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Synthesis, Magnetic and Spectroscopic Study of $(Ph_4As)_2[Re(NCS)_6]\cdot 2H_2O$

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By treatment of $(Ph_4As)_2ReCl_6$ with AgSCN in dimethyl sulfone, a compound of the formula: $(Ph_4As)_2[Re(NCS)_6]\cdot 2H_2O$ **1** (Ph_4As = tetraphenylarsonium cation) is formed. It was isolated by column chromatography on silica gel. The magnetic behaviour of **1** was investigated between 1.72–300 K. $(Ph_4As)_2[Re(NCS)_6]\cdot 2H_2O$ **1** is a magnetically diluted compound with a very small exchange parameter: $zJ' = -0.38$ cm^{-1}. The zero-field splitting parameter 2D equals 14.4 cm^{-1}. 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 [1].

Our work involves the synthesis of a mononuclear Re(IV) complex with thiocyanate ligand. The pseudohalide NCS^- group is known to coordinate to metals in both the terminal and bridging modes. Terminal -NCS or -SCN coordination applies, depending on the preferences of the metal ion. The N-donor end is selected by the relatively 'hard' class A transition series ions and the S-donor by the 'softer' class B ions. According to Pearson's conception, a SCN group coordinated through nitrogen represents a hard base, where as a sulphur coordinated SCN^- group is a soft base [2].

The reported synthesis was found to be reproducible and they yield a mixture of products. Some of them are not characterized. An important step was the isolation of the complexes $(Ph_4As)_2[Re(NCS)_6]\cdot 2H_2O$ **1**, and *cis*-$(Ph_4As)_2[ReCl_4(NCS)_2]\cdot 2CHCl_3$ **2**. The crystal structure of *cis*-$(n\text{-}Bu_4N)_2[ReCl_4(NCS)_2]$ (triclinic, space group $P\bar{1}$, a = 11.245(1), b = 20.174(3), c = 21.320(8) Å, α = 109.06(2), β = 96.46(2), γ = 98.22(5)°, Z = 4) has been determined by single crystal X-ray diffraction analysis. The ambidentate ligand NCS is bonded *via* the N atom [3]. The thiocyanate rhenium(IV), -(V) complexes of the formulas $(Ph_4As)_2[Re(SCN)_6]$ and $(Ph_4As)[Re(SCN)_6]$ are described in [4]. The rhenium(IV) complex was obtained by melting K_2ReCl_6 with KSCN (T = 225°C), the proper caesium, thallium and silver salts were precipitated. The rhenium(V) complex was also obtained using a similar technique: melting $ReCl_5$ with KSCN (T = 230°C). Reaction between $K[Re(SCN)_6]$ and CsCl leads to the caesium complex: $Cs[Re(SCN)_6]$ [5]. The S-coordination ligand to metal was assigned with IR-spectroscopy. The magnetic susceptibilities of a series of rhenium(IV) complexes are described in [6–11].

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Ammonium tetraoxorhenate(VII), tetraphenylarsonium chloride monohydrate, dimethyl sulfone, potassium thiocyanate were purchased from commercial sources and used as received. $(NH_4)_2ReCl_6$ was prepared following [12]. This compound was transformed into the tetraphenylarsonium salt $(Ph_4As)_2ReCl_6$ by precipitation from acidified aqueous solution using $(Ph_4As)Cl$. The AgSCN was obtained by precipitation from water using $AgNO_3$. The reaction was carried out under a stream of argon. A reaction mixture was maintained at 130–135°C in Schlenk's reaction tube surrounded by oil-bath with a temperature controller connected with a magnetic stirrer. To the solution of $(Ph_4As)_2ReCl_6$ (1.18 g; 1.01 mmol) in molten dimethyl sulfone (14.42 g) was added 3.02 g of AgSCN (18.21 mmol). The reaction was stopped after 19 hours. The melt was collected into a mortar and ground into fine powder, which was treated with water to remove the solvent. A red-brown solid (4.68 g) obtained was dried under P_2O_5. The solid was dissolved in 100 ml of acetonitrile. A red-brown solution and a grey precipitate (unreacted starting material and AgCl) was obtained. The mixture was filtered onto a sintered glass filter. The solution was concentrated using vacuum-evaporator to about 100 ml, and red-brown precipitate (1.91 g) was obtained from the cooled solution. The mixture was dried under reduced pressure. The product was dissolved in dichloromethane (30 ml) and chromatographed on the silica gel 60 column with methanol dichloromethane (1:20) as an eluent. The fastest moving red band contained $(Ph_4As)_2[Re(NCS)_6]\cdot 2H_2O$ **1** (7.98 mg), the third yellow band contained *cis*-$(Ph_4As)_2[ReCl_4(NCS)_2]\cdot 2CHCl_3$ **2** (10.27 mg). The elemental analyses of C, H, Cl and N were in agreement with the expected stoichiometry.

