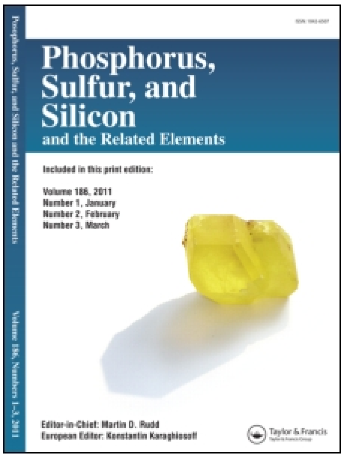


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ELECTRONIC AND LIGAND STRUCTURE DICTATED EFFECTS FOR TRIGONAL, TETRAGONAL AND RHOMBIC SYMMETRIES OF TRANSITION METAL CAGE COMPLEXES

Peter Comba[a]; Alan M. Sargeson[a]
[a] Research School of Chemistry, The Australian National University, Canberra, Australia

To cite this Article Comba, Peter and Sargeson, Alan M.(1986) 'ELECTRONIC AND LIGAND STRUCTURE DICTATED EFFECTS FOR TRIGONAL, TETRAGONAL AND RHOMBIC SYMMETRIES OF TRANSITION METAL CAGE COMPLEXES', Phosphorus, Sulfur, and Silicon and the Related Elements, 28: 1, 137 — 143

To link to this Article: DOI: 10.1080/03086648608072803

URL: http://dx.doi.org/10.1080/03086648608072803

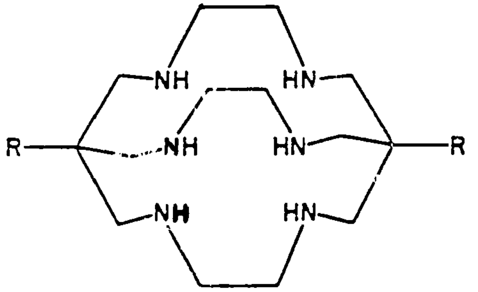
Phosphorus and Sulfur, 1986, Vol. 28, pp. 137–143
0308-664X/86/2802-0137/$15.00/0

ELECTRONIC AND LIGAND STRUCTURE DICTATED EFFECTS FOR TRIGONAL, TETRAGONAL AND RHOMBIC SYMMETRIES OF TRANSITION METAL CAGE COMPLEXES

PETER COMBA* and ALAN M. SARGESON

Research School of Chemistry, The Australian National University,
G.P.O. Box 4, Canberra, A.C.T. 2601 Australia

Spectroscopic and structural data of series of complexes with widely varied metal centers (d^0 to d^{10}) and an identical ligand sphere (figure) are presented. The structures comprise a range from near octahedral to near trigonal prismatic geometries and also involving additional small tetragonal perturbations. The complete series allows for an analysis of the various influences, viz. bonding and non-bonded interactions which dictate the compromise structure. Axial and rhombic distortions in solution and solid state of selected examples are discussed on the basis of electronic and EPR spectroscopy and trigonal distortions are analyzed on the basis of twist angles calculated from X-ray data.



R = H :sar
R = NH_2 :diamsar
R = NH_3^+ :diamH_2sar^{2+}

The sepulchrate and sar type cage ligands (the structures and nomenclature are shown in Figure 1) are unique for their structural simplicity, their versatility as encapsulating agents and the ease with which the ligands and the cage complexes are synthesized. The sepulchrate and sar type cage complexes are therefore very simple and fundamental models for encapsulation of metal centers, transition-metal centers in particular. Also, some labile or usually very reactive metal centers, such as V(IV), Mn(III) and Co(II), e.g., could be studied spectroscopically and structurally for the first time in an unperturbing symmetrical ligand sphere. The large series of transition-metal complexes with a basically constant ligand sphere allowed for many comparative studies (e.g. spectroscopy, electrochemistry, structural aspects, etc.).

