Materials Science, Vol. 20, No. 2, 2002

$(Ph_4P)_2[ReCl_5(tcm)]$
– a new precursor of molecular magnets

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New complex of composition $(PPh_4)_2[ReCl_5(tcm)]$ have been obtained and characterized by IR, UV-Vis spectroscopies and magnetic measurements. The rhenium atom is six-fold co-ordinated with five chloride atoms and one tcm group. The compound contains tcm^- in monodendate function co-ordinated to metal via the N-atom. The temperature dependence of magnetic susceptibility measured over the range of 1.73–300 K showed the presence of a very weak antiferromagnetic interaction (zJ'=-0.78 cm^{-1}) between the rhenium atoms.

Key words: *rhenium(IV), complex compound, magnetism, tcm ligand*

1. Introduction

The tricyanomethanide $(tcm)^-$ ion presents itself as a rather efficient complexing agent. The tcm^- forms co-ordinate bonds with preservation of its planarity. The bonds are N-type metal-to-ligand ones as a consequence of the high electron density on the cyano nitrogen. The tcm^- ion shows a tendency to act as a bridge ligand and hence to form co-ordination polymers [1–8]. Because of the high degree of delocalization of the ionic charge, three cyano-N-atoms are equally capable of establishing co-ordinate bonds. This enables tricyanomethanide to act not only as a monodentate ligand but preferably as a bi-, tri- and tetradentate ligand in bridge function. Ag(tcm), which contains layers of two interpenetrating hexagonal sheets [9] upon reaction with $(Ph_4P)_2ReCl_6$ gives the complex $(Ph_4P)_2[ReCl_5(tcm)]$. The compound contains tcm^- in monodendate function co-ordinated to metal centre via the N-atom.

Rhenium(IV) ion ($5d^3$) of the ground electronic state $^4A_{2g}$ term has three unpaired electrons. The fourth oxidation state is particularly stable in association with classical ligands (predominantly σ-donors) and like other d^3 ions, it adopts octahedral symmetry.

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2. Experimental section

2.1. Synthesis

A mixture of 1.20 g of $(Ph_4P)_2ReCl_6$ (1.11 mmol) and 1.43 g of Ag(tcm) (7.23 mmol) was heated under reflux in 120 ml of acetonitrile (t = 81 °C). The reaction was stopped after 30 hours. The solution was brown. The grey precipitate (0.81 g), mainly AgCl and unreacted starting material was filtered. To the brown solution *n*-hexane was added to precipitate the product. Yellow crystals of the final product were obtained by slow evaporation from a (1:3) *n*-hexane–2-butanone mixture. Anal. Calcd. for $C_{52}H_{40}P_2Cl_5N_3Re$: C, 55.1; H, 3.5; Cl, 15.7; N, 3.7; Re, 16.4 Found: C, 54.5; H, 3.5; Cl, 15.1; N, 3.2; Re, 15.7.

2.2. Physical measurements

Electronic (reflectance) spectra of undiluted sample of complex $(Ph_4P)_2$ $[ReCl_5(tcm)]$ were recorded over the range of 200–800 nm with Hitachi 356 Double Beam Spectrophotometer.

The FIR spectra were measured in Nujol mull (500–50 cm^{-1}) and MIR spectra in KBr pellet (4000–400 cm^{-1}) with Bruker IFS 113V Spectrophotometer.

Magnetic susceptibility of the polycrystalline samples was measured over the temperature range of 1.73–300 K using Quantum Design SQUID-based magnetometer MPMS-XL5 type. The superconducting magnet was operated at the magnetic field strength ranging up to 5 kG.

The corrections for diamagnetism were estimated from Pascal constants [10]. The effective magnetic moment was estimated from the equation:

$$\mu_{\mathrm{eff}} = 2.83\left[\chi_M^{\mathrm{corr}} T\right]^{1/2}\ \mathrm{B.M.}$$

2. Results and discussion

Proposed molecular structure of $[ReCl_5(tcm)]^{2-}$ anion is shown in Fig. 1. The complex $(Ph_4P)_2[ReCl_5(tcm)]$ of symmetry C_{4v} has 11 normal modes of vibration: $\Gamma_{\mathrm{vib}} = 4A_1 + 2B_1 + B_2 + 4E$ [11]. The type of bond of the tricyanomethanides is reflected in a characteristic way by the IR/Raman spectra of the compound, where most significant variations are observed in the range of the CN stretching vibration band. There are three ν(CN) vibrations ($2A_1$, E_1) to be expected in metal-N-tricyanomethanides (local C_{2v} symmetry) and two expected ν(CN) frequencies (A_1, E_1) in metal-C-tricyanomethanides (local C_{3v} symmetry). IR spectrum of $(Ph_4P)_2[ReCl_5(tcm)]$

complex shows two bands in the CN vibration region, at 2240 and 2172 cm^{-1} and a shoulder at 2189 cm^{-1}. It may be interpreted that A_1 and B_1 may possibly coincide.

