev, *Inorg. Chim. Acta*, **169,** 101 (1990).
2. F. D. Rochon, P. C. Kong, and R. Melanson, *Inorg. Chem.*, **29,** 1352 (1990).
3. F. D. Rochon, *private communication.*
4. R. Melanson and F. D. Rochon, *Can. J. Chem.*, **53,** 2371 (1975).

5. R. P. Shibaeva, *Koord. Khim.*, **11,** 129 (1985).
6. V. Yu, Kukushkin, V. K. Belsky, V. E. Konovalov, G. A. Kirakosyan, L. V. Konovalov, A. I. Moiseev, and V. M. Tkachuk, *Inorg. Chim. Acta*, **185,** 143 (1991).
7. V. K. Belsky, V. E. Konovalov, and V. Yu. Kukushkin, *Acta Crystallogr., Sect C*, **47,** 292 (1991).
8. R. Melanson and F. D. Rochon, *Acta Crystallogr., Sect. B*, **33,** 3571 (1977).
9. F. D. Rochon, P. C. Kong, and R. Melanson, *Inorg. Chem.*, **29,** 2708 (1990).
10. R. Melanson and F. D. Rochon, *Acta Crystallogr., Sect B*, **34,** 941 (1978).
11. A. B. P. Lever, *Inorg. Chem.*, **29,** 1271 (1990).
12. J. Chatt, *Coord. Chem. Rev.*, **43,** 337 (1982).
13. Yu. N. Kukushkin, *The Chemistry of the Coordination Compounds*, Vishaya Skhola, Moscow, 1985, p. 182.
14. E. C. Constable, *Inorg. Chim. Acta*, **145,** 49 (1988).