Models clearly show the complete encapsulation of the metal center and its protection from substrates, both leading to high stability and inertness. Therefore, it was possible to investigate a whole series of complexes with a basically constant ligand sphere (i.e. six amines), and widely varied metal centers, virtually all possible d^n electronic configurations.

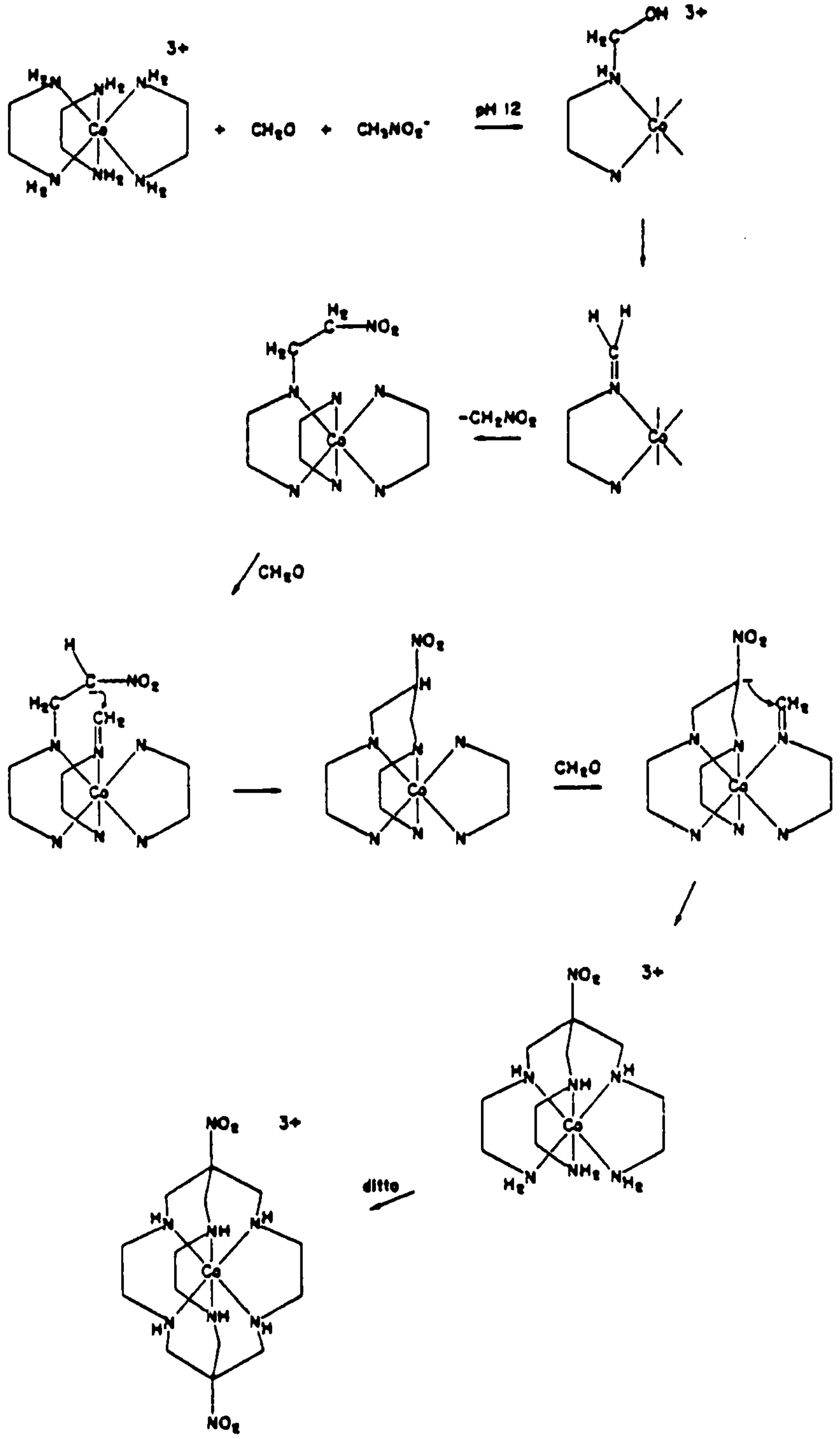
---

*Author to whom all correspondence should be addressed.