Electronic (absorption) spectra of complexes in acetonitrile were recorded over the range 200–800 nm with UV-Visible spectrophotometer CARY 50 Bio (Varian). 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 was measured between 1.72–300 K using Quantum Design SQUID-based magnetometer type MPMS-XL-5. The superconducting magnet was operated at field strengths 0.5 Tesla. The SQUID magnetometer was calibrated with palladium for which the gram magnetic susceptibility was taken as 5.30×10^{-6} cm^3g^{-1} at 293.1 K (NBS, USA). The corrections for diamagnetism were estimated from Pascal constants [13]. The effective magnetic moment was calculated from: $\mu_{eff} = 2.83[\chi_M^{corr}T]^{1/2}$ B.M.

The magnetic properties of complex **1** under the form of $\chi_M T$ *vs*. T (χ_M being the molar magnetic susceptibility) are plotted in Figure 1. The χ_M T values smoothly decrease in a wide temperature range and rapidly decrease at low temperatures. The effective magnetic moment of 3.48 B.M. is reduced in comparison with the spin-only value (3.87 B.M.). The slight decrease of χ_M T at low temperatures can be due either to zero-field splitting of Re^{IV} and /or to intermolecular interactions.

To interpret 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 [14]. Zero-field splitting and ligand field of symmetry lower than cubic lead to the anisotropy of magnetic properties of an ion.

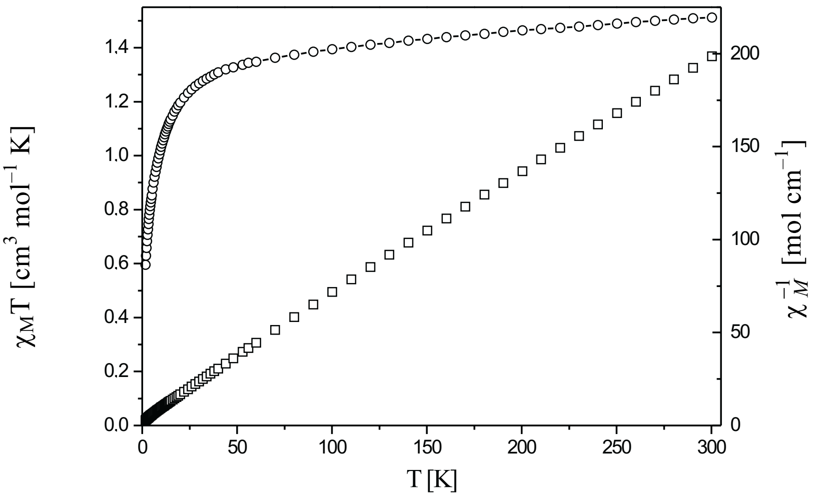

Figure 1. Temperature dependence of χ_MT (O) and χ_M^{-1} (·) for $(Ph_4As)_2[Re(NCS)_6]\cdot 2H_2O$. The solid line is the calculated one.

The relevant spin Hamiltonian is defined by: $H = D[S_{z^2} - 1/3S(S+1)] + g_{\|}DH_zS_z + g_{\perp}B(H_xS_x + H_yS_y)$, 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 were corrected by a factor predicted from the molecular field of the magnetic exchange [15].

$$\chi_{\perp} = \frac{N\beta^2}{4kT} g_{\perp}^2 F_{D\perp};\ \chi_{\|} = \frac{N\beta^2}{4kT} g_{\|}^2 F_{D\|}$$

where

$$F_{D\perp} = \frac{4 + 6\dfrac{kT}{2D}\left[1 - \exp\left(-\dfrac{2D}{kT}\right)\right]}{1 + \exp\left(-\dfrac{2D}{kT}\right)} \quad \text{and} \quad F_{D\|} = \frac{1 + 9\exp\left(-\dfrac{2D}{kT}\right)}{1 + \exp\left(-\dfrac{2D}{kT}\right)}$$

$$\chi_i' = \frac{\chi_i}{1 - \left(\dfrac{2zJ'}{Ng_i^2\beta^2}\right)\chi_i}$$

The average magnetic susceptibility equals $\chi_{av} = 1/3\ \chi_{\|} + 2/3\chi_{\perp}$. Minimization of the agreement factor R $[R = \Sigma(\chi_{exp}T - \chi_{calc}T)^2/\ \Sigma(\chi T_{exp})^2]$ leads to 2D = 14.4 cm^{-1}, g_{av}=1.77, and zJ′ = –0.38 cm^{-1} with R=5.7×10^{-5}. The small exchange parameter suggests the presence of very weak antiferromagnetic interactions between $[Re(NCS)_6]^{-2}$ ions at crystal lattice. This fact confirms the calculated in the interval 300–80 K Curie value C = 1.57 cm^{3}mol^{-1} K and the negative value of Weiss constant θ = –13.9 K.

