

## GEOMETRICAL CHANGES IN IRON(II) COMPLEXES CAUSED BY THE REPLACEMENT OF PHENYL GROUPS IN THE LIGAND TRIPHENYLPHOSPHINE OXIDE BY BENZYL RADICALS

Stanley Ivair KLEIN\*  
Antonio Carlos MASSABNI\*  
José Celso MOREIRA\*\*  
Aldo TANCREDO\*\*\*

**ABSTRACT:** The series of complexes  $[\text{FeL}_4] (\text{ClO}_4)_3$ ,  $[\text{Fe}(\text{NO}_3)_3 \text{L}_2]$  and  $[\text{FeL}_4] [\text{FeCl}_4]$  ( $\text{L} =$  dibenzylphenylphosphine oxide, dbppo; tribenzylphosphine oxide, tbpo) were prepared and the stereochemistry of the new complexes was compared to that of the parent triphenylphosphine oxide (tppo) iron(III) compounds. The effect of the bulkier and alkyl type tppo ligand is to alter the geometry and possible the coordination number of the uncharged nitrate complex only. For the charged complexes no changes in geometry within each series were detected.

**KEY-WORDS:** Complexes; phosphine oxides; iron(III); stereochemistry; ESR spectra.

## INTRODUCTION

The geometries and stoichiometries of iron(III) triphenylphosphine oxide complexes seem to be governed by the type of anion associated with the metal. Thus, the cation in  $[\text{FeL}_4] (\text{ClO}_4)_3$  is square planar, and in  $[\text{FeCl}_2 \text{L}_4] [\text{FeCl}_4]$  it is octahedral. The iron metal is in the centre of a slightly distorted trigonal bipyramid in  $[\text{Fe} (\text{NO}_3)_3 \text{L}_2]$ . ( $\text{L} = \text{tppo}$ ).

\* Departamento de Química Geral e Inorgânica - Instituto de Química - UNESP - 14800 - Araraquara - SP.

\*\* Departamento de Química Tecnológica e de Aplicação - Instituto de Química - 14800 - Araraquara - SP.

\*\*\* Instituto de Geociências e Ciências Exatas - UNESP - 13500 - Rio Claro - SP.

Phosphine oxides bearing benzyl radicals as in dbppo and tbpo<sup>2</sup> are expected to differ from tppo in their steric requirements, and also in the electron donation capacity of their phosphoryl oxygen, since both dbppo and tbpo have increasing alkyl character when related to the strict aryl character of the radicals in tppo. The interplay of such factors could, in principle, affect the type of complex to be formed, either by making the number of coordinated ligands different from those found in the tppo compounds mentioned, or by altering their geometries. In an attempt to detect such possible changes, the work herein reported was undertaken.

## EXPERIMENTAL

The following instruments were used: Metrohm E-182 conductometer for conductance measurements; Mettler FP-2 for melting points. The spectrometers Cary 17, Perkin-Elmer model 567 and Varian E-109 were used to obtain UV-visible, ir and room temperature X-band ESR spectra, respectively. Magnetic moments were measured by the Gouy method.

The preparation of the complexes followed closely that reported earlier<sup>1</sup>. Good analytical data for the new complexes were obtained by the analysis of the metal by complexometric titration, and of the anions (chloride as AgCl; nitrate with nitron and perchlorate with tetraphenylarsonium chloride<sup>3</sup>). The phosphine oxide contents were analysed by recovering the insoluble ligands after decomposition of the complexes with deionized water.

## DISCUSSION

Relevant physical constants for the new complexes are presented in the Table. These, together with good analytical data, fully support the stoichiometries indicated for the compounds.

From the Table, it is clear that the number of ligated phosphine oxides within each series is independent of the phosphine oxide itself, but is still related to the associated anion, and that this number is identical to those for the known tppo complexes.

Electronic and vibrational spectroscopies were of limited use for unveiling the stereochemistry of the compounds. All UV-visible spectra obtained, showed a number of shoulders of difficult assignment, in addition to more intense bands near 450 nm. In the infrared spectra there were sometimes superposition of bands which made it difficult to distinguish between mono and bi-dentate coordination of nitrate groups.