The synthesis of the cage compounds is very cheap, quick and easy and leads to very high yields. The problem of synthesizing cages with cavities that are large enough to accomodate metal ions, is primarily that of making large ring systems where entropy effects are unfavourable. However, if the synthesis is done on ligands coordinated to metal centers the large-ring synthesis may be reduced to several small-ring systems (Scheme 1).[2] Such a template synthesis has additional advantages; the coordinated ligands can be specifically activated by the metal center and through the influence of the metal template the synthesis may be stereospecific. The reaction shown in Scheme 1 occurs with complete retention of chirality. There are now various methods to isolate the metal-free ligands from the parent cage complexes[3] and with some skill and luck many metal ions can be complexed by these ligands.[4]

In the following we are turning to some spectroscopic and structural studies of these systems. EPR and electronic spectroscopy show that solution and solid-state structures are in many cases quantitatively and in most cases qualitatively identical and this is not unexpected for cage systems. One of the most important general results of our spectroscopic studies is that the cage complexes are not generally as highly symmetrical and as similar to each other as one might have expected. One of the reasons is that the cages have a particular cavity size, which actually is tunable within certain limits through conformational changes. E.g., the 1,2-diaminoethane (en)-type chelate five rings may be lel or ob (viz. parallel or oblique to the pseudo C_3 axis, see Figure 1). It is obvious that a cage complex with ob_3 configuration has a somewhat compressed cavity compared with lel_3 cage. And all possible combinations (e.g. lel_3, lel_2ob, etc.) have very particular distortions. Another important aspect is that the cage ligands have a preferred structure and the cage complex structure is then the result of a compromise between metal center and ligand preferences (see below). Also, the modes of distortion are not easy to predict. E.g. a principally Jahn-Teller active species might not be tetragonally distorted in a simple way like the usual elongation of so many hexacoordinate copper(II) systems. The copper(II) hexammine cage system actually is more trigonal prismatic than octahedral (see Table I). In addition it has a quite large rhombic distortion with two short cis bonds and two long pseudo trans bonds. In conclusion we note that we do not really have a series of complexes with an identical ligand sphere. Consequently, one has to be careful if one correlates ligand-field and bonding parameters.

We are now turning to the major perturbation from octahedral geometry which is a the trigonal twist.[5] Actually, this terminology may be misleading since a trigonal prism is not just a distorted octahedron. Although octahedral coordination geometry is still predominant for various reasons trigonal prismatic structures are now well established. We will present here a few new examples, of which the already mentioned copper(II) complex is just one. The study on the twist angles is based on X-ray data and Figure 1 defines the essential parameters. Two factors made this study particularly satisfactory. 1. A whole series of complexes with a constant ligand sphere[6] but widely varied electronic structure or similar electronic structure but variable size of the metal center could be studied. The various influences (bonding and nonbonded interactions) could therefore be separated. 2. The twist angles cover a wide range (ca. 18° to 60°), whereas the other structural parameters such as b, s, etc. are roughly constant and the bond-lengths a are as expected. Such a large range



