# 875. *The Metal–Metal Bond in Binuclear Di-π-cyclopentadienyltitanium*(III) *Chloride*

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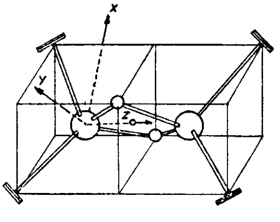
Measurements of the magnetic susceptibility of polycrystalline di-π-cyclopentadienyltitanium(III) chloride reveal the presence of singlet and triplet spin states in thermal equilibrium. These arise from intramolecular titanium–titanium interactions. A qualitative molecular-orbital analysis suggests that bridging chlorine atoms are not only involved in 4-centre bonding with $Ti_2$ pairs, but that they also play a vital role in making the lowest triplet state of the dimer thermally accessible.

THE magnetic properties of cyclopentadienyl derivatives of tervalent titanium (configuration $3d^1$) appear to be uncomplicated. At room temperature [(π-cpd)$_2$Ti] picrate [1] and [(π-cpd)$_3$Ti] [2] have magnetic moments of 2·3 and 1·69 B.M., respectively, which correspond to a single unpaired electron per titanium atom. As the temperature is lowered to 90°K, the susceptibility of the latter compound follows Curie's law.

Unlike these mononuclear derivatives, the compound di-π-cyclopentadienyltitanium(III) chloride is dimeric,[3,4] [(π-cpd)$_2$TiCl$_2$Ti(π-cpd)$_2$], and it has been suggested that pairs of titanium atoms are grouped together by bridging chlorine atoms [4] (see Figure 1). In this event, the probable dimensions of the $[Ti_2Cl_2]^{4+}$ core {estimated here from published *X*-ray data [5] on [(π-cpd)$_2$TiCl$_2$Al(C$_2$H$_5$)$_2$]} make it likely that metal–metal bonding will occur by interaction of $3d$-orbitals centred on each titanium atom.

FIGURE 1. Reference axes for [(π-cpd)$_2$TiCl]$_2$



*Magnetic Properties of Di-π-cyclopentadienyl Titanium*(III) *Chloride*.—We have evaluated this possibility by measuring the variation with temperature of the paramagnetic susceptibility of [(π-cpd)$_2$TiCl]$_2$ between 85 and 350°K (see Figure 2). Instead of obeying some

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[1] F. A. Cotton, H. P. Hanson, and G. Wilkinson, unpublished work, quoted *Prog. Inorg. Chem.*, 1959, **1**, 69.

[2] E. O. Fischer and A. Löchner, *Z. Naturforsch.*, 1960, **15**b, 266.

[3] H. Nöth and R. Hartwimmer, *Chem. Ber.*, 1963, **93**, 2246.

[4] G. Natta, *Angew. Chem.*, 1959, **71**, 205.

[5] G. Natta, P. Corradini, and I. W. Bassi, *J. Amer. Chem. Soc.*, 1958, **80**, 755.

form of Curie or Curie–Weiss law, the susceptibility passes through a maximum value at 170°K and then falls rapidly at lower temperatures. At 350°K, the effective magnetic moment per titanium atom is 1·60 B.M., being only slightly lower than the " spin-only " value, 1·73 B.M., calculated for a single unpaired electron. However, when the temperature is reduced to 85°K, the magnetic moment decreases monotonically to 0·68 B.M. Extrapolation of the $\mu_{\text{eff}}(T)$ curve to lower temperatures indicates that the dimer will become diamagnetic.

The close resemblance of this anomalous magnetic behaviour to that so well established for binuclear copper(II) acetate [6] suggests that, here too, isolated pairs of metal atoms interact to form a lower singlet state ($S = 0$; diamagnetic) and a slightly higher triplet state ($S = 1$; paramagnetic). As the temperature is lowered, the singlet state becomes progressively populated at the expense of the triplet level, so that the susceptibility and magnetic moment both decrease steadily, eventually to zero.