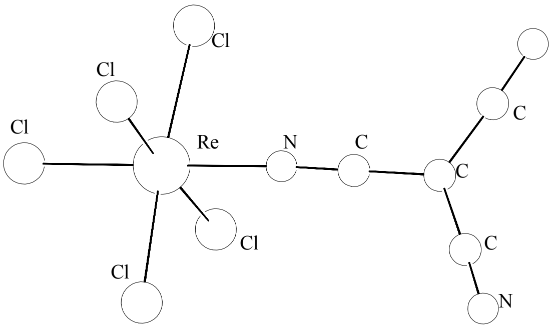

Fig. 1. Proposition of the molecular structure of $[ReCl_5(tcm)]^{2-}$ ion

It is found that, in passing from an octahedral $ML_6(O_h)$ to six co-ordinate square bipiramidal complexes ML_5Z (C_{4v}), the t_{2g} orbital splits into two sets: $b_2(xy)$, $e(xz, yz)$ and the e orbital into sets: $a_1(z^2)$, $b_1(x^2-y^2)$. Bands at 25 063 cm^{-1} (399 nm, $A = 0.85$), 29 412 cm^{-1} (340 nm, $A = 0.86$) and 31 270 cm^{-1} (320 nm, $A = 0.89$) of high absorption coefficients can be attributed to ligand metal charge transfer transitions: $N \rightarrow M$, $Cl \rightarrow M$ [12]. Other bands with lower absorption coefficients in the visible region are due to the ligand field (d-d) transitions. These are bands at 13 123 cm^{-1} (762 nm, $A = 0.36$), 14327 cm^{-1} (698 nm, $A = 0.35$), 21 008 cm^{-1} (476 nm, $A = 0.70$) which can be attributed to $b_2 \rightarrow e$ ($xy \rightarrow xz, yz$); $b_2 \rightarrow b_1$ ($xy \rightarrow x^2-y^2$); $e \rightarrow a_1$ ($xz, yz \rightarrow z^2$), respectively. On the basis of the transitions mentioned above and equations estimated for the d orbitals in a field of C_{4v} symmetry [13], Dq = 1433 cm^{-1}, Dt = 277 cm^{-1}, $Ds = -3913$ cm^{-1} parameters were calculated.

Bands observed in the UV region at 48 544 cm^{-1} (206 nm; $A = 0.96$) and 43 860 cm^{-1} (228 nm; $A = 0.96$) are characteristic of tcm^- [14].

The structure of $[ReCl_5(tcm)]^{2-}$ ion can be described as short square-bipyramid with the electron configuration $(b_2)^1(e)^2$. Such a configuration is also confirmed by the magnetic moment μ_{eff} = 3.29 B.M. (T = 300 K) corresponding three unpaired electrons.

The reduction of magnetic moments in comparison with the spin only value (3.87 B.M.) can be explained on the basis of depopulation of spin-orbit coupled excited states and/or zero-field effects. The magnetic susceptibilities of other rhenium(IV) salts have been reported elsewhere [15–20].

Magnetic properties of complex $(Ph_4P)_2[ReCl_5(tcm)]$ under the form of $\chi_M T$ and χ_M vs. T (χ_M being the molar magnetic susceptibility) are plotted in Fig. 2.

To interpret quantitatively the susceptibility data, we used the approaches in which we considered that the magnetic susceptibility of this complex might be described by the susceptibility of the $^4A_{2g}$ term with zero-field splitting [21].