SCHEME 1

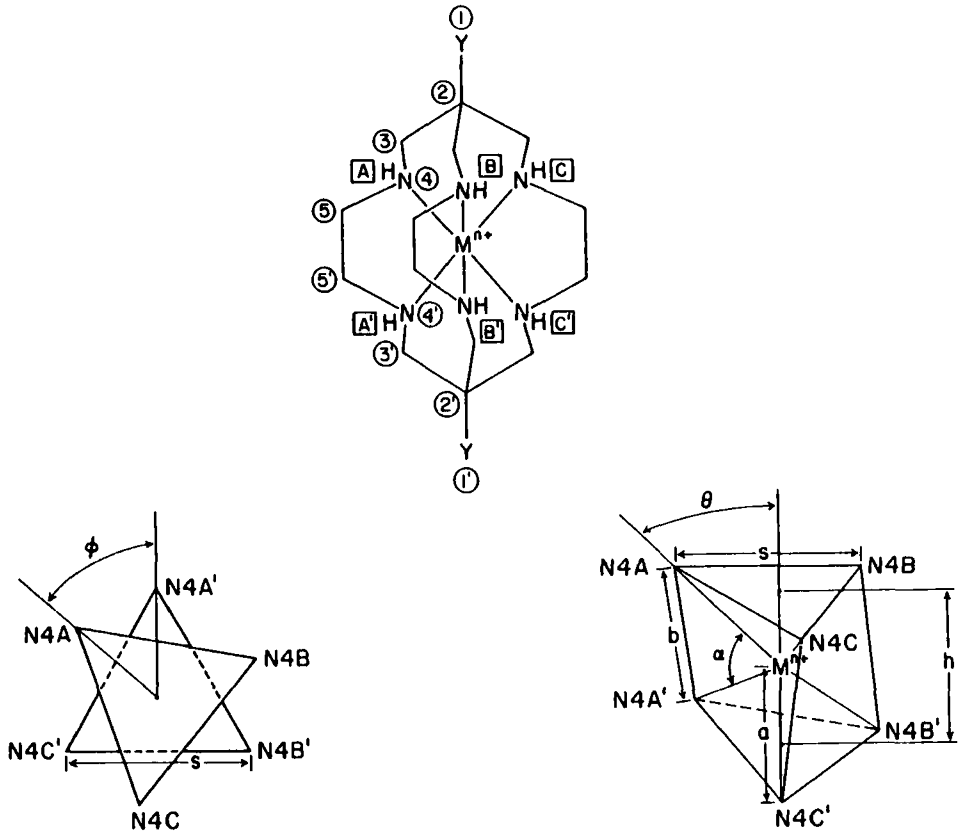


FIGURE 1 Nomenclature and structural parameters of the cage ligands and complexes. Y = H: sar; Y = NH_2: diamsar; Y = NH_3: di(amH)sar^{2+}; Y = NH_2OH: di(NH_2OH)sar^{2+}; 2 = N: sep.

for the twist angles allows for a meaningful analysis even if additional rhombic distortions are neglected.[6]

In Figure 2 the twist angles are plotted as a function of the d-electron occupation of the metal centers. There is a group of metal complexes whose structures are roughly constant and closer to trigonal prismatic than to octahedral and also close to the structure of the diprotonated free ligand. The twist angles of the other complexes vary considerably between this and the octahedral limit. The results can be rationalized with the expected differences in ligand-field stabilization energy (ΔLFSE) between the two extreme structures. From a qualitative energy level scheme (Figure 3), it follows that there is no preference for either geometry for d^0, d^1 (low spin d^2), high spin d^5, high spin d^6 and d^{10} systems. The ligand therefore dictates the structure in these cases. Since the ligand structure is very similar for all complexes, one expects very similar structures for the cases mentioned above, and this is exactly what one observes (Figure 2, Table I). For all other metal centers there exists a preference for octahedral structure with a maximum for low spin d^6. With this simple and qualitative model it is possible to estimate the twist angles within about