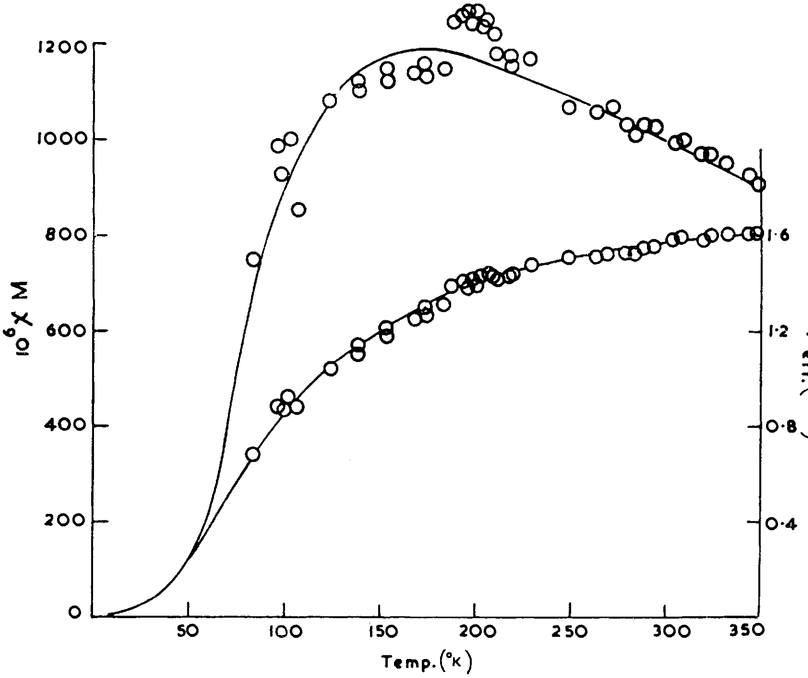

FIGURE 2. Variation of magnetic susceptibility (upper curve; left hand axis) and magnetic moment (lower curve; right hand axis) with temperature for $[(\pi\text{-cpd})_2\text{TiCl}]_2$; full curves calculated from eqn. 3

The aptness of this hypothesis can be evaluated by comparing the experimental results with $\chi_M(T)$ and $\mu_{\text{eff}}(T)$ curves derived from equation (1), which is appropriate to the singlet–triplet model: [6]

$$\chi_M = \frac{g^2N\beta^2}{3kT}\left[1 + \tfrac{1}{3}\exp\left(-\frac{J}{kT}\right)\right]^{-1} \tag{1}$$

Here $J$ represents the difference in zero-point energies of the molecular singlet and triplet levels. $J$ is negative for the present compound, corresponding to a singlet ground state. If the magnetic moment arises from spin alone, then $g = 2$ and equation (1) reduces to:

$$\chi_M = \frac{0{\cdot}5}{T}\left[1 + \tfrac{1}{3}\exp\left(-\frac{J}{kT}\right)\right]^{-1} \tag{2}$$

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[6] B. N. Figgis and R. L. Martin, *J.*, 1956, 3837.

Furthermore, the singlet–triplet separation can be estimated directly from the temperature of maximum susceptibility, $T_c = -\frac{5J}{8k}$, whence $-J = 1{\cdot}6\ kT_c$. The Curie–Weiss law will not be strictly obeyed until $T \gg T_c$ when $\theta \simeq 0{\cdot}4\ kT_c$.

The experimental results are compared in Figure 2 with those calculated (full curve) from equation (3),

$$\chi_M = \frac{0{\cdot}548}{T}\left[1 + \tfrac{1}{3}\exp\left(\frac{275}{T}\right)\right]^{-1} \tag{3}$$

The agreement is good and confirms that our model is essentially correct. The required value of $g$ is 2·10.

We note that the experimental data appear to show undue scatter at 160—200°K, which is nearly coincident with the susceptibility maximum. This feature was reproduced in a series of runs, and may reflect a minor phase transition at this temperature. Indeed, this small anomaly can be accommodated by employing slightly differing values of $g$ and $J$ above and below 170°K [cf. equations (4) and (5)]. However, as the general validity of our model is not consequent on this elaboration, we do not propose to seek further evidence of a solid-state transition.