This magnetic interaction might be transmitted by bonding arrangements such as M-L...L-M [10]. The presence of the bulky $(Ph_4As)^+$ cation results in the diamagnetic dilution because it increases the distance between the paramagnetic Re(IV) center. On the basis of magnetic data we conclude that Re(IV) in **1** exhibits a large zero-field splitting parameter together with weak antiferromagnetic interactions. Infrared evidence for the mode of bonding of the thiocyanate groups in $[Re(NCS)_6]^{2-}$ ion favours attachment through the nitrogen end. Two ν(CN) bands, observed in the IR spectra, at 2054 and 2062 (vs) (two frequency bands ν(CN) come from inequality coordination of SCN^- ion) are shifted to higher wavenumbers, while ν(CS) (844 cm^{-1} (vw)) and δ(NCS) (476 cm^{-1} (w)) bands to lower wavenumbers in comparison with those of AgSCN (2077 cm^{-1}). The absorption spectra in UV/VIS region of acetonitrile solution gave band at 24961 cm^{-1} ($\varepsilon = 3.5\times10^3$ dm^3 mol^{-1} cm^{-1}), which is attributed to N→Re charge transfer transition. Higher energy band observed at 37037 cm^{-1} ($\varepsilon = 1.0\times10^4$ dm^3 mol^{-1} cm^{-1}) is attributed to $2\pi\rightarrow3\pi$ ligand transition. The $2\pi\rightarrow3\pi$ transition is forbidden in the free ion and may become allowed when the thiocyanate ion is bonded to a metal [16]. Available evidence (magnetic properties, visible and IR spectra) reveals that the obtained rhenium complex is six coordinated with NCS ligands.

According to our calculations, a small negative, zJ′ parameter (–0.38 cm^{-1}) for complex $(Ph_4As)_2[Re(NCS)_6]\cdot2H_2O$ **1** informs that $[Re(NCS)_6]^{2-}$ ions are magnetically isolated in the crystal lattice. This may be explained as due to the large size of $(Ph_4As)^+$ cation, which leads to an increase of intermolecular rhenium-rhenium distance.

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REFERENCES

1. Rouschias G., *Chem. Rev.*, **74,** 531 (1974).
2. Pearson R.G., Hard and Soft Acid and Bases, Dowden, Hutchinson&Ross, Stroudsberg, Pensylvania 1973; *J. Am. Chem. Soc.*, **85,** 3533 (1963).
3. Homolya L., Struess S. and Preetz W., *Z. Naturforsch.*, **53b**, 132 (1998).
4. Bailey R.A. and Kozak S.L., *J. Inorg. Nucl. Chem.*, **6**, 419 (1967).
5. Bailey R.A. and Kozak S.L., *Inorg. Chem.*, **6,** 2155 (1967).
6. Mroziński J., *Proc. Conf. Coord. Chem.*, **54,** 293 (1980).
7. Mroziński J., *Bull. Acad. Polon. Sci. Ser. Chim.*, XXVIII **7,** 559 (1980).
8. Mroziński J., *Bull. Acad. Polon. Sci. Ser. Chim.*, XXVIII **10,** 789 (1980).
9. Małecka J., Jager L., Wagner Ch. and Mroziński J., *Polish. J. Chem.*, **72,** 1879 (1998).
10. Tomkiewicz A., Villain F. and Mroziński J., *J. Mol. Struct.*, **555,** 383 (2000).
11. Tomkiewicz A., Bartczak T.J., Kruszyński R. and Mroziński J., *J. Mol. Struct.*, **595**, 225 (2001).
12. Watt G.W. and Thompson R.J., *Inorg. Synth.*, **1,** 178 (1939).
13. König E., Magnetic Properties of Coordination and Organometallic Transition Metal Compounds, Springer-Verlag, Berlin 1966.
14. Figgis B.N., *Trans. Farad. Soc.*, **56**, 1553 (1960).
15. Chiozzone R., González R., Kremer C., De Munno G., Cano J, Lloret F., Julve M. and Faus J., *Inorg. Chem.*, **38,** 4745 (1999).
16. Di Sipio L., Oleari L. and De Michelis G., *Coord. Chem. Rev.,* **1,** 7 (1966).