TABLE - Physical constants of the new complexes

Complexes	m.p. <sup>0</sup> C	$\Delta M$ $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	$\mu_{\text{eff}}$ B.M $\pm 0,02$
[FeCl <sub>2</sub> (dbppo) <sub>4</sub> ] [FeCl <sub>4</sub> ]	126-30	65	10,98
[FeCl <sub>2</sub> (tbpo) <sub>4</sub> ] [FeCl <sub>4</sub> ]	110-2	61	11,29
[Fe(NO <sub>2</sub> ) <sub>3</sub> (dbppo) <sub>2</sub> ]	68-71	12	5,86
[Fe(NO <sub>2</sub> ) <sub>3</sub> (tbpo) <sub>2</sub> ]	78-83	8	5,79
[Fe(dbppo) <sub>4</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	220-5	185	5,90
[Fe(tbpo) <sub>4</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	225-8	181	5,92

Particularly revealing were the ESR spectra of the complexes, which were very similar within each series of charged compounds [FeL<sub>4</sub>] (ClO<sub>4</sub>)<sub>3</sub> and [FeCl<sub>2</sub>L<sub>4</sub>] [FeCl<sub>4</sub>] (L = tppo, dbppo, tbpo), indicative of the maintenance of the square planar and octahedral geometries for the cations<sup>1</sup>.

The ESR spectra for the series of uncharged nitrate complexes are shown in the Figure, and indicate clearly that straight pentacoordination is not retained in the iron metal ligated to the bulky tbppo ligands. Those spectra were analysed according to the methods of DOWSING *et alii*<sup>4,6</sup> and WICKMAN *et alii*<sup>7</sup>. The lines near  $g = 6$  and  $g = 2$  in all spectra indicate systems where  $\lambda$  is close to zero, and therefore all three nitrate complexes possess axial symmetry. In the least sterically hindered tppo and dbppo compounds the line near  $g = 6$  is split, the splitting for the dbppo complex being more pronounced. This indicates deviations from  $\lambda = 0,0$ , which can be associated with progressive distortions from an ideal D<sub>3h</sub> symmetry of a trigonal bipyramidal environment around the metal imposed by the bulk of the dbppo ligand. The calculated parameters are:  $D = 0,55 \text{ cm}^{-1}$ ,  $\lambda = 0,04$  (tppo complex; these values agree precisely with those found earlier<sup>1</sup>, and  $D = 0,62 \text{ cm}^{-1}$ ,  $\lambda = 0,066$  for the new dbppo complex. It is interesting to note that the values  $D = 0,62 \text{ cm}^{-1}$  and  $\lambda = 0,067$  were found for the analogous triphenylarsine oxide complex<sup>1</sup>. This seems to suggest that the later ligand exerts the same geometrical influence as dbppo in this class of nitrate iron(III) compounds.

In considering the distortions mentioned above, it was surprising to find no such splittings in the line near  $g = 6$  in the ESR spectrum of Fe(NO<sub>2</sub>)<sub>3</sub> (tbppo)<sub>2</sub>. The low values  $D = 0,2 \text{ cm}^{-1}$  and  $\lambda = 0,032$  indicate, in fact, a geometry for this complex which is different than that of a mononuclear, trigonal bipyramid.

It is unfortunate that we could not obtain a complementary Q-band spectrum for the tbpo complex. However, circumstantial evidence such as the presence of axial symmetry and a  $\lambda$  value close to zero, seems to be indicative of an octahedral structure. This could

be attained if at least one of the coordinated nitrate groups would be bidentate. In fact, other structures with axial symmetry are possible, as for instance, in dimeric or polymeric species containing bridging nitrate groups. In any case, the infrared spectrum of the compound should be of difficult interpretation.

