

## Topological Degeneracy of Magnetic Orbitals in Organic Biradicals Mediated by Metal Ions: Triplet Ground State in a Titanium(IV) Complex of Schiff Base Diquinone Radical Ligands

Andrea Caneschi, Andrea Dei\* and Dante Gatteschi

Department of Chemistry, Università di Firenze, Via Maragliano 75, 50144 Firenze, Italy

A large intramolecular ferromagnetic interaction is observed in a titanium(IV) complex formed by two tridentate Schiff base semiquinonato radical ligands; this peculiar magnetic behaviour may be rationalised on the basis of the structural properties of the biradical compound.

Topological degeneracy of magnetic orbitals is currently widely used in order to achieve preferred parallel alignment of unpaired electrons in both organic and inorganic molecules.<sup>1</sup> The final aim of deriving molecular-based ferromagnets can in fact be achieved if individual building blocks containing unpaired electrons are assembled in such a way that the magnetic orbitals are kept orthogonal to each other. In this way Hund's rule shows that electron spins will remain parallel to each other. This approach proved to be successful, for instance, in copper(II)–oxovanadium(IV) pairs<sup>2</sup> and in polycarbenes,<sup>3–5</sup> where molecules with an  $S = 5$  ground state have been recently synthesized.<sup>5</sup>

We show here that preferred parallel spin alignment can be observed in organic biradicals which are formed when two Schiff base diquinone radical ligands bind to a diamagnetic metal ion, provided they are properly designed to keep their magnetic orbitals orthogonal to each other.

It is well known that 3d metal ions react with 3,5-di-*tert*-butylcatechol and aqueous ammonia in the presence of air yielding bis complexes of the resulting biquinone ligand.<sup>6–8</sup> On the basis of structural and magnetic data it has been shown that the coordinated ligand can be described, depending on

the nature of the metal ions, either as the monoanion of the 2-(2-hydroxy-3,5-di-*tert*-butylphenylimino)-4,6-di-*tert*-butylcyclohexa-3,5-dienone, L<sup>1</sup>, or the corresponding dianionic semiquinonato analogue L<sup>2</sup>. We have found that when the same reaction is carried out with TiCl<sub>3</sub> a violet crystalline derivative of formula Ti(C<sub>56</sub>H<sub>80</sub>N<sub>2</sub>O<sub>4</sub>) is obtained. The crystallographic characterization shows that this compound must be formulated as a titanium(IV) complex of the ligand L<sup>2</sup>. The metal ion is octahedrally coordinated by the two ligands which occupy the meridional sites of the coordination polyhedron (Fig. 1).<sup>†</sup> The C–O distances are longer than those

<sup>†</sup> Crystal data: C<sub>56</sub>H<sub>80</sub>N<sub>2</sub>O<sub>4</sub>Ti,  $M = 893.16$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.711(4)$ ,  $b = 12.246(5)$ ,  $c = 20.944(10)$  Å,  $\alpha = 89.19(4)$ ,  $\beta = 74.15(4)$ ,  $\gamma = 75.27(4)^\circ$ ,  $V = 2789(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.06$  g cm<sup>-3</sup>. Mo-K $\alpha$  radiation (graphite monochromator,  $\lambda = 0.71069$  Å),  $T = 300$  K. Final conventional  $R$  factors:  $R = 7.75\%$ ,  $R_w = 7.77\%$  for 3337 observed reflections [ $I > 3\sigma(I)$ ] and 509 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

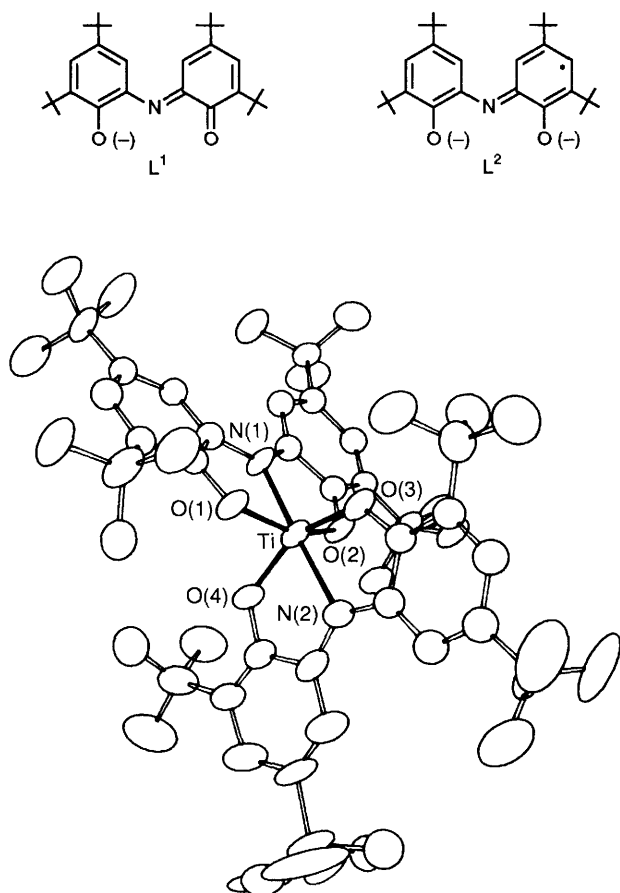


Fig. 1 ORTEP drawing of the asymmetric unit of  $\text{Ti}(\text{L}^2)_2$ . H atoms are omitted for clarity.