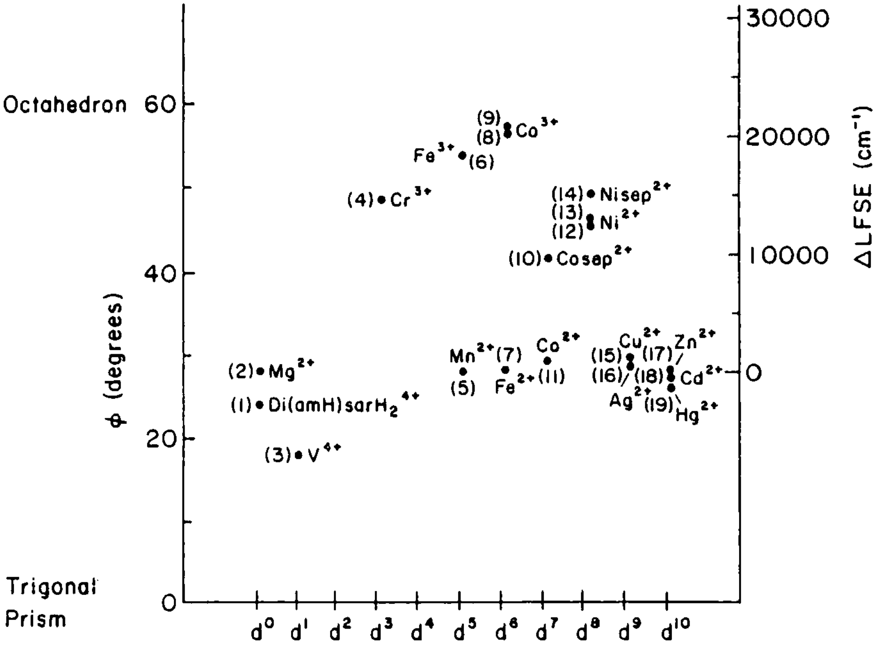


FIGURE 2 Twist angles φ in relation to the d-electron occupation of the metal centers (for numbering, see Table I).

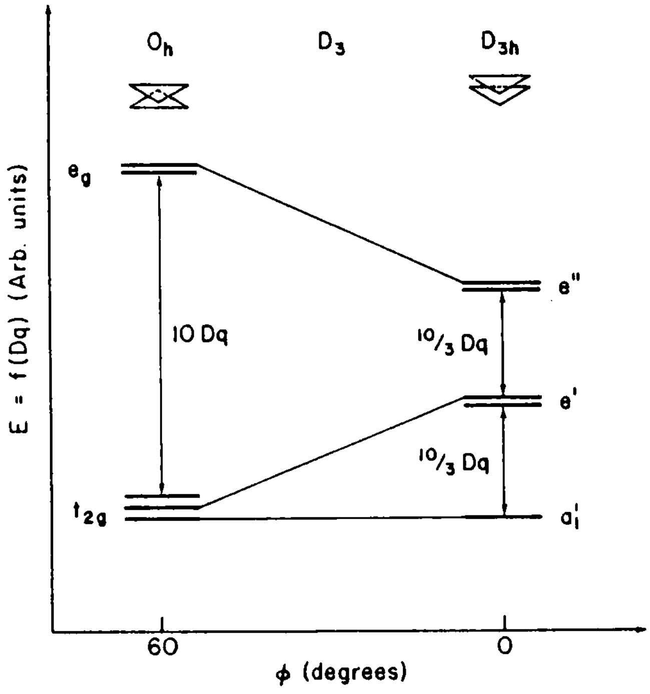


FIGURE 3 Qualitative energy level scheme for trigonal prismatic and octahedral geometries.