Below 170°K;
$$\chi_M = \frac{0{\cdot}49}{T}\left[1 + \tfrac{1}{3}\exp\left(\frac{272}{T}\right)\right]^{-1} \tag{4}$$

Above 170°K;
$$\chi_M = \frac{0{\cdot}54}{T}\left[1 + \tfrac{1}{3}\exp\left(\frac{256}{T}\right)\right]^{-1} \tag{5}$$

It is of interest to compare the magnitude of the present $J$-value of $-192$ cm.$^{-1}$ ($\simeq 0{\cdot}5$ kcal. mole$^{-1}$), with those previously observed for a wide variety of copper(II) complexes with the complementary electron configuration, $3d^9$. From the selected values gathered in Table 1, it is clear that the $d^1$–$d^1$ exchange interaction in $[(\pi\text{-cpd})_2\text{TiCl}]_2$ is of a similar order of magnitude to the $d^9$–$d^9$ interaction in binuclear copper(II) alkanoates but probably much smaller than that in the copper(II) derivative of 1,3-diphenyltriazen (diazoaminobenzene), which is diamagnetic at room temperature.[7]

TABLE 1

Estimated values of $T_c$, $g$, and $J$ for some binuclear compounds of titanium(III) and copper(II)

| | | | $J$ | | |
|---|---|---|---|---|---|
| Compound | $T_c$ | $g$ | (cm.$^{-1}$) | (kcal. mole$^{-1}$) | Ref. |
| $[\text{Ti}_2(\pi\text{-cpd})_4\text{Cl}_2]$ | 170 | 2·10 | 192 | 0·55 | |
| $[\text{Cu}_2(\text{C}_3\text{H}_7\text{CO}_2)_4(\text{C}_6\text{H}_5\text{NH}_2)_2]$ | 107 | 2·18 | 119 | 0·35 | 9 |
| $[\text{Cu}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2]$ | 255 | 2·13 | 284 | 0·82 | 6 |
| $[\text{Cu}_2(\text{C}_3\text{H}_7\text{CO}_2)_4(\text{C}_5\text{H}_5\text{N})_2]$ | 295 | 2·21 | 325 | 0·93 | 9 |
| $[\text{Cu}_2(\text{HCO}_2)_4(\text{C}_5\text{H}_5\text{N})_2]$ | 495 | 2·16 | 550 | 1·57 | 8 |
| $[\text{Cu}_2(\text{dpt})_4]$ | | | $>1000$ | $>3$ | 7 |

TABLE 2

Overlap integrals for *schedo* and *delta* metal–metal bonds

| Compound | M–M bond length (Å) | $t$ | $p$ | $S(3d_{xy}–3d_{xy})$ " *delta* " | $S(3d_{z^2}–3d_{z^2})$ " *schedo* " |
|---|---|---|---|---|---|
| $[(\pi\text{-cpd})_2\text{TiCl}]_2$ | 3·5 | 0 | 8·8 | 0·03 | 0·145 |
| $[\text{Cu(OAc)}_2,\text{H}_2\text{O}]_2$ | 2·6 | 0 | 12 | 0·003 | 0·045 |

*The Nature of the Titanium–Titanium Bond in* $[(\pi\text{-cpd})_2\text{TiCl}]_2$.—Magnetic-susceptibility measurements on the solid do not resolve whether the $d^1$–$d^1$ exchange interaction arises from direct overlap of the titanium $d$-orbitals (metal–metal bonding) or from their overlap *via* filled orbitals centred on the bridging chlorine atoms. However, we have established

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[7] C. M. Harris, B. F. Hoskins, and R. L. Martin, *J.*, 1959, 3728.

[8] R. L. Martin and Hanneke Waterman, *J.*, 1959, 2960.