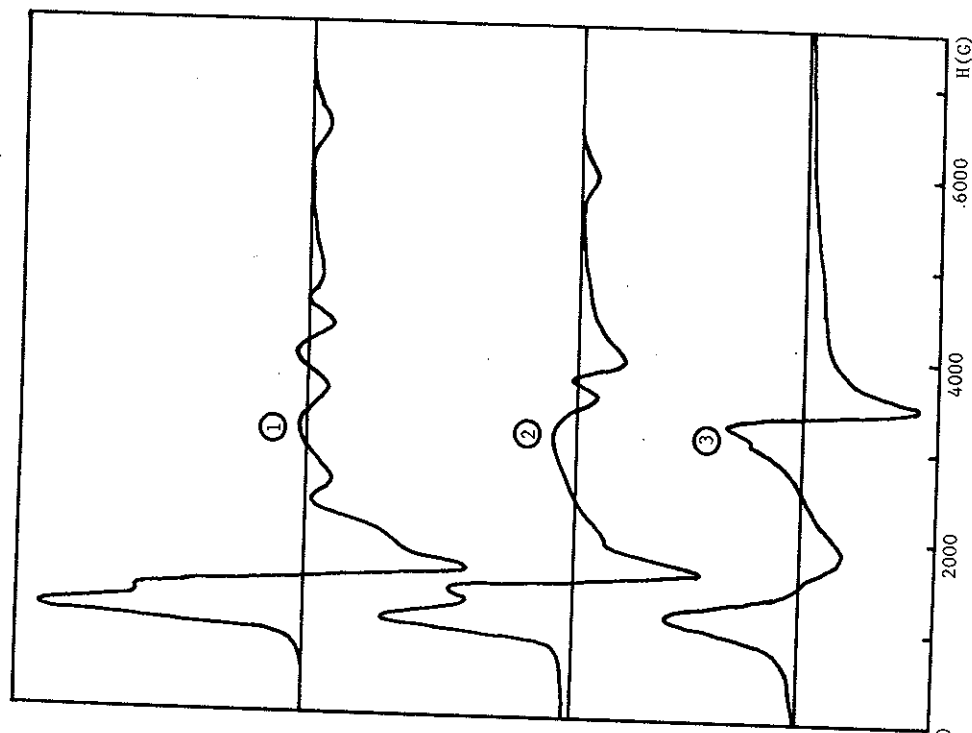


FIG. 1 - ESR spectra of the nitrate complexes (solid sample, 300°K).

- 1)  $[\text{Fe}(\text{NO}_3)_3(\text{tppo})_2]$ ;
- 2)  $[\text{Fe}(\text{NO}_3)_3(\text{dbppo})_2]$ ;
- 3)  $[\text{Fe}(\text{NO}_3)_3(\text{tbpo})_2]$ .

The important conclusion that can be drawn from the present work is that steric effects may not be the sole factor responsible for geometrical changes in iron(III) compounds, since such changes were only detected in the series of uncharged, non-conducting nitrate complexes. This may be taken as an evidence of the importance of electronic effects caused by the change of the aryl type character of tppo by the alkyl character of tbpo.

KLEIN, S. I. *et alii* - Mudanças da geometria dos complexos de Ferro(III) provocadas pela troca de grupos fenil do ligante trifenilfosfinóxido por radicais benzil. *Ecl. Quím., São Paulo*, **13**: 7-11, 1988.

RESUMO: As séries de complexos  $[\text{FeL}_4](\text{ClO}_4)_3$ ,  $[\text{Fe}(\text{NO}_3)_3\text{L}_2]$  e  $[\text{FeL}_4][\text{FeCl}_4]$  (L = dibenzilfosfinóxido, dbppo; tribenzilfosfinóxido, tbpo, foram preparadas e a estereoquímica dos novos complexos foi comparada com a dos compostos semelhantes de trifenilfosfinóxido (tppo) com Ferro(III). O efeito do ligante tbpo mais volumoso e do tipo atômica altera a geometria e provavelmente o número de coordenação somente do complexo neutro de nitrato. Para os complexos com carga não foram observadas alterações na geometria em cada série.

UNTERMOS: Complexos; fosfinóxidos; ferro(III); estereoquímica; espectros de ESR.

## REFERENCES

1. COTTON, S. A. & GIBSON, J. F. - *J. Chem. Soc. (A)*, 859 (1971).
2. MASSABNI, A. C. & SERRA, O. A. - *J. Coord. Chem.*, **7**, 67 (1977).
3. GLOVER, D. J. & ROSEN, J. M. - *Anal. Chem.*, **37**, 306 (1965).
4. DOWSING, R. D. & GIBSON, J. F. - *J. Chem. Phys.*, **50**, 294 (1969).
5. DOWSING, R. D.; GIBSON, J. F.; GOODGAME, D. M. L.; GOODGAME, M. & HAYWARD, P. J. - *J. Chem. Soc. (A)*, 1242 (1969).
6. DOWSING, R. D.; GIBSON, J. F.; GOODGAME, M. & HAYWARD, P. J. - *J. Chem. Soc. (A)*, 187 (1969).
7. WICKMAN, H.; KLEIN, M. P. & SHIRLEY, D. A. - *J. Chem. Phys.*, **42**, 2113 (1965).

Recebido em 05/03/88