TABLE I

Experimental and calculated twist angles ϕ

Complex[a]	ϕ (measd)[b]	ϕ (calcd)[c]
(1) di(amH)sarH$_2$ (NO$_3$)$_4$	23.9	28[c]
(2) Mg(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	27.8	28[d]
(3) V(IV)di(amH)sar-2H (S$_2$O$_4$)$_2$ · 2H$_2$O	17.7	28[c]
(4) Cr(III)diamsar Cl$_3$ · H$_2$O	49.0	49[d]
(5) Mn(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	27.6	28
(6) Fe(III)sar (NO$_3$)$_3$	52.8	51
(7) Fe(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	28.6	28
(8) Co(III)sep (NO$_3$)$_3$	56.7	58[c,e]
(9) Co(III)di(NH$_2$OH)sar Cl$_5$ · 4H$_2$O	58.3	58[c]
(10) Co(II)sep S$_2$O$_6$ · H$_2$O	42.4	31[c]
(11) Co(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	29.0	31
(12) Ni(II)di(amH)sar Cl$_4$ · H$_2$O	45.7	43
(13) Ni(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	47.1	43
(14) Ni(II)sep (ClO$_4$)$_2$	48.0	43[c]
(15) Cu(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	29.8	34
(16) Ag(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	28.8	34
(17) Zn(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	28.6	28
(18) Cd(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	27.4	28
(19) Hg(II)di(amH)sar (NO$_3$)$_4$ · H$_2$O	25.8	28

[a] For nomenclature, see Figure 1.

[b] For details and references, see Reference 5.

[c] Principally different systems (see text).

[d] Fixed points.

[e] For steric and electronic reasons the octahedral limit is somewhat smaller than 60° (56°–58°).

5° (Table I). Included in the treatment is a correction for differences in electronic repulsion. The ligand-field parameters are from spectroscopic studies of the whole series of complexes[7] and we have to assume two fixed points (Mg(II) (2) and Cr(III) (4)). It is clear that more sophisticated models could yield quantitatively more accurate estimates. However, one has to realize that the measured twist angles have, due to the neglected distortions form trigonal symmetry, error limits of up to 7°. The diprotonated metal-free ligand (1), the sepulchrates (8), (10), (14) and the vanadium cage (3) are somewhat different systems and the differences between observed and calculated twist angles is well understood for these cases. The differences are actually very helpful for other studies.[8].

It is now a very important conclusion that the structures of the cage complexes are the result of a compromise between nonbonded interactions and electronic effects, between ligand and metal-center preferences. This is principally nothing new and certainly general for chemical compounds. It however is in sharp contrast to treatments based solely on geometric and/or repulsion models.[9] Our study unambiguously shows the importance of electronic effects.

ACKNOWLEDGMENTS

PC is grateful to the University of Lausanne for financial support to attend the IRIS IV Conference.

REFERENCES AND NOTES

1. Present address: Université de Lausanne, Institut de chimie minéral et analytique, Place du Château 3, 1005 Lausanne, Switzerland.
2. R. J. Geue, T. W. Hambley, J. M. Harrowfield, A. M. Sargeson and M. R. Snow, *J. Am. Chem. Soc.*, **106**, 5478 (1984).
3. A. M. Sargeson, work in progress.
4. a) P. Comba, L. M. Engelhardt, J. M. Harrowfield, G. A. Lawrance, L. L. Martin, A. M. Sargeson and A. H. White, *J. Chem. Soc., Chem. Commun.*, (**1985**), 174; b) P. Comba, I. I. Creaser, L. R. Grahan, J. M. Harrowfield, G. A. Lawrance, L. L. Martin, A. W. H. Mau, A. M. Sargeson, W. H. F. Sasse and M. R. Snow, *Inorg. Chem.*, accepted; c) A. M. Sargeson *et al.*, work in progress.
5. P. Comba, A. M. Sargeson, L. M. Engelhardt, J. M Harrowfield, A. H. White, E. Horn and M. R. Snow, *Inorg. Chem.*, **24**, 2325 (1985).
6. This is not in contradiction to the fact that the ligand sphere is principally not constant (see text), since the largest distortion (i.e. the trigonal twist) is the variable for this study. Additional rhombic distortions are neglected.
7. P. Comba, work in progress.
8. P. Comba and A. M. Sargeson, *Aust. J. Chem.*, accepted.
9. D. L. Kepert, *Prog. Inorg. Chem.*, **23**, 1 (1977), and references therein.