[9] E. Kokot and R. L. Martin, *Inorg. Chem.*, 1964, **3**, 1306.

that the magnetic anomaly is intramolecular rather than intermolecular (co-operative superexchange) by measuring the magnetic susceptibility of $[(\pi\text{-cpd})_2TiCl]_2$ in benzene solution by the nuclear magnetic resonance [10] method at room temperature. The effective magnetic moment per titanium atom, 1·32 B.M., is similar to that of the polycrystalline material, confirming that the source of spin–spin interaction lies predominantly within the dimer.

A qualitative molecular-orbital treatment throws considerable light on whether the spin–spin interaction between pairs of titanium atoms is of the direct or indirect type. We assume that two carbocyclic rings are bound to each titanium atom in such a way that the metal–ring binding is symmetrical about the symmetry axes of the rings. The point symmetry of the binuclear species is then $D_{2h}$ (see Figure 1). The immediate environment of each titanium atom comprises two chlorine atoms and two $C_5H_5$ rings. Although the local symmetry about each titanium atom is $C_{2v}$, it is convenient here to consider sets of $d_\epsilon{}^3s$ hybrid σ-bonding orbitals located on each titanium atom and directed tetrahedrally towards the chlorine atoms and to the centres of each aromatic ring. The four remaining non-bonding $3d_\gamma$ orbitals of the two titanium atoms ($2 \times 3d_{xy}$ and $2 \times 3d_{z^2}$ with co-ordinate axes defined as in Figure 1) can now be combined to give new molecular orbitals transforming in the point group $D_{2h}$ as $a_g(z^2) + b_{1g}(xy)$ (bonding) and $b_{1u}(z^2) + a_u(xy)$ (antibonding), which are available for the two $3d$ electrons of the titanium pair. We make the usual assumption that the magnitude of the splitting between a bonding orbital and its antibonding counterpart is roughly proportional to the relevant overlap integral, to arrive at the bonding scheme for the $Ti_2$ core given in Figure 3a. In this description, the singlet ground state derived from the configuration $[a_g(z^2)]^2$ corresponds to a "*schedo*" σ-bond between the titanium atoms (see Figure 4a). The lowest excited triplet state for the dimer will correspond to the configuration $[a_g(z^2)]^1[b_{1g}(xy)]^1$.

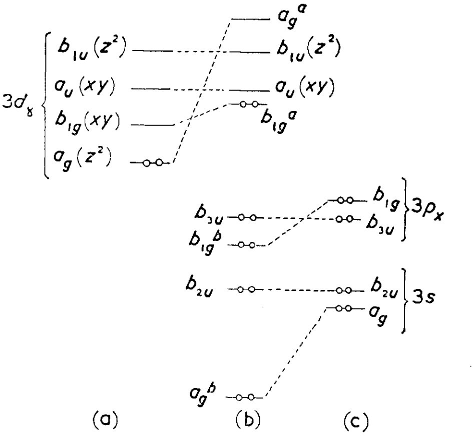

FIGURE 3. Schematic molecular-orbital energy levels for $[(\pi\text{-cpd})_2TiCl]_2$ with the inclusion of chlorine $3s$ and $3p_x$ orbitals

(a) Energy levels for $Ti_2$ core; (b) energy levels for $Ti_2Cl_2$ core; (c) energy levels for $Cl_2$ core; point-group symmetry $D_{2h}$. Not drawn to scale

The actual extent of *schedo* (or δ; Figure 4b) metal–metal bonding will be sensitive to the magnitude of the overlap integral at the assumed Ti–Ti distance of 3·5 Å. An effective nuclear charge of $Z_{\text{eff}} = 4$ for $Ti^{3+}$ (calculated from Slater's rules) leads to values $t = 0$ and $p = 8{\cdot}3$ for the independent variables [11] which give a measure of nuclear asymmetry and internuclear distance of the Ti–Ti bond. When taken with the tabulations of Craig *et al.*[11] and of Roberts and Jaffé,[12] these values lead to the overlap integrals listed in Table 2. Corresponding values for copper(II) acetate are included for comparison.