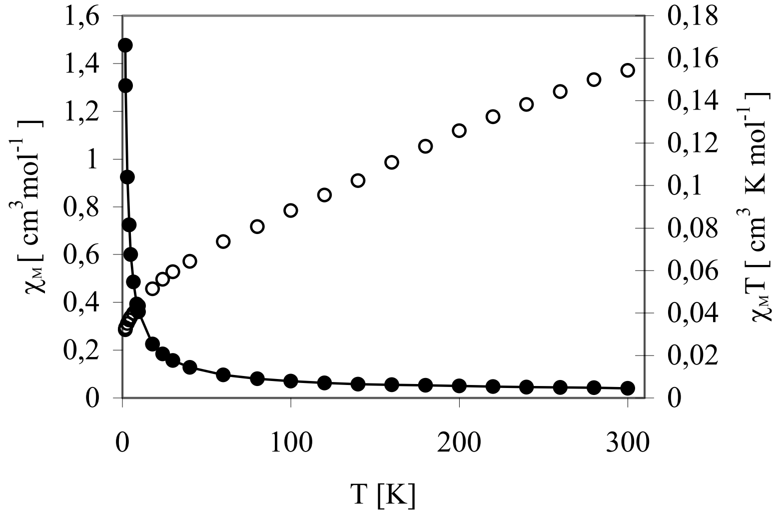

Fig. 2. Thermal dependence of χ_M (●) and $\chi_M T$ (○) for $(Ph_4P)_2[ReCl_5(tcm)]$ complex. Solid line is the calculated curve (Eq. (2), (3))

Zero-field splitting and ligand field of symmetry lower than cubic lead to the anisotropy of magnetic properties of an ion. The relevant spin Hamiltonian is defined by the equation:

$$H = D\left[S_z^2 - 1/3S(S+1)\right] + g_{\|}DH_zS_z + g_{\perp}B(H_xS_x + H_yS_y) \tag{1}$$

where DS_z^2 represents the splitting into two Kramers doublets in the absence of magnetic field. The parallel and perpendicular zero-field susceptibilities for $S = 3/2$ (Eq. (2)) were corrected by a factor predicted from the molecular field (Eq. (3)) [22]:

$$\chi_{\|} = \frac{N\beta^2}{4kT} g_{\|}^2 F_{D_{\|}}, \qquad \chi_{\perp} = \frac{N\beta^2}{4kT} g_{\perp}^2 F_{D\perp} \tag{2}$$

where

$$F_{D_{\|}} = \frac{1 + 9\exp\left(-\frac{2D}{kT}\right)}{1 + \exp\left(-\frac{2D}{kT}\right)}, \qquad F_{D\perp} = \frac{4 + 6\frac{kT}{2D}\left[1 - \exp\left(-\frac{2D}{kT}\right)\right]}{1 + \exp\left(-\frac{2D}{kT}\right)}$$

$2D$ is the zero-field parameter, N – Avogadro's number, $g_{\perp}$, $g_{\|}$ – the spectroscopic splitting factors, β – the Bohr magneton and k – the Boltzmann constant:

$$\chi_i' = \frac{\chi_i}{1-\left(\frac{2zJ'}{N g_i^2 \beta^2}\right)\chi_i} \tag{3}$$

where $i = \|$ or $\perp$, zJ' is the exchange parameter and was applied to calculate magnetic exchange effect by means of a molecular field.

Since our data refer to powered samples, the average magnetic susceptibility is equal to $\chi_{av}=1/3\chi_{\|}+2/3\chi_{\perp}$. Minimization of the agreement factor R ($R = \Sigma(\chi_{exp} - \chi_{calc})^2/\ \Sigma(\chi_{exp})^2$] leads to $2D = 30.47$ cm^{-1}, $g_{av} = 1.65$, and $zJ' = -0.78$ cm^{-1} with $R = 8.95\cdot10^{-4}$.

A small value of the exchange parameter suggests the presence of very weak antiferromagnetic interactions between $[ReCl_5(tcm)]^{2-}$ ions at crystal lattice. This fact confirm: the calculated in the interval 300–80 K the Curie constant value $C = 1.36$ cm$^3\cdot$K$\cdot$mol^{-1} and negative value of the Weiss constant $\theta = -35.4$ K. This magnetic interaction might be transmitted by bonding arrangements such as M–L...L–M [19]. The occurrence of a bulky $(Ph_4P)^+$ cation results in the diamagnetic dilution due to increasing distance between the paramagnetic Re(IV) centres.

On the basis of magnetic data we conclude that Re(IV) in $(Ph_4P)_2[ReCl_5(tcm)]$ exhibits a large zero-field splitting parameter together with weak antiferromagnetic interactions, but we have obtained only twin crystals. After determination the structure of monocrystals of this complex, further discussion of its physicochemical properties will be possible.

Acknowledgements

This work was financially supported by the Polish State Committee for Scientific Research and European Science Fundation Programme *Molecular Magnets*.

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Received 16 February 2002
Revised 24 April 2002