observed in  $\text{L}^1$  complexes (1.34 vs. 1.26 Å) and also slightly longer than in the  $\text{Mn}(\text{L}^2)_2$  complex (1.32 Å) (probably owing to a decreased  $\pi$  character of the metal bond interaction).<sup>7,8</sup> The C–N and C–C lengths are also clearly indicative of the overall ligand charge of the complex. The average Ti–O and Ti–N distances are 1.88 and 2.15 Å, respectively, consistent with the +4 oxidation state of the metal ion. The dihedral angles between the ring planes of the two ligands are 9.7 and 5.4°, respectively. The planes of the two ligands in the coordination polyhedron are orthogonal to each other.‡

Electrochemical measurements in 1,2-dichloroethane solutions indicate that this compound undergoes four one-electron transfer processes at –1.14, –0.67, 0.08 and 0.45 vs.  $\text{Fc}^+/\text{Fc}$  couple. The positive couples involve ligand-centred redox processes. Studies are in progress in order to ascertain the nature of the processes occurring at negative potentials.

The temperature dependence of  $\chi T$  for this derivative is shown in Fig. 2. The room temperature value corresponds to  $\mu_{\text{eff}} = 2.47 \mu_{\text{B}}$ , slightly higher than expected for two uncorrelated  $S = 1/2$  centres within the molecule. However, on cooling  $\chi T$  increases reaching a plateau in the range 35–4 K corresponding to  $\mu_{\text{eff}} = 2.77 \mu_{\text{B}}$ , which is consistent with an  $S = 1$  ground state, thus indicating a ferromagnetic interaction between the radical ligands. The fitting of susceptibility data requires  $J = -56 \text{ cm}^{-1}$  and  $g = 2.00$  (the exchange Hamiltonian is  $JS_1S_2$ ).

‡ In the structure one *tert*-butyl group was found to present a twofold rotational disorder, like in the  $\text{Co}^{\text{II}}$  and  $\text{Mn}^{\text{II}}$  homologues.<sup>7</sup> This group was refined with a variable occupancy factors for the two sets of atoms, *i.e.*, 43% for C(54), C(55), C(56) and 57% for C(541), C(551) and C(561).

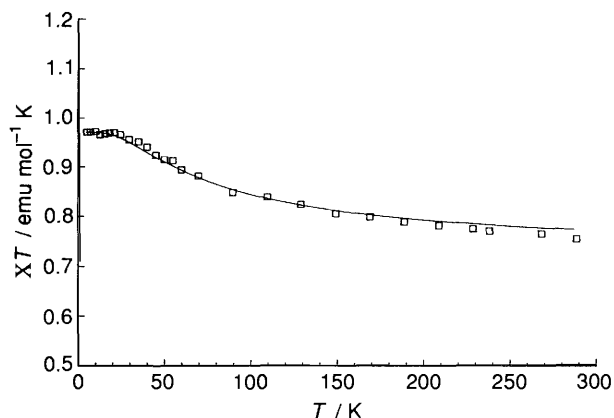


Fig. 2 Temperature dependence of magnetic susceptibility for  $\text{Ti}(\text{L}^2)_2$ . The solid line represents the calculated values with the best fit parameters (see text).

The polycrystalline powder EPR spectra of this derivative show a signal at  $g = 2.00$ , with no spectral features to be assigned as triplet EPR spectra being detected. Similar results were obtained using frozen solutions in different organic solvents.

The ground triplet state is stabilized by the topological degeneracy of the two magnetic orbitals of the radicals. Assuming an overall  $C_{2v}$  symmetry for the complex, the two  $\pi^*$  magnetic orbitals behave as  $b_1$  and  $b_2$ , respectively. They are therefore orthogonal to each other, thus rationalising the observed ferromagnetic coupling. The mechanism by which the two electrons affect each other may involve the empty metal orbitals.

While paramagnetic metal ions have been widely employed in order to synthesize molecular based ferro- or ferri-magnets,<sup>1,9</sup> the use of diamagnetic ions has been much less widespread. Recently Rey *et al.*<sup>10</sup> reported ferromagnetic chains formed by coordination of imino nitroxides to rhodium dimers, the coupling constant being  $5 \text{ cm}^{-1}$ . The example reported here shows that much larger ferromagnetic coupling can be achieved with suitably designed radicals.

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