The magnitude of the overlap integrals for the titanium(III) compounds is surprisingly large. Thus, although the metal atoms in copper(II) acetate are nearly 1 Å closer together

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[10] D. F. Evans, *J.*, 1959, 2003.

[11] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J.*, 1954, 332.

[12] J. L. Roberts and H. H. Jaffé, *J. Chem. Phys.*, 1957, **27**, 883.

than in $[(\pi\text{-cpd})_2TiCl]_2$, the corresponding overlap integrals are very much smaller, reflecting the marked effect of the higher effective nuclear charge on copper. Previously, we have maintained that in copper(II) acetate a singlet–triplet separation of some 300 cm.$^{-1}$ is consistent with an extremely small overlap integral $S(3d_\delta\text{–}3d_\delta)$ of 0·003. By analogy, the overlap integrals in Table 2 require that the present singlet–triplet separation should be of the order of several thousand cm.$^{-1}$ so that $[(\pi\text{-cpd})_2TiCl]_2$ should be diamagnetic.

We suggest here, that this seeming anomaly can be resolved by consideration of the role of the two bridging chlorine atoms. The *X*-ray crystal-structure determination of the closely related dimer $[(\pi\text{-cpd})_2TiCl_2Al(C_2H_5)_2]$ indicates that the chlorine atoms are disposed at 90° to the metal atoms. Accordingly, the two $3p$ chlorine orbitals which lie in the $yz$-plane are thus naturally oriented for metal–chlorine bridge σ-bonding, and we can therefore assume that the bridge bonds contain little *s*-electron character; *i.e.*, the $3p_x$ and $3s$ (of lower energy) chlorine orbitals remain non-bonding, each with two electrons. The sets of two $3p_x$ and of two $3s$ orbitals of the bridging chlorine atoms can each be used separately as the basis for a representation of the $D_{2h}$ group, the former transforming as $b_{1g} + b_{3u}$, the latter as $a_g + b_{2u}$.

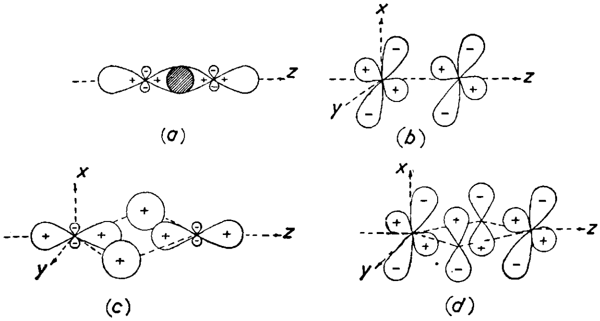

FIGURE 4. The Ti–Ti metal–metal bonding orbitals for $[(\pi\text{-cpd})_2TiCl]_2$
(a) $a_g(z^2)$ *schedo* σ-bonding orbitals; (b) $b_{1g}(xy)$ δ-bonding orbital; (c) $a_g^b$ 4-centre bonding orbital; (d) $b_{1g}^b$ 4-centre bonding orbital

Clearly, two $a_g$ orbitals (one from the titanium pair and one from the chlorine pair) can be combined to give one bonding $a_g^b$ (Figure 4*c*) and one antibonding $a_g^a$ orbital. Likewise, a bonding $b_{1g}^b$ (Figure 4*d*) and an antibonding $b_{1g}^a$ orbital can be formed. Since the $a_g$–$a_g$ interaction is likely to be stronger than the $b_{1g}$–$b_{1g}$ interaction, the relative movements of the energy levels of the $Ti_2Cl_2$ core can be approximated by a diagram of the type given in Figure 3. Both the $b_{2u}$ and $b_{3u}$ orbitals are non-bonding so that effectively ten electrons [one from each $Ti^{III}$ together with eight from the chlorine $3s$ and $3p_x$ sets] can be accommodated in a singlet ground state with the likely configuration: $[a_g^b]^2[b_{2u}]^2[b_{1g}^b]^2[b_{3u}]^2[b_{1g}^a]^2$. Since the $b_{1g}^a$ orbital is destabilised by the interaction with the chlorine atoms the lowest lying excited triplet state with the configuration $[a_g^b]^2[b_{2u}]^2[b_{1g}^b]^2[b_{3u}]^2[b_{1g}^a]^1[a_u]^1$ may now reasonably lie within a few hundred cm.$^{-1}$ of the singlet ground state.

Both the bonding $a_g^b$ and $b_{1g}^b$ orbitals can be described as 4-centre molecular orbitals involving the $Ti_2Cl_2$ core with the remaining lone pairs of electrons being localised in either a $b_{2u}$ orbital, which is weakly antibonding, or a $b_{3u}$ orbital, which is weakly bonding with respect to the two chlorine atoms. The remarkable ease of oxidation [13] of $[\pi\text{-cpd}_2\ TiCl]_2$ is hardly surprising, since the two electrons of highest energy are located in a δ-type orbital ($b_{1g}^a$), which is well exposed to chemical attack (cf. Figure 4*d*).

It emerges from this analysis that bridging chlorine atoms will generally modify an intramolecular metal–metal interaction in one (or both) of two ways: (1) By multicentre bonding, which for the present compound involves a direct four-way overlap of titanium and chlorine atomic orbitals. (2) By localised super-exchange which involves no direct overlap between $3d$ orbitals of each titanium. However, spin-coupling between chlorine-bridged titanium atoms to give singlet and triplet states is achieved by the conventional

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[13] A. F. Reid and P. C. Wailes, *Austral. J. Chem.*, 1965, **18**, 9.

super-exchange mechanism [14] which, however, is " localised " rather than " co-operative " for a molecular compound of the present type.

It is emphasised that no sharp delineation is implied here, the relative contributions of each mechanism being determined by the nature and magnitude of the relevant overlaps. Thus, multicentre bonding is likely to be favoured by the situation depicted in Figure 4c; localised super-exchange by that in Figure 4d.

Finally, we note that the role of bridging chlorine atoms in producing a thermally accessible triplet state in $[(\pi\text{-cpd})_2TiCl]_2$ is not unduly sensitive to the particular description chosen for $\sigma$-binding between titanium and the cyclopentadienyl rings. For the present compound, it is sufficient that two single titanium orbitals can be combined to give molecular orbitals which contain either of the irreducible representations $a_g$ or $b_{1g}$ in the molecular point group $D_{2h}$. Thus, for example, a set of nine hybrid $\sigma$-orbitals might have been envisaged, constructed from five $3d$, one $4s$, and three $4p$ atomic orbitals centred on each titanium atom. If eight of these $\sigma$-bonding orbitals accommodate 16 electrons from two $C_5H_5^-$ rings (regarded now as a 6- rather than a 2-electron donor) and two bridging $Cl^-$ ions, the remaining ninth lobes of each hybrid set can be combined to give molecular orbitals with the requisite $a_g$ and $b_{1u}$ symmetry. Interaction with the $a_g$ ($3s$) orbital of the bridging chlorine atoms can again provide a likely mechanism for reduction of the singlet–triplet separation into the region of observed values.

## EXPERIMENTAL

*Materials.*—Di-π-cyclopentadienyltitanium(III) chloride was kindly given to us by Dr. A. F. Reid, Division of Mineral Chemistry, C.S.I.R.O., Melbourne. It was prepared from magnesium cyclopentadienide and titanium trichloride by the methods described elsewhere.[13]

*Magnetic Measurements.*—The magnetic susceptibility of the solid material was determined by the Gouy method with an apparatus of design similar to that described in detail by Colton.[15]

The magnetic susceptibility in solution was measured by the method recommended by Evans.[10] The displacement of the proton resonance in benzene caused by the paramagnetic solute was measured with a Varian A 60 nuclear magnetic resonance spectrometer.

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[*Received, December 29th,* 1964.]

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[14] R. L. Martin and Hanneke Waterman, *J.*, 1959, 1359.

[15] R. Colton, U.K. Atomic Energy Authority Research Group Report AERE–R4186 (1963).